THE EFFECT OF ADSORPTION ON ENERGY TRANSPORT AT A SOLID–VAPOUR INTERFACE

by

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A thesis submitted in conformity with the requirements for the degree of Master’s of Applied Science
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Abstract

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2014

An apparatus was configured to measure steady-state energy transport between ethanol vapour and a polished copper surface. The magnitude of energy transport increased with pressure until the ratio of the vapour pressure to its saturation pressure reached 0.2. The adsorption of ethanol on copper was measured and the energy transport was found to strongly increase with adsorption until approximately $4 \, \mu\text{mol/m}^2$ was adsorbed, after which the dependence of energy transport on adsorption became weak. An interfacial temperature discontinuity was measured and decreased with the amount of adsorption in a manner opposite to the energy transport. The magnitude of energy transport was found to strongly correlate to the fraction of adsorption sites on the copper occupied by at least one ethanol molecule. The temperature discontinuity demonstrated a strong correlation to the fraction of vacant adsorption sites. The amount of adsorption per se cannot account for the heat flux behaviour at the interface over the entire pressure range examined.
Dedication

The author would like to recognize his parents, Carl Clark and Piroska Fejes, for their gracious support and encouragement of his education.
Acknowledgements

The author would like to gratefully acknowledge the support and guidance of his supervisor, Dr. C.A. Ward, as well as thank his colleagues from the Thermodynamics and Kinetics Laboratory, A. Persad, C. Wu, S. Yaghoubian, and S.H. Zandavi, for their kindness and helpfulness. He would like to recognize the support received from the Natural Sciences and Engineering Research Council of Canada and the European Space Agency.
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Chapter 1

Introduction

Energy transport at a solid-vapour interface is a naturally occurring phenomenon and is used frequently in industry. Understanding how energy is transported across the interface is important for advances in the performance of heating and cooling technologies, from thermal management of electronics to food production [11, 13, 24–26, 32, 33, 49]. Despite the every day occurrence and use of the phenomenon, it is not well understood. Experimental investigations into energy transport at a solid-vapour interface are lacking in the literature and theoretical treatments are incomplete [33]. In this thesis the energy transport at an ethanol vapour and solid copper interface is investigated by measuring the temperature profiles in the bulk phases near the interface. The adsorption of ethanol on copper was measured and its effect on the heat flux was examined. Through comparison with two similar studies, water on gold and silica on gold, the importance of the thermal conductivity of the solid is investigated.

1.1 Background

1.1.1 Thermal Energy Transport at an Interface and the Temperature Discontinuity

Using classical kinetic theory (CKT) Pao predicted the existence of a temperature discontinuity at a liquid-vapour interface where there is evaporation; the vapour temperature at the interface was predicted to be lower than the liquid temperature [8, 36, 37]. This result was nonintuitive and seemed nonphysical
Chapter 1. Introduction . . .

to the investigators. Koffman et al. concluded that this temperature discontinuity was theoretically possible according to CKT, but questioned its possible magnitude, and stated, “the paradox is significant because it casts a shadow of doubt on the fundamental theory” [28]. In an attempt to explain the prediction, Aoki and Cercignani hypothesized that the temperature discontinuity is a result of changes in the kinetic layer or Knudsen layer, a region close to the wall only typically a few mean free paths thick, and suggested there could be a sharp temperature gradient present in this region [3]. Subsequently, Cercignani and collaborators confirmed that a temperature discontinuity could be described analytically, but urged experimental verification [8]. It is questionable if CKT was appropriate for application to liquids and vapours, since it was developed to describe low density gases.

In 1999 Fang and Ward initiated experimental studies on the liquid-vapour interface of water held in a funnel, which was evaporated at steady-state, and measured a temperature discontinuity at the apex of the interface [14]. The apparatus was specially constructed, allowing temperature measurements along the center line of the axisymmetric liquid water at heights increasing by 10 µm, with an uncertainty of only ±0.1 °C — meaning the thermocouple was brought within one mean free path (MFP) of the vapour molecules above the interface. This discontinuity was in the opposite direction of that predicted by CKT, the vapour near the interface was warmer than the liquid. By measuring within a MFP, Fang and Ward dispelled the hypothesis that a sharp temperature gradient was present in the Knudsen layer [3]. CKT was demonstrated to be insufficient to describe the temperature discontinuity at a liquid-vapour interface.

The largest temperature discontinuity measured by Ward and Fang was 7.8 °C, at the maximum evaporation flux [14]. The direction of the temperature discontinuity was confirmed by Ward and Stanga in further work on evaporation and condensation [42], in which they found the the discontinuity was present and the vapour temperature was greater for either process. Persad and Ward examined ethanol evaporation and established the existence of a temperature discontinuity for that process [38]. The direction of the temperature discontinuity confirms the suspicions of the authors over the previous decades who were intuitively unwilling to accept the predictions of CKT.

Through modelling different iterations of kinetic theory, Bond and Struchtrup were able to demonstrate that CKT is insufficient to describe the temperature discontinuity or evaporation flux and claimed that the interfacial energy flux plays a dominant role in determining the temperature discontinuity [6]. They also suggested that the ratio of vapour pressure to saturation pressure and the temperature of the liquid are important factors in determining the interfacial energy flux for a liquid-vapour system. Duan and
Ward applied Statistical Rate Theory (SRT), developed from the concept of transition probability in quantum mechanics and Bolztnan’s definition of entropy, to evaporation at the liquid-vapour interface and to predict the temperature discontinuity without the use of any fitting or experimental parameters [12]. Their predictions were consistent with the measured temperature discontinuities in [14], [42] and [38]. Statistical Rate Theory, unlike CKT, includes the effect of phonons. Duan and Ward’s result suggests that it is important to consider phonons to come to an accurate description of evaporation and the temperature discontinuity at a liquid-vapour interface.

Holyst et al. conducted molecular dynamics simulations of argon, modelled as a Lennard-Jones fluid, evaporating into its own vapour and concluded that the temperature discontinuity is caused by the constraint of equilibrium between momentum flux in the vapour and the liquid pressure in the evaporating film [23, 24]. They observed that the temperature jump is inversely proportional to the vapour density at the interface, and suggested that at high pressures the temperature is continuous at the interface. Babin and Holyst conducted simulations on sub-micrometer evaporating droplets, where energy transport at the interface was found to be the factor constraining the evaporation speed [4].

Ward and others demonstrated, that for a droplet, measuring the contact angle dependence on the liquid pressure at the three-phase line allows the liquid-solid adsorption to be determined [43]. By accounting for adsorption at the solid-liquid and solid-vapour interfaces it has been shown that surface tension, and subsequently the contact angle, of a sessile droplet could be accurately predicted [18, 44]. Furthermore, Ghasemi and Ward demonstrated that when a substrate is heating an evaporating droplet the majority of thermal energy was transported parallel to the solid-liquid interface to the three-phase line, where it was then distributed to the liquid-vapour interface [19]. Due to this observation, they suggested liquid-solid adsorption at the interface may give rise to a thermal resistance perpendicular to the interface.

A picture has formed over time in the literature, where the behaviour of two bulk phases near and at their interface is essential for understanding how energy is transported from one bulk phase to the other. A method of quantifying the effect of the interface is to find the Kapitza, or interfacial thermal, resistance.

1.1.2 Kapitza Resistance

The Kapitza resistance, first discovered in 1941, is a thermal resistance to heat transfer across an interface [39]. It is an experimental property, as no complete theoretical description of the cause of the resistance
is currently available [19]. For a small heat flux across an interface the temperature discontinuity is expected to be proportional to it [39]. The Kapitza resistance is defined,

$$R_k \equiv \Delta T / q$$

(1.1)

where $\Delta T$ is the temperature discontinuity across the interface, the interfacial vapour temperature less the interfacial solid temperature. $q$ is the heat flux per unit area to the interface from the vapour.

The magnitude of the thermal resistance has been attributed to phonon behaviour at the interface [5, 9]. A phonon is defined as a quantum of vibrational energy and they are important in determining the thermal and electric properties of a material. It has been suggested that the interfacial thermal resistance is due to an impedance at the interface which prevents phonons in the bulk phases from transporting energy across the interface, caused by a mismatch in phonon frequencies [32]. It follows that the phonon frequencies at the interface are important in determining the temperature discontinuity and the energy transport across the interface. The phonon frequency mismatch, interfacial bond strength, interface temperatures, and pressure at the interface all known to effect the Kapitza resistance [33]. Murad and Puri performed molecular simulations which showed $R_k$ as decreasing with temperature of the fluid at the interface, and as inversely proportional to the heat flux [32].

Two models have traditionally been used to describe the interfacial thermal resistance — the Acoustic Mismatch Model (AMM) and the Diffuse Mismatch Model (DMM) [41]. The Acoustic Mismatch Model, by analogy to classical wave theory and acoustics, assumes phonons can be treated as waves in a continuum which will only exhibit specular scattering at a perfectly ideal surface [33]. Therefore the level of matching between the acoustic impedance of the materials controls the number of phonons that can transfer energy across the boundary [34]. Conversely, DMM assumes all the phonons scatter diffusively at the interface, accounting for the fact that an interface will not be ideal [33].

It has been found that AMM performs best at low temperatures because the phonon wavelengths are long when compared to the molecular spacing of the solid. DMM is thought to hold for higher temperatures than AMM, but it has not accurately predicted the thermal boundary resistance [34]. In practice neither extreme is true, with AMM providing an upper limit and DMM a lower limit on the transmissivity of phonons across the interface, but both models depend on phonon behaviour at the interface, indicating a reduction in the mismatch of phonon frequencies will reduce the thermal resistance.

Ge et al. found through experimentation using time-domain thermoreflectance that for water and a
hydrophilic surface the Kapitza resistance is a factor of 2-3 smaller than for water and a hydrophobic surface [17]. Harikrishna and collaborators built on this work to experimentally show that the thermal resistance is inversely proportional to the work of adhesion between a solid and liquid for the specific case of a gold-thiol-alkane-ω-group-water system [21]. The ω-group was altered to change the work of adhesion, which is a measure of the bond strength between the water and solid – the minimum work required to disassociate liquid water from the solid in its vapour. Harikrishna and coworkers also observed that the relationship between the work of adhesion and the Kapitza resistance would only hold if it was the factor limiting the energy transport [21]. Stronger bonding at the interface resulted in larger values of heat flux, suggesting the stronger bonds enable greater transfer of vibrational energy from the water to the solid; indicating the adsorption of a fluid on a solid has an important role to play in determining the resistance to thermal energy transport.

Both AMM and DMM consider the characteristics of the bulk phases at the interface, but at the interface between a vapour and a solid an adsorbed layer is present. Using molecular dynamics simulations of silica-water and silicon-water Murad and Puri demonstrated that an adsorbed layer could act to reduce the Kapitza resistance [32]. They did not directly model the adsorption, but observed that the van der Waals attraction between the silicon atoms and water molecules led to a layering of the water molecules on the solid surface. For silica, which is more hydrophillic than silicon, water molecules became organized in layer which penetrated the silica structure, due to nanoporous surface. They found that for the silica-water system, which had a greater number of water molecules layered adjacent to the solid than the silicon-water system, the Kapitza resistance was less than in the silicon-water system. They suggested, based on the theories of energy transport through phonons at the interface, that increasing the fluid pressure or adsorbing additional layers of the fluid will increase the ability of phonons to transfer energy at the interface [32, 39]. Therefore, adsorption of a vapour on a solid will act to increase the heat flux at the interface. The results of the simulations supported the theory that it is due to the adsorbed layer becoming more “solid like” that the thermal resistance is reduced, and that after a certain amount of adsorption is present on a surface the resistance will exhibit much weaker dependance on pressure and temperature [10, 32].

1.1.3 The Adsorption of a Vapour on a Solid

Adsorption is a phenomenon describing the attachment of particles from a fluid phase to the surface of a solid phase. An adsorption isotherm is an important mathematical way to describe the aforementioned
occurrence. Over many decades several isotherm expressions have been developed on different bases, but none could successfully describe the wide range of observed adsorption behaviour.

The Langmuir isotherm is one of the simplest empirical models, assuming the adsorption of single molecules approaches a monolayer [30]. The Langmuir isotherm reaches a plateau if all the adsorption sites are occupied. This isotherm has been found effective at describing a gas adsorbing as single molecules onto a solid, but cannot describe vapour adsorption on a solid [15].

For gases at low temperatures an S-shaped isotherm, being convex at low pressure and becoming concave at high pressure, was measured by Brunauer and colleagues [7]. They developed the BET-isotherm as a theoretical expression to describe their observations, on the basis that the same forces responsible for condensation are responsible for adsorption [7]. Another popular isotherm, the FHH-isotherm, was arrived at independently by Hasley, Frenkel and Hill in an attempt to describe adsorption when more adsorbed layers are present at higher pressures [20, 22]. The BET-isotherm performs best for relative pressures less than 0.35, while the FHH-isotherm performs better for relative pressures above 0.8 [15].

A major shortcoming of these isotherms is that none can describe a finite amount of adsorption as a vapour approaches its saturation pressure. Anderson modified the BET equation to reflect the physical requirement of finite adsorption near and at saturation pressure, based on the empirical data, but did not develop a theoretical basis for the modification [1, 2]. In a review of adsorption isotherms Limousin and colleagues criticize the macroscopic and largely empirical way in which these isotherms are developed, as this does not give insight into the mechanisms of adsorption involved [31].

The Zeta-isotherm, as applied to vapours and solids, was developed by Wu and Ward [44], and extended to gases by Zandavi and Ward [47, 48], who also established a method of predicting the cluster distributions of the adsorbed molecules. The derivation of the isotherm is reviewed in Chapter 4, but importantly it begins from a theoretical basis and does not predict infinite adsorption at the saturation pressure of a vapour. Instead, it predicts that an adsorbed film will form at pressures above the saturation pressure. The Zeta-isotherm assumes an adsorbed vapour can be modelled as clusters of molecules, with one cluster adsorbing for one adsorption site; the way the molecules inside a cluster are organized is not considered. The success in its formulation relies on the limiting of the number of molecules that can be in a cluster, by considering a canonical ensemble (NVT-ensemble, only energy can be exchanged with a reservoir), rather than a grand canonical ensemble (µVT-ensemble, energy and matter can be exchanged with a reservoir). The Zeta-isotherm was shown to be superior to the BET isotherm for describing the adsorption of toluene, heptane and octane on silica [47]. The Zeta-isotherm can be reduced
to the Langmuir [48] or BET [47] isotherms by making certain assumptions about the system and the way molecules adsorb.

1.2 Motivation & Scope

As elaborated on in the preceding discussion of the literature, the understanding of energy transport at a solid-vapour interface is incomplete. Energy is transported through a vapour, across an interface and through a solid, where the interface is thought to be the rate limiting step in this process. The work undertaken for this thesis was conducted with the intent of empirically examining energy transfer and adsorption at a copper-ethanol interface. We will investigate the relationship between adsorption, heat flux and the temperature discontinuity. By using copper, which has one of the largest thermal conductivities for a metal, heat transfer through the solid should not limit the rate at the interface. In conjunction with two other interfacial energy transport and adsorption studies, water-gold [46] and water-silica [45], the effect of the thermal conductivity of the solid compared with the interfacial behaviour is investigated. This comparison affords the opportunity to examine if differing amounts of adsorption at the interface of different solid-vapour systems can be linked to the differences in heat flux.

Chapter 2 describes the apparatus used to experimentally determine the interfacial temperatures and heat flux, as well as the preparation and procedure followed in conducting the experiments. The calibration of the thermocouples for use in the apparatus, the machining and polishing of the copper substrate, and the installation of the substrate in the chamber are detailed.

Chapter 3 covers the analysis and results of the interfacial energy transport experiments. By measuring the temperature profiles in the vapour, the interfacial vapour temperatures were found by extrapolation. The heat flux to the substrate was determined by Fourier’s law. The behaviour of the energy flux, temperature discontinuities, and thermal resistance are confirmed with respect to increasing pressure.

The equilibrium adsorption measurements of ethanol on copper are described and analysed in Chapter 4. The development of the Zeta-isotherm and process for fitting it to the measured data are reviewed. The adsorption behaviour of ethanol-copper and the distribution of adsorbed ethanol clusters is examined with respect to the interfacial heat flux, temperature discontinuity and Kapitza resistance. The relationship between adsorption, energy transport, temperature discontinuity and interfacial resistance is examined.
In Chapter 5 the experimental work done with ethanol-copper is used in conjunction with two other solid-vapour studies, water-gold and water-silica, to examine the effect of the thermal conductivity of the solid on interfacial energy transport. It is confirmed that for two systems, one with a higher thermal conductivity for the solid and the other with greater adsorption, that the thermal conductivity is not limiting the heat flux. It is shown that at low pressure the adsorption controls the heat flux, but that this relationship does not continue at higher pressure ratios; suggesting that there is a threshold amount of adsorption after which increased adsorption does not significantly affect the interfacial thermal resistance.
Chapter 2

Apparatus & Procedure: Study of Interfacial Energy Transport

An apparatus was constructed to measure the temperature profiles near a solid-vapour interface. The top of an otherwise insulated chamber was maintained at room temperature, and a solid substrate inside the chamber, near the bottom, was maintained at a lower temperature. This provides a driving force for heat transfer. There is energy transport through the bulk vapour to the interface, from the interface to the bulk solid, and through the bulk solid to a temperature bath.

The heat transfer from bulk vapour to the interface could take place through conduction, convection or radiation. No vapour is being added or removed from the chamber during an experiment; any heat transfer by convection will be limited to natural convection. Furthermore, since the bottom of the chamber was being cooled by the substrate, and the top of the chamber was being heated, natural convection was suppressed near the interface. In a study done with a similar chamber, different sized thermocouple beads were used to measure a constant temperature profile [14]. If radiation were to have an appreciable effect on the measurements made, the larger thermocouple would have recorded a greater temperature, but this was not the case. Near the interface the fluid was quiescent and conduction was the mode of heat transfer observed, since the temperature profile was linear. By measuring the temperature profiles in the vapour, the heat flux to the substrate was determined by Fourier’s law.

Heat is carried by phonons and electrons in an electric conductor, such as copper, and by phonons alone.
Figure 2.1: A schematic of the apparatus setup. Details of substrate inside the chamber can be seen in Figure 2.2.

in a dielectric vapour such as ethanol. There is no heat conduction through electron movement in the vapour and at the interface, due to the lack of free electrons in the vapour. Therefore, in the system described here, only phonons can be responsible for heat transfer across the adsorbed layer.

2.1 Configuration of the Apparatus

This section details the setup of the various pieces of equipment that make up the apparatus. A schematic of the apparatus that was used to experimentally measure the vapour and solid temperatures is shown in Figure 2.1. The chamber, which contains the copper substrate and vapour, and for which the pressure inside could be controlled, was constructed of stainless steel with four borosilicate glass viewports.

2.1.1 Cleaning of the Chamber Components

All chamber components were rinsed with deionized, distilled and nanofiltered water, having a resistivity of \(18.2\pm0.1\Omega\cdot\text{cm}\) (final filtering done and resistivity measured with a Barnstead Nanopure D4751); cleaned with a water and detergent mixture (Alconox) for approximately 24 hours; and thoroughly rinsed again. The glass and steel components were soaked for approximately 24 hours in acetone (VWR, 99.5%) and rinsed with pure water. In addition to the aforementioned cleaning, any glassware used was subsequently subjected to 24 hours immersion in chromic-sulfuric acid (VWR, 99.9%), followed by rigorous rinsing with pure water.

2.1.2 Configuration for Temperature Measurements

Above the substrate a thermocouple (K-type) was mounted on a 3-axis positioning micrometer (HPT040, Vacuum Generators) — allowing measurements at varying radial positions and heights above the substrate in the vapour phase. The moveable thermocouple (Omega, CHAL-0005), had a wire diameter of 13 \(\mu\text{m}\), and had a bead diameter measured under a microscope of 27 \(\mu\text{m}\). The positioner had an accuracy of \(\pm10\ \mu\text{m}\) in the vertical direction, and \(\pm2\ \mu\text{m}\) in the radial direction. The moveable thermocouple was configured in a U-shape, as seen in Figure 2.11, to limit the possibility of heat conduction down the thermocouple wires to the bead due to the vertical temperature gradient in the vapour. Two perpendicular viewports with a cathetometer and high-zoom video-camera were used to position the moveable thermocouple above the center of the substrate. A high speed camera (Photron Fastcam PCI-R2 with a Sony zoom lens) was used to monitor the thermocouple position during experiments. Twelve K-type thermocouples (Omega, 5TC-TT-36-36), with teflon insulated wiring and a bead diameter of 0.27 mm, were embedded in the substrate at varying depths and radial positions, as described in Section 2.3.

2.1.3 Maintaining the Temperature Gradient in the Chamber

The chamber, except for the viewports, was insulated on the sides and bottom. The top was exposed to room temperature. Since the chamber is stainless steel, heat from the top of the chamber may be conducted under the insulation to the sides of the chamber. A recirculating cooling bath (VWR, Model #: 1156DF) pumped cooled ethylene glycol, 1°C, along insulated tubing which led to the bottom flange, and then to the substrate base. The cooling fluid removed heat from the base of the substrate and was
Figure 2.2: Illustration of the substrate, moveable thermocouple, and recirculating cooling fluid.
Chapter 2. Apparatus & Procedure

2.1.4 Feeding Vapour into the Chamber

The degassing flask contained the working fluid before it was allowed to enter the chamber. The pressure and temperature inside the degassing flask could be brought below saturation values using a cold trap (Labconco CentriVap -84°C) and a mechanical vacuum pump (Welch DuoSeal, Model # 1402B-01). A capacitance diaphragm pressure transducer (Infinicon Sky CDG045, Full Scale: 100 Torr, Accuracy 0.15%, Resolution 0.0015%) and thermocouple were used to monitor these values. Once the vapour was degassed it could be fed into the system from the degassing flask and syringe. The fluid from the syringe pump flowed up a 1.6 mm outer diameter stainless steel tube and out the center hole of the substrate.

2.1.5 Controlling the Chamber Pressure

The chamber was maintained at low pressure (approximately 20 Pa) by the mechanical vacuum pump and could be brought to pressures in the $10^{-5}$ Pa range using the turbo-molecular diffusion pump (Leybold, UHV1100). A pressure transducer (Infinicon CDG045D, Full Scale: 1000 Torr, Accuracy: 0.15%) with a resolution of ±4 Pa was used to monitor the pressure in the chamber when it was closed to the turbopump. The leak rate of the chamber was measured several times, giving values of 1.23 Pa/hr (measured with average pressure of approx. 40 Pa), 1.44 Pa/hr (measured with average pressure of approx. 70 Pa) and 0.72 Pa/hr (measured with average pressure of approx. 1080 Pa). The leak rate was measured over a period of at least 12 hours in each case. A quadruple pole residual gas analyzer (SRS RGA 200) was used to monitor the composition of the chamber through a leak valve leading to the mass spectrometer and the turbopump.

2.1.6 Data Acquisition

All thermocouple and pressure transducer voltages were fed to a data acquisition unit (Aigilent 34970A), which uses two ice-point cells (Omega TRCIII-A and TRCIII) to provide the reference voltage for the readings. The DAQ output to a PC, where Benchlink Data Logger 3 (version 4.3) was used to monitor and record the voltages. The mass spectrometer also output to PC, and RGA Version 3.213.006 application was used to examine the chamber atmosphere composition.
2.2 Calibration of Thermocouples

All the thermocouples for use in the chamber were carefully calibrated prior to their installation.

2.2.1 Method of Calibration

The calibration of all thermocouples for use in experiments was done with a National Institute of Standards and Technology (NIST) certified thermocouple composed of a probe (T100-450-15) and a reader (F100-A2, Accuracy: ±0.02). The device was calibrated and certified by Isotech Inc. (Certificate #: ISO12953), showing a maximum device-under-testing system error of ±0.009°C over the calibration range of -38‰ to 420‰. Since the calibration error was less than the manufacturer cited accuracy, the larger value was used as the error for the T100/F100 pair.

The thermocouples that were being calibrated were attached directly next to the T100 shaft, as seen in Figure 2.3. They were then submerged in the recirculating temperature bath, as seen in Figure 2.4. The vertical gradient in the bath was measured to be 0.003‰/cm, which is negligible compared with the F100 manufacturer cited accuracy of ±0.02‰. The F100 temperatures and voltages were recorded for 30 minutes when the bath was at steady-state. Steady-state was deemed to have been achieved when the standard deviation of the average F100 temperature over 30 minutes was less than the accuracy of the F100.

A cubic polynomial was fit to convert the measured voltages of the thermocouples to the temperatures recorded by the F100, producing a calibration curve which was subsequently checked using a range of temperature check points. If the difference between the measured F100 value and the calculated thermocouple temperature was less than the accuracy of the F100, the calibration curve was considered valid.

2.2.2 Calibration of Thermocouple for Vapour Phase Measurements

The thermocouple for use in the vapour phase was calibrated with a point taken every 5°C, from -30°C to 40°C, with check points taken every 10°C from -33°C to 37°C. The difference between the calculated temperature and the measured temperature was less than the accuracy of the F100 for all checkpoints except -33°C (see Table 2.1), and therefore the calibration curve, as seen in Figure 2.5, was considered valid.
Figure 2.3: The substrate thermocouples before calibration attached to the T100 at the location of the bead inside the shaft (1 in. from tip). None of the exposed wires or thermocouple beads touch each other, or the T100 shaft, to avoid creating any electrical circuits which could interfere with accurate readings.

Figure 2.4: Photograph of the calibration in progress. The T100 probe is wrapped in foam insulation, while the thermocouples that are to be calibrated can be seen entering the temperature bath under this insulation. The temperature bath must be well insulated where the thermocouples enter to be able to reach steady-state.
Figure 2.5: Calibration curve for the vapour-phase thermocouple. For the lowest temperature check point, the magnitude of the difference between the measured temperature and calculated temperature was greater than the F100 error, and so the calibration was only valid to -23 °C. The coefficient of determination and calibration expression for voltage to temperature conversion are shown.

valid through the upper limit of check points to 37°C. The ice-point cells used for the reference voltage for the thermocouples maintained their temperatures within ±0.02°C. The root mean square of the ice point cell error, F100 accuracy and difference between calculated and measured temperatures were taken to estimate an uncertainty of ±0.03°C on temperature measurements in the vapour phase.

2.2.3 Calibration of Thermocouples to be Installed in the Substrate

The twelve thermocouples for use in the substrate were calibrated simultaneously. Care was taken to position the thermocouples around the T100 probe without the beads touching each other or the probe, to avoid the creation of any circuits between the thermocouples or the T100 shaft, as seen in Figure 2.3. A typical calibration curve can be seen in Figure 2.6. A measurement was taken every 2°C, from -16°C to 40°C, with check points taken every 7°C from -13°C to 35°C. The differences between the check points and the calibration curves were less than the F100 accuracy (as seen for a single substrate thermocouple in Table 2.2) and so the calibration was valid. A conservative error estimate was appropriate for the substrate thermocouples because it was necessary to calibrate them before installation in the substrate and the installation process could introduce additional error to the calibration. There were more sources
Table 2.1: The check point values for the calibration of the vapour phase thermocouple. The standard deviation is for the measured temperature from the F100 – it was less than the F100 accuracy of ±0.02 for all check points. The final column is the magnitude of the difference between a measured check point temperature, and a temperature calculated based on the calibration curve – it was less than the F100 accuracy of ±0.02 for all but the check points at -33°C.

<table>
<thead>
<tr>
<th>Measured Temperature (‰)</th>
<th>Standard Deviation (‰)</th>
<th>Calculated Temperature (‰)</th>
<th>Measured - Calculated (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-33.153</td>
<td>0.012</td>
<td>-33.175</td>
<td>0.022</td>
</tr>
<tr>
<td>-33.179</td>
<td>0.006</td>
<td>-33.207</td>
<td>0.028</td>
</tr>
<tr>
<td>-23.055</td>
<td>0.003</td>
<td>-23.068</td>
<td>0.013</td>
</tr>
<tr>
<td>-13.046</td>
<td>0.001</td>
<td>-13.046</td>
<td>0.001</td>
</tr>
<tr>
<td>-3.060</td>
<td>0.004</td>
<td>-3.049</td>
<td>0.011</td>
</tr>
<tr>
<td>-3.065</td>
<td>0.004</td>
<td>-3.066</td>
<td>0.002</td>
</tr>
<tr>
<td>6.958</td>
<td>0.003</td>
<td>6.970</td>
<td>0.012</td>
</tr>
<tr>
<td>16.979</td>
<td>0.001</td>
<td>16.976</td>
<td>0.003</td>
</tr>
<tr>
<td>26.998</td>
<td>0.002</td>
<td>26.989</td>
<td>0.009</td>
</tr>
<tr>
<td>37.007</td>
<td>0.001</td>
<td>37.012</td>
<td>0.004</td>
</tr>
</tbody>
</table>

of error in the substrate temperature measurements than in the vapour phase measurements. The additional error was due to the epoxy coating of the thermocouples, which results in a thin layer of epoxy between the thermocouple bead and the copper; since the thermal conductivity of the epoxy was only 1.038 W/(mK) and the thermal conductivity of the copper was two orders of magnitude larger, there was a larger resistance to heat conduction around the thermocouple bead than in the bulk copper. In addition, due to the installation in epoxy, the thermocouple bead and wiring may have been under physical stresses not present during the calibration. The standard error of the reference ice-point cell, the F100, and the maximum check point difference are summed for an uncertainty on the substrate thermocouple measurements of ±0.05°C.

2.3 Preparation of Copper Substrate

2.3.1 Machining and Polishing of the Substrate

The substrate was machined out of polycrystalline copper (McMaster-Carr, 99.9% purity) using a mill to form the rough shape and a lathe to finish the cylindrical form. The center hole, diameter of 0.635 mm, and the twelve radial thermocouple holes, diameters of 1.041 mm, were made with a jewelers drill. The dimensions of the substrate are seen in Figure 2.7. A stainless steel tube was silver soldered into the 1.6 mm diameter hole. The substrate was stored in ethanol after machining to prevent oxidation.
Figure 2.6: Calibration curve for one of the thermocouples to be embedded in the substrate. All of the substrate thermocouple calibration curves were similar. The coefficient of determination and calibration expression for voltage to temperature conversion are shown.

Table 2.2: The check point values for the calibration of one of the substrate thermocouples. The standard deviation on the measured temperatures from the F100 were less than the F100 accuracy of ±0.02 for all check points. The final column is the magnitude of the difference between a measured check point temperature, and a temperature calculated based on the calibration curve – at all check points the calibration was valid.

<table>
<thead>
<tr>
<th>Measured Temperature (°C)</th>
<th>Standard Deviation (°C)</th>
<th>Calculated Temperature (°C)</th>
<th>Measured - Calculated (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.128</td>
<td>0.003</td>
<td>35.126</td>
<td>0.001</td>
</tr>
<tr>
<td>29.111</td>
<td>0.004</td>
<td>29.109</td>
<td>0.002</td>
</tr>
<tr>
<td>23.124</td>
<td>0.001</td>
<td>23.123</td>
<td>0.001</td>
</tr>
<tr>
<td>17.105</td>
<td>0.003</td>
<td>17.107</td>
<td>0.002</td>
</tr>
<tr>
<td>11.107</td>
<td>0.003</td>
<td>11.111</td>
<td>0.004</td>
</tr>
<tr>
<td>5.104</td>
<td>0.004</td>
<td>5.107</td>
<td>0.003</td>
</tr>
<tr>
<td>1.123</td>
<td>0.007</td>
<td>1.122</td>
<td>0.001</td>
</tr>
<tr>
<td>-0.881</td>
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<td>-0.882</td>
<td>0.001</td>
</tr>
<tr>
<td>-6.892</td>
<td>0.004</td>
<td>-6.899</td>
<td>0.007</td>
</tr>
<tr>
<td>-12.882</td>
<td>0.002</td>
<td>-12.892</td>
<td>0.010</td>
</tr>
</tbody>
</table>
before polishing.

The top surface of the substrate was prepared using the following procedure. The surface was smoothed sequentially, using 120, 240, 320 and 600 grit sandpaper. The substrate was then polished using successively finer suspensions. The first polishing was done with a Gold Label polishing cloth (Allied Co.) coated with a diamond suspension with an average particle size of 6 \( \mu \text{m} \) (Allied Co., Product #: 90-30025-X). The second polishing utilised a White Label (Allied Co.) cloth coated with a lubricant (GreenLube, Allied Co., Product #: 90-209000-X) and a diamond suspension with an average particle size of 1 \( \mu \text{m} \) (Allied Co., Product #: 90-30015-X). The final polishing was done with a Final A (Allied Co.) cloth, the same lubricant as the previous step and an alumina/silica suspension with an average particle size of 0.05 \( \mu \text{m} \) (Allied Co., Product #: 180-70000-X). Between each step the substrate was submersed in fresh ethanol and cleaned using an ultrasonic cleaner.

The aforementioned polishing procedure had been used before on copper to obtain an average surface roughness of 53.1 nm, measured by surface profilmetry [18], but the roughness of this substrate was not measured. Images to qualitatively examine the improvement in surface roughness were taken using a standard optical microscope and can be seen in Figure 2.8. The completed substrate is seen in Figure 2.9.

### 2.3.2 Installation of Substrate in Chamber & Installation of the Substrate Thermocouples

The substrate was connected to the bottom flange of the chamber via a hollow stainless steel shaft that carried the cooling fluid from the temperature bath. A rubber O-ring was positioned between the substrate base and stainless steel to prevent the copper acting as a sacrificial anode for the stainless steel and to ensure no cooling fluid could leak into the chamber.

The twelve substrate thermocouples were inserted into the radial holes and secured in position using thermally conductive adhesive epoxy (Omegabond 101, \( k = 1.038 \text{ W/(mK)} \)). The holes were filled with epoxy using a syringe and the thermocouples were installed in vertical sets of three. Each thermocouple was coated with a thin layer of epoxy to electrically insulate it; if the thermocouples were not electrically insulated from the copper and each other the readings could be affected by electrical conduction between thermocouples through the substrate. Care was taken to maintain the quality of the polish. The substrate attached to the chamber flange with all thermocouples installed can be seen in Figure 2.10. Finally, the bottom flange was fastened to the chamber using a copper gasket to ensure a tight seal. A photograph
Figure 2.7: Schematic for the machining of the copper substrate. Comparing the measured diameter of 17.93 mm, found with a Vernier caliper, to the target of 18.00 mm, we can see that we are less than 3 thou off the desired dimension — within the tolerance. The twelve thermocouple holes on the side are drilled with drill bit size no. 59 (1.041 mm) and the center hole was drilled with drill bit size no. 72 (0.635 mm).
Figure 2.8: The left side of this figure shows the substrate after machining, which can be compared with the images on the right, taken after the polishing was complete. The top set of images show the improvement in the surface quality around the center hole, and the bottom set show the reduction of roughness near the edge of the substrate and in the improved quality of the edge.
of the substrate in the chamber with the moveable thermocouple positioned above the centre hole can be seen in Figure 2.11.

### 2.4 Procedure for Interfacial Temperature Measurements

#### 2.4.1 Preparation for Experiments

**Cleanliness of the Chamber Atmosphere Before an Experiment**

Before each experiment (or “run”) the chamber was evacuated to a pressure of the order $10^{-5}$ Pa or lower using the turbopump. The composition of the chamber was examined with the mass spectrometer before each run (see Table 2.3). It was ensured that contamination of the chamber by mechanical pump oil would not interfere with the temperature measurements.

The composition of the turbopump alone, seen in Column 1 of Table 2.3, was measured at a pressure of order $10^{-7}$ Pa. The turbopump atmosphere was dominated by hydrogen, suggesting the turbopump was clean. The high partial pressure of hydrogen was caused by the low compression ratio of the turbopump for light gases; while heavier gases were more easily compressed at the turbopump exit, hydrogen was not. As seen in Figure 2.12 there were no peaks distinguishable from the background noise at atomic
Figure 2.10: The copper substrate, attached to the bottom flange, with the thermocouples installed in the side holes using epoxy. Any exposed connections between the thermocouple wiring and the wiring out of the bottom of the flange (thermocouple junctions) are wrapped in teflon for protection from any potential reactions with the working fluid.
Figure 2.11: The moveable thermocouple positioned above the centre hole of the substrate. The photo was taken looking down a cathetometer telescope with a digital camera. The thermocouple is U-shaped to suppress the conduction of heat along the thermocouple wires due to the vertical temperature gradient.
mass units (AMU) the pump oil contributes to. The fractional masses of the mechanical pump oil are
distributed over seven different atomic masses, and it is therefore more difficult for the RGA software
to quantify than a component that has a lesser number of fractional masses.

A typical atmosphere composition for the chamber and turbopump before any ethanol was allowed into
the chamber is shown in Column 2 of Table 2.3. The analysis by the SRS RGA software calculated 1.1%
of the chamber atmosphere was mechanical pump oil, but as seen in Figure 2.13 there were no peaks
discernible from the noise at AMU where the pump oil contributes to the partial pressure. Therefore,
the percentage reported by the software was considered negligible and the chamber was considered clean
before each experiment began.

<table>
<thead>
<tr>
<th>Components</th>
<th>1. Turbopump</th>
<th>2. Turbopump and Leak Valve</th>
<th>3. Chamber &amp; Turbopump Before Run</th>
<th>4. Chamber After Run</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (Pa)</td>
<td>5.60 × 10^{-7}</td>
<td>8.40 × 10^{-5}</td>
<td>3.07 × 10^{-6}</td>
<td>7.07 × 10^{-6}</td>
</tr>
<tr>
<td>Components</td>
<td>Argon</td>
<td>Carbon Dioxide</td>
<td>Carbon Monoxide</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Percent (%)</td>
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<td>9.1</td>
<td>11.8</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>3.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>5.6</td>
<td>10.2</td>
<td>86.9</td>
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<tr>
<td></td>
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<td>2.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>0.1</td>
<td>1.1</td>
<td>2.2</td>
</tr>
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<td></td>
<td>13.3</td>
<td>78.5</td>
<td>51.9</td>
<td>7.8</td>
</tr>
<tr>
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<td>6.8</td>
<td>0.7</td>
</tr>
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<td>Oxygen</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
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<td>Turbopump Oil</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
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<td>0</td>
</tr>
<tr>
<td>Hydrogen</td>
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<td>0</td>
<td>7.5</td>
<td>0</td>
</tr>
<tr>
<td>Neon</td>
<td>6.5</td>
<td>0</td>
<td>2.6</td>
<td>0</td>
</tr>
</tbody>
</table>

Degassing the Ethanol

In addition to the cleaning process discussed in Section 2.1, the degassing flask was rinsed twice with
ethanol before it was filled with previously unopened liquid ethanol (Anhydrous Ethyl Alcohol, Green-
Field Ethanol Inc., manufacturer claims 100%). The degassing flask was then sealed against the room
atmosphere. The valve to the flask was opened to the cold trap and mechanical pump. A magnetic stirrer
Figure 2.12: The composition of the turbopump alone at $5.60 \times 10^{-07}$ Pa. Mechanical pump oil contributes to the partial pressures at atomic mass units of 39 (4.9%), 41 (23.6%), 43 (25.9%), 55 (16.6%), 56 (4.9%), 57 (18.9%), and 71 (5.2%). The partial pressures at AMU corresponding to the pump oil are not distinguishable from the noise. Some of the more dominant components are labelled.

Figure 2.13: The mass spectrometer scan of the chamber and turbopump before a run, done at $3.07 \times 10^{-06}$ Pa. Mechanical pump oil contributes to the partial pressures at atomic mass units of 39 (4.9%), 41 (23.6%), 43 (25.9%), 55 (16.6%), 56 (4.9%), 57 (18.9%), and 71 (5.2%). There are no peaks which are discernible from the noise at AMU where the pump oil contributes to the partial pressure. Therefore, the chamber is clean from mechanical pump oil before the run. Some of the more dominant components are labelled.
Achieving Steady–State

Once the ethanol was in the chamber, the temperature bath was set to the desired temperature, 1±0.01°C and the chamber was evacuated to the desired pressure using the mechanical pump. The ethanol pressure was reduced in stages, which allowed the system to approach steady-state in-between, since the evacuation reduced the temperature as well as the pressure. When the desired pressure was being approached the system was closed and allowed to reach steady-state, which could take up to 12 hours. Steady-state was deemed to have been achieved when the standard deviation on the average
pressure was less than the transducer resolution for the duration of an experiment. For each experiment there is some variation in the room temperature, which heats the top of the chamber, but within each experiment it varied around an average value; the effect of this will be discussed in Chapter 3. The temperature bath was stable for the duration of all runs within ±0.1°C.

### 2.4.2 Taking the Interfacial Temperature Measurements

Readings of the vapour temperature were taken with the moveable thermocouple at radial positions of 0, 1, 2, 3, 4, 6, 7, 8, 8.5 and 8.75 mm (±2µm, along the r-axis in Figure 2.2). At each radial position data was recorded for increasing heights above the substrate (along the z-axis in Figure 2.2), from a minimum of 23.5 ± 10 µm to at least 103.5 ± 10 µm, but usually to 0.4 mm. The moveable thermocouple was photographed at different positions and can be seen in Figure 2.15.

To determine the position of the interface the thermocouple was brought down until the surface of the copper was gently touched. At this position the bead was exposed to the vapour, but was also touching the copper, and therefore the temperature could not be determined with certainty, so it was moved up by 10 µm and the first point was recorded. At least ten vertical measurements were taken with spacing of 10 µm. At each point the voltage was recorded for 130 seconds; the period of the ice-point cells. For every radial position this process was repeated. The voltages from the substrate thermocouples, and the chamber pressure transducer were continuously recorded for the duration of the experiment. The data logger sent the information to the PC, where it was stored for later conversion into temperature and pressure.

### 2.4.3 Composition of the Chamber Atmosphere During an Experiment

During the end of each experimental run the valve leading from the chamber to the leak valve was opened, and the leak valve to the mass spectrometer was opened a fraction large enough to see the composition of mass spectrometry scans change, but not large enough to change the pressure in the chamber. Ethanol was dominant in the chamber for all runs. Figure 2.16 shows a typical mass spectrometer reading after a run, for which the SRS RGA software calculated 86.9 % of the atmosphere was ethanol, as listed in Table 2.3. Ethanol contributes to the partial pressures at AMU of 18 (2.4%), 19 (1.0%), 26 (3.7%), 27 (10.5%), 29 (10.1%), 30 (2.6%), 31 (43.9%), 43 (3.3%), 45 (14.9%), and 46 (7.5%) — peaks in the partial pressure at each of these masses were observed and there was overlap with the mechanical pump oil at
Figure 2.15: Images of the moveable thermocouple and substrate taken through a viewport of the chamber with a high-zoom digital video camera. These images are taken through the viewport perpendicular to the one used for Figure 2.11 — the U-shape was not visible from this angle. Left: Thermocouple in vapour – camera looking straight on. Centre: Thermocouple close to substrate surface – camera tilted downward; the center hole of diameter 0.6 mm can be seen. Right: Thermocouple in vapour close to substrate edge – camera tilted downward. The zoom lens has a narrow depth of field, so when it was focused on the thermocouple, the substrate edge appears fuzzy.

43 AMU. No peaks at the other AMU for which the pump oil contributes to the partial pressure were observed. Therefore, the 2.2% mechanical pump oil calculated by the SRS RGA software for this run was considered to be negligible.

The percentage of ethanol reported was expected to be larger, but the tubing between the chamber and the mass spectrometer (see Figure 2.1) had a larger leak rate than the chamber itself. The chamber leak rate was below 2 Pa/hr, while the leak rate between the valve leading to the chamber and the leak valve leading to the mass spectrometer was as high as 10 Pa/hr. This rate was greater than the turbopump pulled the atmosphere through the leak valve when it was only open a fraction. The composition of the turbopump and leak valve tubing, as seen in Column 2 of Table 2.3 demonstrates this; the atmosphere composition was similar to air and the turbopump pressure was higher than when the leak valve was only opened a fraction. Therefore, the estimated percentage of ethanol was diluted by the room atmosphere leaking into the tubing during the mass spectrometry measurements. The longer the leak valve was open to the mass spectrometer, the more diluted the chamber atmosphere became, which presented a challenge in accurately measuring the ethanol concentration. The knowledge that the degassed ethanol introduced to the chamber was pure, that the chamber was initially at approximately $10^{-5}$ Pa, and that there was a leak affecting the mass spectrometry measurements, suggests the true ethanol percentage was higher, especially since the section of tubing in question was closed to the chamber during experiments, but open for the mass spectrometry.
Figure 2.16: The mass spectrometer scan of the chamber and turbopump during the run where $x_V = 0.86$, done at $7.7 \times 10^{-06}$ Pa. There are no peaks which are discernible from the noise at atomic masses where the pump oil contributes to the partial pressure, except at a mass of 43, but ethanol is also present for this mass. Therefore, the chamber is free of mechanical pump oil during the run.
Chapter 3

Analysis & Results for the Study of Interfacial Energy Transport from Ethanol to Copper

The average thermocouple temperatures and their standard deviation were calculated using the calibration curves discussed in Section 2.2.2 and Section 2.2.3. Each vapour phase measurement was averaged over a 130 second period. The substrate thermocouple temperatures and chamber pressure were averaged over the duration of the experimental run. The standard deviation of all temperature measurements in the vapour phase for all experiments was less than the thermocouple error of ±0.03°C, and for all temperature measurements in the substrate, less than the error of ±0.05°C. The temperatures, positions and pressures were input into Wolfram Mathematica, which was used for the analysis. Let the superscript ‘V’ represent the vapour phase, and ‘S’ the solid phase; ‘VS’ signifies a quantity across the interface, and an ‘I’ after a ‘V’ or ‘S’ represents a value at the side of the interface corresponding to that bulk phase.

The saturation pressure was calculated based on the area-weighted-average vapour interfacial temperature (in Kelvin), using Equation (3.1), which was derived from Statistical Rate Theory and verified experimentally [38].

\[ P_{sat}(T) = \exp(52.165 - 6445/T - 3.75424 \ln(T) - 0.0000030053(T^2 - T)) \quad (3.1) \]
A ratio of the measured pressure to the saturation pressure at a given temperature can be calculated and is denoted $x^V$. The thermal conductivity of the ethanol vapour was calculated based on the area-weighted-average interfacial vapour temperature, using Equation (3.2) found from the Design Institute for Physical Properties (DIPPR) [16].

$$k_V(T) = \left(-0.010109T^{0.6475}\right)/(1 - 7332/T - 26800/(T^2))$$ (3.2)

### 3.1 Interfacial Vapour Temperature and Heat Flux

The temperature increase with height was found to be linear based on measurements up to 100 µm above the interface; this was considered the near interface region. A fit was calculated for each collection of measurements at a radial location and was extrapolated to the interface ($z = 0$), as seen in Figure 3.1. The uncertainty in the position, temperature error, and uncertainty in the fit parameters were propagated to calculate the uncertainty in the interfacial vapour temperature. For all runs the vapour interfacial temperature increased towards the edge of the substrate, as seen in Figure 3.2 for the run where $x^V = 0.1$ in. Note that the interfacial temperature was relatively constant for $r = 1$ to 4 mm, the region closer to the center of the substrate. As the edge of the substrate was approached the sharply increasing values of $T^VI$ suggest there may have heat conduction in the horizontal direction as well as the vertical direction past a certain radial position.

The slope of the fit at a radial location was used to determine the local heat flux. The uncertainty in the fitted slope parameter was used to determine the error on the temperature gradient. The values of the local gradients at different radial positions were linearly joined in a piecewise fashion, as seen in Figure 3.3. The total heat flux from the vapour to the substrate was found by integration of the local gradients along the interface, multiplied by the thermal conductivity of the ethanol vapour.

The heat flux from the vapour for each experiment was calculated and plotted against the pressure ratio, as in Figure 3.4. The heat flux increased sharply from $0 < x^V < 0.2$, after which the increase in the flux was not verifiable given the uncertainty on the gradients. It was seen that the previously mentioned variation in room temperature, discussed in Section 2.4.1, does have a noticeable affect on the heat flux. The variation in room temperature for each experiment can be seen in Figure 3.5. For the runs where room temperature was measurably lower than the average across all runs, 29.33°C, (i.e. for $x^V = 0.57$
Figure 3.1: Vapour temperatures at $r = 3$ mm with $x^V = 0.1$. The linear fit through the temperatures near the interface is shown as the dashed line. The fit does not utilise measurements taken more than 100 $\mu$m above the surface because they deviate from the linear trend.

Figure 3.2: $x^V = 0.1$. Vapour interfacial temperatures, calculated from linear fits of the vapour temperatures, along the interface in the radial direction. The dashed line is for illustrative purposes only.
Figure 3.3: $x^V = 0.1$. The gradients of temperature in the $z$-direction at the interface on the vapour side. The local gradients are integrated with the trapezoid rule (integration of the dashed line) and multiplied by the thermal conductivity to find the total heat flux from the vapour. In this case the total heat flux from the vapour is calculated to be $0.021 \pm 0.001 \text{ W}$.

and $x^V = 0.83$) the heat flux from the vapour appears lower than would be expected based on visual inspection of the trend through the points present on either side.

The interaction of ethanol vapour molecules with each other before they collide with the thermocouple may effect the temperature measurements. The temperature measured by the thermocouple is the result of vapour molecule collisions with the thermocouple. If a vapour molecule experiences a collision before coming into contact with the thermocouple, energy is is lost due to that collision. Many successive collisions will reduce the accuracy of a temperature measurement done with a thermocouple. This can be examined using the mean free path (MFP), an estimate of the average length a particle can travel before colliding with another randomly moving particle — the distance a particle travels, divided by the product of the volume over which collisions can take place and the number of particles for a unit volume. The MFP of a vapour molecule was approximated using CKT and can be found using the following expression [40],

\[
MFP = \frac{k_b T^V l}{\sqrt{2\pi} P^V d(T^V)^2}
\] (3.3)
Figure 3.4: The heating of the substrate by the vapour increases with the pressure ratio. The experiments were not done in any particular order with respect to $x^V$. The hollow marker signifies that experiment was done above saturation pressure and there was some condensation visible on the substrate.

Figure 3.5: The average room temperatures for experiments done at different pressure ratios. Notice that for $x^V = 0.57$ and $x^V = 0.83$ the room temperatures do not fall within the uncertainty of the others.
where \( k_b \) is the Boltzmann constant and \( d(T^{VI}) \) is the hard sphere approximation diameter of the molecule, dependant on the interfacial vapour temperature. The MFP assumes each gas molecule has an effective cross-sectional collision area of \( A = \pi (d(T^{VI}))^2 \). The effective volume of particles collided with is then \( V = \pi (d(T^{VI}))^2 \sqrt{2\bar{v}t} \), where \( \sqrt{2\bar{v}} \) is the average relative velocity of the particles based on the molecular speed distribution. The number of particles is determined from the ideal gas law, reflected by the presence of the Boltzman constant, vapour pressure and vapour temperature in Equation (3.3).

The hard sphere diameter of an ethanol molecule can be estimated from the dynamic viscosity of the vapour, which is found from DIPPR [16] to be,

\[
\eta^V(T) = \frac{1.0613 \times 10^{-7} T^{0.8066}}{1 + 52.7/T}
\]  

(3.4)

where \( T \) is in Kelvin. The hard sphere diameter can then be found using the expression provided by Present [40],

\[
d(T^{VI}) = \left( \frac{k_b m T}{[\eta^V(T^VI)]^2 (6\pi^2)^{-1}} \right)^{1/4}
\]  

(3.5)

where \( m \) is the mass of a molecule (kg/molecule). The mean free path over the range of interfacial vapour temperatures was calculated and is plotted in Figure 3.6.

For the two runs at the lowest \( x^V \) the MFP was greater than the minimum height the thermocouple could be above the substrate, 23.15 \( \mu m \) — therefore the vapour phase thermocouple was estimated to be experiencing more collisions with molecules that had not collided with any vapour molecules since colliding with the interface than when the thermocouple was outside of a MFP of the interface. Measuring within the MFP of the interface results in more accurate extrapolation to the interfacial temperature. The MFP ranges from a maximum of 72.0 \( \mu m \) at the minimum pressure ratio to a minimum of 1.8 \( \mu m \) at the maximum pressure ratio.

### 3.2 Interfacial Solid Temperature

The substrate thermocouples were used to determine the temperature at the interface on the solid side. They were checked for reliability by solving the Laplace equation for steady-state heat transfer within
Figure 3.6: The mean free path of ethanol vapour molecules based on the average pressure in the chamber and the area-weighted-average vapour interfacial temperature. For the two experiments at the lowest pressure ratios, the thermocouple was positioned within a MFP for the first temperature measurement.

The control volume (CV) formed by the center line, and the lines through the top, bottom and side thermocouples. A function was fit for the temperature profile along each boundary, these serve as the boundary conditions. The solution was compared with the measured substrate temperatures that were not used in computing the boundary conditions.

The partial differential equation for steady-state axis-symmetric heat flux in a cylinder, Equation (3.6), was solved by dividing the problem into three subproblems using superposition, Equation (3.7), with two homogenous boundary conditions each, and then by separation of variables for each subproblem, Equation (3.8). The centre hole was neglected.

\[ \nabla^2 T = 0 = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial h^2} \]  
\[ T = \sum_{i=1}^{3} T_i \]  
\[ T_i = R_i(r)Z_i(h) \]

Substituting Equation (3.8) into Equation (3.6) and introducing a constant, \( \mu \), yields two ordinary
Figure 3.7: The geometry and control volume for the substrate energy balance. The PDE is solved within the volume contained by the centre line, and lines through the top thermocouples, the bottom thermocouples and the side thermocouples. $f_1(h)$, $f_2(r)$, and $f_3(r)$ are functions fit through the temperatures along the boundary. There are three thermocouples not used to calculate the boundary conditions (solid disks), and these are used to check the solution. $h$ is used as the vertical coordinate, instead of $z$ as in the vapour. The $h$-axis origin is 5.5 mm below the $z$-axis origin (i.e. $h = z + 5.5\text{mm}$).

differential equations, Equation (3.9) and Equation (3.10), which can be applied to each subproblem.

$$\frac{d^2Z_i}{dh^2} = \mu_i Z_i \tag{3.9}$$

$$rR_i' + r^2R_i'' + r^2R_i\mu_i = 0 \tag{3.10}$$

The geometry and setup of the problem is shown in Figure 3.7. The boundary conditions were as follows:

**Subproblem 1:**

- $\nabla^2T_1 = 0$
- $T_1(r = r^*) = f_1(h)$
- $Z_1(0) = 0$
- $Z_1(L) = 0$
- $R_1(0) = \text{finite}$

**Subproblem 2:**

- $\nabla^2T_2 = 0$
- $T_2(h = L) = f_2(r)$
- $Z_2(0) = 0$
- $R_2(r^*) = 0$
- $R_2(0) = \text{finite}$

**Subproblem 3:**

- $\nabla^2T_3 = 0$
- $T_3(h = 0) = f_3(r)$
- $Z_3(L) = 0$
- $R_3(r^*) = 0$
- $R_3(0) = \text{finite}$
**Subproblem 1:** The solution to $Z_1(h)$ is,

$$Z_{1m}(h) = c_m \sin \left( \frac{m}{\pi} h \right) \quad (3.11)$$

Then, solving for $\mu_m$ from Equation (3.9), Equation (3.10) can be seen as the Modified Bessel ODE where $n = 0$.

$$rR' + r^2R'' + R \left( -r^2 \left( \frac{m\pi}{L} \right)^2 - n^2 \right) = 0 \quad (3.12)$$

which has the general solution of form,

$$R_{nm} = C_1 I_n \sqrt{\mu_{1m} r} + C_2 K_n \sqrt{\mu_{1m} r} \quad (3.13)$$

where $I_n$ and $K_n$ are the modified Bessel functions of the first and second kind, respectively. $K_n$ diverges at zero, and so $C_2$ must be zero for the finiteness condition to be met at the center line. By combining the solutions, Equation (3.11) and Equation (3.13) for the separated variables, applying the final boundary condition of $T_1(r = r^*) = f_1(h)$ and utilizing the orthogonality of sines, a solution for subproblem 1 was found.

$$T_1(r, h) = \sum_{m=1}^{\infty} \frac{2}{(L)I_0 \left( \frac{m\Pi r^*}{L} \right)} \int_0^L f_1(h) \sin \left( \frac{m\Pi h}{L} \right) dh \sin \left( \frac{m\Pi h}{L} \right) I_0 \left( \frac{m\Pi r}{L} \right) \quad (3.14)$$

**Subproblems 2 & 3:** For the second and third subproblems Equation (3.10) can be seen as the Bessel ODE where $n = 0$.

$$rR' + r^2R'' + R[(r\mu_{2m})^2 - n^2] = 0 \quad (3.15)$$

which has the general solution of form,

$$R_{nm} = C_1 J_n \sqrt{\mu_{2m} r} + C_2 Y_n \sqrt{\mu_{2m} r} \quad (3.16)$$

$J_n$ and $Y_n$ are the Bessel functions of the first and second kind, respectively. $Y_n$ diverges at zero, and so $C_2$ must be zero for the finiteness condition to be met. Using the boundary conditions on $R_2(r)$, $\mu_{2m}$ can be found and the solution to $Z_2(h)$ was arrived at,

$$Z_{2p}(h) = \sinh(j_{0,p} \frac{h}{r^*}) \quad (3.17)$$

where $j_{0,p}$ is the $p^{th}$ root of $J_0$. 
The Bessel function of the first Kind has the following property of orthogonality,

\[ \int_0^{\infty} [J_n(j r) J_m(r)]r dr = \frac{1}{2}(r^*)^2[J_{n+1}(j r)]^2 \delta_{m p} \]  

(3.18)

where \( \delta_{m p} \) is the Kronecker delta. This allows the solution for \( T_2(r, h) \) to be found,

\[ T_2(r, h) = \sum_{p=1}^{\infty} \frac{2 \int_0^{\infty} f_2(r) J_0 \left( \frac{j_0 r}{r_*} \right) dr \sinh \left( \frac{j_0 h}{r_*} \right) J_0 \left( \frac{j_0 p}{r_*} \right)}{(r^*)^2 \sinh \left( \frac{j_0 L}{r_*} \right) \left[ J_1(j_0 p) \right]^2} \]  

(3.19)

The procedure for solving \( T_3(r, h) \) is similar to that for \( T_2(r, h) \). The solution is,

\[ T_3(r, h) = \sum_{k=1}^{\infty} \frac{2 \int_0^{\infty} f_3(r) J_0 \left( \frac{j_0 r}{r_*} \right) dr \sinh \left( \frac{j_0 L - h}{r_*} \right) J_0 \left( \frac{j_0 k}{r_*} \right)}{(r^*)^2 \sinh \left( \frac{j_0 L}{r_*} \right) \left[ J_1(j_0 k) \right]^2} \]  

(3.20)

Summing \( T_1 \) to \( T_3 \) solves the PDE for an energy balance in the substrate. The solution was tested by calculating the net flux through a reduced control volume (CV) for each run based on the slope of the solution at the edges of the CV. The control volume was from \( h = 1 \) mm to 3 mm, and \( r = 0 \) mm to 5 mm. The net flux for each case was 0.001% or less of the calculated energy coming into the substrate.

The thermal conductivity of copper was calculated using Equation (3.21), with \( T \) in Kelvin, which was obtained with a linear fit through the tabulated data found in [27].

\[ k_s(T) = -0.1T + 431 \]  

(3.21)

The temperatures of the three test points ([r,h] = [2,2], [4,2] & [6,2]) found from the substrate thermocouples are compared with the calculated temperatures found from the PDE solution and checked to ensure they are within the uncertainty in the measured temperatures and position. For all experiments the calculated values fell within the uncertainty of the measured value, but the solution was extremely sensitive to the characteristics of the fitted functions used as the boundary conditions. Figure 3.8 and Figure 3.9 show the test points and the PDE solution for two different runs.

The solution was not robust enough to be extrapolated to the interface (\( h = 5.5 \) mm). This was because the gradients in the vertical direction were too small, given the uncertainty in the temperature, and copper’s large thermal conductivity, for the solution to accurately predict the temperature or heat flux.
at the interface — a larger temperature gradient, or more data points would be needed to achieve this.

The negligible temperature difference between the top two rows of thermocouples (h=2 mm and h=4 mm) suggests the gradients in the copper near the interface were not measurable with this apparatus.

For the runs where \( x^V = 0.94 \) and \( x^V = 1.01 \) one of the ice point cells could no longer maintain 0°C, causing six of the substrate thermocouple readings to become unreliable (at \( r = 6 \text{ mm} \) and \( r = 7.5 \text{ mm} \)). To fix the problem those thermocouples would have to be recalibrated, which would involve disassembling portions of the chamber and attempting to remove the thermocouples without damaging the copper substrate. Since the calculated test temperatures were within the uncertainty of the substrate thermocouples for the first eight experiments conducted, it was assumed this would continue to be true.

Given the difficulty in obtaining the substrate interfacial temperatures by extrapolation of the PDE solution, an alternative method was required. It was assumed that the flux from the vapour was conducted linearly downwards into the substrate, perpendicular to the interface. The substrate thermocouple tem-

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**Figure 3.8:** Left: Solution to PDE when \( h=2 \text{ mm} \). The solution goes through the test points considering the uncertainties. Right: Solution to PDE when \( r=4 \text{ mm} \). For run where \( x^V = 0.27 \).

**Figure 3.9:** Left: Solution to PDE when \( h=2 \text{ mm} \). The solution goes through the test points considering the uncertainties. Right: Solution to PDE when \( r=4 \text{ mm} \). For run where \( x^V = 0.02 \).
temperatures at $z = -1.5$ mm, the vapour heat flux at the interface, and the thermal conductivities of ethanol and copper were used to estimate the interface temperature on the solid side. A fit was found that passed through the local gradients along the interface (see Figure 3.10), and another fit was computed to go through the substrate temperatures (see Figure 3.11) at $\Delta h = 1.5$ mm below the interface. The following expression was then used to calculate the substrate interfacial temperatures,

$$T^{SI} = \frac{k_V (T_{VI\text{average}})}{k_S (T_{S\text{average, } z = -1.5 \text{ mm}})} \left( \frac{\partial T}{\partial z} (r) \right) \Delta h + (T^S_{z = -1.5 \text{ mm}} (r)) \tag{3.22}$$

The error in the interfacial substrate temperatures was found by propagating the error in the fits of the substrate temperatures and vapour gradients.

As seen in Figure 3.12 the calculated substrate interfacial temperatures fell within the uncertainty of the substrate temperatures below the interface. This suggests that the thermal conductivity of the copper was too large to measure a temperature difference, and that the assumption of linear conduction downwards from the surface for the first 1.5 mm of the substrate is appropriate. Therefore, the substrate temperatures at $z = -1.5$ mm are used as the substrate interfacial temperatures when the interfacial
3.3 Results for Heat Flux, Temperature Discontinuity and Kapitza Resistance

Figure 3.13 gives an example of a temperature discontinuity at the interface. From Figure 3.12 and Figure 3.3 it can be seen that the temperature discontinuity and local heat flux are constant within their uncertainty for $0 < r < 4$ mm. Since both the substrate and vapour interfacial temperatures were found to increase with the radial position for $r > 4$ mm, the local values of heat flux at $r = 2$ mm and $r = 4$ mm, in the region where $\Delta T^{SV}$ and the heat flux do not measurably change with $r$, were used. This facilitates the calculation of the Kapitza resistance, since it is found from the temperature discontinuity and heat flux at a specific radial location. The local heat flux, $q^{VI}$ (Figure 3.14), $\Delta T^{SV}$ (Figure 3.15), and $R_k$ (Figure 3.16) are calculated at $r = 2$ mm and $r = 4$ mm, and plotted against the pressure ratio for all runs. $q^{VI}$, $\Delta T^{SV}$, and $R_k$ are all constant within their uncertainty for $x^V > 0.2$. 

**Figure 3.11:** A fit through the top level of substrate thermocouples, 1.5 mm under the surface, for the run where $x^V = 0.37$. The fit is of the form $a + br^4$. The error on values calculated using the fit were found by propagating the error in the fit parameters ($a$ and $b$), which were calculated using the substrate thermocouple temperature uncertainty as weights.
Figure 3.12: For run where $x^V = 0.37$. The hollow circles are the interfacial vapour temperatures, calculated from the linear fit extrapolated to the interface in the vapour. The dashed line is for illustrative purposes only. The solid circles are the measured substrate temperatures 1.5 mm below the interface. The solid line is the calculated substrate interfacial temperature. The calculated substrate interfacial temperature is not appreciably different than the substrate temperature 1.5 mm below.
Figure 3.13: The temperature discontinuity at $r = 4\,\text{mm}$ for the run where $x^V = 0.02$. The temperature discontinuity of $2.9 \pm 0.1^\circ\text{C}$ was the largest measured in the series of experiments.
**Figure 3.14:** The heat flux for all runs at \( r = 2 \) mm and \( r = 4 \) mm. The heat flux increases sharply before \( x^V \approx 0.2 \), after which the flux does not measurably change as the ethanol approaches saturation pressure. The hollow marker signifies that the experiment was done above saturation pressure and there was some condensation visible on the substrate.

**Figure 3.15:** The temperature discontinuity at \( r = 2 \) mm and \( r = 4 \) mm for all runs. The temperature discontinuity decreases sharply before \( x^V \approx 0.2 \), after which it does not decrease appreciably. The largest temperature discontinuity measured was \( 2.9 \pm 0.1 \) °C, found at the lowest pressure ratio. The hollow marker signifies that the experiment was done above saturation pressure and there was some condensation visible on the substrate.
Figure 3.16: The Kapitza resistance at $r = 2$ mm and $r = 4$ mm. The trend exhibited by the Kapitza resistance is similar to that for the temperature discontinuity; it increases sharply once the pressure is reduced below $x^V \approx 0.2$. Since the Kapitza resistance is the local flux divided by the local temperature discontinuity, this behaviour was expected. The hollow marker signifies that the experiment was done above saturation pressure and there was some condensation visible on the substrate.
Figure 3.17: The Kapitza resistance is proportional to the temperature discontinuity.

An increased interfacial vapour temperature results in the temperature difference between the top of the chamber and $T^V$ being reduced, which results in a lesser driving force for heat flux than for runs with a smaller $\Delta T^SV$. It is suspected that the same mechanism responsible for decreasing heat flux at low pressures is responsible for the increase in the temperature discontinuity, due to their opposite behaviour – as the temperature discontinuity decreased the heat flux increased. As the pressure ratio was increased past $x^V = 0.2$ the Kapitza resistance did not display any appreciable dependance on the pressure, which corroborates the conclusion of Murad and Puri, that once a certain amount of vapour is adsorbed the Kapitza resistance will no longer exhibit as great of dependance on pressure [32]. In the next chapter the adsorption of ethanol on copper, which is a factor in accounting for the interface behaviour, is investigated.

It was suggested by Kapitza that the interfacial thermal resistance should be proportional to the liquid interfacial temperature $R_k \propto (T^{LI})^\eta$[39]. In the ethanol-copper experiments the substrate was kept at a constant temperature, so the change in temperature discontinuity represents the change in the interfacial vapour temperature. It was found that the Kapitza resistance can be described as proportional to the temperature discontinuity as seen in Figure 3.17, and that through the same method the local heat flux can be described as proportional to the Kapitza resistance, see Figure 3.18.
Figure 3.18: The local heat flux is proportional to the Kapitza resistance.
Chapter 4

Adsorption of Ethanol on Copper and Relation to Interfacial Energy Transport

As discussed in Sections 1.1.1 and 1.1.2 the adsorption of a fluid on a solid affects the Kapitza resistance and by extension the interfacial energy flux. The adsorption of ethanol on copper was measured and compared with the interfacial energy transport.

4.1 Theory of a Vapour Adsorbed on a Solid Surface

The derivation of the Zeta-isotherm as developed by Wu and Ward [44], and its extension to gases and adsorbed molecule cluster distributions as developed by Zandavi and Ward [48], is reviewed here.

A reaction scheme is assumed where single adsorbed molecules, $A_1$, interact with adsorbed clusters containing multiple molecules, $A_2, A_3 \cdots A_{\zeta_m}$, under equilibrium conditions. The movement of multi-molecule clusters to the vapour phase is neglected. The interactions between clusters of multiple
molecules are neglected. It is assumed that $i = 1, 2 \cdots \zeta_m$ molecules adsorb in a cluster,

\[
A_1 + A_1 \rightleftharpoons A_2,
A_1 + A_2 \rightleftharpoons A_3,
\vdots
A_1 + A_{\zeta-1} \rightleftharpoons A_{\zeta_m}
\] (4.1)

For the adsorbed clusters to be in thermodynamic equilibrium, the chemical potentials of clusters $\mu_i$ must be equivalent to the sum of the chemical potentials of a single molecule,

\[
\mu_i^{SV} = i\mu_1^{SV} \quad i = 1, 2, \cdots \zeta_m
\] (4.2)

The chemical potential for a single molecule is constant with respect to the cluster size. Considering the exchange of single-molecule clusters between the adsorbed and bulk vapour phases, still at equilibrium,

\[
\mu_1^{SV} = \mu_V
\] (4.3)

Each cluster is approximated as a quantum mechanical harmonic oscillator, with each degree of freedom having a frequency $\omega(i)$. Therefore, the energy of a cluster may be expressed as,

\[
\epsilon_k^{(i)} = \epsilon_0^{(i)} + k\hbar \omega^{(i)} \quad k = 0, 1, 2, 3 \cdots
i = 1, 2, 3 \cdots \zeta_m
\]

The zero-point energy of a cluster with $i$ molecules, for a single degree of freedom, is denoted $\epsilon_0^{(i)}$ and $\hbar = h/(2\pi)$ is the reduced Planck constant. The oscillation of the molecules within a cluster, the internal degrees of freedom, are neglected. Then, the total energy of the adsorbed phase, $E^{SV}$, may be expressed by summing the energy over the clusters,

\[
E^{SV}(a_1, a_2 \cdots a_{\zeta_m}, I_1, I_2 \cdots I_{\zeta_m}) = \sum_{i=1}^{\zeta_m} (3a_i \epsilon_0^{(i)} + I_i \hbar \omega^{(i)})
\] (4.4)

where $a_i$ represents the total number of clusters of size $i$, and $I_i$ the number of phonons for a given cluster.

The degeneracy of an energy state, $g_e$, is the number of ways the $I_i$ phonons can be distributed over the
3\(a_i\) oscillators. Consider the oscillators as boxes, and the phonons as balls. For the first box any number of balls could be put inside, let this value be \(N_1\), but for the second box there are only \(N_2 = I_i - N_1\) balls, and for the third \(N_3 = I_i - N_1 - N_2\). For the final oscillator, the number of remaining balls is set, and so there are \(3a_i - 1\) boxes. There are \((3a_i + I_i - 1)!\) ways to order the phonons and oscillators, but the sequence in which they are ordered is irrelevant, so the permutation is divided by \((3a_i - 1)!\)(\(I_i\)!), the number of possible sequences that the boxes and balls could be arranged in.

\[
ge_e = \frac{(3a_i + I_i - 1)!}{(3a_i - 1)!(I_i)!} \tag{4.5}\]

The second degeneracy is configurational; \(g_c\), quantifies the number of ways the clusters can be distributed over the number of adsorption sites per unit surface area, \(M\). For the clusters of one molecule there are \((M)(M-1)(M-2)\cdots(M-a_1+1)\) possible ways to order \(a_1\) clusters over \(M\) adsorption sites, and \(a_1!\) possible sequences. For two molecules there are \((M-a_1)(M-a_1-1)(M-a_1-2)\cdots(M-a_1-a_2+1)\) possible ways to order \(a_2\) clusters over \(M\) adsorption sites, and \(a_2!\) possible sequences. The product of configurational degeneracies for each cluster size is taken to determine the total configurational degeneracy,

\[
ge_c = \frac{M!}{a_0! \prod_{i=1}^a (a_i)!} \tag{4.6}\]

The partition function in general is,

\[
Q = \sum_{i=1}^{\infty} \exp\left(-\frac{E_i}{k_bT}\right) \tag{4.7}
\]

where \(E_j\) is the energy of a given state, and \(k_b\) is the Boltzmann constant. The number of states is taken into account by including the degeneracy in the summation, allowing it to be taken over energy levels instead,

\[
Q = \sum_{I_i=0}^{\infty} g_c g_e \exp\left(-\frac{E_i}{k_bT}\right) \tag{4.8}
\]

An energy level can have 0 to \(I_i\) phonons, and since the number of energy levels is not known, the limit is \(\infty\). Combining Equation (4.8) with Equation (4.4) and substituting for \(g_e\) gives,

\[
Q = \sum_{I_i=0}^{\infty} g_c g_e \prod_{i=1}^a \frac{\zeta_m}{(3a_i - 1)!(I_i)!} \exp\left(-\frac{\sum_{i=0}^a \zeta_m (3a_{i}(i) + I_i h\omega(i))}{k_bT}\right) \tag{4.9}
\]
Using the binomial series formula the above is simplified, and the partition function is found to be,

\[
Q = g \zeta_m \prod_{i=1}^{\zeta_m} (q_i)^{a_i}
\]  

(4.10)

where \( q_i \) is,

\[
q_i = \left( \frac{\exp\left(-\frac{\epsilon_i}{k_b T}\right)}{1 - \exp\left(-\frac{\bar{h} \omega_i}{k_b T}\right)} \right)^3
\]

(4.11)

We suppose \( q_i \) may be written as a product,

\[
q_i = q_1 (q_{v})^{i-1} \quad i = 1, 2, 3 \cdots \zeta_m
\]

(4.12)

The Hemholtz function, \( F = -k_b T \ln(Q) \), can be differentiated with respect to \( a_i \) to give the chemical potential. Then, from Equation (4.11) and \( \partial F/\partial a_i = \mu_i^{SV} \) an expression for the chemical potential of the interfacial phase is found,

\[
\mu_i^{SV} = k_b T \ln\left(\frac{a_i}{a_0 q_i}\right)
\]

(4.13)

The bulk vapour is approximated as an ideal gas, for which the chemical potential is expressed,

\[
\mu^V = k_b T \ln(x^V \exp\left(\frac{\mu^V(T, P_s)}{k_b T}\right))
\]

(4.14)

where \( \mu^V(T, P_s) \) is the reference chemical potential at the saturation pressure, \( P_s \), at the given temperature. From Equation (4.3), this must also be the chemical potential of a single molecule cluster.

The number of adsorbed moles per a unit area is expressed,

\[
n^{SV} = \sum_{i=1}^{\zeta} i a_i
\]

(4.15)

and the number of occupied sites, \( n_{oc} \), is found to be,

\[
n_{oc} = \sum_{i=1}^{\zeta} a_i
\]

(4.16)

The number of vacant adsorption sites per unit area is denoted \( a_0 \),

\[
a_0 = M - \sum_{i=1}^{\zeta} a_i
\]

(4.17)
From Equation (4.13) and Equation (4.14), $a_1$ is found to be,

$$a_1 = a_0 q_1 x^V \exp \left[ \frac{\mu^V(T, P_s)}{k_B T} \right]$$

(4.18)

Then, the number of adsorption sites for any cluster size can be expressed,

$$a_i = a_1 \left( q_v x^V \exp \frac{\mu^S}{k_B T} \right)^{i-1}$$

(4.19)

We now have a closed system involving Equation (4.15), Equation (4.16), Equation (4.17), Equation (4.18) and Equation (4.19). Equation (4.15) is summed and two new parameters are introduced, $c$ and $\alpha^{SV}$,

$$c = \frac{q_1}{q_v}$$

(4.20)

$$\alpha^{SV} = q_v \exp \frac{\mu^V(T, P_s)}{k_B T}$$

(4.21)

Then Equation (4.15) can be summed to express the number of adsorbed moles per unit surface area of the solid,

$$n^{SV} = \frac{M c \alpha^{SV} x^V [1 - (1 + \zeta_m)(\alpha^{SV} x^V)^{\zeta_m} + \zeta_m(\alpha^{SV} x^V)^{1+\zeta_m}]}{(1 - \alpha^{SV} x^V)[1 + (c - 1)\alpha^{SV} x^V - c(\alpha^{SV} x^V)^{1+\zeta_m}]}$$

(4.22)

The terms in the first set of brackets of the denominator in Equation (4.22) appear to introduce a singularity for $\alpha^{SV} x^V = 1$, but if l’Hôpital’s Rule is applied to Equation (4.22) for $\alpha^{SV} x^V \to 1$ a finite limit is found.

$$\lim_{\alpha^{SV} x^V \to 1} n^{SV} = \frac{M c \zeta_m (1 + \zeta_m)}{2(1 + c \zeta_m)}$$

(4.23)

Equation (4.17), the number of vacant adsorption sites, can be now expressed as,

$$\frac{a_0}{M} = 1 - \frac{c \alpha^{SV} x^V ((\alpha^{SV} x^V)^{\zeta_m} - 1)}{\alpha^{SV} x^V (1 + c((\alpha^{SV} x^V)^{\zeta_m} - 1)) - 1}$$

(4.24)

and, Equation (4.19), the number of clusters of size $i$, can be expressed,

$$\frac{a_i}{M} = \frac{c(\alpha^{SV} x^V - 1)(\alpha^{SV} x^V)^i}{\alpha^{SV} x^V (1 + c((\alpha^{SV} x^V)^{\zeta_m} - 1)) - 1}$$

$$i = 1, 2, 3 \ldots \zeta_m$$

(4.25)

In these expressions $M$, $c$ and $\alpha^{SV}$ are independent of $x^V$, but do depend on temperature. These values are not known and must be calculated from measured adsorption isotherms to complete the expression for a given solid-vapour system, but these constants come out of the derivation of the isotherm and therefore have a theoretical basis.
4.1.1 Method of Determination for $\zeta_m$, $M$, $\alpha^{SV}$, and $c$

An error function is defined [48], where the square root of the sum of the squares of the residuals between the measured adsorption at a given pressure, $n_{SV}^{m}(x_V^j)$, and the calculated adsorption at a given pressure for a certain value of $\zeta_m$, $n^{SV}(x_V^j, \zeta_m)$, are divided by the sum of the measured adsorption values.

$$
\Delta(\zeta_m) = \sqrt{\frac{\sum_{j=1}^{N_m} [n^{SV}(P_V^j, \zeta_m) - n_{SV}^{m}(P_V^j)]^2}{\sum_{j=1}^{N_m} n_{SV}^{m}(P_V^j)}} \quad (4.26)
$$

$N_m$ is the number of measurements made, so $P_V^j$, with $j = 1, 2 \ldots N_m$, represents the different pressures that adsorption was measured at. The parameters $M$, $c$ and $\alpha^{SV}$ are fitted to a set of equilibrium adsorption measurements for iterations of $\zeta_m$ increasing by one. Initially $\zeta_m$ is set to one and $M$, $c$ and $\alpha^{SV}$ are found using the nonlinear regression package of Wolfram Mathematica. This procedure is continued until the error function is minimized. At this point increasing the value of $\zeta_m$ will not change the values of the fitting parameters and will not reduce the value of $\Delta(\zeta_m)$.

4.2 Adsorption Measurements of Ethanol on Copper

The adsorption of ethanol on copper powder (Sigma-Aldrich, Average particle size: 10 $\mu$m, Purity: 99%) was measured using an adsorption instrument (Surface Measurements Systems, DVS Advantage) capable of measuring mass with an accuracy of $\pm 0.5$ $\mu$g. The mass of copper was heated for two hours at 200$^\circ$C in dry nitrogen flow, and subsequently cooled to the desired temperature of 10$^\circ$C. The mass was measured once the desired temperature was achieved, and with the sample still exposed to dry nitrogen flow. Ethanol was mixed with dry nitrogen as the carrier gas to control the concentration of ethanol in the flow over the sample; since the absorption of nitrogen was negligible, the partial pressure of ethanol is used to find the pressure ratio. A microbalance recorded the mass difference in the sample due to adsorbed vapour.

Each measurement was taken over a ten minute period after the system was at equilibrium. For lower pressures equilibrium was achieved within an hour. At higher pressures the apparatus had to be left for three hours to reach equilibrium. An adsorption measurement was considered to be made at equilibrium when the standard deviation of the percent adsorbed mass over a 10 minute period was equal to or less than 1% of the percentage adsorbed mass as displayed by the apparatus. For example, the percent
Table 4.1: Zeta-isotherm constants for ethanol adsorbing on copper. Calculated based on the measurements shown in Figure 4.1.

<table>
<thead>
<tr>
<th>$\zeta_m$</th>
<th>$\Delta(\zeta_m)$</th>
<th>$c$</th>
<th>M</th>
<th>$\alpha^{SV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.0188</td>
<td>99.9</td>
<td>2.74</td>
<td>0.757</td>
</tr>
</tbody>
</table>

adsorbed at $x^V = 0.4$ was $8.40 \times 10^{-3}$ % and the standard deviation was $5.97 \times 10^{-5}$ %, meaning the standard deviation in the measured mass over 10 minutes was 0.7% of the adsorbed mass. The results of the measurements are seen in Figure 4.1. The adsorption increased rapidly at low pressure, increased by an approximately regular amount in the middle range of pressures, and began increasing at an accelerating rate towards $x^V = 1$.

The error bars in Figure 4.1 were based on the difference between the measured adsorption and desorption when the partial pressure of the ethanol was zero. With no adsorbate present, the mass before any ethanol was adsorbed and after the ethanol was completely desorbed should have been equivalent, but the desorption measurement gave a negative mass change, indicating a limit on the accuracy of the apparatus for this particle size. The accuracy of the adsorption apparatus was constrained by the total mass of the adsorbent that could be used with the microbalance. A smaller particle size would have resulted in a larger surface area for the same mass of adsorbent, meaning the difference between the reference mass and the measured mass due to adsorption would be greater, resulting in smaller error.

4.3 The Isotherm and Cluster Distributions

Equation (4.22) was used to plot the Zeta-isotherm for copper-ethanol, seen in Figure 4.1, using the method detailed in Section 4.1.1 to calculate the parameters $M$, $c$ and $\alpha^{SV}$, which are shown in Table 4.1. The values of the error function are plotted in Figure 4.2, where it can be seen the function is minimized at $\zeta_m = 50$.

As seen in Figure 4.3, the isotherm can be extended past the pressures at which adsorption was measured. The isotherm extension predicts a large rate of increased adsorption when the pressure is around $x^v = (\alpha^{SV})^{-1}$, after which the isotherm eventually becomes constant, and an adsorbed film is present. If it is assumed that the specific volume per molecule of the adsorbed film clusters beyond saturation pressure is that of the bulk liquid [16], $v_f$ (m$^3$/molecule), and that the adsorbed layer is uniform, then the thickness
Figure 4.1: Gravimetric measurements of the equilibrium adsorption and desorption isotherms of ethanol were made on copper powder. After the copper powder was placed in the adsorption instrument (Surface Measurements Systems), it was heated to 473 K, and held at this condition for two hours. The copper was cooled in the enclosure of the instrument to 283.15 K by dry N$_2$ flow, and the equilibrium adsorption-desorption isotherm measured at 10.8±0.1°C. N$_2$ was used as the carrier gas for the ethanol vapour. The dry mass of copper used is 117.056 mg. The surface area of the copper powder was found to be 439 m$^2$/kg ± 6% by Zandavi and Ward [48], and this is used to change the mass based adsorption values measured from the apparatus to specific molar adsorption per area, as plotted here. The ζ-isotherm is plotted using Equation (4.22) with the parameter values from Table 4.1.
Figure 4.2: A plot showing $\Delta(\zeta_m)$ as $\zeta_m$ is increased. At $\zeta_m = 50$ the error reaches a minimum. Any increases in the value of $\zeta_m$ do not decrease the error or change the values of the fitting parameters, $M$, $c$, and $\alpha_{SV}$.

of the adsorbed film can be estimated [48],

$$\tau_{af} = M\zeta_m v_f$$  \hspace{1cm} (4.27)

where $M$ must be in adsorption sites per unit area, not moles of adsorption sites per unit area, since $\zeta_m$ is a number of molecules. With this approximation the thickness of the adsorbed ethanol film was estimated to be 8 nm.

The fraction of adsorption sites occupied by a cluster of size $i$, $a_i$, can be calculated using the isotherm parameters found in Table 4.1 and Equation (4.25). As seen in Figure 4.4, initially only single molecule clusters were present, and they reached their maximum number of sites at $x_v \approx 0.1$. Past $x_v = (\alpha_{SV})^{-1}$ clusters of size $\zeta_m$ are dominant and continue to increase their share of adsorption sites, while all other cluster sizes eventually decreased in their share of sites. There are no single molecule clusters predicted to be left at approximately $x_v = 1.5$. By examining the cluster distributions it was seen that single molecules are responsible for the sharp rise in the Zeta-isotherm at low pressure.
Figure 4.3: The Zeta-isotherm can be extended past $x_V = 1$ to predict the formation of an adsorbed film [48].

Figure 4.4: The fraction of adsorbate clusters of size $a_\zeta$ present as $x_V$ is increased. Note how $a_1$ clusters, single molecules, are predicted to be adsorbed very rapidly with the initial pressure increase.
Figure 4.5: The heat flux at \( r = 4 \) mm is plotted using the left axis, and the adsorption isotherm is plotted using the right axis. The hollow marker signifies that the experiment was done above saturation pressure and there was some condensation visible on the substrate.

### 4.4 Relation of Adsorption to Energy Transport at the Interface

For \( 0 < x^V < 0.2 \) the total heat flux increased significantly and amount of adsorbed vapour had a sharp initial increase for \( 0 < x^V < 0.1 \), as seen in Figure 4.5. The adsorption of the vapour continued to increase for \( x^V > 0.2 \), but any increase in the heat flux after this point was not larger than the uncertainty in flux values.

By plotting the heat flux against the amount adsorbed (see Figure 4.6) it was seen that the heat flux increased with the moles adsorbed until \( n^{SV} \approx 4 \) \( \mu \text{mol/m}^2 \), after which the magnitude of heat flux increase was within the uncertainty on the heat flux measurements. Therefore the heat flux displayed a strong dependance on the amount adsorbed for \( 0 < n^{SV} < 4 \) \( \mu \text{mol/m}^2 \), after which the dependance of the heat flux on the amount adsorbed was negligible. Similarly, it was seen that the temperature discontinuity (Figure 4.7) and the Kapitza resistance (Figure 4.8) exhibited no dependance on the amount adsorbed for \( n^{SV} > 4 \) \( \mu \text{mol/m}^2 \). This observation supports the results of simulations that suggest the Kapitza resistance dependance on adsorption should decrease as the pressure increases, since the properties of the interfacial phase are thought to depend less on the pressure as the amount of adsorption increases.
Figure 4.6: The heat flux from the vapour shows a strong correlation with the adsorption until \( n^{SV} \approx 4 \) \( \mu \text{mol/m}^2 \). The pressure ratios at which flux is measured are input into the Zeta-isotherm to estimate the amounts adsorbed at each \( x^V \), allowing the total heat flux from the vapour to the interface to be plotted as a function of the amount adsorbed. The hollow marker signifies that the experiment was done above saturation pressure and there was some condensation visible on the substrate.
Figure 4.7: The temperature discontinuity ($r = 4$ mm) has a strong correlation with the adsorption until $n^{SV} \approx 4 \, \mu$mol/m$^2$. The hollow marker signifies that the experiment was done above saturation pressure and there was some condensation visible on the substrate.

Through examination of the predicted cluster distributions and the heat flux together (see Figure 4.9), it was seen that the significant increase in heat flux which occurred for $0 < x^V < 0.2$ corresponds with the significant increase in the adsorption of single vapour molecules, which reach their maximum number of sites before $x^v = 0.2$. As $a_1$ decreases the sites are taken up by two-molecule-clusters first, and then clusters of increasing size, but none of them show a rapid increase as $a_1$ does. It is proposed that the predicted increase in the adsorption of single molecules in this pressure range is responsible for the significant increase in the heat flux in the same pressure range.

The temperature discontinuity and Kapitza resistance were also compared with the cluster distributions, seen in Figure 4.10 and Figure 4.11 respectively. The interpretation that suggests single molecule adsorption is responsible for the sharp initial heat flux increase implies that the adsorption of single ethanol molecules are also responsible for the sharp decrease in the temperature discontinuity and Kapitza resistance in the same region. Then, according to the theory of phonon frequency mismatch discussed in Section 1.1.2, the adsorption of single molecules should be acting to greatly increase the overlap of phonon frequencies at the interface, hence decreasing the Kapitza resistance and allowing a greater heat
Figure 4.8: The Kapitza resistance \((r = 4 \text{ mm})\) exhibits a strong correlation with the adsorption until \(n^{SV} \approx 4 \mu\text{mol/m}^2\). The hollow marker signifies that the experiment was done above saturation pressure and there was some condensation visible on the substrate.

Figure 4.9: Comparison of the cluster distributions with the heat flux at \(r = 4 \text{ mm}\). The vertical axis on the left is for heat flux and the one on the right is for adsorption. The number of molecules in each cluster, \(a_i\) is labelled on the first four curves. The hollow marker signifies that the experiment was done above saturation pressure and there was some condensation visible on the substrate.
flux; however, this is a conjecture since the phonon frequencies of the adsorbed phase are not known.

When the adsorbed single molecules were replaced by multi-molecule clusters the heat flux did not exhibit the same increase as it did for the initial adsorption of single molecules — this suggests that the multi-molecule clusters do not increase phonon resonance further. The heat flux does not decrease as the single molecules are replaced by multi-molecule clusters. Since the single molecules are adsorbed first and in much greater numbers than any other cluster size they show a strong correlation to the increase in heat flux, but if molecules could only adsorb in clusters greater than a single molecule it is not known if the same behaviour of increased heat flux with initial adsorption would be observed. It may not be that the phonon frequencies of the adsorbed single molecules match the phonon frequencies of the bulk phases more closely than the phonon frequencies of other cluster sizes, but that single molecules simply happen to be adsorbed first. For example, if the initial adsorption was predicted to occur by two-molecule clusters a similar correlation between the initial increase in adsorption and heat flux may have been found.

**Figure 4.10:** Comparison of the cluster distributions with the temperature discontinuity at $r = 4$ mm. The vertical axis on the left is for the temperature discontinuity and the one on the right is for adsorption. The number of molecules in each cluster, $a_i$, is labelled on the first four curves. The hollow marker signifies that the experiment was done above saturation pressure and there was some condensation visible on the substrate.
Figure 4.11: Comparison of the cluster distributions with the interfacial thermal resistance at $r = 4$ mm. The vertical axis on the left is for the resistance and the one on the right is for adsorption. The number of molecules in each cluster, $a_i$, is labelled on the first four curves. The hollow marker signifies that the experiment was done above saturation pressure and there was some condensation visible on the substrate.
4.4.1 Correlation of Energy Transport to the Number of Occupied Adsorption Sites

Equation (4.16) was used to find the total number of clusters adsorbed as function of the pressure ratio. For \( x^V = 0.2 \), 94.7\% of the adsorption sites are occupied. For \( x^V > 0.2 \) the vast majority of the increase in the amount adsorbed is due to clusters of increasing size replacing those of smaller size. It was seen that the number of occupied sites and the heat flux exhibited a strong correlation, as seen in Figure 4.12, suggesting that as clusters of increasing size replace those of a smaller size they do not enhance the energy transport at the interface further. The fraction of occupied sites out of the total available sites, \( n_{oc}/M \), was scaled linearly to fit the heat flux,

\[
q^{VI} = a \left( n_{oc}/M \right)
\]

where \( a = 77.71 \). This relationship shows that for ethanol on copper the presence of an adsorbed cluster of any size is much more significant in its effect on the heat flux than the number of cluster sizes present, or the size of each cluster.

The temperature discontinuity was found to correlate to the fraction of vacant adsorption sites at the
interface, which is simply one less the fraction of adsorbed sites, Equation (4.17). The fraction of vacant sites out of the total available sites, $a_0/M$, was scaled linearly to fit the temperature discontinuity,

$$\Delta T^{SV} = d + g\left(\frac{a_0}{M}\right)$$

where $d = 1.067$ and $g = 4.671$. The correlation can be seen in Figure 4.13.

The correlation suggests that the temperature discontinuity is caused by the same phenomenon that controls the energy transport. As the number of vacant sites approached a minimum the temperature discontinuity did not decrease further. Once all the adsorption sites were occupied by a cluster of any size the temperature discontinuity did not decrease further with an increase in the cluster size.

Based on the analysis of the number of occupied or vacant sites, the adsorption of larger clusters once almost all the adsorption sites are occupied does not further enhance the heat flux or decrease the temperature discontinuity in an ethanol copper system.
Chapter 5

Comparison of Energy Transport and Adsorption with Other Systems

Similar studies to those performed with ethanol-copper have been done for water-gold [46] and water-silica [45], both in the Thermodynamics and Kinetics Laboratory. The amount adsorbed plays a role in determining the relative magnitude of the heat flux between systems. For all three systems the heat flux does not increase significantly with adsorption after a certain pressure ratio has been reached. The possible impact of the thermal conductivity of the solid on the interfacial heat flux is investigated.

5.1 Ethanol–Copper vs. Water–Gold

In Figure 5.1 the adsorption of ethanol on copper is compared with the adsorption of water on gold, which was measured using the same adsorption apparatus. The gold adsorbed less water than the copper did ethanol for $0 < x^V < 0.4$, at which point the water-gold adsorption overtook that of ethanol-copper for the remainder of the pressure range examined.

The energy transport was compared between the ethanol-copper and water-gold systems, as seen in Figure 5.2-A. The measurements of heat flux in the water-gold system were done with a higher substrate temperature, 5°C, than in the ethanol-copper system, 1°C; one would expect the heat flux to the gold should be less, since there is less of a driving force for heat flux in the system, i.e. the temperature
Figure 5.1: The equilibrium adsorption measurements and Zeta-isotherm for ethanol discussed in Chapter 4 compared with those for a water-gold system at 5°C. The water adsorbs on gold less than ethanol on copper when $x^V < 0.4$. The ethanol is adsorbing on copper at 10.8±0.1°C, but a difference of 5°C has not produced measurable differences in ethanol-copper or water-gold isotherms measured with this apparatus.
Figure 5.2:

A. Comparison of energy transport in ethanol-copper and water-gold systems. The substrate base temperature was 1°C for the former and 5°C for the latter. There was less potential for heat transfer in the water-gold system and as expected from the difference in substrate temperatures, the flux to the gold was less. The hollow marker signifies that the experiment was done above saturation pressure and some condensation was present on the substrate.

B. Comparison of energy transport dependance on adsorption in ethanol-copper and water-gold systems. In each case the increased adsorption past \( n^{SV} \approx 4 \mu\text{mol/m}^2 \) does not have a strong correlation to any increase in heat flux, since the heat flux is relatively constant.
difference between the top of the chamber and the substrate was less. The thermal conductivity of gold at 5°C is 318.7 W/(m.K), and of copper at 1°C is 403.6 W/(m.K); based on this, if the thermal conductivity of the solid has an effect on the heat flux from the vapour, one would expect the ethanol-copper system to transfer more energy, which was the case.

Despite that the water-gold adsorption became greater than that of ethanol-copper at $x^V \approx 0.4$, as seen in Figure 5.1, the energy transport in the water-gold system did not become greater than that of ethanol-copper (Figure 5.2-A). The water-gold system did not exhibit a large increase in heat flux for $x^V > 0.2$, suggesting that the increased pressure did not have a large effect on the heat flux. The heat flux in both systems was plotted as a function of the amount adsorbed, as seen in Figure 5.2-B, and the heat flux for $n_{SV} > 4$ µmol/m² does not show a significant dependence on the amount adsorbed. Therefore, it may only be the initial adsorption that controlled the heat flux, after which other factors gain prominence.

If, as suggested in the literature, the adsorbed vapour acts to reduce the phonon frequency mismatch between the bulk phases, reducing the resistance to energy transport, then the initial adsorption at low pressure appears to reduce the mismatch more substantially than increased adsorption past a certain threshold.

If the fraction of adsorbed single molecules is compared between water-gold and ethanol-copper (Figure 5.3), it is seen that the adsorption of single ethanol molecules on copper is much greater than the adsorption of single water molecules on gold. The shallower increase for the adsorption of single water molecules on gold accounts for the lesser overall adsorption until $x^V \approx 0.4$. It is not known why single molecules adsorb, and the isotherm increases, more readily for ethanol-copper at lower pressure. The larger adsorption of water on gold above $x^V \approx 0.4$ may be due to stronger polarity of water than ethanol; the water molecules are more strongly attracted to each other and are able to adsorb in larger clusters. The value of $\zeta_m$ for water-gold adsorption was found to be 80 [46], whereas for ethanol-copper $\zeta_m = 50$; one would expect the total adsorption to become greater for water-gold at pressures where clusters of the maximum size are present. In addition, based on the Zeta-isotherm parameters, there are more adsorption sites per unit area for water-gold (4.92 µmol/m²) than for ethanol-copper (2.74 µmol/m²), meaning greater total adsorption was possible.

The temperature discontinuities in the two systems were compared (see Figure 5.4). Since the flux in the water-gold system was less than in the ethanol-copper system, one might expect $\Delta T_{SV}^{\text{Gold}}$ to be larger than $\Delta T_{SV}^{\text{Copper}}$ over the entire pressure range examined, but this was not the case; the temperature discontinuities behaved similarly in both systems.
Figure 5.3: A comparison of single molecule adsorption for ethanol-copper and water-gold.

Figure 5.4: Comparison of the temperature discontinuity in ethanol-copper and water-gold systems. The substrate base temperature is 1°C for the former and 5°C for the latter.
Chapter 5. Comparison with Other Systems . . .

Figure 5.5: The energy transport in the water-gold system did not show the same trend as the number of occupied adsorption sites, as was found for ethanol-copper.

In Section 4.4.1 a strong correlation between the number of occupied adsorption sites and the energy transport at the ethanol-copper interface was discussed. The same linear relation between the energy transport from the vapour to the interface and the number of occupied adsorption sites was sought for the water-gold system, but as seen in Figure 5.5 the correlation was not found. This suggests there is something different about the adsorption in the water-gold system.

The number of occupied adsorption sites in the water-gold system does not plateau in the same manner as the ethanol-copper system, as seen in Figure 5.6. At $x^V = 0.2$ only 33.0% of the sites in the water-gold system are occupied, compared with 94.7% occupied sites for ethanol-copper. It may be that the gold resulted in a special case due to its low reactivity, reflected by its status as a noble metal – the occupation of adsorption sites by water on silica demonstrated a similar trend to that of ethanol on copper.

5.2 Ethanol–Copper vs. Water–Silica

The heat flux and adsorption were measured for water vapour and hydroxylated silica by Wu [45]. As seen from the comparison of isotherms (Figure 5.7) the adsorption of water on silica was initially similar to and then much greater than the adsorption of ethanol on copper. The cause of the greater adsorption at high pressures for water-silica is not known, but the maximum cluster size, $\zeta_m$, for water-silica was
found to be 130 molecules [45], so there will be a larger amount adsorbed as clusters larger than are possible for ethanol-copper or water-gold are present at higher pressures. Furthermore, based on the Zeta-isotherm parameter $M$, there are more adsorption sites per unit area for water-silica ($4.3 \, \mu\text{mol/m}^2$) than for ethanol-copper ($2.74 \, \mu\text{mol/m}^2$), meaning greater total adsorption was possible. The greater number of molecules in a cluster for water-silica may reflect the fact that water is more polar than ethanol.

There is no measurable difference in the temperature discontinuities between the two systems, as seen in Figure 5.8. The temperature discontinuities in the water-silica system were slightly larger in value than those in the ethanol-copper system, but the difference was within the uncertainty.

### 5.3 Rate-Limiting Step

The thermal conductivity of silica (1.4 W/(m.K)) is a fraction of a percent of that for copper (403.6 W/(m.K)) or gold (318.7 W/(m.K)); if the thermal conductivity of the solid was the rate-limiting step for heat transfer between the bulk phases, the heat flux to the silica should be much less than it was for ethanol-copper or water-gold. In addition, the water-silica heat flux was measured with a substrate temperature of 3°C, 2°C higher than the ethanol-copper system, so there is less of a driving force for
Figure 5.7: The equilibrium adsorption measurements and Zeta-isotherm for ethanol discussed in Chapter 4 compared with those for a water-silica system at 15°C. The ethanol is adsorbing on copper at 10.8±0.1‰, but a difference of 5°C has not produced measurable differences in isotherms measured with this apparatus. Much more water adsorbs on silica than ethanol does on copper as the pressure increases.

Figure 5.8: Comparison of temperature discontinuity in ethanol-copper and water-silica systems. The substrate base temperature is 1°C for the former and 3°C for the latter.
heat flux. One expects that both of these factors should lead to the heat flux in the water-silica system being less than that in the ethanol-copper system, but this was not the case — the heat flux to the silica from the water vapour, seen in Figure 5.9, is greater than that from the ethanol to the copper. If the heat flux between the water-gold and water-silica systems are compared the same result is found; the heat flux was larger for water-silica, despite the larger thermal conductivity of the gold.

The greater interfacial energy transport of water-silica as compared with the ethanol-copper and water-gold systems confirms that the thermal conductivity of the substrate material is not the dominant factor when considering the magnitude of interfacial energy transport. That the adsorption of water on silica was larger than for ethanol-copper and water-gold strongly suggests that adsorption at the interface is the rate-limiting mechanism for energy transport between the bulk vapour and solid. However, it was observed that the dependance of heat flux on adsorption was weak to nonexistent for $x^V > 0.2$ for all systems, and for $n_{SV}^{water-gold} > n_{SV}^{ethanol-copper}$ when $x^V > 0.4$ the heat flux in the water-gold system was not larger than in the ethanol-copper system. For $x^V < 0.2$ the amount of adsorption had a significant effect on the heat flux, but that for $x^V > 0.2$ the different amounts adsorbed by the different systems were not reflected in differences of energy transport. This was especially evident though the examination of water-silica, which adsorbs increasingly more than ethanol-copper for $x^V > 0.2$, but does not exhibit the same trend of increasingly greater energy transport.

It was observed that for $x^V > 0.2$ the Kapitza resistance in all three systems was constant within the uncertainty. The increase in adsorption for $x^V > 0.2$ does not have a measurable impact on $R_k$. As previously discussed it has been suggested that an adsorbed layer will result in weaker dependance of the heat flux on pressure and temperature [32]. Once a certain threshold of adsorption has been achieved at the interface the increased adsorption with increased pressure may not improve the phonon frequency matching as significantly as it did at low pressure. The rate-limiting step occurs at the interface for $x^V < 0.2$ and it is influenced by the amount adsorbed. The Kapitza resistance exhibited no correlation to adsorption for $0.2 < x^V < 1.0$, suggesting the amount of adsorption is no longer contributing to the rate of energy transport.
Figure 5.9: Comparison of energy transport in ethanol-copper, water-gold and water-silica systems.
Figure 5.10: A comparison of the Kapitza Resistance as a function of $x^V$ for all three systems. Note how for approximately $x^V > 0.2$ the resistance is the same for all systems and does not change with pressure. The hollow marker signifies that experiment was done above saturation pressure and some condensation was present on the substrate. There is less adsorption at low pressures in the water-gold system than the ethanol-copper system and this may account for the larger Kapitza resistance at these pressures, but more accurate measurements are required to verify this suggestion.
Chapter 6

Conclusions and Recommendations

6.1 Conclusions

The energy transport from the bulk ethanol vapour to the interface increased until $x^V \approx 0.2$, but no increase was verifiable above this pressure, as seen in Figure 3.14. The temperature discontinuities (Figure 3.15) and Kapitza resistance (Figure 3.16) displayed the opposite trend as $x^V$ approaches 0.2, they decreased sharply and were then constant within the uncertainty.

The Zeta-isotherm displayed a sharp increase for $x^V < 0.1$, after which the isotherm increased at a regular rate until $x^V > 0.6$, at which point the isotherm began to show an accelerating increase in adsorption, as seen in Figure 4.1. The sharp initial rise in the adsorption isotherm was compared with the predicted cluster distributions of the adsorbed ethanol. It was shown, see Figure 4.4, that single molecules were adsorbing in much greater numbers than multi-molecule clusters at low pressure ratios; they are responsible for the sharp increase in adsorption for $x^V < 0.1$.

The initial sharp increase in adsorption correlates to the sharp rise in heat flux as the pressure ratio was initially increased (Figure 4.9). It was seen in Figure 4.6 that for up to approximately 4 $\mu$mol/m$^2$ of ethanol adsorbed on copper the heat flux increased with adsorption. The assertion that increasing the pressure, hence increasing the adsorption, enhances thermal energy transport is true at low pressure, but is uncertain for adsorption greater than 4 $\mu$mol/m$^2$ in the ethanol-copper system. The temperature discontinuity displayed the opposite trend to heat flux, decreasing with adsorption until 4 $\mu$mol/m$^2$ was
adsorbed. Increased adsorption of ethanol on copper enhanced the energy transport to the copper and decreased the temperature discontinuity until a threshold of $4 \mu\text{mol/m}^2$ adsorbed was met.

It was seen that the number of occupied sites and the heat flux exhibited a strong correlation, as seen in Figure 4.12, suggesting that as clusters of increasing size replace those of a smaller size they do not enhance the energy transport at the interface further. This relationship shows that for ethanol on copper the presence of an adsorbed cluster of any size is much more significant in its effect on the heat flux than the number of cluster sizes present, or the size of each cluster. The temperature discontinuity was found to correlate to the fraction of vacant adsorption sites at the interface, as seen in Figure 4.13. Once all the adsorption sites were occupied by a cluster of any size the temperature discontinuity did not decrease further with an increase in the cluster size.

It has been shown by comparing the ethanol-copper study with water-gold and water-silica experiments that the thermal conductivity of the solid in a solid-vapour system is not the rate-limiting step for interfacial energy transport. Despite the significantly larger thermal conductivities of copper and gold, the heat flux in the water-silica system was greater over the entire pressure range it was measured for, as seen in Figure 5.9.

It has been suggested that the different amounts of vapour adsorbed by the three systems can account for the differences in interfacial energy transport, but this must be qualified. In both the ethanol-copper and water-gold systems the heat flux was not seen to be significantly increased for adsorption greater than $4 \mu\text{mol/m}^2$ (Figure 5.2), and despite the fact that the water-gold adsorption became greater than that of ethanol-copper at $x^V \approx 0.4$ (see Figure 5.1), the heat flux did not. Furthermore, the increasingly large difference between water-silica and ethanol-copper in the amount adsorbed (Figure 5.7) was not reflected by the energy transport in the water-silica system becoming increasingly larger than that of ethanol-copper, or the temperature discontinuity becoming increasingly smaller.

Therefore, the initial adsorption was important for the initial increase in energy transport, but after a threshold had been met, around $4 \mu\text{mol/m}^2$ in the case of both ethanol-copper and water-gold, the heat flux and temperature discontinuity did not demonstrate a strong dependance on the amount adsorbed. The ratio of the heat flux to the temperature discontinuity, the Kapitza resistance, for all three systems was found to be approximately equivalent and constant within the uncertainty for $x^V > 0.2$, as seen in Figure 5.10, despite the fact that the adsorption continued to increase at different rates for the three systems. Once a requisite amount adsorbed was met, the Kapitza resistance did not decrease further. It is not simply the amount adsorbed that can account for the magnitude of the heat flux or the differences
in interfacial energy transport between different vapour-solid pairs.

### 6.2 Recommendations for Future Work

The relation between the number of occupied sites and the interfacial energy transport must be thoroughly examined for several additional vapour-solid systems to determine the correlation found for the ethanol-copper system was system specific or a general dependance. It was shown the correlation did not hold for a water-gold system, but heat flux data for the water-silica system at lower pressures is needed to determine if it holds for that vapour-solid pair. It may be the adsorption of water on gold is a special case.

Further work must be undertaken to relate the strength of intermolecular bonds between the solid and vapour, and between vapour clusters, to the adsorption. Ethanol is less polar than water, and this may explain why water-silica adsorption was so much greater than ethanol-copper. An experimental study measuring the adsorption of a polar and less polar vapour on the same solid would be beneficial to this end. The copper will react with water, requiring a different solid than used in this study. Also requiring further study is the behaviour of the Zeta-isotherm as the saturation pressure is approached, exceeded, and the maximum cluster size becomes dominant. It is expected a thin film of adsorbed clusters of size $ζ_m$ will be formed for $x^v > (\alpha^{SV})^{-1}$. How heterogeneous droplet formation occurs from this film should be considered.

It has been suggested that resonance in the phonon frequencies between the adsorbed and bulk phases can account for the decreased Kapitza resistance as the pressure rises. This requires theoretical work to quantify the phonon frequencies of different cluster sizes and compare them with the phonon frequencies of the vapour and solid. If the phonon frequencies for two different vapours adsorbed on the same solid were known, the overlap could be computed and compared with the experimentally determined Kapitza resistance to confirm that this is the mechanism of energy transport at the interface. It may be that the initial adsorption of single molecules acts to increase the resonance much more significantly than the additional adsorption of multi-molecule clusters does. To quantitatively show the effect of adsorption on the heat flux both the amount adsorbed, and the level of matching of phonon frequencies between the adsorbed clusters and the bulk phases must be taken into account.

The adsorption behaviour of different material combinations could be taken advantage of to increase the
heat transfer performance of electronic devices. For example, depending on the atmosphere in which a
device operates, a solid layer could be designed to enhance heat transfer to that atmosphere which may
not be the same material typically thought to provide the best cooling performance. Alternatively, an
atmosphere could be chosen that would impede heat transfer due to the weak adsorption between it and
the solid.
Chapter 7

Appendix: Summary of Data

7.1 Data From Interfacial Temperature and Heat Flux Experiments

Tables 7.1 and 7.2 summarize the data used for the analysis of temperature discontinuity, interfacial heat flux and Kapitza resistance. The experiments were done in the order they appear. The interfacial temperatures are an area-weighted average. The net energy through the control volume (CV) was discussed in Chapter 3. TC108 is located at \( r = 2 \text{ mm} \) and \( h = 2 \text{ mm} \). TC111 is located at \( r = 4 \text{ mm} \) and \( h = 2 \text{ mm} \). TC114 is located at \( r = 6 \text{ mm} \) and \( h = 2 \text{ mm} \).
### Table 7.1: Summary of data for interfacial temperatures and flux

<table>
<thead>
<tr>
<th></th>
<th>Run 3.1</th>
<th>±</th>
<th>Run 3.3</th>
<th>±</th>
<th>Run 3.4</th>
<th>±</th>
<th>Run 3.5</th>
<th>±</th>
<th>Run 3.6</th>
<th>±</th>
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<td>$x^V$ (%)</td>
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<td>0.4</td>
<td>83.2</td>
<td>0.3</td>
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<td>1474</td>
<td>4</td>
<td>1037</td>
<td>4</td>
<td>182</td>
<td>4</td>
<td>91</td>
<td>5</td>
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<td>2</td>
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<tr>
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<td>0.001</td>
<td>0.023</td>
<td>0.001</td>
<td>0.024</td>
<td>0.002</td>
<td>0.021</td>
<td>0.001</td>
<td>0.018</td>
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<td>3.56E-05</td>
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</tr>
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<td>0.00131</td>
<td>0.00114</td>
<td>0.00118</td>
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<td>0.04</td>
<td>0.04</td>
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<td>0.04</td>
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<td>0.04</td>
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<tr>
<td>Test TC114 (Measured - Calculated)</td>
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<td></td>
<td></td>
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</tr>
</tbody>
</table>

| Heat Flux, q (W/m²)      | r = 2 mm | 74 | 6 | 72 | 4 | 74 | 5 | 67 | 4 | 59 | 5 |
|                         | r = 4 mm | 74 | 7 | 74 | 4 | 76 | 6 | 71 | 5 | 58 | 4 |
| Temperature Discontinuity, $\Delta T$ (K) | r = 2 mm | 1.2 | 0.1 | 1.0 | 0.1 | 1.0 | 0.1 | 1.5 | 0.1 | 2.0 | 0.1 |
|                         | r = 4 mm | 1.3 | 0.1 | 1.1 | 0.1 | 1.1 | 0.1 | 1.5 | 0.1 | 2.0 | 0.1 |
| Kapitza Resistance, $R_k$ (m²K/W) | r = 2 mm | 0.016 | 0.003 | 0.014 | 0.003 | 0.014 | 0.003 | 0.022 | 0.003 | 0.033 | 0.005 |
|                         | r = 4 mm | 0.018 | 0.003 | 0.015 | 0.003 | 0.014 | 0.003 | 0.021 | 0.003 | 0.034 | 0.005 |
Table 7.2: Summary of data for interfacial temperatures and flux, cont’d

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<th>±</th>
<th>Run 3.11</th>
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<td>Net Energy Through CV (W)</td>
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<td>Net CV / Out CV (%)</td>
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<tr>
<td>Test TC108 (Measured - Calculated)</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>n/a</td>
<td>n/a</td>
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<tr>
<td>Test TC111 (Measured - Calculated)</td>
<td>0.02</td>
<td>0.05</td>
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<td>n/a</td>
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<td>Test TC114 (Measured - Calculated)</td>
<td>0.04</td>
<td>0.00</td>
<td>0.00</td>
<td>n/a</td>
<td>n/a</td>
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</tr>
<tr>
<td>Heat Flux, q (W/m(^2))</td>
<td>r = 2 mm</td>
<td>53</td>
<td>4</td>
<td>82</td>
<td>4</td>
<td>78</td>
<td>7</td>
<td>80</td>
<td>7</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>r = 4 mm</td>
<td>50</td>
<td>5</td>
<td>80</td>
<td>5</td>
<td>77</td>
<td>5</td>
<td>82</td>
<td>4</td>
<td>74</td>
</tr>
<tr>
<td>Temperature Discontinuity, ΔT (K)</td>
<td>r = 2 mm</td>
<td>2.8</td>
<td>0.1</td>
<td>1.1</td>
<td>0.1</td>
<td>1.2</td>
<td>0.1</td>
<td>1.1</td>
<td>0.1</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>r = 4 mm</td>
<td>2.9</td>
<td>0.1</td>
<td>1.1</td>
<td>0.1</td>
<td>1.2</td>
<td>0.1</td>
<td>1.1</td>
<td>0.1</td>
<td>1.2</td>
</tr>
<tr>
<td>Kapitza Resistance, R(_k) (m(^2)K/W)</td>
<td>r = 2 mm</td>
<td>0.053</td>
<td>0.006</td>
<td>0.013</td>
<td>0.002</td>
<td>0.015</td>
<td>0.003</td>
<td>0.014</td>
<td>0.003</td>
<td>0.016</td>
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<tr>
<td></td>
<td>r = 4 mm</td>
<td>0.058</td>
<td>0.008</td>
<td>0.014</td>
<td>0.002</td>
<td>0.015</td>
<td>0.003</td>
<td>0.013</td>
<td>0.002</td>
<td>0.016</td>
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7.2 Data From Adsorption Measurements

The measured adsorption and desorption values of ethanol on copper are listed in Table 7.3.
Table 7.3: Adsorption and desorption measurements of ethanol on copper.

<table>
<thead>
<tr>
<th>Ref. Mass</th>
<th>117.1157 mg</th>
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<tbody>
<tr>
<td>Avg Temp</td>
<td>10.75476 Std. Dev. 0.096723</td>
</tr>
<tr>
<td>$x^V$ (%) (Mass - Ref. Mass)/Ref Mass (%) Adsorption (µmol/m$^2$) Std. Dev.</td>
<td>Adsorption (%)</td>
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<tr>
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<td>-------------</td>
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<tr>
<td>0</td>
<td>4.27E-05 4.50E-05 2.11E-02 -2.10E-03 1.35E-04 -1.04E+00 1.06E+00</td>
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<tr>
<td>3</td>
<td>3.27E-03 4.12E-05 3.29E+00</td>
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<td>4</td>
<td>4.82E-03 4.50E-05 2.39E+00</td>
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<tr>
<td>5</td>
<td>5.03E-03 7.48E-05 2.49E+00 3.41E-03 4.85E-05 1.68E+00 8.02E-01</td>
</tr>
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<td>6</td>
<td>5.53E-03 6.74E-05 2.74E+00</td>
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<tr>
<td>8</td>
<td>5.85E-03 8.30E-05 2.89E+00 4.36E-03 4.85E-05 2.16E+00 7.35E-01</td>
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<td>10</td>
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<td>15</td>
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<tr>
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<td>25</td>
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<td>45</td>
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<tr>
<td>50</td>
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<tr>
<td>55</td>
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<td>85</td>
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Bibliography


