Modelling of wear and tribofilm growth

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Cover figure: An artistic visualisation of a contact between two surfaces with reacted layers, see Fig. B.1 for details.

Modelling of wear and tribofilm growth

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their never ending care and my sister for the all the inspiring energy she provides me with.
Abstract

Wear is a consequence of nature which becomes costly if uncontrolled. Basic wear protection is provided by lubrication which will decrease the severity of the contact between asperities. If the conditions of a contact are such that there can be no hydrodynamic lift off by the oil and most of the contact occurs in between such asperities, the protection is provided by chemically reacted layers, sometimes as thin as just a few nanometers.

In such cases where wear is governed by the most basic wear mechanisms, analytical models and numerical simulation tools have been developed and used to predict the extent of wear. Few of these models consider the interplay between contact mechanics and wear mechanisms. Wear modelling must keep improving.

The goal for this work is to examine the predictive efficiency of current models and initiate construction of reliable models for the chemical growth of wear reducing layers. To achieve this, numerical simulations of contact mechanics are used in Paper A to calculate the wear of contact surfaces and in Paper B as a basis for conditions of chemical growth.

The contact mechanics model is based on a solution to Boussinesq's problem applied to equations for the potential energy by Kalker. The method takes the contact's surface topographies and substrate material properties as input and outputs elastic and plastic deformation, contact pressure and contact area. The numerical implementation is efficiently evaluated by means of FFT-accelerated techniques.

The wear is usually treated as a linear function of contact pressure and in this case the Archard wear equation constitute a feasible approximation. This equation is implemented in the present contact mechanics model to approximately predict the extent of wear, in boundary lubricated contacts, by means of numerical simulations.

The chemistry of lubricant additives is discussed. Using chemical theory for adsorption as by Arrhenius, the molecular perspective of antiwear additives is explored. Mechanical properties of tribochemical antiwear layers are taken into account in the developed method.

The results in Paper A from wear simulations and comparison with an experiment shows the usefulness of wear equations of geometrical contact mechanics.

The chemical model in Paper B for tribofilm growth is applied to rough surfaces allowing comparison of the synergy between contact mechanics and chemistry for different surface contacts. The results show how tribofilms grow on rough or smooth surfaces. The model can be used to compare chemical acitivity for different surface designs.
Appended Papers

Paper A


Paper A introduces a new way to use wear simulations based strictly on contact pressure calculations for a ball on disc contact. The contact is used in the simulation to mimic the behaviour of an reciprocating test. The wear simulation results are compared with the results from the experimental test and limitations as well as advantages of the simulation method are discussed. All experiments were carried out by Joel Andersson. The numerical simulations were performed by Joel Andersson and coded based on code by Andreas Almqvist. Discussions between all authors led to the conclusions and presentation of the results.

Paper B

J. Andersson, R. Larsson, A. Almqvist, M. Grahn, I. Minami "Semi-Deterministic chemo-mechanical model of boundary lubrication", Submitted to Faraday Discussions 156, Southampton 2-4 April, 2012

Paper B includes development of a model for tribofilm growth. The model is first calibrated against experiments with smooth surfaces and is then used to compare efficiency of growth on different rough surfaces. The article was written by Joel Andersson and Roland Larsson. The numerical simulations were performed by Joel Andersson and coded based on code by Andreas Almqvist. The chemical model was developed in discussions between Joel Andersson, Andreas Almqvist, Roland Larsson, Ichiro Minami and Mattias Grahn.
Nomenclature

$\eta$ - Viscosity [Pa·s].

$\kappa$ - Dimensional wear constant [Pa$^{-1}$].

$\lambda$ - Wear depth [m].

$\nu$ - Poisson ratio.

$\xi$ - Spatial coordinate at pressurised point [m].

$\Pi$ - Residual error.

$\rho$ - The distance between a force and a deformed point [m].

$\upsilon$ - Single surface deformation [m].

$\chi_\eta$ - A function of poisson ratio.

$\Psi$ - Boussinesq potential [N].

$\Psi_1$ - Boussinesq potential [N/m].

$\Omega$ - Integration area of a square element [m$^2$].

$a$ - Index for current timestep.

$A$ - Substance concentration [mol/m$^3$].
- Numerical convergence parameter.
- Substance concentration [mol/m³].
- Substance concentration [mol/m³].
- Sliding distance [m].
- Sliding distance for one time step [m].
- Influence coefficients matrix [m].
- Elastic modulus [Pa].
- Contact pressure and tractions in q direction [Pa].
- Boussinesq potential.
- Boussinesq potential.
- The gap between two surfaces [m].
- Dimensonless gap between surfaces.
- Shear modulus [Pa].
- Thickness of tribofilm in x₃ direction [m].
- Highest allowed thickness of tribofilm [m].
- The thicker of two tribofilms on a contact spot [m].
- Tribofilm height on surface i [m].
- Index used to indicate top or bottom surface.
- Index indicating grid node number
- Reaction rate [mol/s].
- Pre-exponential factor [mol/m³s].
- Chemical constants [K].
- Chemical constants [J/s].
- Chemical constants [1/s].
$l_q$ - The length of a surface element [m].

$L_{q}$ - Length of calculation window [m].

$m$ - Order of chemical reaction.

$M$ - Number of nodes on a mesh.

$n$ - Order of chemical reaction.

$p$ - Contact pressure [Pa].

$p(x_1, x_2)$ - Continuous contact pressure [Pa].

$p(j)$ - Contact pressure on meshpoint $j$ [Pa].

$p$ - Non-dimensional contact pressure vector.

$p_{ps}$ - The plastic deformation pressure of the substrate [Pa].

$p_{ptf}$ - The lowest plastic deformation pressure of the film [Pa].

$P$ - Dimensionless contact pressure.

$P_3$ - Normal point load [N].

$q$ - Index used to indicate spatial directions.

$r$ - Radius of contact area for a spherical contact [m].

$R_{qi}, R_q$ - Principal radii of spherical surfaces [m].

$s$ - Integration variable [m].

$S$ - Contact area [m$^2$].

$t$ - Time [s].

$\Delta t$ - Time step [s].

$T$ - Temperature [K].

$u_q$ - Surface deformation in $q$ direction [m].

$U$ - Dimensionless deformation.

$U_p$ - Plastic deformation [m].
\(v\) - Relative surface velocity [m/s].

\(V, V^*\) - Variational principle potential energy [J].

\(w\) - Load [N].

\(x_q\) - Spatial coordinates [m].

\(y\) - Index indicating grid node number.

\(z_i\) - Spherical surfaces [m].
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Part I

Comprehensive Summary
Chapter 1

Introduction

The goal with this licentiate thesis is to develop models for wear and tribochemistry in boundary lubrication. It is part of a pursuit for increased energy efficiency, better wear prevention and decreased fuel consumption of machines. All of this is achieved through continuous improvements of tribological systems. Examples of such improvements are optimizing surface texture, materials, lubricant composition as well as machine design.

Much can be improved by trial and error experiments. But as the number of parameters and design alternatives increase, the range of experimental methods alone is limited by cost. Many companies and researchers therefore implement numerical simulations as a complement to experimental efforts and analytical calculations. Better models renders it possible to test radical design changes at a lower cost. In this licentiate thesis models for tribochemistry and wear in boundary lubrication are developed.

The multidisciplinary character of tribology is often discussed. As in the interface of contacts in relative motion many effects take place, from chemical reactions, physical adhesive effects on the nano scale, to bulk deformation, micro-cracking, rheology, introduction of dust particles and the list goes on. The study of tribology is therefore of interest to a wide span of experts. The scientific language used in this thesis may not be familiar to everybody. Therefore, in the following section, the language of tribology and the concept of boundary lubrication is introduced.

After that, the state of the art is presented and some gaps in the field motivate the objectives.

1.1 Lubrication regimes and wear

Tribology is the study of surfaces in relative motion. Words commonly associated with tribology are friction, wear and lubrication. Friction is the dissipation of energy that occurs between moving objects. Wear is when the energy dissipated detrimentally alters the contacting surface materials. Lubrication is the art of controlling friction and wear by adding lubricant to the tribological system.
CHAPTER 1. INTRODUCTION

Figure 1.1: Schematic interpretation of the Stribeck curve. The curve illustrates how the friction coefficient varies with the Hersey number, or more specifically, it is a function of viscosity ($\eta$), velocity ($v$) and pressure ($p$). At low values of the Hersey number no significant pressure can be built up in the lubricant. i.e. the load has to be carried by surface bulk. This is the boundary lubrication regime. Once the pressure starts to build up in the lubricant and helps to separate the surfaces, increased separation quickly decreases the friction. This is the mixed lubrication regime. Once the highest asperities no longer collide, the surfaces lift off and the volume were viscous losses(friction) occur increase with separation. This is the full film lubrication regime.

1.1.1 Lubrication

The structured study of lubrication, is often associated with Richard Stribeck [1], who studied friction as a function of the Hersey number (velocity ($v$) times viscosity ($\eta$) divided by the pressure ($p$)), in a journal bearing in the first half of the 20th century. Varying these parameters, he found a connection between friction and the Hersey number. When friction is plotted against the Hersey number, the resulting curve is known as the Stribeck curve. The curve indicates a natural division of fluid lubrication into three different lubrication regimes, namely: (see also Fig. 1.1)

1. **Boundary lubrication** is a lubrication regime, where most of the load is carried by the substrate material. In this regime the lubricant is unable to fulfill its role as a load carrier and therefore works mainly as an agent for bringing lubricant additives into the contact. These chemical additives bind chemically and through physisorption to the surface and are able to remain in the contact despite the severe local conditions.
2. In the mixed lubrication regime, the lubricant carries more of the load but there is still the occasional contact between asperities. As the load carrying capacity of the lubricant depends directly on the velocity, viscosity and pressure, the separation between the surfaces and thus the amount of asperity collisions decrease quickly moving to the right in the Stribeck curve.

3. In the full film lubrication regime there is no more contact between the surfaces and all the load is carried by the hydrodynamic pressure formed in the lubricant. Now the sliding resistance occurs inside the lubricant due to viscous losses. This means that increased separation will also increase the friction.

Intuitively most of the wear occurs in the boundary lubrication regime. Therefore it is often desirable to avoid this regime of lubrication all together. Unfortunately, this is not always so easily done. When local pressures are high or when two surfaces are moving with a low relative velocity, boundary lubrication will be the result.

1.1.2 Wear

Wear is undesirable deformation or loss of material on surfaces due to load and relative motion between them. It is usually a destructive and undesirable process. With such a broad definition there are many mechanisms which lead to wear. Wear is a whole field of science, but there are some attempts to establish simplified laws and formulas for wear.

When a contact has failed, the analysis of wear involves the identification of a wear mechanism. If the failure was caused by plastic deformation or by scratching, the wear mechanism was abrasive. If failure was caused by sulfuric corrosion the wear mechanism was tribochemical. If failure was caused by smearing or scuffing deformation the wear mechanism was adhesive. Adhesive and abrasive wear are the most common wear mechanisms. Other wear mechanisms are surface fatigue, fretting and erosive wear.

A commonly used model for adhesive and abrasive wear is the Archard wear law [2,3], which linearly relates the wear per sliding distance to the pressure. More precisely

\[ \lambda = \kappa pd, \]

where \( \lambda \) is the wear depth, \( p \) is the pressure, \( \kappa \) is the dimensional wear coefficient and \( d \) is the sliding distance.

1.2 The state of the art and gap analysis

The chemistry and mechanics during boundary lubrication are subjects studied by means of many different scientific approaches. First principle molecular dynamics simulations are applied to understand nano scale details, e.g. Mosey et al. [4], Naveira Suarez et al. [5] and Minfray [6]. Empirical models based on experimental observations can be used to model the mild wear behavior observed in boundary lubricated contacts, e.g. Archard [3].
CHAPTER 1. INTRODUCTION

Linking between asperity scale and application is dominated by statistical models. In statistical models the surfaces are restricted in terms of shape for instance by assumptions of asperity radii and asperity height by some probability density function. Greenwood, Tripp and Williamson [7,8] introduced such concepts. Extensions of more complicated asperity collisions is motivated by statistical assumptions by many authors [9–11]. A statistical model by Zhang et al. [12] includes several observed phenomena occurring during boundary lubrication. Applying the models to real surfaces can be difficult, as statistical parameters are hard to measure.

Recent developments of numerical tools and faster computers allow for deterministic investigations of contact mechanics, even with rough surfaces. Bosman and Schipper, for example, investigate the combination of surface roughness and multilayer effect on wear [13,14]. The work in [13] shows how numerical simulations can be used to explain tribological wear phenomena. The investigation is focused on the presence of noncrystalline layers. These fine grain layers exhibit plasticity behavior vastly different from the steel bulk.

The height of experimentally observed ZDDP tribofilm, is in the same order of magnitude as the roughness of many standard treated surfaces’ roughness, see e.g. Spikes [15]. This indicates that the geometry of the chemical layer can have an effect on the wear mechanics. Furthermore, the mechanical properties of tribofilms vary with the height of the film, as shown by Demmou et al. [16]. Investigations of how the tribofilms grow and effect roughness on a surface is therefore of interest.

The driving mechanism of the tribofilm growth is believed to be high energies in asperity collisions. The geometrical distribution of asperities leads to high local energy concentration which is believed to be the origin of the bulky structure of the tribofilm. Several possible kinetic models were proposed for the average film height by Fujita et al. [17,18]. In their work, it is speculated around both uniform film growth and local expansion of tribofilm to explain the average film height. Spacer layer interferometry was used to get updates on the tribofilm height as time passes but lack of in situ information leads to a speculative nature of the equations for tribofilms formation and removal. With numerical simulations it is possible to explore what is happening inside the contact, based on a frame of approximations. This is not possible with to do with experimental techniques.

In this licentiate thesis deterministic models for wear and for tribofilm growth governed by energy due to friction power are developed and numerical simulations exploring wear behavior and contact in situ information are conducted.

1.3 Objectives

The objectives of this licentiate thesis are

- Development of a wear model with a time range suitable for comparing with tribological experiments.

- Development of a model for tribofilm growth. The model should incorporate contact mechanics to simulate tribological conditions.

- Extract simulation information from inside a contact during sliding conditions.
1.4 Outline of this thesis

The thesis starts with an introduction of the subject. Chapter 2 introduces some contact mechanics and describes how pressure and deformation are related and numerically calculated. In Chapter 3, lubricants and their additives are discussed from a molecular perspective. The antiwear additive Zinc dialkyldithiophosphates (ZDDP) and how it grows a tribofilm is given special attention. Basic reaction chemistry is introduced. Chapter 4 describes the numerical procedure for solving the contact mechanics and how chemical growth of tribofilms is implemented. Chapter 5 briefly summarize the results from Paper A and Paper B. Chapter 6 ends the licentiate thesis by stating some conclusions and future work.
Chapter 2

Contact mechanics

The essential difference between boundary lubrication and other lubrication regimes is the domination of contact between solids in the material pair. The mathematical description of contact between solids is known as contact mechanics. In contact mechanics, the surface and bulk response to the contact is studied. One extensive book in the field is by K.L. Johnson [19]. Modern contact mechanics is based on theoretical work ranging back to the 19th century, by Boussinesq and Cerruti. The analysis was refreshed by Love, in the book *the mathematical theory of elasticity* [20]. Commonly used notation is introduced by Timoshenko and Goodyear in *theory of elasticity* [21]. The numerical contact mechanics solvers used by the author are based on publications by Kalker [22], Ju and Farris [23], Stanley and Kato [24] and others.

This chapter starts with introducing Hertz theory. After that the methods of minimal potential energy and the variational principle of contact elastostatics is reviewed. Solving the minimization problem numerically utilize implementation of solutions to Boussinesq’s problem by mathematical potential theory, the third topic of this chapter. The chapter ends with a discretization of the variational principle, and incorporation of the deformation solution.

2.1 Hertz Theory

Hertz theory is a theory for the elastic deflection of elastic spheres. A contact pressure $p(x_1, x_2)$ in the area $S$ is found. The contacting bodies are approximated by parabolas in Hertz theory. The spherical surfaces $z_1$ and $z_2$ can be approximated by second degree polynomials according to

$$z_i = (-1)^i \frac{1}{2R_{qi}} x_q^2,$$

with summation over coordinate index $q = 1, 2$ but not over surface indicator index $i = 1, 2$. The $R_{qi}$ represent different principal radii of the surfaces. The approximation of the sphere is valid if the contact radius is small compared to the principal radii. $x_q$ represent the two coordinate directions of the contact plane. It
is convenient to look at the gap between the surfaces $g(x_1, x_2)$ which is of the form

$$g(x_1, x_2) = \frac{1}{R_q} x_q^2.$$  \hfill (2.1.2)

With $\frac{1}{R_q} = \frac{1}{2R_{q_1}} + \frac{1}{2R_{q_2}}$. Eq. (2.1.2) assumes summation over $q$. In order to get contact stresses and start analysing the contact mechanics, a load is applied to each surface. As a result the surfaces $z_i$ are each deformed by an amount $u_i(x_1, x_2)$ in the $x_3$ direction. If the surfaces were not deformed, we can imagine an overlap of the surfaces, corresponding to their distortion in space $\delta_i$. One demand for the idealised mathematical treatment is that substrate overlap is not allowed. This means that

$$u_1(x_1, x_2) + u_2(x_1, x_2) + g(x_1, x_2) = \delta_1 + \delta_2$$ \hfill (2.1.3)

is satisfied in the contact zone, $S$ and

$$u_1(x_1, x_2) + u_2(x_1, x_2) + g(x_1, x_2) > \delta_1 + \delta_2$$ \hfill (2.1.4)

is satisfied out of contact. Hertz found the contact pressure distributions $p(x_1, x_2)$ which results in deformations which satisfy equations 2.1.3 within $S$ and 2.1.4 outside $S$. Hertz theory is valid when the following assumptions are fulfilled.

1. Continuous non-conforming surfaces ($r << \min(R_{q_i})$).
2. Small strains ($r << \min(R_{q_i})$).
3. The contacting bodies are elastic half-spaces $r << \min(R_{q_i})$, $r << \delta$.
4. Frictionless contact.
5. The contact forces are much greater than the body forces.

$\min(R_{q_i})$ represent the smallest of the significant radii of the the contact. $r$ is the radius of the contact zone and $\delta$ is the undeformed distortion. To derive the correct pressure distributions, potential theory is used.

### 2.2 Minimization Problem

In mechanics there are a principles of minimal virtual work for many systems. These principle states that the virtual work vanishes for non-reaction forces. This means there is an expression which must be minimal when a system is in equilibrium. For contact elastostatics Kalker [22] has formulated such a principle. For frictionless contact the expression to be minimised is

$$V = \frac{1}{2} \int \int_S p(x_1, x_2) u_3(x_1, x_2) dS - \int \int_S p(x_1, x_2) g(x_1, x_2) dS.$$ \hfill (2.2.1)

In Eq. (2.2.1) $g(x_1, x_2)$ is the separation between two solid surfaces, $p(x_1, x_2)$ is the normal($x_3$ direction) pressure distribution in the contact and we integrate over a region $S$ where the contact is assumed to occur. $u_3$ is the deformation in normal direction.
2.3. THE BOUSSINESQ POTENTIAL SOLUTION

In order to solve 2.2.1 by variational calculus or numerical methods, the deformation as a function of pressure and the undeformed separation are sufficient. The deformation as a function of pressure was derived by lord Kelvin, Boussinesq and Cerruti.

2.3 The Boussinesq potential solution

Figure 2.1: Notation used in the derivation of deformations on a point \((x_1, x_2, x_3)\) due to point forces on coordinates \((\xi_1, \xi_2)\) on the circular surface

Boussinesq, see e.g. Love [20] has provided solutions for the behaviour of a half plane due to a load distribution on the surface \(S\) with traction components \(f_1, f_2\) and \(f_3\) \((f_3 = p)\). The solution utilize potential theory. No derivation is made here but the solution is presented. Indicies \(q = 1 - 3\) indicate directions \(x_q\), see Fig. 2.1 for the notation. The first potential function \(F_{1q}\) which is used to describe displacements can be written

\[
F_{1q} = \int_S f_q(\xi_1, \xi_2)\Omega d\xi_1 d\xi_2, \quad (2.3.1)
\]

with

\[
\Omega = x_3 \ln(\rho + x_3) - \rho
\]

and

\[
\rho = ((x_1 - \xi_1)^2 + (x_2 - \xi_2)^2 + x_3^2)^{1/2}.
\]
The notation used is illustrated in Fig. 2.1. Another potential $F_q$ is defined,

$$F_q = \frac{\partial F_q}{\partial x_3} = \int_S f_q(\xi_1, \xi_2) \ln(\rho + x_3) d\xi_1 d\xi_2. \quad (2.3.2)$$

To write the deformations in a compact way, Love also uses

$$\Psi_1 = \frac{\partial F_1}{\partial x_3} = \frac{\partial F_q}{\partial x_q}, \quad (2.3.3)$$

with the summation convention applied, and

$$\Psi = \frac{\partial \Psi_1}{\partial x_3} = \frac{\partial F_q}{\partial x_q}. \quad (2.3.4)$$

The components of elastic displacement $u_q$ at any point $A(x_1, x_2, x_3)$ can then be written, according to Love

$$u_1 = \frac{1}{4\pi G} \left( 2 \frac{\partial F_1}{\partial x_3} - \frac{\partial F_3}{\partial x_1} + 2\nu \frac{\partial \Psi_1}{\partial x_1} - x_3 \frac{\partial \Psi}{\partial x_1} \right) \quad (2.3.5)$$

$$u_2 = \frac{1}{4\pi G} \left( 2 \frac{\partial F_2}{\partial x_3} - \frac{\partial F_3}{\partial x_2} + 2\nu \frac{\partial \Psi_1}{\partial x_2} - x_3 \frac{\partial \Psi}{\partial x_2} \right) \quad (2.3.6)$$

$$u_3 = \frac{1}{4\pi G} \left( 2 \frac{\partial F_3}{\partial x_3} - \frac{\partial F_3}{\partial x_3} + (1 - 2\nu) \frac{\partial \Psi_1}{\partial x_3} - x_3 \frac{\partial \Psi}{\partial x_3} \right) \quad (2.3.7)$$

or

$$u_q = \frac{1}{4\pi G} \left( 2 \frac{\partial F_q}{\partial x_3} - \frac{\partial F_q}{\partial x_q} + \chi_q \frac{\partial \Psi_1}{\partial x_q} - x_3 \frac{\partial \Psi}{\partial x_q} \right) \quad (2.3.8)$$

with $\chi_1 = \chi_2 = 2\nu$ and $\chi_3 = 1 - 2\nu$. So if the contact tractions are known beforehand, the deformation can be easily found. A problem arises when the tractions depend on each other. A particularly common way to get ahead is to set the tangential tractions to 0, and thus simplify the problem of finding deformations considerably. This leads to the solution of Boussinesq’s problem. By setting normal tractions to 0, Cerruti’s problem is solved instead.

**Example 2.1. Deformation due to normal point load**

To derive from Eq. (2.3.8) the influence of the load in a point, the point load must first be specified. Considering an area $S$ loaded only in the $x_3$ direction, letting the area go to zero and defining the resulting point load to $P_3$ gives the following expression for the load.

$$P_3 = \int_S f_3(\xi_1, \xi_2) d\xi_1 d\xi_2. \quad (2.3.9)$$

If this load is applied in the origin, $\rho = (x, x_q)^{1/2}$. The potentials $\Psi_1$, $\Psi$ and $\frac{\partial \Psi}{\partial x_3}$ can be calculated (we have normal loading, so $f_1 = f_2 = 0$ and consequently
2.3. THE BOUSSINESQ POTENTIAL SOLUTION

\[ F_1 = F_2 = 0. \]

\[ \Psi_1 = \frac{\partial F_1}{\partial x_q} = \frac{\partial F_1}{\partial x_3} = F_3 = \int_S f_3(\xi_1, \xi_2) \ln(\rho + x_3) d\xi_1 d\xi_2 = P_3 \ln(\rho + x_3) \]

(2.3.10)

\[ \Psi = \frac{\partial \Psi_1}{\partial x_3} = P_3 \frac{\partial}{\partial x_3} \ln(\rho + x_3) = \frac{P_3}{\rho} \]

(2.3.11)

\[ \frac{\partial \Psi}{\partial x_3} = P_3 \frac{\partial}{\partial x_3} \ln(\rho + x_3) = -P_3 \frac{x_3}{\rho} \]

(2.3.12)

These values in Eq. (2.3.8) gives the deformation \( v(x_1, x_2, x_3) \) in \( x_3 \) direction due to the point load in the origin.

\[ v(x_1, x_2, x_3) = \frac{1}{4\pi G} \left( \frac{\partial F_3}{\partial x_3} + (1 - 2\nu) \Psi - x_3 \frac{\partial \Psi}{\partial x_3} \right) = \frac{1}{4\pi G} \left( \frac{P_3}{\rho} + (1 - 2\nu) \frac{P_3}{\rho} + P_3 \frac{x_3^2}{\rho^3} \right) = \frac{P_3}{2\pi G} \left( 1 - \nu \right) \frac{1}{\rho} + \frac{x_3^2}{2\rho^3} \]

(2.3.13)

The Hertz approximation of small angles means that the \( x_3 \) term is small compared to \( x_2 \) and \( x_1 \). Setting \( x_3 = 0 \), an approximation that can be considered valid as long as \( x_3^2 << x_1^2 + x_2^2 \) on the rough surface, the deformation of the surface is acquired.

\[ v(x_1, x_2) = \frac{P_3(1 - \nu)}{2\pi G \rho x_3 = 0} = \frac{P_3(1 - \nu^2)}{\pi E} \frac{1}{\sqrt{x_1^2 + x_2^2}} \]

(2.3.14)

If there is a distributed normal load \( p(x_1, x_2) \) on the surface, the deformation \( v_{\text{tot}}(x_1, x_2) \) will be given by the summed influence (the integral) of the loaded infinitesimal surface elements.

\[ v_{\text{tot}}(x_1, x_2) = \frac{1 - \nu^2}{E \pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{p(s_1, s_2)}{\sqrt{(x_1 - s_1)^2 + (x_2 - s_2)^2}} ds_1 ds_2 \]

(2.3.15)

With two surfaces in contact, acting upon each other with normal forces, we get their total deformation in \( x_3 \) direction \( u_3(x_1, x_2) \),

\[ u_3(x_1, x_2, 0) = \left( \frac{1 - \nu^2}{E_1 \pi} + \frac{1 - \nu^2}{E_2 \pi} \right) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{p(s_1, s_2)}{\sqrt{(x_1 - s_1)^2 + (x_2 - s_2)^2}} ds_1 ds_2 \]

(2.3.16)

or

\[ u_3(x_1, x_2) = \frac{1}{\pi E} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{p(s_1, s_2)}{\sqrt{(x_1 - s_1)^2 + (x_2 - s_2)^2}} ds_1 ds_2 \]

(2.3.17)
2.4 Discretisation

Since there is no explicit formula available to estimate the contact deformation, numerical techniques will have to be utilised and the contact deformations need to be calculated over a discrete mesh. Considering the out of plane deformation on the contact plane, \( u_3(x_1, x_2) \) from square elements with sides of equal dimensions \( 2l_1 \) and \( 2l_2 \) which all are considered to contribute with uniform pressures, the total deformation is given by summing their individual contributions calculated from Eq. (2.3.17)

\[
 u_3(x_1, x_2) = \frac{1}{\pi E^*} \sum_{y=1}^{M} \int_{\Omega_y} \int \frac{ds_1 ds_2}{\sqrt{(x_1 - s_1)^2 + (x_2 - s_2)^2}} p_y
\] (2.4.1)

where \( M \) is the amount of square elements that come into contact and \( \Omega_y \) is the domain of each pressure element with value \( p_y \). This equation will be correct for a fine mesh.

As we are now working on a mesh with \( M \) elements, the origin can be allowed to move across the grid on all the nodes \( j \) of the mesh. So the deformation occurs instead of in the origin at element \( j \).

\[
 u_{3j} = \frac{1}{\pi E^*} \sum_{y=1}^{M} D_{yj} p_y
\] (2.4.2)

For all of the mesh points \( j = 1, 2, 3, ..., \) the integration area \( \Omega_y \) in Eq. (2.4.1) is of the same size but with different coordinate values \( x_1 \) and \( x_2 \), so \( D_{yj} \) is always given by the equation

\[
 D_{yj} = \frac{1}{\pi E^*} \int_{-l_1}^{l_1} \int_{-l_2}^{l_2} \frac{ds_1 ds_2}{\sqrt{(x_1 - s_1)^2 + (x_2 - s_2)^2}}
\] (2.4.3)

which has solution

\[
 D_{yj} = \frac{1}{\pi E^*} \left\{ (x_1 + l_1) \ln \left[ (x_2 + l_2) + \sqrt{(x_2 + l_2)^2 + (x_1 + l_1)^2} \right] \\
 + (x_2 + l_2) \ln \left[ (x_1 + l_1) + \sqrt{(x_2 + l_2)^2 + (x_1 + l_1)^2} \right] \\
 + (x_2 - l_2) \ln \left[ (x_2 - l_2) + \sqrt{(x_2 - l_2)^2 + (x_1 - l_1)^2} \right] \\
 + (x_2 - l_2) \ln \left[ (x_2 - l_2) + \sqrt{(x_2 - l_2)^2 + (x_1 - l_1)^2} \right] \\
 + (x_1 - l_1) \ln \left[ (x_1 - l_1) + \sqrt{(x_2 - l_2)^2 + (x_1 - l_1)^2} \right] \\
 + (x_1 - l_1) \ln \left[ (x_1 - l_1) + \sqrt{(x_2 + l_2)^2 + (x_1 - l_1)^2} \right] \right\}
\] (2.4.4)

Numerically, the influence coefficients \( D_{yj} \) can be calculated for each point on a mesh, and they quickly give the deformation of all elements on the mesh by
multiplying the influence matrix (tensor of degree 2) with the pressure vector. The non-dimensional vector form of Eq. (2.4.2) is

\[ u = Dp. \] (2.4.5)

where, \( u \), \( D \) and \( p \) are the non-dimensional forms of the deformation, influence matrix and pressure, respectively.
Chapter 3

Tribochemistry

Tribochemistry is the study of chemistry under tribological conditions. The most important tool in controlling friction is the lubricant, whose chemical and physical properties are designed for a number of purposes. Lubricant additives are used to further enhance certain properties of the lubricant. In particular, antiwear additives are used to limit destructive consequences of wear. The antiwear additives form protective layers called tribofilms through chemical reactions with the surface.

3.1 Lubricants

Basically any material which is added to a tribological system in order to alter the wear or friction properties is a lubricant. The most common way to lubricate machine components is by an oil base stock which is blended with some lubricant additives. Lubricants enhance the tribological properties of a contact by altering its physical and chemical properties.

Physical properties such as density, viscosity, heat capacity, pour point, cloud point and thermal conductivity are important in full film and mixed lubrication. In boundary lubrication the chemical properties, like polarity, oxidation inhibition, solubility, antiwear properties, anti corrosion properties and cleansing properties like dispersancy and detergency are important. Mechanical properties like shearability or friction are important in all lubrication regimes but cannot be said to be properties of the lubricant but rather they are properties of the tribological system.

A typical engineering lubricant consists of base oil and additives. Base oils can be either synthetic or mineral. On the molecular level oils typically consist of long chains (20-30 atoms) of carbon saturated with hydrogen. Mineral oils are less pure but cheaper and therefore dominate in industry, while synthetic oils operate under extreme conditions e.g. high temperature or special conditions when high purity is desired for instance in scientific applications. As lubrication technology is becoming more advanced, synthetic oil are starting to replace mineral oils in some of its traditional areas.

Focusing on boundary lubrication, the base lubricants’ job is not as important as the job of the additives. The lubricant as a carrier of additives is still important. For instance, an oil with improperly chosen polarity may cause lubricant molecules
to interfere with additives by adhering to the surface and block out reaction cites. See *e.g.* [5] for more information about the effect of base oil polarity on additive efficiency.

### 3.2 Additives

The additive is made soluble in the oil by taking a surface active chemical and adding to it an oliophillic group which is soluble in the base oil. The active chemical is chosen to give the lubricant enhanced properties. Lubricant additives modify properties of the tribological system including antiwear, friction, oxidation, pour point, viscosity and detergency.

Antiwear properties are essential for the lifetime of mechanical parts. The most commonly used antiwear additive is ZDDP. It has an ability to form a protective layer of chemisorbed molecules, only a few hundred nm thick, which greatly improves the wear behavior in steel contacts. This layer is known as a thermal film or tribofilm, depending the driving formation mechanism.

### 3.3 Protective boundary film

The transparent solid called thermal film forms on a steel surface when the ZDDP solution in contact with a surface is heated above 100°C. The film consists of a thin (about 10 nm) outer layer of polyphosphate grading to pyro- or ortho- phosphate in the bulk. The main cation in ZDDP thermal films are Zn, unlike tribofilms whose main cation is Fe [25].

A film often referred to as tribofilm can form at much lower temperatures than the thermal film, even as low as room temperature. The rate of formation depends on the temperature [17]. The tribofilm forms in asperity contacts rather than at large lubricant thickness and if there is a sliding contact rather than a rolling contact [26].

The structure of the tribofilm has been found to be pad-like. This can be observed in scanning force microscopy (SFM) images by Aktary *et al.* [27,28].

It can be observed that the cross section of the film is separated by valleys. The pads consist mainly of glassy phosphate with a thin, outer layer of Zn polyphosphate and with pyro- or ortho-phosphate in the bulk [15]. It has been found that the pads are smart in the sense that they become harder during nano indentation, meaning that they harden under operation [29].

This could be explained by cross-linkage of Zn phosphates under pressure. A computer simulation by Mosey *et al.* indicated cross-linkage in motor oil additives [4]. Despite efforts, the cross-linkage theory has yet to be experimentally verified for lubricant additives [30].

#### 3.3.1 Step by step ZDDP film formation

Marina L. Suominen Fuller *et al.* proposed a model for the ZDDP film formation [31]. In the first step ZDDP is adsorbed on the rubbing surfaces as described
3.4 REACTION CHEMISTRY

in Eq. (3.3.1).

\[ \text{Zn}[(\text{RO})_2\text{PS}_2]_2 \text{ (solution)} \rightarrow \text{Zn}[(\text{RO})_2\text{PS}_2]_2 \text{ (adsorbed)} \]  

(3.3.1)

After some time, ZDDP (partially) converts to a LI-ZDDP in solution,

\[ \text{Zn}[(\text{RO})_2\text{PS}_2]_2 \text{ (solution)} \rightarrow \text{Zn}[\text{O}_2\text{P(SR)}_2]_2 \text{ (LI-ZDDP in solution)} \]  

(3.3.2)

The LI-ZDDP will later adsorb along with ZDDP on the surface,

\[ \text{Zn}[\text{O}_2\text{P(SR)}_2]_2 \text{ (LI-ZDDP in solution)} \rightarrow \text{Zn}[\text{O}_2\text{P(SR)}_2]_2 \text{ (adsorbed)} \]  

(3.3.3)

After this, the adsorbed species of ZDDP and LI-ZDDP react thermooxidatively and a long chain polyphosphate results on the surface (Eq. (3.3.4)).

\[ \text{Zn(RO)}_4\text{P}_2\text{S}_4 + \text{O}_2 \rightarrow \text{Zn(PO)}_3\text{ (adsorbed)} + \text{ sulphur species} \]  

(3.3.4)

As more rubbing occurs phosphates come in contact with water and form short
chain pollyphosphate (Eq. (3.3.5) and/or Eq. (3.3.6)).

\[ 7\text{Zn(PO)}_3\text{ (adsorbed)} + 6\text{H}_2\text{O} \rightarrow \text{Zn}_7(\text{P}_5\text{O}_{16})_2 + 4\text{H}_3\text{PO}_4 \]  

(3.3.5)

\[ 2\text{Zn(PO)}_3\text{ (adsorbed)} + 3\text{H}_2\text{O} \rightarrow \text{Zn}_2\text{P}_2\text{O}_7 + 2\text{H}_3\text{PO}_4 \]  

(3.3.6)

The fully formulated film is a complex matter, with high concentrations of FeO/FeS
layer near the bulk with short chain ployphosphates on top of it and longer chain pollyphosphates on top.

Clearly, the reaction mechanisms of ZDDP are not as simple as one might
wish. Even if the above theory is not exactly correct it is clear that a number of
chemical reactions are involved in the process of building a tribofilm. It is a bold
assumption to make that just one or a few of these reactions is a bottleneck for
growth of tribofilm formation. Still this is one of the many assumptions made in
Paper B.

3.4 Reaction chemistry

In basic reaction chemistry the reaction rate \( \frac{dC}{dt} \) for a chemical reaction
where substances \( A \) and \( B \) react to produce substance \( C \) depends on the
temperature \( T \) and is given by Arrhenius equation [32]:

\[ \frac{dC}{dt} = k(T)A^m \cdot B^n. \]  

(3.4.1)

where

\[ k(T) = K_1e^{-K_2/T} \]  

(3.4.2)

\( A, B \) and \( C \) in Eq. (3.4.1) represent the concentrations of substances \( A, B \) and \( C \)
respectively. \( K_2 \) is a constant which includes the activation energy of the reaction
and the universal gas constant. In the present model, \( K_2 \) must be found from
curve-fits to experiments. \( K_1 \) is the pre-exponential factor which tells about the
probability that a reaction occurs.
Paper B derives an equation for tribofilm growth based on Eq. (3.4.1). It is achieved with a number of simplifications. One knowledge gap in the current understanding of the chemistry of the tribofilm growth is that values of constants $K_1$ and $K_2$ for one or more fundamental reactions has not been found. The chemistry applied in Paper B is motivated as a step to better understanding of the tribofilm reaction mechanisms.

A dream model for prediction of ZDDP growth would be based on knowledge about the detailed reaction kinetics of the molecules and their reaction rate. This could possibly be examined by careful experiments and molecular dynamics simulations. The resulting reaction energies would be used to predict the constants $K_1$ and $K_2$, or show a need to include new adsorption models. Fluid mechanical calculations would predict the local concentration of different chemicals across the surfaces. Contact and thermal mechanics would finally predict the temperature and pressure. Combining all these effects lead to a dream tribolochemical film growth model. The model in Paper B is the start of such a model, one of the first synergetic models for tribofilm behaviour.
Numerical Implementation

In order to create a numerical model which can predict wear mechanisms and wear severity, the models presented so far need to be reformulated for computer implementation and combined in a reasonable fashion. The contact pressure is a good measure on the severity of contact. Just knowing the contact pressure and material combination can intuitively tell quite a lot about how the contact will wear. When the desired goal is to investigate wear in terms of time-development, the simplest implementation is to use for example Archard’s wear law directly. In boundary lubrication, chemical reactions are of great importance to antiwear behavior. In order to study the growth of tribofilms, a simple model for growth and how to apply it is described. The contact mechanics of a tribofilm is important to its antiwear mechanisms. A method accounting for variations in plastic deformation pressure is presented.

4.1 Contact pressure calculation

A discrete version of Eq. (2.2.1) is

\[ V^* = \frac{1}{2} \sum_{j=1}^{M} p_j \left( \sum_{y=1}^{M} D_{yj} p_y \right) - \sum_{j=1}^{M} p_j g_j \]  

(4.1.1)

where \( g_j \) is the gap at node \( j \), \( p_j \) the pressure and \( D_{yj} \) the influence coefficients as in Eq. (2.4.3). The expression in vector form is

\[ V^* (\mathbf{P}) = \frac{1}{2} \mathbf{p}^T \mathbf{Dp} - \mathbf{p}^T \mathbf{g} \]  

(4.1.2)

Any local minimum of this function will mean \( \nabla V^* = 0 \), so

\[ \nabla V^* (\mathbf{P}) = \mathbf{Dp} - \mathbf{g} = 0 \]  

(4.1.3)

for the equilibrium condition of the deformation and pressure.

The calculation of Eq. (4.1.3) can be performed directly, but the calculation speed will depend on the square of the amount of grid nodes \( (M^2) \). If advantage is
CHAPTER 4. NUMERICAL IMPLEMENTATION

taken of the convolution form of $C_{kj}$ (see Eq. (2.4.1)), multiplication in the Fourier plane can directly give the deformation due to a pressure distribution. Applying fast Fourier transform (FFT) the calculation time will be reduced to $M \log M$, a considerable improvement for large grids. A numerical procedure is to guess a pressure and then iterate until the residual

$$\Pi_p = \text{IFFT}(\text{FFT}(C) \cdot \text{FFT}(p)) - g,$$  \hspace{1cm} (4.1.4)

is sufficiently close to 0. in Eq. (4.1.4) FFT indicates (fast) Fourier transformation and IFFT inverse (fast) Fourier transformation. The pressure guess is adjusted according to

$$P_{\text{new}} = P_{\text{old}} - b(U + G).$$  \hspace{1cm} (4.1.5)

Here $P$, $U$ and $G$ are the dimensionless forms of $p$, $u$ and $g$ respectively and $b$ is a factor controlling the magnitude of the pressure adjustment.

A procedure for plastic deformation is also implemented in Paper A and Paper B. The plastic deformation is taken into account by letting points which experience pressures above a certain limit float and stay outside the pressure calculation. This leads to a feasible albeit somewhat slow implementation, as information from points in plastic deformation is discarded in the numerical procedure. The numerical procedure of the load calculation is illustrated by the flowchart in Fig. 4.1. See Sahlin et al. [33,34] for more details on the contact mechanical calculations.

### 4.2 Implementation of Archard’s wear law

When the contact pressure is known, the implementation of Archard’s wear law is extremely simple. Eq. (1.1.1) is rewritten in a form more suitable to the numerical calculation following the procedure described in Paper A, leading to an expression of the form

$$\Delta \lambda_j = \kappa p_j \Delta d.$$  \hspace{1cm} (4.2.1)

Where $\Delta \lambda_j$ is the change of the geometry due to wear, $\Delta d$ is the sliding distance during the current time step and $\kappa$ is the dimensional wear coefficient. This equation is directly implemented in Paper B.

In Paper A the wear simulation is compared to a reciprocating ball on disc experiment lasting for 1 hour of running time. It is then numerically unreachable to do the deterministic calculation of all the contact points. Therefore the contact mechanics is solved and considered constant for a specified amount of reciprocating strokes. The pressure is redistributed by an integral, so that amount of time in contact and contact intensity are both taken into account. To simplify further the simulated movement mimics a periodic repetition of the contact conditions, and no edge effects are taken into consideration. The amount of wear hence depend only on the $x_2$ coordinate value according to

$$\Delta \lambda(x_2) = \kappa \cdot \frac{1}{L_1} \int_0^{L_2} p(x_1, x_2) dx_1 \cdot \Delta t \cdot v.$$  \hspace{1cm} (4.2.2)

This equation can be calculated directly on the grid nodes $x_2$ values. $L_1$, $\Delta t$ and $v$ is the length of the calculation window, the time step and the velocity of the ball which is considered constant. This wear equation is explained further in Paper A.
4.2. IMPLEMENTATION OF ARCHARDS WEAR LAW

Figure 4.1: The numerical procedure of the pressure and deformation calculation, illustrated by a flowchart.
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4.3 Tribofilm mechanics and reaction kinetics

In the tribofilm model the goal is to make a time-dependent calculation of how tribofilms grow and how the mechanics change. The underlying material of both the disk and the ball are assumed to be steel. Observation of the real fully developed tribofilm shows a complicated structure, with FeS and ZnS close to the bulk followed by Fe and Zn polyphosphates with shorter phosphate chain length and in the utmost long-chain polyphosphates of mainly Zn. In order to produce a mechanical film, grown by mathematical formulas, a simple chemical growth model is proposed and a possible model for the contact mechanics is illustrated.

4.3.1 Tribofilm growth model formulation

The nature of tribofilm both concerning growth and antiwear behaviour is still under experimental exploration. The full picture of chemical reactions to formation of tribofilm is not clear, while the composition of the final film is more well examined [15]. The work by Fujita and Spikes [18] is an example of an attempt to describe ZDDP growth by mathematical formulas, but it only shows how the tribofilm grows on a macroscopic scale. The interest and research of the molecular reactions and the qualitative measurements of the antiwear properties remain separated by orders of magnitude. The model in this licentiate thesis is based on contact mechanics and Arrhenius equation. The model is calibrated by experimental data from experiments presented by Suarez [35].

The tribofilm growth model is thoroughly derived in Paper B. The final numerical expression adapted for the notation used in this chapter is

\[ h_j(a+1) = h_j(a) + \Delta t C_6 (h_{max} - h_j(a)) e^{-\frac{K_5}{\mu p_j v}}. \]  \hspace{1cm} (4.3.1)

\( h_j, h_{max}, \Delta t, a, K_6 \) and \( K_5 \) are the tribofilm height at node \( j \), highest allowed value on tribofilm height, time step length, time step number and chemical reaction constants respectively. The terms in the exponent \( \mu, p_j \) and \( v \) are the friction coefficient, the pressure and the relative surface velocity. The constants need to be calibrated against experiments.

Fujita et al. introduced a maximum film height in [18] in their kinetic model for tribofilm growth. Such a maximum film height is also useful in the models developed here. It has been observed in experiments that the mean film height converges to certain values over time. This doesn’t prove that there is a highest film height locally. However, it does help set a numerical boundary for tribofilm height, which prevents escalating film height.

Articles by Bosman et al. [13,14] summarize measurements from articles where measured heights from 60–150 nm have been observed for steel. There are examples of even thicker ZDDP films. Aktary et al. measured up to 500 nm thick thermal ZDDP film patches on gold [27]. In Paper B the value on \( h_{max} \) is set to 70 nm.

The constants \( K_5 \) and \( K_6 \) needs calibration. This is a disadvantage which has to be accepted until the most important reaction energies in tribofilm formation have been identified (and measured or calculated).
4.3. TRIBOFILM MECHANICS AND REACTION KINETICS

4.3.2 Film mechanics

The tribofilm has different behavior from the substrate in terms of elastic modulus and plastic deformation pressure. This can be captured by mathematical formulations in the numerical model. The influence coefficients of Eq. (2.4.3) do not allow variations in elastic modulus across the material, but it is possible to allow variations in plastic deformation pressure.

The values of plastic deformation and its variations is from experimental measurements by Demmou et al. [16]. A simple equation with linear variation in plastic deformation pressure $p_p(h)$ with tribofilm thickness $h$ can be easily implemented. An equation of such a hardness variation is

$$p_p(h) = p_{p_{\text{max}}} - (p_{p_{\text{max}}}-p_{p_{\text{min}}}) \frac{h}{h_{\text{max}}}. \quad (4.3.2)$$

$p_{p_{\text{max}}}$ and $p_{p_{\text{min}}}$ are the highest and lowest plastic deformation pressure values of the film. $p_{p_{\text{max}}}$ has the same value as the substrate hardness and $p_{p_{\text{min}}}$ should be lower for a realistic tribofilm. This method essentially captures the behavior of the tribofilm, which is harder the closer to the surface we come. A chemical explanation is that the length of the phosphate chains, decreasing with height above the substrate on the well developed tribofilm in the ZDDP case. The shorter chains would then have a higher probability of forming a linked structure which would increase the hardness. The contact mechanics change so that from the start, one a node with a thick tribofilm, high pressure will easily deform the tribofilm plastically. As the tribofilm is penetrated deeper the films resistance to plastic deformation will increase.

Considering two surfaces with tribofilm growing on them there are three possible cases for plastic deformation. Either only the thicker tribofilm is plastically deformed, they are both deformed or both tribofilms are penetrated completely. The different cases are seen in Fig. 4.2. Now the hardness is depending on the plastic deformation and the plastic deformation is clearly depending on the hardness. The system can still be solved numerically. The equation for the plastic deformation pressure $p_p$, given that we already know the plastic deformation $U_p$ is given by the equation

$$p_p = \begin{cases} 
  p_{ps} - \frac{p_{ptf}}{2h_{\text{max}}}(h_1 + h_2 - U_p) & \text{if } |h_1 - h_2| \leq U_p < (h_1 + h_2) \\
  p_{ps} & \text{if } (h_1 + h_2) \leq U_p.
\end{cases} \quad (4.3.3)$$

$p_{ps}$ and $p_{ptf}$ denote the plastic deformation pressure of the substrate and the plastic deformation pressure of the film of max film height $h_{\text{max}}$. $h_1$ is the thicker of the two tribofilms. $U_p$, $h_1$ and $h_2$ are in turn plastic deformation and the height of tribofilm on surface 1 and 2 respectively.

A residual error minimisation method can be used to solve the system numerically. The plastic deformation pressure is first calculated assuming no plastic deformation of the film. This initial plastic deformation pressure is used to calculate the deformation and pressure distribution. Then a residual error $\Pi$ is calculated from Eq. (4.3.3), by taking the value of the left hand side minus the calculated
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Figure 4.2: Three possible cases of tribofilm plastic deformation. The tribofilm elements are on surfaces covered by tribofilm which is of different height and is undergoing plastic deformation. 1. The thicker tribofilm with lower hardness is the only one which deforms plastically. 2. Both tribofilms deform plastically. 3. the tribofilm is deforming to an extent which leads to plastic deformation of underlying material.
value of the right hand side of the equation. The scheme is

\[
\Pi = \begin{cases} 
  p_y - p_{ps} - \frac{p_{ps} - p_{pat}^{f,t}}{h_{f1}} (h_{f1} - U_p) & \text{if } U_p < |h_{f1} - h_{f2}|, \\
  p_y - p_{ps} - \frac{p_{ps} - p_{pat}^{f,t}}{2h_{f1}} (h_{f1} + h_{f2} - U_p) & \text{if } |h_{f1} - h_{f2}| \leq U_p < (h_{f1} + h_{f2}), \\
  p_y - p_{ps} & \text{if } (h_{f1} + h_{f2}) \leq U_p.
\end{cases}
\] (4.3.4)

The residual is used to make alterations on the ingoing plastic deformation pressures, so that

\[
p_{p}(a + 1) = p_{p}(a) - d \cdot \Pi(a).
\] (4.3.5)

where \(d\) is a convergence factor which is adapted for smooth convergence. The final plastic deformation is used to deform the surfaces/tribofilms by applying the plastic deformation to first the thicker of the tribofilms, then to both films and finally to the underlying material, if the pressure is high enough.
Chapter 5

Results and Discussion

5.1 Paper A

The results in Paper A compare numerical simulations with an experiment. The Archard wear coefficient is adjusted in the simulation to match the wear volume of the experiment. The validity of the model is therefore a question about shape rather than volume. Figure 5.1 shows a summary of the resulting wear profiles from simulations and experiments in Paper A. The simulation results show that

Figure 5.1: A summary of the results from Paper A. (a) and (b) show experimental results. (c) and (d) shows simulation results. The profiles in line with the sliding direction are on the left and the profiles perpendicular to the sliding direction are on the right.
the curvature of the ball and the movement produce a flatter texture in the sliding direction with rounded edges in the perpendicular direction. The experiment shows the same, with higher roughness and a sinusoidal pattern perpendicular to sliding direction (Fig. 5.1b). The sinusoidal pattern and the roughness was not captured by the simulation. Visual comparison of the wear scar parallel to sliding between Fig. 5.1b and Fig. 5.1d indicate a similar wear scar curvature and thus the importance of contact pressure to wear.

5.2 Paper B

Results in Paper B show the calibration of the model and how the tribofilm grows on surfaces in a few different contact cases. The calibration was performed by trial and error, leading to a reasonable fit of the tribofilm growth for the first meters of rubbing distance for the cases of a low slide-roll ratio. Reasonable because the inclination of the curve resembles experimental measurements and because the asymptotic value for the tribofilm height is about the same in experiments and simulations.

From the rough surface simulations, a few points can be highlighted. In the model, the role of the counter surface seems highly significant for the tribofilm growth. When two smooth surfaces are in contact, they fail to produce the high local contact pressures which really stimulate the growth of tribofilm. Therefore the single surface with the highest growth of tribofilm is the smooth surface in contact with the roughest contact. On the rough surfaces themselves large portions of the surface remains out of contact, and the most of the tribofilm gets worn because the contact area experiences higher pressure.

Studying this contact leads to the conclusion that antiwear films are formed on a contact pair so that the smoother surface is better protected by tribofilm. The rougher surface is allowed to wear down its sharper asperities to a greater extent. Both effects are beneficial for the running in of the contact.
Chapter 6

Conclusions and future work

6.1 Conclusions

The conclusions from Paper A and Paper B are

- Pressure is a strong indicator of the severity of a contact concerning wear but wear models need to take many other factors into account.

- Chemical reaction models in combination with contact mechanical tools can be used to draw important conclusions about wear processes.

- Surface roughness design can be compared and evaluated by implementation of the developed tribochemical model.

6.2 Future work

Pressure, thermodynamics and chemistry are three corner stones in boundary lubrication. The current tribochemical model includes pressure calculations and a chemical model, but the thermodynamical analysis is still mediocre. The physical value of the model would increase greatly with thermodynamical calculations.

The contact mechanical calculations can be developed further. For instance subsurface stress and tangential traction effects are currently neglected but important parts of the wear process.

The chemical model can be developed. Improvements in the thermal mechanical model will directly improve the chemical analysis. Including more substances and reactions, the quality of the model can be improved further.
Part II

Appended Papers
Paper A
Numerical simulation of a wear experiment

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Abstract

A wear model including a deterministic FFT-accelerated contact mechanical tool to calculate pressure and elastic-plastic deformation, is employed to simulate the time dependent wear in a sphere on flat contact. The results of the wear simulations compared to experimental results from a reciprocating test in a ball on disk tribometer. The conditions of the simulations and the experiments are independently adjusted to match up. Similarities and differences shows upon the usefulness and limitation of wear modelling of this type.

Keywords: Wear simulation, FFT, Archard

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A.1 Introduction

predicting wear and scuffing risk in metallic contacts is an important task. Influential factors such as temperature, elastic-plastic deformations, wear, surface topography, material properties and chemistry all contribute to the complex contact conditions. Because of the complexity of the system, an experimental approach is often chosen. While an experimental approach is necessary, the underlying mechanisms behind the wear can prove difficult to probe by just analyzing wear scars and it is difficult to obtain in situ information. Therefore, numerical predictions and matching against simulations is good complement to find out more about governing factors causing wear. Early models for determination of wear, utilizing the Archard wear equation, used the initial pressure distribution throughout the wear life. This was found to give results that diverted from reality [36].

Numerical methods to study wear has been used by Pödra and Andersson [37], incorporating a basic and numerically efficient contact mechanics model known as the Winkler surface model. Using this model, Flodin and Andersson [38] simulated wear of helical gears. Another example of using the same model is by Spiegelberg and Andersson [39] simulating wear in the valve bridge/rocker arm pad of a cam. The model works well numerically but its simplicity carries the drawback that neighboring surface asperities deflect independently of each other. This is only true for very special materials, under limited constraints.

Other models by Pödra and Andersson [2]) have been based on FEM calculations, with the advantage of easy implementation of numerous physical effects. The drawback with these models is that the calculation effort of FEM is much higher than using the winkler surface model.

A optimization technique solving wear problems by a boundary element approach was implemented by Sfantos and Aliabadi [40]. The model was later extended to 3D [41] and Roling contacts (Rodríguez-Tembleque et al. [42]). The work is relevant due to its efficiency in terms of one wear mode, but for future development with variable wear modes the incremental method offers easier implementation.

A fast contact mechanical model involving the interaction between contact points on each surface is used here by implementation of the DC-FFT method described Liu et al [43]. The plastic 3 dimensional deformation is included by the methods of Almqvist and Sahlin et al. [33,34,44]. This deformation behavior corresponds to an ideal plastic behavior of ductile materials, such as steel.

In this study elastic perfectly plastic deformations and wear are simulated for a sphere on flat contact pair. Under consideration of the surface asperities mutual influence by FFT-accelerated numerical methods, deeper insight into the wear mechanism of a tribosystem is expected. Numerical simulations of a sphere on a flat are compared to experimental assessments of the reciprocating motion of a ball on a disk.

The authors find that the Archard wear equation can be used to roughly estimate the wear observed in the experiments. From the numerical simulations it is seen that the pressure and also the real area of contact is in constant change during a wear process. The simulation thus provides insight into the nature of wear. It is also concluded that there is still a great room for improvement to enhance the
predictive capability of wear models.

A.2 Nomenclature

\[ Q = \text{Wear volume per sliding distance}[m^3/m] \]
\[ K = \text{Dimensionless wear constant.} \]
\[ H = \text{Hardness}[\text{Pa}] \]
\[ F_N = \text{Normal force}[\text{N}] \]
\[ h = \text{height change due to wear}[\text{m}] \]
\[ k = \text{Dimensional wear constant } K/H[\text{Pa}^{-1}] \]
\[ p = \text{Pressure}[\text{Pa}] \]
\[ s = \text{Sliding distance}[\text{m}] \]
\[ \Delta h = \text{height change due to wear (discrete)}[\text{m}] \]
\[ \Delta s = \text{Sliding distance (discrete)}[\text{m}] \]
\[ V = \text{Complementary potential energy } [\text{J}] \]
\[ u = \text{The deformation of a surface}[\text{m}] \]
\[ h = \text{The separation between surfaces}[\text{m}] \]
\[ x, y = \text{Spatial coordinates.} \]
\[ x', y' = \text{integration variables.} \]
\[ E^* = \text{reduced elastic modulus}[\text{Pa}] \]
\[ W_v = \text{Wear volume } [\text{m}^3] \]
\[ \rho_s = \text{Density of steel}[\text{kg/M}^3] \]
\[ \Delta t = \text{The size of one timestep } [\text{s}] \]
\[ v = \text{Velocity}[\text{m/s}] \]
\[ L = \text{The length of the evaluation window } [\text{m}] \]
\[ P_b(y) = \text{Time average pressure } [\text{Pa}] \]
\[ M = \text{Number of nodes in x-direction.} \]

A.3 Wear model

Holm [45] introduced the concept of wear volume per sliding distance, \( Q \), being proportional to the normal force for each material pair according to

\[ Q = K \frac{F_N}{H}, \quad (A.3.1) \]

where \( H \) is the hardness. The wear constant \( K \) was interpreted as number of abraded atoms per atomic collision. Archard [3] improved the theory behind Eq. (A.3.1), which is known as the “Archard wear equation”. The wear constant was instead interpreted as the probability that an asperity collision would lead to the formation of a wear particle. The model has been used to predict wear in several different systems, thus being used as a rough universal wear volume predictor. When the equation is accurate, the wear mode is called delamination wear. In this work the Archard wear equation will be interpreted as contribution to wear from normal stresses and sliding at the micro scale. The Archard wear equation is used due mainly to its simplicity and the accuracy to which we calculate the pressure. Of particular interest is wear depth at each point on the surface, \( h \). Rewriting
Eq. (A.3.1) results in
\[ h = kps. \]  

(A.3.2)

Here, the dimensional Archard wear coefficient \( k = K/H \) is used as the proportionality constant to the pressure \( p \) times the sliding distance \( s \). A localized discrete version of Eq. (A.3.2) is used. This means that the wear rate is constant during the sliding. By assuming lateral wear \( \Delta h \) to occur at a point subjected to the pressure \( p \) over a sliding distance \( \Delta s \) Eq. (A.3.2) is used locally in the form of Eq. (A.3.3).
\[ \Delta h = kp \cdot \Delta s. \]  

(A.3.3)

As anyone may realize, all the numerous mechanisms of wear can not be sufficiently represented by the Archard wear model. Wear simulations can with advantage be made more ambitious in the future.

A.4 Numerical model

The numerical model has been set up to reflect the experiments that will be described in section A.5; Experimental details.

A.4.1 Contact mechanics

As real materials experience plastic flow at high pressure, plastic deformation is included in this simulation. To maintain necessary numerical efficiency the transition to fully plastic flow is assumed to be immediate above yield pressure. The yield pressure is set to the same magnitude as the hardness, \( H \). Elastic deflection due to contact between two surfaces has been solved by a fast DC-FFT method [43]. The methods of [33] and [34] are implemented for the perfectly plastic flow.

The DC-fft method originates from the variational formulation of the contact problem by J.J. Kalker [22], namely minimization of the functional
\[ V = \frac{1}{2} \int \int_S p u dS - \int \int_S p h dS \]  

(A.4.1)

where \( p \) is the normal pressure, \( u \) is the deformation in normal direction, \( S \) is the domain of contact and \( h \) is the initial separation of the surfaces in normal direction. The deformation of a half-plane due to a point load was calculated by Kelvin, Cerruti and Bossinesq. The solution is frequently referred to as presented by Love [20]. \( u \) for a distributed load \( p(x', y') \) at \( (x, y) \) is
\[ u(x, y) = \frac{1}{\pi E^*} \int \int \frac{p(x', y')}{\sqrt{(x - x')^2 + (y - y')^2}} dx' dy' \]  

(A.4.2)

Equation (A.4.2) is recognized as a convolution. The numerical method uses the simple form of the fourier transform of a convolution to quickly minimize Eq. (A.4.1) for deformation and pressure. The numerical procedure is explained further in reference [33].

The theory and numerical methods assumes linear elastic perfectly plastic solids which are also infinite half-spaces. The top surface is a sphere with a radius of 5
mm and the opposing surface is perfectly flat. Both surfaces have elastic moduli of 207 GPa, Poisson ratios of 0.3 and a hardness of 4 GPa. The simulated load is 100 N.

### A.4.2 Wear modelling

As the simulations are to be compared to an experiment, described in section A.6.1, a specification of the movement is necessary. Time and velocity are simulated by discrete time increments of $\Delta t = 0.25$ s at an average velocity of $v = 0.1$ m/s. This leads to a sliding distance $\Delta s = 2.5$ mm, which is used to calculate the wear on both surfaces. The wear constant is calculated to give the same wear volume as achieved in the experiment.

$$k = \frac{W_v}{F_N \cdot s}$$  \hspace{1cm} (A.4.3)

Where $W_v$ is the total worn volume of the ball and the disk, $F_N$ is the load in the numerical simulation (and experiment) and $s$ is the total sliding distance of the simulation (and experiment). The wear volume is calculated by the measured mass loss, $\Delta m$ times the density of steel, $\rho_s = 7850$ kg/m$^3$. The resulting wear coefficient is (see also experimental results A.6.1) $k = 3.11 \cdot 10^{-16}$ Pa$^{-1}$.

The contact conditions vary on the disk and on the ball. As the ball is sliding across the disk, the disk surface is allowed time out of contact, while the ball seems to be constantly in contact. Therefore, wear on the two surfaces is treated in two different ways in the simulation. On the sphere, the pressure calculated at the current timestep is immediately used to calculate the wear according to Eq. (A.3.3). The calculation of wear on the flat is more intricate.

To calculate the wear on the flat a sliding direction is first chosen. Along this sliding direction the total wear over one timestep must follow Eq. (A.3.3), considering the momentary pressure distribution as well as how the contact has changed over this timestep. Figure A.1 illustrates how a pressure distribution across the contact is smeared out in the sliding direction. The circular shaded region in Fig. A.1 shows a possible distribution of pressure calculated at the current timestep. The wear during this same timestep is calculated by assuming equal wear in x-direction over the whole sliding window represented by the rectangular shaded area in Fig. A.1.

This distribution of pressure is justified by thinking about how the pressure in each individual point on the flat will change as the sphere moves across it. The points close to the centre of the track on the flat would be expected to initially experience pressure for a longer time at each passing, and also experience a different pressure distribution due to the shape of the sphere. The pressure is assumed to be constant during a time step $\Delta t$. Every worn point in the y-direction on the flat is assumed to experience the whole pressure spectrum. Therefore, the time averaged pressure is equal to the geometrically averaged pressure over the whole contact region. More precisely the pressure averaged over one time step $P_p(y)$ in each contact point on the flat, choosing the sliding direction as $x$ in Fig. A.1 is determined by

$$P_p(y) = \frac{1}{M \cdot \Delta x} \int_0^L P(x, y)dx.$$  \hspace{1cm} (A.4.4)
In order to simulate wear across the flat surface, the momentary pressure is spread out over the wear region before it is used to calculate wear in Eq. (A.3.3), giving a time averaged wear. The circular shaded zone represents a possible pressure distribution at one time instant. The corresponding wear on the flat would be distributed across the underlying rectangular shaded area, in this case resulting in more wear at the centre of the rectangular wear zone.
Here, $L$ represents the length of the entire window of the flat that is worn, $M$ is the amount of grid nodes in the sliding direction and $\Delta x$ is the length in $x$-direction of one grid node. In the current case $L$ is set to 2 mm. The resulting wear depth $\Delta h(y)$ on the flat over a timestep $\Delta t$ is given by combining Eq. (A.3.3) with Eq. (A.4.4), that is

$$
\Delta h(y) = k \cdot \frac{1}{M \cdot \Delta x} \int_0^L P(x, y) dx \cdot \Delta t \cdot v.
$$  (A.4.5)

Equation (A.4.5) is computed at each timestep with an updated pressure distribution.

As the same material is used in the ball and the disk in the experiment, the material parameters are set the same for the sphere and the flat in the simulation. For the same reason the wear is assumed to be equal on the flat and the sphere.

The resulting, numerically efficient model describes an ideal wear process and the deformation of a sphere moving on a flat. The model corresponds to the conditions in the centre of the disk, so the simulation should be compared to the central part of the wear scar.

### A.5 Experimental details

Before and after experiments the contacting surfaces were measured with an optical profilometer, WYKO NT1100, manufactured by Phoenix Arizona USA. Measurements were taken at three different magnifications, rendering samples of size $1.24 \text{mm} \times 0.94 \text{mm}$, $0.62 \text{mm} \times 0.47 \text{mm}$ and $0.31 \text{mm} \times 0.24 \text{mm}$. This was achieved using a $10 \times$ mirau objective with three variations of the field of view lens; producing measurements at $5 \times$, $10 \times$ and $20 \times$ magnification.

The experiments are conducted in a sliding reciprocating rig; the Optimol SRV reciprocating friction and wear tester. The rig is used to estimate surface behavior at reciprocating wear, see e.g. Hardell et al. [46]. The reciprocating movement may introduce greater wear rates, see Ward [47]. The wear scar will however be completely straight compared to a ball on disk setup, where the wear scar is circular. This is in agreement with the numerical model.

A ball sliding on a disk, both made of AISI25100 steel are the samples used in the reciprocating wear tester. The contact is lubricated with 99% pure hexadecane. The hexadecane has low polarity and should minimize chemical interaction with the surface and still reduce the friction to boundary lubrication levels see e.g. Kajdas et al. [48] or Naveira-Suarez et al. [49]. The viscosity of hexadecane, although variable during the running experiment, is about 5 mPas for conditions similar to those of the experiment, see [50]. The radius of the ball is 5 mm. The temperature is preset to $90 \, ^\circ \text{C}$ before the samples are loaded with 100 N and the ball is slid on the disk by a frequency of 25 Hz. A stroke length of 2 mm giving an average velocity of 0.1 m/s is chosen. The test is terminated after 1 hour of sliding.

Before and after the experiment the contacting bodies were weighed in order to quantify the wear-volume.
A.6 Results and discussion

A.6.1 Experimental

The weight of the disk before and after the experiment was measured to 27.6445 g and 27.6443 g respectively, i.e. a weight change of around 0.2 mg. The corresponding change of the balls weight was around 2 mg. This indicates a difference between fundamental assumptions of the numerical model and the experiment, implying that the wear is 10 times greater on the ball than on the disk. The resulting dimensional Archard wear coefficient, using the density of the steel 7850 kg/m³, and Eq. (A.4.3) is calculated to $k = 3.11 \cdot 10^{-16}$ Pa⁻¹.

Surface metrology measurements of the disk surface with the interferometer resulted in $R_a$ values ranging from 6.7 – 10.8 nm, calculated by Veeco’s software Vision 32. This is considered flat enough. The fact that we have variation in $R_a$ value is due to sample point, resolution, measured area and measurement quality. A typical surface roughness topography of the disk is displayed in Fig. A.2. Figure A.3 shows the ball surface before the test. It can be visually verified that the surfaces are initially flat. In Fig. A.2 the scale shows measured roughness in the nanometer scale. For the ball, as seen in Fig. A.3, the roughness is small compared to the ball curvature in the contact area.

![Figure A.2: The roughness of the disk surface before wear.](image)

After running the test for one hour, under the wear conditions described in section A.5, the surfaces were again analyzed in the optical profiler system. The worn ball can be seen in Fig. A.4 and the wear scar on the disc is depicted in Fig. A.5. Plastic flow combined with wear has lead to significant increase in the
roughness. Except for the increase in roughness there are some interesting patterns in the wear scar, which demand an explanation.

Figures A.6 and A.7 show worn profiles of the ball in the perpendicular and parallel directions to sliding direction respectively. Comparing the surface profile parallel with and perpendicular to the wear scar clearly illustrates a pattern. From Fig. A.6 it can be seen that the shape of the ball has been worn down to be almost flat. The variation in height between the end of the wear scar and the highest roughness peaks being about 1 μm. The profile seen in Fig. A.7 has retained a more circular shape, with a corresponding difference in wear scar depth of about 10 μm. Two grooves has formed on each side of the centre of the wear scar. There is conformity of these grooves on the ball and on the disk, as can be seen by comparing Fig. A.5 and Fig. A.4.

If physical properties of the real system are accurately considered in the numerical simulations, there should be identifiable similarities in the results from simulation and experiment. In other words, how well the Archard wear equation predicts the actual wear is investigated.

A.6.2 Numerical

Analysis of the simulated worn profiles shows both interesting similarities and differences compared to the experiment. The contact pressure during sliding can not easily be monitored in an experiment. The real time information about the pressure distribution, is a valuable result form the numerical model, that complements the information obtained from experiments. An image of the in-contact pressure distribution after 200 s and its corresponding contour plot is shown in Fig. A.8.
Figure A.4: The wear scar on the ball.

Figure A.5: The wear scar on the disk.
A.6. RESULTS AND DISCUSSION

Figure A.6: A typical profile of the worn ball in x-direction, parallel to the direction of sliding.

Figure A.7: A typical profile of the worn ball in y-direction, perpendicular to the direction of sliding.
and Fig. A.9 respectively. Curves illustrating a cross section of the initial pressure, and the pressure after 200 s, 500 s, 1500 s and 3600 s are depicted in Fig. A.10.

Figure A.8: The pressure distribution in the simulated contact between the sphere and flat after 200 s.

As can be seen in this figure the load becomes supported by a larger area as the surfaces wear, leading to a lowered and widened pressure distribution with time. It can also see that the magnitude of the pressure is not high enough to cause plastic flow. An improvement of the model would be to consider the local pressures due to rough surfaces. These higher pressure are likely to induce plastic flow.

Figures A.11 and A.12 show the worn profiles perpendicular and parallel to the sliding direction. It can be seen, by comparing with the measured profiles, that the numerical wear model produces a profile somewhat different from that observed in the experiment. For instance nothing of the two grooves perpendicular to sliding direction are seen in the numerical results. The basic shape of the wear scar, on the other hand, are similar in the experiments and simulations. The similarities lie within the flatness seen in profiles along the sliding direction and the curved shape that appears perpendicular to the sliding direction. From the experiment this difference between the shape of the profiles in the two perpendicular directions, is clear by comparing the y-scale in Fig. A.7 and Fig. A.6. It seems like the pressure distribution and the sliding distance are factors influencing wear and that the Archard model can be used to give an idea of were there is risk for wear to occur locally.

A.7 Conclusions

Experimental results from tests in a reciprocating ball on disk tribometer have been compared to the results from numerical simulations of the wear of a spherical and a flat surface. Wear processes were quantified by measuring wear volume and
Figure A.9: A contour plot of the pressure distribution in the simulated contact between the sphere and flat after 200 s.

Figure A.10: The pressure at $y = 0$ along the sliding direction as it changes during the wear simulation over time.
Figure A.11: Worn profiles of the ball surface along the sliding direction predicted by the numerical model. The top curve shows the unworn surface, with profiles after 200 s, 500 s, 1500 s and 3600 s of wear following beneath it.

Figure A.12: Worn profiles of the ball surface perpendicular to the sliding direction predicted by the numerical model. The top curve shows the unworn surface, with profiles after 200 s, 500 s, 1500 s and 3600 s of wear following beneath it.
analyzing profiles from the wear test. The wear process was also analyzed by an
evaluation of the artificially worn surfaces resulting from numerical simulations and
changes in contact pressure during the wear process were calculated.

A direct conclusion from the experiment is that the wear is 10 times larger on
the ball compared to the disk. It could be explained by thermoelastic instability of
asperities, since the ball is constantly in contact and will experience more friction
heating and less time for recovery compared to the local parts of the disk in contact.
It is also possible that there is more oxidation on the disk than on the ball, as the
ball surface is not allowed time out of contact. Clearly, the contact conditions of
the mating surfaces are different which leads to a domination over the pressure
effect on wear.

Simulations with the Archard wear equation was found to match qualitatively
with the wear on a ball and a flat. The difference on the wear scar on a ball between
sliding direction and perpendicular direction was found to be intrinsic properties
of the system, i.e., the pressure calculated by contact mechanical methods has been
shown to have an effect on the predicted wear.

It is questionable whether the Archard wear equation alone can be safely em-
ployed in numerical tools to test new machine designs with contacts like in this
experiment. The variable velocity in the contact, may indicate that wear modes
other than delamination wear are introduced. This is also the case in most engi-
neering applications, where several wear modes are present simultaneously. On one
hand the equation as shown erroneously assumes a constant relation between wear
and pressure for a tribological system. Changes inherent in the full tribological
system clearly changes the value of the constant and thus it is not a constant by
definition. On the other hand first principle simulations can not yet be set up for
complete engineering components. An intermediate feasible approach, would be
to incorporate wear maps in numerical simulations. This could also, with suffi-
cient data, be successfully implemented in reverse engineering concerning material
selection.

Still, wear modelling of this type is in an infant stage and improvements can be
made in the direction of wear equations. Some examples of important factors that
affect wear are roughness, temperature and lubricant additive-surface interaction.
Paper B
Semi-Deterministic chemo-mechanical model of boundary lubrication

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Abstract

A model for tribofilm growth is developed. The model is used in combination with numerical contact mechanics tools to enable evaluation of the combined effects of chemistry and contact mechanics. The model is tuned with experimental data and is thereafter applied to rough surfaces. The growth of the tribofilm is evaluated for 3 different contact cases and short-term tribofilm growth behaviour is analyzed. The results show how tribofilms grow in patches. The model is expected to be used as a tool for analysis of the interaction between rough surfaces.

Keywords: Tribofilm, Tribochemistry, Antiwear, Numerical model
Figure B.1: Two surfaces with 3 layers each are in contact. The base of each surface is the substrate material, steel in this case. An oxide layer has been formed on top of the steel layer. On top of the oxide layer a chemisorbed layer is illustrated. The strings illustrate a physically adsorbed, easily sheared layer. Coordinate directions are indicated, with $x_1$ representing sliding direction.

### B.1 Introduction

Boundary lubrication is the lubrication regime where hydrodynamic action is negligible. Only a fraction of the nominal contact area supports the applied load. Extreme pressures occur at the contacting asperities when surfaces slide relative to each other. The contact temperature may reach several hundred degrees if contact time is sufficiently long. The base fluid of the lubricant has an important role even if it cannot provide hydrodynamic lift and load support. In the boundary lubrication regime, the base fluid acts a carrier of surface active components (additives) that adhere to, or react with, the surfaces and form a thin protective layer—a tribofilm.

Figure B.1 shows a snapshot of two surfaces in sliding contact. Three layers are indicated schematically. More precisely, on top of the base material there is an oxide film and on top of the oxide there is a reacted film. This film is formed from a reaction between lubricant components and the base material or its oxide. The top layer is a physically adsorbed, easily sheared, layer [51].

Asperities will collide as the surfaces slide and all layers may be sheared off if the collisions are severe. This will cause scuffing and may give rise to serious surface damage. The ultimate design of a boundary lubricated system would rely on physical adsorption only. In such a case, the adsorbed molecules provide sufficient load carrying capacity without causing any damage to the reacted layers. This is, however, normally not possible to obtain for engineering surfaces under normal operating conditions. Successful design of a boundary lubricated system is therefore
B.1. INTRODUCTION

based on a balance between wear and growth of the reacted layers. It is thus important to avoid very severe collisions and it is important to have access to lubricant components that can react with surfaces and reform the layers as soon as they are worn off. The severity of collisions is controlled by surface roughness, sliding speed and applied load while lubricant-surface reaction kinetics controls growth of tribofilms.

The vast majority of boundary lubrication studies are experimental and surface analytical and there are many thousands of publications from the past 50 years. Typically, the growth and removal of the reacted layers are studied first by employing tribotests with subsequent (post-mortem) surface analysis using techniques such as Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS), see for instance Spikes [15]. The outcome is detailed knowledge about individual systems and a general understanding of some of the processes. There are, however, very few attempts to describe these complex processes in mathematical terms (for implementation on the continuum level). Given the materials pair, operating conditions, surface roughness and lubricant type there are very few models available which can predict risk of wear under boundary lubrication conditions [52]. Indeed, even the most basic type models can contribute significantly to the understanding of the complex processes governing the growth and removal of tribofilms. Moreover, it would be beneficial to enable predictions of system performance without running an experiment first.

Boundary lubrication has often been said to be too complex to enable modelling and this is most probably the explanation why there are relatively few publications available. Sullivan [53] derived a model for oxidational wear under boundary lubrication conditions. The model was based on the Quinn and Sullivan oxidational wear theory [54] with the addition of a model for physical adsorption of a boundary film. No detailed contact mechanics model was included. Stolarski [55] derived a similar model for the tribofilm considering the contact mechanics by adding a statistical Greenwood and Williamson [8] type of contact model. Chang and co-workers [12] developed a physiochemical micro-contact model. They studied colliding asperities and determined contact pressure and temperature deterministically and they developed a statistical model for physically adsorbed and chemically reacted layers. Their model is based on the Volmer adsorption isotherm for physical adsorption. The reacted layer growth was modelled by an empirical law and Archard’s wear equation was used to describe the wear of the reacted layer. Fujita and Spikes [18] presented another model for growth and removal of reacted films. The model was experimentally validated. They did, however, only study the growth on the global scale not on the roughness scale. Recently, Bosman and Schipper [14] presented a deterministic model of wear in boundary lubricated contacts with rough surfaces. Their wear modelling strategy was based on the Pödra and Andersson time stepping technique [2] for numerical wear predictions.

This paper presents a new model for growth and removal of the reacted layer. Contact mechanics is deterministic and quasi-transient. This means that real rough surfaces are brought into contact and that these are moved relative to each other to simulate a sliding interface [56]. This means that the contact pressure and deformation distributions are time dependent. An experimentally validated model for growth of the reacted tribofilm is developed and layer thickness is updated after
every time step. The varying properties of the layer itself does, in turn, influence the contact mechanics. The effect of different surface roughness on running-in and wear risk is studied for a given materials and lubricant combination. The underlying motivation of the work is to generate knowledge about the micro level mechanical processes of tribofilms in between rough surfaces in sliding contact. Focus is on the contact mechanics of tribofilms. These studies are believed to be helpful in designing better tribological systems. This model will also be a platform for further improvement of the physico-chemical model of additive-surface interaction.

B.2 Nomenclature

\( u_3(x_1, x_2) \) = The out of plane deformation of a surface [m].

\( E^*, E_1 \) and \( E_2 \) = Elastic moduli [Pa].

\( x_i \) = Spatial coordinates [m].

\( y_i \) = Spatial coordinates [m].

\( f_3(x_1, x_2) \) = Stress distribution [Pa].

\( G(x_1, x_2) \) = The out of plane gap between the surfaces [m]

\( \nu \) = Poisson ratio.

\( V \) = Complementary potential energy [J].

\( A, B \) and \( C \) = Substances’ concentration [mol/m³].

\( t \) = Time [s].

\( k(T) \) = Reaction rate [mol/s].

\( m \) and \( n \) = Order of chemical reaction.

\( C_i \) and \( D \) = Constants related to chemical reactions [varies]

\( T, T_{bulk} \) and \( T_{flash} \) = Temperatures [K].

\( B_0 \) = Concentration of substance [mol/m²].

\( h_{max} \) = Highest allowed tribofilm height (x₃ direction) [m].

\( h \) and \( h_n \) = Tribofilm height (x₃ direction) [m].

\( \mu \) = Friction coefficient.

\( p \) and \( p(i, j) \) = Contact pressure [Pa].

\( v \) = Relative surface velocity [m/s].

\( p_{y}, p_{ys} \) and \( p_{yfm} \) = Plastic deformation pressures [Pa].

\( h_1 \) and \( h_2 \) = Tribofilm height on surface 1 and 2 [m].

\( h_t \) = The thicker of two tribofilm elements in contact [m].

\( U_p \) = Plastic deformation of a surface [m].

\( Q \) = Wear volume per sliding distance [m³/m]

\( K \) = Dimensionless wear constant.

\( H \) = Hardness [Pa]

\( F_N \) = Normal force [N].

\( s \) = Sliding distance [m].

\( h_w \) = Height (x₃ direction) change due to wear [m].

\( \kappa \) = Dimensional wear constant \( K/H \) [Pa⁻¹].

B.3 Numerical Model

The novelty of this work lies in the growth and removal of the tribofilm layer and how it is combined with contact mechanics. The model consists of four parts:
B.3. NUMERICAL MODEL

- contact mechanics to find contact pressure and elastic/plastic deformations
- tribofilm growth model
- tribofilm mechanics model
- wear model

The components of the model are described in the following sections.

B.3.1 Contact mechanics

The first step is to find out the pressure as this gives much information about contact severity. In combination with the friction coefficient the pressure gives rise to tangential tractions and therefore friction work in the sliding direction. Friction energy is a key component in the current model for chemical activation of the tribofilm growth.

The contact mechanics calculation seeks the distribution of pressure due to a given load. In turn this is controlled by how the surfaces deform in the contact. An overview of the numerical procedure can be found in Fig. B.2. For the contact mechanics to agree with reality the correct material model must be employed. Most materials have elastic behaviour up to some plastic deformation pressure where the material begins to deform plastically, and when the strains becomes too high the material will fail. The transition between elastic and plastic behaviour is governed by plasticity functions in theoretical contact mechanics. A simple form of elastic-plastic behaviour is elastic-perfectly plastic. This stress-strain behaviour will resemble the behaviour of steel surfaces.

The stress-strain mechanics of tribofilms has been investigated by Demmou et al. [16]. ZnDTP tribofilm experiments and simulations have indicated that the tribofilm hardness varies with the height of the film with high values near the substrate of the film and low values at top of the film [57]. The variation of hardness with penetration depth has also been investigated [16].

The elastic properties of tribofilms are not very well established. For this reason, the elastic modulus of the tribofilm was chosen to be the same as for the steel substrate. This will also keep the model uncomplicated. The model applied here is elastic, perfectly plastic, with the hardness of the tribofilm depending on the thickness of the film while the modulus of elasticity is assumed to be the same for the tribofilm and the steel substrate. Plastic deformation is assumed to occur when pressure reaches the same magnitude as the tribofilm hardness.

The half-plane assumption is used to describe the elastic deformation, i.e. the contacting bodies are assumed to have infinite support. Small asperity angles and negligible influence of tangential tractions are assumed. In this case the deformation \( u_3(x_1, x_2) \) due to stress distribution \( f_3(x_1, x_2) \) in \( x_3 \) direction (perpendicular to the contact plane) is given by

\[
    u_3(x_1, x_2) = \frac{1}{\pi E^*} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{f_3(y_1, y_2)}{\sqrt{(x_1 - y_1)^2 + (x_2 - y_2)^2}} dy_1 dy_2.
\]  

(B.3.1)
Here, 

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

(B.3.2)

is the reduced elastic modulus of the materials, with \( E_1 \) and \( E_2 \) the elastic moduli and \( \nu_1 \) and \( \nu_2 \) the poission ratios of the two materials. According to the variational principle developed for contact mechanics by Kalker [58], the corresponding static solution is found by minimizing the functional

\[ V = \frac{1}{2} \int \int_S f_3(x_1, x_2) u_3(x_1, x_2) dS - \int \int_S f_3(x_1, x_2) G(x_1, x_2) dS. \]  

(B.3.3)

Here, \( G(x_1, x_2) \) denotes the separation distance between two surfaces before deformation. Eq. (B.3.1) may be recognized as a convolution. Once discretized, this type of equation allows for the application of a Fourier transformation and the numerical evaluation can be reduced significantly by employing the FFT (Fast Fourier Transformation). Once the pressure reaches the predefined value for plastic deformation, the node in question is taken out of the calculation as well as the corresponding load. More details about the elastic plastic calculation can be found in Sahlin et al. [33].

B.3.2 Tribofilm growth

In this model it is assumed that a film is formed due to a chemical reaction between two substances. The film is assumed to grow only in the contact spots where rubbing takes place, i.e. it is a tribofilm. One attempt to model tribofilm growth was presented by So and Lin [59]. Their model is based on the Arrhenius equation. The reaction rate \( \frac{dC}{dt} \) for a chemical reaction where substances \( A \) and \( B \) react to produce substance \( C \) depends on the temperature \( T \) and is given by [32]:

\[ \frac{dC}{dt} = k(T) A^m \cdot B^n. \]  

(B.3.4)

where

\[ k(T) = C_1 e^{-C_2/T} \]  

(B.3.5)

\( A, B \) and \( C \) in Eq. (B.3.4) represent the concentrations of substances \( A, B \) and \( C \) respectively. \( C_2 \) is a constant which includes the activation energy of the reaction and the universal gas constant. In the present model, \( C_2 \) must be found from curve-fits to experiments. \( C_1 \) is the pre-exponential factor which tells about the probability that a reaction occurs. Assume that the concentration \( A \) is constant and always equally available in the contact area. The concentration \( B \) depends on the thickness of the tribofilm, as this substance is related to elements present near the substrate surface. When the tribofilm becomes thicker it will act as a barrier and there will be a lower concentration \( B \) available at the top of the layer slowing down the reaction. Assuming that the growth completely stops at a thickness \( h_{max} \).

A first approximation for the variation of the concentration by height \( h \) is linear:

\[ B = \begin{cases} 
B_0(h_{max} - h) & \text{if } h < h_{max}, \\
B_0 & \text{if } h > h_{max}.
\end{cases} \]  

(B.3.6)
B.3. NUMERICAL MODEL

Where $B_0$ is the concentration of reaction substance $B$ at the surface. This means that we have

$$A^n B^n = C_3 (h_{max} - h)^n \text{ for } h < h_{max} \quad (B.3.7)$$

where $C_3 = B_0 A^n$. The expression is finally simplified by setting the order of the relevant reaction to 1, that is $n = 1$. The rate of change of reaction product $C$ is proportional to the film height. Equation (B.3.4) and (B.3.7) can now be combined to:

$$\frac{dh}{dt}_{\text{growth}} = C_4 (h_{max} - h) k(T). \quad (B.3.8)$$

where $C_4$ is a proportionality constant that includes constants $B_0$ and $C_3$ plus the transformation of concentration $C$ into film thickness $h$.

The temperature $T$ can be divided into flash temperature and bulk temperature according to,

$$T = T_{\text{flash}} + T_{\text{bulk}}. \quad (B.3.9)$$

where the Bulk temperature can be obtained from experiment or predictions. The flash temperature is proportional to the (local) friction heating $\mu v p$, see for instance [51]. The bulk temperature is proportional to the global friction heating from the whole contact area. The reaction rate can thus be written as:

$$k(T) = C_1 e^{-\frac{C_5}{\mu v p}}. \quad (B.3.10)$$

where $D$ is a proportionality constant and the exponent $r$ is 1 for Péclet numbers below 5. In this case Eq. (B.3.10) can be simplified to:

$$k(T) = C_1 e^{-\frac{C_5}{\mu v p}}. \quad (B.3.11)$$

where $C_5$ is a new constant that could be found from curve-fits to experiments. The final expression for the tribofilm growth is given by combining Eq. (B.3.11) and Eq. (B.3.8),

$$\frac{dh}{dt}_{\text{growth}} = C_6 (h_{max} - h) e^{-\frac{C_5}{\mu v p}}. \quad (B.3.12)$$

Where $C_6 = C_1 C_4$. A finite difference formulation of the height of the tribofilm has the form

$$h_{n+1}(i, j) = h_n(i, j) + \Delta h. \quad (B.3.13)$$

A discrete equivalent of Eq. (B.3.12) is

$$\Delta h = \Delta t C_6 (h_{max} - h_n(i, j)) e^{-\frac{C_5}{\mu v p(i, j)}}. \quad (B.3.14)$$

Combining Eq. (B.3.14) and Eq. (B.3.12) gives the height of the tribofilm in the numerical model:

$$h_{n+1}(i, j) = h_n(i, j) + \Delta t C_6 (h_{max} - h_n(i, j)) e^{-\frac{C_5}{\mu v p(i, j)}}. \quad (B.3.15)$$
B.3.3 Tribofilm mechanics

The mechanics of the tribofilm is certainly important for its anti-wear properties. The ‘smart’ behaviour of the tribofilm formed by Zinc dialkyldithiophosphate (ZDDP) under pressure, possibly related to pressure induced crystallization as shown by Mosey et al. [4] and observed as variation in the elastic modulus [16] is a phenomenon which should optimally be studied in combination with the contact mechanics. Unfortunately the variation in elastic modulus does not allow for the same numerical efficiency for calculating contact pressure, thus reducing the time-range of the calculation of contact pressure to levels too far from a tribological time-span, such as the time it takes for a contact to be considered run-in.

The plastic deformation pressure variation with film height and penetration depth, however, has been incorporated in the model. This is done by assuming a linear variation of plastic deformation pressure \( p_y \) with height. The plastic deformation pressure will vary from bulk hardness \( p_{ys} \) of 4 GPa to a minimum \( p_{yfm} \) value of 1 GPa at the top of the fully developed tribofilm of height \( h_{max} \). Notice that in practice this height of film will never be reached as the tribofilm grows asymptotically toward this value. Concerning plastic penetration depth \( U_p \), the tribofilm will carry load as if it was the height of the deformed film. This is achieved by iterative minimization of the residual

\[
p_y = \begin{cases} 
  p_{ys} - \frac{p_{ys} - p_{yfm}}{h_{max}} (h_t - U_p) & \text{if } U_p < |h_1 - h_2|, \\
  p_{ys} - \frac{p_{ys} - p_{yfm}}{2h_{max}} (h_1 + h_2 - U_p) & \text{if } |h_1 - h_2| \leq U_p < (h_1 + h_2), \\
  p_{ys} & \text{if } (h_1 + h_2) \leq U_p. 
\end{cases}
\] (B.3.16)

where \( h_t \) is the thicker of \( h_1 \) and \( h_2 \). This way of varying the plastic deformation pressure, or hardness, is an approximation that does not fully mimic stress and deformations of the film and the substrate. It is, however, believed that the approximation is sufficiently good for the purpose of getting representative prediction of contact pressure and real area of contact.

B.3.4 Wear model

The nature of wear is all but simple. Plastic deformation, oxidational wear, corrosion, delamination wear and seizure are some examples of wear modes, which are triggered for different reasons and cause different damage. For this reason the universal wear laws lack general accuracy, and understanding wear in an engineering component often requires a vast amount of experiments.

The Archard wear equation is often used to estimate the sliding wear. In this equation the wear volume is proportional to the sliding distance and pressure. This type of wear model is easily included in the present model since local pressures are computed. The drawback is the non-constancy of the proportionality constant. Indeed, factors other than sliding distance and normal pressure influence wear. But starting with this simple relation between pressure and wear, and excluding effects one by one, a more accurate picture of how a contact wears takes form. In this work, plastic deformation is included separately in the contact mechanics model while all other wear effects are included in the Archard model. Historically, Holm [45] proposed that wear volume \( Q \), is proportional to the normal force \( F_N \)
times sliding distance $s$, for each material pair according to:

$$Q = K \frac{F_N}{H} s,$$  \hspace{1cm} (B.3.17)

where $H$ is the hardness. The wear constant $K$ was interpreted by Holm as number of abraded atoms per atomic collision. Equation (B.3.17) is normally referred to as the “Archard wear equation”. Archard [3] re-interpreted the constant in the equation as the probability that an asperity collision would lead to the formation of a wear particle. The model has been used to predict wear due to many different wear mechanisms, thus being used as a rough wear predictor for wear types other than from delamination wear. In this work, wear is included in the form of the Archard equation and plastic deformation. In the model applied here, the wear depth at each point on the surface is denoted $h_w$. Rewriting Eq. (B.3.17) results in

$$h_w = \kappa p s.$$  \hspace{1cm} (B.3.18)

The dimensional Archard wear coefficient $\kappa = K/H$ is used as the proportionality constant to the pressure $p$ times the sliding distance $s$. A localized discrete version of Eq. (B.3.18) is used. This means that the wear rate is constant during the sliding.

Wear rate $\frac{dh}{dt}$ can be obtained as the time derivative of Eq. (B.3.18)

$$\frac{dh}{dt} = \kappa p v.$$  \hspace{1cm} (B.3.19)

\subsection*{B.3.5 Full numerical model}

The calculation procedure can be illustrated by a flowchart, see Fig. B.2. The calculations in each step described in the numerical model are represented in this flowchart.

When making calculations on real measured surfaces the resolution needed to include a significant amount of asperities quickly becomes too high. Furthermore, as the length scale becomes smaller, not only length but also times become short. For example if a grid of $64 \times 64$ is chosen to resolve a rough surface of area $62 \times 53 \, \mu m$ and the surfaces move at a velocity of $0.25 \, m/s$, one contact calculation corresponds to a time step of about $3 \, \mu s$ and a travel distance of $0.83 \, \mu m$. The tribofilm growth rate is considered to occur slowly in this work, meaning that such small timescales will produce tribofilms of physically insignificant thicknesses.

For the interest of studying how the tribofilm grows on asperities a method based on averaging the influence from the contact pressure is introduced. It is a two step method, were first the contact mechanics are deterministically solved and the pressure for each contact case which arises is calculated. More precisely, a procedure where one surface is moved across the counter surface and the points on the surface exiting the contact over the right boundary, is assumed to re-enter the contact from the left, is employed. The next step involves time averaging of the pressure for each separate node on the surface. In the second step, the averaged pressure at each node is considered constant for about $0.2 \, s$, corresponding to a sliding distance of $53 \, mm$. The constant pressure conditions are used to calculate how the tribofilm grows and the system wears. The process is repeated until the
Figure B.2: Flowchart of the numerical procedure implemented in the boundary lubrication model.
tribofilm behaviour has been sufficiently established. Figure B.3 illustrates the schematics of the averaging method.

Concerning the choice of the resolution of the surfaces, a few aspects should be taken into account. First in the case of the ball on disk contact, the symmetry of the geometry gives fairly quick grid convergence, which means that a less dense grid can be successfully implemented, without severe loss of accuracy. In the case of rough surfaces the issue is more complicated. As the geometry itself is measured with a limited number of data points this sets an upper limit of what we can say is the measured surface. A lower resolution limit is found when contact mechanics change severely due to changes in roughness. In this work the chosen compromise between calculation efficiency and resolution is including all measured points over a small area.

B.4 Simulation Details

The simulation is run in two stages. First a calibration with experiments is performed in order to establish the set of constants in equations (B.3.19) and (B.3.15) and then utilization of this set of constants for real rough surfaces in sliding contact. The calibration is expected to be valid for all cases with the same surface materials and same lubricant.
B.4.1 Calibration

The surfaces used for calibration is a sphere and a flat. These surfaces are generated on a calculation mesh of $32 \times 32$ elements. The spherical surface is set to have a radius of 1 cm. Furthermore, the wear scar on the disk is assumed to be located at a distance of 5 cm from the centre of the disk. This means that a point on the ball is in contact $1/5$ as long as a point on the disk. The effect of this is achieved by storing the disk surface as a matrix containing $3 \times 160$ elements. The size of the calculation grid corresponds to a square area of $0.7 \times 0.7$ mm. The surfaces are loaded with 300 N.

To achieve movement through time the matrices containing surface data are shifted one step at a time in one direction. The predefined Slide-Roll-Ratio (SRR) determines how many steps the surfaces will be shifted. For instance, when the SRR is 5% the ball surface will be shifted 21 times when the disk surface is shifted 20 times. The pressure is solved for in every 5th shift using the same pressure value to calculate film growth and wear. To minimize computation time, the geometry matrices are circulated. The material and tribofilm parameters are chosen to resemble bearing steel with a tribofilm formed by Poly-$\alpha$-Olefin 2wt% ZDDP. The material and tribofilm parameter values are listed in table B.1. The tribofilm simulation data was adapted so that agreement is found to an experiment by Naveira Suarez et al. [60] at an SRR of 0.5%. The constants found from curve-fit to experiments are presented in table B.1. Figure B.4 shows the experimental data used to calibrate the parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_1, E_2$</td>
<td>207 GPa</td>
<td>Young’s modulus</td>
</tr>
<tr>
<td>$\nu_1, \nu_2$</td>
<td>0.3</td>
<td>Poisson ratio</td>
</tr>
<tr>
<td>$h_{max}$</td>
<td>70 nm</td>
<td>max local tribofilm height</td>
</tr>
<tr>
<td>$C_0$</td>
<td>160 kW</td>
<td>Exponential constant of Eq. (B.3.15)</td>
</tr>
<tr>
<td>$C_5$</td>
<td>0.3 $1/s$</td>
<td>linear constant for reaction rate equation</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>$1.63 \cdot 10^{-15}$</td>
<td>Dimensionless Archard wear coefficient</td>
</tr>
<tr>
<td>$y_{ps}$</td>
<td>4 GPa</td>
<td>The limiting pressure of the (steel) substrate</td>
</tr>
<tr>
<td>$y_{pfm}$</td>
<td>1.5 GPa</td>
<td>The limiting pressure of a 200 nm tribofilm</td>
</tr>
</tbody>
</table>

B.4.2 Rough surfaces

As the model has been calibrated it is of interest to measure its usefulness on rough surfaces and evaluate how the tribofilm grows in a sliding contact with rough surfaces. Contact between four rough surfaces is evaluated with the numerical model. The surfaces are once again adapted to behave as bearing steel- no parameter values will be different from those listed in table B.1.

The surfaces are optically measured real surfaces. The smooth surfaces are balls from a Wedeven Ascoiciates Tribology Research Machine (WAM) which have been optically measured in an optical profiler. The rough surfaces are taken from the same unidirectionally ground steel sample measured with the same equipment.
A two step processing of the surface is employed. First, tilt is removed based on the acquired surface heights. Then possible missing data is restored by the application of a Delaunay triangulation based interpolation technique; `TriScatteredInterp` function in MATLAB [61].

After this the surfaces are cut of to preserve a suitable amount of asperities. 64×64 grid points are preserved corresponding for all surfaces to an area of 62μm×53μm. Surface data can be found in table B.2.

Table B.2: Surface roughness parameters. The bearing steel balls are of the type used in the WAM.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Surface information</th>
<th>Sq</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>Unidirectionally ground sample</td>
<td>96 nm</td>
</tr>
<tr>
<td>R2</td>
<td>Unidirectionally ground sample</td>
<td>53 nm</td>
</tr>
<tr>
<td>S1</td>
<td>Bearing steel ball (WAM)</td>
<td>21 nm</td>
</tr>
<tr>
<td>S2</td>
<td>Bearing steel ball (WAM)</td>
<td>20 nm</td>
</tr>
</tbody>
</table>

Short length and time scale simulations applying the technique illustrated in Fig. B.3 are run on the 64×64 grid for the S1-S2, the S1-R1, and the S1-R2 contact cases.

### B.5 Results and discussion

The calibration of constants $C_4$, $C_5$, max tribofilm height $h_{\text{max}}$ and wear coefficient $\kappa$ were first adapted to an experiment as described above. The resulting values on
the parameters were used to predict different cases of SRR in the ball on disk contact. Checking how well the predicted film thickness agrees with the measured mean film thickness from the experiment is seen as a measure of the quality of the model. The values and how they change is then used to test different rough surfaces, which are compared in terms of tribofilm quality and contact severity.

### B.5.1 Calibration of the growth model

The calibration was done by adjusting parameters until the agreement with experiments was considered to be sufficient and the values of the constants of the tribofilm growth were balanced against the sliding wear constant. The resulting curve, which was adapted to 0.5% SRR, is seen in Fig. B.5. Comparing with the experimental curve of Fig. B.4 we can say that the agreement is sufficient. The problem now is that for different SRRs other than 0.5% there is an overshoot of tribofilm height above the set value for $h_{max}$, which means the model will not be able to reconstruct the experimental results completely. In fact, we need a different model to achieve this. This will be discussed in the discussion section.

### B.5.2 Model evaluation

Once the model was calibrated to agree with one case of SRR, other SRR were tried out. Results from choosing 10%, 5%, 2% and 0.5% SRR are seen in Fig. B.5. Corresponding experimental measurements are shown in Fig. B.4. A quick growth in the beginning of the numerical experiment can be observed, with a faster growth for higher SRR, as also observed in the experiment. The domination of wear against tribofilm growth for the higher SRR seems to indicate a model weakness. Although
B.5. RESULTS AND DISCUSSION

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Figure B.6: Mean tribofilm height from the numerical simulation. The contact is between two smooth balls exhibiting the surface roughness S1 and S2, respectively. The height is measured by summing up the nodal tribofilm height of each surface and dividing over surface area. The circled line (black) shows the sum of both surfaces’ tribofilm height. The line with plus signs (red) shows the mean tribofilm height on the surface S1 and the line with asterisks (blue) shows the mean tribofilm height on the surface S2.

an exact match was not achieved, the parameter values will be considered accurate enough for use on the small scale with rough surface contacts.

B.5.3 Rough surfaces contact

Results from the deterministic technique for studying rough contacts are presented here. The results are presented case wise and each contact pair is discussed separately.

The first contact case is between two smooth surfaces (S1 and S2). Figure B.6 shows the mean film height against time.

It can be seen that the two surfaces develop tribofilms in a similar fashion. This is expected as the surfaces are of similar quality and geometry. It can also be seen that the growth process is random. There are ups and downs of the tribofilm height and the tribofilm height is initially higher on the surface S1, while after some time this is switched around in favour of the S2 surface. This chaotic behaviour indicates that the solution can not be interpreted exactly but rather phenomenologically, due to measuring equipment and numerical limitations.

One of the qualities of the numerical model is that we can observe the geometrical shape of either surface or tribofilm at any time of it’s development. Figure B.7 shows the profile of the tribofilm after 0.2, 4 and 20 s. Figure B.7 A – C is the tribofilm on surface S1, and Figure B.7 D – F is the tribofilm on surface S2 as its
counter surface.

Having observed already how the mean tribofilm thickness develops the distributions provide a more detailed perspective. It can be seen that ridges of tribofilm are formed in the sliding direction. These ridges are due to asperities on the counter surface, generating the amount of activation energy necessary to activate tribofilm growth, without wearing down too much film and substrate. With the new insight of wear and tribofilm growth in the specific case an explanation of the average tribofilm behaviour is suggested. It can be seen in Fig. B.7 B and D, that the ridge behaviour is more established on surface S2. This is noteworthy, as at this point of tribofilm formation the average height is lower on this surface. But, as these ridges are developed sooner and at least one of them seems to survive, the long-term effect is that this surface gets a thicker tribofilm.

The mean film thickness of the rough(R1)-smooth(S1) contact can be seen in Fig. B.8.

It is noteworthy that the tribofilm of S1 grows faster in contact with the rougher surface R1 than with the smoother surface S1. It seems that the higher contact pressure caused by the rougher surface is, at least on average, a better initiator of tribofilm growth.

The formation of ridges is in line with this hypothesis in the sense that the rougher surface will produce a wider span of contact pressures on the counter surface, resulting in more possibilities for generating the conditions required for tribofilm growth.

Figure B.9 shows development of a tribofilm for the S1 - R1 contact pair. A-C depicts the tribofilm on surface S1 and D-F is the one on R1, after 0.2, 4 and 20 s from left to right.
B.5. RESULTS AND DISCUSSION

Figure B.8: Mean tribofilm height from the numerical simulation. The contact is between one smooth ball exhibiting the surface roughness S1 and one rougher ground surface exhibiting the surface roughness R1. The height is measured by summing up the nodal tribofilm height of each surface and dividing over surface area. The circled line (black) shows the sum of both surfaces’ tribofilm height. The line with plus signs (red) shows the mean tribofilm height on the surface S1 and the line with asterisks (blue) shows the mean tribofilm height on the surface R1.

Figure B.9: A-C shows the development of tribofilm on the surface S1, after 0.2, 4 and 20 s while rubbing against surface R1. D-F shows the development of tribofilm on surface R1.
Figure B.10: Mean tribofilm height from the numerical simulation. The contact is between one smooth ball exhibiting the surface roughness S1 and one rougher ground surface exhibiting the surface roughness R2. The height is measured by summing up the nodal tribofilm height of each surface and dividing over surface area. The circled line (black) shows the sum of both surfaces’ tribofilm height. The line with plus signs (red) shows the mean tribofilm height on the surface S1 and the one with asterisks (blue) shows the mean tribofilm height on the surface R2.

The initial growth of tribofilm on the rough surface, R1, that is seen in Fig. B.10 D, is different from the growth of tribofilm on the smooth surface S1. The coverage is initially poor, indicating that there are many grooves on this surface, which initially doesn’t come into contact at all. Even after 4 s not much has happened with the tribofilm on the R1 surface. It is only after 20 s, Fig. B.10 F, that some ridge like formation of tribofilm can be observed.

The contact pair S1 - R1 was analyzed using the same procedure as for the other contact pairs (S1 - S2 and S1 - R2). Figure B.10 illustrates the mean film height for S1 - R1 and Fig. B.11 shows the tribofilm on each surface after after 0.2, 4 and 20 s.

The surface R2, which is smoother, in the sense that it exhibits a smaller $S_q$-value, than R1 and rougher than S2 promotes a fast tribofilm growth on its counter surface while also providing a decent ground for growing tribofilm on itself. Therefore, the contact pair S1-R2 produces the thickest accumulated tribofilm of the contact pairs studied here. Unlike the situation on the surface R1, the mean film height enters a stage of tribofilm growth which seems faster than just linear growth. By comparing Fig. B.9 F and Fig. B.11 F it is also observed that the S1-R2 contact pair produces more ridges than S1-R1.

In the present model, the tribofilm is assumed to behave as a linear elastic - perfectly plastic material. It is obvious that the outcome would have been different if a more realistic material model, considering possible variations in modulus of
B.6 Discussion on an alternative empirical model

The model applied so far has been derived from an Arrhenius equation type of reaction building tribofilm. From a mechanist’s point of view, it may be tempting to simply postulate a tribofilm growth model based on friction work which gives a good result for the tribofilm thickness. Clearly work will partially lead to heat development and plastic deformation in the contact and partially to chemical energy. The heat developed will also increase the probability for molecular collisions which will grow the tribofilm. A polynomial expression is numerically convenient. If the global behaviour of the experiments by Naveira Suarez [60] is transferred to a smaller scale a simple model for the tribofilm height is easily implemented. For instance the expression

\[ h = h_{\text{max}} \cdot \frac{W_{\text{tot}}}{W_{\text{tot}} + C}, \]  

(B.6.1)
Figure B.12: Mean tribofilm height as a function of time numerically calculated with SRR of 0.5%, 2%, 5% and 10%.

can be adapted and applied locally to match the average tribofilm height. In this equation, $h_{max}$ is the highest allowed film thickness, $W_{tot}$ is the total friction work following a node and $C_c$ is a constant which determines the required energy for growing the tribofilm of dimension energy. The numerical application of such an expression leads to a form

$$h_{n+1} = h_{max} \frac{h_n C_c + W_{n+1}(h_{max} - h_n)}{h_{max} C_c + W_{n+1}(h_{max} - h_n)}$$ (B.6.2)

for tribofilm growth due to the work

$$W_n = P \Delta x \Delta y \mu \Delta s.$$ (B.6.3)

during the timestep $n$, with $\Delta x$ and $\Delta y$ the lengths of grid nodes, $P$ the. This model was adapted to match the 5% SRR case of Fig. B.4. To achieve a match of the overshot, the growth constant $C_c$ needs to vary, decreasing over the first 1000 m of sliding time.

Making a similar investigation for this model as was done with the chemically derived one, resulted in much better matching with the mean film height of the varying SRR experiments. Figure B.12 shows results from this model. The agreement between this model and the WAM experiments indicate a predictive ability for SRR effects on the Poly-$\alpha$-Olefin and 2% ZDDP system. It also indicates that in fact a chemical running in, lasting slowly over the first hour of running the experiment, is taking place. The causes for the chemical running in could be for instance reduction of reactant concentration with time, a slower ZDDP action due to draining of some catalytic chemical component or oxidation of the Fe surface. However, as for predicting the reaction energies of the chemical reactions (and thus
aiding in finding them), the model is insufficiently anchored to chemical theory to be useful, as far as the authors can see.

B.7 Conclusions

A model for a Deterministic chemo-mechanical modelling of boundary lubrication has been successfully implemented. The module for tribofilm growth has been adjusted to agree with measured mean tribofilm height from experiments in a system of ZDDP in Poly-α-Olefin for different SRR. Evaluation on rough surfaces shows clear differences in protection of different contact cases. The method developed could be used to predict the tribofilm protection efficiency for different surfaces designs.

On the asperity scale, the roughness of the surfaces in contact has large effect on the tribofilm coverage and contact severity. Because of higher contact pressures the tribofilm growth may be overpowered by wear leading to lower tribofilm coverage on a rougher surface. The effects considered in the present model indicate that smoother surfaces form more tribofilm, while inducing less film growth on their countersurface.

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Bibliography


