

FRICION FORCE FOR BOUNDARY LUBRICATION

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ABSTRACT

A thermodynamic model describing the phase transition of first order between structure states of lubricant material in the boundary friction regime is proposed. It is shown that lubricant melts with temperature increase or at shear of rubbing surfaces if the elastic strain (stress) exceeds the critical value. The phase diagram with domains of dry and sliding friction is constructed. The dependences of friction force on temperature of lubricant and velocity of shear of rubbing surfaces are analyzed.

Key words: ultrathin lubricant film, boundary friction, stick-slip regime, phase diagram, elastic stress and strain

INTRODUCTION

At friction of two surfaces divided by lubricant less than 10 atomic layers thick, there comes a boundary friction mode. This mode is basically different from dry and liquid friction [1]. Voluminous lubricants can be in solid or liquid thermodynamic steady phases, but boundary lubricants organize solid-like and liquid-like structures. They are not steady thermodynamic phases, but kinetic regimes of friction. There can be several such regimes [2, 3]. The transitions between such kinetic regimes during sliding lead to a stick-slip mode. The lubricant melting can occur under the mechanisms as of the first order phase transition [2, 4, 5], as of the second one [6, 7]. In particular, in the work [8] the possibility of both transition types is considered.

In the work [7] the thermodynamic theory of melting of a thin layer of lubricant confined between two solid surfaces is proposed. This theory is based on Landau phase transitions theory [5]. This model allows for the loss of shift stability leading to the liquid-like structure of lubricant as at the thermodynamic melting, as when the shear stress exceeds the fluidity limit (shear melting). The influence of these factors is studied also in works [10, 11], which use the excess volume, arising owing to the chaotization of solid medium structure during melting, as the order parameter [12]. The shear modulus of lubricant decreases with increasing of excess volume [10, 11]. In the work [7] the shear modulus, which has zero value in the liquid-like phase, is the order parameter. However, in [7] the melting of lubricant is described as a continuous second order phase transition, but at the boundary friction regime jump-like phase transitions of

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first order are often observed [2, 10, 11]. In these situations the stick-slip motion of rubbing surfaces is established. The author of [7] discussed the possibility of jump-like transition in [13], however, he did not make a corresponding research. The purpose of the given work is the description of the first order phase transition within the framework of model [7].

DENSITY OF FREE ENERGY

The density of free energy for the lubricant has the form [7]:

$$f = \alpha(T - T_c)\phi^2 + \frac{a}{2}\phi^2\varepsilon_{el}^2 - \frac{b}{2}\phi^4 + \frac{c}{3}\phi^6, \quad (1)$$

where T is the temperature of the lubricant, T_c is the critical temperature, ε_{el} is the shear component of elastic strain, α, a, b, c are the positive constants, ϕ is the order parameter (the amplitude of periodical part of microscopic function of medium density [7]).

Parameter ϕ equals zero in liquid-like phase and takes a non-zero value in solid-like structure. In the potential (1) the sign of the third term is changed in comparison with [7,13] and the fourth term is introduced. Such kind of expansion is used for description of first order phase transitions [5,13]. Also in (1) the multiplier a is introduced additionally in the second term. It allows to variate the influence of the elastic energy on the potential.

Let us define the elastic stress as $\sigma_{el} = \partial f / \partial \varepsilon_{el}$:

$$\sigma_{el} = \mu\varepsilon_{el}, \quad (2)$$

$$\mu = a\phi^2. \quad (3)$$

The analysis of potential (1) allows us to obtain the following situations. Let's define the function

$$B(\varepsilon_{el}, T) = \frac{1}{2}a\varepsilon_{el}^2 + \alpha(T - T_c). \quad (4)$$

At $B(\varepsilon_{el}, T) \leq 0$ two symmetric non-zero minimums of potential are realized, being divided by one zero maximum (low curve in *fig. 1*). In this situation the lubricant is solid-like.

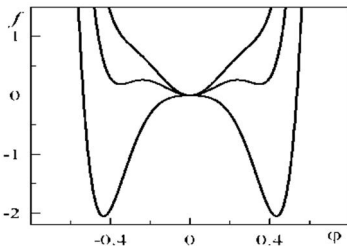


Fig. 1 – Dependence of density of free energy f (J/m^3) (1) on order parameter ϕ (dimensionless variable) at $\alpha=0.7 \text{ J}\cdot\text{K}^{-1}/\text{m}^3$, $T_c = 290 \text{ K}$, $a=4\cdot 10^{12} \text{ Pa}$, $b=285 \text{ J}/\text{m}^3$, $c = 1600 \text{ J}/\text{m}^3$. Curves from bottom to top correspond to the temperatures $T=260 \text{ K}$, 280 K , 290 K and shear strain $\varepsilon_{el} = 3\cdot 10^{-6}$

In the intermediate interval of values $0 < B(\varepsilon_{el}, T) < b^2 / 4c$ zero maximum of potential is transformed to minimum, and in addition two symmetric maximums appear, which separate the central minimum from two symmetric non-zero minimums (middle curve in *fig. 1*).

In such situation the lubricant can have as solid-like, as liquid-like structure, depending on initial conditions. And in case $B(\varepsilon_{el}, T) \geq b^2 / 4c$ single zero maximum of $f(\phi)$ is realized (the top curve in *fig. 1*), which corresponds to zero value of shear modulus μ and liquid-like structure of lubricant according to (3). The abscises of extremums of potential (1) are defined according to equalization

$$\phi_{1,2}^2 = \frac{b}{2c} \mp \sqrt{\frac{b^2}{4c^2} - \frac{B(\varepsilon_{el}, T)}{c}}, \quad (5)$$

where sign "–" corresponds to the symmetric maximums of potential, and sign "+“ corresponds to its symmetric minimums. According to Eq. (5) the melting of lubricant is carried out as when its temperature T increases, as when the mechanical influence occurs, leading to the increase of the shear components of elastic strain ε_{el} . Thus the given model considers the thermodynamic and shear melting.

PHASE DIAGRAM

Let us introduce V as the relative velocity of shear of the rubbing surfaces divided by an ultrathin lubricant film with the thickness h . To find a relation between the shear velocity and elastic strain we will use the Debye approximation relating the elastic strain ε_{el} and the plastic one ε_{pl} [7]:

$$\dot{\varepsilon}_{pl} = \frac{\varepsilon_{el}}{\tau_{\varepsilon}}, \quad (6)$$

where τ_{ε} is the Maxwell relaxation time for internal stress. The total strain in a lubricant is defined as the sum of elastic and plastic components [7, 12]:

$$\varepsilon = \varepsilon_{el} + \varepsilon_{pl}, \quad (7)$$

and sets the velocity of motion of the top block V according to relation [14]:

$$V = h\dot{\varepsilon} = h(\dot{\varepsilon}_{el} + \dot{\varepsilon}_{pl}). \quad (8)$$

The last relationships give the expression for elastic components of shear strain [10, 11]:

$$\tau_{\varepsilon} \dot{\varepsilon}_{el} = -\varepsilon_{el} + \frac{V\tau_{\varepsilon}}{h}. \quad (9)$$

At constant velocity of shear V the stationary value of elastic strain is set according to (9):

$$\varepsilon_{el}^0 = \frac{V\tau_\varepsilon}{h}. \tag{10}$$

According to the principle of minimum of energy the system tends to occupy a state corresponding to minimum of potential $f(\phi)$ at any initial conditions (see fig. 1). Thus the stationary value of the order parameter, defined by the expression (5) is established, and this expression is taken with the sign "+" as the sign "-" in it corresponds to unstable states. In fig. 2 the stationary values of order parameter squared are shown, which calculate according to expression (5), in which the stationary elastic strain ε_{el} is defined according to velocity of shear by the formula (10).

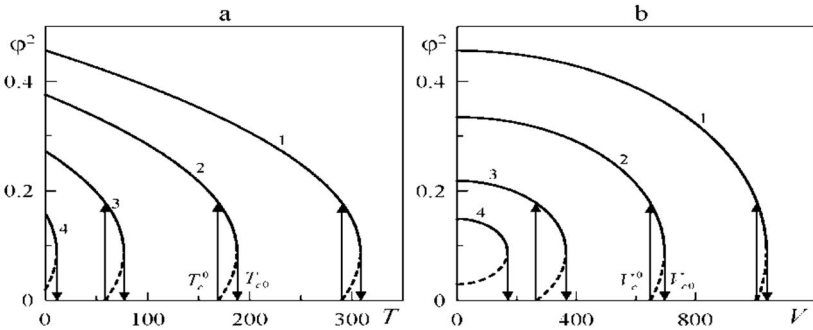


Fig. 2 – Dependence of stationary value of order parameter squared ϕ^2 (dimensionless variable) (5) on temperature of lubricant T (K) and velocity of shear V (nm/s) at parameters of fig. 1 and $h = 10^{-9}$ m, $\tau_\varepsilon = 10^{-8}$ s: a – curves 1–4 correspond to the fixed values of shear velocity $V=0$ nm/s, 650 nm/s, 900 nm/s, 1020 nm/s; b – curves 1–4 correspond to the fixed temperatures $T=0$ K, 170 K, 270 K, 300 K.

Continuous sites of curves correspond to the steady stationary states, and dashed lines correspond to the unstable ones.

At zero velocity of shear (shear stress and strain equal to zero) and small value of temperature T the lubricant is solid-like, because non-zero value of order parameter ϕ is realized, and according to (3) the shear modulus μ does not equal to zero either (fig. 2a, solid part of curve 1). In this case the potential is shown by the lowest curve in fig. 1. If the temperature T exceeds the critical value

$$T_{c0} = T_c - \frac{a}{2\alpha} \left(\frac{\tau_\varepsilon V}{h} \right)^2 + \frac{b^2}{4\alpha c} \tag{11}$$

the order parameter squared undergoes a jump-like change from non-zero value to zero with transition of lubricant in liquid-like state, and the top curve in fig. 1 corresponds to this. If after this transition the value of T decreases, the lubricant solidifies at lower temperature:

$$T_c^0 = T_c - \frac{a}{2\alpha} \left(\frac{\tau_\varepsilon V}{h} \right)^2. \tag{12}$$

Thus jump-like changes of order parameter from zero to non-zero value are observed.

The potential in the intermediate interval $T_c^0 < T < T_{c0}$ is shown by middle curve in fig. 1. Therefore, the dependence $\phi^2(T)$ has hysteresis character and corresponds to the phase transitions of first order. According to fig. 2a the lubricant melts at smaller value of temperature with increase in velocity of shear. The curve 4 corresponds to the situation in which the lubricant can't solidify after melting with decreasing in temperature. When the velocity exceeds a certain critical value, the lubricant is liquid-like ($\mu = 0$) at any temperature.

According to fig. 2b when the velocity exceeds the critical value

$$V_{c0} = \frac{h}{\tau_\varepsilon} \sqrt{\frac{2\alpha(T_c - T)}{a} + \frac{b^2}{2ac}} \tag{13}$$

the melting of lubricant occurs, and when V is less than the value

$$V_c^0 = \frac{h}{\tau_\varepsilon} \sqrt{\frac{2\alpha(T_c - T)}{a}}, \tag{14}$$

the lubricant solidifies. Here the situation is similar to the one presented in fig. 2a.

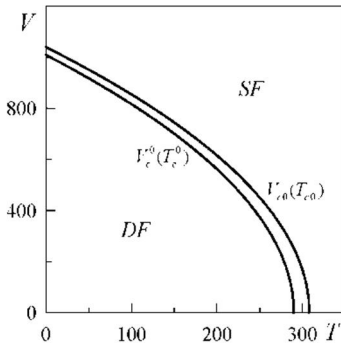


Fig. 3 – Phase diagram with areas of liquid-like (SF) and solid-like (DF) lubricant at parameters of fig. 2

In fig. 3 the dependences of critical velocity of melting of lubricant V_{c0} (13) and of its solidifying V_c^0 (14) on temperature T are shown. Above the curve V_{c0} the lubricant is liquid-like and the sliding friction regime (SF) is realized. In the interval $V < V_c^0$ the lubricant has solid-like structure. Between curves in fig. 3 the potential $f(\phi)$ looks like shown by middle curve in fig. 1, therefore the lubricant condition in this area depends on initial conditions. Thus, the fig. 3 represents the

phase diagram with two stationary friction modes. *Figure 3* can be interpreted also as a dependency of critical temperatures T_{c0} (11) and T_c^0 (12) on velocity of shear V .

FRICTION MAP

At shear of rubbing surfaces in the layer of lubricant elastic stress σ_{el} and viscous stress σ_v appear. The total stress is the sum of these components:

$$\sigma = \sigma_{el} + \sigma_v. \quad (15)$$

The friction force F which interferes with the movement, can be found as a product of total stress and area of rubbing surfaces A :

$$F = \sigma A. \quad (16)$$

Let us define the viscous stress in a lubricant according to [14]

$$\sigma_v = \frac{\eta_{eff} V}{h}, \quad (17)$$

where η_{eff} is the effective viscosity of lubricant material. The boundary lubricant is the non-Newtonian liquid. Such lubricants have complex dependences $\eta_{eff}(\dot{\epsilon})$. For example, viscosity of pseudoplastic lubricants decreases with increasing in shear rate $\dot{\epsilon}$, and for dilatant lubricants the viscosity increases with growth of $\dot{\epsilon}$. Therefore we use the simple approximation [14]

$$\eta_{eff} = k(\dot{\epsilon})^\gamma, \quad (18)$$

allowing to consider both situations, for qualitative analysis. Here the proportionality factor k ($\text{Pa} \cdot \text{s}^{\gamma+1}$) is introduced.

With the account (8) and (18) the expression for viscous stresses (17) take the form:

$$\sigma_v = k \left(\frac{V}{h} \right)^{\gamma+1}. \quad (19)$$

Having substituted (15) and (19) into (16) we obtain the finished equalization for friction force [10,11]:

$$F = \left[\sigma_{el} + k \left(\frac{V}{h} \right)^{\gamma+1} \right] A, \quad (20)$$

where the elastic stress σ_{el} is defined by (2).

The dependence (20) is shown in *fig. 4*. The *fig. 4a* shows that the friction force decreases at fixed shear velocity with increase in temperature. It occurs because of the decrease of the shear modulus. When lubricant melts ($T > T_{c0}$), the friction force doesn't depend on the temperature, because in the frameworks of the considered model the shear modulus equals zero in this situation.

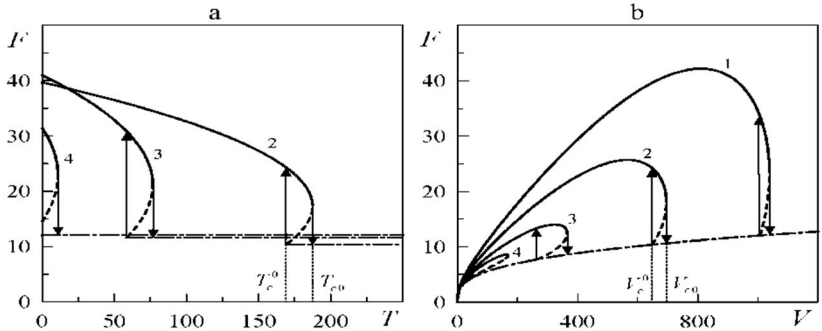


Fig. 4 – Dependence of friction force F (mN) (20) on temperature of rubbing surfaces T (K) and velocity of shear V (nm/s) at parameters of fig. 2 and $\gamma = -2/3$, $A = 3 \cdot 10^{-9} \text{ m}^2$, $k = 4 \cdot 10^5 \text{ Pa} \cdot \text{s}^{1/3}$: a – curves 2–4 correspond to the constant values of shear velocity $V=650 \text{ nm/s}$, 900 nm/s , 1020 nm/s ; b – curves 1–4 correspond to the fixed values of temperatures $T=0 \text{ K}$, 170 K , 270 K , 300 K .

The dependencies have hysteresis, because at phase transition shear modulus (3) has jump-like changes. At parameters of curve 4 the lubricant in case of melting does not solidify at further decreases of temperature (see explanation for fig 2a), therefore friction force has a constant value after melting at different temperatures T .

The fig. 4b shows a different behavior. Here, according to (20), at increase of velocity the total friction force at first grows due to the increase of the viscous stresses σ_v , and because of the increase of the elastic component of F caused by the increase of the elastic component of strain (10). However the shear modulus decreases with growth of velocity leading to reduction of the elastic component of force F . Therefore exists a critical velocity, at which excess the lubricant still remains solid-like, however the total friction force starts to decrease. With further increase of velocity at $V > V_{c0}$ (13) the melting occurs, and elastic stress (2) becomes equal to zero, therefore the first term in (20) equals zero, too, and that leads to abrupt decrease in total friction force. If V increases furthermore, the value F increases due to the viscous component (the second term in (20)). The lubricant solidifies at abrupt increase of force F but at a different value of velocity $V = V_c^0$ (14). Let us note that in fig. 4b the dependencies of friction force after melting coincide for all curves, because the viscous component F depends on velocity of shear only, and doesn't depend on temperature. In fig. 4b, curve 4, the transition to melting is not shown for better recognition of figure. This curve differs from others in the figure, because its solid part (stable value of F before melting) and dashed part (unstable value of F) together make a closed line. In addition, the friction force after melting is al-

ways described by the dependence shown in figure by dash-dotted line (stable value of F after melting), because the lubricant can't solidify with decrease of V anymore. Actually the figure 4 represents a friction map for boundary lubrication regime. This figure shows the lubricant state (solid-like lubricant with big friction force or liquid-like lubricant with small value of friction force) depending on system parameters. In works [10,11] it is shown that in intermediate area of a hysteresis in the figure in the case of real tribological system the stick-slip friction mode is realized. Let us note that the results shown in fig. 4b qualitatively coincide with a new friction map for boundary regime proposed in [14] at generalization of experimental data.

CONCLUSIONS

The behavior of an ultrathin lubricant film confined between two atomically-smooth solid surfaces was investigated. Melting and solidifying of lubricant is presented as first order phase transitions. The research shows that in case of shear of the rubbing surfaces with constant velocity lubricant melts at an excess of the critical values in temperature or elastic shear stress. Since the considered phase transition is the one of the first order, lubricant solidifies at smaller values of the specified quantities. The phase diagram of different regimes of friction is constructed. The received results qualitatively coincide with known experimental data.

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