From Gases and Evaporators risk assessmeNt towards an Integrated management of sea and land pollution incidentS

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T.2.2.1 / D2.2 – LITERATURE SURVEY ON RAPID PHASE TRANSITION

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1. Introduction

The marine industry is on the cusp of a major energy revolution with the introduction of new propulsion fuels for ships. These innovative fuels offer a cleaner, more sustainable alternative to traditional fuel oils, in response to growing environmental concerns and increasingly stringent international regulations. The maritime sector is responsible for around 2.5% of global greenhouse gas (GHG) emissions. To reduce these GHG emissions, the International Maritime Organization (IMO) has set targets to reduce the carbon impact of ships by 40% by 2030 and 70% by 2040, compared with 2008 levels. These drastic reductions are driving the development of new alternative technologies to use more environmentally-friendly fuels. The development of alternative fuels for ship propulsion, such as ammonia, methanol and hydrogen, offers promising prospects for reducing these greenhouse gas emissions. However, the use of these new ship propulsion fuels is not without risks. Ammonia is considered a promising fuel because it is carbon-free, which means it does not produce CO_2 during combustion. However, ammonia is extremely toxic to humans and marine organisms. A leak or spill could lead to serious health consequences and significant environmental damage. With regard to the risks associated with handling and storage, ammonia is stored under high pressure or at low temperature, which requires specific infrastructures with a high probability of explosion and fire. Methanol is another interesting alternative fuel, but it is also a highly flammable and explosive product, which poses safety risks on board ships. Although less toxic than ammonia, methanol is nonetheless toxic to humans and marine life. Prolonged exposure or major spills can have harmful effects on health and the environment. As for hydrogen, this fuel is often presented as the ultimate solution because of its clean combustion, producing only water. However, its use in the marine sector is complex and involves storage issues. Hydrogen is a compressed gas at very high pressure or in liquid form at extremely low temperatures, it is also extremely flammable and can form explosive mixtures with air.

Attention to the environment and the impact of shipping on climate change has encouraged the development of alternative solutions for ship propulsion fuels. While the previous cited products are promising, natural gas (LNG) stands out as a fuel that is already being used by ships (Chen et al., 2018). However, the widespread use of LNG raises significant concerns about the risks and consequences of potential spills into the marine environment. Low-temperature storage conditions coupled with a limited understanding of the physical-chemical models that describe the behavior of these substances when released into the environment, and the likelihood of unconventional accidental scenarios, inevitably lead to considerable concern among authorities and response services (Aursand and Hammer, 2018). In the event of an accidental release of LNG or other low-temperature refrigerated substances into water (e.g. ammonia, hydrogen, ...), the mixing between the two fluids and the temperature difference between the nucleation point of the mixture and ambient temperature can lead to very rapid evaporation rates. This rapid phase change (from liquid to vapor) is known as a rapid phase transition (RPT), and can lead to vapor cloud explosions and potentially the

formation of shock waves (Bariha et al., 2017, Bubbico and Salzano, 2009). Several examples of industrial accidents and large-scale tests have been reported in the literature (Cleaver et al., 2007; Sun et al., 2017).

Such scenarios raise significant concerns, particularly in onshore or port facilities, where congested areas may increase local turbulence phenomena that potentially lead to catastrophic explosions, as shown by the Beirut explosion in 2020. This clearly highlights the risks associated with bunkering procedures (Sun et al., 2017). While the risks associated with dispersing and igniting a cloud of LNG, ammonia or hydrogen are well understood, the phenomenon known as rapid phase transition (RPT), as defined by Reid, 1983, remains a major concern (Luketa-Hanlin, 2006; Shaw et al., 2005; Pitblado and Woodward, 2011; Cleaver et al., 2007, Alderman, 2005; Hightower et al., 2005; Havens and Spicer, 2007; Raj and Bowdoin, 2010; Forte and Ruf, 2017). Assessing the conditions of occurrence and the risks associated with RPT in the event of an LNG spill in water is crucial for maritime LNG operations, whether during transport or use. This assessment is essential for preparing response services and improving accident management. However, Bubbico and Salzano, 2009 explained in their study that the conditions that allow real explosive evaporation to occur are still not well understood. Furthermore, the intensity of the blast wave and its propagation in the surrounding atmosphere, knowledge of which is essential for risk assessment of large-scale facilities, are not easily predictable. This is because the total energy involved in the explosion and the maximum overpressure at the 'source term' depend on numerous factors such as the release rate, the location of the source (above or below sea level), external environmental conditions, the composition of the LNG, the water temperature and the impact velocity of the LNG on the water surface. Bubbico and Salzano, 2009 have developed an acoustic model to define the total energy produced by the RPT of LNG and the explosion overpressure. The results obtained by the authors were compared with the findings of a recent report by Sandia National Laboratory (Sandia, 2004), which re-examined LNG hazards with a focus on ship-to-water spills, and found that:

(i) The overpressures that can be reached by RPT explosions for very large spills (100 $m^3.min^{-1}$) and the possible upper limits of damage to structures have not been assessed;

(ii) The greatest impact of an accidental release on public safety and property occurs within a radius of around 250 m from the spill, and for an intentional release, within a radius of around 500 m from the spill. The results of the comparison obtained by Bubbico and Salzano, 2009 can be used to define exclusion zones, for the protection of people and property along the transit route, even for land-based spills, and for the impact on the public.

The following videos illustrate the risks associated with the RPT phenomenon. The first video deals with experimental tests carried out by Gaz de France in Lorient (France) between 1982 and 1984 (https://youtu.be/h-EY82cVKuA?si=BWFirFv7iSD6qvMW). This video clearly shows the explosion phenomena when LNG is spilled into water. The second video, produced at the Falck Fire Academy (Netherlands), demonstrates the risks associated with extinguishing an LNG fire spilled on the ground. It shows the successive

appearance of explosions and fireballs when extinguishing products are sprayed on the burning LNG slick (https://youtu.be/dCZInpwqzNc?si=IDEIOyuxnLdnF22Y).

The remainder of this document will focus on LNG, as it is currently the most widely transported product in maritime transport and, therefore, the most studied and documented regarding the consequences of RPT.

2. Review of RPT incidents involving LNG spills on water

This section reviews the analysis carried out by Nédelka et al, 2003, which describes RPT incidents involving LNG spills in water. It is important to note that it is difficult to find accounts of this type of accident in the scientific literature. The RPT incidents presented here occurred either during the operation of an LNG plant, or during experimental programs that were not intended to produce RPT events. This list is not intended to be exhaustive, but it does demonstrate the relevance of concerns about RPTs between LNG and water by showing that RPTs can occur in real-life situations and not just in experiments specifically developed to study the RPT phenomenon.

2.1. RPT events during LNG plant operation

Canvey, England, May 1973: RPTs after discharge pipe rupture

During a normal LNG carrier unloading operation, a 100 mm bursting disk on a 350 mm discharge pipe broke. The LNG spilled into one of the LNG tanks, where water had accumulated following recent rainfall. Three explosions were heard, but the only damage was a broken window in an adjacent building.

Arzew, Algeria, March 1977: RPTs after valve rupture

The rupture of an aluminium valve resulted in the release of several thousand cubic meters of LNG over a period of 10 hours. The leak occurred on the ground near a frozen earth tank, the LNG slick spread over the sea and several RPTs were observed. Shock waves and/or projectiles shattered a number of adjacent windows.

Badak, Indonesia, December 1992: LNG leak in the drainage system

An LNG leak occurred during the start-up of a liquefaction train; it was decided to continue operating the train despite the leak. Protective water curtains were deployed to reduce the effects of the vapor cloud generated. Approximately 11 hours after plant start-up, RPTs occurred in a drainage channel lined with a concrete slab. The drainage channel and concrete slab were broken, the adjacent pipe was damaged and concrete

blocks were projected over a distance of around 100 m. No staff member was injured, as the area was evacuated due to the leak.

Fos-sur-Mer, France, September 1995: RPT during an extinguisher demonstration

During a demonstration of the use of a truck-mounted dry powder extinguisher to extinguish a fire in a 25 m^2 LNG tank, an RPT was caused when the contents of a puddle of water were projected into the LNG tank by the flow of the extinguisher. A fireball was produced by the massive increase in the rate of vaporization, doubling the size of the flame for a few seconds. The demonstration continued and the fire was successfully extinguished.

Montoir terminal, France, October 1995: RPT resulting from a vaporizer leak

A leak occurred in the packing gland of a high-pressure valve located at the top of a waterfall film vaporizer unit. The water flowed out of the vaporizer tubes into a basin, where it is normally collected and returned to the river. The leaking LNG was under high pressure (around 100 bars) and came into contact with the water. An RPT occurred, followed by a number of minor accidents.

2.2. RPT events during experimental programs

Nantes, France, 1971: RPT during gas dispersion tests

During an LNG vapor dispersion test at GDF's Nantes test facility, LNG was released onto a layer of water thickness of 100 mm. The LNG was released from a 3 m^3 peak tank. Several RPTs were observed several seconds after the LNG was released. As a result, the structure designed to retain the water and LNG was broken, the stainless-steel tank was bent and ice was ejected outside the pool.

China Lake, USA, 1980: RPTs during Burro gas dispersion experiments

The Burro tests were carried out by the Lawrence Livermore National Laboratory at China Lake between 1978 and 1982 to study the dispersion of vapor clouds. Vapor clouds were produced by releasing LNG onto water. During tests carried out with high LNG flow rates (720 to 1080 m^3/h), severe RPTs were generated both during immediate contact between LNG and water and sometime after spillage. The LNG released during these experiments had a high methane content (>83%). The most severe RPT event produced air overpressures estimated at a TNT equivalent of 3.5 kg.

Nantes, France, March 1982: RPT during an LNG pool fire experiment

During a test to extinguish a fire in an LNG tank at GDF's test facility in Nantes, a new emulsifying product was being evaluated. The product was not satisfactory, and a heterogeneous mixture of foam and water was produced and poured onto the ignited LNG. Approximately 11 minutes after ignition, the fire had still not been effectively extinguished, so it was decided to stop applying the foam. After a further 6 minutes, a violent RPT occurred, the massive increase in the rate of vaporization producing a fireball that reached a height of 40 m, some four times the height of the previous flame. The fireball caused a significant increase in the radiation produced by the fire and lasted for an estimated 5 to 10 seconds.

3. The RPT phenomenon

LNG has been transported in LNG carriers at sea for around 50 years, and is widely acknowledged to have an excellent safety record (Forte and Ruf, 2017). However, spilling LNG or any other cryogenic product at sea can have serious consequences. Indeed, after an accidental release, the vapor associated with the evaporation of the cryogenic fluid forms a cloud of cold gas, denser than air, which can travel downwind to a potential source of ignition. Several scenarios have been identified by various authors (ABS, 2004; Koopman and Ermak, 2007; Luketa-Hanlin, 2006; Melhem et al., 2006; Sandia, 2004; Schubach and Bagster, 1996; Shaw et al., 2005):

- The instantaneous fire creates a fireball,
- A slick fire on the surface of the water
- Vapor cloud explosion (UVCE).

Among the possible accident scenarios, when a cryogenic fluid such as LNG is spilled on water at very high speed, the phenomenon of rapid phase transition (RPT) must be taken into account. This results in the formation of a puddle on the surface of the water, which gradually boils over, often without incident. In some cases, however, rapid vaporization is observed, sometimes accompanied by combustion or other chemical reactions. Although combustion does not necessarily occur, the release of steam, commonly called a "steam explosion" or a "physical explosion", is so violent that the physical effects of the overpressure are similar to an explosion.

3.1. Description of the physical mechanisms involved in an RPT phenomenon

When LNG is spilled onto water, it is initially at a temperature of around -162°C at atmospheric pressure. As the surface water is initially much warmer (between 15°C and 25°C) than the LNG, the high temperature difference between the two fluids causes the LNG to boil. This boiling leads to the formation of a vapor film between the LNG and the water, which greatly reduces heat transfer between the water and the LNG. However, if the vapor film is broken, a transition to a faster heat transfer mode can occur, leading to the nucleate boiling mechanism. The LNG is then heated very rapidly, and a RPT can occur, potentially leading to a steam explosion. In general, the resulting overpressures have been found to be highly variable. Experimental work carried out to characterize the consequences of RPTs has shown that explosions do not always occur in apparently identical experiments, and the severity of RPTs is not the same depending on the LNG fractions involved in the RPT. It has been found that when LNG slicks form on the water surface, an RPT seems more likely when there is some turbulence or mixing of the LNG/water interface (Melhem et al., 2006).

Parallel to this research, RPTs can appear randomly and explosively, in large quantities and all at once. These are RPT events that can release mechanical energies large enough to displace and damage heavy equipment (Luketa-Hanlin, 2006; Pitblado and Woodward, 2011; Forte and Ruf, 2017). These RPTs could theoretically cause secondary structural damage and cascading failures (Havens and Spicer, 2007). However, previous studies in the literature show that it is relatively difficult to predict whether or not an RPT event will occur during a given spill. Aursand et al, 2020 explain that the results of studies carried out by the Lawrence Livermore National Laboratory in the 1980s showed that RPT occurred in around a third of spills. This work also highlighted that a single spill can lead to more than ten separate RPT events, while RPT yields appear to be highly random and can apparently have TNT equivalents ranging from a few grams to 6 kg (around 25 MJ) (Luketa-Hanlin, 2006; Koopman and Ermak,2007; Melhem et al., 2006; Cleaver et al., 1998; ABS Consulting, 2004; Hightower et al., 2004).

Nédelka et al, 2003 states in his article that Gaz de France, Shell Research and British Gas have carried out tests on complete loading/unloading arm rupture scenarios (Nédelka et al., 1989). They carried out 28 instantaneous spills with volumes ranging from 1 to 9 m^3. These tests allowed us to observe numerous RPTs under various spill conditions, and are still used for global validation of RPT consequence assessment (Figure 1). The largest volumes (1 to 9 m^3) and LNG flow rates (average flow rate up to 2300 m^3/h) ever used in supervised testing were observed. The maximum explosion recorded was estimated at 4.15 kg of TNT.

Figure 1 Illustration of an RPT explosion obtained during tests carried out by Gaz de France in Lorient, France - 3rd October 1984 when 9 m³ of LNG was spilled into the sea (Nédelka et al., 2003).

As mentioned above, the mechanism of RPT is the very rapid (explosive) evaporation of a low-temperature cryogenic liquid into another liquid with a higher temperature (in this case LNG in seawater). This phenomenon does not necessarily involve fire or other chemical reactions, but is a purely physical explosive phenomenon, like the explosion of an envelope containing a pressurized gas.

The RPT phenomenon has also received considerable attention in the context of nuclear fuel-coolant interactions in the nuclear power industry (Berthoud, 2000), which has many similar features. Overall, due to the small spatial scales of the physical phenomena involved (film boiling), small temporal scales (rapid nucleation) and low reproducibility, precise quantification of the consequences associated with LNG spills in water is difficult. As explained by Aursand et al., 2018, there are generally two categories of models, trigger prediction models or consequence prediction models:

(i) Models for predicting RPT triggering are used to determine if, when and where RPT will occur. Prediction of RPT triggering is mostly based on the relationship between water temperature and LNG thermodynamic properties, such as the superheat limit (Reid, 1983). Melhem et al. 2006 proposed a more complex method based on a gradual change in the composition of the LNG mixture.

(ii) The second set of models concerns the assessment of the consequences of RPTs, and focuses on evaluating the energy yield of the reaction and calculating the pressure peaks associated with the explosion. These models are based on idealized thermodynamic approaches to estimating the explosive yield of steam explosions. These methods originate from work

carried out in the 1996 to assess the impact of vapor explosions during nuclear fuel leaks in coolants (Cleaver et al., 1998; Berthoud, 2000).

While these methods can be applied directly to immediate RPT phenomena, this is not the case for delayed RPT due to the unknown composition of the LNG at the time of release. The literature distinguishes between early and delayed RPT in large-scale LNG spills (Hightower et al., 2004; Luketa-Hanlin, 2006; Koopman and Ermak, 2007; Bubbico and Salzano, 2009). Early RPT is triggered at the point of a chaotic spill at any time during the spill, while delayed RPT occurs after a while in the outside of the spreading pool. The distinction between the two types of events depend on when and where the phenomenon occurs during a spill. Immediate RPT refers to explosions occurring in the mixing region at any time during the spill event (a phenomenon linked to the dynamics of the release into the water). A delayed RPT, on the other hand, concerns RPTs that are not immediate, i.e. all explosion phenomena occurring in the spreading zone and not in the mixing region (phenomenon linked to external mixing factors). Delayed RPTs occur only after a certain time has elapsed since the start of the LNG spill (of the order of a few minutes).

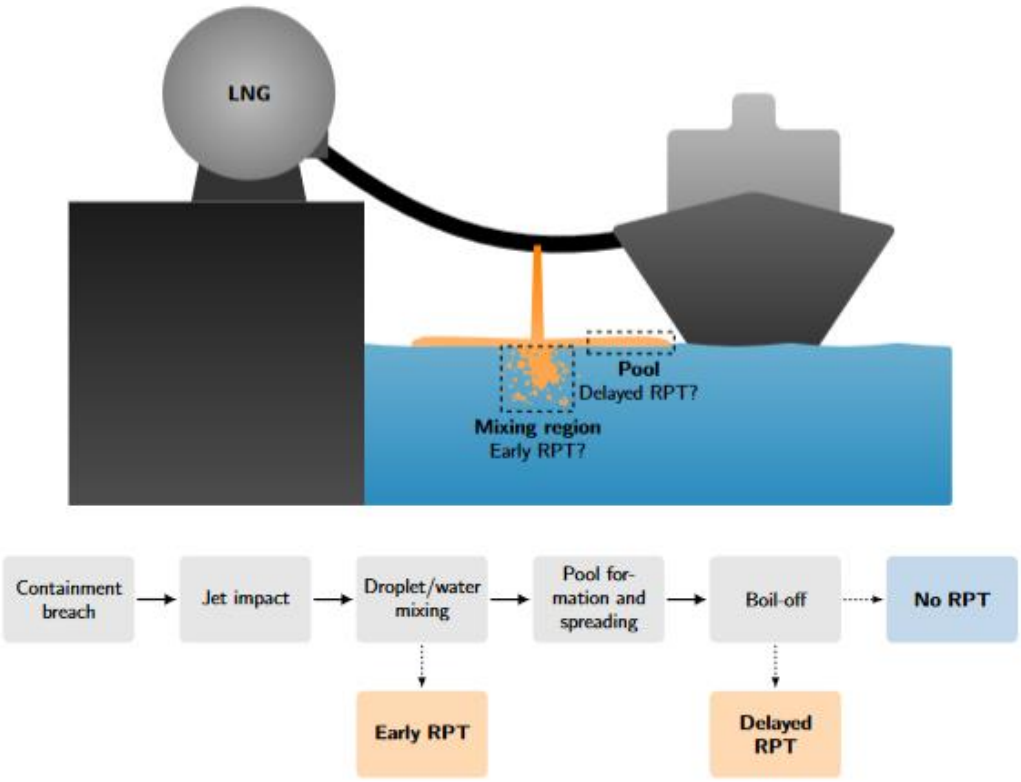

Figure 2 Illustration of a spill scenario resulting from a leak in a supply line. The leak results in the release of a cryogenic fluid in the form of a falling jet. Immediate RPT from the mixing region and delayed RPT from the spreading layer. The associated flow chart shows the possible pathways of the different types of RPT events (Lervåg et al, 2021)

Overall, the practical assessment of the risks and consequences of an LNG spill still seems uncertain, mainly due to the lack of reliable trigger predictions. A 2004 report for the U.S. Federal Energy Regulatory Commission concluded that there was no satisfactory

theoretical method for the practical assessment of RPT risk for LNG carriers (ABS Consulting, 2004), but there is a clear qualitative consensus on RPT mechanisms. According to Aursand et al, 2020, the RPT mechanism can be described by the following phases:

(i) *Film boiling phase*: Initially, after an LNG spill onto water, film boiling occurs. The temperature difference between seawater and LNG is so great that boiling occurs far into the boiling regime. This means that the LNG is isolated from the water by a vapor film composed mainly of methane. This vapour film thermally insulates the LNG from the water and considerably reduces heat exchange between the LNG and the water. The heat flow remains relatively low, and all the thermal energy is used for evaporation, while the LNG remains in its quasi-equilibrium state during boiling (at the bubble point of around -162°C).

(ii) *Collapse of the boiling film (liquid-liquid contact)*: For some reason, an external event triggers the collapse of the boiling film. The mechanisms suggested for boil film collapse depend on whether we are considering early or delayed RPT (this event is often linked to destabilization of the LNG slick by turbulence effects). In both cases, this means that there is considerable direct contact between the water and the LNG, which increases the heat flux by several orders of magnitude.

(iii) *Rapid superheating to the superheat limit*: since a liquid-liquid interface has relatively few nucleation sites, the evaporation rate is initially unable to keep pace with the dramatic increase in heat flow. Much of the heat is expended to superheat the LNG, which means that the liquid is heated significantly. The boiling temperature of water is well above its boiling point. The superheated liquid is in a metastable state and can return to its equilibrium state. The sudden, sharp increase in the rate of heat transfer causes the liquid to overheat and evaporate rapidly. If it is not sufficiently disturbed, there is a maximum temperature to which the liquid must pass, regardless of external disturbances. This is known as the superheat limit.

(iv) *Homogeneous nucleation*: As the liquid approaches its superheat limit, vaporization occurs spontaneously throughout its volume, through homogeneous nucleation. This is the start of a rapid transition from the liquid to the two-phase state.

(v) Explosive expansion: If it were in mechanical equilibrium with its surroundings, the new state would take up more than 100 times the volume of the original superheated liquid state. The fluid is initially constrained to hold within the initial volume, so the pressure rises dramatically before it has time to expand. As this transition occurs rapidly, it is observed as a noisy and destructive steam explosion. The event involves high-pressure waves and the release of considerable energy through the work of expansion of the vapour.

3.2. Modeling LNG spills

Lervag et al., 2021 present a model that considers important mechanisms such as boiling and evaporation, as well as the enrichment of the LNG mixture due to evaporation (Figure 3). When LNG is spilled on water due to a leak, it spreads and begins to evaporate. Vapor bubbles continuously form at the water-LNG interface and rise to the surface. The bubbles displace the liquid phase, reducing the average density of the liquid-vapor mixture. The reduction in density means that the volume, and therefore the height, of the LNG-air surface increases. This in turn affects the spreading rate, which depends on the height of the leading edge (Fyhn et al., 2019).

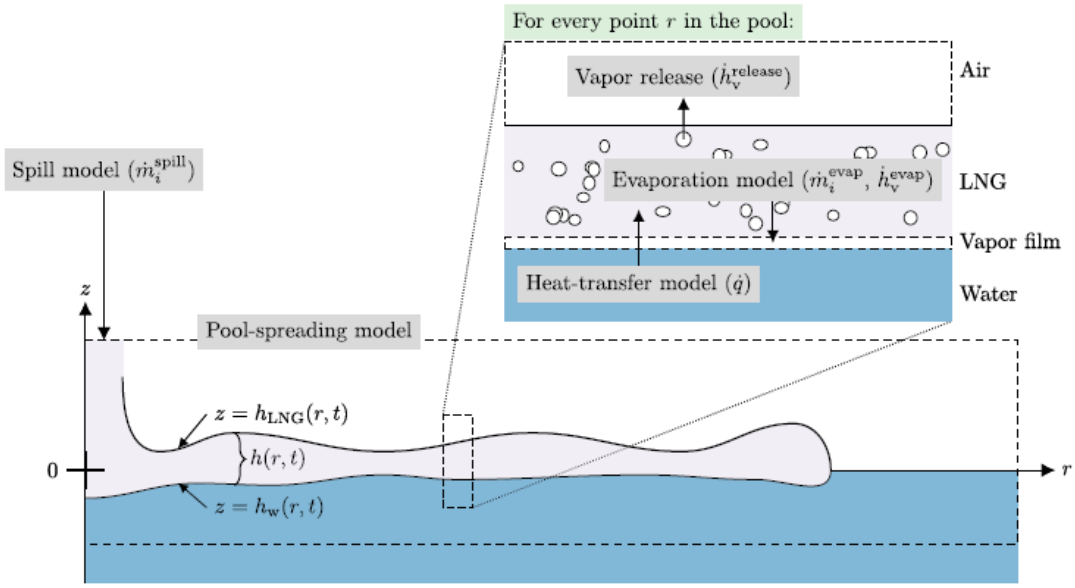

Figure 3 Illustration of the LNG spreading model proposed by Lervag et al., 2021. This spill model calculates the mass added due to spillage, and the heat transfer and evaporation models calculate the mass loss due to evaporation.

The spreading model proposed by Lervag et al., 2021 aims to model the evolution of the geometric characteristics of the LNG slick, which involves tracking its thickness *h* and local thermodynamic state as a function of radius *r* and time *t*. The authors thus propose to calculate the vertical positions *z* of the interfaces from those given by h_w (the coast of the water - LNG interface) and h_{LNG} (the coast of the LNG - Air interface), which can be calculated from h using the following equations:

$$h_w = -(1-\delta)h \quad (1)$$

$$h_{LNG} = \delta h \quad (2)$$

$$\delta = \frac{\rho_w - \rho}{\rho_w} \quad (3)$$

Where ρ_w is the density of the water and ρ is the overall density of the liquid-vapor mixture. Note that $h_w = 0$ corresponds to the reference water level with no LNG spill.

3.3. Modelling the triggering and consequences of an RPT

3.3.1. Prediction of RPT triggering

The main difficulty in predicting the onset of an RPT is in predicting the two essential steps required to trigger it: the sudden collapse of film boiling and the resulting liquid-liquid interaction (trigger event). Different approaches are used depending on whether we are considering an immediate RPT (droplet boiling) or a delayed RPT (pool boiling or sheet boiling).

1. RPT delayed

In the case of a delayed RPT, the LNG will spill onto the water surface and enter a sheet boiling phase. This phenomenon is generally described by the following boiling curve: (Dhir, 1998). The Figure 4 shows a classic sheet boiling curve. The cryogenic fluid is the boiling fluid (blue), while water acts as the hot surface (red). When $T > Tsat$, the surface is considered superheated, and the difference between *T and Tsat* is called the surface superheat temperature. When the surface superheat temperature is moderate, we're in the conventional nucleate boiling regime. When the surface superheat temperature becomes very high, the film boiling regime appears, accompanied by a dramatic drop in heat flow due to the formation of a continuous vapor film limiting heat exchange. The lower end of the film boiling regime is the Leidenfrost temperature (T_L), and its crossing from right to left is called film boiling collapse (Nukiyama, 1934).

In this case, LNG acts as the boiling fluid and water as the hot surface. According to the theory described above, RPT is triggered by the collapse of film boiling, which, for sheet boiling, is defined by the position on the boiling curve:

$$T_L < T_w : \text{film boiling (no RPT)} \quad (4)$$

$$T_L > T_w : \text{Liquid-liquid contact (risk of RPT)} \quad (5)$$

where T_w is the water temperature and T_L the Leidenfrost temperature. The Leidenfrost temperature of a fluid such as LNG is difficult to predict (or even measure) with good accuracy, but has generally been found to be close to, or even slightly below, the fluid's critical temperature (Spiegler et al., 1963),

$$\mathrm{T}_L \approx \frac{27}{32} T_{crit} \quad (6)$$

As written by Aursand et al, 2020, the critical point of an LNG mixture lies in the region of $T_{crit} \approx 203$K (-70°C), which gives, using equation (6), $T_L \approx 171$K (-102°C). For comparison, as water freezing is not normally observed in large-scale LNG spills, the surface has a near-zero temperature, $T_w \approx 0$°C. We are therefore safely in the "Film boiling (no RPT)" part of equation (4). The above calculations are only valid for LNG with its initial (stored) composition. As boiling increases, the composition of the LNG changes, so that the

critical temperature of the mixture increases. According to equation (6), this means that the Leidenfrost temperature also rises. It eventually reaches the water temperature, which, according to equation (4), presents a risk of RPT. Thus, the challenge of predicting the onset of a delayed LNG RPT is reduced to predict when and where the $T_L > T_w$ condition can be satisfied. In our previous work, Aursand and Hammer (2018), this issue was analyzed in terms of the methane fraction required to satisfy the triggering criterion. The results can be summarized as follows. LNG needs to boil down to around 30-50% methane before fulfilling the delayed RPT trigger condition ($T_L \approx T_w$). This depends on the relative quantities of the heavier alkanes. When the trigger condition is met, only 10-20% of the initial LNG quantity remains.

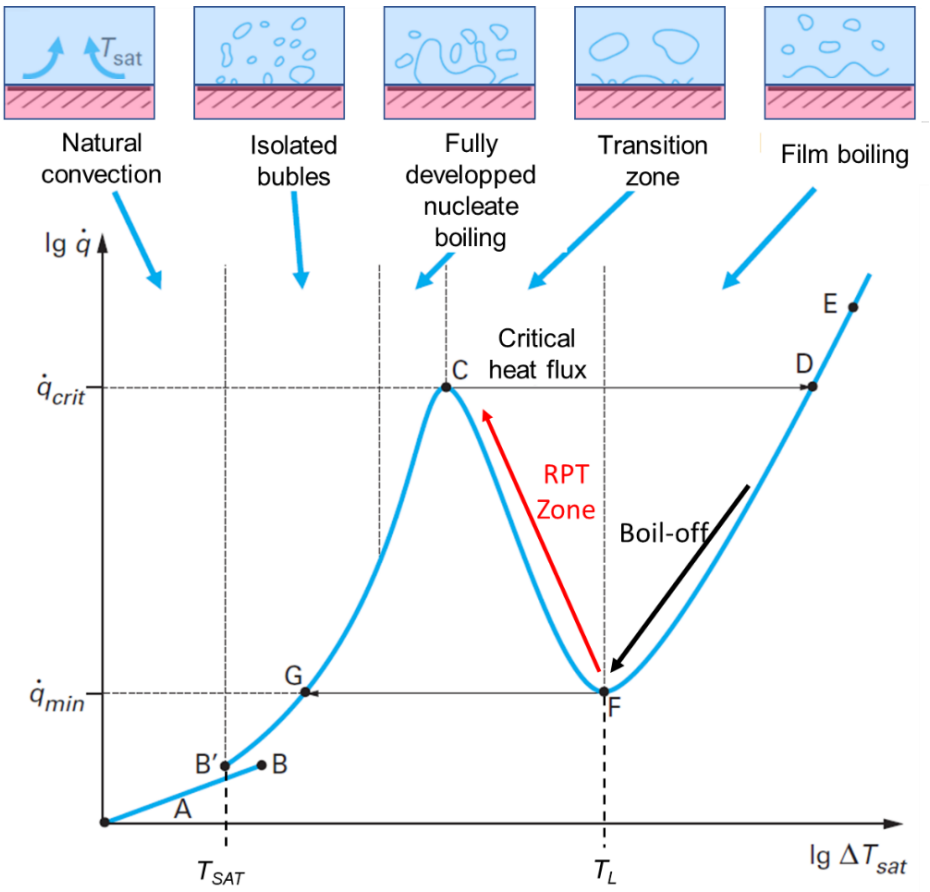

Figure 4 : Illustration of a typical boiling curve for saturated pool boiling, representing boiling heat flux ($\dot{q}$) as a function of surface temperature (T). (adapted from Jocelyn & Lallemand, 2021 and Lervag et al., 2021)

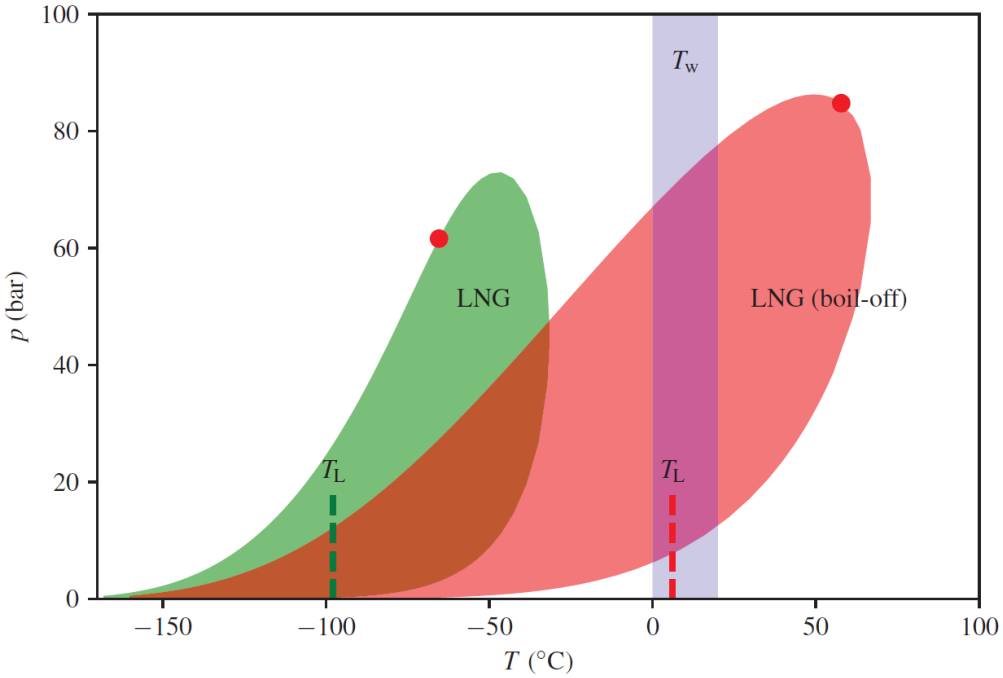

Figure 5 Illustration of how the two-phase region of the LNG mixture (green and red solid shapes) and the critical point (red dot) move towards higher temperatures as methane is removed from the mixture due to boiling. In this particular example, LNG goes from 90% methane to 40% methane. The Leidenfrost temperature (T_L), according to equation (6), then rises to reach typical seawater temperatures (vertical blue zone), thus satisfying the delayed RPT trigger condition (Aursand et al., 2020).

2. Early RPT

As shown in Figure 2 early RPT occurs in the chaotic mixing region below the point of impact of the LNG jet. This turbulent region contains droplets of boiling LNG immersed in water, which initially move downwards due to inertia (jet orientation and velocity), but eventually rise to the surface due to buoyancy. According to the general theory of RPT presented in section 3.1, the triggering event is initiated by a sudden and significant liquid-liquid contact. It is much more difficult to predict this phenomenon in the case of early RPT than in the case of delayed RPT, as the degree of liquid-liquid contact is no longer governed by a simple boiling curve. In this case, a detailed multiphase simulation of the mixing region on sufficiently long-time scales is required, as mentioned by Nédelka et al. 2003, using the CHYMES model, originally developed to simulate fuel/coolant mixing in nuclear accidents (Fletcher & Thyagaraja, 1991) and adapted by British Gas to LNG/water mixing as part of the RPT3 program. This model was re-coded by NTNU (University of Trondheim, Norway) for Gaz de France in the RPT4 program to improve numerical stability and enable simulations of large-scale events.

This model describes, in a cylindrical geometry, the formation of cryogenic fluid/water mixing zones following the impact of a vertical downward jet of cryogenic fluid on a water surface. An example of simulation is shown in Figure 5. The estimation of secondary mixing zones (induced by breaking waves, interaction of the resulting stratified LNG/water interface with obstacles) is not addressed. For a given spill scenario,

the CRYOMIX computer code provides an unstable, localized description of the mixing zone that can be used to obtain an estimate of the volume of reactive mixture, in order to remedy the inadequacy of experimental correlations.

This model describes, in a cylindrical geometry, the formation of mixing zones in a vertical downward jet of cryogenic fluid impacting the water surface. A simulation example is shown in Figure 6. The estimation of secondary mixing zones (induced by breaking waves, interaction of the resulting stratified LNG/water interface with obstacles) is not described. For a given spill scenario, the CRYOMIX computer code provides an unstable, localized description of the mixing zone that can be used to obtain an estimate of the volume of the reactive mixture, in order to remedy the inadequacy of the experimental correlations.

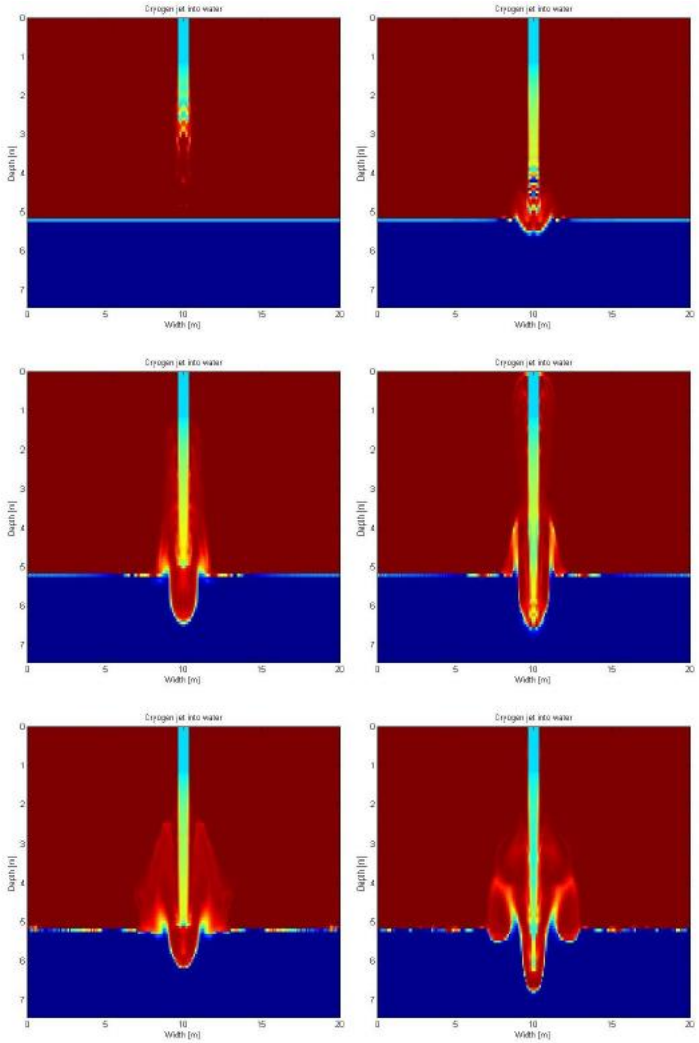

Figure 6 : Example of CRYOMIX simulation results for the impact of a cryogenic fluid descending vertically on the water surface (Nédelka et al., 2003).

3.3.2. Quantifying the impact of the RPT

Aursand and Hammer (2018) have also proposed a method for partially quantifying the consequences of the RPT. According to the theoretical sequence listed in paragraph 3.1

after the collapse of film boiling, there is rapid superheating, homogeneous nucleation and explosive expansion. Aursand et al, 2018 propose to quantify the consequences of RPT by simplifying the last two steps of the chain of events (steps 4-5 of section 3.1) by the following idealized two-step process:

(i) *At equilibrium*: the energy and density of the mixture are calculated precisely at the moment when the mixture reaches the superheat limit after collapse of the boiling film. The temperature of this state is the superheat limit (T_{SHL}) corresponding to the composition at the moment when the trigger criterion was reached. It is then necessary to determine the corresponding quasi-equilibrium state, with the same energy, density and composition. This results in a new intermediate high-pressure state (T^*,P^*).

(ii) *Isentropic expansion*: The intermediate state (T^*,P^*) is called a quasi-equilibrium state because, although it is in local equilibrium, it is not in mechanical equilibrium with the environment (P^* >> 1 atm). This leads to rapid expansion, which is approximated as an isentropic process. The final state of this expansion can then be found as the state at atmospheric pressure, which has the same entropy as the intermediate state at high pressure.

From this analysis, Aursand et al., 2020 note that there are two important figures to remember from such a calculation. Firstly, the maximum pressure (P^*) is the pressure of the intermediate state before expansion. This value can be interpreted as an estimate of the maximum pressure observed in a steam explosion very close to the source. Secondly, the energy yield of the explosion (E) is calculated as the mechanical work done by the expansion process. Since the process is assumed to be isentropic (reversible and adiabatic), it follows from classical thermodynamic analysis that the work done by the process is simply the difference in total enthalpy between the initial and final states of expansion. Note that this simply gives an energy per triggered quantity (i.e. per mole or kilogram), not a total quantity. Even with these simplifying assumptions, performing this calculation involves a rather complex set of thermodynamic algorithms. Firstly, an algorithm to calculate the superheat limit (T_{SHL}) as described by Aursand and Hammer (2018). Secondly, an algorithm to calculate the two-phase equilibrium state, either for values of energy and density, or for values of entropy and pressure. For these calculations, Aursand et al., 2020 use implementations of SINTEF's in-house software (Wilhelmsen et al., 2017), which are based on the algorithms described by Michelsen and Mollerup, 2007. The result of such a calculation is illustrated in Figure 7. As explained by Aursand et al., 2020, this result depends on the initial LNG composition, which can vary. Aursand and Hammer (2018) have studied the range of results for a plausible range of LNG compositions, and give the following conclusions:

(i) The predicted explosive yield of the LNG RPT (*E) is in* the order of 50-80 kJ/kg, equivalent to around 12-20 g of TNT per kg of LNG. In terms of volume of liquid spilled, this corresponds to around 5-10 g of TNT per liter.

(ii) The predicted peak pressure for LNG RPT (P^*) is between 20 bar and 60 bar. It should be noted that the predicted yield is calculated only in terms of energy per

quantity of liquid contributing to the reaction. As there is currently no way of predicting the amount of liquid that will participate in a single event, it is impossible to predict the explosive yield of a single RPT event. However, calculations do provide useful upper limits on the explosive potential of an LNG pool.

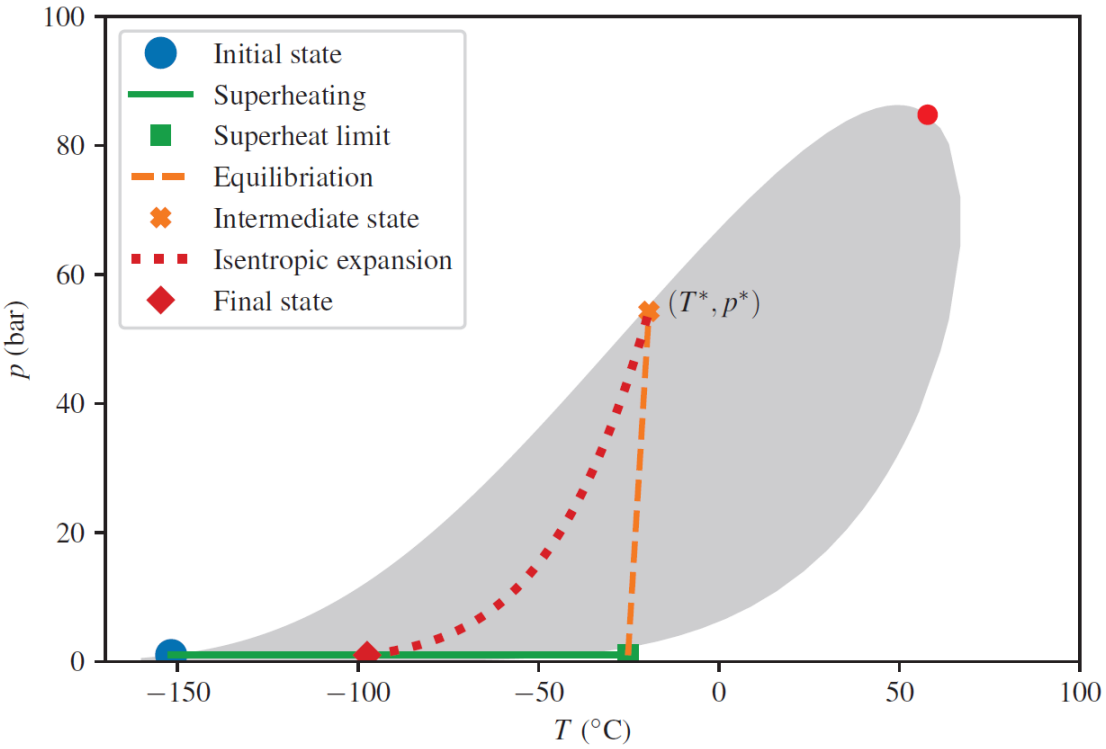

Figure 7 Result of an RPT consequence calculation, for an LNG mixture triggered after boiling to 40% methane. In this example, the theoretical explosive yield (E) is 20 gTNT per kg of LNG, i.e. around 10 gTNT per liter of LNG spilled. The predicted peak pressure ($p*$) is around 55 bar (Aursand et al., 2020).

4. Conclusion

The transition to cleaner shipping fuels is crucial to reducing GHG emissions. However, the use of new fuels such as ammonia, methanol and hydrogen, as well as LNG, requires robust risk management solutions to avoid environmental and safety disasters. Liquefied natural gas (LNG) is already in use and shows promise, but its low-temperature storage and the risk of spills pose serious environmental and safety problems. Accidental spill scenarios of LNG or other cryogenic products (such as ammonia or hydrogen) into water can cause rapid phase transitions, leading to vapour cloud explosions and shock waves.

The rapid phase transition (RPT) can occur when LNG is released on water, resulting from the intense thermal interaction between the LNG at very low temperature (-162°C) and the seawater. This interaction can cause the LNG to boil rapidly, potentially followed by a physical explosion without necessarily involving combustion. The physical mechanisms are due to the initial formation of a vapour film isolating the LNG from the water and the rupture of this film leading to rapid nucleate boiling, and explosive vaporisation. The consequences of RPT can vary considerably depending on the conditions of the spill and the composition of the LNG. Studies have shown that the occurrence and severity of RPTs are unpredictable, with events occurring in around one third of spill cases. Experimental tests have shown that explosions can be comparable to huge explosions.

Modelling these phenomena is complex and relies on the prediction of two types of RPT: early and delayed. Early RPT occurs in a chaotic mixing zone below the spill jet, while delayed RPT occurs after the formation of an LNG slick on water, once the composition of the LNG has been altered by boiling. Current models, although based on acoustic thermodynamic principles, present challenges in accurately predicting the timing and location of RPTs.

LNG spills at sea, although rare, present significant risks, mainly related to non-combustion physical explosions called RPT. The complex mechanisms and variability of conditions make it difficult to predict these events accurately. Current research and modelling provide a basis for understanding and assessing the risks, but uncertainties remain as to the accurate prediction of RPTs. Furthermore, reported incidents of RPT show explosions caused by accidental spills of LNG into water, highlighting the potential dangers. RPT scenarios, involving rapid phase transitions and vapour explosions, remain poorly understood and are a source of concern for public safety and port infrastructures. It is therefore crucial to continue experimental studies and the development of more robust models to improve the safety and risk management associated with the maritime transport of LNG and, more specifically, the use of cryogenic fluids as a propulsion fuel.

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