Thermodynamic and gas dynamic aspects of a BLEVE

by

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Contents

NOMENCLATURE

Upper-case Roman

A	Surface area
$\tilde{A}_i$	Interfacial area density, $[m^2/m^3]$
Ca	Capilary number
D	Thermal diffusivity
Gb	Gibbs number
J	Nucleation rate
Ja	Jacob number
J_e	Evaporation rate
N	Number of molecules per unit volume
Nu	Nusselt number
N_A	Avogadro constant
Pr	Prandtl number
R	Bubble radius
$\dot{R}$	Bubble radius growth rate
$\mathbb{R}$	Universal gas constant
$\bar{R}$	Specific gas constant, $\mathbb{R}/m_M$
Re	Reynolds number
T	Absolute temperature, [Kelvin]
V	Volume, $[m^3]$
W	Work
W_{min}	Minimum work of formation of a bubble
W^*_{min}	Minimum work of formation of a critical bubble
Z	The elevation
$\mathbb{Z}$	Compressibility

Lower-case Roman

c	Speed of sound
c_p	Constant pressure specific heat
c_v	Constant volume specific heat

f	Friction force
g	The gravitational acceleration
h	Enthalpy
$\hat{h}$	Heat transfer coefficient
h_{LG}	Latent heat of vaporization
k	Thermal conductivity
k_B	Boltzmann constant
m_M	Molar mass
m_m	Molecular mass
n	Number density
p	Pressure
q	Heat
$\dot{q}$	Heat transfer rate
$\dot{q}''$	Heat transer rate per square meter
r	radial distance
r^*	Critical bubble radius
s	Entropy
t	Time
u	Velocity
v	Specific volume

Upper-case Greek

Ω	Solid angle of the laser lens
Γ	Mass transfer rate
Γ''	mass transfer rate per square meter

Lower-case Greek

α_c	Condensation coefficient
α_l	Liquid volume fraction
α_v	Void fraction, vapor volume fraction
β	Physical variable in [23]
γ	Specific heat ratio, isentropic component, c_p/c_v
θ	Fraction factor

λ	Physical variable in [23]
μ	Chemical potential
ν	Kinetic viscosity
ξ	Contact angle at the bubble surface
ρ	Density
σ	Surface tension
τ	Time variable in [23]
ϕ	Heterogeneous nucleation factor
φ	Liquid-to-vapour volume expansion factor
χ	Flash fraction
ψ	Perimeter

Superscripts

$*$	Parameters for critial bubble
$1ph$	One-phase
$2ph$	Two-phase

Subscripts

in general

0	Initial state
B	Boiling
b	Bubble
bb	Bubble boundary
c	Critical
h	Isenthalpy
i	Interface
L	left
l	Liquid
m	Mixture
NU	Nucleation
R	Right
SL	Superheat Limit
s	Isentropy
v	Vapor
w	Wall
∞	Infinity or ambient
crk	Crack
frt	Boiling front
ini	Initial
max	Maximum
min	Minimum
sat	Saturation
thr	Threshold
tpl	Thermal protection layer

Abbreviations

BCE	The energy per unit volume transferred to the vapor when the liquid flashes [12]
BLCBE	Boiling Liquid Compressed Bubble Explosion
BLEVE	Boiling Liqid Expanding Vapor Explosion
EOS	Equation of State
MI	Mechanical Impact
EF	External Fire
PLG	Pressure Liquefied Gas
PRV	Pressure Relief Valve
TLOC	Total Loss of Confinement

Chapter 1

Introduction

This first chapter will give an introduction to what is a BLEVE, Boiling Liquid Expanding Vapor Explosion, and its hazards particularly in relation to tunnel safety. It will be shown that several definitions of a BLEVE can be given, depending on the aspect put in focus. In particular distinction can be made between two groups of references, respectively giving an engineering definition and a physical definition. As a result of our literature survey, our own definition of BLEVE will be presented trying to bridge the gap between these two groups of definitions. In the following chapters, we stick to that definition unless specified otherwise.

First of all, we would like to consider some basic concepts, i.e. superheated liquid, explosive boiling and bubble nucleations, by an easy example.

It is well known that when we heat the water in a tea kettle up to the temperature of 100 °C at the atmospheric pressure, the water will start to boil or vaporize. In this case, invisible active nuclei formed on the inner surface of the kettle or at any impurities in the water will grow to be a visible bubble which will detach from the wall and move upwards due to buoyancy. Such a type of bubble nucleation is called *heterogeneous nucleation* since the bubble nucleation only occurs at the locations where there is a boundary between two different phases.

However if we put the water into a very smooth glass and heat it in the microoven, the boiling will not occur even the temperature already exceeds the normal boiling point at the atmospheric pressure. At this moment, the water is said to be *superheated* and if we keep heating the water, a rapid 'explosive-like' boiling, termed *explosive boiling*, will suddenly occur and may cause serious damage to the microoven. In this explosive boiling, the active nuclei are evenly formed throughout the liquid, therefore it is called *homogeneous nucleation.*

Superheating sometimes is referred to as boiling retardation, or boiling delay. It refers to the phenomenon in which a liquid is heated to a temperature higher than its boiling point, without actually boiling. A superheated state can also be reached in another way than by heating, namely by depressurization to a pressure lower than the saturation pressure at the prevailing temperature.

The references in this chapter include: [3], [4], [5], [7], [14], [16], [19], [21], [24], [25], [26], [31], [33], [35], [36].

1.1 Superheated State and Bubble Nucleation

1.1.1 Superheated liquid and superheat limit

In physics, a liquid is said to be *superheated* when its temperature exceeds its saturation temperature of its pressure or its pressure decreases below its saturation pressure of its temperature while the liquid is still not boiling.

$$T_l > T_{sat}(P_l) \qquad \text{or} \qquad P_l < P_{sat}(T_l)$$

In this report, the term 'superheating' refers to the fact of reaching a superheated state, by either of the two methods, rising the temperature or rapid lowering of the pressure and the reader should bear in mind that superheating does not always involves adding heat.

The superheated state is thermodynamically metastable. The superheated liquid will start to vaporize after a time which depends on the nucleation rate. With a small change in the liquid's temperature, the time frame can vary from millions of years to several nanoseconds. See below table in page 112 of [14].

Temperature T (K)	Nucleation rate J $[1/(cm^3 s)]$	Waiting time
560	2.7×10^{-76}	12×10^{68} yr
570	8.5×10^{-20}	3.7×10^{11} yr
575	5.7×10^{-3}	1.8×10^{2} s
580	4.3×10^{9}	2.3×10^{-10} s
590	4.3×10^{23}	2.3×10^{-24} s

Table 1.1: Limit of superheat and nucleation rate in water at atmospheric pressure

Correspondingly there exists a limiting temperature beyond which no superheated liquid can exist as well as a limiting pressure below which no superheated liquid can survive. This limit is the *superheat limit.* Thermodynamic stability analysis indicates that, for a pure liquid, the superheat-limit results when

$$\left(\frac{\partial p}{\partial v}\right)_T = 0 \tag{1.1}$$

In this report, we will use T_{SL} and P_{SL} to represent the superheat limit temperature and the corresponding superheat limit pressure, respectively. Not only the nucleation rate, but also the bubble growth rate depend on how far away the system is from the superheat limit.

Therefore when a liquid is highly superheated, quite differently from our previous knowledge of the normal boiling, the vaporization will commence and proceed in an much shorter time frame. The output is often an 'explosive' boiling which means the rapid volume expansion of the liquid-to-vapor phase transition can be hazardous.

The process of rapid phase transition from highly superheated liquid to vapor is called *explosive boiling* [31]. Explosive boiling occurs when the liquid is suddenly and drastically heated by immersion in a hot medium, or by laser heating, or by passage through a shock wave, or by sudden depressurization as in liquid ejected in space.

So the next question is, what makes the boiling so explosive?

1.1.2 Bubble nucleation

The answer to the question in the previous section is complex, however *bubble nucleation* is definitely the first aspect that should be qualitatively explained.

Before that, the general progress of bubble growth will be introduced.

Everything has its origin, so does a bubble. Consider the appearance of a small sphere of gas (nucleus) in a liquid. To vaporize the liquid and expand in the liquid, the nucleus needs a minimum energy to sustain the growth of the bubble or the two-phase interface. This energy is termed *the minimum work of formation of a bubble* W_{min} and it depends on fluid properties and local pressures as given by Blander and Katz in [4].

$$W_{min} = \sigma A - (p_v - p_l)V_b + i(\mu_v - \mu_l) \tag{1.2}$$

in which i is the number of molecules.

As shown in Fig.(1.1) from [7], W^*_{min}, the maximum of W_{min}, works as the nucleation barrier and corresponds to a critical bubble radius r^*. For nuclei smaller than r^*, more energy is needed for growing and for nuclei larger than r^*, less energy is required.

Heterogeneous nucleation and homogeneous nucleation are two different ways of bubble nuclei generation. Heterogeneous nucleation occurs at the interface of two phases. At this interface, the nucleation can benefit from

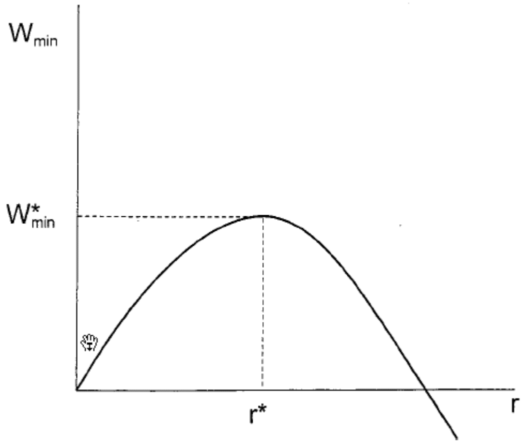

Figure 1.1: The variation of W_{min}, the Gibbs formation energy of a cluster of molecules form a bubble nucleus, as function of the radius of such clusters and the nucleation barrier W^*_{min}

- sufficient external energy supplied to the liquid through the interface, i.e. bubble generation at the heated wall;
- the reduced nucleation barrier originating from any of the following:
  - reduced bubble surface area: the bubble formed at the irregularities and cavities on the solid wall forms only part of a sphere;
  - surface tension reduction: surface tension is a function of temperature which decreases as the temperature increases;
  - reduction of required minimal volume: bubble formed around gaseous/solid impurities.

Therefore heterogeneous nucleation is highly depending on the presence of a heterogeneous interface and nucleation site population on the heterogeneous interface including

- in case of solid-liquid interface: extent of wall wetting, concentration of solid impurities in the liquid...
- in case of gas-liquid interface: area of interface, amount of gas dissolved in liquid ...
- liquid-liquid interface: properties of interface between immiscible liquids...

Homogeneous nucleation in a narrow sense refers to the bubble nucleation due to thermal motion of the liquid molecules themselves, which can occur throughout the liquid. Homogeneous nucleation in broad sense refers to any nucleation which can homogeneously occur throughout the liquid. Some scientists did argue that heterogeneous nucleation could also occur on very small, sub-micron sized contaminant particles in the liquid; experimentally this would be hard to distinguish from homogeneous nucleation (see Section 1.6 in [5]). At present in this project, we use the concept of homogeneous nucleation in narrow sense.

The major difference between homogeneous nucleation and heterogeneous nucleation is the bubble/nuclei number density. It has been widely accepted that homogeneous nucleation could generate bubble number density of 10^{10} - $10^{12}\, m^{-3}s^{-1}$ while in general heterogeneous nucleation has a much lower bubble number density.

Back to the energy discussion. If the conditions are favourable for formation of a huge number of nuclei and sufficiently energy is available for rapid further growth of nuclei to bubbles the vaporization process will be explosive and hazardous. Huge nucleus number density and high energy supply will result in *explosive boiling*. So the violence of boiling/vaporisation depends on

1. Bubble nucleation rate
2. Energy transfer to the nuclei

Interaction between neighbouring bubbles, eventually will also have to be taken into account.

1.2 BLEVE as a hazard

After having introduced some basic physical concepts, we now move on to the engineering field and see what superheated liquid, homogeneous nucleation and explosive boiling can do in real engineering problems.

1.2.1 BLEVE

Let's start with one definition of BLEVE.

BLEVE, *Boiling Liquid Expanding Vapor Explosion*, is an explosion as the consequence of the catastrophic rupture of a pressure vessel containing a liquefied gas. The catastrophic rupture of the vessel will normally directly expose the liquefied gas to the ambient. The sudden depressurization will lead to an explosive vaporization inside the bulk of the liquid. Blast wave and even shock wave can be generated to have destructive impact on the surroundings and human bodies as well as the projectiles. If the liquid is flammable, jet fire, pool fire and fireball will cause fire hazard.

The vessel rupture can be due to mechanical impact, exposure to an external fire, fatigue of the vessel, corrosion and/or a bad construction or malfunctioning component. The direct hazards from a BLEVE normally include blast wave, projectiles, fire engulfment and thermal radiation and/or exposure and health problems if the content is toxic.

1.2.2 Tunnel safety

This study is made in the context of a set of studies on the safety of road constructions in the Netherlands, in particular tunnels. The increase in the number of tunnels in the Netherlands, and the increasing intensity of the traffic through these tunnels, requires good insight in the risks associated with this traffic. An important safety aspect is the risk for the occurrence of a gas explosion in case of an accidental release of a flammable material, or a blast wave due to the failure of the pressure vessel of a truck carrying a liquid at high pressure (BLEVE).

For either case, the hazard depends on the rate at which the potential energy stored inside the tank is released in the limited volume of space in the tunnel. An intense blast wave or shock wave can result and impose a high overpressure on the tunnel structure (as well as on the vehicles and human bodies present in the tunnel. Therefore it is important to be able to predict the strength of this blast wave as function of all relevant aspects (e.g. transported liquid, truck and tunnel type, incident scenario, etc.)

1.2.3 Causes for BLEVE

The statistics on the notable BLEVE incidents during the period of 1926 $\sim$ 1986 [24] can be quite helpful for us to understand the possible causes for a BLEVE incident. Although it can be expected that the percentages have changed due to intensification of traffic and or improved safety regulations since 1986.

Causes	Number of incidents	Percentage
Exposure to fire	17	34.69%
Mechanical damage/failure	12	24.49%
Overfilling	10	20.41%
Runaway reaction	6	12.24%
Overheating	3	6.12%
Vapor-space explosion	1	2.04%

More than 50% of the BLEVE incidents were caused by external heating including exposure to fire, runaway reaction and overheating. More than 20% of the incidents were caused by mechanical damage/failure.

In all of the over-filling accidents, absence of an overpressure-relief device was a major contributing factor. With improving standards of overpressure protection, the frequency of BLEVEs caused by overfilling could be expected to decline significantly. Moreover it is remarkable that the accidents caused by the over-filling often lead to high fatalities.

Incidents caused by vapor-space explosion and mechanical failure are the least frequent and their descriptions also indicated that they were very random and therefore hard to predict.

It is clear that **external heating** (EF) and **mechanical damage** (MI) are the most common causes for BLEVE incidents. In this project, these two accidental modes will receive most attention.

1.3 What are the key elements of a BLEVE ?

The term 'BLEVE' was first introduced by J.B. Smith, W.S. Marsh and W.L. Walls of factory Mutual Research Corporation in 1957. When it was invented it was used to describe a phenomenon rather than to give a clear definition. The five words stand as a block, but the relation of the 'explosion' to the 'expanding vapor' of the 'boiling liquid' is not obvious. And no further specification is given of the type of boiling. This has caused discrepancy in interpretation of the acronym among scientists and the engineers. The discrepancy mainly refers to two points

- whether the explosion is limited to physical explosion or it can include chemical reaction/explosion;
- whether the superheat limit must be reached or not in triggering a BLEVE.

It will shown below that the complicated scenarios possibly involved in BLEVEs bring difficulty in defining a BLEVE.

1.3.1 BLEVE: physical or chemical

Many engineering references consider chemical explosion an essential part of a BLEVE. This is reasonable because most PLG, *Pressure-Liquefied-Gas*, stored in commercial tanks is flammable and external fire is a main reason for tank weakening and total disintegration. Under such circumstances, chemical reaction of the released liquid with the surrounding air, leading to explosion is almost certain to occur. On the other hand, chemical reaction is not a must for a BLEVE to occur even though it can make things much worse. The explosion can be a completely physical one caused by the rapid volume expansion due to rapid vaporization. So there are two possibilities to logically interpret 'Boiling Liquid Expanding Vapor Explosion':

- a physical explosion completely due to liquid boiling and vapor expansion;
- a chemical explosion of flammable liquid which has been intensified by liquid boiling and vapor expansion.

In the INERIS report 2002 [16], BLEVE is qualified as a physical explosion in the sense that it corresponds to a phase change only, in contrast with a chemical explosion corresponding to an oxidation reaction.

But in the engineering literature, especially from the Process Industry, often a tank containing flammable PLG engulfed in an external fire is considered and the standard scenario of a BLEVE also includes a chemical explosion. It goes as follows [19]: As the fire heats the tank, the fluid inside rises in temperature and pressure, roughly following the saturation curve, although, temperature stratification may occur in the liquid and vapor. Normally PRV, *Pressure Relief Valve*, action is introduced when the set pressure is reached. The fluid is vented and may be ignited to form a torch if flammable. The pressure inside the tank is controlled around the set pressure of the PRV if it is still functioning correctly. If for some reason the tank tears open, the fluid is exposed to atmospheric pressure. Therefore the liquid becomes superheated and starts to boil rapidly and violently resulting a pressure rise inside the tank, which may speed up the rupture development until a catastrophic failure of the tank and chemical explosion of the released fuel with the surrounding air. The chemical potential is in general a more powerful explosion than the pure physical explosion, caused by the rapid boiling of the superheated liquid and the rapid vapor expansion.

The standard scenario of the Process Industry literature may not be the most relevant for studies on Tunnel Safety. Mechanical impact, not external fire, can be expected to be the main cause of the failure of the pressure vessel. And the mixing with the surroundings can be completely different in a tunnel geometry. Nevertheless, if external fire occurs, depending on its relative position to the pressure vessel, it can serve as an ignition point to the flammable fluid, a heat source to PLG and/or a weakening factor to the strength of the pressure vessel.

1.3.2 BLEVE: hot and cold

If we now focus on aspects of the rapid vaporisation of a BLEVE, it appears that another discussion point remains on what is essential for a BLEVE. Is it required that the superheat limit is reached or not ? In other words: is homogeneous nucleation essential or not ? Some authors think it is because they believe that it explains why the vaporization is so violent and results in an explosion. The theory presented by R.C. Reid [25] [26] considers that a liquid at a temperature above the limit superheat temperature when it is depressurized to atmospheric pressure gives rise to a BLEVE. This definition has been widely accepted. It explains why both flammable and non-flammable liquids can show a large energy release in the explosion.

Other references do not support the idea that homogeneous nucleation is required. They point out that under certain circumstances, heterogeneous nucleation is hard to distinguish from homogeneous nucleation as discussed in Sec.(1.1.2). (Also, for authors who see the BLEVE in the first place as a chemical explosion, it is not necessary to require that the liquid is at the superheat limit temperature.)

The proposal that a homogeneous nucleation is not needed, in contrast with the theory of Reid, was first made in 1993 [3]. A new concept of Cold BLEVE was proposed. In the experiments reported, 11 automotive propane tanks, either 0.30 or 0.38 m^3 in capacity, were subjected to pool and/or torch fire impingement. Of the 11 tanks tested, 3 were regarded to be true BLEVEs by the experimentalists, resulting in completely opened tanks and completely consumed propane in less than 4 seconds. Other cases only showed a two-phase jetting after tank damage. Among the 3 'true' BLEVEs, two very different kinds of phenomena were observed. One that occurred with a weakened tank at a relatively low temperature is called weak or **Cold BLEVE** and the other two that occurred when the liquid temperature was above the superheat limit* for propane at atmospheric pressure are called strong or **Hot BLEVE**.

Spherical fireballs were observed both in Cold BLEVE and Hot BLEVE, however the altitude of the fireball in Hot BLEVE reached approx. 55 meter within 1.5 second after the total disintegration of the tank, much higher than 20 meter of Cold BLEVE. A ground level cloud fire was observed in Cold BLEVE, while not in Hot BLEVE.

It should be observed that although this representative paper concerns the nature of the vaporisation process it belongs to the part of the literature where the chemical explosion and fireball are considered essential aspects of a BLEVE.

It should be remarked that if local heating by fire is involved, it is hard to determine whether the superheat limit is reached for the bulk liquid or only locally, due to the strong nonlinear dependence of vaporisation properties on distance to the superheat limit. The average temperature of the liquid may not be representative.

1.3.3 BLCBE: a new BLEVE

In 1993, Venart *et al.* proposed **BLCBE**, *Boiling Liquid Compressed Bubble Explosion*, as a new type of BLEVE for explaining some of the more severe BLEVE type industrial incidents [35].

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*The temperatures were empirically estimated, not measured.

A BLCBE is described as a series of events including [36]:

1. partial vessel failure i.e. a crack;
2. rapid depressurization of an already nucleated and now superheated liquid;
3. rapid bubble growth and then constraint of the two-phase system (by either physical, acoustic, or inertial means);
4. repressurization back to nearly the original containment pressure;
5. adaptive and coherent bubble collapse resulting in the formation of power amplified liquid shock waves;
6. wall-pressure wave interaction resulting in total and rapid vessel destruction;
7. mechanical distribution of the liquid contents as an aerosol;
8. heat transfer and total evaporation (and if flammable auto-ignition) of the aerosol.

The key feature of BLCBE is the process of repressurization which compresses the growing bubbles. In this way energy is accumulated inside the bubbles and released simultaneously when the tank totally disintegrates.

This is another way to demonstrate the complex in the possible scenario involved in a BLEVE which may result in explosive hazards, besides R.C. Reid's superheat limit theory.

1.3.4 Conclusion: criteria for defining BLEVE

We need to distinguish chemical BLEVE from physical BLEVE, because these two explosions are different both in their nature and in their consequences. The driving force for physical BLEVE is vaporization due to non-equilibrium between the liquid and gaseous phases. The driving force for chemical BLEVE is combustion, chemical reaction due to non-equilibrium in vapour/gas space. The heat of vaporisation and heat of combustion (with air) are both liquid properties, but the heat of combustion is in general several orders larger than the heat of vaporization. We take the heat of combustion[†] and heat of vaporization[‡] of propane and n-butane for comparison
therefore if the volume expansion is favoured by a good mixing between the superheated liquid and the air (vaporization extracts energy from the air) in both physical BLEVE and chemical BLEVE, the volume expansion in chemical BLEVE is further favoured by the released heat of combustion in a much powerful manner.

[†] data from Wiki, *http : //en.wikipedia.org/wiki/Heat_of_combustion*

[‡] data from Air Liquide, *http : //encyclopedia.airliquide.com*

	Heat of combustion (MJ/kg)	Heat of vaporization (kJ/kg), 1atm
Propane	49.9	425.31
n-Butane	49.2	385.6

Table 1.2: Heat of combustion and heat of vaporization for propane and n-butane

The concepts of BLCBE, has been little explored after it has been proposed. The proposed definition, of scenario, for a BLCBE makes it a more complex event than a BLEVE with a one-way vaporization process. An interesting aspect of the BLCBE hypothesis is that it provides a mechanism for generating a violent explosion even when the superheat limit is not reached.

For a non-flammable liquid only the physical BLEVE is possible. For the flammable liquid, we need to investigate chemical and physical BLEVE together. But in this project we focus on the first part, the physical explosion.

We conclude our criteria for defining BLEVE as below:

- physical BLEVE is of interest in itself and also needs to be better understood to make progress with understanding of chemical BLEVE;

- A chemical BLEVE could be violent also when the superheat limit is not reached, because of the violence of the chemical explosion being dominant. Reaching the superheat limit should not be imposed as a strict requirement. A physical BLEVE can be violent without the superheat limit being reached, only via special scenario's as e.g. the BLCBE. The difference between cold BLEVE and hot BLEVE seems relevant; a requirement superheat limit being reached should not be made.

1.4 BLEVE stage and BLEVE event

Various definitions have been given to BLEVE due to the complicated scenarios involved in BLEVE incidents.

Most definitions coming from Process Industry or Safety Engineering often involve external fire, chemical explosion and fireball. However others think this entire sequence of events is wrongly designated as a BLEVE [33], therefore they reserved the term BLEVE to be the explosive rupture of a pressure vessel, the flash evaporation of liquefied gas and the rapid expansion of its vapor.

1.4.1 Definitions

In our study, we clearly distinguish two concepts, **BLEVE** and **BLEVE event**, as Pinhasi *et al.* did in [21].

BLEVE event is defined to be an event in which a tank containing PLG is suffered mechanical impact and/or external fire and later totally disintegrated.

BLEVE is just the physical expansion (explosion) stage of a BLEVE event.

There are only two requirements for a BLEVE event, as the description of 'an exploding pressure vessel of liquefied gas' in [33], (i) PLG in a certain confinement; (ii) Sudden Total Loss of the Confinement (**TLOC**). Therefore, a BLEVE event can involve chemical explosion and fireball as well, but BLEVE must not.

1.4.2 Three stages of a BLEVE event

A BLEVE event can be divided into three stages with two time frames: (i) the moment of TLOC; (ii) the moment of chemical reaction commences.

Pre-BLEVE stage The process from the initiation of the accident to the moment of TLOC;

BLEVE stage The process from the moment of TLOC to any chemical reaction or chemical explosion commences;

Post-BLEVE stage The process involving chemical reaction or chemical explosion.

By strictly distinguishing BLEVE from BLEVE event, we can successfully explain two so-called 'new BLEVE', Cold BLEVE and BLCBE. Cold BLEVE is a BLEVE event in which the physical expansion in BLEVE stage only employs moderate or weak reinforcement to the chemical explosion in post-BLEVE stage. BLCBE is a BLEVE event with an energy-accumulated pre-BLEVE stage which result in a more violent physical explosion in BLEVE stage.

1.4.3 Features of three stages

In general, the main feature of pre-BLEVE stage is variety. The features of BLEVE stage are rapidness. The main feature of post-BLEVE stage is chemical reaction.

Pre-BLEVE stage in MI includes

- Fluid-structure coupling, crack development coupled with the thermodynamic properties of PLG
- Single or two-phase PLG release through the crack
- Vaporization of the released liquid and expansion of the vapor outside the vessel

Pre-BLEVE stage in EF includes:

- Thermal response of the vessel wall and PLG to the external fire
- Crack initiation and its development
- Combustion of the released vapor/liquid in the formation of pool fire or torch

BLEVE stage includes:

- Rapid exposure of the pressurized vapor and liquid to the ambient
- Projection of the vapor and liquid due to pressure difference
- Rapid vaporization and expansion of PLG
- Gasdynamics of the surrounding air

Post-BLEVE stage, if there exists, includes:

- Chemical reaction/explosion
- Deflagration-to-Detonation Transition along the tunnel

1.5 Summary

In this chapter, the description of BLEVE and its hazards to tunnel safety have been generally discussed. The difficulty lies in how to define a BLEVE which can possibly occur in completely different scenarios and how to bridge the gaps among current existing definitions.

BLEVE and BLEVE event, two different concepts have been proposed. The purpose is to define the very basic and essential features of a BLEVE and exclude all the other unnecessary ones although some are high correlated. We expect, by doing that, the definition of BLEVE would become unique and clear at least within the project of Tunnel Safety.

The BLEVE event is further divided into three stages, pre-BLEVE, BLEVE and post-BLEVE, by two time frames. It will be shown in the following chapters that the theory, the mechanism, the governing equations and the numerical models for different stages are greatly different. Different stages have different problems to solve.

The statistics on BLEVE accidents indicated that external heating and mechanical damage are the main causes for BLEVE accidents. Two specific accidental mode, external fire and mechanical impact, will be mainly focused on in the project of Tunnel Safety.

Chapter 2

Theories of Bubble vaporization

In this chapter, we will give an overview of the theoretical approaches of bubble vaporization. It will be shown that as the liquid superheat increases, the physics for the bubble nucleation and vaporization will change. The classical theories can not properly describe the bubble nucleation and growth at high superheats, especially in the initial phase. Efforts has been made either for upgrading the classical theories or for developing new methods for bubble vaporization research.

The references in this chapter include: [5], [7], [18], [23], [30] and [31].

2.1 Classical theory for spherical bubble dynamics

Rayleigh-Plesset equation can best describe the behavior of a single bubble in an infinite domain of liquid at rest far from the bubble and with uniform temperature far from the bubble. See Chapter 2 in [5].

The generalized Rayleigh-Plesset equation for bubble dynamics is

$$R\frac{d^2R}{dt^2}+\frac{3}{2}\Big(\frac{dR}{dt}\Big)^2+\frac{4\nu_l}{R}\frac{dR}{dt}=\frac{1}{\rho_l}\Big[p_b(t)-p_\infty(t)-\frac{2\sigma}{R}\Big] \tag{2.1}$$

The analytical model for four possible stages* in vapor-bubble growth in a superheated liquid have been respectively described below.

1. Initial or latent stage, the radial velocity of growth is limited by the restraining effect of surface-tension

$$R_0=\frac{2\sigma}{p_{sat}(T_\infty)-p_\infty} \tag{2.2}$$

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[*] Only for sufficiently large liquid superheats, the bubble growth will following above processes. For smaller superheats, the inertial stage will be skipped. At still smaller superheats, both the inertial and the intermediate stages will be skipped.

2. Inertia stage, the upper bound for the growth velocity is

$$\left(\frac{dR}{dt}\right)_{inertial} = \left[\frac{2}{3}\frac{p_{sat}(T_\infty) - p_\infty}{\rho_l}\right]^{1/2} \tag{2.3}$$

3. Intermediate stage, both the inertial and thermal effects control the bubble growth

4. Asymptotic stage, the bubble growth only depends on the inflow of thermal energy, $T_B = T_{sat}(P_\infty)$

$$\left(\frac{dR}{dt}\right)_{thermal} = \left(\frac{3}{\pi}\right)^{1/2} \frac{k_l}{h_{LG}\rho_{sat}(T_B)} \frac{T_\infty - T_B}{(D_l\, t)^{1/2}} \tag{2.4}$$

In the study of Prosperetti and Plesset [23], the vapor-bubble growth in a superheated liquid, with appropriate scaling, was described by a single equation under general conditions, without any parameter of liquid superheat and liquid properties. With an approximation of a thin thermal boundary layer, their model gives an accurate description of the growth of spherical vapor bubbles in a superheated liquid except for very small superheats[†]. If the further approximation of a linear variation of vapor pressure with temperature and of constant physical properties are made, the scaled variables can be introduced to describe the growth under any conditions.

The only unknown parameter in Rayleigh-Plesset equation p_b, the bubble pressure, was approximated to be the saturation pressure of the liquid temperature at the bubble boundary T_{bb}, $p_b = p_{sat}(T_{bb})$. T_{bb} can be obtained from the energy equation,

$$\frac{\partial T}{\partial t} + \frac{R^2}{r^2}\frac{dR}{dt}\frac{\partial T}{\partial r} = \frac{D_l}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right) \tag{2.5}$$

$$T_{bb}(t) = T_\infty - \frac{1}{3k}\left(\frac{D_l}{\pi}\right)^{\frac{1}{2}} \int_0^t h_{LG}\frac{d}{dx}[R^3\rho_{sat}(T_{bb})]\left[\int_x^t R^4(y)dy\right]^{-\frac{1}{2}} dx \tag{2.6}$$

Compared with the results obtained from a more accurate model developed by Donne and Ferranti [10], it is shown that (i) For the reduced temperatures equal to 0.53, 0.514 and 0.47, respectively, at $1\,atm$ ambient pressure, the agreement is quite good except in the early stages of growth; (ii) The results show a poorer agreement in low superheats than in the high and moderate superheats, by changing the ambient pressure from $0.5\,atm$ to $6\,atm$.

In order to obtain a universal equation for bubble growth in superheated liquid, Rayleigh-Plesset equation is further approximated by a linear relation between the equilibrium vapor pressure and the temperature in terms of a dimensionless time variable τ and two physical variable λ and β which contain all the physical parameters of the problem[‡]

[†] The reduced temperatures used in this study never exceed 0.6.

[‡] In the paper, the authors use μ and α instead of λ and β, respectively.

$$V^{\frac{4}{3}}\Big[V\frac{d^2V}{d\tau^2}+\frac{7}{6}\Big(\frac{dV}{d\tau}\Big)^2\Big]=3\Big[1-\lambda\int_0^{\tau}(\tau-\theta)^{-\frac{1}{2}}\frac{dV}{d\theta}-V^{-\frac{1}{3}}\Big] \tag{2.7}$$

with the initial condition of $V(0)=1$ and may further become

$$y^{\frac{4}{3}}\Big[y\frac{d^2y}{dx^2}+\frac{7}{6}\Big(\frac{dy}{dx}\Big)^2\Big]=3\Big[1-\int_0^{x}(x-\xi)^{-\frac{1}{2}}\frac{dy}{d\xi}d\xi-\lambda^2y^{-\frac{1}{3}}\Big] \tag{2.8}$$

with the initial condition of $y(0)=\lambda^6$. If two physical variables $\tilde{R}$ and $\tilde{t}$ are defined to be

$$\tilde{R} = \lambda^2R/R_0 = y^{\frac{1}{3}}, \tag{2.9}$$

$$\tilde{t} = \beta\lambda^2 t = \int_0^x y^{-\frac{4}{3}}(\xi)d\xi \tag{2.10}$$

The relation $\tilde{R}=\tilde{R}(\tilde{t})$ is independent of the physical parameters β and λ except in the initial stages of the growth. The asymptotic relations (2.3) and (2.4) become

$$\Big(\frac{d\tilde{R}}{d\tilde{t}}\Big)_{inertial}=\Big(\frac{2}{3}\Big)^{\frac{1}{2}},\qquad \Big(\frac{d\tilde{R}}{d\tilde{t}}\Big)_{thermal}=\pi^{-1}(3\tilde{t})^{-\frac{1}{2}} \tag{2.11}$$

The results are compared with Donne & Ferranti's again and it is shown that

- The physical variables λ and β do include in a physically meaningful way all the quantities relevant for the growth of vapor bubbles in superheated liquid under a very wide range of conditions.
- The times required for growth to the indicated value of R/R_0 are shown as a function of λ.
- The differences in initial stages still present.
- The scaled growth rate for very large superheat[§] are seen to deviate considerably and these discrepancies have limited effects on the $\tilde{R}(\tilde{t})$ results.

For the study of Prosperetti and Plesset [23], it should be noted that

- This scaled description is valid only for bubbles that have grown by about an order of magnitude beyond their initial radius, so that surface-tension effects have become unimportant. This limitation is inconsequential in practice, particularly for moderate and large liquid superheats.
- The asymptotic stage of bubble growth was accurately described by the scaled formulation. However the rate of bubble growth for large superheats is overestimated in the intermediate stage.
- This classical theory of bubble growth does not describe explosive boiling (see [30]).

[§] In the case of high superheat it may be possible to evaluate the physical properties appearing in β and λ at a temperature different from T_B

2.2 Homogeneous nucleation theory

The modern homogeneous nucleation has been investigated in detail both experimentally and theoretically by Volmer & Weber [37], J. Frenkel [12], V.P. Skripov [32], Blander and Katz [4], and others.

The classical homogeneous nucleation theory estimates the energy barrier to nucleation by treating the droplet or the bubble as composed of a bulk core surrounded by an interface. If a very small bubble is formed within a large homogeneous mass, we can consider that this does not change the state of the matter in the outer phase. In this case, independently of the type of constants imposed on the simple system (for example, $T, p =$ constant or $s, v =$ constant), the minimum work of formation of the bubble is described by the same equation

$$W_{min} = \sigma A - (p_v - p_l)V + i(\mu_v - \mu_l) \tag{2.12}$$

where A is the surface area of the bubble, p_v is the vapor pressure within the bubble, p_l is the surrounding liquid pressure, V is the volume of the bubble, i is the number of molecules inside the bubble and μ_v and μ_l are, respectively, the chemical potentials of the vapor and liquid phases. For a spherical vapor bubble (or a spherical 'cluster' of vapor molecules) of radius r, Eqn.(2.12) reads

$$W_{min} = 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 (p_v - p_l) + i(\mu_v - \mu_l) \tag{2.13}$$

The first term represents the work of surface formation, the second term the volume work directed against the pressure forces, and the third the 'molecular' work. It is well-known that the minimum work W_{min} exhibits a maximum W^*_{min} at the critical bubble radius r^* given by

$$\left(\frac{\partial W_{min}}{\partial r}\right)_{r=r^*} = 0 \quad \text{and} \quad \left(\frac{\partial^2 W_{min}}{\partial r^2}\right)_{r=r^*} < 0 \tag{2.14}$$

Suppose the critical bubble is in mechanical and chemical equilibrium[¶], Eqn.(2.13) can be written in a simpler form as a function of the radius of the critical bubble r^*

$$W^*_{min} = \frac{1}{3}\sigma A^* = \frac{1}{2}V^*(p_v - p_l), \quad A^* = 4\pi r^{*2}, \quad V^* = \frac{4}{3}\pi r^{*3} \tag{2.15}$$

or

$$W^*_{min} = \frac{16\pi\sigma^3}{3(p_v - p_l)^2} \tag{2.16}$$

or in reduced units

[¶] It implies that $p_v = p_l + \frac{2\sigma}{r}$ and $\mu_v(p_v, T) = \mu_l(p_l, T)$, however mechanical equilibrium may not necessarily hold at $r = r^*$ [7]

$$\frac{W^*_{min}}{k_B T} = \frac{4}{27} \frac{[\sigma A^*/(k_B T)]^3}{[(p_v - p_l)V^*/(k_B T)]^2} \tag{2.17}$$

The final step in homogeneous nucleation theory is an evaluation of the mechanism by which energy deposition could occur and the probability of that energy reaching the magnitude, W^*_{min}, in the available time [5]. In the body of a pure liquid completely isolated from any external radiation, this issue is reduced to an evaluation of the probability that the stochastic nature of the thermal motions of the molecules would lead to a local energy perturbation of magnitude W^*_{min}. Most of the homogeneous nucleation theories therefore relate W^*_{min} to the typical kinetic energy of the molecules, namely $k_B T$ and the relationship is couched in terms of a Gibbs number,

$$Gb = \frac{W^*_{min}}{k_B T} \tag{2.18}$$

A number of experssions have been proposed for the precise form of the relationship between the nucleation rate, J, defined as the number of nucleation events occuring in a unit volume per unit time and the Gibbs number, Gb, but all take the general form

$$J = J_0 \, e^{-Gb} \tag{2.19}$$

where J_0 is some factor of proportionality. Various functional forms have been suggested for J_0. A typical form is that given by Blander and Katz [4], namely

$$J_0 = N\Big(\frac{2\sigma}{\pi m_m}\Big) \tag{2.20}$$

where N is the number of molecules per unit volume for the liquid and m_m is the mass of a molecule. Though J_0 may be a function of temperature, the effect of an error in J_0 is small compared with the effect on the exponent, Gb, in Eqn.(2.19).

2.2.1 Extended homogeneous nucleation theory

Despite its success in predicting the superheat limit of liquids assuming the nucleation rates about $J = 10^{10} \sim 10^{12} \, m^{-3} s^{-1}$, the classical homogeneous nucleation theory has been widely criticized for

- ignoring the effect of curvature on surface free energy;
- predicting a finite barrier when the spinodal is approaching;
- its failure to predict the tensile strength of liquid at relatively low temperatures;
- providing low steady-state nucleation rates

Extensions of the classical theory are also criticized for as either being thermodynamically inconsistent or not satisfying the nucleation theorem.

In the study of Delale *et al.* [7], the classical homogeneous nucleation was reconsidered by employing a new phenomenological nucleation barrier in the capillarity approximation that utilizes the superheat threshold achieved in experiments. An algorithm to calculate the superheat limit temperature, critical bubble radius and steady-state nucleation rate has been developed.

By adding a non-negative phenomenological correction term, $F^*(T, p_l) \geqslant 0$, to the free energy for the formation of a vapor bubble of critical size r^*, Eqn.(2.13) for the minimum work of formation for mechanical equilibrium at $r = r^*$ becomes

$$W^*_{min} = 4\,\pi\, r^{*2}\,\sigma - \frac{4}{3}\,\pi\, r^{*3}\,(p^*_v - p_l)_{exp} - F^*(T, p_l) \tag{2.21}$$

The equation to be solved for the superheat limit temperature T_{SL} for a given liquid pressure p_l is

$$\frac{p_l}{p_c} = \frac{p_{v,\infty}}{p_c}\Big\{1 - \frac{\kappa}{\eta}\frac{(1 - T_{SL}/T_c)^{\varepsilon}}{T_{SL}/T_c}\Big[\frac{h_{LG}}{\bar{R}T_c(\mathbb{Z}_v - \mathbb{Z}_l)}\Big]\Big(1 - \frac{\mathbb{Z}_l}{\mathbb{Z}_v}\Big)\Big\} \tag{2.22}$$

where $\bar{R}$ is the specific gas constant; h_{LG} is the latent heat of vaporization at T_{SL}; κ is a substance dependence constant obtained by fitting the experimentally measured T_{SL} at $1\,atm$ into above equation. η is given by the relation

$$\eta = 1 - \frac{\rho_{v,\infty}}{\rho_l} + \frac{1}{2}\Big(\frac{\rho_{v,\infty}}{\rho_l}\Big)^2$$

and the exponent ε, standing for the power law temperature dependence of the expansion work $(p^*_v - p_l)_{exp}V^*$, is estimated to be the same for all substances, ≈ 2.2 as confirmed in experiments.

The phenomenological correction $F^*(T_{SL}, p_l)$[‖] is regarded as a function of T_{SL} and approximated by a fraction θ of $(p^*_v - p_l)_{exp}V^*$ as

$$F^*(T_{SL}, p_l) = \theta(p^*_v - p_l)_{exp}V^* = \frac{8}{3}\pi\theta\, r^{*2}\sigma \tag{2.23}$$

Therefore by extrapolation from T_c down to the superheat temperatures, the steady-state nucleation rate becomes

$$J = \mathbb{Z}_v\Big(\frac{3\sigma\rho_l^2}{\pi m_m^3}\Big)^{1/2} exp\Big[-\frac{4\pi r^{*2}\sigma}{3k_BT_{SL}}(1 - 2\theta)\Big] \tag{2.24}$$

With the two adjustable parameters κ and θ, an excellent agreement is observed between measured and predicted values of the superheat limit temperatures, which are shown to lie

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[‖] $F^*(T, p_l)$ is now evaluated at the superheat limit temperature T_{SL} by extrapolation from T_c.

between the spinodals of the Berthelot and van de Waals equations of state. The nucleation rates were enhanced of 11 to 20 orders of magnitude over the one predicted by the classical theory based on Eqn.(2.12).

2.2.2 Non-classical method on homogeneous nucleation

The classical nucleation theory breaks down near a spinodal (where the critical nucleus is small in amplitude but large in spatial extent) or under conditions where the critical clusters of the new phases are small enough that the curvature of the cluster surface affects its free energy. In recent years, homogeneous nucleation is being investigated by nonclassical methods using the density functional methods or molecular dynamics simulations.

Density functional techniques of statistical mechanics have proven to be powerful approaches to studying nonclassical nucleation of the gas-to-liquid transition and the reverse process of cavitation in expanded liquids. Effects arising from the proximity of spinodals and from surface curvature are built into the density functional approaches used, and deviation from the capillarity approximation (which lies at the heart of classical nucleation theory) can be studied.

In 1998, M. Matsumuto reviewed the studies on microscopic mechanism of phase change for various fluid systems using molecular dynamics simulation [18]. The dynamic behavior of molecules near the surface has been classified into four catagories, evaporation, self-reflection, condensation and molecular exchange. The fourth type, molecular exchange, becomes quite important for some cases such as associating fluids and fluids at high temperatures.

Moreover when the liquid and vapor is in equilibrium, the condensation coefficient α_c is found to be strongly dependent on the temperature due to the molecular exchange since such a behavior does not contribute to the condensation flux.

The condensation and evaporation behavior is much complicated in the case of non-equilibrium conditions. The condensation behavior seems strongly dependent on the temperature and the density of vapor and when hot vapor condensation on cool liquid occurs, the general tendency of α_c is

$$\frac{\partial \alpha_c}{\partial T_v} > 0, \qquad \frac{\partial \alpha_c}{\partial \rho_v} < 0$$

2.3 Kinetic theory analysis of explosive boiling of a superheated droplet

Modern understanding of the kinetics of evaporation from the interface surface can be summarized as follows: for a given temperature T_l of liquid phase, and for a corresponding vapor saturation pressure $p_{sat}(T_l)$, the process depends on one additional free parameter, the ratio $p_{sat}(T_l)/p_\infty$, where p_∞ is the external pressure. Other macroscopic quantities, like temperature, velocity and mass flux, are found to be unique functions of this one parameter. In the case of high reduced temperature (low evaporation coefficient), the pressure ratio has little effect on the evaporation rate unless the ratio is very close to unity. Hence, the changes of vapor pressure inside the bubble have little influence on the evaporation rate. On the other hand, the pressure inside the bubble is influenced by the evaporation rate through hydrodynamics of the radial flow in the liquid phase. Therefore, when the evaporation rate saturates, both bubble growth rate and bubble pressure remain constant. See [31].

Shusser and Weihs [30] developed a mathematical model to predict the growth of an internal vapor bubble produced by homogeneous nucleation within a liquid droplet. The general physical situation is depicted schematically in Fig.(2.1). Their target is to express R_1 and R_2 as functions of time.

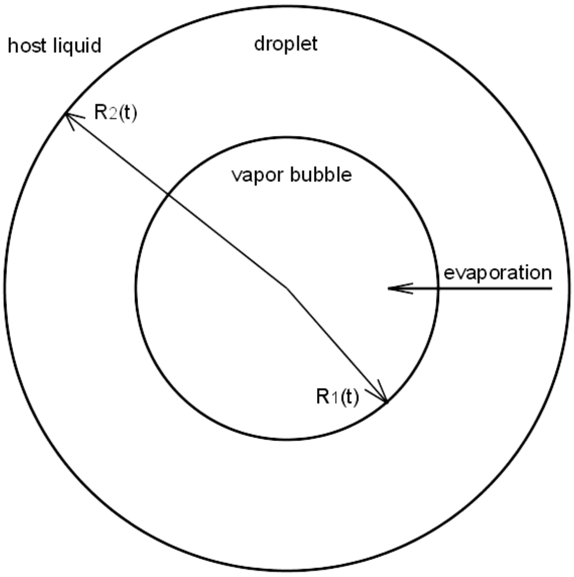

Figure 2.1: Schematic illusion of explosive boiling of a liquid droplet

Equations for droplet radius growth, vapor density in the bubble and the pressure in the bubble are established from conservation equations. Several assumptions have been made based on the previous experimental observations.

1. The vapor is an ideal gas.
2. Both the droplet liquid and the host liquid are invisid and incompressible.
3. The pressure within the vapor bubble is uniform (but can change in time).
4. The flow, bubble and droplet are radially symmetric and the bubble is formed at the center of the droplet[**].

Furthermore, the most important assumption for their model is that the evaporation rate is constant and equal to its maximal possible value, which is the kinetic theory limit to the mass flux that can be attained in a phase-change process. This evaporation rate J_e is given by the Hertz-Knudsen formula

$$J_e = p_{sat}(T_B)\sqrt{\frac{m_M}{2\pi\,\mathbb{R}T_B\acute{y}}} \tag{2.25}$$

where T_B is the boiling temperature for the droplet liquid; $p_{sat}(T_B)$ is the saturation pressure at T_B; $\mathbb{R}$ is the universal gas constant.

Applying above assumptions to the mass and momentum conservation equations, the equations for droplet radius growth $\dot{R}_2$, vapor density in the bubble ρ_v and the pressure in the bubble p_i are established respectively.

$$\dot{R}_2 = \Big(\dot{R}_1 - \frac{J_e}{\rho}\Big)\frac{R_1^2}{R_2^2} \tag{2.26}$$

$$\rho_v = \frac{J_e}{\dot{R}_1} \tag{2.27}$$

$$p_i = \rho_v \frac{\mathbb{R}}{m_M} T_B \tag{2.28}$$

Finally the approximate formula for bubble radius growth is given

$$\dot{R}_1 = b_0\Big(\frac{2}{3}\frac{J_e}{\rho_{hl}}\frac{\mathbb{R}}{m_M}T_B\Big)^{1/3} \tag{2.29}$$

where ρ_{hl} is the density of the host liquid and b_0, an emperical coefficient, is estimated to be 1.

[**] In the appendix, the assumption of concentricity was inspected and it shows that the error in pressure will be within 10% if the deviation of the bubble center from the droplet center is less than 25% of the droplet radius.

Within $100\mu s$, the calculated bubble radius growth agrees with the experimental results in [?] quite well with a little overestimation but still much better than the model developed by Shepherd and Sturtevant in [?] and the rate estimated from classical inertial growth. It is found by calculation that the bubble pressure can not drop if the host liquid has a greater density than the droplet liquid and vice versa. Shusser and Weihs conclude that the process of explosive boiling is characterized by bubble formation by homogeneous nucleation and evaporation rate that is equal to its kinetic theory limit.

‡

In the follower paper of Shusser *et. al* [31], their 1999 model has been justified. Shusser and Weihs 1999 model used an approximate algebraic relationship for vapor pressure inside the bubble p_i. The full form was retained to check the accuracy their approximation in this study.

After comparison the results with the experimental data in [29], the best agreement was obtained for the evaporation coefficient of 0.06 corresponding to a reduced temperature 0.88 for butane. This very low value is also in agreement with the results of molecular dynamics simulations [18].

The time dependence of the evaporation rate J_e was calculated. The error in the Shusser and Weihs 1999 model does not exceed 5.5% for the whole duration of the process and remains below 1% after $30\mu s$. The approximated vapor pressure inside the bubble p_i in Shusser and Weihs 1999 model has been justified as well since the error is significant only during very short period of the initial growth of the evaporation rate, in nanosecond.

Besides the high dependence of the pressure inside the bubble on the evaporation rate when the latter is low, low evaporation rate also influences the thermodynamic state of the vapor. It is shown that the vapor is highly superheated for $a_w = 0.06$ and the temperature of the vapor is about 98% of the temperature of the superheated liquid, i.e. by far larger than the saturated vapor temperature.

There is about 10% difference in the bubble pressure computed from Shusser and Weihs 1999 model and from this paper.

2.4 Summary

In this chapter, we have introduced several representative theoretical approaches relevant to the bubble vaporization.

The classical theory of bubble vaporization mainly focuses on describing the behavior of bubble growth in slightly superheated liquid. In such a case, the liquid superheat could not overcome the energy barrier for critical bubbles therefore the bubble nuclei can only form on the sites where either the energy barrier is reduced or extra energy is fed to the liquid. The bubble growth is proceeding in a time frame that thermodynamic equilibrium between the liquid and vapor at the bubble surface is obtainable. A precise description of the bubble growth based on thermodynamic equilibrium can be established.

As the liquid is superheated further, due to density fluctuation, the energy barrier can be overcome by liquid particles themselves besides the two possibilities mentioned above. The classical homogeneous nucleation theory is trying to explain how the bubble nuclei is initiated at high superheats in two aspects: i) how much is the energy barrier? ii) how much is the bubble nucleation rate? However it has been shown that classical homogeneous nucleation theory has been widely criticized for describing the initial phase of bubble nucleation. Some efforts has been made trying to extend the validity of the classical homogeneous nucleation.

In recent decades, other methods have been developed to research bubble nucleation at extremely high superheat, i.e. molecular dynamic simulation and the kinetic model developed by Shusser, Ytrehus and Weihs. These methods have succeeded in modelling the homogeneous nucleation for a very small amount of liquid molecules. However for a real large-scale BLEVE problem, the molecular dynamic simulation is too expensive for modelling tons of liquid and the kinetic model is not sufficient as the length scale of the liquid increases, from the diameter of one single droplet to the diameter of a large tank.

Chapter 3

The BLEVE event

In this chapter, we will discuss the whole BLEVE event trying to reveal the latest research on each stage and the unsolved problems open to our study.

The characteristic feature of pre-BLEVE is 'variety and uncertainty'. The characteristic feature of BLEVE stage is 'rapidness'. The characteristic feature of post-BLEVE stage is 'chemical explosion'.

The reference in this chapter include: [1], [2], [6], [8], [9], [11], [15], [19], [21], [22], [25], [26], [27], [28], [29], [33] and [34].

3.1 Pre-BLEVE stage

The pre-BLEVE stage is the first stage of a BLEVE event. What we concern in this stage includes

- How does a crack appear and propagate along the tank?
- Will the tank totally disintegrate? If yes, when and how will it be?
- What is the state of the PLG and the ambient when the tank totally disintegrates?

All these information is essential as the initial conditions for the BLEVE stage. However the variety and uncertainty in pre-BLEVE stage brings great difficulties to provide definitive initial conditions for the BLEVE stage.

3.1.1 Crack development

In 1996, Lenclud and Venart established models for the blowdown process of partially filled pressure liquefied vessels, in which both single and two-phase discharge were considered* [15].

A crack opening model was developed using the Crack Opening Displacement theory and plastic displacement assumptions.

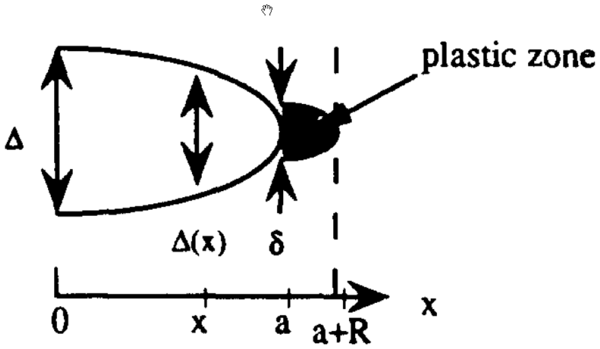

Figure 3.1: Crack displacement concept

The crack lengthes were obtained as a function of time from high-speed cinematography and the crack widthes were assumed to be the sum of two components, an elastic displacement and a plastic displacement. Consequently the crack area was described as a function of time.

$$A_{crk} = \pi a^2 \Big(\frac{1}{C} + \frac{\Delta}{2a}\Big)$$

in which a is the crack length; C, the shape aspect ratio i.e. the ratio of crack length to the plastic deformation width, is assumed to be constant; Δ is the crack opening displacement shown in Fig.(3.1).

For a single-phase discharge, an expression for the unsteady compressible choked flow through time-varying openings was developed. The predicted time-dependent pressure was found to be in reasonable agreement with the experiments.

‡

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[*] We will mainly concentrate on their single-phase model since the two phase models they used can not adequately describe the experimental results even when the model parameters were adjusted to suit the experimental results.

The research on crack development is also carried out in another working package L-1 of the project Tunnel Safety by numerical methods.

We expect the output of working package L-1 will include

- Moment of the tank total disintegration as a function of tank material, liquid initial state, initial crack area/shape/location or external fire intensity;
- Crack area as a function of time.

At present, the working package L-1 only uses a constant tank pressure for their crack development prediction. It will be shown later that the pressure in the tank oscillates with time in a crazy manner, therefore it can be expected that the real tank total disintegration will happen ahead of the current prediction of working package L-1.

3.1.2 Vessel over-pressure

In the study of Chen *et. al* [6], a small-scale experiment was established to investigate the possible processes that could lead to a BLEVE and observe the thermo-hydraulic interactions which ooccur immediately following the partial loss of confinement through a simulated crack. The schematic of the experimental setup is shown in below figure.

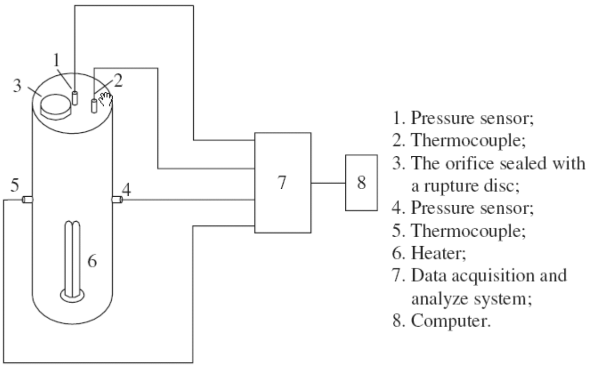


Figure 3.2: Experimental setup

The vessel made of stainless steel is 800 mm in height and 5 mm in thichness. Its diameter is 250 mm. A rupture disk is installed on the top of the vessel. The power of the heater is 6 kW. Working fluid is water. The highest data acquisition frequency is 500 kHz/s[†].

[†] The step-shaped pressure curve can be a good proof of the low resolution of the pressure sensor used in the experiments.

According to the authors, two pressure peaks result after the pressure is released (see Fig.(3.3)): the first pressure peak seems to occur because of the vapor pressure caused by the swelled two-phase layer after the initial venting, the second one was reasoned as a dynamic impact or 'liquid hammer' and is maintained by bubbles collapse or something like cavitation at the surface of the inner wall of the head space that ocurs with the ejection of two-phase flow.

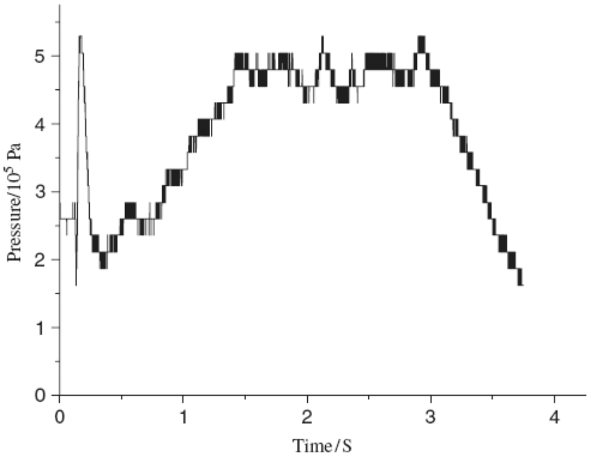


Figure 3.3: The whole pressure curve measured by the pressure sensor installed on the top of the vessel (60% liquid height; 130 °C; 6.67% orifice area)

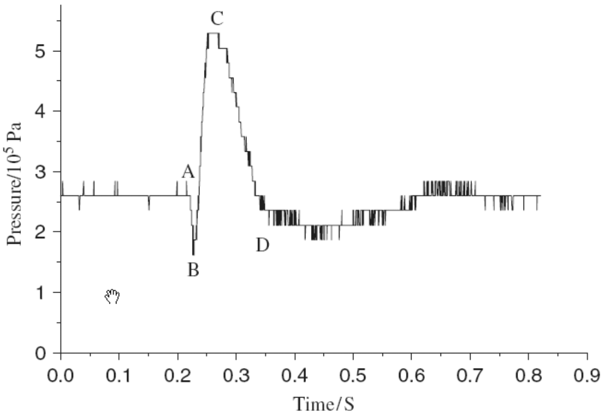


Figure 3.4: The enlarge diagram of the first pressure peak in Fig.(3.3).

If we carefully observe the initial stage of the pressure curve in Fig.(3.4) and the pressure curve in Fig.(3.5), we will find several interesting points:

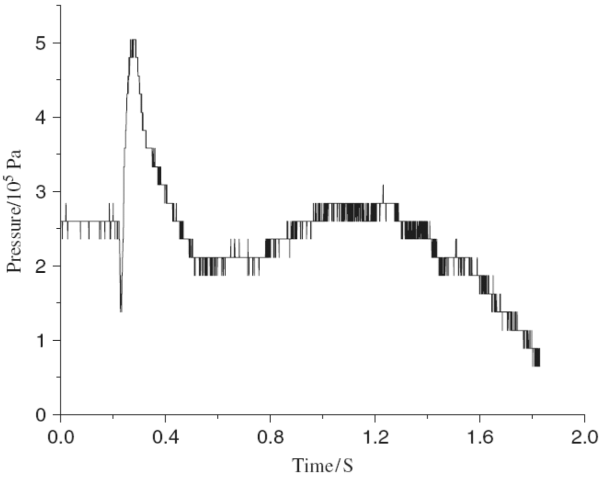


Figure 3.5: The whole pressure curve measured by the pressure sensor installed in the wall of the vessel at middle height (60% liquid height; 130 °C; 6.67% orifice area)

- The initial high pressure is maintained for more than 200 *ms* after the rupture disk is broken;
- Suddenly a pressure drop occurs throughout the tank as observed in the pressure curves of the top and middle sensors. So far we don't know the reason for this rapid pressure drop;
- The sudden pressure drop is immediately followed by a rapid repressurization, possibily because of the massive bubble nucleation/growth or the dynamic impact of the lading on the sensor;
- Before the first peak is finished, all the lading in the tank behaves roughly the same at least in pressure aspect, their positions do not matter too much.
- After the pressure field is established, the pressure near the crack has the highest value and is maintained for nearly 1.5 *s* even after the pressure at the middle height already start to decrease.

The authors also carried out some research on the light height, orifice size and the degree of liquid superheating. The results indicate that they all have different influence on the magnitue of the measured over-pressure. No empirical equation has been derived.

‡

In the study of McDevitt *et. al* [19], two sets of experiments have been performed to study the initiation of a BLEVE: (i) Tank test and (ii) Shock tube test. The target of their research is to determine what actually causes the pressure waves inside the tank which lead to a BLEVE.

In the tank test, one litre tank (26 cm long with a diameter of 7.5 cm and a thickness of 0.635 cm) was filled with R-12 or R-22 (88 v%). The tank was ruptured by a .3006 full metal jacketed rifle bullet. The pressure at the end of the tanks was recorded.

In the shock tube test, experiments were then conducted with liquids at the same conditions as the tank tests in a shock tube equipped with windows. Liquid was suddenly exposed to atmospheric pressure while a spark photograph was taken and the pressure response recorded.

Results show that

- The initial drop in pressure is followed by a rapid pressure rise, caused by the boiling of liquid. As shown in the pressure history of tank tests, the pressure drops slightly, then rises to a level 30% higher than the inital pressure, which happens within 2 ms.
- The pressure measured by the transducer opposite to the burst disk in shock tube tests indicates that at first the pressure decreases approx. 10% at a constant speed for about 0.02 ms, then the pressure keeps constant[‡] for about 0.03 ms, then within 0.01 ms the pressure is recovered to a level higher than the initial pressure again.
- An explosion kernel originating near the rupture location in the shockk tube has been found in the photograph. This explosion is called *initial explosion.*

The initiation of BLEVE was described by the authors as follows:

1. The liquid in the vicinity of the break experiences the pressure drop.
2. The depressurization causes the liquid near the break to be in a superheated state.
3. After the rarefaction wave has traveled a finite distance, the superheated liquid behind this wave will homogeneous nucleate and cause a pressure wave.
4. This pressure wave (or blast wave) then overtakes the rarefaction wave before it has propagated far from the break.
5. The blast wave eventually stops any further boiling and the fluid on the end of the tank only experiences this blast.
6. Blast wave is the cause for the catastrophic failure of the container. The volume of the fluid involved in the initial explosion determines the magnitude of the blast (pressure) wave.

[‡] this constant pressure is still higher than the amtospheric pressure

According to the authors, the probability of an explosion is 100% if the fluid is on the spinodal curve and is less than 100% if the initial temperature of the liquid is below the superheat temperature limit, according to McDevitt's private communications with R.C. Reid on his theory on BLEVEs.

‡

We take three representative experiments in [6] and [19] for comparison in below table.

	Chen *et. al* 2007	McDevitt *et. al* 1990 Tank	McDevitt *et. al* 1990 Shock tube
Vessel (mm)	Height: 800 Diameter: 250 Thickness: 5	Height: 260 Diamter: 75 Thickness: 0.635	Length: 914 Width: 25 Height: 38
Crack location	top (vapor)	top (vapor)	bottom (liquid)
Crack area	D65 hole	.3006 bullet hole	D25 hole
Liquid	water	R-22	R-12
Loading level	60%	88%	94%
Initial temp.	130 °C	$\sim$ 65 °C	$\sim$ 90 °C
Initial press.	$\sim 2.7\,bar$	$27\,bar$	$27.7\,bar$
Initial venting time	$\sim 200\,ms$	$\sim 1.2\,ms$	$260\,\mu s$
1st press. drop to	$\sim 1.5\,bar$	$\sim 23\,bar$	$\sim 25.86\,bar$
1st press. peak	$\sim 5.2\,bar$	$\sim 35\,bar$	$\sim 28\,bar$

Table 3.1: Comparision of the study of [6] and [19]

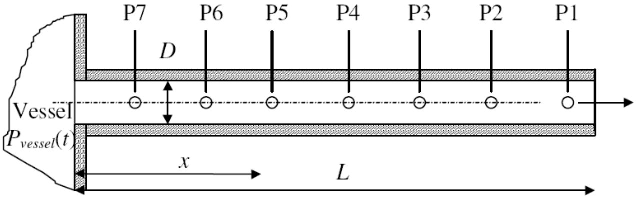
This comparision shows the possible relevant parameters to the pressure variation in the tank.

3.1.3 Liquid/mixture discharge rate

A two-phase model was developed for evaluating coolant discharge rates from loss-of-coolant accidents (LOCA) [22].

The equations of motion of a rapidly expanding two-phase flow are non-linear and hyperbolic. They also exhibit wave propagation features. Therefore a numerical scheme that incorporates the method of characteristics to solve the governing equations was developed which includes

- EVUT (equal velocity unequal temperature) model for two-phase flow;
- Bubble breakup model depending on Rayleigh-Taylor and Kelvin-Helmholtz instability criteria respectively;



L	1700mm
P1	1652mm
P2	1425mm
P3	1225mm
P4	1025mm
P6	825mm
P5	625mm
P7	425mm
D	88mm

Figure 3.6: Schematic description of the experimental channel, [2]

- An approximate slip velocity model for calculating the Kelvin-Helmholtz instability criterion for bubbles.

The instability criteria were presented in terms of the Weber and Eotvos numbers, respectively. The initial nucleation sites number density n_0 is chosen so that the numerically predicted pressure undershoot would correspond to the value predicted by Elias and Chambre 1993 model [11].

The code was used to predict a set of experimental data provided by Barták [2]. The comparison between the numerical simulation and the experimental results indicates that

- The inclusion of the bubble breakup mechanism is essential since constant bubble density (without bubble breakup mechanism) failed to reproduce the experimental results.
- This model reprocueds quite accurately the wavy transients of both hot and relatively colder tests, both in amplitudes and pressure oscillation frequencies.
- The two instabilities had a similar influence on the bubble breakup rate.
- The critical dimensionless number for Kelvin-Helmholtz instability was more convenient in usage.
- The Rayleigh-Taylor instability criterion needs modifying to reproduce the experimental data.

3.1.4 Boiling front propagation

In the study of Reinke and Yadigaroglu [27], research has been carried out on the boiling front propagation in several metastable superheated liquids. The important observations and findings include

- The real superheat at the boiling front is lower than the nominal superheat due to the pressure increase at the boiling front;

- Above a certain superheat threshold, vaporization occurs only in boiling front and below a certain superheat threshold, no boiling front but only slow bubbling, which agrees with previous studies;
- No significant influence of the cross-section area on the front velocity for pipe size in the range from 14 to 80mm which is contrary to certain previous findings [13] which suggest an asymptotic threshold value at larger pipe diameters;
- The vaporization and fragmentation of the superheated liquid at the boiling front appears to be self-amplified;
- The boiling front travels at a constant average velocity which is much lower than the local speed of sound. The measured velocity varies predominantly linearly with the liquid superheat;
- Linear empirical equations have been established between the velocity of boiling front propagation and the nominal superheat for butane, propane, and water;
- **Most importantly, the boiling front had a velocity significantly lower than that expected from isentropic phase change.**

Two flash fractions, χ_h for isenthalpic flash fraction and χ_s for isentropic flash fraction, are defined as follows[§]

$$\chi_s = \frac{s_{l1} - s_{l2}}{s_{v2} - s_{v2}} < \frac{h_{l1} - h_{l2}}{h_{v2} - h_{v2}} = \chi_h = \frac{c_{pl}\Delta T_{12}}{h_{LG2}} = Ja$$

in which l denotes for liquid and v denotes for vapor. 1 represents the single-phase in the upstream of the boiling front while 2 represents the two-phase mixture in the downstream. The definition of the isenthalpic quality assumes that the vapor/liquid mixture is at rest after the vaporization; this results in the highest possible quality since 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 comparison between the experimental data and these two limiting qualities indicates that the flash quality values for propane are between these two lines and very close to the isenthalpic line. Therefore the assumption of isentropic phase change will lead to considerable overestimation of the two-phase flow velocity.

Reinke and Yadegaroglu also attempt to predict the acceleration pressure drop and the two-phase front velocity from the conservation equations of mass, momentum and energy. However the measured pressure drop is found to be 1.3667 times as large as the calculated values, which has been reasoned as the neglection of the frictional, form, and gravititional

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[§] For initial liquid state and final two phase state at rest, Jacob number Ja is identical to isenthalpic flash fraction χ_h.

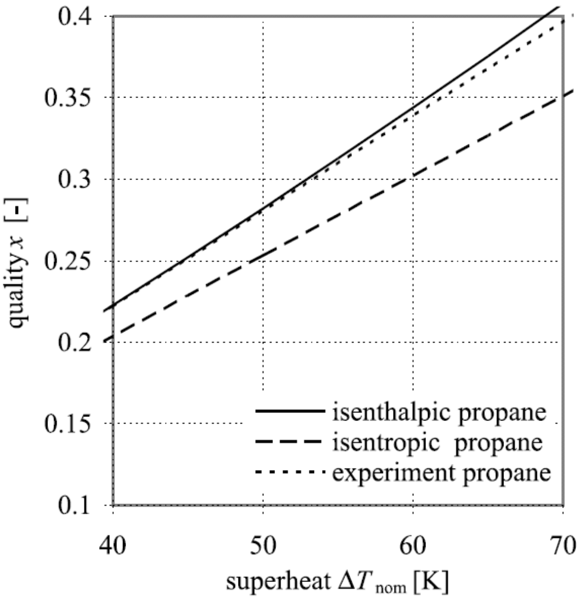

Figure 3.7: Isenthalpic, isentropic and experimental quality x for propane

pressure drops in the pipe. The calculated two-phase flow velocities u_{TPF} are higher than the measured ones as well. The lower the velocity, the higher the difference.

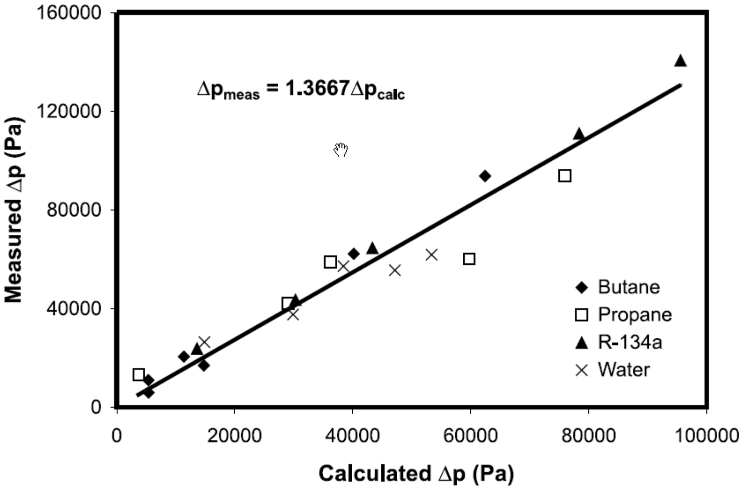

Figure 3.8: Comparison of the predicted press drop with measured values

Non-dimensional analysis was carried out to correlate the experimental data so as to determine the threshold temperature for boiling front propagation and to predict the boiling front velocity u_{frt} as a function of the superheat. If the representative temperature is $T_{sat,frt}$ for all the fluids, the superheat at the threshold of boiling front propagation is given by

$$Ja^*_{thr} = 10.11 Pr_l^{0.971} \tag{3.1}$$

and if the representative temperatures are T_{ini} for liquid and $T_{sat,frt}$ for gas,

$$Ja^*_{thr} = 8.997 Pr_l^{1.325} \tag{3.2}$$

For the boiling front velocity u_{frt}, since the slopes of the correlation lines differed from fluid to fluid, an average slop is used in deriving a general correlation.

$$\begin{aligned} Ja_{thr} &= Ja^*_{thr}\frac{\rho_v(T_{sat,frt})}{\rho_l(T_{ini})} && (3.3)\\ Ca &= 0.0813(Ja - Ja_{thr}) && (3.4) \end{aligned}$$

in which the capilary number Ca is defined as $(\mu u_{frt})/\sigma$.

It should be remarked that

- The highest initial temperature in this study is corresponding to approx. $0.81T_c$. The real superheat at the boiling front is even lower than the one calculated from the initial temperature. Therefore this study mainly describes the superheated liquid behavior in pre-BLEVE stage;
- The measured flash quality values are exactly on the isenthalpic line at lower superheats. As the superheat increases, the experimental data deviates from the isenthalpic line and towards the isentropic line.
- The conclusion that no significant influence of the cross-section area on the front velocity is noticeable.

3.1.5 Tank in pool fire engulfment

A simple mathematical mode has been proposed [28], which describes dependences of various parameters on time in an accident of LPG tank in pool fire engulfment. These parameters include temperature, pressure and mass of LPG, temperature of the vessels' wall and thermal protection layer.

The system of equations include empirical equations for the liquid vaporization, the temperatures of the liquid and the vessel wall, and the one-dimensional thermal diffusion equation for thermal layer.

The computed vessel pressure and temperature were compared with the experimental results for different kinds of thermal layer protections.

In two cases of thick thermal layer $60mm$ and $10mm$, poor agreements were observed in the maximum vessel pressure in which the computation overestimated the maxima greatly. For the rest 6 cases of thin thermal layers or no thermal layers, the maxima were almost successfully predicted except a small delay in the time for the maxima to be reached.

The predicted wall temperature as a function of time was poorly agreed with experimental data.

3.1.6 Open question in pre-BLEVE stage

The open question left for us in the pre-BLEVE stage is mainly the status of the liquid/two-phase mixture and the ambient at the moment of tank total disintegration, which includes

- Bubble number density, bubble volume distribution or void fraction in average;
- thermodynamic state of the liquid and the vapor, respectively;
- thermodynamic state of the ambient.
- the shape of liquid/two-phase mixture after tank total disintegration

To experimentally investigate above problems, more parameters besides the ones listed in Table (3.1) should be investigated, i.e. different crack increasing rates, different moments of tank total disintegration, different durations of tank total disintegration etc.

To numerically solve above problems, fluid-structure coupling analysis must be performed to get the correct initial condition for the research in BLEVE stage.

However an easy way to simplify the pre-BLEVE stage is to assume that the pre-BLEVE stage lasts extremely short in time. The liquid can be regarded as undisturbed after the tank total disintegration. In this way, the initial conditions for BLEVE stage can be easily achieved.

3.2 BLEVE stage

The BLEVE stage is the most important stage of a BLEVE event. If no chemical reaction afterwards, the output of the BLEVE stage is the output of the whole BLEVE event, normally a rapind expansion of two-phase mixture following a blast wave propagating in the air.

The feature of the BLEVE stage is rapidness. Some researchers reason that the rapind expansion of the superheated liquid is due to the homogeneous bubble nucleation and the high vaporization rate at the superheat limit. In the lab-scale experiments, a single liquid droplet is injected into a bubble column and gradually heated to be superheated. Suddenly the droplet explodes. The behavior of the droplet and the bubble growth inside the droplet is recorded by high-speed photography, meanwhile the pressure perturbation is measured. Some researchers believe for real commercial Pressure-Liquefied-Gas, the heterogeneous nucleation will dominate the initial phase of the BLEVE stage due to the presence of the rough tank wall and the impurities in the liquid. Therefore they also carried out studies on the role of heterogeneous nucleation in the BLEVE stage.

For the numerical simulation of the BLEVE stage, some simple numerical models have been developed which are able to describe the shock wave generated in BLEVE stage. Direct experimental validation is still required for those models.

3.2.1 Superheat limit and BLEVE

Thermodynamic stability analysis indicates that, for a pure liquid, the superheat-limit results when

$$\left(\frac{\partial p}{\partial v}\right)_T = 0 \tag{3.5}$$

An interesting correlation between the superheat limit temperature and the pressure was developed by Reid in [25] from the bubble-column data. In this study, T_{SL}/T_c was plotted as a function of p/p_c and found to increase with p/p_c for several liquids and particularly

$$T_{SL}/T_c \simeq 0.89 \sim 0.90 \quad \text{when } p = 1\,atm$$

Reid also proposed a new method of estimating the superheat-limit temperature based on the kinetic theory with which he could estimate the numerical values of the rate of formation of critical-size embryos and thus vapor bubbles from a given volume of liquid. If the nucleation rate is chosen to be $10^{12}m^{-3}s^{-1}$, the superheat-limit temperature for n-pentane is $421K$ closing to the experimental value. Fortunately, the results are relatively insensitive to the choice of the nucleation rate[¶].

An important result is that kinetic theory indicates no significant bulk nucleation until a definite temperature is reached. Then, in a range of only a few degrees, the rate changes

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[¶] The predicted value of T_{SL}/T_c as a function of p/p_c was plotted in curves which are in qualitative agreement with the data from previous studies. Unfortunately, few data exist to test this prediction at that moment.

from a value which is negligible small to a very large value.

Reid used his superheat-limit hypothesis to explain the explosion caused by rapid depressurization of hot, saturated liquids in an accident of pressurized-liquid tank or BLEVE [26]. Two requirements were proposed for the possible explosion:

- The temperature of the hot (heated by fire) liquid must be above the superheat-limit temperature at $1\,atm$;
- The drop in tank pressure must be very rapid.

The strength of the explosion immediately following a tank failure has been linked to the degree of superheat at the time the tank failed.

3.2.2 Prediction of the superheat limit

In the work of Abbasi *et al.* [1], attempts have been made to develop a framework with which superheat limit temperature T_{SL} of a new substances can be theoretically determined. Seven cubic equation of state (EOS) have been transformed and numerically solved for T_{SL}.

A comparison between the predictions and the observed values reveals that for a large number of chemicals the transformed Redlich-Kwong EOS is able to predict T_{SL} within 1% deviation from the experimental values.

$$p = \frac{\bar{R}T}{v-b} - \frac{a}{T^{1/2}v(v+b)} \tag{3.6}$$

in which v is the specific volume; $\bar{R} = \mathbb{R}/m_M$. Applying the mathematical description of the critical point

$$\left(\frac{\partial p}{\partial v}\right)\bigg|_{T_c} = 0 \qquad \text{and} \qquad \left(\frac{\partial^2 p}{\partial v^2}\right)\bigg|_{T_c} = 0$$

to Eqn.(3.6), they get the values of b and a in terms of critical volume as

$$b = \frac{v_c}{\kappa} \qquad \text{and} \qquad a = \frac{\kappa(\kappa+1)^2}{(2\kappa+1)(\kappa-1)^2}\bar{R}T_c^{3/2}v_c \tag{3.7}$$

where $\kappa = 2^{2/3} + 2^{1/3} + 1$. v_c can be further eliminated from the expressions of b and a, hence RK-EOS in reduced coordinates is

$$p_r = \frac{3\kappa T_r}{\kappa v_r - 1} - \frac{\kappa^2}{T_r^{1/2}v_r(\kappa v_r + 1)} \tag{3.8}$$

When the concept of minimuzation of pressure at maximum superheat as given by Eqn.(3.5) is applied to above equation, it produces highly non-linear algebraic equations to be solved numerically.

3.2.3 Bubble growth at the superheat limit

In the experimental study of Shepherd and Sturtevant [29], short-exposure photographs and fast-response pressure measurements have been used to construct a description of the complete explosion process of superheated droplets. An empirical model of evaporation after onset of instability has been established.

The results showed that

- the measured superheat limits agreed well with published data;
- only one single bubble forms within the droplet during each explosion and the growth proceeds in microsecond time frame;
- the effective velocity of the vapor-liquid interface was high initially but reached a constant value within a short time if the bubble expansion of the order of 5 μs;
- a large-amplitude small-scale roughening (interfacial instability) of the bubble surface is observed in the early stage of the evaporation;
- a series of toroidal waves driven by vapor jetting form on the interface are observed after the bubble has grown large enough to contact the outer edge of the droplet;
- violent oscillations of the bubble that occur on a millisecond time scale, after evaporation of the liquid is complete, cause the disintegration of the bubble into a cloud of tiny bubbles.

From there results the authors were able to deduce that

- very high rates of mass transfer[‖] occured from the liquid to the growing bubble which might be the result of the observed instability and wrinkling of the evaporating surface, the Landau mechamism of instability applies to rapid evaporation at the superheat limit and Rayleigh-Taylor instability applies to the bubble disintegration;
- the implied density of the vapor in the bubble was high;

[‖] The evaporative mass flux is two-order of magnitude greater than the one predicted by conventional bubble-growth theories without account for the effects of instability. Indeed the evaporative mass flux is of the same order as the maximum possible one-way flux across a smooth interface given by kinetic theory, namely $\frac{1}{4}n\bar{c}$, where n is the number density and $\bar{c}$ is the mean molecular speed

- from energy considerations, it was likely that the bubble content was not single phase but was made up of both dense vapor and liquid;
- The estimated mean density within the bubble is more than 1/2 of the critical density for butane, and of the order of the liquid density.

With the fraction θ of the bubble surface across which evaporation actually takes place, the evaporation flux rate $\dot{m}_0$ and the bubble radius increasing rate $\bar{\dot{R}}$ assumed constant, an empirical model of evaporation after onset of instability are established.

$$\begin{aligned} V_b &= \frac{4}{3}\pi \bar{\dot{R}}^3 t^3 && (3.9)\\ M_b &= \frac{4}{3}\pi \bar{\dot{R}}^2 t^3 \theta \dot{m}_0 && (3.10)\\ \rho_{eff} &= \theta \frac{\dot{m}_0}{\dot{R}} && (3.11)\\ \overline{\frac{dp}{dt}} &= \frac{2\rho_\infty \bar{\dot{R}}^2}{\tau}\left[\bar{\dot{R}} - \theta\,\frac{\dot{m}_0}{\rho_l}\right] && (3.12) \end{aligned}$$

in which V_b, M_b, ρ_{eff} and $\overline{dp/dt}$ are the bubble volume, the total mass within the bubble, the effective vapor density within the bubble and the far-field pressure, respectively.

The time for liquid initially contained a drop of radius R_0 to completely boil is proportional to R_0:

$$t_0 = R_0\left[\theta \frac{\dot{m}_0}{\rho_l}\bar{\dot{R}}^2\right]^{-\frac{1}{3}} \tag{3.13}$$

The maximum far-field pressure at the end of the evaporative stage is proportional to t_0, and therefore R_0:

$$p_{max} = \overline{\frac{dp}{dt}}\, t_0 \tag{3.14}$$

After the evaporative instability becomes nonlinear and saturated, the evaporation process seems to be quasi-steady:

- The bubble radius increasing at constant speed, $\dot{R}$.
- The far-field pressure increasing at a roughly linear rate $\overline{dp/dt}$.
- The evaporative flux is a constant $\dot{m}_0$.
- θ, the fraction of the bubble surface across which evaporation actually takes place, is assumed to be constant 0.5 calculated from the present experimental data.

3.2.4 Heterogeneous nucleation factor

In the study of Deligiannis and Cleaver [8], a two-fluid model has been used to evaluate the initial depressurization of a subcooled or saturated liquid. The role of nucleation and its effect on the interfacial area, and hence heat and mass transfer, is assessed and compared with available experimental data.

They derived the interfacial heat transfer $\dot{q}_i$ as a function of the bubble number density and the void fraction, in contrast to the arbitrarily assumed constant number density and bubble radius used in previous models

$$\dot{q}_i = 3.9 n_b^{2/3} \alpha_v^{1/3} \cdot Nu \cdot k_l (T_i - T_k) \tag{3.15}$$

in which T_i is the interfacial temperature; T_k is the temperature of phase k. The bubble number density n_b is computed from one-dimensional transport equation

$$\frac{\partial n_b}{\partial t} + u \frac{\partial n_b}{\partial z} + n_b \frac{\partial u}{\partial z} = H_{HOM} + H_{HET} - H_{COAL} \tag{3.16}$$

in which H_{HOM}, H_{HET}, H_{COLA} are the change in n_b arises from homogeneous nucleation in the bulk of the liquid, heterogeneous nucleation on the surfaces and the rate at at which bubbles coalesce, respectively. Utilizing the conservation equations for mass and energy together with the state equation $\rho_v = \rho_v(p, h_v)$, above equation can be written as

$$\begin{aligned} \frac{Dn_b}{Dt} - \frac{n_b}{\rho_v c_v^2} \frac{Dp}{Dt} - \frac{n_b}{\alpha_v} \frac{D\alpha_v}{Dt} &= H_{HOM} + H_{HET} - H_{COAL} && (3.17) \\ &- \frac{n_b}{\rho_v \alpha_v} (\dot{m}_{iv} + \dot{m}_{NU}) + \frac{n_b}{\rho_v^2 \alpha_v} BCE \left[\frac{\partial \rho_v}{\partial h_v} \right]_p && (3.18) \end{aligned}$$

where c_v is the speed of sound in the vapor phase; subscript NU stands for nucleation; BCE is the energy per unit volume transferred to the vapor when the liquid flashes [12]. Once H_{HOM}, H_{HET} and H_{COAL} are known, above equation can be solved by the method of characteristics.

In many experimental studies, the temperature difference is less than the superheat for homogeneous nucleation. Therefore H_{HOM} can be considered negligibly small and at the beginning of a depressurization H_{COAL} might also be considered small.

Heterogeneous nucleation factor ϕ is introduced to derive an equation for heterogeneous nucleation rate from the one for homogeneous nucleation rate:

$$H_{HOM} = N\Big(\frac{2\sigma N_A}{\pi \cdot m_m \cdot B}\Big)^{1/2} \exp\Big(-\frac{16\pi\sigma^3}{3k_B \cdot T_l \cdot \Delta P^2}\Big) \tag{3.19}$$

$$H_{HET} = N^{2/3}\frac{(1-M)}{2}\Big(\frac{2\sigma N_A}{\pi \cdot m_m \cdot B \cdot \phi}\Big)^{1/2} \exp\Big(\frac{-W^*_{min} \cdot \phi}{k_B T_l}\Big) \tag{3.20}$$

where N is the number of molecules per unit volume; B is equal to 2/3 in this study; $M = (\sigma_{sl} - \sigma_{sv})/\sigma_{lv}$ where σ_{sl}, σ_{sv} and σ_{lv} are the surface tensions between liquid and solid, vapor and solid, and vapor and liquid, respectively.

Because of the inherent difficulties in prescribing a value of ϕ, the nucleation model relies on carefully selection of ϕ to agree with the experiment; It was suggested by Deligiannis and Cleaver that a potentially more reliable determination of ϕ could be achieved by matching the results from unsteady thermal non-equilibrium model calculations with the position of the minimum pressure. It is shown that once this value is fixed, the initial rate of depressurization and the rate of pressure recovery agrees quite well with experiment in Fig.(3.9).

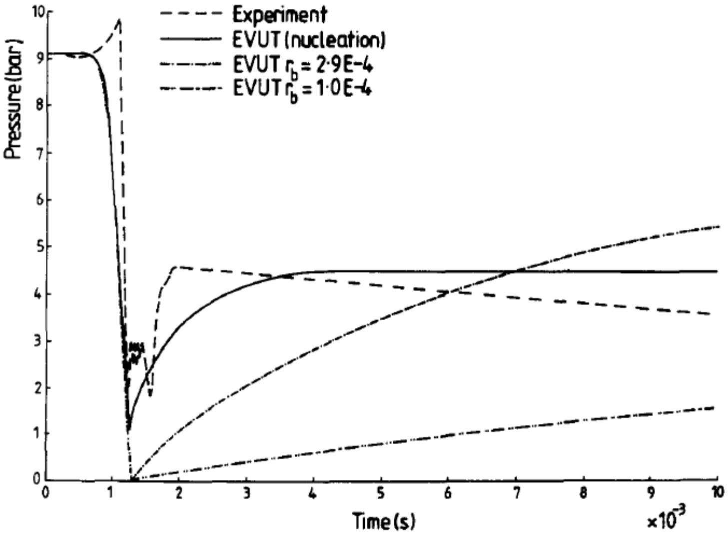

Figure 3.9: Initial depressurization

The influence of different values of ϕ on the initial pressure history has been discussed. Crowded effect, compression wave, slip and bubble rotation and enhanced surface tension will reduce the nucleation rate. An averaged value of ϕ could be determined from experiments.

‡

In the following study of Deligiannis and Cleaver [9], they carefully investigated the heterogeneous nucleation factor ϕ during a transient liquid expansion. ϕ is well-defined for an isolated bubble, but for swarms of bubbles it is statistical in nature and difficult to determine analytically.

The calculated value of ϕ has been statistically correlated with the initial temperature of the liquid T_0, the pressure drop $\Delta p = p(T_0) - p_{min}$, the time to the minimum pressure Δt and the mean depressurization rate $\Delta p/\Delta t$.

ϕ is found to be mainly dependent on the liquid superheat Δp and T_0.

$$\phi \sim T_0,\ \Delta p$$

The averaged value of ϕ for all the wall nuclei in the vessel should not depend on the rate of pressure release in the vessel, but only on the pressure and temperature at the positions where nucleation is most dominant; in this case where the pressure is a minimum. For very rapid discharges, the temperature of the liquid at this point varies little from the initial temperature. Hence

$$\phi \sim T_0, p_{min}$$

For both the water and the freon test, p_{min} shows a close correlation with T_0

$$p_{min} \sim T_0$$

therefore ϕ should only be a function of T_0

$$\phi = \phi(T_0)$$

or in reduced temperature

$$\phi = \phi(T_0/T_c)$$

The correlation of ϕ with T_0/T_c suggests that very fast discharges ($> 2000\, bar/s$) provide a robust method of attempting to quantify the heterogeneous nucleation factor. Since T_l hardly changes from T_0 during the nucleation process, the functional relation of ϕ with T_l may be of value of modeling non-equilibrium two-phase flows in which nucleation is known to play an important role.

3.2.5 Numerical simulations for BLEVE stage

In the study of van den Berg *et al.* [33], [34], a new method is presented to calculate the blast effects originating from an exploding vessel of liquefied gas.

A safe assumption they made on the vapour source strength or the flash-evaporation rate is that the evaporation process is **expansion-controlled**[**]. In such cases, the vapor pressure of a flashing liquid is imposed as the boundary condition for the gas dynamics of expansion.

An acoustic blast model was developed from the solution of the wave equation. With the assumption of linearly growing liquid release rate, the blast overpressure can be computed from

- a volume source in a half-space[††]:

$$\frac{\Delta p}{p_0} = \frac{\gamma}{2\pi r c_0^2} \frac{2V\chi\varphi}{(\Delta t)^2}$$

- a volume source in a tube:

$$\frac{\Delta p}{p_0} = \frac{\gamma}{2Ac_0} \frac{V\chi\varphi}{\Delta t}$$

where Δp is the wave overpressure; p_0 is the ambient pressure; c_0 is the ambient speed of sound; A is the cross-sectional area of the tube; V is the volume of the liquefied gas; χ is the flash fraction and φ is the liquid-to-vapour expansion factor; r is the distance from source; t is time.

The computational results from various release times indicate **the magnitue and duration of the blast effect** from a collapsing vessel of liquefied gas is highly dependent on the release time and thereby on the exact rupture mode of the vessel and the consequent liquid release development. The authors remark that any experimental observations on BLEVE blast effects can only make any sense if the rupture mode of the vessels used and the consequent release scenario can be controlled and are fully repeatable. The modelling showed that the rupture of a pressure vessel containing a liquefied gas in free space develops blast of a significant strength only if the vessel nearly instantaneously disintegrates. The blast effects could be minor if the crack and the consequent release of a vessel take just a fraction of a second, i.e., $0.5s$.

The gas dynamics of the expanding vapour and the sourrounding atmosphere was further computed by numerically solving the Euler equations and

- if the rupture of the vessel and the subsequent liquid release are nearly instantaneous, the boundary conditions consists in the vapour pressure of the superheated liquid;

[**] It means that intrinsically the evaporation of superheated liquid can occur infinitely fast, therefore extrinsic circumstances including the liquid release rate and the gas dynamics (inertia) of the vapour and the surrounding air will determine the evaporation rate.

[††] In [33], $(\varphi - 1)$ replaces φ in all these equations.

- if the failure of the vessel is not instantaneous, a steady release rate of liquid is assumed over some span of time. The boundary condition consist in the steady vapour mass flow for the duration of the release time.

The results from one-dimensional gas dynamic model indicate

- The shorter the release time, the higher the blast wave overpressure and the earlier the decay process sets in. For longer release times, the gas dynamic solution approximates the acoustic volume source results quite well;
- The strong blast wave emitted particularly in the vessel's lateral directions, which successively reflects at both tunnel walls and overtakes the leading shock wave while propagating down the tunnel;
- The tunnel structure in the direct vicinity of the BLEVE is loaded with approximately the full vapour pressure of the flashing liquid. Downstream, the blast overpressure quickly decreases as a consequence of the intense energy dissipation in the strong shock phenomena.

‡

In 2004, Pinhasi, Dayan and Ullmann developed a new numerical model, consisting of EVUT (equal velocities unequal temperatures) model for the two-phase domain and one-dimensional unsteady compressible flow equations for the air domain, in order to investigate the thermodynamic and the dynamic state of the BLEVE stage [21].

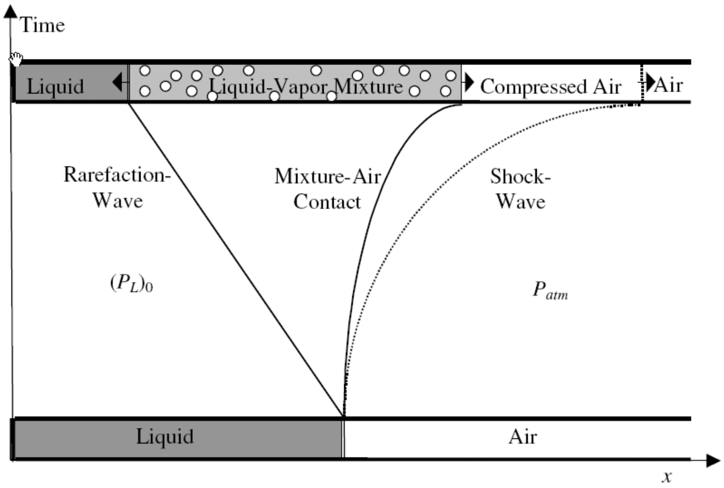

Figure 3.10: Typical wave action in the $x - t$ plane following BLEVE

The hyperbolic and non-linear equations of motion were solved by the method of characteristics. This model allows calculation of

- Bubble nucleation and growth processes in the liquid
- Front velocity of the expanding liquid
- Shock wave pressure formed by the liquid expansion through the air

In this study, the computational results have been compared with two exact solutions for shock tubes under two different pressure ratios, $p_L/p_R = 10$ and $p_L/p_R = 100$.

For the case of the pressure ratio equal to 10, the results match the exact solution quite well in Fig.(3.11). Slight deviations were observed in the velocity of sound and Mach number in the case of the pressure ratio equal to 100 in Fig.(3.12), which has been reasoned that due to the homotropic flow assumption in the exact solution, in contrast to the isentropic assumption of the numerical model.

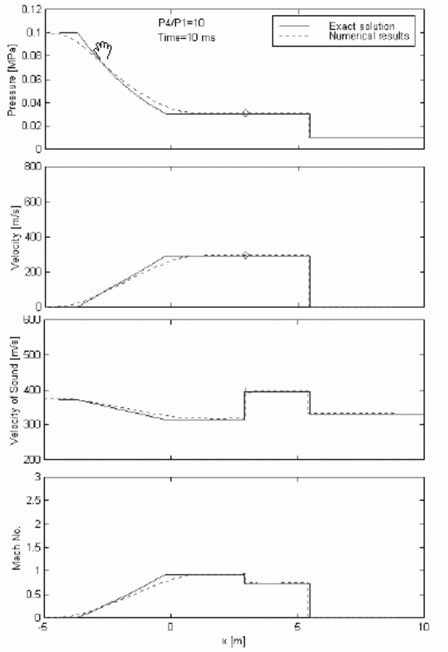

Figure 3.11: Profile of the flow properties for test case $p_L/p_R = 10$ at time $t = 10\,ms$

Velocity, pressure, velocity of sound and Mach number have been computed using this model for initial temperature ranging from 0.7 to 0.95 respectively. The initial bubble number density n_b^0 are chosen to be (i) a value to support the pressure-undershoot predicted by the pressure-undershoot model for relative low initial superheat [11]; or (ii) the

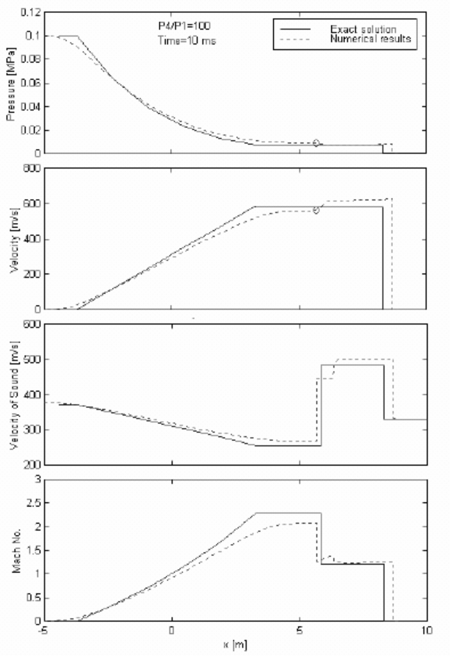

Figure 3.12: Profile of the flow properties for test case $p_L/p_R = 100$ at time $t = 10\,ms$

maximum level $10^{12}\,m^{-3}s^{-1}$ [32] for high superheats closing to the superheat limit. The computation results indicates that

- For the relative low initial temperature $T_0/T_c = 0.75$, the depressurization is characterized by rapid boiling.

- The shock wave formation was found to occur at temperature higher than $T_0/T_c = 0.90$ and shortly after formation, the shock strength increases rapidly with time and thereafter increases gradually.

- The formation of the shock at $T_0/T_c = 0.90$ occurs after $\sim 1.5\,ms$ and begins slightly earlier at higher initial temperatures. Nonetheless its inception begins essentially after a period of approx. $0.5\,ms$ (necessary for the material particles acceleration).

The comparison between Pinhasi *et. al* 2004 model and the TNT equivalence model indicates that the simple energy model tends to **over-estimate the BLEVE consequences**. The majot reason for this discrepancy lies in the difference of teh vapor formation mechanism. In the energy model, the liquid is assmued to flash instantaneously and the entire vapor is formed prior to the expansion. However in the actual case, there is a process of vapor formation during expansion.

3.2.6 Open questions in BLEVE stage

The goal of research in BLEVE stage in our project is to quantitatively describe how the bubble nucleation/vaporization proceeds in the real BLEVE stage.

In the lab-scale experiments, we can use the vessel of polished inner wall and purified liquid to suppress the heterogeneous nucleation. But we can not do that in a real-scale BLEVE event. The difference between the lab-scale experiments and the real-scale BLEVE event is not only the length scales, but also the volume density of the heterogeneous sites, the relative ratios between various length scales etc. We can research various bubble nucleation/vaporization in the lab, but for the engineering computation, we must either include all the possibilities or use a smart average to weight all the possibilities.

Simply to say, we must be able to mathematically describe all the possible bubble nucleation/vaporization for a real BLEVE event, including the onset condition, the nucleation rate and the vaporization rate. This is the most tricky and challenging problem in our project.

3.3 Post-BLEVE stage

The post-BLEVE stage, accordig to our definition, is an optional stage of a BLEVE event. Due to the flammability of most PLG stored in commercial tanks, it is frenquently occurring in a BLEVE event. Therefore the chemical explosion in post-BLEVE stage has been widely researched and many BLEVE-related studies are often involving fires in different formats, including pool fire, jetting fire, fireball etc.

To intepret the chemical explosion in post-BLEVE stage, we must be able to quantitively describe the status of the two-phase PLG and the ambient air before the chemical reation commences. All these are based on a clear and definitive understanding the rapid expansion of the highly superheated liquid in pre-BLEVE and BLEVE stages. In our project, we will mainly concentrate on pre-BLEVE and BLEVE stage of the BLEVE event and leave the post-BLEVE stage for future studies.

3.4 Summary

Chapter 4

Equations and models for two-phase flow

In this chapter, we will summarize the conservative equations and constitutive models for two-phase flow and bubble vaporization.

The traditional conservative equations have two simplified formats for two-phase flow, EVET (equal velocity and equal temperature) and EVUT (equal velocity and unequal temperature) models. The latter have been widely used in the numerical simulation of two-phase flows.

The bubble vaporization in two-phase flow is a process of mass and heat transfer, therefore the source terms in the continuity, momentum and energy equations need to be described by constitutive models which include the the mass transfer rate at the interface, interfacial friction, wall friction, interfacial heat transfer and wall heat transfer into the liquid and the vapor phase, respectively.

The reference in this paper includes: [4], [8], [15], [17], [20], [21], [22], [32], [33] and [34].

4.1 Conservative equations

In rapid expansion phenomena, viscous and heat diffusion are relatively slow processes that entail negligibel effects. Neglecting viscous and axial heat flux terms, the conservation equations for the flow are therefore:

$$\frac{\partial}{\partial t}(\alpha_k\rho_k) + \frac{1}{A}\frac{\partial}{\partial x}(A\alpha_k\rho_k u_k) = \Gamma_{i,k} \tag{4.1}$$

$$\begin{aligned}\frac{\partial}{\partial t}(\alpha_k\rho_k u_k) + \frac{1}{A}\frac{\partial}{\partial x}(A\alpha_k\rho_k u_k^2) + \alpha_k\frac{\partial p_k}{\partial x}\\ = \Gamma_{i,k}u_k - f_{i,k} - f_{w,k} - \alpha_k\rho_k g\frac{\partial Z}{\partial x}\end{aligned} \tag{4.2}$$

$$\begin{aligned}\frac{\partial}{\partial t}\Big[\alpha_k\rho_k\Big(h_k + \frac{1}{2}u_k^2\Big)\Big] + \frac{1}{A}\frac{\partial}{\partial x}\Big[A\alpha_k\rho_k u_k\Big(h_k + \frac{1}{2}u_k^2\Big)\Big] - \alpha_k\frac{\partial p_k}{\partial t}\\ = \dot{q}_{i,k} + \dot{q}_{w,k} + f_{i,k}u_k + \Gamma_{i,k}\Big(h_k + \frac{1}{2}u_k^2\Big) - \alpha_k\rho_k u_k g\frac{\partial Z}{\partial x}\end{aligned} \tag{4.3}$$

In these equations, the subscript k (l or v) denotes the phase (liquid or vapor, respectively). The source terms $\Gamma_{i,k}$, $f_{i,k}$, $f_{w,k}$, $\dot{q}_{i,k}$ and $\dot{q}_{w,k}$ are the mass transfer rate at the interface, interfacial friction, wall friction, interfacial heat transfer and wall heat transfer into phase k per unit volume, respectively. Likewise, A is the cross-section area of the duct, Z is the elevation and x is the space independent variables.

The summation of the liquid and gaseous volume fractions equals by definition unity ($\alpha_l + \alpha_v = 1$). It is assumed that gravity is the only influential external force. For conservation of mass, momentum and energy at any two-phase interface, the following relations must hold:

$$\Gamma_{i,v} + \Gamma_{i,l} = 0 \tag{4.4}$$

$$\Gamma_{i,v}u_v - f_{i,v} + \Gamma_{i,l}u_l - f_{i,l} = 0 \tag{4.5}$$

$$\dot{q}_{i,v} + f_{i,v}u_v + \Gamma_{i,v}\Big(h_v + \frac{1}{2}u_v^2\Big) + \dot{q}_{i,l} + f_{i,l}u_{i,l} + \Gamma_{i,l}\Big(h_l + \frac{1}{2}u_l^2\Big) = 0 \tag{4.6}$$

4.1.1 Simplified conservative equations: EVET model

The EVET model is based on the assumptions that the phases are of equal local pressures (i.e. $p_l = p_v = p$), equal temperatures (i.e. $T_v = T_l = T$), and no slip conditions ($u_v = u_l = u$ and $f_{i,k} = 0$). According to these assumptions, the one-dimensional conservation equations reduce to (similar to single phase equations) [22]:

$$\begin{aligned}
\frac{\partial \rho_m}{\partial t} + \frac{\partial}{\partial x}(\rho_m u) &= -\rho_m u \frac{1}{A}\frac{dA}{dx} && (4.7)\\
\rho_m \frac{\partial u}{\partial t} + \rho_m u \frac{\partial u}{\partial x} + \frac{\partial p}{\partial x} &= -f_w - \rho_m g \frac{\partial Z}{\partial x} && (4.8)\\
\rho_m \frac{\partial h_m}{\partial t} + \rho_m u \frac{\partial h_m}{\partial x} - \frac{\partial p}{\partial t} - u\frac{\partial p}{\partial x} &= \dot{q}_w + f_w u && (4.9)
\end{aligned}$$

where the mixture density and the mixture enthalpy are

$$\begin{aligned}
\rho_m &= \alpha_l \rho_l + \alpha_v \rho_v && (4.10)\\
h_m &= \frac{\alpha_l \rho_l h_l + \alpha_v \rho_v \rho_v h_v}{\rho_m} && (4.11)
\end{aligned}$$

To complete the sef of governing equations, the thermal and equations of states for saturated fluid conditions are introduced:

$$\rho_k = \rho_{k,sat}(p), \quad h_k = h_{k,sat}(p) \tag{4.12}$$

4.1.2 Simplified conservative equations: EVUT model

The EVUT (equal velocity, unequal temperature) model is the simplest way of describing the sudden depressurization of an initially subcooled or saturated liquid contained in a vessel. For EVUT model, the existence of equal local pressure between phases (i.e. $p_l = p_v = p$) and no slip conditions (i.e. $u_l = u_v = u$ and $f_{i,k} = 0$) are assumed and the temperature difference between two phases is allowed.

The EVUT model in Pinhasi *et al.* [21] and [22] reads

$$\begin{aligned}
\frac{\partial}{\partial t}(\alpha_k \rho_k) + \frac{\partial}{\partial x}(\alpha_k \rho_k u) &= \Gamma_{i,k} - \alpha_k \rho_k u \frac{1}{A}\frac{dA}{dx} && (4.13)\\
\rho_m \frac{\partial u}{\partial t} + \rho_m u \frac{\partial u}{\partial x} + \frac{\partial p}{\partial x} &= -(f_{w,l} + f_{w,v}) - \rho_m g \frac{dZ}{dx} && (4.14)\\
\alpha_k \rho_k \frac{\partial h_k}{\partial t} + \alpha_k \rho_k u \frac{\partial h_k}{\partial x} + \alpha_k \frac{\partial p}{\partial t} - \alpha_k u \frac{\partial p}{\partial x} &= \dot{q}_{i,k} + \dot{q}_{w,k} + f_{w,k} u && (4.15)
\end{aligned}$$

The mixture density is given by $\rho_m = \alpha_v \rho_v + \alpha_l \rho_l$ and the set of equations is subject to the thermodynamic state equation of each phase: $\rho_k = \rho_k(p, h_k)$.

‡

The EVUT model in Deligiannis & Cleaver [8] is

$$\frac{\partial}{\partial t}(\alpha_k\rho_k)+\frac{1}{A}\frac{\partial}{\partial x}(A\alpha_k\rho_k u)=\Gamma_{i,k}+\Gamma_{NU} \tag{4.16}$$

$$\begin{aligned}\frac{\partial}{\partial t}(\alpha_k\rho_k u)+\frac{1}{A}\frac{\partial}{\partial x}(A\alpha_k\rho_k u^2)+\alpha_k\frac{\partial p}{\partial x} &= \Gamma_{i,k}u-f_{i,k}-f_{w,k}\\ &\quad -\alpha_k\rho_k g\frac{\partial Z}{\partial x}+\Gamma_{NU}u \end{aligned} \tag{4.17}$$

$$\begin{aligned}&\frac{\partial}{\partial t}\Big[\alpha_k\rho_k\Big(h_k+\frac{u^2}{2}\Big)\Big]+\frac{1}{A}\frac{\partial}{\partial x}\Big[A\alpha_k\rho_k u\Big(h_k+\frac{u^2}{2}\Big)\Big]-\alpha_k\frac{\partial p}{\partial t}\\ &=\dot{q}_{i,k}+\dot{q}_{w,k}+f_{i,k}u+\Gamma_{ik}\Big(h_k+\frac{u^2}{2}\Big)_i-\alpha_k\rho_k u g\frac{\partial Z}{\partial x}+BCE\end{aligned} \tag{4.18}$$

The subscript w, i and NU denote transfer from the wall, the interface and the nucleation, respectively. BCE is the energy per unit volume transferred to the vapor when the liquid flashes.

4.2 Constitutive models

Constitutive equations for wall and interfacial heat and mass transfer must be provided for closure of the conservation equations for two-phase flow.

4.2.1 Interfacial source terms

According to [21] and [22], the interfacial mass and heat transfer have below relations.

$$\Gamma_{i,v}h_{LG} = \dot{q}_{i,net} \tag{4.19}$$

$$\dot{q}_{i,net} = \tilde{A}_i\dot{q}''_{i,net} \tag{4.20}$$

$$\Gamma_{i,v} = \tilde{A}_i\Gamma''_{i,net} \tag{4.21}$$

where $\dot{q}''_{i,net}$ and $\Gamma''_{i,net}$ are the interfacial transfer rate per square meter for heat and mass, respectively; $\tilde{A}_i$, the interfacial area density, is defined to be the interfacial area per unit volume. If the bubbles are assumed to be spherical and having the similar diameters, $\tilde{A}_i$ can be expressed to be

$$\tilde{A}_i = 4\pi R^2 n_b \tag{4.22}$$

where n_b is the number density of nucleation sites. Also the void fraction can be written as

$$\alpha_v = \frac{4}{3}\pi R^3 n_b \tag{4.23}$$

The bubble growth is assumed to be heat diffusion controlled. Therefore the heat supply to the bubble interface can be expressed as

$$q''_{i,net} = \hat{h}[T_l - T_{sat}(p_l)] \tag{4.24}$$

The heat transfer coefficient $\hat{h}$ can be derived from solutions for the diffusion rate of heat transport from a liquid at constant superheat state to a bubble interface, which is

$$\hat{h} = \frac{k_l Nu}{2R_b} \tag{4.25}$$

in which the Nusselt number is a function of the Jacob number,

$$Nu = \frac{12}{\pi}\left[1 + \frac{1}{2}\left(\frac{\pi}{6Ja}\right)^{2/3} + \frac{\pi}{6Ja}\right] \tag{4.26}$$

$$Ja = \frac{c_{p,l}\rho_l(T_l - T_{sat})}{\rho_v h_{LG}} \tag{4.27}$$

The unknowns in above equations are R, n_b and $\Gamma''_{i,net}$. If the void fraction can be solved from the two-phase EVUT model, at least one more equation is needed to solve the interfacial source terms.

In Pinhasi *et al.* [21], the net inerfacial mass transfer flux (or the net evaporation rate) is given [see [32]]

$$\Gamma''_{i,net} = \frac{p_{sat} - p_v}{\sqrt{2\pi m_m k_B T}} \tag{4.28}$$

In Pinhasi *et al.* [22], a bubble breakup model is developed for solving the number density of the bubbles n_b.

‡

A new model for the interfacial heat transfer was developed in term of the bubble number density and the void fraction [8]

$$\dot{q}_i = 3.9 n_b^{2/3} \alpha_v^{1/3} \cdot Nu \cdot k_l \cdot (T_i - T_k) \tag{4.29}$$

where subscript k denotes liquid or vapor, respectively. Instead of arbitrarily assuming constant number density and bubble radius, they use a transport equation for the number density of bubbles n_b for one-dimensional flow

$$\frac{\partial n_b}{\partial t} + u\frac{\partial n_b}{\partial z} + n_b\frac{\partial u}{\partial z} = H_{HOM} + H_{HET} - H_{COAL} \tag{4.30}$$

In most experimental studies the temperature difference is less than the superheat for homogeneous nucleation. Bubble generation does not occur in the bulk of the liquid but mainly on the walls of the container or on impurities in the liquid. Therefore, H_{HOM} can be considered negligible small. At the beginning of a depressurization H_{COAL} might also be considered small. Hence the nucleation rate is mainly dependent on heterogeneous nucleation rate, given by Blander and Katz [4].

$$H_{HET} = N^{2/3}\frac{(1-m)}{2}\Big(\frac{2\sigma N_A}{\pi \cdot m_m \cdot B \cdot \phi}\Big)^{1/2} \exp\Big(\frac{-W^*_{min} \cdot \phi}{k_B T_l}\Big) \tag{4.31}$$

where N is the number of molecules per unit volume; B is equal to 2/3 in this study; $m = (\sigma_{sl} - \sigma_{sv})/\sigma_{lv}$ where σ_{sl}, σ_{sv} and σ_{lv} are the surface tensions between liquid and solid, vapor and solid, and vapor and liquid, respectively.

ϕ is the heterogeneous factor, < 1, which physically implies that the molecular clusters formed on a rough surface or suspended particles need less energy to survive. Bubbles formed in this manner assume a shape bounded by a plane and a portion of spherical surface. ξ is the contact angle at the bubble surface. Blander and Katz [4] show that ϕ and ξ are linked by

$$\phi = \frac{2 - 3cos\xi + (cos\xi)^3}{4} \tag{4.32}$$

4.2.2 Wall source terms

The source terms between the wall and the two-phase flow are descibed by following models in [20]. The term for the channel wall heat transfer, $\dot{q}_{w,k}$ to the vapor ($k = v$) or liquid ($k = l$) is connected to the void fraction as

$$\dot{q}_{w,k} = \alpha_k \dot{q}_w \tag{4.33}$$

The total heat flux $\dot{q}_w$ must be supplie as input the program as a function of the position x along the channel. For adiabatic flow conditions there is not external heat input, thus $q_w = 0$.

For single-phase liquid flow, the wall friction per unit volume of the mixture is

$$f_{w,k}^{1ph} = \alpha_k \rho_k f_w \frac{\psi}{A} = \frac{1}{2} \alpha_k \rho_k u^2 C_f \frac{4}{D} \tag{4.34}$$

where ψ is the duct perimeter (for a pipe $\psi = \pi D$); C_f is the friction coefficient.

For two-phase flow, a friction multiplier, η^2, is incorporated so that

$$f_{w,k}^{2ph} = \alpha_k \rho_k f_w \frac{\psi}{A} = f_{w,k}^{1ph} \cdot \left(\eta^2 \frac{\rho_m}{\rho_l} \right) \tag{4.35}$$

The friction coefficient C_f dependence on the Reynolds is

$$C_f = \left\{ \begin{array}{ll} 16/Re_D & Re_D < Re_{D,cr} \\ 0.046/Re_D & Re_D > Re_{D,cr} \end{array} \right. \tag{4.36}$$

where the critical Reynolds for laminar-turbulence transition, $Re_{D,cr} = 1462.27$.

The two-phase friction multipliers equations adopted in term of quality, χ, are

$$\begin{array}{cl} \alpha_v < 0.3 & \eta^2 = \left[1 + \chi\left(\frac{\rho_l}{\rho_v} - 1\right)\right]^{0.8} \left\{1 + \chi\left[\frac{(3.5\mu_v + 2\mu_l)\rho_l}{(\mu_l + \mu_v)\rho_v} - 1\right]\right\}^{0.2} \\ 0.3 < \alpha_v < 0.8 & \eta^2 = \left[1 + \chi\left(\frac{\rho_l}{\rho_v} - 1\right)\right]^{0.8} \left\{1 + \chi\left[3.5\frac{\rho_l}{\rho_v} - 1\right]\right\}^{0.2} \\ 0.8 < \alpha_v < 0.95 & \eta^2 = \left[1 + \chi\left(\frac{\rho_l}{\rho_v} - 1\right)\right]^{0.8} \left\{1 + \chi\left[\frac{\mu_l \rho_l}{\mu_v \rho_v} - 1\right]\right\}^{0.2} \\ \alpha_v > 0.95 & \eta^2 = \left[1 + \chi\left(\frac{\rho_l}{\rho_v} - 1\right)\right]^{1.8} \left(\frac{\mu_v}{\mu_l}\right)^{0.2} \left(\frac{\rho_v}{\rho_l}\right)^{0.8} \end{array} \tag{4.37}$$

For homogeneous flow, the flash quality $\chi = \alpha_v \rho_v / \rho_m$.

4.3 Specific models

4.3.1 Acoustic volume source term

In the study of van den Berg *et. al* [33] and [34], they derive a volume source term for gas explosion using the acoustic volume source [17] as an analogue.

- a volume source in a half-space:

$$\frac{\Delta p}{p_0} = \frac{\gamma}{2\pi r c_\infty^2} \frac{d\Phi}{dt}$$

- a volume source in a tube:

$$\frac{\Delta p}{p_0} = \frac{\gamma}{2Ac_\infty}\Phi$$

where Φ is the volume source strength, γ is the ratio of specific heats and c_∞ is the ambient speed of sound. A striking feature is that a steady release of superheated liquid in three-dimensional space does not give rise to any overpressure while it does give rise to blast in a tube.

With the assumption of linearly growing liquid release rate, the blast overpressure in a half-space can be computed from

$$\frac{\Delta p}{p_0} = \frac{\gamma}{2\pi r c_\infty^2}\frac{2V\chi\varphi}{(\Delta t^2)} \tag{4.38}$$

and the blast overpressure in a tunnel tube can be computed from

$$\frac{\Delta p}{p_0} = \frac{\gamma}{2Ac_\infty}\frac{V\chi\varphi}{\Delta t} \tag{4.39}$$

in which a flash fraction $\chi = 50\%$ and a liquid-to-vapor expansion factor $\varphi = 260$ are approximated for propane.

4.3.2 Crack opening and choked flow

In 1996, Lenclud and Venart established a model for the observed crack propagation and opening on pressure tanks [15]. Crack lengths are obtained from high speed cinematography. Crack widths are assumed to be the sum of two components, an elastic displacement and a plastic displacement.

The elastic displacement Δ is derived as a function of the crack length and the internal pressure from LEFM, *Linear Elastic Fracture Mechanism*, using crack opening displacement theory.

To introduce plastic displacement into the mode, they made two assumptions:

- the crack shape after the vent is elliptical;
- the shape aspect ratio C, i.e. the ratio of the length a to the plastic deformation width w, is constant over time.

As a result, half the actual crack width is the sum of the elastic and plastic components:

$$b = \frac{a}{C} + \frac{\Delta}{2}$$

and the crack area is then:

$$A_{crk} = \pi a^2 \Big(\frac{1}{C} + \frac{\Delta}{2a}\Big)$$

The crack length extension can be inferred to be a double step process, each of which proceeds at constant velocity:

$$\begin{array}{rrcl} 0 < t < t_1 & 2a & = & u_1 t \\ t_1 \le t < t_{Af} & 2a & = & u_2 t + C_2 \\ t \ge t_{Af} & 2a & = & 2l_f \end{array}$$

in which t_{Af} is the timing of final crack length and $2l_f$ is the final crack length and the values of u_1, t_1, u_2 and C_2 are determined by high speed cinematography. Therefore the model for crack area as a function of time and internal pressure can be derived.

A choked flow model is first presented in this study in which a time-varying area and a discharge coefficient are introduced. The establishment of choked flow is assumed instantaneous, the flow here is considered to be choked during the whole process, the process is considered isentropic and the gas perfect.

The equation for internal pressure is

$$p = p_0 \Bigg\{ \Big(\frac{p'}{p_0}\Big)^{-(\gamma-1)/(2\gamma)} + \frac{\gamma-1}{2}\Big(\frac{2}{\gamma+1}\Big)^{0.5(\gamma+1)/(\gamma-1)} + \frac{C_D A'_{crk} \Delta t}{V_v}\sqrt{\frac{\gamma p_0}{\rho_0}} \Bigg\}^{-2\gamma/(\gamma-1)} \tag{4.40}$$

in which p_0 and ρ_0 are the initial density and pressure of the gas, respectively. p' and A'_{crk} represent the pressure of the gas and the crack area at previous moment, respectively. C_D is the discharge coefficient. Δt is the time step. V_v is the volume of the gas.

4.3.3 Bubble breakup model

The conservation equation for the bubbel number density n_B is given in Pinhasi *et al.* [22]:

$$\frac{\partial n_b}{\partial t} + \frac{\partial}{\partial z}(n_b u) = \psi \tag{4.41}$$

where ψ is the intensity of the bubble breakup, given by the Kelvin-helmholtz and Rayleigh-Taylor instabilities respectively.

4.3.4 Slip velocity model

To calculate the Kelvin-Helmholtz instability criterion for bubbles, one must know the bubble dimension, the mixture properties and the difference between the phase velocities (the wlip velocity).

If the wlip velocity between phases is much smaller than the flow average velocity, $|u_v - u_l| \ll |u|$, one can write the material derivatives as $D_v/Dt \simeq D_l/Dt$ and the vapor equation of motion is

$$2\frac{\rho_v}{\rho_l}\frac{Du_v}{Dt} - 3\frac{Du_l}{Dt} + \frac{D(\Delta u)}{Dt} + (\Delta u)\frac{1}{V_b}\frac{DV_b}{Dt} = \frac{1}{V_b}\frac{\Gamma}{\rho_l}(\Delta u) - \frac{2}{\rho_l V_b} f_D \qquad (4.42)$$

in which u_l and u_v are the velocities for liquid and vapor, respectively, $\Delta u = u_v - u_l$; Γ is the evaporation rate; V_b is the bubble volume and f_D is the drag force on a bubble.

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