MICROSCOPIC ICE FRICTION

by

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Dipl. Ing., Technische Universität Berlin, Germany, 2006

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE STUDIES
(Chemical and Biological Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA
(VANCOUVER)

April 2010

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ABSTRACT

Microscopic ice friction was studied systematically across all ice friction relevant friction regimes using several metallic interfaces. A rheometer with a newly designed fixture for friction measurements was used in these studies. The investigations focus on the influence of material properties, such as surface wettability, roughness, surface structure, surface nanopatterning, and thermal conductivity.

Using a femtosecond laser process certain dual scale roughness structures were created to mimic the lotus leaf on the surface of inherently hydrophilic metal alloys. After laser irradiation the samples show initially superhydrophilic behavior with complete wetting of the structured surface. However, over time these surfaces become hydrophobic to superhydrophobic. The change in wetting behavior correlates with the amount of carbon found on the structured surface. The explanation for the time dependency of the surface wettability lies in the combined effect of surface morphology and surface chemistry.

With regard to ice friction this controlled lotus-like roughness significantly increases the coefficient of friction at low sliding speeds and temperatures well below the ice melting point. However, at temperatures close to the melting point and relatively higher speeds, roughness and hydrophobicity significantly decrease ice friction. This decrease in friction is mainly due to the suppression of capillary bridges.

The influence of surface structure on ice friction was also investigated isolated from the effect of surface roughness. It is shown that grooves oriented in the sliding direction also significantly decrease friction in the low velocity range compared to scratches and grooves randomly distributed over a surface.

The isolated effect of thermal conductivity on ice friction is investigated by thermally insulating the slider and the friction fixture with fiberglass. A decrease of the friction coefficient in the boundary friction regime and an earlier onset of the mixed friction regime in terms of sliding velocity are reported. Furthermore, the dependence of the ice friction coefficient on sliding velocity is compared for different sliding materials. It was concluded that the influence of thermal conductivity decreases with increasing sliding velocity.
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ACKNOWLEDGEMENTS

I would like to acknowledge the following people and organizations that helped me in various ways throughout the duration of this project.

Firstly, I am very grateful to my supervisor, Prof. Savvas G. Hatzikiriakos, and my co-supervisor, Prof. Peter Englezos, for their strong support with skillful guidance, and encouragement not only throughout my PhD thesis but also with regard to my future career. Especially, I want to thank them for giving me the freedom to try new ideas and thereby getting the joy of independent research.

Professor Edward Lozowski and Professor Darren Stefanyshyn are acknowledged for their respective inputs and the fruitful discussions.

I want to thank Dr. Todd Allinger and the Own The Podium 2010 initiative for financially supporting and setting the framework of this research. Furthermore, I want to thank Speedskating Canada and in particular Jeff Scholten, Alexander Moritz, Francois Girard, and Robert Tremblay for the valuable collaboration.

I would also like to extend this acknowledgement to Dr. Saeid Kamal, without whom the realization of the laser idea would not have been possible.

In addition, I want to thank Christos, Rosie, and Dan, as well as my entire lab group for the fruitful discussions, the encouragement, and the fun we shared.

Last but not least, I would like to specially thank my parents, who are always there for me.
Dedicated to

Maja und Willi
CO-AUTHORSHIP STATEMENT

The work of this thesis consists of four different manuscripts, which correspond to chapters one to four.

During all this work, my research supervisor Prof. Savvas G. Hatzikiriakos, co-supervisor Prof. Peter Englezos, and I participated in the identification and the design of the research work.

All of the experimental work was carried out by me as part of my Ph.D. research project.

The data analysis was performed by me after several insightful discussions with my supervisors.

Finally, I did the final preparation for each manuscript after careful revision and approval of my research supervisors.
1 INTRODUCTION

Friction is an extremely important technological concern in almost every application that involves moving parts. This work focuses on friction of metal runners on ice with the particular objective of trying to find ways of minimizing this friction. Therefore, appropriate steel alloys are chosen as runner materials. The influence of the surface roughness is addressed in detail. Next to polishing runners according to ice sport’s common practice, the frictional effect of roughening the surface and structuring it with distinct micro- and nanopatterns is researched. These particular patterns are copied from nature and imitate the lotus leaf exposing a superhydrophobic surface. In addition, heat trapping at the interface by insulating the slider with fiberglass is studied.

1.1 Literature Review

1.1.1 History of Ice Friction Studies

Even though friction on ice has only been investigated during the last 150 years, the study of friction has a long history as shown in Figure 1-1.

Figure 1-1: Timeline of friction studies.

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1 A version of this chapter has been accepted for publication. Kietzig, A.-M., Hatzikiriakos, S.G., Englezos, P., Physics of Ice Friction, Journal of Applied Physics (2009).
First encounters with frictional forces date back to the Neanderthal Age about 200,000 B.C. when people used frictional heat to make fire by rubbing wood on wood or striking flint stones. The first report of sliding on ice comes from Scandinavia around 7,000 B.C. Rock carvings illustrate the use of a sledge for the transport of heavy goods. The next interesting historic record dates back to 2,400 B.C.. Egyptian carvings show that a lubricant, possibly water, was poured in front of a sledge to facilitate sliding (Dowson, 1998; Persson, 2000). The first recognition of the force of friction was found in Aristoteles’ (384-322 B.C.) *Questiones Mechanicae* (Dowson, 1998). Another almost 2000 years passed before friction was studied for the first time quantitatively by Leonardo da Vinci (1452-1519). He investigated the influence of the apparent area of contact upon frictional resistance, distinguished between rolling and sliding friction, studied the benefits of lubricants, and made the first observations of wear. In fact, he postulated the two laws of friction:

1. ‘*Friction produces double the amount of effort if the weight be doubled*’ - The force of friction is directly proportional to the applied load.

2. ‘*The friction made by the same weight will be of equal resistance at the beginning of its movement although the contact may be of different breadth and length.*’ - The force of friction is independent of the apparent area of contact for a given load.

However, since da Vinci’s records were only published at the end of the 19th century, these laws are often referred to as Amonton’s laws (Dowson, 1998; Persson, 2000). The French physicist Guillaume Amonton (1663-1705) rediscovered and thereby confirmed da Vinci’s findings in 1699. Furthermore, he identified roughness as the fundamental cause of friction, and defined friction as the force required to lift interlocking asperities over each other during the sliding motion (Dowson, 1998). Leonard Euler (1707-1783) contributed to friction studies with a clear distinction of static and dynamic friction and introduced the symbol $\mu$ for the coefficient of friction (Dowson, 1998). In 1785, Charles Augustin Coulomb (1736-1806) investigated five main factors for frictional resistance. He studied the nature of materials in contact and surface coatings, the extent of the surface area, the normal pressure, the length of time
that surfaces stay in contact, and the frictional behavior under vacuum as well as under varying ambient conditions namely temperature and humidity.

Coulomb was the first to formulate friction force as an equation:

\[ F_T = \mu F_N \]  

(1-1)

where \( F_T \) is the frictional force, \( F_N \) the normal force, and \( \mu \) the coefficient of friction, which was assumed to be independent of the sliding velocity. This is sometimes referred to as the 3\textsuperscript{rd} law of friction. However, it was found later that this only holds as long as the sliding velocity is not too low or not too high (Dowson, 1998; Persson, 2000).

It was not until 150 years ago that ice became a matter of scientific investigations. Faraday brought two ice cubes into contact, which instantly froze together (Faraday, 1859). He concluded that the ice surface is covered with a liquid-like layer. This marked the beginning of research efforts to understand ice, and the role its surface plays in ice friction. Shortly after Faraday’s experiment, Thomson explained it by attributing the existence of the liquid-like layer to pressure melting (Thomson, 1860). Reynolds was the first to investigate systematically the matter of sliding on ice (Reynolds, 1900-1903). Following Thomson’s ideas he wrongly attributed the low friction on ice to pressure melting; this explanation for the ease of skating was widely accepted among scientists for almost 40 years, until Bowden and Hughes (1939) suggested that frictional heating might be the main contributor to the low friction coefficient on ice; this is today the generally accepted theory to explain ice friction.

The understanding of the underlying mechanisms of friction on ice is particularly important in a broad field of applications, such as motorized vehicle traffic in winter road conditions (Chang et al., 2001; Roberts and Richardson, 1981; Higgins et al., 2008), glacial movements, cargo transportation through northern sea ways, design of offshore structures and ice breakers (Nakazawa et al., 1993), and ice sports (Colbeck et al., 1975). High friction on ice is desired for motorized vehicle traffic in winter road conditions and the grip of shoe soles on ice to avoid accidents. However, in the field of cargo transportation through northern sea ways and the design of offshore structures low friction materials are desired to limit maintenance and operation costs, e.g. 70\% of the
power of an ice breaker ship is consumed to overcome ice friction (Petrenko, 1995). The reduction of ice friction is also important in competitive sports (de Koning et al., 2000; Rebsch et al., 1991). This review mainly concentrates on the application in ice sports. The reason is that most of the published data in literature refer to such applications and the experimental setups address issues arising in ice sports. However, the knowledge gained can be applied to the other areas mentioned above. Another reason is that in competitive sports the urge for a faster speed is unbroken and keeps athletic competitions interesting (ISU, 2009). As a result researchers around the world continuously search to find ways of minimizing ice friction. The development of world records in long track speed-skating over time is illustrated in Figure 1-2. During speed-skating the contribution of ice friction to the overall frictional loss is about 20% (de Koning et al., 2000).

![Figure 1-2: Average speed of long track speed skating world records (men) (data from ISU, 2009).](image)

Colbeck (1994) published an excellent review on snow friction. There are many similarities in snow and ice friction. Many experiments on snow friction are actually carried out on ice, whose behavior is less complex. The application of snow friction research lies mainly in the fields of snow sports and avalanche research.
A review of the many different factors influencing ice friction and their interdependence with respect to different friction regimes clarifies our understanding of ice friction and sheds more light on the complexity of ice.

### 1.1.2 Friction Regimes

Following, the basic physical concepts of dry, boundary, mixed, and hydrodynamic friction are introduced with respect to the thickness of the lubricating liquid-like layer on ice. The latter greatly influences the amount of friction on ice.

#### 1.1.2.1 Dry Friction

Dry friction describes the sliding contact of two surfaces in absence of any kind of lubricating layer. A solid surface is never completely flat but shows a distinct profile of surface asperities and valleys. When two asperities of different surfaces come into contact, adhesive bonds of chemical or physical nature are formed between these mating asperities. If the surfaces are moved relative to one another, the adhesive bonds are sheared. The force necessary to break the adhesive bonds between contacting asperities is the tangential friction force $F_T$ given by:

$$ F_T = \tau_c A_c $$

where $\tau_c$ is the shear strength, necessary to shear the asperity contact, and $A_c$ the area of real contact between the asperities of the mating surfaces.

Bowden (1952) proposed that the real area of contact ($A_c$) between two surfaces is directly proportional to the applied load ($F_N$) and the softer material’s hardness ($H$).

$$ A_c = \frac{F_N}{H} $$

Accordingly, the friction coefficient can be written as:

$$ \mu = \frac{\tau_c}{H} $$
Thus, dry friction is characterized by the work necessary to break solid surface adhesive bonds. It depends on the applied load and the hardness of the surfaces but is independent of the sliding speed (Persson, 2000; Bhushan, 2002; Bowden and Tabor, 2001).

Real dry friction on ice under atmospheric conditions cannot exist. Even at very low temperatures a very thin liquid-like film lubricates the sliding interface. This film has a thickness of a few molecular layers (Petrenko and Whitworth, 1999).

1.1.2.2 Boundary Friction

Boundary friction is characterized by a lubricating layer with the thickness of only a few molecular layers between the sliding surfaces (Bhushan, 2002). Boundary lubrication on ice is characterized by the temperature \( T \) in the contact zone being everywhere below the melting temperature \( T_m \), and the thickness of the lubricating liquid-like layer \( h \) being far smaller than surface roughness \( R \) (Kozlov and Shugai, 1991).

\[
\text{everywhere in contact zone: } T < T_m, \ h << R
\]

The lubricating liquid-like layer reduces solid-solid contact between the surfaces. In total, the friction coefficient of boundary lubrication is typically lower than that of dry friction (Bhushan, 2002).

1.1.2.3 Mixed Friction

Mixed friction occurs when the surface temperature rises above the melting temperature \( T_m \) of ice at some points within the contact zone and the thickness of the liquid-like layer \( h \) is still less than the characteristic roughness of the surfaces \( R \) (Kozlov and Shugai, 1991).

\[
\text{at some points in contact zone: } T > T_m, \ h < R
\]

In this regime the load of the slider is partly supported by the surface asperities and partly by the lubricating layer. It is obvious that the increased thickness of the lubricating layer reduces solid-solid adhesion and enhances the lubrication.
Accordingly, the decrease in friction force compared to boundary lubrication can be demonstrated in:

\[ F_f = A_c \alpha \tau_c + \left(1 - \alpha\right) \eta \frac{v}{h} \]  

(1-5)

where \( \alpha \) is the fraction of unlubricated area, \( \tau_c \) the shear strength of the solid contact, \( v \) the velocity of the slider, \( \eta \) the viscosity, and \( h \) the thickness of the lubricating layer (Bhushan, 2002).

However, at the same time a wetting lubricant enforces the build-up of capillary water bridges between the asperities, as illustrated in Figure 1-3.

![Figure 1-3: Capillary bridges between asperities of contacting surfaces during sliding.](image)

The capillary bridges act as bonds between the slider and ice surfaces and exercise a drag force on the slider (Colbeck, 1988). However, capillary bridges do not support the applied load. These capillary bridges act like liquid bonds and result in additional frictional resistance. Hence, capillary bridges should be taken into account to complement Equation 5. The problem herein is, however, that no physical or experimental model exists to describe the contribution of capillary bridges to the friction force.

1.1.2.4 Hydrodynamic Friction

If everywhere in the contact zone the temperature is above the melting temperature \( (T_m) \), and the thickness of the lubricating layer between the two surfaces is greater than the height of the asperities, friction is called hydrodynamic (Kozlov and Shugai, 1991).
In this friction regime the lubricating layer, not the surface asperities, carries the applied load. If the load is very high, a part of the lubricating layer might be squeezed out between the surfaces. However, for hydrodynamic friction, it is assumed that the thickness of the lubricating layer remains greater than the height of the asperities. Following the area of real contact is identical to the surface area \( A \) of the slider (Bhushan, 2002). No solid-solid contact occurs during the sliding movement. Consequently, shearing of solid-solid adhesive bonds no longer contributes to the friction force. The frictional force can be described as

\[
F_r = \tau_i A
\]

where \( \tau_i \) is the shear strength of the lubricating liquid-like layer or an “effective” shear stress developed from shearing of the liquid-like layer. This can be simply expressed as

\[
\tau_i = \frac{\nu \eta}{h}
\]

As in the case for mixed friction capillary drag forces should be included in the case of water lubrication.

Fowler and Bejan (1993) pointed out that the lubricating film under a slider on ice becomes thicker towards the trailing end. Consequently, friction mechanisms on ice can include all types of friction except for pure dry friction.

Figure 1-4 summarizes the various regimes of ice friction in a schematic. Note the drop of the coefficient of friction with the film thickness in the boundary friction regime due to reduced solid-solid contact. On the other hand, the coefficient of friction increases with film thickness as it becomes fully hydrodynamic, as discussed above. Accordingly, there is an optimal film thickness associated with minimum friction for each slider system. It is also noted that there is a smooth transition between the different regimes indicated by the dashed lines; also the scaling of the axis has to be understood in qualitative terms. Exact values for the film thickness are dependant on the respective experimental and material inherent parameters.
1.1.3 Origin of the Lubricating Liquid-Like Layer on Ice

Ice sports are possible because of the existence of a liquid-like layer on the ice surface at temperatures below 0 °C. There are three different mechanisms that contribute to the thickness of the liquid-like layer. These are surface melting, pressure melting, and frictional heating.

1.1.3.1 Surface Melting

Faraday (1859) suggested the existence of a liquid-like layer as an inherent part of the ice surface. This layer exists even without the contact of another body, in other words no friction is required for its existence. At its surface the hexagonal structure of ice \( h \) breaks down (Figure 1-5).
Figure 1-5: Surface structure of ice 1h (Ikeda-Fukazawa and Kawamura, 2004).

Experimental proof for the existence of the liquid-like layer was given with diverse experimental techniques. The temperature range, in which the liquid-like layer was observed in different experiments, shows a wide variability depending on the technique applied (Figure 1-6).

![Figure 1-6: Experimental techniques to investigate the liquid-like layer on ice](adapted from Petrenko and Whitworth, 1999).
Therefore it is not surprising that scientists came to different conclusions about the general nature of the liquid-like layer and more precisely the onset temperature of its formation. Different theories were developed to clarify the underlying physics. However, in spite of the vast experimental evidence, the scientific explanation for the presence of the liquid-like layer is still under debate. For a more detailed review the reader is referred to Petrenko and Whitworth (1999). Here some of the prevailing theories are summarized briefly.

Fletcher (1962, 1968) attributed the formation of the liquid-like layer to electrostatic interactions, whereas Lacmann and Stanski (1972) justified the existence of the liquid-like layer on nature’s tendency to minimize the energy of a system. This theory of free surface energy minimization was further advanced by Dash et al. (1995). They claimed that a system, whose free surface energy of a solid-vapor interface \( \gamma_{sv} \) is higher than the sum of the energies of the solid-liquid \( \gamma_{sl} \) and the liquid-vapor \( \gamma_{lv} \) interface, will “lower its free energy by converting a layer of the solid to liquid”.

\[
\gamma_{sv} > \gamma_{sl} + \gamma_{lv}
\]  

(1-8)

While this theory holds for several solids, experimental evidence for ice shows that the free surface energy of ‘dry’ ice is in fact not larger than the combined surface energies of the wetted system (Knight, 1971; Elbaum et al., 1993; Makkonen, 1997).

Fukuta (1987) suggested subsurface pressure melting as an explanation for the liquid-like layer on ice. Since water molecules at the ice surface only have water molecule neighbors from one side, they experience an inward pull. This pull exerts a pressure on the layers below. Makkonen (1997) has shown that this pressure is large enough to reduce the melting point of the ice surface layer by about 13 K. It should be noted that even though subsurface pressure melting might contribute to the thickness of the liquid-like layer, it fails to explain its presence at lower temperatures.

Low-energy electron diffraction (LEED) experiments coupled with molecular dynamics simulation gave further insight into the forces leading to a liquid-like layer on ice. Surface molecules tend to vibrate and rotate constantly in order to minimize dangling bonds. Kroes (1992) pointed out that through the movement of the molecules the outer
ice layers become partially charged. Simulations of Devlin and Buch (1995) confirmed that the breakdown of the solid structure is indeed energy minimizing, since thereby the number of dangling bonds can be reduced. Furthermore, they found that the surface is dynamically disordered. This was further explained by the results of Furukawa and Nada (1997), which indicated that molecules diffuse within the two outermost layers, which leads to this highly disordered surface. Finally, the study of Marterer et al. (1997) revealed that at a temperature as low as 90 K molecular vibration is so high that the outermost atoms could no longer be detected by LEED.

1.1.3.2 Pressure Melting

For many years pressure melting was considered to be the explanation of choice for the low friction coefficient on ice. While it might contribute to the formation of a lubricating layer close to the melting point, pressure melting cannot explain the low friction on ice at lower temperatures. The pressure $p$ exerted on the ice can be calculated by $p = F_N / A_C$. A major problem in friction studies in general is the calculation of the exact area of contact $A_C$. Since surfaces are never perfectly smooth, contact takes actually place between a certain number of asperities. With ice being a comparatively soft material the contact area of a slider on ice depends on the applied load. Furthermore, it also depends on the ambient temperature, because the ice softens with increasing temperature reaching the melting point.

As an example consider an ice-skater ($F_N = 700$ N), whose skate is in contact with the ice over an area of $1 \times 10^{-4}$ m$^2$ (assuming a contact length of the skate with the ice of 0.1 m and width of $10^{-3}$ m). Accordingly, the additional pressure here is $\Delta p = 7$ MPa. Based on the phase diagram of water $dp/dT$ is approximately -9.9 MPa/K at 0 ºC and 0.1 MPa. Therefore, a pressure increase of $\Delta p = 7$ MPa will only result in a change of the melting temperature of $\Delta T = -0.7$ K ($\Delta T = \Delta p / -9.9$ MPa/K). With the herein assumed contact area pressure melting cannot contribute much to a liquid layer on ice, as the melting temperature of ice can only be lowered by about 1 K depending on the slider. Colbeck (1995) illustrated that only 0.005 % of an ice skate is in actual contact with the ice for pressure melting and frictional heating to contribute equally to the heat production. The resulting very high contact pressure, however, would result in high wear
rates and great losses in the film thickness by squeeze out of the lubricating layer, so that the friction coefficient would be higher than observed in experiments.

1.1.3.3 Frictional Heating

On the basis of their experiments Bowden and Hughes (1939) suggested that frictional heating plays a fundamental role in the low friction coefficient on ice. Heat generated by the frictional motion raises the temperature at the contacting points to the melting temperature of ice. Hence, the ice surface melts locally at the contacting asperities, whereby a non-continuous melt water film is formed. This film contributes to the lubrication of the slider on ice. However, not all the energy from frictional heating is available for melting the ice due to energy consumption through material deformation and energy losses by heat conduction into the ice and the slider. Furthermore, the authors point out that this lubricating layer can become continuous, if the ambient temperature is close to the melting point of ice. They also note that the observed friction at 0 ºC increases if a small quantity of water is added to the ice. However, any further conclusions regarding the drag effect of capillary bridges were not drawn in this study and as discussed previously their contribution to the coefficient of friction can be significant. In conclusion, it can be said that frictional heating is the most important contributor to the low friction on ice.

1.1.4 Experimental Methods for the Measurement of Ice Friction

Various experimental setups have been developed to measure friction on ice. Instrumented skates were used to measure real-life friction parameters (Colbeck et al., 1997; de Koning et al., 1992); rather big slider models were developed to have greater control over various parameters during field experiments (Bowden, 1953; Kuroiwa, 1977; Slotfeldt-Ellingsen and Torgersen, 1983; Itagaki et al., 1987). However, to really understand ice friction at a fundamental level laboratory equipments proved to be most suitable (Bowden and Hughes, 1939; Evans et al., 1976; Calabrese, 1980; Oksanen and Keinonen, 1982; Lehtovaara, 1987; Akkok et al., 1987; Kozlov and Shugai, 1991; Jones et al., 1994; Petrenko, 1995; Strausky et al., 1998; Buhl et al., 2001; Liang et al., 2003;
Montagnat and Schulson, 2003; Albracht et al., 2004; Ducret et al., 2005; Marmo et al.,
2005; Bäurle, 2006; Higgins et al., 2008). In this section the various experimental setups,
advantages and disadvantages are summarized and discussed thoroughly.

1.1.4.1 Real-Life Experiments

Colbeck et al. (1997) analyzed real-life ice skating with an instrumented skate. They have used thermocouples to assess the temperature at the skate surface and therewith gave experimental proof for the frictional heating theory. However, the friction coefficient could not be measured with this skate.

De Koning et al. (1992) were first to attempt real-life analysis of ice skating with an instrumented skate. They developed ice skates, which are instrumented with strain gages and transducers. These skates enabled the measurement of the push-off and friction force during skating. Experiments were made on different indoor and outdoor ice skating rinks with an experienced ice skater. The advantage of these experiments is that real-life skating conditions were analyzed. However, real-life experiments show limited control over the different variables. Different ice rinks use different ice making procedures and different locations imply different air temperatures, relative humidities, and water qualities, which will all have an effect on the measured friction coefficient. Furthermore, experiments with only one skater are not statistically significant and imply unpredictable variability. The results are greatly dependent on the skater’s daily performance, i.e. his skating technique might not have been the same on different days at different locations, which results in different loads and pressure as well as in different velocities. Some of the friction results are presented below and compared with results obtained from other experimental setups.

1.1.4.2 Slider Models

Bowden (1953) used small sledges with rounded front edges cut from different materials to measure friction on snow and ice. He applied a certain procedure to prepare the ice surface. It is unclear how the sledges were accelerated.
Kuroiwa (1977) reported ice friction measurements with real skate blades mounted to a frame. This slider model was ejected from a catapult to reach its sliding speed; thereby the velocity can be more closely monitored.

Slotfeldt-Ellingsen and Torgersen (1983) and Itagaki et al. (1987) also used automatically accelerated slider models of different size and weight to measure friction on ice. In contrast to Bowden (1953) and Kuroiwa (1977) they also applied an ice making procedure to further limit variability.

Friction measurements with slider models as described above reduce the unpredictable human factor in the experiments and increase the controllability of parameters such as the ice used, velocity, and load. However, other parameters, such as ice and air temperature, still contribute to variability in the measurements. One particular problem of slider models is that their sliding track cannot be completely predicted. Therefore, the slider model is likely to take different routes over the ice in each experiment. If this unpredictability is to be eliminated by using prepared tracks, the friction on the sidewalls of the track will contribute to the overall measured friction.

1.1.4.3 **Linear Experimental Devices**

Different linear devices were used by Jones et al. (1994), Montagnat and Schulson (2003), Ducret et al. (2005) and Marmo et al. (2005). These pieces of equipment vary in their setup, but they all share the characteristic that the movement of the slider on the ice surface is guided by a control mechanism during the experiment. Accordingly, the problem of unpredictable sliding tracks is solved with linear experimental devices. Furthermore, the ice making procedure, the load and velocity settings are all well controlled. Montagnat and Schulson (2003) and also Ducret et al. (2005) also ensured a certain temperature setting by conducting the experiment in a cold room or freezer unit. Compared to other laboratory equipment, as will be explained further down, linear experimental devices have the advantage that friction between the slider and the ice can be investigated on a fresh ice surface.
1.1.4.4 Rotational Experimental Devices

Different kinds of rotational devices were used to measure friction on ice. Similar to linear experimental devices discussed above, load and velocity can easily be set by the experimenter. One advantage of these setups is the rather small size of the equipment, which facilitates the use of cold boxes and temperature chambers. Accordingly, many setups include close surveillance of the ice and air temperature and even relative humidity. Furthermore, artificial ice surfaces can be created following an ice making procedure to limit variability.

Experiments with a rotary viscometer were carried out by Kozlov and Shugai (1991). This setup utilizes a flat metal ring that slides against a hollow cylinder. This setup necessitates measurements of the vertical displacement of the ring, since the rotation melts the ice at the cylinder wall.

Many experimenters made use of an ice ring or disc, which rotates against a stationary ice sample. Strausky et al. (1998), Buhl et al. (2001), and Liang et al. (2003) successfully applied this setup for their analysis of ice friction. While these setups enable good controllable settings and limited variability, the sample continuously slides over the same ice. Accordingly, edge effects in front of the slider sliding over a fresh ice surface cannot be assessed as seen under real ice sport conditions or in other applications.

A setup with discontinuous ice-slider contact was applied by Evans et al. (1976) and Petrenko (1995), who used a lathe setup with an ice cylinder rotating against a sample. Accordingly, not the whole circumference of the ice cylinder is in contact with the slider. Therefore, a particular area on the ice cylinder can refreeze before getting into contact with the slider again.

Another solution to the edge effect issue was shown by Bäurle (2006), who used a similar setup as described above with an ice turntable and a stationary sample mounted to an arm above it. The ice track with a diameter of 1.60 m is large enough to ensure that the ice surface refreezes before the next pass under the sample. Bowden and Hughes (1939), Oksanen and Keinonen (1982), and Lehtovaara (1987) applied a variation of this setup with a rotating ice surface and the sample mounted to an arm, which permits
horizontal movement of the slider, as to ensure that the samples sees fresh ice after each turn.

Similarly, another variation of rotational experimental devices was used by Calabrese (1980), Akkok et al. (1987), and Albracht et al. (2004). These experiments were carried out on a stationary ice surface with a rotating sample. Calabrese (1980) used a ring; again there exists the problem with the continuous contact between the slider and the ice. Akkok et al. (1987) used a ball on disk setup, which allows the ice to refreeze after the slider passes. Albracht et al. (2004) even avoided sliding over the same track by using a spiral track for their pin slider.

In summary, it can be stated that in order to gain a better understanding of the different parameters that influence ice friction, laboratory devices such as those described above are necessary. They ensure good control over the settings such as ice and air temperature, humidity, velocity, and load. In addition the use of a certain ice making procedure further limits undesired variability in the results. On the other hand, small scale devices often have the characteristic of continuous ice-slider contact or a slider that slides over the same track. While this might not have an impact on the overall analysis and understanding of ice friction, it is rather different to what is seen in actual ice sports. To analyze the real overall ice sport performance in terms of race time, field experiments with athletes serve best. Hereby, a certain number of athletes have to be involved in the experiment to ensure statistical significance and eliminate variation resulting from the human factor. Studies comparing results obtained from real-life experiments involving humans with those from a lab setup are most welcome.

1.1.5 Influence of Different Parameters on the Friction Coefficient

Based on the information from ice friction experiments carried out by different researchers the influence of the different parameters on the friction coefficient will be discussed next in separate sections for each important parameter independently. In many cases, results from various sources are compared to identify consistency of experimental results in the literature. In some cases such comparisons were proven difficult as experimental findings were performed under different operating conditions.
1.1.5.1 Temperature $T$

Since the first ice friction studies by Bowden and Hughes (1939), many researchers have confirmed the dependence of the friction coefficient on temperature (Evans et al., 1976; Calabrese, 1980; Roberts and Richardson, 1981; Slotfeldt-Ellingsen and Torgersen, 1983; Akkok et al., 1987; Itagaki et al., 1987; Derjaguin, 1988; de Koning et al., 1992; Liang et al., 2003; Albracht et al., 2004; Bäurle, 2006; Higgins et al., 2008). Some researchers merely report a decrease of the friction coefficient with increasing temperature (Roberts and Richardson, 1981; Itagaki et al., 1987; Evans et al., 1976; Akkok et al., 1987; Derjaguin, 1988; Liang et al., 2003; Bäurle, 2006; Higgins et al., 2008). This is the case when friction is dominated by boundary friction conditions (Bäurle, 2006; Higgins et al., 2008). However, to obtain the full picture of the dependence of ice friction on temperature, it is necessary to consider all friction regimes, as introduced in Figure 1-4.

Figure 1-7 depicts four sets of experimental results on the temperature dependence of the friction coefficient on ice across the whole range of friction regimes.

![Figure 1-7: Temperature dependence of the friction coefficient.](image-url)
Overall, the various data sets show the same trend, which has also been confirmed in snow friction studies (Bowden, 1953; Buhl et al., 2001). The coefficient of friction decreases first with increasing temperature and rises again when the temperature approaches 0 °C. The minimum coefficient of friction is obtained between -2 and -7 °C depending on the method of measurement, the slider’s normal load, the linear sliding speed, and the slider material. Obviously, at lower temperatures the friction is dominated by solid-solid interactions, typical for the ice friction curve to the left of the minimum, as illustrated in Figure 1-4. At temperatures close to the melting point the thickness of the lubricating liquid-like layer becomes large enough; this not only facilitates the sliding but also adds to the resistance through the built-up of capillary bridges. The relevant friction regime is that of mixed friction beyond the minimum in the friction curve (Figure 1-4) and with a further increase in film thickness hydrodynamic friction. However, the onset of this increase in friction depends largely on the slider material, the normal load and the linear sliding velocity. Table 1-1 summarizes the differences in the operating parameters between the experiments and therewith provides explanation for the differences between the four sets of data.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Slider material</th>
<th>$F_N$ [N]</th>
<th>$\nu$ [m/s]</th>
<th>$A_c$ [mm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calabrese (1980)</td>
<td>Steel ring (AISI 1018)</td>
<td>889.6</td>
<td>&lt; 1</td>
<td>1,235</td>
</tr>
<tr>
<td>Slotfeldt-E. and Torgersen (1983)</td>
<td>HDPE slider block</td>
<td>100</td>
<td>0.3</td>
<td>15,000</td>
</tr>
<tr>
<td>Albracht et al. (2004)</td>
<td>Cr-steel pin</td>
<td>1</td>
<td>0.13</td>
<td>$\approx$ 2</td>
</tr>
<tr>
<td>de Koning et al. (2000)</td>
<td>Steel skate blade (“Viking special”)</td>
<td>700</td>
<td>8</td>
<td>$\approx$ 400</td>
</tr>
</tbody>
</table>

As it is discussed below the sliding velocity, the applied normal force, the area of contact and the material of construction of the slider significantly influence the coefficient of friction.
1.1.5.2 Sliding Velocity $\nu$

Bowden (1953) first observed that friction against ice decreases with increasing velocity. Evans et al. (1976), who were first to model ice friction mathematically, confirmed these findings both experimentally and theoretically. Many other researchers found the same dependency using different experimental set-ups and materials (Kuroiwa, 1977; Calabrese, 1980; Akkok et al., 1987; Montagnat and Schulson, 2003; Marmo et al., 2005; Bäurle et al., 2006). Figure 1-8 illustrates some of these findings.

At higher velocities more frictional heat is produced than at slower speeds, resulting in a greater melt water production and therewith more lubrication, which facilitates the sliding motion; this is the case in the boundary friction regime and also the mixed friction regime before drag forces outweigh the benefits from a thicker lubricating layer (compare to Figure 1-4). Overall, the five different sets of data shown here all agree with the predictions of theoretical models (presented below), which describe the velocity dependence in the boundary regime with $\mu \propto \nu^{-1/2}$ (Evans et al., 1976 (for high velocities); Okasanen and Keinonen, 1982 (for friction dominated by thermal conductivity); Stiffler, 1986; Akkok et al., 1987). Many other sets of data not plotted here

![Figure 1-8: Velocity dependence of the friction coefficient (enhanced lubrication).](image-url)
show a similarly decreasing trend in the coefficient of friction with increasing velocity. The differences among the various sets are attributed to the different experimental setups and operating conditions, such as slider material, normal force, temperature, and apparent contact area (see Table 1-2 for details).

**Table 1-2: Experimental parameters for the data sets plotted in Figure 1-8.**

<table>
<thead>
<tr>
<th>Reference</th>
<th>Slider material</th>
<th>$F_N$ [N]</th>
<th>$T$ [°C]</th>
<th>$A_c$ [mm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evans et al. (1976)</td>
<td>Mild steel rod</td>
<td>45.4</td>
<td>-11.5</td>
<td>$\approx 300$</td>
</tr>
<tr>
<td>Marmo et al. (2005)</td>
<td>Ice hemisphere over steel</td>
<td>2.1 / 2.4</td>
<td>-11.5</td>
<td>$\approx 2$</td>
</tr>
<tr>
<td>Akkok et al. (1987)</td>
<td>Steel cylinder</td>
<td>75</td>
<td>-20</td>
<td>$\approx 50$</td>
</tr>
<tr>
<td>Calabrese (1980)</td>
<td>Steel ring (AISI 1018)</td>
<td>889.6</td>
<td>-18</td>
<td>1,235</td>
</tr>
<tr>
<td>Bäurle et al. (2006)</td>
<td>PE block</td>
<td>84</td>
<td>-10</td>
<td>$\approx 200$</td>
</tr>
</tbody>
</table>

Once drag forces considerably contribute to the overall friction force in the mixed friction and especially in the hydrodynamic friction regime the scaling of the friction coefficient with linear velocity changes dramatically. The coefficient of friction increases with velocity as first observed by Oksanen and Keinonen (1982) in their ice against ice experiments at temperatures above -5 °C. They extended the mathematical model developed by Evans et al. (1976) and found that the thickness of the melt water layer and therewith the coefficient of friction is proportional to $\nu^{1/2}$ for temperatures close to the melting point. Other researchers have confirmed these findings with different slider materials on ice as illustrated in Figure 1-9 (de Koning et al., 1992; Jones et al., 1994; Albracht et al., 2004; Bäurle et al., 2006).

The increase in friction with velocity can be explained through the increase in drag forces from shearing the lubricating layer in the hydrodynamic friction regime. The onset of this increase is obviously largely dependent on the size, weight, and material of
construction of the slider, as well as the experimental temperature. Again differences in the experimental setup and operating conditions of the different sets of data are summarized in Table 1-3.

![Graph showing velocity dependence of friction coefficient](image)

**Figure 1-9:** Velocity dependence of the friction coefficient (added drag by melt water).

| Reference               | Slider material            | $F_N$ [N] | $T$ [°C] | $A_c$ [mm$^2$] |
|-------------------------|---------------------------|-----------|----------|----------------|-----------------|
| Jones et al. (1994)     | Formica block             | 196.2     | $\approx 0$ | 15,000         |
| Albracht et al. (2004)  | High alloy steel pin      | 1         | -7       | $\approx 2$   |
| Bäurle et al. (2006)    | PE block                  | 52        | $\approx 0$ | 1,000          |
| de Koning et al. (2000) | Steel skate blade         | 706       | -4.6     | $\approx 400$ |
|                         | (“Viking special”)        |           |          |                |
In summary, it can be stated that by varying temperature or velocity widely all friction regimes from boundary to hydrodynamic can be identified in ice friction.

1.1.5.3 Normal Force $F_N$

It is clear from the above discussion that the applied normal force and the apparent area of contact between the slider body and the ice surface play significant roles in the resulting coefficient of friction.

It is generally accepted in the literature that the friction coefficient of a slider against ice decreases with increasing normal force at a given temperature and velocity (Bowden and Hughes, 1939 (ice-ice); Oksanen and Keinonen, 1982 (ice-ice); Akkok et al., 1987; Derjaguin, 1988; Buhl et al., 2001 (PE-snow); Albracht et al., 2004; Bäurle et al., 2007). Derjaguin (1988) has shown in his experiments, carried out with a steel slider, that for increasing loads at temperatures close to the melting point the friction coefficient becomes independent of the normal force. Similarly, Oksanen and Keinonen (1982) have shown with their ice against ice experiments that at low temperatures (-15°C) and slow sliding velocities ($\nu=0.5\text{m/s}$) the coefficient of friction decreases with increasing normal force. However, at temperatures close to the melting point (-1°C), the decrease is less pronounced (Figure 1-10a and Table 1-4 for experimental conditions).
Figure 1-10: Normal force dependence of the friction coefficient
a) data from Oksanen and Keinonen (1982); b) data from Albracht et al. (2004).
Table 1-4: Experimental parameters for the data plotted in Figures 1-10a and b.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Slider material</th>
<th>$v$ [m/s]</th>
<th>$T$ [°C]</th>
<th>$A_c$ [mm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oksanen and Keinonen (1982)</td>
<td>Ice on ice</td>
<td>0.5</td>
<td>-5</td>
<td>11,475</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>Albracht et al. (2004)</td>
<td>PTFE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al alloy</td>
<td>1</td>
<td>-7</td>
<td>$\approx 2$</td>
</tr>
<tr>
<td></td>
<td>Cr-Ni steel</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Likewise, Calabrese’s (1980) experiments with a steel slider and loads above 400 N resulted in a coefficient of friction, which is entirely independent of the applied load. Considering different slider materials, Akkok et al. (1987) have shown that the coefficient of friction of a glass slider indeed decreases with normal force, while the corresponding results with a steel slider show no dependence. Similarly, Albracht et al. (2004) also confirmed the decreasing trend of the coefficient of friction with normal force for a PTFE slider, while they have found that the friction coefficients of their aluminum alloy and chrome-nickel-steel sliders are independent of the applied normal force (Figure 1-10b and Table 1-4 for experimental conditions).

Interestingly, the independence of normal force was found for high load sliders made of high surface energy materials in experiments carried out at higher speeds and/or temperatures closer to the ice melting point. This indicates that these results refer to the hydrodynamic friction regime, where complete wetting of the slider dictates the results.

1.1.5.4 Apparent Area of Contact $A_c$

Bowden and Hughes (1939) first performed experiments on the influence of the geometric area of the slider surface on the friction coefficient. Their experimental results have shown little dependence on the geometric contact area. However, Bäurle et al. (2007) have recently studied the influence of the geometric size of the slider under more
controlled conditions. Figure 1-11 illustrates Bäurle et al.’s (2006, 2007) experimental data with exponential curves fitted through the data points.

![Graph](image)

**Figure 1-11:** Area and normal force dependence of the friction coefficient with T=-5°C, \( v=3.3-5\text{m/s} \) (data from Bäurle et al., 2007).

The friction coefficient increases with increasing geometric contact area of the slider. The exponential growth curves show that the coefficient of friction tends to become independent of the applied force with larger contact areas. The initial sharp increase in the friction coefficient contradicts Leonardo da Vinci’s second law of friction, which implies that the friction coefficient is independent of the apparent area of contact, and Bowden’s (1952) discussion of the influence of the area of contact on the coefficient of friction. Bäurle et al. (2007) explain their results by the nature of the ice. For a very small geometric contact area the actual contacting asperities are located closer together, so that a larger amount of frictional energy is produced per unit area. This results into a thicker lubricating layer per unit area and an actual contact of close to 100 %. The larger the geometric area of the slider, the more the contacting points are spread out. Hence, the dominating friction regime for a very small slider might already be hydrodynamic for a given temperature, velocity and normal force setting, while the friction coefficient of a larger sample at the exact same experimental setting might still be controlled by asperity
interactions. Furthermore, Figure 1-11 illustrates again that the slider with the larger load shows lower friction, due to a greater amount of contacting points, which contribute to frictional heating and therewith to a thicker water layer. In conclusion, it is important to take the apparent contact area of different slider samples into consideration when comparing results of different researchers, as done above.

### 1.1.5.5 Roughness and Surface Structure

In 1699, Amonton attributed friction to roughness (Dowson, 1998). This led to the assumption that smooth surfaces show less friction. Ice sports’ athletes still follow this rule today. Calabrese (1980) measured the friction coefficient as a function of sliding speed for steel with different degrees of roughness and confirmed that roughening increases the friction coefficient. Itagaki et al. (1987) came to a similar conclusion after comparing different steel types with rough and smooth polish. Similarly, Ducret et al. (2005) report that an increased roughness of the ice surface increases the friction coefficient of Ultra-High-Molecular-Weight-Polyethylene (UHMWPE) sliding against ice at a very low sliding velocity of 2.5 mm/s. Generally, increasing the roughness of a surface leads to an increased surface area and more interlocking asperities during the sliding movement, which increases the wear rate and overall friction. Also, Marmo et al. (2006) point out that roughness leads to a decreased actual thickness of the lubricating film. Melt water gets trapped in valleys between asperities, and a less uniform temperature profile exists due to hot spots at asperity tips.

Aside from roughness in general, Itagaki et al. (1987) are to the best of my knowledge the only source that mentions the influence of surface structure on ice friction. They found in their experiments that their samples with polished grooves in sliding direction showed similarly low friction as highly polished sliders. However, they do not further explain this finding.

To the best of my knowledge only few studies exist on the influence of roughness and surface structure on ice friction and none of them addresses friction across all friction regimes.
1.1.5.6 **Wettability**

Bowden (1953) has conducted experiments on the wettability of different materials and found that friction was highest for surfaces that wet easily, especially close to the melting point. This can be explained by the enhanced build-up of capillary bridges between the sliding surfaces, which becomes especially important in the mixed and hydrodynamic friction regime. However, it should be considered that a change in hydrophobicity was only achieved by using a different material. Therefore, the impact of hydrophobicity cannot be investigated independently of other material inherent parameters, such as thermal conductivity and material hardness. Furthermore, as was pointed out before, roughness and material surface structure play an important role, as well. However, no reference was made to the surface roughness of different materials. Colbeck (1988) recognized the importance of capillary forces on snow friction. He has found that snow grains that do not support the slider’s load directly are bonded to the slider surface by capillary bridges, whose formation is favored through increased melt water production with increasing sliding speed. Further investigations of the adhesion between water and static rough, hydrophilic and hydrophobic surfaces have shown that hydrophobicity clearly reduces the capillary bonding (Colbeck, 1996; Colbeck, 1997). After recognizing the importance of surface wettability on capillary bonding, it is clear that it also plays an important role in ice friction especially close to the melting point. Wettability being a material property and also a function of surface roughness is a significant factor to consider when conducting ice friction experiments, in particular since its influence is not yet fully understood or included in a model describing ice friction.

1.1.5.7 **Relative Humidity RH**

Calabrese (1980) performed friction experiments with steel sliding against ice at different relative humidity conditions. His results are shown in Figure 1-12.
Relative humidity has a strong influence on the onset of the sliding movement. The higher the humidity, the more lubricated is the sliding interface and the lower the frictional resistance. Unfortunately, no further experimental data exist for the influence of humidity at higher temperatures. Possibly at higher temperatures, where a thicker liquid layer exists, humidity is expected to have a minor effect on the coefficient of friction. However, this remains to be seen experimentally.

1.1.5.8 Thermal Conductivity $\lambda$

Applying the frictional heating theory to ice friction, Bowden and Hughes (1939) performed experiments on the influence of the slider’s thermal conductivity on the friction coefficient. They compared the friction coefficient of a hollow ski with a copper surface to the one of the same ski construction filled with mercury. Air has a thermal conductivity of about 0.025 W/mK and mercury of 8 W/mK. The friction of the mercury filled ski was higher compared to the hollow air filled ski. Even though no further details are given about the exact experimental conditions, this result implies that the friction of a good thermal conductor is higher because less heat is available at the surface to melt the
ice. Further experiments carried out by Itagaki et al. (1987) with steels of different thermal conductivity have also shown this relationship between thermal conductivity and the friction coefficient. However, Albracht et al. (2004) were not able to find a significant influence of thermal conductivity on ice friction in their experiments with different materials. Generally, as pointed out for wettability investigations, using different materials for the analysis of thermal conductivity cannot show the isolated effect of this parameter on ice friction. Using materials of different thermal conductivity always brings along a change in other material parameters such as wettability and material hardness, too. However, all analytical models on ice friction, as discussed below, include thermal conductivity as a major component in describing the melt water film thickness and therewith the resulting coefficient of friction.

1.1.6 Ice Friction Models

From the above discussion of the isolated effect of single factors on ice friction it became clear that the different parameters interact significantly (for further information on the interdependence refer to Appendix A). This interdependence is one of the reasons that complicate the modeling of ice friction across the different friction regimes. Nonetheless, there has been a major effort to model ice friction and the most interesting of those models are briefly introduced here.

Evans et al. (1976) developed the first theoretical explanation for the dependence of the friction coefficient on frictional heating. They defined the total frictional force $F_T$ in terms of heat generated per unit displacement. Accordingly, the total frictional heat is described as the sum of three heat components.

$$F_T = F_S + F_I + F_M$$

These are the heat conducted away from the interface through the slider material $F_S$, the amount of heat which diffuses into the ice $F_I$, and the heat that remains for melting the surface $F_M$. By assuming that the surface is at the melting temperature of ice and taking the length of contact from their experimental observations, this results into the following equation for the friction coefficient $\mu$
\[ \mu = \frac{A \lambda_S (T_m - T_o)}{F_N \nu} + \frac{B (T_m - T_o)}{F_N \sqrt{\nu}} + \mu_M \]  

(1-10)

with \( T_m \) and \( T_o \) being the melting and the ambient temperature respectively, \( \lambda_S \) being the thermal conductivity of the slider, \( \nu \) being the sliding velocity, \( A \) being a constant depending on the actual contact area, and \( B \) being a constant depending on the actual contact area, thermal conductivity and diffusivity of ice. The authors point out that it is not possible to calculate the contribution of the melt friction coefficient \( \mu_M \) directly, but an upper limit can be derived from experiments. Furthermore, from experimental and theoretical considerations they find the thickness of the lubricating layer to be smaller than the combined surface roughness, which indicates an overall mixed friction regime. Since the slider constantly moves over fresh ice, the temperature gradient \( \Delta T_{we} (= |T_{contact} - T_{ice}|; \text{absolute value of the temperature difference between the contacting interface and the bulk ice}) \) is generally greater than the one for the slider \( \Delta T_{slider} (= |T_{slider} - T_{contact}|; \text{absolute value of the temperature difference between the bulk slider material and the contacting interface}) \), except for the case of a very conductive slider material. Their experiments with copper, Perspex\textsuperscript{TM}, and steel indicate that 40 to 60 % of the frictional heat are conducted away from the surface through the slider independent of the ambient temperature. The author’s experiments have shown that the measured friction coefficient depends on the applied normal force according to \( \mu \propto F_N^{1/3} \). This disagreement with Equation 1-10 results from the fact that the model (Equation 1-10) does not fully describe the dependence of the actual contact area on load.

The authors found that the dependency of the friction coefficient on velocity differs at higher and lower speeds. For velocities lower than 3.16 m/s the friction coefficient corresponds to \( \mu \propto 1/\nu \) indicating that heat conduction into the slider \( F_S \) dominates, whereas for higher velocities \( F_I \) takes over and \( \mu \propto 1/\sqrt{\nu} \) explains the experimental results more closely. The results indicate that with increasing slider speed other mechanisms gain importance for friction on ice. However, other mechanisms, such as fluid mechanics of the squeezed lubricating film, were not included in the theory. Another interesting observation is that wear of the ice track increased greatly above -2 \(^\circ\)C.
with significant softening of the ice. The authors point out that wear of the slider surface will generally be higher on new fresh ice than observed in their studies, where a rod formed a track on an ice cylinder. However, the theory does not take energy losses by wear processes into account.

Oksanen and Keinonen (1982) further elaborated this model. With the assumption that the lubricating layer is the main origin of frictional resistance, the authors combine the theory of Evans et al. (1976) with hydrodynamic friction. Based on the assumption that the frictional motion results in a non uniform heat transfer, they derive a model for the friction coefficient. The frictional heat $Q_f$ generated by the motion during a certain time interval $\frac{b}{v}$ is

$$Q_f = \mu F_v v \frac{b}{v}$$  (1-11)

with $b$ being the length of a contacting point. Equating this with the heat consumption equations from Evans et al. (1976) results into:

$$\mu = \frac{n^{1/4} A_c^{3/4}}{F_N} \left\{ \frac{1}{2} \left[ \frac{1}{(2v)^{1/2}} \Delta T_i (\lambda_i c_i \rho_i)^{1/2} + \Delta T_s (\lambda_s c_s \rho_s)^{1/2} \right] + \frac{1}{8v} \left[ \Delta T_i (\lambda_i c_i \rho_i)^{1/2} + \Delta T_s (\lambda_s c_s \rho_s)^{1/2} \right]^2 + \eta_0 v \rho_0 \right\}^{1/2}$$  (1-12)

where $n$ stands for the number of contacting points, $A_c$ for the actual area of contact, $\lambda_i$ and $\lambda_s$ for the thermal conductivity, $c_i$ and $c_s$ for the specific heat capacity, and $\rho_i$ and $\rho_s$ for the density of ice or the slider material respectively, $\rho_0$ for the density of and $\eta_0$ for the viscosity of water.

Here, the authors identify two regions with different relationships between the friction coefficient and the velocity. In the case of a great temperature gradient for the ice $\Delta T_{ice}$ thermal conductivity dominates over viscous shearing (the first part of Equation 1-12). The same is true when the thickness of the lubricating layer is very small, suggesting that the produced heat is mainly conducted away and not available for melting the ice. The velocity dependency of the friction coefficient is then described by $\mu \propto 1/\sqrt{v}$ in the model. If the temperature gradients for the ice $\Delta T_{ice}$ and the slider $\Delta T_{slider}$ are both small, which means that the ambient temperature is close to 0 °C, friction is governed by

32
viscous shearing and melting of the ice (the second part of Equation (1-12)). The model gives a velocity dependency of $\mu \propto \sqrt{v}$ in this case. Furthermore, the authors point out that in the mixed region between the two cases discussed above the strength of the effects is determined by the velocity. At low velocities, thermal conductivity plays the greater role. At high velocities the time for heat conduction is reduced, resulting in more heat available for melting the ice. Even though the model indicates increased frictional resistance close to the melting temperature, it does not mention a potential contribution of capillary drag forces. Furthermore, energy losses due to wear mechanisms and squeeze out of the lubricating layer are ignored in the model. However, the proposed relationships between the sliding velocity and the resulting friction coefficient correspond reasonably well to experimental results, as shown in chapter 1.1.5.2.

In contrast to the analytical models above, Akkok et al. (1987) do not consider the melting temperature as an upper bound for the surface temperature but rather the softening temperature of ice. They argue that after reaching the softening temperature frictional motion wears the surface so much that the originally touching materials are no longer in contact. This is important, since through this kind of wear process no energy is consumed in the phase change, but all heat is conducted away. The heat is assumed to be only conducted into the ice and not through the slider. The following model was developed,

$$\mu = C \frac{A_c(T_c - T_I)}{F_N} \left( \frac{\lambda_s \rho_s c_s}{vb} \right) \frac{1}{2}$$

where $C$ is a constant, $A_c$ the actual area of contact, $T_c$ and $T_I$ are the temperature at the contact and the ice respectively. This model and further experiments confirm the results of Evans et al. (1976) and Oksanen and Keinonen (1982) with $\mu \propto 1/\sqrt{v}$. Furthermore, they emphasize that the velocity dependency changes at high temperatures, when hydrodynamic friction dominates. Concerning the dependency on load, their model gives $\mu \propto 1/\sqrt[4]{F_N}$ for partial contact, while the regression analysis on their experimental data gives $\mu \propto 1/\sqrt{F_N}$. The results of Evans et al. (1976) lie in between these two. This
variance indicates again that effects like the squeeze of the lubricating layer might play an important role here.

The analytical models so far recognize heat conduction and friction dominated by viscous shearing as two extreme cases in the determination of the overall frictional resistance. However, other important mechanisms are left on the side. Squeeze flow, for example, is not considered, which decreases the thickness of the lubricating layer at high loads and fast speeds.

Stiffler (1984, 1986) included squeeze as a type of wear in his model. He derived the following model for the friction coefficient for a conducting surface:

\[
\mu = \frac{2\lambda_s A_s (T_m - T_0)}{F_N (\pi \alpha_s l_c \nu)^{1/2}}
\]  

(1-14)

with \( \alpha_s \) being the thermal diffusivity of the slider material and \( l_c \) the characteristic length of the contact. This analysis assumes hydrodynamic friction with a thickness of the lubricating layer that is larger than the combined roughness of both surfaces. He mentions that this assumption is unrealistic for an ice skater and concludes that the model is not suitable for this application.

Colbeck (1988) developed a comprehensive model for snow friction, which recognizes the different mechanisms of friction acting at the same time:

\[
\mu = \mu_s + \frac{\mu_D \mu_w}{\mu_D + \mu_w}
\]  

(1-15)

with \( \mu_s \) being friction due to capillary drag, \( \mu_D \) being dry friction due to asperity interactions, and \( \mu_w \) being wet friction due to shearing of the water film. The calculation of \( \mu_w \) is based on the shear stress calculation for a Newtonian fluid with \( \mu_w = \mu_o v / h \), with \( \mu_o \) being the water viscosity at 0 °C, and \( c \) a constant that considers the area of contact but is based on the assumption that snow friction is independent of the applied load. The latter was found to not hold true for small sliders on ice as explained in this chapter’s sections 1.1.5.3 and 1.1.5.4. Dry friction \( \mu_D \) is based on the heat flow calculations, first introduced by Evans et al. (1976). It is summarized in \( \mu_D = \varepsilon e^{\beta h} \), where \( \beta \) and \( \varepsilon \) are coefficients. While \( \varepsilon \) is not further defined, Colbeck (1988) discusses four
different cases of heat flow to derive at a value for $\beta$. These four cases are heat flow into the ice only, heat flow at contacts only, entire lower surface at 0 °C, and heat flow assuming an average temperature gradient. For an exact calculation for a particular slider information about the actual area of contact and the division of heat flow into slider and ice would be needed. $\mu_S$ is approximated by $\mu_S = \gamma h^3$, with $\gamma$ being a constant. Even though this model is based on several assumptions regarding the constants, it gives a good example of the interaction of the different mechanisms controlling friction on snow and also ice.

A recent friction algorithm by Penny et al. (2007) is based on skate thermodynamics. The thickness of the lubricating layer is modeled by taking melting, squeeze flow, and heat conduction to the ice into account. However, since the skate might also conduct heat from the surrounding ambience to the ice-slider interface, heat conduction to and/or from the slider is neglected. It is recognized that the thickness of the melt water layer increases along the length of the skate blade and reaches a steady state once the three factors considered (melt, squeeze, and conduction) balance one another. While the model shows reasonable agreement with the experimental data of de Koning et al. (1992) in regard to the sensitivity to ice temperature and sliding velocity, normal force dependency is not investigated further. Furthermore, it needs to be investigated, how suitable the algorithm is to model ice friction at very low sliding velocities, where heat conduction and wear effects are more important.

Bäurle et al. (2006, 2007) recently developed a numerical model specifically for their tribometer experiment (explained in Section 1.1.4.4) but with observations valid for general ice friction problems. The analysis is based on equating heat generation with possible energy dissipation mechanisms. Considering a non uniform frictional contact with some areas being almost dry and some areas covered by lubricating water, the total friction force $F_T$ is calculated by

$$F_T = \mu_{dry}F_N\frac{A_{dry}}{A_{app}} + \frac{\eta v A_{rel}}{h_{wf}}(A_{app} - A_{dry})$$

(1-16)

with $h_{wf}$ being the thickness of the lubricating water film; $A_{dry}$ and $A_{app}$ being the dry and apparent contact areas respectively, and $A_{rel}$ the relative real contact area. A constant
temperature is assumed within the water film. However, the heat diffusion process depends on the change of the water film thickness \( h_{wf} \) along the ice-slider interface which is described as

\[
\frac{\partial h_{wf}}{\partial t} = \frac{1}{L} \left( \frac{\eta v^2}{h_{wf}} - k \cdot \partial_z T \right)_{z=0} - \frac{8h_{wf}^3 \sigma_0}{3\eta D^2}
\]

(1-17)

with \( L \) being the volumetric latent heat of fusion and \( \partial_z T \) the average temperature gradient at the interface. The last term describes the loss of lubricating water by squeeze, with \( \sigma_0 \) being the perpendicular pressure and \( D \) the contact spot diameter, which changes during the contact according to \( D = D_0 \sqrt{\frac{\Delta_{rel}}{\Delta_{rel,0}}} \), with \( D_0 \) being the initial static contact spot diameter, and \( \Delta_{rel,0} \) being the initial relative real contact area. The model is based on one-dimensional calculations of heat generation and conduction perpendicular to the interface into slider and ice. Changing conditions along the ice-slider interface are taken into account by conducting several calculations along the contact length. While describing the general trend of decreasing friction with increasing temperature reasonably well, the model fit to experimental data was improved by including a correction factor to allow for three-dimensional heat flow into the slider. Through \( \Delta_{rel} \) melting and roughness are considered in this numerical model. \( h_{wf} \) is related to \( \Delta_{rel} \) through the bearing ratio curve of the ice surface. Furthermore a rough slider moving over rough ice results in intermittent contact of the surfaces allowing sections of the surfaces to cool before the next contact, which reduces \( h_{wf} \). The authors determine \( \Delta_{rel} \) by fitting their model to their experimental results. This model allows for implications of slider parameters such as thermal conductivity and roughness on the resulting ice friction.

Summarizing, only few analytical models for calculating the friction coefficient on ice exist. One problem with all these models is the estimation of the real contact area. An error can easily be introduced to the calculation, since the size and density of the surface asperities are unknown and have to be approximated. At the same time, adjusting the value for this variable is an easy way to adjust model results so that they fit
experimental data. In general, the different models provide a good idea about the main effects interacting in frictional heating. However, other important mechanisms were not yet fully included in the theoretical analysis. The contribution of capillary drag forces to frictional resistance is not yet separated from overall hydrodynamic friction due to the lack of a sound physical understanding. The influence of material parameters such as surface wettability and roughness on drag force, squeeze flow, and the overall friction coefficient still need to be investigated in greater detail and included into a model.

1.1.7 Summary

Studies on ice friction impact not only ice sports, but also other fields like glaciology, or ship hull design for cargo ship transportation through cold regions. While this review focuses on the application in ice sports, the findings are also relevant to other fields of application and thus contribute to their scientific understanding.

The nature of the liquid-like layer on ice is still a subject of scientific discussion. Surface melting is not yet fully understood and the ice as a material is still an interesting topic for research. In section 1.1.2 it is pointed out that a minimum for friction on ice exists in the regime of mixed friction. This minimum was reported in terms of the optimal ice surface temperature for skating between -9 °C and -6 °C (de Koning et al., 1992; Liang et al., 2003). From the above discussion it is apparent that the location of this minimum depends on many factors. On the basis of the frictional heating theory, the influence of parameters like temperature, normal force, and velocity is fairly well understood. Different mathematical models explain ice friction depending on these parameters, as introduced in section 1.1.6. These models consider heat conduction effects, hydrodynamic friction, and partly squeeze flow. However, friction regimes with a thinner lubricating layer are not well defined in models. Wear effects and capillary bridges between the slider and the ice were not yet successfully included into a model. Furthermore, the effect of material parameters like roughness, hardness, and surface wettability still needs to be investigated in greater detail theoretically and experimentally, and their influence on the build-up of capillary bridges and the overall drag force has to be included into an ice friction model.
1.2 Thesis Objectives

This thesis is devoted to the microscopic investigation of the friction of metallic sliders against ice. An effort has been made to understand the influence of material properties, such as surface wettability, surface roughness, and thermal conductivity on ice friction. The central focus of this work is how to reduce ice friction by controlling those material inherent factors of metallic sliders. The motivation for this work is the upcoming Winter Olympic Games of 2010 in Vancouver, Canada.

The particular objectives of this work can be summarized as follows:

1. to measure ice friction under controlled conditions (temperature, normal force, sliding velocity) across all friction regimes using a rheometer with a newly designed friction fixture.

2. to find a way to mimic the lotus effect on metallic sliders and therewith to change the slider’s surface wettability in order to investigate the influence of hydrophobicity on ice friction.

3. to study the influence of roughness and surface structure of the slider on the resulting ice friction.

4. to investigate the effect of the slider material’s thermal conductivity on ice friction.

1.3 Thesis Organization

The present chapter of the thesis discusses the basic motivation of the present work. It includes a historical overview of friction studies, basic information related to the different friction regimes, and a brief introduction into the theories explaining the existence of the liquid-like layer on ice relevant to ice friction. In addition, this chapter includes a review on the different experimental methods previously used for ice friction studies and the therewith identified different parameters influencing the friction coefficient. Different ice friction models are also discussed. This chapter is based on a review paper that was accepted for publication (Kietzig, A.-M., Hatzikiriakos, S.G.;

Chapter 2 describes a novel approach that can be used to dramatically change the wettability of metallic alloys from hydrophilic to hydrophobic or nearly superhydrophobic by simultaneously micro- and nano-structuring the surface with a femtosecond laser. This chapter is based on a journal paper that has already been published (Kietzig, A.-M., Hatzikiriakos, S.G.; Englezos, P., *Patterned Superhydrophobic Metallic Surfaces*, Langmuir, 25, 4821–4827, 2009).

Chapter 3 examines the effect of those patterned hydrophobic metallic surfaces on ice friction. Apart from the influence of wettability on ice friction, the impact of surface roughness and surface structure is also discussed. This chapter is based on a journal paper that has already been published (Kietzig, A.-M., Hatzikiriakos, S.G., Englezos, P., *Ice Friction: The Effects of Surface Roughness, Structure, and Hydrophobicity*, Journal of Applied Physics, 106, 024303, 2009).

Chapter 4 includes the discussion of the influence of thermal conductivity on ice friction. The isolated effect is presented by insulating the slider with fiberglass. In addition different slider materials are compared with special focus on their respective thermal conductivity. This chapter is based on a manuscript that was accepted for publication (Kietzig, A.-M., Hatzikiriakos, S.G., Englezos, P., *Ice Friction: The Effects of Thermal Conductivity*, accepted for publication by Journal of Glaciology, 2009).

Finally, the conclusions, contributions to the knowledge and recommendations for future research are summarized in Chapter 5. A general summary of the most significant findings from this work is presented.
1.4 References


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2 PATTERNED SUPERHYDROPHOBIC METALLIC SURFACES

2.1 Introduction

When a rain drop falls onto a lotus leaf, it hardly wets the surface. The water droplet rolls off easily carrying away with it any contaminating particles (Solga et al., 2007; Forbes, 2008). This superhydrophobic behavior, also called lotus effect, is attributed to the particular roughness of the lotus leaf’s surface. The surface of a lotus leaf is made up of a certain dual scale roughness structure (Barthlott and Neinhuis, 1997). Micrometer scale asperities in random distribution are covered by fine nanometer scale hairs. The hairs amplify the surface tremendously (Cheng et al., 2006). When water gets into contact with the leaf, the droplets only rest on the peaks of the asperities. Air is trapped between the surface and the drop. Therefore, the drop is supported by a composite surface made out of leaf and air, as described by the Cassie-Baxter equation (Cassie and Baxter, 1944). The resulting contact angle of water on the lotus leaf is as high as 162° (Neinhuis and Barthlott, 1997). Surfaces are considered superhydrophobic, when they show a contact angle of more than 150°, and the contact angle hysteresis is less than 5° (Feng, 2002).

After the first investigations of the lotus leaf, efforts have focused on understanding this roughness induced superhydrophobicity in experiments and models (Onda et al., 1996; Shibuichi et al., 1996; Öner and McCarthy, 2000; Marmur, 2003; Marmur, 2004; Patankar, 2004; Nosonovskv and Bushan, 2005; Burton and Bushan, 2005). Hydrophobic surfaces were created using lithography techniques in combination with self-assembled monolayers (Shiu et al., 2004; Burton and Bushan, 2005) and with silanization agent (Öner and McCarthy, 2000). Superhydrophobicity was achieved on surfaces with aligned carbon nanotubes (Li et al., 2002; Lau et al., 2003; Otten and Herminghaus, 2004; Zhu et al., 2005), solidified alkylketene dimer wax (Onda et al., 1996), electrodeposited ZnO (Li et al., 2003), and anodically oxidized aluminum

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(Shibuichi et al., 1998). The common characteristic of all these surfaces is a certain micro roughness. Laser irradiation has been proven to be an effective technique to create dual scale roughness structures on silicone (Her et al., 1998; Dolgaev et al., 2001; Zorba et al., 2006; Zorba et al., 2008). Yoon et al. (2008) created superhydrophobic laser-structured poly(dimethylsiloxane) surfaces, while Groenendijk et al. (2006, 2008) irradiated a stainless steel mold with a femtosecond laser to create a dual scale roughness structure. This mold was subsequently used to create a replicate of this structure on hydrophobic polymers, which became superhydrophobic due to the dual scale roughness structure. However, the wetting behavior of the laser structured steel mold was not reported.

Rendering an initially hydrophilic surface to hydrophobic was achieved by Baldacchini et al. (2006), by coating a laser irradiated silicon surface with fluorosilane. Zorba et al. (2006) have achieved a similar change in wetting behavior of silicone, however, without additional coating after the laser treatment. This and Bhattacharya’s et al. findings on hydrophobic clustered copper nanowires (2008) are to the best of my knowledge the only reports on altering a material’s surface wettability from hydrophilic to hydrophobic without using a coating.

In this chapter, it is shown that different metallic alloys with initially smooth, hydrophilic surfaces become nearly superhydrophobic and some even superhydrophobic over time after being irradiated with a femtosecond laser. The laser irradiation immediately created a certain dual scale roughness structure on the samples’ surfaces and appears to be responsible for carbon deposition on the substrate’s surface.

### 2.2 Experimental Section

#### 2.2.1 Materials

The different alloys chosen for the experiments are stainless steel AISI 304L, stainless steel AISI 630, low-alloy steel AISI 4140, high speed tool steel AISI M2, mold steel AISI P20 coated with Armoloy® thin dense chromium (TDC) coating of about 4 µm thickness, and titanium alloy Ti-6-4. All samples are about 1mm thick and polished.
to an average roughness value ($R_a$) of about 800 nm. This is defined as the average length of protrusions above their mean value, a measure of roughness standard in literature.

### 2.2.2 Surface Laser Irradiation

The samples’ surfaces were irradiated with a horizontally polarized beam of an amplified Ti:Sapphire laser (seed laser Coherent Mira HP, amplifier Coherent Legend) with 800 nm wavelength, 1 kHz repetition rate, and about 150 fs pulse width. The beam was focused to a spot size of 30 µm. The scan line overlap was set to be 50 %. An x-y-translation stage moved the sample under the laser beam with 0.25 mm/s, resulting in 120 pulses/spot. The samples were irradiated at normal incidence in air. Three different structures were created on each material with a fluence of 0.78 J/cm$^2$, 2.83 J/cm$^2$, and 5.16 J/cm$^2$ respectively.

### 2.2.3 Surface Analysis

The morphology of the surface structures was analyzed with scanning electron microscopy (SEM) and atomic force microscopy (AFM). The samples were ultrasonically cleaned in acetone, before assessing wettability by measuring the contact angle. A 1 µL droplet of distilled deionized water was dispensed on the sample surface and the contact angle was determined by analyzing droplet images and using the software FTA32 Version 2.0. Similarly, contact angle hysteresis was determined by comparing the advancing and receding contact angles of the growing and shrinking droplet respectively (Groenendijk and Meijer, 2006; Groenendijk, 2008). X-ray photoelectron spectroscopy (XPS) analysis was used to quantify the elemental composition of the surface.

### 2.3 Results and Discussion

#### 2.3.1 The Effect of Fluence on Surface Structure

The SEM images (Figure 2-1) clearly show the effect of the laser irradiation on the surface roughness of the samples. The pristine surfaces are characterized by scratch
marks from the polishing process. After the laser process the surfaces show regular protuberances. With increasing fluence this surface structure becomes coarser. For the AISI P20+Cr sample the SEM images clearly show that the coating got damaged by irradiation of 0.78 J/cm$^2$. For higher fluences the coating was completely removed.

**Figure 2-1:** SEM images of pristine and laser structured surfaces (same scale applies to all images).
Figure 2-2 shows the laser induced surface structure at higher magnification exemplarily for AISI 304L.

For all fluences and materials a periodic ripple structure is superimposed onto the more chaotic protuberances. For the structures created with 0.78 J/cm² trenches perpendicular to the ripples isolate fine bumps with average diameters of about 2.5 µm.
With increasing fluence these bumps become larger and the overall microstructure appears coarser (geometric details are given in Table 2-1). Independent of the applied fluence, however, these micro-scale bumps are covered by a fine ripple structure with about 500 nm spacing. Such a surface with roughness patterns on two different length-scales is characteristic for such laser structured surfaces (Birnbaum, 1965; Bäuerle, 1996; Groenendijk and Meijer, 2006).

Structural characteristics, measured by AFM, such as average surface roughness $R_a$, average bump diameter $d$, and average bump height $z$ are summarized in Table 2-1. All dimensions are reported in $\mu$m.

<table>
<thead>
<tr>
<th>Material</th>
<th>$R_a$</th>
<th>$d$</th>
<th>$z$</th>
<th>$R_a$</th>
<th>$d$</th>
<th>$z$</th>
<th>$R_a$</th>
<th>$d$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L</td>
<td>0.32</td>
<td>2.5</td>
<td>3</td>
<td>0.45</td>
<td>4</td>
<td>3.5</td>
<td>1.12</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>630</td>
<td>0.35</td>
<td>2.5</td>
<td>2.5</td>
<td>0.42</td>
<td>4</td>
<td>3.5</td>
<td>0.76</td>
<td>9</td>
<td></td>
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<tr>
<td>4140</td>
<td>0.30</td>
<td>2.5</td>
<td>2</td>
<td>0.37</td>
<td>4</td>
<td>3</td>
<td>1.03</td>
<td>9</td>
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<td>3</td>
<td>0.61</td>
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<td>2</td>
<td>0.37</td>
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<td>0.69</td>
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<td>5.5</td>
<td>1.23</td>
<td>6</td>
<td>10</td>
<td>1.72</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>
2.3.2 Time Effects on Surface Hydrophilicity/Hydrophobicity

Directly after the laser treatment, the droplets were found to wet the structured area on all samples completely; initially all samples exhibit superhydrophilic behavior. Over time, however, the contact angle started to increase. Due to the small size of the structured area the water drop wets the entire structured area until the contact angle exceeds 20°. Therefore, only after that lower limit the change in contact angle could be monitored. Figure 2-3 shows the dependence of the contact angle on time for all six materials and the three different fluences respectively. Each measurement point displayed here is the average of 3 individual measurements.

*Figure 2-3:* Contact angle evolution over time for a) 0.78 J/cm$^2$, b) 2.83 J/cm$^2$, and c) 5.16 J/cm$^2$. 
The contact angle evolution can be described approximately with exponential growth regressions of the type

$$\frac{\theta}{\theta_{eq}} = 1 - e^{-\frac{t}{\lambda}}$$

(2-1)
where $\theta_{eq}$ is the equilibrium contact angle (maximum angle towards which the data converges), and $\lambda$ is a time constant, which represents the time until 63.2% of the maximum contact angle value is reached. An example for such a regression is shown in Figure 2-4 for AISI 630 irradiated with 2.83 J/cm$^2$.

![Figure 2-4: Exponential growth regression on contact angle evolution over time of AISI 630 irradiated with laser of fluence 2.83 J/cm$^2$.](image)

Tables 2-2 and 2-3 summarize the values for $\theta_{eq}$ and $\lambda$ respectively for all samples. Following an initial sharp increase the contact angles gradually reach a steady state. For all alloys the low fluence structures show a faster increase (small time constant $\lambda$) in contact angles compared to the samples irradiated with a higher fluence. Table 2-2 shows that after only one day all the structures irradiated with 0.78 J/cm$^2$ reached at least 63% of their steady state contact angle. Especially the titanium alloy and tool steel M2 are noticeably slower in becoming hydrophobic for the structures irradiated with 2.83 and 5.16 J/cm$^2$. Table 2-3 summarizes the steady state contact angles for all structures. The structures created with irradiation of 2.83 J/cm$^2$ and 5.16 J/cm$^2$ converge to contact angles between 110° and 130° depending on the alloy, while the samples irradiated with
0.78 J/cm² result in less than 10 days in steady state contact angles between 130° and 150°.

Table 2-2: Contact angle regression coefficient \( \lambda \) (days) for all fluences.

<table>
<thead>
<tr>
<th>material</th>
<th>0.78 J/cm²</th>
<th>2.83 J/cm²</th>
<th>5.16 J/cm²</th>
</tr>
</thead>
<tbody>
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<td>304L</td>
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</tr>
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<td>3.43</td>
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</tr>
<tr>
<td>M2</td>
<td>0.10</td>
<td>8.17</td>
<td>16.92</td>
</tr>
<tr>
<td>P20+Cr</td>
<td>0.26</td>
<td>5.34</td>
<td>5.63</td>
</tr>
<tr>
<td>Ti-6-4</td>
<td>0.49</td>
<td>12.27</td>
<td>26.35</td>
</tr>
</tbody>
</table>

Table 2-3: Contact angle regression coefficient \( \theta_{eq} \) (°) for all fluences.

<table>
<thead>
<tr>
<th>material</th>
<th>0.78 J/cm²</th>
<th>2.83 J/cm²</th>
<th>5.16 J/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L</td>
<td>147</td>
<td>127</td>
<td>123</td>
</tr>
<tr>
<td>630</td>
<td>145</td>
<td>126</td>
<td>125</td>
</tr>
<tr>
<td>4140</td>
<td>144</td>
<td>112</td>
<td>119</td>
</tr>
<tr>
<td>M2</td>
<td>139</td>
<td>122</td>
<td>132</td>
</tr>
<tr>
<td>P20+Cr</td>
<td>132</td>
<td>119</td>
<td>129</td>
</tr>
<tr>
<td>Ti-6-4</td>
<td>143</td>
<td>132</td>
<td>124</td>
</tr>
</tbody>
</table>

To further assess the hydrophobic behavior, contact angle hysteresis was measured on the irradiated surfaces once they reached their steady state contact angle. Figure 2-5 shows a growing and shrinking drop sequence exemplarily for AISI 304L irradiated with 0.78 J/cm². With the advancing contact angle of 153° and the receding contact angle of 150.5°, the hysteresis for this particular sample is less than 3°. Accordingly this sample meets the requirements of a superhydrophobic surface. The hysteresis values \( \Delta \theta \) (°) for all samples are summarized in Table 2-4. Overall, the
hysteresis values are very low with more than two thirds of the samples exhibiting values below 3°.

![Figure 2-5: Contact angle hysteresis sequence of AISI 304L irradiated with 0.78 J/cm².](image)

**Table 2-4:** Contact angle hysteresis Δθ (°) for all fluences.

<table>
<thead>
<tr>
<th>material</th>
<th>0.78 J/cm²</th>
<th>2.83 J/cm²</th>
<th>5.16 J/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L</td>
<td>&lt;3°</td>
<td>&lt;3°</td>
<td>&lt;2°</td>
</tr>
<tr>
<td>630</td>
<td>&lt;1°</td>
<td>&lt;3°</td>
<td>≈3°</td>
</tr>
<tr>
<td>4140</td>
<td>&lt;2°</td>
<td>&lt;2°</td>
<td>&lt;2°</td>
</tr>
<tr>
<td>M2</td>
<td>≈6°</td>
<td>&lt;3°</td>
<td>&lt;2°</td>
</tr>
<tr>
<td>P20+Cr</td>
<td>&lt;3°</td>
<td>&lt;4°</td>
<td>&lt;4°</td>
</tr>
<tr>
<td>Ti-6-4</td>
<td>&lt;4°</td>
<td>≈3°</td>
<td>≈6°</td>
</tr>
</tbody>
</table>

2.3.3 **Elemental Surface Analysis**

X-ray photoelectron spectroscopy (XPS) analysis was performed on the untreated and treated surfaces of all materials. Figure 2-6 exemplarily shows the spectra for stainless steel 304L before laser irradiation (Figure 2-6a), immediately after irradiation (Figure 2-6b) and 52 days after irradiation (Figure 2-6c).
Figure 2-6: XPS spectra for 304L before and after laser irradiation with 5.16 J/cm².
After irradiation with 5.16 J/cm\(^2\) one sample of stainless steel 304L was stored in vacuum until it could be analyzed by XPS (Figure 2-6b); the total exposure time to air between the laser treatment and the analysis is estimated to be about 5 hours. It is apparent that the relative amount of carbon increases with time, comparing the spectra before (Figure 2-6a), shortly after laser irradiation (Figure 2-6b), and after a longer period of time (Figure 2-6c), when the contact angle has reached its equilibrium value. While the surface of the untreated alloy consists of iron, nickel and chromium oxides, shortly after the laser irradiation the nickel and chromium peaks are smaller. After 52 days nickel and chromium is not detectable anymore, and the surface is solely made up of iron oxides and carbon. Table 2-5 and Figure 2-7 summarize the relationship between the contact angle and the carbon content for all alloys.

### Table 2-5: Carbon content and contact angle \(\theta_{eq} (^\circ)\) for all alloys.

<table>
<thead>
<tr>
<th>sample</th>
<th>C (atom %)</th>
<th>(\theta_{eq} (^\circ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>substrate</td>
<td>26.56</td>
<td>84</td>
</tr>
<tr>
<td>304L 0.73 J/cm(^2)</td>
<td>63.92</td>
<td>147</td>
</tr>
<tr>
<td>304L 2.83 J/cm(^2)</td>
<td>49.13</td>
<td>127</td>
</tr>
<tr>
<td>304L 5.16 J/cm(^2)</td>
<td>54.69</td>
<td>123</td>
</tr>
<tr>
<td>630 substrate</td>
<td>26.07</td>
<td>83</td>
</tr>
<tr>
<td>630 0.73 J/cm(^2)</td>
<td>55.15</td>
<td>145</td>
</tr>
<tr>
<td>630 2.83 J/cm(^2)</td>
<td>46.86</td>
<td>126</td>
</tr>
<tr>
<td>630 5.16 J/cm(^2)</td>
<td>41.79</td>
<td>125</td>
</tr>
<tr>
<td>4140 substrate</td>
<td>11.55</td>
<td>70</td>
</tr>
<tr>
<td>4140 0.73 J/cm(^2)</td>
<td>51.69</td>
<td>143</td>
</tr>
<tr>
<td>4140 2.83 J/cm(^2)</td>
<td>40.22</td>
<td>112</td>
</tr>
<tr>
<td>4140 5.16 J/cm(^2)</td>
<td>51.00</td>
<td>119</td>
</tr>
<tr>
<td>M2 substrate</td>
<td>38.81</td>
<td>75</td>
</tr>
<tr>
<td>M2 0.73 J/cm(^2)</td>
<td>41.29</td>
<td>138</td>
</tr>
<tr>
<td>M2 2.83 J/cm(^2)</td>
<td>50.89</td>
<td>122</td>
</tr>
<tr>
<td>M2 5.16 J/cm(^2)</td>
<td>50.67</td>
<td>132</td>
</tr>
<tr>
<td>sample</td>
<td>C (atom %)</td>
<td>( \theta_{eq} ) (°)</td>
</tr>
<tr>
<td>------------</td>
<td>------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>substrate</td>
<td>12.33</td>
<td>60</td>
</tr>
<tr>
<td>P20+Cr</td>
<td>0.73 J/cm(^2)</td>
<td>31.47</td>
</tr>
<tr>
<td></td>
<td>2.83 J/cm(^2)</td>
<td>43.82</td>
</tr>
<tr>
<td></td>
<td>5.16 J/cm(^2)</td>
<td>43.72</td>
</tr>
<tr>
<td>substrate</td>
<td>27.32</td>
<td>65</td>
</tr>
<tr>
<td>Ti-6-4</td>
<td>0.73 J/cm(^2)</td>
<td>32.42</td>
</tr>
<tr>
<td></td>
<td>2.83 J/cm(^2)</td>
<td>39.55</td>
</tr>
<tr>
<td></td>
<td>5.16 J/cm(^2)</td>
<td>41.90</td>
</tr>
</tbody>
</table>

**Figure 2-7:** Relationship between steady state contact angle and carbon content for all alloys.

From Figure 2-7 it can be seen that the equilibrium contact angle positively correlates with the carbon content. The overall correlation coefficient is 0.78, with the higher carbon content corresponding to higher hydrophobicity. However, it is to note that there are some exceptions to this trend. Sample 304L irradiated with 2.83 J/cm\(^2\) exhibits a lower relative carbon content but higher equilibrium contact angle than the sample irradiated with 5.16 J/cm\(^2\). Also the M2, P20+Cr, and Ti-6-4 samples irradiated with...
0.78 J/cm² have a lower carbon content than those irradiated with higher fluences but still show higher hydrophobicity.

**2.3.4 Discussion and Explanation of Results**

The present work started with the intention to utilize laser light to create a certain dual scale roughness structure on steel. This was achieved successfully. However, we noticed that the initially hydrophilic samples became hydrophobic over time. More experiments with metallic substrates of different compositions and different laser energies were performed to explore whether this effect was actually reproducible. The multiple substrates analyzed have convincingly demonstrated that this effect is totally reproducible.

In 1936, Wenzel reported the influence of roughness on the contact angle. Generally, Wenzel’s equation states that roughness increases the intrinsic wetting behavior of a surface. However, this relationship fails to give a solution for the contact angle on extremely rough surfaces and for the change from hydrophilic to hydrophobic behavior (Johnson and Dettre, 1964). Cassie and Baxter (1944) further investigated the relationship between roughness and hydrophobicity and realized that contact angles on composite surfaces are higher than predicted by Wenzel’s equation. Composite surfaces are characterized by incomplete wetting. This is represented by the Cassie-Baxter equation, which can also explain a switch from hydrophilic to hydrophobic wetting behavior (Patankar, 2004). In our case, however, the surface structure cannot solely be responsible for the observed high contact angles. The structure is in place immediately after the laser treatment. If the high hydrophobicity was due only to the laser induced roughness, the samples would have been hydrophobic directly after the laser treatment, since the structure does not change over time. Therefore, the final hydrophobicity and the evolution of the contact angle over time are due to other factors. The XPS results suggest that the observed change in wettability can be attributed to a certain extend to the presence of carbon and its compounds on the laser irradiated surfaces discussed above.
We propose the decomposition of carbon dioxide into carbon with an oxygen deficient and therefore active metal oxide scale as a potential explanation assuming that laser energy is accountable for the creation of such a scale. Active magnetite Fe$_3$O$_{4-\delta}$ ($0<\delta<1$), for example, is a non-stoichiometric oxygen deficient iron oxide scale, which was found to catalyze the dissociative adsorption of carbon dioxide (Tamaura and Tabata, 1990; Zhang et al., 2000a; Zhang et al., 2000b). Carbon dioxide becomes carbon monoxide and zero valence carbon, and oxygen anions are transferred into lattice vacancies of the alloy to form a stoichiometric metal oxide like Fe$_3$O$_4$ as reported by Tamaura and Tabata (1990). Furthermore, Zhang et al. (2000) illustrated in their experiments with pure CO$_2$ that at room temperature the reaction rate is very slow. This could serve as an explanation for the observed gradual increase in contact angle over time.

Directly after the laser treatment we already detected an increased amount of carbon on the surface, which is believed to come from the fast decomposition reaction at the time when the laser beam first hits the surface. We suggest that the high energy from the very short laser pulse activates the decomposition reaction and results in the initial carbon deposition on the irradiated surface. However, the carbon from this initial fast decomposition is not enough to cover the entire structure and shield the hydrophilicity of the underlying iron oxides. This intrinsic hydrophilicity of the polar metal oxides is then amplified by the surface roughness according to Wenzel’s theory, which clearly explains the initial superhydrophilicity of the laser irradiated alloys.

Over time the CO$_2$ decomposition reaction continues slowly and non-polar carbon accumulates on the rough surface. Together with the laser created dual scale roughness structure the result is a superhydrophobic surface. This can be compared to the high hydrophobicity of carbon nanotubes (Feng et al., 2002; Lau et al, 2003; Li et al., 2002).

To support this theory different substrates made from AISI 304L were irradiated with 5.16 J/cm$^2$ and kept in different media immediately after the laser treatment. The results are shown in Figure 2-8.
Figure 2-8: Contact angle development of 304L samples irradiated with 5.16 J/cm² stored in different media.

One sample was stored in N₂ for two weeks. After it was taken out, the contact angle was measured continuously and the sample showed approximately the same behavior as the one exposed to ambient air. Another sample was immersed into boiling water for two days after the laser treatment. Even after being exposed to air this sample never became hydrophobic but remained superhydrophilic with a steady state contact angle θ_{eq} of 21°. Tamaura and Tabata (1990) have detected hydrogen gas after active magnetite was exposed to H₂O instead of CO₂. Accordingly, water is decomposed similarly to CO₂ over active magnetite. Therefore, we assume that the active magnetite sites of our sample were deactivated by oxygen ions from the water to form more hydrophilic iron oxides. A third sample was stored in CO₂ and only taken out once a day to perform contact angle analysis. This sample initially shows the same increase in contact angle as the one kept in air. However, its steady state contact angle is higher. Due to H₂O traces in an ambient air environment H₂O decomposition is likely to take place parallel to CO₂ decomposition at the active surface, which results in less carbon on the irradiated surface compared to the same surface stored in a CO₂ environment.
It was shown that the CO\textsubscript{2} decomposition rate is highest for the greatest oxygen deficiency (Tamaura and Tabata, 1990; Zhang et al., 2000b). Comparing the same alloy irradiated with different fluences, it is obvious that the time it takes for the samples to reach their steady state increases with increasing fluence. This can possibly be explained by the difference in the degree of oxygen deficiency, which results in less carbon on the surface. If the presented explanation on the origin of the gradual increase in hydrophobicity is valid, these results suggest that higher laser fluence creates less active magnetite and/or less oxygen deficiency.

2.4 Summary and Conclusions

In summary, it has been shown that after fs-laser irradiation hydrophilic metal alloys of different composition with typical contact angles between 60° and 85° show initially superhydrophilic behavior and subsequently become nearly superhydrophobic and some even superhydrophobic with time. The distinctive laser induced dual scale roughness structure definitely plays a significant role in the extreme wetting behaviors. However, the change in and the time dependency of the wetting behavior indicate that the explanation lies in the combined effect of surface morphology and surface chemistry. With this work we have shown a possibility to modify the wetting behavior of common engineering materials.
2.5 References


3 THE EFFECTS OF SURFACE ROUGHNESS, STRUCTURE AND HYDROPHOBICITY

3.1 Introduction

The study of ice friction is important in fields as diverse as road safety, glacial movements, ice sports, design of offshore structures and ice breakers (Nakazawa et al., 1993). High friction on ice is desired for motorized vehicle traffic in winter road conditions and for the firm grip of shoe soles on ice (Roberts and Richardson, 1981; Chang et al., 2001; Higgins et al., 2008). On the other hand, low friction is desired in ice sports, such as speed skating, luge, skeleton, and bobsleigh (Rebsch et al., 1991; de Koning et al., 1992).

A comprehensive understanding of ice friction calls for the investigation of sliding over a wide range of temperatures and sliding speeds. Depending on the temperature and sliding velocity, different processes/mechanisms prevail, which divide the ice friction map (typical for other surfaces) in different friction regimes, namely boundary, mixed and hydrodynamic friction, as introduced in chapter 1. The transition between these regimes is not abrupt, but it generally depends on the combined effect of many different parameters, such as temperature, sliding velocity, applied normal force, contact area, roughness of slider and ice, wettability and surface structure of the slider material (Colbeck, 1994; Buhl et al., 2001; Bhushan, 2002).

Boundary friction is characterized by a lubricating layer with the thickness of only a few molecular layers between the sliding surfaces. This reduces solid-solid contact at the interface, while the slider’s load is mainly supported by the surface asperities (Kozlov and Shugai, 1991; Bhushan, 2002). In the mixed friction regime the load of the slider is supported by both the surface asperities and the lubricating layer. The increased thickness of the lubricating layer reduces solid-solid adhesion and enhances the lubrication. At the same time a wetting lubricant enforces the build-up of capillary

---

bridges between the asperities (Colbeck, 1988). Capillary bridges do not support the applied load, but they act as bonds between the surfaces and exercise a drag force on the slider. The build-up of these liquid bonds results in additional frictional resistance. However, no physical model or experimental evidence exists to fully describe the contribution of capillary bridges to the friction force. In the hydrodynamic friction regime the lubricating layer and not the surface asperities, carries the applied load. If the load is relatively high, part of the lubricating layer is squeezed out between the surfaces (Colbeck, 1988). However, it is assumed that the thickness of the lubricating layer remains greater than the height of the asperities. Following the area of real contact is identical to the surface area ($A$) of the slider (Bhushan, 2002). No solid-solid contact occurs during the sliding movement. Consequently, shearing of solid-solid adhesive bonds no longer contributes to the friction force.

Fowler and Bejan (1993) pointed out that the lubricating film under a slider on ice becomes thicker towards the trailing end. Consequently, friction mechanisms on ice can include all of the above introduced types of friction. The most important regime for winter sports is mixed friction, where both solid-solid contact and also capillary drag play a significant role (Colbeck, 1994).

While several studies exist on ice friction, most of these report on the effects of temperature (Bowden and Hughes, 1939; Evans et al., 1976; Calabrese, 1980; Roberts and Richardson, 1981; Slotfeldt-Elligsen and Torgersen, 1983; Akkok et al., 1987; Itagaki et al., 1987; Derjaguin, 1988; de Koning et al., 1992; Liang et al., 2003; Albracht et al., 2004; Higgins et al., 2008), sliding speed (Evans et al., 1976; Kuroiwa, 1977; Akkok et al., 1987; de Koning et al., 1992; Jones et al., 1994; Albracht et al., 2004; Montagnat and Schulson, 2003; Marmo et al., 2005; Bäurlle et al., 2006), applied load (Bowden and Hughes, 1939; Oksanen and Keinonen, 1982; Akkok et al., 1987; Derjaguin, 1988; Buhl et al., 2001; Albracht et al., 2004; Bäurlle et al., 2006), area of contact (Bowden and Hughes, 1939; Bäurlle et al., 2007), and moisture (Calabrese, 1980). Very few studies have placed emphasis onto the effects of surface roughness on ice friction (Calabrese, 1980; Itagaki et al, 1987; Marmo et al., 2005; Ducret et al., 2005). This effect is the main focus of this chapter.
The surface roughness of the slider and ice respectively has a major impact on the onset and width of the different friction regimes. In 1699, Amonton attributed friction to roughness (Dowson, 1998). This led to the assumption that smooth surfaces show less friction. Generally, increasing the roughness of a surface leads to an increased surface area and more interlocking asperities during the sliding motion, which increases the wear rate and overall friction especially in the boundary friction regime. Experimental findings generally support this assumption (Calabrese, 1980; Itagaki et al., 1987; Ducret et al., 2005).

Bowden (1953) has conducted experiments on the influence of wettability of different materials on ice friction and found that friction was highest for surfaces that wet easily, especially close to the melting point. This can be explained by the enhanced build-up of capillary bridges between the sliding surfaces, which become especially important in the mixed and hydrodynamic friction regime. Recent studies regarding surface roughness at the micro- and nanoscale that enhance hydrophobicity (lotus effect) or hydrophilicity have shown that material wettability and roughness at the nanoscale are closely related (Onda et al., 1996; Shibuichi et al., 1996; Öner, 2000; Marmur, 2003; Marmur, 2004; Patankar, 2004; Nosonovsky and Bushan, 2005; Burton and Bushan, 2005). For example the superhydrophobic behavior of the lotus leaf is attributed to its dual scale roughness surface structure (Barthlott and Neinhuis, 1997). Micrometer scale asperities in random distribution are covered by fine nanometer scale hairs. The hairs amplify the surface tremendously (Cheng et al., 2006). When water gets into contact with the leaf, the droplets only rest on the peaks of the asperities. Air is trapped between the surface and the drop. Therefore, the drop is supported by a composite surface made out of leaf and air, as described by the Cassie-Baxter equation (Cassie and Baxter, 1944). A composite surface with high air-liquid and low solid-liquid contact is advantageous in order to obtain a very high contact angle, i.e. high hydrophobicity. At the same time contact angle hysteresis, the difference between the advancing and receding contact angle of a moving water drop, should be low, which implies that a water drop easily rolls off a surface. These findings are relevant to ice friction suggesting that fewer capillary bridges would build up between such a composite slider surface and ice, which corresponds to less adhesive forces between the interfaces. Accordingly, friction especially in the mixed
and hydrodynamic friction regime will be reduced compared to a smooth surface of the same material.

In this chapter, a systematic study is undertaken to exploit the effect of surface nanopatterned structuring on ice friction. To the best of my knowledge there are no studies in the literature on the influence of roughness at the nanoscale across all friction regimes. Especially, the interdependence of roughness and wettability of a slider against ice has never been investigated before. The particular types of slider surfaces considered are metallic. The previous chapter describes that by creating certain dual scale roughness structures by femtosecond laser irradiation different metal alloys become gradually (time effect) and finally nearly superhydrophobic with contact angles up to about 150°. The transition from hydrophilic to superhydrophobic wetting behavior was attributed to the combined effect of surface morphology and surface chemistry. Using these nanopatterned nearly superhydrophobic surfaces, we now examine how superhydrophobicity in combination with the nanopatterning affects ice friction across all ice friction regimes.

3.2 Experimental Methods and Materials

3.2.1 Ice Surface Preparation

One of the main experimental challenges of this work was the preparation of ice surfaces that give reproducible results. Small bumps and imperfections on the ice surface can lead to a great variability of the experimental data. To obtain similar ice surfaces the following experimental protocol was followed. Distilled deionized water was used with a typical inorganic content of less than 18.2 MΩ.cm at 25 °C, a total organic carbon content of less than 10 ppb, and an effectively neutral pH value. To minimize bubble formation in the ice the water was boiled to minimize the dissolved gas content. About 6 ml of water were poured into dishes of 40 mm diameter and frozen in a commercial freezer unit. The obtained ice surfaces were smoothed to ensure comparability. The smoothing process was performed in a cold room set at -4 °C using a commercial drill press with a smooth high-density polyethylene pad attached to a sanding tool.
3.2.2 Slider Sample

3.2.2.1 Material and Geometry

Different steel alloys were chosen as materials for the slider, namely stainless steel AISI 304L, mold steel AISI P20, high speed tool steels AISI M2 and AISI D2. Slider samples were prepared in the shape of rings with an outer diameter $d_o$ of 25.4 mm and an inside diameter $d_i$ of 21.4 mm and about 1 mm in thickness.

3.2.2.2 Surface Preparation

To ensure comparability of the slider surface, all rings were polished with silicon carbide sandpaper to an average roughness value ($R_a$) of about 600 nm +/- 50 nm with random polishing marks in all directions. Roughness is defined as the average length of protrusions above their mean value, a measure of roughness standard in literature. Some rings were irradiated with a horizontally polarized beam of an amplified Ti:Sapphire laser (seed laser Coherent Mira HP, amplifier Coherent Legend) with 800 nm wavelength, 1 kHz repetition rate, and about 150 fs pulse width. The beam was focused to a spot size of 30 µm. The scan line overlap was set to be 50 %. An x-y-translation stage moved the sample under the laser beam with 0.25 mm/s, resulting in 120 pulses/spot. The samples were irradiated at normal incidence in air with a fluence of 5.16 J/cm$^2$ respectively. More details on the procedure and the resulting patterns can be found in chapter two.

3.2.2.3 Surface Analysis

All polished rings were analyzed regarding their surface roughness using a non-contacting profilometer (WYKO) using light interferometry with a vertical resolution of less than 0.1 nm and a spatial resolution of 40 nm. However, this approach could not be used for the laser irradiated rings with their black surface absorbing the light. Hence, the morphology of these surface structures was analyzed using AFM (Nanosurf EasyScan2) and SEM (Hitachi S-2300).

The wettability of the slider samples was assessed by measuring the contact angle. A 1 µL droplet of distilled deionized water (specifications above) was dispensed on the sample surface and the contact angle was determined by analyzing droplet images.
and using the software FTA32 Version 2.0. Similarly, contact angle hysteresis was determined by comparing the advancing and receding contact angles of the growing and shrinking droplet respectively.

### 3.2.3 Experimental Setup

The ice friction experiments were carried out with a commercial rheometer (Physica MCR 501) using a modified parallel-plate geometry. The parallel plates are enclosed in an environmental chamber that can produce temperatures as low as -150 °C through the use of an evaporator and liquid nitrogen. The rotating top plate in the parallel plate setup is substituted by a ring slider sample attached to a sample holder, and the stationary bottom plate is the ice dish (Figure 3-1b). To account for non-perfect parallelism between the two surfaces the ice dish holder is mounted via a miniature ball coupling and a compression spring to the rigid lower shaft (Figure 3-1a).

![Figure 3-1: Rheometer with newly designed friction fixture for ice friction experiments.](image)

The experiments using this feature ensured good control of the temperature within the chamber, the set rotational speed, and the applied normal force. All results reported here were obtained with a fixed normal force of 3 N. Each experiment was run for 60 seconds with torque data collected every 0.03 seconds by the rheometer; the first 20 seconds were ignored in the analysis to ensure a steady state torque. The torque signals from second 20 to 60 were averaged and the friction coefficient \( \mu \) for the parallel plate configuration was calculated according to
\[ \mu(v_R) = \frac{T}{2\pi R^3 \tau_{zz}} (3 + \frac{d \ln T}{d \ln v_R}) \]  

(3-1)

where \( \tau_{zz} \) is the normal stress, \( T \) the measured torque, \( R \) the outer radius, and \( v_R \) the linear velocity at the outer radius respectively (for the derivation of Equation 3-1 refer to Appendix B). For the annulus configuration, which was used for the reported experiments, this calculation is simplified to

\[ \mu(v_R) = \frac{T}{\bar{r} F_N} \]  

(3-2)

where \( \bar{r} = \frac{1}{2} (r_o + r_i) \) is the average radius of the slider ring and \( F_N \) is the applied normal force.

To limit variability of experimental results each ice surface was used for only two runs, before it was polished again using the commercial drill press as described above. To ensure a controlled temperature of the ice and slider, runs were started five minutes after the ice sample was placed into the chamber. There was a five minute waiting period in between consecutive runs to ensure that a potential melt water film from the previous experiment had refrozen. At each temperature setting runs with different linear speeds were randomized to average out changes in the slider sample’s surface over time. In the end, ten runs were carried out for each sliding velocity setting.

\[ 3.3 \text{ Results and Discussion} \]

To compare our findings with those reported by other researchers, we have performed ice friction experiments over a wide range of temperatures and sliding velocities using a ring-slider made out of steel AISI 304L. The results are depicted in Figure 3-2 as a 3-D plot showing the friction coefficient as a function of temperature and sliding velocity.
At all temperatures with increasing velocity the friction coefficient initially decreases sharply, passes through a minimum before it exhibits a slight increase. After the minimum the slight increase in the friction coefficient could be noticed for velocities above about 1 m/s, which can be attributed to added drag through capillary bridges (comparable to results from Colbeck’s theoretical investigations (1988), and most recent experiments (Jones et al., 1994; Albracht et al., 2004)). Furthermore, at around -4 °C a minimum in the friction coefficient can be observed. For temperatures below this minimum the friction coefficient decreases with increasing temperature due to enhanced lubrication and reduced solid-solid contact. The opposite effect, an increase in friction with increasing temperature, for temperatures above -4 °C results from the additional resistance caused by capillary bridges and viscous shearing of the melt film (Colbeck, 1988). A clear minimum in the coefficient of ice friction depending on temperature has also been reported by Calabrese (1980), de Koning et al. (1992), and Albracht et al. (2004). Accordingly, our experimental setup has been proven useful in analyzing ice friction especially in the mixed friction regime, where all different friction mechanisms come into play. The friction coefficient values reported in Figure 3-2 are values typically reported in the literature (Calabrese et al., 1980; Slotfeldt-Ellingsen and Torgersen, 1983;
Akkok et al., 1987; Jones et al., 1994; Albracht et al., 2004; Marmo et al., 2005; Bäurle et al., 2006).

### 3.3.1 Roughness and Hydrophobicity

The polished surfaces are characterized by scratch marks that result from the polishing process (Figure 3-3 for steel AISI 304L).

![SEM image of polished SS304L (magnification x500).](image)

**Figure 3-3**: SEM image of polished SS304L (magnification x500).

The average roughness $R_a$ is about 0.6 µm determined by a non-contacting profilometer as discussed above. The laser structured surface shows a distinct dual scale surface structure (Figure 3-4). Micro-scale bumps with an average diameter and average height of 9 µm are covered by a fine ripple structure with about 500 nm spacing. The laser structured slider surface is about twice as rough as the polished surface with $R_a$ of 1.12 µm.
Figure 3-4: SEM images of SS304L irradiated by a femtosecond laser with a fluence of 3.16 J/cm² (magnification x500 and x4000).

The laser process not only creates a lotus-like dual scale roughness on the steel surface but also renders the initially hydrophilic steel surface hydrophobic, as explained in chapter two. While the contact angle of a water droplet on the polished slider is about 84° and the hysteresis (the difference between the advancing and receding contact angles) 18°, this particular laser-structured ring-slider (Figure 3-4) is hydrophobic with a contact angle of 128° and a hysteresis value of less than 5° (average of six individual measurements across the ring surface).
Ice friction experiments were carried out with both sliders (Figure 3-3 and 3-4) at -15 °C, -7 °C, and -1.5 °C. The results are shown in Figure 3-5 for steel AISI 304L.

**Figure 3-5:** Friction of polished and laser irradiated AISI 304L sliders at a) -15 °C, b) -7 °C, and c) -1.5 °C.
At -15 °C both sliders show a decreasing coefficient of friction with increasing velocity (Figure 3-5a). These findings agree reasonably well with predictions of various ice friction models, which describe the velocity dependence of the coefficient of friction in the boundary lubrication regime with a scaling law as \( \mu \propto \nu^{-1/2} \) (Evans et al., 1976; Akkok et al., 1987; Oksanen and Keinonen, 1982; Stiffler, 1986). Overall, the rougher laser-structured slider results in higher friction coefficients practically along the whole velocity range. This is expected in the boundary friction regime, where interlocking asperities dominate the resistance.

Figure 3-5b illustrates the friction behavior for both rings at -7 °C. Again for very slow velocities interlocking of asperities dominates the friction; therefore, the laser-structured slider exhibits higher friction. However, with increasing velocity the difference between the two sliders becomes gradually smaller. While for velocities between about 0.1 and 0.5 m/s the observed friction coefficients for both sliders are very similar, the laser-irradiated slider already shows a slightly lower friction coefficient. The relative insensitivity of the friction coefficient at sliding velocities above 0.5 m/s is characteristic for the mixed friction regime, where the friction reduction from enhanced lubrication is almost outweighed by the increased friction from capillary drag (Colbeck,
This also explains why the rougher laser-structured slider, which is hydrophobic in contrast to the polished ring, exhibits a lower friction coefficient at these high velocities.

The effect of hydrophobicity of the slider is even more pronounced and obvious at -1.5 °C. Oksanen and Keinonen (1982) were first to show that the coefficient of friction increases with velocity in their ice against ice experiments at temperatures above -5 °C. They extended the mathematical model from Evans et al. (1976) and found that the thickness of the melt water layer and therewith the coefficient of friction is proportional to $v^{1/2}$ for temperatures close to the melting point. Other researchers confirmed these findings with different slider materials on ice (de Koning et al., 1992; Jones et al., 1994; Albracht et al., 2004; Bäurle et al., 2007). Figure 3-5c shows the same clear and sharp increase in the coefficient of friction for the polished hydrophilic slider at velocities higher than 0.5 m/s. However, the laser structured slider shows steadily decreasing friction with increasing velocity. Only for very slow speeds the rough laser-irradiated slider shows higher friction, that is when solid-solid contacts dominate the frictional contact. The increase in friction with increase of velocity for the polished slider can be explained by the over proportional increase in drag forces from shearing the lubricating layer in the mixed and hydrodynamic friction regime. Accordingly, it is not surprising that in the same velocity range the friction coefficient of the laser-irradiated rough but hydrophobic slider still decreases with velocity. The hydrophobic nature of the slider surface reduces the build up of capillary bridges.

The same behavior was also found for other steels, such as mold steel AISI P20 (contact angle/hysteresis of pristine slider: 60°/12° and irradiated slider: 121°/3°) and high speed tool steel AISI M2 (contact angle/hysteresis of pristine slider: 75°/16° and irradiated slider: 131°/4°). These results are plotted in Figures 3-6 and 3-7 at two temperatures. The trends are identical. Overall, at -1.5 °C and a sliding velocity of 1.45 m/s the ice friction coefficients of the hydrophobic laser-irradiated sliders were found to be 55-70 % less than those of the polished sliders, an effect quite significant.
Figure 3-6: Friction of polished and laser irradiated AISI P20 sliders at a) -7 °C and b) -1.5 °C.
To summarize, the influence of wettability on ice friction has been demonstrated especially in the experiments carried out close to the ice melting point. It is clear that the laser induced hydrophobicity results into fewer capillary bridges between the slider interfaces and ice and therewith leads to a delayed onset of the increase of the friction.
coefficient with velocity (mixed friction regime). Generally, the onset of the different friction regimes largely depends on the nature of the slider material. In particular, at lower temperatures and low velocities increased roughness results in higher friction coefficients as is expected from theory in the boundary friction regime, where asperity interactions define the friction force. This is the first ice friction study that investigates the influence of not only roughness but also hydrophobicity systematically across the different regimes and points out their respective significance with all other material parameters such as thermal conductivity and hardness being kept constant.

### 3.3.2 Surface Structure

More experiments at -7 °C were conducted on the isolated effect of surface structure for hydrophilic steel surfaces, i.e. controlling roughness without laser irradiation. We have noticed that the orientation of polishing marks plays a significant role on ice friction. After this initial observation the effect of the orientation of the polishing marks was more closely investigated. Figure 3-8 shows optical microscopy images of two 304L steel rings both polished to a $R_a$ value of 600 nm.

![Figure 3-8: Optical microscopy images of AISI 304L slider with a) random polishing marks, b) concentric grooves.](image)

The difference in the two rings, however, can clearly be seen; one shows random polishing marks in all directions, while the other shows almost concentric grooves, which correspond with the sliding direction.
Figure 3-9 shows coefficient of friction curves for the two types of sliders labeled as concentric and random for three different materials (AISI 304L, AISI P20, and AISI D2). All rings were polished to a $R_a$ value of about 600 nm.

Figure 3-9: Sliders of different surface structure at -7 °C; a) AISI 304L, b) AISI P20, and c) AISI D2.
The 304L slider with the random polishing marks (Figure 3-9a) is the same as already discussed in Figure 3-5. All sliders with random marks show the typical dependence of the coefficient of friction on velocity with $\mu \propto v^{-1/2}$ (as introduced in chapter 1.1.5.2). With increasing speed the friction decreases due to better lubrication and less interlocking asperities as also discussed before. For high speeds friction increases again slightly as the friction reduction by enhanced lubrication is offset by the additional capillary drag; a minimum in the coefficient of friction can be observed, as discussed above. The coefficient of friction of the slider with the concentric grooves, however, stays almost constant and independent of sliding velocity. At very low velocities it is obvious that a slider with grooves in the sliding direction would show lower friction than an equivalent slider with random polishing marks. Ice friction at very low velocities is dominated by interlocking asperities typical for the boundary friction regime. While the ice surface asperities constantly meet new asperities of the slider with random scratches, its asperities run rather smoothly in the concentric grooves of the other slider type. This explains the far lower coefficient of friction at low velocities. Similarly, Itagaki et al. (1987) found in their experiments that their samples with polished grooves in sliding direction showed similarly low friction as highly polished sliders.
With increasing speed, however, where typically a decrease in the friction coefficient can be seen for sliders with random scratches, no significant changes are observed for the slider rings with concentric grooves. It seems like the additional melt water cannot reduce friction by lubricating the sliding interface, or in other words the decrease in friction from enhanced lubrication is immediately balanced off by added capillary drag of melt water being trapped in the grooves. Since our experiments are carried out with a ring, the melt water has no easy way to escape the concentric grooves. When the amount of melt water increases and can no longer be retained within the size of the grooves at the applied normal force, it is squeezed out. Accordingly, it seems like reduced asperity interaction through melt water and increased capillary drag balance out each other with increasing velocity. The same results are found for all three types of materials used in this work (see Figures 3-9a, b and c).

3.4 Summary and Conclusion

The effect of surface nanopatterning, hydrophobicity and structure on ice friction was studied systematically over a wide range of temperatures and sliding velocities. It has been shown that hydrophobicity of the slider material reduces friction significantly in the mixed and hydrodynamic friction regime, where capillary bridges between the surfaces play a significant role on the frictional force. The change in wettability of steel sliders from hydrophilic to hydrophobic was achieved without changing the base material and therefore properties such as hardness and thermal conductivity kept the same. This allowed for the first time the more detailed investigation of the contribution of capillary drag to the overall friction. Furthermore, the laser-irradiation facilitates the creation of well defined rough surfaces, which shed light into the influence of uniform roughness on ice friction especially in the boundary and mixed friction regime. In addition to roughness alone, it has been shown that the orientation of scratches and grooves from the polishing process have a major impact on ice friction across all friction regimes. Scratches and grooves oriented in the sliding direction significantly decrease friction particularly for boundary friction dominated by asperity contact. On the other hand, sliders with grooves in sliding direction do not exhibit a clear minimum in friction within
the mixed friction regime. Overall, it was demonstrated that controlled roughness with random asperities in sliding direction can increase friction particularly at low sliding speeds. Such controlled roughness on polymeric and elastomeric materials might be the answer for designing tires, shoe soles and polymeric films with better grips, with such properties needed in many applications.
3.5 References


4 THE EFFECT OF THERMAL CONDUCTIVITY

4.1 Introduction

Friction is a major technological issue in almost every application that involves moving parts. Even though quantitative friction studies go back to Leonardo da Vinci (1452 – 1519), it was not until 150 years ago that friction on ice became the focus of scientific investigations. The material ice is inherently complex with its self sustained lubricating melt water film, which varies in thickness depending on the combined effect of parameters such as temperature, sliding velocity, applied normal force, contact area, roughness of slider and ice, wettability and surface structure, thermal conductivity and hardness of the slider material (Bhushan, 2002; Colbeck, 1994; Buhl et al., 2001). The thickness of the lubricating liquid like layer defines which friction processes/mechanisms prevails namely boundary, mixed and hydrodynamic friction (Bhushan, 2002; Persson, 2000; Bowden and Tabor, 2001).

Friction facilitated by a lubricating layer of no more than a few molecular layers is known as boundary friction. Yet thin, this layer reduces solid-solid contact at the interface, while the slider’s load is mainly supported by the surface asperities (Bhushan, 2002; Kozlov and Shugai, 1991). In the mixed friction regime the load of the slider is supported by both the surface asperities and the lubricating layer, which is thicker than in the boundary friction regime. While this water film reduces solid-solid adhesion and enhances lubrication, it also results in the build up of capillary bridges between the asperities (Colbeck, 1988). In the hydrodynamic friction regime the lubricating layer and not the surface asperities carries the applied load. Following the area of real contact is identical to the surface area ($A$) of the slider (Bhushan, 2002). No solid-solid contact occurs during the sliding movement. Consequently, shearing of solid-solid adhesive bonds no longer contributes to the friction force.

Ice friction applications such as ice sports are characterized by a lubricating water film, which becomes thicker towards the trailing end of the slider and therewith involves

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4 A version of this chapter has been accepted for publication. Kietzig, A.-M., Hatzikiriakos, S.G., Englezos, P., Ice Friction: The Effect of Thermal Conductivity (2009).
all types of friction (Fowler and Bejan, 1993). Overall, however, the most relevant regime for ice sports is mixed friction, where both solid-solid contact and also capillary drag play a significant role (Colbeck, 1994). Especially, for sports such as speed skating, luge, skeleton, and bobsleigh, ways to reduce friction on ice are sought (de Koning et al., 1992; Rebsch et al., 1991).

While several studies exist on ice friction, most of these report on the isolated effects of temperature (Bowden and Hughes, 1939; Evans et al., 1976; Calabrese, 1980; Roberts and Richardson, 1981; Slotfeldt-Elligsen and Torgersen, 1983; Akkok et al., 1987; Itagaki et al., 1987; Derjaguin, 1988; de Koning et al., 1992; Liang et al., 2003; Albracht et al., 2004; Higgins et al., 2008), sliding speeds (Evans et al., 1976; Kuroiwa, 1977; Akkok et al., 1987; de Koning et al., 1992; Jones et al., 1994; Montagnat and Schulson, 2003; Albracht et al., 2004; Marmo et al., 2005; Bäurlé et al., 2006), applied load (Bowden and Hughes, 1939; Oksanen and Keinonen, 1982; Akkok et al., 1987; Derjaguin, 1988; Buhl et al., 2001; Albracht et al., 2004; Bäurlé et al., 2006), area of contact (Bowden and Hughes, 1939; Bäurlé et al., 2007), and moisture (Calabrese, 1980). The effect of material inherent parameters, such as thermal conductivity and surface wettability, is more complicated to investigate; e.g. using materials of different thermal conductivity always brings along a change in other material parameters such as wettability and material hardness, too. Furthermore, a drastic change in one of these material inherent parameters can easily change the prevailing friction regime. Therefore it is not surprising that only few experimental studies have emphasized onto the effects thermal conductivity has on ice friction (Bowden and Hughes, 1939; Itagaki et al., 1987; Albracht et al., 2004).

The very first reports on experiments investigating the influence of thermal conductivity on ice friction go back to Bowden and Hughes (1939). They compared the friction coefficient of a hollow ski with a copper surface to the one of the same ski construction filled with mercury. Air has a thermal conductivity of about 0.025 W/mK and mercury of 8 W/mK. The friction of the mercury filled ski was higher compared to the hollow air filled ski. Even though no further details are given about the exact experimental conditions, this result implies that the friction of a good thermal conductor is higher because less heat is available at the interface to melt the surface of the ice. The
same relationship between thermal conductivity and the coefficient of friction on ice was found by Itagaki et al. (1987) with steels of different thermal conductivity. Albracht and others (2004) investigated the friction behavior of Al alloy, alloy steel, and PTFE. A significant influence of thermal conductivity on ice friction was not found. However, this conclusion is not demonstrated in their published experimental results. It is not clear, for what experimental conditions i.e. for velocity range, and therefore which friction regimes their conclusion are based on.

All empirical models based on the frictional heating theory include thermal conductivity of the slider as a major component in describing the melt water film thickness and therewith the resulting coefficient of friction (Evans et al., 1976; Oksanen and Keinonen, 1982; Stiffler, 1984; Stiffler, 1986; Akkok et al., 1987; Colbeck, 1988). Bäurle and others (2007) simulated the effect of thermal conductivity in their numerical model and found that an increase in thermal conductivity of the slider by a factor of 3 results into an increase of the friction coefficient by about 30% at -5 °C. However, the only experimental findings confirming this dependency are from experiments conducted with few different materials (Bowden and Hughes, 1939; Itagaki and others, 1987).

In this paper, the isolated effect of thermal conductivity and heat trapping at the interface on ice friction is studied using fiberglass insulation for the slider. Results of ice friction are performed and presented for fourteen different common engineering metal alloys and steels over a range of different temperatures and sliding velocities. Thereby, a thorough analysis of the influence of thermal conductivity on ice friction across all relevant friction regimes is given.

### 4.2 Methods and Materials

The experimental setup, the ice and slider surface preparation are explained in chapter 3.2. Here different materials, mainly metal alloys, were chosen for the slider. They are listed in Table 4-1 with their respective thermal conductivity at -7 °C and contact angle, as measured on the polished slider sample.
Table 4-1: Slider and holder materials, their density $\rho$, thermal conductivity $k$, heat capacity $c_p$, and contact angle $\theta$ at -7°C.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density $\rho$ [kg/m$^3$]</th>
<th>Thermal conductivity $k$ [W/m.K]</th>
<th>Heat capacity $c_p$ [J/kgK]</th>
<th>Contact angle $\theta$ [(°) (+/- 2°)]</th>
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<tr>
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<td>6</td>
<td>710</td>
<td>88</td>
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<td>74</td>
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<td>85</td>
</tr>
<tr>
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<td>420</td>
<td>86</td>
</tr>
<tr>
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<td>460</td>
<td>68</td>
</tr>
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<td>16</td>
<td>460</td>
<td>91</td>
</tr>
<tr>
<td>AISI M2</td>
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<tr>
<td>Nitinol</td>
<td>6450</td>
<td>19</td>
<td>320</td>
<td>38</td>
</tr>
<tr>
<td>AISI 420</td>
<td>7600</td>
<td>22</td>
<td>460</td>
<td>68</td>
</tr>
<tr>
<td>AISI P20</td>
<td>7800</td>
<td>28</td>
<td>460</td>
<td>95</td>
</tr>
<tr>
<td>AISI P20+Ni</td>
<td>7800</td>
<td>32</td>
<td>460</td>
<td>66</td>
</tr>
<tr>
<td>holder</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AISI 303</td>
<td>7800</td>
<td>14</td>
<td>500</td>
<td>-</td>
</tr>
<tr>
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<tr>
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<td>0.04</td>
<td>844</td>
<td>-</td>
</tr>
</tbody>
</table>

Apart from different steels and metal alloys, Nitinol and Momentive’s TpG$^\text{®}$ are unique materials, which are discussed here in greater detail. Nitinol is a superelastic nickel titanium shape memory alloy. Under stress it changes its metallic crystal phase from austenitic to martensitic. After releasing the stress, this crystal transformation is
fully reversible. Therefore, the plastic strain induced is largely recoverable, and the alloy “remembers” its shape. As a thermal management material TpG®, which stands for thermal pyrolytic graphite, is another interesting material. Its in-plane thermal conductivity is as high as $k = 1700 \text{ W/mK}$, while its thermal conductivity in z-direction is only about 6 W/mK. In the application of ice friction, this allows the frictional heat created at the interface to be equally distributed along the whole slider surface, and at the same time only very little heat is conducted away into the slider.

The experimental setup (Figure 4-1), the ice and slider surface preparation are explained in detail in chapter 3. In the following some key points will be emphasized. The thin slider samples are mounted on an aluminum holder, which is held by a stainless steel shaft in the experimental equipment. It is important to note that the aluminum holder serves as a heat sink due to its high thermal conductivity ($k = 235-250 \text{ W/m.K}$) compared to the thermal conductivities of the used sliders ($k = 6-32 \text{ W/m.K}$).

The surfaces of the slider samples were polished to an average roughness value $R_a$ of about 600 nm using silicon carbide sandpaper. It should be noted that care was taken to arrive with random polishing marks in all directions, as it was found previously that the orientation of these marks plays an important role on ice friction (chapter 3).

All slider samples were prepared in the shape of rings with an outer diameter of 25.4 mm and an inside diameter of 23.4 mm and about 1 mm in thickness. For the ice friction experiments with thermally insulated sliders, a 3 mm thick fiberglass disk (thermal conductivity $k = 0.04 \text{ W/mK}$) was mounted in between the slider ring and the ring holder (Figure 4-1c).

**Figure 4-1:** Rheometer a) and b) with newly designed friction fixture for ice friction experiments; c) with fiberglass insulation.
Before contact angle measurements were carried out on the polished surfaces, the samples were ultrasonically cleaned in Aceton. Contact angle measurements were repeated six times at different spots along the slider ring to account for local variations in the surface roughness. The contact angles reported in Table 1 represent the averaged local measurements of the advancing contact angles.

The ice friction experiments were carried out at a fixed normal force of 3N. Torque data recorded by the rheometer were averaged out over the period of 20 to 60 seconds. This period falls within the transient state of heat conduction for our experimental setup.

4.3 Results and Discussion

4.3.1 Thermal Insulation of the Slider with Fiberglass

To investigate the influence of thermal conductivity on ice friction we ran experiments with fiberglass insulated metal sliders over a wide range of temperatures (-1.5, -4, -7, -10 °C) and sliding velocities (0.0036 – 1.45 m/s), in order to cover the relevant friction regimes. Our experimental setup ensures constant and identical ice and ambient temperatures (±0.1 °C). With the thermal conductivity of ice being 2 W/mK, the frictional heat produced by the sliding motion at the interface is conducted mainly through the sliders, whose thermal conductivity is higher and in some cases considerably higher (Table 4-1). Fiberglass with a thermal conductivity of 0.04 W/mK prevents the heat to be conducted away from the ice-slider interface along the ring holder. This results into a local temperature increase of the slider’s interface.

The experimental results reported in this work represent an average of the torque recorded over a forty-second period, excluding the first 20 seconds of each experiment. A simple finite difference, unsteady, 1-D heat transfer model (similar to that reported by Bäurle et al., 2007) for our experimental setup simulates the heat flux through slider, insulation if applicable, holder, and shaft. It was found that this period (20s-60s) lies within the transient heat transfer period (steady-state temperature has not been reached).
However, the relative differences of the surface temperature between the slider of different thermal conductivity are manifested at the early stages of the process and remain almost unchanged with time (simply the profiles close to the surface are slowly translated to higher temperature). Therefore, it is possible to compare friction curves obtained from different slider materials and attribute these to differences in the thermal conductivity of the slider to a certain degree. This is due to the high thermal conductivity of the aluminum (slider’s holder). For the fiberglass experiments, however, the slope of the temperature gradients changes more significantly and the surface temperature reaches 0°C more rapidly. This creates a thicker water layer that reduces friction. Accordingly, these results cannot be used for an inter-material comparison of their ice friction performance, and can solely be used to assess the effect of the insulation.

Figure 4-2 illustrates the effect of the insulation in a 3-D bar chart showing the friction coefficient as a function of temperature and sliding velocity.
**Figure 4-2:** 3D bar chart of temperature and velocity dependence of the ice friction coefficient for a) Stellite 6B and b) Stellite 6B insulated with a fiberglass disk.
In Figure 4-2a the ice friction behavior of Stellite 6B slider is shown. At all temperatures with increasing velocity the friction coefficient initially decreases, passes through a minimum before it exhibits a slight increase. After the minimum the increase in the friction coefficient could be noticed for velocities above about 1 m/s, which can be attributed to added drag through capillary bridges (comparable to results from Colbeck’s theoretical investigations (1988), and most recent experiments (Albracht et al., 2004; Bäurle et al., 2006)). Furthermore, at around -4 °C a minimum in the friction coefficient can be observed. For temperatures below this minimum the friction coefficient decreases with increasing temperature due to enhanced lubrication and reduced solid-solid contact. The opposite effect, an increase in friction with increasing temperature, for temperatures above -4 °C results from the additional resistance caused by capillary bridges and viscous shearing of the melt film (Colbeck, 1988). A clear minimum in the coefficient of ice friction depending on temperature has also been reported by Calabrese (1980), de Koning et al. (1992), and Albracht et al. (2004). Accordingly, this experimental setup allows for investigations in the mixed friction regime, which is the most interesting, since different mechanisms interplay.

Figure 4-2b illustrates the ice friction behavior of the Stellite 6B slider insulated with a fiberglass disk (Figure 4-1c). It is clearly noticeable that the friction on ice for the slower velocities is largely reduced. This indicates that the insulation indeed traps the heat at the interface and therefore ensures a thicker lubricating layer, which again results in lower friction. The minimum in terms of sliding velocity, however, is shifted to lower speeds. Therewith the increase in friction towards hydrodynamic friction starts at lower speeds and comparing the two graphs it also becomes clear that the minimum with the fiberglass insulation is actually at a higher friction coefficient than it is the case for the non-insulated Stellite 6B slider.

Figure 4-3 illustrates the ice friction curves in a 2D plot for different materials with and without fiberglass insulation at -7 °C.
Figure 4-3: Sliders of with and without fiberglass insulation at -7 °C; a) Stellite 6B, b) AISI P20, c) AISI 304L, and d) AISI M2.
Figure 4-3 a-c show the same trend. As described above the fiberglass insulation reduces the ice friction coefficient for slow sliding velocities tremendously. This is expected in the boundary friction regime and to the left of the friction minimum in the mixed friction regime, where interlocking asperities and little lubricating melt water dominate the friction. Overall, the insulation dampens the friction curve, which results in
a wider mixed friction regime and a less pronounced minimum. For Stellite 6B and AISI P20 the friction minima for the non-insulated slider lie noticeably below the fiberglass insulated ice friction curves. In the case of AISI 304L the curve for the insulated slider is at about the same level as the minimum for the non-insulated slider. However, for AISI M2, whose ice friction curve is already rather low with a wide minimum, the fiberglass insulated slider exhibits higher friction. This is comparable to Figure 4-3a and 4-3b for velocities around the minimum.

In conclusion, insulating the slider with fiberglass results in the frictional heat being trapped close to the interface and prevents its conduction along the sample holder. Therefore, more heat is available to melt the ice and lubricate the sliding interface. In the boundary friction regime and the left side of the mixed friction regime this results in a decrease in friction, a wider mixed friction regime (Figure 4-3a-c), and/or an earlier onset of the mixed friction regime (in terms of sliding velocity) (Figure 4-3a). At the same time the insulation and therewith thicker melt water layer can result in higher friction due to added capillary drag by water bridges around the friction minimum for the particular slider (Figure 4-3a, b, d).

4.3.2 Comparison of Different Materials and the Impact of Thermal Conductivity on Friction

As becomes obvious from the above discussion and Figure 4-3, different materials have different ice friction curves under the same experimental settings, which is largely due to the different material compositions and the therewith related material inherent properties. One material inherent property is thermal conductivity, as discussed above. However, the difference in the frictional material response to thermal insulation as illustrated in Figure 4-3 is also due to other material properties, such as surface wettability, surface roughness, and material hardness.

Keeping the interaction of the different material inherent properties in mind, it is obvious that different materials exhibit different ice friction curves under identical experimental conditions. This is further illustrated in Figure 4-4.
Figure 4-4: Ice friction curves for different materials at -7 °C.

Generally, most materials follow the same typical friction curve with decreasing friction in the boundary friction regime, a minimum in the mixed friction regime and depending on the location of the minimum a subsequent increase in the friction coefficient with velocity. It is interesting to note that most materials show a minimum at the same velocity. However, investigating this further it becomes clear that all these
materials are steels and therefore this common characteristic is probably attributable to their similar chemical composition.

Nitinol’s friction curve, however, shows a significantly different behavior. Its friction coefficient increases continuously with the sliding velocity. Even at very slow sliding speeds this material behaves as typical for the mixed friction regime past the minimum. This assumption can be supported with the very high surface wettability of this material (Table 4-1), which enhances the build up of capillary bridges, which again contribute to the frictional resistance. However, the behavior might also be related to the change in Nitinol’s crystal structure under stress. Definitely, this material offers ground for future research and due to its atypical behavior it is excluded from the subsequent analysis.

TpG®’s friction curve should also be mentioned briefly, as it shows the lowest friction in the low velocity range of all materials under comparison. This can be attributed to its non-uniform thermal conductivity behavior. In plane the thermal conductivity is very high, which ensures an even temperature across the whole surface and little difference between the temperature at the tips of surface asperities and spots that are not in actual contact with the ice. At the same time the low thermal conductivity in normal to sliding direction traps the frictional heat at the interface, which results in a thick melt water film and therewith the lowest observed friction in the boundary regime.

Certainly the thermal conductivity of the different materials play a significant role in the observed behavior, although other material properties might also be important, alas difficult to assess. From the heat transfer model of Bäurle and others (2007) an increase of the thermal conductivity of slider by a factor of 3 causes an increase in the coefficient of friction by about 30% at -5 °C. In our case, the thermal conductivity of P20 is 4 times that of Ti-6-4. Taking the three slowest velocities at -7 °C (Figure 4-4), the friction coefficient of P20 is found 65-85% higher than that of Ti-6-4. Similarly taking the thermal conductivity of P20 which is 2 times that of Stellite 6B, the friction coefficient of P20 is found 15-25% higher than that of Stellite 6B. These results seem reasonable with respect to the trend described by Bäurle et al.’s (2007) findings. It is noted that the experimental conditions of the present work are similar to those used by Bäurle and
others (2007) with the exception of a much higher normal force used, that is of 84 N versus 3 N used in the present work.

Below a simple correlation analysis is performed and it is shown how far the obtained friction results across different materials can be attributed to their thermal conductivity. Figure 4-5 summarizes the contribution of thermal conductivity on ice friction across different materials at different sliding velocities.

![Figure 4-5: The contribution of thermal conductivity to ice friction at different sliding velocities.](image)

To show the general trend linear regression lines are plotted through the data for different sliding velocities. Table 4-2 summarizes the slopes of the different lines and their respective fit to the data.
Table 4-2: Regression slope and fit to Figure 4-5.

<table>
<thead>
<tr>
<th>velocity $\nu$ [m/s]</th>
<th>$d\mu/dk$ $[10^{-3}]$</th>
<th>$R_{k,v}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.004</td>
<td>3.3</td>
<td>0.7050</td>
<td>0.4970</td>
</tr>
<tr>
<td>0.036</td>
<td>2.3</td>
<td>0.6595</td>
<td>0.4349</td>
</tr>
<tr>
<td>0.108</td>
<td>0.9</td>
<td>0.4714</td>
<td>0.2222</td>
</tr>
<tr>
<td>0.361</td>
<td>-0.2</td>
<td>0.2447</td>
<td>0.0599</td>
</tr>
</tbody>
</table>

The slope of the trend lines ($d\mu/dk$) and especially the Bravais-Pearsson correlation coefficient ($R_{k,v}$) show clearly that for low sliding velocities there is a positive dependency of the friction coefficient on thermal conductivity. With increasing sliding velocities this dependency decreases until $\nu = 0.361$, which is the velocity, where many materials display a minimum in the ice friction coefficient. This again indicates that left of the minimum (in the regime of boundary and mixed friction) higher thermal conductivity of the slider material results in more heat being conducted away into the slider, so that less heat remains available to melt the ice at the interface and to contribute to lubrication.

4.4 Summary and Conclusion

The effect of thermal conductivity on ice friction was studied systematically for a variety of metal alloys over a wide range of temperatures and sliding velocities by insulating slider materials with fiberglass. It has been shown that the lower the thermal conductivity of the slider material is, the lower is the friction coefficient in the boundary and partly in the mixed friction regime, where interlocking asperity contacts contribute to the frictional resistance. Generally, thermal insulation dampens the friction curves and widens the mixed friction regime.

Figure 4-6 summarizes these findings in a qualitative friction map in terms of temperatures versus sliding velocity. The influence of thermal conductivity on the exact location and height of the ice friction minimum is not straightforward, as other material inherent properties, such as surface wettability and material hardness also play a
significant role. Overall it was demonstrated by the comparison of many different slider materials that thermal conductivity loses its influence on ice friction with increasing sliding velocity.

Figure 4-6: Qualitative friction map on the influence of thermal conductivity on the different friction regimes depending on temperature and sliding velocity.
4.5 References


5 CONCLUSIONS, CONTRIBUTION TO THE KNOWLEDGE AND RECOMMENDATIONS

5.1 Conclusions

The possibilities to reduce ice friction across all friction regimes were studied using a commercial rheometer with a friction fixture, which was newly designed as part of this work. The instrument has shown good suitability for the task, since it allowed the analysis of microscopic ice friction under controlled conditions. Good agreement with experimental results and model predictions from literature was found for the ice friction coefficients obtained for varying sliding velocities and temperatures. It was confirmed that the experimental setup enabled the evaluation of ice friction across different friction regimes.

The difference in the friction curves of different materials was attributed to several slider inherent factors studied in greater detail; such as roughness, surface structure, and thermal conductivity in the friction regimes, where solid-solid interactions dominate, and surface wettability, where capillary bridges contribute to the resulting ice friction.

It was identified that currently the understanding of the influence of surface wettability on ice friction is limited. The idea was initially to create a lotus-like dual scale roughness structure on the steels surface and to subsequently render this surface hydrophobic with a polymer coating. However, the surprising finding was that the laser processing method already changed the chemistry of the steel’s outermost surface layer, which resulted in the observed hydrophobicity or near-superhydrophobicity. Therewith, a way was found to render inherently hydrophilic steels hydrophobic in a one step process by using a femtosecond laser without changing the bulk material’s properties.

With slider samples rendered hydrophobic using the femtosecond laser process the working hypothesis could be confirmed that low wettability reduced the build-up of capillary bridges and therewith ice friction in the regime dominated by the latter. These results are published for the first time in the literature thus providing the possibility to
assess the influence of wettability on ice friction without changing the bulk material properties or applying a coating.

At the same time, the effect of roughness on ice friction was investigated. Femtosecond laser structured slider samples exhibit a controlled dual-scale roughness structure. As expected, the friction coefficient against ice was observed to be higher for those structured samples compared to polished sliders in the friction regimes controlled by solid-solid interactions, such as boundary friction and mixed friction before the friction minimum. However, the influence of roughness decreases with increasing sliding velocity.

Another approach was taken to analyze the impact, which surface roughness has on ice friction by separately looking at the surface structure. While surface roughness was kept constant, the orientation of polishing grooves in regard to the sliding direction was changed from random to concentric. It was found that the orientation of grooves in sliding direction reduces ice friction in the boundary friction regime. However, no clear minimum in the friction curves of sliders with concentric grooves could be found in the velocity range covered in this investigation. Once capillary bridges contribute to the overall ice friction, it seems like the decrease in friction from enhanced lubrication is immediately balanced off by added capillary drag of melt water being trapped in the grooves.

The final material inherent factor investigated within this thesis is thermal conductivity. Again the analysis of its impact was initially approached without changing materials but insulating the slider material with fiberglass. It was found that trapping the frictional heat at the surface resulted in less friction in the boundary regime due to an increased thickness of the liquid-like layer on the ice surface. Also, it was observed that the insulation dampens the friction curve, which results in a wider mixed friction regime and a less pronounced minimum. Furthermore, the comparison of different metallic slider materials was presented. It was shown that the influence of thermal conductivity decreases with increasing sliding velocity due to decreasing solid-solid interaction along the different friction regimes. A friction map indicating the influence of thermal conductivity was created as a rough guide to material selection. However, in conclusion
it is pointed out that the comparison of different materials is complicated even with similar roughness preparation, due to different chemical composition, thermal conductivity and wettability.

5.2 Contribution to the Knowledge and Significance to the Field of Study

Several contributions to knowledge have resulted from this research work. These are identified as follows:

1. It is reported for the first time in literature a method of changing the surface wettability of metallic surfaces by a one step femtosecond laser process. This finding cannot only be applied to ice friction applications but actually creates a completely new, exciting research field.

2. Based on the above mentioned finding, the contribution of surface wettability and therewith the influence of capillary bridges across all regimes relevant to ice friction was shown for the first time without having to change the material or the type of coating.

3. The impact of roughness on ice friction was illustrated in the boundary friction regime. In addition, the influence of surface structure was isolated from overall roughness and it was found that this distinction is important and that surface structure has a major influence on the observed friction curve.

4. With fibreglass as a thermal insulator for the slider the influence of thermal conductivity was assessed. It was found that heat trapping at the surface changes the ice friction curve for a particular slider material.
5.3 Recommendations for Future Work

Several important aspects for the study of ice friction are yet to be studied. These are recommended below for possible future research work.

1. In this study the influence of roughness and surface structure was examined at two different levels (laser structured dual roughness versus polished, and concentric versus random grooves). A more detailed study with more different degrees of roughness and surface structures will result in more quantitative information about their respective influences.

2. Related to point 1 it would be of interest to run more ice friction experiments at different normal force settings. Especially, higher normal forces than those used in this thesis research can give additional information about wear and deformation processes during ice friction in order to extend the study of Montagnat and Schulson (2003), Marmo et al. (2005), and Higgins et al. (2008).

3. By using slider samples of the same base material but different wetting behavior (i.e. samples, which were previously irradiated by a femtosecond laser and therefore are at different stages of becoming hydrophobic over time) it becomes possible to assess the influence capillary bridges have on the resulting ice friction in greater detail.

4. Information on wear and deformation processes on both ice and slider resulting over a prolonged period are also of interest in the study of the actual area of contact between the slider and the ice. Bäurle et al. (2007) have provided further insight into this area of ice friction research. However, it is unknown how the real contact area changes in the long term under sliding motion due to wear and/or deformation processes.

5. Furthermore, the herein investigated factors (roughness, surface structure, wettability) still need to be included into a model predicting the friction of a certain slider on ice.

6. The correlation and scale up of results from laboratory experiments to real life conditions will help the material selection for many different applications. Therefore, field experiments need to be carried out. For the application of
speed skating this means either using a suitable sled model or actual glide testing with athletes.

7. Beyond the use in reducing ice friction, superhydrophobic metallic surfaces, as functional surfaces offer potential for application in completely different areas of research. These range from the prevention of condensation and water coalescence (Onda et al., 1996; Shibuichi et al., 1996), as well as the prevention of contamination (Schmidt et al., 1994) and fouling (Genzer and Marmur, 2008), to the enhancement of lubricity and durability, and to the increase in biocompatibility of such surfaces (Genzer and Marmur, 2008).
5.4 References


APPENDIX A: Interdependence of Parameters Influencing Ice Friction

Figure A-1: Qualitative model for the interdependence of important parameters influencing ice friction.
Legend to figure A-1:

Colors:
- blue parameters given by the athlete.
- purple parameters given by ambient conditions
  Temperature is shaded in two colors to symbolize, that only the initial ice temperature is given. Once the slider moves over the ice, the temperature is defined by frictional mechanisms.
- green parameters represent slider material characteristics, which can be altered intentionally.

Parameters:
- \( F_N \): load
- \( v(s) \): velocity of the slider
- \( t \): time of contact between particular point of slider and ice
- \( k(s) \): thermal conductivity of slider material
- \( Q_f \): frictional heat
- \( Q(i) \): heat conducted to ice
- \( T(i) \): temperature of ice
- \( H(i) \): hardness of ice
- \( V(l) \): volume of meltwater
- \( S \): amount of liquid squeezed out between slider and ice
- \( h(l) \): height of liquid-like layer
- \( RH \): relative humidity
- \( \theta \): contact angle of water on slider
- \( R(s)_{hp} \): roughness of hydrophobic slider surface
- \( H(s) \): hardness of the slider
- \( \mu_{\text{dry}} \): coefficient of dry friction
- \( \mu_{\text{hyd}} \): coefficient of hydrodynamic friction
APPENDIX B: Derivation of Friction Expression

![Parallel plate design](image)

Figure B-1: Parallel plate design.

Starting with the definition for torque $T$ and for the friction coefficient $\mu$, the friction coefficient can be defined as a function of linear velocity $v_R$.

Torque:

$$ T = \int_0^{2\pi R} \int_0^R \tau_{th} \cdot r \cdot rdrd\theta $$

$$ \Rightarrow \quad T = 2\pi \int_0^R \tau_{th} r^2 dr $$  \hspace{1cm} (B-1)

Friction coefficient:

$$ \mu = \frac{\tau_{th} A}{F_N} = \frac{\tau_{th}}{\tau_{zz}} $$

$$ \Rightarrow \quad \tau_{th} = \mu \tau_{zz} $$  \hspace{1cm} (B-2)

Note: friction coefficient depends on velocity!

from (B-1) with (B-2)

$$ T = 2\pi \int_0^R \mu(v) \cdot \tau_{zz} \cdot r^2 dr $$  \hspace{1cm} (B-3)
Change of variables:

\[ \omega = r \omega \]  
(B-4)

for \( r = 0 \):

\[ \nu_0 = 0 \]  
(B-5)

for \( r = R \):

\[ \nu_R = R \omega \]  
(B-6)

\[ \Rightarrow \quad \omega = \frac{\nu_R}{R} \]  
(B-7)

from (B-4):

\[ r = \frac{\nu}{\omega} \]  
(B-8)

with (B-7)

\[ r = f(\nu) = \frac{\nu \cdot R}{\nu_R} \]  
(B-9)

\[ dr = \frac{\partial f(\nu)}{\partial \nu} d\nu \]

with (B-9)

\[ dr = \frac{R}{\nu_R} d\nu \]  
(B-10)

from (B-3) with (B-5), (B-6), (B-9) and (B-10):

\[ T = 2\pi R^3 \tau_{zz} \frac{1}{\nu_R^3} \int_0^{\nu_R} \mu(\nu) \nu^2 d\nu \]  
(B-11)

\[ \left( \frac{T}{2\pi R^3 \tau_{zz}} \right) \nu_R^3 = \int_0^{\nu_R} \mu(\nu) \nu^2 d\nu \]  
(B-12)

To eliminate the integral, differentiate both sides by using the Leibniz rule:

\[ \frac{\partial}{\partial z} \int_{a(z)}^{b(z)} f(x, z) dx = \int_{a(z)}^{b(z)} \frac{\partial f}{\partial z} dx + f(b(z), z) \frac{\partial b}{\partial z} - f(a(z), z) \frac{\partial a}{\partial z} \]
\[
\frac{d}{dv_R} \left[ \frac{T}{2\pi R^3 \tau_{zz}} \right] v_R^3 = \left( \int_0^{v_R} \frac{\partial}{\partial v_R} (\mu(v)v^2) dv + \left[ \mu(v)v^2 \right]_{v=v_R} \frac{\partial v_R}{\partial v_R} - \left[ \mu(v)v^2 \right]_{v=0} \frac{\partial(0)}{\partial v_R} \right)
\]

(B-13)

\[
\frac{d}{dv_R} \left[ \frac{T}{2\pi R^3 \tau_{zz}} \right] v_R^3 = \mu(v_R)v_R^2
\]

(B-14)

since \( T = T(v_R) \):

\[
\frac{v_R^3}{2\pi R^3 \tau_{zz}} \frac{dT}{dv_R} + 3v_R^2 \frac{T}{2\pi R^3 \tau_{zz}} = \mu(v_R)v_R^2
\]

(B-15)

\[
\mu(v_R) = \frac{T}{2\pi R^3 \tau_{zz}} \left( 3 + \frac{v_R}{T} \frac{dT}{dv_R} \right)
\]

(B-16)

Taking \( \left\{ \frac{v_R}{T} \frac{dT}{dv_R} \right\} \) from (A-16) to further analyze:

\[
\frac{v_R}{T} \frac{dT}{dv_R} = \frac{v_R}{T} \frac{dT}{dv_R}
\]

(B-17)

According to logarithmic differentiation: \( f'(x) = f(x)(\ln f(x))' \)

\[
\frac{v_R}{T} \frac{dT}{dv_R} = \frac{v_R}{T} \frac{d\ln T}{dv_R}
\]

(B-18)
\[ f = v_R \frac{d \ln T}{d \ln v_R} \]
\[ d \frac{f}{dx} = \ln 1 \]

Because of the chain rule:
\[ \frac{d}{dx} f = \frac{dg}{dx} \cdot \frac{d}{dg} f \rightarrow \frac{d}{dx} f = \frac{1}{x} \frac{d}{d \ln x} f \]
\[ v_R \frac{d \ln T}{d \ln v_R} = v_R \frac{1}{v_R} \frac{d \ln T}{d \ln v_R} \]
\[ = \frac{d \ln T}{d \ln v_R} \]

Therefore it follows from (B-19) with (B-16):

\[ \mu(v_R) = \frac{T}{2 \pi R^3 \tau_{zz}} \left( 3 + \frac{d \ln T}{d \ln v_R} \right) \] (B-20)

An approximation for the ring design:

Figure B-2: Friction fixture for rheometer.
Based on the mean radius of the ring (B-3) simplifies to:

\[ T = \mu \tau_{ss} \cdot R \cdot A \quad \text{(B-21)} \]

\[ T = \mu \frac{F_N}{A} \cdot R \cdot A \quad \text{(B-22)} \]

\[ \mu = \frac{T}{F_N R} \quad \text{(B-23)} \]