1. Introduction

Friction is important during the converting and end-use of almost every paper product [1]. For example, high friction is essential for sack paper and linerboard in corrugated containers during transportation and storage [2], for controlling the paper roll behaviour and for good runnability of the paper in a printing press [1]. The reliability of copiers and printers [3] as well as the suspension from currency bills from automatic teller machines [4] depend on a constant level of friction between the paper sheets during sheet-feeding. Low paper-paper friction and low paper-metal friction are required for example during the corrugating of fluting [1].

It is therefore surprising how little is known about the factors affecting the friction of paper. Most of the research in this field focuses on the effect of surface roughness and operational conditions [5-8]. However, contradictory conclusions are drawn in these reports. Broughton and Gregg [9] report that the smoothening of a paper surface decreases the friction and conclude that friction arises from surface asperities. On the other hand, Fellers et al. [10] report that smoothening increases the friction of paper and propose that the higher friction due to an increased area of real contact. Jones and Peel [5] conclude from their results that the smoothening of a paper surface has no effect on the friction. Few articles address the influence of lipophilic contaminants on the friction of paper, despite the fact that they have a substantial effect [1,9,11,12], (papers II-IV). Despite the enormous amount of literature on friction, wear and lubrication, very few authors have applied the fundamental principles from that field of research to paper systems [1,12,13], (papers II-IV). A systematic study of the friction of paper cannot be made without an understanding of the basic principles and concepts of friction, lubrication and wear, i.e. the science of tribology. For this reason, this thesis starts with a literature review about important and relevant aspects of tribology.

Tribology is the interdisciplinary science and technology of interacting solid surfaces in relative motion. The topics covered by this term include lubrication, friction and wear. The expression tribology originates from the Greek word tribos, which means rubbing [14]. It extends over the scientific fields of physics, chemistry, solid mechanics, fluid mechanics, heat transfer, materials science and lubricant rheology [15].

Friction is the resistance to motion whenever one solid body moves over another. It is one of the oldest problems in physics and is of great practical importance in many industrial operations. Minimizing friction is essential for the energetic efficiency of many processes and it has become a crucial factor in small-scale moving devices, such as miniature motors, magnetic storage devices and aerospace components. Friction is not however just a nuisance. Without friction there would be no violin music and it would be impossible to walk or to drive a car. Thus, in many applications it is desirable to maximize friction [14].
2. Basic concepts of tribology

2.1 Historical aspects

Among the disciplines of engineering, tribology has the longest pedigree. More than 400,000 years ago, our hominid ancestors used friction when they chipped stone tools. Friction was essential when the Neanderthals by 200,000 B.C. succeeded in generating fire by rubbing wood on wood and by striking together flint stones. Early civilizations, like the Sumerian and Egyptian, discovered the usefulness of lubricants in improving the performance of chariots and in facilitating transport by sleds. Figure 1 shows a painting from the tomb of Tehuti-Hetep at El-Beshed dated at about 1880 B.C., where the Egyptian method of moving stone statues is illustrated. The painting shows that the statue is moved by means of a sled, without the aid of rollers or levers. A most interesting detail in the painting is a man standing and pouring lubricant from a jar onto the ground immediately in front of the sled [16].

![Figure 1: A painting from the tomb of Tehuti-Hetep at El-Beshed (dated about 1880 B.C.), illustrating the transportation of an Egyptian colossus.](image)

2.2 General aspects of friction

Friction is the resistance to motion during sliding or rolling that is experienced when a solid body moves tangentially over another with which it is in contact. The resistive tangential force, which acts in a direction directly opposite to the direction of motion is called the friction force. The coefficient of friction is the quotient obtained when the friction force is divided by the normal force acting on the contact. The measured value of the friction force or of the coefficient of friction is dependent not only on the materials per se but also on factors that are independent of the material, such as sliding speed, resting time and the environmental conditions. Therefore, friction is not a material property but a system response [15].

In view of the long history of problems associated with friction, one might think that friction is a simple and well-understood subject. However, nothing could be more wrong. The frictional forces acting between two macroscopic bodies are ultimately due to electromagnetic forces between electrons of different atoms at the contact interface. Thus, an exact treatment of the friction forces means that it is necessary to consider the impossible task of studying the coupling between all the electrons using quantum electronics, e.g. the complete Schrödinger equation for these particle systems. The concept of friction is a substitute for such a microscopic approach, where the frictional force acting on a block sliding on a substrate is usually considered to be a function only of the center of mass velocity of the block. If wear
processes are neglected, this means that friction arises from the transfer of translational kinetic energy into heat motion. These energy losses may be due to deformation of the contact during loading/unloading [14] or due to adhesion hysteresis [17].

Generally, effective equations of motion of particle systems can be formulated only by eliminating many degrees of freedom. However, the analytical solution of the problem of a block sliding on a solid substrate is very complicated and a systematic reduction in the degrees of freedom can only be performed approximately. The number of degrees of freedom decreases if the size of the studied system is reduced. Consequently, for sufficiently small systems, well-defined friction concepts can be elucidated [14].

2.2.1 Nanotribology
A fundamental understanding of adhesion and friction requires an understanding of the mechanisms on the atomic/molecular scale between the interactions of two materials when they are brought into contact and caused to slide with respect to each other. Due to surface roughness, contact between two macroscopic bodies occurs at many asperities and the importance of investigating single asperity contacts in friction studies has long been recognized. The recent emergence of nanoscale probing techniques, like the Atomic Force Microscope (AFM) or the Surface Force Apparatus (SFA), has for the first time opened the way towards systematic investigations of interfacial problems at the nanolevel [15].

2.2.2 Friction phenomena
Consider the case where a solid body, referred to as the sled, comes into contact with a surface and a normal load, \( N \), is applied on the sled. Next consider that a tangential force, \( F \), is applied on the sled. The value of the tangential force required to initiate relative motion is then the static friction force, \( F_s \). This is usually greater than the tangential force required to maintain relative motion at constant sliding speed, which is known as the kinetic friction force, \( F_k \). Figure 2 shows the typical development of the tangential force as a function of time for such a system [15].

![Figure 2: The development of the tangential force as a function of time required to initiate and to maintain relative movement between two solid bodies, where \( F_s \) is the static friction force and \( F_k \) is the kinetic friction force.](image-url)
Provided that neither the chemistry nor the structure of the surface changes during sliding, there is a general argument that the kinetic friction must be either equal to or lower than static friction. A paradoxical situation would otherwise occur if the kinetic friction were higher than the static friction and the magnitude of pulling force lay between that of the static and kinetic friction force: On the one hand sliding would be initiated because the pulling force exceeded the static friction force but on the other hand sliding would be hindered because the kinetic friction force exceeded the pulling force. The contradiction is inescapable and leads to the conclusion that the static friction cannot be lower than kinetic friction. [18].

Occasionally, the recorded development of the tangential force as a function of traversed distance (or time) may repeatedly rise and fall along the sliding path, as shown in figure 2. This behavior is called stick-slip friction and is the opposite to steady sliding, where the tangential force maintains a constant value over the traversed distance. A classic explanation of this phenomenon is that the static coefficient of friction is markedly larger than the kinetic coefficient of friction. However, the reasons behind stick-slip friction are generally attributed to elastic mechanisms by spring elements which store and release strain energy. Spring elements are present in virtually every aspect of the friction system: at the contact interface, at the force transducer and in the machine frame, to mention a few. Employing a stiff-machine concept when designing the friction-testing device may minimize the tendency for stick-slip behavior to occur [14,15].

2.3 The laws of friction

Two laws of friction are generally obeyed over a wide range of applications. These laws are often attributed to the French physicist Guillaume Amontons, who rediscovered them in 1699, although Leonardo da Vinci was the first to describe them about 200 years earlier. According to the first law, the friction force, \( F \) is proportional to the load,

\[
F = \mu W
\]

where the constant \( \mu \) is known as the coefficient of friction, which is independent of load. This law is violated when the substrate surfaces are lubricated or coated by oxide films with low shear strength. In these cases, a lubricant film or oxide film separates the substrate surfaces. The coefficient of friction is constantly low under low loads and increases to a higher level once a critical load is exceeded. This behavior is due to the collapse of the lubricant film or oxide film leading to more direct contact between the substrate surfaces and thus higher friction. [15].

The second law states that the friction force is independent of the apparent area of contact. This law may not be true for very soft materials, where the real contact is effectively the same as the apparent area of contact [15].

To these two laws, a third “law” is sometimes added. It states that friction is independent of the sliding speed and this law is not generally valid. The dependence of friction with sliding speed is not well understood and contradictory results are reported in the literature. It is often observed that the coefficient of friction decreases very slightly with increasing velocity. The shear rate, which is dependent on the sliding velocity, influences the mechanical properties of many materials, especially polymers. In most cases, the strength of the material increases at higher shear rates due to hardening. Consequently, the size of the real contact area decreases and this causes friction to decrease [15]. However, another theory predicts that for solid
surfaces the friction forces, $F$, should increase logarithmically with sliding velocities, viz. $F \sim \ln(v/v_0)$, where $v_0$ is the characteristic phonon velocity [19], which is also supported by data from AFM measurements [20,21].

### 2.4 The real area of contact

All surfaces of solid bodies are rough on an atomic scale. For nominally smooth surfaces the surface roughness manifests itself on different scales, on the micrometer scale, on the submicrometer scale and eventually at the atomic level. When two surfaces are brought into contact, the real area of contact is only a small fraction of the apparent area of contact, schematically shown in figure 3. This is because the surface roughness causes contact to occur only at discrete spots, sometimes referred to as junctions. The sum of the junction areas constitutes the real area of contact. The real area of contact is dependent on the surface texture, on the material properties and on the interfacial loading conditions. When two surfaces in contact move relative to each other, the friction force is contributed to the adhesion between the junctions and other sources of surface interactions. Upon loading, contact between the two surfaces will initially occur only at a few points to support the load. Due to the small size of the real contact area the stresses at the contact regions may exceed the yield strength of the material, and this will cause the surface to deform at the contact regions [22]. The mode of deformation is either elastic, elastic-plastic, viscoelastic or viscoplastic. As the normal load increases, a larger number of asperities on the two surfaces come into contact, and existing contact areas grow to support the load [15,20].

![Figure 3: Schematic representation of an interface, showing the apparent area of contact, $A_a$, and the real area of contact on a micrometer scale. The inset shows the details of a contact on a submicrometer scale.](image)

Thus, the problem of relating friction to the surface texture and to the material properties involves the determination of the real area of contact, and an understanding of the mechanics of the contact of solid bodies is essential to gain more fundamental knowledge about friction. Many theories to describe the mechanics of contacts between solid bodies exist, but no single theory holds for all conditions. These theories are the essence of a scientific field called contact mechanics.

### 2.5 Adhesion, surface energy and surface tension

The work of adhesion or surface energy is the free energy change, or reversible work done, to separate two different liquid or solid media 1 and 2 with given unit areas from contact to infinity in vacuum. If the two media are identical, the work is referred to as the work of cohesion. The surface energy or surface tension is the free energy change $\gamma$ when the surface
area of a medium is increased by unit area. For a medium 1, the change in free energy \( \gamma_1 \) due to creating unit area is equivalent to the work \( W_{11} \) required to separate two half-unit areas from contact [23]:

\[
\gamma_1 = 0.5W_{11}
\]  

(2)

When two unlike bodies 1 and 2 are brought together reversibly, the free energy change per unit area is the free change in energy of adhesion, \( \Delta G_{12}^a \), which equals the negative of the work of adhesion, \( W_{12} \) [24]. For this process

\[
\Delta G_{12}^a = \gamma_{12} - \gamma_1 - \gamma_2 = -W_{12}
\]

(3)

where \( \gamma_1 \) and \( \gamma_2 \) are the surface energies of the two separated media respectively and \( \gamma_{12} \) the free energy change in expanding the “interfacial” area between the two media by unit area. \( \gamma_{12} \) is also known as the interfacial energy or interfacial tension. For solids, the separation is irreversible and involves the dissipation of heat.

Adhesion occurs when two bodies are pressed together, either under a normal load or under combined normal and shear forces. It involves chemical interactions, for example covalent bonds, electrostatic bonds, metallic bonds and hydrogen bonds, as well as physical interactions, like van der Waals forces. Generally, the physical interactions are much weaker than the chemical interactions. Adhesive forces act only at the areas of real contact between two bodies. Adhesion significantly increases if a shear displacement is added to the normal load, due to the induction of plastic flow which causes a dramatic increase in the real contact area. Surface contaminants, like films of hydrocarbons, generally reduce adhesive strength [23]. For friction, adhesion plays an important role because it influences the shear strength of the contacts and the size of the contact area [25].

2.5.1 Capillary condensation

Under ambient conditions, water vapor spontaneously condenses around contact sites between hydrophilic surfaces, and water menisci are formed [23]. The Laplace pressure, \( P \), in such a meniscus pulls the contacting surfaces together and contributes to the total adhesion force. (This is the primary force acting in the creation and consolidation of paper.) \( F_{Lap} \), the force due to Laplace pressure, acting between a sphere of radius \( R \) and a flat surface is

\[
F_{Lap} \approx -4\pi \gamma_w R \cos \theta_w ,
\]

(4)

where \( \gamma_w \) is the surface tension of water and \( \theta_w \) its contact angle on the surface. (In this text, we adopt the convention that attractive forces are negative and repulsive forces positive.) Equation 4 is valid only if the liquid forms the same contact angle on the sphere and on the surface. If water forms different contact angles, \( F_{Lap} \) can be expressed as [26]:

\[
F_{Lap} \approx -2\pi \gamma_w (\cos \theta_{1,w} + \cos \theta_{2,w}) ,
\]

(5)

where \( \theta_{1,w} \) and \( \theta_{2,w} \) are the contact angles on the two surfaces.

The phenomenon of capillary condensation is utilized in nanolithography, which enables surfaces to be patterned with molecules on the nanoscale. AFM tips are impregnated with the compound to be deployed and the compound molecules are delivered to the surface via
capillary transport as the tip is scanned over a surface [27]. Capillary forces dramatically change the properties of granular media. For example, the attractive forces between grains of sand increase if the sand gets wet. This is the reason why sand castles can only be built with wet sand rather than dry sand [28].

2.6 Adhesion and friction
When a solid body comes into contact with a surface the friction force $F$ that develops due to relative movement is the sum of the individual friction forces $f_i$ developing at the junctions. The individual friction force acting at a junction may be considered to be equal to the product of the contact area $a_i$ of the junction and the shear strength $\tau_i$ of the junction. The friction force is then expressed as

$$F = \sum_{i=1}^{n} f_i = \sum_{i=1}^{n} a_i \tau_i$$  \hspace{1cm} (6)

The sum of the individual contact areas constitutes the area of real contact, $A_r$. By replacing the $\tau_i$ with the average shear strength of the junctions, $\tau$, equation 4 can be re-written as

$$F = A_r \tau$$  \hspace{1cm} (7)

In the simplest attempt to incorporate the concept of adhesion to the theory of friction, the friction force is assumed to originate only from adhesive forces and defined as follows [22]:

$$F_a = A_r \tau_a$$  \hspace{1cm} (8)

where $F_a$ is the friction force, $A_r$ is the area of real contact and $\tau_a$ is the average shear strength per unit area of the dry contacts. In the case of contact with a liquid film (for example a lubricant) partially covering the surface, $F_a$ may be calculated from

$$F_a = A_r \left[ \alpha \tau_a + (1-\alpha) \tau_i \right]$$  \hspace{1cm} (9)

where $\alpha$ is the fraction of the real contact area that is not covered by the film and $\tau_i$ is the shear strength of the lubricant film, which is governed by the viscosity and thickness of the fluid film. If the normal load is considered to be equal to the product of the real contact area and the mean real pressure, $p_r$, the coefficient of friction is for dry contacts then given by

$$\mu_a = \frac{F_a}{W} = \frac{A_r \tau_a}{A_r p_r} \hspace{1cm} (10a)$$

$$= \frac{\tau_a}{p_r} \hspace{1cm} (10b)$$

These formulae are however based on very rough approximations and other friction sources like deformation processes or contact area growth have been neglected [15].
2.7 The friction of viscoelastic materials

Paper is a viscoelastic material, which means that it is subject to elastic and viscous (time-dependent) deformations upon loading. The frictional properties of viscoelastic materials are different from those of other materials. The inherent coefficient, $\mu_i$ of friction may be regarded as consisting of two components, the coefficient of friction related to the force needed to shear adhered junctions, $\mu_a$, and the coefficient of friction related to the force needed to supply the energy of deformation, $\mu_d$:

$$\mu_i = \mu_a + \mu_d$$ (11)

In viscoelastic materials, $\mu_d$ may give a significant contribution to $\mu_i$. The deformation forces arise from elastic hysteresis losses [22]. Two types of deformation can occur during sliding: Firstly, microscopic interactions, which account for plastic deformation and displacement of interlocking surface asperities, and secondly, the macroscopic interactions that arise from ploughing induced by surface asperities especially when the surfaces are of different hardnesses [15].

2.8 Lubrication

The friction between two clean solid bodies may be very high and it can be decreased by lubrication. The material that lowers the friction between two solid bodies is called a lubricant. Lubricants can be divided into solid lubricants, usually powders or thin films on a surface, and liquid lubricants. The term solid lubricant embraces a wide range of materials that provide low friction and wear. Solid lubricants are added to fluid lubricants for those applications where sliding contact occurs, for example during start-up processes under high loads or low sliding speeds. These lubricants are also referred to as boundary lubricants. Fluid lubrication can be achieved by liquids or even gases, as in the case of a stream of air that is used to separate paper sheets in feeding operations in copy machines or printers [15].

2.8.1 Hydrodynamic lubrication

Hydrodynamic lubrication is also known as fluid-film lubrication or thick-film lubrication. The principle of hydrodynamic lubrication is that a thin layer of fluid is compressed between the surfaces. The hydrodynamic pressure created by the film is sufficient to support the load, and thus prevents direct contact between the surfaces. The foundation of fluid film lubrication theory is given by the Reynolds equation. This equation establishes a relation between the geometry of the surfaces, relative sliding velocity, the properties of the fluid and the normal load [15].

The coefficient of friction in the hydrodynamic regime can be up to three decades smaller than in the unlubricated case. The frictional properties arise purely from the shearing of the lubricant fluid, which is governed by the bulk physical properties of the fluid, notably its viscosity [29].

2.8.2 Boundary lubrication

Boundary lubrication occurs when the normal load is increased and the relative speed is decreased so that the film between the two surfaces becomes thinner leading to a greater degree of contact between the surfaces. Under these conditions, the bulk properties of the lubricant are relatively unimportant, and the friction is dependent on the physical and
chemical interactions of the lubricant with the solid bodies. The lubricating compound comprises an active head-group that attaches to the surface and an inert tail that does not interact with the surface. In boundary lubrication, the lubricant molecules form a monomolecular layer on each surface. Figure 4 shows a diagram of two surfaces that are lubricated by boundary lubrication. Depending on the normal load applied, the surfaces are at least partly separated by the film molecules, although the film gradually breaks down and is worn away. Due to the normal and lateral stresses, the lubricant molecules migrate from the high-load regions to regions where the normal stress is lower. Sliding of the film may initiate an orientation of the film molecules so that their tails point in the direction opposite to the movement [15,18].

![Figure 4: Schematic view of boundary lubrication, where two surfaces are separated by two monomolecular layers of a lubricant. The lubricant molecules are drawn as black circles with a straight tail, representing the active head-group that attaches to the surface and the inert tail respectively. Sliding of the film may initiate an orientation of the film molecules so that their tails point in the direction opposite to the movement.](image)

The boundary films can be formed by physical adsorption, chemical adsorption or chemical reaction. Generally, the ductility of the films increases in this order. A physisorbed film can be either monomolecular or multimolecular, whereas a chemisorbed film is monomolecular [15].

The efficiency of a boundary lubricant is dependent on its shape and the degree of interaction between its molecules and the substrate surface. The criterion for efficient boundary lubrication may be stated as follows: The substrate surface should have a high surface energy, so that there will be a strong tendency for the lubricant molecules to adsorb onto the surface. The substrate surface should be readily wettable by the lubricant molecule, so that it can spread and form a monomolecular film and the lubricant molecule should be comprised of an active group that can adsorb onto the substrate and inert tail. The interactions between the lubricant and the substrate should be strong to maintain good stability of the film under normal and lateral stresses. The lubrication effect then arises from the fact that the shear strength between the two monomolecular films is much lower than that between the clean substrate surfaces. The reason why alkanes are ineffective boundary lubricants is because they lack an interacting head-group and are thus completely inert. Ring molecules or branched molecules tend to be poorer boundary lubricants than straight-chain molecules, because steric hindrance prevents the formation of densely packed monomolecular films [15,18].

Figure 5 shows the effect of the chain length of saturated fatty acids adsorbed on a glass surface on the friction between the glass surface and a stainless steel surface [30]. Here, the coefficient of friction is plotted against the number of carbon atoms in the carbon chain of the fatty acid. It can be seen that the coefficient of friction decreases linearly at the beginning of
the curve. Those fatty acids with 14 or more carbon atoms in the carbon chain lower the friction coefficient to a constant low level and no further decrease in the friction coefficient is observed after this point.

Figure 5: The effect of the chain length of saturated fatty acids adsorbed on a glass surface on the friction coefficient against stainless steel [30].

Boundary lubricants such as fatty acids form vertically oriented monolayers on a substrate surface, where the molecules may be slightly tilted with respect to the surface. The tendency to form such layers and their stability increases with increasing chain length of the fatty acid due to a stronger cohesion between the chains. The results shown in figure 5 suggest that monolayers composed of fatty acids with chain lengths below 12 carbon atoms behave as liquids and have a poor durability during shearing. Those with chain lengths of 12-15 carbon atoms behave like a plastic solid with medium durability. The monolayers composed of fatty acids with chain lengths above 15 carbon atoms behave as solid crystals and have a high durability [30].

2.9 Friction-testing devices in tribology

A large number of different testing devices exist to measure the friction between different materials. The testing devices are designed to simulate the conditions of wear and friction for the particular application of interest. A complete survey of the different principles regarding these devices is beyond the scope of this thesis. Therefore, this section is devoted to a presentation of two of the most common test principles for the measurement of friction [29].

2.9.1 The horizontal-plane principle

Many friction testers are based on the horizontal-plane principle, which is schematically shown in figure 6. The basic principle of this type of friction tester is that a solid rests on another solid in a horizontal plane and that the force required to initiate or to maintain horizontal motion is recorded. This force may be a pulling force, as illustrated in figure 6, or a pushing force. Every friction system has elastic properties, which originate from for example the contact interface, the force transducer and the machine frame. In figure 6, the elastic properties are represented by the spring constant, k.
Figure 6: A diagram of a friction tester based on the horizontal-plane principle. A solid of mass M is resting on another solid body in a horizontal plane and exerts the normal force, \( N = Mg \), on the body, where g is the gravitational constant. In friction measurements the force required to initiate or to maintain horizontal motion is recorded. The elastic properties of the friction system are represented by the spring constant, k.

2.9.2 The inclined plane principle
The most primitive friction-testing device is based on determining the angle at which a solid body resting on an inclined plane begins to slide when the inclination angle, \( \theta \), is slowly increased. Only the static coefficient of friction can be determined by this method [14]. Figure 7 shows the force equilibrium for this system. The normal force, projected to the inclined plane is \( Mg \cos \theta \), where \( M \) is the mass of the body, \( \theta \) is the angle of inclination and g is the gravitational constant.

Figure 7: The force equilibrium for a solid body of mass M resting on an inclined plane at an angle of inclination \( \theta \). The body exerts a force N on the plane where g is the gravitational constant.

At the sliding angle, \( \theta_s \), the tangential pulling force, \( Mg \sin \theta_s \), is equal to (or in practice slightly exceeds) the static friction force and the static coefficient of friction, \( \mu_s \), can be calculated according to

\[
\mu_s = \frac{Mg \sin \theta_s}{Mg \cos \theta_s} = \tan \theta_s
\]

(12)

This test method has been very popular for the measurement of paper-to-paper friction in the paper industry. It should be mentioned, however, that it is very inaccurate and has poor reproducibility. The main reasons for the poor performance can be attributed to the low degree of controllability during testing, regarding the resting time, sliding speed and the rotation of the sled during the friction test [8].
3. The components of paper

3.1 The components of wood fibres
The wood fibres that comprise the paper are composite materials that consist mainly of polymeric matter, viz.: cellulose, hemicellulose and lignin. A myriad of lipophilic low-molecular-weight compounds that can be removed by extraction also exist in the tree. These lipophilic compounds are therefore referred to as wood extractives. The relative amounts of these components vary between different tree species and also within a tree species. Norway spruce (*picea abies*), for example contains about 42% cellulose, 28% hemicellulose, 27% lignin and about 2% extractives [31].

Figure 8 shows an image captured by environmental scanning electron microscopy (ESEM) of a surface of an uncoated paper grade, in this case a liner. This grade of paper comprises the outermost layer of cartonboard. The figure illustrates that paper is not a homogenous material and that the paper surface is very rough on the micrometer-scale.

![Figure 8](image)

Figure 8: A typical surface of an uncoated paper grade, in this case a liner. The image was captured by environmental scanning electron microscopy (ESEM).

3.2 Lipophilic compounds in pulp and paper
Wood extractives or wood resins are terms used for low-molecular-mass lipophilic compounds (LCC) in wood, pulp and paper. These components can be classified into different groups according to their different chemical structures, morphological occurrences and biological functions in the tree. Extractives from both softwood and hardwood consist mainly of fats and waxes present in the parenchyma cells. Resin channels in softwood also contain resin acids. During pulping and bleaching, fats are partly hydrolyzed to free fatty acids [31].

When recycled fibres are the fibre source for papermaking, the lipophilic constituent may also include substances picked up during the life cycle, notably metal soaps, binders, ink oils, waxes, adhesives, rubbers, styrenes, acrylates and polyethylenes [32]. The metal soaps are insoluble in water and precipitate as solid metal salts onto the fibre [33,34] and may incorporate other lipophilic compounds [35].
4. The friction between paper surfaces

Different grades of paper exhibit very different frictional behaviors, which are not always in accordance with the requirements for the specific paper grade. Therefore it is important to understand the fundamental reasons behind the differences in friction between different papers.

Many theories have been put forward to describe the origin of the friction between paper surfaces. Bayer and Sirico followed the ideas of Bowden and Tabor and suggested that the coefficient of friction between paper surfaces includes an adhesion component and a deformation component. Bayer and Sirico treated the deformation component as arising predominantly from abrasion rather than from adhesion hysteresis [36]. Back considered that the cohesion of the fiber network and the local deformations around the area of surface contact determine the frictional properties of paper, and he dismissed the suggestion that the surface energy was the only significant influence on static friction [1]. Borch, in contrast, maintained that interfacial adhesion controls friction [3]. Inoue et al. found that a smooth paper surface has a higher friction than a rough surface, suggesting that adhesion rather than interlocking of surface asperities is the dominant mechanism [37]. Fellers et al. propose that friction is essentially independent of the macroscopic surface roughness of the paper sheet, but that it is dependent on the “micro-roughness” of the contact areas together with the intermolecular interactions between the contact areas [10]. Heslot et al. show that paper-to-paper friction is affected by the dynamics of the system [13]. They studied the effect of contact time, sliding velocity and machine stiffness on the coefficient of friction between two sheets of cartonboard. The results showed that the static coefficient of friction increases logarithmically with increasing contact time and that the kinetic coefficient of friction passes through a minimum when plotted against the sliding velocity. The results obtained in his study are in accordance with the results of friction trials with entirely different materials [38]. Heslot et al. conclude that low-velocity friction dynamics obeys quite general laws whose functional form is independent of the material.

4.1 The decrease in friction with consecutive slides

Many uncoated paper grades exhibit a frictional behavior that is rarely observed for other materials. When paper are cause to slide against paper the friction decreases with consecutive slides in the same direction. [1,8,39]. The decrease in paper-to-paper friction has been associated with progressive damage to the paper surface, such as ruptured fiber bonds and the creation of surface debris [39]. In another study however, no surface debris could be collected [1]. It has also been observed that paper maintains a high level of friction when the sliding direction is reversed after each slide [8]. An explanation based on the orientation of structural elements has been suggested [8] but a deeper understanding for this phenomenon has been lacking. This frictional behavior is discussed in the study described in paper I.

4.2 The influence of low-molecular-mass lipophilic compounds on paper friction

Paper-to-paper friction is strongly influenced by the presence of low-molecular-mass lipophilic compounds, such as wood extractives and surface contaminants [11]. Nevertheless only a few studies have described how these compounds influence paper friction [1,9,11], (papers II-IV).
The mechanism by which lipophilic compounds affect friction is not well understood. The effect of extractives and contaminants on the paper friction has in some investigations been partly attributed to the fact that they modify the surface free energy of the paper [1,9,11]. In other studies, no correlation was found between the paper-paper-friction of different paper grades and the surface energy characterized by contact angle measurements [40]. Several authors propose a mechanism for the lubrication of paper surfaces by low-molecular-mass lipophilic compounds that is closely related to boundary lubrication [1,11], (paper II).

5. Methodology

In this section the materials and methods employed in the work described in this thesis and the principles of the tools used for physical and chemical characterization are outlined.

5.1 Friction testers

Since friction is not fundamentally a material property but is rather to be seen as a system response, the value obtained for the friction of paper is dependent on many material-independent factors, such as the measurement conditions [8] and the dynamics of the measurements [13]. In this investigation great effort was therefore devoted to maintaining these factors as constant as possible so that the friction could be measured under controlled and reproducible conditions. This was achieved by using highly automated friction testers, which allowed a high degree of control regarding the resting time, sliding speed and sled movement. In this way, the measured differences in friction could indeed be attributed to differences between the papers.

The friction tester used in the studies described in paper II was an in-house customized device. A description of this apparatus is given by Johansson et al. [8]. In the other studies on paper friction (papers II, III and V) an “Amontons II” from Mu measurements (USA) was employed. The Amontons II is based on the design elements of the in-house customized device but has been improved regarding friction force sensing and rigidity. Both friction testers are based on the horizontal-plane principle, which means that one surface is moved relative to the other on a horizontal plane. They are designed to meet the standards required for reproducible and accurate friction measurements on paper, according to ISO 15359 [41]. Prior to the friction measurements, the test sheets were conditioned for 18-21 hours at 23°C and 50% RH and thereafter cut to test pieces (165 x 60 mm) in a special cutting device that allows contact-free handling of the test areas of the papers [8]. On each sample, three slidings were performed, yielding six friction coefficients. However, only the first static coefficient of friction (S1), the third static coefficient of friction (S3) and the third kinetic coefficient of friction (K3) are reported. These have been found to be the most important friction coefficients for the characterization of paper surfaces [8].

A diagram of the Amontons II is shown in figure 9. The Amontons II consists of a table that moves along its length axis and a sled that is kept in position by sensitive plates when the table moves. A clip fixes the paper test strip on a rubber surface that is mounted on the table. The other test strip is mounted on the lower side of the sled by means of a clamping device (not shown in the figure). At the beginning of a measurement the sled is lowered mechanically (not shown in the figure) until it rests freely on the test surface.
Figure 9: A diagram of the friction tester, Amontons II. Due to the friction force the sled tends to move along with the table but it is held back by two sensitive plates that are coupled to stiff load cells. The friction force is determined by measuring the deflection of the sensitive plates.

The coefficients of friction were calculated by dividing the friction force by the weight of the sled. Figure 10 shows, as an example, the static and kinetic coefficients of friction between two sheets of filter paper during the first, second and third slides in the same direction, where the coefficients of friction are plotted against time. During the first four seconds the table moves at a speed of 60 µm/s and a friction force is slowly built up causing the coefficient of friction to increase. The peak value during this period is defined as the static coefficient of friction. After four seconds, the table accelerates to a constant speed of 20 mm/s and friction drops to a lower level. The kinetic coefficient of friction is evaluated from the mean force between 40 and 60 mm of the traversed slide path.

Figure 10: The coefficients of friction of clean filter paper is plotted against running time. Data from the first, second and third slides over the same track and the values taken for the static and the kinetic coefficients of friction are shown. The development of the coefficient of friction with increasing number of slides is indicated by an arrow.
The decrease in friction with the number of consecutive slides can be clearly seen in figure 10. Occasionally, stick-slip behavior was observed during a friction measurement, especially for low-friction surfaces. This behavior was attributed to spring elements in the soft rubber on top of the table. The rubber was however essential to minimize buckling of the paper, which could otherwise give rise to uncontrollable contributions to the friction force.

It was observed, that for the same paper grades, the values of the friction coefficients obtained from the in-house customized device were about 30% lower than those give by the Amontons II. Nevertheless, the accuracy and reproducibility were good for both friction testers with 95% confidence limits varying between 1% and 3% of the average value. The performance of the load cells of the devices was checked by force calibration and no operational flaws were detected. The results of Johansson et al. may explain the difference in the obtained friction values [8]. They report that the harder the backing under the paper strip on the table, the higher are the coefficients of friction. Therefore the discrepancy in the friction data obtained in this work may be attributed to the fact that the material properties of the rubber layer may have changed during time. This means that the friction values reported in paper II cannot be compared to those reported in papers I, III and IV.

5.2 Measurement of fiber rising tendency

The paper samples in the study described in paper I were tested with respect to fiber rising tendency, i.e. the total area of fibers at the surface that had the ability to rise out of the plane of the surface, using a Fibro 1000 by Fibro system AB (Sweden) [42]. Figure 11 shows the principle of the device. A paper test piece is mounted on a conveyor belt and moves over the edge of a metal blade. At the curvature, the fiber ends point out of the plane of the paper surface and an image along a 4 mm long line is captured by a CCD camera every 0.3 mm in the moving direction. The result is given as the projected area of the fibers on the monitor in mm² per unit width of the test piece.

![Figure 11](image)

Figure 11: The principle of measuring the fiber rising tendency with the Fibro 1000. A paper test strip moves over the edge of a metal blade. At the point of curvature, the fiber ends point out of the plane of the paper surface and an image is captured by a CCD camera for subsequent analysis.

5.3 Environmental Scanning Electron Microscopy (ESEM)

In the studies described in papers I and IV, paper samples were imaged using an Environmental Scanning Electron Microscope (ESEM) model 2020 from Electroscan/Philips. ESEM enables samples to be imaged at high magnifications and high resolution under ambient conditions without the need for sample preparation. In an electron microscope, an electron beam is focused onto a specimen by an electromagnetic condenser lens and scanned
over the surface. The interaction between primary beam electrons and the specimen generates secondary electrons, which are used for topographic imaging. As the beam moves from point to point, the signal strength of the secondary electrons varies. These differences are due to different path lengths that have their origin in the topography of the specimen. [43].

5.4 Impregnation of filter papers
In the studies presented in papers II and III, filter papers based on cotton cellulose (“filter paper 00H” from Munktell AB, Sweden) were impregnated with low-molecular-mass lipophilic compounds to study their effect on paper-to-paper friction. The compounds were dissolved in organic solvents and the solution was then poured into glass basins. The filter papers were impregnated by dipping them into the solution, where they were kept for 60 seconds. Thereafter they were withdrawn from the solution and dried on plates under restraint. Friction was measured on the top side of the papers, i.e. the side that was not in contact with the plates.

The model compounds used in the investigation described in paper II were different wood extractives representing major components in wood resin. The model compounds were various fatty acids, fatty alcohols, alkanes, resin acids, sterols, triglycerides and betulin. The model compounds used in the investigation described in paper III were magnesium salts of different fatty acids and abietic acid. These lipophilic acids have much higher vapor pressures when they are present as salts instead of free acids so that the atomic composition of adsorbed layers of these compounds can be studied with vacuum techniques, such as XPS (see section 5.7).

5.5 Quantification of low-molecular-mass lipophilic compounds in paper
The amount of low-molecular-mass lipophilic compounds (LLC) in a paper was determined by extraction and quantification of the extracted compounds by gas chromatography-mass spectrometry (GC-MS) and ion chromatography (IC).

5.5.1 Extraction of paper
The removal of LLC from paper samples, (papers III and IV) was achieved by solvent extraction. Two different extraction devices, a SoxTec™ and a Soxhlet extractor, were employed. These devices are both based on the regeneration of fresh solvent by reflux. The SoxTec™ apparatus used was a SoxTec™ System 2 HT2 extractor from Foss AB (Sweden), which is schematically shown in figure 12. This apparatus works in two modes, where the extraction is performed by keeping the sample, placed in a porous cellulose extraction socket, in a beaker filled with the solvent. A heater keeps the solvent at its boiling temperature so that extraction is achieved at elevated temperatures. The extraction socket is attached to a steel rod. Solvent vapor condenses at a cooler that is placed on top of the extractor, and drops of fresh solvent are guided to the rod and roll down into the extraction socket. Rinsing of the sample is achieved in the other mode, where the extraction socket is lifted above the level of the extract. Drops of solvent then continue to roll down the rod, through the socket and into the beaker [44].
Figure 12: A diagram of the SoxTec™ System 2 HT2 extractor showing its two work modes, the extraction mode (mode A) and the rinsing mode (mode B).

The traditional Soxhlet extractor consists of a specially shaped glass tube divided into several sections that are connected via an arrangement of pipes, as illustrated in figure 13. The solvent/extract is placed in a round flask and placed at its boiling point by means of a heater. Solvent vapor is led to the extraction chamber, which also contains the sample. The vapor condenses in a cooler on the top of the extractor and the solvent drops slowly fill the extraction chamber, so that a cold extraction of the sample is achieved. The extract runs from the bottom of the extraction chamber into a small U-shaped pipe. New extract continuously fills the U-shaped pipe until it is siphoned over into the round flask at the bottom, whereafter a new sequence starts. In this way the sample is extracted and rinsed in batches as long as the solvent is refluxed in the system [45].

Figure 13: A diagram of the Soxhlet extractor. It is a specially shaped glass tube divided into several sections that are connected via an arrangement of pipes. Regenerated solvent fills the extraction chamber up to a certain level, whereafter the solvent/extract is siphoned over into a round-bottomed flask at the bottom.
5.5.2 GC-MS analysis

In the studies described in papers III and IV the low-molecular-mass lipophilic compounds extracted from the paper samples were quantified by GC-MS, where a gas chromatograph (GC) is interfaced with a mass spectrometer (MS). Gas chromatography is the technique of choice for the separation of thermally stable and volatile organic and inorganic compounds. Sometimes the compounds in the sample must be derivatised in order to improve their volatility. This can be done by silylating active hydrogens in the polar groups of the compounds, a technique commonly used for the analysis of fatty acids and fatty alcohols. The principle of gas chromatography is to separate the compounds in the sample in a long column, called the stationary phase, while they pass through the column with the help of a carrier gas, called the mobile phase. The compounds have different affinities for the mobile and the stationary phases, and this separates them from each other when they travel through the column. Many different techniques are available for identification of the separated compounds. The detector of choice is the mass spectrometer because it enables both a qualitative and a quantitative analysis of the separated compounds. The mass spectrometer produces charged particles that consist of the parent ion and ionic fragments of the original molecule, and it sorts these ions according to their mass-to-charge ratio [46].

For the GC-MS-analysis, a Hewlett Packard 5890 Series II gas chromatograph interfaced with a Hewlett Packard 5989 B mass spectrometer was used.

5.5.3 Ion Chromatography

In the study described in paper III, the extracts from impregnated paper samples were analyzed by ion chromatography (IC) using a Dionex ED/GP 40 equipped with an Ion Pac AS11-HC column interfaced with a Dionex ED-40 electrochemical detector. IC is a method of separating ions based upon ion-exchange resins. The ions are pumped through a column containing the resin and ions with different affinities to the ionic groups of the resin are separated before they pass the detector. The detection system is based on the measurement of electrolytical conductance [47].

5.6 Contact angle and surface energy measurements

Different liquids that were deposited on impregnated filter papers (paper III) and impregnated cellulose films (paper V) and their contact angles were measured to characterize the surface chemistry and to determine the surface energy, respectively.

Work must be done to create any new surface. The surface tension, \(\gamma\), is the work required to increase the surface area by 1cm\(^2\). In the case of a liquid, the surface tension is numerically equal to the surface energy. In this context the term surface energy will be used, except when forces are discussed in which case the term surface tension will be used. In contrast to a liquid surface, the surface energy of solids, denoted here \(\gamma_{sv}\) or \(\gamma_s\), can only be estimated indirectly. This is done by determining the contact angle formed by liquid droplets on the surface of the solid. The force balance for such a system is described by Young’s equation:

\[
\gamma_{sv} = \gamma_{sl} + \gamma_l \cos \theta
\]  \(\text{(13)}\)

where \(\gamma_{sv}\) is the surface tension of the solid-vapor interface, \(\gamma_{sl}\) is that of the solid-liquid interface, \(\gamma_l\) is that of the liquid-vapor interface and \(\theta\) is the contact angle between the droplet and surface of the solid. The force balance is schematically described in figure 14.
Figure 14: The force balance of a drop of liquid on the surface of a solid body, where $\gamma_{sv}$ is the surface tension of the solid-vapor interface, $\gamma_{sl}$ that of the solid-liquid interface and $\gamma_{lv}$ that of the liquid-vapor interface, and $\theta$ is the contact angle between the droplet and the surface of the solid. The force component of $\gamma_{lv}$ that is pointing perpendicularly out of the surface, $\gamma_{lv}\sin\theta$, is balanced by the forces in the strain field of the solid (not shown in the figure).

Combination of equations (3) (section 2.5) and (13), yields the Young-Dupré equation, which relates the work of adhesion to $\gamma_{lv}$ and the contact angle:

\[
W_{sl} = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} = \gamma_{sl} + \gamma_{lv}\cos\theta + \gamma_{lv} - \gamma_{sl} = \gamma_{lv}(1 + \cos\theta)
\]  

(14)

According to the combining rule, the free energy of adhesion, $\Delta G^a$ of any interface is equal to the geometric mean of the free energies of cohesion of the separate phases, $\Delta G^c$. For a system where an apolar liquid droplet rests on the surface of an apolar solid, this rule is formulated as

\[
\Delta G_{sl}^a = \sqrt{\Delta G_{sl}^c \Delta G_{sl}^c}
\]  

(15)

which, by using equations (2) and (3) (section 2.5), can be rewritten as

\[
W_{sl} = 2\sqrt{\gamma_s \gamma_l}
\]  

(16)

where $W_{sl}$ is the work of adhesion, and $\gamma_s$ and $\gamma_l$ are the surface energies of the solid and of the liquid, respectively. For analogous systems where either the liquid or the solid or both are polar, the surface tension of the liquid can be divided into three components: a dispersive component, an acid-component and a base-component.

In a similar manner, the surface energy of polar surfaces can be divided into a dispersive component, an acid-component and a base-component:

\[
\gamma_s = \gamma_s^d + 2\sqrt{\gamma_s^+ \gamma_s^-}
\]  

(17)

where $\gamma_s$ is the total surface energy, $\gamma_s^d$ its dispersive component, $\gamma_s^+$ its acid-component, and $\gamma_s^-$ its base-component. The combining rule is then expressed as
\[ W_d = 2\left( \sqrt{\gamma_{ls} \gamma_{ls}^d} + \sqrt{\gamma_{ls} \gamma_{ls}^i} + \sqrt{\gamma_{ls} \gamma_{ls}^b} \right) \]  

where \( \gamma_d \) stands for the dispersive component, \( \gamma^+ \) for the acid-component and \( \gamma^- \) for the base-component. The surface tension components of the liquid are denoted by \( \gamma_l \) and the surface energy components of the surface are denoted by \( \gamma_s \). Thus, by combining equations (14) and (17) an expression is obtained that relates the free energy of the liquid in equilibrium with its vapor and the contact angle to the dispersive and polar contributions to the adhesion across the liquid-solid interface. If the contact angles of three suitable liquids on the surface of a given solid are measured a set of three equations can be formulated, which enables the surface energy of the solid to be determined in terms of its dispersive component, \( \gamma_s^d \), acid-component, \( \gamma_s^+ \) and base-component, \( \gamma_s^- \): 

\[ \begin{align*}
\gamma_{h1}(1 + \cos \theta_1) &= 2\left( \sqrt{\gamma_{ls} \gamma_{ls}^d} + \sqrt{\gamma_{ls} \gamma_{ls}^i} + \sqrt{\gamma_{ls} \gamma_{ls}^b} \right) \\
\gamma_{h2}(1 + \cos \theta_2) &= 2\left( \sqrt{\gamma_{ls} \gamma_{ls}^{i+}} + \sqrt{\gamma_{ls} \gamma_{ls}^i} + \sqrt{\gamma_{ls} \gamma_{ls}^b} \right) \\
\gamma_{h3}(1 + \cos \theta_3) &= 2\left( \sqrt{\gamma_{ls} \gamma_{ls}^{i+}} + \sqrt{\gamma_{ls} \gamma_{ls}^i} + \sqrt{\gamma_{ls} \gamma_{ls}^b} \right)
\end{align*} \]

where the numbers 1, 2 and 3 refer to the three different liquids. For each liquid, \( \gamma_{h1}, \gamma_{h2}, \gamma_{h3}^- \) and \( \gamma_l \) are known, and this means that the equation system can be solved with respect to the unknown variables, i.e. the surface energy components, \( \gamma_s^d, \gamma_s^+ \) and \( \gamma_s^- \) [24].

In the study described in paper IV the surface energies of regenerated cellulose films were determined by contact angle goniometry using water, ethylene glycol and diiodomethane. Contact angles were measured using a manual contact angle goniometer (Model 100-00-115/220 from Ramé-Hart, Inc., NJ). The value at five seconds after deposition of the droplet on a test surface was recorded. The surface energies were calculated according to equation (19). In the study described in paper III, equilibrium contact angles of diiodomethane deposited on the surface of impregnated filter papers was studied with a Dynamic Absorption Tester, Fibro DAT 11000 from Fibro Systems AB (Sweden). The instrument applies a liquid droplet to the surface while a high-speed video camera captures images as the droplet spreads and/or is adsorbed. Images of the droplet are automatically captured every 20 milliseconds and the saved images are evaluated by image analysis in terms of drop volume, height, the quotient between base diameter and base area and the contact angle.

### 5.7 X-Ray photoelectron spectroscopy

In the study described in paper III, X-ray photoelectron spectroscopy (XPS) was employed to characterize layers of low-molecular-mass lipophilic compounds deposited on filter papers. XPS is a powerful tool both for studying the electronic structure and bonding of molecules and for the surface analysis of solids. In XPS, the sample surface is irradiated by X-Ray photons and, as a result of the photoelectric effect, electrons contained in the material may be ejected if the energy of the incoming photons is greater then the binding energy holding the electrons within their orbitals. The electrons ejected have a relatively low kinetic energy and can only travel short distances in matter, and this means that XPS has a high surface sensitivity [48]. It also means that the electrons from the outermost atoms of the studied material are over-represented in the XPS spectrum. In XPS, inner shell electrons (1s electrons) and Auger electrons are detected.
Photoelectrons generated by a given element result in discrete peaks in the XPS spectrum. The position of each peak is dependent on to the chemical environment of the atom and this means that detailed information about the bonding of the atoms can be obtained from the shifts of the peaks. Figure 15 shows an XPS spectrum of clean filter paper based on cotton cellulose (area = 165 x 165 mm²), where the intensity of the detection signal (counts per second) is plotted against the binding energy of the emitted electrons (eV). The figure shows that the surface of clean filter paper contains mainly oxygen (O 1s) and carbon (C 1s). The high-resolution domain of the spectrum reveals that the C 1s peak consists of four overlapping peaks, each corresponding to a major bond type [49]. Peak C1 originates from carbon atoms bonded only to carbon or hydrogen atoms, referred to as aliphatic carbon, peak C2 originates from carbon atoms bonded to a single oxygen atom other than a carbonyl, peak C3 originates from carbon atoms bonded to two non-carbonyl oxygen atoms or to a single oxygen atom, and peak C4 originates from carbon atoms bonded to a carbonyl and a non-carbonyl oxygen atom. The overlapping carbon peaks are isolated by a mathematical deconvolution, or curve-fitting technique [50]. It can be seen that the C2 peak dominates in the spectrum of clean filter paper, which is expected because the carbons in cotton cellulose are bonded to either hydroxyl groups or single oxygen atoms. The C1s high-resolution domain of the XPS spectrum of filter paper impregnated with 4.5 µmoles/g paper of magnesium distearate is also shown in figure 15. (The adsorbed amount was determined by GC-MS analysis of the extract of the filter papers.) It can be seen that the ratios of the peak areas changed after impregnation and that the C1 peak became dominant. This is because aliphatic carbon is the main type of carbon in low-molecular-mass lipophilic compounds such as magnesium distearate.
Figure 15: XPS spectrum of clean filter paper based on cotton cellulose, where the intensity of the detection signal (counts per second) is plotted against the binding energy of emitted electrons (eV). Both the low-resolution domain of the entire spectrum and the high-resolution domain of the C1s peak are shown. The C1s peak consists of four overlapping peaks, indicated by arabic numerals. Peak C1 originates from the carbon atoms bonded only to carbon or hydrogen atoms, referred to as aliphatic carbon, peak C2 originates from carbon atoms bonded to a single oxygen atom other than a carbonyl, peak C3 originates from carbon atoms bonded to two non-carbonyl oxygen atoms or to a single oxygen atom, and peak C4 originates from carbon atoms bonded to a carbonyl and a non-carbonyl oxygen atom. The C1s high-resolution domain of the XPS spectrum of filter paper impregnated with magnesium distearate is also shown.

In the study described in paper III, an AXIS 165 from KRATOS/Shimadzu Corp. (Japan) was employed to characterize layers of low-molecular-mass lipophilic compounds that were deposited on the surface of filter papers. A qualitative value for the thickness of a layer was developed by calculating the ratio of the area of the C1 peak to that of the sum of the carbon and oxygen peaks, C1/(C+O).
5.8 Atomic force microscopy (AFM)

In the study described in paper IV, a Nanoscope III™ atomic force microscope (AFM) from Digital Instruments was employed to measure the adhesion and the friction between regenerated cellulose films and functionalized AFM tips. Figure 16 shows the principle of the AFM. The system consists of two components: (1) a piezoelectric scanner on which the substrate surface is mounted that moves in the X-, Y- and Z-directions and (2) a detection system which measures the interaction between the surface and a tip that is mounted on the lower side at the end of a cantilever. The detection system consists of a laser which generates a beam of light that is reflected from the cantilever into a photosensitive detector (PSD). The PSD is divided into four segments, labeled A-D in figure 16. The position of the spot is determined by a circuit which generates a voltage from the photodiode segments. When the cantilever is in its equilibrium position, the laser spot is positioned at the intersection of the PSD segments and any change in the signal intensity between the PSD segments is interpreted as a cantilever deflection. The cantilever may vertically deflect due to topographic features on the surface during an image scan or due to adhesion during normal force measurements. The deflection changes the vertical position of the laser spot on the PSD and yields a differential signal between its top elements (A+B) and its bottom elements (C+D). During friction measurements, the friction between the tip and the sample surface causes the cantilever to torque. This results in a change in the horizontal position of the laser spot on the PSD, yielding a differential signal between its left-hand elements (A+C) and its right-hand elements (B+D).

**Figure 16:** A diagram showing the principle of an atomic force microscope. Interactions between the sample and a tip mounted at the end of a cantilever cause the cantilever to deflect, and the deflection is recorded by monitoring changes in the location of a reflected laser spot on a photodetector. The cantilever is mounted on a chip (not shown in the figure) and forms an angle, $\phi$, with respect to the surface. A feedback loop maintains a constant normal load during topographic measurements and during friction measurements.
5.8.1 Topographic measurements
During topographic measurements, the surface is in contact with the tip and is scanned in the X- and Y-directions. Features on the sample surface vertically deflect the cantilever and cause the vertical position of the laser spot on the PSD to change. The position is read by a feedback loop (see figure 16), which generates a voltage that moves the scanner in the Z-direction to restore the spot to its original position. A topographic image of the sample is recorded by monitoring the changes in voltage of the scanner in the z-direction when the surface is scanned along its X- and Y-axes.

5.8.2 Adhesion measurements
The AFM also provides information about the surface forces acting between the tip and the sample surface. In adhesion measurements, the feedback loop is disabled and the scanner moves repeatedly up and down with respect to the cantilever. The surface forces cause the cantilever to vertically deflect. The magnitude of the adhesive force is determined by applying Hooke’s Law, i.e. by multiplying the deflection of the cantilever due to adhesion by its normal spring constant. Figure 17 shows the raw data from an adhesion measurement, called a “deflection-displacement curve”, where the normal deflection signal is plotted against the vertical displacement of the scanner. In this case, a hydroxyl-functionalized tip was brought into contact with a cellulose film. The figure shows several points, labeled A-E, which are typical for deflection-displacement curves. The measurement starts at point A, where the cantilever is not touching the surface. As the surface approaches the tip the attractive forces grow stronger. When the force gradient becomes higher than the normal spring stiffness of the cantilever, the tip jumps into contact [51]. This jump occurs at point B in figure 17, and the jump in this particular case is very small. After contact, the sample is moved further in the same direction and this causes the cantilever to deflect upwards. The slope of the line of the deflection-displacement curve in the constant compliance regime, which is marked by a rectangle in figure 17, is equal to the normal sensitivity of the PSD, and this converts the normal deflection of the cantilever from a voltage to a metric distance. This calibration should be carried out on a hard material, such as glass, to avoid contact deformation [52]. After loading the cantilever to a desired force (point C in figure 17), the movement of the piezo is reversed. Adhesion between tip and sample surface causes the cantilever to vertically bend until the elastic force that is built up in the cantilever equals the adhesion force (point D), after which the tip detaches from the surface (point E). The adhesion force can then be calculated according to

\[ F_N = k_{N,lev} \frac{\Delta U_N}{S_N}, \]

where \( k_{N,lev} \) is the normal spring constant of the cantilever, \( \Delta U_N \) is the vertical deflection signal during the pull-off of the tip from the surface, and \( S_N \) the normal sensitivity of the PSD.
Figure 17: The normal deflection signal of the cantilever plotted against the vertical displacement of the scanner. The sample, which is mounted on the scanner, is being moved towards the cantilever and back again. The figure also shows several points, labeled A-E, which are typical for deflection-displacement curves and the normal deflection of the cantilever at these points. (The deflections are exaggerated in the figure.) The constant compliance regime, in which the normal sensitivity, $S_N$, is determined, is marked by a square. The normal deflection voltage, $\Delta U_N$, during pull-off due to adhesion is also shown.

5.8.3 Lateral force measurements

In lateral force measurements, the feedback loop is activated and the surface to be studied is brought to contact with the AFM tip. The surface is moved laterally with respect to the cantilever, back and forth along a line. Friction causes the cantilever to twist laterally in the direction opposite to the scanning direction and this generates a torsion signal due to the difference in intensity between the right-hand and the left-hand elements of the PSD. In this way friction loops can be recorded, as in figure 18, where the torsion signal (V) is plotted against the lateral displacement of the sample. In this case, a hydroxyl-functionalized tip was brought into contact with a cellulose film. Figure 18 also shows the topographic profile of the scanned line. It can be seen that the topography of the surface contributes to the torsion signal. This artifact is due to the torsion of the cantilever when the tip encounters a step feature on the surface. The influence of topography on the torsion signal that is common to both scanning directions can be partly cancelled by calculating the average torsion signal, $\bar{\Delta U_T}$, based on the average torsion signals recorded during the trace, $\Delta U_T^+$, and retrace, $\Delta U_T^-$ [53], i.e.
\[ \Delta \hat{U}_T = \frac{\Delta \hat{U}_T^+ - \Delta \hat{U}_T^-}{2}. \]  

\[ F_L = \frac{k_{lv}}{h_{\text{eff}} S_{\text{lv}}} \Delta \hat{U}_T, \]  

\textbf{Figure 18:} A friction loop, where the torsion signal is plotted against the lateral displacement of the sample when the sample is being moved back and forth along a scanning line. The figure also shows a cross section of the cantilever and its torque during the trace and retrace. At the beginning of a measurement, the tip adheres to the sample surface and an elastic force is built up in the cantilever during the initial displacement that causes the cantilever torque to increase. When the elastic force equals the friction force, the surface starts to slide under the tip. During the scan, the average torsion signal during sliding, \( \Delta \hat{U}_T^+ \), is recorded. At the end of the run the slide direction is reversed, causing the torque angle to reverse and the average torsion signal during sliding, \( \Delta \hat{U}_T^- \), is recorded. The topographic profile of the scanned line is also shown in the figure. An example of the increase in torsion signal during trace and retrace due to a step feature on the surface along the scanning line is indicated with a broken line in the figure.

The average lateral force, \( F_L \), is given by
where \( k_{\Phi}^{lev} \) is the torsional spring constant of the cantilever, \( S_\Phi \) the torsional sensitivity of the PSD, \( \Delta \bar{U} \) the average torsion signal and \( h_{\text{eff}} \) the effective height or radius of rotation at which the lateral force acts. The effective height is given by

\[
h_{\text{eff}} = (h_{\text{tip}} + 0.5t) \cos \varphi ,
\]

where \( h_{\text{tip}} \) is the height of the tip, \( t \) the thickness of the cantilever and \( \varphi \) the mounting angle of the cantilever (\( \approx 9.5^\circ \)). \( S_\Phi \) can be determined by calculating the initial slope of a friction loop over a displacement of a few nanometers on a hard surface [54].

### 5.8.4 Contact stiffness

In force measurements with AFM, the contact stiffness is an important factor to be considered. The force, \( F \), to be measured is assumed to obey Hooke’s Law, i.e. \( F = k \cdot x \), where \( x \) is the deflection of the cantilever and \( k \) the total stiffness of the system, which is approximately equal to the spring constant of the cantilever. However, the cantilever and the contact act like springs in series so that \( k \) includes both the cantilever stiffness, \( k_{\text{lev}} \), and the contact stiffness, \( k_{\text{cont}} \) [52] according to:

\[
k = \left[ \frac{1}{k_{\text{lev}}} + \frac{1}{k_{\text{cont}}} \right]^{-1}.
\]

This means that the deflection of the cantilever which is being measured reflects the magnitude of force only if \( k_{\text{lev}} \ll k_{\text{cont}} \). In order to judge whether Hooke’s Law is applicable for the determination of adhesion and friction forces for a system, the normal and lateral spring constants must be compared to the normal and lateral contact stiffnesses, respectively. The normal contact stiffness for a sphere-plane contact, \( k_{\text{cont}}^N \) in the Hertz case [25] is given by

\[
k_{\text{cont}}^N = 2aE^*,
\]

where \( a \) is the contact radius. \( E^* \), the effective modulus, is given by

\[
\frac{1}{E^*} = \frac{(1-\nu_1^2)}{E_1} + \frac{(1-\nu_2^2)}{E_2},
\]

where \( \nu_1 \) are the Poisson’s ratios and \( E_i \) the Young’s moduli of the contacting materials. The contact radius in equation 25 is a function of the applied normal load. At the start of the pull-off phase of an adhesion measurement the applied load is zero. The contact radius during pull-off may be calculated using the JKR theory [55] as:

\[
a^3 = 6\pi R^2 W_{12} / E^*,
\]

where \( R \) is the sphere radius and \( W_{12} \) the work of adhesion. For a contact between a regenerated cellulose film (1) and a gold-coated functionalized AFM tip (2), \( E_1 = 4 \text{Gpa} \) [56], \( \nu_1 = 0.1 \) [56], \( E_2 = 50 \text{ Gpa} \) [57] and \( \nu_2 = 0.44 \) [57], \( W_{12} = 92 \text{ mJ/m}^2 \) and \( R = 55 \text{ nm} \). According to equations (24), (25) and (26) these data give \( k_{\text{cont}}^N \approx 49 \text{ N/m} \), which may be compared with

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the normal stiffness of the cantilever, 0.4 N/m (determined by measuring the normal vibration of the cantilever suspended in air [58], see section 5.8.5). Thus, due to its greater compliance, the cantilever is deformed in adhesion measurements to a much greater extent than the contact and the adhesion force is well approximated by equation (20).

The lateral contact stiffness, $k_{\text{cont}}^L$, for a sphere-plane contact is given [52] by

$$k_{\text{cont}}^L = 8aG^* ,$$  

(27)

where $G^*$ is the effective shear modulus given by

$$\frac{1}{G^*} = \frac{1-\nu_1}{G_1} + \frac{1-\nu_2}{G_2} ,$$  

(28)

where $G_i$ ($i=1,2$) are the shear moduli of the contacting materials and $G_i = E_i/(2(1+\nu_i))$. At a given applied normal load, N, the contact area according to JKR theory [55] is given by

$$a^3 = \frac{R}{E^*} (N + 3\pi RW_{12} + \sqrt{6\pi RW_{12}N + (3\pi RW_{12})^2} ) .$$  

(29)

In the study described in paper V, the average normal load during friction measurements was 10 nN, so that for the contact between a film of regenerated cellulose and a gold-coated AFM tip $k_{\text{cont}}^L \approx 170$ N/m. This value is to be compared to the lateral stiffness of the cantilever, 140 N/m (determined by following the analysis by Ducker and Neumeister [59], see section 5.8.5). Thus, in friction measurements both cantilever and contact deform to similar extents, i.e. the torsion of the cantilever, which we detect, does not reflect the true friction force. It is the opinion of the present author that the term lateral force should be used instead of friction force when friction results from AFM measurements are presented.

5.8.5 Cantilever calibration
AFM cantilevers must be calibrated to obtain the spring constant in order to convert the measured deflection into a force. Many methods of obtaining the normal spring constant are reported in the literature. These include the measurement of a cantilever’s resonance frequency with [60] or without [61] the attachment of a small end-mass, the measurement of the static deflection of a cantilever under the force of a known end-mass [62] and the calibration against a cantilever of known spring constant [63]. The calibration method employed in the study described in paper V was based on measuring the area of the first resonance peak in a power spectrum of a thermally vibrating cantilever [58].

The determination of the torsional spring constant is more difficult and such studies are scarce. Many calibration methods are based on the measurement of the twist of the cantilever when it experiences a known torsional force [64-69]. In the study presented in paper V, the torsional stiffness, $k_\phi$, was calculated from the dimensions and the material properties of the cantilever following the analysis of Neumeister et al. [59].
6. The friction hysteresis of paper (paper I)

Many uncoated paper grades exhibit a frictional behavior that is rarely observed for other materials where paper-to-paper friction decreases with consecutive slides in the same direction. [1,8,39]. It has also been observed that paper maintains a high level of friction when the sliding direction is reversed after each slide [8]. Explanations for these phenomena have been lacking. The purpose of the investigation described in paper I was to characterize the dependence of paper-to-paper friction on the sliding direction of the previous slide for various paper grades covering a wide range of fiber types and manufacturing conditions.

6.1 Materials and methods

The papers studied were filter paper, impregnated filter paper, sack paper, laboratory-made paper, copy paper, newsprint, backing paper, gloss-coated paper, matt-coated paper and cast-coated paper. Static and kinetic friction forces and coefficients of friction were measured using an “Amontons II” from Mu Measurements (USA) according to ISO 15359 [41]. The values for the friction coefficients were averaged from six measurements and 95% confidence limits varied between 1 to 3 % of the mean. The papers were also characterized with respect to fiber rising tendency and they were imaged by environmental scanning electron microscopy (ESEM).

To study the influence of a lubricant on paper-to-paper friction, filter paper sheets were impregnated with a solution containing 5 mmol/L stearic acid (Kebo AB, Sweden) dissolved in acetone, by dipping them into the solution for 60 seconds. In addition to paper-to-paper friction experiments, one experiment was performed where filter paper was caused to slide against a clean glass plate. An Environmental Scanning Electron Microscope (ESEM) was used to image the paper surfaces before and after 10 repeated slides in the same direction.

For the determination of friction hysteresis, two types of experiments were performed for all the paper grades.

1. Repeated slides where the sliding direction was reversed after each slide (R-trials).
2. Repeated slides in the same direction (S-trials).

Figure 19 shows the static coefficient of friction of the filter paper plotted against the number of slides for a sequence of R-trials and S-trials. The following test procedure was carried out for the investigated papers: In the first four slides the sliding direction was reversed after each slide and a high level of friction was usually obtained and the mean value was recorded. During the next slides the sliding direction was kept the same and the friction generally decreased to a lower level and the mean value was recorded. This lower plateau was typically reached after 10 slides. This sequence of R- and S-trials was carried out five times using the same pair of papers. The difference between the maximum and minimum values of the static friction coefficient was recorded for each sequence of R-and S-trials and the friction hysteresis, $FH$, was determined, which was defined as

$$FH = 100 \cdot \frac{1}{5} \sum_{n=1}^{5} \frac{F_{n,\text{max}} - F_{n,\text{min}}}{F_{n,\text{max}}} \%.$$

(30)
In equation (30), \( n \) denotes the number of sequences, \( \overline{F}_{n,\text{max}} \) denotes the mean value recorded when the sliding direction was reversed after each slide and \( \overline{F}_{n,\text{min}} \) denotes the mean value recorded when the sliding direction was kept unchanged.

**Figure 19:** The static coefficient of friction versus the number of runs for a sequence of R- and S-trials. The difference between the maximum value obtained during the R-trials and the minimum value obtained during the S-trials is also indicated.

### 6.2 Fiber alignment caused by sliding

In order to examine whether any physical changes took place during sliding, filter paper, i.e. the paper with the most pronounced friction hysteresis, was examined by ESEM before and after sliding. Figure 20 shows ESEM images of the filter paper surface before and after 10 repeated slides in the same direction. For clarification, the sliding direction of the opposite paper is also shown. It is evident from the figure that sliding causes fibers to rise out of the plane of the paper surface so that they align themselves in the sliding direction.

**Figure 20:** ESEM image of a filter paper surface before and after 10 repeated slides against another filter paper in the same direction. For clarification, the sliding direction of the opposite paper is also shown.
6.3 Friction hysteresis and fiber-rising tendency
It was suspected that the reason why different paper grades exhibited different degrees of friction hysteresis could be traced to differences in the extent of reorientation of fibers during sliding. It was also suspected that the extent of reorientation of fibers was related to the fiber rising tendency of the papers. In figure 21, the friction hysteresis of the paper grades is plotted against the corresponding total area of raised fibers. The figure shows a good correlation between the friction hysteresis and the total area of raised fibers.

![Figure 21: The friction hysteresis of the papers plotted against the corresponding total area of raised fibers per unit width of the test piece.](image)

6.4 Conclusions: The origin of friction hysteresis
Based on these results, it is proposed that the friction hysteresis of paper has its origin in the extent of interlocking of the fiber ends of contacting paper surfaces. The extent of interlocking depends on the orientation of fibers on the paper surface relative to the sliding direction, as is illustrated in figure 22. When the sliding direction is reversed after each slide (R-trials), fibers of the contacting paper surfaces are pushed into each other and interlock during sliding causing high friction. For consecutive slides in the same direction (S-trials), fibers of the contacting paper surfaces always become oriented in the sliding direction, which minimizes interlocking and causes low friction.
Figure 22: The orientation of fiber ends on contacting paper surfaces with respect to sliding direction during the measurement of static friction for R-trials and S-trials, respectively.

No friction hysteresis was observed when a filter paper was caused to slide against a glass plate indicating that no interlocking of fibers can occur when a paper surface slides against a non-fibrous surface. For many uncoated paper grades it is also observed that friction decreases with the number of slides after the first slide when sliding is being carried out in the same direction, see for example figure 10, section 5.1. The high friction during the first slide was probably associated with the work necessary to raise and align the fibers on a paper surface in the sliding direction from their initial orientation, as shown in figure 20.

It is concluded that the friction hysteresis of paper is governed by the degree of interlocking of the fibers of contacting paper surfaces, which in turn is affected by the orientation of the fibers relative to the sliding direction.
7. The identification of lubricants in paper (paper II)

Section 7 summarizes the study described in paper II in which the influence on paper-to-paper friction of low-molecular-mass lipophilic compounds (LLC) that occur in paper was investigated. More specifically, the influence of different model compounds, which represented major components in wood resin, was studied and the compounds were judged by their ability to lubricate the paper surface.

7.1 Materials and methods

Commercial filter papers based on cotton cellulose (Munktells filter paper 00H, Sweden) were chosen as model paper. The filter paper sheets were impregnated with 24 different wood extractives in order to study the individual influences of these wood extractives on paper-to-paper friction. The model compounds, which represent major components of wood resin, were different saturated fatty acids and fatty alcohols, unsaturated fatty acids, triglycerides, resin acids, alkanes, sterols and betulin. Friction was measured according to ISO 15359 [41] using the in-house customized friction tester [8] described in section 5.1. The values for the friction coefficients were averaged from six measurements and 95% confidence limits varied between 1 to 3 % of the mean.

7.2 The influence of chain length

Figure 23 shows the coefficients of friction of filter paper impregnated with solutions in acetone of different saturated fatty acids at a concentration of 5mM. The aim of this experiment was to study the influence of chain length of a fatty acid on the lubricating effect of that compound.

Figure 23 shows that the coefficients of friction decreased with increasing chain length from a high level to a low level of friction around a chain length of 14-16 carbon atoms. The same
behavior was observed when filter papers were impregnated with different fatty alcohols. These results are in accordance with those obtained in experiments with lubricated steel surfaces rubbed over glass surfaces [30], figure 5, section 2.8.2. In figure 5, however, the coefficient of friction decreases linearly with increasing chain length in the regime between 8 and 14 carbon atoms in the chain of the fatty acid. In the corresponding interval in figure 23, the friction decreases first after 12 carbon atoms in the chain of the fatty acid. (Note that no fatty acid with 9 or less carbon atoms in the chain was tested in this case.) The different behaviors may perhaps be attributed to the fact that the fatty acids were deposited on different surfaces. The lubricating ability of a fatty acid is dependent on its interaction with the substrate surface. The interaction between a fatty acid and a steel surface is very different from that between a fatty acid and a paper surface, because the fatty acid is bonded much more strongly to a steel surface.

### 7.3 The influence of unsaturation in fatty acids

In figure 24, the coefficients of friction for the filter paper sheets impregnated with stearic acid (no double bond, saturated), oleic acid (one double bond, mono-unsaturated) and linoleic acid (two double bonds, di-unsaturated) are plotted against the number of double bonds in the fatty acid. The acids shown in figure 24 all have 18 carbon atoms in the hydrocarbon chain.

Figure 24 shows that the friction was markedly higher for the filter papers impregnated with the unsaturated fatty acids than for the filter papers impregnated with stearic acid. S1 and S3 were independent of the number of double bonds in the unsaturated acid and only K3 was slightly lower for the filter papers impregnated with the mono-unsaturated oleic acid than for the filter papers impregnated with the di-unsaturated linoleic acid.

![Figure 24: S1, S3 and K3 for filter papers impregnated with 5 mM of three fatty acids with 18 carbon atoms in the carbon chain: stearic acid (no double bonds), oleic acid (one double bond) and linoleic acid (two double bonds). The reference friction values obtained from the filter papers dipped into pure acetone are also shown.](image-url)
7.4 Comparison with results reported in the literature

Most of the results in the study described paper II are in agreement with those obtained from earlier investigations [1,9,11,12]. Some results and conclusions presented in paper II are however in contradiction to those obtained by Back and Gurnagul. Back [1] states that resin acids increase paper-to-paper friction when they are deposited on paper, whereas the results in paper I show that resin acids decrease paper-to-paper friction. Back used sheets based on pulp from unbleached softwood and hardwood and sheets based on cotton linters and dissolved lubricants were deposited by impregnation. He impregnated the sheets with solutions of abietic acid and dehydroabietic acid and measured the friction of impregnated sheets and of impregnated sheets that had been stored in an oven at 105 °C. His results showed in fact that the friction of the sheets decreased when they were impregnated with abietic acid. The friction of the sheets also decreased when they were impregnated with dehydroabietic acid, except in one case when the sheets based on cotton linters were stored in the oven after impregnation and an increase in friction was achieved. It is the opinion of the present author that the conclusion that resin acids increase paper-to-paper friction does not hold based on the results of Back’s experiments. Secondly, Back [1] states in his article that extractable lipophilic compounds were present in his substrate papers and that they might have been re-distributed during impregnation. This violates the principle of the impregnation procedure per se, because the study of the influence of model compounds on the friction of paper requires clean substrate papers.

Gurnagul [11] states that oleic acid is a more efficient lubricant than stearic acid, whereas the results in paper II show the opposite. Gurnagul used paper based on thermo-mechanical pulp for the substrate paper. It is well known that this paper grade contains considerable amounts of lipophilic compounds. Again, this choice of substrate paper violates the principle of the impregnation procedure because the study of the influence of model compounds on the friction of paper requires clean substrate papers. On the basis of these facts, the results and conclusions presented in paper II provide a better foundation for understanding the effect of wood extractives on paper-to-paper friction.

7.5 Conclusions: The effect of wood extractives on paper friction

In paper II, a model to describe the effect of these wood extractives on the friction of paper is proposed. According to this model, the friction between paper surfaces is highest when no wood extractives are present on the surfaces. The high friction arises from the strong adhesive forces that act between the pure paper surfaces. Further, the model states that a wood extractive must meet several structural criteria in order to lubricate a paper surface. Firstly, it must have a hydrophilic group that can attach to the paper surface. Secondly it must have a linear hydrocarbon backbone of sufficient length, and thirdly, it must have the ability to form tightly packed ductile vertically oriented molecular films on the paper surface. When the paper surfaces are covered by ductile molecular films of wood extractives, friction is determined by the shear forces between the molecular films. These forces are much weaker than those acting between unlubricated paper surfaces and therefore friction decreases when paper surfaces are coated by molecular films of wood extractives. Furthermore, figure 24 shows that the introduction of one cis-double bond was enough to neutralize the most efficient lubricating performance of stearic acid. It is reasonable to assume that the cohesive interaction

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1 This is probably only an approximate description of their orientation. Surfactants, such as fatty acids usually form monolayers on substrate surfaces where the molecules are slightly tilted with respect to the surface [18].
between the hydrocarbon chains is stronger for stearic acid because the chains are less sterically hindered compared to the more folded chains of oleic acid, which facilitates the formation of a vertically oriented monolayer. The difference in cohesive interaction is also reflected by a significant difference in the melting points [23] of the fatty acids (70 °C for stearic acid and 16 °C for cis-9-octadecenoic acid [70]).

8. The role of chemical structure of LLC for lubrication
(paper III)

Although it is not specifically stated in the study described in paper II, the authors proposed a type of lubrication by which wood extractives decrease paper-to-paper friction that is, in effect, boundary lubrication. The purpose of the investigation described in paper III was to clarify whether wood extractives and other low-molecular-mass lipophilic compounds that occur in paper can act as boundary lubricants on paper surfaces. The main objective of that study was to investigate the role of chain length and chemical structure of LLC for their orientation relative to the paper surface, which is an important criterion for boundary lubrication.

Magnesium salts of different lipophilic acids were used as model compounds for LLC and were deposited from solutions on filter paper sheets by impregnation. Static and kinetic coefficients of friction of the impregnated filter papers were determined using an “Amontons II” from Mu measurements (USA). The adsorbed layers of magnesium salts deposited were characterized by contact angle goniometry and X-Ray photoelectron spectroscopy (XPS).

In pre-trials, filter papers were impregnated with free fatty acids but it was noted that the acids evaporated in the vacuum chamber of the XPS, making a quantitative analysis of the atomic composition of a surface by XPS impossible. It was chosen to convert the fatty acids to magnesium salts, because they have low volatility but are still soluble in organic solvents.

8.1 Materials and methods

Magnesium salts of the different fatty acids and abietic acid were prepared by precipitation. The fatty acids used were saturated fatty acids of different chain length ranging from 4 to 18 carbon atoms in the carbon chain and three unsaturated fatty acids (cis-9-octadecenoic acid, trans-9-octadecenoic acid and cis,cis-9,12-octadecadienoic acid).

The magnesium salts were deposited on sheets of filter paper based on cotton cellulose (“00H”, Munktell AB, Sweden) by impregnation from solution. The compounds used for impregnation used in this investigation were magnesium salts of butyric acid, hexanoic acid, octanoic acid, decanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid and octadecanoic acid, cis-9-octadecenoic acid, trans-9-octadecenoic acid, cis,cis-9,12-octadecadienoic acid and abietic acid. Impregnation solutions were prepared by dissolving the magnesium salts in toluene. Mg butyrate, Mg-dihexanoate and Mg-dioctanoate were not fully soluble in toluene and were instead dissolved in methanol. The filter papers were impregnated by dipping them in an impregnation solution for 60 seconds and dried under restraint on washed plates.
To compare the different magnesium salts, it was necessary to obtain full coverage of a paper surface by the magnesium salts. However, it was more important to maintain the same molar amount of Mg salt in the impregnated filter papers so that the XPS spectra of the impregnated filter papers could be interpreted in terms of chemical structure and orientation of the compounds relative to the paper surface rather than of differences in the adsorbed amounts. For the adsorbed amount, we chose the value at which Mg-dioctadecanoate formed a monolayer on the paper surface, viz.: 4.5 \( \mu \text{mole/g} \) paper. The packing density of surfactant monolayers increases with increasing linearity [71]. Further, it is proposed that the intermolecular distance between fatty acid molecules in monolayers decreases with increasing length of the hydrocarbon chain [72]. Therefore, it can be argued that the magnesium salts other than Mg-dioctadecanoate, which were composed of either shorter or non-linear lipophilic acids, must have formed at least a monolayer on the paper surface at 4.5 \( \mu \text{mole/g} \). That value was determined by determining the contact angle of diiodomethane as a function of the adsorbed amount of Mg-dioctadecanoate. (The adsorbed amount was increased by increasing the concentration of the impregnation solution.) According to the Cassie equation, the contact angle, \( \theta \), of a liquid resting on a chemically heterogeneous surface composed of compounds 1 and 2 is related to the contact angles of the liquid on the pure compounds, \( \theta_1 \) and \( \theta_2 \), by the relation

\[
\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2 ,
\]

where \( f_1 \) and \( f_2 \) are the fractions of the surface area covered by the respective compounds [73,74]. At full coverage \( f_1 = 0 \) and \( \theta = \theta_2 \). In our investigation, the contact angle on the impregnated filter paper was plotted as a function of added amount of fatty acid and it was noted that the contact angle increased steeply from 0° to a final constant plateau of 91°. The amount of Mg-dioctadecanoate necessary to reach that plateau, 4.5 \( \mu \text{mole/g} \), was taken as the amount at which a monolayer had formed.

The amounts of the other Mg-salts adsorbed on the filter papers were controlled by adjusting the concentration of the impregnation solutions: Filter papers were impregnated with solutions of different concentrations for each compound and the amount adsorbed was determined by chemical analysis (see the following section). That concentration of the impregnation solution that gave the desired value for the adsorbed amount of a compound on the filter paper was used in the subsequent experiments, i.e. friction tests, XPS analysis and contact angle goniometry.

The amount of LLC adsorbed in the sheets was determined by extraction and quantitative analysis of the extract. The sheets were extracted for 48 hours using a Soxhlet extractor [45] with a mixture of 98% chloroform and 2% formic acid. The solutions containing the lipophilic compounds were evaporated under a stream of nitrogen gas. All extracts, except those from the filter papers impregnated with Mg-dibutyrate and Mg-dihexanoate, were re-dissolved in dichloromethane, after addition of an internal standard, 14-methyl pentadecanoic acid and analysed by GC-MS. The silylated products of Mg-dibutyrate and Mg-dihexanoate were too volatile and evaporated during silylation. The extracts of the filter papers impregnated with these compounds were instead re-dissolved in Milli-Q water containing 10% methanol for quantification by ion chromatography. The results of the quantification by IC and GC-MS were based on the average of two measurements and deviations were typically 10 % of the mean.
Friction tests were carried out according to ISO 15359 [41] using the “Amontons II” from Mucmeasurements (USA). The values for the friction coefficients were averaged from six measurements and standard deviations varied between 1 to 3% of the mean.

The surface chemistry of the impregnated filter papers was investigated by studying the interaction of diiodomethane with the surface of selected paper samples. Attempts were made to study the interaction of water and ethylene glycol with the paper surfaces. Their contact angles, however, decreased from an initially high value (typically 110°) to zero within a few seconds, probably due to transfer of the magnesium salts from the surface/air to the water/air interface. Diiodomethane was chosen as test liquid because it gave stable equilibrium contact angles. Contact angles were recorded with a Dynamic Absorption Tester, Fibro DAT 1100 [75] (Fibro systems AB, Sweden). The instrument applies a liquid droplet to the surface, and a high-speed video camera captures images as the droplet spreads and/or is adsorbed. Images of the droplet are automatically captured every 20 milliseconds and the images are evaluated by image analysis. The contact angles were based on the averages of 10 readings. The standard deviations were less than 5% of the average value.

Only filter papers impregnated with the magnesium salts of saturated fatty acids with 8 carbon atoms or more in the carbon chain and that of trans-9-octadecenoic acid gave high equilibrium contact angles. In the case of the other compounds, diiodomethane gave initial contact angles of 50-80° but it was immediately adsorbed by the paper so that no equilibrium contact angles could be recorded.

An AXIS 165 by KRATOS/Shimadzu Corp. (Japan) was employed to characterize the atomic composition of the paper surface in order to monitor differences in thickness of the layers of magnesium salts deposited on filter paper. The analysis depth of XPS is about 10 nm for paper, which is larger than the length of the fatty acids used in this study, which varied between 1 and 2 nm. A qualitative value for the thickness of a layer was developed by calculating the ratio of the area of the C1 peak to that of the sum of the carbon and the oxygen peaks, C1/(C+O), see section 5.7. At incomplete coverage, however, the C1/(C+O) ratio reflected the surface coverage of paper by the magnesium salt rather than the thickness of the layer [76].

8.2 Four types of frictional behaviors
The results in the study described in paper III showed that kinetic friction in many cases was higher than the corresponding static friction. This behavior was attributed to changes in the surface chemistry of the filter papers that were induced by sliding and are discussed in sections 7.2.3-7.2.7. With the impregnated papers, four types of frictional behavior were observed, which reflected the stability of the lubricant layer. The types of behavior were labeled “stable”, “semi-stable”, “unstable” and “non-lubricating” and are shown in figure 25, where the coefficients of friction during the first and the third runs are plotted against running time. The figure shows the friction data for filter papers impregnated with the representative magnesium salts that gave rise to one of the four types of frictional behavior. The other compounds that gave rise to each type of behavior are listed in the figure. The development of the coefficient of friction with increasing number of slides is indicated by an arrow. The frictional behavior was characterized as follows:

a) For the “stable” case: the levels of both static and kinetic friction were low and the coefficients decreased with increasing number of runs, the kinetic coefficient of friction being
either lower than or equal to the static coefficient of friction, indicating the presence of a stable and wear-resistant lubricating layer.

b) For the “semi-stable” case: the static friction was low and the kinetic friction was medium, the coefficients of friction decreasing with increasing number of runs. During the first run, the kinetic coefficient of friction was equal to the static coefficient of friction but in subsequent runs the kinetic friction coefficient was higher than the corresponding static friction coefficient. The static coefficient of friction during a particular run was always lower than the kinetic coefficient of friction of the previous run. This indicates the presence of a semi-stable lubricating layer that was stable at a low sliding speed but was worn off at high sliding speed.

c) For the “unstable” case: the levels of friction were medium to high and increased with increasing number of runs to the same level as that of the clean filter paper. The kinetic coefficient of friction was higher than the corresponding static coefficient of friction and increased with increasing running time, indicating wear and permanent damage to the lubricating layer.

d) For the “non-lubricating” case: the levels of friction were high and the coefficients of friction decreased with increasing number of runs, the kinetic coefficient of friction always being lower than the static coefficient of friction. The levels of friction were of the same magnitude as those of clean filter paper, indicating the absence of any lubricating layer.

![Figure 25](image)

**Figure 25:** The coefficient of friction of the impregnated filter papers plotted against running time and the four types of frictional behavior observed, which reflected the stability of the lubricant film. The figure shows data for filter papers impregnated with representative magnesium salts that gave rise to a particular frictional behavior. Other compounds that gave rise to a particular behavior are listed in the figure. The development of the coefficient of friction with increasing number of slides is indicated by an arrow.

### 8.3 Contact angle data

The surface energy of a solid hydrocarbon is much lower when the chains are oriented normal to rather than parallel to the surface [77] and high contact angles with diiodomethane can be
expected on a surface covered with a monolayer of vertically oriented hydrocarbons. Contact angle data in table 1 show that only filter papers impregnated with the magnesium salts of trans-9-octadecenoic acid and saturated fatty acids with 8 or more carbon atoms in the carbon chain yielded high and stable contact angles for diiodomethane, indicating that these salts formed such monolayers. Filter papers impregnated with the Mg-dibutyratate, Mg-dihexanoate, Mg-di-cis-9-octadecenoate, Mg-di-cis,cis-9,12-octadienoate and Mg-diabietate adsorbed diiodomethane, indicating that these compounds did not form vertically oriented monolayers.

### 8.4 The effect of chain length on friction

In figure 26, S3 and K3 values for filter papers impregnated with magnesium salts of saturated fatty acids with different chain lengths are plotted against the number of carbon atoms in the fatty acid. The adsorbed amount was kept at approximately 4.5 mmole/g paper. The figure shows that the frictional behavior of magnesium salts of the different fatty acids changed with increasing chain length. The magnesium salts of fatty acids containing up to six carbon atoms were not lubricating, those containing 8 to 12 carbon atoms gave “semi-stable” lubricating layers and those containing more than 14 carbon atoms gave “stable” layers.

![Figure 26: The third static coefficient of friction (S3) and the third kinetic coefficient of friction (K3) for filter papers impregnated with magnesium salts of saturated fatty acids with different chain lengths plotted against the number of carbon atoms in the fatty acid (the adsorbed amount was approximately 4.5 µmole/g paper). The type of frictional behavior is indicated. The reference friction values of clean filter paper are also shown.](image)

It is evident in figure 26 that the coefficients of friction of the impregnated filter papers decreased and that the resistance to wear of the lubricating layer of magnesium salt increased with increasing chain length of the fatty acid. The fatty acid must have 8 or more carbon atoms in the carbon chain for lubrication to be achieved. In addition, contact angle data in table 1 in paper III show that only these magnesium salts (together with the magnesium trans-9-dioctadecenoate) yielded high equilibrium contact angles for diiodomethane, indicating that they formed vertically oriented monolayers. The assumption that these compounds are first able to form such monolayers with 8 carbon atoms in the carbon chain is also supported by XPS measurements. In figure 27, C1/(C+O) values for filter papers are plotted as a function
of the number of carbon atoms in the carbon chain of the fatty acid. Equilibrium contact angles for diiodomethane on impregnated filter papers are shown in brackets. (Equilibrium contact angles could not be determined on clean filter paper and on filter paper impregnated with Mg-dihexanoate because diiodomethane was adsorbed.) Figure 27 shows that the C1/(C+O) ratio was 4-6% up to 6 carbon atoms and jumped abruptly to 42% at 8 carbon atoms and gradually increased to 79% with increasing number of carbon atoms. The abrupt change in C1/(C+O) can be explained by the spontaneous formation of vertically oriented films, as illustrated by the insets in figure 27. The gradual increase in the C1/(C+O) ratio with increasing number of carbon atoms in the fatty acids above 8 carbon atoms is probably due to an increase in the thickness of vertically oriented monolayers with increasing number of carbon atoms in the hydrocarbon chain.

Figure 27: The C1/(C+O) ratio of filter papers impregnated with magnesium salts of different saturated fatty acids plotted as a function of the number of carbon atoms in the carbon chain of the fatty acid. The amount of magnesium salt adsorbed by the filter papers was kept at approximately 4.5 µmole/g. The numbers in brackets show equilibrium contact angles of diiodomethane on impregnated filter papers. The insets show the assumed orientation of the hydrocarbon chain of the magnesium salt on the surface. The values for clean filter paper are also shown.

8.5 Effect of stereochemistry of unsaturated fatty acids on lubrication

Table 1 in paper III shows that magnesium di-trans-9-octadecenoate was a more efficient lubricant than magnesium di-cis-9-octadecenoate. The table also shows that filter papers impregnated with magnesium di-trans-9-octadecenoate gave stable contact angles for diiodomethane, indicating that this compound formed a vertically oriented monolayer. In contrast, diiodomethane was adsorbed on filter papers impregnated with magnesium di-cis-9-octadecenoate, indicating that this compound did not form such a layer. It is reasonable to assume that the cohesive interaction between the hydrocarbon chains of the magnesium salts is stronger for the “more linear” trans isomer because the chains are less sterically hindered than the “more folded” cis isomer, and that this facilitates the formation of a vertically oriented monolayer. The difference in cohesive interaction is also reflected by a significant difference in melting point [23] of the fatty acid isomers (45 °C for trans-9-octadecenoic acid and 16 °C for cis-9-octadecenoic acid [70]). In view of the contact angle data, a higher value of the
C1/(C+O) ratio was expected for filter paper impregnated with the Mg di-trans-9-octadecenoate, but both magnesium salts had similar values (>20%). A possible explanation for these seemingly contradictory results is that Mg-di-cis-9-octadecenoate perhaps formed thick but disordered layers on the paper surface, and that these gave a high value for C1/(C+O) but instable contact angles, whereas Mg di-trans-9-octadecenoate formed a vertically oriented monolayer, which gave not only a high value for C1/(C+O) but also a high equilibrium contact angle. It is reasonable to assume that a disordered film of the cis isomer would be worn off more easily than an ordered film of the trans isomer. Table 1 in paper III shows that magnesium di-cis,cis-9,12-octadecenoate was a poor lubricant and that magnesium diabietate had no lubricating effect at all, despite their high C1/(C+O) values on filter paper (17.3 and 39.9 %, respectively). However, the unstable contact angles of diiodomethane on papers impregnated with these compounds indicate that none of these compounds formed vertically ordered monolayers on the paper surface. By analogy with the case of Mg-di-cis-9-octadecenoate, the high values for C1/(C+O) recorded on Mg di-cis,cis-9,12-octadecenoate and Mg-diabietate were probably due to the formation of disordered thick layers of magnesium salts which were easily worn off during sliding and thus gave poor lubrication or no lubrication, respectively.

8.6 Conclusions: Boundary lubrication of paper surfaces

The study presented in paper III was aimed at clarifying whether low-molecular-mass lipophilic compounds (LLC) that occur in paper can act as boundary lubricants. The main objective of that study was to investigate the role of chain length and chemical structure of LLC for their orientation relative to the paper surface, which is an important criterion for boundary lubrication.

The results show that the ability of a magnesium salt of a lipophilic acid used in this study to decrease paper-to-paper friction depends on its ability to form vertically oriented monolayers on the paper surfaces. Further, the resistance to wear of a layer depends on the degree of linearity and length of the carbon chain of the lipophilic acid. These phenomena are probably due to a strong cohesion between the hydrocarbon chains of lipophilic acids, which increases the stability of the monolayer. The results reported in the studies describer in papers II and III are in good agreement with the results reported in the literature on the effect of boundary lubricants on friction [15,78-81], and it is concluded that boundary lubrication is the type of lubrication by which low-molecular-mass lipophilic compounds that occur in paper decrease paper-to-paper friction.
9. The effect of boundary lubricants on the friction of commercial paper grades (paper IV)

This section describes the main results of the study described in paper IV, which was aimed at finding the origin of the differences in friction of commercial linerboards based on recycled fiber (old corrugated containers, OCC). In addition, results from an unpublished study are described that was aimed at elucidating the effect of boundary lubricants on the friction of different commercial paper grades.

9.1 Materials and methods

9.1.1 Samples

Four different commercial linerboards based on OCC were investigated. In all the measurements, the side of each board that was intended to face outwards in the corrugated board was analyzed. The linerboards were subjected to two different extraction stages, whereby new samples were generated. The frictional properties of the OCC-based papers were compared to those of Munktell’s filter paper 00H. The origin of the samples and the sample labeling are described in detail in table 1. In addition, the four sheets were calendered to enable the influence on friction of smoothening of the paper surface to be studied. Papers A and B were known to be manufactured from the same pulp. However, paper B was reported to have been surface-coated with CaCO$_3$ particles to increase friction, which was confirmed by ESEM and energy dispersive X-ray spectroscopy (EDS). Samples A0-D0 were calendered at a line-load of 30 kN/m using a pilot calender.

<table>
<thead>
<tr>
<th>Paper</th>
<th>Origin</th>
<th>Sample labeling</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>OCC, pulp x</td>
<td>Before extraction</td>
</tr>
<tr>
<td>B</td>
<td>OCC, pulp x, Surface-coated</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>OCC, pulp y</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>OCC, pulp z</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>Munktell’s Filter paper 00H</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: The origin of the papers and the sample labeling used in this investigation.

The paper sheets were investigated in an ESEM model 2020 from Electroscan/Philips. Figure 28 shows ESEM images of samples A0 and B0. It can be seen that sample B0 contained large particles, which probably originated from the surface coating. The papers C and D were manufactured from different pulps than papers A and B. The ESEM images of the other samples were similar to that of sample A0. ESEM studies showed that samples B1 and B2 did not contain large particles. The particles were obviously removed in the extraction process.
Figure 28: ESEM images of the samples A0 and B0. Sample B0 contained large CaCO$_3$ particles. The ESEM images of the samples C0 and D0 were similar to that of sample A0.

9.1.2 Extraction and GC-MS analysis
The low-molecular-mass material was removed from the linerboards by solvent extraction. Two different extraction devices, a SoxTec™ and a Soxhlet extractor, were employed. The solvent used in this study consisted of 98% chloroform and 2% formic acid. The bulk amount of LLC in the papers was quantified by analyzing the extracts by GC-MS, see sections 5.5.1 and 5.5.2. The results from the quantification by GC-MS were based on duplicates. The deviation from the average was not greater than 10%.

The identified LLC were divided into the following groups:
1. Long-chain saturated fatty acids, with a carbon chain of 15 carbon atoms or more
2. Fatty alcohols
3. Sterols
4. Short-chain saturated fatty acids with a carbon chain of less than 15 carbon atoms
5. Unsaturated fatty acids
6. Alkanes
7. Betulinol
8. Resin acids

The first three groups represent compounds that may act as boundary lubricants (BL) on paper surfaces. The amount of LLC in the prolonged extracted samples A2-D2 was set to zero in the tables and figures since no significant amounts were obtained when the samples were extracted further.

2 The observant reader might have noticed that the authors of the study described in paper II only include fatty acids with at least 16 carbon atoms to the group of lubricating fatty acids. However, (due to temporary intellectual shortcomings) in paper IV, the authors also included pentadecanoic acid to this group, despite the lack of evidence that this acid decreases paper friction. However, for his defense, the author of this thesis points out that pentadecanoic acid constituted less than 2% of the group of boundary lubricants.
9.1.3 Impregnation of the filter paper
To study the influence of LLC on the friction of a clean filter paper, an experiment was carried out where a filter paper was impregnated with the extract obtained from the first extraction stage of paper A. Paper A was chosen as the source of LLC because it had the lowest friction, so that it was expected that the extract from this paper would have the largest effect. The extraction was carried out in such a way that the concentration of LLC in the impregnated filter paper roughly equaled that of sample A0. Sheets were impregnated by putting them into a large glass basin, so that the bottom of the basin was completely covered by the pieces, and the extract was then poured into the basin. After about 12 hours, the solvent had completely evaporated and the filter paper pieces had adsorbed the extractives.

9.1.4 Friction tests
Friction was measured according to ISO 15359 [41] using an “Amontons II” from Mu measurements. In this investigation it was decided to use the data obtained from the third sliding. The given friction values were obtained from measurements where the sliding direction corresponded to the cross direction of the paper. The values for the friction coefficients and the corresponding 95% confidence limits were based on the average of six to eight measurements. The confidence limits obtained varied between 0.01 and 0.03.

9.1.5 Surface roughness measurements
The surface roughness measurements were carried out using a Perthometer PRK profiler from Mahr GmbH (Germany). The surface roughness is given for different bandwidths as the root mean square (RMS), i.e. the square root of the arithmetic mean of the square of the vertical deviation from a reference line. The bandwidths analyzed were 0.0625-0.125 mm, 0.125-0.25 mm, 0.25-0.5 mm, 0.5-1 mm, 1-2 mm, 2-4 mm, 4-8 mm and 8-16 mm.

9.2 The effect of extraction on friction
Originally, the four linerboards had very different friction values. Figure 29 shows the third static and the third kinetic coefficient of friction of the investigated samples. Before extraction, the order among the papers with increasing friction was A, C, B and D and there was no significant difference between the static and kinetic coefficients of friction. After the first extraction stage, the coefficients of friction dramatically increased. It was noted that they increased to the same level, despite the different values before extraction. After the second extraction stage, the coefficients of friction increased further, at least to the level of the filter paper. However, after the second extraction stage, the differences in friction between the papers were larger than those after the first extraction stage. Figure 30 shows that the coefficients of friction of the filter paper (sample F0) decreased after impregnation (sample FI) with the extract of sample A0 and roughly to the level of sample A0.
Figure 29: The third static (S3) and the third kinetic coefficient of friction (K3) of the investigated papers before and after the extraction stages. For comparison, the friction coefficients of clean filter paper and of the filter paper impregnated with the extract from sample A0 are also shown.

9.2.2 Low-molecular-mass lipophilic compounds and friction

Figure 30 shows two curves, where the third static coefficient of friction, S3, is plotted against the amount of the LLC and the amount of boundary lubricants (BL, i.e. the long-chain saturated fatty acids, fatty alcohols and sterols) expressed as milligram per gram dry paper. It is evident in this figure that the coefficients of friction of the papers followed a very general trend, where the friction was low when the amounts of LLC and BL in the paper were high. Figure 30 also shows that although sample B0 had about the same amount of LLC as sample A0 it had a significantly higher friction. The deviation from the general trend was attributed to the ploughing effect of the large CaCO₃ particles, which were identified by ESEM (figure 28). Paper B nevertheless followed the general trend after it had been extracted.
Figure 30: The third static coefficient of friction plotted against the total amount of low-molecular-mass compounds (total LLC) and boundary lubricants (BL) expressed as milligram per gram dry paper. The symbols representing the amount of boundary lubricants are marked with a flag.

Figure 29 shows that the coefficient of friction dramatically increased to the level of clean filter paper after removal of LLC from the papers. Conversely, the friction of clean filter paper decreased to about the same low level of sample A0 after impregnation with LLC from that paper. Figure 30 shows a quantitative relationship between S3 and the content of LLC and boundary lubricants in the papers. It is concluded that the paper-to-paper friction of the linerboards was quantitatively governed by the degree of lubrication by LLC.

The amount of boundary lubricants was fairly proportional to the amount of LLC. The results from the studies described in papers II and III showed that boundary lubricants are the only compounds among the LLC that decrease paper friction. Therefore, it can be assumed that the decrease in friction with increasing amount of LLC shown in figure 31 was probably due to the increasing amounts of boundary lubricants.

9.2.3 Surface roughness and friction

In figure 31, the third static coefficient of friction of the linerboards samples is plotted against the corresponding RMS surface roughness of the band 1-2 mm, which was arbitrarily chosen to show the effect of calendering. The choice of bandwidth for the comparison was not critical since similar trends were observed when the static coefficient of friction was plotted against the corresponding RMS roughnesses of the other bands. From figure 31 it is evident that all the uncalendered linerboard samples had a surface roughness of about 4 µm but very different coefficients of friction. Calandering of the samples A0-D0 decreased the surface roughness of the samples to about 50 % of its original value but left the coefficient of friction unchanged.
Figure 31 shows that friction was independent of the surface roughness of the paper samples, which is in accordance with the results obtained from other investigations [5,10]. The explanation given in the study described in paper IV is as follows: The pressure acting on the asperities at the contact regions under the influence of a normal load is so high that it deforms the asperities on the paper surface. According to the adhesive friction model of Bowden and Tabor [82], the coefficient of friction is dependent on only two mechanical properties, the shear strength of the contacts and the plastic yield stress of the material, which implies an independence of surface roughness.

The AFM study described in paper V showed that the lateral force between an AFM tip and a cellulose surface initially increased with scan size and then remained approximately constant after a scan size of about 30 nm (see figure 2, paper V). The increase in lateral force with increasing scan size was attributed to an increase in surface roughness. It was suggested that lateral forces measured at scan sizes below 30 nm were associated with sliding within topographic domains of the cellulose film. Thus, in that study, it was observed that the friction was dependent on surface roughness. A possible explanation for the seemingly contradictory results presented in papers IV and V may be that paper-to-paper friction is independent of the surface roughness at large length scales which is decreased by calandering.

9.3 Boundary lubricants in different paper grades (unpublished results)

In this section the results from an unpublished study that was directed towards investigating the effect of boundary lubricants on the friction of different commercial paper grades are described. In this investigation, the third static coefficient of friction (S3) was determined for different paper grades that covered a wide range of fiber types and manufacturing conditions and different contents of both low-molecular-mass-lipophilic compounds (LLC) and boundary lubricants (BL). Paper-to-paper friction was measured according to ISO 15359 [41] using an
“Amontons II” from Mu measurements. The amount of LLC in the papers was determined by extraction and quantitative analysis of the extracts, as described in sections 5.5.1 and 5.5.2. Newsprint contains triglycerides, which have too low volatility for analysis with GC-MS. Therefore, prior to the analysis, all the extracts were hydrolyzed with 1.5 mM potassium hydroxide at 70°C for 1 hour to convert triglycerides to free fatty acids. The papers studied were different grades of sack paper, kraftliner, newsprint and testliner. In figure 32, the third static coefficient of friction of the various paper grades is plotted versus the amount of LLC (a) and BL (b), respectively, in the papers.

![Graph](image)

**Figures 32:** The third static coefficient of friction of various paper grades plotted versus the amount of LLC (a) and BL (b), respectively, in the papers (expressed as mg/g paper). Data for extracted and unextracted papers are shown.

The sack paper and kraftliner samples had high friction levels, and the newsprint and the testliner samples had low friction levels. After extraction, however, all these paper grades attained a common level of friction, equal to the level of clean filter paper and independent of the level of friction prior to the extraction. There was a poor correlation between the level of friction of a paper and its content of LLC (figure 32a). For instance, the coefficient of friction of those paper samples that contained between 1 and 1.5 mg/g of LLC varied between 0.3 and 0.7. In addition, the content of LLC in the papers with a coefficient of friction of 0.4 and below varied between 1.0 and 3.2 mg/g. The correlation between the level of friction of a paper and its content of LLC was poor because the boundary lubricants, i.e. those compounds among the LLC that affect friction, constitute only a minor fraction of the LLC. On the other hand, as is evident in figure 32, there was a good correlation between the amount of boundary lubricants and friction, the friction decreasing with increasing amount of boundary lubricants.

### 9.4 Conclusions: The effect of boundary lubricants on paper friction

The results of the study described in paper IV and of the unpublished study described in section 9.3 show that there was a quantitative relationship between the coefficient of friction of a paper and the amount of boundary lubricants in that paper. Moreover, removal of boundary lubricants by extraction caused the coefficient of friction of the different paper grades to rise to the level of clean filter paper (S3 ≈ 0.75) despite their having different levels prior to the extraction. These results indicate that the coefficient of friction of a paper is quantitatively dependent on the content of boundary lubricants such as long-chain saturated fatty acids and fatty alcohols.
10. Examining the forces that influence paper-to-paper friction (paper V)

In paper II a friction model is proposed which states that the high friction between clean paper surfaces arises from a high shear strength due to strong adhesive forces between the contacts. The model also states that the lubricating effect of the low-molecular-mass lipophilic compounds (LLC) in paper depends on their ability to form vertically oriented monolayers on the paper surface so that friction is determined by the attractive forces between the layers. The forces between these layers are weaker than those acting between clean paper surfaces and this gives a low friction. In the study presented in paper III it is concluded that the type of lubrication by which LLC that occur in paper decrease paper friction is in effect boundary lubrication. This section presents the main results from the study described in paper V, which was directed towards examining the attractive forces that influence the friction between the surfaces of hydrophilic polymers and explaining the mechanism by which boundary lubricants decrease the friction.

10.1 Materials and methods

The friction and the adhesion of model systems were measured with an atomic force microscope, AFM, (“Nanoscope III” from Digital Instruments, USA) at different humidities using chemically modified AFM tips and regenerated cellulose films. Lateral forces were averaged from 40 measurements carried out at four different locations on the sample surface and the standard deviations were typically 5% of the mean. Adhesion forces were averaged from 100 measurements carried out at five different locations on the sample surface and the standard deviations varied between 7 and 15% of the mean. Measured adhesion forces were compared with theoretical adhesion forces obtained from two models.

10.1.1 Model surfaces

Regenerated cellulose films ("Spectra/Por-4" from Spectrum Laboratories, Inc., Rancho Dominguez, CA) were used for model surfaces. The films were thoroughly cleaned with trichloroethylene and acetone using a Soxhlet extractor. The effectiveness of this treatment has been verified previously through X-ray photoelectron spectroscopy by evaluating the chemical composition and the carbon-bonding environment of the surface using C1s peak deconvolution [83]. Cleaned films were mounted onto metallic AFM sample discs with a one-component epoxy adhesive. A surface roughness of about 5 nm for the cellulose films was determined from 10 x 10 µm AFM height images.

To obtain fatty acid monolayers, droplets of a dilute fatty acid solution (5 mg/L), using acetone as solvent, were deposited onto a cellulose film with a syringe. During deposition the solution immediately spread on the cellulose surface and formed a uniform liquid layer. After about 5 minutes, the acetone had evaporated, leaving the fatty acids physiosorbed on the cellulose surface. The amount of fatty acid necessary to form a monolayer on the cellulose surface was determined from contact angle measurements according to the method described in section 8.1. The fatty acids used for deposition were decanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, octadecanoic acid and 9-cis-octadecenoic acid.

10.1.2 Tip modification and characterization

To mimic a clean polymer surface and polymer surface coated with fatty acids, gold-coated AFM tips were functionalized [84] by impregnation with 11-mercaptopoundecanol and
dodecanethiol, respectively. Thiols were dissolved in degassed ethanol to obtain 1 mmol/L impregnation solutions. Gold-coating of the cantilevers was performed in a customized thermal evaporator. First, 15 Å of chromium was deposited as an adhesion promoter, followed by the deposition of 200 Å of polycrystalline gold. After gold deposition, the cantilevers were immediately exposed to impregnation solutions to allow thiol chemisorption. The radius of an AFM tip was deduced from the topographic profiles of step features on gold surfaces obtained from AFM-images [85].

10.1.3 Humidity control
High relative humidity (~ 40 %) was maintained by an ultrasonic humidifier and low relative humidity (~ 8 %) was achieved by purging the AFM-head with dried Nitrogen gas. For the latter, a silicon plug with an inlet for dry Nitrogen gas was designed (Figure 33). The plug was equipped with a hygrometer probe (extracted from “Thermo-Hygro”, VWR Scientific Products) and a strip coated with the α-particle emitter Polonium 210 (extracted from "Staticmaster", NRD, Inc., Grand Island, NY) to minimize Coulomb forces at low humidity due to static charge build-up.

![Figure 33: Schematic of the silicon plug used to maintain low humidity and to control static charge build-up in the AFM-head.](image)

10.2 Surface energy measurements and calculation of theoretical adhesion forces
Friction and adhesion, measurements were carried out with the four different contact combinations obtained by employing two different AFM tips, a clean cellulose film and a cellulose film impregnated with octadecanoic acid. The surface free energies of the cellulose films were determined by contact angle goniometry using three liquids (water, ethylene glycol and diiodomethane) and solving Fowkes’ equation [77], see section 5.6. The surface free energies of the coated AFM tips were estimated from the contact angles of the liquids on gold surfaces that were impregnated with either 11-mercaptoundecanol or dodecanethiol. Measured adhesion forces were compared with predicted adhesion forces from two models.

Depending on the humidity at which the measurement was carried out, two different models were employed to calculate the theoretical adhesion force. It was assumed that the surface forces acting within the contact area between a tip and a surface could be described by JKR contact mechanics. The pull-off force $F_{132}$, between a tip, 1, and a surface, 2, in medium 3, predicted by the JKR theory is [55]
\[ F_{132} \approx \frac{3}{2} \pi R W_{132} , \]  
(32)

where \( R \) is the tip radius and \( W_{132} \) is the work of adhesion. It was further assumed that at low humidities (RH = 8\%), medium 3 was essentially air so that \( F_{132} \approx k, \gamma_{13} \approx \gamma_{1}, \gamma_{23} \approx \gamma_{2} \) and \( W_{132} \approx W_{12} \). \( W_{12} \) is given by [86]

\[ W_{12} \approx \sqrt{\gamma_{1} \gamma_{2}} , \]  
(33)

where \( \gamma_{1} \) and \( \gamma_{2} \) are the surface free energies of the tip and surface, respectively, and they can be obtained by solving Fowkes’ equation [77]. The adhesion force at low humidity is thus given by

\[ F_{132} = F_{S3} \approx \frac{3}{2} \pi R \sqrt{\gamma_{1} \gamma_{2}} \]  
(34)

It was assumed that at high humidity (RH = 40\%), the contact between a tip and a surface was surrounded by a water meniscus and that the total adhesion force, \( F_{tot} \), was given by the sum of the surfaces force, \( F_{SW} \), with contact occurring across water and the force due to the Laplace pressure, \( F_{Lap} \), acting in a water meniscus formed around the contact region, i.e.:

\[ F_{tot} = F_{SW} + F_{Lap} . \]  
(35)

\( F_{SW} \) was calculated using the JKR theory,

\[ F_{SW} \approx \frac{3}{2} \pi R W_{SW} . \]  
(36)

\( W_{SW} \) is given by [23]

\[ W_{SW} = \gamma_{1w} + \gamma_{2w} - \gamma_{12} , \]  
(37)

where \( \gamma_{1w} \) is the interfacial energy across the tip/water interface, \( \gamma_{2w} \) the interfacial energy across the surface/water interface and \( \gamma_{12} \) the interfacial free energy. \( \gamma_{1w} \) and \( \gamma_{2w} \) are obtained from Young’s equation [18,23], i.e.

\[ \gamma_{1w} = \gamma_{1} - \gamma_{w} \cos \theta_{1} \]  
(38)

\[ \gamma_{2w} = \gamma_{2} - \gamma_{w} \cos \theta_{2} , \]  
where \( \gamma_{w} \) is the surface tension of water and \( \theta_{1} \) and \( \theta_{2} \) are the contact angles of water on the respective surface. \( \gamma_{12} \) is defined by [86]

\[ \gamma_{12} = \gamma_{1} + \gamma_{2} - W_{12} . \]  
(39)

Combining equations (35), (36), (37) and (38) leads to
\[ W_{SW} = \sqrt{\gamma_1 \gamma_2} - \gamma_p (\cos \theta_1 + \cos \theta_2) . \]  \hspace{1cm} (40)

\( F_{Lap} \) was calculated by multiplying the Laplace pressure with the projected area of the water meniscus, assuming a small meniscus radius \([23,26]\). Following this analysis, the force due to the Laplace pressure in a water meniscus around the contact region between a sphere, 1, and a flat surface, 2, is

\[ F_{Lap} \approx -2\pi R \gamma_p (\cos \theta_1 + \cos \theta_2) . \]  \hspace{1cm} (41)

The total pull-off force at high humidity is thus given by

\[ F_{tot} \approx -\pi R \left[ \frac{3}{2} \sqrt{\gamma_1 \gamma_2} + \frac{1}{2} \gamma_p (\cos \theta_1 + \cos \theta_2) \right] . \]  \hspace{1cm} (42)

10.3 The effect of humidity and surface chemistry on friction and adhesion

To investigate the effect of humidity and surface chemistry on friction and adhesion, a \( 2^3 \)-factor trial was carried out by varying the relative humidity (RH) between 8\% and 40\%, the chemical functionality of the AFM tip (hydroxyl- or methyl-functionality) and the type of surface tested (clean cellulose and cellulose lubricated with octadecanoic acid). In figure 34 the lateral force for the different contact combinations is plotted against the applied normal load.

![Figure 34](image_url)

Figure 34: The lateral force between cellulose and two chemically functionalized AFM tips and the lateral force between cellulose impregnated with octadecanoic acid (lubricated cellulose) and the tips plotted as a function of the applied normal load. Filled symbols mark data collected at high humidity (RH = 40\%) and open symbols mark data collected at low humidity (RH = 8\%).

Figure 34 shows that the lateral forces linearly depended on the applied normal load, obeying a modified form of Amonton’s Law,

\[ F_{lat} = F_{lat}^0 + \mu N , \]  \hspace{1cm} (43)
where $F_{\text{lat}}$ is the lateral force, $N$ the applied normal load, $F_{\text{lat}}^0$ the lateral force at zero applied load, due to adhesion [21] and $\mu$ is the the coefficient of friction, i.e. the slope of a line.

It is evident from Figure 34 that both $\mu$ and $F_0$ significantly increased with humidity, that lateral force was always higher when the hydroxyl-functionalized tip was used, and that it was low, and less dependent on humidity when cellulose was impregnated with octadecanoic acid.

The data show that the more hydrophilic the contacting surfaces were the higher was the friction. These observations indicate that capillary condensation may have a strong influence on the friction between hydrophilic polymer surfaces under ambient conditions.

An increase in friction with increasing humidity has been observed in macroscopic friction tests on granular media [87] and paper [8]. However, the effect of humidity on friction of regenerated cellulose films is opposite to its effect on the friction of mica, where friction decreases with increasing humidity [88-91]. This decrease in friction at high humidity is due to the formation of multiple layers of water so that the shear forces in the liquid layer govern friction. This is, in essence, hydrodynamic lubrication [15], which requires steady sliding between the surfaces. Steady sliding probably occurs more easily between smooth surfaces, such as mica rather than rough surfaces. In the study presented here, friction was affected by surface roughness, which caused an irregular stick-slip pattern. A strong adhesion likely increased friction during the “stick” part of that pattern. Therefore an increase in friction with increasing humidity should be expected because capillary condensation increases the adhesion during pull-off.

In Figure 35 the coefficients of friction for the different contact combinations are plotted against measured adhesion force, $F_{\text{ad}}$.

![Figure 35: The coefficients of friction for the different contact combinations plotted against measured adhesion force, $F_{\text{ad}}$. Filled symbols mark data collected at high humidity (RH = 40%) and empty symbols mark data collected at low humidity (RH = 8%). The connecting lines are drawn to guide the eye.](image-url)

Although adhesion forces and coefficients of friction increased with humidity, the dependence on humidity decreased with increasing hydrophobicity of the contacting surfaces (figure 35).
10.4 Comparison of the measured adhesion forces with predictions from different adhesion models

The measured adhesion forces were compared to values predicted by two different theoretical models (Table 2). It was assumed that at 8% relative humidity, contact occurred across air and that adhesion was due to surface forces, $F_{SA}$, and these were calculated using JKR theory. Further, it was assumed that at 40% relative humidity, the total adhesion force, $F_{tot}$, had two contributions: (1) the surface force acting within the contact area, $F_{sw}$, with contact occurring across water, where $F_{sw}$ was calculated using JKR theory, and (2) the force due to the Laplace pressure contribution, $F_{Lap}$, acting across a water meniscus around the contact region.

Table 2 shows that for contacts involving at least one hydrophilic surface, theory predicts that the surface force acting within the contact area is repulsive when contact occurs across water ($F_{SW}$) but that it is attractive when contact occurs across air ($F_{SA}$). The table also shows that $F_{Lap}$ for these cases always was attractive and that $F_{Lap}$ overcompensated the repulsive contribution of $F_{SW}$ so that the net force, $F_{tot}$, became attractive. Theory predicted that $F_{Lap} \approx 0$ for the contact between the methyl-functionalized tip and the cellulose surface covered by stearic acid (contact angle data for this case showed that $\theta_1 = 100^\circ$ and $\theta_2 = 80^\circ$, i.e., $\cos \theta_1 + \cos \theta_2 = 0$). In this case $F_{SW}$ was however attractive so that the net adhesion force became attractive.

<table>
<thead>
<tr>
<th>Contact combination</th>
<th>RH = 8% $F_{SA}$ (nN)</th>
<th>$F_{SW}$ (nN)</th>
<th>RH = 40 % $F_{Lap}$ (nN)</th>
<th>$F_{tot}$ (nN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose – OH tip</td>
<td>-15.8</td>
<td>16.3</td>
<td>-42.9</td>
<td>-26.3</td>
</tr>
<tr>
<td>Cellulose – CH$_3$ tip</td>
<td>-11.2</td>
<td>2.4</td>
<td>-18.2</td>
<td>-15.7</td>
</tr>
<tr>
<td>Lubr. cell - OH tip</td>
<td>-13.8</td>
<td>4.9</td>
<td>-24.7</td>
<td>-19.7</td>
</tr>
<tr>
<td>Lubr. cell – CH$_3$ tip</td>
<td>- 9.6</td>
<td>~ 0</td>
<td>~ 0</td>
<td>- 9.6</td>
</tr>
</tbody>
</table>

Table 2: Predicted values for the adhesion forces for four contact combinations at two different humidities.

The theoretical models predicted that the magnitude of the adhesion force for the most hydrophobic contact (i.e. for the contact between the lubricated cellulose and the methyl-functionalized tip) is independent of the presence of a water meniscus around the contact.

In Figure 36, measured adhesion forces, $F_{adh}$ for the different contact combinations at the two different humidities are compared with the theoretical predictions.
Figure 36: Measured adhesion forces, $F_{ad}$, for the contact combinations between the different surfaces and tips at two different humidities, compared with theoretical predictions. The error bars show the standard deviations of the measured adhesion forces. NOTE: In the corresponding figure in paper V (figure 6), “$F_{SW}$” should read “$F_{SA}$”.

Figure 36 shows that the measured adhesion forces at 40 % RH were higher than the corresponding adhesion forces at 8 % RH and that the measured data were well predicted by the theoretical models. The adhesion forces measured with the methyl-functionalized tip were consistently higher than the predicted values. Imperfect coverage of the gold-coated tip by the thiols is a possible explanation for this behavior [92] as it leads to more hydrophilic surfaces with higher surface energy. The agreement between measured and predicted adhesion forces is better for the hydroxyl-functionalized tip. This is probably due to a better coverage of the gold tip by 11-mercaptoundecanol, in contrast to decanethiol, because the tails of 11-mercaptoundecanol can crosslink with each other via hydrogen bonds, improving the stability of the monolayer [93]. A comparison of the results in Figure 36 with the theoretical adhesion forces in table 2 indicates that adhesion at high humidity involving at least one hydrophilic surface is dominated by capillary forces acting in a water meniscus formed around the contact region, whereas at low humidity adhesion becomes more dependent on the surface forces acting across the contact region. The results presented in Figures 35 and 36 and the theoretically predicted adhesion forces suggest that the degree of capillary condensation between surfaces of hydrophilic polymers, may be effectively suppressed by a monolayer of long-chain saturated fatty acid.

10.5 The influence of different fatty acids on friction

Cellulose films were impregnated with different fatty acids to study their effect on the surface chemistry and the friction. Table 2 in paper V lists the fatty acids used for deposition, their number of carbon atoms and the equilibrium contact angles of water on cellulose films impregnated with the fatty acids.
The table shows that hexadecanoic acid and octadecanoic acid yielded the most hydrophobic surfaces, which gave the highest contact angle (80°) with water. Since the surface energy of solid films of hydrocarbons is lower when the chains are oriented normal to rather than parallel to the surface [77], the high contact angles shown in the table suggest that these fatty acids formed monolayers on cellulose with vertically oriented chains. The contact angle of water on cellulose impregnated with tetradecanoic acid rapidly decreased from ~60° to its equilibrium value at 46°, likely due to transfer of fatty acids from the solid/vapor to the liquid/vapor interface.

In figure 37, the coefficients of friction of clean cellulose films and of cellulose films impregnated with the saturated fatty acids listed in table 2 in paper V are plotted against the number of carbon atoms in the fatty acid. The lateral force measurements were performed at 40% RH using a hydroxyl-functionalized tip. Coefficients of friction were determined by calculating the slope of the lines obtained when the lateral force was plotted against the applied normal load, see equation (43).

![Figure 37: The coefficient of friction of cellulose surfaces impregnated with different fatty acids plotted against the number of carbon atoms in the fatty acid.](image)

Figure 37 shows that the coefficient of friction between the impregnated cellulose films and the hydroxyl-functionalized tip abruptly decreased from 0.7 to 0.15 at a chain length of 14 to 16 carbon atoms.

The ability of a surfactant such as a fatty acid to decrease friction depends on its ability to form a vertically oriented monolayers on a surface [15] and the tendency to form such a layer increases with increasing length of the hydrocarbon chain [18]. Furthermore, the stability and wear resistance of a layer increases with increasing chain length [78-80] and increasing degree of linearity [81] of the hydrocarbon chain of the surfactant. Contact angle data in table 2 in paper V show that only cellulose films impregnated with hexadecanoic acid and octadecanoic acid gave high equilibrium contact angles with water indicating that these compounds formed vertically oriented hydrophobic monolayers. These layers might have suppressed the degree of capillary condensation, and this could explain the low coefficients of
friction of the cellulose films impregnated with these compounds. The low and instable contact angles of water on the cellulose films impregnated with the shorter fatty acids indicate that these acids did not form vertically oriented monolayers. They were probably worn off during sliding, which could explain the high friction.

10.5.1 Comparison with the results from studies on impregnated filter papers (unpublished results)

In figure 38, static coefficients of friction from the third sliding (S3) of filter papers impregnated with the saturated fatty acids listed in table 2 in paper V have been added to the data in figure 37. The friction measurements on the filter papers were carried out according to ISO 15359 [41] using an “Amontons II” from Mu measurements.

![Graph showing coefficient of friction against number of carbon atoms in fatty acid]

**Figure 38:** The coefficients of friction of cellulose surfaces impregnated with different fatty acids plotted against the number of carbon atoms of the fatty acid. In addition, third static coefficients of friction (S3) of filter papers impregnated with these fatty acids are shown.

Figure 38 shows that the third static coefficient of friction of the impregnated filter papers decreased from 0.7 to 0.3 at a chain length of 14 to 16 carbon atoms, i.e. around the same chain length as in the case of the AFM experiments. By analogy to the observations from the AFM measurements, the jump from a high to a low level of friction for the impregnated filter papers may be attributed to the formation of vertically oriented monolayers of fatty acids on a paper surface.

10.6 Conclusions: Capillary condensation between surfaces of hydrophilic polymers

The friction significantly increased with humidity, and there was a strong correlation between the ability of a fatty acid to form a hydrophobic surface and its lubricating performance. Measured adhesion forces at high humidity were well predicted by the theory that took into account the effect of the Laplace pressure acting in a water meniscus formed at the periphery of the contact region. The model showed that the adhesion forces at high humidity were
dominated by the contribution from the force due to the Laplace pressure. Moreover, the theory predicted that the Laplace contribution to the total adhesion force acting between the hydrophobic tip and the hydrophobic surface was about zero and that, in this case, the adhesion was governed by the attractive surface force acting across the contact. This indicates that the degree of capillary condensation can be effectively suppressed by an increase in hydrophobicity of the contacting surfaces, leading to a decrease in adhesion and friction. These results suggest that the friction of surfaces of hydrophilic polymers under ambient conditions is greatly influenced by the degree of capillary condensation. Furthermore, lubrication by fatty acids is achieved by the formation of a vertically oriented, hydrophobic monolayer that can withstand the stresses during sliding and increase the hydrophobicity of the polymer surface and thereby suppress capillary condensation. The study described in paper V demonstrates that nanoscopic friction measurements on carefully controlled model surfaces are a powerful tool to reveal the types of forces governing macroscopic friction phenomena.

It is a common experience in the paper industry that sizing especially with alkyl ketene dimers (AKD) causes the level of paper-to-paper friction to decrease, which is often not in accordance with the quality requirements of the paper grade. The results of the study described in paper V indicate that it may be difficult to avoid that problem since the hydrophobization of a paper surface probably suppresses capillary condensation around the contacts formed between the paper surfaces, and this leads to a lower friction.

11. The relation between the friction of a paper and its surface coverage by boundary lubricants (partly unpublished results)

In this section, selected results from the study described in paper III and unpublished results are described which were directed towards investigating the effect on paper-to-paper friction of the coverage of a paper surface by a boundary lubricant. This investigation was motivated by the results presented in section 9.3, which show that even very small amounts of boundary lubricants decrease paper-to-paper friction. A rough estimation shows, however, that the internal area of a paper is too large to be covered by the boundary lubricants at the amounts found in papers. The specific area of pulp fibers is of the order of 1 m² per gram paper as determined by nitrogen gas adsorption [94]. Assume that the average molecular area of a boundary lubricant in paper equals that of stearic acid, which is about 25 Å² [95]. The amount of lubricant necessary to cover 1 m² is then approximately 6.7 µmole/g paper or about 1.9 mg/g paper (using the molecular mass of stearic acid). This amount is much higher than the amount found in commercial papers with low friction levels (see figure 34 in section 9.3). This discrepancy could be explained by a selective accumulation of boundary lubricants on those regions of a paper surface which constitute the contact areas between two sheets of paper.

11.1 Effect of increasing amounts of a lubricant on paper friction

In figure 39, the third static coefficient of friction (S3) of filter papers impregnated with different amounts of magnesium dioctadecanoate is plotted against the amount adsorbed by the paper, expressed as µmole/g dry paper. The figure shows that S3 abruptly decreased from a high level to a low level between 1 and 1.2 µmole/g. The figure also shows that friction did not thereafter decrease further with increasing amount of Mg dioctadecanoate, indicating that the paper surface became “saturated” with regard to its frictional response.
In Figure 40, the third static coefficient of friction (S3) is plotted as a function of the C1/(C+O) ratio for clean filter paper and for filter paper impregnated with Mg-dioctadecanoate containing 0.8, 1.2 and 4.2 μmole/g paper. The insets show the assumed arrangement of the molecules of magnesium dioctadecanoate on the paper surface.

Figure 40 shows that the coefficient of friction dropped sharply to low levels already at C1/(C+O) ≈ 6 %, which corresponded to 1.2 μmole/g paper. Diiodomethane was adsorbed by
the papers containing 0.8 and 1.2 µmoles/g paper, (see table 2, paper III) indicating that the surface was incompletely covered by the magnesium salt at these concentrations. The low values of the C1/(C+O) ratio also indicate incomplete coverage. Thus, despite incomplete surface coverage, the Mg-dioctadecanoate maximally decreased friction. This phenomenon can perhaps be explained by a selective accumulation of the compound on the elevated areas, which are the most probable contact regions between rough surfaces, such as paper surfaces. Only these areas need to be covered by lubricant molecules to decrease the paper-to-paper friction. It is reasonable to assume that such an accumulation may occur due to the impregnation procedure: Since the paper sheets were dried on plates, the solvent mainly evaporated in the direction towards the top side of the paper. The Mg-dioctadecanoate molecules were probably dragged to the topside and their concentration in the solvent layer increased as the solvent evaporated. Elevated areas on the top side were probably the last regions to become dry, leading to an accumulation of Mg-dioctadecanoate. In figure 40, the assumed arrangement of Mg-dioctadecanoate molecules with increasing concentration in a paper is indicated. At low concentration the molecules are assumed to cover mainly elevated areas and at higher concentration to cover other regions of the paper surface.

11.2 Cellulose partially covered by stearic acid

The lateral distribution of high- and low-friction areas on a heterogeneous surface can be determined with lateral force microscopy, LFM. In LFM, an atomic force microscope is used to monitor the lateral force across an area and in this way “lateral force maps” may be obtained. Figure 41 shows (a) a “lateral force map” and (b) the corresponding height map of a cellulose surface impregnated with 0.4 nanomoles of octadecanoic acid, i.e. a partially covered cellulose surface.

![Figure 41](image1.png)

*Figure 41:* (a) A representative friction force map and the corresponding height map (b) of a cellulose surface impregnated with 0.4 nanomoles of octadecanoic acid. The scanned area was 1 x 1 µm and the lateral force map was recorded at an applied normal load of 10 nN. The measurements were carried out at 40% RH using a hydroxyl-functionalized tip.
Figure 41 shows that the lateral force of the partially covered cellulose surface was generally high in valleys and that it was low on the peaks of asperities and on high plateaus, indicating an accumulation of stearic acid. The reason for such an accumulation may be attributed to the impregnation procedure, see section 11.1. Figure 41 indicates that lubricant molecules may indeed become selectively accumulated on elevated areas, as suggested in the study described in paper III.

11.3 Conclusions: Accumulation of boundary lubricants on contact regions
The results presented in section 11 show that complete coverage of a paper surface by boundary lubricants is not a prerequisite for maximum lubrication. This phenomenon may be attributed to a selective accumulation of lubricants on elevated areas, which are also the most probable contact regions between rough surfaces, such as paper surfaces [15]. This may explain why even very low amounts of boundary lubricants are sufficient to reduce paper-to-paper friction.

12. The proposed friction model
The results described in this thesis indicate that both the fibrous structure and the surface chemistry influence paper-to-paper friction. More specifically, the degree of interlocking of the fibers of contacting surfaces governs the magnitude of friction hysteresis, whereas the presence of boundary lubricants on a paper surface influences the level of paper-to-paper friction. Based on these results the present author proposes the following model to explain the effect on the level of paper-to-paper friction of boundary lubricants that occur in paper.

12.1 Friction hysteresis
The magnitude of friction hysteresis, i.e. the dependence of friction on the direction of the previous slide, is governed by the degree of interlocking of the fibers of contacting surfaces and is fairly independent on the surface chemistry. The extent of interlocking depends on the orientation of fibers on the paper surface relative to the sliding direction. When the sliding direction is reversed after each slide, fibers of the contacting paper surfaces are pushed into each other and interlock during sliding causing high friction. For consecutive slides in the same direction, fibers of the contacting paper surfaces always become oriented in the sliding direction, which minimizes interlocking and this gives a low friction. Furthermore, the high friction during the first slide during a friction test is probably associated with the work necessary to raise and align the fibers on the paper surface in the sliding direction from their initial orientation.

12.2 The effect of boundary lubricants
The effect of boundary lubricants on the friction between paper surfaces is schematically illustrated in figure 42. The high level of friction between clean paper surfaces arises from a high shear strength due to strong adhesive forces between the contacts. At ambient humidity, this force is dominated by the contribution of the force due to Laplace pressure acting in water menisci that spontaneously form around the contacts between paper surfaces due to capillary condensation. The lubricating effect of low-molecular-mass lipophilic compounds (LLC) depends on their ability to form ordered monolayers on the surface that can withstand the stresses induced during sliding, so that friction is determined by the attractive forces between the layers. The monolayers increase the hydrophobicity of the paper surfaces, and this
suppresses capillary condensation. The adhesion force is then governed by the weak surface force acting inside the contact, causing low friction.

Figure 42: The proposed friction model to describe the effect of boundary lubricants: Capillary condensation occurs around the contacts between clean paper surfaces and between paper surfaces covered by non-lubricating compounds causing a strong attractive force between the contacts. The strong attractive force leads to high shear strengths between the contacts leading to a high friction. Lubricated paper surfaces are covered by monolayers of low-molecular-mass lipophilic compounds that separate the paper surfaces so that the interactions between the monolayers govern friction. These monolayers increase the hydrophobicity of the paper surfaces, which suppresses capillary condensation. The adhesion force is then governed by the weak surface force acting inside the contact, leading to a low friction.

In some observations, the kinetic friction between lubricated paper sheets was higher than the static friction. This behavior was attributed to wear of a lubricant layer at high sliding speed.

The results in section 9.3 show that the level of paper-to-paper friction of different paper grades is very dependent on the content of boundary lubricants. Further, un lubricated paper surfaces seem to have a common level of friction. Figure 32 shows that the third static coefficient of friction for extracted paper grades was about 0.75, which is close to the value of filter paper based on cotton cellulose. Based on these results, the present author proposes that the level of friction, $F$, between two sheets of paper is largely governed by the degree of coverage of contact regions by boundary lubricants, i.e.

$$ F \approx \phi F_1 + (1 - \phi) F_2, \quad (44) $$

where $\phi$ is the fraction of coverage of the contact areas by boundary lubricants, $F_1$ the level of friction of between lubricated paper surfaces and $F_2$ the level of friction between un lubricated paper surfaces.
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Niklas Garoff
14. References


