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SOME PRINCIPLES OF BUILDING THE MOLECULAR MODELS FOR TRIBOSYSTEMS WITH MESOMORPHIC BOUNDARY LUBRICATION LAYER

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Problems related to computer molecular modelling for imitation of tribosystem consisting of a couple of friction surfaces and a dividing lubrication layer have been studied. Tribological tasks that potentially can be resolved with the help of this concept and classification of the models used have been described. Principles of calculation environment organization for tribosystem models have been articulated. The main limitations of software and algorithmic solutions in this area have been listed. The potential of computer models for forecasting tribosystem parameters and new lubrication materials development have been evaluated and described.

Key words*: boundary lubrication layer, mesogenic lubricant, molecular modeling, molecular dynamics, friction, software.*

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НЕКОТОРЫЕ ПРИНЦИПЫ ПОСТРОЕНИЯ МОЛЕКУЛЯРНЫХ МОДЕЛЕЙ ТРИБОСИСТЕМ С МЕЗОМОРФНЫМ СМАЗОЧНЫМ СЛОЕМ

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Рассмотрен комплекс проблем, связанных с применением компьютерного молекулярного моделирования для имитации трибосистемы, состоящей из пары поверхностей трения и разделяющего их смазочного слоя. Описаны трибологические задачи, которые могут быть решены с помощью этой идеологии, дана классификация используемых моделей. Сформулированы принципы организации вычислительной среды для работы с моделями трибосистем. Дан перечень основных ограничений, налагаемых на программно-алгоритмические решения в этой области. Оцениваются перспективы компьютерных моделей для прогнозирования параметров трибосистем и разработки новых смазочных материалов.

Ключевые слова*: граничный смазочный слой, мезогенные смазочные материалы, молекулярное моделирование, молекулярная динамика, трение, программное обеспечение.*

Introduction

One of the most interesting and complicated goals of modern tribology is building a tribosystem model at the molecular level as an integral whole by ways of computer molecular modelling (CMM). By tribosystem we mean the unity of three components: two friction surfaces and dividing them lubrication layer (LL).

A tribosystem model can be two-dimensional and three-dimensional. Two-dimensional models are built "manually. They serve only for visualization of longitudinal section of the friction couple. Configuration of lubrication material (LM) particles and a form of their flat supramolecular packing are assigned arbitrarily and optimization calculations are not fulfilled.

Using modern software of molecular dynamics which helps to build images of molecular objects of different complexity levels it is possible to get a three-dimensional tribosystem with account of chemical nature and molecular structure of each of the three system components: friction surfaces and LL. Herewith a three-dimensional image of the layer is created with due account of intermolecular interaction of LM particles both between themselves and with solid surfaces.

The tribosystem CMM with a lubrication layer allows to monitor the LL structural features including films of molecular width. It becomes important especially in the case when the lubrication layer consists of molecules with anisometric structure, for example, active adsorptional and /or mesogenic. Herewith the possibility appears not only to monitor the two-dimensional layer image in the cross section but to have information about all the particles of the described tribosystem in any arbitrary section. In addition, it gives the possibility for calculating many parameters of tribosystem.

We think that CMM can be applied to the larger extent to the problems of studying lubrication process than to wear and tear. Herewith modelling of hydrodynamical lubrication mode is more accessible. The task of wear and tear modelling is complicated by the fact that one has to deal with real contact zones characterized by profound structural surface reconstruction, high temperature and inevitable chemical reactions. It is impossible to reproduce such a multifactor process in full "multiparticle" model. There are attempts to describe solid body interaction on the example of one or several atomic links [1]. Currently the task of modelling the liquid layer structure is more achievable technically.

To build a full universal molecular model of the tribosystem possessing a reliable forecasting capability is a very uneasy task. The solution depends on the calculation method, special software and mainly on the progress in setting calculation problems and algorithms. The goal of these studies is creating automated systems for constructing new LM which efficiency will depend on their optimal supramolecular structure (we have named them "LM of structural activity").

Below we describe some typical tasks, which often take place in developing models of liquid friction simulation.

The main tasks of modelling tribosystems with lubricant presence

Static two-dimensional models

There are many different artificial "voluntaristic" methods for describing suggested special molecule organization within the LL (for example, models U.B. Hardy [2], A.U. Adamson [3], B.V. Deryagin [4] and others). The main goal of these images is to visualize the tribosystem structure in longitudinal section. These methods differ mainly by description of transition from adsorbed near surface films to volumetric "mesial" zone state. They are different: from the simplest "Langmuir railing" formed by surfactants up to complex multilayer models. It is quite specific that most of these methods do not have any sufficient experimental proofs confirming their validity. Hence, a new approach related to CMM opens new possibilities in this regard. A number of new researches published recently in different countries show reassuring prospects for investigations in this direction [5–8].

Static three-dimensional models

The static model is needed for describing a tribosystem without friction. To create a static model we need a model of two friction surfaces placed at a distance of working clearance from each other. The width of clearance is set depending on which lubrication mode we are going to study: boundary, hydrodynamic or mixed.

The main object of the research here is three-dimensional cluster, which is placed into the working clearance. The cluster has the set of geometrical sizes: length (in the direction of the suggested sliding vector), depth (perpendicular to this vector) and width (measured by normal line to the friction surfaces). It is well understood, that the width is equal to the working clearance size and the depth and length are selected out of the following ideas (quite controversial).

- The length and depth of the cluster must be big if possible. Their size must be big enough for the number of LM particles be sufficient to give the valid information about the layer characteristics due to the larger statistics of individual interactions.
- The length and depth of the layer at edges of the four sides have boundary zones where interactions will be degenerated. At subsequent calculations these boundary zones will have to be cut at the depth of several molecular sizes so that they do not influence the calculation result.
- The length and depth limitations are connected with the unallowable large volume of calculations required for too big cluster and the need to take into account the computing power.

Based on these requirements the researcher must take a compromise solution about the optimal volume of the molecular cluster and the corresponding number of its particles.

The next task is to fill in the working clearance within the limits of the set cluster size with particles of the LM concerned. Herewith one needs to understand that the results of the subsequent calculations strongly depend on with which orientations and with which intermolecular distances the molecules were placed into the cluster body. We offered the following solution of this problem.

1. The virtual space within the cluster is divided into cubical cells of the similar size. The cell size must allow the LM molecule be placed within it.
2. One LM molecule must be placed into each cell.
3. The molecule axis position is randomized to provide the maximum disorderliness of molecules in the cluster by sequential turning of the molecule around the three spatial axes at some randomly selected angles.
4. The cluster optimization procedure is started during which the particles move closer to each other, herewith each of them gets a steady position corresponding to the minimum interaction energy with neighboring particles and solid surfaces.

To assign all the cluster particles the spatial positions corresponding to the minimum of energy the optimization procedure is applied. This computer calculation is usually fulfilled with a number of sequential iterations and is stopped by the set break criterion when the energy minimum is reached.

During the optimization, separate particles move closer to each other under the intermolecular forces in the LL with allowance made for the field of force of the friction surfaces. These tribosystem models provide more specific information about the molecular structure, allow to get correct images of the LM distribution in the cross section of the layer and possible orientation effects. Finally, according to the results of the CMM out of offered hypothetic models of molecular packs we can select the ones justified by optimization calculations.

In case the LM is a mixture of two or more components we can see the influence of the components concentration over the mixture structure, to forecast the synergism or antagonism phenomenon in additives. (For example, it is well known, that the mixture of iogenic and non-iogenic surfactants often shows synergism at surface activity parameter).

Complication of the LM composition can represent even a more interesting task: for example, including nano-particles into it – nano-spheres, nano-tubes, nano-onions, graphene nano-plates, etc. [8]. The image of the LL will get significantly more complicated: new nano-size surfaces will appear in the system which will compete with solid surfaces in the process of adsorption. In this case, the width of the working clearance in the tribosystem must be increased to place the sufficient number of nano-particles into it so that their influence over the molecular rheology of the ultradisperse system could be recorded. The task will get even more complicated at that due to the particles interaction with solid surfaces.

It is interesting to note such fact. At transition from two-dimensional model to the three-dimensional one the visibility of orientational effects is lost. Change in degree of supramolecular orientations of LL in a three-dimensional picture becomes only numerical factor. It testifies that all previous attempts to reflect the LL structure by two-dimensional picture were in vain.

Dynamic three-dimensional models

Transition from the static model to the dynamic one and giving such system a virtual shift is a more complicated task. This moving model is interesting because it gives the possibility to follow the structure evolution of the LL during friction. We can monitor the level of mobility of the adsorption layer participles, changes in the molecules orientation in the shift process, the layer evolution during friction parameters changes (surface nature and LM).

Transformation of the static model into the dynamic one demands significantly more powerful calculation resource. The reasons are as follows. To evaluate the result of the LL change because of friction the friction path must significantly exceed the size of molecules in the LM. At the same time, the elementary shift

step must be significantly less than the molecule length. After each step, the optimization procedure should take place, and this means that there must be many iterations (not less than several hundreds) until the lubrication layer has noticeable structural changes. That is why we suppose that the need for applying multiprocessor systems will appear for "shift" tasks in the first place.

Accounting of friction parameters

a) Solid surfaces roughness

The roughness of solid surfaces is a very important thing for a real friction process. Modelling roughness of friction surfaces when creating a molecular model of the tribosystem is complicated by the fact that the heights scale of roughness of real surfaces in machines details (about 1 mcm) significantly surpasses the allowable LM cluster sizes in the molecular model. To assess the roughness influence over the lubrication process one needs to aim at achieving the situation when one cluster includes at least several typical kinds of roughness.

The further complication of the solid surface model will very likely lead to the need to saturate the surfaces with models of surface structure defects. The need may appear when the wear and tear research is required.

b) Temperature and pressure

Thermostating and pressure coupling in the tribosystem is very seldom described in molecular dynamics research works (see, e. g., [9]). In assessing orientation effects in the LL the temperature is surely an important characteristic since it influences the adsorption speed, kinetics of surface reactions and the level of supramolecular organization. Thermo- tasks can appear when attempting to model the wear and tear process in tribosystem where the heat generation by real contact zones and heat streams from these zones into the lubrication layer must be calculated. We suppose that such problem definition is far too complicated for now to resolve it by methods of molecular dynamics.

If there is a need to define the friction ratio in the tribosystem we need to take into account the normal load when modelling. The question of how to shift the macroscopic pressure applied to the friction couple to the molecular cluster has not been resolved yet.

c) Sliding speed

It is difficult to guess how the real sliding speed, which in the majority of real friction couples reaches meters per second can be directly calculated in such a small scale of our modelled object. It is possible that the temperature influence can be calculated in models indirectly, for example, via heat radiation as a result of internal friction in the LL or via changes of frequency in temperature impulses generated by real intermetal contact points.

Creating computing environment for tribosytems modelling

Since there was no special software originally developed for solving tribological tasks available, we decided to develop a special software complex based on the module principle. We developed a complex mathematical model of the tribosystem allowing to describe the friction process in liquid LL with account of molecular structure and supramolecular LM self-organization (Figure).

The central block is the main part of the model. It provides for molecular cluster optimization. We selected HyperChem software for the central block. To resolve additional tasks for creating a tribosystem we developed additional software modules interacting with the central block and forming entrance data array and processing data output [10, 11].

We patented a number of software programs serving for the work of modules in the national software database (see Fig.). The blocks for thermostating and pressure coupling and the block for modelling roughness of solid surfaces shown at the figure are now under construction. The work of the software complex as a whole aimed at calculating comparative efficiency of different triboactive LM is described in number of programs made by us during several last years.

The following assumptions were made for the complex model: 1) molecular system is limited in volume by minimal allowable LM cluster sizes; 2) there are no edge effects of molecular clusters outside of solid boundaries; 3) solid surfaces have no defects, are chemically inactive, homogenous and smooth molecule-wise; both surfaces are made of the same material; 4) there is no LM domain structure; 5) there are no chemical reactions on surfaces and in the cluster volume; 6) solid surface is used in modelling only as a source of field; 7) boundary adsorbed LM layer is rigidly connected with solid surfaces.

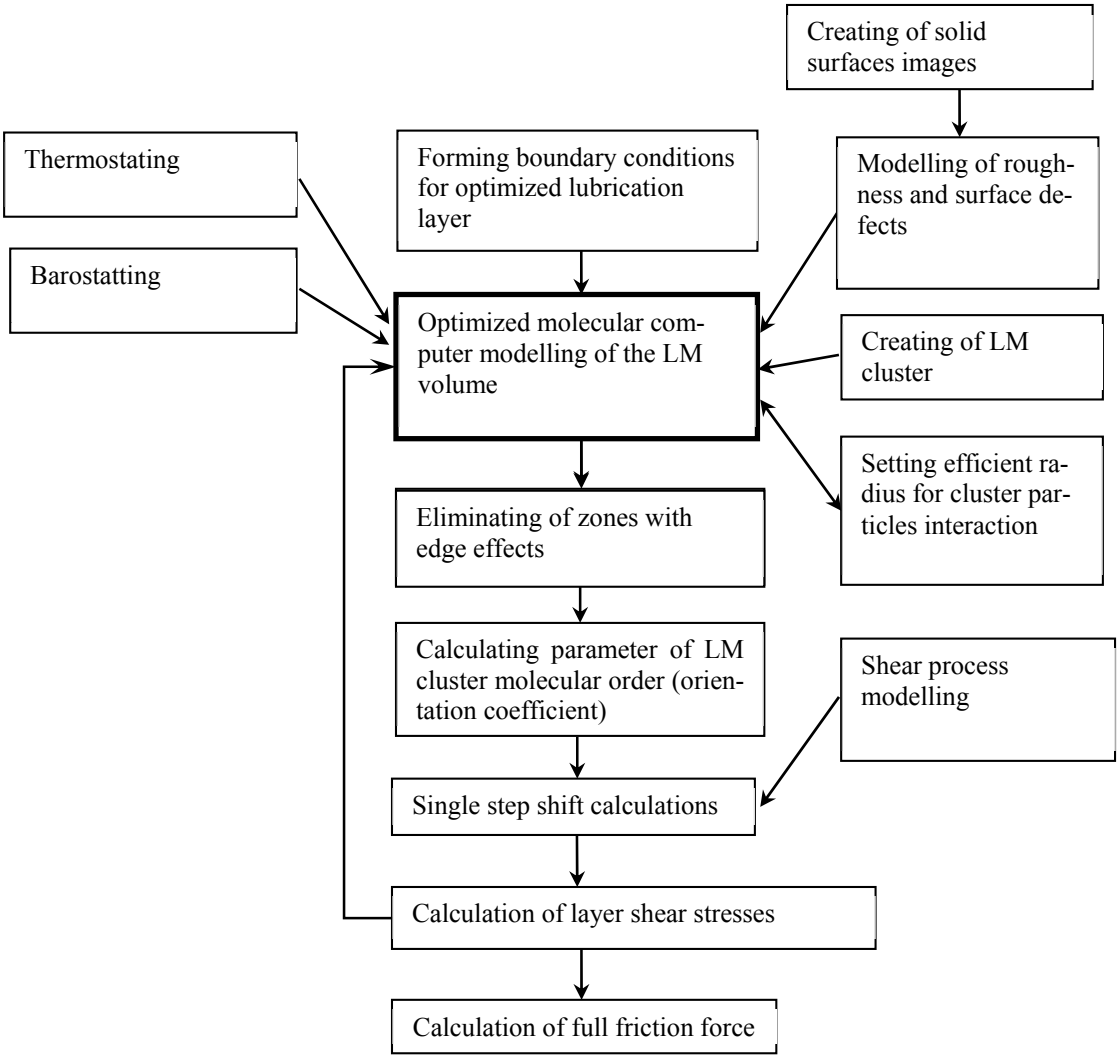

Figure. Complex optimizing mathematical model of tribosystem with LL

We created a three-dimensional dynamic model of a tribosystem. Molecular cluster consisting of particles forming the layer served as a basis of the LM model. Flat crystal grates of alpha-iron with depth of two atomic layers were built as solid friction surfaces.

For CMM we selected triboactive substances with anisometric molecular structures. The cluster volume (number of particles) must be enough for showing supramolecular effects. Firstly, single molecule images were built, and then particles were placed there at random with the help of randomization procedure.

Then the randomized cluster was optimized and the procedure of discrete shift was launched. To assess the supramolecular organization level after the first optimization we calculated the LM order parameter – "orientation coefficient" [17]. Then we optimized the system after each single shift and assessed this coefficient value.

Limitations for modelling of tribosystems with a LL

Tribosystem as an object of modelling by CMM demands a big number of particles for objective analysis. This fact, and also a number of other limitations provide for an unallowable increase of time for calculations. Below we show which details of modelling procedure increase the calculation time, which difficulties need to be overcome to make the calculation time reasonable.

A. Modelling of solid surfaces

1. The level of perfectness of the crystal grate (modelling defects of surface structure), the "depth" of the solid surface model.
2. Modelling non-homogenous and nonmetallic surfaces (polymer, elastomer, textile fiber, composite, etc.).
3. Modelling of roughness.

B. Modelling of LL

1. Sizes of molecules of LM components, especially tri boactive component.
2. The number of particles in the LM model cluster (working volume).
3. Molecular conformations.
4. Eliminating edge effects at a cluster boundary.
5. The presence of solvent within the LM composition, concentration of the triboactive component.

C. Software, calculation algorythms

1. Selecting an optimization method and its software solution. Ways of "parallelizing" calculations.
2. Introducing efficient radiuses of interaction.
3. The value of discretization step of the shift process.
4. Thermostating.
5. Pressure coupling.
6. Selecting output parameters of the model: shift process characteristics, friction force and friction ratio, molecular order parameter, etc.

D. Hardware parameters

1. One or multi-processor computers.
2. Processor clockspeed.

Conclusion

We have described the main essentials related to the problem definition of CMM of tribosystems with LL, principles of computing environment, the main difficulties and limitations. We have shown that the problems of describing the supramolecular organization of hydrodynamic LL can be successfully resolved at the current level of this research area development. Approaches to modelling processes of dry and mixed friction and wear and tear are not clear yet and, in our view will demand decades of research. We have presented phases and results of CMM type selected by us in the Table below.

Table. Phases of creating molecular model of hydrodynamic LL and expected results

№	Problem name	Description	Useful result
1	Creating a lubrication material cluster	A model of microscopic cluster out of LM molecules is built	We can calculate parameters of supramolecular structure including for the mixture of non-homogenous LM
2	Creating friction surfaces	The image of solid friction surface or two parallel surfaces with a set clearance are built	Gives the opportunity to assess differences in the structure of surfaces
3	Creating static three-component tribosystem	Two parallel surfaces with a clearance filled with lubrication material are built	After optimization of the LL cluster we can study the layer structure characteristics with account of differences on the surface and in volume
4	Applying a shear process to the tribosystem	Modelling tangential transition usually with the help of sequential iterations.	The possibility to follow the development of the lubrication layer at shift
5	Order parameter calculation	The change of orientation coefficient of molecular cluster is calculated	Assessment of volumetric orientation processes in the LL.
6	Assessment of the stressed state of the LL	Calculation of layer constraints in LL and generalfriction force	Possibility anti-frictional characteristics of the LL forecasting.

It is necessary to note that it is essential to add real tribotechnical experiment to the results of CMM at this stage of research. It is important to analyze correlations between calculated and experimental data for broad range of LM and friction modes. It will provide for more accurate definition of the application area and potentials of the new approach, will speed up its application when developing reliable and cost efficient tribosystems of the new generation.

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