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<https://doi.org/10.15407/ujpe66.11.993>

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## DESCRIPTION OF THE STATIONARY STRUCTURAL STATES OF A BOUNDARY LUBRICANT MAKING USE OF THE RELATION BETWEEN THE DENSITY-MODULATION AND EXCESS-VOLUME ORDER PARAMETERS

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*A second-order phase transition between the structural states of a boundary lubricant sandwiched between atomically smooth solid surfaces has been described in the framework of the Landau theory of phase transitions, by using the density modulation and the excess volume as the order parameters. A relation between those order parameters is found. The stationary states of a lubricant and their dependences on such control parameters as the lubricant temperature, the elastic strain in the lubricant layer, and the external load on the friction surfaces are studied. The melting kinetics was simulated in the framework of a mechanical analog of the tribological system with elasticity.*

*Keywords:* boundary lubricant, friction force, stick-slip mode, order parameter, phase transition.

### 1. Introduction

In recent years, a variety of micromechanical systems have been widely used in various domains of science and technology. Those devices are applied in biomedicine, while developing new energy sources, in positioning systems in micro- and nanoelectronics, and so forth. During the operation of such systems, there arises a friction force between the contacting parts. This force must be strictly controlled, because if its allowable values are exceeded, the mechanisms may fail prematurely. To reduce friction, lubricants are used in the surface contact area [1–3]. In micromechanical systems, the thickness of a lubricant layer, as a rule, does not exceed several atomic diameters, and the friction surfaces are atom-

ically smooth [4, 5]. Many experiments evidence that the properties of lubricants in this boundary friction mode differ substantially from those of bulk lubricants. The boundary friction mode is characterized by such phenomena as the shear melting; stick-slip motions of various types; an anomalous increase in the viscosity of the lubricant layer, when its thickness decreases; the deviation of the melting and solidification temperatures from their counterparts for the same bulk substances; memory effects; complicated dependences of the viscosity on the temperature, layer thickness, pressure, and velocity gradient; a huge increase (sometimes up to 10 orders of magnitude) in the relaxation times in thin layers [4, 5], and so on. Despite a large number of experimental [3, 4, 6] and theoretical [7–10] works, as well as the results of computer simulation [5, 11–

16], there is yet no single approach that can describe all the mentioned features. Therefore, the study of the boundary friction processes is of increased relevance, in particular, in the framework of the thermodynamic representation of the problem considered in this paper [17].

In the earlier works on this topic [10, 18–20], a phenomenological theory of the boundary friction based on the Landau theory of phase transitions of the second order was proposed. To describe the states of a lubricant, an order parameter  $\varphi$  was introduced. It is associated with the periodic component (a density modulation) of the microscopic density of the medium. In the liquid-like state of a lubricant, the density modulation disappears, and the introduced order parameter vanishes,  $\varphi = 0$ . But if the lubricant is in the solid state, the order parameter  $\varphi > 0$ . It should be noted that, as was shown by L.D. Landau [21], the melting in bulk materials can take place exclusively in accordance with the mechanism of phase transitions of the first order. However, the symmetry of the phase state of a boundary lubricant is substantially affected by the atomic relief of the friction surfaces, which remain solid after the melting of the lubricant layer. Therefore, the phase transitions of the second order between liquid- and solid-like states of a lubricant in the boundary friction mode are often observed. This phenomenon was discovered both experimentally [4] and theoretically [10], including a computer simulation [11–15].

At the same time, there are known the works, where the possibility of a phase transition of the first order is denied [22]. However, the type of a phase transition depends on the shape of lubricant molecules. For example, for polymer molecules, the phase transition of the first order does take place, as is evidenced by the computer simulation [5].

The specific features of phase transitions of the first order were studied by us in works [23–25] in the framework of the ideology proposed in works [10, 18, 19]. In particular, we have developed an approach in which the excess volume  $f$  arising, when the lubricant melts owing to the structure randomization of the solid body [26, 27], is used as an order parameter. The advantage of this approach consists in that it explicitly involves the influence of an external load on the friction surfaces, which is introduced via normal external stresses  $-n$ . As the magnitude of  $n$  increases, the excess volume  $f$  decreases

owing to the compression of the lubricant layer by the confining walls. Two approaches were considered: the asymmetric [27] and symmetric [26] expansions of the thermodynamic potential. The former case describes the phase transition between two non-zero values of the excess volume  $f$ . The latter concerns the systems, where the ordered solid state of a lubricant corresponds to the zero value of the excess volume, but  $f$  becomes different from zero at the melting, as the temperature grows. In both scenarios, the transitions between the phase states of the lubricant layer are described as step-like phase transitions of the first order.

The approaches mentioned above operate with the order parameters that have different physical meanings, but they describe the same boundary friction process. Therefore, it is useful to establish a relation between the order parameters  $\varphi$  and  $f$ . In so doing, one should bear in mind that such a relation may not always be found. For example, in the case of vitrification transition [22], there can arise a situation where the value of the excess volume  $f$  changes in the course of melting, so it can play the role of order parameter. At the same time, the approach operating with the density modulation  $\varphi$  as the order parameter cannot be applied in this case, because the density modulation acquires zero values at the vitrification transition in both phases (i.e., there is no long-range order in the alternation of atoms).

A partial relation between the density-modulation,  $\varphi$ , and excess-volume,  $f$ , order parameters was found in work [17]. However, the issue concerning the relation between the indicated order parameters still remains far from the complete understanding. Thus, the aim of this work was to determine such a relation in the case of the phase transition of the second order.

## 2. Thermodynamic Model of the Phase Transition of the Second Order

### 2.1. The density modulation as the order parameter

#### 2.1.1. Formulation of the model

In works [10, 18, 19], the amplitude  $\varphi$  of the periodic component of the microscopic medium-density function was chosen as the order parameter. In the liquid state, the microscopic density function is homogeneous, so  $\varphi = 0$ . In the solid state, the lubri-

cant layer has a crystalline structure, and  $\varphi \neq 0$ . At temperatures close to the phase transition, the series expansion of the free energy in the order parameter  $\varphi$  takes the form [21]

$$\Phi_{\text{therm}} = a_1\varphi^2 + \frac{b}{4}\varphi^4, \quad (1)$$

where the quantities  $a_1$  and  $b$  depend on the temperature and pressure. If the lubricant temperature  $T$  is close to the phase transition temperature  $T_c$ , then we may write [21]

$$a_1 = \alpha(T - T_c). \quad (2)$$

Energy (1) corresponds to the undeformed state of a lubricant. If the lubricant layer undergoes elastic strains  $\varepsilon_{\text{el}}$ , the deformation energy  $\mu\varepsilon_{\text{el}}^2/2$ , where the shear modulus  $\mu = a\varphi^2$ , must be added to the free energy (1). As a result, the power series expansion of the free energy density  $\Phi_\varphi$  in the density-modulation order parameter  $\varphi$  looks like [10]

$$\Phi_\varphi = \alpha(T - T_c)\varphi^2 + \frac{a}{2}\varphi^2\varepsilon_{\text{el}}^2 + \frac{b}{4}\varphi^4 + \frac{g}{2}(\nabla\varphi)^2, \quad (3)$$

where the last summand describes a spatially inhomogeneous distribution of the order parameter. In work [25], the melting of a lubricant was simulated taking the spatially inhomogeneous distribution of the order parameter into consideration in the framework of the method of dimensionality reduction (MDR) [28], and it was shown that the gradient term insignificantly affects the system behavior. Therefore, for simplicity, we consider a homogeneous system, which is equivalent to the condition  $g = 0$  J/m.

Elastic stresses arising in the lubricant layer are determined as  $\sigma_{\text{el}} = \partial\Phi_\varphi/\partial\varepsilon_{\text{el}}$  [10], so

$$\sigma_{\text{el}} = a\varphi^2\varepsilon_{\text{el}} = \mu_s\varepsilon_{\text{el}}, \quad (4)$$

where the shear modulus  $\mu_s$  of the lubricant equals zero in the liquid-like state of the lubricant and acquires non-zero values in the solid-like state. The stationary values of the order parameter,  $\varphi_0$ , and the shear modulus,  $\mu_{s,0}$ , are determined from the condition  $\partial\Phi_\varphi/\partial\varphi = 0$  [10]. As a result, we obtain

$$\varphi_0 = \sqrt{\frac{2\alpha(T_c - T)}{b} - \frac{a}{b}\varepsilon_{\text{el}}^2}, \quad (5)$$

$$\mu_{s,0} = a\varphi_0^2 = \frac{a[2\alpha(T_c - T) - a\varepsilon_{\text{el}}^2]}{b}. \quad (6)$$

Expressions (5) and (6) make it possible to find the critical values for the elastic strain and the temperature,

$$\varepsilon_{\text{el},c0} = \sqrt{\frac{2\alpha(T_c - T)}{a}}, \quad (7)$$

$$T_{c0} = T_c - \frac{a\varepsilon_{\text{el}}^2}{2\alpha}; \quad (8)$$

i.e., if they are exceeded, the lubricant melts.

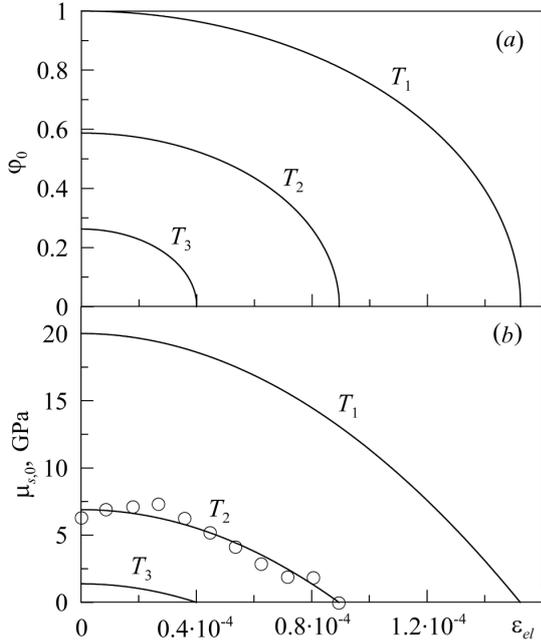
Although the microscopic density of a substance can be measured in a computer experiment [11–15, 17], and the values of the order parameter  $\varphi$  can be found experimentally, it is much more convenient – for the sake of universality – to present  $\varphi$  in a normalized dimensionless form. We assume the order parameter  $\varphi$  is normalized to its maximum value. As a result, the normalized  $\varphi$  acquires the values within an interval from 0 to 1. The value  $\varphi = 1$  corresponds to the most ordered lubricant, which is realized, according to Eq. (5), at the zero absolute temperature,  $T = 0$  K, and in the absence of elastic strains,  $\varepsilon_{\text{el}} = 0$ . Equation (5) together with the condition  $\varphi_{\text{max}} = 1$  at  $T = 0$  K and  $\varepsilon_{\text{el}} = 0$  leads to the following relation between the expansion parameters [17]:

$$b - 2\alpha T_c = 0, \quad (9)$$

i.e., they are additionally restricted.

Note that, provided we know precisely measured critical values (7) and (8), all expansion parameters of  $\Phi_\varphi(\varphi)$  in formula (3) can also be determined exactly. However, such a procedure demands a specific set of experimental data for a specific system, which is absent in the literature. Furthermore, our task is to give a qualitative description. Therefore, we do not confine ourselves to the description of a specific system, but choose the parameters in such a way that the values of critical temperatures and strains are in the experimentally observed intervals [4]. However, in so doing, we select the expansion parameters to satisfy relation (9).

Figure 1 demonstrates the dependences of the stationary values of the order parameter,  $\varphi_0$ , and the shear modulus,  $\mu_{s,0}$ , on the elastic strains  $\varepsilon_{\text{el}}$  for various lubricant temperatures  $T$ , provided that the model parameters are fixed. The parameter values were chosen to ensure an approximate correspondence of the melting temperature, the critical strain, and



**Fig. 1.** Dependence (5) of the order-parameter stationary value  $\varphi_0$  on the elastic strains  $\varepsilon_{el}$  (a) and dependence (6) of the shear-modulus stationary value  $\mu_{0,s}$  on the elastic strains  $\varepsilon_{el}$  at the fixed temperatures  $T_{1-3} = 0, 190,$  and  $270$  K for the expansion parameter values  $T_c = 290$  K,  $\alpha = 0.8 \text{ J}\cdot\text{K}^{-1}/\text{m}^3$ ,  $a = 2 \times 10^{10}$  Pa, and  $b = 464 \text{ J}/\text{m}^3$  (b). The symbols in panel (b) demonstrate computer simulation results presented in work [16]

the critical shear modulus to the intervals of experimentally observed values. From Fig. 1, it is easy to see that if the temperature equals zero,  $T_1 = 0$  K, and if the strain is absent,  $\varepsilon_{el} = 0$ , then the maximum values of the order parameter  $\varphi_0$  and the shear modulus  $\mu_{s,0}$  are realized. In this case, the latter is numerically identical to the value of the constant  $a$  in the  $\Phi_\varphi(\varphi)$  expansion (3). So, the expansion parameter  $a$  gives the maximum value of the shear modulus  $\mu_s$  in the absence of thermal fluctuations ( $T = 0$  K) and external perturbations ( $\varepsilon_{el} = 0$ ). The figure also demonstrates that the order parameter and the shear modulus values decrease with the growth of a strain  $\varepsilon_{el}$  and the lubricant temperature  $T$  because expansion (3) takes the thermodynamic and shear meltings [10] into account. We note that the order parameter vanishes continuously with the growth of indicated quantities. Therefore, according to the ideology of the Landau phase transition theory, a phase transition of the second order takes place [21, 29].

### 2.1.2. Comparison with simulation and experimental results

The model described above is based on the free energy expansion (3). A proper choice of the expansion ensures the adequacy of the developed model. Above, we briefly described the considerations resulting in the choice of free energy in form (3). A more detailed description of potential (3) and an analysis of the physical nature of the shear melting can be found in works [10, 20]. However, the shear melting model, which is described in this work, is phenomenological, i.e., it is based on experimental results. Therefore, in order to additionally confirm the adequacy of the proposed approach, we compare the model with both the real experiment and the simulation results obtained by other authors. In particular, the symbols in Fig. 1, b correspond to the dependence of the shear modulus on the strain obtained in work [16], where the behavior of atomically thin layers sandwiched between solid surfaces, when the latter undergo a shifting, was studied with the help of molecular statistics methods. In work [16], all dependences include dimensionless quantities. Therefore, in order to compare our approach with the result of a simulation performed in work [16], the dependence  $\mu(\varepsilon)$  from work [16] was so scaled along both axes that the simulation results could be satisfactorily superimposed on the theoretically calculated curve. However, the selected scales are not arbitrary. For example, the scale along the  $\varepsilon_{el}$ -axis is dictated by an  $\varepsilon_{el}$ -value at which the shear modulus vanishes.

The authors of work [16] presented the dependences of the elastic stresses  $\sigma_{el}$  on the strain  $\varepsilon_{el}$ , which are given by Eqs. (4) and (6) in our model. Combining those equations, we obtain

$$\sigma_{el} = \frac{a [2\alpha(T_c - T) - a\varepsilon_{el}^2] \varepsilon_{el}}{b} \times H(1 - \varepsilon_{el}/\varepsilon_{el,c0}), \quad (10)$$

where  $H(x)$  is the Heaviside function, and the value of  $\varepsilon_{el,c0}$  is determined again by expression (7). In order to include as many dependences as possible into comparison, it is convenient to present Eq. (10) in the dimensionless form. As the strains  $\varepsilon_{el}$  increase, Eq. (10) describes the growth of stresses  $\sigma_{el}$  from zero to the maximum value

$$\sigma_{el}^{\max} = \frac{2\sqrt{a}}{b} \left( \frac{2}{3}\alpha(T_c - T) \right)^{3/2}, \quad (11)$$

which is attained at the strain

$$\varepsilon_{el}(\sigma_{el}^{\max}) = \sqrt{\frac{2\alpha(T_c - T)}{3a}} = \frac{\varepsilon_{el,c0}}{\sqrt{3}}. \quad (12)$$

Let us introduce the dimensionless stresses  $\tilde{\sigma}_{el} = \sigma_{el}/\sigma_{el}^{\max}$  and strains  $\tilde{\varepsilon}_{el} = \varepsilon_{el}/\varepsilon_{el,c0}$ . Then Eq. (10) looks like

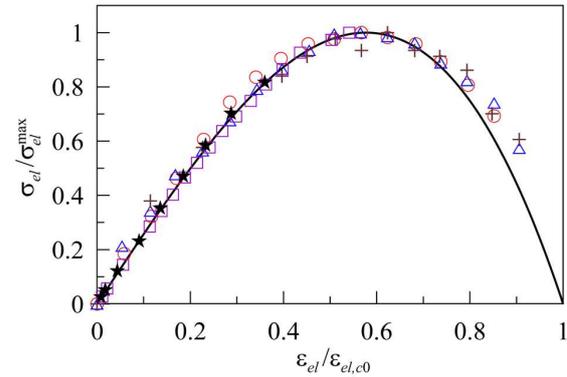
$$\tilde{\sigma}_{el} = \frac{3\sqrt{3}}{2} (1 - \tilde{\varepsilon}_{el}^2) \tilde{\varepsilon}_{el} \times H(1 - \tilde{\varepsilon}_{el}). \quad (13)$$

In Fig. 2, the solid curve illustrates the dimensionless dependence (13). The symbols in the figure correspond to the data obtained in work [16] for mono-, di- and triatomic lubricant layers sandwiched between solid surfaces, as well as to the results of real experiments described in work [30]. Experimentally measured were the stresses between atomically smooth mica surfaces, which were separated by a lubricant layer  $0.7 \pm 0.2$  nm in thickness and which performed periodic motions with a frequency of 250 Hz. The squares ( $\square$ ) demonstrate the results of an experiment in which 3-methyl-undecane ( $\text{CH}_3\text{-C}_{11}$ ) was used as a lubricant, and the surface load was 2 mN. The stars ( $\star$ ) illustrate an experiment in which the surfaces were separated by a perfluorohexaglyme layer with the zero external load. Figure 2 demonstrates a rather good agreement of theoretical results with the experimental results and the results of a computer simulation. All of this confirms the adequacy of the proposed theory, which is based on potential (3).

It should be noted that the dependence  $\sigma_{el}(\varepsilon_{el})$  can be experimentally measured only up to the maximum of elastic stresses, because the decreasing part of the dependence corresponds to unstable states. That is why all experimental results shown in Fig. 2 are within the interval  $0 < \sigma_{el} < \sigma_{el}^{\max}$ . However, the simulation results are shown in a wider interval, which confirms the decrease of the dependence  $\sigma_{el}(\varepsilon_{el})$ , when the elastic strains exceed the critical value (12).

## 2.2. The excess volume as the order parameter

In Section 2.1, a model was formulated in which the density modulation  $\varphi$  is used as the order parameter. Its value decreases, as the lubricant melts,



**Fig. 2.** The solid curve is the dimensionless dependence of the elastic stresses on the strains [formula (13)]. The stresses are measured in the  $\sigma_{el}^{\max}$ -units (11), and the strains in the  $\varepsilon_{el,c0}$ -units (7). The symbols correspond to the results of a simulation in work ([16]) for monoatomic ( $\circ$ ), diatomic ( $\Delta$ ), and triatomic ( $+$ ) lubricant layers sandwiched between shifted surfaces. The results of real experiments taken from work [30] are shown by the symbols  $\square$  and  $\star$

which occurs as either the temperature  $T$  or the shear strains  $\varepsilon_{el}$  increase. According to the phenomenological Landau theory of phase transitions, any physical quantity that distinguishes the phase states of the substance and can be used to expand the free energy in a series can serve as the order parameter. In other words, the order parameter must be a continuous function within some interval.

A good candidate for the role of an order parameter is the excess volume  $f$ , which appears in a lubricant owing to its expansion at the melting. In accordance with the paradigm of works [31, 32], let us define the excess volume as

$$f = \frac{\rho_{rcp} - \rho}{\rho}, \quad (14)$$

where  $\rho$  is the lubricant density, and  $\rho_{rcp}$  is the maximum possible value of  $\rho$ . Expression (14) follows from the definition of the relative excess volume,  $f \equiv \delta Q/Q$ , where  $\delta Q$  is an extra volume that appears, when the lubricant is heated or melts, and  $Q$  is the minimum lubricant volume. The physical meaning of the parameter  $f$  is described in more details in Section 5 of work [17].

While describing the phase transition of the second order, the expansion of the free energy in a power series in the excess volume order parameter  $f$  is based on an ideology proposed in works [26, 27] and has the

form<sup>1</sup> [17, 33]

$$\Phi_f = \frac{1}{2}\lambda (\varepsilon_{ii}^{\text{el}})^2 + \mu (\varepsilon_{ij}^{\text{el}})^2 + \left[ \phi_0^* - \frac{1}{2}\bar{\lambda} (\varepsilon_{ii}^{\text{el}})^2 - \bar{\mu} (\varepsilon_{ij}^{\text{el}})^2 - \alpha'T \right] f^2 + \frac{1}{4}\phi_1 f^4, \quad (15)$$

with the positive expansion constants  $\lambda$ ,  $\mu$ ,  $\phi_0^*$ ,  $\bar{\lambda}$ ,  $\bar{\mu}$ ,  $\alpha'$ , and  $\phi_1$ . The first and second invariants of the strain tensor in expression (15) are given by the formulas [17, 27, 34] (see Appendix A)

$$\varepsilon_{ii}^{\text{el}} = \frac{n}{\lambda_{\text{eff}} + \mu_{\text{eff}}}, \quad (16)$$

$$(\varepsilon_{ij}^{\text{el}})^2 = \frac{1}{2} \left[ \left( \frac{\tau}{\mu_{\text{eff}}} \right)^2 + (\varepsilon_{ii}^{\text{el}})^2 \right], \quad (17)$$

respectively, in which the external normal stresses  $n$  determine the load at the friction surface,  $\tau$  is the shear stresses, and  $\mu_{\text{eff}}$  and  $\lambda_{\text{eff}}$  are elastic parameters. Note that the coefficient in front of  $f^2$  in expression (15) changes its sign to the negative one as the temperature  $T$  or the elastic strains  $\varepsilon_{\text{el}}$  increase, which leads to the melting because the stationary value  $f_0$  of the order parameter, becomes non-zero at that.

According to Eq. (15), the elastic stresses  $\sigma_{ij}^{\text{el}}$  arising in the lubricant layer are determined by the formula [17, 26, 27]

$$\sigma_{ij}^{\text{el}} = 2\mu_{\text{eff}}\varepsilon_{ij}^{\text{el}} + \lambda_{\text{eff}}\varepsilon_{ii}^{\text{el}}\delta_{ij}, \quad (18)$$

where the effective elastic parameters

$$\mu_{\text{eff}} = \mu - \bar{\mu}f^2, \quad (19)$$

$$\lambda_{\text{eff}} = \lambda - \bar{\lambda}f^2, \quad (20)$$

are introduced. They decrease at the melting, when the excess volume  $f$  increases. From expression (18), we get the following relation for determining the shear component of elastic stresses [33, 34]:

$$\tau = \mu_{\text{eff}}\varepsilon_{\text{el}}, \quad (21)$$

where  $\varepsilon_{\text{el}}$  is the elastic component of the shear strain.

<sup>1</sup> Note that the free energy expansion in the standard form, which is used to present the general expression for the free energy of a deformed isotropic body [33], contains terms with the coefficients  $\mu$ ,  $\bar{\mu}$ ,  $\lambda$ , and  $\bar{\lambda}$ . The expansion of the free energy in a power series in the order parameter  $f$  is based on the same consideration as was used when deriving expression (3).

The model, where the density modulation  $\varphi$  is the order parameter, does not contain the external load explicitly. Therefore, in order to determine a relation between the density-modulation,  $\varphi$ , and excess-volume,  $f$ , order parameters, let us firstly consider a simplified case with no external load,  $n = 0$ . Then, the first invariant (16) equals zero,  $\varepsilon_{ii}^{\text{el}} \equiv 0$ , and the second one (17) is reduced to the square of the shear strain,  $(\varepsilon_{ij}^{\text{el}})^2 \equiv \varepsilon_{\text{el}}^2/2$ , with an accuracy to a constant. As a result, potential (15) acquires a simpler form,

$$\Phi_f = \frac{\mu}{2}\varepsilon_{\text{el}}^2 + \left( \phi_0^* - \frac{\bar{\mu}}{2}\varepsilon_{\text{el}}^2 - \alpha'T \right) f^2 + \frac{1}{4}\phi_1 f^4. \quad (22)$$

The condition  $\partial\Phi_f/\partial f = 0$  brings about the following stationary values for the order parameter and the shear modulus, respectively:

$$f_0 = \sqrt{\frac{\bar{\mu}\varepsilon_{\text{el}}^2 + 2\alpha'T - 2\phi_0^*}{\phi_1}}, \quad (23)$$

$$\mu_{\text{eff},0} = \mu - \frac{\bar{\mu}}{\phi_1} (\bar{\mu}\varepsilon_{\text{el}}^2 + 2\alpha'T - 2\phi_0^*) \times H(\bar{\mu}\varepsilon_{\text{el}}^2 + 2\alpha'T - 2\phi_0^*). \quad (24)$$

Dependences (23) and (24) are illustrated in Fig. 3 for fixed model parameters. It follows from the figure that the growth of the elastic strains  $\varepsilon_{\text{el}}$  and the temperature  $T$  makes the excess volume  $f_0$  larger, which diminishes, in turn, the shear modulus  $\mu_{\text{eff},0}$ .

Consider the curve corresponding to the temperature  $T_1$  in more details. Its behavior has an essential difference from that demonstrated in Fig. 1. In Fig. 1, *b*, the shear modulus decreases monotonically with the strain (or temperature) growth, and the point of a phase transition of the second order is at the value  $\mu_{s,0} = 0$  in the  $\mu_{s,0}$ -dependences. At the same time, in Fig. 3, *b*, along the dependence corresponding to the temperature  $T_1$ , the shear modulus firstly remains constant (it has a maximum at  $f_0 = 0$ ). Then, above the phase transition point, it begins to decrease. Such a difference between the two approaches takes place only at low temperatures. In the relevant temperature interval of the corresponding experiments [4], the both approaches describe the same behavior (see the  $T_2$ - and  $T_3$ -curves in Fig. 1, *b* and Fig. 3, *b*).

### 2.3. Relation between the density-modulation and excess-volume order parameters

A relation between the above-mentioned models of the boundary friction cannot always be established.

In particular, in the case of vitrification transition, the density modulation  $\varphi$  vanishes in both phases, so it cannot be used as the order parameter. But then it is possible to apply the model with the excess volume  $f$  as the order parameter.

A generalized situation can be considered, in which the order parameter must possess two components (a function of the density modulation and the excess volume). In this case, the thermodynamic potential  $\Phi(\varphi, f)$  becomes a 3D-dependent quantity in the order-parameter space. This approach will make it possible to describe a broader class of systems, because the latter will include the models discussed above, if one component of the order parameter changes insignificantly (for instance, it can be the zero value of the density modulation  $\varphi$  at the vitrification transition).

Furthermore, from this three-dimensional representation of the free energy, we can pass to the situations considered in this paper, if we know a relation between the order parameters  $\varphi$  and  $f$ , which can be found experimentally in every case. Let us establish such a relation by assuming that the shear moduli  $\mu_s$  and  $\mu_{\text{eff}}$  in both models describe the same quantity. This is an approximation, because, as was shown above, the models can demonstrate a physically different behavior at low temperatures. However, the application of such an approximation makes it possible to change from a description of the boundary friction process via the density modulation to an equivalent description via the excess volume, and vice versa. The problem of developing a unified approach in which the free energy is a function of the two-component order parameter remains open at that.

### 2.3.1. Change from the excess-volume order parameter to the density-modulation one

The equivalence condition for the shear moduli,  $\mu_s = \mu_{\text{eff}}$  [see expressions (4) and (19)] brings us to the relation

$$f^2 = \frac{\mu}{\bar{\mu}} - \frac{a}{\bar{\mu}} \varphi^2. \quad (25)$$

Substituting it into expression (22) for the free energy  $\Phi_f(f)$ , we obtain an equivalent potential in the form

$$\Phi_{f \rightarrow \varphi} = \left[ \frac{\phi_0^* \mu}{\bar{\mu}} - \frac{\alpha' T \mu}{\bar{\mu}} + \frac{\phi_1 \mu^2}{4 \bar{\mu}^2} \right] +$$

$$+ \left( \frac{a}{2} \varepsilon_{\text{el}}^2 + \frac{\alpha' T a}{\bar{\mu}} - \frac{\phi_0^* a}{\bar{\mu}} - \frac{\phi_1 a \mu}{2 \bar{\mu}^2} \right) \varphi^2 + \left( \frac{\phi_1 a^2}{4 \bar{\mu}^2} \right) \varphi^4. \quad (26)$$

By comparing this expressions and expression (3) for  $\Phi_\varphi(\varphi)$ , we can find the following relations for the expansion parameters:

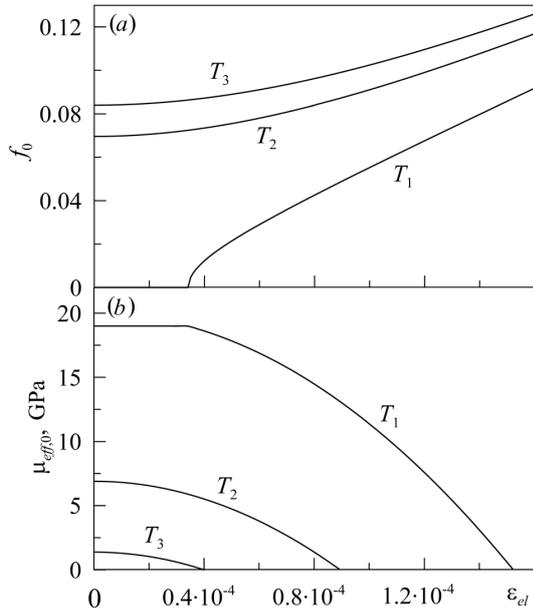
$$b = \frac{\phi_1 a^2}{\bar{\mu}^2}, \quad \alpha = \frac{\alpha' a}{\bar{\mu}}, \quad T_c = \frac{\phi_0^*}{\alpha'} + \frac{\phi_1 \mu}{2 \alpha' \bar{\mu}}. \quad (27)$$

Then the normalization condition (9) for the order parameter  $\varphi$  takes the form

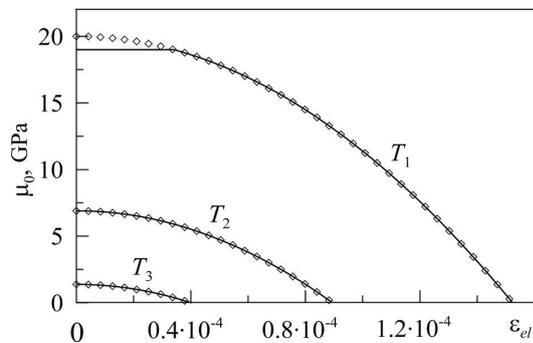
$$\bar{\mu} = \frac{\phi_1 (a - \mu)}{2 \phi_0^*}. \quad (28)$$

From whence, an important property follows. We note that, according to Eqs. (4) and (19), the parameters  $a$  and  $\mu$  determine the maximum values of the shear modulus. Therefore, in order to describe the same system in the framework of two models, the indicated parameters must acquire identical values, which, taking expression (28) into account, gives  $\bar{\mu} = 0$ . This value has no physical sense, because, in such a case according to expression (19), the effective shear modulus  $\mu_{\text{eff}}$  does not change with the growth of the excess volume  $f$ . This fact leads to the conclusion that two concerned models of boundary friction cannot match each other absolutely exactly in the whole range of control parameters, and the condition  $\bar{\mu} > 0$  dictates that the inequality  $a > \mu$  must be satisfied. Bearing all that in mind, the parameters were given the numerical values indicated in the captions to Figs. 1 and 3.

To go further, it is pertinent to choose the parameters of the potential  $\Phi_{f \rightarrow \varphi}(\varphi)$  [Eq. (26)] that they should correspond as much as possible to the expansion parameters of  $\Phi_\varphi(\varphi)$  [Eq. (3)], since the aim of this work is to establish a relation between two approaches to the description of the boundary friction mode. In the system of equations (27), the values of the parameters  $a$ ,  $b$ ,  $\alpha$ , and  $T_c$  are already known (see the caption to Fig. 1). We know that  $\mu < a$ . Therefore, let us put  $\mu = 1.9 \times 10^{10}$  Pa. Now, system (27) contains three equations with four unknowns, i.e., it is insufficient. This occurs, because the potential  $\Phi_\varphi$  [Eq. (3)] in the homogeneous case is determined by four constants:  $\alpha$ ,  $T_c$ ,  $a$ , and  $b$ . The potential  $\Phi(f)$  [Eq. (22)] is determined by five constants:  $\mu$ ,  $\bar{\mu}$ ,  $\phi_0^*$ ,  $\alpha'$ , and  $\phi_1$ . Therefore, if there is a correspondence between the potentials described by



**Fig. 3.** Dependence (23) of the order-parameter stationary value  $f_0$  on the elastic strains  $\epsilon_{el}$  (a) and dependence (19) of the effective-shear-modulus stationary value  $\mu_{eff,0}$  on the elastic strains  $\epsilon_{el}$  at the fixed temperatures  $T_{1-3} = 0, 190,$  and  $270$  K for the expansion parameter values  $\phi_0^* = 1450$  J/m<sup>3</sup>,  $\phi_1 = = 7.25 \times 10^6$  J/m<sup>3</sup>,  $\alpha' = 100$  J · K<sup>-1</sup>/m<sup>3</sup>,  $\mu = 1.9 \times 10^{10}$  Pa, and  $\bar{\mu} = 2.5 \times 10^{12}$  Pa (b)



**Fig. 4.** Dependences of the shear-modulus stationary value  $\mu_0$  on the elastic strains  $\epsilon_{el}$ . The solid curves are the dependences shown in Fig. 3, b; the symbols correspond to the dependences shown in Fig. 1, b

formula (26), the equivalent constants (27) should be so chosen that one of the parameters has to be selected arbitrarily. Let  $\phi_0^* = 1450$  J/m<sup>3</sup>, which allows finding all parameters in expansion (26) when solving system (27) (the determined values are quoted in the caption to Fig. 3).

Since potential (26) corresponds to expression (22), the stationary values of the shear modulus  $\mu_{eff,0}$  coincide with the dependences shown in Fig. 3. The solid curves in Fig. 4 demonstrate dependences corresponding to the potential  $\Phi_f(f)$  [Eq. (22)], which are also depicted in Fig. 3, b. Symbols in Fig. 4 illustrate dependences corresponding to the potential  $\Phi_\varphi(\varphi)$  [Eq. (3)], which are shown in Fig. 1, b. As one can see, the curves perfectly coincide at the temperatures  $T_2$  and  $T_3$ , which testifies to the possibility of a numerically exact equivalent description of the stationary states of the boundary lubricant in the framework of both models.

However, the behavior described by the  $T_1$ -curve differs substantially, because the potential  $\Phi_f(f)$  [Eq. (22)] describes the phase transition of the second order between the zero and non-zero values of the excess volume  $f$ . When the temperature  $T$  or the strains  $\epsilon_{el}$  increase from zero to the phase transition point, then, according to expression (19), the value of the shear modulus remains unchanged,  $\mu_{eff} = \mu$ , because the zero stationary value,  $f_0 = 0$ , is realized (see the  $T_1$ -curve in Fig. 3). After the temperature or the strain exceeds its critical value, the excess volume becomes different from zero, and the shear modulus  $\mu_{eff}$  decreases as the control parameters grow further. However, the  $T_2$ - and  $T_3$ -curves in Fig. 4 demonstrate a decrease of the shear modulus in the whole interval of control parameters. This happens, because the excess volume  $f_0 \neq 0$  at zero strains  $\epsilon_{el}$  (see Fig. 3, a). Hence, at a temperature, where the excess volume has a value different from zero in the absence of strains, the both models describe the stationary states of a lubricant identically, so that an exact correspondence between them can be established.

Let us consider once more the dependences corresponding to the temperature  $T_1$  in Fig. 4. For them, the parameters  $\mu = 1.9 \times 10^{10}$  Pa and  $a = 2 \times 10^{10}$  Pa provide the maximum values of the shear modulus. As follows from the figure, the closer are the  $\mu$ - and  $a$ -values, the wider are the intervals of control parameters, where the exact correspondence between the models exists. As was shown above, the inequality  $a > \mu$  is always satisfied. Therefore, for the models to match, it is necessary to choose  $\mu \rightarrow a$ , with the obligatory condition  $a > \mu$  (it is necessary for expression (28) to be positive). Then, as one can see from Fig. 4, the difference between the models takes place only at temperatures close to zero, which are of no

practical importance. Moreover, the free energy expansion is written for temperatures near the phase transition point, and the error of such a description increases substantially, when moving away from the critical temperature  $T_c$ .

Note that always  $a > \mu$ . Then, if the potential  $\Phi_{f \rightarrow \varphi}(\varphi)$  [Eq. (26)] gives the stationary values of the order parameter  $\varphi$  close to 1 (at low temperatures  $T$ ), expression (25) leads to values  $f^2 < 1$ , which corresponds to a negative number under the root in Eq. (23). However, besides the stationary value (23), there always exists the stationary value  $f_0 = 0$ , which is just realized in this case and which corresponds to a constant value of the shear modulus,  $\mu_{\text{eff}} = \mu$  [see Eq. (19)]. The stationary value  $\mu_s$  of the shear modulus is determined directly from expression (26), and it decreases with the growth of control parameters, as is shown in Fig. 1. Therefore, potentials (26) and (22) behave differently at low temperatures. However, if potential (26) is used, relation (25) is always checked, and  $f_0 = 0$  (accordingly,  $\varphi_0 = \sqrt{\mu/a}$ ) is put, if  $f^2 < 1$ , then the application of Eqs. (26) and (22) brings about the same behavior in both cases. The described contradiction is caused by the fact that, when expression (25) is substituted into the free energy (22), the potential component determined by the last term at  $f^4$  is always positive, irrespective of the  $f^2$ -value in expression (25). Furthermore, potential (22) provides a permanent increase of the excess volume with the growth of control parameters. At the same time, if the critical values of control parameters, above which the stationary value  $\varphi_0 = 0$  is realized, are exceeded, potential (26), according to Eq. (25), gives a constant value of the excess volume,  $f_0 = \sqrt{\mu/\bar{\mu}}$ .

### 2.3.2. Change from the density-modulation order parameter to the excess-volume one

Hence, using relation (25) between the order parameters  $f$  and  $\varphi$ , we found expression (26) for the free energy  $\Phi_{f \rightarrow \varphi}(\varphi)$ , which corresponds to the potential  $\Phi_f(f)$  [Eq. (22)]. Although the thus determined potential is reduced to the form  $\Phi_\varphi(\varphi)$  [Eq. (3)], nevertheless, it describes principally different properties of a lubricant in a certain interval of parameters (at low temperatures  $T$ ). So, it is also of interest to find the potential as a function of the excess volume  $f$ , proceeding from the initial expansion of  $\Phi_\varphi(\varphi)$  [for-

mula (3)]. For this purpose, relation (25) written in the form

$$\varphi^2 = \frac{\mu}{a} - \frac{\bar{\mu}}{a} f^2 \quad (29)$$

will be used. When substituting Eq. (29) into Eq. (3), we obtain the potential

$$\begin{aligned} \Phi_{\varphi \rightarrow f} = & \left[ \frac{\alpha\mu(T - T_c)}{a} + \frac{b\mu^2}{4a^2} \right] + \frac{\mu}{2} \varepsilon_{\text{el}}^2 + \\ & + \left( \frac{\alpha\bar{\mu}(T_c - T)}{a} - \frac{\bar{\mu}}{2} \varepsilon_{\text{el}}^2 - \frac{b\mu\bar{\mu}}{2a^2} \right) f^2 + \frac{b\bar{\mu}^2}{4a^2} f^4. \end{aligned} \quad (30)$$

It is equivalent to expression (3) for  $\Phi_\varphi(\varphi)$ . To within a constant, the free energy (30) is reduced to expression (22) for the potential  $\Phi_f(f)$ , provided the change of variables

$$\phi_0^* = \frac{\bar{\mu}}{a} \left( \alpha T_c - \frac{b\mu}{2a} \right), \quad \phi_1 = \frac{b\bar{\mu}^2}{a^2}, \quad \alpha' = \frac{\alpha\bar{\mu}}{a}. \quad (31)$$

Then the solution of the system of equations (31) is already given in terms of the parameters indicated in the captions to Figs. 1 and 3, because they comprise a solution of the completely equivalent system of equations (27).

Potential (30) brings about the following expression for the stationary value of the order parameter:

$$f_0 = \sqrt{\frac{a^2 \varepsilon_{\text{el}}^2 + 2\alpha a(T - T_c) + b\mu}{\bar{\mu}b}}, \quad (32)$$

which, if relation (27) or (31) is taken into account, coincides with expression (23). Furthermore, using relation (25) between the order parameters [or the equivalent expression (29)], we obtain formula (5). Note that if the temperature  $T$  grows in a certain interval starting from the zero value, there can arise a situation, where the expression under the root in Eq. (32) is negative. Then potential (30) has a minimum equal to zero and the stationary value is  $f_0 = 0$ , which, according to Eq. (29), leads to a constant value  $\varphi_0$  of the density modulation (see the solid  $T_1$ -curve in Fig. 4). In this case, contradictions similar to those described above do not arise.

Since the potential  $\Phi_{\varphi \rightarrow f}(f)$  [Eq. (30)] is equivalent to expression (22) for  $\Phi_f(f)$  to within a constant, it governs the behavior that is similar to that exhibited in Fig. 3. On the other hand, this potential corresponds to expression (3) for  $\Phi_\varphi(\varphi)$ , so it also

leads to the results shown in Fig. 1. Hence, expressions (3) for the free energy  $\Phi_\varphi(\varphi)$ , (22) for  $\Phi_f(f)$ , (26) for  $\Phi_{f \rightarrow \varphi}(\varphi)$ , and (30) for  $\Phi_{\varphi \rightarrow f}(f)$  describe the same stationary states of lubricant. The behavior distinctions observed in Fig. 4 take place only at low temperatures and are induced by different values of the expansion parameters  $a$  and  $\mu$ , because always  $a > \mu$  [see formula (28) and the relevant explanation].

Furthermore, it is easy to determine the lubricant temperature  $T$  above which the both models are equivalent. For this equivalence to take place, it is necessary that the expressions under the roots in Eqs. (23) and (32) be positive in the absence of strains,  $\varepsilon_{el} = 0$ . Those expressions are positive, if the lubricant temperature  $T$  is higher than the critical value,

$$T > T^* = \frac{\phi_0^*}{\alpha'} \quad (33)$$

If this inequality is satisfied, the both models considered in this paper demonstrate identical results in the whole interval of control parameters. This statement, according to the last expression in Eqs. (27) (at a fixed value of  $T_c$ ), agrees with the fact that, in order to broaden the width of the interval, where the models give the same result, it is necessary that the value of the parameter  $\mu$  be as close as possible to the value of  $a$ . For the expansion parameter values used in this work, we obtain the value  $T^* = 14.5$  K.

#### 2.4. Influence of the external load

The research performed above confirms that the process of boundary friction can be described identically using the density modulation  $\varphi$  or the excess volume  $f$  as the order parameter. The former model is more universal [expression (3) for  $\Phi_\varphi(\varphi)$ ], because it is valid in the whole interval of control parameters, so it does not need additional conditions. However, an essential shortcoming of this model is the fact that it does not consider the influence of external loads, which is very important in this problem, because external loads can change the behavior of tribological systems in a critical manner [4]. The fact that the process of boundary friction in the absence of external loads ( $n = 0$  Pa) can be identically described using the both models leads to an idea of that there is a correspondence between the approaches, which allows the model based on the potential  $\Phi_\varphi(\varphi)$  to be

so modified that it would involve the influence of external loads on the friction surface. Let us find such a correspondence.

First, let us write the potential  $\Phi_f(f)$  [Eq. (15)] with  $n \neq 0$  in a simpler form. According to expressions (17) and (21), the second invariant of the strain tensor can be expressed via the first invariant as follows:

$$(\varepsilon_{ij}^{el})^2 = \frac{\varepsilon_{el}^2 + (\varepsilon_{ii}^{el})^2}{2}, \quad (34)$$

where  $\varepsilon_{el}$  is the elastic strain component, which is the control model parameter. After the substitution of expression (34) into the free energy (15), we obtain

$$\Phi_f = \frac{\mu}{2} \varepsilon_{el}^2 + \frac{\lambda + \mu}{2} (\varepsilon_{ii}^{el})^2 + \left[ \phi_0^* - \frac{\bar{\mu}}{2} \varepsilon_{el}^2 - \frac{\bar{\lambda} + \bar{\mu}}{2} (\varepsilon_{ii}^{el})^2 - \alpha' T \right] f^2 + \frac{1}{4} \phi_1 f^4. \quad (35)$$

Taking potential (35) as an example, let us consider the change from the order parameter  $f$  to the order parameter  $\varphi$  in the general case, i.e., when the external normal stresses  $n$  differ from zero.

The substitution of relations (25), (16), (19), and (20) into potential (35) gives the expression

$$\Phi_{f \rightarrow \varphi, n} = \Phi_{f \rightarrow \varphi}(\varphi) + \frac{n^2 \bar{\mu} / 2}{\bar{\mu} \lambda - \bar{\lambda} \mu + a \varphi^2 (\bar{\lambda} + \bar{\mu})}, \quad (36)$$

where  $\Phi_{f \rightarrow \varphi}(\varphi)$  is defined by formula (26). In the absence of external load ( $n = 0$  Pa), the application of relations (27) makes it possible to reduce potential (36) to  $\Phi_\varphi(\varphi)$  [Eq. (3)] with an accuracy to a constant. Hence, expression (36) generalizes the model proposed in works [10, 18, 19] because it additionally takes the external load applied to the surfaces into account. When finding the stationary values for the order parameter and the shear modulus directly from expression (36), the curves shown by symbols in Fig. 4 are obtained in the whole interval of control parameters, without a necessity to introduce additional conditions and restrictions.

Figure 5, *a* illustrates the dependences of the potential  $\Phi_{f \rightarrow \varphi, n}$  [Eq. (36)] on the order parameter  $\varphi$  for various values of the external load growing from  $n_1$  to  $n_5$ . In particular, if the load  $n_1 = 0$  Pa, then potential (36) is reduced to  $\Phi_{f \rightarrow \varphi}(\varphi)$  [Eq. (26)]. From the figure, it follows that the growth of the external load increases the stationary value of the order

parameter  $\varphi_0$  corresponding to the minimum of the potential  $\Phi_{f \rightarrow \varphi, n}$  [Eq. (36)] (see also Fig. 5, b). According to expression (6), this leads to the growth of the shear modulus  $\mu_{s,0}$  of a lubricant, i.e., the lubricant becomes more solid-like. Physically, this occurs due to the fact that the growth of the external load leads to a forced ordering of the molecules in the lubricant layer [4].

It is worth noting that if the parameters have the values that were used to plot the curves corresponding to the temperatures  $T_4$  and  $T_5$  in Fig. 5, b, then the increase of the magnitude of external normal stresses  $n$  gives rise to a phase transition of the second order between the zero (in the liquid-like structure) and non-zero (in the solid-like structure) stationary values of the order parameter  $\varphi_0$ . At the temperatures  $T_1$ ,  $T_2$ , and  $T_3$ , the lubricant is in the solid-like state even under the zero load,  $n = 0$  Pa, because  $\varphi_0 \neq 0$  at  $n = 0$  Pa. Hence, model (36) makes allowance for the influence of the temperature  $T$ , the elastic strains  $\varepsilon_{el}$ , and the external load  $n$ , whose set of values determines the phase state of the lubricant. In works [23, 24, 26, 27], a relation between the elastic strain in the lubricant layer and the relative velocity of the friction surfaces was obtained. Thus, the main control parameters governing the friction modes were taken into consideration.

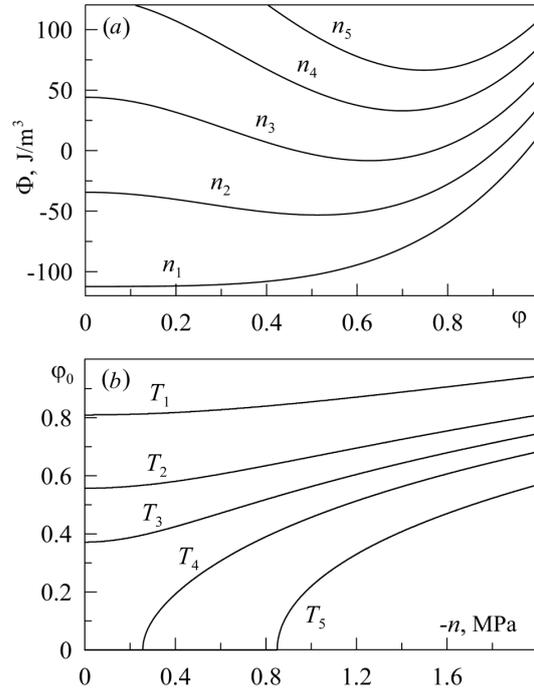
Note that potential (36) can be transformed into a polynomial form, if we carry out a series expansion of the term describing the external load,

$$\begin{aligned} \frac{n^2 \bar{\mu} / 2}{\bar{\mu} \lambda - \bar{\lambda} \mu + a \varphi^2 (\bar{\lambda} + \bar{\mu})} &= \\ &= \frac{n^2 \bar{\mu}}{2 (\bar{\mu} \lambda - \bar{\lambda} \mu)} \sum_{m=0}^{\infty} \left[ \frac{-a (\bar{\lambda} + \bar{\mu}) \varphi^2}{(\bar{\mu} \lambda - \bar{\lambda} \mu)} \right]^m. \end{aligned} \quad (37)$$

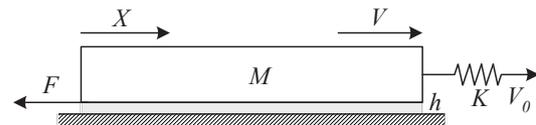
However, in so doing, we should account for that series (37) converges only provided the condition

$$\varphi < \varphi_c = \sqrt{\frac{\bar{\mu} \lambda - \bar{\lambda} \mu}{a (\bar{\lambda} + \bar{\mu})}} \quad (38)$$

is obeyed, where the selected values of the model parameters bring about the critical value of the order parameter  $\varphi_c = \sqrt{30030}/260 \approx 0.667$ . Note that, according to inequality (38), it is possible to choose such values of model parameters – e.g., by enlarging the value of the parameter  $\lambda$  – that substantially broaden



**Fig. 5.** Dependence (36) of the free energy  $\Phi_{f \rightarrow \varphi, n}$  on the order parameter  $\varphi$  for the parameters  $\lambda = 10^{10}$  Pa,  $\bar{\lambda} = 10^{11}$  Pa, the elastic strains  $\varepsilon_{el} = 0$ , and the lubricant temperature  $T = 300$  K (a). The other parameters are the same as in Figs. 1 and 3. The curves  $n_1$  to  $n_5$  correspond to the values of normal stresses  $n = 0, -1.2, -1.7, -2.1,$  and  $-2.4$  MPa, respectively. Dependences of the order-parameter stationary value  $\varphi_0$  on the external normal stresses  $-n$ , corresponding to potential (36) for the same parameters as in panel a (b). The curves  $T_1$  to  $T_5$  correspond to the temperatures  $T = 100, 200, 250, 300,$  and  $400$  K, respectively



**Fig. 6.** Mechanical analog of the tribological system

the convergence interval. However, since we have the exact expression (36) for the potential  $\Phi_{f \rightarrow \varphi, n}(\varphi)$ , the application of formula (37) is optional.

### 3. Kinetics of the Tribological System

Consider a mechanical analog of tribological system, which is shown in Fig. 6. A spring with the stiffness  $K$  is connected to a block with the mass  $M$ . The block is located on a smooth surface, being separated from it by a lubricant layer with the thickness  $h$ . The

free end of the spring is driven at the fixed velocity  $V_0$ . When the block moves, there arises a friction force  $F$ , which resists the motion. Let us denote the current coordinate of the block as  $X$ . Then the corresponding equation of motion looks like [10, 35]

$$M\ddot{X} = K(V_0t - X) - F. \quad (39)$$

This equation includes the friction force  $F$ , which can be found using the models described above. For this purpose, we have to know the relation between the shift velocity  $V$  and the elastic strains arising in the lubricant layer. Let us use the Debye approximation, which relates the elastic,  $\varepsilon_{\text{el}}$ , and plastic,  $\varepsilon_{\text{pl}}$ , strain components via the formula [10]

$$\dot{\varepsilon}_{\text{pl}} = \frac{\varepsilon_{\text{el}}}{\tau_\varepsilon}, \quad (40)$$

where the relaxation time parameter  $\tau_\varepsilon$  is introduced.

The total strain in the lubricant layer consists of the elastic and plastic components,

$$\varepsilon = \varepsilon_{\text{el}} + \varepsilon_{\text{pl}}, \quad (41)$$

and determines the velocity  $V$  of the block according to the law [36]

$$V = h\dot{\varepsilon} = h(\dot{\varepsilon}_{\text{el}} + \dot{\varepsilon}_{\text{pl}}). \quad (42)$$

The last three equations bring about the following expression for the elastic component of shear strain:

$$\tau_\varepsilon \dot{\varepsilon}_{\text{el}} = -\varepsilon_{\text{el}} + \frac{V\tau_\varepsilon}{h}. \quad (43)$$

As a rule, the relaxation time  $\tau_\varepsilon$  is very short, which allows the stationary value of elastic strain

$$\varepsilon_{\text{el}} = \frac{V\tau_\varepsilon}{h} \quad (44)$$

to be used with a sufficient accuracy within the approximation  $\tau_\varepsilon \dot{\varepsilon}_{\text{el}} \approx 0$ . Expression (44) means that the elastic strain  $\varepsilon_{\text{el}}$  in the lubricant layer with a constant thickness  $h$  is determined by the block velocity  $V$ . The elastic strains equal zero at rest ( $V = 0$  m/s) because the external perturbation of the system is absent. The friction force that acts in the system and is shown in Fig. 6 is determined as the product of total stresses and the contact area  $A$  of the friction surfaces,

$$F = (\sigma_{\text{el}} + \sigma_v) A, \quad (45)$$

where the viscous stresses  $\sigma_v$  are calculated according to the formula [36]

$$\sigma_v = \frac{\eta_{\text{eff}} V}{h}, \quad (46)$$

and the effective viscosity of lubricant,  $\eta_{\text{eff}}$ , is determined by the following dependence, which was obtained experimentally [36]:

$$\eta_{\text{eff}} = k(\dot{\varepsilon})^\gamma. \quad (47)$$

Here, the coefficient of proportionality  $k$  with the dimensionality  $\text{Pa}\cdot\text{s}^{\gamma+1}$  is introduced. For pseudoplastic fluids,  $\gamma < 0$ ; dilatant fluids are characterized by the index  $\gamma > 0$ . In the case of Newtonian fluids,  $\gamma = 0$ , because, in accordance with Eqs. (47) and (42), the viscosity does not depend on the velocity gradient.

Taking Eqs. (42) and (47) into account, expression (46) for viscous stresses can be written in the form

$$\sigma_v = k \left( \frac{V}{h} \right)^{\gamma+1}. \quad (48)$$

Substituting this formula into Eq. (45), we obtain the final expression for the friction force<sup>2</sup> [23],

$$F = \left[ \sigma_{\text{el}} + k \operatorname{sgn}(V) \left( \frac{|V|}{h} \right)^{\gamma+1} \right] A, \quad (49)$$

where the elastic stresses  $\sigma_{\text{el}}$  are determined by expression (4) or (21), depending on the applied model.

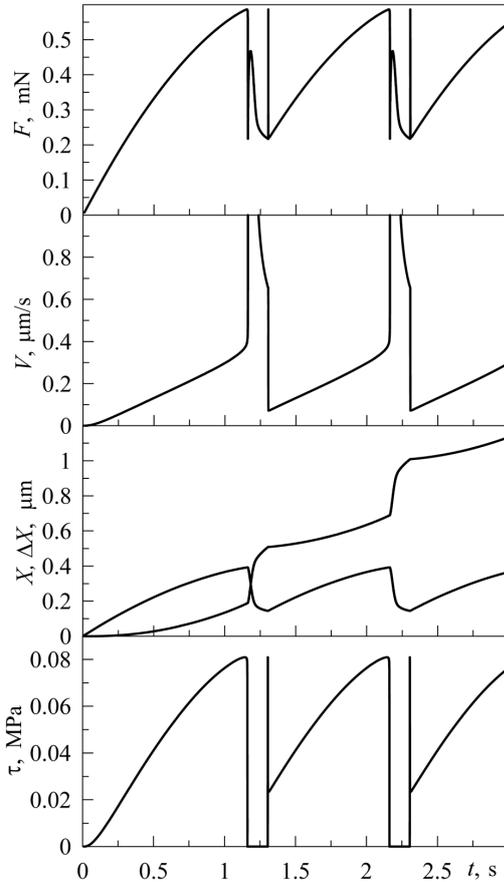
### 3.1. The excess volume as the order parameter

To describe the lubricant behavior, let us write the kinetic relaxation equation of the Landau–Khalatnikov type [37],

$$\frac{\partial x}{\partial t} = -\delta \frac{\partial \Phi}{\partial x}, \quad (50)$$

where  $x$  is an order parameter, and the kinetic coefficient  $\delta$  characterizes the inertial properties of the system. Consider firstly a situation where the excess volume  $f$  is used as the order parameter,  $x \equiv f$ . After substituting the free energy  $\Phi_f(f)$  [Eq. (35)] into

<sup>2</sup> Here, the sign function  $\operatorname{sgn}(x)$  and the absolute value of the shift velocity,  $|V|$ , are used, because the velocity itself,  $V$ , can acquire negative values.

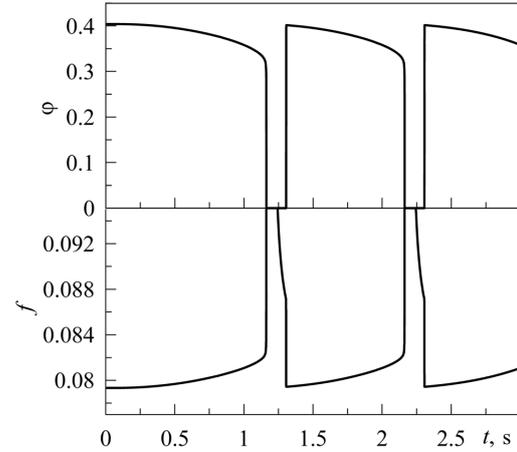


**Fig. 7.** Dependences of the friction force  $F$  [Eq. (49)], the block shift velocity  $V$ , the block coordinate  $X$ , the spring elongation  $\Delta X = V_0 t - X$ , and the elastic stresses  $\sigma_{el}$  on the time  $t$  at the parameters  $M = 0.4$  kg,  $K = 1500$  N/m,  $\delta = 100$  Pa $^{-1}$  s $^{-1}$ ,  $h = 10^{-9}$  m,  $\tau_\varepsilon = 10^{-7}$  s,  $A = 5 \times 10^{-9}$  m $^2$ ,  $\gamma = -2/3$ ,  $k = 5 \times 10^3$  Pa $\cdot$ s $^{1/3}$ ,  $T = 250$  K,  $V_0 = 500$  nm/s, and  $n = -0.3$  MPa. The other parameters are the same as in Figs. 1, 3, and 5

Eq. (50), the latter looks like

$$\frac{1}{\delta} \frac{\partial f}{\partial t} = -f \left[ 2\phi_0^* - \bar{\mu} \left( \frac{V\tau_\varepsilon}{h} \right)^2 - 2\alpha'T \right] - \phi_1 f^3 - \frac{n^2 f (\bar{\lambda} + \bar{\mu})}{[\lambda + \mu - f^2 (\bar{\lambda} + \bar{\mu})]^2}, \quad (51)$$

where relation (44) between the relative shift velocity of friction surfaces,  $V$ , and the elastic strain in the lubricant layer,  $\varepsilon_{el}$ , is used. Equation (51) tells us that an increase of the external load (of the magnitude of normal stresses  $n$ ) leads to a forced ordering in the



**Fig. 8.** Dependences of the order parameters  $\varphi$  and  $f$  on the time  $t$  corresponding to the dependences shown in Fig. 7

lubricant because the excess volume  $f$  decreases at that. To calculate the time evolution of the main parameters of the tribological system shown in Fig. 6, we numerically solved the system of kinetic equations (39) and (51). The friction force  $F$  was determined from Eq. (49), and the elastic stresses  $\sigma_{el} \equiv \tau$  according to expression (21)<sup>3</sup>. The relation  $\dot{X} = V$  has also to be taken into account. The indicated system of equations was solved using the Euler and 4th-order Runge–Kutta methods. Both of them gave rise to identical results.

In Fig. 7, the numerically calculated time dependences of the friction force  $F$ , the block velocity  $V$ , the block coordinate  $X$ , the spring tension  $\Delta X$ , and the elastic stresses  $\tau$  arising in the lubricant layer are depicted. As follows from the figure, the stick-slip mode of boundary friction is established in the system, when periodic phase transitions between the solid-like and liquid-like structural states of the lubricant take place. The specific features of this type of the stick-slip motion mode, as well as its origin, were considered in work [23] in detail in the framework of the model for the phase transition of the first order.

Figure 8 additionally exhibits the time,  $t$ , dependences of the excess-volume,  $f$ , (cut from above) and density-modulation,  $\varphi$ , order parameters, which cor-

<sup>3</sup> Since the model does not restrict the value of the excess volume  $f$ , then, according to Eq. (19), we must put  $\mu_{eff} = 0$  if  $f > \sqrt{\mu/\bar{\mu}}$ . Accordingly, the parameters  $\lambda$  and  $\bar{\lambda}$  should be chosen so that the condition  $\lambda_{eff} > 0$  be always obeyed for all realized values of the order parameter  $f$ .

respond to the dependences shown in Fig. 7. It follows from the figure that the system actually undergoes phase transitions, with the density modulations being smaller for larger excess volumes.

### 3.2. The density modulation as the order parameter

Substituting the free energy (36) into Eq. (50),<sup>4</sup> we obtain the explicit kinetic equation

$$\frac{1}{\delta} \frac{\partial \varphi}{\partial t} = -\varphi \left[ 2\alpha (T - T_c) + a \left( \frac{V\tau_\varepsilon}{h} \right)^2 \right] - b\varphi^3 + \frac{n^2 \bar{\mu} a \varphi (\bar{\lambda} + \bar{\mu})}{[\bar{\mu}\lambda - \bar{\lambda}\mu + a\varphi^2(\bar{\lambda} + \bar{\mu})]^2}. \quad (52)$$

To simulate the process of lubricant melting, it is necessary to follow a procedure similar to that described in the previous section. The only difference consists in that it is necessary to use Eq. (52) instead of Eq. (51). The elastic stresses  $\sigma_{el}$  entering expression (49) for the friction force  $F$  are determined by expression (4). However, the application of Eq. (52) has an important detail. In particular, if Eq. (52) is integrated numerically, its root  $\varphi = 0$  remains stable, even if it corresponds to the maximum of the potential  $\Phi_\varphi(\varphi)$ . In work [23], to avoid such a situation, additive noise with low intensity was additionally introduced into Eq. (52). The role of this noise consists in that in the described situation with  $\varphi = 0$ , the system will transit from the unstable state into the stable one corresponding to the energy minimum. Thus, the account for fluctuations is necessary due to the specific features of a numerical calculation. The integration of Eq. (51) does not invoke such problems.

## 4. Conclusions

In this work, the thermodynamic theory of the structural states at the boundary friction, which was proposed by V.L. Popov, has been generalized. The generalization consists in that the load on the friction surfaces is introduced into the model in a natural way via the magnitude of external normal stresses. It is shown that the increase of normal stresses leads to an increase in the stationary values of the density-modulation order parameter and the shear modulus

of a lubricant. The lubricant can melt, if its temperature grows, the elastic strain component increases (it appears in the lubricant layer at its shear), or the external load decreases. The model described in this work summarizes the results previously obtained while studying the kinetics of boundary friction in the absence of external loads. Since the load on the surface often has a critical effect in boundary-friction experiments and the proposed generalization allows the description of the load effect, the work can serve as a basis for further theoretical research.

*The author is grateful to Dr.Sci. Prof. S.I. Denysov for a detailed analysis of dissertation work [17]. This activity generated an idea to establish a relation between two theoretical approaches to the description of boundary friction. In the presented work, this idea has been realized in the case of the phase transition of the second order. The author also thanks Dr.Sci. Prof. V.L. Popov and Dr.Sci. Prof. A.E. Filippov for discussing the results of the work, as well as a number of critical comments and propositions, which made the work substantially better.*

*The work contains the results of research carried out as a part of a scholarship work in the framework of the nominal scholarship of the Verkhovna Rada of Ukraine for young scientists-doctors of sciences (the resolution of the Verkhovna Rada of Ukraine No. 1641-IX from 14 July 2021).*

## APPENDIX A

### Determination of the strain tensor invariants

Hooke's law for an isotropic body is written in the form [33]

$$\sigma_{ij} = \lambda \varepsilon_{ii} \delta_{ij} + 2\mu \varepsilon_{ij}. \quad (A1)$$

Let us choose the principal deformation axes as the coordinate axes. Then the strain tensor  $\varepsilon_{ij}$  has only diagonal components. Let us consider a plane-deformed state of lubricant, for which  $\varepsilon_{22} = 0$ . The diagonal components of the stress tensor in the selected coordinate system are

$$\sigma_1 = \lambda(\varepsilon_{11} + \varepsilon_{33}) + 2\mu\varepsilon_{11}, \quad (A2)$$

$$\sigma_2 = \lambda(\varepsilon_{11} + \varepsilon_{33}), \quad (A3)$$

$$\sigma_3 = \lambda(\varepsilon_{11} + \varepsilon_{33}) + 2\mu\varepsilon_{33}. \quad (A4)$$

The tangential stresses [34]

$$\tau_2 = \frac{\sigma_3 - \sigma_1}{2} = \mu(\varepsilon_{33} - \varepsilon_{11}), \quad (A5)$$

act along the lubricant boundary, and the stress normal to the lubricant boundary equals [34]

$$n_2 = \frac{\sigma_3 + \sigma_1}{2} = (\lambda + \mu)(\varepsilon_{11} + \varepsilon_{33}), \quad (A6)$$

<sup>4</sup> Expression (36) describes the free energy  $\Phi_\varphi$  [Eq. (3)] making allowance for the term corresponding to the external load and proportional to  $n^2$ .

Then, from Eqs. (A5) and (A6), we obtain

$$\varepsilon_{11} = \frac{1}{2} \left( \frac{n_2}{\lambda + \mu} - \frac{\tau_2}{\mu} \right), \quad (\text{A7})$$

$$\varepsilon_{33} = \frac{1}{2} \left( \frac{n_2}{\lambda + \mu} + \frac{\tau_2}{\mu} \right). \quad (\text{A8})$$

Accordingly, the first two invariants of the strain tensor – Eqs. (16) and (17) – are as follows:

$$\varepsilon_{ii} = \varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33} = \frac{n_2}{\lambda + \mu}, \quad (\text{A9})$$

$$\varepsilon_{ij}\varepsilon_{ji} = \varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2 = \frac{1}{2} \left[ \left( \frac{\tau_2}{\mu} \right)^2 + (\varepsilon_{ii})^2 \right]. \quad (\text{A10})$$

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Received 04.04.21.

Translated from Ukrainian by O.I. Voitenko

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ЗВ'ЯЗОК МІЖ ПАРАМЕТРАМИ ПОРЯДКУ  
МОДУЛЯЦІЇ ГУСТИНИ І НАДЛИШКОВОГО ОБ'ЄМУ  
ПРИ ОПИСІ СТАЦІОНАРНИХ СТРУКТУРНИХ  
СТАНІВ МЕЖОВОГО МАСТИЛА

В рамках теорії фазових переходів Ландау з використанням модуляції густини і надлишкового об'єму в ролі па-

раметрів порядку описано фазовий перехід другого роду між структурними станами межового мастила, затиснутого між атомарно-гладкими твердими поверхнями. Знайдено зв'язок між таким чином визначеними параметрами порядку. Досліджено стаціонарні стани мастильного матеріалу в залежності від керуючих параметрів – температури мастила, пружної деформації в змащувальному шарі і зовнішнього навантаження на поверхні тертя. Проведено моделювання кінетики плавлення в рамках механічного аналога трибологічної системи із пружністю.

*Ключові слова:* межове мастило, сила тертя, переривчастий режим ковзання, параметр порядку, фазовий перехід.