

SELF-ORGANIZATION AND DISSIPATIVE STRUCTURE FORMATION IN NON-CRYSTALLINE MATERIALS

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A model is proposed to describe dissipative structures formation in non-crystalline materials. To investigate temperature dependencies of the share of atoms in liquid-like states and mean-square atomic displacements. It is shown that system transits into non-equilibrium state when the melt freezing rate increases which corresponds of dissipative structures formation in non-crystalline materials.

Introduction

Non-crystalline state of matter represents peculiar self-organizing system with certain degree of ordering and life time, which are determined by external control parameters (temperature, pressure, electromagnetic radiation), and includes sufficiently wide range of materials from glassy matters with organic and non-organic origin to bio-object [1,2,3]. It provides broad range of their properties and character of interaction with external fields.

Example of self-organizing systems is dissipative structures formation, when freezing the melt, for which all above enumerated requirements are fulfilled (technology of freezing process causes presence of open system; feedback is provided by interaction of field of dynamic displacements, viscosity and force constants; transition realizes under certain rate of external conditions change). Solution of this problem is connected with investigation of structure and properties of equilibrium (crystalline, quasicrystalline, liquid) and strongly non-equilibrium (non-crystalline) materials in the vicinity of phase transition.

Model of system

Crystallization of the melt takes place during equilibrium liquid-crystal phase transition, as temperature lowers under thermodynamic equilibrium. Transition model must take into account anharmonicity of atomic oscillations, what is provided by use of self-consistent phonons theory (SCPT) [4] so long as classic harmonic and quasi-harmonic approximations for system in transforming temperature region are not applicable. When heating, as amplitude of heat oscillations increases, quantity of defects goes up, what

leads to their uniting. In phase transition vicinity concentration of such fluctuation essentially rises and as homogeneous atomic heat oscillations has considerable influence on the physical properties of the system [5].

As we approach the temperature T of the solid to the melting temperature T_m , the concentration of the point defects (the internodal atom (vacancy) type) or the extended defects (the dislocation type) increases sufficiently. Such defects taken separately are not the disordered phase nuclei. However, if they are accumulated within a certain macroscopic domain, then such area of disordering corresponds to the structure inherent to the liquid-like (soft) states, i.e. it has a shearing instability, a high level of dynamic displacements and the instability related to the defect formation. Hence, within the phase transformation interval along with the homogeneous fluctuations (i.e. the thermal displacements

The soft states are the specific structural states with the additional degree of freedom in the configurational space. These states are due to the spatial fluctuations of the short-range order parameters (the number and the length of the bonds, the interbond angles) around their average value and the formation of the defect states in the highly non-equilibrium conditions and are intrinsic in the non-crystalline solids. Atoms in the soft states process a considerable level of static displacements and, consequently, the vibrational anharmonism and the lability to the spatial rearrangements. The bonding topology and the configurational parameters which describe the soft states are accounted for and detailed in terms of certain structural models. We shall analyse the general tendencies of the formation of macroscopically

ordered structures in non-crystalline solids away from the equilibrium state, therefore, we shall use the universal characteristics of the soft states.

Consider the system of N similar atoms of mass M , the portion N_f of which being in

$$H = \sum_{l=1}^N T_f(l) \sigma_f(l) + \frac{1}{2} \sum_{l \neq l', f, f'} \Phi_{ff'}(\vec{r}_{ll'}) \sigma_f(l) \sigma_{f'}(l'), \quad (1)$$

where $T_f(l) = \frac{\vec{p}^2(l)}{2M}$ is the kinetic energy of the atom l , $\Phi_{ff'}(\vec{r}_{ll'})$ is an interatomic interaction potential and $\sigma_f(l)$ characterises two sets of locally observed microscopic states:

$$\sigma_f(l) = \begin{cases} 1, & \text{if the atom } l \text{ is in the state } f; \\ 0, & \text{if the atom } l \text{ is not in the state } f. \end{cases}$$

The possibility of the formation of the liquid-like states in the solid is, consequently, $\sigma_f = \langle \sigma_f(l) \rangle = N_f/N$. Let us introduce the effective Hamiltonian of the system:

$$H_0 = \sum_f H_{0f} + (1 - \sigma_2)^2 \sum_{l, l', \alpha} I_\alpha(l, l') v_\alpha(l), \quad v_\alpha(l) = \sum_m v_\alpha(l/m) \sigma_2(m), \quad (2)$$

$$H_{0f} = \sigma_f \sum_l T_f(l) + \frac{\sigma_f^2}{2} \sum_{l, l', \alpha, \beta} \left[\Phi(\vec{R}_{ll'}) + \frac{1}{2} u^\alpha(l, l') \tilde{\Phi}_f^{\alpha\beta}(l, l') u^\beta(l, l') \right],$$

whose model parameters, i.e. the fraction of atoms in the liquid-like states σ_f , the force constants $\tilde{\Phi}_f^{\alpha\beta}(l, l')$ and the mean-square relative displacements of atoms

$y_{\alpha\beta}(l, l') = \langle u^\alpha(l, l') u^\beta(l, l') \rangle$ are calculated on the basis of the variational principle for the free energy functional:

$$F \leq F_0 + \langle H - H_0 \rangle_0, \quad F_0 = \sum_f F_{0f} - TS, \quad F_{0f} = -\Theta \ln \left\{ SP e^{-\frac{H_{0f}}{\Theta}} \right\}, \quad (3)$$

Here $S = -k_b \ln \left[\prod_f \left\{ \frac{g_f!}{N_f! (g_f - N_f)!} \right\} \right]$ is the entropy, g_f is a statistical weight of the state f , $\mathbf{r}_l = \mathbf{R} + \mathbf{u}_l + \mathbf{v}_l$, \mathbf{u}_l and \mathbf{v}_l are the dynamic and the static displacements of atoms, $u_\alpha(l, l') = u_\alpha(l) - u_\alpha(l')$ are the relative

displacements, $v_\alpha(l/m)$ are the static displacements of the atom l when the atom m is in the liquid-like state, $\Theta = k_b T$. The variation of F over the parameters σ ($\sigma = \sigma_2$), $\tilde{\Phi}_f^{\alpha\beta}(l, l')$, $y_{\alpha\beta}(l, l')$ at fixed temperature T and pressure P :

$$\delta F = \left[\frac{\partial F}{\partial \sigma} \right]_{y_{\alpha\beta}, \tilde{\Phi}_f^{\alpha\beta}} \cdot \delta \sigma + \left[\frac{\partial F}{\partial \tilde{\Phi}_f^{\alpha\beta}} \right]_{\sigma, y_{\alpha\beta}} \cdot \delta \tilde{\Phi}_f^{\alpha\beta} + \left[\frac{\partial F}{\partial y_{\alpha\beta}} \right]_{\sigma, \tilde{\Phi}_f^{\alpha\beta}} \cdot \delta y_{\alpha\beta} \quad (4)$$

allows one to determine their temperature dependence for the equilibrium ($\delta F = 0$) and non-equilibrium ($\delta F \neq 0$) transformations. Let us find the functional equations to determine

the probability of the formation of the liquid-like states, force constants and mean-square displacement of atoms. Using equations (2) and (3) for σ we find:

$$\frac{\partial F}{\partial \sigma} = \frac{\partial F}{\partial \sigma} + \frac{\partial}{\partial \sigma} \langle H - H_0 \rangle_0 = \bar{T}_2 - \bar{T}_1 + 2\sigma(\bar{\Phi}_2 - \bar{\Phi}_1) - 2\bar{\Phi}_1 - 4\bar{T}(1 - \sigma)\sigma - 2N \ln \frac{\frac{g_2 - 1}{g_1 - 1}}{1 - \sigma}. \quad (5)$$

Here the following notation has been introduced: $\bar{T}_f = \sum_l \left\langle \frac{\bar{P}_f^2(l)}{2M} \right\rangle$,

$$\bar{\Phi}_f = \frac{1}{2} \sum_{l,l'} \langle \Phi_f(l,l') \rangle, \quad \bar{T} = \left\langle \sum_{l,l',\alpha,m} I_\alpha(\bar{r}_{ll'}) v_\alpha(l/m) \right\rangle.$$

Similarly, the functional equations with

$$\frac{\partial F}{\partial y_{\alpha\beta}(l,l')} = \frac{\partial}{\partial y_{\alpha\beta}(l,l')} \langle H - H_0 \rangle_0 = \frac{1}{4} \left(\langle \nabla_{ll'}^\alpha \nabla_{ll'}^\beta \Phi_f(\bar{r}_{ll'}) \rangle \sigma_f^2 - \bar{\Phi}_f^{\alpha\beta}(l,l') \right), \quad (6)$$

$$\frac{\partial F}{\partial \bar{\Phi}_f^{\alpha\beta}(l,l')} = \frac{\partial F_0}{\partial \bar{\Phi}_f^{\alpha\beta}(l,l')} + \frac{\partial}{\partial \bar{\Phi}_f^{\alpha\beta}(l,l')} \langle H - H_0 \rangle_0 = \frac{\hbar}{2MN} \sum_k \frac{\sin^2 \frac{\bar{k}\bar{r}_{ll'}}{2}}{\omega(\bar{k})} \coth \frac{\hbar\omega}{2\Theta} - \frac{y_{\alpha\beta}(l,l')}{4}. \quad (7)$$

In the non-equilibrium non-crystalline state, ($\delta F \neq 0$). Expanding F into a power series in the system deviation from the equilibrium state and restricting ourselves to the first terms of the expansion, we have:

$$F = F_0 + \frac{1}{2} \sum_{i,j} a_{ij} \eta_i \eta_j + \frac{c}{3} \eta^3 + \frac{b}{4} \eta^4, \quad (8)$$

where the following notations are used:

$$\eta = \sigma - \sigma_e, \quad \eta_y = \left\{ \eta_y^\alpha \right\}, \quad \eta_y^\alpha = y_\alpha(l,l') - y_\alpha(l,l')_e, \\ \eta_\Phi = \left\{ \eta_\Phi^\alpha \right\}, \quad \eta_\Phi^\alpha = \bar{\Phi}^{\alpha\alpha}(l,l') - \bar{\Phi}^{\alpha\alpha}(l,l')_e,$$

$$a_{ij} = \left(\frac{\partial^2 F}{\partial \eta_i \partial \eta_j} \right)_e, \quad c_{ijk} = \frac{1}{2} \left(\frac{\partial^3 F}{\partial \eta^3} \right)_e, \quad b_{ijk} = \frac{1}{6} \left(\frac{\partial^4 F}{\partial \eta^4} \right)_e$$

and the allowance was made for $\left(\frac{\partial F}{\partial \eta_i} \right)_e = 0$ (the subscript "e" corresponds to the equilibrium state).

To describe the kinetics of the order parameter variation we shall use the Landau-Khalatnikov regression equation [7]

$$\frac{\partial \eta_i}{\partial t} = -\gamma_i \left(\frac{\partial F}{\partial \eta_i} \right)$$

which allows one in relations

$$\lambda^{-1} \frac{\partial \eta}{\partial t} = -a_0 \eta - c \eta^2 - b \eta^3 - D_\eta \nabla \eta, \quad a_0 = - \left(a_{11}^2 - \frac{a_{12}}{a_{22}^2} - \frac{a_{13}}{a_{33}^2} \right). \quad (10)$$

The expansion coefficients are the functions of the temperature, pressure and control parameter, i.e. the cooling rate is:

respect to the quantities $y_{\alpha\beta}(l,l')$ and $\bar{\Phi}_f^{\alpha\beta}(l,l')$ are found:

(8) to obtain the following system of non-linear kinetic equations:

$$\lambda^{-1} \frac{\partial \eta}{\partial t} = -a_{11} \eta - a_{12} \eta_y - a_{13} \eta_\Phi - c \eta^2 - b \eta^3 - D_\eta \nabla \eta, \\ \lambda^{-1} \frac{\partial \eta_y}{\partial t} = -a_{12} \eta - a_{22} \eta_y, \quad \lambda^{-1} \frac{\partial \eta_\Phi}{\partial t} = -a_{13} \eta - a_{33} \eta_\Phi. \quad (9)$$

The first terms in these equations describe the energy dissipation with relaxation time of $\tau_{ij} = a_{ij}^{-1}$, while the second terms define the collective mode interaction.

Let us draw on the Prigogine principle of mode subordination which holds for highly non-equilibrium systems [8]. According to this principle:

$$\frac{\partial \eta_y}{\partial t} = 0, \quad \frac{\partial \eta_\Phi}{\partial t} = 0.$$

This allows one to reduce the number of

order parameters: $\eta_y = - \left(\frac{a_{12}}{a_{22}} \right) \eta$, $\eta_\Phi = - \left(\frac{a_{13}}{a_{33}} \right) \eta$ and rewrite (9) in the following form:

$a_0 = a_0(T, P, q)$. Since in the equilibrium state: $\delta F = 0$, $\delta^2 F > 0$ and $\eta = 0$, then, to ensure this, $a_0(T, P, q)$ must be a positively defined matrix,

i.e. $a_0(T, P, q) > 0$. In the non-equilibrium state $\delta F \neq 0$, $\eta \neq 0$. To provide the formation of the stationary states with non-zero order parameter, it is essential that $a_0(T, P, q) < 0$. Thus, at the transition to the non-equilibrium state with non-zero order parameter:

$$\eta = \frac{-2c \pm \sqrt{4c^2 - 4a_0b}}{6b}, \text{ and the expansion}$$

coefficient is $a_0(T_c, P_c, q_c) = 0$. Here the following conditions must hold: $c(T_c, P_c, q_c) = 0$, $b(T_c, P_c, q_c) > 0$, since, with the approach to the point T_c, P_c, q_c from the equilibrium state side, an even derivative should be positive. Thus, in the process of melt cooling and at the transition to the non-

crystalline state, $a_0(T_c, P_c, q_c)$ can be approximated by:

$$a_0(T_c, P_c, q_c) = -\tilde{a}_0 \ln(\arctan[\tilde{q}]), \quad \tilde{q} = \frac{q - q_c}{q_c},$$

which is transformed to $a_0(T_c, P_c, q_c) \approx -a_0 \tilde{q}$ as $\tilde{q} \ll 0$.

Thus, started from expressions (5)-(10), we arrive at the following self-consistent system of equations with respect to the relative fraction of atoms s in the liquid-like states, the mean-square atomic displacements $y_{\alpha\beta}(l, l')$ and force constants $\tilde{\Phi}_f^{\alpha\beta}(l, l')$:

$$F_1(\sigma) = 0, \quad F_2(y) = 0, \quad F_3(\Phi) = 0. \quad (11)$$

Here:

$$F_1(\sigma) = \tilde{T}_2 - \tilde{T}_1 + 2\sigma(\tilde{\Phi}_2 - \tilde{\Phi}_1) - 2\tilde{\Phi}_1 - 4\tilde{T}(1 - \sigma)\sigma - 2\Theta N \ln \frac{\frac{g_2 - 1}{\sigma} + \tilde{a}_0 \tilde{q} \eta - c\eta^2 - b\eta^3 - D_n \nabla^2 \eta}{\frac{g_1 - 1}{1 - \sigma}},$$

$$F_2(y) = \frac{\hbar}{2MN} \sum_{\vec{k}} \frac{\sin^2 \frac{\vec{k} \vec{r}_{ll'}}{2}}{\omega(\vec{k})} \coth \frac{\hbar \omega}{2\Theta} \frac{y_{\alpha\beta}(l, l')}{4} \frac{\eta_y}{\tau_y},$$

$$F_3(\Phi) = \frac{1}{4} \left(\left\langle \nabla_{ll'}^\alpha \nabla_{ll'}^\beta \Phi_f(\vec{r}_{ll'}) \right\rangle \sigma_f^2 - \tilde{\Phi}_f^{\alpha\beta}(l, l') \right) - \frac{\eta_\Phi}{\tau_\Phi}.$$

This system allows the temperature properties of the system to be studied both at the equilibrium ($\eta = 0$) and highly non-equilibrium ($\eta \neq 0$) transformations.

Self-consistent description of non-equilibrium systems

Consider the application of the above concepts to the studies of the stability and metastable states formation in the certain solid-state model in the high-temperature region ($\theta \gg \hbar \omega_L$, ω_L is a maximum frequency of vibrations). Let us describe the interatomic interaction through the effective pair potential of the following type $\Phi(r) = \Phi_1(r) + \Phi_2(r)$, where its short-range component $\Phi_2(r)$ can be approximated by the hard-sphere potential ($\Phi_2(r) = \Phi_0$ at $r < a$ or $\Phi_2(r) = 0$ at $r > a$) and the long-range one $\Phi_1(r)$ can be presented in the form of a sum of the central Morse-like potential:

$$\left(\Psi(r) = V_0 \left[\exp\left\{-12 \frac{r-a}{r}\right\} - 2 \exp\left\{-6 \frac{r-a}{r}\right\} \right] \right) \text{ and}$$

the non-central potential

$$\left(G(\delta) = -G_0 \exp\left\{-4 \left(\frac{\delta}{a}\right)^2\right\} \right), \text{ where } \delta \text{ is the}$$

deflection of the atom in the plane normal to the direction of the bond, G_0 and V_0 are the potential parameters.

Solution results of self-consistent system (12) in equilibrium and non-equilibrium states with the use of the iteration procedure are shown in Fig.1. In temperature dependencies ($\tau = \theta/V_0$ is a reduced temperature) of share of atoms in liquid-like states we can mark out five distinctive parts which correspond to different system states:

- stable: part a-b - crystalline ordered state, part e-f - liquid disordered state;
- metastable: part b-c - super-heated crystal, part d-c - super-cooled liquid;
- virtual system state: part c-d - state is thermodynamically unstable.

During increase of the melt freezing rate, the narrowing of temperature range of metastable regions existence and phase

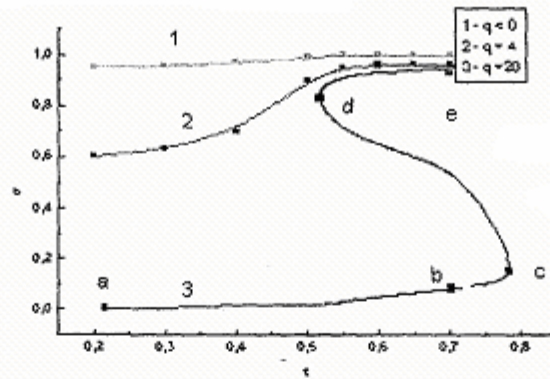


Fig. 1. Temperature dependence of the share of atoms in liquid-like states.

transition point shift to lower temperatures area are observed. When q reaches certain critic value metastable regions completely vanish and system transits into non-equilibrium state. The degree of the system deviation from equilibrium is defined by deviation of order parameter from its equilibrium value (Fig.1).

Non-crystalline materials formation needs considerable system deviation from equilibrium state when phase transition takes place. Deviation value is defined by external control parameter-freezing rate. As freezing rate is higher than critic to represent transition character we must take into account occurred in the system bifurcations, which lead to dissi-

pative structures formation. For example, in region $q < q_c$, system is in equilibrium under different values of external control parameter [10].

During the melt cooling under strongly non-equilibrium conditions the part of system energy, which is in the atoms and molecules heat motion, transits in macroscopic organized motion by spatial-temporal correlation. This motion stipulates formation of complex spatial system organization (dissipative structure), when the largest dissipation of the energy is observed. In stationary case, formed dissipative structures are stable formations with distinctive shape and volume, and as shape so volume is stable to low disturbances.

REFERENCES

1. Mar'yan M.I. Izv. VUZov. , **12**, 5 (1990).
2. Bablojanc A . Molecules, dynamics and life. - New York, Chichester Brisbane, Toronto, Singapore (1986) 374.
3. Mar'yan M.,Kikineshy A , Mishak A. Phil. Mag. B, **68** , 5, 688 (1993).
4. Plakida N.M. Double-time Green's function method in the theory of anharmonic anharmonic crystals./ Stat.physics and quantum field theory, Moscow,Nauka,(1973) 205 p.
5. Yukalov V.I. Phys. Rev. B: Condens. Matter. **32** ,32, 436(1985).
6. Keizer J. Statistical thermodynamics of non-equilibrium processes. - New York. Springer - Verlag (1987) 608.
7. Николис Г., Пригожин И. Познание сложного, Мир. Москва, (1990) 342.
8. Haken H. Phys. Script., **35**, 247 (1987).
9. Shatalov A.A., Mar'yan M.I., Kikineshy A.A. Proc. Conf. Intelligent Materials. Paris - (1996) 105.
10. Tadic B. Phil. Mag. B. **77**, 2, 277 (1998).

САМООРГАНІЗАЦІЯ ТА ФОРМУВАННЯ ДИСИПАТИВНИХ СТРУКТУР В НЕКРИСТАЛІЧНИХ МАТЕРІАЛАХ

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Розглянуто модель формування дисипативних структур в некристалічних матеріалах. Досліджено температурну залежність долі атомів в рідкоподібних станах, середньоквадратичних зміщень атомів. Показано, що в залежності від швидкості охолодження відбувається перехід системи в нерівноважний стан, який супроводжується формуванням дисипативних структур.