Surface Boiling of Superheated Liquid

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Prof. Dr. G. Yadigaroglu, examiner
Prof. Dr. S. Banerjee, co-examiner
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Abstract

A basic vaporization mechanism that possibly affects the qualitative and quantitative prediction of the consequences of accidental releases of hazardous superheated liquids was experimentally and analytically investigated. The studies are of relevance for the instantaneous failure of a containment vessel filled with liquefied gas. Even though catastrophical vessel failure is a rare event, it is considered to be a major technological hazard. Modeling the initial phase of depressurisation and vaporization of the contents is an essential step for the subsequent analysis of the spread and dispersion of the materials liberated. There is only limited understanding of this inertial expansion stage of the superheated liquid, before gravity and atmospheric turbulence begin to dominate the expansion. This work aims at a better understanding of the vaporization process and to supply more precise source-term data. It is also intended to provide knowledge for the prediction of the behavior of large-scale releases by the investigation of boiling on a small scale.

Release experiments with butane, propane, R-134a and water were conducted. The vaporization of liquids that became superheated by sudden depressurisation was studied in nucleation-site-free glass receptacles. Several novel techniques for preventing undesired nucleation and for opening the test-section were developed. Releases from pipes and from a cylindrical geometry allowed both linear one-dimensional, and radial-front two-dimensional propagation to be investigated. Releases were made to atmospheric pressure over a range of superheats.

It was found that, above a certain superheat temperature, the free surface of the metastable liquid rapidly broke up and ejected a high-velocity vapor/liquid stream. The zone of intense vaporization and liquid fragmentation proceeded as a front that advanced into the test fluids. No nucleation of bubbles in the bulk of the superheated liquid was observed. The propagation of the front exhibited spatial and temporal fluctuations. However, the average measured front velocities and pressures showed rather stationary features - depending on the fluid, the pressure and the superheat. For example, a boiling front velocity of up to 1.3 m/s with a corresponding two-phase flow velocity of 115 m/s was noted for butane with an initial superheat of 73 K when released to the atmosphere. Fluid acceleration led to a pressure of 0.9 bar higher in the superheated liquid than in the ambient atmosphere. For the pipe sizes in the range from 14 to 80 mm investigated, no significant influence of the cross-sectional area on the boiling front velocity was noted.

Boiling front propagation appeared as a complex interaction of vaporization and fragmentation of the superheated liquid. Vaporization caused vapor and liquid motion, which in turn led to the break-up of the initially stagnant liquid. The surface area was consequently enlarged and, among other effects, higher superheated liquid from the bulk was transported to the liquid/vapor interface. Explosive boiling appeared as a process of self-amplifying vaporization which led to the violent phenomena observed. Below a certain threshold, front propagation was not noted, since a limited latent heat could not create enough surface area and corresponding vapor mass fluxes for sustained flashing. In addition, the vaporization could not carry away the surplus saturated liquid.
The findings for the rapid phase transition were qualitatively described in detail. The importance of instabilities, either driven by hydrodynamic or thermal effects and possible nucleation mechanisms were evaluated. The front movement could be modeled by a correlation considering the dominant thermophysical properties and assuming a process controlled by instationary heat conduction and surface properties of the liquid. The results were then related to the explosive cloud expansion following the breach of small glass containers. This vaporization process observed in former experiments was modeled by assuming a boiling front advancing from the outside to the center of a volume of superheated liquid. However, certain measured characteristic velocities and times could be matched only by assuming additional vaporization in the core of the liquid. It remains to be investigated to what extent the current findings can be extrapolated to other conditions, such as higher superheat, different pressures, larger scales and inhomogeneous liquids or liquid-gas or liquid-vapor mixtures.
**Kurzzusammenfassung**


Bei den mit Butan, Propan, R-134a und Wasser durchgeführten Versuchen wurde die durch schlagartige Druckentspannung hervorgerufene Verdampfung in nukleationskeimfreien Glasgefäßen untersucht. Neuartige Techniken zur Vermeidung unerwünschter Nukleation sowie zur Behälteröffnung ermöglichten in Rohren und einer zylindrischen Geometrie eine lineare, eindimensionale und eine radiale, zweidimensionale Verdampfungsentspannung. Mit unterschiedlichen Anfangsüberhitzungen erfolgten die Freisetzungen jeweils zur atmosphärischen Umgebung hin.

Oberhalb einer bestimmten Überhitzungstemperatur rauhte sich die freie Oberfläche der metastabilen Flüssigkeit auf und beschleunigte einen Dampf-/Flüssigkeitsstrom. Eine Zone starker Verdampfung und intensiven Aufbrechens der Flüssigkeit bewegte sich als Front in das Testvolumen, wobei sich im Inneren der überhitzten Flüssigkeit keine Blasen bildeten. Das Voranschreiten der Front war zeitlichen und räumlichen Schwankungen unterworfen. In Abhängigkeit von Flüssigkeit, Druck und Temperatur ergaben sich nach Mittelung allerdings stationäre Werte. Als Beispiel der auftretenden Größenordnungen sei eine Butanfreisetzung zur Umgebung mit einer Anfangsüberhitzung von 73 K erwähnt. Die Siedefront bewegte sich mit einer mittleren Geschwindigkeit von 1,3 m/s, und das zweiphasige Verdampfungsprodukt erreichte eine Geschwindigkeit von 115 m/s. Die Fluidbeschleunigung erhöhte den Druck in der überhitzten Flüssigkeit gegenüber der Umgebung um 0.9 bar. Bei untersuchten Rohrdurchmessern im Bereich von 14 bis 80 mm beeinflusste die Flüssigkeitsquerschnittsfläche die Siedefrontgeschwindigkeit nur unwesentlich.

Phasengrenzfläche nicht ausreichend vergrößerte und die auftretenden Dampfmassenströme eine andauernde Verdampfung nicht aufrecht erhielten. Ausserdem wurde der Überschuss an gesättigter Flüssigkeit nicht ausgetragen.

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<td>$a$</td>
<td>m/s$^2$</td>
<td>acceleration</td>
</tr>
<tr>
<td>$B$</td>
<td>-</td>
<td>mass transfer number</td>
</tr>
<tr>
<td>$Ca$</td>
<td>-</td>
<td>capillary number</td>
</tr>
<tr>
<td>$c_D$</td>
<td>-</td>
<td>drag coefficient</td>
</tr>
<tr>
<td>$c_p$</td>
<td>J/(kg K)</td>
<td>heat capacity at constant pressure</td>
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<tr>
<td>$c_v$</td>
<td>J/(kg K)</td>
<td>heat capacity at constant volume</td>
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<tr>
<td>$c_{v0}$</td>
<td>J/(kg K)</td>
<td>heat capacity at constant volume of ideal gas</td>
</tr>
<tr>
<td>$d$</td>
<td>m</td>
<td>diameter</td>
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<tr>
<td>$Ec$</td>
<td>-</td>
<td>Eckert number</td>
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<tr>
<td>$g$</td>
<td>m/s$^2$</td>
<td>acceleration of gravity</td>
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<td>J/kg</td>
<td>enthalpy</td>
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<tr>
<td>$j$</td>
<td>m/s</td>
<td>volumetric flux per unit area</td>
</tr>
<tr>
<td>$Ja$</td>
<td>-</td>
<td>Jakob number</td>
</tr>
<tr>
<td>$M$</td>
<td>kg</td>
<td>mass</td>
</tr>
<tr>
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<td>kg/s</td>
<td>mass flow rate</td>
</tr>
<tr>
<td>$\tilde{M}$</td>
<td>kg/mol</td>
<td>molar mass</td>
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<td>$m$</td>
<td>kg/(s m$^2$)</td>
<td>mass flux per unit area</td>
</tr>
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<tr>
<td>$On$</td>
<td>-</td>
<td>Ohnesorge number</td>
</tr>
<tr>
<td>$p$</td>
<td>N/m$^2$</td>
<td>pressure</td>
</tr>
<tr>
<td>$Pr$</td>
<td>-</td>
<td>Prandtl number</td>
</tr>
<tr>
<td>$R$</td>
<td>J/(mol K)</td>
<td>ideal gas constant</td>
</tr>
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<td>$r$</td>
<td>m</td>
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<tr>
<td>$Re$</td>
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<tr>
<td>$s$</td>
<td>J/(kg K)</td>
<td>entropy</td>
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<tr>
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<td>s</td>
<td>time</td>
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<td>$u$</td>
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<tr>
<td>$x$</td>
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<td>Quality</td>
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**Greek Symbols**

<table>
<thead>
<tr>
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<tr>
<td>$\alpha$</td>
<td>m$^2$/s</td>
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<tr>
<td>$\delta$</td>
<td>m</td>
<td>Boundary layer thickness</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>-</td>
<td>Void fraction</td>
</tr>
<tr>
<td>$\eta$</td>
<td>N s$^2$/m</td>
<td>Dynamic viscosity</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>W/(m K)</td>
<td>Thermal conductivity</td>
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<tr>
<td>$\lambda$</td>
<td>m</td>
<td>Wavelength</td>
</tr>
<tr>
<td>$\nu$</td>
<td>m$^2$/s</td>
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<td>kg/m$^3$</td>
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<td>$\sigma$</td>
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**Indices**

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</tr>
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<td>crit</td>
<td>Critical state, critical wavelength</td>
</tr>
<tr>
<td>cl</td>
<td>Cloud</td>
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<tr>
<td>fr</td>
<td>Front</td>
</tr>
<tr>
<td>G</td>
<td>Gas / Vapor</td>
</tr>
<tr>
<td>L</td>
<td>Liquid</td>
</tr>
<tr>
<td>LG</td>
<td>Difference between liquid and gas states</td>
</tr>
<tr>
<td>lim</td>
<td>At superheat limit</td>
</tr>
<tr>
<td>nom</td>
<td>Nominal</td>
</tr>
<tr>
<td>real</td>
<td>Real</td>
</tr>
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<td>Two-phase flow</td>
</tr>
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<td>1</td>
<td>Metastable state</td>
</tr>
<tr>
<td>2</td>
<td>Final state</td>
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Chapter 1
Introduction

Sufficient depressurization or heating shifts a liquid to a state where its temperature is far above the saturation point corresponding to its momentary pressure. A "metastable" or "superheated" liquid is formed which can vaporize spontaneously to reach the stable equilibrium state. The liquid-vapor transition, which is termed "flashing", potentially occurs in a violent and rapid manner. Because the resulting mass fluxes of the vapor are orders of magnitude higher than in pool boiling, for instance, and because of the explosion-like character of phase change, superheated liquids are of increasing scientific interest. On one hand, the intense heat and mass flux that they are capable of attaining make them attractive for controlled application in technical processes. On the other hand, their explosive vaporization rate poses the threat of a serious thermohydraulic explosion in both natural and technical processes. Table 1.1 lists examples of the flashing of superheated liquid as a function of its origin. The present investigation focuses particularly on the shaded phenomena, that is, on effects relating to the catastrophic failure of pressure vessels filled with liquefied gas.

This work is motivated by the fact that in industry various substances are stored as liquid in pressure vessels at temperatures exceeding their normal boiling point. A tank failure involving an instantaneous and complete loss of the walls will result in the sudden vaporization of a large volume of superheated liquid. In a first stage of such an accident, the inertial expansion may lead to a destructive pressure wave damaging the immediate vicinity of the release location. This locally dangerous stage is followed by gravitational slumping (if the vapor/aerosol cloud is heavier than air) and a turbulent dispersion of the vapor due to wind and related effects. Because the released substances are often explosive and/or toxic in nature, they pose a threat to people, property and nature in an extended area around the release site. Public awareness of the risk posed by liquefied gases grew considerably after several severe accidents occurred in the recent past. For example, the 1984 explosion of liquefied natural gas in

Table 1.1: Flashing phenomena in superheated liquids

<table>
<thead>
<tr>
<th>Phenomenon</th>
<th>Beneficial effect</th>
<th>Hazardous effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sudden heating</td>
<td>Electric steam generation (Braeunlich 1992)</td>
<td>Heating of liquid by chemical reaction</td>
</tr>
<tr>
<td>Sudden pressure reduction</td>
<td>Desalination and purification of water, superheated jets for cleaning and combustion technologies</td>
<td>Hydrothermal explosion in craters, geysers</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sudden, complete or partial failure of storage vessels, nuclear or chemical reactors or pipes</td>
</tr>
</tbody>
</table>
Mexico City caused the deaths of more than 500 people (Prugh 1991).

As several studies have shown, modelling of the dispersion process is fairly sensitive to the assumptions made about the distribution and condition of the fluids at the end of the inertial expansion (Raj 1991). This means that in order to improve the simulation of gas dispersions and the assessment of the consequences of an accident on the surroundings, progress must be made in acquiring a fundamental understanding of the initial stage of a vapor explosion. Different theoretical and experimental approaches have previously been taken to predict the behavior of superheated liquid during the failure of a pressure vessel. However, an understanding of the boiling mechanism determining the rate of vaporization is still lacking.

The approach taken in this work was to analyze the liquid-vapor transition of a geometrically complex volume by considering a fraction of the overall volume and ensuring that vaporization occurred only on the free surface of this volume. The primary goal was to obtain experimental insight into the mechanism and the rate of vaporization. With novel facilities and techniques developed here to suppress undesired nucleation, superheated liquid was discharged from receptacles free of nucleation sites. In four different test fluids, boiling fronts appearing as a thin zone of violent vaporization and fragmentation were observed to propagate into the metastable liquid. Various aspects of these boiling fronts were documented by pressure measurements and high-speed movie recordings and videos. The results were analyzed and compared with other investigations of the vaporization of superheated liquid.

The most important achievement of this work is the systematic investigation of the influence of superheat, geometry and properties of the fluid on boiling front propagation. Several aspects are documented for the first time, for example, boiling front propagation in a cylindrical geometry. In the range of conditions investigated, boiling fronts were found to propagate independently of cross-sectional size. Above a certain threshold, the velocity increased roughly linearly with superheat. Self-enforcing fragmentation lead to the explosive nature of vaporization. The two-phase velocities measured were in the range of the radial expansion speed of unconfined spherical releases of superheated liquid. However, due to the still limited amount of available data and uncertainties about its generality, universal scale-up laws remain to be further developed and confirmed. Furthermore, the phenomena could be observed in a temperature range necessarily limited upwards and the effect of nucleation sites such as distributed impurities or bubbles in the superheated liquid could not be studied in detail.

Despite some quantitative uncertainties, the experiments provided direct experimental confirmation that boiling fronts constitute a potential vaporization mechanism during large-scale vessel failure. Therefore, this work should contribute to a better understanding of the physics of unconfined releases of superheated liquid. It is expected that models for accident analysis can be improved and the handling of hazardous fluids can be made safer.

The following chapter reviews previous findings related to the vaporization of superheated liquid. The experimental techniques developed and used are then presented; this chapter describes two different facilities for investigating releases on a small scale, as well as techniques developed for suppressing undesired nucleation. In the fourth chapter, the various qualitative and quantitative findings obtained for vaporization via a boiling front are summarized. The subsequent analysis of Chapter 5
1. Introduction

and 6 focus on explaining the boiling mechanism and relating it to the relevant thermophysical properties of the fluid. In the last chapter, the results of boiling front propagation are used to obtain a quantitative prediction of the behavior of unconfined spherical releases of superheated liquid.
Chapter 2
Background and Motivation

This work is aimed at investigating the explosive vaporization of an unconfined volume of superheated liquid. It is mainly motivated by the current lack of knowledge about the catastrophic failure of pressurized tanks filled with liquefied gas. The consequences of such accidental releases are largely controlled by the boiling of superheated liquid. In the following, a review of previous investigations relating to this type of phase change from different fields of research is given. The relevant work can be divided into the following topics:

- Detailed investigations of liquid-vapor phase-change (i.e.: single bubble growth, explosive boiling at limit of superheat, flashing, boiling front propagation)
- Motivations for studying the unconfined release of superheated liquid (i.e.: dense gas dispersion following catastrophic vessel failure)
- Studies of the unconfined release of superheated liquid (i.e.: small and large-scale releases)

Thermodynamic considerations play a central role in the analysis of liquid-vapor phase-change phenomena. Therefore, prior to addressing the above issues, the thermodynamics of superheated liquids will be introduced.

2.1 Thermodynamics of Superheated Liquids

The idealized thermodynamic steps involved in depressurizing a saturated liquid and vaporizing the superheated liquid are illustrated in Fig. 2.1.

Initially, a liquid is present at a temperature $T_0$ and the corresponding saturation pressure $p_0$. Decreasing the pressure in the absence of a phase change (removing the weight from the piston) leads to an isothermal, adiabatic shift of the liquid from a saturated (0) to a superheated state (1). This state, also known as a metastable state, is stable for a certain time until a sufficiently strong disturbance initiates the phase change. Part of the liquid then undergoes an isobaric phase change to reach a stable equilibrium state at a temperature $T_2$ corresponding to the new pressure $p_2$. This process can be plotted in a $p-v$ diagram as shown in Fig. 2.2.

Figure 2.2 shows the saturation curve with the critical point (C) separating the liquid from the vapor side. The metastable state of a pure liquid is visualized as lying on an isotherm that extends from the stable single-phase liquid region into the two-phase region. The form of an isotherm is given by the equation of state (e.g. Van-der-Waals equation of state) as $p = f(T,v)$. This equation, together with the criterion of Maxwell (Carey 1992), gives the limit between stable liquid and metastable states, i.e., the saturation curve. The isotherms below the critical temperature show two extreme values where $(\partial p/\partial v)_T = 0$. Mechanical stability requires that $(\partial p/\partial v)_T < 0$ (Carey 1992). As can be seen from Fig. 2.2, the isotherm between the shaded regions of
metastable states violates this stability criterion, that is, a single-phase fluid cannot exist in this region. The extreme point of the isotherm where the slope \( (\partial p/\partial v)_T \) changes from negative to positive values is named the limit of intrinsic stability, the superheat limit or the spinodal limit.

Connecting the various minima of all isotherms below the critical temperature forms what is known as the spinodal line which is, in addition to the saturation curve, the second limit of the region of theoretically possible metastable liquids. Similar regions and boundaries can be found for metastable vapor, as plotted in Fig. 2.2, but are not discussed further here.

Figure 2.2 also shows the steps of a sudden depressurization of liquid as illustrated in Fig. 2.1. Initially, the liquid is kept at a slightly subcooled \((0a)\) or saturated state \((0)\). The isothermal depressurization then shifts the liquid to the superheated condition of point \((1)\). From there, boiling or evaporation forms a two-phase system with the liquid and the vapor at states \((2)\). In general, as the liquid enters deeper into the metastable range, the likelihood of a phase change increases. At the spinodal line a phase change is virtually certain to occur, that is, homogeneous nucleation starts. A more precise prediction of the duration and mechanism of phase change from the metastable state will be described later in more detail.

Projecting the saturation surface and the liquid spinodal line on a \(p-T\) diagram and considering a relevant fluid for this process at typical experimental conditions leads to Fig. 2.3. The figure shows the saturation curve and the liquid spinodal line for propane. The saturation data is plotted from tabular data (see Appendix B), while the spinodal line was calculated using the Van-der-Waals equation of state (Carey 1992) and the critical data from Table 3.2.
2. Background and Motivation

As can be seen from Fig. 2.3, the metastable liquid can be characterized by its superheat temperature \( \Delta T \), as the difference between actual temperature and saturation temperature at constant pressure (line 2-1):

\[
\Delta T = (T_{\text{actual}} - T_{\text{sat}}) \quad p = \text{const}
\]  
(2.1)

Similarly, the underpressure below the saturation pressure at the same temperature can be taken to describe the metastable liquid (line 0-1):

\[
\Delta p = (p_{\text{actual}} - p_{\text{sat}}) \quad T = \text{const}
\]  
(2.2)
2. Background and Motivation

Specifying only one of these two related quantities does not describe the specific state of a metastable liquid, since the same degree of superheat can be attained at different temperatures or pressures.

Another important parameter, that describes the possible vapor mass fraction after phase-change of a metastable liquid due to adiabatic depressurization, is the Jakob number $Ja$ which is defined as the ratio between the energy available due to superheat and the heat necessary for the vaporization of saturated liquid:

$$Ja := \frac{h_{11} - h_{12}}{h_{\alpha\alpha} - h_{12}}$$

(2.3)

In this definition, the intrinsic enthalpies are used. For the initial (1) and final (2) state at rest, the Jakob number $Ja$ is identical to the isenthalpic mass fraction or isenthalpic flash fraction $x_h$. Similarly, an isentropic flash fraction $x_s$ can be defined which is larger than the isenthalpic flash fraction $x_h$:

$$Ja = x_h = \frac{h_{11} - h_{12}}{h_{\alpha\alpha} - h_{12}} > x_s = \frac{s_{11} - s_{12}}{s_{\alpha\alpha} - s_{12}}$$

(2.4)

This means that less vapor is produced during an isentropic vaporization process than in an isenthalpic process. Assuming a constant heat capacity $c_{pL}$ results in:

$$Ja = \frac{c_{pL} \Delta T_{12}}{h_{\alpha\alpha}}$$

(2.5)

Frequently, the Jakob number is multiplied by the liquid/vapor density ratio to yield the modified form:

$$Ja^* = \frac{c_{pL} \Delta T_{12}}{h_{\alpha\alpha}} \frac{\rho_{12}}{\rho_{\alpha\alpha}}$$

(2.6)

In general, the Jakob number of metastable liquids is limited by $0 < Ja < 1$, that is, adiabatic flashing is not sufficient to vaporize all the liquid. However, liquids with a high heat capacity or what are known as retrograde fluids potentially have sufficient latent heat to vaporize all the liquid upon adiabatic expansion. As Thomson and Sullivan (1975) calculated, this requires a ratio of the specific heat capacity to the ideal gas constant of $c_v^0/R > 11.2$. Among others, Kurschat (1990) proved this phenomenon experimentally by using perfluorohexane ($C_{6}F_{14}$) with $c_v^0/R = 39.3$ resulting in complete vaporisation, whereas water with $c_v^0/R = 3.5$ (Baehr 1984) could not be completely vaporized by adiabatic phase-change.

2.2 Liquid-Vapor Phase-Change

The preceding chapter presented the different thermodynamic states occurring during depressurization of liquid below saturation and its following vaporization. Information about probability and duration, however, requires a precise knowledge of the mechanism of phase change. Besides film boiling, the transformation from the liquid to the gaseous state occurs via the two mechanisms of evaporation and nucleate boiling. If the vapor pressure of the liquid is lower or only slightly above the total pressure in the vapor space, calm evaporation (essentially mass transfer) with vapor transition through a flat free surface will occur. In the case of nucleate boiling, the liquid gets
locally superheated sufficiently to allow nucleation, vapor is generated more vigorously at various nucleation sites inside or at the boundary of the liquid volume.

In the classical literature, a distinction is made between film and nucleate boiling. In film boiling, the temperature of the heating surface is so high that the surface is blanked by a continuous vapor film from which bubbles are released into the liquid. Ideally, there is no contact between the liquid and solid surfaces. In nucleate boiling, two mechanisms can be identified: heterogeneous and homogeneous nucleation. Heterogeneous nucleation is defined as the generation of vapor at the interface between the liquid and preexistent gas, whereas homogeneous nucleation is characterized by vapor generation occurring completely within a pure liquid phase (Carey 1992).

While evaporation of a stagnant liquid can occur even without superheat, nucleation always requires a fluid that is at least locally metastable. Homogeneously nucleated liquids vaporize with explosive violence, whereas heterogeneously nucleated liquids boil at a lower superheat but may nevertheless be producing vapor in a violent manner.

Another particular case of boiling to be considered is that involving surface instabilities (generation of surface waves) propagating into the superheated liquid from an initially flat surface. In this type of boiling, no nucleus is required as in the case of homogeneous or heterogeneous nucleation but disturbances produce local variations of the vapor mass flux from the free surface and thus create pressure differences. These in turn lead to further disturbances of the surface which again amplify the vapor generation (Prosperetti and Plesset 1984). However, since this unstable boiling is also observed on bubbles growing rapidly at higher superheats, the question as to whether vaporization enhanced by instabilities of the interface should be considered separately, is purely academic.

2.2.1 Classical Theory of Single Bubble Growth

The present work focuses on vaporization by boiling fronts propagating into superheated liquid. Previous studies on depressurization and thermal explosion phenomena involving transient boiling were based on the prediction of bubble growth, since bubbles offer a large interfacial area for the liquid-vapor transition. To check the suitability of bubble growth models for application to the current problem, the theory of vapor-bubble growth in a superheated liquid is presented in the following.

Vapor bubble growth in a superheated liquid requires the formation of a vapor nucleus. Taking into account the mechanical stability, assuming thermodynamic equilibrium and using the Clausius-Clapeyron equation, the following relation gives the minimum or critical radius of a vapor volume from which bubbles will grow (Collier and Thome 1994):

\[
  r^* = \frac{2\sigma}{\rho_{\text{gas}} h_{\text{lg}} \Delta T} \quad (2.7)
\]

Only bubbles with a larger radius, \( r > r^* \), will grow while those bubbles with a radius smaller than critical will condense again. Low surface tension and high superheat result in a small critical radius for bubble growth, as can be seen from equation (2.7).
The formation of a bubble embryo is followed by bubble growth. Two limiting cases of the expansion process can be distinguished. During the initial stage of bubble growth, after formation of stable bubble nuclei, the process is inertia-controlled, i.e. the expansion is controlled by the velocity at which the vapor can push back the surrounding liquid. The second stage of bubble growth is controlled by heat transfer. At this later stage, the liquid superheat near the interface has been significantly depleted so that heat for vapor production has to be transported from the surrounding liquid to the liquid-vapor interface. The temperature gradient in a thin thermal boundary layer surrounding the bubble determines the rate of vaporization (Prosperetti and Plesset 1978). Since this thermally-controlled heat transfer typically occurs at scales of millimeters and milliseconds, it is of major importance in the context of this work. Carey (1992) gives an expression for the bubble size corresponding approximately to the transition between inertia-controlled and heat-transfer-controlled growth. For superheated propane at 1 bar and 0 °C, the transition occurs approximately at a bubble diameter of $d_{\text{trans}} = 0.06$ mm. For the spherically symmetric period of phase growth in an unconfined infinite medium, Plesset and Zwick (1954) derived the following relation for the increase in bubble radius with time:

$$r = \sqrt{\frac{12}{\pi}} \sqrt{\frac{\rho_L c_p \lambda_L}{\rho_g (h_g - h_L)}} \frac{1}{\Delta T} \sqrt{t}$$

(2.8)

which can be modified using equation (2.6) to obtain:

$$r = \sqrt{\frac{12}{\pi}} \sqrt{\alpha} \, J_a^* \sqrt{t}$$

(2.9)

Equation (2.9) shows that, in addition to the thermal diffusivity $\alpha = \lambda_L/\left(\rho_L c_p\right)$, the Jakob number $J_a^*$ is the key parameter in describing the growth of the bubble. It also implies that the radius of the bubble $r$ increases with the square root of time $t$, which in turn indicates a slowdown in the velocity of bubble growth with time. Equations (2.8) or (2.9), which will be referred to as the classical theory of bubble growth, were found to be in good agreement with experimental results.

More exact theoretical solutions of the differential equations for heat transfer and a further refinement of the bubble growth process are given by Scriven (1959) and Prosperetti and Plesset (1978). Mikic et al. (1970) describe bubble growth, including the transition from the inertia-controlled to the thermally controlled expansion period. Beside these, there are quite a few bubble growth models which consider temperature and pressure environments of various complexity at different stages of bubble growth. In technical systems with heated solid surfaces, the classical theory of bubble growth mentioned above must be modified to account for the lack of spherical symmetry and the nonuniformity of the temperature field in the surrounding liquid.

By using the classical growth equation (2.8 or 2.9), the specific mass flux of vapor across the moving bubble interface can be calculated as follows:

$$\dot{m}_{\text{interface}} = \frac{d}{d t} \left( \frac{M_{\text{bubble}}}{A_{\text{bubble}}} \right) = \frac{1}{3} \rho_g \frac{d r}{d t} = \sqrt{\frac{3}{\pi}} \sqrt{\frac{\rho_L c_p \lambda_L}{(h_g - h_L)}} \frac{1}{\Delta T} \frac{1}{\sqrt{t}}$$

(2.10)
This expression shows that the specific vapor flux decreases with time, as the radius increases. For a certain size of bubble, the mass flux can be expressed by:

$$\dot{m}_{\text{interface}} = \frac{6 \rho_l c_{pl}}{\pi \rho_a} \lambda_l \frac{1}{r} \left( \frac{\Delta T}{h_0 - h_l} \right)^2$$

Equation (2.11) tells us that high mass fluxes can be observed with particular ease for small bubbles and that the vaporization rate increases for a given bubble size with the square of the superheat.

2.2.2 Explosive Boiling at Limit of Superheat

Stable growth of a vapor bubble requires achievement of a critical radius, as determined by equation (2.7). In most technical and natural boiling processes, this minimum volume of gas is provided by pre-existing vapor or inert gas inclusions in small cavities on solid surfaces. These natural or machine-formed pits, scratches, or other irregularities allow heterogeneous nucleation, that is, bubbles will grow at low superheat from these sites.

If heterogeneous nucleation is suppressed, however, a liquid may be heated to temperatures far above its normal boiling point because the critical radius has to be reached by statistical fluctuations of the molecular density within the liquid phase. In this case, bubble growth begins spontaneously from vapor-like clusters of molecules. This onset of homogeneous nucleation has been theoretically and experimentally investigated.

Theoretical prediction of homogeneous nucleation is possible by considering the thermal fluctuations in metastable liquids. These provide a small but finite probability that clusters of molecules with vapor-like energies come together to form a vapor embryo (Collier and Thome 1994). According to the Boltzmann equation for the distribution of molecular clusters, the probability of vapor formation increases exponentially with superheat. At a certain threshold, the size of such a cluster is extremely sensitive to the superheat of the liquid, so that a small temperature increase leads to an increase in the probability of vapor nuclei of a critical size \( r^* \) by some orders of magnitude. The maximum possible superheat is then reached. This is known as the kinetic limit of superheat and offers a second way of predicting homogeneous nucleation, in addition to the thermodynamic limit based on the equation of state discussed in the previous section.

The kinetic limit of superheat or the onset of homogeneous nucleation is derived in the classical work of Volmer (1939). This publication gives an historical overview of related phenomena and addresses the calculation of the nucleation rate of superheated liquids. A more recent book by Skripov (1974) allows a general insight into the thermodynamics of metastable liquids. It presents, for example, thermophysical properties of the superheated state and experimental techniques for investigating homogeneous nucleation. Reviews of the physical properties of superheated liquids are also given by Lienhard (1988) and Shamsundar and Lienhard (1992).

Experiments with various highly superheated liquids were compared with this classical theory of nucleation (reviewed by Skripov 1974). Similarly to the early work of Moore (1956), in most of the subsequent experiments, single liquid droplets rising in an
2. Background and Motivation

Table 2.1: Calculated and measured limits of superheat $\Delta T_{\text{lim}}$ at 1 bar

<table>
<thead>
<tr>
<th></th>
<th>n-butane ©</th>
<th>propane ©</th>
<th>water ©</th>
</tr>
</thead>
<tbody>
<tr>
<td>theoretical superheat limit $\Delta T_{\text{lim}}$ [°C]</td>
<td>105.1</td>
<td>55.2°</td>
<td>307.6</td>
</tr>
<tr>
<td>experimental superheat limit $\Delta T_{\text{lim}}$ [°C]</td>
<td>104.9</td>
<td>52.9</td>
<td>302.1</td>
</tr>
</tbody>
</table>

(Calculation and data found in ©: Blander and Katz 1975; © Thormaehlen 1985)

Immiscible "host" liquid with a vertical temperature gradient were used; these became superheated during their rise. Explosive vaporization occurred close to the theoretically predicted homogeneous nucleation temperature (Jarvis et al. 1975, Blander and Katz 1975, Shepherd and Sturtevant 1982, Frost and Sturtevant 1986, Nguyen et al. 1988, Frost 1988, McCann et al. 1989). As an example, in Table 2.1 the calculated kinetic limit of superheat and the experimentally observed onset of homogeneous nucleation are compared for a number of fluids that were investigated in the present work.

In some of the above experiments, the superheat for nucleation was considerably less than that predicted by the homogeneous nucleation theories. According to the experimental work of Yang and Maa (1987), the presence of microbubbles is a possible reason for this lowering of the superheat limit. Differences between measured and calculated results were in particular observed for water, whereas for many light hydrocarbons the superheat limit was correctly predicted by the kinetic theory. As a rule of thumb, the limit of superheat $\Delta T_{\text{lim}}$ at 1 bar of the latter substances was below the critical temperature $T_{\text{crit}}$ by a factor of 0.9. In the neighborhood of 1 bar, the limit of superheat varied only slightly with pressure (McCann et al. 1989).

The studies on superheated drops not only focused on the onset of homogeneous nucleation, but also examined the explosive nature of vaporization in more detail. Shepherd and Sturtevant (1982) observed that instabilities distorted and roughened the liquid-vapor interface. They attributed the tearing of the interface to a significant increase in the surface area available for evaporation. This increased the rate of vaporization by two orders of magnitude compared with the predicted value that did not consider the effects of surface instability. A high-velocity two-phase flow stream moving away from the interface was produced. It was suggested that the Landau mechanism of instability was playing a dominating role in the initial fragmentation process (Shepherd and Sturtevant 1982). Additional studies on the explosive boiling of droplets were performed by Frost and Sturtevant (1986) and Frost (1988). Depending on the ambient pressure, a different dynamic behavior of the bubbles growing inside drops was observed; increasing the pressure moderated the explosion of superheated droplets. Nguyen et al. (1988) developed a model to predict the pressure field around an exploding liquid particle, while McCann et al. (1989) performed measurements to verify this aspect of vaporization. Lesin et al. (1994) give more data on the interface velocities of an exploding superheated droplet.

The superheat limit for propane given here is derived from the kinetic limit of superheat. It differs from that of Fig. 2.3 which is based on the thermodynamic limit of superheat considering the Vander-Waals equation of state. The curvature of the spinodal line depends on the type of state equation (Skripov 1974).
Whereas the above experiments investigated boiling at the highest possible superheat, Owen and Jalil (1991) focused on determining the lowest superheat required to observe flashing or violent boiling of single drops. They found no disintegration of water drops kept in a quiet steam environment at low temperatures, but explosive vaporization was recorded at superheats exceeding $\Delta T_{1bar} \approx 20$ K. Compared to the investigation of the onset of homogeneous nucleation, where stable water drops were observed even at superheats of $\Delta T_{1bar} = 200$ K (Thormaehlen 1985), these experiments showed that the explosive character of the vaporization could already be observed at fairly low superheat at conditions typical for heterogeneous nucleation. Similar findings were obtained by Maa and Tung (1980) who established that, with increasing size, the drops became unstable at decreasing superheat. Sufficently large drops asymptotically reached the constant value of superheat required for flashing due to heterogeneous nucleation. In order to predict the incipience of flashing, Maa and Tung suggested that this asymptotic value for heterogeneous nucleation should be used rather than that obtained from the theory for homogeneous nucleation. Besides the effect of droplet size, it can be assumed that the flashing of the liquid will be further promoted in a turbulent environment.

It can be concluded that explosive bubble growth inside superheated drops can occur irrespective of whether it was initiated by homogenous or heterogeneous nucleation. It is characterized by much higher mass-transfer rates than would be predicted by the classical bubble-growth theory, which presumes a smooth, undisturbed bubble surface. In explosive boiling liquid may also be contained inside the bubbles.

Depressurization or transfer of heat are two ways of superheating a liquid experimentally. Examples of using heat transfer are the investigations of homogeneous nucleation presented here, where either a host liquid (Moore 1956) or pulse heating of a wire (Skripov 1974) served as the energy source for small droplets. Uniform superheating of a larger volume of fluid can be achieved by depressurization. In the following sections, research having a particular emphasis on investigating the vaporization mechanism caused by sudden depressurization will be reviewed, firstly by considering general flashing phenomena and secondly by considering the particular mechanism of phase-change by boiling fronts. Studies on unconfined releases of stagnant superheated liquid due to sudden depressurization will subsequently be presented.

### 2.2.3 Various Flashing Phenomena

A liquid might become superheated either during its flow through a variable pressure field or by suddenly depressurizing a stagnant volume of liquid. Either quasi continuous or instantaneous releases (blow-down phenomena) can occur. The transients related to the depressurization of stagnant liquid will depend on the ratio between the initial volume (reservoir or pipe volume) and the cross-sectional outflow area. Vaporization can range from flashing with extreme changes in temperature and pressure, e.g. due to sudden rupture/opening of pipes, to quasi-continuous outflow, e.g. during blow-down from large tanks through small pipes.

The accelerational and frictional pressure drop causing flashing of liquid flowing continuously in a pipe was investigated by several authors (e.g. Fletcher 1984). Miller (1985) visually recorded that bubbles were fewer in number by more than an order of
magnitude and grew faster than expected from various theoretical treatments, e.g. using conduction-controlled bubble growth theory. Nucleation was limited to the walls and was not seen in the bulk.

Brown and York (1962) and Lienhard and Day (1970) investigated the flashing influence on the break-up of jets continuously expanding in a low-pressure space and found a minimum superheat necessary for flashing to occur. Kitamura et al. (1986) found that this critical requisite superheat decreased with increasing liquid velocity or nozzle diameter. Using short nozzles, Wildgen and Straub (1989) observed boiling at the free surface of the jet. Kurschat (1990) released jets of retrograde, highly superheated fluid and produced its complete evaporation. In the case of retrograde liquids with a Jakob number $J_a > 1$, the heat was transported only over distances of molecular order of magnitude leading to no heat-transfer limitation. Bharathan and Penny (1984) investigated the vaporization of superheated liquid jets for application to flash evaporation processes.

Releases from initially stagnant liquid were performed by Hooper (1969), Edwards and O’Brien (1970), Lienhard et al. (1978) and Alamgir et al. (1980), for example. They measured pressure transients in pipes evolving at rates of depressurization of up to $1.62 \text{ Mbar/s}$. The resulting metastable liquids were even found to reach negative pressures. Thus, fluids were subjected to tension for several milliseconds in release experiments where a considerable “pressure undershoot” was observed. Bartáček (1990) addressed the expansion wave propagating in an abruptly opened pipe. He found that this initial pressure undershoot was stopped by explosion-like vapor generation leading to a period of quasi-static pressure during vaporization.

Between the above extremes of continuous flashing in liquid flow and instantaneous vaporization of stagnant superheated liquid, various studies were carried out with releases of different path lengths. Depressurization times ranged from milliseconds with highly transient flow phenomena to days characterized by quasi-steady outflow. Current studies focus on cases such as interacting flashing in a pressure vessel and in a depressurization pipe where the fluid becomes depressurized (e.g., Hervieu 1992, Mayinger 1995).

Since flashing occurs in a variety of situations, no general correlation or model is available to predict the exact flow behavior, for example. Numerous models for flashing flow have, therefore, been proposed. Mayinger (1981) and Gerliga and Skaložubov (1986) reviewed the modeling of flashing flows. Yang et al. (1986), Watanabe et al. (1987) and Riznic and Ishii (1989) proposed models for the vapor generation in flashing liquids during blowdown. Qian (1988) and Gopalakrishna (1989) considered flashing in initially stagnant liquids and presented simulations based on modeling the effects of collective bubble growth. Leung and Epstein (1991) examined the effects of noncondensible gases on flashing. Deligiannis and Cleaver (1992) showed that nucleation could be correlated by introducing a factor accounting for heterogeneities in the liquid. Shin and Jones (1993) proposed a model for nucleation and the flashing mechanism in nozzles. Despite these various attempts to model flashing flow, it is still difficult to predict the results of depressurization experiments a priori, because of various non-quantifiable effects (e.g. influence of surface conditions of liquid and walls, presence of dissolved gases or impurities). This means that even recent flashing models (e.g. Giot 1994, Kolev 1995) still depend on major experimental input to determine the density of nucleation sites, for example.
2.2.4 Boiling Front Propagation in Bubbly Liquid

The boiling behavior of single superheated drops was extensively investigated in the context of homogeneous nucleation. Of equal engineering relevance is the vaporization of a larger volume of superheated liquid, which can in principle take place in the presence or absence of nucleation sites in the bulk of the liquid. This work focuses on boiling which is restricted to the free surface. However, similarities to this type of vaporization are also found in some investigations with bulk and wall nucleation which will be reviewed in this section.

Friz (1965) recorded high-speed films of the depressurization of liquid water in a vertical glass pipe. In the experiments, the liquid was only partly degassed and no special precautions were taken to eliminate nucleation sites from the glass walls. After opening a rupture disk at the top of the pipe, Friz observed bubble formation over the whole length of the glass test section. This bubbly mixture remained stagnant until it was reached by an “acceleration front” or zone of phase change which traveled from the exit into the liquid/bubble mixture. At initial superheats of up to 25 K and releases to 1 bar ambient pressure, velocities of the vaporization zone reached a maximum of 2 m/s. The acceleration front, propagating at a constant medium velocity, produced a vapor/liquid mixture flowing downstream of the front. The work of Friz is the first known to the author where such a propagating vaporization zone was reported.

In similar experiments with retrograde liquids, Chaves (1984) noticed a depressurization wave initiating bubble growth in a boundary layer along the walls. This was followed by a “vaporization wave” with rapid expulsion of a two-phase flow. Perfluorohexane (C₆F₁₄) expanding from different initial temperatures to a vacuum reservoir showed speeds of the vaporization front propagating into the superheated bubbly liquid of about 25 m/s. Even though intentional, the critical flow limitation did not allow sufficient superheating for complete vaporization of the retrograde liquid in the pipe (see Kurschat 1990).

2.2.5 Boiling Front Propagation without Bulk Nucleation

The first experiments with completely suppressed bulk and wall nucleation were performed by Grolmes and Fauske (1974). Similarly to Friz, they released fluids from a glass pipe and observed a “boiling front” propagating into a stagnant volume of superheated liquid. Bulk nucleation was prevented, however, by intensive cleaning, rinsing of the test section and/or by degassing and extensive prior boiling of the test fluid. A violent phase transition was observed to occur only at the free surface, in a narrow, bubble-like structured layer. This front moved forward at velocities of about two orders of magnitude lower than the speed of sound in the superheated liquid. A two-phase jet was formed downstream of the vaporization zone and accelerated. Methanol, water and refrigerant R-11 with initial superheats of 70 to 80 K showed front velocities in the range of 0.3 to 0.5 m/s when released into a low-pressure reservoir.

Grolmes and Fauske also observed a minimum superheat required for boiling front propagation to occur. Some close-up recordings of the violent surface flashing revealed that depressurization leads to the development of surface waves of different patterns, this being attributed to variations in surface tension. At low superheat, only pure evaporation took place, that is, only vapor left the free surface with convective
2. Background and Motivation

Fig. 2.4: Mechanism of instability growth on free surface of highly superheated liquid (Prosperetti and Plesset 1984)

liquid motion supporting the heat transfer. At higher superheat, more violent flashing started, either from a disturbance at the liquid/vapor/glass contact line or from the shattering of a large single bubble. The disturbances spread across the whole free surface so that at the end the whole surface was covered by a bubbly structure that ejected a two-phase mixture away from the superheated liquid.

Later, Prosperetti and Plesset (1984) and Mesler and Bellows (1988) analyzed the observations of Grolmes and Fauske (1974), trying to explain the vaporization mechanism. Prosperetti and Plesset carried out a linear stability analysis of an evaporating liquid surface. They found that at large evaporating mass flow rates the instabilities were very strong, leading to an interface increase as illustrated in Fig. 2.4.

Due to favorable conditions for heat conduction, the evaporating mass flux across a disturbed surface was increased at the liquid troughs and decreased at the liquid crests. As a result, the acceleration of the vapor at the interface led to higher pressures in the troughs than on the crests. This pressure difference induced liquid motion toward the crests which amplified the surface deformation and in turn pushed the troughs deeper into the highly superheated liquid.

Mesler and Bellows (1988) proposed a secondary nucleation mechanism to explain the production of a sufficiently large interface leading to violent surface flashing. Secondary nucleation refers to the production of vapor nuclei by entrainment of small bubbles into superheated liquid by falling drops. The chain reaction potentially leading to explosive vaporization is illustrated in Fig. 2.5.

The chain reaction is initiated by a bursting bubble at the liquid surface. The remnants of the film covering the bubble coalesce to drops which fall and entrain some small bubbles into the liquid. These serve as nuclei for new bubbles to grow. Mesler and Bellows (1988) found clear evidence for this mechanism in experiments conducted at low superheat. However, when boiling occurred explosively fast at high superheat, no visual evidence was obtained due to the limited speed of the recording. Both Mesler and Bellows and Prosperetti and Plesset found the proposed mechanisms to be at least partly responsible for boiling front propagation.

Clearly, such a mechanism considering collapsing bubbles only can take place particularly at low superheat, when the modest vapor generation rate is unable to entrain droplets away from the surface. However, “bursting” of liquid, such as
described in chapter 4.4.2, a short distance away from the surface could project smaller drops on the interface. Thus, explosive vaporisation rather than rupturing bubbles could entrain nucleation sites into the liquid at high superheat.

Peterson et al. (1984) studied the vaporization of suddenly depressurized refrigerant R-11 in different set-ups. At superheats of at most 18 K they noticed vaporization with mass transfer rates of 10 - 12 times the rates for quiet evaporation alone. This increase was attributed to liquid motion and entrainment of drops from the free surface of the refrigerant into the vapor stream. Later, Das et al. (1987) reported a phase-change front starting from the free surface. In a set-up similar to that of Grolmes and Fauske, they released water into an evacuated chamber. They found that the velocity of the front increased linearly with superheat and with the square of the pipe diameter, whereas impurities in the test fluid decreased the velocity of the boiling front. However, no direct visual evidence of boiling front movement was obtained because the propagation velocity was measured indirectly, that is, by an array of photosensors. From their description, it cannot be ruled out that the boiling front propagated into a bulk of bubbly liquid, as in the experiments of Friz (1965), for instance.

In the work of Hill (1991) (see also Hill and Sturtevant 1990), boiling fronts were investigated more extensively. Hill distinguished the two consecutive stages of boiling front propagation, the transient start-up and the period of quasi-steady propagation, and described them in detail. By opening a rupture disk positioned on a glass pipe, saturated refrigerants R-12 and R-114 were released from typical initial temperatures of 20°C at different expansion reservoir pressures ranging from 0 to 1 bar absolute. Similarly to Grolmes and Fauske, nucleation in the bulk and on the walls of the glass test section was suppressed, so that Hill could film the nucleation behavior on the free surface, that depended on the superheat. At low superheat, single bubbles started growing - preferentially along the glass/liquid/vapor circumference line. After a certain

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Fig. 2.5: Chain reaction for producing vapor bubble nuclei by secondary nucleation (as proposed by Mesler and Bellows 1988)
period of up to 100 ms and the formation of clusters of bubbles or large single bubbles, a sudden explosive vaporization within these clusters or bubbles initiated the propagation of the boiling front. In a few instances, solid particles falling into the metastable liquid triggered the onset of boiling front propagation. At higher superheat, random sites of nucleation appeared within a few milliseconds on the whole free surface and led to the immediate formation of a boiling front.

After initiation of explosive vaporization, and independently of the start-up mode, the boiling front propagated into the superheated liquid. Although there were fluctuations in the characteristics of the flashing zone that were strong at some times and places, this process was termed “quasi-steady” propagation because, after averaging in space and time, the vaporization front showed rather stationary features. The velocity, the pressure inside the stagnant superheated liquid and the two-phase mass flux flowing downstream from the boiling front remained constant. Hill observed propagation velocities in the range from 0.2 to 0.6 m/s.

The boiling front consisted of a layer of bubble-like structures, i.e., visual evidence was found for both closed bubbles and open hemispherical caps which were continuously generated, grew, broke up and/or collapsed. The typical size of bubbles and/or open caps decreased with increasing boiling front velocity, i.e., with increasing superheat. Further downstream and within one centimeter from the leading front contour, explosive fine-scale fragmentation occurred. The liquid-vapor transition accelerated a two-phase mixture to velocities of up to 35 m/s, depending on the superheat. The highly nonuniform two-phase stream contained drops with diameters reaching at most 0.1 mm and a few bubbles of less than 1 mm in diameter.

Hill found that below the self-start threshold for the onset of movement of the boiling front as observed by Grolmes and Fauske, the boiling front propagation could still be initiated by external triggering. In his case, a boiling front moving through a more volatile liquid (R-114) started the boiling front propagation in a less volatile substance (R-12) resting below. The lower limit for artificial triggering, the absolute superheat threshold, was lower than the self-start threshold by a few degrees Kelvin. The mechanism of vaporization was described as a mutually interactive process of liquid fragmentation leading to increased evaporation which in turn enhanced liquid motion. However, due to the very complex interaction of mass and heat transfer and the limited experimental conditions, a usable model for the velocity of the vaporization process could not be given.

In subsequent experiments, Sugioka (1991) investigated the effect of particles on the behavior of the boiling front essentially using the same set-up as Hill (1991). He found that boiling fronts appeared above a critical superheat, and propagated six times faster in the presence of glass beads than under similar conditions without particles. Some of the experiments were conducted in a centrifuge to investigate the influence of gravity on particle acceleration. Particle acceleration due to vapor drag of at most 500 g was measured.

2.3 Motivation for Studying Unconfined Releases

In the past, the threat of vapor explosions was the main motivating factor for research on the behavior of highly superheated liquids. Sudden heating followed by rapid
2. Background and Motivation

vaporization of metastable liquid is one possible cause of such physical explosions and represents an extremely hazardous and destructive situation. Such problems have been reported in the paper industry in connection with smelt-dissolving tank operations, in the metals industry in connection with the accidental spillage of molten materials into water (Reid 1983), in the nuclear industry in connection with interactions between water and molten fuel elements (Corradini 1993) and in the transportation industry in connection with spills of liquid natural gas onto water (Reid 1978). Fletcher and Theofanous (1994) give a review of recent progress achieved in understanding such phenomena.

Catastrophic Vessel Failure

The sudden depressurization of an initially saturated or subcooled liquid is involved in another family of accident scenarios. In particular, the instantaneous disintegration of a pressure vessel containing a liquefied substance, leading to an instantaneous release of all its contents is considered as a major technological accident. Substances such as ammonia, chlorine, cyclohexane and butane are stored and handled in the chemical and process industry. The potential hazards associated with the storage of these toxic and/or explosive liquefied gases have been brought to the attention of the chemical industry and the general public on the occasion of past incidents that involved fatalities. Davenport (1983) reports on 71 different incidents, some of which involved more than 200 fatalities and extensive property loss. Prugh (1991) lists more than 50 major incidents, among them the storage catastrophe in Mexico City. This accident, involving the release of several thousand tons of liquefied petroleum gas (LPG), which is a mixture of hydrocarbons (mainly propane and butane) caused the death of more than 500 people. The release and spreading of toxic superheated liquid in Bhopal in 1984 caused at least 2,500 casualties (Banerjee 1987). Thus, accidental releases of superheated liquid following catastrophic failure have been responsible for widespread injury and property damage in the past.

Several surveys have been carried out to assess the probability of vessel failure. Smith and Warwick (1983) determined a catastrophic failure rate of $4.2 \times 10^{-5}$ per pressure vessel year, where catastrophic failure was defined as an incident severe enough to necessitate major repair. However, this data included not only storage tanks but also process equipment, such as steam generators. In another study, the probability of vessel failure resulting in a large, spontaneous release of stored propane was given as $1.3 \times 10^{-7}$/year (Basler and Hofmann 1992). It included fire as a possible cause. Sooby (1993) reported a failure rate of $3 \times 10^{-8}$/year for cold vessel failure, i.e., the immediate uncontrolled release of the total contents of a storage vessel due to spontaneous rupture. However, external events such as vehicle and aircraft impact were ignored. Vilchez et. al (1995) emphasized impact during transportation as a main contributor to accidents. In summary, it can be stated that complete failure of a pressure vessel rarely occurs, but when it does so, the consequences are potentially devastating.

The scheme of Fig. 2.6 shows a succession of possible events during an accident involving a vessel containing pressurized liquefied gas. It can only give a rough overview of explosion accidents, since the actual course of events quite often
2. Background and Motivation

Accidental Phase

- Collision, overpressure or impact
- Fire impingement
- Thermal rupture

Release Phase

- Instantaneous release: Complete disintegration of vessel
- Continuous release: Crack formation, pipe and flange break

Hazards Phase

- Projectile hazards
- Pressure blast wave
- Temperature fall
- Fire and explosion hazards
- Toxic clouds

Fig. 2.6: Scheme of events during failure of pressure vessel containing liquefied gas

represents an interaction of different phenomena and depends on various factors such as the condition of the fluids, the presence of ignition sources, the proximity to other storage or process facilities, the degree of confinement, the release rate and direction, the topography, the weather conditions, etc. The TNO Yellow Book presents various flow charts to identify the different modes of release of hazardous material (TNO 1992).

At this point it should be mentioned that different expressions are used in the literature to describe accidents involving the sudden generation and vaporization of superheated liquid. Rapid phase transitions (RPTs), vapor explosion, steam explosion, unconfined vapor explosion, explosive boiling, thermal explosions, catastrophic vessel failure, boiling liquid compressed-bubble explosion (BLCBE) and boiling liquid expanding-vapor explosion (BLEVE) are some of the various terms encountered (Reid 1983, Venart et al. 1993). They are to some extent defined differently, for instance it is not clear whether a vapor explosion implies ignition and a fireball or not.

Dense Gas Dispersion

As seen in Fig. 2.6, the complete collapse of a vessel and the instantaneous release of superheated liquid might lead to hazards such as projectile discharge and the emission of a destructive blast wave. This work was mainly motivated by the need for a more precise prediction of the spread of heavy gases originating from the liberation of superheated liquid. Vessel failure with release of toxic or flammable gases is characterized by the following subsequent stages:

- inertial expansion (driven by internal energy)
- gravitational spreading and liquid fall-out
- atmospheric dispersion

The initial phase of boiling and aerosol formation is clearly of particular importance for modeling the following consequences. Different approaches, of varying complexity, have previously been taken to predict the behavior of such denser-than-air clouds. Reviewing the research, Raj (1991) concluded that there was an urgent need to
conduct analyses, tests and further research on all aspects of source modeling. He stated that the hazard contours predicted by different models were mainly dependent on the assumed initial conditions. Thus, the error in source estimation far outweighed the error in estimating any other environmental parameter or even choosing a different model (Hanna et al. 1991).

The uncertainty in the entrainment of air into the two-phase cloud was probably the main reason why dense-gas dispersion models frequently showed poor agreement with experimental data (e.g. Havens 1992). Another important parameter in dispersion modeling was the amount of liquid forming a pool during a release. In a study to evaluate eleven dispersion models from different European countries, Amendola et al. (1992) found that there existed major differences in the results based on different assumptions, for example, whether a pool was formed or not, or the amount of liquid "rained out" compared to the amount of liquid forming an aerosol/vapor mixture. Progress towards a fundamental understanding of the initial stage of the bursting of pressure vessels was therefore found to be a precondition for an improved modeling of dense-gas dispersion.

### 2.4 Integral Studies of Unconfined Releases

Several studies on vessel failure involving pressurized liquefied gas were reviewed by Leslie and Birk (1991). In their overview, however, they considered only vessels failing due to or in the presence of a fire. This work concerns the initial phase of an unconfined vaporization of a volume of superheated liquid, that is vaporization of superheated liquid resulting from "cold" vessel failure with instantaneous loss of containment without the involvement of any chemical reactions. The first major experimental work on this type of release of superheated liquid was carried out at BASF, Germany. In a series of experiments, the rupture of small and some large metal vessels was investigated (see Hess et al. 1973, 1974, Maurer et al. 1977, Giesbrecht et al. 1981, for example). It was found that the time required for complete opening of the vessel was short compared with the time required for flashing. Expansion velocities were measured for the clouds which spread in a hemispherical pattern. Later, Hasegawa and Sato (1977) investigated the rupturing of glass spheres. Although these studies focused on the subsequent ignition and fireball expansion and analyzed the flashing process only to a limited extent, they provided information about pool formation, that is, liquid not vaporized during the initial phase and collecting on the ground. At a low flash fraction ($x < 0.2$ for propylene) almost all the liquid of a release fell to the ground and formed a pool, whereas at a high flash fraction ($x > 0.36$ for propylene) the released fluid remained in the air in the form of an aerosol cloud.

Bettis (1987) used a metal sphere opening into two hemispheres to investigate in detail the characteristics of the aerosol generated and moving outwards in a radial plane. The test fluids, the initial temperature, the fill level and the release volume were varied. Pettitt (1990) and Tickle and Webber (1991) conducted similar experiments by rupturing glass spheres. Despite some pressure and temperature measurements, the vessel contents were again considered as a "black box" because it was difficult to obtain information originating from inside the vaporizing volume. In view of the lack of sound knowledge of the driving heat and mass transfer mechanism, these "global"
views of boiling could only produce experimental findings in the form of empirical correlations.

Later, Schmidli and co-workers shattered a large number of spherical glass vessels containing refrigerants or hydrocarbons, releasing their contents as a vapor/aerosol cloud (Schmidli 1993, Schmidli et al. 1990, 1992, 1995). Data and models were obtained for cloud formation and cloud expansion for the inertia-driven stage (before gravitational and atmospheric spreading started to dominate). For the phase of cloud expansion, Schmidli (1993) observed a constant radius velocity of the spherically expanding cloud. By nondimensional analysis, he derived the following correlation for the radius velocity of the cloud \( u_{cl} \), which represented his experimental data and measurements of Tickle et al. (1991) fairly accurately, irrespective of its degree of generality:

\[
\begin{align*}
\frac{u_{cl}}{\mu_L} = 0.165 \times 10^{-3} \left( \frac{c_{pl} \Delta T}{h_{LG}} \right)^{1.8} \left( \frac{p_L}{\rho_G} \right) \left( \frac{\sigma}{\mu_L} \right)
\end{align*}
\] (2.12)

In addition to showing the effect of fluid properties, equation (2.12) expresses the almost quadratic increase of cloud expansion velocity \( u_{cl} \) with superheat \( \Delta T \).

Some close-up recordings indicated that boiling starts preferentially on the surface of the superheated liquid. Even though a fundamental description of vapor generation could not be given because of the difficulty in obtaining information originating from inside the liquid, a fairly extensive database could be established and the dominating properties and parameters were determined.

The observed expansion of the cloud resulting from a sudden release was compared with predictions obtained from simple models. These were based on isentropic expansion down to atmospheric pressure (see Hardee and Lee 1975) followed by a spreading phase during which air is entrained (see Opschoor 1992). However, the comparisons showed that these models inaccurately predicted the experimental results, for example, by overestimating the expansion velocity.

In summary, various integral release investigations made it obvious that a better understanding of the driving boiling mechanism responsible for the rapid phase transition in the superheated liquid is required. The influence of thermophysical properties on vaporization is of particular importance. Otherwise, attempts to scale-up results and/or apply them to other substances will contain major uncertainties.

2.5 Summary of Previous Findings

This chapter reviewed various previous findings with relevance to this work. Some more detailed investigations will be mentioned later in this text. At this stage, ten key points summarize the main conclusions:

1. Sudden depressurization or heating generates metastable or superheated liquids which pose the threat of serious vapor explosions for the immediate vicinity.

2. Accidental spreading of superheated liquid may create toxic/flammable clouds which are hazardous for an extended area around a release site.
3. Modeling of atmospheric dispersions resulting from such failures is sensitive to input regarding the initial conditions. However, information about the source term is limited.

4. Instantaneous and complete vessel failure is a rare but extremely serious accident. There is a need to achieve a better understanding of the phenomena occurring during vessel failure, such as the boiling mechanism, in order to prevent and mitigate such incidents.

5. The latent heat of a superheated liquid is insufficient to adiabatically vaporize the entire liquid (except for retrograde fluids). Depending on the superheat, liquid pools and/or an aerosol cloud will be formed after catastrophic vessel failure.

6. Both heterogeneous and homogeneous nucleation of superheated liquid lead to violent vaporization with mass-transfer rates that are orders of magnitude higher than in conventional boiling (e.g. bubble growth during pool boiling).

7. In the absence of nucleation sites in the bulk of a superheated liquid, vaporization is restricted to the free surface, which propagates as a boiling front into the metastable liquid.

8. Boiling fronts propagate at velocities that are orders of magnitude slower than the pressure rarefaction wave of a liquid, so a liquid layer may remain superheated for an extended period until it is reached by a boiling front.

9. A boiling front is characterized by a complex interaction of fluid motion, fine-scale fragmentation and enhanced vaporization which results in the ejection of a two-phase flow of high velocity.

10. An analytical description of boiling fronts and an evaluation of their influence on large-scale vaporization is still outstanding.

2.6 Outline of Present Work

The objective of this thesis is to investigate the general behavior of unconfined releases of superheated liquid. The work is intended to fill some of the gaps in current knowledge of catastrophic vessel failure. The results could contribute to the development of an improved overall assessment of routine hazards of liquefied gas releases, starting from the nature of the failure and resulting in a prediction of concentration contours as a function of time after the start of an accident.

The study focuses on the boiling mechanism and the thermophysical properties influencing the liquid-vapor transition of a volume of superheated liquid not in contact with nucleation sites. The propagation of boiling fronts will be investigated in particular, since these might play a dominant role in the vaporization process. In general, the data found in the literature for boiling front propagation are rather limited with respect to substances and experimental conditions. No data can be found that covers both boiling front propagation and expansion of unconfined clouds under corresponding conditions. This work is intended to narrow this gap by studying experimental releases from receptacles of different geometries.

The experimental set-ups and the four fluids investigated are presented in Chapter 3. The findings of the experiments, particularly the occurrence of boiling fronts, are
presented and discussed in Chapter 4. Various pressure, temperature, video and film recordings are documented. Chapter 5 and 6 present a proposed qualitative model of the observed boiling phenomena which leads to a correlation approach for modeling the vaporization. In Chapter 7 these results are then adapted and compared to previous experiments examining an unconfined spherical release of superheated liquid. This leads to suggestions for future work and conclusions in Chapter 8.
The objective of the experimental work was to investigate the physical processes occurring during the vaporization of an unconfined volume of superheated liquid, that is, during the period where the walls are no longer in contact with metastable liquid. As mentioned in the previous chapter, earlier experiments were based on the rupture of small-scale vessels, e.g. glass spheres. However, these investigations could provide only limited information originating from inside the vaporizing liquid volume. For example, the spherically expanding vapor cloud did not permit an easy examination of the nucleation mechanism from outside. However, such information is needed for a description of the formation of aerosol/vapor clouds.

A new approach was therefore taken, namely by assuming that under specified conditions boiling occurs only on the surface of a volume of superheated liquid. With this hypothesis, a large-scale release could be simplified to an investigation of small-scale one-dimensional phenomena, as illustrated in Fig. 3.1.

As shown in Fig. 3.1, the failure of the envelope of a tank filled with saturated liquid is considered. The bulk is no longer in contact with the walls and vaporization occurs only at the surface. The same phenomena as that occurring in such an extended volume of liquid should also be observable in just a section of it, for example in a glass receptacle whose walls do not offer any sites for nucleation. More specifically, it is assumed that boiling proceeds by a front propagating into the stagnant test fluid. Experiments were needed to verify these assumptions and to clarify whether the geometry or the surface characteristics of the wall would have an impact on the phenomena observed.

Two different release facilities were designed on the basis of this idea. The first set-up allowed releases from a pipe geometry and a study of the downward propagation of a boiling front. The greater part of the experimental work was performed with this facility. The other device, designed at a later stage of the project, allowed the opening of a circumferential cross section between two parallel glass plates. This resulted in a full 360° radial outflow from a flat cylindrical vessel and permitted boiling fronts advancing from the outside to the center of a volume of superheated liquid to be recorded. Both set-ups and their operation, including safety considerations, are presented in the subsequent sections. The test fluids and some of their thermophysical properties will be listed at the end of this chapter.

### 3.1 Experimental Set-Up for Releases from a Glass Pipe

The objective of the first set-up was to study the boiling front propagation of various fluids at different superheats and with various cross-sectional areas. The design criteria for the set-up were such that it should:

- not provide nucleation sites which would influence the boiling,
3. Experimental Equipment, Methods and Fluids

Fig. 3.1: Investigation of a large-scale release with total loss of containment by a small-scale release from the free surface of a glass pipe

- permit sudden depressurization to ambient pressure, that is, complete opening of the test section in a millisecond time scale,
- allow the investigation of propane, butane, water and R-134a in a range of absolute pressures from 1 to 10 bar corresponding to temperatures from -42 °C to 150 °C,
- allow a maximum degree of film recording and pressure and temperature measurements,
- allow use of differently-sized test sections.

These requirements resulted in the design outlined in Fig. 3.2.

The central part of this set-up consisted of exchangeable glass pipes (GP) having a length of 500 mm with inner diameters up to 80 mm. They were made of borosilicate glass and were sealed with flat rings of thermally stable rubber. The plane joints of the pipes were fixed between an arrangement of rings and flanges consisting either of stainless steel or aluminum. The rings at the top (RT) and the bottom (RB) allowed penetration by instrumentation, e.g. mounting of pressure transducers and thermocouples. The rings also provided various line connections to the glass pipe (GP). The bottom of the test volume was closed by a glass disk (GD) which permitted observation in the direction of the pipe axis. The top end of the pipe was closed by a rupture disk (RD). This could be opened by a new type of opening mechanism, which is described in more detail in section 3.1.2.

The pipe was surrounded by a temperature conditioning jacket (TCJ) or a box having
two opposite sides made of high-temperature-resistant glass (TRG), its other sides were of aluminum plates. This was designed to allow illumination and observation of the pipe test section. The clearance between pipe and box was filled with a transparent
liquid (water, ethylene glycol/water mixture, silicone oil depending on temperature) which had a similar refractive index to that of the pipe glass. Because of this and of the rectangular cross section of the box, the pipe contents (e.g. TL) could be visualized almost without optical distortion.

Tests were performed with dimethyl sulfoxide and a saccharose/water mixture, whose refractive indices are similar to that of glass, in order to reduce the optical distortion further. However, the slightly improved image quality could not justify the additional costs and complications arising from the use of these heat transfer liquids.

Forced convection driven by the pump of a connected thermostat (Haake DC3-K15) allowed heat removal or supply to the pipe via the transparent liquid. Depending on the heat-transfer agent used, the temperature could be adjusted in a range from -15°C to 150°C. As noted before, this temperature range could be established by using an ethylene glycol/water mixture, demineralized water or silicone oil in the temperature ranges -15 - 5°C, 0 - 100°C and 90 - 150°C, respectively. Because of the high flow rate of the liquid in the jacket and the insulation of the aluminum sides, the temperature field surrounding the glass pipe was fairly homogeneous with a measured difference between the minimum and maximum temperature of less than 1 K.

For experiments with initial temperatures below the dew point of the ambient air, the observation glasses at the bottom and the sides of the box were enclosed in thin chambers made of acrylic glass. Nitrogen (N₂) flowing through these spaces at a low rate prevented condensation of ambient humidity on the observation glasses.

The entire release facility could be rotated by 180° to allow different release directions. However, the experiments were always conducted from a vertical pipe with the rupture disk at the top. The effect of different release directions was checked by the second set-up that allowed circumferential releases.

The test fluid was placed in the glass pipe in such a way that it did not contact any "rough" solid surfaces. At the bottom, the test fluid was buffered by a denser, non-mixing liquid (BL), such as demineralized water in the case of propane as a test fluid. At the sides, the test liquid was only in contact with smooth glass surfaces. The column of test fluid placed this way did not show undesired nucleation, either on the walls or in the bulk. Further aspects of the suppression of undesired nucleation are given in section 3.1.3.

The test fluids were piped as gases and condensed in the glass pipe. For this purpose, the fluid was pressurized in its storage tank by its own vapor pressure, which was adjusted by a temperature-controlled bath surrounding the test-liquid container. This temperature was slightly higher than that of the heat transfer agent surrounding the glass pipe. The test liquid therefore vaporized in the pressure bottle and condensed within the glass pipe. While propane, butane and R-134a were heated in their transport bottles by placing them in an adequate open water basin, the water used as a test liquid was heated in a 3-dm³ pressure vessel placed in an oil bath. An immersion heater controlled by a thermostat was used for heating the oil up to 150°C.

The hose and tube connections were made of either PVC or PTFE, while only stainless steel pipes were installed for the water experiments. They were connected with Swagelok® fittings and controlled with Nupro® valves. A Nupro safety valve (SV) limited the maximum pressure in the pipe (GP), although the opening mechanism with its rupture disk (RD) already provided protection against overpressure. Other line
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connections to two solenoid valves allowed remotely-controlled emergency opening of both the vapor and the liquid space of the test section. Lines to a vacuum pump and to a nitrogen bottle allowed the absolute pressures to be adjusted from 0.05 to 11 bar.

3.1.1 Modifications to the Set-Up for Releases from a Glass Pipe

Modifications were made to the previously described set-up for various detailed studies. Figure 3.3 shows several accessories which were used only for investigating certain aspects.

The largest pipe diameter of 80 mm allowed other receptacle geometries to be installed inside it. A glass funnel provided a test section with decreasing cross-sectional area. At the bottom, it was connected directly to the outside via a line and a valve to allow separate drain of the funnel and the volume surrounding it. This geometry was used to investigate the influence of the cross-sectional area on the velocity of the boiling front. Since the funnel was not as pressure resistant as required, it had to be placed inside the larger 80-mm pipe. During experiments, buffer liquid filled the space between the pipe walls and the funnel, as well as the lower part of the funnel. The cross-sectional area of the funnel decreases at the bottom to approximately 1/50th of the value at the top ($d_{\text{top}} = 70$ mm, $d_{\text{bottom}} = 10$ mm, height = 150 mm). Besides the funnel, a flattened pipe section (rectangular cross section in field of view: 60 x ca. 4 mm, height: 100 mm; see Fig. 3.3) and a small glass pipe ($d = 14$ mm) were also installed and operated inside the large pipe in a similar manner.

For a few experiments, a mirror inclined at 45° was placed within the volume of the buffer liquid. In comparison to filming through the glass disk at the bottom, this reduced the distance between camera and boiling front considerably and allowed closer inspection of the vaporization in the downstream direction.
To determine how homogeneously the test liquid could be heated in the glass pipe, the glass at the bottom of the pipe was replaced by a steel disk onto which a slideable thermocouple had been placed. This allowed the temperature along the pressurized pipe to be measured over the whole cross section. It was found that a typical time of 10 min between end of filling and release was sufficient to obtain a temperature gradient of less than 1 K from the top to the bottom of the test-liquid volume. Since the temperature in the test liquid could not be recorded during an experiment (see following subsection 3.1.4), it was thought that the thermocouple should be moved out of the superheated liquid prior to each experiment. Unfortunately, this procedure did not allow proper boiling front measurements because small amounts of test liquid continued to stick to the thermocouple even after it had been withdrawn from the test liquid down into the buffer-liquid zone. This resulted in vapor generation in the buffer liquid during the depressurization, thus precluding undisturbed propagation of boiling fronts. Therefore, the temperature field in the bulk was measured only in a few tests independently of actual experimental runs. It was found, however, that the temperature in the buffer liquid deviated by less than 1 K from the temperatures in the test liquid. The temperature of the buffer liquid was therefore taken to be the actual temperature of the test liquid. Other ways of inserting moveable thermocouples through the glass wall or from the top were thought to be unnecessary or too complicated.

The 0.1 dm$^3$ glass cylinder of Fig. 3.3 allowed the test liquid to be stained. Coloring agent was injected into it by a needle and mixed with the condensing test liquid. In order to prevent solid impurities from entering the test section, the drain of the coloring receptacle was positioned at a medium height in the center of the glass cylinder, since most of the impurities collected either at the bottom or at the top of the still liquid. The colored liquid could flow into the glass pipe through a separate line and mix there with other test fluid.

In some experiments with 80-mm pipes, an orifice (OR) with an opening of 30 mm was mounted directly beneath the rupture disk. It allowed the effect of an elevated pressure downstream of the boiling front to be investigated (Fig. 3.2).

A two-meter-long acrylic glass pipe of 80 mm internal diameter could be placed on top of the rupture disk for making measurements of the two-phase flow velocity at different distances from the vaporization zone. Movie recordings allowed the propagation of fine droplets to be traced.

3.1.2 Opening Mechanism

In order to achieve instantaneous depressurization, the exit of the pipe had to permit "rapid" opening. Conventional valves attained opening times only of the order of several hundredths of a second and thus limited the mass flux rate during opening time to an undesirable degree. Therefore, an opening mechanism based on the principle of a rupture disk became necessary. This allowed complete opening of even large cross-sections within milliseconds or even less, since, in the typical materials used, a crack spreads roughly at the speed of sound. Since the use of glass or brittle elements would lead to an undesired production of multiple fragments, metal was chosen as the disk material.

In its simplest form, a rupture disk is a metal diaphragm fixed between two flanges and pressurized on one side. Opening can be initiated by cutting it with a blade or a needle.
However, complete clearance of the cross section can be achieved only within a narrow pressure range. The upper limit of this range is given by the pressure of spontaneous rupture. The lower limit is set by the toughness of the metal: at low pressures a blade penetrates the diaphragm without initiating an opening of the entire flow area. Since these limits varied from one run to another in tests, the simple technique based on pricking the metal diaphragm did not lead to reliable opening of the system. A mechanism which permitted reliably-triggered full opening over an extended range of pressures was necessary.

To satisfy this need, a new mechanism was developed. It exploited the fact that the maximum tension in a loaded diaphragm placed between two flanges is always reached at the flange circumference. This maximum value increases overproportionally with increasing flange diameter. Thus, a small enlargement of a circular flange diameter leads to a major increase in tension of the rupture sheet. An opening mechanism was developed on the basis of this observation and of a series of time-consuming tests. Its principle is shown in Fig. 3.4, where three stages of the opening process are outlined.

The metal sheet is fixed by two rings (1,2) on a counter-flange (3). Only the cross section enclosed by the inner ring (2) is pressurized, and the diaphragm (4) is supported by the rounded edge of this ring (step §). Upon triggering, the inner ring (2) lifts off, leading to an increased pressurized area of the diaphragm (step ②). This in turn leads to increased tension at the circumference of the diaphragm, which is now supported at the sharp-edged outer ring (1) which cuts it and opens the cross section (step ③). In the actual experiments, brass sheets with thicknesses ranging from 0.05 to 0.15 mm were used, although other materials such as aluminum could have been employed as well. For an 80-mm internal diameter of the inner ring, a controlled opening between 2 and 14 bar could be achieved.

The advantages of the above mechanism can be summarized in the following:

- Independently of the inside pressure, opening is possible upon mechanical activation over a certain range of containment pressures.
- The simple mechanism works reliably and creates round openings.
- The double-ring arrangement eliminates the problem in which the blade merely penetrates the diaphragm without opening the entire flow area.
• The mechanism operates independently of orientation and permits a comparatively smooth opening without any initial pressure increase in the containment.

• No obstacles remain in the flow cross section (e.g. no knives, blades).

• The actual tearing period even for "large" cross sections is reduced to less than a millisecond.

• Instead of expensive commercial rupture disks, ordinary foil made of sheet metal can be used. This reduces the cost per opening by approximately two orders of magnitude.

This novel opening mechanism was granted a registered patent (Reinke 1995).

The mechanism outlined in Fig. 3.5 was designed to use the above principle for opening a receptacle. It locked and then released upon triggering the inner ring. This action was based on a detent which was levered out by a lift-cylinder-driven wedge. To avoid electrical installations near the release zone, the cylinder was driven by pressurized nitrogen from a pressure flask through a remote solenoid valve. The detent was connected to one side of a swinging arm holding the inner ring and could be tightened by two screws. The opposite site of the frame was fixed by long metal beams connected to a distant pivot. When the detent was unlocked, the frame could swing out in an almost parallel manner without using a complicated mechanical structure for guidance because of the distant position of the pivot.

3.1.3 Suppression of Undesired Nucleation and Filling Procedure for Test Fluids

In general, the experiments were conducted in such a way that test fluid investigated at small scale was subjected to the same experimental conditions as those expected in an extended volume of superheated liquid, e.g. in a storage tank. This required that the materials contacting the test fluid did not offer nucleation sites, i.e. locations from which bubble growth could start. However, even experiments with a smooth, untreated glass surface provided gas-filled cavities from which nucleation would start, particularly in the case of highly superheated liquid and/or non-wetting fluids. Thus, simply filling test liquid without further treatment into a glass receptacle caused undesired heterogeneous nucleation on the walls upon sudden depressurization. A new elaborate preconditioning procedure became, therefore, necessary.

Buivid and Sussman (1978) investigated the superheat of liquids attainable without occurrence of flashing in the presence of solid, gas-free particles. They showed that contact with solid surfaces causing changes in the wetting angle reduced the attainable degree of superheat by only a few degrees. They concluded that it was not necessary to remove impurities but rather to eliminate their gas-filled cavities. In fact, impurities were visible in some of our own experiments, but they did not cause nucleation because they had been previously degassed. On the contrary, filtering the liquid during filling (Nupro TF filter retaining particles exceeding 0.5 µm) proved insufficient in avoiding undesired nucleation, because it did not eliminate the gas in cavities on the glass.

Beside filtering, treatment with ultrasound was tested as a means of eliminating gas-filled cavities. This method is successfully used to clean even small-sized pores, e.g. of...
Fig. 3.5: Mechanism for lifting rupture disk support
(Nitrogen moves piston which levers out detent by pushing a wedge. This releases the beam which is connected via two screwed shanks to the arm holding the inner ring.)

Medical equipment. For test purposes, an ultrasound vibrator was placed inside the water-filled glass pipe. However, the device (Telsonic, resonator RS-36-30, generator RG-36-150, 300 W) proved unable to visibly remove any gas inclusions, except on its own metal surface.

Finally, a new preconditioning method was developed and used for denucleating the test section. Its principle was to:

- empty all cavities by vacuuming,
fill these cavities with a buffer liquid (which fills out the test volume completely) by pressurizing the buffer liquid during introduction of test fluid,

introduce the test fluid and simultaneously remove the buffer liquid without exposing the walls of the test section to a gas atmosphere.

This approach resulted in the following experimental procedure. In order to eliminate impurities from the walls, the pipe was brushed carefully and rinsed with demineralized water. Afterwards, the test section was sealed with a diaphragm and almost completely filled with a liquid that was denser and had a higher boiling point than the test substance. This liquid did not mix with the test fluid. These requirements were fulfilled, for example, by using demineralized water in the case of propane as the test fluid. A vacuum pump was then used to evacuate the contents of the pipe down to 0.05 bar. This emptied the remaining gas-filled cavities of the glass, and subsequent pressurization with the test fluid filled them with liquid or covered them with a liquid film. The glass was thus unable to provide any further nucleation sites for the test liquid.

Another source of nucleation sites was the buffer liquid at the bottom of the pipe. During the filling process, this layer collected some impurities which could not be completely excluded by filtering. The contamination collecting at the surface of the buffer fluid was of particular concern since it remained in contact with the superheated test liquid. Before filling with test liquid, therefore, the top layer of the buffer liquid was sucked off by a small pipe (TO in Fig. 3.2) reaching into the glass pipe, and impurities floating on the buffer liquid were carried away. During this procedure, the buffer liquid was continuously replaced by liquid from the device via the flexible connections (CC). This vessel could be shifted in the vertical direction to produce a level change in the test pipe (GP) without using any pumping device.

The pipe was subsequently filled with test fluid. In order to avoid contamination, the fluid was introduced into the pipe as superheated vapor originating from the heated storage vessels. As the test liquid condensed and collected, the buffer liquid was lowered using either the device with the flexible connections (CC) shown in Fig. 3.3 or by releasing it through a valve. In its final position within the pipe, the test liquid was only in contact with buffer liquid and with glass walls which had been continuously covered by liquid since the initial vacuuming. So there was no way that gas or vapor-filled cavities could form on the glass surface exposed to the test fluid.

After the desired amount of test liquid had accumulated, for example to a height of 15 cm, it was allowed to rest for at least ten minutes in the glass, in order to reach the temperature of the conditioning fluid. Since the pressure had to be maintained during this time but no further condensation was to occur, either the pressure of the storage flask was reduced or the pipe was pressurized with nitrogen. By again lowering the level of the buffer liquid, the test liquid was brought into its final position within the glass pipe and the experiment could be triggered.

For certain investigation, glass receptacles (flattened pipes, funnel) were placed inside the glass pipe as already mentioned. These could be emptied through a separate line at their bottom. By opening this line, the glass receptacle could be completely emptied and filled with test liquid (TL) while the level of the buffer liquid (BL) surrounding the receptacle would drop down just to the upper rim of the receptacle. The receptacle
The above general procedures for "denucleation" and filling of the test section had to be adapted for each test fluid because of their different boiling points and densities. For example, for water it proved impossible to find a reasonable buffer fluid that had both a higher density and a higher boiling point. The necessary preparations required for the different fluids are summarized in Table 3.1.

Even though the above technique allowed boiling fronts to be observed in a large number of cases, there were still a few occurrences of undesired nucleation on the glass walls or at the buffer-liquid/test-fluid interface. Particularly at "high" superheats (see Table 4.1), unwanted bubble growth distorted the boiling front propagation, and these experiments could not be used for the present analysis. Often, undesired nucleation on the glass wall was observed in experiments with water, while almost no unwanted nucleation occurred in experiments with refrigerant R-134a.

3.1.4 Measuring Methods and Data Acquisition

As already noted, little is currently known about the very first stage of a sudden release of superheated liquid. This is partly due to the highly transient and explosive character of the process. Therefore, the main feature of an improved experimental investigation had to be a robust and fast-acting measuring and data storage system. This was required for recording the following:

- the mechanism of boiling front propagation,
- the velocity of advancing boiling fronts,
- the velocity of the two-phase flow stream,
- the temperature history of the superheated liquid,
- the pressure history at up- and downstream locations of boiling fronts,
- droplet sizes.

The appropriate visualization, measuring and storage devices for these tasks are presented in the following sections.

At this point, it should be remarked that many other aspects of the process could have been investigated in detail. However, the phenomenon of boiling at the free surface had rarely been studied before so that the relevant data and the resulting theory are rather fragmentary. At the beginning of the present project, it was simply assumed that boiling fronts might possibly influence the vaporization following catastrophic vessel
### Table 3.1: Preparations for limiting nucleation to free surface of liquid

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Buffer Liquid (bottom insulation)</th>
<th>Denucleation of Glass Walls and Buffer Liquid</th>
<th>Filling and Conditioning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane</td>
<td>water at test fluid temperature</td>
<td>vacuuming to 0.05 bar of the glass receptacle completely filled with water at ( T &lt; 30 , ^\circ\text{C} ), followed by heating to test fluid temperature at 1 bar</td>
<td>condensation of test fluid on top of water and simultaneous lowering of water level</td>
</tr>
<tr>
<td>Propane</td>
<td>water at test fluid temperature; at ( T &lt; 0 , ^\circ\text{C} ): salt water</td>
<td>vacuuming to 0.05 bar of the glass receptacle completely filled with water at release temperature of test fluid</td>
<td>condensation of test fluid on top of water and simultaneous lowering of water level</td>
</tr>
<tr>
<td>R-134a</td>
<td>R-134a cooled to ( T &lt; T_{\text{sat,1 bar}} = -26 , ^\circ\text{C} ) by miniature heat exchanger at bottom</td>
<td>vacuuming to 0.05 bar of the glass receptacle completely filled with water at ( T &lt; 30 , ^\circ\text{C} ), followed by heating to test fluid temperature at 1 bar</td>
<td>condensation of test fluid which collects at bottom and simultaneous outflow of water from the top of test fluid</td>
</tr>
<tr>
<td></td>
<td>R-113 at test fluid temperature</td>
<td>vacuuming to 0.6 bar of glass receptacle completely filled with R-113 at ( T &lt; 20 , ^\circ\text{C} ), followed by heating to test fluid temp. at 1 bar</td>
<td>condensation of test fluid on top of R-113 and simultaneous lowering of R-113 level</td>
</tr>
<tr>
<td>Water</td>
<td>water at bottom cooled to ( T &lt; T_{\text{sat,1 bar}} = 100 , ^\circ\text{C} ) by miniature heat exchanger or by simultaneous in- and outflow</td>
<td>vacuuming to 0.05 bar of glass receptacle completely filled with water at ( T &lt; 30 , ^\circ\text{C} ), followed by heating to test fluid temperature at 1 bar</td>
<td>condensation of test fluid on buffer water, simultaneous outflow at bottom and water replacement by condensed water at top</td>
</tr>
</tbody>
</table>

failure. Besides, it was not even known how these fronts might be investigated experimentally (The fundamental work of Hill (1991) was located after our own first experimental releases). Therefore, the objective of the experiments was to obtain a basic understanding of the boiling mechanism and to determine the key parameters influencing it. After the first successful tests, it was decided to focus on the period of quasi-steady boiling front propagation of different test fluids. Additionally, the influence of superheat and of the release geometry was to be investigated. These factors seemed to be of major relevance for the vaporization of an extended volume of superheated liquid and of major importance for practical problems. Additionally, they seemed to be accessible with available or designable hardware.

Other detailed studies could have addressed additional factors, such as the initiation of explosive boiling, the temperature distribution in the vaporization zone, or the characteristics of the two-phase flow region. In fact, due to the complex interactions at the boiling front and their consequences for large-scale unconfined releases, a multitude of parameters and mutual influences could have been investigated. However, this would have been beyond the financial scope and time frame of the project. Particularly the development of new experimental techniques (denucleation of glass, opening mechanism, droplet-size measurement, circumferential release facility)
required very time-consuming efforts. For these various reasons, only the six basic aspects listed at the beginning of this section were analyzed. Some further technical limitations of the measurements are described in the following sections.

**Visualization Instruments**

Flow visualization was realized by means of high-speed movies and video recordings. A Hycam high-speed camera with a maximum rate tuned to almost 8000 full frames per second was used, whereas the video camera (CCD-Panasonic NV MS 95 E) allowed a frequency of 50 frames per second with a shutter time of 1/16000 s for sharp imaging. In a few instances, a second camera (CCD-Panasonic F10) was used for parallel recordings of the boiling front and the two-phase flow region. Still photographs were taken with a Nikon F801S camera.

The majority of experiments was conducted to record a number of intermediate time steps for determining the velocity of boiling fronts under different conditions. This did not require the kind of temporal resolution provided by the high-speed camera, so most of the experiments were recorded with the video camera. Quite apart from being much cheaper, the video allowed an immediate analysis to be performed of the recorded experiment, whereas a week usually elapsed after recording before the movies could be viewed because of the external processing of the film. The video proved to be particularly advantageous during the very time-consuming period required for developing the experimental techniques. In addition, the single video frames could be digitized, saved to a file and printed (with a Panasonic VCR 7330 connected to a PC-based frame grabber). With the date and time faded into the video, the prints permitted easy listing and retrieval of the experimental runs.

The movie recordings were made where a high frame frequency and improved image resolution were required. Special high-speed film with a reinforced base capable of withstanding the forces acting during acceleration and deceleration, rated 200- or 400-ASA, black and white, was used (30 m Eastman 7222 or 38 m Kodak RAR 2498, respectively). Since the film accelerated asymptotically towards a final frequency during recording, the momentary frame rate had to be recorded to allow a precise analysis. For this purpose, a light-emitting diode within the camera marked adjustable time steps on the film. For detailed studies, single frames of the 16-mm negative films were enlarged to photos and afterwards scanned and transformed into electronic files. A 38-m film gets recorded at a final frame rate of 8000 frames/second in about 0.9 s and results in almost 5000 frames. The recording had to be precisely synchronized with the release. As was described in section 3.1.2, the opening of the disk was triggered by a solenoid valve which pressurized a piston. This led to a certain delay between triggering the valve and the actual opening of the rupture disk. A self-made electronic device with a relay was used to open the valve at will, either before or after starting the camera. This device switched a 220-V line within a time range of one second before and after starting the camera. By adjusting two potentiometers, the desired moment of recording could be controlled. The video tapes required no special synchronization to the experiments as the recording time was practically unlimited.

A spotlight with a 2500-W quartz bulb served as the illumination source (Strand Lighting Alto 8/16) and could be used from a distant, safe position (3 m). The best image quality for both the movie and video recordings was obtained by back-lighting
the object through the temperature-conditioning jacket and using a light-diffusing sheet of paper.

**Data Acquisition System**

The sequences of temperature and pressure signals obtained during the experiments had to be sampled, stored and displayed for immediate and later analysis. Two data acquisition devices were used for this purpose: a digital storage oscilloscope (LeCroy 9314M) and a PC-based data acquisition system (PC + Keithley 500).

The digital storage oscilloscope (DSO) had four channels with a memory of 50,000 data points each and a maximum sampling rate of 100 MHz. The maximum time resolution of the system was fixed by adjusting the duration of recording. The 8-bit analog/digital converter allowed an accuracy of < 1% of the full scale. The storage was triggered by temperature or pressure signals attaining adjustable changes of negative slope.

Data could be transferred via the RS-232-C interface to a PC or stored directly on an internal 3.5" floppy drive in DOS format. Different settings of the oscilloscope could also be stored on this disk. A self-made compression program allowed the size of the recorded files to be reduced by filtering out those points which deviated from the previously stored values within an adjustable range. The ASCII-formatted file could then be conveniently imported to a spreadsheet for further analysis. For documentation purposes, hard copies of the screen showing the settings and the results were plotted on paper immediately after each experiment.

A PC-operated system was used for data acquisition at lower sampling rates (< 62.5 KHz). It consisted of an external unit equipped with two analog/digital converters offering a total of 24 differentially-ended channels. A card insert in a DOS-PC and a data acquisition software (Asyst 3.0) allowed the system to be configured and operated. The software and the various module combinations allowed fairly flexible adjustment to the experimental requirements. In principle, the system allowed completely automated experiments to be performed. For reasons of convenience, however, the use of the system was limited to long-term recordings, e.g. monitoring the temperature of the buffer liquid, the temperature-conditioning jacket and the ambient temperature.

**Temperature Measurements**

An exact modeling of the observed boiling process must be based on a precise knowledge of the thermophysical properties of the test liquid. These, in turn, depend partly on the temperature which must, therefore, be determined as precisely as possible. In general, it would have been desirable to obtain as much data as possible, e.g. in the form of a high resolution temperature field across the boiling front. However, in the case of surface boiling of superheated liquid, the possibilities of obtaining temperature readings with the available equipment are rather limited.

The main reason for this limitation is that any solid transducer placed into metastable liquid serves as an artificial nucleation site. At best, it just records the local saturation temperature of the liquid. In addition, the violent boiling requires a fairly robust layout (thick wires). As our own calculations and experiments have shown, this would have
increased the response time of the TC to such an extent that the thermocouples would have been incapable of tracing the temperature transients. Besides, as Hill (1991) mentioned and as is shown in Chapter 5, the particularly interesting thermal boundary layer between the highly superheated liquid and the vapor space is much thinner than the diameter of a sufficiently strong thermocouple. Therefore, the recordings were limited to determining the temperature of the test liquid prior to release. In addition, the temperatures of the vapor space above the test liquid, of the conditioning liquid, of the test liquid and of the ambient air were measured.

The thermocouples used were 1 mm thick, K-type chromel alumel thermocouples with a sensitivity coefficient of 41 μV/K. The various thermocouples were connected to a multichannel sampling thermometer (Keithley 740) with a digital display, or to the data acquisition board of the PC. The readings from the digital display were compared to readings from two officially-calibrated mercury thermometers. This allowed correction curves to be established for the range from -50°C to 160°C, which resulted in an accuracy of the temperature readings of better than 0.5 K.

No special efforts were made to perform temperature measurements in the two-phase flow region. Besides the problem of provoking nucleation and the difficulties in measuring highly transient temperatures, the release of the rupture disk would have destroyed any fragile sensing device. Consequently, in the analysis it was assumed that the two-phase region over the length of the acrylic glass pipe, which was about 2 m, is at saturation at the conditions prevailing near its origin. Ways of measuring temperatures optically (e.g. infrared light, holographic interferometry) were evaluated, but were found to require an unjustifiable amount of work and funding for their successful application.

**Pressure Measurements**

While the temperature in the superheated liquid was known or assumed to be the initially measured temperature, the pressure of the metastable liquid during the release could not be predicted a priori. For this reason, and because the pressure determined the superheat in the test liquid, it had to be recorded with high temporal resolution prior to and during boiling front propagation.

The pressure generated by the boiling front was measured up- and downstream of the rings placed at the test pipe ends. To prevent undesired nucleation in the superheated liquid, the lower pressure transducer was mounted in the buffer fluid below the test liquid. It was assumed that this arrangement would not significantly modify the signal originating from the boiling front (e.g. by damping or reflection at the interface). A Kistler 603b piezoelectric transducer was used for this location because it was suitable for contact with water. Another reason for placing the pressure transducer in the buffer liquid was its sensitivity to temperature changes. The flashing of superheated liquid at the surface of the transducer would have caused extreme errors in the pressure recordings because it is accompanied by temperature drops of up to 80 K in our experiments. A transducer with a natural frequency of 400 kHz and an operation range of 0-200 bar was sufficient for the measurements. The charge signal provided by the piezoelectric cell is proportional to the pressure change and was converted by a Kistler 5005 charge amplifier to a voltage and then sampled with the DSO. The pressure drop triggered the data storage in the DSO.
3. Experimental Equipment, Methods and Fluids

A second transducer, flush-mounted in the upper service ring, measured the static pressure in the vapor/aerosol space. This Kulite XCQ-062-17A transducer was sufficiently insensitive to temperature changes, but was not suitable for use in water. It could therefore be used only for propane, butane or R-134a runs. This miniature strain-gauge type transducer had a natural frequency of 1.6 MHz and could be excited with the maximum direct current from a 7-V battery. The voltage signal was filtered (cut-off frequency 300 kHz) and amplified by a Princeton Applied Research Model 113 S/N amplifier. The DSO was again used for data sampling.

The Kulite strain-gauge transducer measured the absolute pressure. This allowed the pressure to be accessed directly on a digital display. The piezoelectric cell could only measure pressure variations of limited duration because of its inherent cell discharge. However, although the discharge time constant was sufficiently long for our experiments, it required pre-setting of the device several seconds prior to each experiment.

The pressure transducer readings were compared with the measurements of a high-precision barometer operating at around 1 bar (Wallace & Tiernan FA 129) and with a calibrated mechanical pressure gauge (Kobold Manometer 1875) which showed an accuracy of about 2% of the measured value for both transducers.

Droplet Size Measurements

In the analysis of accident scenarios where superheated liquid is released, it is required to predict the size of the droplets created. This assessment is of paramount importance for accurately modeling the dispersion of the aerosol/gas cloud that is generated. The analysis of droplet sizes also relates to the issue of the pool formation by spilled liquid, which must also be considered in modeling gas dispersion originating from releases of liquid.

Thus, beyond a study of vaporization at the boiling front, it is necessary to obtain data on drop sizes and drop velocities. In this work, a simple experimental technique based on the principle of paper witness cards was used. In this technique, the impaction diameter of a stained droplet impinging on paper allowed the initial diameter of the droplet before impingement to be determined. Superheated droplets evaporated immediately after contacting the paper. The diameter of the colored spot remaining on the paper gave information about the initial droplet size. A collection of spots on paper could be converted to the original droplet sizes by using a predetermined spreading correction factor.

The paper stain technique was used to obtain data at an early stage of this work and to check the feasibility of other more sophisticated techniques for obtaining data during a very rapid and transient process. Beside its simplicity, the other advantage of the paper method was that it allowed a spatially distributed matrix of small paper sheets to be arranged. These would allow to study in an uncomplicated manner the expanding aerosol cloud and the liquid fall-out at various points. The costly direct measuring techniques (e.g., pulsed laser holography, high-speed movie recording with synchronized laser illumination) only allow measurements in small volumes during a single experiment. Additionally, the more sensitive methods are usable only under laboratory conditions.
As it turned out, the shortcomings of the paper technique were a lack of precision, particularly for small drop sizes. In addition, the calibration did not completely cover the range of velocities that occurred in the experiments and the paper technique does not provide the time history of the droplet population unless moving orifices are installed. Thus, the paper sheets recorded the integral results of an experiment.

In a first step, a spreading factor relationship had to be established which related the measured spot diameters produced on paper to the original drop diameters. The experimental set-up used for this purpose and the required analysis with its limitations are described in Appendix A. The calibration experiments, which were performed only with propane, produced the following correlation:

\[ d_{\text{drop}} = 0.310 d_{\text{stain}}^{0.781} \]  
(3.1)

In the present work, the paper technique was applied only to releases from pipes. Since paper held in the escaping high-speed jet would have been immediately covered by the massive concentrated impingement of many drops, the resulting blurred paper would have been useless. So the paper was rotated at high speed to distribute the impingement from a single run over a larger area. An orifice additionally reduced the density of the impinging drops. Since the rotational speed of the wheel used for calibration (Appendix A) was limited by dynamic imbalance, a new rotating device for collecting drops had to be designed. This and the complete arrangement are shown in Fig. 3.7.

![Fig. 3.7: Rotating paper disk](image)

The disk, rotating at ca. 450 rpm., carried paper sheets. These passed in front of the rectangular orifice (2 cm x 7 cm) once about every 0.13 s. This was the typical duration of a single release with boiling front propagation. Video recordings of a scale placed at the upper side of the aluminum disk allowed individual impingements to be related to a specific instant during the release.

Information about the travel velocities of drops can be obtained from macroscopic views of the release process (expansion of aerosol/air cloud). Other studies showed that the travel velocity of the leading drops in an expanding vapor/aerosol mixture is similar to the expansion velocity of the cloud (Bettis 1987, Schmidli et al. 1990).
3.2 Experimental Set-Up for Circumferential Releases

The second set-up was designed to study boiling front propagation in a geometry closer to that of the catastrophic vessel failure under consideration. The main purpose of the second set-up was to check whether boiling fronts propagate from the surface to the core of bulk superheated liquid and if this propagation is independent of the direction of gravity. As in the case of releases from pipes, only depressurizations to 1 bar ambient pressure were planned, since this is most similar to the vessel failure in question and was easy to realize in experiments. The other design criteria for the set-up were that it should:

- not influence the boiling in the central part by providing nucleation sites,
- permit sudden depressurization to ambient pressure,
- allow investigation of propane in a range of absolute pressures from 1 to 10 bar corresponding to temperatures from -42°C to 30°C,
- allow a maximum degree of film recording,
- allow a full 360° circumferential unobstructed release.

These requirements resulted in the release principle outlined in Fig. 3.8. The corresponding detailed design is shown in Fig. 3.9.

Two circular glass plates were placed opposite to each other in parallel. They were held in place by stainless steel flanges, which in turn were suspended in a structure of steel bars. These had to take up the force acting on the two glass-flange sections of the set-up. For a test volume pressurized to 10 bar, this resulted in a force of about 80 kN. The circumferential opening between the steel flanges was closed by an aluminum ring. This could be slid away, as shown in Fig. 3.8, to open the flat cylindrical volume filled with superheated liquid. A long swinging suspension allowed an almost parallel guidance of the ring. To obtain the sudden force required to move the ring, a weight
Fig. 3.9: Experimental set-up for releasing superheated liquid in the radial direction
was dropped by triggering an electromagnet. The falling weight was connected by a 
rope to the swinging arm, allowing it to move suddenly. A complete opening of the 
discharge cross-section occurred in less than 0.02 s.

Initially, an attempt was made to close the circumferential release cross section by 
rubber elements pressed together by a steel band under high tension. Upon triggering, 
this steel band should open and release the rubber elements. However, this technique 
did not allow sufficient sealing or required excessively heavy stressing of the bands and 
rubber elements. The aluminum ring described above moveable in the axial direction 
was therefore chosen as the opening mechanism. The main problem in using this ring 
was that the rubber seals became blunt due to the violent cold stream of released fluid, 
so that the ring did not open properly, i.e. canted. Even a more advanced guiding 
structure could not prevent this problem, so that finally the rings were coated with a 
special rubber grease prior to each experiment.

The glass disks (Schott Maxos®) with a diameter of 25 cm allowed an overpressure of 
10 bar. Larger diameters allowing the same pressure were not available at a justifiable 
price. The required space for sealing and fixing with flanges limited the field of view to 
a diameter of 22 cm. The flanges holding the glass disks were closed by acrylic glass 
disks forming a cavity for the temperature-conditioning fluid. This arrangement 
allowed the temperature on the outside of the glass disks to be adjusted. A 
conditioning liquid with a homogeneous temperature profile was desired, but when the 
temperature difference between the ambient and the test fluid was significant, even 
insulation did not eliminate the temperature gradient due to the heat losses through the 
various metal flanges. A more sophisticated temperature conditioning system would 
have been expensive. The initial temperature in the liquid was therefore adjusted 
essentially to be the ambient temperature.

Another cylindrical chamber was fitted on top of the acrylic glass disks of the 
temperature-conditioning cavity (Fig. 3.9 shows only one chamber even though 
chambers were placed on both sides of the release volume). For experiments with 
initial temperatures below the dew point of the ambient air, this space was filled with 
nitrogen and thus prevented condensation of ambient humidity on the observation 
glasses. The other reason for installing these cylindrical chambers was to keep the 
aerosol fog released out of the field of view.

Since the conditioning liquid was transparent, the circular test section could be 
illuminated from one side and observed from the other. The set-up was placed in an 
upright position so that the expected circular boiling front would face different 
directions of gravity.

The preconditioning of the test section between the two glass disks was similar to that 
used for the experiments with the glass pipes. For denucleation, the gas and vapor 
inclusions in the cavities of the glass were eliminated by vacuuming and subsequently 
replaced by a buffer liquid. Test fluid was then introduced and buffer liquid 
simultaneously removed without exposing the receptacle walls of the test section to a 
gas atmosphere. As a consequence of the vacuum created prior to each experiment, the 
flanges had to support the glass disks on both sides. The width of the outlet cross 
section was therefore smaller (1 cm) than the distance between the two glass disks (2.5 
cm), resulting in a narrowing of the outflow passage.
In contrast to the pipe experiments, where there was always an interface between the buffer and the test liquids, no interface was left inside the test section for the circular-release experiments. Thus, there was no possible accumulation of impurities at such interfaces. Nucleation along the circumference of the steel flanges could not be prevented anyway, and started there instantaneously after opening, as the experiments showed. It should be emphasized that in the experiments with a circular release, the test liquid was not condensed but poured directly into the release facility as liquid without any special precautions regarding impurities. The storage flask containing the test fluid (propane) was emptied from the bottom and not from the top as in the case of pipe experiments.

As already remarked, the main goal was to visualize the propagation of boiling fronts in a circular geometry. The data acquisition was therefore limited to only a few basic parameters. The same equipment that was described for the pipe experiments was used for this purpose. The temperatures were measured at the top and bottom, or with the slideable transducer in the core of the liquid prior to the experiments. The pressure transients were not recorded during these experiments since, in contrast to the experiments with pipes, the pressure transducers could not be placed inside the buffer liquid. The experimenters thought of installing a small glass tube filled with buffer liquid inside the test section. This pipe would have been connected to a pressure transducer mounted at the bottom of the flange. In this way, the pressure in the core of the superheated liquid could have been measured through the column of buffer liquid without causing nucleation. Due to limited manpower, however, this technique could not be applied.

### 3.3 Release Location and Safety

Due to the properties of the test liquids and the character of the experiments, various safety precautions had to be taken. The experimental work involved the following hazards:

- **Propane and butane vapors are flammable/explosive when mixed with air.**
- **Propane, butane and R-134a vapors are denser than air.**
- **Preheating the test fluids (prior to experiments to allow later condensation in the test facility) may cause an unacceptable overpressure in their transport or storage containers.**
- **Vaporizing propane and R-134a at ambient pressure can attain temperatures below -42°C and -28°C, respectively.**
- **Vaporizing water at ambient pressure and the heat transfer agent attain temperatures above 100°C.**
- **Sharp-edged metallic rupture disks are ejected from the opening mechanism at high velocity.**
- **Glass pipes/enclosures are partly operated beyond their safe pressure limits and possible disintegration by brittle fracture can release glass projectiles.**
- **Sudden vaporization creates considerable noise.**
The effects of potential explosions during the experiments posed the threat of significant injuries from cuts, freezing, burning, etc. The harmful effects of inhalation of vapors or suffocation and frightening neighbors had also to be considered. The setup and the procedures of experiments consequently had to satisfy several safety criteria.

For limiting the consequences of an ignition of flammable gases, the release facilities were placed outdoors in an open shelter. The construction (12 m x 8 m) was covered with a 4 m high metallic roof. Three sides of the shelter were partially closed with metal plates, leaving a free passage for air at the top and the bottom. By this means, a potential pressure wave could dissipate in an almost unhindered manner and a dense unignited gas cloud could quickly disperse. An accumulation of gas denser than air was impossible since the facility was located at a certain elevation. While the actual release experiments were conducted in the open shelter, the sensitive devices (digital storage oscilloscope, PC, thermostat, vacuum pump, amplifier, speed and control unit of the high-speed camera, etc.) were operated in a neighboring heated container. This control room was completely closed on its side facing the release, thus preventing any harmful gases from entering.

Since a maximum of 2 dm$^3$ of test liquid was instantaneously released to the ambient air, an incident could involve a considerable volume of reactive gas. For example, propane has a liquid/vapor density ratio of 206 ($\rho_{L,\text{sat}}$ (20°C) = 500 kg/m$^3$, $\rho_{G,\text{sat}}$ (-42.1°C) = 2.42 kg/m$^3$) and a lower explosion limit in air of 2.1 Vol.-% (Bartknecht 1993). This results in a flammable/explosive vapor/air mixture of 19 m$^3$ under ideal conditions. Ignition of such a volume of gas had to be prevented under any circumstances. So all sources of sparks and heat were sufficiently shielded from the released gas. For example, the light source was kept in a partly closed box, no other electrical installations were placed in the vicinity of the release site (except for low-voltage transducers and two shielded solenoid valves), and the opening mechanism was driven pneumatically or by totally enclosed electromagnets. In addition, all facilities were electrically grounded.

The controlled preheating of test liquid was mainly performed in a water bath or, in the case of water as test fluid, in an oil bath. Two thermostats connected in series were used to stop the heating when the safety limit was reached. In addition, a safety valve prevented any overpressure in the vessels.

Commercial glass pipes were used for the “one-dimensional” releases. Unfortunately, these usually had to be operated at pressures exceeding the safety limits specified by the manufacturer. However, these pressure ratings were found to be on the safe side and the pipes could be operated at much higher pressures. For example, the permissible overpressure in an 80-mm glass pipe was specified as approximately 1 bar, while 22 bar were attained in tests without breaking it. However, the pipes were found to be quite sensitive to improper installation (e.g. direct glass/metal contact). Each new installation of a pipe was therefore checked by filling it with water to a pressure twice as high as that expected during the experiment. Nevertheless, failure of the pipes or the glass plates could not be excluded. Under extreme conditions, this would have resulted in the sudden spreading of glass fragments, hot/cold test fluid and temperature-conditioning agent. To preclude this, the glass sections of the different set-ups were additionally enclosed by acrylic glass or metal plates. This was also necessary to protect against the uncontrolled ejection of a fragment of the metallic rupture disk.
The filling procedure, described in section 3.1.3, and the triggering of the experiment were performed from a location 2 m away from the test site. Again, this site was protected by metal and acrylic glass plates. Two solenoid valves could be operated from there to trigger emergency vents placed in the vapor and liquid spaces of the test facilities. The valve connected to the liquid space was opened preferentially. Thus, the contents could be released without thermally overstressing the glass pipe, since the pressure (corresponding to the saturation temperature of the liquid) would not drop significantly during release, except at the end when the pipe would be almost completely emptied.

As an additional safety precaution, all heating devices were switched off and the flasks containing test fluid were closed when personnel was absent from the test site. Since other people working in the vicinity of the test site could be alarmed and endangered by the sudden loud bang of a release, a horn gave advance warning prior to each experiment.

It should be remarked that these safety requirements and other procedures not explicitly mentioned here complicated the experiments to a considerable extent. For example, some of the experiments had to be conducted under rather adverse weather conditions as a consequence of the required outdoor location of the set-up. In addition, some of the sensitive instrumentation used outside the container (cameras, pressure transducers, etc.) required a daily set-up which took up a great deal of time. The various steps involved in the pressure pre-testing of the glass equipment were also fairly time consuming.

### 3.4 Test Fluids

The phenomena taking place during and the consequences of large-scale releases of superheated liquids depend mainly on the thermophysical properties of the fluids involved. Four fluids were chosen to obtain a range for the key parameters that influence boiling: butane, propane, refrigerant R-134a and water. Butane (n-butane) and propane are of direct relevance to catastrophic vessel failure because of their frequent pressurized storage and the potential formation of vapor clouds that are denser than air. R-134a (tetrafluoroethane) and water were selected because of their very distinct physical properties (e.g. the typical liquid/vapor density ratio at saturation of propane is greater than that of water by a factor of seven and its typical latent heat is greater by a factor of five, see Table 3.2). Particularly, for establishing correlations, it is important to provide data using fluids with significantly varying thermophysical properties. It is also of scientific relevance to study the boiling behavior of bulk superheated water because of its wide technical applications and involvement in natural phenomena.

The test fluids were also selected largely for reasons of convenience and to allow a direct comparison with the work of, e.g., Schmidli (1993). However, refrigerants R-114 and R-12, that were utilized in previous studies, were not used because of their harmful effect on the environment when released into the atmosphere.

Representative properties of the test fluids can be found in Table 3.2. The thermodynamic data of this table for which no source is given were calculated using the correlations of Appendix B. Appendix B also lists correlations for R-114 and R-12,
### Table 3.2: Properties of test fluids

<table>
<thead>
<tr>
<th></th>
<th>n-Butane</th>
<th>Propane</th>
<th>R-134a</th>
<th>Water</th>
</tr>
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<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C₄H₁₀</td>
<td>C₃H₈</td>
<td>C₂H₂F₄</td>
<td>H₂O</td>
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<tr>
<td><strong>Molecular mass</strong></td>
<td>M̄ [g/mol]</td>
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<tr>
<td>n-Butane</td>
<td>58.1</td>
<td>44.1</td>
<td>102.0</td>
<td>18.0</td>
</tr>
<tr>
<td>Propane</td>
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<tr>
<td>R-134a</td>
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<tr>
<td>Water</td>
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<tr>
<td><strong>Critical pressure</strong></td>
<td>p_{crit} [bar]</td>
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<tr>
<td>Water</td>
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<tr>
<td><strong>Critical temperature</strong></td>
<td>T_{crit} [°C]</td>
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<td>96.7</td>
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<td>Water</td>
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<tr>
<td><strong>Critical density</strong></td>
<td>p_{crit} [kg/m³]</td>
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<td>512</td>
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<td>R-134a</td>
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<td>Water</td>
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<tr>
<td><strong>Boiling point</strong></td>
<td>T_{sat} at 1 bar [°C]</td>
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<td>-0.7</td>
<td>-42.1</td>
<td>-26.1</td>
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<td>Water</td>
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<td><strong>Saturation pressure</strong></td>
<td>p_{sat} [bar]</td>
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<td>p_{L,sat} [kg/m³]</td>
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<td><strong>Liquid/vapor density</strong></td>
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<td><strong>Sat. liquid isobaric specific heat</strong></td>
<td>c_{pL} at 1 bar [J kg⁻¹ K⁻¹]</td>
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<td><strong>Isentropic quality</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>20 K</td>
<td>0.118</td>
<td>0.099</td>
<td>0.115</td>
<td>0.037</td>
</tr>
<tr>
<td>40 K</td>
<td>0.234</td>
<td>0.205</td>
<td>0.225</td>
<td>0.071</td>
</tr>
<tr>
<td>60 K initial superheat AT at release to ambient at 1 bar [-]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.310</td>
<td>0.304</td>
<td>0.333</td>
<td>0.105</td>
</tr>
<tr>
<td>Propane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-134a</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Max. superheat</strong></td>
<td>T_{lim} obtained at 1 bar [°C]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butane</td>
<td>105</td>
<td>53</td>
<td>-</td>
<td>302</td>
</tr>
<tr>
<td>Propane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-134a</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Jakob No. Ja at superheat limit at 1 bar [-]; (eq. 2.5)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.63</td>
<td>0.50</td>
<td>-</td>
<td>0.38</td>
</tr>
<tr>
<td>Propane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-134a</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sat. surface tension</strong></td>
<td>σ at 1 bar [N/m]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.0149</td>
<td>0.0155</td>
<td>0.0148</td>
<td>0.0589</td>
</tr>
<tr>
<td>Propane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-134a</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sat. liquid thermal conductivity</strong></td>
<td>λ_{L} at 1 bar [W m⁻¹ K⁻¹]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.115</td>
<td>0.134</td>
<td>0.105</td>
<td>0.677</td>
</tr>
<tr>
<td>Propane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-134a</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Approximate price</strong></td>
<td>[CHF/kg]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butane</td>
<td>20</td>
<td>3</td>
<td>26</td>
<td>-</td>
</tr>
</tbody>
</table>

which allow comparisons with the experiments of other researchers. The properties of all other fluids for which no correlation was established are mentioned explicitly in the text.

It should be noted that none of the fluids used can be completely vaporized by an adiabatic release to atmospheric pressure (see: Jakob No. Ja at superheat limit at 1 bar in Table 3.2). This means that without further heat transfer, such a released substance will always create a vapor/liquid mixture. The difference in isentropic quality and liquid/vapor density ratio among the test fluids is also of particular relevance.

No extra measures were taken to purify the fluids in their delivered state. Additional information about these test fluids (e.g. purity) and auxiliary agents can be found in Appendix C.
Chapter 4
Experimental Results

Release experiments including pressure and temperature measurements, high-speed cinematography and video recordings have illuminated various aspects of the vaporization process, i.e. the phase change via boiling fronts. First studies of the boiling fronts and of the two-phase expansion of propane and butane allowed a comparison with the results of the unconfined, spherical releases examined in previous projects (Schmidli 1993). The findings at this intermediate stage of the work suggested an investigation of the influence of different release directions and led to the design and use of a set-up allowing circumferential releases. In the meantime, investigations of water and R-134a releases were continued. The various findings will be presented in this chapter, starting with the experimental matrix and an overview of boiling front propagation. The following more detailed results will be summarized at the end.

4.1 Experimental Test Matrix

One of the main objectives was to study the dependence of boiling front velocity on the superheat of four test liquids. Since the fluids were always released to the environment at an atmospheric pressure of \( p = 1 \) bar, the superheat had to be varied by changing the initial temperature \( T_\text{in} \). The latter was measured prior to depressurization in the center of the then slightly subcooled liquid and determined the nominal degree of superheat \( \Delta T_{\text{nom}} \) following decompression according to:

\[
\Delta T_{\text{nom}} = T_\text{in} - T_{\text{sat}, 1 \text{ bar}}
\]  

Other parameters that were changed during the course of the experiments were the pipe diameter and its geometry. Table 4.1 gives an overview of the different investigations depending on the substance. An overview of the experimental runs used for the analysis in this work is given in Appendix D.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Range of superheat ( \Delta T_{\text{nom}} ) [K]</th>
<th>Internal pipe diameters [mm]</th>
<th>Pressure data at base, exit</th>
<th>Movie close-up</th>
<th>Drop size</th>
<th>Orifice at exit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>30 - 72</td>
<td>14 - 80</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Butane</td>
<td>23 - 73</td>
<td>40, 80</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-134a</td>
<td>23 - 68</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Water</td>
<td>7 - 38</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td>base</td>
</tr>
</tbody>
</table>
In theory, boiling fronts in pure superheated liquids should be observable in the temperature range extending from the boiling point to the limit of superheat. In the experiments, the threshold of boiling front propagation, that is, the lowest superheat at which boiling front propagation was observed, led to the lower limit of tested superheat. The upper limit of superheat was given by the safety pressure margins of the glass pipe, except in the case of water, where nucleation on the glass walls could not be prevented at an initial temperature exceeding $T = 138 \, ^\circ\text{C}$. Pressure measurements for water experiments were performed at a single location because only one rapid-acting water-resistant pressure transducer was available.

The more detailed studies were conducted mainly with propane (two-phase flow measurements, perpendicular views of boiling front, droplet size, etc.) because of its convenient experimental requirements and its price. In addition, the circumferential releases were conducted solely with propane. A total of more than 200 experiments were carried out, but many of them could be used for analysis, mainly because of undesired nucleation on the glass walls and buffer liquid.

### 4.2. Overview of Boiling Front Propagation

The experiments with superheated butane, propane, R-134a and water proved the assumption that under certain conditions and after eliminating any nucleation sites in the surroundings of the fluid, the nucleation is restricted to the free surface of the liquid. By opening the test section and depressurizing the test liquid, a phase-change front travelling violently into the superheated liquid became visible. The boiling zone exhibiting intense vaporization and fine-scale fragmentation produced a two-phase flow of high velocity downstream since the latent heat was insufficient for vaporizing all the liquid ($Ja < 1$). The example in Fig. 4.1, showing the video sequence of a

![Fig. 4.1](image)

Propagation of a boiling front (advancing from top to bottom) inside stagnant superheated liquid (Run 117, R-134a, superheat $\Delta T_{\text{super}} = 68 \, \text{K}$, velocity of boiling front $u_{\text{fr}} \approx 0.97 \, \text{m/s}$, pipe inner diameter $d_i = 40 \, \text{mm}$, 50 Hz frame rate)
release of superheated R-134a from a vertical glass pipe, illustrates this situation. Similar results were obtained using butane, propane and water.

On the first frame of Fig. 4.1, the pipe is closed and the liquid and vapor are in a saturated or slightly subcooled state. The buffer liquid, in this case R-113, can be seen below the test fluid. The following frames show the propagation of the boiling front from left to right in steps of 20 ms, after opening and depressurization of the glass pipe. The boiling front travelled into the now superheated R-134a where the contour of the phase boundary changed continuously during propagation. Tips of the front sped forward while other areas remained almost stationary for some time. The random nature of tip acceleration led to a highly irregular shape. The boiling front can be seen in the upper part of the frames as well as the ejected two-phase flow.

Figure 4.2, which shows a single frame of a high-speed movie recording taken at a frequency of 4500 frames/s, shows an enlarged view of the boiling front region. Again, the superheated liquid can be found at the bottom (white area) of the frame while the two-phase flow is accelerated towards the top of the frame.

Fig. 4.2:
Enlargement of a boiling front (advancing from top to bottom) inside stagnant superheated liquid (Run 121, propane, superheat $\Delta T_{\text{nom}} = 50$ K, flattened pipe section)

The boiling front, where explosive vaporization and fine-scale fragmentation occurred, appeared to be several millimetres thick. Bubble-like structures covering a range of diameters up to a few millimeters grew and disappeared during the advancement into the metastable liquid. The vapor-liquid mixture left the vaporization plane almost perpendicularly. Bursts frequently occurred within the front and spread from one point of the front to other locations. Because of this and the irregular shape of the boiling
front, the resulting two-phase jet was not continuous and uniform near the front. In summary, recordings such as those of Fig. 4.2 illustrate that violent surface boiling is a complex interaction of vaporization, liquid fragmentation and two-phase acceleration.

Depressurization and boiling front propagation lead to a pressure-time history which was recorded by the two pressure transducers. These were located in the buffer liquid below the test fluid and in the vapor space underneath the rupture disk, respectively. A typical example of their recording is displayed in Fig. 4.3.

Figure 4.3 shows that after opening the glass pipe, the pressure at the exit decreased to the ambient pressure within 20 ms, whereas the pressure at the base remained at a plateau above the surrounding pressure for 200 ms. The duration of this plateau corresponded to the period of constant boiling front propagation. The origin of pressure fluctuations is not understood in detail. However, the oscillations in the plateau are attributed to the integral effect of reflected pressure waves and randomly-occurring bursts in the boiling zone.

The elevated pressure below the approaching boiling front (base pressure) was due to the accelerational and frictional pressure drop between the superheated liquid and the exit of the pipe. This elevated pressure lead to a smaller degree of superheat, $\Delta T_{\text{real}}$, in the stagnant metastable liquid, which is expressed as:

$$\Delta T_{\text{nom}} \geq \Delta T_{\text{real}} = T_{\text{in}} - T_{\text{sat.L}}$$  \hspace{1cm} (4.2)

where $T_{\text{sat.L}}$ is the saturation temperature at the pressure behind the front, which should be nearly identical to the measured pressure. In the example of Fig. 4.3, with the liquid assumed to be uniformly superheated, $\Delta T_{\text{nom}} = 66$ K was thus reduced as $\Delta T_{\text{real}} = 51.3$ K.

Considering only those images recorded after the onset of front propagation (such as the four on the right side of Fig. 4.1) and averaging the advancing boiling-zone
4. Experimental Results

contour over space and time, the mean velocity of the front $u_f$ could be determined. Although locally and temporarily strong fluctuations were observed in the appearance of the flashing layer, it was found that the front travelled at an average constant velocity. Other quantities showed rather stationary features as well, such as the pressure upstream of the vaporization zone after the sudden initial drop leading to the pressure plateau of Fig. 4.3.

This work focuses on the vaporization of a large volume of superheated liquid that does not contact surfaces which provide nucleation sites. The process and analysis of explosive boiling can be divided into two consecutive stages: the transient start-up period and the period of quasi-steady boiling front propagation (Hill 1991). Quasi-steady boiling front propagation is of major importance for the investigation of the overall effect of the vaporization, because the major proportion of liquid is released during this period. Thus, the following treatment gives qualitative and quantitative results mainly for the period of quasi-steady boiling front propagation. In contrast, the short transient start-up period, that is the onset of boiling front movement, contributes only to a small extent to the overall mass fluxes. The observations made during the start-up period will be presented only in brief.

4.3 Transient Start-Up of Boiling Front Propagation

After the test fluid was filled and preconditioned to the desired temperature, the experiments were triggered by opening the rupture disk. The vapor above the test liquid could expand and a rarefaction wave traveled through the vapor space at its local speed of sound. The sudden depressurization caused the saturated vapor above the test fluid to partly condense. This fog formation became visible by a sudden drop in the transparency of the vapor space (Fig. 4.4: 1st to 2nd frame). The decompression

![Fig. 4.4: Onset of boiling front propagation (Run 009, propane, $\Delta T_{nom} = 49$ K)](image)

1.: $t = 0$ ms
2.: $t = 5.8$ ms
3.: $t = 11.5$ ms
4.: $t = 51.0$ ms
wave then traveled through the liquid, so that it became superheated and started to vaporize. At moderate superheat, as in the example of Fig. 4.4, the preferred location for the first bubbles to appear was the liquid/vapor/glass contact line (3rd frame). At random locations on this line, bubbles grew and their surface became roughened. New bubbles appeared, successively covering the whole free liquid-vapor interface from the outside toward the center. Within a few milliseconds, the typical appearance of a boiling front emerged, i.e. the characteristic cauliflower-like surface pattern was seen (4th frame).

At higher superheat than that of Fig. 4.4, this onset of violent flashing generally occurred more quickly, i.e. explosive vaporization across the whole free surface started immediately after the arrival of the decompression wave at this surface. For example with propane at $\Delta T_{\text{nom}} = 62$ K, the whole free surface was covered by a boiling front within less than the exposure time of a single frame of a high-speed recording ($t < 0.2$ ms). At lower superheat, for example with propane at $\Delta T_{\text{nom}} = 29$ K, it was observed that the free surface remained unchanged until a single bubble appeared from which other bubbles started to grow. Later, a burst occurred within this slow growing, foam-like structure and initiated boiling all over the free surface.

The start-up appeared to be fairly irregular, particularly at lower superheat. In one instance, the free surface remained unchanged for several milliseconds, while in another run, a large bubble grew rapidly into the superheated liquid immediately after opening. However, the following quasi-steady boiling front propagation, e.g. the propagation velocity, appeared to be very similar even though the onset appeared to be very different. After start-up, therefore, the boiling front is unaffected by events preceding its creation. Besides the dependence on superheat, it seems that the start-up is influenced by various unquantifiable factors such as impurities or the surface quality of the glass.

The initial pressure drop above and below the liquid filled section of the pipe was recorded by two transducers mentioned in section 4.2, as shown in Fig. 4.3. This initial transient is shown in Fig. 4.5 in an expanded view. Upon opening, the pressure at the exit decreased. The initial oscillation of the base pressure shortly before the pressure decreased at the exit was probably due to the lifting of parts of the opening mechanism.

Different depressurization rates were observed. While the compressible vapor space pressure decreased at an average of ca. 2 kbar/s, a rate of ca. 4 kbar/s was noted for the transducer at the base. For a certain period of the experiment, a lower pressure was recorded at the base than at the exit.

The expanded view of Fig. 4.5 shows that the pressure near the rupture disk started decreasing approximately 1 to 1.5 ms earlier than the pressure at the base, i.e. in the buffer liquid. Considering the position of the pressure transducers, the vapor space as well as the volumes of the buffer and test liquid, this difference can be explained by the travel velocity of the rarefaction wave. The depressurization velocity corresponded to the speed of sound in the different media of the experiments. Given the travel height $h$ and the speed of sound $u_{\text{crit}}$ of each single-phase fluid (butane vapor: $h = 18$ cm, $u_{\text{crit}} = 198$ m/s; liquid butane: $h = 18$ cm, $u_{\text{crit}} = 710$ m/s; liquid water: $h = 19$ cm, $u_{\text{crit}} = 1550$ m/s) the resulting duration of travel was 1.28 ms (speed of sound data from Lemmon et al. 1993). Thus, it is clear that the speed of sound determined the delayed pressure fall at the base pressure transducer.
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Fig. 4.5: Base and exit pressure profiles: rupture and start-up of boiling
(Run 092, butane, $\Delta T_{\text{nom}} = 66$ K, $u_h = 0.93$ m/s)

In general, the initial pressure fluctuations were rather irregular. This can be interpreted as the integral result of reflections at liquid interfaces and the bottom of the pipe. From both the film and pressure recordings, it appears that sudden superheating led to irregular boiling start-up and pressure oscillations. These levelled off after several milliseconds when the period of quasi-steady boiling front propagation was reached.

4.4 Qualitative Description of Quasi-Steady Boiling Front Propagation

The absence of nucleation sites in the bulk led to vaporization which was restricted to the free surface of the superheated liquid. Three characteristic zones can be distinguished: the superheated liquid, the boiling front zone and the two-phase flow region. These will be discussed separately in the following sections. Some of these observations were already made by Hill (1991), but are repeated here to obtain a complete description of the vaporization process.

4.4.1 Superheated Liquid Layer

As discussed later, rapid boiling front propagation required a minimum degree of superheat. Below this threshold of quasi-steady propagation, only slow evaporation or bubble motion was observed. The phenomena observed in the superheated liquid layer were different in the two cases.
4. Experimental Results

Fig. 4.6: Motion of the interface between the buffer and the test liquids (elliptical grey area near the bottom) due to the approach of the boiling front (Run 084, butane, $\Delta T_{\text{nom}} = 55$ K, $u_T = 0.76$ m/s, $d_{\text{pipe}} = 80$ mm)

**Rapid Boiling Front Propagation**

Figures such as 4.3 and 4.5 show that in this case the whole liquid volume became superheated within a few milliseconds and remained in this metastable state until it was reached by the boiling front. In the above example, the liquid-vapor interface moved with a velocity of approximately 1 m/s, which was slower by orders of magnitude than the speed of sound in any of the several fluid layers in the pipe. The fastest boiling front observed during the experiments propagated at a velocity of 1.3 m/s.

For the experiments with butane, propane and R-134a, the buffer liquid remained below the test fluid. This separation line was clearly visible in the video recordings. Figure 4.6 shows the movement of this interface during an experiment. Upon opening the rupture disk, the interface between the test and buffer liquid was slightly disturbed and some irregular wave patterns developed. During the vaporization of the test liquid, these oscillations calmed down and the surface flattened. The initial movement was therefore attributed to small mechanical perturbations caused by the sudden movement of the opening mechanism. Only in the immediate vicinity of the boiling front as shown in the right frame of Fig. 4.6 did the interface move significantly due to the push from the approaching boiling front. As the boiling front approached, the interface closest to the vaporization zone was pushed downwards whereas other areas of the interface rose. This protrusion was observed particularly in experiments with a high front velocity. Obviously, a locally intense vaporization led to pressure differences in the boiling front region, inducing local motion in the superheated liquid. An interface motion at start-up was not noted in all the experiments. For example, the interface between R-134a and R-113 as the test and buffer liquids, respectively, showed almost no movement at all.

Similar observations were made in some experiments in which propane was stained in layers of different intensity to make the fluid movement visible (see section 3.1.4 on drop-size measurements). Within the resolution of the film and video systems (less than a millimeter), no convective mixing could be seen until the arrival of the boiling front. Only in the vicinity of the boiling front, in a zone of less than one centimeter away
4. Experimental Results

Fig. 4.7: Case of slow boiling. Left frames: Cooling and liquid motion underneath the interface; Right frame: residual, saturated ("cold") liquid boiling below the interface (Run 095, butane, $\Delta T_{\text{nom}} = 32$ K, $u_l = 0.045$ m/s)

from the phase-change line, did the motion become visible, i.e. liquid was pushed aside by leading bubble tips speeding forward into the superheated liquid.

Experiments below the Threshold of Rapid Boiling Front Propagation

The vaporisation below the threshold of rapid boiling front propagation was much slower and some convection and mixing inside the superheated liquid could be observed. Figure 4.7 shows the structures evolving in the stagnant superheated liquid at a temperature slightly below the onset of boiling front propagation.

At low superheat and consequently at low vaporization rate, as in the run of Fig. 4.7, the vaporization that started at the free surface caused the liquid to cool down. Due to the resulting differences in density, fluid motion was induced which led to convective heat transfer from the bulk of the liquid to the free surface. The decrease in temperature was indicated by the changes in the refractive index shown in Fig. 4.7. Underneath the liquid-vapor interface, the zone affected by mixing is visible in Fig. 4.7 (two frames on the left). Since in this case the latent heat and the vapor production were insufficient to carry away any surplus cooled liquid, and the process was much slower, mixing occurred, and the volume from which heat was removed increased. As the superheat near the interface was depleted, the heat required for vapor production had to be transported over an increasing distance from the lower layers of the liquid to the liquid-vapor interface. Eventually, convective liquid motion affected the whole column of liquid through which the vaporization zone slowly propagated. Finally, a volume of saturated or "cold" liquid was left in the pipe (Fig. 4.7, right image). Thus, the vaporization was characterized by two stages: the propagation of a boiling front and an extended period of slow bubbling in the residual liquid.
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Since below the threshold of rapid boiling front propagation, the fluid remained in the test section a long time, the vaporization cannot be considered as adiabatic any longer because heat transfer from the surrounding glass walls to the fluid became significant.

The above phenomenon of convective liquid motion in the metastable liquid is not observed during boiling front propagation at higher superheat and consequently high boiling front velocity, which is the situation of main interest here. Therefore, the experiments lead to the conclusion that, except for the small pressure fluctuations caused by the varying momentary vaporization rates, the state of the stagnant liquid is not substantially changed during the period of rapid, quasi-steady boiling front propagation. The liquid remained superheated and isothermal during these experiments. Additionally, the metastable liquid in the pipe can be considered as motionless except in the immediate vicinity of the boiling front.

Properties of the Superheated Liquid

In principle, the range of superheats considered here could extend from the saturation temperature to the limit of superheat for homogeneous nucleation; see for illustration Fig. 2.3. Within these limits, the isothermal depressurization caused the density and enthalpy of the stagnant liquid to change in principle, but these variations were negligible compared to experimental uncertainties, such as the temperature measurements. For example, an isothermal depressurization of saturated, liquid propane at $T = 10 \, ^\circ\text{C}$ to the metastable state at $p = 1 \, \text{bar}$ with $\Delta T_{\text{nom}} = 52 \, \text{K}$ leads to a density decrease of $\Delta \rho = 0.2\%$ of the initial value (according to $dp/dv$ of the Van-der-Waals equation of state). Therefore, for further analysis, the thermophysical properties such as the density and enthalpy of the superheated liquid will be assumed to be the saturation properties at the same temperature.

4.4.2 Boiling Front Zone

The zone stretching between the continuous single phase of superheated liquid and the steady two-phase flow region will be considered as the boiling front in the following treatment. Vaporization, fragmentation and acceleration of the fluid occurs within this zone, giving the typical profile of Fig. 4.2. In the following subsections, the observed structure and dynamics of the boiling front are presented in detail.

Boiling Front Structure

The surface of the boiling front was covered by bubble-like structures. In most cases, the leading tip of the front was visible as a hemispherical liquid-vapor interface, that is, the downstream end of the leading cavities was surrounded by other neighbouring vaporizing interfaces. Unlike inspecting the surface of an approaching boiling front, it was very difficult to access information from inside the boiling layer. A view into the region which was behind the most advanced edge of the front by more than half the typical diameters of the hemispheres, was very difficult. Even though some of the movie recordings were taken in a narrow glass receptacle (e.g., Fig. 4.2) and not in a round pipe, it could not be shown definitely whether completely closed bubbles floating at the top of the liquid or open caps were present. Therefore, even though the
terms *bubble* or *cap* will be used frequently in the following, this does not necessarily imply a closed volume of vapor or an open buckle from which vapor escapes away from the superheated liquid.

In several cases, the surfaces of the bubbles appeared to be smooth and glassy while in others they were characterized by an irregular surface pattern. It is difficult to generalize and quantify this phenomenon because of this extreme disparity. In general, however, small bubbles appeared to be smoother than larger bubbles. Some of the rounded interfaces acted as hosts carrying various other smaller hemispherical structures. The appearance of a boiling front recalled a fractal pattern, where larger scale profiles were covered by typical structures at a smaller scale. For example the contour line of a boiling front (e.g., at the scale of Fig. 4.1 or larger) consisted of a bubbly structure (e.g., at the scale of Fig. 4.2) where the larger bubbles were again covered by smaller caps, etc. As the larger bubbles grew and eventually burst or disappeared the smaller ones that grew on their surface replaced them. It is, therefore, rather difficult to characterize the front by the distribution of a typical cap size at the leading front edge because a certain bulging can be interpreted as the sub- or superstructure of another interface. Roughening on the surface appeared random in orientation and on many scales of length.

Film recordings with a perpendicular view onto the boiling front were taken only in a few instances. The back-lighting technique was impractical because it would have required inserting the lamp into the two-phase flow. So only a low degree of contrast was obtainable with the existing illumination source. Figure 4.8 gives an example of such a recording. The cauliflower structure is apparent. Larger bubbly structures are covered by smaller ones.

The size of the leading bubbles reached several millimeters and varied with temperature, that is, it decreased with increasing superheat. The approaching front therefore appeared with a finer structured surface at high superheat than at low superheat. As an example, Fig. 4.9 compares the appearance of boiling fronts at $\Delta T_{\text{nom}} = 30$ K and 69 K of butane. The higher the superheat and the corresponding boiling front velocity, the finer the bubble structure became.
4. Experimental Results

Fig. 4.9: View of boiling front at different superheats (butane; left: Run 097, $\Delta T_{\text{nom}} = 30$ K, $u_r = 0.064$ m/s; right: Run 102, $\Delta T_{\text{nom}} = 69$ K, $u_r = 1.2$ m/s; view field: 94 x 83 mm)

In general, every observable volume of gas was in contact with the vapor space or separated only by a thin film from it, that is, no nucleation event isolated from the boiling front region was noted within the superheated liquid. At superheats above the threshold temperature, no visual evidence was found for nucleation in the bulk of the liquid, except in experiments where the bubble nucleation could be clearly attributed to wall nucleation or nucleation on preexistent nuclei. It can be concluded that vaporization occurred only upon contact of liquid with the boiling front.

Even though optical distortion limited the view into the bubbles, the inside of the leading bubbles appeared essentially to be filled with pure vapor. Any liquid drops or fragments passing through these cavities would have been visible. Similar findings were made by Frost (1985), who observed that any aerosol or two-phase flow or a small-scale surface distortion refracted incoming light and caused a vapor space to appear opaque in photos. The leading transparent cavities can therefore be assumed to be filled with pure vapor only.

Since the stored thermal energy was insufficient to vaporize all the liquid, the surplus of fluid had to pass through the boiling layer. In general, as will be shown later, for the current experiments, the proportion of unvaporized liquid penetrating through the boiling layer was always more than 50% of the total mass flux. The growing bubbles acted as a volume source which moved the incompressible liquid to the side. Since there was no visual evidence for liquid flowing inside the visible part of bubbles, it had to flow around the leading vapor cavities. The boiling front surface appeared to be covered mostly by vapor cavities such that the cross-sectional flow area for the liquid was narrowed. This observation as well as reasons of mass continuity imply that the liquid was accelerated as it entered the vaporization layer.

Downstream of the typical cap structure, i.e. at a depth of about one diameter of the largest smooth bubble, the view of the boiling region appeared increasingly blurred. This blur was found even in movie recordings taken at frequencies of several thousand frames per second. Rough estimates made by considering the exposure time and the resolution of the film (such as of Fig. 4.2) indicated that the flow of vapor and liquid several millimeters behind the front already reached a speed at least one order of magnitude faster than the propagation velocity of the boiling front. Vapor became the continuous phase and the flow appeared to be finely sprayed but not evenly distributed.
Despite this, the liquid particles streamed in threads perpendicularly away from certain sites of the boiling layer. The preferred locations for the origin of such streaks were the troughs between the hemispherical caps, or in general the zones lagging behind other leading tips. The liquid flow appeared to be concentrated there, because stronger light extinction was observed at these sites.

**Boiling Front Dynamics: Contour Changes**

Beside the structure described so far, the dynamics of the boiling front are of interest. In fact, an understanding of the boiling mechanisms can only be obtained by studying frame sequences taken at high spatial and temporal resolution. Otherwise the structures of single frames are difficult to interpret.

Film recordings showed that as the boiling front advanced, its contour changed continuously. Tips of the front sped forward while other areas remained almost stationary for several milliseconds. The latter regions may have accelerated later on or were joined by the laterally expanding front originating from leading bubbly tips. Figure 4.10 illustrates typical contour changes appearing during boiling front movement. It shows how the boiling front moved into the superheated liquid in time steps of 20 ms. Each contour line represents the most advanced edge of the boiling front surface at a certain instant. The collection of front lines over a certain time period indicates that the shape of the front changed continuously. The position of the most advanced point therefore moved laterally, as is illustrated in Fig. 4.11. In this case, the leading tip was found to move mainly near the center of the cross section.

From Fig. 4.11 it could be concluded that the core of the superheated liquid was the preferred location for leading boiling front tips to appear. However, it should be kept in mind that the two-dimensional projection of the three-dimensional boiling front surface does not provide any information about the position of the prevailing leading edge in the third dimension, i.e. its distance from the camera. A point visible on a single frame in the center of the glass pipe may be in the core of the pipe or on its walls. Thus, a single view perpendicularly toward the boiling front leaves an uncertainty about the three-dimensional appearance of the boiling front. However, it was concluded from other perspectives and illumination directions than, for example, those of Fig. 4.1, that the leading tips were evenly distributed across the whole surface of the front.

The contour of the boiling front changed continuously, but the stabilizing effect of the statistical nature of tip acceleration smoothed or flattened the shape of the front. Another effect, which limited tailing, was the lateral motion of the boiling fronts because any advancing tip pulled a cone-like vapor/aerosol space behind it. It was not surprising to observe that the axial difference between the most advanced and the most retarded points of the boiling front increased with cross-sectional size. Since the lateral movement of points on the boiling front covered smaller cross sections faster than larger ones, the most retarded and most advanced points in the axial direction of a boiling front lay closer together in smaller pipe diameters than in larger conduits.
Figure 4.12 shows a comparison of experiments conducted at the same superheat but with different pipe sizes. As can be concluded from Fig. 4.12, the front contour in some runs became rather distorted, i.e. in a pipe with an internal diameter of 80 mm the maximum axial difference between the most advanced and most retarded points reached 45 mm. Even identical experiments showed extreme differences in behavior: experiments performed under the same initial conditions led to dissimilar contours of the liquid/vapor boundary. The differences between the runs in Fig. 4.12 were averaged according to pipe diameter to allow easier interpretation. The average lines in Fig. 4.12 illustrate that the axial scatter in local boiling front positions increased with pipe diameter or cross-sectional area.
Boiling Front Dynamics: Single Bubble Growth

Growing bubbles or open caps came continuously into view at the propagating front, which then exhibited a roughness at a variety of scales. Some bubbles disappeared, that is, they were obscured by other advancing bubbles. In some cases they moved downstream, probably due to a push from flowing liquid. New vapor cavities had downstream origins. In general, however, they appeared from some irregular location on the surface of a host bubble. Often, a larger bubble divided into two or more smaller structures. Figure 4.13 illustrates the repeating cycle of bubble/cap generation, growth, roughening and/or disappearance on the surface of a boiling front. For example, the right side of frames 1 to 8 shows the growth of two larger structures. When reaching approximately three millimeters in diameter, their surfaces become rough (frames 10 and 11) and several new smaller bubbles start growing from them (frames 12 and following).

Some sufficiently strong disturbances produced bulging on a vapor cap. In some instances, this was initiated by a drop hitting the interface from the downstream direction. Such events were noted in a few high-speed movie recordings. In other recordings, roughening of the surface occurred during bubble expansion without any prior impingement of liquid.
Fig. 4.13: Boiling front propagation in a glass prism (Run 121, propane, \(\Delta T_{\text{nom}} = 50\) K, \(u_b = 1.2\) m/s, frame rate 4700 Hz, view field 35 mm x 28 mm)
**Boiling Front Dynamics: Bursts**

Smooth transparent caps were observed downstream, and bursts frequently occurred within the zone of fluid acceleration. They appeared preferentially at locations of high motion and high density of liquid spray. For example, the liquid spray mass flux seemed to be increased at lagging points along the front contour, and it was from there that most of the bursts originated. These explosions generated a blast wave which was visible as a sudden radially expanding field of light extinction. From the initial site, the explosion spread over the whole layer, that is, the arrival of the wave triggered new reactions in the manner of a chain reaction. When an explosion occurred, the boiling front in its immediate vicinity was accelerated. The bursts expanded with approximately the same velocity as the speed of the two-phase flow.

The bursts were difficult to detect on single frames. Only by viewing a film sequence was it possible to observe these dynamic high-speed explosion phenomena. At high superheat, the bursts occurred closer to the leading edge of the front (within a few millimeters); at low superheat they took place further inside the two-phase region (in some cases a centimeter downstream). At low superheat the bursts were less frequent and were clearly distinguishable as single events while at higher superheats explosive bursts were sweeping across the boiling front layer almost continuously.

In some instances, this phenomenon of violent bursts was also observed at the sites where undesired nucleation occurred. This was typically a bubble that grew to a considerable size and expelled the whole liquid column above it. Later, when only a thin film of liquid was left on the glass wall, bursts were observed on this film. These explosions propagated across the whole field of view from top to bottom. While the large single bubbles were still transparent during growth, the light from the back was extinguished when the bursts caused a fine-scale structure.

**Boiling Front Dynamics: Transition from Single Bubble Growth to Violent Boiling with Front Propagation**

A characteristic feature of the boiling fronts was the violent vaporization and/or fragmentation of liquid which made them distinctively different from “slow” evaporation or smooth single-bubble growth. To understand the nature of boiling front propagation, it is quite instructive to study the transition from pure vaporization to violent boiling front propagation at the interface of a single growing bubble. An example of such a transition was filmed in a flattened pipe and is shown in Fig. 4.15. Fig. 4.14 illustrates the position of the camera view field relative to the glass receptacle and the time scale of the frames of Fig. 4.15.
4. Experimental Results

Fig. 4.14: View field and time axis of the 15 frames displayed in Fig. 4.15 (flattened pipe insert described in section 3.1.1)

Fig. 4.15: See next page for continuation
4. Experimental Results

Fig. 4.15: Transition from pure vaporization to boiling front propagation at a bubble interface in a flattened pipe (propane, $\Delta T_{\text{nom}} = 63$ K, view field: 30 mm x 27 mm, time steps: see Fig. 4.14)

The frame sequence of Fig. 4.15 shows part of an expanding bubble interface. The right side of the images shows the vapor-filled inside of a flattened bubble between two glass walls covered by a film of buffer liquid (water). The left side shows the superheated propane.

The first frame shows part of a bubble which has already grown to a diameter of approximately $d = 30$ mm (based on simultaneous video recording). The ring patterns and structures visible within the bubble on the vapor side are probably due to vaporization of propane on the thin water film. However, these do not seem to have influenced further boiling of the propane.
The bubble was still fully transparent at this stage, indicating that it consisted of pure vapor. As the interface moved from right to left, it was disturbed at some point by two bubble-like caps growing around a fold which remained stationary in the following frames. Frames 2 to 7 show how the depth of the notch increased. In frame 9, small bubbly structures growing perpendicularly from the liquid notch became visible. On the next frame, explosive vaporization started. By including frames 11 and 12, it can be seen that within a millisecond the contour line of this structure disappeared and a black fog-like zone expanded. Frames 9 to 12 were taken in time steps of 0.29 ms. This change of transparency was probably due to fine-scale fragmentation. Small particle sizes below the film resolution and acceleration of this aerosol led to complete light refraction. A similar process occurred in the upper part of the frame, i.e. a zone with complete light extinction spread at the fold of two vapor cavities. A washboard-like ripple pattern can be seen along the stretched aerosol zone and away from the side of the superheated liquid (upper third of frame 10). This indicates a high relative motion of gas over the surface of the liquid film remaining on the glass walls. The next frames 10 to 14 show the rapid spread of the aerosol-generating sites. Away from the interface, the aerosol streamed to the right side of the frames and filled up the former bubble volume. Smaller caps than before could now be observed at the contour line along the volume of the superheated liquid. A two-phase flow sped away from there and the typical structure of a boiling front was established.

Some of the above phenomena, such as the ripple formation, may have been an art-effect caused by the narrow cross-sectional area of the glass receptacle and the shearing forces of the film between the glass wall and the vapor stream. It is not known whether such behavior will also be found in a “wall-free” environment. However, the observation of explosive boiling and fine-scale fragmentation found preferentially in the fold between neighbouring bubble hemispheres was supported by a number of other close-up studies of the boiling process.

The preferred conditions for explosive vaporization occurring during boiling front propagation can be summarized from recordings such as those of Fig. 4.15. It appears that liquid/vapor fronts at high superheat and moving rapidly generate a dramatic increase of their surface area. This in turn leads to increased vaporization which, in general, induces a higher local motion between gas and liquid. Due to intense mixing and fragmentation, warmer liquid from the vicinity of the front is rapidly moved to the free surfaces. Thus, at conditions of high superheat, shortly after initiation, explosive boiling appears as a self-amplifying process. The phase change proceeds as a self-sustaining mechanism, continuously generating new surface area for further vaporization.

### 4.4.3 Two-Phase Flow Zone

After fragmentation and vaporization, and leaving the zone of violent bursts, the fluid flowed as a finely dispersed spray. A liquid film flowing along the wall of the tube was seen in the glass pipe and in an acrylic glass pipe installed downstream of the rupture disk. The core was not filled with pure vapor but with aerosol passing at high velocity. Thus, the appearance of the two-phase zone resembled a wispy annular structure. The fragmentation within the boiling layer was characterized by random bursts at the liquid/vapor interface as already noted. Similarly, the resulting two-phase flow was not continuous and uniform; instead, fragments of liquid were randomly expelled from the
boiling layer. Thus, fluctuations in the two-phase flow region were visible. Drops appeared in long, streaky structures rather than in swarms.

4.4.4 Boiling Front Propagation during Circular Releases

The initial plan was to investigate different release directions by inclining the entire release facility to produce different angles of the glass pipe. However, the use of a buffer liquid for suppressing nucleation at the bottom of the test liquid, appeared to make this approach difficult. Therefore, a facility allowing circumferential releases, i.e. in the radial direction from a cylindrical volume, was designed and used (Figs. 3.8 and 3.9). In addition, the circular geometry appeared to be more similar to the conditions found in the large-scale, unconfined, spherical or cylindrical releases from failing storage tanks.

The circumferential releases using superheated propane proved the assumption that under certain conditions and after eliminating any nucleation sites in the surroundings of the fluid, vaporization would occur by a boiling front travelling from the outside to the center of the cylindrical volume of liquid. By opening the test section and depressurizing the test liquid, a phase-change front travelling violently into the superheated liquid became visible. The boiling zone produced a two-phase flow in the radial direction. As an example, Fig. 4.16 shows frames of a high-speed movie sequence of a circular release of liquid propane. The axis of the cylindrical test volume was horizontal.

Upon opening, a vaporization zone in the upper part of the test volume became visible. A boiling front propagated into the superheated liquid. At this initial stage, the irregular shape of the contour and the transparency resembled the experiments conducted in the glass pipe. Approximately the upper quarter of the view-field height was reached by the vaporization layer when bubbles appeared all along the remaining circumference of the view field. From there, the vaporization spread in a rather irregular pattern toward the center of the circular volume. In comparison to the pipe experiments, some bubbly structures grew to a fairly large size during this stage of the experiment (several centimeters in diameter). Later, bursts occurred within the bubbles. At the end, all the fluid was vaporized. Even though in some experiments the front appeared more circular with equal front propagation from all sides, the uneven shape development of the front in Fig. 4.16 represents a more typical result.
Fig. 4.16: Radial boiling front propagation during release through a circular cross section; gravity acts downwards (Run 141, propane, $\Delta T_{\text{nem}} = 49$ K, $u_g = 1.3$ m/s, $\Delta t_{\text{frames}} = 7.9$ ms)

4.5 Quantitative Characterization of Boiling Front Propagation

Several variables were quantified for further studies. The influences of various parameters on boiling front velocity were of particular interest, since this velocity determines the consequences of the boiling of superheated liquid, e.g. the expansion velocity of a released vapor cloud.

4.5.1 Boiling Front Propagation Velocity

For the following analysis, movie and video recordings were digitized and the resulting contour plots (such as Fig. 4.10) measured. This allowed the average velocity of points of the boiling front to be determined. An example of the time dependence of the average boiling front position is shown in Fig 4.17.
4. Experimental Results

Fig. 4.17: Time dependence of average boiling front position (Runs 033, 034; propane; \( \Delta T_{\text{nom}} = 47 \) K; average velocity of boiling front \( u_f = 0.43 \) m/s)

Figure 4.17 shows two runs, with essentially the same initial temperature. The almost constant slope indicates a period of constant boiling front velocity and illustrates the quasi-steady nature of boiling front propagation. The average velocity of the fronts shown is \( u_f = 0.43 \) m/s, which is three orders of magnitude less than the speed of sound in the pure liquid \( (u_{\text{cm}} = 870 \) m/s). This again confirms that depressurization and propagation of the phase-change front into the superheated liquid are decoupled processes. The above runs involved the highest columns of superheated liquid used (ca. 300 mm). The liquid at the bottom remained superheated for more than 0.6 s until it was reached by the boiling front.

4.5.2 Effect of Flow Cross-Section on Boiling Front Velocity

The results of the current investigations can be applied to other geometries and scales if the influence of the test-cell geometry on boiling front velocity is known. If the fluid in the test section behaves essentially as if it were part of a more extended volume on a larger scale, then the pipe wall must not influence the boiling behavior. Even though nucleation on the glass walls was successfully suppressed, experiments were needed to verify whether the geometry of the wall had an impact on the phenomena observed. So the objective of the first measurements was to investigate the influence of the cross-sectional area, i.e., the pipe diameter, on the boiling front velocity.

The experimental set-up of Fig. 3.2 allowed differently-sized pipes to be installed and, indeed glass tubes of different diameters were used. A glass funnel provided, however, a more efficient way of investigating the effect of diameter. The funnel was filled with test fluid, that rested on top of the buffer liquid at its bottom. During front movement from the top to the bottom of the funnel, the diameter decreased from ca. 70 mm to 10 mm, which equals a decrease in cross-sectional area by almost a factor of 50. Thus, instead of replacing the pipe diameter several times and conducting many experiments, a single run allowed the behavior to be investigated in a continuously varying cross-section. Figure 4.18 shows a boiling front in the funnel geometry.
Experimental Results

The contour at each time step was recorded as in Fig. 4.10. The averaged successive front position for three runs with propane is shown in Fig. 4.19. The velocity obtained from the successive measured front locations is also plotted.

The previous finding of quasi-steady boiling front velocity is confirmed. The fronts in Fig. 4.19 advanced roughly linearly with time, i.e. their velocity remained almost unchanged during front propagation. Despite the large decrease in diameter of the funnel, the propagation velocity was reduced only slightly. This minor decrease may possibly be attributed to a small temperature gradient within the test liquid. Because the stagnant buffer liquid was mixed only by free convection, the heat exchange between the test liquid and the surrounding buffer liquid was limited. Accordingly, the temperature at the top of the funnel was probably slightly higher. The boiling front propagated faster at higher superheats, as will be shown further on. Thus, the small temperature drop toward the bottom of the funnel might have decreased the front speed actually measured. In view of this possible reason for the velocity decrease, the propagation velocity can be interpreted as remaining largely unaffected by the pipe diameter in the range investigated.

As presented in the next subsection, the experiments focused on the influence of different degrees of superheat on the propagation velocity. Experiments with pipes of different diameter were conducted with propane and butane, as shown in Fig. 4.20. Thus, the influence of cross-sectional area could again be observed.

As can be seen in Fig. 4.20, the boiling front velocity increased with superheat. At first glance, this increase occurred independently of pipe size. Only boiling front velocities in the "prism", i.e., the flattened pipe section of Fig. 3.3, differ significantly. Obviously, the narrow gap of ca. 4 mm between the parallel glass walls increased the boiling velocity.

Figure 4.21 was obtained by linearly correlating the data of Fig. 4.20 for propane segregated by pipe diameter. The trend lines in Fig. 4.21 indicate a slight dependence on diameter. A middle speed was measured for the smallest pipe diameter of 14 mm while the fastest and slowest propagations were noted in the 80 mm and the 40 mm pipes, respectively; the differences are, however, small. The spread of data for a certain
pipe size or at a certain superheat are of the same order of magnitude, and the limited amount of data are insufficient to allow more detailed interpretation.

Therefore, it can be stated that within the investigated range of internal pipe diameters from 14 mm to 80 mm, no significant influence of cross-sectional area on boiling front velocity is evident. However, as the pipe diameter decreases to the scale of the bubbly structures at the boiling front (as in the glass prism), the behavior of the front is significantly influenced by the presence of the glass walls. Then, the front velocity can no longer be considered as independent of the cross-sectional size.

This last conclusion is supported by the findings of Sugioka (1991), who placed glass beads 0.4 - 0.7 mm in diameter in columns of refrigerants R-12 and R-114. The boiling front, which traveled through the superheated liquid in this sphere bed, attained velocities six times greater than without packing. Thus, small cross sections of the kind appearing between the glass beads increased the boiling front velocity significantly. The size of the glass beads and of the cavities between them were smaller than that of the bubbles observed without glass beads.
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**Fig. 4.20**: Influence of cross-sectional area on boiling front velocity at different superheats for propane and butane (propane with linear regression line)

**Fig. 4.21**: Linear regression of boiling front velocity with superheat for different pipe diameters in propane (see Fig. 4.20 for comparison)
4.5.3 Effect of Superheat on Boiling Front Velocity

Beside the geometry and use of the four test fluids, the other parameter varied was the initial temperature. Since the test substances were always released to atmospheric pressure, this lead to a varying nominal superheat. The results are summarized in Fig. 4.22 (see Appendix E for comparison to plots versus real superheat).

Even though the same superheat led to different boiling front velocities, some characteristic similarities were observed for all four fluids. In general, the boiling front velocity, $u_h$, can be described by the following equation:

$$u_h = (0.0307 \Delta T_{nom}/K - 0.977) \text{ m/s}$$

where $\Delta T_{nom}$ is the nominal superheat. The values of $u_h$ for butane, propane, R-134a, and water are shown in the graphs below.

Fig. 4.22: Velocity of boiling fronts for butane, propane, R-134a and water ($\triangle$/$\odot$: data used/not used for linear correlation; lines indicate linear regression line and an 80% confidence limit, see Appendix E for comparison with data plotted versus the “real” superheat)
velocity increased with superheat, as already mentioned in the previous section. The maximum observed speed of 1.3 m/s was reached with butane at a superheat of $\Delta T_{\text{nom}} = 73$ K. Above a certain threshold, the boiling front speeds showed a dependence on the degree of superheat that was roughly linear over the range of conditions investigated.

Below this threshold ($\Delta T_{\text{nom, butane}} < 32$ K; $\Delta T_{\text{nom, propane}} < 27$ K; $\Delta T_{\text{nom, R-134a}} < 29$ K; $\Delta T_{\text{nom, water}} < 10$ K), no front propagation, but rather “quiet boiling” was observed (see Fig. 4.7). Thus, boiling front propagation required a minimum superheat, which varied with the fluid. This finding of a lower threshold for boiling front propagation confirmed the results of Grolmes and Fauske (1974) and Hill (1991), which were obtained for other fluids. Apparently, below the threshold, the released latent heat is not sufficient to produce a vapor stream strong enough to carry away the surplus liquid. In view of the existence of this lower limit for boiling front occurrence, it can be concluded that boiling front propagation is determined only partly by the stored thermal energy. Otherwise, the front movement should have taken place at any arbitrarily low superheat.

The spread in the data is quite noticeable, particularly for various runs with propane at a superheat of ca. $\Delta T_{\text{nom}} = 47$ K. Neglecting uncertainties in the temperature measurements, the most plausible reason found for this scatter was the varying fill level of the test liquid. In general, the runs in the 40 mm pipe started with a higher column of test fluid than the runs in the 80 mm pipe (greater by a factor of roughly 1.5) because of the less time-consuming filling (condensation) of the small pipes. Therefore, the averaging of the velocity was generally based on fewer time steps in the case of 80 mm pipes. Because of the random nature of boiling front propagation, a shorter period of averaging caused a wider spread in the data, e.g. at ca. $\Delta T_{\text{nom}} = 47$ K the measurements in the 80 mm pipe varied from about 0.5 to 0.9 m/s, whereas the boiling front velocity in the 40 mm pipe ranged from about 0.4 to 0.6 m/s. Particularly long runs with high liquid columns, such as Run 033 and Run 034 in Fig. 4.17, where the velocity was averaged over about thirty time steps, led to a difference in propagation velocity of less than 1%. Therefore, the spread in data is likely to be related to the varying duration of the runs, i.e. the fill level.

The dependence of the velocity on superheat was correlated by linear regression. The resulting straight line and its corresponding equation together with the 80% confidence limits are given in Figure 4.22. The linear correlations are summarized in Table 4.2.

The experimental data for water deviated from the linear trend noted for the other test fluids. Initially, it was thought that the increasing mass flux of the two-phase mixture reached critical flow, i.e. choking occurred. However, the analysis presented in the

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<th>Table 4.2: Boiling front propagation parameters</th>
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<td>Lower threshold [K] (correlations of Fig. 4.22 with $u_f = 0$ m/s)</td>
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<td>$d(u_f)/d(\Delta T_{\text{nom}})$ [m s$^{-1}$ K$^{-1}$]</td>
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following chapter resulted in mass fluxes which were too low to be critical, i.e. to explain the non-linear front velocity increase in water. In any case, the onset of boiling front propagation was measured to be near $\Delta T_{\text{onset,water}} = 10$ K. For practical reasons, the remaining data points were correlated by a line crossing the horizontal axis at this superheat in Fig. 4.22.

As illustrated in Fig. 4.7, some saturated liquid remained in the test section after termination of the vaporization with slow bubbling below the threshold of boiling front propagation. This fraction, that was not carried away by the two-phase jet, could be measured by comparing the initial and final liquid levels in the pipe. Only a few experiments could be analyzed because in most of the runs below the threshold temperature single bubbles appearing in the bulk expelled the whole liquid column. However, the remaining relevant experiments where only "slow bubbling" occurred could be analyzed; the results are plotted in Fig. 4.23.

Considering also the thresholds of Table 4.2, it was found that the amount of residual liquid decreased roughly linearly to zero as the initial superheat approached the threshold for boiling front propagation. At lower superheats, the major part of the liquid remained unvaporized in the pipe. Since in the experiments the saturation temperature was below the temperature of the surrounding conditioning liquid, heat transfer to the test fluid and slow bubbling took place after the main initial vaporization process. The liquid eventually vaporized completely.

The above measurements were taken within three seconds after explosive boiling stopped. During this time, heat transfer from the conditioning liquid and the related vaporization and the expulsion of liquid from the pipe reduced the amount of fluid left in the pipe. Therefore, the theoretical fraction of liquid remaining in an adiabatic pipe as plotted in Fig. 4.23 (calculation based on Eq. 2.3) was not reached. Particularly, near the onset of front propagation the non-adiabatic vaporization and the removal of liquid led to a lower fraction of residual fluid than could be theoretically expected.
4.5.4 Effect of Boiling Front Velocity on the Pressure in the Superheated Liquid

The thermal energy stored in the metastable liquid is consumed for vaporization. Mass conservation and the increase in specific volume of the two-phase flow leaving the interface produces a high-velocity jet. As a result, the vapor/liquid mixture leaving the interface produces a thrust on the superheated liquid leading to the pressure plateau shown in Fig. 4.3. In addition, there is a frictional pressure drop between the boiling front and the ambient air to which the mixture is released at the pipe exit. The base pressures of various runs, i.e. the pressures in the superheated liquid, resulted in the plot of Fig. 4.24.

The data for Fig. 4.24 were obtained by considering only approximately the middle 80% of the length of the typical quasi-steady pressure plateau shown in Fig. 4.3. Any influence on the averaged pressure value plotted in Fig. 4.24 by the arbitrary selection of limits for this range was insignificant since at least several hundred data points were recorded during the relevant time period.

As might be expected, the pressure difference between the superheated volume and the ambient air assumed to be at $p_{atm} = 1$ bar, to which the liquid was released, generally increased with rising boiling front velocity $u_{fr}$ and superheat $\Delta T_{nom}$. Under similar conditions, particularly high back pressures were noted for R-134a and water while the values for butane and propane were very similar and generally lower.

Table 3.2, listing the thermophysical properties of the fluids, indicates particularly high liquid/vapor density ratios for water which led to relatively high vapor velocities. This in turn leads to a high back pressure. R-134a is set apart from the other test fluids by its high vapor density $\rho_{sat}$ and high quality $x$ after vaporization from a certain initial superheat. These properties explain the high thrust pressure of R-134a. A more
4. Experimental Results

Fig. 4.25: Pressure trace under limited outflow conditions (upper plot) and difference between base and exit pressures (lower plot; release from $d_{\text{pipe}} = 80 \text{ mm}$ through $d_{\text{orifice}} = 30 \text{ mm}$, Run 087, propane, $\Delta T_{\text{nom}} = 62 \text{ K}$, $u_b = 0.33 \text{ m/s}$)

detailed analytical study of the reduction of nominal superheat by an increase in pressure will be given later in section 5.1.1.

4.5.5 Effect of Pressure on Boiling Front Velocity

The contents of the test section were always released to the atmosphere. This defined the pressure downstream of the vaporization zone as $p_{\text{atm}} = 1 \text{ bar}$. In order to vary the pressure in the boiling front zone at a constant initial temperature, an orifice was introduced into the flow channel. The limited outflow area led to an increased pressure in the test section volume. The influence of the total pressure on front propagation could be investigated by this means.

As in the case of full opening (see Fig. 4.3), the release through an orifice led to an immediate fall in pressure after cutting the rupture disk. However, the depressurization rate was much smaller than in experiments without an orifice (see Fig. 4.3 for comparison). A pressure plateau was again formed during boiling front propagation. The pressure transducer upstream of the orifice now recorded a pressure higher than the atmospheric pressure and very similar to the pressure measured at the base. In fact, a detailed look at the base and exit pressure curves (bottom of Fig. 4.25) showed a
Fig. 4.26: Influence of the orifice on pressure in the superheated liquid $p_{\text{base}}$ and on the boiling front velocity $u_f$ for butane and propane.

typical fluctuation of ± 0.1 bar with a pressure that was higher by an average of 0.044 bar at the transducer located at the bottom of the stagnant superheated liquid. Thus, the orifice increased the total pressure in the test section and reduced the pressure gradient between the stagnant superheated liquid and the exit of the pipe.

Figure 4.26 depicts the effect of the orifice on the pressure in the stagnant superheated liquid and on the boiling front velocity for several runs. Experiments with propane and butane with or without an orifice are compared. The orificing of the flow area from $d = 80$ mm to $d = 30$ mm resulted in a higher pressure in the superheated liquid ($p_{\text{base}}$), as shown in the left plot. The right plot indicates that a higher pressure in the boiling front region at a constant initial temperature led to a reduced boiling front velocity. This relation is plotted in Fig. 4.27 in another form. In general, an increasing boiling front velocity led to a rise in pressure, but with a steeper increase in the case of flow limitation in the two-phase region.

The structure of the boiling front at an elevated pressure was not investigated by close-up recordings. However, a comparison of regular video images, as in Fig. 4.28, shows

Fig. 4.27: Pressure in the superheated liquid $p_{\text{base}}$ vs. boiling front velocity $u_f$. 
4. Experimental Results

Fig. 4.28: Boiling front appearance with (left) and without (right) orifice (propane; $\Delta T_{\text{nom}} = 51$ K; left: Run 081, $u_r = 0.16$ m/s; right: Run 082, $u_r = 0.70$ m/s)

that the contour line appeared rougher at limited outflow conditions and correspondingly lower boiling front velocities. At the same initial superheat, bubbles of larger size were noticed than at lower total pressure. In fact, a rough comparison with experiments at a lower total pressure (without an orifice) showed that the resulting appearance was similar to that of the runs conducted at a lower superheat but an equal boiling front velocity.

Due to the limited time available, only one orifice size was tested to study the qualitative pressure influence. In summary, it could be shown that boiling front propagation also occurred at elevated pressures, something that is important to know for situations with limited outflow from containments. From these experiments, it can be concluded that a higher total pressure at the same initial superheat leads to a lower velocity and a "rouglier" structure of the boiling front.

4.5.6 Effect of Boiling Front on Two-Phase Flow Velocity

For measuring the two-phase flow velocity, a two meter long, transparent acrylic glass pipe with the same internal diameter as the test section (80 mm) was placed on top of the opening mechanism. Video recordings of this pipe did not provide a sufficient frame rate for studying the two-phase flow. So high-speed movie recordings with frequencies of more than 6000 frames/s were made. Because of the costs of high-speed filming, only a limited number of experiments was conducted.

The camera was placed approximately 0.9 m downstream of the boiling front and recorded the two-phase flow over a length of approximately 0.1 m. For analysis, the motion of "swarms" of liquid fragments and aerosol was measured. A thin liquid film visible on the glass walls (annular flow) could clearly be distinguished from the high-velocity flow in the pipe. Attempts to trace the flow with polystyrene chips failed. Putting them above the rupture disk was unsuitable since they would have been accelerated with the initial velocity of the expanding pure vapor space. This velocity was considerably higher than that of the later two-phase flow at steady state that was to be measured. Placing them into the pressurized vapor space above the test liquid resulted in their fine-scale disintegration due to the sudden pressure drop after opening the rupture disk. So clearly recognisable liquid droplet swarms were identified and
4. Experimental Results

Fig. 4.29: Two-phase flow velocity downstream of the boiling front

(Propane; ■: Run 125-127; + : test with growth of a single bubble on the glass walls during front propagation leading to a higher velocity than in the undisturbed case at the corresponding superheat; front velocity measured but data not used in further analysis)

followed from frame to frame and their average propagation rate was taken as the two-phase flow velocity.

Figure 4.29 displays the results for the two-phase flow velocity during the steady boiling front propagation. As can be seen, increasing superheat enhanced the velocity of the two-phase mixture. Similarly, the two-phase flow velocity increased with rising boiling front velocity. A significant difference was measured between the boiling front and two-phase flow velocities, reaching a ratio of $u_{\text{TPF}}/u_{\text{t}} = 65$ within the observed range.

For the above measurements, the passage of the liquid/vapor mixture over a length of 10 cm downstream of the boiling front was analyzed, as mentioned. At the typical frame rate and two-phase flow velocities, at most 15 time steps of a moving pattern could be monitored. Within the range of uncertainty, no acceleration could be detected by analyzing these. It can be concluded that at the above distance of 90 cm away from the boiling zone and under quasi-adiabatic conditions, the fluid mixture moved at constant velocity. More detailed tracking of the two-phase flow acceleration process downstream of the vaporization zone was not performed, since this would have required a considerable amount of additional, costly, high-speed filming.

4.5.7 Effect of Release Direction and Gravity on Boiling Front Propagation

Contour plots displaying the temporal change of the boiling front could be obtained from recordings such as those of Fig. 4.16. As an example, the change of shape of the superheated liquid remaining between the glass disks is shown in Fig. 4.30.

It can be seen that at the beginning vaporization occurred only in the upper part of the test volume. It then started all around the circumference. In later steps, the liquid in the center of the test section was not at rest, but was pushed in various directions: in the plots, the liquid area of a later time step sometimes partly covers the area of an earlier time step. It is likely that the central superheated liquid was also moved during start-up when the front movement was noted only in the upper part, i.e. it was pushed toward
4. Experimental Results

Contours of the boiling front during its propagation towards the center of the superheated liquid (Run 140, propane, $\Delta T_{\text{nom}} = 47$ K, $u_f = 1.5$ m/s (radial average))

the bottom of the test section. However, the liquid could not be marked, so its movement remained unnoticed in these experiments.

In another experiment, the circular cross section was not emptied from buffer liquid completely, so that at the lower fourth of the circular view field an interface between buffer and test liquid remained. Another interface, that is the line between test liquid and vapor, was visible in the upper part of the circular view field. Upon opening the test section, vaporization started at the top of the superheated liquid volume. This pushed the buffer and test liquids downwards. Already in the next frame of the video sequence (0.02 s later) the interface between buffer and test liquid was no longer visible. Considering the distance travelled by the interface (2 cm) this movement of liquid volume indicates an acceleration of at least ten times the earth gravity. This supports the assumption that liquid was moved already during start-up of the run shown in Fig. 4.30. In this case, the motion of the liquid/vapor interface is the combined result of boiling front propagation and liquid movement.

The decreasing amount of superheated liquid could be determined from plots such as that of Fig. 4.30. Transforming the irregular volumes to equivalent cylindrical forms allowed to determine the decrease of diameter with time. Figure 4.31, including the recordings of other experiments as well, shows that the decrease in average volume proceeds irregularly in time. A slow radial decrease is observed at the beginning. Later the equivalent radial velocity increases; however, the contour line at this time deviates strongly from a cylindrical shape (e.g. at times later than 40 ms in Fig. 4.30). Comparing the average speed to front velocities measured in pipes at the same superheat shows, that at the beginning similar velocities are noted, however, at later
4. Experimental Results

Fig. 4.31: Average velocity of boiling front during circular release and during propagation in a pipe (propane)

stages, the equivalent velocity for the cylindrical volume proceeds faster. Due to the limited temperature conditioning capability of the test section used for these experiments (see section 3.2), only a limited range of superheats was investigated.

4.5.8 Droplet Size Measurements

In a few experiments, colored propane was released and its two-phase jet impinged on rotating paper sheets as described in section 3.1.4. After vaporization of the superheated drops, circular spots were left on the paper which could then be examined. The original drop size could be determined in conjunction with the calibration presented in Appendix A. The results of this data collection and transformation are presented here.

This simple technique was used only to get an order of magnitude of typical drop sizes. Its major deficiencies were a limited resolution to drop sizes not smaller than ca. \( d_{\text{drop}} = 0.05 \text{ mm} \) (corresponding to a spot diameter of 0.1 mm) and the inaccuracy stemming from the indirect method of measuring the drop size. Because of these limitations, only a limited amount of data was taken. This method cannot be used as a substitute for more advanced techniques.

The experiments were conducted with propane, using three different superheats (\( \Delta T_{\text{m}} \approx 48 \text{ K, } 54 \text{ K, } 61 \text{ K} \)) and two different distances from the initial liquid fill level (\( d = 1.1 \text{ m, } 1.6 \text{ m} \)). The jet travelled through still ambient air and the core of the aerosol had to pass through an orifice before hitting the paper. From each run, five areas of the impact sheets with a diameter of 2 cm were analysed. Every clearly distinguishable spot with a diameter larger than 0.05 mm was recorded resulting in approximately 550 analysed impingements. However, ambiguities rose from the fact that some spots overlapped and/or that contours were not contrasted on the evenly colored background of similar color by smaller drops. The result of this data collection and transformation is plotted as the lognormal cumulative drop-size distributions of Fig. 4.32. The figure shows the trends obtained by fitting the actual data points to lognormal distributions. It should be emphasised, that this pattern does not represent the actual drop size distribution in the two-phase flow but rather the result of the data.
4. Experimental Results

Fig. 4.32: Fitted drop-size distributions in detectable range from five experiments with propane

collection with the limitations described above. As one consequence, the above arithmetic mean is certainly not the average value of all aerosol particles downstream the boiling front but only of the noted proportion.

Qualitatively, it can be concluded from Fig. 4.32 that increasing superheat leads to smaller drop sizes. While at a superheat of $\Delta T_{\text{nom}} = 61$ K ($T_{\text{initial}} = 19^\circ$C) no drops could be analysed because all sizes were below the detectable range, in runs at lower superheat, numerous impingements were left on the paper, e.g. the largest drops reached diameters of up to 3 mm (not shown in Fig. 4.32). From the evenly sprayed paper regions it can, however, be assumed that the majority of drops were below the analysable range.

From Fig. 4.32 the changes of the droplet spectrum with distance become evident. The more distant location at 1.6 m leads to a droplet population of smaller size on the average. For a quantitative prediction of drop diameter decrease with increasing distance, however, the data is too incomplete.

In summary it can be stated that the mean drop size decreases with growing superheat and distance from the boiling front zone. The recordings of drops impinging on paper supported the impression that the vaporization leads to fine fragmentation of the unvaporized liquid. For propane at superheat of $\Delta T_{\text{nom}} = 60$ K and at distance of 1.6 m from the boiling front no drop diameter greater than 0.05 mm was found. To which extent secondary effects, such as reentrainment from the liquid film on the walls of the pipe played a role cannot be stated. This would certainly be an artefact not occurring at large-scale unconfined releases.
4.6 Summary of Experimental Results for Boiling Front Propagation

A liquid can be brought to a superheated state by sudden depressurization. Within a certain range (bounded by a lower threshold degree of superheat and by the onset of homogeneous nucleation), boiling can be limited to the free surface of the liquid volume. This requires the absence of nucleation sites (cavities, impurities) in contact with the liquid to suppress any ordinary wall boiling.

The boiling, which proceeds via a phase-change front into the stagnant superheated liquid, is characterized by a vigorous, fine-scale break-up of the superheated liquid, caused by an extremely fast phase transition. A liquid/vapor mixture is accelerated perpendicularly away from the free surface of the metastable liquid. The boiling layer, consisting of a bubbly structure, is irregular in shape and continuously changes its contour during the quasi-steady propagation phase as the integral result of several randomly occurring interacting processes. Explosive bursts within the boiling front are the outcome of a self-amplifying cycle of vaporization, liquid fragmentation and liquid-surface enlargement.

In releases from a circular geometry, boiling appears only on the outer cylindrical surface of the superheated liquid. The vaporization zone travels toward the center of the superheated liquid, leading to a radially expanding stream of vapor/liquid mixture. The major effects of varying superheat on the front characteristics are summarized in Table 4.3.

Several quantitative relationships could be determined. In the range of cross sections investigated, it was found that the wall proximity and the size of the receptacle do not influence the propagation of the boiling front. Only with diameters reaching the same order of magnitude as the typical scale of bubbles at the front was a front velocity increase due to a narrow cross section observed.

Boiling front propagation requires a minimum of superheat. Above this temperature, the fronts propagate at a quasi-constant velocity, which increases roughly linearly with superheat (see Table 4.2). An increasing boiling front velocity leads to an increase in pressure in the superheated liquid due to the acceleration of the two-phase mixture. The boiling front velocity is in turn reduced by an elevated pressure in the boiling front region, for example due to an orifice placed in the two-phase stream. The velocity of the two-phase stream increases with superheat and corresponding boiling front velocity. In the facility used for circular releases, higher circularly-averaged front velocities appear than in the one-dimensional case.

Drop sizes of the two-phase stream emerging from the boiling front are typically well below one millimeter, hence one concludes that the explosive boiling leads to fine-scale fragmentation.
Table 4.3: Summary of some qualitative findings for typical boiling front propagation in pipe geometry

<table>
<thead>
<tr>
<th>Location and aspect</th>
<th>Low superheat at or below onset of boiling front propagation (e.g. butane at $\Delta T_{nom} = 30$ K)</th>
<th>Medium superheat above onset of boiling front propagation (e.g. butane at $\Delta T_{nom} = 40$ K)</th>
<th>High superheat (e.g. butane at $\Delta T_{nom} = 70$ K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiation of boiling front propagation on free surface</td>
<td>Nucleation of slow-growing bubbles possibly after several milliseconds delay time</td>
<td>Immediate nucleation at liquid/vapor/glass contact line</td>
<td>Immediate nucleation on whole free surface</td>
</tr>
<tr>
<td>Contour line of boiling front</td>
<td>Rough, almost complete bubbles visible</td>
<td>Medium</td>
<td>Fine scale</td>
</tr>
<tr>
<td>Bubbly structure of boiling front</td>
<td>Rough bubbles, reaching maximum diameter of the order of centimeters</td>
<td>Reaching maximum diameters in the range of several millimeters</td>
<td>Maximum diameters not more than a few millimeters</td>
</tr>
<tr>
<td>Visible convective motion in stagnant superheated liquid</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Residual liquid after termination of boiling front propagation</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Bursts in zone behind leading surface plane</td>
<td>Random bursts as single events at a distant location from the leading surface</td>
<td>Irregular bursts, but more frequent than at low superheat</td>
<td>Almost continuously sweeping on whole front area, within a few millimeters downstream leading edge</td>
</tr>
<tr>
<td>Two-phase region appears</td>
<td>Highly unsteady, liquid chunks/drops in millimeter range</td>
<td>Unsteady, spray-like</td>
<td>Spray-like, evenly distributed</td>
</tr>
</tbody>
</table>
Chapter 5
Analysis of Boiling Front Experiments

The final objective of this work is to predict the magnitude of energy conversion which can result from the sudden unconfined depressurization of liquid. If a boiling front is the dominating vaporization mechanism in such a process, it is important to describe its behavior and to understand the influence of thermophysical properties on the propagation velocity. In turn, and with respect to catastrophic vessel failure, this velocity is of importance since it influences the characteristics of the expanding aerosol cloud that is formed.

The following analysis relates several quantities such as the pressure in the stagnant liquid, the boiling front velocity and the two-phase quality and velocity. Thereafter, calculations are presented which concern the influence of downstream pressure on boiling rate, the critical flow conditions and releases in cylindrical geometry. Finally, the growth of single bubbles in superheated liquid is analysed and quantitatively compared to the behavior of the boiling front.

5.1 Interfacial Jump Condition

A quantitative macroscopic investigation of the boiling front allows conclusions to be drawn about the phase transition at microscopic level. An analysis using a control volume moving with the phase interface is carried out first.

5.1.1 Conservation Equations

In schematic form, a boiling front can be considered as a moving one-dimensional discontinuity of the phases. The transition from the stagnant liquid phase to two-phase flow is assumed to occur in a front of negligible thickness. Although violently unstable at the microscopic level, the front is assumed to progress at steady speed, as illustrated in Fig. 5.1.

Consider the control volume of Fig. 5.1 moving with the steady boiling front velocity. The superheated liquid (1) enters the control volume from the left at the velocity \( u_1 \) corresponding to the average boiling front velocity \( u_{bf} \). The phase discontinuity within this frame of reference is at rest. Frictional effects are ignored and adiabatic flow in the control volume is assumed. Further, the two-phase flow leaving on the right (2) is presumed to be a homogeneous stream at \( u_2 \) which is taken as the two-phase velocity \( u_{TPF} \). If \( u_{TPF} \) is considered to be the two-phase
5. Analysis of Boiling Front Experiments

mixture velocity in an absolute frame of reference, then \( u_2 \) should have been \( u_2 = u_{spf} + u_h \). Since \( u_{spf} \gg u_h \), \( u_2 = u_{spf} \) is a good approximation. The cross sectional areas at (1) and (2) are the same.

Since there is no source or sink within the control volume of Fig. 5.1, the upstream and downstream states are related by the following equations for the conservation of mass, momentum and energy.

\[
\rho_1 u_1 = \rho_2 u_2 \tag{5.1}
\]
\[
\rho_1 + \rho_1 u_1^2 = \rho_2 + \rho_2 u_2^2 \tag{5.2}
\]
\[
h_1 + \frac{1}{2} u_1^2 = h_2 + \frac{1}{2} u_2^2 \tag{5.3}
\]

Assuming equal velocities between the phases at 2, the two-phase density \( \rho_2 \) is given by:

\[
\frac{1}{\rho_2} = (1 - x_2) \frac{1}{\rho_{L2}} + x_2 \frac{1}{\rho_{G2}} \tag{5.4}
\]

where \( x_2 \) is the flowing quality at 2. The enthalpy at 2 is given by:

\[
h_2 = (1 - x_2) h_{L2} + x_2 h_{G2} \tag{5.5}
\]

and the pressure drop between 1 and 2 is:

\[
\Delta p = p_1 - p_2 \tag{5.6}
\]

Taking:

\[
\rho_1 = \rho_{L1}; h_1 = h_{L1}; u_1 = u_h; u_2 = u_{spf}
\]

where \( \rho_{L1}, h_1 \) correspond to saturation at \( T_1 \)

and \( h_{L2}, h_{G2}, \rho_{L2}, \rho_{G2} \) correspond to saturation at \( p_2 \).

The effects of slip in the two-phase flow are discussed in section 5.1.5 and in Appendix G.

Given the temperature \( T_1 \) and the exit (release) pressure \( p_2 \) (generally assumed to be 1 bar), the above three conservation equations contain four unknowns, \( u_h, u_{spf}, \Delta p \) and \( x_2 \). Thus, a fourth expression, for instance relating the experimental conditions to the boiling front velocity \( u_h \) is needed.

Using only the mass and energy conservation equations (5.1) and (5.3) and the above substitutions, the algebraic transformation leads to a quadratic expression for \( x_2 \):

\[
x_2^2 + \left( \frac{h_{G2} - h_{L2}}{u_h^2} \right)^2 \left( \frac{\rho_{L1}}{\rho_{L2}} \right)^3 + \left( \frac{\rho_{L1}}{\rho_{L2}} \right)^3 = 0
\]

which can be further simplified and solved by assuming:
Influence of boiling front velocity $u_f$ on downstream quality $x_2$ at constant nominal superheat $\Delta T_{\text{nom}}$ for propane for release to $p_2 = 1$ bar and measured increase of boiling front velocity with nominal superheat

$$\frac{\rho_{\text{liq}}}{\rho_{\text{g}}} = 1$$  \hspace{1cm} (5.8)

The assumption of Eq. (5.8) does not introduce a relevant error in the range considered, as our own calculations have shown.

Equation (5.7) indicates that at constant nominal superheat, i.e. initial temperature and corresponding enthalpy $h_{\text{liq}}$, a range of boiling front velocities $u_f$ is possible, depending on the downstream quality $x_2$. As shown in Fig. 5.2, a release at a certain nominal superheat can produce a considerable range of boiling front velocities $u_f$ with only slight changes in the quality $x_2$. The relationship between quality and front velocity is unknown a priori. For further analysis, therefore, the measured velocity must be used.

The locus of the measured $u_f$ points on the various superheat lines provides the relationship between the front velocity and quality at the front and is also shown in Fig. 5.2. It is based on the linear correlation of Fig 4.22 resulting from propane data. In general, an increase in superheat leads to an increase in both boiling front velocity and two-phase quality.

With a known quality $x_2$ the homogeneous two-phase flow velocity $u_{\text{TPF}}$

$$u_{\text{TPF}} = \left(1 + x_2 \left(\frac{\rho_{\text{liq}}}{\rho_{\text{g}}} - 1\right)\right) u_f$$  \hspace{1cm} (5.9)

and, by additionally considering the momentum equation (5.2), the accelerational pressure drop $\Delta p$ can be calculated:

$$\Delta p = \left(\frac{\rho_{\text{liq}}}{\rho_{\text{g}}} - 1\right) \rho_{\text{liq}} x_2 u_f^2$$  \hspace{1cm} (5.10)
Equations (5.7) and (5.9) allow the sensitivity of the two-phase flow velocity to the downstream quality to be calculated. Figure 5.3 shows that slightly increasing the quality \( x_2 \) at constant nominal superheat \( \Delta T_{\text{nom}} \) significantly decreases the two-phase flow velocity \( \nu_{\text{TPF}} \). Again the line of values resulting from the control volume analysis using the measured boiling front velocity is also plotted.

The same findings as those predicted by Eq. 5.7 were obtained using a control volume within a fixed frame of reference. However, a phase interface moving in the control volume results in having to solve cubic rather than quadratic expressions for the quality \( x_2 \), which leads to algebraic complications in the calculations. Therefore, an analysis based on a fixed-coordinate system was not performed but is merely attached in Appendix F.

### 5.1.2 Relation of some Parameters during Boiling Front Propagation

The equations given above can be used to calculate several relations based on the measured boiling front velocity. The linear correlation of Fig. 4.22 for \( u_{\text{fr}} = f(\Delta T_{\text{nom}}) \) in the relevant range above the lower limit of boiling front propagation of propane is used as an example to illustrate these dependencies:

\[
\begin{align*}
  x_2 &= f(\Delta T_{\text{nom}}), \\
  \nu_{\text{TPF}} &= f(\Delta T_{\text{nom}}) \quad \text{and} \\
  \Delta p &= f(\Delta T_{\text{nom}}).
\end{align*}
\]

Additionally, the Jakob numbers \( Ja \) and \( Ja^* \), and the real superheat \( \Delta T_{\text{real}} \) in the metastable liquid due to the accelerational pressure increase \( \Delta p \), are displayed in different plots. The physical properties were obtained using the correlations of Appendix B.

The plots on the left of Fig. 5.4 show that increasing the nominal superheat \( \Delta T_{\text{nom}} \) also increases the downstream quality \( x_2 \), the two-phase flow velocity \( \nu_{\text{TPF}} \) and the pressure difference \( \Delta p \) between the stagnant superheated liquid and the region immediately above the boiling front. The acceleration effect due to the liquid/vapor phase transition increases the pressure at the boiling front and induces a lower superheat in the metastable liquid with \( \Delta T_{\text{real}} < \Delta T_{\text{nom}} \).
5. Analysis of Boiling Front Experiments

Fig. 5.4: Boiling front characteristics of propane based on measured front velocity $u_F$ (assuming homogeneous two-phase flow)

All relationships are based on a linear increase in boiling front velocity with superheat. The resulting dependencies on $\Delta T_{nom}$ and $x_2$ are, however, non-linear. The quality $x_2$ and the real superheat $\Delta T_{real}$ increase with $\Delta T_{nom}$ according to a power law with an exponent of less than one, whereas the two-phase flow velocity $u_{TPF}$ and the pressure drop $\Delta p$ increase with an exponent greater than one. Similar trends are observed for the effect of quality $x_2$, as shown by the right plots of Fig. 5.4. The lowest plot on the right indicates the increasing divergence between real and nominal superheat.

Figure 5.4 resulted from the linear correlation for the front velocity shown in Fig. 4.22. However, the measured data have a scatter, i.e. a range of boiling front velocities $u_F$ is measured at a certain superheat. Similarly, the same boiling front velocity might be observed at different superheats. The sensitivity of the quality $x_2$ and two-phase flow
5. Analysis of Boiling Front Experiments

5.1 Change of quality $x_2$ and two-phase flow velocity $u_{TPF}$ with varying boiling front velocity $u_b$ and superheat $\Delta T_{nom}$ at constant superheat and front velocity, respectively, for propane released to 1 bar

For Fig. 5.5, the points with the strongest spread in the data of Fig. 4.22 were chosen, i.e. $\Delta T_{nom} = 47$ K and $u_b = 1$ m/s. The left plot shows that a significant change in the front velocity at constant superheat leads only to minor changes in the quality but to a considerable change in the two-phase flow velocity ($u_{TPF}$ ↑: 125 %; $x_2$ ↓: 0.9 %; $u_b$ ↑: 122 %). For a constant boiling front velocity and a rising superheat, the right plot indicates a similar increase in both the quality and the two-phase flow velocity ($\Delta T_{nom}$ ↑: 22 %; $x_2$ ↑: 24 %; $u_{TPF}$ ↑: 19 %). The very strong dependence of $u_b$ on $x_2$ (and

---

**Fig. 5.5**: Change of quality $x_2$ and two-phase flow velocity $u_{TPF}$ with varying boiling front velocity $u_b$ and superheat $\Delta T_{nom}$ at constant superheat and front velocity, respectively, for propane released to 1 bar

**Fig. 5.6**: Boiling front velocity and pressure drop across the boiling front as a function of quality for four test fluids ($x_2$ for water at a different scale)
consequently on $\Delta T_{\text{nom}}$) explains the scatter observed. Moreover, a given initial superheat or boiling front velocity may lead to a significant spread in the two-phase flow velocities.

In the above analysis only propane was considered. The behavior of the other fluids investigated, i.e. butane, R-134 and water is summarized in Fig. 5.6, which includes propane for easy comparison as well. Again, the plots result from the linear correlations of the boiling front velocity of Fig. 4.22, covering only the range of quality where boiling front propagation was observed. Butane, propane and R-134a show rather similar trends of boiling front velocity with $x_2$ while water vaporization already sets in at a significantly lower quality. In comparison to the other fluids, R-134a and water show the highest accelerational pressures for corresponding quality.

**Fig. 5.7:** Two-phase velocity, nominal and real superheat for different qualities and four test fluids. Bottom: relation between boiling front velocity and two-phase flow velocity.
5. Analysis of Boiling Front Experiments

Fig. 5.8: Isenthalpic, isentropic and experimental quality $x_2$ for propane and water

The effect of this pressure increase is displayed in Fig. 5.7. At the upper limit of the range investigated this leads, particularly for water, but also for R-134a, to a near flattening in the increase of real superheat $\Delta T_{\text{real}}$ with increasing quality: the pressure exerted on the stagnant liquid by the ejected two-phase flow attenuates the increase in nominal superheat $\Delta T_{\text{nom}}$. The main contributing factor to this behavior is certainly the large liquid/vapor density ratio, in particular of water. This parameter is probably also the main contributor to the different two-phase flow velocities plotted in Fig. 5.7. Water, having a much larger latent heat, already reaches the same two-phase flow velocities at $1/7$th to $1/8$th of the quality of the other fluids. Propane, butane and R-134a reach similar two-phase flow velocities at comparable qualities.

The lower plot of Fig. 5.7 depicts the increase of two-phase flow velocity $u_{\text{TPF}}$ with boiling front velocity $u_b$. Since the quality increases with front velocity, the two-phase velocity increases in a non-linear way. A particularly strong increase is noted for R-134a and water.

5.1.3 Difference between Isenthalpic and Isentropic Flow

The analysis with the control volume around the boiling front allows the downstream quality $x_2$, determined semi-theoretically*, to be compared with theoretical predictions. The isenthalpic quality discussed in section 2.1 assumes that the vapor/liquid mixture is at rest after vaporization; this results in the highest possible quality because no latent heat is converted to kinetic energy. In contrast, the isentropic quality results in maximum conversion to kinetic energy, thus leading to the lowest quality. The experimental values are between these two limiting cases, as shown in Fig. 5.8. They are very near the isenthalpic results. Therefore, the phase-change at a boiling front cannot be described as an isentropic process. In recalling the sensitivity to quality

* "Semi-theoretical" because the measured boiling front velocity $u_b$ is used as an input.
5. Analysis of Boiling Front Experiments

2.5

I

1.5-

0.5

butane
propane
R-134a
water

--- theoretical

--- regression of data

Fig. 5.9: Measured and calculated pressure $p_1$ of stagnant superheated liquid

changes illustrated in Fig. 5.3, it becomes obvious that the assumption of an isentropic phase change will lead to a considerable overestimation of the two-phase flow velocity. Similar findings were obtained for explosive vaporization after release from spherical vessels by Schmidli (1993). It was found that the expansion velocities were significantly lower than those predicted by assuming an isentropic phase change and a corresponding transformation to kinetic energy.

5.1.4 Pressure Results

The experimental data for the boiling front velocity $u_b$ and the calculated values of $x_2$ from Eq. (5.7) were used to calculate the accelerational pressure drop $\Delta p$ across the boiling front. Assuming that this pressure drop was the one measured between the pressure transducer in the stagnant liquid and the exit (measured to be $p_2 = 1$ bar), the absolute pressure $p_1$ in the superheated liquid could be calculated and compared with the measured data. As an example, in Fig. 4.3 the calculated pressure $p_1$ was plotted and found to be somewhat lower than the measured value. Several such runs were analyzed, where each run with the corresponding boiling front velocity and the relevant fluid properties had to be considered separately. The results are compared in Fig. 5.9.

The measurements of the base pressures $p_1$ during the period of constant boiling front propagation are found to be higher than the theoretical predictions. This might result from neglecting the frictional and gravitational pressure gradient in the pipe above the boiling front. On the other hand, the general trend is well predicted, which suggests that the control-volume analysis is valid. Distinctively different behavior by any of the fluids used cannot be observed. An analysis considering a lower velocity for the liquid (slip flow) would have resulted in even lower theoretical predictions.
5. Analysis of Boiling Front Experiments

5.1.5 Two-Phase Flow Velocity

In experiments, the velocities of the boiling front and of the mist stream flowing ca. 0.9 m downstream of the boiling front were measured simultaneously as discussed in section 4.5.6. Together with the superheat measurements, this allowed a comparison to be made with calculations using the control-volume analysis (Fig. 5.10; left). It happened that the runs conducted for measuring the two-phase velocity were at higher boiling front velocities than the average of the many other propane runs (Fig. 5.10; right). Correspondingly, this also resulted in the calculated two-phase flow velocities being above average. The measured liquid velocity was lower than calculated. At low velocities in particular, the difference becomes significant. This can be attributed to the limiting assumption of homogeneous two-phase flow in the control-volume analysis.

In Appendix G, a boiling front model is derived which takes the ratio of the true velocities of the gas and liquid phase into account. The velocity ratio $S$ (or “slip”) is defined as

$$ S = \frac{\dot{u}_g}{\dot{u}_l} $$

For the average trend of the propane runs, this analysis leads to the plot of Fig. 5.11. Thus, an increasing velocity ratio $S$ leads to a significant decrease in liquid velocity. In the calculation for Fig. 5.11 it was found that the lesser kinetic energy required for the liquid phase made more energy available for vaporization, leading to a slightly higher quality $x_2$ at an increased velocity ratio $S$.

In Fig. 5.11, the measured four velocities of the liquid phase are plotted. However, the exact actual ratio $S$ cannot be derived from their position since the lines of constant slip $S$ are based on the average trend relation $\dot{u}_l = f(\Delta T_{nom})$. Figure 5.10 shows that the four two-phase flow velocity measurements deviated somewhat from the average trend and therefore cannot be compared with the plotted trend lines. However, using the actual measured front velocity $\dot{u}_f$ together with the corresponding superheat $\Delta T_{nom}$ for the control volume analysis (rather than the $\dot{u}_l = f(\Delta T_{nom})$ relationship) and calculating the
5. Analysis of Boiling Front Experiments

Fig. 5.11: Influence of velocity ratio $S$ (continuous lines: vapor velocity; dotted lines: liquid velocity) on two-phase flow velocity and experimental data for propane ($u_b$ - data for calculation of lines from Fig. 4.22)

Fig. 5.12: Velocity ratio at different measured liquid-phase velocities ($\blacksquare$, +: see Fig. 4.29)

5.1.6 Boiling Front Propagation at Elevated Pressure

The presence of an orifice at the exit of the test pipe increased the pressure in the stagnant superheated liquid and the two-phase flow region (see Fig. 4.25). The real superheat of the metastable liquid decreased correspondingly. For a nominal superheat ranging from 50 to 65 K, a pressure increase ranging from roughly 0.14 to 0.22 bar due to the presence of an orifice was noted. To evaluate the influence of superheat on boiling front velocity, the pressure increase is used to calculate the real superheat for both, experiments with and without orifice. The data collected for several runs and the corresponding $S$ ratio leads to Fig. 5.12. This plot shows that a velocity ratio of one is approached at high velocities.

In general, it can be concluded that homogeneous flow conditions are approached at high superheat, i.e. high boiling front and two-phase flow velocities. At elevated velocities, the average size of the liquid particles can be assumed to be smaller. Finer-sprayed liquid is expected to be entrained easier by the vapor velocity, partly, at least, explaining this trend.
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Fig. 5.13: Velocity decrease of boiling front due to elevated pressure by orifice and difference between real and nominal superheat for propane data

The analysis carried out for a control volume allow three methods to determine the real superheat. Given the initial temperature it is possible to:

1. use the measured pressure in a given run in the superheated liquid,

2. use the measured boiling front velocities of different runs and calculate the pressure in superheated liquid based on the analysis for a control volume,

3. use the correlated velocities of the runs (from correlation of Fig. 4.22) and calculate the pressure in the superheated liquid based on the analysis for a control volume.

The first possibility is chosen here since it is the most direct and based on experimental data only. Figure 5.13 shows the difference resulting from the use of nominal or real superheat (see Appendix D for all runs). Particularly at high superheat and at a corresponding high acceleration pressure, the real superheat is considerably lower than the nominal one. As indicated by the lines resulting from a linear regression, the boiling front velocity increases faster with real superheat than with nominal superheat.

Similarly, in the experiments with an orifice the real superheat in the metastable liquid is lower than the nominal superheat. But even comparing on the basis of real superheat, lower front velocities were measured. Therefore, it is concluded that the same real superheat in the metastable liquid does not necessarily lead to the same front velocity irrespective of orificing. It appears that the pressure level at the front is another velocity determining factor. Indeed, in the experiments with an orifice at the exit, the glass pipe and the boiling front are at elevated pressure. The pressure in the pipe decreases already in the vicinity of the boiling front; investigations of Sugioka (1991) showed that the major part of vaporization and acceleration occurred in a zone extending only a few centimeters in the downstream direction from the boiling front. The front velocity cannot therefore be described solely by the real superheat but appears to be influenced by the pressure level at the front as well.
As mentioned in section 2.1, the same superheat can be reached at different front pressures. As shown in Fig. 4.26, the pressure in the superheated liquid was not that different in the experiments with or without the orifice. Therefore, the influence of the pressure in the superheated liquid cannot be evaluated by the present experiments. Releasing propane with an initial temperature of 18 °C to 1 bar, for example, will probably result in a different vaporization rate than a release from 1.5 °C to 0.5 bar, even though a $\Delta T_{\text{nom}} = 60$ K is provided in both cases. For example, the vapor density and the latent heat are affected by the front pressure. Therefore, at the same real or nominal superheat but different pressures, various front velocities will result.

In summary, it can be concluded that the correlations for boiling front velocity based only on $\Delta T_{\text{nom}}$ are applicable for a certain release or downstream pressure. Any other release pressure or an additional pressure drop (such as that resulting from orificing) in the flow direction, even if the same real superheat is maintained, will lead to a different vaporization behavior.

5.1.7 Critical Flow Condition

The critical flow rate is the maximum flow rate that can be attained by a compressible fluid as it passes from a high-pressure region to a sufficiently low-pressure region. Although the flow rate of a compressible fluid from the high-pressure region can be increased by reducing the receiving-end pressure, it attains a maximum when this pressure reaches the critical downstream pressure value. Since the boiling process generates a two-phase flow of high velocity, it is of interest to investigate any possible critical flow limitation on boiling front propagation. In principle, not only the vaporization and fragmentation in the boiling front zone, but also the flow limitation in the two-phase flow region could determine the rate of phase change. The conditions for the occurrence of critical flow are therefore investigated.

Critical flow has been studied extensively in two-phase systems. Assuming thermodynamic equilibrium and an isentropic expansion downstream of a stagnation point, two models, among the multitude that have been proposed, can be used to calculate the maximum mass flux. In the homogeneous equilibrium model it is assumed that the liquid and vapor phase at the location of maximum mass flux move at the same velocity ($S = 1$), whereas in the approach of Moody (1965), a velocity ratio of:

$$S = \left( \frac{\rho_L}{\rho_g} \right)^{\frac{1}{3}}$$

is postulated. With this assumption, and conserving mass, momentum and energy between the stagnation point (1) and the point of maximum mass flux (2) the critical mass flux can be derived as follows (Mayinger 1982):

$$m_{\text{crit}} = \sqrt{\frac{2 \left[ h_{11} - h_{12} - h_{LGD} \left( s_{1} - s_{L2} \right) / s_{L2} \right]}{S \left( s_{C2} - s_{1} \right) + s_{1} - s_{L2}} \left[ \frac{s_{1} - s_{L2}}{s_{L2} \rho_{L1}} + \frac{s_{1} - s_{C2}}{s_{L2} \rho_{G2}} \right]}}$$

The homogeneous and Moody models are used here to obtain a range of estimates for the critical mass flux. Indeed Mayinger (1982) shows that measured critical mass fluxes are between the values obtained by Moody's approach and the homogeneous
5. Analysis of Boiling Front Experiments

![Graph showing critical mass flux vs. stagnation pressure for propane and water](image)

**Fig. 5.14**: Critical mass flux of initially saturated stagnant propane and water at $p_1$ and experimental mass fluxes through the orifice (for Run 087 the cross-section of the orifice was used for calculating the experimental mass flux.)

assumption. Equation (5.12) has to be solved iteratively by successively reducing the receiving end-pressure $p_2$. The results, together with the maximum flow rates observed during the experiments ($= p_1 u_b$) are plotted in Fig. 5.14.

The critical mass flux of saturated liquid increases with the stagnation pressure, as shown in Fig. 5.14. A velocity ratio of one, i.e. homogeneous flow, leads to the lower theoretical prediction. The maximum flow rates observed in this work were much smaller than any prediction of critical flow. Choked flow, i.e. flow limitation due to reaching the maximum mass flow rate, can consequently be excluded as an effect that limits the boiling front velocity in these experiments.

### 5.2 Boiling Front Velocity in Cylindrical and Pipe Releases

The circumferential releases showed that boiling fronts propagate from the outside to the center of a cylindrical volume of superheated liquid. During this advance, the contour line of the unvaporized liquid appeared increasingly irregular, leading to an increasing ratio between free surface area available for boiling and volume of liquid.

In addition to propagation of the boiling front, liquid motion occurred and influenced the movement of the interface. The motion was caused by start of vaporization at the top of the liquid, leading to an unequal accelerational pressure distribution around the periphery of the liquid. Thus, movement of the free surface appeared as the combined effect of boiling front propagation and liquid motion. However, it is difficult to say which fraction of interface movement had to be attributed to vaporization by a boiling front since, particularly at the beginning of an experiment, the outflow rates were unknown. At least as long as the liquid boundary was not completely visible in the view field of the facility (e.g., in Fig. 4.30 at $t < 47$ ms the contour of the liquid volume was not completely in the view field) liquid could leave the central volume without
Fig. 5.15: Fill level in release facility (1) and area ratio $A_{\text{cylindrical front}} / A_{\text{outflow}}$ (2) ($r_0 = 11 \text{ cm in facility used}$)

passing the visible liquid/vapor interface. In that case, the mass-flux across the visible interface could not be determined by the decrease in liquid volume.

As already noted in section 4.5.7, the direct gravitational effect alone cannot explain the movements of the liquid. During the typical duration of an experiment (80 ms) gravitational fall would cause a displacement of 3 cm. However, such displacements of liquid were observed in the experiments even within less than 8 ms (e.g., Fig. 4.30: time step from 55 to 63 ms).

Another aspect, producing differences from the releases from pipes and possibly influencing the vaporization, is the exit geometry of the facility for circumferential releases. For technical reasons (vacuum before filling), the gap between the flanges at the outflow cross section was smaller than the distance between the glass plates (Fig. 3.9). Therefore, the ratio between the idealized cylindrical surface of a boiling front in the test section and the outflow cross-section between the flanges changed during propagation, as shown in Fig. 5.15. This arrangement led to an "orifice effect" of the flanges during approximately the first half ($r/r_0 > 0.4$) of an idealised circular propagation. This in turn increased the frictional pressure drop leading probably to a reduced vaporization rate at the front according to previous findings for pipes (section 5.1.6). Towards the end of vaporization ($r/r_0 < 0.4$), the area ratio led to a lower pressure drop supporting higher vaporization rates.

Comparing the equivalent radius decrease rate in cylindrical geometry to the boiling front velocity in linear geometry and considering the above effects, results in the velocity differences listed in Table 5.1.

Table 5.1 shows that interface motion during circumferential release is the integral result of various effects. Since data is missing on, e.g., liquid motion and pressure inside the liquid, it is difficult to compare these results to boiling front propagation in pipes. In summary, the release experiments could not prove or disprove the equality of boiling front velocities in one- and two-dimensional releases but showed that bulk nucleation did not occur in cylindrical geometry also.
Table 5.1: Increase (+) or decrease (-) of equivalent radius velocity in circumferential releases compared to boiling front velocity in a pipe due to several effects

<table>
<thead>
<tr>
<th>effect</th>
<th>beginning of experiment</th>
<th>towards end of experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>irregular shape of liquid volume</td>
<td>±</td>
<td>+</td>
</tr>
<tr>
<td>narrow exit cross-section</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>liquid motion (unequal pressure distribution, gravity)</td>
<td>+</td>
<td>±</td>
</tr>
</tbody>
</table>

(Reading example: Liquid motion leads to higher (+) equivalent-radius velocity in circumferential releases than boiling front velocity in pipes at the beginning of an experiment.)

5.3 Growth Rates and Mass Fluxes of Bubbles in Superheated Liquid

This section contains certain experimental results that were not presented in Chapter 4, since they are compared to bubble growth theory directly here.

Close-up recordings revealed that the surface of the boiling front appeared to be covered with bubble-like structures. A fraction of the superheated liquid which was reached by the boiling front vaporized in this leading front zone (Fig. 4.2), whereas another part passed through and reached the region of fragmentation and acceleration downstream. For further analysis, it is important to study the fraction of vapor which is typically released by the leading bubble structure, or more generally, to know the typical mass fluxes occurring during the conduction-controlled growth stage of a bubble in superheated liquid.

5.3.1 Measured and Theoretical Growth Rates of Bubbles or Caps

Parasitic Bubbles

In some experiments, single bubbles grew on the glass walls or on the interface between the buffer and the test liquid. Even though these bubbles were not desirable, as they disturbed the boiling front propagation, their growth rate could be measured and compared with the theoretical prediction of Eq. (2.8). The theory describes the growth of a smooth vapor bubble in a uniformly superheated liquid during the stage controlled by heat conduction. Figure 5.16 shows the increase in bubble diameter with time, the average of the shortest and longest diameters being used in the case of non-spherical bubbles. The calculated increase of the diameter $d$ with the square root of time $t$ is also shown.

As seen from the examples of Fig. 5.16, the bubbles roughly followed the prediction of Eq. (2.8), particularly during the initial stage. Later, however, the bubbles grew faster than predicted. This change of behavior coincided with a roughening of the bubble surface. It appears that the increased surface area enhanced the mass transfer, leading
5. Analysis of Boiling Front Experiments

Fig. 5.16: Measured and calculated growth of individual bubbles in superheated liquid to faster bubble growth. Other deviations from theory were possibly caused by factors such as the slightly increased pressure due to simultaneous growth of several bubbles leading to a slightly lower superheat, the inhomogeneous volume of superheated liquid near the glass walls and the buffer liquid, or disturbances due to liquid flow.

Boiling Front Bubbles or Caps

The typical increase in bubble diameter on the boiling front surface was also measured, even though it was difficult to determine the starting time of bubble growth and to monitor complete hemispherical structures, i.e. to determine their diameter. The measured growth of individual bubbles/caps is shown in Fig. 5.17. Due to the unknown starting-time, in Fig. 5.17 the first measured diameter was placed at a time corresponding to the same theoretical diameter. Any growth of a bubble with a higher slope than the calculated increase indicates faster growth than according to the theory.

In general, the boiling front bubbles showed growth velocities of the order of the theoretical predictions. In contrast to the measured single bubbles, their growth appeared more irregular. After a period of slower growth than predicted, some bubbles exhibited an increased growth velocity which coincided with roughening on their surface. However, most of the bubbles grew slower than predicted and some even decreased in size. Comparison of Fig. 5.17 to Fig. 5.16 shows that single bubbles grew to considerably larger size than the structures at the boiling front.

The smaller maximum sizes and the slower growth velocity of boiling front bubbles can be attributed to open caps since the vapor flux across the interface is in that case not coupled with volumetric expansion. A reduced heat supply to the interface would be another potential reason for the slow-down of bubble growth. Such a reduction could, for example, be due to the vicinity of also growing neighboring bubble with which the superheat available in the liquid is shared. However, the flow conditions with superheated liquid passing around the vapor spaces are more likely to increase heat transfer rather than decrease it.
Despite the deviation of data from theoretical predictions, it can be concluded that the bubble growth model of Eq. (2.8) for the period controlled by heat conduction gives a good approximation of the vaporization rate occurring in the leading caps of the boiling front. The typical fluxes of vapor flowing into the vapor cavity can be derived from the bubble growth rate. This was done with Eq. (2.11) and is plotted in Fig. 5.18 (left plot). Small bubbles at an early stage of growth and at high superheat show a particularly large specific mass-flux across the liquid-vapor interface.

Using Fig. 5.18 (left plot), one can obtain the order of magnitude of the typical vapor fluxes resulting from the leading surface of the boiling front. These can be compared to the overall vapor mass flow determined from the experiments. In Fig. 5.18 (right plot) the average vapor mass flux from a boiling front, i.e. the mass flow rate averaged over the pipe cross-section, is plotted versus the superheat. Bubble diameters in the range typically observed at the front (several millimeters in diameter) produce lower mass fluxes. Thus, a significantly higher mass flux is noted for boiling fronts than across the interface of single bubbles in the range of diameters observed.

In another approach, the surface of a boiling front is considered to be a plane layer covered with bubble hemispheres. Several assumptions have to be made to obtain an "order-of-magnitude" calculation to determine the vapor mass flux from this bubbly
Typical vapor mass fluxes into the bubble in superheated propane for different bubble radii and superheats. The vapor mass flux of the experimental runs averaged over the pipe cross section is plotted on the right diagram for comparison.

Surface, since the exact surface characteristics, e.g. shape, surface area, size distribution etc. could not be assessed. For simplicity, the leading front is considered as an assembly of open hemispheres. This assumes a packing of structures of uniform diameter in the way sketched in Fig. 5.19. As in the control-volume analysis of section 5.1, the caps are fixed within a moving frame of reference. Assuming a static appearance of the front structure, the major part of the cross section is covered by hemispherical vapor spaces. Liquid flows through the remaining interstitial area. Even though this flowing liquid fraction depends on superheat or local quality, the main part of the liquid flows through these "channels" (see Fig. 5.4 regarding the quality \( x \)). For reasons of continuity and because of the decreased cross-sectional area, the liquid velocity increases during its passage around the vapor cavities.

It is assumed that the mechanism controlling heat conduction for bubble growth, Eq. (2.8), is also valid and applicable to a hemispherical geometry. The shaded hemispherical part contributes only to vaporization and typically releases the vapor through the circular cross-section at the top. The assumed hemispherical shape of the bubble increases the liquid-vapor interface in comparison to its projected flat circular area. The area ratio \( A_{\text{hemisphere}} / A_{\text{circular opening}} = 2 \) leads to an increase of the phase-change area. Considering the integral opposing effects of both the increased surface area due to the hemispherical shape of the cap and the reduced vapor generating cross-sectional area due to the space occupied by flowing liquid, it becomes obvious that these together do not significantly increase the specific mass flux averaged over the whole cross section.

Figure 5.20 shows that during the experiments with propane, a vapor flux averaged over the whole cross section of up to 300 kg m\(^{-2}\) s\(^{-1}\) was reached, and that this would have required a close packing of a layer of vapor caps 50 \( \mu \)m in diameter. The visual observations, however, do not suggest that the surface is covered by so many small-
sized caps, although the diameter of the caps in question is below the resolution of the photographic equipment used.

Another possibility is that difference between typical vapor fluxes in bubble growth and boiling front propagation could be a result of particularly high vaporization rates in the early stages of bubble growth. The average mass flux of bubbles during growth was calculated to investigate this aspect. The specific mass flux across the bubble interface is calculated according to Eq. (2.10) as follows:

\[ \dot{m}_{\text{instantaneous}} = \text{const} \Delta T \frac{1}{\sqrt{t}} \]  

Averaging over the whole period of bubble growth leads to:

\[ \dot{m}_{\text{average}} = \text{const} \Delta T \int_0^t \frac{1}{\sqrt{t}} \, dt = 2 \text{const} \Delta T \frac{1}{\sqrt{t}} = 2 \dot{m}_{\text{instantaneous}} \]  

According to Eq. (5.14), the average vapor flux during bubble growth is twice as high as the mass flux at the final bubble size. Therefore, no visible hemisphere would have produced the quantity of vapor that would have been necessary to explain the vapor fluxes originating from the boiling front. Only numerous small bubbles not growing to the sizes typically observed at the front could lead to the measured vapor stream. Again, such visual evidence for such small-scale structures could not be obtained in the experiments.

The above calculations may raise objections because they ignore several effects such as the non-smooth appearance of the bubbles and the random, pulsing propagation of the front. Nevertheless, the difference in orders of magnitude between the vapor fluxes leads to the conclusion that the major part of the vaporization does not occur in the
liquid-vapor interface of the bubbly structure. It is more likely that the main part of the vapor flux is generated further downstream, i.e. in the region where bursts and fine-scale fragmentation occur.

5.3.2 Model Based on Balance of Forces around the Growing Cap

Observation of the boiling front suggests that vaporization pushes the liquid-vapor interface into the superheated liquid. In turn, the greatest fraction of incompressible liquid has to pass around the growing vapor spaces. It is therefore instructive to establish a force balance relating the acceleration of the vapor in the cavities and the forces acting on the liquid due to flow around the cavities. The effect of superheat is of particular interest, since it was noted in the experiments that the front appeared to have a finer structure with increasing superheat.

Since the exact structure and dynamics in the front are unknown, several simplifying assumptions for an analysis have to be made. In the simplest form, propagation at constant velocity and a static appearance of the boiling front can be assumed. Fluid flow is assumed to proceed without friction. Considering a front of uniformly sized caps as illustrated in Fig. 5.19, the pressure inside an open cap induced by the acceleration of vapor can be calculated. Assuming that vapor is produced only across the hemispherical interface $A_{\text{hemisphere}}$ and released through the downstream cross section $A_{\text{circular opening}}$, the pressure drop can be calculated to be:

$$\Delta p = \rho_v u_v^2 = \rho_v \left( \frac{A_{\text{hemisphere}}}{\rho_v} \right)^2$$

(5.15)

The specific mass flux of Eq. 5.15 can be determined by Eq. (2.11). Small bubble caps in particular lead to high vapor fluxes and a corresponding significant pressure inside. As the bubble grows and the curvature decreases, the thrust also decreases and caps that become too big would be "pushed away" and "smoothed out" by the liquid stream. The accelerational pressure drop of the incompressible frictionless liquid can be calculated according to the Bernoulli equation:

$$\Delta p = \rho_v / 2 \left[ \left( \frac{A_{\text{pipe}}}{A_{\text{flow channel}}} \right)^2 - 1 \right] u_v^2 + g d$$

(5.16)

where $A_{\text{flow channel}}$ is the interstitial flow area.

Equation (5.16) is the pressure drop in the liquid due to the reduced liquid flow area in the front as the liquid flows upwards around a hemispherical cap plus the hydrostatic pressure over a distance roughly equal to the cap diameter, as shown in Fig. 5.19. The pressure drops of Eqs. (5.15) and (5.16) should be equal and knowing the mass flux of the vapor from the experiments, a corresponding bubble diameter could be calculated. The result is plotted in Fig. 5.21. According to the plot, a strong decrease of bubble size with increasing superheat is noted near the onset of boiling front propagation at $\Delta T_{\text{nom}} = 27$ K. The growing liquid speed (equal in the moving frame of reference to the boiling front velocity) induces a stronger liquid acceleration which has to be compensated by an increasing thrust on the vapor side. This is achieved by an increasing specific mass flux of vapor from the interface, which is supported by a higher superheat. However, the main factor in increasing the pressure is the effect of a
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Fig. 5.21 : Cap diameter \(d\) balancing the pressures due to the acceleration of the liquid by decrease of its flow area and by vapor thrust for propane (flow area decrease = \((1-\frac{A_{\text{flow channel}}}{A_{\text{pipe}}})\) 100)

reduced radius. As mentioned previously, the smaller curved interfaces allow higher specific mass fluxes. In Fig. 5.21, therefore, the typical diameter strongly decreases and then reaches a minimum. According to the model, a slight increase in diameter occurs at high superheat. This results from the particularly strong increase of the accelerational pressure in Eq. 5.15, which depends on \(\Delta p - \Delta T_{\text{nom}}^4\).

In general, the above calculations agree with the qualitative experimental finding that the bubbly structure appears to have a finer structure with increasing superheat. However, the predicted sizes \((d << 1 \text{ mm})\) are well below the diameters that were typically observed in the experiments \((d > 1 \text{ mm})\). So some of the assumptions in the above model are inadequate. Either the vaporization across the interface is higher or the accelerational pressure drop is less. The neglect of the vapor shear may also be a factor.

Another possible explanation for the different sizes noted in calculations and measurements is that the fast bubble growth at the initial stage leads to a liquid acceleration which cannot be maintained due to deceleration at a later stage of bubble growth. However, the inertial liquid flows away from the vapor cavity by inertia without requiring any further thrust. It has so far been impossible to estimate the relevance of this expansion due to liquid inertia. This would require a dynamic rather than a static calculation as in the above model.

5.3.3 Model Based on Radial Bubble Growth Velocity

In still another approach, the radial velocity of a growing bubble was calculated to explain the observed decrease in bubble diameter with superheat. According to Eq. (2.8), the radius increases as:

\[
r = \text{const} \ t^{\nu_2}
\]

The radius velocity can be calculated to be:

\[
r = \text{const} \ 0.5 \ t^{-\nu_2}
\]

Equation (5.18) predicts a decrease in growth velocity with time, i.e. larger bubbles grow more slowly. This is depicted in Fig. 5.22, which shows the radial velocity of the
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Fig. 5.22: Radial velocity of growing bubble at different diameters and superheats compared with boiling front velocity for propane.

Fig. 5.23: Bubble diameter at certain superheat to obtain the same radius velocity as the boiling front velocity for propane.

The analysis of boiling front experiments involves understanding the dynamics of bubble growth and their impact on the boiling front velocity. A key observation is the relationship between bubble diameter and superheat at which the radial velocity matches the boiling front velocity. This is given by:

\[ d = \text{const}^2 / u_b \]  

(5.19)

Inserting the measured relation \( u_b = f(\Delta T_{\text{son}}) \) for propane (from Fig. 4.22) in Eq. (5.19) results in Fig. 5.23, which shows a strong decrease in bubble size above the temperature for onset of boiling front propagation. Later, the diameter again increases, similar to the situation shown in Fig. 5.21. However, the calculated diameters are now generally larger and are in the range typically observed in the experiments. The average size of the population has to be below the line because larger diameters show smaller radial expansion velocities than the average \( u_b \). In addition, the fluctuating velocity of the front has to be compensated by intermittent faster growth of the bubbles.

From the similarity of calculated bubble diameters and the sizes observed in the experiments, the conclusion could be drawn that thermally-controlled bubble growth determines the boiling front velocity. On the other hand, such bubble growth cannot explain the rates of vaporization observed in the experiments. It seems that the main vaporization occurs further downstream, where intense fine-scale fragmentation obviously occurs. At this stage, where essential information about the complex boiling front structure and dynamics is missing, it appears unreasonable to refine the modeling since the assumptions would have to be based largely on unverifiable information. The attempts made here provide, however, useful guidance towards understanding the phenomena and excluding certain assumptions.

5.3.4 Thermal Boundary Layer around a Growing Bubble

A bubble in superheated liquid growing in the stage controlled by heat conduction is surrounded by liquid providing the heat for vaporization. For further analysis, it is
important to know about the depth of the liquid layer which is affected by this heat removal. For a plane liquid/vapor interface moving due to vaporization, such as an idealized boiling front, Hill (1991) derived a simple approach to calculate the thickness of the thermal boundary layer. In his model, the front is considered as a heat sink advancing into the superheated liquid with a constant velocity \(u_r\) as illustrated in Fig. 5.24. The solution for energy conservation in a control volume moving with the interface is given as:

\[
\frac{T(x) - T_r}{T_i - T_r} = 1 - e^{-\frac{u_r x}{\alpha}}
\]  

(5.20)

where \(\alpha\) is the thermal diffusivity of the liquid.

The thickness of the boundary layer grows with increasing thermal diffusivity \(\alpha\) and decreasing velocity of the interface \(u_r\). Assuming a velocity similar to that for a typical boiling front propagation of \(u_r = 1\) m/s and taking the thermal diffusivity \(\alpha\) of propane and water at saturation at 1 bar, for example, leads to thicknesses of the boundary layer according to Eq. (5.21) of \(\delta = 0.10\) \(\mu\)m and \(\delta = 0.17\) \(\mu\)m, respectively. Thus, the layer affected by the temperature drop is extremely thin. In principle, this layer should be even thinner when considering a spherical geometry.

Even though the above analysis appears rather superficial, it can be concluded that the smooth bubble caps growing at the leading surface of a boiling front are surrounded by boundary layers with thicknesses of the order of the above calculations, i.e. in the range of several microns. This shows that the latent heat used for vaporization is transported only over “short” distances. If the stored thermal energy of superheated liquid is to be transported at a high rate to the vaporizing interface, this requires a fine-scale fragmentation of the liquid. Only by increasing the interfacial area relative to the liquid volume can the vapor production be significantly enhanced.

### 5.4 Drop Size Distribution in Two-Phase Flow

In the previous chapter, the characteristic sizes appearing in the two-phase flow zone were presented. For different superheats and distances, the sizes of drops were recorded after travel through still air. Even though an exact size distribution could not
be given, the medium size of the drops was found to be $d_{\text{median}} < 0.08 \text{ mm}$ at a superheat of $\Delta T_{\text{nom}} > 48 \text{ K}$ and at a distance of more than $1.1 \text{ m}$ from the boiling front.

Various modes of drop rupture are conceivable (see Pilch and Erdman 1987). For example, the explosive vaporization of single superheated drops was investigated in several works (see Chapter 2.2.2). This led to fine-scale fragmentation of the drops; however, detailed size distributions were not obtained. In the experiments of this work, the travel of drops through still air influenced the drop size distribution as well, but the exact mixing with air was not known and was not analysed. Therefore, in order to get an upper limit of drop size distribution, the exposure of liquid to a high-velocity stream of vapor will be further considered as the only break-up mechanism. Thus, thermal fragmentation is ignored and only aerodynamical break-up is investigated.

The upper limit of stable drop size is given by the $We$ number criterion (Pilch and Erdman 1987):

$$We = \frac{\rho_v (u_v - u_{\text{drop}})^2}{\sigma} \frac{d_{\text{drop}}}{12}$$  \hspace{1cm} (5.22)

Increasing the velocity difference between drop and accelerating vapor leads to smaller drop sizes. Since the acceleration process of liquid in the front is not known in detail, the liquid was assumed to be at rest initially. The conditions for break-up are most favorable near the boiling front, i.e. in the region with the highest relative motion of vapor and liquid. In addition, the violent bursts that lead to fine-scale fragmentation of the superheated liquid are found only in this zone. Later on, vapor and liquid flow at closer velocities, and deceleration in stagnant surrounding air will not lead to further fragmentation. The vapor flux originating from the boiling front could be determined by the control volume analysis. Thus, the maximum stable drop sizes were calculated for different superheats by Eq. (5.22) as shown in Fig. 5.25.

The plot shows a decrease of the upper, acceleration-controlled stable drop size with growing superheat due to increase of vapor velocity. Comparing the results obtained by the $We$ number criterion to the experimentally determined drop sizes demonstrates that the majority of measured drops was smaller than predicted by stability theory. This would support that the $We$ number is a relevant parameter for calculating the upper limit of drop size. On the other hand there were still drops with a larger diameter than possible according to the $We$-stability limit. To which extent secondary effects, such as
reentrainment in the annular flow region of the pipe played a role can not be stated. This would certainly be an artefact not occurring at large-scale unconfined releases because of the missing possibility of collection of saturated liquid on the walls.

In summary, missing details about liquid break-up and acceleration of fluid do not allow to evaluate the dominating break-up mechanism or to investigate secondary effects such as collection and reentrainment of liquid. Therefore the drop size analysis remains with open questions.
Chapter 6
Boiling Front Mechanism

The propagation of a boiling front appears to be the result of vaporization, liquid fragmentation and fluid acceleration. In the following, an attempt is made to establish a model which relates the various observed and measured phenomena qualitatively. In a first step, a schematic mechanism is proposed. Later, the applicability and relevance of other approaches such as secondary nucleation mechanisms or instability effects are discussed. Since boiling at the free surface appears to be a complex process, detailed quantitative modeling requires elaborate numerical studies which are beyond the scope of this work. A more practical approach is therefore taken by performing an evaluation based on non-dimensional analysis at the end of this chapter.

6.1 Proposed Model of Boiling Front

Figure 6.1 illustrates an idealized boiling front, based on the assumption of an assemblage of differently sized open hemispheres. Even though in a real situation this local appearance changes continuously, the overall composition and size distribution can be assumed to be constant. Part of the superheated liquid is vaporized across the interface. Due to expansion and acceleration of the vapor, the interface is pushed into the superheated liquid. The major part of the liquid is not vaporized but is moved aside by the growing vapor cavities. It has to penetrate through the open channels that are

![diagram](image_url)

**Fig. 6.1:** Schematic boiling front model
not covered by vapor. The fluid consequently accelerates. Later, the vapor flowing at a higher velocity further increases the liquid velocity due to shear. Due to the relative motion of the liquid and vapor, the liquid becomes fragmented into fine particles and an aerosol stream is generated. Like a chain reaction, the increased surface area and the vapor flux lead to a highly turbulent environment that increases the fine-scale break-up of the liquid. As a result of this unstable self-reinforcing process, vaporization develops into explosive boiling. The frequent explosive bursts are probably the final result of this unstable increase in surface area. The leading bubble structure, i.e. the visible transparent caps, provide a “trigger stream” of vapor for the initiation and growth of instabilities leading to more intense vaporization further downstream.

Considering the thickness of the thermal boundary layer, it appears that heat is removed only from a very thin volume around a bubble. An increased amount of hot liquid is available for providing heat for vaporization and for entrainment by the intense fragmentation in the front region. Initially, homogeneous nucleation was considered as a possible reason for the burst since the pressure in the superheated liquid decreases as it passes through the boiling front due to its acceleration. Thus, the liquid flowing through the idealized boiling front of Fig. 6.1 would face a velocity increase by a factor of 10, which in turn would lead to a pressure decrease. However, the superheat limit in the relevant range is rather insensitive to pressure changes. The slight decrease in pressure between the stagnant metastable liquid and the two-phase flow is certainly insufficient for initiating homogeneous nucleation. However, it seems that explosive boiling, so far investigated mainly in the context of the superheat limit and for single drops (see section 2.2.2), is a phenomenon that also occurs at lower degrees of superheat, particularly in the turbulent environment of a boiling front.

In any case, the bursts contribute to the advancement of the boiling front by successive pulses. These fluctuations of the front velocity are noted particularly at low superheat. After a local burst, the front in that region speeds forward.

6.2 Origin and Nature of Vapor Cavities

In the previous section, a qualitative model explaining the vaporization mechanism at a boiling front was proposed. However, the origin of the growing vapor cavities at the leading edge which come continuously into view has not yet been considered in detail. Boiling front propagation is characterized by a dramatic increase in the interface between the superheated liquid and the vapor. The scheme of Fig. 6.2 gives a classification of the relevant possible mechanisms of interface creation.

According to this scheme, vapor cavities might penetrate from the free surface into the metastable liquid, i.e. they are open from the beginning of their growth. In contrast, nuclei inside the superheated liquid are at least at the initial stage of their growth closed. The likelihood and importance of these two mechanisms is discussed in more detail in the following two sections.

6.2.1 Preexistent Nuclei and Secondary Nucleation

Assuming that bubble growth starts from nuclei already present before the boiling process is initiated, the reason must be sought for the destabilization of such initially stable nuclei by the approaching front. In addition, it should be clarified why this
activation of nuclei occurs only at the boiling front and not in the bulk liquid upstream. The decrease in hydrostatic pressure due to an approaching flashing front could be a possible explanation. However, this influence is negligible compared to the fluctuations in absolute pressure in different experiments and during single runs. It is rather unlikely that the slight decrease in hydrostatic pressure could activate a nucleus; this mechanism can thus be excluded as a source of activation of nuclei.

Another consequence of an approaching flashing front is that it cools down the liquid in a thin thermal boundary layer, which can be shown to be thicker than the critical radius of a bubble nucleus. Besides increasing the surface tension, the colder boundary layer decreases the degree of superheat of the liquid surrounding the bubble. Thus, rather than activating nuclei, a boiling front would tend to deactivate preexisting nuclei. It can therefore be concluded that there is no evidence that the bulk of the liquid contains nuclei which are destabilized by an approaching depressurization front.

The secondary mechanism of Fig. 2.5 proposed by Mesler and Bellows (1988) might be of relevance as another possible source for vapor cavities (see also Fig. 6.1). In a modified form of this mechanism proposed here, liquid fragments would not originate from collapsing bubbles but would be produced by downstream bursts and be back-catapulted through the leading caps onto the liquid/vapor interface. This would create both small entrained quantities of vapor in the metastable liquid and disturbances on the interface (the vapor cap). New bubbles could grow from the entrained vapor, whereas the surface disturbances could activate an instability mechanism.

Examples of these two effects were indeed found in the film recordings, but in a rather limited number. In a few instances it was seen that particles did hit the interface, giving rise to the growth of a vapor cavity. In enlarged view fields, it was observed that the front in the immediate vicinity of a burst became finer in structure and advanced faster. This observation could be explained by liquid particles accelerating onto the front and...
introducing vapor nuclei. The spray would serve as a trigger stream shifting the average size of the caps to a lower value and thus enhancing vapor production. The nuclei introduced this way would grow, and at a later stage the bubbles would break open in the downstream direction. In turn, this increase in vaporization rate would have the secondary effect of amplifying the thrust pressure and the liquid fragmentation rate.

The above observations support the relevance of secondary nucleation for boiling front propagation. However, a roughening of the surface was often noted, also at low superheat where no prior movement of liquid fragments was detected. This might be due to the limited camera resolution compared to the velocity and size of the moving particles. However, it appears more likely, particularly in the absence of bursts, that secondary nucleation is only partly responsible for vapor cap generation. It was found that bursts and liquid impingement are not necessary for front propagation, e.g. at low superheat. However, they might accelerate boiling front propagation. The secondary nucleation mechanism might contribute to an increased generation of nucleation sites, particularly at higher superheats, where bursts occurred almost continuously and closer to the leading surface.

Besides the acceleration of particles, the bursts also generate pressure waves with rapid movement of vapor. The arrival of these pressure fluctuations at the liquid/vapor interface might induce disturbances. New vaporization sources could possibly develop from these disturbances. This would explain why the bursts amplify the advancement of the boiling front even without the visual impact of liquid fragments on the liquid. However, the strength of the bursts and the effect of pressure oscillations on the stability of the interface are unknown.

Since secondary nucleation seems to be at least partly responsible for the structure of the front, there appears to be some feedback from the downstream region, affecting the vaporization rate at the leading contour. This aspect makes modeling particularly difficult, since a quantitative evaluation of this influence requires more detailed studies of both the nature of the explosive bursts and the increase in mass transfer due to secondary nucleation.

### 6.2.2 Importance of Instabilities for Boiling Front Propagation

**Landau instability**

Instabilities at the free surface have to be considered as another possible mechanism for area increase. In relation to boiling front propagation, vaporization may not start from a nucleus as in the case of homogeneous or heterogeneous nucleation but from a disturbance on the surface. The Landau instability, originally described in connection with the instability of laminar flames, was adopted by several authors for the analysis of vaporizing superheated liquid (Shepherd and Sturtevant 1982 and Frost and Sturtevant 1986). The interface-disturbing effect of the vapor accelerating away from a superheated liquid was investigated by Prosperetti and Plesset (1984) and was reviewed in section 2.2.5. The theory was developed for vapor acceleration from a plane surface of superheated liquid. The geometry of a boiling front during quasi-steady propagation differs significantly from this situation. For an order-of-magnitude
estimation, however, the surface of a bubble can also be assumed to provide a location for the activation of thermal instabilities at a smaller spatial scale.

The calculations of Prosperetti and Plesset (1984) were performed for a liquid undergoing steady evaporation from its plane interface, as already noted. For a perturbed surface and a constant temperature distribution, the calculations yield a threshold for the occurrence of instability. This gave the minimum required vapor velocity \( u_0 \) for the onset of instabilities:

\[
u_0 = \left( \frac{2 \rho_L}{3 \rho_o} \right)^{\frac{1}{2}} \left( \frac{\sigma}{\rho_L g} \right)^{\frac{1}{2}}
\]

(6.1)

For saturation conditions at \( p = 1 \) bar, these vapor velocities must be \( u_0 > 1.61 \) m/s for propane and \( u_0 > 5.12 \) m/s for water (corresponding to specific mass fluxes of 3.8 kg m\(^{-2}\) s\(^{-1}\) and 3.1 kg m\(^{-2}\) s\(^{-1}\), respectively). The wavelength of the fastest-growing instability then reaches \( \lambda_{\text{onset}} = 1.6 \) cm for water and decreases with increasing mass flux according to the calculations of Prosperetti and Plesset.

These values for the specific vapor mass flux and the fastest-growing wavelength can be compared to the mass fluxes occurring inside a thermally-controlled growing bubble. The maximum bubble diameters that can still produce the required vapor velocities at the bubble interface for the onset of instabilities are plotted in Fig. 6.3. Since the specific mass flux from a growing bubble decreases with time and bubble diameter, only diameters smaller than those plotted above can reach the unstable range. At the lower limit for the onset of instabilities, the wavelength of the fastest-growing wave \( \lambda_{\text{onset}} \) is greater than any of the bubble sizes plotted above. This wavelength \( \lambda_{\text{onset}} \) decreases only with increasing vapor velocity or with specific vapor flux.

Further calculations showed that bubbles with diameters within the range of the required wavelength and necessary vapor fluxes are found only at an early stage of bubble growth, i.e. at times and sizes which could not be resolved any further with the camera equipment available in the experiment. It is therefore concluded that if thermal

Fig. 6.3: Maximum bubble diameter and growth time for reaching vapor velocities at a bubble interface above the threshold for the onset of instabilities
instabilities of the Landau type were activated they would become effective only during the early stages of bubble growth and so could not explain observed disturbances occurring at larger drop sizes.

Shepherd and Sturtevant (1982) and Frost and Sturtevant (1986) calculated the Landau instability for violent vaporization of liquid drops and found instabilities only for small sizes. For ether drops vaporizing at the superheat limit at ambient pressure, they predicted instabilities growing in the range of 0.4 < \lambda < 16 \mu m, which is at an earlier stage than thermally controlled bubble growth. However, they detected a high sensitivity of the instability to assumptions about the temperature distribution in the boundary layer. Frost and Sturtevant (1986) pointed out that disturbances visible in the millimeter range represent the late, nonlinear, and saturated stage of the instability. This finding is similar to conclusions of section 5.3.2 which indicated that the filmed growth of caps at the boiling front could possibly be attributed to inertia effects caused at earlier times rather than be caused by actual vaporization induced forces.

Rayleigh-Taylor Instability

Another possible mechanism for explaining the roughening and break-up at the interfaces of the vapor cavities at the boiling front is the Rayleigh-Taylor instability. It applies to two fluids of different density that are accelerated towards each other. The minimum wavelength of a perturbation which will grow is found to be (Carey 1992):

\[
\lambda = 2\pi \sqrt{\frac{\sigma}{(\rho_1 - \rho_0) a}}
\]  

(6.2)

While a high surface tension and a low density difference will stabilize the surface, an increasing acceleration \(a\) of the fluid of higher density into the one of lower density will lead to a smaller wavelength, i.e. instabilities at a smaller scale.

In the case of boiling fronts, the vapor caps expand into the liquid. Considering the model of Fig. 5.19 and Fig. 6.1 and the related assumptions, the liquid passes around the vapor cavities through the remaining interstitial area. By this, it accelerates from an initial velocity \(u_1\) to a higher velocity \(u_2\) which is essentially determined by the reduced liquid cross-sectional flow area in the boiling front. Thus, the liquid of higher density accelerates into the vapor of lower density as described by the Rayleigh-Taylor instability.

Applying the instability criteria requires certain assumptions about the acceleration of the liquid into the vapor. Considering liquid acceleration to occur within half the diameter \(d\) of a certain cap size and assuming a narrowing of the cross-sectional area from \(A_1\) to \(A_2\) leads to:

\[
\frac{1}{2} d = \frac{1}{2} a t^2
\]  

(6.3)

\[
u_2 = u_1 \frac{A_1}{A_2} = a t + u_1
\]  

(6.4)

From these equations, the acceleration can be calculated to be:

\[
a= \frac{\left(\frac{A_1}{A_2} - 1\right)u_1}{d}
\]  

(6.5)
The liquid acceleration obtained can be implemented into Eq. (6.2) leading to a lower limit of destabilizing disturbances on the leading surface of the interstitial liquid. However, an upper limit for the wavelength $\lambda$ is given by the size of the liquid jet. If $\lambda$ is too large, an unstable Rayleigh-Taylor wave does not fit on the cavity (Kitscha and Kocamustafaogullari 1989). For an order of magnitude estimation it is sufficient to assume that the upper limit corresponds approximately to the diameter of the cap such that:

$$d > \lambda > 2\pi \frac{d}{(\rho_L - \rho_v) \left( \frac{A_1}{A_2} - 1 \right) u_t^2}$$

(6.6)

The resulting minimum possible diameter $d$ for onset of instability is displayed for various area ratios $A_1/A_2$ in Fig. 6.4, where $u_t$ is taken as the boiling front velocity $u_t$ corresponding to a certain superheat $\Delta T_{\text{nom}}$. The hydrodynamical stability analysis shows a decreasing minimum stable jet size (corresponding to a cap size $d$) for an increase of superheat (and corresponding boiling front velocity) and a decrease of cross-sectional flow area. This qualitative result is in accordance with the experimental findings that the boiling front appeared to have a finer structure with increasing superheat.

From the film recordings, the area ratios $A_1/A_2$ can be estimated to be roughly more than 10. For a superheat of $\Delta T_{\text{nom}} = 50$ K this would lead to an onset of instability on the surface of the bubbles at sizes larger than 0.2 mm. Figure 5.17 indicates that bubble diameters of several millimeters were typically observed in the experiments. However, the quantitative predictions of Eq. (6.6) are rather questionable because of the difference between the underlying theoretical assumptions and the reality (narrow bubble packing instead of plane interfaces in continuous liquid, growing bubbles, pulsing advancement). On the other hand, the leading liquid/vapor interfaces are subject to acceleration and a finer structure of the boiling front is noted particularly at high boiling front velocities. Thus, acceleration-induced fragmentation seems to be
another mechanism that could explain the growth limitation of cavities at the front leading edge.

**Kelvin-Helmholtz Instability**

Vaporization at the leading edge leads to a relative motion of liquid and vapor in the downstream direction. This relative fluid movement may possibly lead to an unstable change in the morphology at the interface of the fluid streams. Such a fluid-dynamic instability is described by the Kelvin-Helmholtz mechanism. In the absence of gravity, the stability condition of Kelvin-Helmholtz is given by Carey (1992):

\[
\lambda > \frac{2\pi \sigma (\rho_l + \rho_v)}{\rho_l \rho_v \Delta \nu^2}
\]  

(6.7)

This equation implies that disturbances above a certain critical value will increase and enlarge the surface area: the higher the velocity difference between the gas and the vapor \( \Delta \nu \), the smaller the wavelength \( \lambda \) for the onset of instability. Considering typical vapor velocities downstream from the front of 50 m/s averaged over the pipe cross-section at \( \Delta T_{\text{nom, propane}} = 50 \text{ K} \) this results in a \( \lambda > 0.03 \text{ mm} \). Thus, the vapor velocities have the potential to create instabilities with wavelength in the range of typical size of boiling front structures which are several millimeters.

Experimental investigations have been used to determine the critical wavelength for certain flow structures, such as jets. However, it is rather difficult to define such conditions for the current problem. First of all, the vaporization in the boiling front appears locally as a highly unsteady phenomenon. Pulsing advancement initiated by bursts in the downstream region leads to highly-transient flow conditions. In addition, the exact structure, such as the liquid and vapor flow path through or within the front, is essentially unknown. The velocity differences attained locally and temporarily cannot therefore be quantified. Consequently, it can only be assumed that instabilities of the Kelvin-Helmholtz type appear and that they reinforce the cycle of surface enlargement, vaporization and relative liquid/vapor movement. Visual evidence for the presence of Helmholtz instability is provided, for example, by the ripple pattern downstream from leading bubbles (Fig. 4.15, frame 10).

A quantification based on known correlations requires many questionable assumptions. Our attempts to implement theories for the stability of liquid jets, for example, were unable to clarify the contribution of the Kelvin-Helmholtz instabilities to boiling front propagation. In any case, an alteration of the interface morphology results in dramatic changes in heat and mass transport at the interface. More sophisticated modeling must take into account non-linear instability phenomena, and even advanced models will depend on major empirical input. On the other hand, the experimental data and close-up studies are still rather incomplete.

### 6.3 Quantitative Prediction of Boiling Front Behavior

An important objective of this work is the quantitative prediction of boiling front propagation depending on the thermophysical properties of the fluid involved. If knowledge about the mechanism to be described is unavailable, an analysis based only on a systematic investigation of all possible combinations of non-dimensional
parameters can be carried out. At the beginning of such an analysis, the relevant variables are listed. In a next step, the Buckingham Pi-Theorem (Li and Lam 1976) is used to establish a matrix from which several non-dimensional numbers can be derived depending on the rank of the matrix. More familiar numbers are obtained by combining some of these quantities. Like the analysis of Schmidli (1993), the analysis for boiling front propagation determined the capillary number $Ca$, the Eckert number $Ec$, the Jakob number $Ja$, the Prandtl number $Pr$, the Ohnesorge number $On$, the Weber number $We$ and three additional numbers as relevant parameters.

Since two vaporization mechanisms appeared clearly in the experiments, i.e. slow bubbling below a certain threshold and boiling front propagation above a certain superheat, the analysis was separated into two steps: Determination of the onset temperature for front propagation, and prediction of the increase in velocity with superheat. The various non-dimensional numbers were plotted against each other for this purpose. Least-square fitting methods were used to relate the numbers to each other in a way giving the best representation of experimental data. The desired boiling front quantities could be predicted by taking into account the thermophysical properties and the initial conditions of the fluid. However, it was found that an approach based on the assumption of heat conduction as the dominating factor in vaporization described in section 6.3.1 led to a more successful representation. The results of the non-dimensional analysis are, therefore, not presented here. Instead, the following section gives only the most successful approach used in this work for describing the data.

### 6.3.1 Correlation for Onset of Boiling Front Propagation

From the results obtained so far, it appeared that boiling front propagation resulted from the interacting processes of vaporization, liquid fragmentation and fluid acceleration. The explosive nature of the boiling was mainly attributed to the self-amplifying process of surface-area creation. Since vaporization driven by latent energy at $Ja < 1$ always requires heat conduction from the bulk to the free surface of the liquid, the first step in a phenomenological description was to use the elementary relation for transient heat conduction. At the onset of boiling front propagation, the momentary vaporization becomes sufficient to create new surface area. The dependence of the instantaneous heat flux across an interface separating two substances at different temperatures is given by the following relation (VDI-Wärmeatlas 1994):

$$ q = \sqrt{\lambda_L \rho_L c_{pl}} \Delta T $$

(6.8)

It was then assumed that a certain velocity of vapor accelerating away from the surface triggered further fragmentation. This vapor velocity $u_G$ is given by:

$$ u_G = \frac{\dot{m}_G}{\rho_G} = \frac{\dot{q}}{h_{lg} \rho_G} = \frac{\sqrt{\lambda_L \rho_L c_{pl}} \Delta T}{h_{lg} \rho_G} $$

(6.9)

The onset superheat for boiling front propagation $\Delta T_{onset}$ could be derived from this by taking the thermophysical properties corresponding to saturation at the release pressure $p = 1$ bar:
Correlated and calculated superheat temperatures for onset of boiling-front propagation $\Delta T_{\text{onset}}$ (for R-12 and R-114 only ranges in which onset of front propagation occurred could be deduced from previous studies and, therefore, are not plotted here - see text; methanol and R-11 data of Grolmes and Fauske (1974))

$$\Delta T_{\text{onset}} = c_1 \frac{h_{\text{LG}} \rho_G}{\sqrt{\lambda_L \rho_L c_{\text{pl}}}}$$  \hspace{1cm} (6.10)

By taking the values for the onset of boiling front propagation in Table 4.2 and minimizing the sum of the squared differences between this measured data and the predictions of Eq. (6.10), the value of the constant was obtained as $c_1 = 0.0117 \text{ m s}^{-1}$. The comparison of the measured and correlated superheats for the onset of boiling front propagation is shown on the left-hand side of Fig. 6.5*. The comparisons with data of others are discussed below.

Equation (6.10) gives a good representation of the measured data. The maximum deviation from the correlation is found for butane, with an underprediction of the onset superheat by 2 K. It cannot be clarified whether this deviation is a result of a poor representation of the data or if insufficient measurements (e.g., limited data, experimental errors) explain the difference. At any rate, no other approach, for example, eliminating the dimensional form of the above correlation (by using $Ja^*$, $Re$, $We$ number, etc.) improved the prediction of the experimental data. The results obtained from the relations arising from the work of Prosperetti and Plesset (1984) (Eq. 6.1) were no better than the simple form of Eq. (6.10) either.

The above findings were compared to previous ones cited in the literature, but only three sources with relevant data were found: Grolmes and Fauske (1974), Hill (1991) and Schmidli (1993). Their results led to several considerations relating to the effects of the cross-sectional size and the absolute release pressure.

* Properties for methanol and R-11 are taken from Maddox (1983) and Lemmon et al. (1993), respectively.
Effect of Cross Section on the Threshold

While the boiling front velocity was found to be independent of cross-sectional size in the current work, according to Grolmes and Fauske the onset temperature for sustained front movement is influenced by the pipe diameter. In a systematic investigation of methanol and refrigerant R-11 they found a decrease of the threshold temperature from ca. 51 K to 23 K and from 59 K to 33 K with pipe diameters ranging from 2 mm to 20 mm, respectively. An asymptotic approach toward a threshold value at larger pipe diameters was found.

The dependence of the onset of violent vaporization on the diameter was not studied in detail in this work. In fact, the threshold was determined by extrapolating the correlated data to $u_\infty = 0$ m/s. Since the pipe diameters used in this work were typically larger than those of Grolmes and Fauske (1974), it can be assumed that the thresholds in Fig. 6.5 are close to the asymptotic value. Hill (1991) explained the influence of the diameter on the threshold by the increased probability of vapor cavities (impurities, scratches) with increasing diameter. Thus pipes with larger cross-sections had a longer circumferential length, and this led to more contacts between the superheated liquid and the gas cavities in the glass or impurities. The experimental results of Grolmes and Fauske for methanol and refrigerant R-11 are also plotted in Fig. 6.5. Their measurements with the largest pipe diameter for R-11 deviate from the value predicted using Eq. (6.10) by at most 3 K.

Effect of Release Pressure on the Threshold

Grolmes and Fauske performed their releases from different initial temperatures to different reservoir pressures. They do not state explicitly the exact conditions under which the measurements for determining the onset were conducted. But it can be assumed that the reservoir pressure was much below the ambient pressure with $p_{\text{reservoir}} \ll 1$ bar. However, only the saturation properties at $p = 1$ bar were used for the onset correlation of Eq. (6.10). Varying the release pressure changes the prediction for boiling front onset because it is based on the saturation properties (for example propane: $p_{\text{sat}} = 0.5$ bar $\rightarrow T_{\text{onset}} = 15$ K; $p_{\text{sat}} = 2.0$ bar $\rightarrow T_{\text{onset}} = 53$ K). The above correlation gives, however, approximately the correct result at different release pressures, using the properties for $p_{\text{sat}} = 1$ bar. The dependence of the constant factor ($c_1$) on pressure needs to be investigated.

Hill also investigated the threshold temperature of R-114 and R-12, performing the release from a saturation temperature of $T_{\text{sat}} = 20$ °C to a reservoir at $p \leq 1$ bar. He found a threshold between $35$ K $< T_{\text{onset}} < 45$ K for R-114 and of $T_{\text{onset}} < 45$ K for R-12, whereas Eq. (6.10) predicted $T_{\text{onset}} = 37$ K for R-114 and $T_{\text{onset}} = 34$ K for R-12 with saturation values of $p = 1$ bar. Thus, the results of Eq. (6.10) do not contradict the measured data for the initiation of front propagation.

In the work of Schmidli, superheated liquid was released from shattered glass spheres to $p = 1$ bar. No explosive vaporization was noted below a range of superheat of $37$ K $< \Delta T_{\text{nom}} < 47$ K for R-114, while the onset temperature was at least below $\Delta T_{\text{nom}} < 47$ K for propane, $\Delta T_{\text{nom}} < 43$ K for butane and $\Delta T_{\text{nom}} < 43$ K for R-12. These findings do not contradict the values of Fig. 6.5. Even though the experiments of Schmidli were of a different nature, these measurements support the relevance of the above correlation.
A more detailed comparison of the current work with the experimental findings of Schmidli will be given in the next chapter.

The main conclusion that can be drawn from the above is that the Eq. (6.10) with properties always evaluated at 1 bar predicted the threshold of superheats for several experiments (including some releases to pressure below atmospheric); the pressure-dependence and that of the coefficient $c_1$ should be further investigated. The correlation predictions are unlikely to be valid at small pipe sizes ($d_{pipe} < 20\,\text{mm}$). On the other hand, the qualitative variation of the threshold value for different fluids is well represented. Further systematic studies of the effects of pressure and diameter on the onset temperature are required.

6.3.2 Correlation for Front Velocity

Knowing the threshold for boiling front propagation, the next step in correlating the data is to determine the velocity increase with nominal superheat ($du_f/\Delta T_{nom}$). As for the onset limit, it can be assumed that the velocity is influenced mainly by heat conduction. The sensitivity to the break-up of the liquid is another important factor. As expressed by the We number, liquid fragmentation is facilitated by a low surface tension $\sigma$, which was therefore taken as an additional factor in the correlation. Other attempts were also made, for example using non-dimensional factors. However, the best representation of the data is found in Eq. (6.11) with $c_2 = 1.149\,\text{N} \cdot \text{m}^{-1} \cdot \text{s}^{1/2}$.

$$\frac{d(u_f)}{d(\Delta T_{nom})} = c_2 \frac{\sqrt{\lambda_p \rho_L c_p}}{h_{LG} \rho_G \sigma}$$

(6.11)

Combining Eqs. (6.10) and (6.11) yields the line equation for $u_f$:

$$u_f = c_2 \frac{\sqrt{\lambda_p \rho_L c_p}}{h_{LG} \rho_G \sigma} \Delta T_{nom} - \frac{c_1 c_2}{\sigma}$$

(6.12)

In Fig. 6.6, the predictions are compared with experimental data. A good prediction is obtained particularly for propane, butane and R-134a. The water data do not fall on a straight line and, as a consequence, the predictions deviated from the measurements, to some extent significantly. It is impossible to say whether this deviation should be attributed to irregularities during the experiments or to some fundamentally different characteristics of water.

The predicted and experimental results are plotted again in Fig. 6.7. The confidence limits indicate the probability of deviations from the predictions. It appears that for a predicted boiling front velocity of $u_f = 1\,\text{m/s}$, for example, approximately 80% of the experimental data is found in a range of $\pm 0.1\,\text{m/s}$ of the predicted value. The most extreme deviations are again found for water.

An attempt was made to compare the above results with previous studies. Unfortunately, the limited data available included only velocity measurements with releases to reservoir pressures of $p < 1\,\text{bar}$. In some of these experiments choking occurred and/or the reservoir pressure was not specified. However, a data point of Hill (1991) indicates that the measured boiling front velocity was lower than predicted at a given superheat. The above correlation predicts for $\Delta T_{nom} = 67\,\text{K}$ and refrigerant R-12 a front velocity of $u_{fr} = 0.78\,\text{m/s}$, while Hill measured $u_{fr} = 0.57\,\text{m/s}$ at $p = 0.5\,\text{bar}$. A
Fig. 6.6: Boiling front prediction by Eq. (6.12) and experimental data

The qualitative result of this comparison is that the boiling front is slower than predicted by Eq. (6.12) in releases to pressures lower than \( p = 1 \) bar. This contradicts findings of Chapter 5.1.6, where slower front velocities were noted for higher front pressure.

It has not yet been evaluated to what extent the above correlation can be extrapolated to a release pressure other than \( p = 1 \) bar. As already found in section 5.1.6, the boiling
front is not solely a function of the superheat $\Delta T_{\text{nom}}$. It is also uncertain as to how the above correlation can be used at higher superheats than those measured here. Thus the correlation will certainly not predict the boiling front velocity correctly if choking occurs at high superheat.

It currently appears impossible to put the various qualitative observations into a more general model, since fundamental data is missing. In any case, the given correlations allow, for a limited range of conditions to predict the boiling front velocity, which is the key parameter for studying the subsequent stages after vaporization, such as aerosol dispersion.
Chapter 7
Role of Boiling Fronts in Spherical Releases

This work is motivated by consideration of the worst case of vessel failure, i.e. the instantaneous complete failure of the complete containment leading to the highest possible rate of release of superheated liquid. In previous studies, the catastrophic disintegration was studied without considering the boiling mechanism in particular. "Global" measurements for a limited number and size of vessels were obtained in most cases. It was shown experimentally that a small tank envelope could tear and swing open in the manner sketched in Fig. 3.1 and that the short opening time did not allow the development of defined openings for jet formation (Hess et al. 1973). In any case, it is assumed that shortly after the initiation of a catastrophic failure, the vessel walls no longer affect the boiling process.

There have been very few experiments on the rupture of vessels with an emphasis on the initial vaporization of the liquid. Previous investigations focused mainly on the subsequent dispersion or ignition rather than on the inertial expansion. The most extensive investigation was conducted by Schmidli (1993), but only at a small scale releasing up to 2 dm$^3$ of test liquid. In order to simulate complete failure, spherical glass bottles were shattered and the cloud developing from the vaporizing superheated contents was measured. In the following, the results obtained for boiling fronts are compared with these findings. Despite an extensive search in the literature and several research institutions, it proved impossible to locate data relating to scales typical for industrial installations.

7.1 Lower Limit of Explosive Boiling

As for the threshold for the onset of boiling front propagation, Schmidli found that explosive vaporization occurred only above a minimum degree of superheat. Below this limit, expressed by a range of Jakob numbers $50 < Ja^* < 55$, only gravitational slumping of the released superheated liquid was noted (see also section 5.3.1). However, this non-explosive behavior was observed only for R-114. Schmidli's criterion can be compared to the threshold condition for the onset of boiling front propagation listed in Table 4.2. Transforming the given superheat temperatures to their corresponding Jakob numbers $Ja^*$ results in:

$$Ja^*_{\text{butane}} = 42, \quad Ja^*_{\text{propane}} = 34, \quad Ja^*_{\text{R-134a}} = 44 \quad \text{and} \quad Ja^*_{\text{water}} = 30$$

The above Jakob numbers $Ja^*$ for the threshold are lower than the value given by Schmidli. This can be interpreted in different ways. First, it is doubtful whether the Jakob number $Ja^*$ alone is sufficient for predicting the threshold of explosive boiling. It is also questionable whether the limit for R-114 noted above is generally applicable to other fluids as well. The fact that the Jakob numbers $Ja^*$ at the onset of boiling front propagation differ suggests that this parameter alone is insufficient for describing the threshold.
On the other hand, it could be argued that these differences indicate that boiling front propagation and the vaporization following spherical unconfined release are based on different underlying boiling mechanisms. This cannot be proved or disproved since no single test fluid was used for investigating both thresholds in boiling front studies and in unconfined spherical releases. As a conclusion, it can be stated that the finding of a lower limit of explosive boiling in directed releases from pipes and in spherical releases qualitatively emphasizes the existence of the same underlying boiling mechanism.

### 7.2 Two-Phase Flow Velocities

For the initial stage of unconfined releases, a constant expansion velocity $u_{ci}$ of the aerosol cloud was measured (Schmidli 1993) for certain refrigerants and hydrocarbons. Limited data is available for the expansion velocity, depending on superheat and duration of expansion. In the following sections, it is intended to explain the cloud expansion quantitatively by considering boiling fronts as the driving mechanism for vaporization.

#### 7.2.1 Direct Comparison of Aerosol Velocities

From the fluids used by Schmidli (1993) only propane and butane were studied in this work. The measured velocities $u_{ci}$ are plotted in Fig. 7.1.

The velocity of two-phase flow originating from boiling fronts can be compared with these measurements for spherical releases. The correlation of Fig. 4.22 and the control volume analysis presented in section 5.1.1 are used for this purpose. The latter yields the quality of the mixture expelled from the boiling front and the two-phase flow velocity.

In a first simple approach, the difference between spherical and linear expansion is neglected and the two-phase velocities for the two different cases are directly compared in Fig. 7.1. The comparison shows that the velocities are of the same order of magnitude in the two different geometries. However, the calculated linear expansion...
velocities are higher by a factor of about 1.5 than these from the spherically expanding cloud. The finding that butane expands faster than propane in the unconfined releases is confirmed by the expansion in a linear geometry only at high superheat.

7.2.2 Mass Conservation during Cloud Expansion

The above results emphasized the need to study the difference between spherical and linear release in more detail and to investigate the time dependence of spherical cloud development. In the first step of such an analysis, the superheated spherical volume is assumed to vaporize solely on its outer envelope as sketched in Fig. 7.2. This vaporization shell moves toward the center of the volume with the velocity \( u_f \) measured for boiling fronts at the corresponding superheat. The front expels a liquid-vapor mixture in the radial direction. This mixture is then assumed to push the surrounding air away without any mixing. Therefore, three zones can be distinguished during vaporization: the spherical liquid volume of radius \( r_{\text{liquid}} \), the vapor-liquid shell with an outer radius \( r_{\text{cloud}} \) and the surrounding air. According to this model, the time dependence of the mass of superheated liquid in the center \( M_L \) can be calculated as:

\[
M_L = M_{L0} - \int_0^t M_L \, dt
\]

(7.1)

with the mass flow rate leaving the liquid core of

\[
\dot{M}_L = \rho_L 4\pi r_{\text{liquid}}^2 u_f
\]

(7.2)

and the mass of the vapor-liquid mixture in the surrounding shell \( M_{L,\text{cloud}} \):

\[
M_{L,\text{cloud}} = M_{\text{cloud}} + M_{L,\text{cloud}} = x \int_0^t \dot{M}_L \, dt + (1-x) \int_0^t \dot{M}_L \, dt
\]

(7.3)

Since air entrainment is excluded in the model of Fig. 7.2, no heat supply is possible for further vaporizing saturated liquid originating from the boiling front. Essentially, only vapor from the front will contribute to the adiabatic, volumetric expansion of the cloud. The total cloud volume with \( r_{\text{cloud}} \) is calculated by adding the volumes of liquid and vapor and considering their corresponding densities. The temporal change of the different volumes is shown in Fig. 7.3. While the core radius decreases at a constant rate, the total mass flow rate from the liquid core slows down due to the decrease in surface area. The cloud radius velocity strongly decreases together with the non-linear increase in radius with vapor volume. Due to the slower boiling front velocity \( u_f \), a
lower superheat leads to a longer period of vaporization. In addition, a lower final volume is found because of the decreasing quality with smaller superheat.

In the examples of Fig. 7.3, a complete vaporization of the saturated liquid would have led to a spherical volume with a radius of \( r = 0.48 \) m. In case of mixing with air, the only other energy source that could have been available would have been the specific heat of the air. To cool down dry air from the ambient temperature to the saturation temperature of the released propane at ambient pressure for providing vaporization heat requires a considerable amount of air because of its limited heat capacity. A simple heat balance ignoring kinetic energy shows that complete vaporization of \( V_{\text{propane},1} = 2 \) dm\(^3\) initially superheated to \( \Delta T_{\text{nom}} = 47 \) K with air at an ambient temperature of \( T = 15 \) °C requires a volume of \( V_{\text{air}} = 5.3 \) m\(^3\). In this case, a homogeneous mixture of propane vapor (\( V_{\text{propane}} = 0.48 \) m\(^3\)) and additional air for complete phase change results in a sphere with a radius of \( r = 1.1 \) m. A simultaneous increase of superheat to \( \Delta T_{\text{nom}} = 60 \) K and of the ambient air temperature to \( T = 25 \) °C results in a sphere of \( r = 1.0 \) m. This is significantly more than for the case of Fig. 7.3 without mixing.

The idealized cloud development could also be compared to the experimental growth of clouds shown in Fig. 7.3 (Schmidli 1993). The measured increase in cloud radius is shown for a release of \( V = 2 \) dm\(^3\) of propane at initial superheats of \( \Delta T_{\text{nom}} = 47 \) K and \( 60 \) K. As was mentioned previously, these releases were characterized by an initial phase of constant radial expansion velocity. The speed depended on the superheat but not on the vessel size, although the initial volume determined the duration of the constant rate of radius increase. For releases from identical volumes, a larger superheat led to a faster cloud increase and a shorter period of cloud expansion. After an initial phase, the radius velocity slowed down drastically, and this was followed by slow gravitational and atmospheric dispersion. This later phase is not considered in this analysis and is not included in Fig. 7.3.
The comparison shows that the measured clouds expanded faster and in a shorter period than calculated according to the model of Fig. 7.2. During the initial stage, the volume became larger than could be expected even for complete vaporization. It can be concluded from these mass continuity considerations that air was indeed mixed into the clouds in the experiments. However, complete vaporization did not occur during the initial expansion phase since the total volume was not sufficiently large to provide the energy needed for total vaporization from the air.

7.2.3 Conclusions for further Analysis of Cloud Expansion

It can be concluded from the previous sections that mixing of the released vapor and/or liquid is occurring with ambient air. This leads to larger clouds than would be possible by the expansion of the vapor alone. Therefore, the model assumption of completely separated regions of air and released substance of Fig. 7.2 is not really adequate. Mixing of air with vapor would have required the passage of vapor streams into air and vice versa. Such flows of gases of similar density could have been visible on the recordings. Instead, however, the regular shape of the expanding aerosol cloud did not indicate any presence of such counterflow phenomena during the initial stage.

Therefore, it is concluded that only liquid fragments could have the capability of penetrating into the ambient air as observed in the experiments. Their initial acceleration and inertia would have been high enough to reach the velocity and duration of travel that were noted for the outer contour of the expanding cloud.

Figure 7.3 shows that the period of constant expansion finishes earlier than would have been expected for boiling front propagation from the outside of the liquid volume only. The duration of constant expansion coincided with increased pressure measurements in the core of the superheated liquid. After a time similar to the period of initial expansion, the signals of the pressure transducer levelled off to the steady ambient value. Thus, the sudden slow-down of the radial expansion indicated the end of vaporization. Two mechanisms would explain why this behavior differed from the above model assumptions: either the boiling fronts were faster (by a factor of approximately six) or boiling was not occurring on the free surface of the superheated liquid only. The two alternatives are discussed below.

During the investigation of boiling fronts, it was found that an increase in interface pressure slowed down the front propagation. Similarly, a lower pressure in the downstream region increased the front velocity. By comparing linear and spherical expansions, it can be expected that a lower front pressure occurs in spherical geometry since the frictional pressure drop is reduced. So the assumption of an increased velocity would be reasonable for a spherical geometry. On the other hand, the increase in front velocity required to explain the duration of the expansion leads to a significantly higher two-phase flow velocity (by a factor of 6). However, a higher velocity for aerosol originating from boiling fronts was already noted by directly comparing the two phase-flow velocities in Fig. 7.1. A further increase in boiling front speed would additionally increase this two-phase velocity, an assumption which certainly does not match the observations. It is therefore unreasonable to attribute higher boiling front velocities to the shorter measured duration of vaporization.

An increase in front velocity was already noted in this work for the case of cylindrical releases as compared to the linear ones (see section 4.5.7). However, the analysis of
this phenomenon in section 5.2 was unable to clarify whether the increased velocity was an effect due to the cylindrical geometry or whether the velocity increase was an artefact, i.e. the increased contact of the liquid with the glass surface accelerated the boiling process. Considering the exit geometry it was concluded that the pressure was higher in the downstream direction than in releases from pipes because of the reduction in flow area. These experiments cannot therefore be used to derive a conclusion for velocity differences between linear, cylindrical and spherical releases.

The other possible explanation for faster boiling in the Schmidli experiments was that vaporization did not occur only on the surface of the liquid. For the spherical releases, it appears that the condition and treatment of the liquid were very similar to those in the current experiments. The only possibly important difference was the filling procedure. For the unconfined releases, the test fluid was poured into the glass flasks in the liquid state, while in the current investigation the fluid was condensed in the pipe. It might be supposed that this difference promoted vapor nucleation in the bulk. In a few instances, however, our pipes were also directly filled by liquid without the occurrence of bulk nucleation in the following experiment. Besides, in all our cylindrical releases the test substance was introduced in the liquid state, without this leading to dispersed nucleation. The other indication of the absence of bulk nucleation was given by a few unconfined spherical releases where close-up recordings showed that nucleation occurred only at the liquid-glass interfaces, at least during the first milliseconds after shattering of the glass (Schmidli 1993). Any dispersed nucleation would already have become visible at that stage since it was observed from our pipe experiments that any nucleation source in the bulk (e.g. preexistent bubbles) started growing immediately after depressurization.

While dispersed nucleation in the bulk of the superheated liquid can thus be excluded, some devices placed inside the liquid might have supported vaporization. The flasks of Schmidli were most often equipped with both temperature and pressure transducers. In fact, the close-up recordings were the only instances when there were no internal installations except for a thermocouple at the top. From the experience obtained in our pipe experiments, it is safe to assume that bubbles were growing, particularly from the surface of the pressure sensor. It is very likely that these pushed the surrounding liquid away, leading to a liquid shell of decreasing thickness. Depending on the strength of the internal source, this could even stretch the outer liquid surface where simultaneously nucleation was occurring. Unfortunately, the difference between unconfined releases with or without internal installations was not investigated and their effect on the expansion characteristics of the cloud remained unknown. Nevertheless, the effect of such an assumed second internal vaporization zone will be discussed in the following by proposing a model with two zones of vaporization.

7.2.4 Vaporization in Two Zones of Superheated Liquid

Compared with the proposal of Fig. 7.2, a model which leads to a shorter expansion duration and a constant expansion velocity during vaporization is required. Moreover, it should allow penetration of liquid fragments into ambient air at velocities similar to those of cloud expansion. A simplified model for this mechanism is proposed and illustrated in Fig. 7.4.
As in the first model, vaporization is assumed to occur by a boiling front moving with \( u_{fr,a} \) at the outer surface. In a first step, no mixing of air with the substance released is assumed. In the center of the liquid, a single internal vapor source of spherical geometry is considered. This assumption approximates the growth of a bubble at the pressure transducer, which was positioned in the center of the liquid. Growth of this internal volume leads to a thinning of the surrounding liquid shell even without boiling on the outer surface. During vaporization, four zones are assumed to appear: the spherical vapor volume in the core of radius \( r_{liq,i} \), the surrounding liquid envelope with an outer radius \( r_{liq,o} \), the vapor-liquid shell with an outer radius \( r_{c,i} \), and the surrounding air.

The typical growth history of a bubble could have been used to obtain the growth of the inner vapor volume. To keep the analysis simple, however, a constant vapor volume radial expansion velocity was used. This was the velocity of a vaporization front moving relative to the expanding interface into the superheated liquid with a constant velocity \( u_{fr,i} \) and vaporizing a liquid mass flow rate:

\[
M_{li}^* = \rho_L 4\pi r_{iq,i}^2 u_{fr,i}
\]  

where the radius changes due to front movement and expansion of gas in the core. Taking into account the time dependence of the radius and assuming complete vaporization of this liquid stream in the core leads to a differential equation which can be integrated to obtain the internal radius of the liquid \( r_{liq,i} \):

\[
r_{liq,i} = \frac{\rho_L}{\rho_G} u_{fr,i} t
\]  

In the following step, the decreasing volume of the expanding shell must be calculated. It can be expressed as

\[
M_L = M_{li} - \int_0^t (M_{li}^* + M_{lo}^*) \, dt
\]  

with the mass flux across the outer surface of

\[
M_{lo}^* = \rho_L 4\pi r_{liq,o}^2 u_{fr,o}
\]

Equation (7.6) can be transformed into a differential equation of first order. Finally, several algebraic transformations and an integration yield an analytical solution for the change of radius \( r_{liq,o} \) with time. Due to its transcendental nature, an explicit solution
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Fig. 7.5: Comparison of experimental increase of cloud radius (Schmidli 1993) and variation of liquid and vapor volume radii according to the model of Fig. 7.4 with time (propane, $\Delta T_{\text{nom}} = 47$ K, liquid initial volume $V = 2$ dm$^3$, $u_{\text{fr},i} = 0.0259$ m/s, $u_{\text{fr},o} = 0.5904$ m/s, $x = 0.2625$, duration adjusted by varying $u_{\text{fr},i}$ to $t = 0.025$ s as in the experiment of Schmidli)

for $r_{\text{liq},o}$ cannot be obtained and only numerical solutions are possible. The integration constant must be determined by the initial conditions, i.e. by setting a certain initial liquid volume. The remaining independent parameter is the propagation velocity $u_{\text{fr},i}$ of the vaporization zone in the core, which must be assigned values lower than the velocity at the outer liquid radius $u_{\text{fr},o}$ to obtain reasonable results (see example in Fig. 7.5). The velocity $u_{\text{fr},i}$ could be varied in such a way that the vaporization finished after a certain time, i.e. vaporization from the core and the surface used up all the initial liquid. The total cloud volume described by $r_{\text{cloud}}$ was calculated by adding the volumes of liquid and vapor and considering their corresponding densities. The temporal change of the different volumes is shown in Fig. 7.5.

The plot shows the monotonous increase of the internal liquid radius and the initial slight decrease and following increase of the external liquid radius. After a predetermined time, the two radii meet, marking the end of the vaporization. The simultaneous vaporization in two zones leads to a faster vaporization of the liquid. Even though the mass vaporized inside is much smaller than on the outside, it speeds up the vaporization significantly because the external vaporization area is enlarged. Compared to the “one-front” model, the “double-front” model leads to an almost constant rate of increase of the outer cloud radius, as can be seen in Fig. 7.5.

In Fig. 7.5, the time for complete vaporization was forced to be $t = 0.025$ s by adjusting $u_{\text{fr},i}$. This period corresponded to measurements of the vaporization duration for the unconfined release of propane ($V = 2$ dm$^3$) at a superheat of $\Delta T_{\text{nom}} = 47$ K. This required a front velocity in the core of $u_{\text{fr},i} = 0.0259$ m/s.

Similarly, the different radii of the double-front model could be calculated for different cloud expansion durations, i.e. core front velocities $u_{\text{fr},i}$. The effect of different vaporization periods is shown in Fig. 7.6. A stronger increase in vapor volume in the core leads to faster expansion of the outer surface of the liquid, which accelerates its vaporization. Again, the second internal vapor source leads to an extended period of
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Fig. 7.6: Radii change according to the model of Fig. 7.4 with time. For the meaning of the different lines see Fig. 7.5 (propane, $\Delta T_{\text{nom}} = 47$ K, initial liquid volume $V = 2 \text{ dm}^3$, $u_{f,1} = 0.1038 \text{ m/s}$ for $t = 0.01 \text{ s}$ duration for complete vaporization, $u_{f,1} = 0.0109 \text{ m/s}$ for $t = 0.04 \text{ s}$, $u_{f,0} = 0.5904 \text{ m/s}, x = 0.2625$)

constant expansion of the vapor cloud for both cases investigated. Reducing the front velocity in the core to $u_{f,1} = 0 \text{ m/s}$ results in the plot of Fig. 7.3 for the outer cloud radius.

Figure 7.6 shows a slightly larger final cloud volume for a short duration of vaporization. This effect results from the model assumptions, which say that the center contains pure vapor and the outer shell consists of a vapor/liquid mixture whose quality depends on the boiling front velocity. Since the proportion of initial mass vaporized in the core is higher in fast vaporization, this leads to a larger total volume according to the model. Even though only a small proportion of the mass vaporizes in the core (for $t = 0.04 \text{ s}$ of Fig. 7.6 ca. 1% of the total mass), its expansion leads to a considerable acceleration of the vaporization process.

Thus, the model of Fig. 7.4 correctly predicts the shorter duration of vaporization observed in experiments by assuming internal vapor formation. However, the measured expansion velocities are faster and a larger visible volume is reached than that obtained without allowing mixing. In the next chapter, therefore, the model of Fig. 7.4 will be extended to allow penetration of saturated liquid into ambient air.

7.2.5 Velocity Field around Vaporizing Superheated Liquid

Due to their inertia, liquid drops can penetrate much further into still ambient air than vapor at the same initial velocity. As a modification of the model of Fig. 7.4, it is therefore assumed that liquid fragments are accelerated at the outer surface by the vapor stream. While the vapor velocity in a spherical geometry quickly slows down in the radial direction because of the increasing volume available for expansion, it is assumed that the accelerated liquid continues to propagate due to its inertia. Because they are accelerated in the high vapor-speed region of the boiling front, the droplets pass the vapor region and enter into the ambient air. While the saturated drops would
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Fig. 7.7: Velocity field around a spherical volume of vaporizing superheated liquid according to the model of Fig. 7.4; the numbers in the legend give the velocity in [m/s] (propane, \( \Delta T_{\text{nom}} = 47 \) K, initial liquid volume \( V = 2 \text{ dm}^3 \), \( u_{\text{F1}} = 0.0259 \text{ m/s}, u_{\text{F0}} = 0.5904 \text{ m/s}, x = 0.2625 \))

not vaporize in their own vapor, they would lose mass in the air region because of the assumed higher ambient temperatures. Besides this decrease in size, they would simultaneously be decelerated in the outer parts of the vapor region and in the air volume.

The velocity field around an expanding vapor source must be known in order to calculate the deceleration and acceleration of droplets in gas. Assuming incompressible gas flow from a spherical source gives the following for the vapor flow rate leaving the surface of the liquid volume:

\[
M_{\text{v0}} = \frac{x \rho_{\text{L}} V_{\text{L0}}}{\rho_{\text{g}}} = x \rho_{\text{L}} 4\pi r_{\text{L0}}^2 u_{\text{v0}}
\]  

(7.8)

The vapor mass flow rate at any other more distant spherical envelope of radius \( r \) is given by:

\[
M_{\text{v}} = \frac{x \rho_{\text{L}} 4\pi r^2 u_{\text{v}}}{\rho_{\text{g}}}
\]  

(7.9)

Neglecting the relatively slow motion of the liquid interface, these two equations are combined to give the vapor velocity at a given radius \( r \) and a certain position of the outer liquid surface which is expressed by its radius \( r_{\text{L0}} \) and is a function of time \( t \):

\[
u_{\text{v}}(r,t) = \frac{x \rho_{\text{L}}}{\rho_{\text{g}}} u_{\text{v0}} \frac{r_{\text{L0}}^2}{r^3}
\]  

(7.10)

Using Eq. (7.10) and plotting velocity contours for various distances and times leads to Fig. 7.7. The flow field results from the vaporisation as illustrated in Fig. 7.5. The highest velocities appear at the boiling front. The velocity slows down in the radial direction due to the spherical expansion. Because of expansion of the outer surface, the velocity field moves away from the core with time, leading to the arched shape of the illustration for the radial velocity change with time. Since the vapor and air are
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Fig. 7.8: Velocity field around a spherical volume of vaporizing superheated liquid according to the model of Fig. 7.4; the numbers in the legend give the velocity in [m/s] (propane, $\Delta T_{nom} = 60$ K, initial liquid volume $V = 2$ dm$^3$, $u_{r,i} = 0$ m/s (= model of Fig. 7.2), $u_{r,o} = 0.97$ m/s, $x = 0.337$)

assumed to be incompressible, the vapor pushes the surrounding air outwards. Thus, Eq. 7.10 can also be applied to the surrounding region of air.

For comparison, the velocity distribution is plotted for the case without vaporization in the center of the liquid. The example of Fig. 7.8 shows a run with a higher superheat than that of Fig. 7.7. Higher velocities for the vapor are therefore noted at the outer surface of the liquid and at more distant locations. The shrinking surface area of the liquid leads to a sudden decrease of vaporisation with time. Complete vaporization of the liquid takes longer and a decreasing velocity is noted in the radial direction.

7.2.6 Drop History in Gas Velocity Field

The above velocity fields were calculated for the vaporized fraction of the fluid originating from the boiling front. It is of interest to see how the gas velocity influences liquid drops exposed to it. In particular, the question of how the drop velocity and its size change with distance and time is to be studied. For this purpose, the momentum equation is used to calculate the acceleration and deceleration of droplets at several discrete radial positions depending on the velocity of the surrounding continuous phase. The decrease in size due to evaporation mass transfer is also calculated for each time step.

The effect of gravity is ignored since the typical accelerations and velocities noted during the initial stage of unconfined releases are much longer than those that could be attributed to gravitational effects. Additionally, it is assumed that the drops appear as spheres at saturation condition. It is assumed that any superheat was already depleted during the intense fragmentation and mixing processes in the boiling front region. The steps for calculating the droplet history are shown in the flow chart of Fig. 7.9.
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General input: thermophysical properties of released substance and air; initial conditions of substance and air and resulting vapor/air velocity field

Initial conditions: diameter of drop $d_{\text{drop}}$; radial drop position $r_{\text{drop}}$; drop velocity $u_{\text{drop}}$; $t = 0$ s

next time step $t + \Delta t$

stop calculation if $d_{\text{drop}} = 0$ m

continue calculation

$d_{\text{drop}}(t + \Delta t) = d_{\text{drop}}(t) + \frac{dd_{\text{drop}}}{dt} \Delta t$

diameter decrease:

$\frac{dd_{\text{drop}}}{dt} = \frac{2 Nu \lambda_{\text{vapor}} \Delta T}{h_{\text{LG}} d_{\text{drop}} \rho_{\text{L}}}$

Nusselt number

$Nu = (2 + 0.57 Re^{0.5} Pr^{0.33})(1 - B)^{-0.7}$

Prandtl number

$Pr = \mu_{\text{vapor}} c_{p, \text{vapor}} / \lambda_{\text{vapor}}$

mass transfer number

$B = c_{p, \text{vapor}} (T_{\text{air}} - T_{\text{drop}}) / h_{\text{LG}}$

$r_{\text{drop}} > r_{\text{cloud}}$: drop vaporization in air

$r_{\text{drop}} < r_{\text{cloud}}$: no drop vaporization

new drop position

$r_{\text{drop}}(t + \Delta t) = r_{\text{drop}}(t) + [u_{\text{drop}}(t + \Delta t) + u_{\text{drop}}(t)] \Delta t / 2$

Initial conditions:

calculate gas velocity (vapor/air) at drop position $u_{G} = f(r_{\text{drop}})$ by Eq. (7.10)

velocity difference between drop and gas $\Delta u = u_{\text{drop}} - u_{G}$

$r_{\text{drop}} < r_{\text{cloud}}$: use vapor properties of released fluid for gas

$r_{\text{drop}} > r_{\text{cloud}}$: use air properties for gas

Reynolds number $Re$

$Re = \rho_{G} |\Delta u| d_{\text{drop}} / \eta_{G}$

drag coefficient $c_{D}$

$c_{D} = 24 / Re(1 + 0.15 Re^{0.687})$

drop mass $m_{\text{drop}}$

$m_{\text{drop}} = \rho_{L} \pi / 6 d_{\text{drop}}^{3}$

drop acceleration/deceleration

$\frac{du_{\text{drop}}}{dt} = -c_{D} \rho_{G} \pi / 8 d_{\text{drop}}^{2} \Delta u |\Delta u| / m_{\text{drop}}$

new drop velocity

$u_{\text{drop}}(t + \Delta t) = u_{\text{drop}}(t) + du_{\text{drop}} / dt \Delta t$

Fig. 7.9: Scheme for calculation of drop history in gas velocity field around vaporising spherical volume of superheated liquid ($c_{D}$ - correlation: Clift et al. (1978); $Nu$ - correlation: Renksizbulut and Yuen (1983))
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Fig. 7.10: History of drop starting from the surface of a liquid volume exposed to the velocity of spherical release (propane, \(d_{\text{drop}} = 0.4\) mm, \(\Delta T_{\text{com}} = 47\) K, initial liquid volume \(V = 2\) dm\(^3\), \(u_{t,1} = 0.0259\) m/s, \(u_{t,2} = 0.5904\) m/s, \(x = 0.2625\), duration adjusted to \(t = 0.025\) s as in the experiment, \(T_{\text{air}} = 0\) °C)

Starting from the calculated liquid contour change with time, the velocity of the gas at a certain radial position which determines the local relative motion is known. The position of the vapor/air boundary determines whether the properties of air or vapor are to be used. This boundary also determines whether vaporization takes place, a process which the model restricts to the air region. The thermophysical properties used for the calculations are listed in Appendix B. The history of a drop originating from the surface of the liquid at the start of vaporization is shown in Fig. 7.10.

In the example of Fig. 7.10, a drop with an initial diameter of \(d_{\text{drop}} = 0.4\) mm is considered. The velocity field accelerates the drop to a velocity of about \(u_{\text{drop}} = 9\) m/s. Its radial position consequently changes. The droplet distance relative to the outer liquid surface (middle thick line) increases, but the drop remains in the vapor space, i.e. vaporization does not start and the droplet diameter remains constant. Only after leaving the vapor space and entering the air region does the diameter of the drop start to decrease.

A smaller drop behaves differently in an identical flow field. Figure 7.11 shows the history of a drop with \(d_{\text{drop}} = 0.05\) mm. Because of its lower inertia, this drop reaches a higher velocity than larger drops at the beginning. It passes through the vapor zone and enters the air space. There it starts to vaporize so that it already disappears before the complete vaporization of the liquid volume.

By comparison of plots such as Fig. 7.10 and Fig. 7.11, it becomes obvious that small drops reach high velocities at earlier times than larger ones. On the other hand, large drops travel farther until they are completely vaporized. Under given conditions, it can
now be investigated which initial drop size reaches the longest radial distance at certain times after the start of vaporization. If a collection of drops with a range of sizes starts from the liquid surface, the radial position reached by the fastest of these drops after different times can be found. This was done for a collection of differently-sized drops without an initial velocity and is illustrated in Fig. 7.12.

Various drop sizes lead to maximum travel distances after different times, as shown by the sharply dropping lines in Fig. 7.12. The thick line in Fig. 7.12 envelopes the maximum travel distance of drops at certain times. It appears that this envelope of many drop histories increases almost linearly with time. Drops starting at a stage later than the beginning of the release are not considered, even though they might possibly pass the larger slower-moving drops released at an earlier time.

It can be assumed that the leading drops constitute the visible cloud which is observed in experiments. Their low temperature (for propane $T_{sat,1\text{bar}} = -42 \, ^\circ\text{C}$) would lead to the immediate condensation of air humidity. Therefore, the line of maximum distances travelled by drops can be compared to the expansion of clouds investigated by Schmidli (1993). The experimental observations at corresponding superheat and identical duration of vaporization are plotted in Fig. 7.13.

The comparison shows that the measured clouds expanded faster than the leading drops in the model. In fact, the collection of differently-sized drops is only slightly faster than the expanding volume of vapor. To reach higher velocities the drops were not to be accelerated by the stream of pure vapor alone. Thus, it was assumed that the drops were not at rest at the beginning, but started from the boiling surface with a
certain velocity. This was found to be a reasonable assumption since the bursts in the downstream region discussed in section 4.4.2 accelerated particles at the boiling front to high velocities. Figure 5.11 indicates a certain velocity ratio \( S \) for the two-phase flow region, leading to a lower velocity of the liquid than of the vapor stream. Thus, the velocity of the liquid originating from the boiling process can be assumed to lie somewhere between zero and that of the homogeneous two-phase jet. The result for an initial velocity of \( u_{\text{drop,initial}} = 19 \text{ m/s} \) assigned to all particles is shown in Fig. 7.14.

As shown in Fig. 7.14, the modified model of Fig. 7.4 successfully predicts the behavior of an expanding liquid/vapor cloud at the initial stage. The two parameters

![Fig. 7.12: Trajectories of differently sized drops (conditions as in Fig. 7.10)](image)

![Fig. 7.13: Travel distance of differently-sized drops and outer radius of vapor volume in comparison to measured cloud expansion, drops starting from rest (conditions as in Fig. 7.10)](image)
adjusted were the front velocity in the core $u_{fr,1}$ needed to obtain the correct vaporization duration, and the initial velocity of the drops $u_{drop,initial}$ to reach a similar radius velocity as that noted in the experiments. A similar result was obtained when considering the case of an initial superheat of $\Delta T_{norm} = 60$ K. Again, choosing the appropriate $u_{fr,1}$ in the core and the correct initial velocity for the whole droplet population led to a good prediction of the observed behavior.

Several objections might be raised against this simplified approach. For example, the assumption of a single concentric internal vapor volume increasing with constant radius velocity might not be adequate for the considered spherical releases. Choosing the initial velocity of the drops accelerated away from the boiling front might also be considered as rather arbitrary. On the other hand, the currently missing data does not allow the model proposed above to be validated further. To do this, several additional investigations would have been necessary. Thus the acceleration of liquid fragments from the boiling front or the global effect of distributed nucleation in unconfined releases of superheated liquid would have been interesting topics of investigation.

Various other details could be studied and sensitivity studies as well as the examination of additional cases undertaken. However, since detailed experimental data is missing, their relevance as well as the examination of additional cases is uncertain. The objective of this chapter was to show the possible influence of boiling fronts on the vaporization of larger volumes of superheated liquid. On the basis of simplifying but realistic assumptions it was shown that boiling fronts combined with other effects have the potential to explain the observed phenomena.

Fig. 7.14: Travel distance of differently-sized drops and outer radius of vapor volume in comparison with measured cloud expansion, all drops start with an initial velocity of $u_{drop,initial} = 19$ m/s (conditions as in Fig. 7.10)
Chapter 8
Summary, Conclusions and Recommendations

A survey of past experimental and analytical work revealed that only a limited understanding exists of the boiling mechanisms involved in the sudden release of superheated liquid. This is particularly true for the accidental spillage of liquefied gas following the complete failure of pressure vessels. Previous investigations, such as the work of Schmidli (1993) and Hill (1991), focused on the global effect of the vaporization of liquid volumes or analyzed the sudden phase transition of metastable liquid at a fundamental level. While Hill provided fundamental information about the vaporization phenomena of boiling fronts, Schmidli presented results on the unconfined release of superheated liquid.

Despite their efforts, however, the limited number of experiments and the missing link between basic boiling phenomena and the overall effects led to major uncertainties in predicting the consequences of severe accidents. To reduce this gap in knowledge, the aim here was to quantify and obtain a better understanding of the boiling process and to propose new models for facilitating predictions of large-scale phenomena. The present work, therefore, addresses experimental and theoretical studies of liquid releases. In particular, the behavior of boiling fronts travelling into superheated liquid and their potential effects on unconfined releases from spherical vessels were analyzed.

Experimental Work

Several novel techniques were developed and successfully applied for the experiments. For example, in order to provide conditions such as those found in large volumes of liquid, a receptacle behaving in an essentially inert manner toward the superheated liquid was needed. The resulting procedure of vacuuming and subsequently pressurizing the glass section with a buffer liquid represented a new method for eliminating nucleation sites from glass surfaces for the purpose of investigating boiling fronts. The quick-opening mechanism for releases from glass pipes based on the controlled break of a rupture disk was new, in the sense that it could be triggered in a certain range independently of the pressure on the disk. In addition, the set-up allowing the radial release of a cylindrical volume of superheated liquid was unique since it permitted an undisturbed view of boiling fronts advancing in the radial direction for the first time.

Butane, propane, R 134a and water were selected as the test substances because of their sufficiently different physical properties and/or their technical importance. These fluids also allowed a direct comparison to previous unconfined releases or permitted the findings on boiling fronts to be extended to liquids other than those previously investigated. In general, the experimental conditions were chosen to obtain findings of industrial relevance, i.e. the substances were released to atmospheric pressure. The maximum nominal superheat was limited to about 70 K by technical and safety reasons.
The experiments confirmed that in the absence of nucleation sites on the walls or in the bulk, boiling was restricted to the free surface of the superheated liquid. Initially saturated or slightly subcooled liquid did not show bulk nucleation in the absence of floating bubbles or impurities, even without prior purification by condensation. Instead, only the free surface broke up, expelling a stream of vapor and liquid. The front propagated with a locally fluctuating velocity and with changes in its shape but at globally constant velocity.

The leading contour of the boiling front consisted of a bubble-like structure, i.e. of cavities filled with pure vapor which were mostly open in the downstream direction. These caps expanded and pushed away superheated liquid. During their growth, some of the caps acquired a rough surface from which new hemispherical structures started growing. Other vapor cavities shrank in size or were moved downstream by liquid flow. The boiling front, with typical cap diameters in the range of a few millimeters, appeared to have a finer structure at higher superheat. While a small proportion of liquid vaporized into the caps, the major part of the liquid passed around this cauliflower-like structure and penetrated into a zone of more violent vaporization. Relative motion between gas and superheated liquid enlarged the surface area, which in turn enhanced the vaporization rate. Boiling was interpreted as a self-amplifying fragmentation process where vapor from the leading vapor caps triggered intense vaporization further downstream in the boiling-front layer. The violent, unstable nature of the phase change became evident by bursts occurring in the boiling front.

Averaging allowed the quasi-steady front velocity to be determined. While the vaporization zone advanced at up to 1.3 m/s, the two-phase stream moved faster by two orders of magnitude. This fluid acceleration induced a higher pressure in the superheated liquid than that prevailing in the ambient atmosphere. As a result, the real superheat in the metastable liquid lagged behind that obtained from the initial temperature in the experiments and attenuated vaporisation at the leading edge of the boiling front. The boiling-front velocity grew roughly linearly with superheat, but below a lower limit no sustained front advancement was observed. Instead, slow bubbling with insufficient vapor generation for the removal of saturated liquid was noted. No significant influence of cross-sectional size on boiling front velocity was found for pipes with diameters ranging from 14 mm to 80 mm. It was concluded that these measured front velocities would also appear in larger cross-sections. However, in closely spaced conduits reaching the typical diameters of the leading vapor caps, higher boiling-front velocities were noted. The total pressure could be identified as another front velocity determining parameter. Higher pressures exerted on the interface during vaporization reduced the velocity of the front.

An important finding of the present investigation was that boiling fronts also appeared in cylindrical geometries. In an arrangement mimicking the complete failure of the walls of a container, a volume of superheated liquid became vaporized by a front moving from the outer surface toward the center. The core of the liquid remained metastable for several tenths of a second until the arrival of the vaporization zone. The velocity of the front could not be determined exactly in these circular-release geometry experiments due to liquid flow being superimposed on the boiling-front advancement and perturbations due to the restrictive geometry of the outlet opening. However, it appeared to be in the same range as in the glass pipes. By examining the velocities and accelerations of boiling fronts, it was concluded that gravity had no direct significant effect on the boiling velocity.
Analytical Work

A control-volume analysis, using the correlated boiling-front velocity as an input, allowed the downstream quality to be derived. The calculations revealed the phase transition to be non-isentropic, leading to smaller velocities of the two-phase stream than the maximum possible ones. The measured pressures induced by fluid acceleration were in good agreement with the theoretical predictions using the control-volume analysis. Comparison of calculated and measured velocities of the liquid downstream of the boiling front indicated that significant slip occurred at superheats slightly above the onset limit. At higher superheat, the difference in flow velocity between the liquid and vapor phases decreased. This coincided with findings of a shift of droplet-size distribution to smaller sizes at higher superheat.

The vapor generation could not be clearly attributed to a single instability or nucleation mechanism but was found to be most likely the combined effect of several interacting phenomena. Both secondary nucleation and the instability mechanisms of Rayleigh-Taylor, Kelvin-Helmholtz and Landau were found to be possibly at least partly responsible for the process of surface generation, vaporization and liquid fragmentation. Visual or analytical evidence was found for all these mechanisms. However, their influence was difficult to quantify because of their mutual complex interaction. In addition, local flow conditions were unknown due to the irregular structure and the highly transient flow and heat transfer conditions at the front.

Since data were gathered over a wide range of superheats, correlations could be developed for the first time describing the increase of boiling-front velocity with superheat. Because of its complexity, the behavior of the front could only be modeled by a correlational approach. In a first step, the onset superheat for boiling-front propagation had to be analyzed, while at a second stage the increase of front velocity with superheat had to be modeled. For both objectives, correlations based on non-dimensional numbers were tried as a first attempt with limited success. The best fit of the experimental data was obtained by assuming a process dominated by non-stationary heat conduction. The results for determining the threshold could also be compared with a few measurements of other workers. The data was predicted with errors of less than 9 %, which was found to be satisfactory in view of the uncertainties in the conditions of earlier experiments and the spread of our own data. Similarly, theoretical considerations allowed the increase of boiling-front velocity to be correlated by additionally introducing surface effects. As a result, the front velocities for releases to an ambient pressure of 1 bar for a given initial superheat could be predicted with a certain precision. For example, at a predicted velocity of 1 m/s, 80 % of the experimental data were found within a range of ±10 % of the correlated value. Considering the deviation in the measured velocities, this was found to be a good result. The most extreme divergences from the model were found for water. On the basis of the correlation, the main thermophysical properties governing the front speed for releases to the ambient atmosphere were identified. These were the density, the heat conductivity, the specific heat capacity and the surface tension of the liquid, and the density of vapor for saturation at 1 bar.
Role of Boiling Fronts in Unconfined Releases

The unconfined expansion of superheated liquid released to the environment was investigated in previous experiments. Several characteristic parameters of these experiments were compared for evaluating the possible role of boiling fronts in such a mode of release. As for the boiling fronts, the existence of a lower threshold for the onset of violent boiling during an unconfined release was noted. The appearance of this threshold at similar superheat temperatures indicated similar boiling mechanisms in both types of release. The small-scale experiments that produced the data compared here were characterized by a period of constant cloud expansion; duration and the radial expansion velocity were measured. However, differences were found when directly comparing the velocity of the two-phase stream originating from a boiling front to the radial expansion velocities of spherical expanding vapor/liquid clouds. In addition, the duration of the unconfined release could not be explained by assuming that a phase change occurred only on the free surface. It was therefore concluded that vaporization had also started in the core of the volume in the older work (e.g. at points such as the pressure transducer immersed into the liquid volume, for example). Consideration of this additional phase-change location led to a shorter duration of vaporization. This "double-front" model allowed the characteristic constant expansion velocity feature of the spherical cloud to be explained, but the volume and velocity observed in the experiments could not be attained. In fact, conservation of mass and energy required the assumption of air entrainment into the cloud or, vice-versa, penetration of liquid into the ambient air. In addition, the inclusion of liquid expulsion in the model allowed all the experimentally observed phenomena to be covered. In its final form, the model predicted the velocity, the duration and the volume for the initial expansion period sufficiently well, but required the internal vaporization rate and the initial velocity of droplets to be adjusted. The proposed model could not be further validated because of lack of detailed experimental data for both the unconfined releases of superheated liquid and the velocities of liquid particles in the vicinity of the boiling front.

Main Objectives for Future Work

This experimental and analytical work investigated the explosive vaporization of superheated liquid. Fundamental findings on boiling fronts were obtained and related to those from unconfined releases. However, the existing data is still rather limited, and does not allow sufficiently direct comparisons for validating the assumed influence of boiling fronts on unconfined releases of superheated liquid. In addition, the scenario of catastrophic failure of vessels for storing liquefied gas addressed here is likely to occur at higher superheats than those investigated so far. Different initial fluid conditions, e.g. the presence of interior bubbles, can also be assumed. More work taking these current limitations into account is thus required, to allow a reliable prediction of the consequences of vessel failure.

A major objective for the study of boiling fronts will be to conduct experiments with the test substance at higher superheats, i.e. higher pressures. The concept that was developed of placing a fragile and pressure limited glass receptacle into a more stress resistant containment would allow investigations at much higher pressures. While the test fluid would be in contact with the smooth surfaces of the glass and the buffer liquid, the receptacle could be placed in a robust steel containment equipped with small
high-pressure observation windows. This arrangement would allow the releases from receptacles with larger cross section than those investigated so far as well.

Another objective should be to obtain more precise data on the two-phase stream that is generated, particularly the drop-size distribution and its temporal and spatial development. Several small-scale experiments giving information about the influence of nucleation sites distributed in the liquid and their effect on the overall expansion velocity would also be desirable. A complete simulation of the complex phase change at the boiling front remains a challenge for future work, but it appears unlikely that reasonable results will be obtained in the near future, as detailed experimental information on the structure and dynamics of the front is still missing and difficult to obtain.

Besides these objectives for boiling fronts, it appears necessary to broaden the existing data base on unconfined releases as well. The effect of impurities or equipment installed inside of the superheated liquid on overall expansion behavior was not systematically investigated so far. Further detailed measurements of the temperature and concentration distributions in an expanding cloud would help to establish more precise models. It was hoped that the experimental approach for investigating vaporization at a small-scale in glass vessels free of nucleation sites could obviate the outlay for a large-scale experimental effort. However, it appears unavoidable to perform more experiments on an industrial scale to assure and validate the scale-up methods.
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Last but not least, my gratitude also goes to all the other persons who are not named above, but who played a more important role in my life than this work. Their personalities contributed, in one way or another, to successfully complete this work and were the main source of motivation.
Appendix A

Calibration of Drop Size Measurements

A.1 Experimental Set-Up for Calibration of Droplet Traces

For determining droplet sizes based on the principle of paper witness cards, a correlation between original droplet sizes and their resulting impingement diameter had to be established. The diameter of a dyed droplet impinging on paper allowed to determine the initial diameter of the droplet before impingement. The droplets evaporated immediately after contacting the paper. The diameter of the colored spot remaining on the paper gave information about the initial droplet size. A collection of spots on paper could be converted to the original droplet sizes by using a predetermined spreading factor correction. For establishing this spreading factor relationship, the experimental set-up as sketched in Fig. A.1 was used.

The drops were generated by releasing pressurized liquid (propane) from a containment which consisted of a glass cylinder (0.5 dm$^3$) fitted with a quick-opening valve (not shown in Fig. A.1) or fitted with a rupture disc. For coloring, a completely dissolving substance was required. For propane, an agent used for dying benzene was used (BASF-Petrol-Coloring Agent "Sudanrot").

After fragmentation and droplet formation, the drops were directed through two masks onto rotating paper. The latter was ordinary endless paper used for printers. Later, the same kind of paper was used in the actual experiments. A video camera recorded images of the droplets, as shown in Fig. A.1. Simultaneous recording of the passing drops and of the actual position of the marked paper, allowed to assign droplet spots on the paper to video-images of passing drops. This was achieved by dividing the view field of the video camera in two sections. In the upper half of the image the passing

![Fig. A.1: Sketch of experimental set-up for correlating the initial drop size with the resulting spot diameter on paper after impingement](image-url)
drops were captured whereas the lower half was directed by a tilted mirror on the moving scale near the impingement point of the drops on the paper. Since the field of view and the frame rate were limited, numerous runs had to be performed, to record a sufficient amount of drops. Drops impinging at high velocity ($u_{\text{drop}} > 10 \text{ m/s}$) were difficult to capture with the available instrumentation. Because of the required resolution they could be filmed only on one frame. However, with the given exposure duration the length of the trace left by the drop could be used for determining the drop velocity.

A.2 Calibration Results

Droplets with velocities $u_{\text{drop}} \leq 16 \text{ m/s}$ and with diameters $d_{\text{drop}} \leq 6.2 \text{ mm}$ were measured. The gathered data could be successfully represented by a correlation of the form (suggested by Sommerville and Matta 1990):

$$d_{\text{drop}} = a \left( d_{\text{stain}} \right)^b$$

with:

- $d_{\text{drop}} = \text{mean droplet diameter} \quad [\text{m}]$
- $d_{\text{stain}} = \text{mean spot diameter} \quad [\text{m}]$
- $a, b = \text{coefficients} \quad [-]$.

The experimental data, together with this correlation, are shown in Fig. A.2 ($a = 0.310, b = 0.781, 0.4 \text{ mm} \leq d_{\text{stain}} \leq 30 \text{ mm}$).

![Fig. A.2: Correlation of the initial drop size with the resulting spot diameter on paper after impingement of saturated propane droplets with different velocities at atmospheric pressure](image)

The diameter of spots increased with the initial drop size. Practical application of the droplet/spot correlation required that the impact velocity did not essentially influence the relationship. As can be concluded from Fig. A.2, the drop velocity indeed did not show a significant influence on the spreading behaviour. However, it should be noted
that the large drops accumulated in the region of low velocities whereas the small drops gathered in the high speed region.
Appendix B

Fluid Properties

For convenient usage, several thermophysical properties listed in different sources were represented by the correlations of the following pages. The sources of the data are referenced at the end of this Appendix. The range of the original data is given there as well. As input, either the absolute temperature $T$ or the absolute pressure $p$ are used. For input and output only the basic SI units: $J$, $K$, $kg$, $m$, $N$, $Pa$, $s$, $W$ are used. In general, the original data points were considered in such sufficient number so that temperature steps of 10 K and corresponding saturation pressure steps, covered the whole data range of interest.

The drop histories shown in Chapter 7 were based on the following condition and properties of air (VDI-Wärmeatlas 1994):

- $t_{\text{air}} = 0^\circ\text{C}$
- $\rho_{\text{air}} = 1.275 \text{ kg m}^{-3}$
- $c_{p,\text{air}} = 1006 \text{ J kg}^{-1} \text{ K}^{-1}$
- $\lambda_{\text{air}} = 0.0245 \text{ W m}^{-1} \text{ K}^{-1}$
- $\eta_{\text{air}} = 17.1 \times 10^{6} \text{ kg m}^{-1} \text{ s}^{-1}$
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Table B.1: Correlated fluid properties

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<td>PC$_{Mix}^{*}$</td>
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<tr>
<td>PC$_{Mix}^{*}$</td>
<td>$-0.000019163429690592E+10^{p}y^{2}+0.0593142243042354E+10^{p}y^{3}+0.00860358627994236E+20^{p}y^{4}+0.00963204687702046E-23^{p}y^{5}$</td>
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<tr>
<td>PC$_{Mix}^{*}$</td>
<td>$-0.000018163429690592E+10^{p}y^{2}+0.0593142243042354E+10^{p}y^{3}+0.00860358627994236E+20^{p}y^{4}+0.00963204687702046E-23^{p}y^{5}$</td>
</tr>
<tr>
<td>PC$_{Mix}^{*}$</td>
<td>$-0.00001063429690592E+10^{p}y^{2}+0.0593142243042354E+10^{p}y^{3}+0.00860358627994236E+20^{p}y^{4}+0.00963204687702046E-23^{p}y^{5}$</td>
</tr>
<tr>
<td>Table B.1: Correlated fluid properties</td>
<td></td>
</tr>
<tr>
<td>----------------------------------------</td>
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<tr>
<td><strong>Range of Data</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Source</strong></td>
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**n-Butane**

<table>
<thead>
<tr>
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<th>Equation</th>
</tr>
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<tbody>
<tr>
<td>( T_{0,m} )</td>
<td>( \lambda_{0,m} )</td>
</tr>
<tr>
<td>( 16485.205 \times 10^{-3} )</td>
<td>( 19.9 \times 10^{-3} )</td>
</tr>
<tr>
<td>( 6.06134 \times 10^{-2} )</td>
<td>( 0.617 \times 10^{-3} )</td>
</tr>
<tr>
<td>( 3.370 \times 10^{-1} )</td>
<td>( 0.270 \times 10^{-3} )</td>
</tr>
<tr>
<td>( 2.6018 \times 10^{-3} )</td>
<td>( 0.180 \times 10^{-3} )</td>
</tr>
<tr>
<td>( 1.38 \times 10^{-3} )</td>
<td>( 0.170 \times 10^{-3} )</td>
</tr>
<tr>
<td>( 0.641 \times 10^{-4} )</td>
<td>( 0.160 \times 10^{-4} )</td>
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**R-134a**

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<td>( \rho_{0,m} )</td>
<td>( \lambda_{0,m} )</td>
</tr>
<tr>
<td>( 1.641 \times 10^{-3} )</td>
<td>( 1.99 \times 10^{-4} )</td>
</tr>
<tr>
<td>( 6.061 \times 10^{-5} )</td>
<td>( 0.617 \times 10^{-5} )</td>
</tr>
<tr>
<td>( 3.370 \times 10^{-6} )</td>
<td>( 0.270 \times 10^{-6} )</td>
</tr>
<tr>
<td>( 2.601 \times 10^{-6} )</td>
<td>( 0.180 \times 10^{-6} )</td>
</tr>
<tr>
<td>( 1.38 \times 10^{-6} )</td>
<td>( 0.170 \times 10^{-6} )</td>
</tr>
<tr>
<td>( 0.641 \times 10^{-7} )</td>
<td>( 0.160 \times 10^{-7} )</td>
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**Source**

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<td>T&lt;sub&gt;LI&lt;/sub&gt;</td>
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<td>&lt;sub&gt;LI&lt;/sub&gt;</td>
<td>-1730.35166883+3.98786274037x+0.0434497938783x+1.5372979386551E+07x+8</td>
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<td>P&lt;sub&gt;G&lt;/sub&gt;</td>
<td>-979.125913861772532197657205x+0.272451672413182x+2.03154835449165137x+4.9138362874233E+06x+6.2991830272190669+5.9161910012195E-12x+6</td>
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<td>T&lt;sub&gt;G&lt;/sub&gt;</td>
<td>-0.0615781996424433+6.3411702333664E-05x-0.83758745336786E-10x+2.33522940139132x+3.0.0751156825213794E-20x+4.0.09679398337683E-25x+5</td>
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<tr>
<td>&lt;sub&gt;G&lt;/sub&gt;</td>
<td>0.00098895747080023x-3.0.00016883977386561E-35x+6</td>
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<tr>
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<td>= 19026.933863066606628646120388+1.66512291888183x+2.60804197003379E+03x+3.512162364404606x+4</td>
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<tr>
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<td>-31.3829.16302076645320.21135488171E-05x-2.35157281328118E-10x+2.7688.06653176474E+13x+3.1204.751510167466E-20x+4.91.7579498387737E-25x+5.2.684526531366E-30x+6</td>
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<tr>
<td>C&lt;sub&gt;G&lt;/sub&gt;</td>
<td>= 1616.92476399771.14.197196603333x+0.094823265820887x+2.83469111787534E-04x+3.3.947235963062E+07x+4</td>
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<tr>
<td>C&lt;sub&gt;G&lt;/sub&gt;</td>
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<tr>
<td>S&lt;sub&gt;L&lt;/sub&gt;</td>
<td>= -814.64013607473x+1.3.172090711942x+0.0389966697993x+5x+2.64657841214582E-09x+3.4.15124024767169E+08x+4</td>
</tr>
<tr>
<td>S&lt;sub&gt;G&lt;/sub&gt;</td>
<td>= -264.82877773723.22.342502344869x+0.1468769432078x+2.3012027569998E+04x+3.2.3102046632062x+4</td>
</tr>
<tr>
<td>N&lt;sub&gt;A&lt;/sub&gt;</td>
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<tr>
<td>T&lt;sub&gt;L&lt;/sub&gt;</td>
<td>= -0.0187764332574094x-0.000242452467741293x+1.2172917873941E+06x+2.76466532686064x+3.2.3.728461540124E+12x+5</td>
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<tr>
<td>T&lt;sub&gt;G&lt;/sub&gt;</td>
<td>= -0.000308011711237350.00000037216173789x+1.5.898200499966E-09x+3.2.5.00892533580253E-11x+3.1.8266119499533E+14x+6</td>
</tr>
<tr>
<td>G&lt;sub&gt;L&lt;/sub&gt;</td>
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<table>
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<td>= -943.91045618041x-2.5791.693167015x+246.14220213992x+2.1.04333433757241x+3.1.8350018831112E-03x+3.1.89780773969858E-07x+5</td>
</tr>
<tr>
<td>T&lt;sub&gt;LI&lt;/sub&gt;</td>
<td>= -20.9163042783x+0.00100998081834517x+6.0.453025739318E-09x+2.0.047519049684E-14x+3.6.0560504080295x+2.0.4x+4.3.112581503415x+26x+5.0.0328596764249E-32x+6</td>
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<tr>
<td>&lt;sub&gt;LI&lt;/sub&gt;</td>
<td>= 2532.205290448075x+6.9207148136099x+0.3.679529098039777x+2.0.000876939887451x+3.7.8516874520507E-07x+7</td>
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<tr>
<td>P&lt;sub&gt;G&lt;/sub&gt;</td>
<td>= 270.3860136815.46.69135276323x+1.0.56506127366161x+2.0.0227917288585387x+3.7.72089658538044E-06x+4.1.161352283498E+08x+5.7.01116181616068E-12x+6</td>
</tr>
<tr>
<td>T&lt;sub&gt;G&lt;/sub&gt;</td>
<td>= 0.0637555311257242x+8.5368337195266x+1.38.340004052582E-10x+2.0.80529409256416E-15x+3.2912519634734E-20x+4.0.06955552943963x+5x+3.0.081865687897018E-30x+6</td>
</tr>
<tr>
<td>&lt;sub&gt;G&lt;/sub&gt;</td>
<td>+0.00554971.364125736E-35x+7.0.000156562879554784E-40x+8</td>
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</table>
Table B.1: Correlated fluid properties

<table>
<thead>
<tr>
<th>Source</th>
<th>Range of Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>VDI-Wärmeatlas (1994); Dupont (1992); Lemmon et al. (1993); Maddox (1983); Institut International du Froid (1992);</td>
<td></td>
</tr>
<tr>
<td>①: 315 - 440 K; ②: 0.081 bar - 7.3 bar; ③: 185 - 305 K; ④: 0.075 - 11 bar; ⑤: 220 - 360 K; ⑥: 0.078 - 12 bar; ⑦: 273 - 370 K; ⑧: 203-313 K; ⑨: 0.08 - 10 bar; ⑩: 243 - 313 K; ⑪: 299 -313 K; ⑫: 190 - 320 K; ⑬: 0.050 - 11 bar; ⑭: 191 -323 K; ⑮: 251 - 323 K; ⑯: 225 - 355 K; ⑰: 0.08 - 9.7 bar; ⑱: 273 - 357 K</td>
<td></td>
</tr>
</tbody>
</table>
## Appendix C

### Test Fluids and Auxiliary Agents

<table>
<thead>
<tr>
<th>Substance</th>
<th>Purpose</th>
<th>Purity/Specifications</th>
<th>Deliverer/Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>butane</td>
<td>test fluid</td>
<td>&gt; 99.5 %</td>
<td>Garba Gas, CH</td>
</tr>
<tr>
<td>propane</td>
<td>test fluid</td>
<td>&gt; 99.0 %</td>
<td>Shell-Gas, CH</td>
</tr>
<tr>
<td>R-134a tetrafluoroethane</td>
<td>test fluid</td>
<td>&gt; 99.8 %</td>
<td>DuPont, CH</td>
</tr>
<tr>
<td>water</td>
<td>test fluid</td>
<td>distilled</td>
<td>-</td>
</tr>
<tr>
<td>water</td>
<td>buffer liquid for propane and butane; heat-transfer agent for propane, butane and R-134a; cleaning</td>
<td>demineralized</td>
<td>-</td>
</tr>
<tr>
<td>salt water</td>
<td>buffer liquid for propane</td>
<td>water + pure sodium chloride</td>
<td>-</td>
</tr>
<tr>
<td>ethyleneglycol-water mixture</td>
<td>heat-transfer agent for propane</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>silicone oil</td>
<td>heat-transfer agent for water</td>
<td>Min 200</td>
<td>Wacker-Chemie, D</td>
</tr>
<tr>
<td>nitrogen</td>
<td>pressure tests; pressurisation of test fluid; opening of rupture disc; condensation prevention</td>
<td>-</td>
<td>Garba Gas, CH</td>
</tr>
<tr>
<td>glass detergent</td>
<td>cleaning of glass surfaces</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>methanol</td>
<td>cleaning of glass surfaces</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>silicone grease</td>
<td>joint grease for sealings</td>
<td>Baysilone-Paste</td>
<td>Bayer, D</td>
</tr>
<tr>
<td>saccharose water</td>
<td>compensation of optical distortion</td>
<td>-</td>
<td>Merck, D</td>
</tr>
<tr>
<td>dimethylsulfoxide</td>
<td>compensation of optical distortion</td>
<td>-</td>
<td>Merck, D</td>
</tr>
<tr>
<td>petrol colouring agent</td>
<td>colouring of propane</td>
<td>Sudan red 412 liquid</td>
<td>BASF, D</td>
</tr>
<tr>
<td>R-113 trichlorotrifluoroethane</td>
<td>buffer liquid for R-134a</td>
<td>-</td>
<td>DuPont, CH</td>
</tr>
<tr>
<td>mineral oil</td>
<td>heat-transfer agent for water steam generator</td>
<td>BP-Transcal 160</td>
<td>BP Oil, CH</td>
</tr>
<tr>
<td>silicone oil</td>
<td>buffer liquid for water</td>
<td>Rhodorsil 508 V 70</td>
<td>Rhône-Poulenc, F</td>
</tr>
<tr>
<td>silicone rubber</td>
<td>adhesive / sealant rubber</td>
<td>Silastic 744 RTV</td>
<td>Dow Corning, B</td>
</tr>
</tbody>
</table>
Appendix D

Quantitative Experimental Results

Table D.1 contains the data of releases from pipes used for analysis in this work. The non-listed runs were not used for quantitative analysis mainly because of parasitic bubble growth in the superheated liquid or because they were pressure tests conducted with nitrogen.

Table D.1: Quantitative results of pipe releases

<table>
<thead>
<tr>
<th>Run</th>
<th>Fluid</th>
<th>Pipe Ø [mm]</th>
<th>ΔT [K]</th>
<th>u₀ [m/s]</th>
<th>p₁ [bar]</th>
<th>uTF [m/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
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<td>48.5</td>
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<td>48.4</td>
<td>0.570</td>
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<td>44.4</td>
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<td>14</td>
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<td>47.3</td>
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<td>16</td>
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<td>Funnel</td>
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<td>Funnel</td>
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<td>0.777</td>
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<td>Funnel</td>
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<td>1.035</td>
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<td>1.153</td>
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<td>Run</td>
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<td>Pipe Ø [mm]</td>
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<td>u_{fr} [m/s]</td>
<td>P_1 [bar]</td>
<td>u_{TPF} [m/s]</td>
</tr>
<tr>
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Appendix E
Real and Nominal Superheat in Liquid

In Fig. 4.22 the measured boiling front velocities are plotted versus the nominal superheat $\Delta T_{\text{nom}}$. In Figs. E.1 and E.2 the same results are plotted versus the real superheat $\Delta T_{\text{real}}$. For clarity, the results for water are shown in the additional expanded

Fig. E.1: Plots of the measured front velocities versus the nominal and the real superheat of butane, propane and R-134a
Fig. E.2: Plots of the measured front velocities versus the nominal and the real superheat of water

view of Fig. E.2. The calculation of the real superheat for each experiment is based on the analysis of a control volume as illustrated in Fig. 5.1, that is the calculation of the pressure in the superheated liquid resulting from Eqs. (5.7) and (5.10). As data input, the nominal superheat $\Delta T_{\text{nom}}$, i.e. the initial superheat, and the boiling front velocity $u_{fr}$ were used.

Figures E.1 and E.2 show the attenuating effect of higher boiling front velocity $u_{fr}$ on superheat in the metastable liquid. In general, the real superheat $\Delta T_{\text{real}}$ is lower than the nominal superheat $\Delta T_{\text{nom}}$. This effect is illustrated in Fig. 5.7 as well, where the superheat was determined taking the correlated boiling front velocity from Fig. 4.22.

Data representation and analysis in this work are based on the nominal superheat rather than the real superheat. One practical reason for this treatment is that the real superheat in the metastable liquid is not known a priori but depends on the boiling front velocity. Therefore, any correlation for the front velocity based on the real superheat requires either additional information about the actual boiling front velocity or an iterative calculation procedure. While the nominal superheat allows immediate information about the initial properties of the fluid, such as enthalpy and density, information based on the real superheat requires a "back-calculation" in order to obtain the front conditions.

Another reason for using the nominal superheat is related to modelling. It could be argued that the real superheat is most adequate for calculating the heat transfer dominated phenomena. However, the real superheat only applies to the stagnant superheated liquid. As described in section 5.3.1, the major fraction of liquid passes around the leading vapor cavities and gets accelerated. Further downstream the dominant part of vaporisation occurs - limited by a maximum possible quality $x$. The
pressure in any fraction of superheated liquid being accelerated without loosing latent heat decreases and, correspondingly, the superheat increases. Thus, the heat transfer determining superheat is higher than that given by the real superheat and approaches the nominal superheat. Since the local pressures and flow structures are not known in detail it was found not reasonable to consider the real superheat instead of the nominal one in the analysis. Besides, the difference between nominal and real superheat was often small compared to other uncertainties for the order-of-magnitude calculations related to vaporization.
Appendix F:
Stationary Control Volume Analysis

In the following, a control volume analysis is carried out for a system with a fixed coordinate system and a moving boiling front. The coordinate system for the conservation equations of mass, momentum and energy is shown in Fig. F.1.

First, the conservation equations are integrated:

**Mass Conservation**

\[
\frac{\partial (\rho \cdot A)}{\partial t} + \frac{\partial (\rho \cdot u \cdot A)}{\partial z} = 0
\]

Integrating from \(z_1\) to \(z_2\):

\[
\int_{z_1}^{z_2} \frac{\partial (\rho \cdot A)}{\partial t} \, dz + \int_{z_1}^{z_2} \frac{\partial (\rho \cdot u \cdot A)}{\partial z} \, dz = 0
\]

Conservation of mass at the boiling front is obtained by performing this integration, considering that the limit of integration \(z^*\) is variable and that the front velocity is given as:

\[-u_f = \frac{\partial z^*}{\partial t}\]

Note that:

\(A_1 = A_2 = A\).
Appendix F

For stagnant liquid:
\[ u_i = 0 \]
Thus mass conservation at the boiling front reduces to:
\[ \rho_1 \cdot u_e = \rho_1 (u_2 + u_e) \]

**Momentum Conservation**

Neglecting frictional losses:
\[
\frac{\partial (\rho \cdot u \cdot A)}{\partial t} + \frac{\partial (p \cdot A + \rho \cdot u^2 \cdot A)}{\partial z} = 0
\]
Integrating from \( z_i \) to \( z_2 \):
\[
\int_{z_i}^{z_2} \frac{\partial (\rho_1 \cdot u_1 \cdot A_1)}{\partial t} dz + \int_{z_i}^{z_2} \frac{\partial (\rho_2 \cdot u_2 \cdot A_2)}{\partial t} dz + \int_{z_i}^{z_2} \frac{\partial (p \cdot A + \rho \cdot u^2 \cdot A)}{\partial z} dz
\]
\[
+ \int_{z_i}^{z_2} \frac{\partial (p \cdot A + \rho \cdot u^2 \cdot A)}{\partial z} dz = 0
\]
Integration, considering again the time dependent integration limits, yields the conservation of momentum across the boiling front:
\[ p_1 + \rho_1 \cdot u_1 (u_i + u_e) = p_2 + \rho_2 \cdot u_2 (u_e + u_z) \]
Since
\[ u_i = 0 \]
\[ p_1 = p_2 + \rho_2 (u_z^2 + u_2 \cdot u_e) \]

**Energy Conservation**

\[
\frac{\partial (\rho \cdot u^0 \cdot A)}{\partial t} + \frac{\partial (\rho \cdot h^0 \cdot u \cdot A)}{\partial z} = 0
\]
(u^0: total internal energy - not velocity)
Integrating from \( z_i \) to \( z_2 \):
\[
\int_{z_i}^{z_2} \frac{\partial (\rho_1 \cdot u^1 \cdot A_1)}{\partial t} dz + \int_{z_i}^{z_2} \frac{\partial (\rho_2 \cdot u^2 \cdot A_2)}{\partial t} dz + \int_{z_i}^{z_2} \frac{\partial (\rho \cdot h^0 \cdot u \cdot A)}{\partial z} dz
\]
\[
+ \int_{z_i}^{z_2} \frac{\partial (\rho \cdot h^0 \cdot u \cdot A)}{\partial z} dz = 0
\]
Similarly, the conservation of energy across the boiling front results in:

\[
\rho_1 \cdot h_1 (u_1 + u_b) - p_1 \cdot u_b + \frac{1}{2} \cdot \rho_1 \cdot u_1 \cdot u_b + \frac{1}{2} \cdot \rho_1 \cdot u_b^3 = \rho_2 \cdot h_2 (u_2 + u_b) - p_2 \cdot u_b + \frac{1}{2} \cdot \rho_2 \cdot u_2 \cdot u_b + \frac{1}{2} \cdot \rho_2 \cdot u_b^3
\]

Since \( u_1 = 0 \),

\[
\rho_1 \cdot h_1 \cdot u_b - p_1 \cdot u_b = \rho_2 \cdot h_2 (u_2 + u_b) - p_2 \cdot u_b + \frac{1}{2} \cdot \rho_2 \cdot u_2 \cdot u_b + \frac{1}{2} \cdot \rho_2 \cdot u_b^3
\]

The integration above results in the basic equations for the stationary control volume:

\[
\rho_1 \cdot u_b = \rho_2 (u_2 + u_b)
\]

\[
p_1 = p_2 + \rho_2 (u_2^2 + u_2 \cdot u_b)
\]

\[
\rho_1 \cdot h_1 \cdot u_b - p_1 \cdot u_b = \rho_2 \cdot h_2 (u_2 + u_b) - p_2 \cdot u_b + \frac{1}{2} \cdot \rho_2 \cdot u_2 \cdot u_b + \frac{1}{2} \cdot \rho_2 \cdot u_b^3
\]

where

\[
h_2 = (1 - x_1) \cdot h_{32} + x_2 \cdot h_{33}
\]

Assuming homogeneous flow:

\[
\frac{1}{\rho_2} = (1 - x_1) \cdot \frac{1}{\rho_{32}} + x_2 \cdot \frac{1}{\rho_{33}}
\]

Algebraic transformation leads to the following expression for the quality \( x_2 \):

\[
\left[ \frac{1}{2} \rho_1 \left( \frac{1}{\rho_{32}} - \frac{1}{\rho_{32}} \right)^3 \right] \cdot x^3
\]

\[
+ \left[ \frac{3}{2} \cdot \rho_1 \left( \frac{1}{\rho_{32}} - \frac{1}{\rho_{32}} \right)^2 + \rho_1 \cdot \frac{1}{u_b} (h_{32} - h_{32}) \left( \frac{1}{\rho_{32}} - \frac{1}{\rho_{32}} \right) + \frac{3}{2} \cdot \rho_1 \left( \frac{1}{\rho_{32}} - \frac{1}{\rho_{32}} \right)^2 \left( \frac{p_{32}}{p_{32}} - 1 \right) \right] \cdot x^2
\]

\[
+ \left[ -\rho_1 \cdot h \cdot \frac{1}{u_b} \left( \frac{1}{\rho_{32}} - \frac{1}{\rho_{32}} \right) + 3 \cdot \rho_1 \left( \frac{p_{32}}{p_{32}} - 1 \right) \left( \frac{1}{\rho_{32}} - \frac{1}{\rho_{32}} \right) + \rho_1 \left( \frac{1}{\rho_{32}} - \frac{1}{\rho_{32}} \right) \right] \cdot x
\]
This third order equation can be solved by the Cardanic formula where one of the three real solutions gives the quality $x$. Similar to Eqs. (5.7) and (5.8), the two-phase velocity $u_{\text{TPF}}$ and the pressure drop $\Delta p$ or the base pressure $p_1$ can be calculated. In Table F.1 the results by considering a fixed or a moving control volume can be compared.

### Table F.1: Comparison of sample calculations for fixed and moving control volume for propane (boiling front velocity $u_b$ according to correlation of Fig. 4.22)

<table>
<thead>
<tr>
<th>degree of superheat $\Delta T_{\text{nom}}$ [K]</th>
<th>30</th>
<th>50</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>boiling front velocity $u_b$ [m/s]</td>
<td>0.094</td>
<td>0.678</td>
<td>1.262</td>
</tr>
<tr>
<td>quality $x$ [-] moving control volume</td>
<td>0.164631</td>
<td>0.280263</td>
<td>0.395921</td>
</tr>
<tr>
<td>quality $x$ [-] stationary control volume</td>
<td>0.164631</td>
<td>0.280268</td>
<td>0.395948</td>
</tr>
<tr>
<td>two-phase flow velocity $u_{\text{TPF}}$ [m/s] moving control volume</td>
<td>3.552866</td>
<td>41.0417</td>
<td>101.1783</td>
</tr>
<tr>
<td>two-phase flow velocity $u_{\text{TPF}}$ [m/s] stationary control volume</td>
<td>3.453958</td>
<td>40.31133</td>
<td>99.80062</td>
</tr>
<tr>
<td>$u_{\text{TPF}}$ difference [m/s]</td>
<td>0.098908</td>
<td>0.730372</td>
<td>1.377638</td>
</tr>
<tr>
<td>base pressure $p_1$ [N/m$^2$] moving control volume</td>
<td>100177.4</td>
<td>114191.9</td>
<td>161570.9</td>
</tr>
<tr>
<td>base pressure $p_1$ [N/m$^2$] stationary control volume</td>
<td>100176.9</td>
<td>114154.8</td>
<td>161424.2</td>
</tr>
</tbody>
</table>

As can be seen from the Table F.1, the differences are negligible and probably due to computational errors. Because of different assumptions, the two-phase velocity $u_{\text{TPF}}$ leaving a moving control volume is increased approximately by the boiling front velocity $u_b$ in comparison to the stationary control volume. There is no substantial difference for the base pressure $p_1$ calculated by either method.
Appendix G: Moving Control Volume Analysis with Velocity Ratio of Vapor and Liquid

The mass, momentum and energy balances for a control volume moving with the boiling front lead to the following set of equations:

\[ \rho_1 u_i = \rho_{a2} u_{a2} \varepsilon + \rho_{l2} u_{l2} (1 - \varepsilon) \]
\[ p_1 + \rho_1 u_i^2 = p_2 + \rho_{a2} u_{a2}^2 \varepsilon + \rho_{l2} u_{l2}^2 (1 - \varepsilon) \]
\[ h_i + \frac{1}{2} u_i^2 = (h_{a2} + \frac{1}{2} u_{a2}^2) x + (h_{l2} + \frac{1}{2} u_{l2}^2) (1 - x) \]

Substituting

\[ \varepsilon = \frac{1}{1 + S \frac{\rho_{a2} (1 - x)}{\rho_{l2}}} \]
\[ S = \frac{u_{a2}}{u_{l2}} \]
\[ \Delta p = p_1 - p_2 \]
\[ u_r = u_i \]
\[ h_i = h_{l1} \]

and assuming that

\[ \frac{\rho_{l1}}{\rho_{l2}} = 1 \]
\[ \rho_1 = \rho_{l1} = \rho_{l2} \]

results in a third order equation for the quality \( x \):

\[ x = f (u_r, h_{l1}, h_{l2}, h_{a2}, \rho_{l1}, \rho_{l2}, \rho_{a2}, S) \]

This equation can be solved by the Cardanic formula resulting for \( S > 1 \) in one and for \( S \leq 1 \) in three real solutions. With the known quality \( x \) other quantities such as \( u_{l2} \) and \( u_{a2} \) can be calculated as plotted in Fig. 5.11. Fig. G.1 shows the effect of an increasing velocity ratio \( S \) on the acceleration induced pressure drop \( \Delta p \). It can be seen that the
Assumption of homogeneous flow maximises the acceleration induced pressure. In turn, the real superheat $\Delta T_{\text{real}}$ increases in case of $S > 1$ approaching the nominal superheat $\Delta T_{\text{nom}}$. 

**Fig. G.1:** Influence of velocity ratio $S$ on pressure in metastable liquid for propane
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