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Tribological Stress of Lubricating Greases in the Light of System Entropy

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Abstract: Lubricating greases show a structural degradation due to friction stress. The shear process dissipates energy. This results in a breakdown of the thickener structure, heat and entropy generation. Tribo-systems are energy driven systems. The stressed lubricating grease is modeled as a subsystem and presents an open thermodynamic system. Investigations were made to obtain more information about the correlation of system entropy and structural degradation of a lubricating grease. Experimental studies were done to estimate the role in terms of entropy transport for the open system. The degradation-entropy theorem was applied with the help of an empirical model to describe the correlation between degradation process and entropy production for the special case of a closed and stationary system.

Keywords: lubricating grease; structural degradation; entropy

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1. Introduction

Lubricating greases are markedly visco-elastical lubricants with the main task to separate solid surfaces in a tribo-contact. They consist of a base oil and a so-called thickener. This thickener (it is often a metal soap) forms a three-dimensional network and delivers the elastical part of the visco-elastical properties. In a real tribo-contact, such a lubricant is extremely stressed by pressure, temperature and shear rate. The consequences of an applied friction stress can be indirectly observed by a change of the rheological and tribological behaviour. These are well known as thixotropic effects or even better as artificial thixotropy.

With regard to the thickener structure, a strong change in geometry and distribution of the fibres or agglomerates can be detected [1]. The aim of this paper is the description of the tribo-process as an energy driven process. The energetic situation inside the system determines the initiation of additional dissipative processes. In our case, these processes are the degradation of agglomerates and the change of the thickener distribution.

2. Some Phenomenological Observations

Lubricating greases have a wide range of application. For example, 90% of all ball bearings are lubricated with grease. The process conditions in such machine elements are extreme, and the lubricant is stressed by very high pressure, temperature, and unusually high shear rates.

Lubricating grease with an Li-soap structure is characterized by long thickener fibres. An impression is presented in Figure 1.

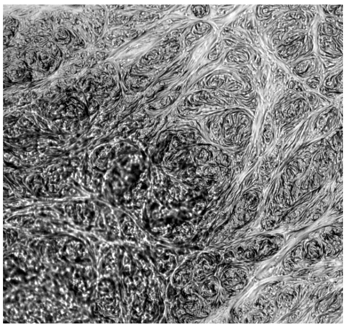
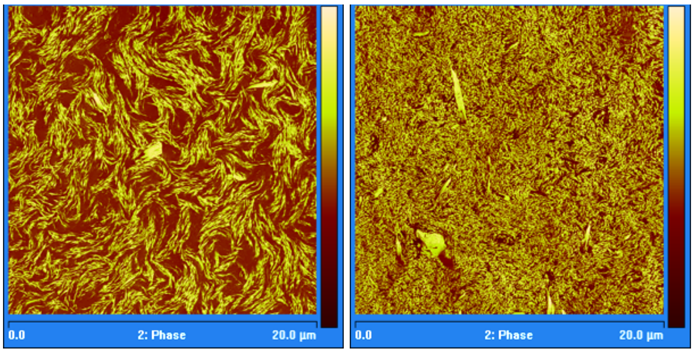


Figure 1. Picture of an oil covered grease structure. Made with reflecting microscope, window size = 470 µm.

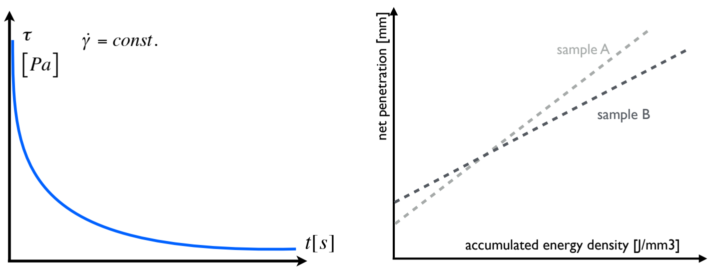
Experimental methods to simulate a stress situation of the lubricants are rheometer tests. The test conditions are far away from reality, but it is possible to observe the influence of shear rate, temperature and pressure during a shear process. Investigations of the effects of a shear process on the grease structure by using atomic force microscope (AFM) comes from University of Huelva (Huelva, Spain) [1,2].

The AFM pictures from Franco et al. (Figure 2) show the consequences of applied shear stress to a lubricating grease very clearly. It is also possible to interpret friction tests in the direction of the structural degradation process because the time dependent friction behaviour is an indirect expression of the structural degradation. An interesting investigation from [3] used the penetration measurement to observe the effects of applied friction energy (Figure 3).



(**a**) (**b**)

Figure 2. (**a**): unsheared Li-model grease; (**b**): 2 h sheared in a rheometer with $\dot{\gamma}$ = 100 s^{-1} and T = 150 °C, window size = 20 µm [1].



(**a**) (**b**)

Figure 3. (**a**): Illustration of a typical behaviour of a stressed grease (rheometer curve); (**b**): Change of penetration caused by introduced mechanical energy as described by [3].

The change of rheological properties like the complex modulus G^* caused by the degradation process is used by [2] as a measure of structural degradation of greases (see Figure 4).

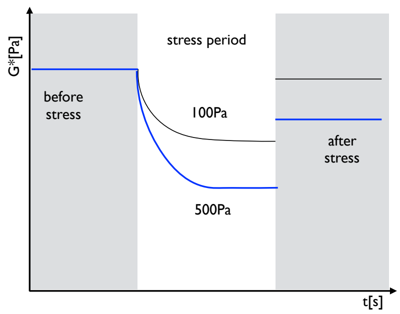


Figure 4. A three-step test (unstressed-stressed-unstressed) to compare the complex modulus as described by [2].

3. The Role of Entropy Transport and Entropy Production

3.1. General Remarks

First, it has to be pointed out that this investigation is strictly dealing with mechanical degradation. Chemical reactions are not involved. The term degradation is used in the sense of a physical process. Degradation means an overstepping of physical bonds (change of the agglomerates).

All processes that we observe are irreversible. The structural degradation process is analogous to the loss of material in solids (caused by friction), an irreversible process. The energetic situation of a stressed volume element of the lubricant has to be considered to analyse the process. A description of a wear process (loss of material) from a thermodynamical point of view is given by [4]. Abdel-Aal describes the tribo-process as a thermodynamically driven process. He points out that the release of friction energy agitates the surface layers and disturbs the order of the system. The system response is lowering of the energy level of the surface layers by adopting a dissipative mechanism. The obtained energy dissipation of disturbance energy leads to a system work-behaviour in a state of minimum energy expenditure.

3.2. Energetic Stressability and Energetic Relief

An idea has been developed of an open thermodynamic system for a stressed lubricating grease. A sub-system inside a general tribosystem consists of the situation of a contact grease volume element against a grease volume element. Such a volume element is stressed by fluid friction, and an exchange of material is assumed as a transport of thickener into the system (m_{in}-unstressed) and out of the system (m_{out}-stressed). The illustration is presented in Figure 5.

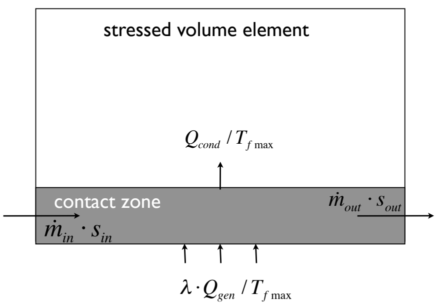


Figure 5. The stressed volume element of a grease film as an open thermodynamic system [5].

The entropy of a system is influenced by two terms

$$\frac{dS}{dt} = \frac{dS_E}{dt} + \frac{dS_I}{dt}, \tag{1}$$

or in another form

$$\rho \frac{ds}{dt} = -\nabla J_s + \gamma. \tag{2}$$

The first term describes the entropy flux, and the second term presents the entropy production, with

$$\gamma > 0 \tag{3}$$

for every real process.

The entropy production is linked to the process of structural degradation, but all other phenomena, such as heat transport and mass transport, also deliver a contribution to the entropy production term. Derived from a general entropy balance [6], it is [7] who proposed a description for the strength of entropy source with

$$\gamma = \frac{\sigma : \epsilon}{\rho \cdot T} + \frac{K^*}{\rho \cdot T^2} |\nabla T|^2 + \sum_k S_k \frac{dn_k}{dt}. \tag{4}$$

The first term presents the traction work, the second term presents the heat conduction, and the third term considers the exchange of material. For greases, different dissipative mechanisms are imaginable (presented with the first term)—for example, a process of energy accumulation, a process of energy transformation, and a transition process of a critical energy level:

$$\frac{dS_{transition}}{dt} = \frac{G' \cdot \gamma_{crit}^2 \cdot V}{T\dot{d}t}, \tag{5}$$

$$\frac{dS_{accumulation}}{dt} = \frac{G' \cdot \gamma_{elastic}^2 \cdot V}{T\dot{d}t}, \tag{6}$$

obtained from an oscillating rheometer test, with γ as the amplitude of deformation and G' as the storage modulus.

To quantify Equation (4), it is [7] who propose the work with heat quantities as presented with

$$\gamma = \frac{\lambda \dot{Q}_{gen}}{T} - \frac{\dot{Q}_{cond}}{T} + \sum_{in} \dot{m}s - \sum_{out} \dot{m}s. \tag{7}$$

These quantities are the heat dissipated by friction, the conducted heat, and the heat transported through the wear particles (related to the idea presented in this paper, it is the heat transported by the grease structure).

The influence of the energetic relief on a tribo-system realised by entropy transport out of the system for a stationary non-equilibrium state is presented by [5]

$$e^*_{Rrheo} = T_f \cdot (\rho_{out} \cdot s_{out}) - \frac{T_f}{V_{out}} (m_{in} s_{in} - S_Q). \tag{8}$$

Here, the parameter $e^*_{Rrheo} [J/mm^3]$ presents a measure of the capability of the system to withstand energetic stress. For a general degradation process, e^*_{Rrheo} presents the relationship between friction energy E_f and volume of the degraded structure V_{out}. In Equation (8), the expression $(\rho_{out} \cdot s_{out})$ can be interpreted as an entropy density linked to the structure that leaves the system.

3.3. Degradation-Entropy Generation Theorem in the Light of Structural Changes of Grease

Bryant, Khonsari and Ling [8] developed an approach to link the entropy production to a degradation process, and finally to the wear process. The conditions are a closed system and the stationary state.

The starting point is a definition of a degradation measure $w = w\left(p_1, p_2, ..., p_i, ..., p_m\right)$ that is a non-negative, non-decreasing continuous function, where $p_i\ (i = 1, 2..., m)$ are one or more dissipative degradation processes. Each $p_i = p_i\left(\zeta_i^j\right)$ depends on a set of time dependent phenomenological variables $\zeta_i^j = \zeta_i^j,\ j = 1, 2, ..., m_i$. The degradation measure is obtained with

$$w = w\{p_i\left(\zeta_i^j\right)\} = \sum_i w_i \quad i = 1, 2, ..., n; \quad j = 1, 2, ..., m_i \tag{9}$$

and the entropy generation from the degradation mechanism

$$S_I = S_I\{p_i\left(\zeta_i^j\right)\} = \sum_i S_{Ii} \quad i = 1, 2, ..., n. \tag{10}$$

With the rate of degradation dw/dt and rate of entropy generation dS_I/dt and following the expression of entropy for stationary state $dS_{Ii}/dt = \sum_j X_i^j \cdot Y_i^j$ as a product of generalized forces X_i^j and generalized flows J_i^j [8]: $X_i^j = \partial S_I/\partial p_i\left(\partial p_i/\partial\zeta_i^j\right)$; $J_i^j = \partial\zeta_i^j/\partial t$ and $Y_i^j = \partial w/\partial p_i\left(\partial p_i/\partial\zeta_i^j\right)$. More applications to the tribological behaviour of solids can be found in [9].

For the presented investigation, a single variable system is defined for an application to the structural degradation process of lubricating greases. This means that the degradation $w = w\{p\left(\zeta\right)\}$ describes a single process $p\left(\zeta\right)$ with one phenomenological variable ζ.

The degradation process is the process of structural degradation $P_{st} = P_{st}\left(E_f\left(P_E\right)\right)$ with a complete dissipation of friction energy E_f (overstep of a critical energy level) caused by supply of energy P_E. The irreversible entropy generated during this friction process is presented as $S_I = S_I\left(E_f\left(P_E\right)\right)$.

The following can be formed

$$\frac{dP_{st}/dt}{dS_I/dt} = \frac{dP_{st}}{dE_f}\frac{dE_f}{dP_E}\frac{dP_E}{dt} \cdot \frac{dE_f}{dS_I}\frac{dP_E}{dE_f}\frac{dt}{dP_E}, \tag{11}$$

analogous to [8]

$$\frac{dP_{st}/dt}{dS_I/dt} = \frac{Y}{X} = \mathbf{B}, \tag{12}$$

with **B** being the degradation coefficient.

It has to be pointed out that both phenomena, the loss of material for solid friction and the change of the grease structure for fluid friction, are combined in one term: *wear.* Both phenomena are caused by friction and both have an irreversible character.

It can be characterized:

- wear of solid bodies is measured as a volume of loss of material V_{wear},
- wear of lubricating greases can be measured as an increasing number of solid units n_p.

The formulated idea can be expressed as

$$E_f \sim n_p. \tag{13}$$

An assumption is made that the introduced friction energy E_f is proportional to the number of solid units, or even better the numbers of particle n_p (e.g., agglomerates). This is illustrated with Figure 6. A proportionality factor is defined and Equation (13) is rewritten

$$dE_f = E_p \cdot dn_p, \tag{14}$$

and related to time

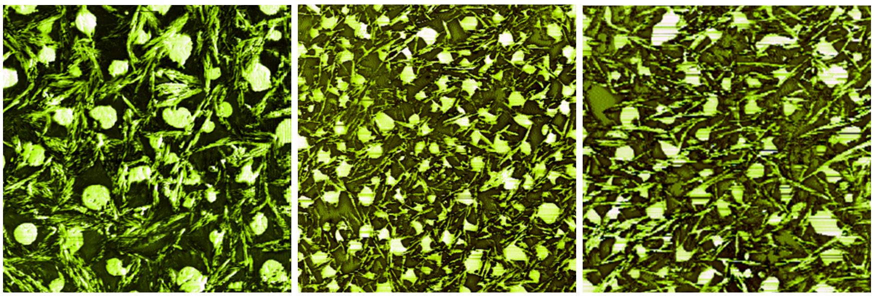


Figure 6. Change of grease structure caused by increasing shear rates in a rotational rheometer test as described by [10]. Dark areas present the base oil and bright areas the thickener (here a Li-Ca-soap was used as a thickener).

$$\frac{dE_f}{dt} = E_p \cdot \frac{dn_p}{dt}. \tag{15}$$

It is

$$\frac{dS_I}{dt} = \left(\frac{dS_I}{dE_f} \cdot \frac{dE_f}{dP_E}\right) \frac{dP_E}{dt}, \tag{16}$$

following [8] for stationary state, and, for closed systems, it is $dS_I/dE_f = 1/T$.

It is obtained that

$$\frac{dE_f}{d\gamma} = \tau \cdot V, \tag{17}$$

with the time dependent phenomenological variable $\zeta = P_E = \gamma$ (deformation), the shear stress τ, and the volume of the stressed sample V. It is

$$\frac{dP_{st}}{dt} = Y \cdot J = B \cdot X \cdot J, \tag{18}$$

and

$$\frac{dn_p}{dt} = \frac{B \cdot \tau \cdot V}{T} \cdot \frac{d\gamma}{dt}. \tag{19}$$

Using Equation (14), it follows

$$\frac{dn_p}{dt} = \frac{\tau \cdot V}{E_p} \cdot \frac{d\gamma}{dt}. \tag{20}$$

Comparing Equations (19) and (20) delivers

$$E_p = \frac{T}{B}. \tag{21}$$

4. Materials and Methods

Different tests are done to obtain information about the friction and wear process of a stressed grease. Experimental work are performed with a Rheometer MCR 302 from Anton Paar (Graz, Austria). A rheometer with a plate–plate system is used to stress a grease sample and to measure different parameters during the process. The experiments deliver some input data to investigate the proposal

(Equation (7)). Especially, tests were done to show the influence of the transported entropy out of the system, according to Equation (8).

4.1. Materials

Model greases with 3 thickener types have been used (see Table 1). These were polyurea (Pu), high dispersed silica (Gel) and lithium-12-hydroxysterat (Li). The samples were made in NLGI-2 grade (grades are defined by the National Lubricating Grease Institute, Lee's Summit, MO, USA).

Table 1. Used model greases. All samples are without additives and made with polyalphaolefin/ mineral-base oil.

Grease Sample	Thickener Type	Base Oil ν_{40} (mm^2s^{-1})	*PP* (°C)	*P*w60 (0.1 mm)	Thickener Content
Li-2	Lithium-12-hydroxyoctadecanoate	100	−24	283	9.5%
Pu-2	Polyurea	100	−24	279	11.1%
Gel-2	high dispersed silica	100	−24	290	8.6%

It mean *PP* the pourpoint and *P*w the worked penetration.

4.2. Experimental Methods

The experimental procedure consists of three steps [11]. A rheometer with a plate–plate system with a standard surface roughness was used. The diameter of the plate was 25 mm, and the gap height was constant at 1 mm.

After a time period without any motion, a stress period realised by a shear test in a rotational mode is first created (constant shear rate $\dot{\gamma}$ an test time t = 900 s). Second, an amplitude sweep with an oscillatory measurement (Figure 7) has been done to reach the crossing point of G′ and G″ (Figure 8). The oscillatory test starts with an amplitude of 10^{-2}%. In addition, the temperature evolution during the stress period of the rheometer tests were measured with the temperature measurement system of the rheometer.

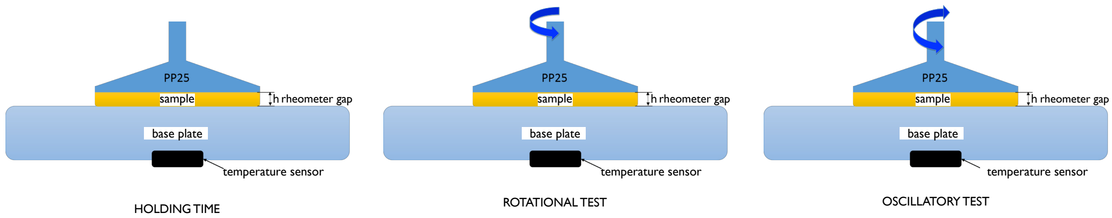


Figure 7. Test procedure with a stress period in rotational modus, and an oscillatory test to check the structural degradation

The second step of the rheometer test (rotational mode) was done to stress the grease sample by a fluid friction or shear process. The test time was defined. The third step was an oscillating test. This has been done in order to get information about the intensity of structural degradation during the stress period before. The result is an indirect expression of the structural degradation (here, it is called wear of lubricating greases). The indirect measure for the wear of the greases is the expended energy to reach the crossing point of G′ and G″ (this step is illustrated in Figure 8). In addition, the temperature sensor system of the rheometer was used to observe the temperature during the stress period. Some simplifications were made to use the rheometer tests for an observation of the energetic situation of the stressed grease.

All tests were made in a special air-conditioned laboratory room. The temperature was measured inside the lower plate in the center of the plate. An assumption was made that the temperature presents the constant temperature of the sample. The idea was developed that a contact zone exists in the defined system. A higher temperature can be found inside this contact zone because fluid friction is introduced (T_{max}) (as shown in Figure 5). Compared to solids, greases have a low energy level for changing the structure. Only intermolecular forces (van der Waals) have to be overcome, which means that an extremely small part of the energy is converted into heat. In other words, the situation to find new dissipative processes occurs very quickly.

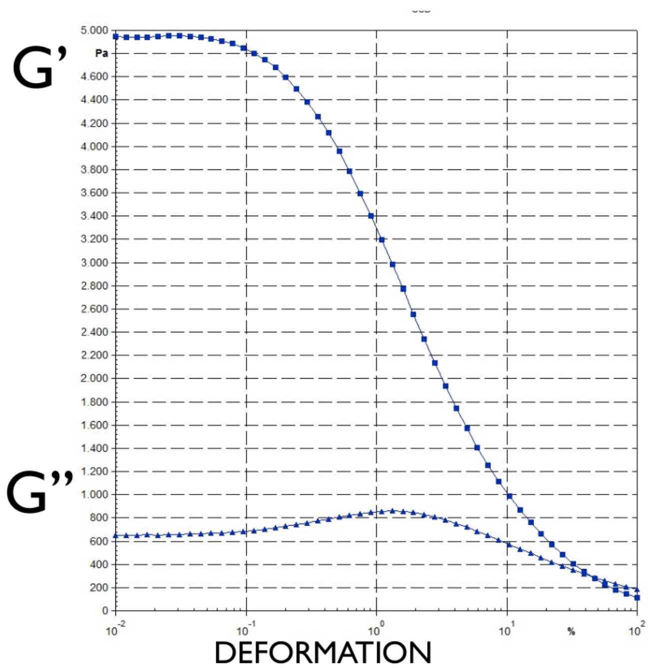


Figure 8. Last step of the test procedure (oscillatory measurement): evolution of the storage modulus G′ and loss modulus G″.

5. Results and Interpretation

5.1. Temperature Measurements

The measured temperature differences of three grease samples are presented in Figure 9. The standard deviation for the repeated tests and for the different shear rates has a range between s = 0.004 K and s = 0.09 K. For each shear rate, the test was repeated three times.

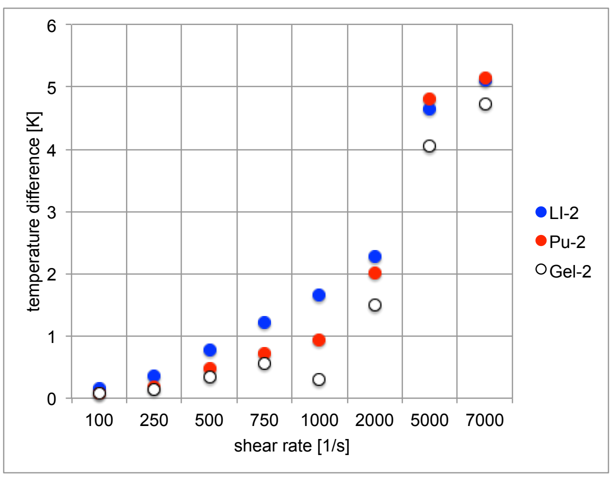


Figure 9. Obtained temperature differences during the shear test (t = 900 s).

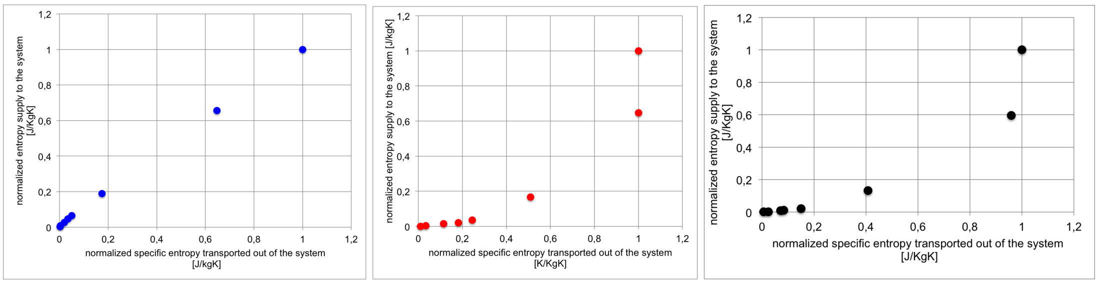
5.2. Influence of the Entropy Transport

According to Equation (8), the transport of entropy out of the system (linked with degraded structure) leads to an improvement of the capability to sustain tribological stress.

Figure 10 presents at the abscissa the specific entropy that leaves the system and at the ordinate the entropy supply to the system (that is proportional to the friction energy that stresses the system) The specific entropy was estimated according to the different thickener types and contents with

$$s_{in} = c \cdot ln\left(\frac{T_{stressed}}{T_{unstressed}}\right), \quad (22)$$

$$s_{out} = c \cdot ln\left(\frac{T_{fmax}}{T_{stressed}}\right). \quad (23)$$



(**a**) (**b**) (**c**)

Figure 10. Comparison of the wear behaviour between three model greases of NLGI-2. (**a**): Li-; (**b**): PU- and (**c**): Gel-sample.

This idea is illustrated in Figure 5. To estimate the T_{max} caused by the introduced friction energy, an assumption was made that only a small part of E_f is converted into heat. As described earlier, the energetic situation for the stressed grease to initiate new dissipative processes (e.g., degradation of the thickener) occurs very quickly. The specific entropy was calculated with Equation (23). The specific heat was computed corresponding to the composition (base oil/thickener). The maximum temperature was calculated with the friction energy (stress test), and the stress temperature was the measured temperature. The entropy supplied to the system comes from the friction energy during the stress test (and maximum temperature) (see Figure 5).

For very low entropy supply to the system, Figure 10 shows for the two model greases on the right side a significant transport of entropy. For the grease on the left side, the entropy transport for low entropy supply is less distinctive. In other words, the system for the two model greases on the right side reacts with higher entropy transport to the stress compared with the left model grease.

The wear behaviour of the lubricant is characterised by the expended energy to reach the crossing point in an amplitude sweep of an oscillating measurement (constant frequency). Figure 11 presents the behaviour of the samples with NLGI-2 grade. A high amount of energy (abscissa) means a low intensity of degradation and vice versa.

In the light of Equation (8), Figure 11 has to be linked with Figure 10. The red and black points represent the two model greases on the left side of Figure 10. For low shear rates (abscissa), a more or less constant behaviour (no significant degradation process) can be observed. In contrast, the blue points (model grease on the right side in Figure 10) also show a significant structural degradation for low shear rates.

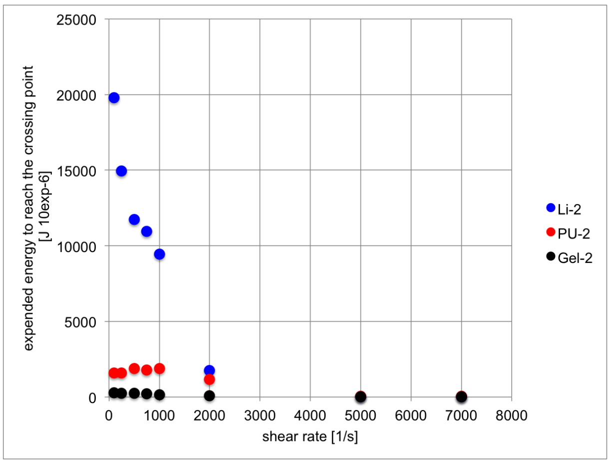


Figure 11. Expended mechanical energy to reach the crossing point of G' and G'' (intensity of structural degradation).

We can summarise that the two model greases (red and black points) choose the transport of entropy out of the system to get an energetic relief, and structural degradation is not significant. This is in accordance with Equation (8). It seems for the model grease on the left side (blue points) that this is not a possible way, and the system reacts with a significant degradation process to relieve the stress situation.

5.3. Influence of Entropy Production

The source term in an entropy balance can be described with Equation (4) and consists of three terms. The third term was selected to investigate the fact if a different behaviour of the model greases, as shown in Figures 10 and 11, can be detected. The third term describes the contribution of the matter exchange to the entropy production.

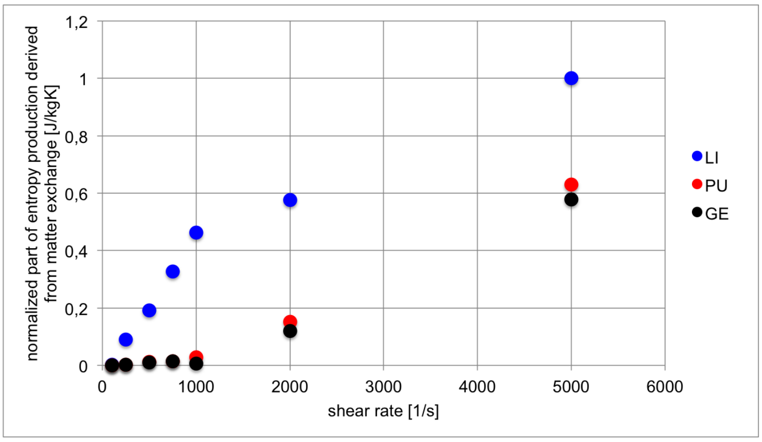


Figure 12. Comparison of the three samples related to the entropy production caused by the matter flow.

Assuming that the masses that come in and go out are the same, but the temperatures are different, the difference is created inside the system and is a part of the entropy generation balance.

It is interesting to detect that again the model grease (blue points) has a different behaviour compared with the other samples (Figure 12). Probably, the intensive structural degradation at low shear rates (Figure 11) leads to this significant process for the blue point sample.

For a steady-state and closed system, Equation (19) describes the correlation between structural degradation and entropy production. Until now, it has only been possible to describe the structural degradation vs. entropy production in a qualitative analysis.

Assuming the so-called degradation coefficient **B** Figure 13 will be obtained, please note that **B** is the slope of curve dn_p vs. S_I.

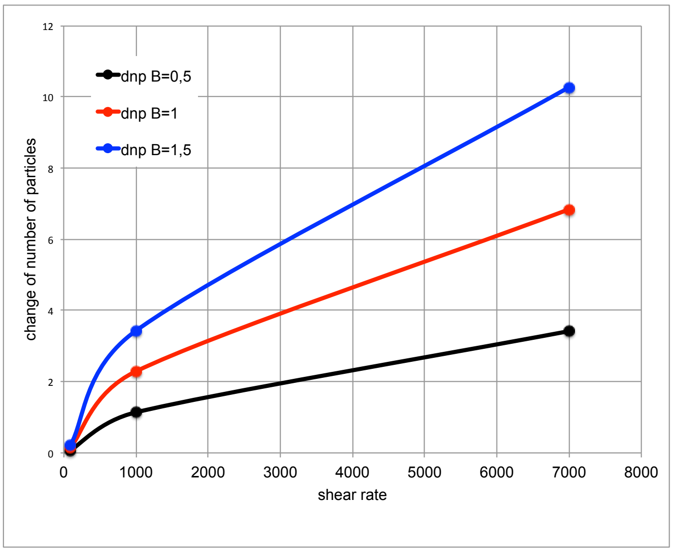


Figure 13. Change of particle number per time with assumed degradation coefficient **B**.

6. Conclusions

The effect of fluid friction leads to a structural degradation of lubricating greases. The mechanical degradation means a destruction of the thickener. The tribological behaviour is understood as a consequence of the energetic situation of the stressed lubricant.

To compare the degradation process of different greases, an indirect measure from oscillatory tests was used. This measure is the mechanical energy that is applied to a stressed grease in an oscillatory test to obtain a complete flow of the sample. The behaviour is influenced by the thickener type and geometry.

Three model greases with different structural degradation behaviours were investigated. The correlation between entropy transport and degradation process becomes clear by linking the tests from Figures 10 and 11. A high energetic relief will be obtained with a high amount of specific entropy transported out of the system. This is confirmed by Equation (8).

The experimental possibilities in this paper allow for an investigation of entropy production to observe the third term (mass exchange) in an entropy balance (Equations (4) and (7)). The same differing behaviours of the model greases were found (Figure 12). The decision of the system to relieve the stress situation with a more intensive degradation for the Li-sample in Figure 10 probably leads to this striking difference.

In the last part of the paper, an application of the so-called entropy generation-degradation theorem by [8] on the grease was tried. The theorem describes the connection between entropy production and a degradation process for a closed stationary system. An empirical model for the structural degradation is proposed that describes more directly the degradation process. An expression is obtained that connects the entropy production and the degradation of the grease structure. A qualitative example is given.

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Conflicts of Interest: The author declare no conflicts of interest.

Abbreviations

B	degradation coefficient [-]
E_f	friction energy [J]
G'	storage modulus [Pa]
G''	loss modulus [Pa]
Q_{gen}	heat generation [J]
Q_{cond}	heat conduction [K]
S	entropy [J/K]
S_E	entropy transport [J/K]
S_I	entropy production [J/K]
V	volume of degraded matter [m^3]
T	temperature [K]
m	mass [kg]
n_P	number of particles [-]
p_i	dissipative process [-]
s	specific entropy [J/kg]
w	degradation measure [-]

References

1. Franco, J.M.; Delgado, M.A.; Valencia, C. Combined oxidative-shear resistance of castor oil-based lubricating greases. In Proceedings of the 3rd Arnold Tross Colloquium, Hamburg, Germany, 8 June 2007.
2. Sanchez, M.C.; Franco, J.M.; Valencia, C.; Gallegos, C.; Urquiola, F.; Urchegui, R. Atomic force microscopy and thermorheological characterisation of lubricating greases. *Tribol. Lett.* **2011**, *41*, 463–470.
3. Rezasoltani, A.; Khonsari, M.M. On the correlation between mechanical degradation of lubricating greases and entropy. *Tribol. Lett.* **2014**, *56*, 197–204.
4. Abdel-Aal, H. Concerning the Thermo-Thermodynamical aspects of wear regime transition in dry tribosystems. *Ann. Univ. Dunaries Jos Galati Fascicle VIII* **2015**, *8*, 41–47.
5. Kuhn, E. Correlation between system entropy and structural changes in lubricating grease. *Lubricants* **2015**, *3*, 332–345.
6. De Groot, S.R.; Mazur, P. *Basics of Thermodynamic of Irreversible Processes*; General Publishing Company: Toronto, ON, Canada, 1984.
7. Abdel-Aal, H. Thermodynamic modeling of wear. In *Encyclopedia of Tribology*; Wang, Q.J., Chung, Y.-W., Eds.; Springer: New York, NY, USA, 2013.
8. Bryant, M.D.; Khonsari, M.M.; Ling, F.F. On the thermodynamics of degradation. *Proc. R. Soc. A* **2008**, *464*, 2001–2014.
9. Amiri, M.; Khonsari, M. On the role of entropy generation in process involving fatigue. *Entropy* **2012**, *14*, 24–31.
10. Roman, C.; Valencia, C.; Franco, J.M. AFM and SEM assessment of lubrica-ting grease microstructures: Influence of sample preparation protocol, frictional working conditions and composition. *Tribol. Lett.* **2016**, *63*, 1–12.
11. Kuhn, E. The energetic situation of the structural degradation of lubricating greases. In Proceedings of the Lubmat-Conference 2014, Manchester, MA, USA, 25–27 June 2014.