NON-EQUILIBRIUM EVOLUTIONAL THERMODYNAMICS OF BOUNDARY FRICTION

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The general thermodynamic model of ultrathin lubricant film melting is proposed. The critical value of shear velocity, at which lubricant melts according to the shear melting mechanism, was found. It was shown that at temperature of rubbing surfaces above the critical value it melts even at zero shear velocity since total thermodynamic melting is realized. Found features coincide qualitatively with experimental data.

Keywords: *BOUNDARY FRICTION, SHEAR MODULUS, STICK-SLIP REGIME, SHEAR STRESS AND STRAIN, ULTRATHIN LUBRICANT FILM.*

1. INTRODUCTION

Relevance of the investigations in the field of boundary friction increases with the development of technology. This kind of friction appears in tribological systems at the thickness of lubricant material less than 10 atomic layers, or when two interacting surfaces separated by a lubricant layer contact with each other due to irregularities, roughness, etc. Boundary friction is often realized at the rubbing friction [1], therefore it requires the detailed study.

In view of the complexity of the physical and chemical processes flowing in and around the contact of interacting solids, the processes occurred during friction are beyond description from the point of view of the classical mechanics. To ascertain the tribological and rheological properties of frictional systems in the regime of boundary friction, the investigations of atomic-smooth mica surfaces separated by ultrathin lubricant layer are actively carried out. It was shown in the same experiments that liquid lubricant can manifest the properties peculiar to solids [2]. The distinctive feature is the presence of stick-slip motion [3], when the relative shear velocity of interacting surfaces changes in motion due to periodic melting and lubricant solidification. Lubricant can melt both in the usual manner due to the temperature increase and in accordance with the shear melting mechanism at excess of the shear velocity critical value. In this case lubricant states are not the equilibrium thermodynamic phases and represent the kinetic friction regimes, between which the transitions leading to the stick-slip friction are possible. Therefore, speak not of the liquid and solid lubricant structures,

but of the slip and stick states. Peculiarities of these states because of the thinness of lubricant layer are not studied yet in full measure.

To describe the abovementioned processes in view of their complexity the phenomenological models, which allow to explain the experimentally observed results [4-7], are the most frequently used. The molecular dynamics methods [8, 9] are widespread as well. Three friction regimes are found in [6] subject to the stochastic effects, namely, the sliding regime corresponding to small shear velocities, the regular stick-slip regime and the sliding regime at large shear velocities. Existence of such regimes is confirmed by the experiments in [1-3, 10].

Approach, which takes into account thermodynamic and shear melting of a lubricant layer, is proposed earlier in [7] within the synergetic Lorentz model. Within the mentioned theory the fluctuation effect of the main parameters [11-14] on the system is studied. It is shown that fluctuations can lead both to the periodical stick-slip friction regime [12] and the regime, when phase transitions in lubricant occur stochastically [14]. The reasons of the stick-slip melting and hysteresis observed in the experiments [15-17] are considered in [18].

At the same time, traditional use of the system of Lorentz equations for the mechanics problems face some contradictions on the stage of problem definition. Consideration of strains and stresses as relatively independent quantities in the sense that for each of them a separate evolutional equation is written does not contradict the principles of "classical" mechanics and thermodynamics. Moreover, at such statement symmetry of types of thermodynamic fluxes, which predetermines strict correspondence of signs in mixed terms of evolutional equations, is absent. Way out of the situation can be found if use multidimensional thermodynamic potentials, which the system of evolutional equations of the Landau-Khalatnikov type [9] should follow from using the standard differentiation procedure. Earlier this approach was used for the description of processes of severe plastic deformation (SPD) [20-23].

2. BASIC EQUATIONS

In accordance with the general scheme [20], the internal energy for the model, where contributions from the large shear strains ε_{ij}^e and over the entropy s are simultaneously taken into account, is of the following form:

$$
\begin{aligned}
u = u_0^* &+ \sigma_0 \varepsilon_{ii}^e + \frac{1}{2}\lambda\left(\varepsilon_{ii}^e\right)^2 + \mu\left(\varepsilon_{ij}^e\right)^2 + \alpha s^2 + \beta s \varepsilon_{ii}^e + \\
&+ t_0 \tilde{s} - \frac{1}{2} t_1 \tilde{s}^2 + \frac{1}{3} t_2 \tilde{s}^3 - \frac{1}{4} t_3 \tilde{s}^4 + \\
&+ \frac{c}{2}\left(\nabla f\right)^2 + \phi_0 f - \frac{1}{2}\phi_1 f^2 + \frac{1}{3}\phi_2 f^3 - \frac{1}{4}\phi_3 f^4 - \\
&- m_1 \tilde{s} f + m_2 \tilde{s}^2 f + m_3 \tilde{s} f^2 - m_4 \tilde{s}^3 f - m_5 \tilde{s}^2 f^2 - m_6 \tilde{s} f^3,
\end{aligned}
\tag{1}
$$

where u_0^*, σ_0, λ, μ, α, β, t_0, t_1, t_2, t_3, c, ϕ_0, ϕ_1, ϕ_2, ϕ_3, m_1, m_2, m_3, m_4, m_5, m_6 are the constants of expansion. And, in turn,

$$t_0 = t_0^* + X_3^{(0)}\varepsilon_{ii}^e + X_5^{(0)}\left(\varepsilon_{ii}^e\right)^2 + X_6^{(0)}\left(\varepsilon_{ij}^e\right)^2 + \alpha_t s,$$
$$t_1 = t_1^* + X_4^{(0)}\varepsilon_{ii}^e;$$
(2)

$$\phi_0 = \phi_0^* + g\varepsilon_{ii}^e + \frac{1}{2}\bar{\lambda}\left(\varepsilon_{ii}^e\right)^2 + \bar{\mu}\left(\varepsilon_{ij}^e\right)^2 + \alpha_\phi s,$$
$$\phi_1 = \phi_1^* + 2e\varepsilon_{ii}^e + \frac{1}{2}\tilde{\lambda}\left(\varepsilon_{ii}^e\right)^2 + \tilde{\mu}\left(\varepsilon_{ij}^e\right)^2,$$
$$\phi_2 = \phi_2^* + q\varepsilon_{ii}^e;$$
(3)

$$m_1 = m_1^* + X_3\varepsilon_{ii}^e + X_5\left(\varepsilon_{ii}^e\right)^2 + X_6\left(\varepsilon_{ij}^e\right)^2,$$
$$m_2 = m_2^* + X_4\varepsilon_{ii}^e,$$
$$m_3 = m_3^* + Y\varepsilon_{ii}^e.$$
(4)

Here elastic stresses are taken into consideration to within quadratic terms through the first two strain tensor invariants ε_{ii}^e, $\left(\varepsilon_{ij}^e\right)^2 = \varepsilon_{ij}^e\varepsilon_{ji}^e$, where summation is realized over repeated indexes. In this case the first invariant represents the trace of the strain tensor $\varepsilon_{ii}^e = \varepsilon_1^e + \varepsilon_2^e + \varepsilon_3^e$, and the second one is determined by expression [24]

$$\left(\varepsilon_{ij}^e\right)^2 = \left(\varepsilon_1^e\right)^2 + \left(\varepsilon_2^e\right)^2 + \left(\varepsilon_3^e\right)^2.$$
(5)

Two new basic values, namely, the non-equilibrium entropy $\tilde{s}$ and the disorder parameter f are introduced here as well. The non-equilibrium entropy describes that part of a thermal motion, which is conditioned by non-equilibrium and non-uniform behavior of thermal distribution. And just this part of the entropy evolves during external action tending to the stationary value. Equilibrium entropy is changed in time because of the relaxation of non-equilibrium entropy and the transition of the last one into the equilibrium subsystem. The disorder parameter physically means the excess volume, which appears due to chaotization (amorphization) of the condensed matter structure during melting.

Expression (1) is written in the most general form with conservation of all terms up to the 4-th order. The expression is simple and symmetrical. In the first line all equilibrium variables are taken into account in quadratic approximation. In the second line, the terms depending on the non-equilibrium entropy and equilibrium parameters are presented. In the third line, − the terms depending on the disorder parameter and equilibrium parameters. And in the last line, the mixed terms per both types of non-equilibrium variables and equilibrium parameters are written. Odd powers of non-equilibrium variables are positive, the even ones are negative, and all signs in explications of the coefficients are positive.

We write the corresponding evolutionary equations for non-equilibrium parameters X_i in the form

$$\tau_{X_i} \dot{X}_i = \frac{\partial u}{\partial X_i}, \tag{6}$$

where τ_{X_i} is the relaxation time. While describing using equations (6), the system tends not to the minimum of the internal energy, but to its maximum that corresponds to the strongly non-equilibrium processes, which occur in the open systems under the external energy pumping [20]. In our case the energy gain is realized due to the straining of lubricant layer under the shear of rubbing surfaces. And equation for the disorder parameter takes on the form

$$\tau_f \frac{\partial f}{\partial t} = c\nabla^2 f + \phi_0 - \phi_1 f + \phi_2 f^2 - \phi_3 f^3 - m_1 \tilde{s} + $$
$$+ m_2 \tilde{s}^2 + 2m_3 \tilde{s}f - m_4 \tilde{s}^3 - 2m_5 \tilde{s}^2 f - 3m_6 \tilde{s}f^2, \tag{7}$$

and for the non-equilibrium entropy $\tilde{s}$ we obtain

$$\tau_s \frac{\partial \tilde{s}}{\partial t} = t_0 - t_1 \tilde{s} + t_2 \tilde{s}^2 - t_3 \tilde{s}^3 - m_1 f + $$
$$+ 2m_2 \tilde{s}f + m_3 f^2 - 3m_4 \tilde{s}^2 f - 2m_5 \tilde{s}f^2 - m_6 f^3, \tag{8}$$

where terms with the sign "+" describe the increment of non-equilibrium entropy due to external energy sources (work), with the sign "−" − its removal into the equilibrium subsystem.

Evolutionary equation for the equilibrium entropy differs from the usual form (6), since change in the equilibrium entropy is carried out because of the transition of its non-equilibrium form to the equilibrium one. Diminution in the non-equilibrium entropy is taken into account by negative terms in the evolutionary equation (8). This means that the same terms should take into account the equilibrium entropy increment. Therefore the evolutionary equation of equilibrium entropy can be written as follows

$$\tau_s \frac{\partial s}{\partial t} = t_1 \tilde{s} + t_3 \tilde{s}^3 + m_1 f + 3m_4 \tilde{s}^2 f + 2m_5 \tilde{s}f^2 + m_6 f^3 + \tau_s L, \tag{9}$$

where L is the diminution of equilibrium entropy due to thermal conductivity. Connected with L quantity of heat escapes to the space surrounding the lubricant, in particular, to the rubbing surfaces, which act as the thermostat. Since diminution of non-equilibrium entropy and its transition to the equilibrium subsystem is the same process, the relaxation times in expressions (8) and (9) are equal.

Using the found value of equilibrium entropy, it is easy to determine the current lubricant temperature. In accordance with the expression for internal energy, the state equation in the following form will be true:

$$T = \frac{\partial u}{\partial s} = 2\alpha s + \alpha_t \tilde{s} + \alpha_\phi f + \beta \varepsilon_{ii}^e. \tag{10}$$

Find analytical expression for the component L in equation (9). In the case of non-uniform heating of the medium, the thermal conductivity equation represents usual continuity equation [25]

$$T \frac{\partial s}{\partial t} = \kappa \nabla^2 T, \tag{11}$$

where the thermal conductivity coefficient κ is supposed to be constant. Assumed that the lubricant layer and atomic-smooth surfaces have different temperatures T and T_e, respectively, for the normal component ∇_z^2 with a satisfactory accuracy one can use the approximation $\kappa \nabla_z^2 T \approx (\kappa / h^2)(T_e - T)$, where h is the lubricant thickness or distance between interacting surfaces. Taking into account the last expression, equation (11) will be simpler written as

$$\frac{\partial s}{\partial t} = \frac{\kappa}{h^2} \left(\frac{T_e}{T} - 1 \right) + \frac{\kappa}{T} \left(\nabla_x^2 + \nabla_y^2 \right) T, \tag{12}$$

where quantity h^2/κ acts as the relaxation time, during which the temperature adjustment in the lubricant thickness due to the thermal conductivity processes occurs. Taking in (9) $L = \partial s / \partial t$ from (12), we obtain the final expression for the equilibrium entropy evolution

$$\tau_s \frac{\partial s}{\partial t} = t_1 \tilde{s} + t_3 \tilde{s}^3 + m_1 f + 3 m_4 \tilde{s}^2 f + 2 m_5 \tilde{s} f^2 + m_6 f^3 +$$
$$+ \tau_s \frac{\kappa}{h^2} \left(\frac{T_e}{T} - 1 \right) + \tau_s \frac{2\alpha\kappa}{T} \left(\nabla_x^2 + \nabla_y^2 \right) s + \tau_s \frac{\alpha_\phi \kappa}{T} \left(\nabla_x^2 + \nabla_y^2 \right) f, \tag{13}$$

where temperature T is given by the equation (10). In accordance with (1), elastic stresses are determined as $\sigma_{ij}^e = \partial u / \partial \varepsilon_{ij}^e$:

$$\sigma_{ij}^e = \sigma_0 \delta_{ij} + \lambda \varepsilon_{ii}^e \delta_{ij} + 2\mu \varepsilon_{ij}^e + \beta s \delta_{ij} +$$
$$+ \left(X_3^{(0)} \delta_{ij} + 2 X_5^{(0)} \varepsilon_{ii}^e \delta_{ij} + 2 X_6^{(0)} \varepsilon_{ij}^e \right) \tilde{s} - \frac{1}{2} X_4^{(0)} \tilde{s}^2 \delta_{ij} +$$
$$+ \left(g \delta_{ij} + \bar{\lambda} \varepsilon_{ii}^e \delta_{ij} + 2 \bar{\mu} \varepsilon_{ij}^e \right) f -$$
$$- \left(e \delta_{ij} + \frac{1}{2} \tilde{\lambda} \varepsilon_{ii}^e \delta_{ij} + \tilde{\mu} \varepsilon_{ij}^e \right) f^2 + \frac{1}{3} q f^3 \delta_{ij} -$$
$$- \left(X_3 \delta_{ij} + 2 X_5 \varepsilon_{ii}^e \delta_{ij} + 2 X_6 \varepsilon_{ij}^e \right) \tilde{s} f + X_4 \tilde{s}^2 f \delta_{ij} + Y \tilde{s} f^2 \delta_{ij}. \tag{14}$$

Expression (14) can be represented in the form of effective Hooke's law [25]

$$\sigma_{ij}^e = \sigma_v \delta_{ij} + 2\mu_{eff} \varepsilon_{ij}^e + \lambda_{eff} \varepsilon_{ii}^e \delta_{ij} \tag{15}$$

with effective elastic parameters

$$\mu_{eff} = \mu + X_6^{(0)} \tilde{s} + \bar{\mu} f - \frac{1}{2} \tilde{\mu} f^2 - X_6 \tilde{s} f, \tag{16}$$

$$\lambda_{eff} = \lambda + 2 X_5^{(0)} \tilde{s} + \bar{\lambda} f - \frac{1}{2} \tilde{\lambda} f^2 - 2 X_5 \tilde{s} f. \tag{17}$$

In (15) the following strain-independent term appears

$$\sigma_v = \sigma_0 + \beta s + X_3^{(0)}\tilde{s} - \frac{1}{2}X_4^{(0)}\tilde{s}^2 + gf - ef^2 + \frac{1}{3}qf^3 - X_3\tilde{s}f + X_4\tilde{s}^2f + Y\tilde{s}f^2. \quad (18)$$

The first and the second invariants are defined as (see Application)

$$\varepsilon_{ii}^e = \frac{n - \sigma_v}{\lambda_{eff} + \mu_{eff}}, \quad (19)$$

$$(\varepsilon_{ij}^e)^2 \equiv \varepsilon_{ij}^e \varepsilon_{ji}^e = \frac{1}{2}\left[\left(\frac{\tau}{\mu_{eff}}\right)^2 + \left(\varepsilon_{ii}^e\right)^2\right], \quad (20)$$

where n and τ are, respectively, the normal and the tangent components of the stresses acting on the lubricant from interacting surfaces[1]. Here we have taken into account that elastic moduluses, which are in charge of the elastic strains, are effective, and the contribution σ_v, which is strain-independent, is subtracted from the stresses.

We will use the Debye's approximation, which connects the elastic strain ε_{ij}^e with the plastic one ε_{ij}^{pl} [4]:

$$\dot{\varepsilon}_{ij}^{pl} = \frac{\varepsilon_{ij}^e}{\tau_\varepsilon}. \quad (21)$$

The total strain in the layer is determined as

$$\varepsilon_{ij} = \varepsilon_{ij}^e + \varepsilon_{ij}^{pl}. \quad (22)$$

This strain specifies velocity of the upper block V_{ij} in accordance with [2]

$$V_{ij} = h\dot{\varepsilon}_{ij} = h(\dot{\varepsilon}_{ij}^e + \dot{\varepsilon}_{ij}^{pl}), \quad (23)$$

where h is the lubricant thickness. The strain relaxation time in (21) depends on the lubricant state

$$\tau_\varepsilon = K(\gamma_0 - \gamma_1 f), \quad (24)$$

where the constants γ_0 and γ_1 and the coefficient K are introduced. For stick lubricant $K = K_{sol}$.

According to the last expression, τ_ε is large in a stick state, and therefore ε_{ij}^e is large, too. For a slip state τ_ε decreases, and ε_{ij}^e also decreases. Combining relations (21)-(24), we obtain expression for the elastic shear strain:

$$\dot{\varepsilon}_{ij}^e + \frac{\varepsilon_{ij}^e}{K(\gamma_0 - \gamma_1 f)} = \frac{V_{ij}}{h}. \quad (25)$$

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[1]Shear stress τ is determined from (15) at $i \neq j$, i.e., $\delta_{ij} = 0$.

Experimental data explicitly states that in a slip state elastic strains relax very fast [2], i.e., the relaxation time for a slip state will be essentially less. Formula (24) at $K = K_{sol}$ contains a tendency of the relaxation time decrease with melting (with the increase in f), but such dependence is true only for a stick state and nearby the transition point [4]. Therefore for slip lubricant we should assume $K = K_{liq} < K_{sol}$.

It is known that in the most cases the lubricant melting has hysteresis behavior [6, 15-17]. For theoretical description of the hysteresis phenomena a number of publications were performed, in particular, within the Lorentz model [18]. In this case in order to take into account the pointed phenomena one should highlight two characteristic values of the disorder parameter: at $f > f_{liq}$ lubricant melts, and when $f < f_{sol}$ it solidifies.

3. VELOCITY EFFECT AND SHEAR MELTING

Lubricants of the thickness of some atomic diameters behave differently from bulk lubricants, and therefore the standard formalism cannot be used for their description, since a number of principally new effects which should be taken into account appear. The one of them is the stick-slip motion [2] schematically represented in Fig. 1.
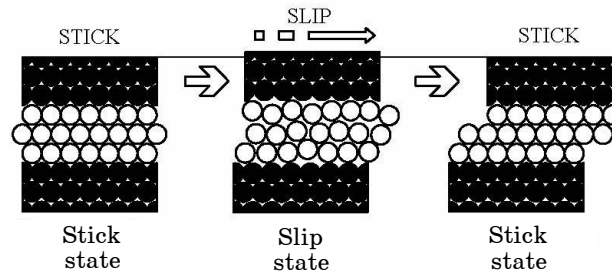
Fig. 1 − Schematic realization of the stick-slip friction regime [2]

If shift the upper interacting surface to the right, at first lubricant is stick, then at the excess of the critical value of elastic shear stresses σ_{ij}^e it sharply transforms into slip phase due to disordering of the atoms. In this case the upper surface rises since the change in the lubricant volume takes place. In a slip state the relaxation of σ_{ij}^e immediately occurs, and lubricant solidifies again because of the wall compression under the action of load. This process is periodical. The one of the main differences from the bulk lubricant behavior in this mechanism consists in the following: the action of shear stresses σ_{ij}^e leads not only to the shear but to the increase in the lubricant volume.

This fact is in good agreement with the results obtained using the molecular dynamics methods [8], and can be presented using the modified relation (19)

$$\varepsilon_{ii}^e = \frac{n - \sigma_v + \sigma_{ij}^e \varepsilon_{ij}^a}{\lambda_{eff} + \mu_{eff}}. \qquad (26)$$

Here we have introduced the dimensionless tensor constant ε_{ij}^a, which specifies the degree of dilatation (lubricant expansion at shear under the action of σ_{ij}^e). Here we should also take into account that the action of shear stresses leads to the increase in the lubricant thickness h. The relative increase in the volume[2] due to the growth of the lubricant thickness can be expressed in the following way:

$$\frac{\delta V}{V_0} = \frac{A\delta h}{Ah} = \frac{\delta h}{h},$$ (27)

where A is the contact area. Equated the contribution into relative increase in the volume from (26) due to shear stresses and the last expression, we obtain the change in the lubricant thickness

$$\delta h = h\frac{\sigma_{ij}^e\varepsilon_{ij}^a}{\lambda_{eff} + \mu_{eff}}.$$ (28)

In consequent calculations the thickness h in (25) should be replaced by the expression $h + \delta h$. Now the model is completed, since along with the thermodynamic melting the shear melting is taken into account. Further, within the present paper we consider the uniform case for simplification, and we assumed that $\nabla^2 \equiv 0$ in relations (7) and (13).

The result of joint numerical solution of the equations (7), (8), (13), (25) is shown in Fig. 2.

At zero velocity shear stresses are equal to zero, excess volume f decreases, and lubricant gradually solidifies due to the wall compression. When system starts moving ($V_{ij} = V_1 \neq 0$), lubricant melts under the action of rising stresses σ_{ij}^e, and the disorder parameter increases in this case. When f reaches the value $f = f_{liq}$, lubricant melts completely, and since the relaxation time in (25) becomes much less stresses start decreasing. In this case lubricant solidifies again, since in a molten state it is maintained by the elastic stresses. When it solidifies completely ($f = f_{sol}$), due to the increase in the relaxation time in (25) parameter f increases again up to the value of f_{liq}, and the process is repeated again. According to the aforesaid, the periodical stick-slip regime of melting/solidification is established. We should note that at $V_{ij} = V_1$ the disorder parameter decreases immediately at excess of f_{liq}, and when lubricant solidifies and $f = f_{sol}$ the disorder parameter decreases for a while and only then increases. This is connected with the fact that for the increase of f some minimum value of stresses is necessary, and since velocity is small this value, in accordance with (25), is developed slowly. Therefore after solidification excess volume can decrease until the corresponding stress value will be reached. With the velocity increase up to the value $V_{ij} = V_2$ peak frequency of stick-slip regime increases because at this velocity stresses develop faster

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[2]Physical meaning of the first invariant in (26): it is the relative change in the volume $\delta V/V_0$, where δV is the volume change; V_0 is the initial volume before deformation.
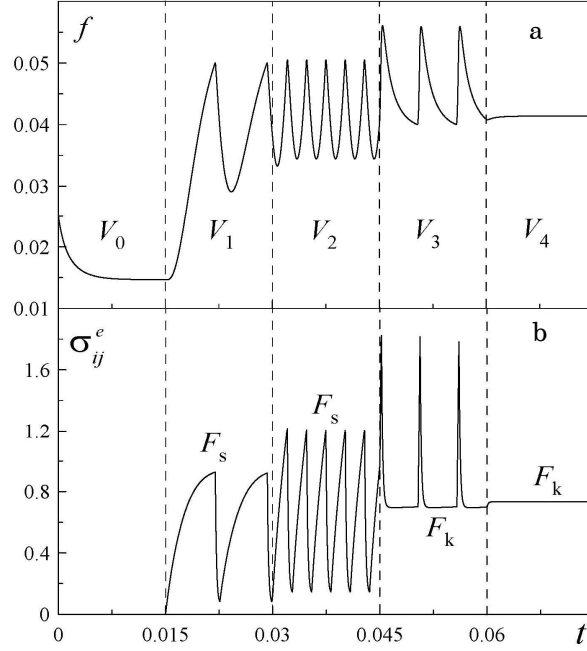
Fig. 2 *− Dependences of the excess volume f (dimensionless quantity) and shear stresses* σ_{ij}^{e} *(15) (MPa) on the time t (s) at the following parameters:* $\sigma_0 = 0,1$ *Pa;* $\lambda = 200$ *Pa;* $\mu = 10^8$ *Pa;* $\alpha = 4,1$ *$K^2 \cdot m^3/J$;* $\beta = 2,2$ *K;* $X_3^0 = 2,02$ *K;* $X_6^0 = 4 \cdot 10^6$ *K;* $t_1^* = 150$ *$K^2 \cdot m^3/J$;* $X_4^0 = 50$ *$K^2 \cdot m^3/J$;* $g = 0,1$ *Pa;* $\overline{\mu} = 4 \cdot 10^5$ *Pa;* $\phi_1^* = 500$ *J/m^3;* $e = 10,8$ *Pa;* $\tilde{\mu} = 24$ *Pa;* $m_1^* = 3$ *K;* $X_3 = 1,12$ *K;* $X_6 = 4040$ *K;* $\tau_f = 1$ *$J \cdot s/m^3$;* $\tau_s = 0,1$ *$K^2 \cdot s \cdot m^3/J$;* $\kappa = 10^{-11}$ *$W/(K \cdot m)$;* $\alpha_t = 0,2$ *$K^2 \cdot m^3/J$;* $\alpha_\phi = 0,2$ *K;* $h = 10^{-9}$ *m;* $T_e = 300$ *K;* $\varepsilon_{ij}^a = 1$ *; n = − 10^5 Pa;* $\gamma_0 = 0,0025$ *s;* $\gamma_1 = 0,005$ *s;* $K_{sol} = 1$ *;* $K_{liq} = 0,07$ *;* $f_{sol} = 0,04$ *;* $f_{liq} = 0,05$ *. The non specified parameters are equal to zero. The values of shear velocities V_{ij}: $V_0 = 0$ nm/s; $V_1 = 2$ nm/s; $V_2 = 4$ nm/s; $V_3 = 21$ nm/s; $V_4 = 22$ nm/s*

in the system. Correspondingly, lubricant melts faster, and during the same period system has time for a greater number of melting/solidification transitions. With more increase in the velocity $V_{ij} = V_3$, peak frequency decreases again, since at large velocities in equation (25) stresses relax to a larger stationary value, at which lubricant solidifies slower. In this case on the dependence of $\sigma_{ij}^e(t)$ long kinetic regions $\sigma_{ij}^e = $ const are visible. In this regime at $f > f_{liq}$ the disorder parameter increases for a while and then decreases. With further rise of the shear velocity $V_{ij} = V_4$, stick-slip regime vanishes and the kinetic friction regime of a slip lubricant with the friction force F_k is established. This occurs because with the velocity larger than the critical one ($V_{ij} > V_c$) stresses σ_{ij}^e appear in lubricant, and they are enough to provide the value $f > f_{sol}$, at which lubricant cannot solidify. We note that with the

increase in the velocity on the dependence $\sigma_{ij}^e(t)$ the values of stresses, which correspond to the kinetic friction regime with the friction force F_k, increase. This fact agrees with the mechanical model [5] proposed before. Thus, with the velocity increase, peak frequency of stick-slip regime increases at first, then it decreases due to appearance of long kinetic regions, and at excess of the critical velocity value $V_{ij} > V_c$ stick-slip regime vanishes. The described behavior agrees well with the experimental data shown in Fig. 3.
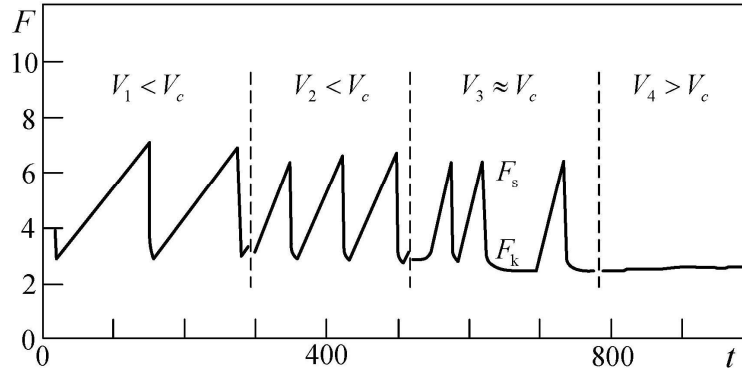

Fig. 3 – Dependence of the friction force F (mN) on the time t (s) for hexadecane layer at temperature 17 °C (T < T$_c$) with the increase in the slip velocity V. Kinetic slip regime [2] occurs above the critical velocity V$_c$ ≈ 400 nm/s

4. TEMPERATURE EFFECT

Lubricant can melt not only due to shear melting with the velocity increase, but also in usual manner at the temperature rise. To investigate the temperature effect we will obtain the time dependences for the excess volume and stresses similar those shown in Fig. 2. In this case we assume that the value of shear velocity V_{ij} is constant and will increase temperature T_e of shifting surfaces. The mentioned dependences are presented in Fig. 4.

It is seen from Fig. 4 that at small temperatures of rubbing surfaces $T_e = T_{e0}$ frequency of the stick-slip transitions is large, and the kinetic region on the dependence $\sigma_{ij}^e(t)$ is not observed. This implies that lubricant after melting starts solidifying immediately. With the temperature rise ($T_e = T_{e1}$) peak frequency becomes less as well as their height. Decrease in the peak height indicates the reduction of the static friction force F_s. With more increase in the temperature ($T_e = T_{e2}$), the kinetic region σ_{ij}^e = const becomes pronounced, i.e., for some time lubricant exists in a molten state at constant stresses. However, due to the dissipation excess volume decreases, lubricant nevertheless solidifies, and the stick-slip regime is realized. At $T_e = T_{e3}$, kinetic region becomes determinative, since here lubricant is in a slip state for most of the time. And, finally, at $T_e = T_{e4}$ lubricant melts, and the kinetic friction region is realized.
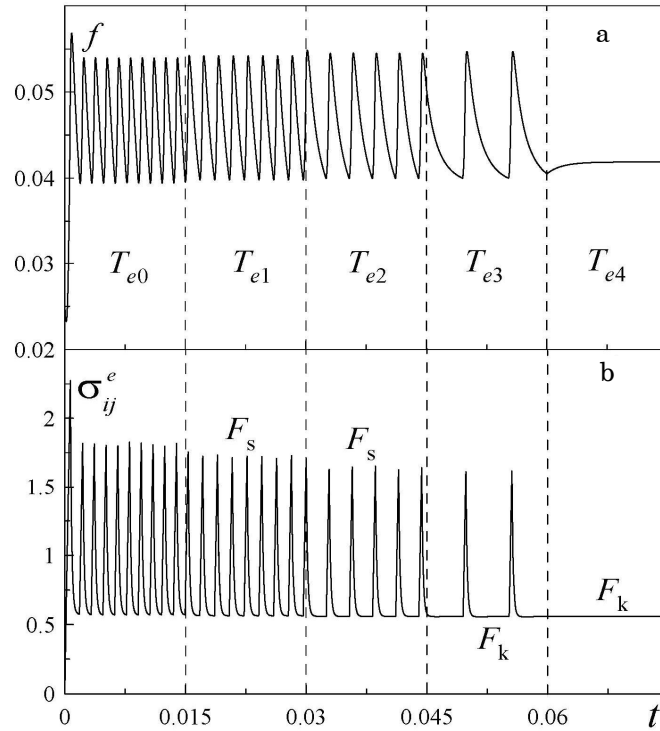
Fig. 4 − Dependences of the excess volume f (dimensionless quantity) and elastic shear stresses σ_{ij}^e (MPa) on the time t (s) at the parameters of Fig. 2 and shear velocity V = 27 nm/s. Temperatures of rubbing surfaces are T_{e0} = 50 K; T_{e1} = 230 K; T_{e2} = 400 K; T_{e3} = 490 K; T_{e4} = 550 K

5. LOADING EFFECT

Experiments for the investigation of the boundary friction are carried out at different loads on the interacting surfaces. It is established that external pressure critically influences the system behavior [2]. In Fig. 5 we present the time dependences of the stresses at constant values of the system temperature and shear velocity but for the increase in the external load n.

In Fig. 5a $T_e < T_c$, and the stick-slip regime is realized. It is seen that with the load rise friction force increases, since amplitude of the stick-slip transitions increases. If magnify temperature up to the value $T_e > T_c$ (see Fig. 5b), the stick-slip regime vanishes, and the kinetic regime is realized, where with the pressure rise friction force increases as well. The described features qualitatively coincide with the experimental dependences obtained in the work [2].
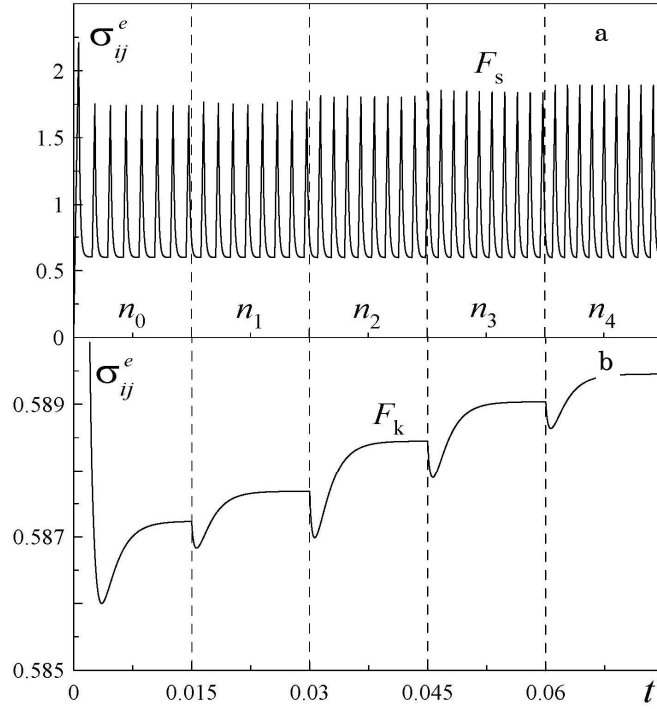
Fig. 5 − *Dependences of the elastic shear stresses* σ_{ij}^{e} *(MPa) on the time t (s) at the parameters of Fig. 2, V_{ij} = 18 nm/s and the external normal pressures n_0 = − 0,05 MPa; n_1 = − 0,1 MPa; n_2 = − 0,2 MPa; n_3 = − 0,3 MPa; n_4 = − 0,4 MPa: T_e = 200 K (a) and T_e = 600 K (b)*

6. CONCLUSIONS

The proposed thermodynamic model allows to describe the effects observed during the ultrathin lubricant film melting. Both the usual melting due to the temperature rise and melting due to the disordering under the action of applied stresses are considered.

It is shown that the reason of appearance of the stick-slip friction regime observed in the experiments is the fast relaxation of elastic stresses when lubricant reaches a slip state. At temperature of rubbing surfaces, which is not enough for melting in the state of rest, at such relaxation lubricant solidifies again and stays in a stick state during the time necessary for the appearance of stresses, at which melting occurs. Also the pressure effect on the melting process is considered, and it is shown that with the pressure rise friction force increases. The obtained dependences qualitatively coincide with the experimental ones. It is possible to achieve the quantitative coincidence, however since there are many parameters in the model, it is quite labor-consuming process, and to find the theory parameters it is necessary to carry out a number of supplementary experiments. Moreover, in each specific experimental situation the parameters values will be different since they depend on the lubricant properties, type of the rubbing surfaces, etc.

APPENDIX: determination of the strain tensor invariants

For isotropic matter the following equality is true [25]:

$$\sigma_{ij} = \lambda \varepsilon_{ii} \delta_{ij} + 2\mu \varepsilon_{ij}. \tag{A.1}$$

We choose the main strain axes as the coordinate ones, and then the strain tensor ε_{ij} has only diagonal components. Consider plain strain lubricant state when $\varepsilon_{22} = 0$. Diagonal components of the stress tensor in such coordinate system take the following form

$$\sigma_1 = \lambda \left(\varepsilon_{11} + \varepsilon_{33} \right) + 2\mu \varepsilon_{11}, \tag{A.2}$$

$$\sigma_2 = \lambda \left(\varepsilon_{11} + \varepsilon_{33} \right), \tag{A.3}$$

$$\sigma_3 = \lambda \left(\varepsilon_{11} + \varepsilon_{33} \right) + 2\mu \varepsilon_{33}. \tag{A.4}$$

The tangential stress acting along the lubricant boundary is equal to

$$\tau_2 = \tfrac{1}{2} \left(\sigma_3 - \sigma_1 \right) = \mu \left(\varepsilon_{33} - \varepsilon_{11} \right), \tag{A.5}$$

and the stress normal to the lubricant boundary is written as

$$n_2 = \tfrac{1}{2} \left(\sigma_3 + \sigma_1 \right) = \left(\lambda + \mu \right) \left(\varepsilon_{11} + \varepsilon_{33} \right). \tag{A.6}$$

Then from **(A.5)** and **(A.6)** we have

$$\varepsilon_{11} = \frac{1}{2} \left(\frac{n_2}{\lambda + \mu} - \frac{\tau_2}{\mu} \right), \tag{A.7}$$

$$\varepsilon_{33} = \frac{1}{2} \left(\frac{n_2}{\lambda + \mu} + \frac{\tau_2}{\mu} \right). \tag{A.8}$$

Correspondingly, the first two strain tensor invariants **(19)** and **(20)** are determined as

$$\varepsilon_{ii} = \varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33} = n_2 \big/ \left(\lambda + \mu \right), \tag{A.9}$$

$$\varepsilon_{ij} \varepsilon_{ji} = \left(\varepsilon_{11} \right)^2 + \left(\varepsilon_{22} \right)^2 + \left(\varepsilon_{33} \right)^2 = \frac{1}{2} \left[\left(\frac{\tau_2}{\mu} \right)^2 + \left(\varepsilon_{ii} \right)^2 \right]. \tag{A.10}$$

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