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1. Introduction

Lubricating greases are colloid disperse systems with visco-elastical properties. These special lubricants have a wide range of application. More than 90% of the ball bearings are grease lubricated but also gears and journal bearings are application examples for greases.

The composition of greases consists of a base oil and a thickener (of course some additives can be found in commercial lubricants). The thickener forms a network which leads to a complex rheological and tribological behaviour.

Tribological contacts lubricated by greases are often working under mixed friction conditions.

The situation inside the grease film determines the content of fluid friction. The situation inside the tribological gap influences the content of solid friction.

A special phenomenon is the structural degradation due to the effects of friction. It leads to a dependence on time of the grease behaviour.

Aims of this chapter are the description of the liquid friction process inside the grease film and of the procedure of structural degradation. Both phenomena have a strong influence on the friction and wear behaviour of the whole tribo-system.

2. General definitions and terminology

The presented work is based on a conception of friction and wear that investigates the process from an energy point of view. Some ideas differ from well-known definitions so that they need to be introduced here for better understanding.
A tribological contact describes the geometrical situation of rubbing bodies with interactions in the sense of the tribological process.

Friction is (only) an energy expenditure.

Wear is a production of irreversibility due to affected friction energy. It covers all elements of a tribo-system [1].

This chapter distinguishes between wear volume and volume of the removed material.

Wear volume is presented by the material area where irreversible friction effects lead to an excess of a critical energetic level. (in contrast to the removed material volume (loss of material)).

Mixed friction describes an energy expenditure in several states of friction that exists simultaneously inside the same tribo-system (see also [2]). A direct contact of the solid bodies is not necessary for mixed friction of a lubricated couple (mix of solid and liquid friction).

Lubricating greases are colloid disperse systems with visco-elastical properties.

The grease structure is characterised by the geometry and the distribution of the thickener, the interactions between the thickener and the tribo-system and the ability of storing energy.

3. Energy balance for a grease lubricated contact

Grease lubricated contacts are often working in mixed friction. That means liquid friction (grease film) and solid friction (asperity deformation) have to be considered. An idea of the situation inside the lubricated contact is presented in the next figures.

Figure 1. Grease lubricated contact with two rough surfaces

The surface profile is modelled with a spherical shape of the asperities and the gap configuration can be illustrated with Fig.2.

The situation of a single contact in consideration of the simple idea of lubricant layers inside the grease film is presented in Fig.3.
The grease topography comes from IR-microscopy and presents the density distribution. In Fig.3 the contact of two density areas inside the grease film is highlighted.

Investigations of the surface profile and of the density distribution of the grease lead to a discrete contact model. Random variables are asperity height $\xi_{1,2}$, radius of the modelled asperity shape $\rho_{1,2}$ and the observed density $\delta_{1,2}$. All random parameters can be described with the Gaussian distribution.

For the contact probability $F$ illustrated in Fig.3 (left) can be obtained [3]

$$F(z,u,\rho) = \int_{1}^{z} \int_{0}^{\xi_2} f(\xi_1) f(\xi_2) d\xi_1 d\xi_2 \cdot \int_{\rho_{1,2}}^{\rho} f(\rho_1) d\rho_1 \cdot \int_{\delta_{1,2}}^{\delta} f(\delta_1) d\delta_1 \cdot \int_{\delta_{1,2}}^{\delta} f(\delta_2) d\delta_2$$

(1)

An energy balance is created by investigation of a single grease lubricated contact. The expended energy is formed as a sum of different contents

$$W_{\text{friction}} = \sum_{i=1,n} W_{i-\text{friction}}$$

(2)
The assumption of mixed friction leads to the consideration of two main contents of the friction energy.

\[ W_{\text{mixed friction}} = W_{\text{solid}} + W_{\text{fluid}} \]  

(3)

A proposal is made with

\[ W_{\text{solid}} = e_{\text{elast/plast}} \cdot V_{\text{elast/plast}} \cdot n_{\text{elast/plast}} \]  

(4)

\[ W_{\text{liquid}} = e_{\text{rheo1,2,3}} \cdot V_{\text{rheo1,2,3}} \cdot n_{\text{rheo1,2,3}} + e_{\text{solidif}} \cdot n_{\text{solidif}} \cdot V_{\text{solidif}} + e_{\text{tensile}} \cdot V_{\text{tensile}} \cdot n_{\text{tensile}} + e_{\text{wave}} \cdot V_{\text{wave}} \cdot n_{\text{wave}} \]  

(5)

In Eq.(4) and (5) the notation energy density for the selected mechanism multiplied by stressed volume and by the number of contacts with the same mechanism is used. For a single contact \( n=1 \) holds. The solid friction from Eq.(4) considers the deformation (elastically/plastically) of the stressed asperities. Information about this is given in [4].

The summands in Eq.(5) describe the shearing process in different gap situations (index rheo), solidification effects in the center of the observed gap (index solidif), tensile stress in the outlet of the contact (index tensile) and the formation of a friction wave (index wave).

Figure 4. Different stress situations for the grease inside the contact geometry \((r_{\text{rheo1,2,3}})\)
4. Liquid friction inside the grease film

4.1. Stress situation inside the gap geometry

As mentioned before a micro single contact of a grease lubricated couple is observed and the stress situation is analysed. The idea of the process model developed here is illustrated in Fig.5.

Figure 5. Grease lubricated gap between two asperities (micro single contact). Shear stress is the most important stress mechanism of the grease. Normal force (+) leads to solidification effects. Normal force (-) leads to tensile stress.

In addition the possibility of a friction wave inside the grease film is observed. The idea is clarified in the Fig.6.

Figure 6. Schematic representation of a friction wave caused by the contact of volume elements of the grease film with different properties
4.2. Empirical proposals to quantify the friction energy

The experimental work is focused on the quantification of the energy expenditure during the shear process of a lubricant. This requires an experimental procedure that simulates the liquid friction inside the grease film.

A proposal is made by the use of a rheometer [5], [6]. Shearing a grease sample in a rotating or oscillating test can be interpreted as a fluid friction experiment. All reaction measured by the rheometer is caused by the grease behaviour. The plate and cone in a rheometer configuration does not lead to the state of mixed friction. Although the test conditions are fare from real contact situation rheometer tests are helpful for fundamental investigations of fluid friction.

A picture of a cone-plate configuration is shown in Fig.7.

![Figure 7](image)

**Figure 7.** Evolution of the observed shear stress (left) during a rheometer experiment with a cone-plate system (right) in rotational modus.

The energy per volume that is necessary to shear the grease during the experiment can be obtained from a shear test (Fig.7). The experimental conditions are constant shear rate and constant test temperature. To compare different grease samples the test time for each experiment has to be held constant.

An empirical proposal [7] is made with

$$
e_{\text{rheo}} = \dot{\gamma}_{\text{const}} \int_0^t \tau(\varsigma) d\varsigma$$

with $e_{\text{rheo}}$ the energy density for the shear process [$J/m^3$], $t$ the test time [s], $\dot{\gamma}$ the shear rate [1/s] and $\varsigma$ the current time [s].

A more interesting experimental procedure is an oscillating rheometer test [Fig.8]. The grease behaviour can be observed in a wide range of the oscillating amplitude. For the investigation
of fluid friction inside the grease film experiments within the linear visco-elastical range can be analysed.

To quantify the friction behaviour the following proposal [3] can be used

\[ e_{\text{rheo-elast}} = \frac{G' \cdot \gamma_{\text{elast}}^2}{\cos \delta} \]  

(7)

\( G' \) is the storage modulus [Pa], \( \gamma \) is the deformation [-] and \( \delta \) is the phase different angle. Eq. (7) describes the energy per volume \([J/m^3]\) to deform the sample elastically and is related to the thickener.

![Figure 8. Typical evolution of the storage modulus and the loss modulus during an amplitude sweep (oscillating measurement)](image)

**4.3. Results from experimental work**

The energy expenditure expressed by the rheological energy density \( e_{\text{rheo-elast}} \) presents the liquid friction behaviour of the investigated grease samples. Equation (7) observes only the shear mechanism inside the tribological gap. To compare the greases the same deformation (oscillating amplitude) has to be used. Some greases with the same thickener type (Li-soap) and the same base oil (mineral oil) were observed by a variation of soap content and test temperature.
An increase of the soap content leads to an increase of the liquid friction. Experiments with a temperature $\vartheta = 50^\circ C$ and the same grease samples deliver the results in Fig.10.

Compared with the test temperature of $\vartheta = 20^\circ C$ lower values of the energy densities are obtained. This behaviour is in accordance with the experience that fluid friction is decreasing with an increasing temperature. A more or less linear correlation of energy density and soap content can be observed.
Figure 11. Critical energy level vs. soap content

Figure 12. Energy densities for the crossing point vs. soap content
5. Irreversible effects due to friction

5.1. Idea of the structural degradation of lubricating greases

A typical curve obtained from rheometer experiments for constant shear rate and temperature (rotational mode) shows a strong dependence on time. The drop of shear stress versus stress time is an indirect expression of the structural degradation and well known from many papers [8],[9],[10].

To illustrate the friction effects AFM-investigations made by [11] are presented below (Fig. 13). The change of thickener structure caused by the liquid friction is evident. The geometry and distribution of the thickener is completely different to the initial situation and it can be assumed that the new grease structure shows a different tribological behaviour.

Volume elements inside the grease film are modelled to observe the tribological process. Because of the thickener distribution these volume elements have different properties as elasticity, density, level of accumulated energy, level of critical energy etc. The consequence of the property distribution is a different tribological behaviour of the observed volume elements forming a lubricant layer. The contact situation of two assumed grease layer composed of different volume elements is presented in Fig. 14.

![Figure 13. Left- fresh grease sample, right- grease stressed in a rheometer [11]](image)

Liquid friction between two modelled grease layer. Different volume elements have different rheological and tribological properties.

An energy stress is applied to the control volume if liquid friction take place (Fig.15). Due to this energy stress an energy accumulation process, a dissipation process and a transition process (overstep of a critical energy level) starts.
Figure 14. Liquid friction between two modelled grease layer. Different volume elements have different rheological and tribological properties.

Figure 15. Modelled volume element inside the grease film. Left – unstressed, right – stressed by liquid friction.

The degradation of the grease structure begins with a transition process within a volume element. Overstepping a critical energy density initiates an irreversible change of the structure.

A contact model is developed to describe the energetic situation of critical exceedance.

To quantify the number of exceedance of critical energy level a stationary Gaussian process is used. Information about the conditions and definitions can obtained in [1] and [12].

\[
E[N_0(\omega)] = \lim_{\varepsilon \to 0} \frac{1}{L} \int_0^L E[A(x, \varepsilon) \cdot h'(x)] dx
\]  

\[
E[N_0(\omega)] = \frac{1}{2\pi} \sqrt{\frac{m_2}{m_0}} \frac{\varepsilon^2 \sqrt{m_0}}{m_0}
\]
Initial situation is described with Eq. (8) and the expectation of the number of overstepping $N_0$ can be determined with Eq. (9). This proposal uses spectral moments $m_2; m_0$.

An example [1] was quantified by using density distribution from IR-microscopy to determine the parameter $m_2; m_0$. A mean value of the critical energy level was assumed.

**Figure 16.** New model to describe the energetic situation for the transition process inside the grease film [1]

**Figure 17.** Influence of the critical energy level of the number of oversteps [1]
5.2. Thermodynamic investigations

5.2.1. General aspects

Friction process within a tribo-system is an irreversible process. It means that input of friction energy leads to irreversible effects. This approach interpreted friction and wear process as an cause-effect-chain. Different authors tried to find relations between the system behaviour expressed by mass loss (wear) and entropy flow/production [15]-[19]. Abdel-Aal [18] expressed the conjecture that relation between frictional heat generation and heat dissipation is related to wear transition. This author pointed out [19] that there exists a one to one relationship between entropy generation and mass loss. Doelling et al. [17] give the argumentation that there exists a strong correlation between components wear and entropy flow.

Ling et al. [13] give an experimental description of a correlation between wear and entropy flow in lubricated sliding systems.

“Sliding wear is an irreversible degradation of surfaces induced by friction. On a microscopic scale irreversible physical interactions between the sliding surfaces – including plastic deformation of asperities, fracture, delamination, abrasive plowing, and corrosive wear, among others – creates friction resistance forces, dissipates power, and generates irreversible entropy. Since the physical interactions responsible for friction and wear monotonically produce entropy, entropy becomes a time base for wear” [13].

“The entropy production, in fact, enable one to bridge the atomic scale phenomena with the macro scale response” [14] in [13]. “In addition friction and wear, from the vantage point of thermodynamics irreversible transform mechanical energy into other forms through dissipative processes. Therefore, entropy production is believed to be a propitious measure for a systematic study of wear and friction” [15].

All these investigations pointed out that the application of irreversible thermodynamics is a promising tool to analyse the tribological processes.

5.2.2. Entropy and structural degradation

The aim of this chapter is a description of relation between energetic situation of the tribo-system and the degradation of grease structure. Tribo-systems as solid surface 1, solid surface 2 and lubricant are investigated but also subsystems as lubricant layer 1 against lubricant layer 2.

Source of irreversible processes are thermodynamic forces \( X_i (i = 1, 2, \ldots) \) (gradient of temperature, gradient of concentration\ldots). These forces Xi evoke corresponding flows \( I_i (i = 1, 2, \ldots) \) (heat flow, diffusion flow\ldots) The generalisation of classical thermodynamic to describe irreversible effects leads to an investigation of local equilibrium. That means there exist macroscopic small system areas that are provided in equilibrium while the whole system is out of equilibrium. Two principles of thermodynamic are used: the linear dependence of flows and thermodynamic forces, and the Onsager-reciprocity [20].
For the entropy generation can be written
\[ \frac{dS}{dt} = \sum_i I_i \cdot X_i \]

The variation of entropy is influenced by two terms
\[ dS = dS_{\text{out}} + dS_{\text{in}} \] (10)

Heat transfer across the boundary of the modelled system (subsystem) delivers the entropy \( dS_{\text{out}} \). Entropy related to mechanisms taking place inside the system is described with \( dS_{\text{in}} \) (entropy production). The intention is to relate the entropy production inside the system with different irreversible effects caused by the friction process within the grease layer. It can be written
\[ \rho \cdot \frac{dS}{dt} + \text{div} \sigma = \Theta \] (11)

with \( \sigma \) - entropy flow density \((\sigma = \mathcal{I}/T; \mathcal{I} = \text{heat flow density})\) and \( \Theta \) - local entropy increase per unit time \((\Theta = -(\mathcal{I}, \text{grad}T)/T^2)\) [20]

Written in differential form and related to time
\[ \frac{dS}{dt} = \frac{dS_{\text{in}}}{dt} - \frac{dQ_{1-2}}{dt} + s_i \cdot \frac{dm_i}{dt} - s_a \cdot \frac{dm_a}{dt} \] (12)

with \( s_i \cdot \frac{dm_i}{dt} \) - entropy transported into the system with mass transport; \( s_a \cdot \frac{dm_a}{dt} \) - entropy transported out of the system by mass loss. \( S_{\text{in}} \) describes the entropy production inside the system and \((\pm)S_{Q1-2}\) leads to a change of system entropy by heat transfer across the system boundaries.

Eq. (12) describes the entropy balance for an open thermodynamic system (with exchange of mass). As Abdel-Aal [18] pointed out only the entropy source strength, namely entropy created in the system, should be used as a basis for systematic description of the irreversible process (degradation of materials).

The process of structural degradation can be described as a process of energy accumulation, energy dissipation and transition of critical energy levels. Each of these mechanisms delivers a contribution to an entropy balance and will change the production term in Eq.(10) and (12). Entropy production (for the observed volume element) is determined by fluid friction and its effects. The process of solid friction (for a mixed friction contact) delivers only a heat portion into the modelled system. The tribo-subsystem can be illustrated with Fig.18.
The transport processes modeled from the investigated tribo-system are presented in Fig. 19, 20 and 21.

As a consequence of the modelled mechanisms for the entropy production can be written as

*Figure 18.* Tribo-subsystem (grease layer against grease layer) inside the general tribo-system

*Figure 19.* Observed contact situation (section of a complete tribological system). Solid rubbing body and some modelled grease layers. Heat transport: Q1 - heat amount from solid friction transported into the solid material and into the grease layer; Q2 - heat amount from liquid friction flows into layer 1 and 2; Q3 - same as Q2; $Q_{\text{COND}}$ presents the heat flow by conduction from layer to layer; $V$ - velocities of the observed layers
As a consequence of the modelled mechanisms for the entropy production can be written with

\[
\frac{dS_{\text{in}}}{dt} = \frac{dS_{\text{acc}}}{dt} + \frac{dS_{\text{diss}}}{dt} + \frac{dS_{\text{trans}}}{dt}
\]  

(13)

It means the process of energy accumulation the process of energy dissipation and the transition of an critical energy level produce entropy. Any chemical potential is disregarded in this investigation. We may rewrite Eq.(12)

\[
\frac{dS}{dt} = \left( \frac{dS_{\text{acc}}}{dt} + \frac{dS_{\text{diss}}}{dt} + \frac{dS_{\text{trans}}}{dt} \right) - \frac{dQ_{\text{in}}}{dt} + s_e \cdot \frac{dm_e}{dt} - s_h \cdot \frac{dm_h}{dt}
\]  

(14)
An assumption is made that heat flow gets a (−) that means for a balance that heat leaves the observed volume element.

It can be proposed

\[ S_{\text{acc}} = \frac{\epsilon_{\text{def}} \cdot \zeta_R \cdot V_{\text{acc}}}{T_{\text{acc}}} \]  

(15)

with \( \epsilon_{\text{def}} \) the energy density used for deformation process, \( \zeta_R \) describes the part of friction energy which is accumulated, \( V_{\text{acc}} \) the accumulation volume and \( T_{\text{acc}} \) the temperature of accumulation process.

\[ S_{\text{trans}} = \frac{G \cdot \gamma^2 \cdot \cos \delta}{c} \]  

(16)

from oscillating rheometer measurements (see Eq.(7)). The temperature situation is assumed as \( T_{\text{solid}} > T_{\text{layer1}} > T_{\text{layer2}} \). Furthermore it is assumed that different temperature appears for different mechanism. It means

\[ T_{\text{acc}} \neq T_{\text{diss}} \neq T_{\text{trans}} \]

In general it is conceivable that part of heat generated by solid friction (asperity deformation) enters the first modelled grease layer. Part of this thermal load will be conducted into the next lubricant layer. Liquid friction between the modelled layers leads to a transport of heat into the layers.

An interesting description of the entropy production term for different processes at sliding interfaces comes from [21].

To link the energetic situation with the structural degradation the entropy production term has to be simplified. The friction energy \( W_f \) is observed with the temperature \( T_f \). It can be obtained

\[ \epsilon^{\text{rheo}}_{\text{Rhei}} = T_f \cdot (\rho_a \cdot s_a) - \frac{T_f}{V_a} (S_a - S_{Q1-2}) \]  

(17)

An interpretation delivers \( (\rho_a \cdot s_a) \) as an entropy density leaving the system with the mass exchange. It means an increasing energetic release by entropy flow out of the system with the degraded structure leads to an increasing capacity to withstand stresses expressed by \( \epsilon^{\text{rheo}}_{\text{Rhei}} \).
To use some experimental results some assumption were made. The specific entropy can be determined by

\[ s = c \cdot \ln \left( \frac{T_{\text{str}}}{T_{\text{unstr}}} \right) \]  

(18)

with index \( \text{str} \) for the stressed layer and \( \text{unstr} \) for the unstressed layer. Test temperature in the rheometer was used for \( T_{\text{unstr}} \). An increasing temperature with an increasing soap content during the friction process was assumed because all measurements show a direct correlation between soap content and fluid friction (see Fig. 10). To link the specific entropy leaving the system with the degradation process the parameter \( e_{\text{Rheo}}^* \) for the crossing point (rheometer tests) is used.

Fig. 22 presents the tendency of \( e_{\text{Rheo}}^* \) vs. \( s \).

**Figure 22.** Correlation between \( e_{\text{Rheo}}^* \) (the crossing point) and specific entropy

Fig. 22 presents the assumed correlation between energetic stress and energetic release.

Finally some conclusions were made

\[ \frac{dS}{dt} > \dot{S}_{\text{prod}} + \dot{S}_{Q1-2} + \dot{m} \cdot s_e \]  

(19)
• A significant energetic release by the transport of degraded structure out of the system can be observed.

\[
\frac{dS}{dt} = \dot{S}_{\text{prod}} + \dot{S}_{Q_{1-2}} + \dot{m} \cdot s_e
\]  

(20)

• No significant energetic release by the transport of degraded structure out of the system can be observed.

\[
\frac{dS}{dt} < \dot{S}_{\text{prod}} + \dot{S}_{Q_{1-2}} + \dot{m} \cdot s_e
\]

• An additional entropy source happens (for example the mentioned friction wave).

6. Conclusions

Some new definitions of general tribological subjects are made. A proposal for an energy balance of a grease lubricated contact is given and empirical proposals for quantification are presented. With the help of rheometer tests the fluid friction was investigated and results are illustrated. The degradation process of the grease structure is described with energetic parameters. An open thermodynamic system is created and described. The influence of the energy flow on the degradation process is presented too.

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