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Report

The risk for rapid phase transition in LNG spilled on water

An overview of the Predict-RPT project

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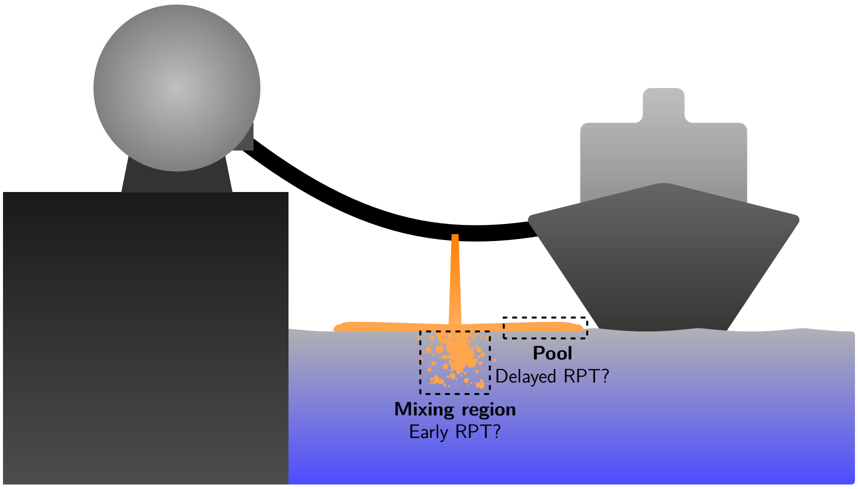

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ABSTRACT

This report summarizes the results of the Predict-RPT project, a competence building project financed from 2015 to 2019 by the MAROFF program of the Research Council of Norway. The aim of the project has been to improve the safety of maritime LNG activities (transportation and fuel usage) by enabling quantification of risks and consequences of large-scale RPT events. The project has focused on deriving a detailed risk assessment tool for delayed RPTs, and this tool and other main findings have been documented in nine scientific papers. In addition, a simplified risk assessment tool has been developed and published as a webtool (`https://predictrpt.herokuapp.com/`). For delayed RPTs, the predicted explosive yield from LNG is in the range of 50–80 kJ/kg LNG and the predicted peak pressure (near source) from an LNG RPT is in the range of 20–60 bar.

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Contents

1 Introduction

Transport of liquefied natural gas (LNG) is increasing in a Norwegian, European and Global context. It is often necessary to transfer LNG in loading arms and lines directly above the sea. Examples include refuelling of LNG-driven ships and passenger ferries and loading and unloading of LNG-carriers at liquefaction plants and LNG terminals. During these operations, LNG may accidentally be spilt onto the sea. The water will be at least 160 °C warmer than the LNG and at certain conditions the LNG is quickly heated due to the large temperature difference. The quick heating rate causes the LNG to overheat, and in some cases the degree of overheat in the LNG will be so large that it can no longer exist as a liquid. At this point, large volumes of the LNG may instantaneously vaporize, thereby creating a local overpressure. The expansion that follows is a physical explosion that may cause harm to personnel and equipment. This is the rapid phase transition (RPT) of LNG.

Although historically the number of RPT accidents has been relatively low, large-scale experiments have demonstrated that RPT explosions can occur during LNG spills under industrially relevant conditions. The increased use of LNG, for example in commercial transport vessels, can lead to more incidents as well as a higher risk of injuries and loss of life. It is therefore important to understand the RPT phenomenon during LNG spills on water.

Predicting the risk of rapid phase-transition events in LNG spills (Predict-RPT) is a competence building project financed from 2015 to 2019 by the MAROFF program of the Reseach Council of Norway. The main aim of the project has been to improve the safety of maritime LNG activities (transportation and fuel usage) by enabling quantification of risks and consequences of large-scale RPT events. This included to fill the known knowledge gaps, improve the national knowledge-base on the subject, and develop a model/tool for assessing risk and consequence.

The present document is the final report of the project summarizing its outcomes. Section 2 presents the current theory of RPT and triggering of these events. This is followed by key messages for stakeholders in Section 3, a practical procedure for LNG RPT risk-assessment in Section 4 and recommendations for risk reduction in Section 5. The risk-assessment procedure consists of a simplified risk assessment framework developed within the project. Section 6 provides an overview of the main results of the project. A detailed and a simplified RPT risk assessment tool have been derived within the project. The simplified tool is presented in Section 4. The features of the detailed tool is explained in Section 6. Section 6 also includes an overview of the project work published in scientific papers. The overview contains brief summaries of the main contribution of each paper towards an increased understanding of the RPT phenomenon.

2 Introduction to LNG Rapid Phase Transition (RPT)

2.1 Liquefied Natural Gas (LNG)

Natural gas is a common fossil fuel used for heating, cooking, propulsion and electricity-generation across the globe. Its main component is methane (about 90%), with the remainder consisting of progressively smaller amounts of the heavier alkanes ethane, propane, butane, etc. Natural gas is being extracted from increasingly remote sources, and this situation requires solutions for long-range transportation. For this purpose, the natural gas is sometimes cooled down below its boiling point (−162 °C) to form Liquefied Natural Gas (LNG) [1]. LNG is transported across the world's oceans in large carriers, and a single carrier may carry up to about 260 000 m^3 of LNG. Combined with the fact that there is an increasing trend towards both processing and usage of LNG at sea, this means that there are many scenarios where LNG may inadvertently spill and come in contact with seawater. In such scenarios there is a risk of Rapid Phase Transition (RPT) events.

2.2 The phenomenon of RPT

When LNG is spilled into water it will in the majority of cases eventually boil off without further incident. However, in some cases it is observed to suddenly, and seemingly at random, undergo a localized explosive vaporization. This is an RPT event, and is considered one of the main safety concerns of the LNG industry [2, 3]. Still, the attention given to RPT risk in LNG safety reviews is highly variably, ranging from significant discussion [3, 4, 5, 6] to little more than a brief mention [7, 8, 9, 10, 11].

RPT is not an explosion in the common meaning of the word, since it does not involve combustion or other chemical reactions. RPT events are what is sometimes called a vapor explosion or a physical explosion. It is still destructive in nature, and poses a danger to both people and equipment. Its peak pressures and released mechanical energy can be large enough to displace and damage heavy equipment [5, 3, 11] and could theoretically cause secondary structural damage and cascading containment failures [9]. Whether or not an RPT event will occur in any given spill has been notoriously difficult to predict. From extensive tests performed by LLNL in the 1980s [5, 12, 13] it was found that RPT occurred in about one third of spills. It was also observed that a single spill may lead to more than ten distinct RPT events. The yields of single RPT events seem quite random, and may apparently have TNT equivalents of anything from a few grams to 6 kg (about 25 MJ) [12, 13, 14, 15, 16].

The general macroscopic chain-of-events of a marine LNG spill is as follows:

1. **Containment breach**: Due to some unintended event, the containment of LNG in a tank or transfer line is broken. If the breach is above sea level, the LNG may fall towards the water surface in the form of a jet.

2. **Jet impact**: The LNG jet impacts the water surface, which will break it up into separate droplets.

3. **Droplet/water mixing**: If the momentum the jet is large enough, the droplets will initially penetrate the surface and become submerged in water. This forms a chaotic *mixing region*.

4. **Pool formation and spreading**: Since the density of LNG is about half of that of water, the droplets will be buoyant and will eventually rise to the surface. This forms an LNG pool that spreads on top of the water surface.

5. **Boil-off**: The boiling point of LNG is at about −162 °C, while the water holds a temperature of about 0 °C, so the spreading pool will start boil while spreading. Since methane is by far the most volatile component, the resulting vapor is almost purely methane. This causes a gradual compositional change, which increases the relative amounts of the heavier alkanes such as ethane, propane and butane.

See Fig. 1 for an illustration of the scenario, and Fig. 2 for an overview of the chain-of-events. As indicated in the figures, there is an established distinction between two kinds of RPT events depending on when and where it occurs in a spill event [5, 12]:

- **Early RPT**: This is defined as any RPT that occurs in the mixing region at any time during the spill event.
- **Delayed RPT**: This is defined as any RPT that is not an Early RPT, which means that it must occur somewhere in the spreading pool, not in the mixing region. Reports indicate that Delayed RPT only occurs a considerable time (on the scale of minutes) after the start of the LNG spill event.

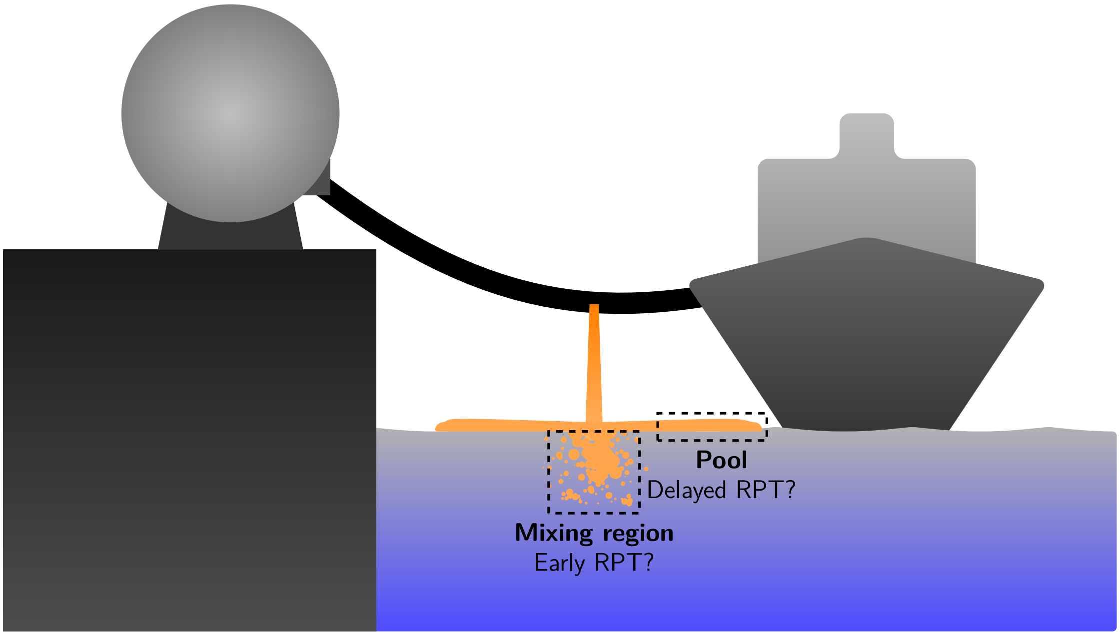

Figure 1: An illustration of a spill-scenario, where a breach in a fueling line causes the release of cryogen in the form of a falling jet. Also shown are the origins of the two kinds of RPT event: *early RPT* from the mixing region, and *delayed RPT* from the spreading pool.

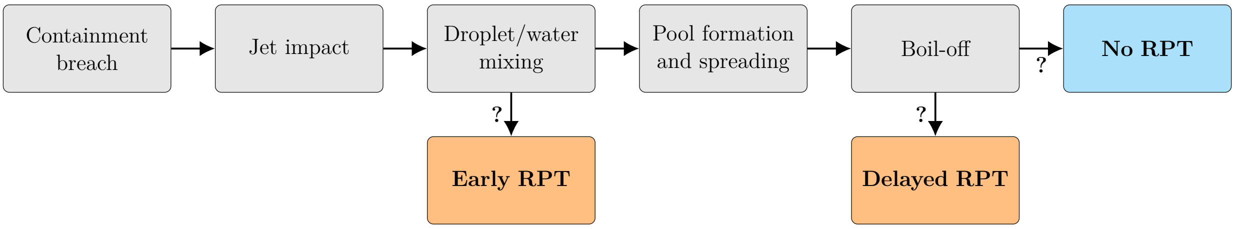

Figure 2: The macroscopic chain-of-events in an LNG spill on water, and the possible pathways to the two kinds of RPT event. The jet from a containment breach impacts the water and forms a mixing region beneath the surface. At this location there is a known possibility of *early RPT*. Then, since the cryogen density is lower than that of water, the droplets will rise up and form a spreading and boiling pool on top. This pool will undergo a compositional change due to boil-off, and may eventually meet the requirements for *delayed RPT*.

2.3 The theory of RPT

After the possibility of LNG RPT was discovered in the 1960s, a handful of research groups went to work on understanding the mechanisms behind the phenomenon. By the first half of the 1970s, they had arrived at a general consensus for a theory of RPT [17, 18, 19, 20, 21, 22]. This is a theory about what occurs on the small scales at the local time and position where a single RPT event is observed, and is relevant for both early and delayed RPT. The theory may be summarized by the following chain-of-events:

1. **Film-boiling stage**: The temperature difference between the sea water and the LNG is so large that boiling occurs far into the *film boiling* regime. This means that the LNG pool or droplet is insulated from the water by a vapor film consisting mainly of methane. Because of this the heat flux stays relatively low and the evaporation stays in a quasi-equilibrium regime. All of the energy transferred into the LNG is spent on evaporation, and the LNG temperature stays close to the bubble-point, which is initially about −162 °C.

2. **Film-boiling collapse (liquid-liquid contact)**: For some reason there is a sudden and localized *film-boiling collapse*. The suggested mechanisms for film-boiling collapse will depend on whether one is considering early or delayed RPT. In either case, this means that there is considerable direct contact between the water and the LNG, which increases the heat flux by orders of magnitude.

3. **Rapid superheating to the superheat limit**: Because a liquid-liquid interface has relatively few nucleation sites, the evaporation rate is initially unable to keep up with the dramatic increase in heat flux. Instead, much of the heat is spent on *superheating* the LNG, which means that the liquid is heated significantly beyond its boiling temperature. The superheated liquid is in a meta-stable state, and may transition to its corresponding equilibrium state if disturbed. If not disturbed sufficiently, there is a maximum temperature at which the liquid must transition regardless of external disturbances. This is called the *superheat limit*.

4. **Homogeneous nucleation**: Once the liquid approaches its superheat limit, vaporization spontaneously occurs throughout its volume by *homogeneous nucleation*. This is the start of a rapid transition from a liquid state to a two-phase state.

5. **Explosive expansion**: If in mechanical equilibrium with its surroundings, the new state would take up over 100 times the volume of the original superheated liquid state. The fluid is initially forced to fit in the original volume, so the pressure increases dramatically before it has time to expand. Since this transition happens fast, it is observed as a loud and destructive vapor explosion. The event involves high-pressure waves and considerable energy release through expansion work.

2.4 Predicting triggering of RPT

The main challenge when predicting the occurrence of RPT is predicting step two, the sudden film-boiling collapse and subsequent liquid–liquid contact. We refer to this as the **triggering event**. The approach depends on whether one considers early RPT (droplet boiling) or delayed RPT (pool boiling).

2.4.1 Delayed RPT

For delayed RPT, the relevant mode of boiling is *pool boiling*. This is usually quantified in terms of the *boiling curve* [23], sometimes called the *Nukiyama curve* after the person who first characterized it back in the 1930s [24]. A general illustration of a boiling curve is shown in Fig. 3.

In the present case, LNG takes the role of the boiling fluid and water takes the role of the hot surface. According to the theory described above RPT is triggered on film-boiling collapse, which for pool boiling is defined by the position on the boiling curve:

$$\begin{aligned} T_\mathrm{L} &< T_\mathrm{w} &&: \text{Film boiling (no RPT)} \\ T_\mathrm{L} &> T_\mathrm{w} &&: \text{Liquid-liquid contact (risk of RPT)}, \end{aligned} \tag{1}$$

where T_w is the temperature of the water. The Leidenfrost temperature of a fluid such a LNG is difficult to predict (or even measure) with good accuracy, but it has generally been found that it is close to, but slightly below, the fluid's critical temperature [25],

$$T_\mathrm{L} \approx \frac{27}{32} T_\mathrm{crit} \tag{2}$$

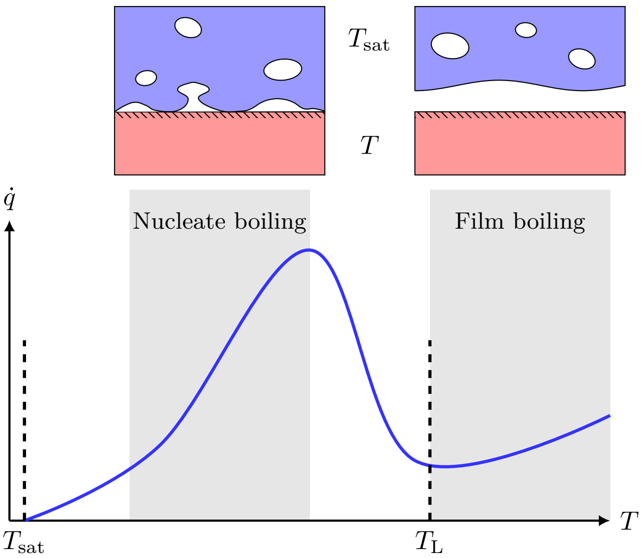

Figure 3: Illustration of a typical boiling curve for saturated pool boiling, showing boiling heat flux ($\dot{q}$) as a function of surface temperature (T). Once $T > T_{\mathrm{s}}$ the surface is considered superheated, and the difference $T - T_{\mathrm{s}}$ is called the *surface superheat*. At moderate surface superheat we are in the conventional *nucleate boiling regime*. However, once the surface superheat becomes very large there is a transition into a *film-boiling regime*, which comes with a dramatic drop in heat flux due to the formation of a continuous vapor film. The lower end of the film boiling regime is the Leidenfrost temperature (T_{L}), and crossing this from right to left is called *film-boiling* collapse.

The critical point of a typical LNG mixture is in the region of $T_{\mathrm{crit}} \approx 203\,\mathrm{K}$ ($-70\,^{\circ}\mathrm{C}$). By comparison, since the water is normally not observed to freeze in large-scale LNG spills, the surface holds a temperature of approximately $T_{\mathrm{w}} \approx 0\,^{\circ}\mathrm{C}$. This means that we are safely in the “Film boiling(No RPT)” part of Eq. (1).

However, this is only true for LNG with its initial (stored) composition. As boil-off proceeds, the composition changes in such a way that the critical temperature of the mixture increases. According to Eq. (2), this means that the Leidenfrost temperature will also increase. Eventually it reaches the water temperature, which according to Eq. (1) gives a risk of RPT. See Fig. 4 for an illustration of this *LNG RPT boil-off* effect.

Thus, the challenge of predicting the triggering of delayed LNG RPT is reduced to the prediction of when and where the condition $T_{\mathrm{L}} > T_{\mathrm{w}}$ may be satisfied. In our previous work, Aursand [26], this was analyzed extensively in terms of the methane fraction necessary to satisfy the triggering criterion. In short, the results were the following:

- The LNG must boil down to approximately 30-50 mol% methane before meeting the condition for delayed RPT triggering ($T_{\mathrm{L}} \approx T_{\mathrm{w}}$). This depends on the relative amounts of the heavier alkanes.
- By the time the triggering condition is met, only 10-20% of the original amount of LNG is remaining.

2.4.2 Early RPT

As indicated in Fig. 1, so-called early RPT occurs in the chaotic mixing region beneath the point of LNG jet impact. This region contains film-boiling LNG droplets submerged in water, which initially move downwards due to inertia but eventually move back to the surface due to buoyancy. According to the general theory of RPT presented in Sec. 2.3, the triggering event is initiated by sudden significant liquid-liquid contact. Predicting this for early RPT is much more difficult than in the case of delayed RPT, since the degree of liquid-liquid contact is no longer governed by a simple boiling curve. In this case it would require a detailed multi-phase simulation of the mixing region over sufficiently long time-scales. This has to our knowledge not been achieved, and we consider early RPT an unsolved problem in the LNG industry.

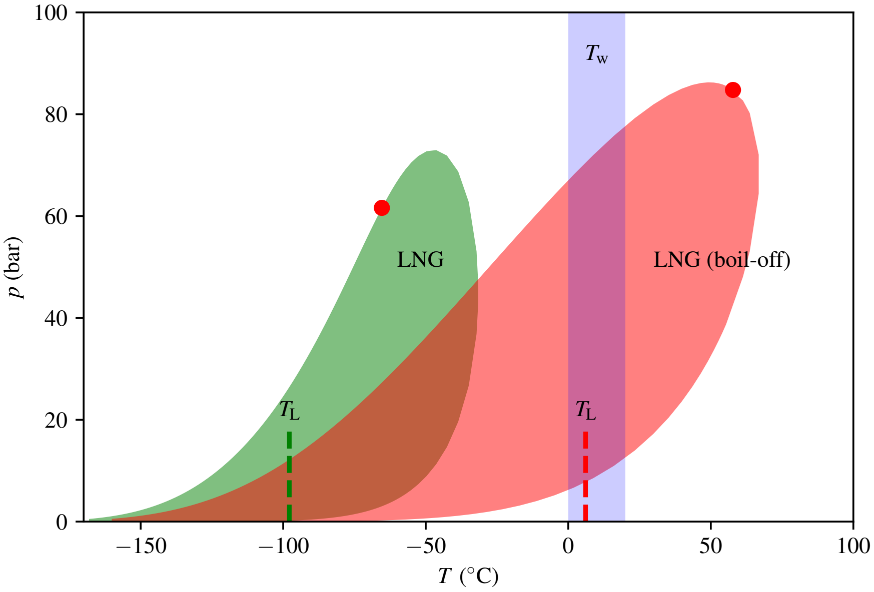

Figure 4: An illustration of how the two-phase region (filled shapes) and the critical point (red dot) shifts to higher temperatures as methane is removed from the mixture due to boil-off. In this particular example the LNG boils down from 90 mol% methane to 40 mol% methane. This causes the Leidenfrost temperature (T_{L}), according to Eq. (2), to shift up into the typical seawater temperatures (blue bar), which satisfies the condition for delayed RPT triggering.

2.5 RPT consequence quantification

Our work in Aursand [26] also included a method of partially quantifying the consequence of RPT. According to the theoretical chain-of-events listed in Sec. 2.3, after film-boiling collapse (Leidenfrost transition) there is rapid superheating, homogeneous nucleation and explosive expansion. Here we enable consequence quantification by simplifying the final two steps in the chain-of-events (steps 4-5) by the following idealized two-step process:

1. **Equilibration**: Calculate the energy and density of the mixture exactly when it reaches the superheat limit after film-boiling collapse. The temperature of this state is the superheat limit (T_{SHL}) corresponding to the composition at the time when the triggering criterion was reached. Then, find the corresponding quasi-equilibrium state, with the same energy, density and composition. This yields a new high-pressure intermediate state (T^*, p^*).
2. **Isentropic expansion**: The intermediate state (T^*, p^*) is called a quasi-equilibrium state because while it is in local equilibrium, it is not in mechanical equilibrium with the surroundings ($p^* \gg 1$ atm). This leads to a rapid expansion, which is approximated as an isentropic process. The end-state of this expansion may then be found as the state at atmospheric pressure that has the same entropy as the high-pressure intermediate state.

There are two significant numbers to take away from such a calculation:

- **Peak pressure** (p^*): This is found as the pressure of the intermediate state before expansion. The value may be interpreted as an estimate for the peak pressure seen in the vapor-explosion event very close to the source.
- **Explosive energy yield** (E): This is found as the mechanical work done by the expansion process. Since the process is assumed to be isentropic (reversible and adiabatic), it follows from classical thermodynamics that the work done by the process is simply the difference in total enthalpy between the initial and final states of the expansion. Note that this merely yields an energy per amount triggered (i.e. per mole or kilogram), not a total amount.

Even with these simplifying assumptions, performing this calculation involves a set of quite complex thermodynamic algorithms:

- An algorithm to calculate the superheat limit (T_{SHL}). Here we use the method described in Aursand [26].
- An algorithm to calculate the two-phase equilibrium state, given either values for energy and density or values for entropy and pressure. Here we use the implementations in SINTEF's `Thermopack` software [27], which are based on algorithms described by Michelsen and Mollerup [28].

The result of such a calculation is shown in Fig. 5. Of course, this result will depend on the initial LNG composition, which will vary some. In Aursand [26] the range of outcomes given a plausible range of LNG compositions was explored, and the conclusions were the following:

- The predicted explosive yield from LNG RPT (E) is in the range of 50–80 kJ/kg, which is equivalent to about 12–20 gTNT per kg LNG. In terms of spilled liquid volume, this is about 5–10 gTNT per litre.
- The predicted peak pressure from LNG RPT (p^*) is in the range of 20–60 bar.

Note that the predicted yield is only found in terms of energy per liquid amount that participates in the event. Since there is currently no way of predicting how much liquid will participate in any single event, the explosive yield of single RPT events cannot be predicted. However, it is possible to estimate the total amount of LNG which is in the risk zone of LNG. Hence, the calculations give a useful upper bound on the explosive potential of an LNG pool.

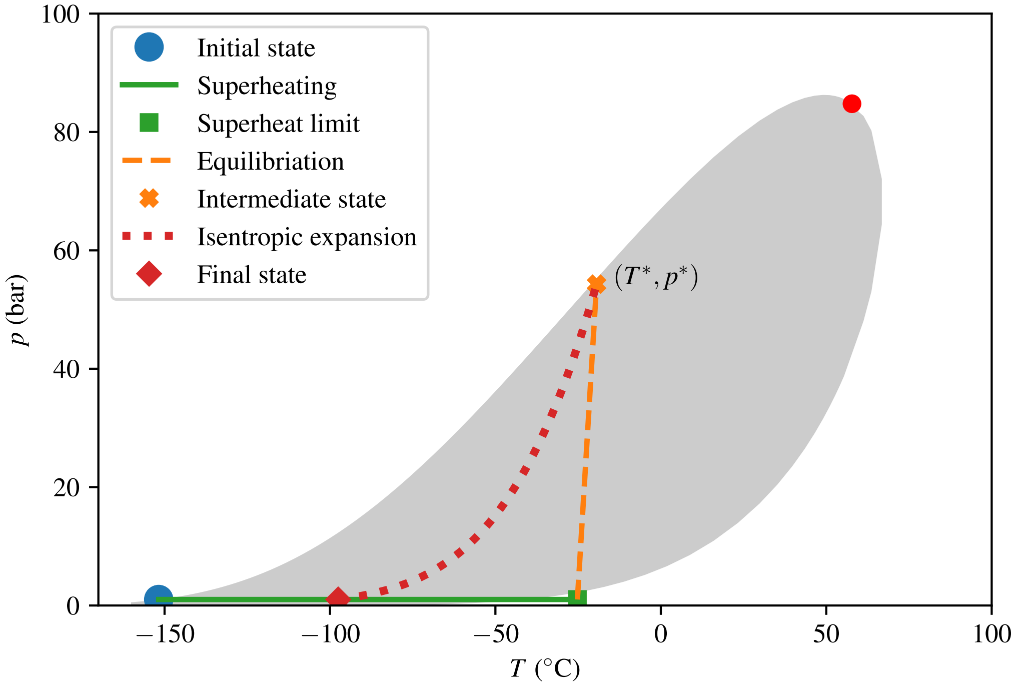

Figure 5: The result of an RPT consequence calculation, as described in Sec. 2.5, for an LNG mixture that is triggered after boiling down to 40 mol% methane. In this particular example the theoretical explosive yield (E) is 20 gTNT per kg LNG, or about 10 gTNT per liter of spilled LNG. The predicted peak pressure (p^*) is about 55 bar.

3 Key messages for stakeholders

Rapid Phase Transition (RPT) is an explosive event that may occur when LNG spills onto water. It is known from large-scale spills tests that it is relatively likely (approximately one third of spills), and that the explosive yields may be significant (up to several kg of TNT equivalent). In the literature there is an established distinction between **Early RPT**, which occurs in the mixing-region beneath jet impact, and **Delayed RPT**, which occurs above water in the spreading LNG pool. Prediction of Early RPT remains an unsolved problem, while prediction of Delayed RPT is possible to some extent. The latter has has been the main focus of Predict-RPT.

In the Predict-RPT project we developed a methodology for estimating when the criteria for Delayed RPT are met. Given a plausible range of LNG compositions we came to the following general conclusions [29]:

- **The LNG must boil down to approximately 30-50 mol% methane before meeting the condition for delayed RPT triggering.**
- **By the time the triggering condition is met, only 10-20% of the original amount of LNG is remaining.**

In Predict-RPT we developed a methodology for estimating the consequence of LNG RPT. Given a plausible range of LNG compositions we came to the following general conclusions [29]:

- The predicted explosive yield from LNG RPT is in the range of 50–80 kJ/kg, which is equivalent to about **12–20 g TNT per kg LNG**. In terms of spilled liquid volume, this is about 5–10 gTNT per litre. Note that the predicted yield is only found in terms of energy per LNG amount that participates in the RPT event. There is currently no method of predicting the exact amount of LNG that will participate in a single RPT event.
- The predicted peak pressure (near source) from an LNG RPT is in the range of **20-60 bar**.

See Sec. 4 for a guide on how to perform the risk assessment for a specific LNG mixture. Based on the theory developed in Predict-RPT, we may suggest the following risk-mitigation measures:

- Adjust the LNG composition **by reducing the amounts of the heavier alkanes (propane, butane, ...) relative to the amount of ethane**. This will reduce the alkane factor (ζ in Eq. (5)), and will reduce both the risk and the consequences of RPT. For alkane factors below 1.1, triggering should be very unlikely.
- **Make the methane-fraction of the LNG as high as possible**. This should preferably be done without conflicting with the point above, i.e., without reducing the amount of ethane relative to the heavier components.

4 Practical procedure for LNG RPT risk-assessment

4.1 RPT peak pressure and explosive yield

In Aursand and Hammer [29] we developed the following step-by-step procedure for LNG RPT risk assessment, based on a given LNG mixture:

1. Approximately specify the LNG mixture in question in terms of the first four alkanes,

$$z = [z_1, z_2, z_3, z_4], \tag{3}$$

   where each number represents the molar fraction of methane (C1), ethane (C2), propane (C3), and n-butane (C4), respectively. If the mixture is given in terms of mass fractions w_i, the molar fractions may be found from

$$z_i = \frac{w_i/M_i}{\sum_j w_j/M_j}, \tag{4}$$

   where M_i is the molar mass of species i (see Tab. 1).

2. Calculate the **Alkane factor**,

$$\zeta(z) = \frac{M_2 z_2 + M_3 z_3 + M_4 z_4}{M_2(1 - z_1)}, \tag{5}$$

   which is essentially the average molar mass of the non-methane part of the mixture, relative to the molar mass of pure ethane (M_2). Typical LNG mixtures generally yield values in the range $\zeta \in [1.1, 1.4]$.

   - **If ζ is less than 1.1 we predict that delayed RPT will not occur, and the risk-assessment stops here.**

3. Calculate the **Leidenfrost fraction**,

$$z_{\mathrm{L}} = 1 - \frac{0.36}{\zeta - 0.73}, \tag{6}$$

   which is the methane-fraction that the mixture must boil down to before meeting the criterion for delayed RPT triggering. One may also calculate the **reduction factor**,

$$\nu = (1 - z_1)\,\frac{\zeta - 0.73}{0.36}, \tag{7}$$

   which is the fraction of initial moles remaining at the time when the triggering criterion is reached.

4. Calculate the predicted **peak pressure**,

$$p^* = \left[1 - \mathrm{e}^{-5.6(\zeta-1)}\right] \cdot 62\,\mathrm{bar}, \tag{8}$$

   which is the estimated maximum explosive pressure close to the source of the RPT event.

5. Calculate the predicted **explosive energy yield**. In terms of triggered moles of LNG, it is found from

$$E = \left[4.731\zeta^3 - 24.65\zeta^2 + 41.75\zeta - 20.60\right] \cdot 1\,\frac{\mathrm{kJ}}{\mathrm{mol}}. \tag{9}$$

   The yield in terms of triggered mass may then be found from

$$E^{(\mathrm{mass})} = \frac{E}{z_{\mathrm{L}} M_1 + \zeta(1 - z_{\mathrm{L}}) M_2}. \tag{10}$$

4.2 Risk assessment for an axisymmetric continuous spill

In Ref. [30], we present a simple set of equations for predicting the radius, time, and potential mass of a delayed RPT event for an idealized case of an unbounded, axisymmetric continuous spill of LNG onto water. It is assumed that the spill has a constant mass rate S (kg/s) within a spill radius $r < r_0$. The spilled LNG has composition $z = (z_1, z_2, z_3, z_4)$. We assume that only the methane is evaporation and we approximate the specific enthalpy of evaporation ΔH by the methane value ΔH_1, which is listed in standard chemical tables. Furthermore, we assume that the heat flux $\dot{q}$ from sea water into LNG is roughly independent of position and composition. The following equations are implemented in a web based tool that can be accessed at https://predictrpt.herokuapp.com/.

With the above assumptions, we find that the radius of RPT is

$$r_{\mathrm{RPT}} = \sqrt{\frac{S(1-\hat{z}_{\mathrm{L}})\,\Delta H_1}{2\dot{q}}}, \tag{11}$$

where $\hat{z}_{\mathrm{L}}$ is given by Eq. (6) except in terms of mass fractions. The time of RPT is then given by

$$t_{\mathrm{RPT}} = \frac{r_{\mathrm{RPT}}}{u_{\mathrm{LE}}}, \tag{12}$$

where u_{LE} is the spill leading-edge velocity and is approximately given by

$$u_{\mathrm{LE}} \simeq \sqrt[3]{\frac{S g_{\mathrm{eff}}}{4\pi\rho r_0}}. \tag{13}$$

Here $g_{\mathrm{eff}} = \delta g$ is the effective acceleration of gravity, and δ is the a buoyancy factor based on the densities of water and LNG, $\delta = (\rho_{\mathrm{w}} - \rho)/\rho_{\mathrm{w}}$.

Finally, the following is a worst-case estimate of the total mass of LNG that at any time $t > t_{\mathrm{RPT}}$ may trigger in an RPT event,

$$M_{\mathrm{RPT}} = \hat{z}_{\mathrm{L}} S(t - t_{\mathrm{RPT}}). \tag{14}$$

5 Recommendations for risk reduction

RPT risk can generally be reduced by either reducing the alkane factor (ζ) or by increasing the initial fraction of methane (z_1), while keeping the other constant. One can also do both simultaneously. This will have the following positive effects:

- Reducing the *reduction factor* (ν): This would mean that a smaller fraction of the original amount of LNG will be remaining at the time when triggering is possible.
- Possibly reducing the alkane factor to $\zeta < 1.1$: This would mean that no delayed RPT is possible.
- A significant reduction in the predicted peak explosive pressure.
- A slight reduction in the predicted explosive yield per triggered mass.

It may be tempting to achieve an increase in the initial methane fraction by reducing the second most prominent component (ethane). However, this can be counter-productive as it will increase ζ. According to this model, a more surefire way of reducing risk will be to reduce the amounts of the heavier hydrocarbons propane and butane. This will ensure that both the pressure and energy yield of the vapor explosion is reduced. Only when these are down to very small fractions should one start removing C2 to further reduce risk.

Table 1: Molar mass of the prominent alkanes in LNG

Name		M (kg/mol)
Methane	(“C1”, CH_4)	0.01604
Ethane	(“C2”, C_2H_6)	0.03007
Propane	(“C3”, C_3H_8)	0.04410
n-Butane	(“C4”, C_4H_{10})	0.05812

6 Main results of the Predict-RPT project

6.1 Framework for delayed RPTs

A simulation framework for delayed RPTs has been developed within the project. The framework contains sub-models that describes the important phenomena that occur from the LNG is spilled on the water until superheated conditions are reached and there is a risk for delayed RPTs. Accurate thermodynamical data for hydrocarbon mixtures have been implemented into the framework through the use of SINTEF's in-house library.

The spreading of LNG is described through a simplified, state-of-the-art CFD model developed within the project. The model is presented in Fyhn et al. [31], and summarized in Section 6.2.

The heat flow into the LNG layer is described by a set of heat transfer correlations. Several such sets have been evaluated as part of the project work, and the set with the best agreement against existing experimental data has been implemented into the framework. The evaporation of LNG is described by assuming that all heat transfered into the LNG results in evaporation of LNG.

The superheat limit is an important parameter for predicting the overpressure caused by the rapid evaporation. As described by Aursand et al. [32], see also Section 6.2, we have shown that for single- and multi-component fluids, the classic nucleation theory provides estimates for the superheat limit of LNG that agree well with experimental data. In the simulation framework, this superheat limit has been included in the model as a part of the estimation of the overpressure and potential energy yield in an RPT event. Section 2.5 describes in detail how these two parameters are estimated.

6.2 Overview of scientific papers

The advances made in the Predict-RPT project are documented in eight published journal papers. A final paper is ready for submission to a scientific journal. Six of the papers stems from the work undertaken by the PhD. The PhD student submitted his thesis [33] to the committee in December 2018 and defended in March 2019. The thesis included a 130-page monograph summarizing the research in addition to the journal papers. His most significant work was performed while staying in Chicago as a Fulbright Scholar at Northwestern University, working with Professor Stephen H. Davis, a highly renowned expert in fluid mechanics. The most novel result was published in the Journal of Fluid Mechanics, arguably the world's most prestigious journal in the field.

The spinodal of single- and multi-component fluids and its role in the development of modern equations of state Aursand et al. [32] investigates the superheated and supersaturated states with the aim of identifying the most suitable superheat limit for fluids. The paper describes a robust methodology for obtaining the spinodal of multicomponent fluids which may even be described by the most sophisticated equations of state available. For a selection of modern equations of states, vapour and liquid spinodal curves, superheat and supersaturation limits from classic nucleation theory and available experimental data for the superheat limit are compared. It is shown that for the selected equations of state, there are large inconsistencies in the predicted spinodals. The classical nucleation theory is shown to predict nucleation rates that are order of magnitude for the experiments. However, the limit of superheat measured in experiments agree within 1.0 K and 2.4 K with predictions from the classical nucleation theory for single- and multi-component fluids, respectively. The paper has received a significant attention and was the fourth most downloaded paper during the last 90 days four months after being published.

Modelling planar film boiling of arbitrary inclination with the lubrication approximation Aursand [34] is the first paper published by the PhD student of the Predict-RPT project. It is also the first, of three papers on inclined planar film boiling. In the paper a model for inclined planar film boiling is derived. The model is based upon the lubrication approximation, and serves as the starting point for investigating the film boiling around a droplet in the mixing zone of an LNG spill. It is shown that the dynamics of the film thickness are governed by the Bond and evaporation numbers. A semi-implicit finite-volume method is derived to solve the highly nonlinear model.

Using the derived method it is shown that the planar film boiling model can be used to study transient vapour film growth and the travelling wave instabilities that may occur.

Inclination dependence of planar film boiling stability In Aursand [26], the lubrication approximation derived by Aursand [34] is combined with a quasi-equilibrium evaporation model to investigate the transition from a steady state to an unstable and oscillating vapour film. In addition to the Leidenfrost point, where the film completely breaks down, this transition is key to predict the heat transfer properties of the insulating vapour film. A relatively simple stability criterion for the steady-state solution is derived for planar, non-horizontal film boiling. The limit is tested against against an experimental data set from the literature. Given the nature of the model with its lack of free empirical parameters, it is seen to display a reasonable accuracy.

Inclined film boiling: Film stability and heat transfer In this third paper on inclined film boiling a long-wave model is elaborated and used to investiage the stability of inclined saturated film boiling. [35] A quasi-parallel stability analysis is performed and the result is combined with a heat-transfer model to establish a heat-transfer coefficient. A comparison against relevant data for film-boiling heat-transfer within an error of 15 %.

Thermocapillary instability as a mechanism for film boiling collapse Aursand, Davis, and Ytrehus [36] investigates the Leidenfrost temperature of pure fluids by a thorough investigation of the physical mechanisms that leads to the film breakdown. A novel model of horizontal saturated film boiling that includes features such as non-equilibrium evaporation based on kinetic theory, thermocapillary and vapour thrust stresses and van der Waals interactions is established. From linear stability analysis of the model it is concluded that the vapour film collapse depends upon the balance of thermocapillary instabilities and vapour thrust stabilization. Hence, a purely theoretical prediction of the Leidenfrost temperature could be established. For a certain set of evaporation coefficients, the resulting prediction is consistent with the average Leidenfrost temperature of all fluids that it was possible to find data for.

Predicting triggering and consequence of delayed LNG RPT Using thermodynamics and nucleation theory, Aursand and Hammer [29] develop a model for delayed RPT in LNG spills. The model includes predictions of triggering and the consequence of vapour explosion per mass unit of LNG. As a part of the work it is discovered that these two features of an LNG RPT can be described by two independent parameters, the initial fraction of methane and the molar mass of the remaining non-methane part. Correlations for risk assessment which do not necessitate the use of the underlaying advanced algorithms were developed. In addition, practical advices for risk mitigation were presented. These have also been reproduced in the current report in Section refsec:riskassessment.

Comparison of kinetic theory evaporation models for liquid thin-films Aursand and Ytrehus [37] investigates the applicability of non-equilibrium evaporation models from kinetic theory in the context of fluid mechanics and heat transfer problems. The Boltzmann-equation Moment Method is found to be a good trade-off between complexity and accuracy for practical purposes. Further, it is found that the use of none-equilibrium evaporation models has a significant impact, quantitatively and qualitatively, on the results.

A consistent reduction of the two-layer shallow-water equations to an accurate one-layer spreading model Fyhn et al. [31] is the result of a joint work with a summer-researcher from NTNU. The paper presents a consistent and accurate approximation (or simplification) that allows us to consider only the layer that is spreading. This is useful as it allows us to model the spreading of LNG on water by consider only the LNG layer. The paper shows that this simplification is accurate within criteria that are satisfied in the relevant RPT scenarios. Through the work presented in Fyhn et al. [31] it has been shown that the one-layer description have a better performance that previous assumed near the edge of an LNG spill. The resulting speed of spill fronts have been compared against theoretical predictions in earlier works. Numerical results from from the one-layer model has been compared with results from experiments and show a good agreement.

A coupled model to predict the onset of rapid phase transitions in spills of cryogenic liquids Lervåg et al. [30] is the final scientific paper of the Predict-RPT project. The paper presents the simulation framework developed for delayed RPTs. Results from a simulation is presented to show the height and temperature profiles of a spill scenario, and the corresponding risk-picture for an LNG spill. The selected spill scenario is representative for spills from loading arm failure of a larger LNG fuelled vessel. Finally, a simplified model for continuous spills is presented. The model is able to predict the location of the inner radius of the RPT risk zone and the time until onset of the risk-zone with good agreement when compared to detailed simulations. These results can be combined with the results of Aursand et al. [32] to form a simplified risk assessment procedure of LNG RPTs as presented in Section 4.

References

[1] S. Kumar, H.-T. Kwon, K.-H. Choi, W. Lim, J. H. Cho, K. Tak, and I. Moon. "LNG: An eco-friendly cryogenic fuel for sustainable development". In: *Applied Energy* 88.12 (2011), pp. 4264–4273. DOI: 10.1016/j.apenergy.2011.06.035.

[2] R. C. Reid. "Rapid phase transitions from liquid to vapor". In: *Advances in Chemical Engineering* 12 (1983), pp. 105–208. DOI: 10.1016/S0065-2377(08)60252-5.

[3] R. M. Pitblado and J. L. Woodward. "Highlights of LNG risk technology". In: *Journal of Loss Prevention in the Process Industries* 24.6 (2011), pp. 827–836. DOI: 10.1016/j.jlp.2011.06.009.

[4] P. Cleaver, M. Johnson, and B. Ho. "A summary of some experimental data on LNG safety". In: *Journal of Hazardous Materials* 140.3 (2007), pp. 429–438. DOI: 10.1016/j.jhazmat.2006.10.047.

[5] A. Luketa-Hanlin. "A review of large-scale LNG spills: Experiments and modeling". In: *Journal of Hazardous Materials* 132 (2006), pp. 119–140. DOI: 10.1016/j.jhazmat.2005.10.008.

[6] Stephen Shaw, John Baik, and Robin Pitblado. "Consequences of underwater releases of LNG". In: *Process Safety Progress* 24.3 (2005), pp. 175–180. DOI: 10.1002/prs.10088.

[7] J. A. Alderman. "Introduction to LNG safety". In: *Process Safety Progress* 24.3 (2005), pp. 144–151. DOI: 10.1002/prs.10085.

[8] M. Hightower, L. Gritzo, and A. Luketa-Hanlin. "Safety implications of a large LNG tanker spill over water". In: *Process safety progress* 24.3 (2005), pp. 168–174. DOI: 10.1002/prs.10089.

[9] J. Havens and T. Spicer. "United states regulations for siting LNG terminals: Problems and potential". In: *Journal of Hazardous Materials* 140.3 (2007), pp. 439–443. DOI: 10.1016/j.jhazmat.2006.10.020.

[10] P. K. Raj and L. A. Bowdoin. "Underwater LNG release: Does a pool form on the water surface? What are the characteristics of the vapor released?" In: *Journal of Loss Prevention in the Process Industries* 23.6 (2010), pp. 753–761. DOI: 10.1016/j.jlp.2010.06.003.

[11] K. Forte and D. Ruf. "Safety Challenges of LNG Offshore Industry and Introduction to Risk Management". In: *ASME 2017 36th International Conference on Ocean, Offshore and Arctic Engineering*. American Society of Mechanical Engineers. 2017, V03BT02A016–V03BT02A016. DOI: 10.1115/OMAE2017-61027.

[12] R.P. Koopman and D.L. Ermak. "Lessons learned from LNG safety research". In: *Journal of Hazardous Materials* 140 (2007), pp. 412–428. DOI: 10.1016/j.jhazmat.2006.10.042.

[13] G.A. Melhem, S. Saraf, and H. Ozog. "LNG Properties and Hazards, Understanding LNG Rapid Phase Transitions (RPT)". In: *An ioMosaic Corporation Whitepaper* (2006).

[14] P. Cleaver, C. Humphreys, M. Gabillard, D. Nédelka, R. Heiersted, and J. Dahlsveen. "Rapid Phase Transition of LNG". In: *12th International Conference on Liquefied Natural Gas, LNG12*. Perth, Australia, 1998, (6.5) 1–13.

[15] ABS Consulting. *Consequence Assessment Methods for Incidents Involving Releases from Liquefied Natural Gas Carriers*. Tech. rep. GEMS 1288209. Report for the Federal Energy Regulatory Commission, 2004.

[16] M. Hightower, L. Gritzo, A. Luketa-Hanlin, J. Covan, S. Tieszen, G. Wellman, M. Irwin, M. Kaneshige, B. Melof, C. Morrow, and D. Ragland. *Guidance on risk analysis and safety implications of a large liquified natural gas (LNG) spill over water*. Tech. rep. Sandia Report SAND2004-6258. Albuquerque, New Mexico: Sandia National Laboratories, 2004.

[17] D. L. Katz and C. M. Sliepcevich. "LNG/Water Explosions: Cause & Effect". In: *Hydrocarbon processing* 50.11 (1971).

[18] D. L. Katz. "Superheat-limit explosions". In: *Chemical Engineering Progress* 68.5 (1972), p. 68.

[19] E. Nakanishi and R.C. Reid. "Liquid Natural Gas - Water Reactions". In: *Chem. Eng. Progress* Vol. 67 (12) (1971), pp. 36–41.

[20] T. Enger and D. E. Hartman. "Explosive boiling of liquefied gases on water". In: *Proceeding of the conf. on LNG import and terminal safety*. Boston, 1972.

[21] T. Enger and D.E. Hartman. "Mechanics of the LNG-water interaction". In: *AGA Distribution Conference, Atlanta*. 1972.

[22] T. Enger, D. E. Hartman, and E. V. Seymour. "Explosive Boiling of Liquefied Hydrocarbon/Water Systems". In: *Advances in Cryogenic Engineering: Proceedings of the 1972. Cryogenic Engineering Conference. National Bureau of Standards. Boulder, Colorado. August 9–11, 1972*. Ed. by K. D. Timmerhaus. Boston, MA: Springer US, 1973, pp. 32–41. ISBN: 9781468431117. DOI: 10.1007/978-1-4684-3111-7_4.

[23] V. K. Dhir. "Boiling heat transfer". In: *Annual review of fluid mechanics* 30.1 (1998), pp. 365–401. DOI: 10.1146/annurev.fluid.30.1.365.

[24] S. Nukiyama. "The maximum and minimum values of the heat Q transmitted from metal to boiling water under atmospheric pressure". In: *Journal of Japan Society of Mechanical Engineers* 37 (1934), pp. 367–374.

[25] P. Spiegler, J. Hopenfeld, M. Silberberg, C. F. Bumpus, and A. Norman. "Onset of stable film boiling and the foam limit". In: *International Journal of Heat and Mass Transfer* 6.11 (1963), pp. 987–989. DOI: 10.1016/0017-9310(63)90053-X.

[26] E. Aursand. "Inclination dependence of planar film boiling stability". In: *International Journal of Multiphase Flow* 106 (2018), pp. 243–253. DOI: 10.1016/j.ijmultiphaseflow.2018.05.010.

[27] Ø. Wilhelmsen, A. Aasen, G. Skaugen, P. Aursand, A. Austegard, E. Aursand, M. Gjennestad, H. Lund, G. Linga, and M. Hammer. "Thermodynamic Modeling with Equations of State: Present Challenges with Established Methods". In: *Industrial & Engineering Chemistry Research* 56.13 (2017), pp. 3503–3515. DOI: 10.1021/acs.iecr.7b00317.

[28] M. L. Michelsen and J. M. Mollerup. *Thermodynamic models: Fundamentals and computational aspects*. second. Holte, Denmark: Tie-Line Publictions, 2007. ISBN: 8798996134.

[29] E. Aursand and M. Hammer. "Predicting triggering and consequence of delayed LNG RPT". In: *Journal of Loss Prevention in the Process Industries* 55 (2018), pp. 124–133. DOI: 10.1016/j.jlp.2018.06.001.

[30] Karl Yngve Lervåg, Hans Skarsvåg, Jabir Ali Ouassou, Eskil Aursand, Morten Hammer, Gunhild Reigstad, Øivind Wilhelmsen, Eirik Holm Fyhn, Magnus Aa. Gjennestad, Peder Aursand, and Åsmund Ervik. "A coupled fluid-dynamical, heat-transfer, and thermodynamical model to predict the onset of rapid phase transitions in spills of cryogenic liquids". In: *IN PROGRESS* (To be submitted Q1 2020).

[31] Eirik Holm Fyhn, Karl Yngve Lervåg, Åsmund Ervik, and Øivind Wilhelmsen. "A consistent reduction of the two-layer shallow-water equations to an accurate one-layer spreading model". In: *Physics of Fluids* 31 (12 2019). DOI: 10.1063/1.5126168.

[32] P. Aursand, M. Gjennestad, E. Aursand, M. Hammer, and Ø. Wilhelmsen. "The spinodal of single- and multi-component fluids and its role in the development of modern equations of state". In: *Fluid Phase Equilibria* 436 (2017), pp. 98–112. DOI: 10.1016/j.fluid.2016.12.018.

[33] Eskil Aursand. "Film boiling and rapid phase transition of liquefied natural gas". PhD thesis. 2019.

[34] E Aursand. "Modelling planar film boiling of arbitrary inclination with the lubrication approximation". In: *Proceedings of the 9. National Conference on Computational Mechanics MekIT'17*. Ed. by B. Skallerud and H. I. Andersson. Trondheim: CIMNE, 2017.

[35] E. Aursand and S. H. Davis. "Inclined film boiling: Film stability and heat transfer". In: *International Journal of Multiphase Flow* 111 (2019), pp. 175–187. doi: 10.1016/j.ijmultiphaseflow.2018.11.017.

[36] E. Aursand, S. H. Davis, and T. Ytrehus. "Thermocapillary instability as a mechanism for film boiling collapse". In: *Journal of Fluid Mechanics* 852 (2018), pp. 283–312. doi: 10.1017/jfm.2018.545.

[37] E. Aursand and T. Ytrehus. "Comparison of kinetic theory evaporation models for liquid thin-films". Submitted to *International Journal of Multiphase Flow* in 2018.