SYNERGETIC THEORY OF A LIQUID–GLASS TRANSITION

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We represent a liquid–glass transition as the spontaneous appearance of the elastic fields of stress and strain shear components that is caused by the cooling of a liquid with a rate that is higher than the critical value. The kinetics of a liquid–glass transition is described by the equations coinciding formally with the synergetic Lorenz system where the strain acts as the order parameter, the conjugate field is reduced to the elastic stress, and the temperature is as the control parameter. Using the adiabatic approximation we find the steady-state values of these quantities and the effective relaxation time. Taking into account the strain defect of the shear modulus we show that the process of a liquid–glass transition is realized according to the mechanism of a first–order transition. The critical rate of the cooling turns out proportional to the thermometric conductivity and the nonrelaxed shear modulus value as well as inversely proportional to the temperature defect of the relaxed modulus and the square of the heat conductivity distance of a sample.
Key words: liquid–glass transition, shear components of elastic stress and strain, viscoelastic medium, Lorenz system, shear modulus, cooling rate.

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I. INTRODUCTION

Within the phenomenological framework the basic distinction between a liquid and a glass consists in the character of the relaxation law of the shear components of the elastic stress: if in an ideal glass they are kept infinitely long, in a liquid such relaxation is going on for the finite time [1]

$$\tau = \eta/G, \tag{1}$$

where η is the dynamical shear viscosity, G is the shear modulus. In naive manner it is possible to assume that a glass transition is caused purely by kinetic effect of a liquid freezing for which viscosity η gets an infinite value for a finite shear modulus G [2]. However in the course of the usual second-order phase transition, where an infinite increase of the τ at critical point is also observed the situation is reverse. Really, proceeding from viscoelastic liquid to a general case formula (1) takes the form of $\tau = \chi/\gamma$, where χ is the generalized susceptibility, γ is the kinetic coefficient (in Eq. (1) they are reduced to the quantities G^{-1}, η^{-1}, respectively) [3]. The infinite increase of a susceptibility χ occurs and a kinetic coefficient γ has no peculiarity at phase transition. It is equivalent to the limit to zero of the shear modulus G for the viscosity η in Eq. (1). This situation corresponds to the viscoelastic transition [4].

Usually at a glass transition thermodynamic peculiarities are observed as an increase of heat capacity [5]. Therefore it is possible to believe that the process of a glass transition is not always reduced to purely mechanical supercooling of a liquid at which shear viscosity gets infinite value. Moreover it is known that liquids as metallic melts undergo a glass transition only at supercritical cooling rates [5]. This circumstance can be explained on the basis of elementary qualitative arguments [6]. The quantitative theory will be stated below. The starting point of our approach is that a glass transition is ensured by the self-organization of elastic fields of stress σ and strain ε shear components, on the one hand, and the temperature T, on other hand [16]. The relationship of the two first components is a well known fact which in the elementary case is reflected by the Maxwell model [1]. The influence of temperature is ensured by a critical increase of the shear modulus $G(T)$ with the decrease of the temperature: in a liquid state $G = 0$, and in a glass one $G \neq 0$.

II. BASIC EQUATIONS

Let us note at first the basic supervision, on which the derivation of the synergetic equations stated below is constructed. The complete gauge field consists of purely force and material components (the former is defined by the field equations, and the latter is reduced to the order parameter representing self-organization effect) [8]. So, in magnet we have [9]

$$\mathbf{H} + 4\pi\mathbf{M} = \mathrm{rot}\mathbf{A}, \tag{2}$$

where the field $\mathbf{H}$ determines the force contribution, and the magnetization $\mathbf{M}$ is the material component. The complete intensity, i.e. magnetic induction $\mathbf{B}=\mathrm{rot}\mathbf{A}$, is reduced to a derivative of the vector potential $\mathbf{A}$. A similar situation takes place for the ferroelectric [9]

$$\mathbf{D} - 4\pi\mathbf{P} = -\nabla\varphi, \tag{3}$$

where the electric induction $\mathbf{D}$, the polarization $\mathbf{P}$, and the potential φ define the force, the material, and the complete components of the electrical field, respectively.

For the examined case of a viscoelastic liquid the tensor of the total strain $\widehat{\varepsilon}_t$ acts as the gauge field, and the potential is reduced to the vector of displacement $\mathbf{u}$. With the account of symmetry of $\widehat{\varepsilon}_t$ they are connected by the expression [1]

$$\widehat{\varepsilon}_t = \frac{1}{2}\left(\nabla\mathbf{u} + \mathbf{u}\nabla\right). \tag{4}$$

Similar to Eqs. (2) and (3) complete strain $\widehat{\varepsilon}_t$ consists of the purely elastic component $\widehat{\varepsilon}$ and the material one $\widehat{\varepsilon}^0$. In the case of thermoelastic effect this component is caused by the change of temperature and is reduced to the dilatation [1]:

$$\widehat{\varepsilon}^0 = \varepsilon^0 \widehat{I}, \quad \varepsilon^0 \equiv \alpha\left(T - T_0\right), \tag{5}$$

where α is the thermal expansion coefficient, T_0 is the equilibrium temperature, $\widehat{I}$ is the unit tensor. In the case under consideration the material component is caused by the appearance of the nonzero value of the shear modulus $G(T)$ with decrease of the temperature. This fact is expressed conveniently writing down the shear component of strain tensor $\varepsilon^0 \equiv G^{-1}(G - G(T))$ in linear approximation of temperature:

$$\varepsilon^0 = G^{-1}\left|\frac{dG(T)}{dT}\right|_{T=0} T, \tag{6}$$

where G is the characteristic value of shear modulus.

We shall proceed now to a direct derivation of the synergetic equations for the viscoelastic medium. The basic of them is reduced to the Maxwell equation [1]

$$\dot{\varepsilon} = -\varepsilon/\tau + \sigma/\eta. \tag{7}$$

Here the dot stands for a derivative with respect to time, the first term in the right-hand side describes the Debye relaxation during time (1), the second term describes the flow of a viscous liquid caused by the shear components of the elastic stress. It is important to mean, that only purely force (instead of material) components of the strain ε and the stress σ are in Eq. (7). In the stationary case $\dot{\varepsilon} = 0$ the kinetic equation (7) is transformed into the Hooke law

$$\sigma = G\varepsilon. \tag{8}$$

The equation for determining the time dependence $\sigma(t)$ of the elastic stress takes the form of

$$\dot{\sigma} = -\sigma/\tau_\sigma + g_\sigma \varepsilon T, \tag{9}$$

where τ_σ, g_σ are the positive constants. As well as in the Maxwell equation (7) the first term in the right-hand side of Eq. (9) describes the dissipation process of a stress relaxation to the equilibrium value $\sigma = 0$. However it flows rather during the macroscopic time τ, than the microscopic one τ_σ. The value τ_σ is reduced to Debye time $\sim 10^{-12}$ s, so that the important for a further condition $\tau_\sigma \ll \tau$ is satisfied. The second term in Eq. (9) takes into account the positive feedback between the elastic strain ε and the temperature T which leads to an increase of the elastic stress σ and, thus, causes self-organization. The physical sense of this term is understandable easily for a steady-state case where $\dot{\sigma} = 0$, and Eq. (9) takes the form

$$\sigma = \left(a_\sigma/v\right) T\varepsilon, \tag{10}$$

where the dimensionless positive constant is introduced

$$a_\sigma \equiv g_\sigma \tau_\sigma v, \tag{11}$$

v is the atom volume. Comparing Eq. (10) with the expression following from Eq. (6) for the material component $\sigma^0 = G\varepsilon^0$, we see that at $\varepsilon = 1$ they coincide. From here it follows that the nonlinear term in Eq. (9) takes into account the connection between the material and the elastic components of the strain. The parameter of this connection defined by Eq. (11) has the form

$$a_\sigma = v\left|\frac{dG}{dT}\right|, \quad \left|\frac{dG}{dT}\right| \equiv \left|\frac{dG(T)}{dT}\right|_{T=0}. \tag{12}$$

The kinetic equation for the temperature can be obtained by analogy with the derivation of the heat conductivity equation stated in Sect. 31 [1]. Thus, it is necessary to start from the continuity equation for the heat $\delta Q = T\delta S$:

$$T\dot{S} = -\nabla\mathbf{q}. \tag{13}$$

Here the heat current is given by the Onsager equation

$$\mathbf{q} = -\kappa\nabla T, \tag{14}$$

where κ is the heat conductivity. In the elementary case of the thermoelastic stress the entropy

$$S = S_0(T) + K\alpha\varepsilon^0 \tag{15}$$

consists of the purely thermodynamic component S_0 and the elastic contribution (5), where K is the compression modulus (see Sect. 6 in [1]). In the case of liquid-glass transition it should be pass from the dilatational component $K\alpha\varepsilon^0$ to the elastic energy $-\sigma\varepsilon/T$ of the shear component divided by temperature (here the sign "minus" takes into account connection $T\delta S = p\delta V \Rightarrow -\sigma\delta\varepsilon$ at $S_0 =$ const which is caused by the contrary choice of the pressure p and the stress σ signs). As a result Eq. (13) takes the form of

$$T\dot{S}_0(T) - \sigma\dot{\varepsilon} = \kappa\nabla^2 T. \tag{16}$$

After Fourier transformation the coordinate derivation ∇ is replaced by $i\mathbf{k}$ ($\mathbf{k}$ is the wave vector) and taking into account the definition of heat capacity $c_p{=}TdS_0/dT$, Eq. (16) assumes the form:

$$c_p\dot{T} = -\kappa\mathbf{k}^2 T + \sigma\dot{\varepsilon}. \tag{17}$$

Substituting here the expression for $\dot{\varepsilon}$ from Eq. (7) we obtain the term σ^2/η describing the trivial effect of the dissipative heating of a viscous liquid flowing under the action of the stress σ.

The process of a liquid-glass transition has the following peculiarity. It is necessary to ensure the heat removal with intensity $\mathbf{q}_0$ contrary to above. The value of $\mathbf{q}_0$ is not reduced to the Onsager component and is fixed by external conditions. In view of these circumstances equation for the temperature takes the final form

$$\dot{T} = -T/\tau_T - g_T\varepsilon\sigma + Q. \tag{18}$$

Here $\tau_T = c_p/\kappa k^2$ is the relaxation time that is caused by thermometric conductivity $\chi{\equiv}\kappa/c_p$, $g_T{\equiv}(\tau c_p)^{-1}$ is the constant of negative connection,

$$Q = Q_0 + \sigma^2/\eta c_p, \quad Q_0 \equiv -i\mathbf{k}\mathbf{q}_0/c_p, \tag{19}$$

where Q_0 is the external component and the square term is the contribution of the elastic stress. The obvious account of this term leads to significant complication of the subsequent analysis, though results in trivial renormalization of quantities. Therefore further component Q in Eq. (18) is supposed to be constant. Let us note that during the derivation of Eq. (18) we accepted equilibrium value of the temperature $T_{00} = 0$. Obviously, otherwise when the liquid is cooled to temperature $T_{00} \neq 0$, Eq. (19) gets the term T_{00}/τ_T.

III. CONDITIONS OF A LIQUID–GLASS TRANSITION

The further problem is the solution of the system of differential equations (7), (9), (18) that determines the self-consistent variation of the elastic fields of the strain $\varepsilon(t)$ and stress $\sigma(t)$ and the temperature $T(t)$. In the analytical form it is possible only provided that the hierarchic conditions

$$\tau_\sigma \ll \tau, \quad \tau_T \ll \tau \tag{20}$$

are satisfied [10]. They mean that in the course of their evolution the stress and the temperature follow the change of the strain [11]. As was specified earlier the first of these conditions is satisfied always. Using the definition of the thermometric conductivity $\chi = \kappa/c_p$, the kinematic viscosity $\nu = \eta/\rho$, where ρ is the medium density, and the sound velocity $c = (G/\rho)^{1/2}$, the second condition in Eq. (20) it is conveniently to give the form of

$$(ck)^2 \ll (\chi k^2)(\nu k^2). \tag{21}$$

We see that the characteristic distance of the heat conductivity of the system $2\pi/k$ does not exceed the value of

$$L = 2\pi\frac{(\chi\nu)^{1/2}}{c}. \tag{22}$$

The physical sense of this condition is expressed by the hydrodynamic inequality

$$\tau_T\tau_\varepsilon\omega_{\mathbf{k}}^2 \ll 1, \tag{23}$$

meaning that geometric average value of the heat conductivity time τ_T and the convection time τ_ε is much shorter that the reciprocal frequency of a sound (here we takes into account expressions $\tau_\varepsilon^{-1}{\equiv}\nu k^2$, $\omega_{\mathbf{k}}{=}ck$, $\tau\tau_\varepsilon\omega_{\mathbf{k}}^2{=}1$). In the glassing systems this condition is satisfied automatically.

Further it is convenient to write equations (7), (9), (18) in the form

$$\tau\dot{\varepsilon} = -\varepsilon + \sigma/G, \tag{24}$$

$$\tau_T\dot{T} = (\tau_T Q - T) - (a_T v)\,\varepsilon\sigma, \tag{25}$$

$$\tau_\sigma\dot{\sigma} = -\sigma + (a_\sigma/v)\,\varepsilon T, \tag{26}$$

where definition (11) is used and the dimensionless constant

$$a_T \equiv \frac{\tau_T g_T}{v} = \frac{\tau_T\tau_\varepsilon\omega_{\mathbf{k}}^2}{c_p v} \tag{27}$$

is introduced (according to Eq. (23) the condition $a_T \ll 1$ is satisfied).

Taking into account Eq. (20) the left–hand side of Eqs. (25) and (26), containing short relaxation times τ_σ, τ_T, it is possible to set equal to zero. Therefore these equations give expressions for the temperature and the elastic stress in terms of strain value [17]

$$T = \frac{\tau_T Q}{1 + \varepsilon^2/\varepsilon_m^2}, \tag{28}$$

$$\sigma = \frac{a_\sigma}{v}(\tau_T Q)\,\varepsilon\left(1 + \frac{\varepsilon^2}{\varepsilon_m^2}\right)^{-1}, \tag{29}$$

where the notion

$$\varepsilon_m^{-2} \equiv a_T a_\sigma = \frac{1}{c_p}\left|\frac{dG}{dT}\right| \tau_T \tau_\varepsilon \omega_{\mathbf{k}}^2 \tag{30}$$

is introduced and Eqs. (12), (27) are taken into consideration in the second equality. In accordance with Eq. (28) the temperature T decreases monotonically with increase of the strain ε from the value $T^0 \equiv \tau_T Q$ at $\varepsilon = 0$ to $T^0/2$ at $\varepsilon = \varepsilon_m$. Obviously this decrease is caused by the negative feedback in Eq. (25), that is reflection of the Le Chatelier principle for analised problem. Really the reason of the liquid's self-organization resulting in a glass transition is a positive feedback between the strain and the temperature in Eq. (26). Hence the increase of the temperature should intensify the self-organization effect. However according to Eq. (28) the system behaves so that the consequence of self-organization, i.e., growth of the elastic strain, leads to a decrease of its reason temperature. Eq. (29) expressing the elastic stress in terms of the strain has the linear form of the Hooke law at $\varepsilon \ll \varepsilon_m$ with the effective shear modulus

$$G_{ef} \equiv (a_\sigma/v)\, \tau_T Q = \left|\frac{dG}{dT}\right| \tau_T Q, \tag{31}$$

where the second equality follows from Eq. (12). At $\varepsilon = \varepsilon_m$ the function $\sigma(\varepsilon)$ has a maximum and at $\varepsilon > \varepsilon_m$ it decreases which does not have physical sense. Thus, the constant ε_m, defined by Eq. (30), has the meaning of the maximum strain. As it is visible from Eqs. (30) and (31) the increase of the temperature defect of the modulus $|dG/dT|$ leads to a decrease of the maximum strain ε_m and the increase of effective modulus G_{ef} whose value is proportional to the characteristic temperature $T^0 = \tau_T Q$. On the other hand, the ratio of the characteristic values of the heat energy $E_T = c_p \tau_T Q$ and the elastic one $E_\varepsilon = G_{ef}\varepsilon_m^2$

$$\frac{E_T}{E_\varepsilon} = \tau_T \tau_\varepsilon \omega_k^2 \tag{32}$$

is a small value in accordance with Eq. (23).

Substituting Eq. (29) in Eq. (24) we find the evolution equation of a system in the course of the glass transition:

$$\eta\dot{\varepsilon} = -\frac{\partial V}{\partial \varepsilon}. \tag{33}$$

Its form is determined by dependence $V(\varepsilon)$ of the synergetic potential on the strain:

$$V = \frac{G\varepsilon_m^2}{2}\left[\frac{\varepsilon^2}{\varepsilon_m^2} - \frac{T^0}{T_c}\ln\left(1 + \frac{\varepsilon^2}{\varepsilon_m^2}\right)\right], \tag{34}$$

where the characteristic temperatures

$$T^0 \equiv \tau_T Q, \tag{35}$$

$$T_c \equiv \frac{vG}{a_\sigma} = G\left|\frac{dG}{dT}\right|^{-1} \tag{36}$$

are introduced and Eq. (12) is used in the second equality of Eq. (36). It is interesting to note that the ratio of these temperatures

$$\frac{T^0}{T_c} = \frac{G_{ef}}{G} \tag{37}$$

is reduced to the ratio of the effective elasticity modulus (31) to its characteristic value G. At $T^0 \le T_c$ dependence (34) has a monotonously increasing shape with the minimum at point $\varepsilon = 0$. It means that in the stationary state ($\dot{\varepsilon}=0$) the elastic strain is absent. Thus, the liquid state is realized in which the strain caused by the external stress relaxes during the time

$$\tau_{ef} = \tau\left(1 - T^0/T_c\right)^{-1}. \tag{38}$$

The relaxation time increases infinitely with the growth of the effective temperature T^0 to the critical value T_c, and at $T^0 > T_c$ the system is transformed into the glass state. Here the dependence (38) gets the multiplier 1/2, and the minimum of the synergetic potential corresponds to the elastic strain

$$\varepsilon_0 = \varepsilon_m\left(T^0/T_c - 1\right)^{1/2}. \tag{39}$$

From the physical view point the process of a glass transition is caused by the fact that at $T^0 > T_c$, in accordance with Eq. (37), the effective shear modulus G_{ef} exceeds the characteristic value G. According to Eqs. (35) and (36) the initial reason of a glass transition is the increase of the cooling rate Q to the values exceeding critical quantity

$$Q_c \equiv \frac{G}{\tau_T}\left|\frac{dG}{dT}\right|^{-1} = \left(\frac{2\pi}{L}\right)^2 \frac{\kappa}{c_p} G\left|\frac{dG}{dT}\right|^{-1}. \tag{40}$$

Here at the definition of heat conductivity time $\tau_T = c_p/\kappa k^2$ the value of the wave number $k = 2\pi/L$ is determined by the heat conductivity distance L of a sample. From parameters that determine the value Q_c it is possible to select the kinetic and the synergetic quantities. The first parameters define the heat conductivity time τ_T, and the second ones describe the self-organization process of the elastic and the temperature fields. According to Eq. (40) the first group contains the thermometric conductivity κ/c_p and the heat conductivity distance L of a sample. The growth of the thermometric conductivity results in the increase of the Q_c, and the increase of the heat conductivity distance of a sample has the stronger square contrary effect. The influence of the synergetic factors is defined by the ratio of the shear modulus G to its temperature defect $|dG/dT|$: the less this ratio is the smaller the critical value of the quenching rate becomes. In other words the systems, predisposed to a glass transition, have a relatively small value of the shear modulus strongly dependent on the temperature. Such a situation is realized in polymers [12], among metal glasses the eutectics satisfy to this property [5].

IV. INFLUENCE OF DEFORMATIONAL DEFECT OF MODULUS

The Maxwell equation (7) assumes the use of the idealized Genki model. For the dependence $\sigma(\varepsilon)$ of the stress on the strain this model is represented by the Hooke expression $\sigma = G\varepsilon$ at $\varepsilon < \varepsilon_m$ and the constant $\sigma_m = G\varepsilon_m$ at $\varepsilon \geq \varepsilon_m$ (the stress $\sigma > \sigma_m$ leads to viscous flow with the deformation rate $\dot{\varepsilon} = (\sigma - \sigma_m)/\eta$). Actually, the dependence $\sigma(\varepsilon)$ curve has two regions: the first one, Hookean, has the large slope fixed by the shear modulus G, and is followed by a more gently sloping section of the plastic deformation whose tilt is defined by the hardening factor $\Theta < G$. Obviously the above picture means that the shear modulus, introduced (in terms of the relaxation time (1)) in Eq. (7), depends on the strain value. We use the simplest approximation

$$G(\varepsilon) = \Theta + \frac{G - \Theta}{1 + \varepsilon/\varepsilon_p}, \tag{41}$$

which describes the above represented transition of the elastic deformation mode to the plastic one. It takes place at characteristic value of the strain ε_p which, obviously, does not exceed the maximum value ε_m (in other case the plastic mode is not displayed). As a result the relaxation time (1) gets the dependence on the strain value:

$$\frac{1}{\tau(\varepsilon)} = \frac{1}{\tau_p}\left(1 + \frac{\theta^{-1} - 1}{1 + \varepsilon/\varepsilon_p}\right), \tag{42}$$

where the relaxation time is introduced for the plastic flow mode (cf. Eq. (1))

$$\tau_p = \eta/\Theta, \tag{43}$$

and the quantity

$$\theta = \Theta/G < 1 \tag{44}$$

is the parameter describing the ratio of the tilts for the deformation curve on the plastic and the Hookean domains. Note that the expression type of Eq. (42) was offered, for the first time, by Haken [11] for the description of the rigid mode of the laser radiation. We used it [10] for the description of the first-order phase transition kinetics, however Eq. (42) had contained the square of the ratio $\varepsilon/\varepsilon_p$ (so the V vs. ε dependence had the even form in [10]). At description of the structural phase transitions of a liquid the characteristic of the third order invariants breaking the specified parity is present [13]. Therefore in approximation (42) we used linear term $\varepsilon/\varepsilon_p$, instead of the square one $(\varepsilon/\varepsilon_p)^2$. It is visible, that the following below dependence (46) is not already even.

Within the adiabatic approximation (20) the system of the Lorenz equations (24) – (26), where instead of the τ it is necessary to use dependence $\tau(\varepsilon)$, is reduced as well as higher, to the Landau-Khalatnikov equation (33). However in the synergetic potential (34) the factor G is replaced on Θ and the odd term appears proportional to $G - \Theta$:

$$V = \Theta\frac{\varepsilon_m^2}{2}\left[\frac{\varepsilon^2}{\varepsilon_m^2} - \frac{T^0}{T_{c0}}\ln\left(1 + \frac{\varepsilon^2}{\varepsilon_m^2}\right)\right] + (G - \Theta)\varepsilon_p^2\left(\frac{\varepsilon}{\varepsilon_p} - \ln\left|1 + \frac{\varepsilon}{\varepsilon_p}\right|\right). \tag{45}$$

Here the critical temperature

$$T_{c0} \equiv \frac{v\Theta}{a_\sigma} \tag{46}$$

is introduced (cf. Eq. (36)). At a small value of the effective temperature (35) dependence (46) has a monotonically increasing shape with its minimum at point $\varepsilon = 0$ corresponding to a steady state of a liquid. As is seen from Fig. 1 at the value

$$T_c^0 = T_{c0}\left\{\left(D^{1/2} - q/2\right)^{1/3} - \left(D^{1/2} + q/2\right)^{1/3} - \frac{\alpha^2}{12}\left[\left(\theta^{-1} + 9\right)^2 - 2^2 3^3\right] + 1\right\}; \tag{47}$$

$$\alpha \equiv \varepsilon_p/\varepsilon_m, \quad D \equiv (p/3)^3 + (q/2)^2,$$

$$p \equiv -\frac{1}{3}\left\{(\alpha/2)^2\left[\left(\theta^{-1} + 9\right)^2 - 2^2 3^3\right] - 3\right\}^2 + \left(\alpha^2/\theta\right)\left[(\alpha/\theta)^2 - 5/\theta + 3^2\right] + 3,$$

$$q \equiv \frac{2}{3^3}\left\{(\alpha/2)^2\left[\left(\theta^{-1} + 9\right)^2 - 2^2 3^3\right] - 3\right\}^3 - \frac{1}{3}\left\{(\alpha/2)^2\left[\left(\theta^{-1} + 9\right)^2 - 2^2 3^3\right] - 3\right\} \times$$

$$\times\left\{\left(\alpha^2/\theta\right)\left[(\alpha/\theta)^2 - 5/\theta + 3^2\right] + 3\right\} - \left[(\alpha/\theta)^2 + 1\right]^2$$

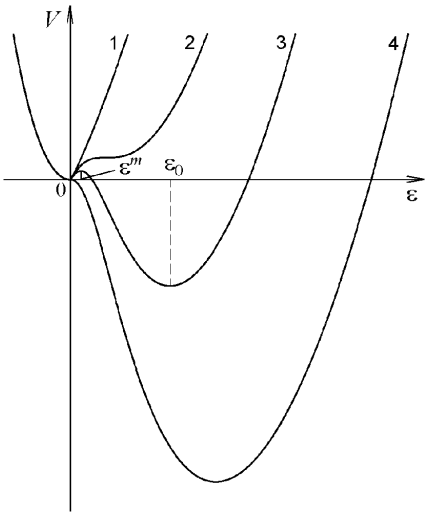

Fig. 1. The dependence of the synergetic potential on the elastic strain at various temperatures: 1) $T^0 < T_c^0$; 2) $T^0 = T_c^0$; 3) $T_c^0 < T^0 < T^c$; 4) $T^0 \geq T^c$.

a plateau appears, which for $T^0 > T_c^0$ is transformed into a minimum corresponding to the strain $\varepsilon_0 \neq 0$ and a maximum ε^m that separates the minima corresponding to the values $\varepsilon = 0$ and $\varepsilon = \varepsilon_0$. With a further growth of the effective temperature T^0 the ordered phase minimum, corresponding to a glass state $\varepsilon = \varepsilon_0$, grows deeper, and the height of the interphase barrier decreases vanishing at the critical value

$$T^c \equiv T_{c0}/\theta = (G/\Theta)T_{c0}, \tag{48}$$

which exceeds critical temperature (46). The steady-state values of the strain in a glassy state have the form (see Figs. 1 and 2):

$$\left.\begin{matrix}\varepsilon_0\\ \varepsilon^m\end{matrix}\right\} = \varepsilon_m \left[2\epsilon \cos\left(\frac{\varphi}{3} \pm \frac{2\pi}{3}\right) - \frac{\alpha}{3\theta}\right]; \tag{49}$$

$$\epsilon \equiv -\mathrm{sign}\,\omega\,(\psi/3)^{1/2}, \quad \cos\varphi \equiv -\omega/2\epsilon^3,$$

$$\psi \equiv \left(\frac{T^0}{T_{c0}} - 1\right) + \frac{(\alpha/\theta)^2}{3},$$

$$\omega \equiv \frac{2\alpha}{3\theta}\left[\left(\frac{\alpha}{3\theta}\right)^2 + 1\right) + \alpha\frac{T^0}{T_{c0}}\left(\frac{\theta^{-1}}{3} - 1\right).$$

At $T^0 \geq T^c$ the dependence $V(\varepsilon)$ has the same character as in the absence of the modulus defect (see the curve 4 in Fig. 1).

The specified peculiarities correspond to the positive strain values ε. On the negative half-axis with the increase of $|\varepsilon|$ a very weak minimum of the V vs. ε dependence is observed, which is followed by the infinite increase of the potential V at $\varepsilon = -\varepsilon_p$. Thus, the negative values of the elastic fields ε, σ are not realized practically.

The characteristic circumstance of our scheme is that energy barrier inherent in the synergetic first-order transition is displayed only at the presence of the deformational defect of the modulus. Since the latter takes place always, it follows that a liquid-glass transition represents synergetic first-order transition. The examined situation is much more complex than usual phase transitions. Really, in the latter case the steady-state value of the system's temperature T_0 is reduced to the value T_{00} fixed by thermostat (it was supposed above $T_{00} = 0$). In our case the medium's temperature exceeds the value T_{00} on magnitude T^0 determined by Eq. (35). The value T^0 is reduced to the critical value T_c for the synergetic second-order transition, that has place in the absence of the modulus defect (see section III). The same situation is realized when we take into account the modulus defect if $T^0 > T^c$. In the $T_c^0 \leq T^0 \leq T^c$ interval the temperature is realized

$$T^m = \frac{T^0}{1 + (\varepsilon^m/\varepsilon_m)^2}, \tag{50}$$

whose value is defined by a maximum position of the dependence (46). Since values T_c and T^m are the minimum values of the temperature at which a glass transition begins, the above means that the negative feedback between the elastic strain ε and the stress σ (see last term in Eq. (25)) reduces the medium's temperature so much that only in the limit does it ensure the self-organization process. According to Eqs. (49), (50) in the interval $T_c^0 \leq T^0 \leq T^c$ the value T_0 smoothly increases from the minimum value

$$T_m = \frac{T_c^0}{1 + \left[3^{-1/2}\left(\frac{T_c^0}{T_{c0}} + \frac{(\alpha/\theta)^2}{3} - 1\right)^{1/2} - \frac{\alpha}{3\theta}\right]^2} \tag{51}$$

to the maximum value T^c. Since in the important range of values of the parameters α and θ limited by the maximum value

$$\theta^m = (\alpha^2/2)\left(\sqrt{1+\alpha^2} - 1\right)^{-1} \tag{52}$$

the minimum system's temperature (51) is lower than the minimum thermostat temperature (47), as it is visible from Fig. 3, in the $(T_c^0,\ T^c)$ interval the temperature T_0 of the medium is always lower than its value T^0 ensured by the cooling of the system with the rate $Q = T^0/\tau_T$. At point $T^0 = T^c$ the values T_0, T^0 are equal, and for $T^0 > T^c$ always $T_0 = T^0 \equiv T^c$.

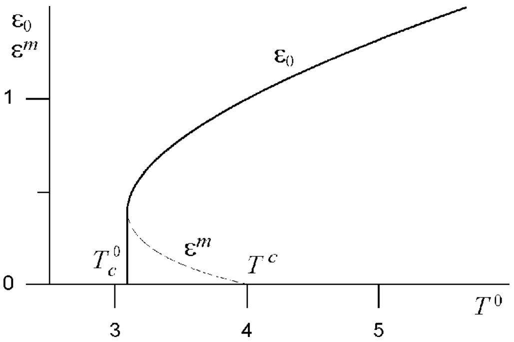

Fig. 2. The dependence of the steady-state values of the strain on the thermostat temperature at $\varepsilon_m = 1,\ T_{c0} = 1,\ \theta = 0,25,\ \alpha = 0,5$ (the solid curve corresponds to the steady state value ε_0, the dashed curve meets the unstable one ε^m).

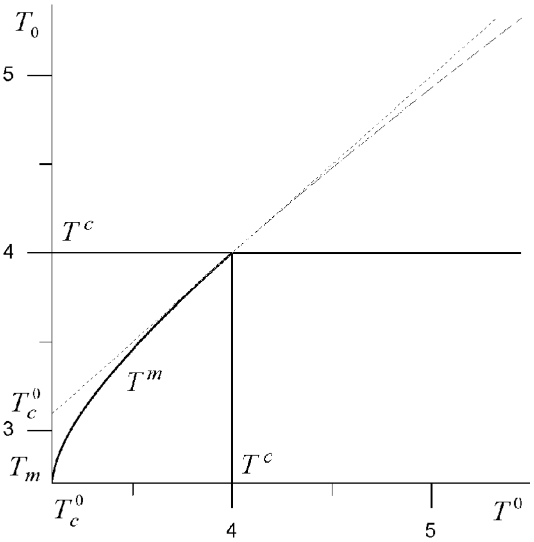

Fig. 3. The dependence of the steady-state value of the system temperature T_0 on the thermostat temperature T^0 ($T_{c0} = 1,\ \theta = 0,25,\ \alpha = 0,5$).

The above analysis is based on the assumption that a glass transition process is caused by the self-organization of shear components of the strain and the stress elastic fields, on the one hand, and the sample temperature, on the other hand. Thus, the strain ε acts as the order parameter, the conjugate field is reduced to the elastic stress σ, and the temperature T is the control parameter. The initial reason of self-organization is the positive feedback between T and ε (see Eq. (26)). According to Eqs. (10), (12) it is caused by the temperature dependence of the characteristic value of the shear modulus. In above expressions we did not take into account the deformational defect of the modulus, therefore the value of the shear modulus G appeared there. However from the reasonings, following from section IV, we see that actually it is necessary to take not the initial value G of the shear modulus which does not change with temperature practically but of the modulus Θ determining the slope of σ vs ε dependence within the region of plastic deformation. Therefore the replacement G by Θ ought to be made in formulas (6), (8), (12), (24), (30), (31), (34), (36), (37), (40). Then, in view of Eq. (48), expression (40) for the critical cooling rate Q^c takes the form of

$$Q^c = \left(\frac{2\pi}{L}\right)^2 \frac{\kappa}{c_p} G \left|\frac{d\Theta}{dT}\right|^{-1}. \qquad (53)$$

It is characteristic that Q^c is defined by both the nonrelaxed shear modulus G and relaxed one Θ.

The kinetics of a glass transition is determined by the Landau-Khalatnikov equation (33), where the synergetic potential has the form (46) inherent in the first-order transition. In supercooled liquid with $\eta = \infty$ the freezing of system can takes place ($\dot{\varepsilon} \to 0$) even in the nonstationary state $\partial V/\partial\varepsilon \neq 0$.

The advanced consideration is phenomenological in nature, that is pertinent to compare with the microscopic theory [14,15]. Within the framework of this theory along with the thermostat temperature T_{00} the intensity of the quenched disorder acts as the state parameter:

$$h^2 \equiv N^{-1}\sum_i (\sigma_i - \bar{\sigma})^2 - N^{-1}\sum_i (\sigma_i(t) - \sigma(t))^2; \quad (54)$$

$$\bar{\sigma} \equiv N^{-1}\sum_i \sigma_i, \quad \sigma(t) \equiv N^{-1}\sum_i \sigma_i(t).$$

This quantity is the difference between the microstress σ_i dispersion and the dispersion of microscopic values $\sigma_i(t)$, which changes close above used [18] macroscopic value $\sigma(t)$ during time $\sim\tau_\sigma$ in fluctuation manner (in Eq. (54) N is the number of atoms, over which the summation is carried out). According to [15] the field $h \neq 0$ results in the appearance of the term $-\left(h^2/2\right)\varepsilon^2$ in the effective Hamiltonian, whose role is acted by the synergetic potential (46) in our case. From here it follows that the quenched disorder

$$h^2 = 2G\left(Q_0 - Q_{c0}\right)/Q^c \qquad (55)$$

appears only at cooling rates exceeding the value

$$Q_{c0} = Q^c\left(1 - \Theta/2G\right). \qquad (56)$$

The obtained dependencies allow to express the results of the microscopic theory in terms of the experimentally observable value: cooling rate Q_0. For the parameters q and Δ we have $q \propto h^{2/3}$, $\Delta \propto h^{2/3} - h_c^{2/3}$ where the critical field h_c corresponds to the cooling rate (53) at which a glass transition leads to the ergodicity breaking. In accordance with [8], for the viscoelastic medium the non-ergodicity parameter $\Delta \propto \eta_g - \eta$ is determined by a difference of the viscosities of a glassy (nonergodic) and a liquid (ergodic) states. As a result accounting for relationship (55) we obtain the expressions:

$$q \propto \left[\left(Q_0 - Q_{c0}\right)/Q^c\right]^{1/3}, \tag{57}$$

$$\Delta \propto \left[\left(Q_0 - Q_{c0}\right)/Q^c\right]^{1/3} - h_c^{2/3}, \tag{58}$$

where $Q_0 > Q_{c0}$. Thus, with the exceeding of the cooling rate in the vicinity of a glass transition point Q^c (at value $Q_{c0} \lesssim Q^c$), the liquid acquires the memory whose parameter begins to increase very rapidly at the point $Q_0 = Q_{c0}$. According to Eq. (58) the defect of the shear viscosity $\eta_g - \eta \propto \Delta$ grows similar sharply at the point of a glass transition. Obviously, the specified peculiarities should be observed experimentally.

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[16] In connection with use of the synergetic concept for the description of a glass transition it is necessary to note that such scheme was already offered earlier [6]. However instead of the temperature the density of site occupation, inversely proportional to nuclear volume was used there. Such model is lattice by means, but is not continual. It yields the critical value not for cooling rate, but for free volume [7].

[17] Note that if the square in σ term in Eq. (18) keeps, the dependencies (28), (29) are expressed in terms of the square equation solutions, that much more complicates the analysis.

[18] Due to adiabatic approximation used above we have proceed from microstress $\sigma_i(t)$ to macroscopic values $\sigma(t)$.