The onset of Marangoni convection for evaporating liquids

by

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The stability of evaporating liquids is examined. The geometries investigated are semi-infinite liquid sheets, bounded liquid sheets, sessile droplets, and funnels.

Stability parameters are generated to characterize the stability of evaporating semi-infinite liquid sheets, \((\text{Ma}/E\nu)_\infty\), and bounded liquid sheets, \((\text{Ma}_n/E\nu)_F\). The derivation is made possible by introducing evaporation as the specific heat transfer mechanism at the interface, and using the statistical rate theory expression for evaporation flux so there are no fitting parameters. It is demonstrated that a single parameter can be used to predict the onset criterion instead of two parameters.

A linear stability analysis is performed for spherical sessile droplets evaporating on substrates constructed of either insulating or conducting materials. A stability parameter is generated to characterize the stability of sessile droplets evaporating on insulating substrates, \(\chi_{sID}^D\), and conducting substrates, \(\chi_{sCD}^D\). The results indicate that spherical sessile droplets evaporating on insulating substrates are predicted to transition to Marangoni convection. Since there are currently no experimental results to compare the theory with, another analysis is performed for liquids evaporating from funnels, which can be compared with existing experimental observations.

A linear stability analysis predicts stable evaporation for funnels constructed of insulating materials, in contrast to the sessile droplet case, and generates a new stability parameter, \(\chi_s\), for funnels constructed of conducting materials. The stability parameter
is free of fitting variables since the statistical rate theory expression for the evaporation
flux is used. The theoretical predictions are found to be consistent with experimental ob-
servations for H\textsubscript{2}O evaporating from a funnel constructed of poly(methyl methacrylate)
(PMMA) and for H\textsubscript{2}O and D\textsubscript{2}O evaporating from a funnel constructed of stainless steel.

A parametric analysis is performed on the new stability parameter for liquids evap-
orating from funnels constructed of conducting materials, $\chi_s$, indicating that smaller
interfacial temperature discontinuities, higher evaporation rates, and smaller radii corre-
spond to less stable systems. It is also illustrated that calculations using statistical rate
theory predict an instability, which is consistent with experimental observations, whereas
using the Hertz-Knudsen theory does not predict any instability.
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Chapter 1

Introduction

1.1 Motivation

Recent technological advancements, particularly in the field of microelectronics, require enhanced thermal management techniques. The microelectronics industry has dual design challenges of increased power demand and a reduction in size of devices. These requirements yield devices with increasing power density, which also requires dissipation of higher heat flux at the chip level to maintain acceptable junction temperatures. The primary failure mechanism in electronics during operation is due to high chip temperature [4]. Therefore thermal management solutions will play an important role in the future of microelectronic devices.

The main design constraints in thermal management systems are cost and size, which indicates that systems must be as effective as possible in a small space. Methods with the highest heat transfer effectiveness are those exploiting the change-of-phase process due to large values of latent heat [5]. Heat pipes and evaporative spray cooling are two examples of cooling systems that take advantage of the phase change process. Heat pipes work by: 1) removing heat that evaporates the working fluid, 2) the vapour flows to the condenser section driven by the pressure difference between the hot evaporator
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and cold condenser section, 3) the vapour is condensed there, 4) driven by capillary forces the liquid flows back to the evaporator section through a capillary structure [6]. The three basic factors that determine the liquid driving potential and thereby the heat transport capability are the surface tension, the contact angle, and the geometry of the solid surface at the three-phase boundary line. The higher the surface tension and the lower the solid-liquid contact angle, the higher the driving potential and heat transport capability [7]. Evaporative spray cooling is a process whereby a cooling agent is sprayed onto an electronic module and the heat dissipated from the equipment causes evaporation of the liquid [8].

Whether the cooling systems are heat pipes, evaporative spray cooling, or possibly future alternatives exploiting the change-of-phase process, there are design issues that require a fundamental understanding of the evaporation process, particularly in small-scale geometries where surface tension is an important factor. In applications where surface tension forces have a dominant role, there is a possibility of benefiting from the transport of thermal energy caused by Marangoni convection [2, 1, 9, 10, 11].

Marangoni convection refers to the flow of fluid generated by unbalanced surface tension forces at an interface. Since surface tension is a function of temperature and concentration, variations in either of these properties can cause the surface tension forces to change, leading to convection. In this work only pure liquids are considered and so convection is generated by temperature variations, known as thermocapillary convection.

It has been demonstrated that Marangoni convection can play an important role in transporting thermal energy during evaporation [2, 1, 9, 10, 11]. In certain circumstances as much as 98% of the energy required for evaporation is transported by thermocapillary convection [11]. Circulation of the fluid enables transport of energy from the three-phase boundary line along the interface, which facilitates evaporation. In both cooling examples noted above, increased energy transport by Marangoni convection could be used to enhance the effectiveness of the cooling system. In order to capitalize on the effects of
Marangoni convection, an understanding of the onset is necessary. This research study is performed in order to address the important unresolved issues relating to the onset of Marangoni convection.

The issues addressed in this study are:

- The role of evaporation in the onset of Marangoni convection.

- There are geometrical effects that have not been examined, specifically the effect with spherical interfaces bounded in the direction of the polar angle.

- The presence of fitting variables in onset criterion complicates experimental comparisons.

In summary, the motivation for this study is to provide a fundamental understanding of the onset of Marangoni convection for evaporating liquids with bounded interfaces. A possible benefit of this understanding is to facilitate the design of more effective thermal management devices, such as heat pipes or evaporative spray cooling systems. In the following sections a summary is provided of studies that address Marangoni instability for evaporating liquids and studies that consider the geometrical effects on the onset of Marangoni convection.

### 1.2 Marangoni convection in evaporating liquids

The seminal work on Marangoni instability was published by Pearson in 1958 [3]. It was the first investigation to provide a stability analysis demonstrating that surface tension effects could destabilize a liquid sheet that was heated from below, and generate convective cells. The analysis was performed for a semi-infinite liquid sheet to isolate the interface from boundary effects. An important point about Pearson’s analysis is that he describes the thermal boundary conditions at the interface as being “of crucial importance” and states that “the aim...is not to provide an exhaustive description of these
phenomena and their relevant idealizations, but rather to provide a general treatment
that illustrates the fundamental surface tension mechanism and comprehends its many
realizations.” He also points out that he is “not concerned...with a thorough analysis
of heat transfer to and from the liquid layer, though these matters become relevant in
the investigation of any particular physical phenomenon.” The reason these quotes have
been stated is to emphasize the generalizations made in the Pearson analysis, specifically
the introduction of a heat transfer coefficient, which favour mathematical tractability
over physical compatibility. The study provided a crucial insight into the destabilizing
effects of surface tension forces, and prior to this explanation it was believed that the
hexagonal convective cell patterns observed in the experiments of Bénard [12] were solely
a result of buoyancy forces, which were theoretically described by Lord Rayleigh [13].

Pearson had thought that it might be possible to treat the “allied problem of liquid
cooling by evaporation in a similar fashion” to his analysis, given the correct set of
approximations. It has been demonstrated that his analysis does not apply to evaporating
liquids [10, 14, 15, 16], and the primary reason for this is that his approximation of
a discrete temperature discontinuity at the interface was experimentally found to be
in the opposite direction to what he had assumed (i.e. the interfacial vapour phase
temperature is actually greater than the interfacial liquid phase temperature). So the
problem of describing Marangoni instability for evaporating liquids has been addressed
in some recent investigations.

Margerit et al. [17] investigated an evaporating semi-infinite liquid sheet lying on an
impermeable hot horizontal plate and bounded on the top by a permeable parallel cold
plate. To describe the evaporation process they used the Hertz-Knudsen relation and the
Onsager-Casimir reciprocity relations. The experiments of Fang and Ward [18] were used
by Margerit et al. to determine the values of some of the interfacial coefficients and the
remaining unknown coefficients were included in additional parameters and described a
priori. They began the analysis with a two-sided model (describing the effects of both
the liquid phase and its overlying vapour); however, during their analysis they reduced the problem to a one-sided model and lumped the vapour effects into an equivalent Biot number. So the result of their work is a one-sided description of Marangoni instability for evaporating liquid sheets, with a Biot number containing unknown coefficients (fitting parameters). In a later work [19], Haut and Colinet studied the effect of including an inert gaseous component in the vapour phase, and showed that the one-sided approach is valid by comparison to a numerical simulation of the two-sided problem. Their work demonstrated that complications can arise in using the Hertz-Knudsen expression for the evaporation flux since unknown fitting coefficients in the stability criterion inhibit comparisons to experimental studies.

Experiments were performed by Chai and Zhang [20] to investigate Marangoni instability for a thin evaporating liquid layer. They investigated twelve different hydrocarbons evaporating on a heated plate with insulated side walls. Aluminum powder was mixed into the fluids for imaging the Marangoni convection. They showed that the onset of the instability did not match with the critical Marangoni numbers predicted by Pearson’s [3] theory and proposed that a new mechanism for initiating an instability is present, caused by the evaporation itself. They did not elaborate on the mechanism that would cause this, neglected to mention the vapour effects, and did not report the measured temperature profiles in the vapour phase, even though they had some experiments where they show evaporation and generation of convection cells with zero or positive temperature gradients in the liquid phase. They demonstrated that evaporation contributes to Marangoni instability, which had been uncertain prior to their experiments.

Liu et al. [15] described the results of Chai and Zhang [20] using a two-sided model of the semi-infinite evaporating liquid layer. They used kinetic theory to describe the evaporation, with the accommodation coefficient lumped into the Biot number, and used the spectral numerical method to solve the system. Their critical Marangoni number includes the temperature difference of both the vapour and liquid phases, but they did
not investigate the link between evaporation and heat fluxes or the effect of a temperature discontinuity at the interface. Similar to Margerit et al., Liu et al. demonstrated the difficulty in generating a stability criteria free of fitting parameters when Hertz-Knudsen theory is used for the evaporation flux. They also left an open question as to the role of evaporation and interfacial temperature discontinuities in the onset of an instability.

A theoretical investigation by Bestehorn [21] analyzed Marangoni convection for thin films of evaporating liquids. He included the evaporation flux (and in particular the change of evaporation with temperature) into an equivalent Biot number, and solved the system numerically with these parameters included as fitting coefficients. He was unable to obtain quantitative comparison with experimental observations due to the unknown fitting parameters; however, the qualitative comparison was consistent and in agreement with previous studies. Specifically, the onset Marangoni numbers and physical Marangoni numbers are higher for evaporating systems, and the evaporation process has a destabilizing effect. Therefore, this was another study in which fitting parameters complicated experimental comparisons.

Experimental studies by Duan and Ward [2, 1] demonstrated the presence of Marangoni convection in experiments with H₂O and D₂O evaporating from funnels constructed of stainless steel. They found that it was possible to have quiescent evaporation and as the evaporation rate was increased there was a transition to Marangoni convection. The geometry of a funnel is significantly different from the semi-infinite sheet geometry used in previous theoretical investigations of Marangoni convection. In particular the liquids evaporating from a funnel had a spherical interface that was in direct contact with the funnel wall. Therefore, it was not possible to apply previous onset predictions to these experiments to understand the transition behaviour. The observations also demonstrate that there was a transition to Marangoni convection without temperature gradients in the liquid phase normal to the interface. Therefore, a new mechanism was generating Marangoni convection, possibly related to the bounded interface, and a new stability
analysis would be required to understand it. Another experimental investigation was performed by Thompson et al. [10] with H$_2$O evaporating from a funnel constructed of polymethyl methacrylate (PMMA). Since PMMA has a thermal conductivity one-third that of water, the funnel wall was insulating in this case. They found that as the evaporation rate was progressively increased there was no transition to Marangoni convection observed, indicating that there may be an effect from the funnel wall material on the stability of the interface.

A theoretical investigation by Das, MacDonald, and Ward [22] was performed for the evaporation of semi-infinite and bounded liquid sheets. The onset Marangoni numbers that resulted from this study contained no fitting parameters since statistical rate theory was used to describe the evaporation flux instead of the Hertz-Knudsen relation. The geometry considered was firstly that of a semi-infinite sheet and secondly boundaries were introduced to study the effect of finite size on the instability. They demonstrated that the predictions of the onset of Marangoni convection were different (i.e. at much higher values) to those predicted by the Pearson theory, which is consistent with the experimental observations noted above for evaporating systems with finite boundaries. However, the geometry was sufficiently different from the funnels used in the experiments of Duan and Ward [2, 1] that no quantitative comparison could be made for those experiments.

A recent experimental investigation by Song and Nobes [16] observed Marangoni convection in water evaporating from a quartz cuvette. They confirmed the inability of the Pearson theory to predict the onset condition for their experiments. Their results also indicate the possibility of the boundary material playing a role in the onset of Marangoni convection. Their experimental system had a depth much greater than the thin film experiments performed previously, thus negating the semi-infinite approximation, and their cuvette wall was constructed of quartz for optical reasons. They noted a convective flow pattern believed to be in a different direction to that observed by Duan and Ward [2, 1] and suggested that the wall material might be playing a role in the nature of the
instability.

In summary, the traditional Marangoni number, based on the theoretical investigation of Pearson, cannot be applied to evaporating liquid layers. The experimental investigations listed above indicate that the onset condition for evaporating liquid layers is at a higher Marangoni number and they demonstrate that the effect of evaporation is significant. Theoretical investigations have resulted in Marangoni numbers for evaporating liquids containing fitting parameters, which makes direct comparison to experimental results difficult. The use of a statistical rate theory expression for evaporation flux results in an onset criterion that is free of fitting parameters; however, the existing experimental observations are either lacking in enough details to provide a validation of the prediction from this theory or have a sufficiently different geometry (i.e. a funnel). Recent experimental observations indicate that the geometry, and specifically the boundary wall material, may play a crucial role in the onset of Marangoni convection. Therefore, a new stability analysis is required to understand these experimental observations [2, 1, 10], and the statistical rate theory expression for evaporation flux should be used so there are no fitting parameters in the stability parameters.

1.3 Geometrical effects on Marangoni convection

As can be seen from the previous section many of the studies of Marangoni instability analyze semi-infinite thin fluid sheets, following the original framework used by Pearson [3]. However, physical systems of interest often have geometries that deviate from semi-infinite sheets. Examples of this are the microelectronic cooling systems noted above with the fluid either tightly confined in tubes or sprayed (resulting in the formation of sessile droplets), and the funnels used in the experiments of Duan and Ward [2, 1]. In this section the effects of geometry on the onset of Marangoni convection are discussed.

Rosenblat et al. [23, 24] provided the first nonlinear analysis of Marangoni convection
in bounded containers. Part 1 of their investigation [23] was for circular cylindrical
containers and part 2 [24] was for rectangular containers. They considered layers of fluid
with the depth dimension either comparable to or smaller than the horizontal dimensions
of the container, and assumed that the upper free surface was non-deformable, and the
side walls were adiabatic and impermeable, but “slippery” (velocity can have a non-zero
value along the boundary). The slippery condition was used to allow the linear stability
theory to be solved using normal modes (separation of variables). In both parts of their
study they found that the instability is a function of the aspect ratio of the container for
bounded containers and predict an increase in the value of the onset Marangoni number
with decreasing aspect ratio of the fluid. Since their study considered nonlinear effects
they were able to analyze the shapes expected for the convection rolls and concluded
that the shape of the container impacts the cell shape. In particular they predicted that
hexagonal cells would not be expected in the bounded containers they investigated. Their
study demonstrates the importance of geometrical effects on Marangoni instability.

An experimental investigation was performed by Koschmieder and Prahl [25] to in-
vestigate the theoretical predictions made by Rosenblat et al. [23, 24]. Their experiments
confirmed that the onset predictions and the shape of the resulting convection cells are
both strongly dependent on the physical side walls (lateral bounding) of the container.
They found that in the circular container the form of the patterns they observed corre-
sponded to the theoretical predictions, although the order of appearance of the patterns
was different from the order of appearance predicted by Rosenblat et al. [23]. They were
surprised by the appearance of triangular cells in the square container; however, they
did not believe a comparison of their results with the theoretical results of Rosenblat et
al. [24] was appropriate, because they considered rectangular containers, of which the
square planform is only a very degenerated special case. With respect to the onset of
convection as a function of the aspect ratio of the layer, their measurements confirmed
in a qualitative way the increase in the value of the onset Marangoni number when the
aspect ratio decreases. Thus, this study provided experimental proof to go along with
the theoretical evidence from Rosenblat et al. [23, 24], that geometry has a significant
impact on Marangoni instability.

Dauby and Lebon [26] performed a numerical investigation to examine the “slippery”
side wall condition from Rosenblat et al. [23, 24], and describe the experimental
observations of Koschmieder and Prahl [25]. A number of other similar investigations
were undertaken [27, 28, 29, 30]. Dauby and Lebon analyzed Marangoni convection in
three-dimensional rectangular finite containers with rigid adiabatic lateral walls with the
“no-slip” condition applied. The “no-slip” condition at the sidewalls makes the method
of separation of variables inapplicable for the linear problem, so to solve the full three-
dimensional problem a spectral Tau numerical method was employed. They find that
the slippery walls assumption results in the absence of transcritical bifurcations, and
the prediction of the shape of the cells is affected. They also found very good agreement
with Koschmieder and Prahl’s experiments [25] since all the convective patterns observed
experimentally for square boxes with aspect ratios smaller than eight were found as sta-
table solutions of their model. Therefore, their study demonstrates the importance of the
boundary conditions when analyzing the stability of a bounded interface.

Krmpotić et al. [31] analyzed the Marangoni convection of a bounded square container
considering both surface tension and gravity effects. For their boundary conditions they
assumed that the lateral walls were impermeable, the tangential vorticity was zero on
them (slippery condition), and they were adiabatic. They found that the sequence of
modes that interact was only fixed by the geometry of the container and by the thermal
properties of the side walls and not by the characteristics of the fluid or by the relative
importance of Rayleigh and Marangoni convective mechanisms. This study provided
further proof that the geometrical effects are crucial, even in the case when buoyancy
effects are considered as well.

Ha and Lai [14] investigated Marangoni instability of an evaporating droplet in a
passive gas medium. This was one of the first studies considering a spherical interface and they considered an entire droplet, unbounded in any direction. As the droplet evaporated it absorbed heat from its interior which resulted in a temperature reduction near the surface. As the evaporation proceeded the temperature reduction and thermal boundary layer thickness near the free surface became larger and the consequent variation in surface tension resulted in a Marangoni instability. An interesting conclusion they noted was that the onset condition was a strong function of the droplet initial temperature with which the value of the onset Marangoni number increases. This study provided evidence that Marangoni instability is present in systems with spherical interfaces.

In a follow-up study Ha and Lai [32] used the energy method to investigate the Marangoni instability of an evaporating droplet. They found similar trends with those acquired by their linear stability analysis [14]. Both studies indicated that, as time proceeded, both the decrease of the surface temperature and the growth of the thermal boundary layer near the free surface were conducive to the onset of instability. The onset Marangoni number and wave number increased with the droplet initial temperature. The onset Marangoni numbers predicted by the energy method were found to be smaller than those calculated by the linear stability analysis. However, the subcritical region between the predictions calculated by these two methods was narrow. The consistency indicated the validity of a linear stability analysis as an approach to investigate the Marangoni instability of an evaporating droplet.

Another study considering the evaporation of a whole spherical droplet was performed by Kim et al. [33]. They investigated a droplet subjected to an impulsive change in boundary condition (transient heat conduction) on the basis of the propagation theory.

As noted above Das, MacDonald, and Ward [22] investigated Marangoni instability for an evaporating liquid sheet bounded by lateral walls. They considered evaporation at the free surface, assumed isothermal side walls (as opposed to adiabatic), and used the no-slip condition along the walls. Their results were consistent with the trends discovered
by Rosenblat et al. [23, 24] in regards to the effect of the aspect ratio of the system. Their study confirmed that a bounded interface can have a different onset Marangoni number, but the analysis was for flat interfaces and not spherical interfaces.

In summary, there have been a number of studies analyzing the Marangoni instability of laterally bounded liquid sheets. Most of these consider adiabatic side walls and the study by Das, MacDonald, and Ward [22] considers isothermal side walls. Experimental investigations have confirmed the importance of the container size for the onset of Marangoni convection and for the shape of the resulting convection cells. The studies analyzing spherical interfaces consider only entire droplets with no bounding in any direction. Much has been learned from the studies of bounded liquid sheets and perfect spheres but with many applications involving geometries that have less idealized geometrical configurations, analyses are required for geometries that are more physically realistic. Also, the experimental observations for liquids evaporating from funnels [2, 1, 10] indicate an interesting transition to Marangoni convection that takes place for conducting funnel materials but not insulating materials. To the best of the author’s knowledge there have been no theoretical investigations of the onset of Marangoni convection for a spherical interface bounded in the direction of the polar angle for all azimuthal angles (i.e. a sessile droplet bounded at 90° or a funnel bounded at 45°).

1.4 Scope of thesis

The first objective in this thesis is to use the statistical rate theory expression for the evaporation flux to produce a stability parameter free of fitting parameters (and without a heat transfer coefficient) and analyze the stability for a liquid sheet, for both semi-infinite and bounded cases. This analysis is an extension of the Das, MacDonald, and Ward [22] work noted above. Once a stability parameter is defined that is free of fitting parameters it will be demonstrated that the surface thermal effects and the stability prediction are
intrinsically linked for physical systems, and so cannot be arbitrarily assigned as has traditionally been done in the past. This analysis demonstrates the advantages of using statistical rate theory in assessing the stability of evaporating systems, and this analysis forms a basis for analyses of systems with geometries more relevant to experiments and applications.

The geometry of a sessile droplet is ubiquitous in applications, such as the evaporative spray cooling example noted above [8], and in experiments, such as the experiments demonstrating the energy transport enhancement from Marangoni convection listed above [11]. A linear stability analysis is performed for the sessile droplet geometry with evaporation included as the heat transfer mechanism at the interface. The statistical rate theory expression for evaporation is used to generate a stability parameter free of fitting parameters. The sessile droplet geometry is described in general by considering liquids with spherical interfaces maintained on a substrate material that are bounded in the direction of the polar angle (at 90°). The criteria for marginal stability is established. Similar to previous studies, it is assumed that the marginally stable state of a system corresponds to a neutral stability and exceeding this criteria generates an instability. The analysis is performed for two different cases: substrates that are insulating, and substrates that are conducting. A stability parameter is developed for evaporating sessile droplets on insulating substrates and conducting substrates. However, there are no experimental results to compare the stability predictions with. Therefore, a new analysis is performed for a funnel geometry, which can be compared to existing experimental observations [2, 1, 10].

A linear stability analysis is performed for liquids evaporating from funnels. The analysis parallels that of the droplet case above except the boundary conditions are altered since the boundary is located at a polar angle of 45° in this case. This analysis is also performed for two different cases: funnels constructed of insulating materials, and funnels constructed of conducting materials. The results of the stability analysis are
used to develop the expression for a stability parameter which provides a *quantitative*
prediction for the transition from a quiescent state to a state with Marangoni convection
for liquids evaporating from funnels constructed of conducting materials. Since the sta-
tistical rate theory expression for evaporation flux is used [34], the onset criterion has no
fitting parameters and can be compared directly to the experimental observations.

The theoretical predictions are then compared with experimental observations. The
theoretical predictions for liquids evaporating from funnels constructed of insulating ma-
terials are compared with the experiments with H$_2$O evaporating from a funnel con-
structed of PMMA [10]. The predictions for a transition to Marangoni convection cal-
culated with the new stability parameter are compared to the experimental results with
H$_2$O and D$_2$O evaporating from funnels constructed of stainless steel [2, 1].

Finally, a parametric analysis is performed to determine the relationship between the
stability parameter and the interfacial vapour phase temperature, interfacial liquid phase
temperature, the evaporation flux, and the radius of the spherical interface. As part of
this analysis two different methods of expressing the evaporation flux are also compared.
The first method is the statistical rate theory expression used in the analysis noted above
and the second is the Hertz-Knudsen expression. Both expressions are used to generate
predictions and the results are compared and discussed.
Chapter 2

Onset of Marangoni convection for evaporating liquid sheets

In the Introduction, it was mentioned that the original stability analysis for Marangoni instability, performed by Pearson [3], could not be applied to evaporating systems. The analysis in this Chapter will be for semi-infinite and bounded liquid sheets. The purpose is to demonstrate how evaporation can be introduced into a stability analysis for this traditional geometry prior to performing the stability analyses for more complicated geometries in the following Chapters. A crucial element of this analysis is to demonstrate that using the statistical rate theory expression for the evaporation rate, enables the introduction of evaporation without the need for fitting parameters. This Chapter also illustrates that an evaporation parameter and stability parameter, which are comprised of physical variables, are necessarily linked due to the energy balance at the interface. Therefore the parameters may not be arbitrarily assigned and a single parameter can be found which has a narrow range of values for the onset criterion. Also, the evaporation parameter appears in similar form in the subsequent Chapters, even when different geometries are analyzed. The introduction of evaporation and discovery of a single parameter in this Chapter sets the basis for the stability analyses and the following chapters
address the challenge of performing stability analyses for evaporating liquids with more complex geometrical configurations

2.1 Introducing evaporation into the stability analysis

This section will summarize the crucial equations and techniques from both the Pearson [3] and Das, MacDonald, and Ward [22] studies to demonstrate how evaporation is included in the stability analysis.

2.1.1 Pearson’s interfacial approximations

As was stated in the Introduction, by referencing quotes from his publication, Pearson states that his objective was to demonstrate that surface tension effects could initiate a Marangoni instability, so he made approximations at the interface to facilitate the mathematical calculations since he was unconcerned with the specific heat transfer mechanisms. He analyzed a semi-infinite liquid layer that was heated from below. In summarizing Pearson’s analysis, his notation is replaced with the notation used in this thesis.

For simplicity, the assumption made at the interface was to consider a discrete jump in temperature at the free surface, whereby the overlying phase was colder than the liquid phase. A general heat transfer coefficient was defined at the interface

\[ h_t = \frac{\partial Q}{\partial T^L} \bigg|_{T^L} , \]

which represents the rate of change with temperature of the rate of loss of heat per unit area from the upper surface to its upper environment. \( Q \) is the rate of heat loss per unit area from the upper free surface, \( T^L \) is the temperature of the liquid, and an \( I \) subscript denotes a property at the interface.
The final interfacial energy balance that resulted from the perturbation analysis was

$$\frac{\partial \theta}{\partial z} + \text{Bi} \theta = 0,$$

where $\theta$ is the temperature perturbation, $z$ is the vertical direction (perpendicular to the interface), and Bi is the Biot number, defined as

$$\text{Bi} = \frac{h_t \delta}{\kappa L},$$

where $\delta$ is the thickness of the liquid layer, and $\kappa_L$ is the thermal conductivity of the liquid.

Since the heat transfer coefficient, $h_t$, is defined in general terms, it becomes problematic when a comparison to experiments must be made. Physical systems typically have more than one mechanism of heat transfer at an interface, and so the rate of change of the heat flux with respect to temperature has proven to be difficult to calculate accurately. What Pearson did when he successfully demonstrated the ability of surface tension forces to destabilize the liquid layer, was to plot neutral stability curves for arbitrarily assigned values of the Biot number, as shown in Fig. 2.1. Since a Bi value of zero is the easiest calculation to make, experimental systems were designed in order to achieve a Bi value of zero and validate the theory. An example is the famous study by Schatz et al. [35], which is considered to be one of the best experimental validations of the Pearson theory.

A downside to the requirement of a zero value for the Biot number is the inability to apply the theory to more general physical systems of interest. Due to the advantageous benefits associated with energy transport by Marangoni convection it is desirable to have a theoretical prediction for onset that could be used in design work or to analyze the conditions required to initiate Marangoni convection. Also, as noted in the Introduction, the theory is not applicable to evaporating systems, primarily due to the discrete temperature jump introduced at the interface, which is in the opposite direction of experimental observations [10].
2.1.2 Analysis for evaporating liquid sheets

Instead of introducing a general parameter at the interface to describe a wide array of heat transfer conditions it is possible to include a specific mechanism that is dominant. Evaporation is ideal for this role, since its magnitude is large relative to other heat transfer mechanisms, and by using the statistical rate theory expression for evaporation flux, the evaporation process can be described using only physical variables, with no fitting parameters, and so the stability can be compared to experiments.

The system investigated in the analysis [22] is shown in Fig. 2.2. The arrows in Fig. 2.2 demonstrate the path of water molecules through the permeable solid layers.
to indicate that the liquid water layer is evaporating. Also of note in the figure are the temperature profiles shown as dashed lines, which correspond to the case where the interfacial energy balance considers conduction through the liquid layer and the energy required for evaporation at the interface.

Figure 2.2: Schematic of physical system used in theoretical analysis. Arrows indicate direction of mass flow, representing evaporation.

The final interfacial energy balance for the evaporation perturbation problem is [22]

$$\frac{\partial \theta}{\partial z} + (Ev) \theta = 0,$$  \hspace{1cm} (2.4)

where $\theta$ is the temperature perturbation. The evaporation parameter, $Ev$, that was a result of linearization and non-dimensionalization during the perturbation analysis, as explained in detail in the publication [22], is defined as follows

$$Ev = \frac{\delta}{\kappa L} \left( \frac{\partial j_{ev}}{\partial T} \right)_{T} \left( h_{0}^{V} - h_{0}^{L} - j_{ev}^{c_{p}} \right),$$  \hspace{1cm} (2.5)

where $h_{0}^{V}$, $h_{0}^{L}$, and $c_{p}$, are the interfacial enthalpy of the vapour and liquid (initial, unperturbed values), and the specific heat of the liquid. The expression for the evaporation flux, $j_{ev}$, is given by statistical rate theory, which is discussed in the next section. It is also noted that Eq. (2.5) requires the derivative of evaporation flux with respect to the interfacial liquid temperature, so an expression is required that can be differentiated.
The evaporation parameter in Eq. (2.4) serves to replace the Biot number in Eq. (2.2). From Eq. (2.5) it can be seen that the heat transfer coefficient has been eliminated and if the expression for the evaporation rate is generated from statistical rate theory, the parameter is based only on physical variables. Part of Pearson’s prediction that the evaporation problem would involve a parameter that depends on the rate of evaporation and the latent heat of vaporization has been vindicated by this analysis; however, it was only possible to derive this parameter with a new perturbation analysis that removed his generalizations.

For evaporating systems, the evaporation parameter is analogous in function to the Biot number for non-volatile systems. It can be deduced that the evaporation parameter represents the ratio of the resistance of the fluid layer to conduction heat transfer to the resistance of the energy transfer for the evaporation process. Therefore, for increasing $Ev$ numbers, the temperature gradient across the fluid layer becomes larger. The temperature gradient across the fluid layer is the driving force behind the generation of the instability and therefore this parameter plays an important role. Similar to the non-volatile case where the predicted onset points are dependent on the value of the Biot number, the predicted onset points depend heavily on the value of the evaporation parameter in the case of evaporating systems, and hence, a broad range of predicted onset points is observed.

The expression for the evaporation parameter in Eq. (2.5) is a critical factor in the investigation of stability for evaporating liquids. A very similar form of this expression appears in the subsequent analyses for bounded spherical interfaces, and in each case the parameters plays a critical role in the stability of the system. As this parameter appears in the upcoming analyses it will be noted and discussed for each case individually.

It was found that for a system of evaporating water, $Ev$ has a minimum value of approximately 20 and a maximum value that approaches infinity. The minimum value was obtained by setting $T_f^L$ at $-40^\circ C$ and optimizing the $Ev$ value with respect to the
depth, evaporation rate, the ability of the system to reach an unstable state, and an
ergy balance at the interface. The value of $-40^\circ$C was selected since the trend is that
lower values of $T^L_I$ yield lower $Ev$ values (described in detail in the following sections), and
because there is evidence in the literature [36] that $-40^\circ$C may be the lowest temperature
at which liquid water can exist. This minimum value is noted for interest but since there
have been no experiments capable of reaching such a low temperature for liquid water
(to the best of the author’s knowledge), values this low are not considered throughout
this analysis. Instead, $Ev$ values associated with actual physically attainable scenarios
are considered.

2.1.3 Statistical rate theory expression for evaporation flux

As noted above, the evaporation parameter (Eq. (2.5)) requires the derivative of evapo-
ration flux with respect to the interfacial liquid temperature. Statistical rate theory can
be used to generate an expression for evaporation flux, $j_{ev}$, [34, 37], which has no fitting
parameters and can be differentiated. The statistical rate theory expression is based on a
quantum mechanical first order perturbation analysis of the unidirectional condensation
and evaporation fluxes. The thermodynamic properties of the vapour phase are included
in determining the expression for the unidirectional evaporation flux. This is in contrast
to other kinetic relations, such as the Hertz-Knudsen theory, described in the next sec-
tion, where the unidirectional evaporation flux is considered to be independent of the
thermodynamic properties of the vapour phase. A detailed derivation of the statistical
rate theory expression for evaporation flux can be found in [34, 37]. The expression for
$j_{ev}$ is [34]

$$j_{ev} = 2mK_e \sinh\left(\frac{\Delta s_{lv}}{k_b}\right),$$

(2.6)

where

$$K_e = \frac{\eta P_s(T^L_I)}{\sqrt{2\pi mk_bT^L_I}},$$

\[ \eta = \exp \left[ \frac{v_f(T_I^L)}{k_b T_I^L} \left( P_e^L - P_s(T_I^L) \right) \right], \]

\[ \Delta s_{lv} = \ln \left[ \left( \frac{T_V^S}{T_I^L} \right)^4 \frac{P_s(T_I^L)}{P_V} \right] + \ln \left[ \frac{q_{vib}(T_V^S)}{q_{vib}(T_I^L)} \right] + 4 \left( 1 - \frac{T_I^L}{T_I^V} \right) + \left( \frac{1}{T_I^V} - \frac{1}{T_I^L} \right) \sum_{l=1}^{3n-6} \left[ \frac{\theta_l}{2} + \frac{\theta_l}{e^{\theta_l/T_I^V} - 1} \right] + v_f(T_I^L) \left[ P_V^* + \frac{2\gamma_{LV}(T)}{r_I} - P_s(T_I^L) \right], \]

\[ \theta_l = \frac{\hbar \omega_l}{k_b}, \]

\[ q_{vib}(T) = \prod_{l=1}^{3n-6} \frac{e^{-\theta_l/T}}{1 - e^{-\theta_l/T}}, \]

and \( P_e^L \) must satisfy

\[ P_e^L - \frac{2\gamma_{LV}(T)}{r_I} = \eta P_s(T_I^L), \]

where \( k_b \) is the Boltzmann constant, \( \hbar \) is the reduced Planck constant, \( m \) is the mass of a molecule undergoing evaporation, \( \omega_l \) is a molecular phonon, \( v_f \) is the specific volume of the liquid at saturation, \( \gamma_{LV} \) is the surface tension at the liquid-vapour interface, \( P_s(T_I^L) \) is the saturation pressure, and \( P_e^L \) is the liquid pressure that would exist at equilibrium. The values of the properties for H\(_2\)O are listed in [2], and D\(_2\)O in [1].

### 2.1.4 Hertz-Knudsen expression for evaporation flux

Another expression that has been used for the evaporation flux is one based on the Hertz-Knudsen theory which uses kinetic theory and assumes a Maxwellian distribution for the velocities of the molecules [38]

\[ j_{ev}^{HK} = \frac{1}{\sqrt{2\pi}} \left( \eta(T_I^L, T_I^V) \frac{P_s(T_I^L)}{\sqrt{RT_I^L}} - \eta(T_I^L, T_V^S) \frac{P_V^*}{\sqrt{RT_I^V}} \right), \]
where \( R = k_b/m \) is the gas constant, \( \eta(T_L^L, T_L^I) \) is the mass evaporation coefficient, and \( \eta(T_L^L, T_V^I) \) is the mass condensation coefficient. At present there is no method to determine these coefficients directly. As noted in the Introduction, Margerit et al. [17] used the Hertz-Knudsen expression and the Onsager-Casimir reciprocity relations in their stability analysis, but ultimately were left with unknown fitting parameters in their results.

In order to generate an expression that is free of fitting parameters the statistical rate theory expression for evaporation flux is used in Eq. (2.5).

The statistical rate theory and Hertz-Knudsen expressions for evaporation flux are compared in more detail in Chapter 6 with respect to a parametric analysis of the stability parameter for liquids evaporating from a funnel.

### 2.2 Single parameter for a semi-infinite liquid sheet

Since the surface heat transfer mechanisms are necessarily linked to the temperature gradient maintained throughout the liquid phase by the interfacial energy balance, it seemed suspect that the Biot number could be arbitrarily assigned, as was done in early studies [3]. When the evaporation parameter, \( Ev \), was derived for the stability of evaporating liquid systems it became clear that it could not be arbitrarily assigned with respect to the Marangoni number, due to the physical parameters in both expressions, and that there must be a link between the two parameters in order to ensure an energy balance at the interface.

An investigation of \( Ev \) values led to the discovery of a precise onset indicator. Dividing the Marangoni number by the evaporation parameter results in a parameter that has a narrow range of values representing the onset points. Fig. 2.3 displays the marginal stability curves and the onset values are represented by the minimum value of each curve with respect to the value of the wave number \( (k) \). There are five distinct curves plotted
in the figure and their close proximity demonstrates the narrow range of predicted onset points for a span of \( Ev \) values between 250 and 2250. To emphasize the narrow range of predicted onset values the selected \( Ev \) range spans an order of magnitude, however the curves still virtually overlay each other. The full range of predicted onset points is from 32.1 to 32.5 as opposed to many orders of magnitude that is found with the Marangoni number. The inset of Fig. 2.3 allows a comparison to the broad range of expected onset points when using the Marangoni number as the prediction parameter for the same range of \( Ev \) values. Predicting precise onset points of a Marangoni instability for physical systems is now attainable for evaporating liquids.

Figure 2.3: Stability curves for a range of \( Ev \) values from 250 to 2250 versus the new stability parameter. The inset shows stability curves with respect to the Marangoni number.

The reason for the narrow range can be ascertained by analyzing the equation for the
new parameter

\[
\left( \frac{Ma}{Ev} \right)_\infty = 8k \left( 1 + \frac{k \coth k}{Ev} \right) \frac{(k - \cosh k \sinh k)}{(k^3 \coth k - \sinh^2 k)},
\]

where the expression in the numerator for the Marangoni instability was derived in the publication [22], and is similar in form to the Pearson result since the only change in the analysis was the replacement of the Biot number with the evaporation parameter. The only dependence of the right hand side on \(Ev\) is from the \(\left( 1 + \frac{k \coth k}{Ev} \right)\) term. As \(Ev\) approaches infinity this term becomes 1 and even for the lowest value calculated for water of \(Ev \approx 20\), this term is only 1.14. Therefore the value of the whole expression changes little with respect to \(Ev\) values that are based on evaporating water.

Due to the narrow range afforded by the new parameter, a median value can be selected that represents the majority of cases, 32.2, particularly those of experimental and practical interest, while maintaining a high degree of accuracy. It is evident that with a single onset point, higher \(Ev\) values require higher Marangoni numbers for onset. Therefore, systems with higher \(Ev\) values are technically more stable according to the corresponding values of the Marangoni number. However, as was stated above, higher \(Ev\) values correspond to systems with larger temperature gradients across the fluid layer. It is concluded then that these two effects offset each other. A system with a higher \(Ev\) value is technically more stable; however, it also has a higher temperature gradient across the fluid layer, which is the destabilizing factor. This manifests itself in a single parameter that shows a relatively common onset point for systems of evaporating water when both \(Ev\) and \(Ma\) effects are considered together.
2.3 Parametric investigation of the evaporation parameter

Since the evaporation parameter has no arbitrary coefficients and no fitting parameters, it can be examined parametrically to understand how it fluctuates when the physical variables are altered. As seen in Eq. (2.5), the evaporation parameter is a function of $T_V^I$, $T_L$, $j_{ev}$, and $\delta$, so each of these parameters are evaluated individually to determine their effect on the values of $Ev$.

There are currently no experiments of evaporating liquid sheets with the measurements and precision necessary to analyze the evaporation parameter. For this parametric analysis, the values from an experiment analyzed later in this thesis are used. The experiment is EVD5 from Duan and Ward [1], which is the same experiment used as the basis for the parametric analysis in Chapter 6. Details of this experiment are provided in Chapter 5. The experiment is for D$_2$O evaporating from a funnel, which is not a physical match to the analysis in this section, but the data is merely used as a base point around which each of the parameters are individually varied.

2.3.1 Effect of interfacial vapour phase temperature

In this section, the effect of $T_V^I$ on the evaporation parameter, $Ev$, is determined. Based on the EVD5 experiment, $T_L^I$ is set at 3.61°C, $j_{ev}$ at 0.221 g/m$^2$s, $\delta$ at 4.4 mm, and the value of $T_V^I$ is varied. It is noted that there is no depth, $\delta$, value in this experiment due to the differing geometry, so the value of the radius of the spherical interface is used instead. The result is plotted in Fig. 2.4.

It can be seen that as $T_V^I$ is increased, the evaporation parameter also increases. The change is relatively insignificant as a percentage of the value of $Ev$, and as compared with the change resulting from varying $T_L^I$ and $\delta$ in the following sections. As was discussed above in relation to the single parameter, an increase in $Ev$ does not necessarily
correspond to a more stable system (since the parameters are linked); however since $Ma/Ev$ is a constant, a larger value of $Ev$ indicates that the onset Marangoni number for the system is also larger. Therefore, if the stability were to be described in relation to the destabilizing effect of the Marangoni number, as was traditionally done in previous studies, where two separate parameters were used, the system is technically more stable for larger $Ev$ values. This is no longer a comprehensive measure of stability; however, it enables a comparison with the stability trends predicted by previous studies. Thus, increasing values of $T^V_I$ correspond to more stable configurations.

### 2.3.2 Effect of interfacial liquid phase temperature

In this section, the effect of $T^L_I$ on the evaporation parameter, $Ev$, is determined. Based on the EVD5 experiment, $T^V_I$ is set at 4.04°C, $j_{ev}$ at 0.221 g/m²s, $\delta$ at 4.4 mm, and the
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value of $T^L_I$ is varied. The result is plotted in Fig. 2.5.

![Graph showing the relationship between Evaporation parameter ($E_v$) and $T^L_I$ (°C).]

Figure 2.5: Evaporation parameter plotted versus $T^L_I$ for $T^V_I$ fixed at 4.04°C, $j_{ev}$ at 0.221 g/m²s, and $\delta$ at 4.4 mm.

It can be seen that as $T^L_I$ is increased, the evaporation parameter also increases; thus, increasing values of $T^L_I$ correspond to more stable configurations, in relation to the traditional measure of Marangoni numbers. The investigation of Marangoni instability for an entire evaporating droplet, analyzed by Ha and Lai [14], also predicted that warmer liquid temperatures correspond to a more stable system. The change is more significant than the change associated with $T^V_I$.

2.3.3 Effect of evaporation flux

In this section, the effect of $j_{ev}$ on the evaporation parameter, $E_v$, is determined. Based on the EVD5 experiment, $T^V_I$ is set at 4.04°C, $T^L_I$ at 3.61°C, $\delta$ at 4.4 mm, and the value of $j_{ev}$ is varied. The result is plotted in Fig. 2.6.
Figure 2.6: Evaporation parameter plotted versus $j_{ev}$ for $T_{f}^{V}$ fixed at 4.04°C, $T_{f}^{L}$ at 3.61°C, and $\delta$ at 4.4 mm.

It can be seen that as $j_{ev}$ is increased, the evaporation parameter decreases; thus, increasing values of $j_{ev}$ correspond to less stable configurations. However, the axis in Fig. 2.6 illustrates that the effect is negligible, so the evaporation parameter remains relatively constant over a large range of evaporation rates. What should be noted here is that, although the evaporation parameter is constant, higher evaporation rates would require a larger temperature gradient through the liquid phase to balance the energy required for evaporation at the interface, which destabilizes the liquid layer. Therefore in a physical system an increase in the evaporation rate would destabilize the interface. This example illustrates why consideration of the whole system is important, and why the arbitrary assignment of general parameters in past theoretical analyses could obscure the physical onset criterion.
2.3.4 Effect of depth

In this section, the effect of \( \delta \) on the evaporation parameter, \( E_v \), is determined. Based on the EVD5 experiment, \( T_V^* \) is set at 4.04°C, \( T_L^* \) at 3.61°C, \( j_{ev} \) at 0.221 g/m²s, and the value of \( \delta \) is varied. The result is plotted in Fig. 2.7.

![Figure 2.7: Evaporation parameter plotted versus \( \delta \) for \( T_V^* \) fixed at 4.04°C, \( T_L^* \) at 3.61°C, and \( j_{ev} \) at 0.221 g/m²s.](image)

It can be seen that as \( \delta \) is increased, the evaporation parameter increases; thus, increasing the depth of the liquid layer corresponds to more stable configurations, in relation to the traditional measure of Marangoni numbers. However, as was the case for the previous parameters, this is not a comprehensive measure of stability.
2.4 Single parameter for the finite liquid perturbation case

The stability of a finite-sized system can also be expressed in terms of a single stability parameter. Based on the analysis for a liquid sheet bounded in the lateral direction [22], an expression for the new single parameter can be generated

\[
\left( \frac{Ma_n}{Ev} \right)_F = \frac{\frac{8n\pi}{A} \left( 1 + \frac{n^2 \pi^2 \coth \frac{n\pi}{A}}{Ev} \right) \left( \frac{n\pi}{A} - \sinh \frac{n\pi}{A} \cosh \frac{n\pi}{A} \right)}{\left( \frac{n\pi}{A} \right)^3 \coth \frac{n\pi}{A} - \sinh^2 \frac{n\pi}{A}}.
\] (2.9)

The stability curves are plotted in Fig. 2.8 for the first ten modes. The plot was generated for an \( Ev \) value of 700, but because the new single parameter is being plotted, this plot is relevant for a broad range of evaporating systems since there is little dependence on the value of \( Ev \). It can be seen that the finite size of the system can alter the predicted onset points for low values of the aspect ratio \( (A) \) but as this value is increased the predicted onset points converge to the value for the semi-infinite case.

2.5 Chapter summary

In summary, it was demonstrated that the Pearson analysis is not applicable for predicting the onset of Marangoni instability for evaporating systems due to generalizations and an inverse temperature discontinuity at the interface. A single parameter was generated to characterize the stability of evaporating liquid sheets. The derivation was made possible by introducing evaporation as the specific heat transfer mechanism at the interface and expressing the evaporation flux with statistical rate theory. A parametric investigation of the new parameter demonstrated that warmer temperatures correspond to a more stable system. It is interesting to note that a similar result was found for the evaporating spherical droplets studied by Ha and Lai [14]. The parametric analysis also illustrated the importance of the physical link between the parameters due to the surface energy
Now that evaporation has been included in the stability analysis for the traditional geometrical configuration of liquid sheets, the analysis can be expanded to more complex configurations in the upcoming Chapters. Also the existence of a single parameter indicates that when the statistical rate theory expression for evaporation flux is used, and the onset criterion contains only physical variables, the stability of an evaporating liquid can be expressed in terms of one parameter, and not two. There is inherently a link between the stability criterion and the energy balance at the interface.

Figure 2.8: Plot of stability curves versus the new parameter for a finite system ($Ev = 700$).
Chapter 3

Stability of an evaporating sessile droplet

In this chapter a stability analysis is performed for evaporating spherical sessile droplets. This geometry is sufficiently different from the semi-infinite and bounded liquid sheets analyzed in the past to yield an entirely new stability parameter for the case of a sessile droplet evaporating on an insulating substrate, $\chi_s^{ID}$, and on a conducting substrate, $\chi_s^{CD}$.

3.1 Problem definition

The investigation is performed for an evaporating spherical sessile droplet with an interface at $r = r_I$ that is bounded at a polar angle of $\pi/2$ by a substrate, as shown in Fig. 3.1. The system is axisymmetric about the $\phi = 0$ centreline. The surrounding fluid is the vapour phase of the liquid and has a temperature at a boundary far from the interface of $T_\infty$. Here the polar angle is given by $\phi$ as $\theta$ is used to denote the temperature perturbation. For reference, the spherical co-ordinate notation used in this thesis is illustrated in Fig. 3.2. For the linear stability analysis the velocity and temperature in the liquid phase and the temperature in the vapour phase are perturbed and analyzed. The temperature of the vapour phase is included to ensure a balance of energy, and the effect of velocity
in the vapour phase is assumed to be negligible. 

Typically, investigation of Marangoni instability is for liquid layers, with an interface that is not in contact with a boundary surface, and the temperature gradients normal to the interface generate the instability. However, in a spherical sessile droplet geometry, temperature gradients in the liquid phase would also result in tangential temperature

Figure 3.1: Schematic of spherical sessile droplet geometry.

Figure 3.2: Notation used in this thesis for the spherical co-ordinate system.
gradients along the interface, which would cause Marangoni convection. Therefore, in order to have an initially stable state to perturb from, it is a requirement that the liquid phase be isothermal. This assumption is consistent with experimental observations [10]. The initial state therefore requires that the energy necessary for evaporation be provided by conduction through the vapour phase.

It is also noted that if the substrate were sufficiently capable of insulating the liquid phase it might be possible to set up temperature gradients in the liquid phase without inducing a tangential temperature gradient along the interface. In such a case it might be possible to set up a traditional Marangoni instability if the temperature gradient in the liquid phase normal to the interface were sufficiently large enough. This form of instability is beyond the scope of this thesis since the interest is in systems with an initially isothermal liquid phase.

The analysis is performed for two different types of substrates, insulating and conducting. This is done because the stability analysis showed a significant difference in the stability for these two cases. Also, the experimental observations that the theoretical predictions for the funnel case are compared with, indicated different stability behaviour for funnels constructed of different materials. More details on this are provided in the chapter for the stability analysis for the funnel case (Chapter 4) and the chapter with the experimental comparison (Chapter 5). Using two different types of substrate materials in the analysis enables a comparison of the thermal properties of the substrate, insulating versus conducting, and allows for comparison to the results for the funnel case.

3.2 Governing equations and boundary conditions

The liquid phase is assumed to be incompressible and buoyancy effects to be negligible (accomplished by exploiting the neutral buoyancy point of water or conditions of near free fall), so the governing equations are mass, momentum, and energy conservation as
follows

\[ \nabla \cdot \mathbf{U} = 0, \quad (3.1) \]

\[ \frac{\partial \mathbf{U}}{\partial t} + \mathbf{U} \cdot \nabla \mathbf{U} = -\frac{1}{\rho} \nabla P + \nu \nabla^2 \mathbf{U}, \quad (3.2) \]

\[ \frac{\partial T^L}{\partial t} + \mathbf{U} \cdot \nabla T^L = \alpha \nabla^2 T^L, \quad (3.3) \]

where \( \mathbf{U} \) is the velocity in the liquid phase, \( \rho \) is the density of the liquid, \( P \) is the pressure, \( \nu \) is the kinematic viscosity, \( T^L \) is the temperature of the liquid phase, and \( \alpha \) is the thermal diffusivity in the liquid.

As noted above, the effect of velocity in the vapour phase is assumed to be negligible, so only energy conservation is required for the vapour phase

\[ \frac{\partial T^V}{\partial t} = \alpha^V \nabla^2 T^V, \quad (3.4) \]

where \( T^V \) is the temperature of the vapour phase, and \( \alpha^V \) is the thermal diffusivity in the vapour phase.

At \( \phi = \pi/2 \) there is a rigid side wall so the boundary conditions on the velocity are

\[ U_r = U_{\phi} = 0. \quad (3.5) \]

At the bounding wall, the energy boundary conditions must be listed individually for each substrate type. For the insulating case

\[ -\frac{1}{r} \frac{\partial T^L}{\partial \phi} \bigg|_{\phi=\pi/2} = 0. \quad (3.6) \]

For the conducting substrate an energy balance is required in the liquid phase between the substrate and evaporation at the liquid-vapour interface, so that instead of Eq. (3.6) the condition is

\[ \left( \int_0^{r_I} \frac{\partial T^L}{\partial \phi} \sin \phi dr \right)_{\phi=\pi/2} = \left( \int_0^{\pi/2} \frac{\partial T^L}{\partial r} r^2 \sin \phi d\phi \right)_{r=r_I}. \quad (3.7) \]
Chapter 3. Stability of an evaporating sessile droplet

At $\phi = 0$ there is an axisymmetric boundary which yields

$$\frac{\partial U_r}{\partial \phi} = 0,$$

$$U_\phi = \frac{\partial U_\phi}{\partial \phi} = 0,$$

$$\frac{\partial T_L}{\partial \phi} = 0,$$

$$\frac{\partial T_V}{\partial \phi} = 0.$$

At $r \to \infty$ the vapour phase temperature satisfies

$$T^V = T_\infty.$$  \hspace{1cm} (3.12)

At $r = r_I$ there is evaporation at a free surface, which is a discontinuous liquid-vapour interface. The boundary conditions can therefore be generated using discontinuity conditions for the balance laws as follows

$$\rho U_r = j_{ev},$$

$$\nu \rho \left( \frac{1}{r_I} \frac{\partial U_r}{\partial \phi} + \frac{\partial U_\phi}{\partial r} - \frac{U_\phi}{r_I} \right) = \frac{\gamma_T}{r_I} \frac{\partial T_L}{\partial \phi},$$

$$\kappa^V \frac{\partial T^V}{\partial r} - \kappa^L \frac{\partial T_L}{\partial r} - \left( \frac{c_\sigma U_\phi}{r_I} \frac{\partial T_L}{\partial \phi} \right) = j_{ev} h_{fg},$$

where $j_{ev}$ is the evaporation flux at the interface, $\gamma_T$ is the change of surface tension with respect to temperature, $\kappa$ is the thermal conductivity (with V and L superscripts denoting the liquid and vapour phases), $c_\sigma$ is the surface thermal capacity [2], and $h_{fg}$ is the enthalpy of vaporization. It is noted in Eq. (3.14) that the vapour phase is not included. Since the viscosity of the vapour phase is negligible compared to the viscosity of the liquid phase, the vapour phase velocity would not contribute to this equation, and so the vapour phase velocity can be considered negligible, as was noted above.
3.3 Initial steady-state solution

Initially, it is assumed that the liquid is evaporating with no Marangoni convection. The initial state is defined based on the stable evaporation observed in the experiments [2, 1, 10]. Therefore, it is assumed that there is an isothermal liquid phase whereby the energy required for evaporation is provided by conduction through the vapour phase, and the vapour phase temperature gradient normal to the interface is uniform along the interface. It is also assumed that the initial evaporation rate is low enough so that the effect of flow through the liquid phase is negligible, and the initial velocities are zero. Thus

\[ U_{ini} = 0, \]
\[ P_{ini} = P_0, \]
\[ T_{ini}^L = T_0, \]
\[ T_{ini}^V = T_{ini}^V(r), \]

where the \( ini \) subscript denotes the initial state, and a 0 subscript or superscript denotes the initial, unperturbed value of the variable.

With the low flow rate assumption and dependence only in the radial direction, the initial temperature distribution in the vapour phase is governed by a simplified form of Eq. (3.3) as follows

\[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T_{ini}^V}{\partial r} \right) = 0. \]

When the assumptions listed above are applied at the free surface, \( r = r_I \), the energy balance can be written as

\[ \kappa^V \beta = j_{ev} h_{fg}, \]

where the uniform vapour phase temperature gradient normal to the interface is denoted
as \( \beta \). Therefore, the boundary conditions from Eqs. (3.15) and (3.12) are

\[
\left. \frac{\partial T^V_{ini}}{\partial r} \right|_{r=r_I} = \beta, \tag{3.22}
\]

\[
T^V_{ini}(r \to \infty) = T_\infty. \tag{3.23}
\]

The solution of Eq. (3.20) with Eq. (3.22) and Eq. (3.23) is

\[
T^V_{ini}(r) = T_\infty + \beta \left( -\frac{r^2}{r} \right). \tag{3.24}
\]

This initial steady-state solution will provide the basis for perturbations in the linear stability analysis.

### 3.4 Perturbation equations

Based on the initial state, the following perturbations are introduced

\[
U(r, \phi, t) = u(r, \phi, t), \tag{3.25}
\]

\[
P(r, \phi, t) = P_0 + p(r, \phi, t), \tag{3.26}
\]

\[
T^L(r, \phi, t) = T_0 + \theta^L(r, \phi, t), \tag{3.27}
\]

\[
T^V(r, \phi, t) = T_\infty + \beta \left( -\frac{r^2}{r} \right) + \theta^V(r, \phi, t), \tag{3.28}
\]

and it is reiterated that the velocity perturbation and pressure perturbation are for the liquid phase only, so no superscript is included on them.

Since the evaporation flux and enthalpy of vaporization depend on the liquid and vapour temperatures, a perturbed form of these parameters is required. They can be expanded as

\[
j_{ev} = j^0_{ev} + \frac{\partial j_{ev}}{\partial T^L} \theta^L + \frac{\partial j_{ev}}{\partial T^V} \theta^V, \tag{3.29}
\]

\[
h_{fg} = \left( h^V_0 - h^L_0 \right) - c_p^L \theta^L + c_p^V \theta^V, \tag{3.30}
\]

where \( c_p \) is the specific heat capacity. It can be seen from Eq. (3.29) that an expression for the evaporation flux is required, which will allow for the derivative to be taken with
respect to both liquid and vapour temperatures. For the reasons noted above in the previous chapter, the statistical rate theory expression for evaporation flux, Eq. (2.6), is used.

The following non-dimensionalizations are introduced

\[ r = r^* r_I, \quad (3.31) \]
\[ t = \frac{t^* r_I^2}{\nu}, \quad (3.32) \]
\[ U_r = \frac{U_r^* \alpha}{r_I}, \quad (3.33) \]
\[ U_\phi = \frac{U_\phi^* \alpha}{r_I}, \quad (3.34) \]
\[ P = \frac{P^* \rho \nu \alpha}{r_I^2}, \quad (3.35) \]
\[ T_L = T_L^* \beta r_I, \quad (3.36) \]
\[ T_V = T_V^* \beta r_I, \quad (3.37) \]

When the perturbations and scalings are substituted into the conservation equations, Eqs. (3.1) - (3.4), the following linearized equations result (the asterisk is dropped from the variables and the analysis is non-dimensional from here onwards)

\[ \nabla \cdot \mathbf{u} = 0, \quad (3.38) \]
\[ \frac{\partial \mathbf{u}}{\partial t} = -\nabla p + \nabla^2 \mathbf{u}, \quad (3.39) \]
\[ \Pr \frac{\partial \theta^L}{\partial t} - \nabla^2 \theta^L = 0, \quad (3.40) \]
\[ \frac{\nu}{\alpha V} \frac{\partial \theta^V}{\partial t} - \nabla^2 \theta^V = 0, \quad (3.41) \]

where \( \Pr \) is the Prandtl number in the liquid phase \((\nu/\alpha)\). The pressure term can be eliminated by taking the curl of Eq. (3.39) twice yielding

\[ \frac{\partial}{\partial t} \nabla^2 \mathbf{u} - \nabla^4 \mathbf{u} = 0, \quad (3.42) \]

A linearized and non-dimensional set of governing equations has now been derived, Eqs. (3.38), (3.42), and (3.40), and the linear stability analysis can be performed. The linearized and non-dimensional boundary conditions are derived in the following section.
3.5 Marginal stability

As noted in the Introduction, it is assumed that the marginally stable state of a system corresponds to neutral stability and exceeding this criteria generates an instability. The marginally stable state of the system can be described if the following form is assigned to the perturbations

\[ u_r = u_{rs}(r, \phi) \exp(\sigma t), \quad (3.43) \]
\[ u_\phi = u_{\phi s}(r, \phi) \exp(\sigma t), \quad (3.44) \]
\[ \theta^L = \theta^L_s(r, \phi) \exp(\sigma t), \quad (3.45) \]
\[ \theta^V = \theta^V_s(r, \phi) \exp(\sigma t). \quad (3.46) \]

The governing equations, Eq. (3.38), Eq. (3.42), Eq. (3.40), and Eq. (3.41) become

\[ \nabla \cdot u_s = 0, \quad (3.47) \]
\[ \sigma \nabla^2 u_s - \nabla^4 u_s = 0, \quad (3.48) \]
\[ \text{Pr}\sigma \theta^L_s - \nabla^2 \theta^L_s = 0, \quad (3.49) \]
\[ \frac{\nu}{\alpha \nu} \sigma \theta^V_s - \nabla^2 \theta^V_s = 0. \quad (3.50) \]

The exchange of stabilities is assumed to be valid, so that \( \sigma \) is real, the marginally stable states are characterized by \( \sigma = 0 \), and Eq. (3.48), Eq. (3.49), and Eq. (3.50) become

\[ \nabla^4 u_s = 0, \quad (3.51) \]
\[ \nabla^2 \theta^L_s = 0, \quad (3.52) \]
\[ \nabla^2 \theta^V_s = 0. \quad (3.53) \]

The perturbations, Eqs. (3.25) - (3.30), and stability equations, Eqs. (3.43) - (3.46), can now be substituted into the boundary conditions from Section 3.2. At \( \phi = \pi/2 \), substituting into Eq. (3.5) yields

\[ u_{\phi s} = 0. \quad (3.54) \]
It is noted that slip is allowed along the boundary wall in the perturbed velocity. In order to generate meaningful solutions to the stability problem, slip must be allowed. This is a common condition in stability analyses with bounded interfaces [23, 24, 31], and also in situations involving contact lines [39] to prevent a singularity in the stress condition near the contact line.

For the insulating substrate, at $\phi = \pi/2$, substituting into Eq. (3.6) yields

$$-\frac{1}{r} \frac{\partial \theta_s^L}{\partial \phi} \bigg|_{\phi=\pi/2} = 0. \quad (3.55)$$

For the conducting substrate, substituting into Eq. (3.7) yields

$$\left( \int_0^{1} \frac{\partial \theta_s^L}{\partial \phi} \sin \phi dr \right) (\phi=\pi/2) = \left( \int_0^{\pi/2} \frac{\partial \theta_s^L}{\partial \phi} r^2 \sin \phi d\phi \right) (r=1). \quad (3.56)$$

At $\phi = 0$, Eqs. (3.8) - (3.11) become

$$\frac{\partial u_{rs}}{\partial \phi} = 0, \quad (3.57)$$

$$u_{\phi s} = \frac{\partial u_{\phi s}}{\partial \phi} = 0, \quad (3.58)$$

$$\frac{\partial \theta_s^L}{\partial \phi} = 0, \quad (3.59)$$

$$\frac{\partial \theta_s^V}{\partial \phi} = 0. \quad (3.60)$$

For $r \to \infty$, Eq. (3.12) becomes

$$\theta_s^V = 0. \quad (3.61)$$

At $r = 1$, Eqs. (3.13) - (3.15) become

$$u_{rs} = \frac{r_1^2 \beta}{\rho \alpha} \left( \frac{\partial j_{ev}}{\partial T} \frac{\partial \theta_s^L}{\partial \theta_s^L} + \frac{\partial j_{ev}}{\partial T} \frac{\partial \theta_s^V}{\partial \theta_s^V} \right), \quad (3.62)$$

$$\frac{\partial^2 u_{rs}}{\partial r^2} - \frac{\partial u_{rs}}{\partial \phi^2} + 2 \frac{\partial u_{rs}}{\partial r} - \cot \phi \frac{\partial u_{rs}}{\partial \phi} - 2u_{rs} = -\frac{\gamma T r_1^2}{\rho \nu \alpha} \left( \frac{\partial^2 \theta_s^L}{\partial \phi^2} \dot{\theta}_s^V + \cot \phi \frac{\partial \theta_s^L}{\partial \phi} \right), \quad (3.63)$$

$$\frac{\kappa^V \partial \theta_s^V}{\kappa^L} + \frac{r_1}{\kappa^L} \left( -\frac{\partial j_{ev}}{\partial T} \frac{h_0^V}{h_0^L} - j_{ev}^L \right) \theta_s^V \dot{\theta}_s^V \dot{\theta}_s^L \dot{\theta}_s^L, \quad (3.64)$$
Equation (3.63) has been simplified to eliminate the dependence on \( u_\phi s \) by first differentiating by \( \phi \) then substituting in the continuity equation, Eq. (3.47), and finally substituting the undifferentiated initial form to yield the form shown above. With this simplification only a solution for \( u_{rs} \) is required in the stability analysis. For convenience the dimensionless groupings from these equations are defined as follows

\[
\xi_{CL} = \frac{r_1^2 \beta}{\rho \alpha} \frac{\partial j_{ev}}{\partial T_L},
\]

(3.65)

\[
\xi_{CV} = \frac{r_1^2 \beta}{\rho \alpha} \frac{\partial j_{ev}}{\partial T_V},
\]

(3.66)

\[
\xi_M = \left( -\frac{\gamma T r_1^2 \beta}{\rho \nu \alpha} \right),
\]

(3.67)

\[
K = \frac{\kappa_V}{\kappa_L},
\]

(3.68)

\[
\xi_{TV} = \frac{r_1}{\kappa_L} \left( \frac{\partial j_{ev}}{\partial T_V} (h^V_0 - h^L_0) - j^0_{ev} c_p^V \right),
\]

(3.69)

\[
\xi_{TL} = \frac{r_1}{\kappa_L} \left( \frac{\partial j_{ev}}{\partial T_L} (h^V_0 - h^L_0) - j^0_{ev} c_p^L \right),
\]

(3.70)

and it is noted that each of these parameters contain only properties or measurable variables, thus making them physical parameters. The conditions at \( r = 1 \) are rewritten

\[
u_{rs} = \xi_{CL} \theta^L_s + \xi_{CV} \theta^V_s,
\]

(3.71)

\[
\frac{\partial^2 \nu_{rs}}{\partial r^2} - \frac{\partial^2 \nu_{rs}}{\partial \phi^2} + 2 \frac{\partial \nu_{rs}}{\partial r} - \cot \phi \frac{\partial \nu_{rs}}{\partial \phi} - 2 \nu_{rs} = \xi_M \left( \frac{\partial^2 \theta^L_s}{\partial \phi^2} + \cot \phi \frac{\partial \theta^L_s}{\partial \phi} \right),
\]

(3.72)

\[
K \frac{\partial \theta^V_s}{\partial r} + \xi_{TV} \theta^V_s = \frac{\partial \theta^L_s}{\partial r} + \xi_{TL} \theta^L_s.
\]

(3.73)

The \( \xi_M \) term in Eq. (3.72) is traditionally called the Marangoni number. In this analysis \( \xi_M \) is defined by Eq. (3.67), so it represents the Marangoni number for a spherical system with an initially isothermal liquid phase and a temperature gradient in the vapour phase. The stability criterion will be developed by substituting the solutions for the velocity and temperature perturbations into Eq. (3.72) and solving for \( \xi_M \).

It can be seen in Eq. (3.69) and Eq. (3.70) that the \( \xi_{TV} \) and \( \xi_{TL} \) parameters are very similar to the evaporation parameter from the liquid sheet analysis in Chapter 2, given
as Eq. (2.5). This factor appears in the analysis for the sessile droplet in spite of being based on a different stability analysis with a differing geometry. As was the case for the liquid sheet analysis this parameter is crucial for the onset criterion of bounded spherical interfaces, which will be demonstrated in the following sections.

The change-of-phase at the liquid-vapour interface allows a non-zero value for the radial velocity in Eq. (3.71). The liquid and vapour phase temperatures are coupled because the contributions from both phases are included in the energy balance of Eq. (3.73). The $\xi_{CL}$ and $\xi_{CV}$ terms relate a temperature change (in the liquid and vapour phase respectively) to the radial velocity at the interface of an evaporating fluid.

It is noted that the boundary conditions, Eqs. (3.54) - (3.61) and (3.71) - (3.73) do not comprise a complete set and so the governing equations, Eqs. (3.51), (3.52), and (3.53), are not closed. All of the boundary conditions have been implemented for the physical problems being investigated in this study, with Eqs. (3.55) and (3.56) being of particular importance. If the stability analysis proceeds in a general form using only the boundary conditions listed above, it is found that the coefficients are cancelled from the stability parameters derived in the following sections, so no additional boundary conditions are required to adequately describe the stability.

It would be possible to close the system with respect to the temperatures if there were an additional boundary condition predicting the magnitude of the temperature discontinuity between the interfacial liquid and vapour phase temperatures. At present, to the best of the author’s knowledge, no such expression exists. A temperature discontinuity is included in Eq. (3.73), which ensures a balance of energy and also enables any magnitude of temperature discontinuity to be applied. If a heat flux is given, it is possible to use statistical rate theory to predict one of the interfacial temperatures given the other one. However this requires an additional input and therefore does not close the system. If the theory were to be developed, it is possible to use a kinetic expression, similar to the statistical rate theory expression for the evaporation flux, to describe the energy flux at
the interface. If such an expression were to be developed it would possible to have the
capability to predict the magnitude of the temperature discontinuity at an evaporating
interface. The development of such an expression is a significant undertaking and is
beyond the scope of this work, but it is mentioned here to provide some insight for the
closing of the system.

3.6 Insulated substrate

In this section, an analysis is performed for spherical sessile droplets evaporating on
insulating substrates, using the equations derived above.

3.6.1 Liquid phase temperature

The general solution to Laplace’s equation, Eq. (3.52), for the liquid phase temperature
perturbation bounded at the origin is given as

$$\theta_s^L(r, \phi) = \sum_{n=0}^{\infty} \left( A_n r^n + B_n r^{-n-1} \right) P_n(\cos \phi),$$

where $P_n(\cos \phi)$ are the Legendre polynomials. In order for the solution to be bounded
at the origin, $B_n = 0$ for all $n$. Substituting into Eq. (3.55) yields

$$-\frac{1}{r} \frac{\partial \theta_s^L}{\partial \phi} \bigg|_{\phi=\frac{\pi}{2}} = -\sum_{n=0}^{\infty} (n + 1) A_n r^{n-1} P_{n+1}(0) = 0.$$  \hfill (3.75)

Therefore, $A_n = 0$ for all odd values of $n$. The boundary condition from Eq. (3.60) is
satisfied

$$\frac{\partial \theta_s^L}{\partial \phi} \bigg|_{\phi=0} = 0.$$  \hfill (3.76)

The expression for $\theta_s^L$ is

$$\theta_s^L(r, \phi) = \sum_{n=0}^{\infty} (A_n r^n) P_n(\cos \phi),$$

for only even values of $n$. This expression will be used in Section 3.6.4 to derive the
stability criterion.
### 3.6.2 Vapour phase temperature

The general solution for the temperature in the vapour phase is

\[
\theta_v^s (r, \phi) = \sum_{n=0}^{\infty} \left( C_n r^n + D_n r^{-n-1} \right) P_n (\cos \phi). \tag{3.78}
\]

Since the vapour phase does not include the origin, the \( D_n \) coefficients remain, and instead \( C_n = 0 \) for all \( n \), from the boundary condition at \( r \to \infty \), Eq. (3.61). When Eq. (3.78) is substituted into Eq. (3.73), one finds

\[
\sum_{n=0}^{\infty} \left( D_n (\xi_{TV} - K (n + 1)) \right) P_n (\cos \phi) = \sum_{n=0}^{\infty} \left( A_n (n + \xi_{TL}) \right) P_n (\cos \phi), \tag{3.79}
\]

for even values of \( n \). Therefore \( D_n = A_n (n + \xi_{TL})/(\xi_{TV} - K (n + 1)) \). The expression for \( \theta_v^s \) is

\[
\theta_v^s (r, \phi) = \sum_{n=0}^{\infty} \frac{A_n (n + \xi_{TL})}{(\xi_{TV} - K (n + 1))} r^{-n-1} P_n (\cos \phi), \tag{3.80}
\]

for even values of \( n \).

A result of the coupling in the energy balance, Eq. (3.73), the expressions for both \( \theta_s^L \) (Eq. (3.77)) and \( \theta_s^V \) (Eq. (3.80)), contain the \( A_n \) coefficient. The \( A_n \) coefficient is the only unknown in Eq. (3.80) since \( K, \xi_{TV} \), and \( \xi_{TL} \) are physical parameters, defined in Eq. (3.68), Eq. (3.69), and Eq. (3.70) respectively, containing properties or measurable parameters.

### 3.6.3 Liquid phase radial velocity

The general solution to the spherical biharmonic equation, Eq. (3.51), is given as [40]

\[
u_{rs}(r, \phi) = \sum_{n=0}^{\infty} \left( E_n r^{n+2} + F_n r^n + G_n r^{1-n} + H_n r^{-1-n} \right) P_n (\cos \phi). \tag{3.81}
\]

In order for the solution to be bounded at the origin, \( G_n = 0 \) for \( n > 1 \) and \( H_n = 0 \) for all \( n \). The boundary condition from Eq. (3.57) is satisfied

\[
\frac{\partial u_{rs}}{\partial \phi} \bigg|_{\phi=0} = 0. \tag{3.82}
\]
When Eq. (3.81) is substituted into Eq. (3.71), one finds
\[
G_0 + G_1 \cos \phi + \sum_{n=0}^{\infty} (E_n + F_n) P_n(\cos \phi) = \sum_{n=0}^{\infty} A_n \left( \xi_{CL} + \frac{\xi_{CV} (n + \xi_{TL})}{\xi_{TV} - K (n + 1)} \right) P_n(\cos \phi).
\]
(3.83)

There are no additional boundary conditions to limit which of the coefficients in Eq. (3.83) are used in the expression for \(u_{rs}\)
\[
u_{rs}(r, \phi) = G_0 r + G_1 \cos \phi + \sum_{n=0}^{\infty} (E_n r^{n+2} + F_n r^n) P_n(\cos \phi),
\]
(3.84)
so the stability problem is solved considering all of the coefficients and the resulting solutions are analyzed with respect to their physical validity.

### 3.6.4 Examination of the coefficients

In order to derive the stability criterion Eq. (3.72) is rearranged and the \(s\) subscript is added to distinguish from the physical definition of \(\xi_M\) given above in Eq. (3.67)
\[
\xi_{Ms} = \frac{\left( \frac{\partial^2 u_{rs}}{\partial r^2} - \frac{\partial^2 u_{rs}}{\partial \phi^2} + 2 \frac{\partial u_{rs}}{\partial r} - \cot \phi \frac{\partial u_{rs}}{\partial \phi} - 2 u_{rs} \right)}{\left( \frac{\partial^2 \theta_{Ls}}{\partial \phi^2} + \cot \phi \frac{\partial \theta_{Ls}}{\partial \phi} \right)}.
\]
(3.85)
Substituting in the solutions for \(\theta_{Ls}^L\) (Eq. (3.77)), \(\theta_{Vs}^V\) (Eq. (3.80)), and \(u_{rs}\) (Eq. (3.84)) yields
\[
\xi_{Ms} = \frac{1}{A_n} \left( -2E_n (n + 1) (n + 2) + 2F_n (n^2 + n - 1) \right),
\]
(3.86)
for even values of \(n\), and \(n > 0\).

The \(E_n\) and \(F_n\) coefficients in Eq. (3.86) are investigated individually. There are two possible cases, Eq. (3.83) can either be solved for \(E_n\) with \(F_n\) set equal to zero (Case \(E\)), or for \(F_n\) with \(E_n\) set equal to zero (Case \(F\)). Utilizing combinations of these terms would result in a description of the stability parameter with ambiguous constants, which would have to be eliminated, so only these two cases are considered. Case \(E\) yields
\[
\xi_{E_{Ms}} = -\left( \frac{2(n+2)}{n} \right) \left( \xi_{CL} + \frac{\xi_{CV} (n + \xi_{TL})}{\xi_{TV} - K (n + 1)} \right),
\]
(3.87)
and Case F yields

$$\xi_{Ms}^F = -\left(\frac{2(n^2 + n - 1)}{n(n+1)}\right) \left(\xi_{CL} + \frac{\xi_{CV}(n + \xi_{TL})}{\xi_{TV} - K(n+1)}\right), \tag{3.88}$$

for all even values of \(n\) greater than zero. The form given in Eq. (3.88) is a multiple of Eq. (3.87), so only Eq. (3.87) needs to be analyzed since the multiplier is larger for all even values of \(n\) greater than zero, and therefore the parameter is larger and corresponds to the least stable case.

### 3.6.5 Stability parameter for an insulated substrate

To examine the stability, the result from the perturbation analysis, Eq. (3.87), is equated to the physical definition of \(\xi_M\) from Eq. (3.67)

$$-\left(\frac{2(n+2)}{n}\right) \left(\xi_{CL} + \frac{\xi_{CV}(n + \xi_{TL})}{\xi_{TV} - K(n+1)}\right) = \xi_M. \tag{3.89}$$

Substituting in Eq. (3.65), Eq. (3.66), and Eq. (3.67) and rearranging terms yields

$$-\frac{r_i^2 \beta}{\rho \alpha} \left(\frac{2(n+2)}{n}\right) \left[\left.\frac{\partial j_{ev}}{\partial T}\right|_I + \left.\frac{\partial j_{ev}}{\partial T'}\right|_I \left(\frac{n + \xi_{TL}}{\xi_{TV} - K(n+1)}\right)\right] = -\frac{\gamma_T r_i^2 \beta}{\rho T \nu}. \tag{3.90}$$

The \(\xi_{TL}\) and \(\xi_{TV}\) terms were not substituted for, since no simplification results from the substitution. The terms common to both sides of the equation can be cancelled

$$-\left(\frac{2(n+2)}{n}\right) \left[\left.\frac{\partial j_{ev}}{\partial T}\right|_I + \left.\frac{\partial j_{ev}}{\partial T'}\right|_I \left(\frac{n + \xi_{TL}}{\xi_{TV} - K(n+1)}\right)\right] = -\frac{\gamma_T}{\nu}. \tag{3.91}$$

An expression has now been generated that relates the evaporation properties of the fluid to the ratio between the surface tension forces and viscous forces. In order to generate a stability parameter that is dimensionless, Eq. (3.91) is rearranged

$$\frac{\nu}{\gamma_T} \left[\left.\frac{\partial j_{ev}}{\partial T}\right|_I + \left.\frac{\partial j_{ev}}{\partial T'}\right|_I \left(\frac{n + \xi_{TL}}{\xi_{TV} - K(n+1)}\right)\right] = \left(\frac{n}{2(n+2)}\right). \tag{3.92}$$

The stability parameter, \(\chi_{ID}^s\) (the ID superscript refers to the case of a sessile droplet on an insulating substrate), is defined as the left hand side of Eq. (3.92)

$$\chi_{ID}^s = \frac{\nu}{\gamma_T} \left[\left.\frac{\partial j_{ev}}{\partial T}\right|_I + \left.\frac{\partial j_{ev}}{\partial T'}\right|_I \left(\frac{n + \xi_{TL}}{\xi_{TV} - K(n+1)}\right)\right], \tag{3.93}$$
for even values of $n$ greater than zero. It is emphasized that $\chi^{ID}$ is comprised entirely of physical variables that are either properties or parameters that can be measured, so this expression could be compared directly with experimental observations. In contrast to the conventional stability investigations for non-volatile fluids and semi-infinite systems, the stability parameter does not depend on temperature gradients, since $\beta$ was cancelled in Eq. (3.90). For this geometry it would not be possible to develop normal temperature gradients in the liquid phase without also developing tangential temperature gradients and initiating Marangoni convection. The presence of a bounding wall in contact with the interface results in significantly different stability behaviour. Therefore, the expression for the stability parameter is instead a function of the conditions at the interface. Also the importance of including the vapour phase thermal contributions in the interfacial energy balance, Eq. (3.73), is noted since the vapour phase contributions are present in the stability parameter, particularly the $K$ term, which is the ratio of thermal conductivity of the vapour and liquid phases.

Although this stability parameter could be compared directly to experiments, unfortunately at this time there exist no experiments to compare with. So instead of this comparison, a similar analysis is performed for a funnel geometry (boundary wall at $\phi = \pi/4$) in the next chapter, and those results are compared to experiments for that geometry, which do exist [2, 1, 10]. Also, a comparison between the results for the sessile droplet case performed above and the funnel case is made following the stability results for the funnel case in the next chapter.

### 3.7 Conducting substrate

In this section an expression is developed to predict the onset of Marangoni convection for spherical sessile droplets evaporating on conducting substrates.
3.7.1 Liquid phase temperature

Similar to the analysis above, the general solution to Laplace’s equation is Eq. (3.74), and in order for the solution to be bounded at the origin, $B_n = 0$ for all $n$. Substituting into Eq. (3.56), both integrals are found to be equivalent, so Eq. (3.56) is satisfied. The boundary condition from Eq. (3.60) is also satisfied

$$\frac{\partial \theta_s^L}{\partial \phi} \bigg|_{\phi=0} = 0. \quad (3.94)$$

Therefore, the expression for $\theta_s^L$ is

$$\theta_s^L(r, \phi) = \sum_{n=0}^{\infty} (A_n r^n) P_n (\cos \phi). \quad (3.95)$$

This expression will be used in Section 3.7.4 to derive the stability criterion.

3.7.2 Vapour phase temperature

Similar to the analysis above, the general solution to Laplace’s equation is Eq. (3.78), and in order for the solution to be bounded at $r \to \infty$ according to Eq. (3.61), $C_n = 0$ for all $n$. Substituting into Eq. (3.73) yields

$$\sum_{n=0}^{\infty} (D_n (\xi_{TV} - K (n + 1))) P_n (\cos \phi) = \sum_{n=0}^{\infty} (A_n (n + \xi_{TL})) P_n (\cos \phi). \quad (3.96)$$

Therefore $D_n = A_n (n + \xi_{TL})/(\xi_{TV} - K(n + 1))$. The expression for $\theta_s^V$ is

$$\theta_s^V(r, \phi) = \sum_{n=0}^{\infty} \frac{A_n (n + \xi_{TL})}{(\xi_{TV} - K(n + 1))} r^{-n-1} P_n (\cos \phi). \quad (3.97)$$

Similar to the insulated substrate case, due to the coupling in the energy balance, Eq. (3.73), the $A_n$ coefficient is present in both $\theta_s^L$ (Eq. (3.95)) and $\theta_s^V$ (Eq. (3.97)), and is the only unknown in Eq. (3.97) since $K$, $\xi_{TV}$, and $\xi_{TL}$ are physical parameters, defined in Eq. (3.68), Eq. (3.69), and Eq. (3.70) respectively, containing properties or measurable parameters.
3.7.3 Liquid phase radial velocity

Similar to the analysis for an insulated substrate, the general solution to the spherical biharmonic equation is Eq. (3.81), and for the solution to be bounded at the origin \(G_n = 0\) for \(n > 1\) and \(H_n = 0\) for all \(n\). The boundary condition from Eq. (3.57) is satisfied

\[
\frac{\partial u_{rs}}{\partial \phi} \bigg|_{\phi=0} = 0. \tag{3.98}
\]

When Eq. (3.81) is substituted into Eq. (3.71), one finds

\[
G_0 + G_1 \cos \phi + \sum_{n=0}^{\infty} (E_n + F_n) P_n(\cos \phi) = \sum_{n=0}^{\infty} A_n \left( \xi_{CL} + \frac{\xi_{CV} (n + \xi_{TL})}{\xi_{TV} - K (n + 1)} \right) P_n(\cos \phi). \tag{3.99}
\]

There are no additional boundary conditions to limit which of the coefficients in Eq. (3.83) are used in the expression for \(u_{rs}\)

\[
u_{rs}(r, \phi) = G_0 r + G_1 \cos \phi + \sum_{n=0}^{\infty} (E_n r^{n+2} + F_n r^n) P_n(\cos \phi), \tag{3.100}
\]

so the stability problem is solved considering all of the coefficients and the resulting solutions are analyzed with respect to their physical validity.

3.7.4 Examination of the coefficients

Similar to the analysis above, the \(\xi_{Ms}\) expression in Eq. (3.85) is used to solve for the coefficients. Substituting in the solutions for \(\theta_s^L\) (Eq. (3.95)), \(\theta_s^V\) (Eq. (3.97)), and \(u_{rs}\) (Eq. (3.100)) yields

\[
\xi_{Ms} = \frac{1}{A_n} \left( \frac{-2E_n (n + 1) (n + 2) - 2F_n (n^2 + n - 1)}{n (n + 1)} \right). \tag{3.101}
\]

The \(E_n\) and \(F_n\) coefficients in Eq. (3.101) are investigated individually. There are two possible cases, Eq. (3.99) can either be solved for \(E_n\) with \(F_n\) set equal to zero (Case E), or for \(F_n\) with \(E_n\) set equal to zero (Case F). Utilizing combinations of these terms
would result in a description of the stability parameter with ambiguous constants, which would have to be eliminated, so only these two cases are considered. Case $E$ yields
\[
\xi_{Ms}^E = - \left( \frac{2(n+2)}{n} \right) \left( \xi_{CL} + \frac{\xi_{CV} (n + \xi_{TL})}{\xi_{TV} - K(n+1)} \right),
\]
(3.102)
and Case $F$ yields
\[
\xi_{Ms}^F = - \left( \frac{2(n^2 + n - 1)}{n(n+1)} \right) \left( \xi_{CL} + \frac{\xi_{CV} (n + \xi_{TL})}{\xi_{TV} - K(n+1)} \right).
\]
(3.103)
The form given in Eq. (3.103) is a multiple of Eq. (3.102), so only Eq. (3.102) needs to be analyzed since the multiplier is larger for all values of $n$ greater than zero, and therefore the parameter is larger and corresponds to the least stable case.

### 3.7.5 Stability parameter for a conducting substrate

Following the same framework as the stability analysis for the insulated case above, to examine the stability the result from the perturbation analysis, Eq. (3.102) is equated to the physical definition of $\xi_M$ from Eq. (3.67)
\[
- \left( \frac{2(n+2)}{n} \right) \left( \xi_{CL} + \frac{\xi_{CV} (n + \xi_{TL})}{\xi_{TV} - K(n+1)} \right) = \xi_M.
\]
(3.104)
Substituting in Eq. (3.65), Eq. (3.66), and Eq. (3.67) and rearranging terms yields
\[
- \frac{r_j^2 \beta}{\rho \alpha} \left( \frac{2(n+2)}{n} \right) \left[ \frac{\partial j_{ev}}{\partial T_L} \bigg|_I + \frac{\partial j_{ev}}{\partial T_V} \bigg|_I \left( \frac{n + \xi_{TL}}{\xi_{TV} - K(n+1)} \right) \right] = - \frac{\gamma T r_j^2 \beta}{\rho \nu \alpha}.
\]
(3.105)
The $\xi_{TL}$ and $\xi_{TV}$ terms were not substituted for, since no simplification results from the substitution. The terms common to both sides of the equation can be cancelled
\[
- \left( \frac{2(n+2)}{n} \right) \left[ \frac{\partial j_{ev}}{\partial T_L} \bigg|_I + \frac{\partial j_{ev}}{\partial T_V} \bigg|_I \left( \frac{n + \xi_{TL}}{\xi_{TV} - K(n+1)} \right) \right] = - \frac{\gamma T}{\nu}.
\]
(3.106)
An expression has now been generated that relates the evaporation properties of the fluid to the ratio between the surface tension forces and viscous forces. In order to generate a stability parameter that is dimensionless, Eq. (3.106) is rearranged
\[
\frac{\nu}{\gamma T} \left[ \frac{\partial j_{ev}}{\partial T_L} \bigg|_I + \frac{\partial j_{ev}}{\partial T_V} \bigg|_I \left( \frac{n + \xi_{TL}}{\xi_{TV} - K(n+1)} \right) \right] = \left( \frac{n}{2(n+2)} \right).
\]
(3.107)
The stability parameter, $\chi^{CD}_s$ (the CD superscript refers to the case of a sessile droplet on a conducting substrate), is defined as the left hand side of Eq. (3.107)

$$\chi^{CD}_s = \frac{\nu}{\gamma_T} \left[ \left. \frac{\partial j_{ev}}{\partial T_L} \right|_I + \left. \frac{\partial j_{ev}}{\partial T_V} \right|_I \left( \frac{n + \xi_{TL}}{\xi_{TV} - K(n + 1)} \right) \right],$$

(3.108)

Similar to $\chi^{ID}_s$, $\chi^{CD}_s$ is comprised entirely of physical variables that are either properties or parameters that can be measured, so this expression could be compared directly with experimental observations if any presently existed.

It is noted that the stability parameters for insulating, $\chi^{ID}_s$, and conducting, $\chi^{CD}_s$, substrates are similar. The only difference being the retention of the even values of $n$ for the insulating case, but all values of $n$ for the conducting case. Therefore, this analysis predicts that insulating and conducting substrates have similar stability behaviour. In the following Chapter it will be demonstrated that for the funnel geometry this is not the case, since the stability predictions are significantly different for funnels constructed of insulating and conducting substrates.

As stated above, there are no experiments to compare this theory with. However, there are experiments that indicate the prediction is consistent for a sessile droplet evaporating on a PDMS substrate, particularly in comparison to the experimental observations for the case of evaporation from a funnel constructed of PMMA. This will be demonstrated in Chapter 5. Also, experiments that could be used to validate this theory are proposed at the end of that chapter.
Chapter 4

Stability of liquids evaporating from funnels

The stability analysis performed in the last chapter is adjusted for a different geometry in this chapter in order to facilitate a comparison to experimental results. The geometry is for liquids with spherical interfaces evaporating from funnels instead of spherical sessile droplets evaporating from substrates. The change corresponds to the boundary condition, which is located at $\phi = \pi/2$ for the sessile droplet, but shifted to $\phi = \pi/4$ for the funnel case. This shift in the location of the boundary results in different modes influencing the stability for the differing geometry, which gives rise to important changes in the stability parameter. Since there are experimental observations for the case of liquids evaporating from funnels [2, 1, 10], the new analysis can be compared to experimental observations to determine if it is consistent with physical systems.

4.1 Problem definition

The problem is identical to that in the preceding chapter except for the geometrical shift of the boundary wall; therefore the system being investigated is an evaporating liquid with a spherical interface at $r = r_f$, that is bounded at a polar angle of $\pi/4$ by the funnel
Figure 4.1: Schematic of system analyzed in the linear stability analysis.

wall, as shown in Fig. 4.1. All other details of the system are the same as that analyzed in the previous chapter, for the sessile droplet.

4.2 Governing equations and boundary conditions

The governing equations for marginal stability are those derived in the previous chapter as Eq. (3.51) and Eq. (3.52).

The boundary conditions are also the same, except for the conditions at the funnel wall, which is located at $\phi = \pi/4$. The velocity boundary condition is

$$u_{\phi s} = 0,$$  \hspace{1cm} (4.1)

and it is noted that along the funnel wall slip is allowed in the perturbed velocity. For the insulated funnel wall the condition is

$$- \frac{1}{r} \frac{\partial \theta^L}{\partial \phi} \bigg|_{\phi=\frac{\pi}{4}} = 0.$$  \hspace{1cm} (4.2)

For the conducting funnel wall the energy balance in the liquid phase between the funnel
side wall and evaporation at the liquid-vapour interface is

\[
\left( \int_0^1 - \frac{\partial \theta_s^L}{\partial \phi} \sin \phi dr \right)_{\phi = \pi/4} = \left( \int_0^{\pi/4} \frac{\partial \theta_s^L}{\partial r} r^2 \sin \phi d\phi \right)_{r=1} = 0. \tag{4.3}
\]

### 4.3 Insulated funnel wall

In this section the analysis is performed for liquids evaporating from funnels constructed of insulating materials.

#### 4.3.1 Liquid phase temperature

The solution to Laplace’s equation, Eq. (3.52), is that given above as Eq. (3.74) for the liquid phase temperature perturbation, and for the solution to be bounded at the origin, \( B_n = 0 \) for all \( n \).

When Eq. (3.74) is substituted into Eq. (4.2), one finds

\[
- \frac{1}{r} \frac{\partial \theta_s^L}{\partial \phi} \bigg|_{\phi = \pi/4} = A_1 \frac{1}{\sqrt{2}} + \frac{3A_2}{2} r + \frac{9A_3}{4\sqrt{2}} r^2 + \ldots = 0. \tag{4.4}
\]

Since this expression must equal zero for all values of \( r \), \( A_n = 0 \) for \( n > 0 \). It is noted that this is a significant difference to the solution for the sessile droplet case, since all even values of \( n \) remained in that case, but here only the \( n = 0 \) mode remains.

The boundary condition from Eq. (3.60) is satisfied

\[
\frac{\partial \theta_s^L}{\partial \phi} \bigg|_{\phi = 0} = 0. \tag{4.5}
\]

The expression for \( \theta_s^L \) is thus a constant

\[
\theta_s^L(r, \phi) = A_0. \tag{4.6}
\]

For the case with an insulated funnel wall, the liquid phase temperature perturbation is constant everywhere. Since the temperature is constant along the free surface, there will be no Marangoni convection and the system is predicted to be stable. Thus, the stability has been established and solutions for the vapour phase temperature and radial velocity are not required.


## 4.4 Conducting funnel wall

In this section an expression is developed to predict the onset of Marangoni convection for liquids evaporating from funnels constructed of conducting materials.

### 4.4.1 Liquid phase temperature

Similar to the analysis above, the general solution to Laplace’s equation is Eq. (3.74), and in order for the solution to be bounded at the origin, $B_n = 0$ for all $n$. Substituting into Eq. (4.3), it is found that both integrals are equivalent, so Eq. (4.3) is satisfied. The boundary condition from Eq. (3.60) is also satisfied:

$$\left. \frac{\partial \theta_s^L}{\partial \phi} \right|_{\phi=0} = 0. \quad (4.7)$$

Therefore, the expression for $\theta_s^L$ is

$$\theta_s^L(r, \phi) = \sum_{n=0}^{\infty} (A_n r^n) P_n (\cos \phi). \quad (4.8)$$

The conducting case therefore yields an expression, Eq. (4.8), for the liquid phase temperature perturbation that depends on $\phi$, in contrast to the expression for the insulating case, Eq. (4.6).

Since the result for $\theta_s^L$ in Eq. (4.8) is the same as that for the sessile droplet evaporating on a conducting substrate in Eq. (3.95), the remaining analysis will be identical. Since the thermal boundary condition of Eq. (4.3) has already been satisfied in the same manner as Eq. (3.56) for the sessile droplet case, there will be no additional changes to this analysis. Therefore, the analysis is not repeated here and the stability parameter, $\chi_s$, will be the same as $\chi_s^{CD}$ and can be listed here for liquids evaporating from funnels constructed of conducting materials

$$\chi_s = \frac{\nu}{\gamma_T} \left[ \frac{\partial j_{ev}}{\partial T_L} \right]_I + \frac{\partial j_{ev}}{\partial T_V} \left|_I \left( \frac{n + \xi_{TL}}{\xi_{TV} - K(n + 1)} \right) \right]. \quad (4.9)$$
As was noted above, \( \chi_s \) is comprised entirely of physical variables that are either properties or parameters that can be measured, so this expression can be compared directly with experimental observations.

### 4.5 Comparison between sessile droplet and funnel cases

For both sessile droplet and funnel geometry, the stability parameter was found to be the same for boundaries constructed of conducting materials. However, the results for the insulating case were considerably different. For the sessile droplet case, a stability parameter was generated; thus, a transition to Marangoni convection was predicted to occur. In contrast, the funnel case was found to be stable regardless of the evaporation rate. This indicates that the location of the funnel wall at \( \phi = \pi/4 \) serves to suppress the modes that are causing the instability in the sessile droplet case. To ascertain the physical validity of these predictions a comparison to experimental observations is made in the following chapter.
Chapter 5

Comparison with previous experimental observations

In this chapter, the theoretical predictions are compared to experimental observations [2, 1, 10]. It is noted that the liquid phase in these experiments was isothermal prior to the onset of Marangoni convection. Since there were no temperature gradients in the liquid phase, there could not have been any buoyancy-driven convection; hence, the observed transition to convection was the result of surface tension effects.

5.1 Experiments with a PMMA funnel

For liquids evaporating from funnels constructed of an insulating material, the theoretical analysis in Section 4.3 predicts that there will be no Marangoni convection and the system is stable. In the experiments of [10], H$_2$O was evaporating from a funnel constructed of PMMA. Since the thermal conductivity of PMMA is less than one-third that of water, the funnel is considered to be insulating. In these experiments the system was observed to be stable and there were no conditions in the investigation whereby Marangoni convection could be initiated. Therefore, the theoretical result correctly describes the observations in the experiments [10].
5.2 Experiments on a PDMS substrate

Experiments have been performed with a sessile droplet evaporating on a substrate constructed of polydimethylsiloxane (PDMS) [41], which has a thermal conductivity lower than water and can be considered insulating with respect to liquid water. There are some considerable differences between the theoretical analysis in Chapter 3 and the experimental conditions. Notably, the sessile droplet was not spherical and no experiments were performed with an isothermal liquid phase to ascertain if there was a transition from quiescent evaporation to Marangoni convection. However, a rough comparison can be made between the funnel constructed of PMMA where no Marangoni convection was observed [10], and the experiments for a sessile droplet on a substrate constructed of PDMS, where Marangoni convection was observed. The differences between the experiments and theory prevent a proper comparison; however, the experimental observations indicate the possibility of Marangoni convection for a sessile droplet, which is consistent with what the theory predicts, and suggests that the result is physically plausible. Experiments that can be used to thoroughly validate the theory for sessile droplets are recommended in Section 5.6.

5.3 Experiments with a stainless steel funnel

The predictions for a transition to Marangoni convection calculated with the stability parameter derived in Section 4.4 are now compared to the experimental results with H$_2$O and D$_2$O evaporating from funnels constructed of stainless steel [1, 2].

The values measured during the D$_2$O experiments [1] are listed in Table 5.1. In experiments EVD1 through EVD4, quiescent (stable) evaporation was observed as the evaporation rate was progressively increased from one experiment to the next. EVD5 was the first experiment where a convecting state was observed. Thus, a transition to Marangoni convection is expected to occur between EVD4 and EVD5.
Table 5.1: Conditions for the D$_2$O experiments [1].

<table>
<thead>
<tr>
<th>Experiment</th>
<th>EVD1</th>
<th>EVD4</th>
<th>EVD5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P^V$ (Pa)</td>
<td>651.9±13.3</td>
<td>642.6±13.3</td>
<td>625.3±13.3</td>
</tr>
<tr>
<td>$r_I$ (mm)</td>
<td>4.4±0.01</td>
<td>4.4±0.01</td>
<td>4.4±0.01</td>
</tr>
<tr>
<td>$j_{ev}$ (g/m$^2$s)</td>
<td>0.059±0.001</td>
<td>0.089±0.001</td>
<td>0.221±0.002</td>
</tr>
<tr>
<td>Throat $T^L$ ($^\circ$C)</td>
<td>3.60±0.02</td>
<td>3.58±0.02</td>
<td>3.61±0.02</td>
</tr>
<tr>
<td>Extrap. $T^V_I$ ($^\circ$C)</td>
<td>4.41±0.64</td>
<td>4.33±0.64</td>
<td>4.04±0.64</td>
</tr>
<tr>
<td>Onset $\chi_s$ ($n = 1$)</td>
<td>0.167</td>
<td>0.167</td>
<td>0.167</td>
</tr>
<tr>
<td>Onset $T^V_I$ ($^\circ$C)</td>
<td>3.641</td>
<td>3.621</td>
<td>3.652</td>
</tr>
<tr>
<td>Interface observed</td>
<td>Quiescent</td>
<td>Quiescent</td>
<td>Convection</td>
</tr>
<tr>
<td>Prediction</td>
<td>Quiescent</td>
<td>Quiescent</td>
<td>Possible convection</td>
</tr>
</tbody>
</table>

Similarly, the values measured during the H$_2$O experiments [2] are listed in Table 5.2. In experiments EV5 through EV7, quiescent (stable) evaporation was observed as the evaporation rate was increased. EV8 was the first experiment where a convecting state was observed, so a transition is expected to occur between EV7 and EV8 for the H$_2$O experiments.

It is crucial that the modes present in the experimental observations be determined, since the expression for the stability parameter for liquids evaporating from funnels constructed of conductings materials [Eq. (4.9)] places no limit on which mode will generate the instability. Temperature measurements made along the interface are summarized in Fig. 5.1, which was reproduced from reference [2]. It can be seen that during the quiescent evaporation in experiment EV5 the temperature along the interface was uniform, within the measurement error bars. In contrast, for evaporation with Marangoni convection present, experiment EV19 shows a continuous increase in temperature from
Table 5.2: Conditions for the H$_2$O experiments [2].

<table>
<thead>
<tr>
<th>Experiment</th>
<th>EV5</th>
<th>EV7</th>
<th>EV8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$PV$ (Pa)</td>
<td>787.9±13.3</td>
<td>783.9±13.3</td>
<td>777.3±13.3</td>
</tr>
<tr>
<td>$r_I$ (mm)</td>
<td>4.4±0.01</td>
<td>4.4±0.01</td>
<td>4.4±0.01</td>
</tr>
<tr>
<td>$j_{ev}$ (g/m$^2$s)</td>
<td>0.057±0.001</td>
<td>0.070±0.001</td>
<td>0.100±0.002</td>
</tr>
<tr>
<td>Throat $T^L$ (°C)</td>
<td>3.56±0.03</td>
<td>3.53±0.03</td>
<td>3.53±0.03</td>
</tr>
<tr>
<td>Extrap. $T^V_I$ (°C)</td>
<td>4.42±0.64</td>
<td>4.31±0.64</td>
<td>4.23±0.64</td>
</tr>
<tr>
<td>Onset $\chi_s$ ($n = 1$)</td>
<td>0.167</td>
<td>0.167</td>
<td>0.167</td>
</tr>
<tr>
<td>Onset $T^V_I$ (°C)</td>
<td>3.625</td>
<td>3.595</td>
<td>3.595</td>
</tr>
<tr>
<td>Interface observed</td>
<td>Quiescent</td>
<td>Quiescent</td>
<td>Convection</td>
</tr>
<tr>
<td>Prediction</td>
<td>Quiescent</td>
<td>Quiescent</td>
<td>Possible convection</td>
</tr>
</tbody>
</table>

the apex to the contact line. This is indicative of one large circulation cell present in the bulk liquid phase, since the presence of many cells would require temperature fluctuations along the interface caused by the hot and cold regions in the ascending and descending regions of each circulation cell. Therefore, it is concluded that there is one large circulation cell in the experimental observations. For the spherical harmonics, the presence of one circulation cell indicates that only the $n = 1$ mode is present, because higher values of $n$ would result in the presence of additional cells. The stability parameter can be simplified for these experiments, so Eq. (4.9) is written as

$$\chi_s(n = 1) = \frac{\nu}{\gamma_T} \left[ \frac{\partial j_{ev}}{\partial T^L} \bigg|_I + \frac{\partial j_{ev}}{\partial T^V} \bigg|_I \left( \frac{1 + \xi_{TL}}{\xi_{TV} - 2K} \right) \right], \quad (5.1)$$

and the onset is predicted to occur for a value of 1/6, from Eq. (3.107).

The interfacial radius, $r_I$, listed in Table 5.1 and Table 5.2 is the radius shown in Fig. 4.1, which was calculated based on the geometry such that the funnel wall corresponded to the origin of the spherical coordinate system and was located at an angle of $\pi/4$. This
Figure 5.1: The interfacial liquid temperature measured as a function of distance from the center line of the funnel in three different experiments. The conditions in EV5 and EV8 are listed in Table 5.2. Experiment EV19 is one for which Marangoni convection is present. (Reproduced from [2].)

is an approximation, which differs from the “interface radius” reported in [1] because that radius was calculated for a different purpose by considering the curvature of the interface and not for the location of the funnel wall. The difference between these two values results in a negligible change for the calculations performed in this analysis.

The interfacial vapour phase temperature, $T^V_I$, listed in Table 5.1 and Table 5.2 is labeled as the extrapolated value (“Extrap.”). The $T^V_I$ values reported in the experimental papers [1, 2] correspond to a temperature measurement that is approximately 40 $\mu$m away from the interface (in the normal direction). This is a result of the bead diameter of the thermocouple (approximately 50 $\mu$m), the gap required to ensure the bead was not in contact with the liquid phase, and the accuracy of the cathetometer used for positioning ($\pm$10 $\mu$m). The stability is sensitive to the value of $T^V_I$ so the value at the interface is
Table 5.3: Coefficients for the $T^V$ fit using Eq. (3.24).

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>$T_\infty$ (°C)</th>
<th>$\beta$ (°C/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVD1</td>
<td>28.75 ±1.97</td>
<td>5531 ±456</td>
</tr>
<tr>
<td>EVD4</td>
<td>26.73 ±2.04</td>
<td>5091 ±474</td>
</tr>
<tr>
<td>EVD5</td>
<td>26.07 ±0.93</td>
<td>5006 ±216</td>
</tr>
<tr>
<td>EV5</td>
<td>33.46 ±1.38</td>
<td>6601 ±319</td>
</tr>
<tr>
<td>EV7</td>
<td>30.55 ±0.72</td>
<td>5963 ±167</td>
</tr>
<tr>
<td>EV8</td>
<td>30.95 ±1.01</td>
<td>6071 ±233</td>
</tr>
</tbody>
</table>

required and an understanding of its uncertainty range. The temperature measurements were made as close to the interface as possible (thermocouple bead located 40 µm away) and at regular intervals progressively further from the interface (in a direction normal to the interface). These data points are used to generate a fit, which is extrapolated to the location of the interface. The fit corresponds to the solution for the vapour phase temperature in the initial stable state reported above as Eq. (3.24). Values for $T_\infty$ and $\beta$ are found and listed in Table 5.3 for each experiment. The measured data points and the fits are plotted in Fig. 5.2 for each of the experiments to elucidate the method, results, and estimated error.

The estimated error range listed in Table 5.1 and Table 5.2 for the extrapolated $T^V$ values is a result of the temperature measurement inaccuracy, the uncertainty in the interface location, and the fitting and extrapolation errors. The cathetometer uncertainty of ±10 µm leads to an uncertainty of ±20 µm in the location of the interface since both the steady state position of the interface, where evaporation is taking place, and the thermocouple bead location rely on positioning performed with the cathetometer. Although the temperature measurement inaccuracy is ±0.02°C, the combination of bead and interface location uncertainty, and the fitting and extrapolation errors raises the
Figure 5.2: Plot of the experimental data (points) and the fit (solid lines) for the vapour phase temperatures in the experiments. The interface is located at $r = r_I = 4.40$ mm.
estimated error to ±0.64°C.

The stability parameter for liquids evaporating from funnels constructed of conducting materials, χₚ, defined in Eq. (4.9), is a function of the interfacial liquid and vapour temperatures, the vapour phase pressure of the system, and the radius of the spherical interface. The expression for the evaporation flux, jₑ, derived from statistical rate theory is sensitive to values of the vapour phase pressure [34]. The equipment provided a measurement range of ±13.3 Pa which is not accurate enough to predict jₑ. However, the evaporation rate was measured with a syringe pump for these experiments, with a high degree of accuracy (±0.001 g/m²s). So instead of calculating the value of jₑ from the experimental measurements the value can be inserted directly and the stability parameter investigated as a function of the evaporation flux also

\[ \chi_p = \chi_p(j_e^0, T_V, T_L, P_V, r_I). \]  

(5.2)

Once the evaporation flux is inserted directly into the calculation of \( \chi_p \), the effect of the vapour phase pressure on the values of \( \chi_p \) becomes negligible.

### 5.4 Stability prediction for the D₂O experiments

In this section, it is determined if the stability parameter, χₚ, predicts the transition to Marangoni convection observed in the experiments of [1]. The fluid used in this study was D₂O, and the properties are given in [1]. As noted above the onset value is 1/6 (0.167).

If the value of \( \chi_p \) is calculated directly from the experimental values listed in Table 5.1, without considering the uncertainty ranges, the value of \( \chi_p \) is found to be less than the onset value (0.167) and the system is predicted to be stable for all of the experiments. However, it must be determined if an instability is predicted to occur within the uncertainty ranges of the experimental data. Since \( T_V \) has the largest uncertainty range, it is
examined first while holding the other experimental parameters in Eq. (5.2) constant, and the value which would be required for the onset of an instability is calculated.

The results of the investigation are summarized in Table 5.1. The instability is predicted to occur at a $T^* V^*$ value of approximately $3.641^\circ C$ for EVD1, $3.621^\circ C$ for EVD4, and $3.652^\circ C$ for EVD5. These results are listed to three decimal places based on the calculation requirement; however, it is noted that this level of accuracy exceeds the precision capability of measurements. The onset $T^* V^*$ value for EVD5, in which Marangoni convection was observed, lies within the possible range; however, the values for EVD1 and EVD4, which were observed to be quiescent, do not lie within the possible range. The uncertainty ranges for $j_{ev}$, $T^* f$, and $r_I$ were also investigated and there were no values within the ranges that predicted an instability for EVD1 and EVD4. Therefore, the theory is consistent with experimental observations, since it predicts that a transition to Marangoni convection is possible between EVD4 and EVD5.

5.5 Stability prediction for the H$_2$O experiments

In this section, it is determined if the stability parameter predicts the transition to Marangoni convection observed in the experiments of [2]. The fluid used in this study was H$_2$O, and the properties are given in [2].

Similar to the D$_2$O case, if the value of $\chi_s$ is calculated directly from the experimental values listed in Table 5.2, without considering the uncertainty ranges, the value of $\chi_s$ is less than the onset value (0.167) and the system is predicted to be stable for all of the experiments. As was done above, it must be determined if an instability is predicted to occur within the uncertainty ranges of the experimental data, beginning with an investigation of $T^* V^*$ while holding the other experimental parameters in Eq. (5.2) constant, and calculating the value which would be required for the onset of an instability.

The predicted $T^* V^*$ values are found to be outside of the uncertainty ranges for fixed
values of $j_{ev}$, $T_l^L$, and $r_I$. If $T_l^L$ is allowed to vary within its uncertainty range it is found that for the highest values of $T_l^L$ ($0.03^\circ$C above the values listed in Table 5.2) the predicted $T_l^V$ values are within the uncertainty range for EV8. The results of the investigation are summarized in Table 5.2. The instability is predicted to occur at a $T_l^V$ value of approximately $3.625^\circ$C for EV5, $3.595^\circ$C for EV7, and $3.595^\circ$C for EV8. The onset $T_l^V$ value for EV8, in which Marangoni convection was observed, lies within the possible range; however, the values for EV5 and EV7, which were observed to be quiescent, do not lie within the possible range. Therefore, the theory is consistent with the experimental observations, since it predicts that a transition to Marangoni convection is possible between EV7 and EV8.

## 5.6 Recommended experiments

In this section, experiments are recommended that could provide validation of the theory for evaporating sessile droplets, and provide a more rigorous examination of the stability for liquids evaporating from funnels.

### 5.6.1 Sessile droplet experiments

The experiments required to validate the theory derived in Chapter 3 would be similar to those mentioned above on the PDMS substrate [41]. Similar to the experiments performed by Duan and Ward [2, 1], the evaporation rate should be set low enough so that quiescent evaporation is maintained in the sessile droplet, with an isothermal liquid phase. Then the evaporation rate can be progressively increased at very small intervals (preferably even smaller than the ones taken by Duan and Ward) to ascertain the conditions when a transition to Marangoni convection occurs. Experiments should be performed on two different types of substrates, an insulating one and a conducting one. PDMS would suffice for the insulating substrate, and materials like gold or copper
would suffice for the conducting case.

5.6.2 Funnel experiments

The funnel experiments were performed with great care and the precision achieved was among the leading edge available currently in terms of methodology and equipment. The only improvement to the existing experiments would be to use smaller intervals when progressively increasing the evaporation rate to more accurately pinpoint the transition to Marangoni convection.

Other recommended experiments would require a mechanism to eliminate buoyancy driven convection, such as experiments with near free-fall conditions. If buoyancy could be eliminated it would enable the experiments to be run at a wider range of temperature (not restricted to the neutral buoyancy point of water) and much higher evaporation rates, which would allow for more rigorous validation of the onset predictions. Also it would allow predictions to be made for other fluids and validation of the theory for use in applications with different working fluids.
Chapter 6

Parametric analysis of the stability parameter

As was discussed above and summarized in Eq. (5.2), the new stability parameter for liquids evaporating from funnels constructed of conducting materials, $\chi_s$, is primarily a function of the interfacial vapour phase temperature, the interfacial liquid phase temperature, the evaporation flux, and the radius of the spherical interface. The experimental comparison in Chapter 5 indicates a strong link between these parameters and the stability. In this chapter the direct effect of the parameters on the stability is investigated by performing a parametric analysis, in which each parameter is analyzed individually while the others are held constant.

The analysis is performed using two expressions for the evaporation flux. The first is the statistical rate theory (SRT) expression used in the previous analysis, Eq. (2.6), and the second is the Hertz-Knudsen expression, Eq. (2.7). The derivatives of each $j_{ev}$ expression with respect to $T_L^i$ and $T_V^i$ are substituted into the expression for the stability parameter, Eq. (4.9), and the parametric analysis is performed for both versions. Since there is currently no technique for determining the accommodation coefficients in the Hertz-Knudsen expression, they were set equal to 1, which has been shown to be a fair
approximation under some circumstances [38].

The methodology for the analysis will be to use the data from the EVD5 experiment as a starting point and vary each parameter individually. The analysis was performed for a number of the experiments and the results were found to be identical, so the EVD5 experiment was selected for no particular reason, but it is representative of all of the experiments. Listing more than one set of parameter curves would only serve to complicate the results and ensuing discussion.

It should be emphasized that this parametric analysis is not a physically based analysis, since it is not believed that the three parameters can be independently varied. There is reason to believe from experimental observations [34] that there is a link between the temperature discontinuity at the interface and the evaporation flux. However, there is presently no expression describing this relationship and the result may depend on a number of factors that have not been rigorously investigated, such as the thermal boundary conditions of the system, the temperature in the bulk phases, and the presence of Marangoni convection. So these parameters are varied independently, exclusively to determine their influence on the onset of Marangoni convection.

6.1 Effect of interfacial vapour phase temperature

In this section, the effect of $T^I_V$ on the stability parameter for liquids evaporating from funnels constructed of conducting materials, $\chi_s$, is determined. Based on the EVD5 experiment $T^I_L$ is set at 3.61°C, $j_{ev}$ at 0.221 g/m²s, $r_I$ at 4.4 mm, and the value of $T^I_V$ is varied. The result is plotted in Fig. 6.1 where the top plot is for SRT and the bottom plot for Hertz-Knudsen.

It can be seen for the SRT version of the stability parameter (top plot), that as $T^I_V$ is decreased from the measured value of 4.04°C, the system becomes unstable. An interesting phenomenon is that since $T^I_L$ is fixed in this case, as $T^I_V$ is decreased, it
Figure 6.1: Top: stability parameter calculated using SRT is plotted versus $T_V^L$ for $T_I^L$ fixed at 3.61°C, $j_{ev}$ at 0.221 g/m²s, and $r_I$ at 4.4 mm. Bottom: stability parameter calculated using Hertz-Knudsen is plotted for the same conditions as the top plot.
approaches the value of $T_L$ (3.61°C); thus, the temperature discontinuity at the interface ($\Delta T_I = T_I^V - T_I^L$) is decreasing. Therefore, the analysis indicates that as $T_I^V$ decreases the system becomes less stable, or alternatively, as the temperature discontinuity decreases the system becomes less stable.

It can be seen from the bottom plot that if the Hertz-Knudsen expression is used to calculate the stability parameter, there is never predicted to be an instability for any value of $T_I^V$. The resulting values of $\chi_s$ are negative and five orders of magnitude lower than the onset value. It is also noted that the plot shows a reasonably small range of $T_I^V$ values; however, in the analysis the values were spanned over a much larger range to investigate if any values would generate a prediction of instability, and none did. This result disagrees with experimental observations, since Marangoni convection was observed for this experiment, and reaffirms the choice of SRT for the analysis in the previous chapters.

6.2 Effect of interfacial liquid phase temperature

In this section, the effect of $T_L$ on the stability parameter, $\chi_s$, is determined. Based on the EVD5 experiment $T_I^V$ is set at 4.04°C, $j_{ev}$ at 0.221 g/m²s, $r_I$ at 4.4 mm, and the value of $T_I^V$ is varied. The result is plotted in Fig. 6.2 where the top plot is for SRT and the bottom plot for Hertz-Knudsen.

It can be seen for the SRT version of the stability parameter (top plot), that as $T_I^V$ is increased from the measured value of 3.61°C, the system becomes unstable. Similar to the $T_I^V$ analysis it is again interesting to observe the effect of decreasing the temperature discontinuity. Since $T_I^V$ is fixed in this case, as $T_I^L$ is increased, it approaches the value of $T_I^V$ (4.04°C); thus, the temperature discontinuity at the interface is decreasing. Therefore, the analysis indicates that as $T_I^L$ increases the system becomes less stable, or alternatively and consistent with the $T_I^V$ case, as the temperature discontinuity decreases the system
Figure 6.2: Top: stability parameter calculated using SRT is plotted versus $T_I^L$ for $T_I^V$ fixed at 4.04°C, $j_{ev}$ at 0.221 g/m²s, and $r_I$ at 4.4 mm. Bottom: stability parameter calculated using Hertz-Knudsen is plotted for the same conditions as the top plot.
becomes less stable. Also of note in Fig. 6.2, is the onset line has a slope since it is a function only of $T_L$, whereas in the other plots where $T_L$ is held constant, it has a constant value. The trend is that the onset value decreases as $T_L$ is decreased.

Similar to the above case, it can be seen from the bottom plot that if the Hertz-Knudsen expression is used to calculate the stability parameter, there is never predicted to be an instability for any value of $T_L$. Again, this result disagrees with experimental observations and reaffirms the choice of SRT for the analysis in the previous chapters.

### 6.3 Effect of evaporation flux

In this section, the effect of $j_{ev}$ on the stability parameter, $\chi_s$, is determined. Based on the EVD5 experiment $T_V$ is set at 4.04°C, $T_L$ at 3.61°C, $r_I$ at 4.4 mm, and the value of $j_{ev}$ is varied. The result is plotted in Fig. 6.3 where the top plot is for SRT and the bottom plot for Hertz-Knudsen.

It can be seen for the SRT version of the stability parameter (top plot), that as $j_{ev}$ is increased from the measured value of 0.221 g/m$^2$s, the system becomes unstable. Firstly, this result is compatible with what would be expected physically, since an instability that results from evaporation should result in a system that becomes less stable as the evaporation rate is increased. Secondly, from Fig. 6.3 it can be seen that the evaporation rate expected to yield an instability for fixed interfacial temperature values, is more than two orders of magnitude higher than what was observed in the experiments. There is no experimental data for liquids evaporating from funnels at such high rates. It would be interesting to have some experiments at higher evaporation rates, which results in a system farther from equilibrium, and ascertain the stability behaviour.

Similar to the above two cases, it can be seen from the bottom plot that if the Hertz-Knudsen expression is used to calculate the stability parameter, there is never predicted to be an instability for any value of $j_{ev}$. Again, this result reaffirms the choice of SRT
Figure 6.3: Top: stability parameter calculated using SRT is plotted versus $j_{ev}$ for $T_I^Y$ fixed at 4.04°C, $T_I^L$ at 3.61°C, and $r_I$ at 4.4 mm. Bottom: stability parameter calculated using Hertz-Knudsen is plotted for the same conditions as the top plot.
for the analysis in the previous chapters.

6.4 Effect of radius of spherical interface

In this section, the effect of \( r_I \) on the stability parameter, \( \chi_s \), is determined. Based on the EVD5 experiment \( T_{I}^V \) is set at 4.04°C, \( T_{I}^L \) at 3.61°C, \( j_{ev} \) at 0.221 g/m²s, and the value of \( r_I \) is varied. The result is plotted in Fig. 6.4 where the top plot is for SRT and the bottom plot for Hertz-Knudsen.

It can be seen for the SRT version of the stability parameter (top plot), that as \( r_I \) is decreased from the measured value of 4.4 mm, the system becomes unstable. This indicates that liquids evaporating from smaller funnels are less stable. This result could be extended to sessile droplets as well, since the stability parameter is the same in both the funnel analysis and sessile droplet analysis when conducting materials are used for the boundary. This would indicate that smaller sessile droplets are less stable.

Similar to the above cases, it can be seen from the bottom plot that if the Hertz-Knudsen expression is used to calculate the stability parameter, there is never predicted to be an instability for any value of \( r_I \). Again, this result reaffirms the choice of SRT for the analysis in the previous chapters.

6.5 Comparison of kinetic relations

The results of this parametric analysis demonstrate the importance of the kinetic relation used to express the evaporation flux at the interface on the onset criterion. Use of the Hertz-Knudsen theory results in an onset parameter that predicts no instability would be possible for the system regardless of the value of the physical parameters. A possible explanation for this is that assigning the accommodation coefficients a value of 1 may have resulted in the loss of some temperature dependence; however, this is difficult to address since the coefficients are unknown with certainty, and seems unlikely
Figure 6.4: Top: stability parameter calculated using SRT is plotted versus $r_I$ for $T^V_I$ fixed at 4.04°C, $T^L_I$ at 3.61°C, and $j_{ev}$ at 0.221 g/m²s. Bottom: stability parameter calculated using Hertz-Knudsen is plotted for the same conditions as the top plot.
that there is significant temperature dependence given the results of a recent study [42]. Another explanation is that the unidirectional evaporation flux is independent of the thermodynamic properties of the vapour phase for the Hertz-Knudsen expression, as mentioned in Chapter 2, and the vapour phase properties are important for predicting the onset criterion in this case.

What has been illustrated is that using the statistical rate theory expression for evaporation flux results in a parameter that predicts an onset to Marangoni convection under the conditions described above, which is consistent with the fact that an onset was observed in experiments [2, 1].
Chapter 7

Conclusions

Stability parameters were generated to characterize the stability of evaporating semi-infinite liquid sheets, \((\text{Ma}/E)^\infty\), and bounded liquid sheets, \((\text{Ma}_n/E)^F\). The derivation was made possible by introducing evaporation as the specific heat transfer mechanism at the interface, and using the statistical rate theory expression for evaporation flux so there were no fitting parameters. A parametric investigation of the new parameter demonstrated that the interfacial liquid temperature and depth of the liquid layer have the largest effect on the stability of the system, and warmer temperatures corresponded to a more stable system. It was also demonstrated that a single parameter can be used to predict the onset criterion instead of two parameters, and that arbitrarily assigning one parameter is not possible due to the link between the stability and the interfacial energy balance.

A linear stability analysis was performed for spherical sessile droplets evaporating on substrates constructed of either insulating or conducting materials. Stability parameters were generated to characterize the stability of sessile droplets evaporating on insulating substrates, \(\chi^{ID}_s\), and conducting substrates, \(\chi^{CD}_s\). Since there are currently no experimental results to compare the theory with, another analysis was performed for liquids evaporating from funnels.
The boundary conditions were modified and a linear stability analysis was performed for liquids evaporating from funnels constructed of either insulating or conducting materials, so the theoretical results could be compared to experimental observations [2, 1, 10]. The stability analysis for liquids evaporating from funnels constructed of insulating materials predicted that there would not be a transition to Marangoni convection and the system would remain stable for all evaporation rates. The stability analysis for liquids evaporating from funnels constructed of conducting materials yielded an expression for a stability parameter, $\chi_s$, comprised of only physical variables defined at the liquid-vapour interface and no fitting parameters. Therefore the parameter was used to generate a prediction for the onset of Marangoni convection and it was compared directly with experimental observations. The differing results from these two analyses demonstrated the importance of the thermal properties of the boundary wall on the stability of bounded systems.

The theoretical result for the insulated case correctly described the observations of quiescent (stable) evaporation in the experiments with H$_2$O evaporating from a funnel constructed of PMMA [10]. In comparison, experimental observations for a sessile droplet evaporating on a PDMS substrate, indicate that a transition to Marangoni convection is possible for sessile droplets evaporating on insulating substrates. This is qualitatively consistent with the theoretical result from the sessile droplet analysis; however, a quantitative comparison could not be made since the experiments lacked a stable case to compare with.

The new stability parameter for liquids evaporating from funnels constructed of conducting materials, $\chi_s$, was used to calculate onset predictions for the experiments with H$_2$O and D$_2$O evaporating from a funnel constructed of stainless steel [2, 1]. The predictions were consistent with the experimental observations for both liquids. The experimental data did not have the precision or range required to provide a rigorous validation of the theoretical result.
A parametric analysis was performed on the new stability parameter. The analysis demonstrated that smaller interfacial temperature discontinuities, higher evaporation rates, and smaller radii correspond to less stable systems. It was also illustrated that calculations using statistical rate theory predict an instability, which is consistent with experimental observations, whereas using the Hertz-Knudsen theory does not predict any instability.
Bibliography


