Computing of the Molecular Orientation State of the Lubrication Layer

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Abstract

The algorithm and software for computing the order parameter value describing structural sequence in the molecular model of the boundary lubrication layer have been created. It has been shown that computer estimation of a supramolecular self-organization together with a new method of polarization tribometry can enhance the efficiency of new lubrication composition creation.

Keywords: Lubrication materials; Lubrication layer; boundary lubrication; molecular modeling

1. Introduction

Lubrication activity of boundary layers of adsorption origin to a great extent is determined by the level of lubrication media molecules orientation in relation to friction surfaces. Currently this level is increased by introducing additions with characteristics allowing to form volume and superficial supramolecular structures (mesomorphic nanostructured systems) \cite{1} to the lubrication media. By all means, the most important role in protecting surfaces from wear and tear is played by boundary lubrication layers, the structure of which is formed under the influence of force field of the solid surface \cite{2,3}.

B.V. Deryagin has shown that the friction value is changed on the solid bodies surface depending on the molecules orientation in the adsorption layer. When the molecules orientation is horizontal (in relation to the base) the friction is at minimum. When the quantity of molecules of surface-active media in adsorption layer (when their

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orientation is changed from horizontal to vertical) grows the maximum friction takes place in case of their maximum disordered positions. When further the number of molecules is increased the adsorption layer acquires the most vertical orientation, the friction lessens and with further growth of the number of molecules does not change [3].

Molecular structures of boundary layer described in literature are varied and are built on the basis of general theoretical conceptions and are not likely to be verified by the experiment. However, new methods of computer molecular dynamics which have recently been developed allow researching the question of the layer structure soundly and in detail. This ideology was firstly presented by us in the work [4]. We are speaking about applying the complex of molecular modelling for describing molecular array composing the lubrication layer. Modern complexes of molecular modelling allow building adequate models of complex molecules. Examples of images of anisometric molecules able for orientation process are shown on Figure 1. The position of each particle of this array is determined by its interaction with neighboring particles and with the solid surface. The example of modelling the interaction between the singular molecule of the mesogenic lubrication material with the metal surface (iron) is depicted on Figure 2.

In transition from the singular molecule model to the group of particles we face the necessity of the system “optimization”. The essence of optimization lies in the computer software varying the position of each molecule in such a way that the system as a whole has a minimum energy. This molecular image of the lubrication layer can be subjected to pressure and/or shift. In doing that the array is deformed and each discrete step of the layer deformation is accompanied by the cyclic optimization process. The above mentioned process of supramolecular self-organization appears which is seen in the change of the molecular parameter order. The quantitative evaluation of this parameter is a real goal of the present work.

![Molecular models of some mesogenic molecules of tribo-active additives](image)

**2. The quantitative estimation of the orientation effect in the lubrication layer with mesogenic additives**

The description of orientation effects in array of molecules in the lubrication layer comes to the computing the system “order parameter”. The orientation ratio can serve as one of the methods of its determination. The calculation of this ratio must be the part of a more complication calculation complex, the function of which is the molecular modelling of the friction pair with lubrication layer [5].

So, we have a group of virtual models of molecules which are moving closer to each other to create a lubrication layer in a 3-dimensional space firstly occupying random (chaotic) orientation. When imitating the friction process the shift process provides for orientating molecular axes in the direction of friction. Here appears the task of calculating the order parameter of the molecular system. This parameter must change in the process of friction depending on the structure of molecule of the triboactive component. This data can help in choosing applicable (from the point of view of tribostructuring) additions for lubrication compositions. The work [6] shows that this ratio can be calculated with the help of one of the two formulas:
\[ k_1 = \frac{\sum_{i=1}^{N} |\sin(\varphi_i)|}{N}, \quad k_2 = \frac{\sum_{i=1}^{N} |1 - \cos(\varphi_i)|}{N}, \tag{1} \]

where \( k_1, k_2 \) are different representations of the orientation ratio, \( N \) – the number of molecules, \( \varphi_i \) – the deviation angle of the \( i \)-molecule axis in relation to the main direction of molecules, “director” (in this case in relation to the sliding vector direction). \( k_1 \) is used in the case when the molecules under study have a “plane of symmetry”.

Fig. 2. Molecular model for testing the software (sodium stearate on the iron surface)

The degree of the orientation order in the liquid crystal can also be determined with the help of another parameter [7]:

\[ k = -\frac{1}{2} + \frac{3}{2} \left\langle \cos^2 \vartheta \right\rangle, \tag{2} \]

where \( \vartheta \) – is an angle which is created between the long molecule axis with the director’s direction, and angle brackets mean the statistic average for all the molecules. In ideal parallel orientation \( k = 0 \). In nematic phase the \( k \) parameter takes the average meaning \( 0 < k < 1 \), which depends on the temperature and concentration of molecules of the bar-shape form. (But we need to point out that to disk-shape molecules expression (2) is evidently not applicable).

Let’s stress out that in 2-dimension case when molecules possess the ease of rotation only in one plane \( xy \) (the case of molecular monolayer), the order parameter (2) will look like:

\[ k = 2 \cdot \left\langle \cos^2 \vartheta \right\rangle - 1, \tag{3} \]

To calculate the order parameter, it is necessary to have a number of axes direction vectors for all the molecules of the group. Placing the molecule axis inside of the molecule in ideal case must be done with the help of the least square method in 3 dimensions though this solution will demand more time for calculation.
To calculate the molecule axis position will be complicated when using large molecules which have complex forms, “swinging” joints and conformation abilities. The rigid “fixation” of the singular molecule form before the optimization procedure and using the molecule conditional axis for particles of the same nature can currently serve as an acceptable solution. Thus, neglecting the possible conformations significantly simplifies the task of describing the molecular array orientation.

3. Building the algorithm for order parameter calculation

Based on the completed analysis of the expressions for determining orientation ratio we have tested these formulas on the pre-developed program. As an object of calculation we have used the bar-shaped molecules. We have selected expression (3) for using in the developed software for calculating the order parameter as in our view it determines the ratio under question to the fullest extent. When the molecules are fully ordered the order parameter is converging to 1. Also, based on the above given data we can make a conclusion that the axis angling of molecules to the surface, which too must be determined in the software algorithm, influences the lubrication characteristics as well. To build molecular axes we have used the least square method and for that purpose we have minimized mean square deviations of atoms from the bar-shaped molecule.

The software has been developed on the VBA language. This approach extends the functionality of the software and gives the user additional tools for processing data using Excel [8] options. The results have been visualized in the table and graphic forms with the possibility of exporting to the file format and subsequent analysis (Figure. 3).

In cells T2:V7 the calculated co-ordinates of the most remote atoms of molecules concerning which the main axes are under construction. On the plot the main axes («directors») of molecules sodium stearate placed on iron surface which molecular model is presented on Figure 2 are shown. In cells Y2:AA4 the results of calculations of corners cosinuses are presented, which axes form with semiaxes of co-ordinates. In cells AC3, AC4 results of calculation of an average corner of calculation of all molecules concerning friction surface and order parametre are presented.

In the final view the received the algorithm chart for calculating \( k \) value is shown on Picture 4. The chart consists of 10 blocks and includes both entering data on the molecules array of the lubrication layer and calculation procedures themselves.

![Fig. 3. Sample of working window of the software](image-url)
Figure 4. Software algorithm for searching orientation ratio of lubrication layer molecular structure

1. Start (open the file for processing)

2. Character-at-a-time data is read from the file in which Cartesian coordinates of the molecules positions are represented as a z-matrix (in extension)

3. File ending is checked
   - Yes
   - No

4. Symbols are converted into coordinates and are entered into the cells of the table

5. The number of atoms in the molecule is determined

6. Maximum and minimum values are determined from the array of atom coordinates in each molecule and references values of the identified atoms in the data array are saved

7. The axis is drawn in each molecule (by building a vector based on atoms (points) having maximum and minimum values on X axis)

8. Directing cosines and axis angles of each molecule in relation to the global coordinates system are determined in all the 3 directions X, Y, Z

9. The order parameter is calculated based on the formula: \( k = \frac{1}{2} \left(3 \cos^2 \theta - 1\right) \)

10. The general molecule axis order is determined (the extend of variances in directing angles):
    1. Three standard deviations (SD) are determined in relation to directing angles of all the molecules (SD by \( \cos \theta \), SD by \( \cos \theta \), SD by \( \cos \theta \))
    2. Average value of SDs is determined
    3. Average incline angle of molecules axes to the surface is calculated.

11. All the computed values are output into the table
    The graph of molecule axis positions is built in the Cartesian coordinates

12. End
In the context of the described model approach the question comes to mind as to how to evaluate the adequacy of calculations beside having the tribological experiment. Here we can use methods of lubrication layer analysis in the polarized light [9]. Attempts are known to have been made to combine getting a polarized picture of the studied friction and the process of the controlled friction [10, 11]. Based on these principles the device developed by us — “polarization tribometer” — allows getting complex information “in situ” about the processes of structuring and visco-elastic qualities of lubrication materials with triboactive additions of adsorption (structuring) action.

This device is able to simultaneously receive indicated values of the rotational moment of the friction pair at constant sliding velocity and controlled working clearance and register response of the optical signal formed by the laser bear and polarizer. It gives helpful information about the role of supramolecular self-organization effects in the boundary lubrication layer. Registered effects demand analytical description from the point of view of rheology of the lubrication material flooding in thin layers with consideration for mesogenic media physics. We have touched upon advantages and limitations of the molecular modelling method for diagnosing lubrication layers in work [13].

4. Conclusion

Thus, the computing problem has been solved: to calculate the order parameter for molecular array forming the boundary lubrication layer between the two friction surfaces. The orientation ratio statistically evaluating the extent of supramolecular order of the lubrication layer is computed. This parameter can be used, for instance, for preliminary selection and comparison of efficiency of triboactive additions which possess mesomorphic characteristics.

In our view, in comparison with traditional methods of diagnostics computer molecular modelling together with new optical experimental methods has a visible potential for creating new lubrication materials.

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