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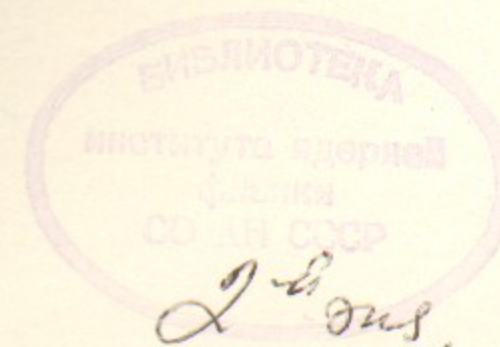
MODEL OF STRUCTURAL PHASE TRANSITIONS IN AMORPHOUS SYSTEMS

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Abstract

Within the framework of the statistical theory of crystal ordering the polimorphic (structural) phase transitions (PPT) in amorphous systems (liquid, glass) are studied. The PPT changes the parameters of the tangent lattice, the latter is the generalisation of the crystal lattice onto the case of amorphous systems. The local structure parameters are introduced as the invariants of the crystal-order parameters. The simple hamiltonian is proposed and the corresponding phase diagram is studied in the mean-field approximation (MFA). The system displays the line of the I-order phase transitions (PT) in the liquid, terminating in the critical point of "structural boiling". It is shown that on the line of the coexistence the local structure of crystal and liquid may be different. Some physical implications are indicated. The possibility of the application of the theory to some physical systems is briefly discussed.

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1. The statistical theory of the condensed matter (crystal, liquid, glass) proposed recently by Patashinskii and Shumilo [1,2] gives the "unified "description of the properties and structure of both anisotropic and amorphous phases, by introducing the idea of the tangent lattice. Namely, the atoms of the small volume δV of the condensed matter (containing $n_o \sim 10^2 \div 10^3$ atoms) can be mapped onto the lattice sites of an ideal lattice. Changing the position and orientation in space of the ideal lattice one can achieve its tangency to the physical system in volume δV. Then, the coincidence of the atoms' positions and their images in the lattice is maximal. The mapping can be continued along the paths in the volume of the system and is characterized by the rotation $\hat{g}(\vec{r})$ of the ideal lattice from the fixed initial orientation to its tangent position in each volume $\delta V(\vec{r})$. This rotation is the important characteristic of the mapped configuration of atoms. The bifurcation of the mapping which may rise when moving along the closed path reflects some properties of the linear defects of the structure. The physical picture of the configurations we are dealing with is as follows. Along any path which does not cross the line of the defect the distribution of atoms ressembles that of the thin pivot cut from the monocrystal along some line and bent in a continuous way. It's important that the domain of such a "good" material is connected and that any 2-dimensional section of the system passes mainly through the "good" material. The "patches" due to the intersection with the lines of the defects are disconnected.

It's well known that in crystals the competition of the types of lattices gives rise to the polimorphic phase transition (PPT) with the discontinuous change of the type of the lattice. The picture of the amorphous state described above enables one to study the phase transition (PT) with the discontinuous change of the type of local lattice also in an amorphous system. The requirements for such a PT are that the two competing types of local order which define the types of the tangent lattices differ strongly so that the intermediate configurations have great values of energy. As the result, the connection property of the "good" material yields the surface energy between the domains with different local structures. The order

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parameters describing the PPT in the amorphous system are the scalar characteristics of the local structure - the invariants of the tensor moments of density of atoms. The more detailed study of these parameters and the liquid-liquid PT is given in paper [3] of Patashinskii. When moving along the line of the PPT in the amorphous system (liquid) into the domain of high temperatures, this line can terminate in a critical point. The thermodynamical study of the PPT was given in paper of Patashinskii and Shumilo [4].

In our earlier works we studied the models of melting, crystallization [5,6] and the PPT in crystals [7] in the case when the local order was fixed and the only degrees of freedom were that described by rotation $\hat{g}(\vec{r})$. In compound systems with a few components their relative rotation may change the total local order while the local order of the components maintains fixed. Such the systems can be studied in the framework of papers [5,6].

The aim of this paper is to perform such the calculations for the system in which the change of the local order is possible due to the relative rotation of fixed local structures of its two components.

2. In the crystal phase the global point-symmetry changes at the PPT. On the contrary, in amorphous systems the global symmetry keeps isotropic, i.e. there are not any long-range correlations of the relative orientations of the local crystal order parameters (the structure tensors $T_{\alpha\beta\gamma\delta}$ [5]). On the other hand, from the arguments presented above it follows that there can exist the long-range correlations of the invariants ψ_i of these tensors (see [3]). Then, the PPT in an amorphous matter would be a phase transition (PT) with the (discontinous) change of local structure parameter $\langle \psi_i \rangle$, where the brackets denote the statistical-mechanics average. To study such the PT, one must account for the fluctuations of the positions of atoms in $\delta V(\vec{r})$, giving rise to the fluctuations of invariants ψ_i. Instead, we will use the more simple in treatment parametrisation of the set of the local configurations. Namely, consider in each point $\vec{r}$ the two ideal lattices, characterized by local crystal order parameters $T^{(i)}_{\alpha\beta\gamma\delta}(\vec{r})$, ($i = 1,2$). The fluc-

tuations of their relative orientations give rise to the fluctuations of the invariants ψ_i of the total local crystal order parameter $T_{\alpha\beta\gamma\delta}(\vec{r}) \equiv T^{(1)}_{\alpha\beta\gamma\delta}(\vec{r}) + T^{(2)}_{\alpha\beta\gamma\delta}(\vec{r})$ of the tangent lattice. Let's define the simplest local structure parameter, i.e. the invariant of the tensor $T_{\alpha\beta\gamma\delta}(\vec{r})$:

$$p(\vec{r}) = T^{(1)}_{\alpha\beta\gamma\delta}(\vec{r}) \, T^{(2)}_{\alpha\beta\gamma\delta}(\vec{r}) . \qquad (1)$$

In this paper Einstein's summation convention is used. Note that $p(\vec{r})$ has the meaning of the local energy of interaction of the two lattices [5,6].

Consider the following hamiltonian of the crystal-amorphous structure

$$-\mathcal{H}(\vec{r},\vec{r}') = J \sum_{i=1}^{2} T^{(i)}(\vec{r}) T^{(i)}(\vec{r}') + \gamma \left\{ T^{(1)}(\vec{r}) T^{(2)}(\vec{r}') + T^{(1)}(\vec{r}') T^{(2)}(\vec{r}) \right\}$$
$$+ U(p(\vec{r}), p(\vec{r}')), \qquad (2)$$

where, for the sake of simplicity, the tensor indices are not written out explicitly. The first two terms are the standard crystal order hamiltonians [5,6], the third one describes the interaction of the crystal-order parameters of the two lattices. The last term, describing the interaction of the invariants, plays the crucial role in the PPT in the amorphous phase (i.e. when $\langle T^{(i)}_{\alpha\beta\gamma} \rangle = 0$). It should fulfill the two following conditions. First, the interaction of the local structure parameters $p(\vec{r})$ and $p(\vec{r}')$ of the two neighbouring $\delta V(\vec{r})$ and $\delta V(\vec{r}')$ must be of the "ferromagnetic" type since, as stated above, the policrystallic configurations of atoms are of small probability. Second, the local (i.e. in each point $\vec{r}$) energy should have at least two minima, corresponding to two nonequal values of invariants. The stability of these minima should depend on the parameters of the hamiltonian. The simplest hamiltonian $U(p(\vec{r}), p(\vec{r}'))$ satysfying these requirements is

$$U(p(\vec{r}), p(\vec{r}')) = \frac{\alpha}{2} \left(p(\vec{r}) + p(\vec{r}') \right) + \mu \, p(\vec{r}) p(\vec{r}'), \qquad (3)$$

where $\mu > 0$.

3. Since we are mainly interested in revealing the effect of the PPT in amorphous systems, we'll make some simplifying assumptions which do not affect qualitatively the results. First, we'll consider the simple case of the locally cubic system, i.e. when the tensors $T^{(i)}_{\alpha\beta\gamma\delta}(\vec{r})$ have the cubic point-symmetry. The generalization to the case of the other point-symmetries can be done easily following the lines of [7]. Next, we'll study the case when the allowed orientations of the local crystallographic axes of $T^{(i)}_{\alpha\beta\gamma\delta}(\vec{r})$ with respect to a fixed coordinate system form a discrete set $S^{(i)}$. The qualitative results are the same as in the case of the continuous rotation of $T^{(i)}_{\alpha\beta\gamma\delta}(\vec{r})$; the problem of the equivalence of the two approaches was studied in [6]. For the set $S^{(i)}$ we take the four orientations $\{\hat{g}^{(i)}_k, k=1,...4\}$ defined in [5], and study the case when $\hat{g}^{(1)}_k = \hat{g}^{(2)}_k$. Then, the hamiltonians $\mathcal{H} = -T^{(i)}(\vec{r})T^{(k)}(\vec{r})$ ($i, k = 1, 2$) are the ones of the 4-state Potts model [5].

The thermodynamics of the system with the hamiltonian $\mathcal{H}$, eqs (2),(3) will be studied in the mean-field approximation (MFA) approach of [5-7]. The MFA equations are

$$\langle T^{(i)}_{\alpha\beta\gamma\delta}\rangle = Z^{-1} \sum_{\{\hat{g}^{(1)}_k, \hat{g}^{(2)}_k\}} T^{(i)}_{\alpha\beta\gamma\delta} e^{-\beta\mathcal{H}_{MFA}}, \quad (4a)$$

$$\langle p\rangle = Z^{-1} \sum_{\{\hat{g}^{(1)}_k, \hat{g}^{(2)}_k\}} p\, e^{-\beta\mathcal{H}_{MFA}}, \quad (4b)$$

where

$$Z = \sum_{\{\hat{g}^{(1)}_k, \hat{g}^{(2)}_k\}} e^{-\beta\mathcal{H}_{MFA}}, \quad (4c)$$

$$-\mathcal{H}_{MFA} = \sum_{j,i=1}^{2} C_{ij}\langle T^{(i)}\rangle T^{(j)} + \alpha p + \mu\langle p\rangle p, \quad (4d)$$

$$C_{11} = C_{22} = J \quad ; \quad C_{12} = C_{21} = \gamma .$$

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Here, β denotes the inverse temperature. The solutions $\langle T^{(i)}_{\alpha\beta\gamma\delta}\rangle_0$ and $\langle p\rangle_0$ of eqs. (4) extremalize the thermodynamic potential F :

$$\left.\frac{\partial F}{\partial\langle T^{(i)}_{\alpha\beta\gamma\delta}\rangle}\right|_0 = 0 \quad ; \quad \left.\frac{\partial F}{\partial\langle p\rangle}\right|_0 = 0 . \quad (5)$$

4. In our discrete model the invariants $p(\vec{r})$ can take only two values since $T_{\alpha\beta\gamma\delta}(\hat{g}_K)T_{\alpha\beta\gamma\delta}(\hat{g}_L) \sim \delta_{KL}$. From 16 relative orientations of the axes of $T^{(i)}_{\alpha\beta\gamma\delta}(\vec{r})$ in our model 4 correspond to the coincidence of the local lattices $(\hat{g}^{(1)}_k = \hat{g}^{(2)}_k, k=1,...4)$ while the other 12 $(\hat{g}^{(1)}_k, \hat{g}^{(2)}_L, k \neq L = 1,...4)$ describe an "orthogonal" relative orientations of the axes of $T^{(i)}_{\alpha\beta\gamma\delta}(\vec{r})$. The solutions of eqs. (4) displaying at $T \equiv \beta^{-1} = 0$ such the properties globally (i.e. in each point $\vec{r}$) will be referred to, correspondingly, as the "parallel" (p) and "orthogonal" (O) phases.

For the p -phase straightforward but tedious algebra yields the following results. The temperature dependence of the crystal-order parameters $\langle T^{(i)}_{\alpha\beta\gamma\delta}\rangle$ can be expressed via one scalar amplitude $h(\beta)$:

$$\langle T^{(i)}_{1123}\rangle(\beta) = \langle T^{(i)}_{2213}\rangle(\beta) = \langle T^{(i)}_{3312}\rangle(\beta) = h(\beta) \quad (i=1,2). \quad (6)$$

The orientation of the two lattices, corresponding to eq.6 at $\beta^{-1} = 0$ is given by $\hat{g}^{(1)}_k = \hat{g}^{(2)}_k$ for some fixed k. As shown in [5] the temperature dependence of these three parameters yields that of all the others. The thermodynamics of the p -phase can be studied via the MFA eqs. (4) which take the form

$$F_p = \frac{27}{4 \cdot 28}\frac{\mu}{J+\gamma}\langle p\rangle^2 + \frac{81}{4}h^2 - \frac{1}{\beta}\ln Z_p, \quad (7a)$$

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$$Z_P = e^{-\tilde{\beta}(\tilde{\alpha}+\tilde{\mu}\langle P\rangle)}\left\{\left(e^{-6\bar{\beta}h}+3e^{2\bar{\beta}h}\right)e^{4\bar{\beta}(\tilde{\alpha}+\tilde{\mu}\langle P\rangle)}+\right.$$

$$\left.+12\,ch\,2\bar{\beta}h\right\},\qquad (7b)$$

$$h = \frac{4}{27}\frac{1}{Z_P}e^{-\tilde{\beta}(\tilde{\alpha}+\tilde{\mu}\langle P\rangle)}\left\{\left(-e^{-6\bar{\beta}h}+e^{2\bar{\beta}h}\right)e^{4\bar{\beta}(\tilde{\alpha}+\tilde{\mu}\langle P\rangle)}+\right.$$

$$\left.+4\,sh\,2\bar{\beta}h\right\},\qquad (7c)$$

$$\langle P\rangle = 42\left(\frac{4}{27}\right)^2\frac{1}{Z_P}e^{-\tilde{\beta}(\tilde{\alpha}+\tilde{\mu}\langle P\rangle)}\left\{\left(e^{-6\bar{\beta}h}+3e^{2\bar{\beta}h}\right)e^{4\bar{\beta}(\tilde{\alpha}+\tilde{\mu}\langle P\rangle)}-\right.$$

$$\left.-4\,ch\,2\bar{\beta}h\right\},\qquad (7d)$$

where $\tilde{\beta}=14\cdot\frac{4}{27}\beta$, $\bar{\beta}=(J+\gamma)\tilde{\beta}$, $\tilde{\mu}=\mu\frac{4}{27}$, $\tilde{\alpha}=\alpha\cdot\frac{4}{27}$ and index "p" denotes the parallel phase.

Analogously, for the o-phase the crystal order parameters are defined by two scalar amplitudes $x(\beta)$, $y(\beta)$

$$\langle T^{(1)}_{1123}\rangle(\beta)=\langle T^{(2)}_{1123}\rangle(\beta)=y(\beta),\qquad (8a)$$

$$\langle T^{(1)}_{2213}\rangle(\beta)=\langle T^{(1)}_{3312}\rangle(\beta)=-\langle T^{(2)}_{2213}\rangle(\beta)=-\langle T^{(2)}_{3312}\rangle(\beta)=x(\beta).\qquad (8b)$$

The orientation of the two lattices corresponding to eq. 8 at $T=0$ is given by $\hat{g}^{(1)}_k$, $\hat{g}^{(2)}_l$ for some fixed numbers $k\neq l$. The thermodynamics of the o-phase will be examined with the help of the MFA equations (4):

$$F_o = \frac{27}{4\cdot 28}\mu\langle P\rangle^2 + \frac{27}{2}(J-\gamma)x^2 + \frac{27}{4}(J+\gamma)y^2 - \frac{1}{\tilde{\beta}}\ln Z_o,\qquad (9a)$$

$$Z_o = 2\,e^{-\tilde{\beta}(\tilde{\alpha}+\tilde{\mu}\langle P\rangle)}\left\{e^{4\bar{\beta}(\tilde{\alpha}+\tilde{\mu}\langle P\rangle)}2\,ch\,2\bar{\beta}y + e^{-2\bar{\beta}y}ch\,4\mathring{\beta}x+\right.$$

$$\left.+e^{2\bar{\beta}y}+4\,ch\,2\mathring{\beta}x\right\},\qquad (9b)$$

$$y = \frac{8}{27}\frac{1}{Z_o}e^{-\tilde{\beta}(\tilde{\alpha}+\tilde{\mu}\langle P\rangle)}\left\{e^{4\bar{\beta}(\tilde{\alpha}+\tilde{\mu}\langle P\rangle)}2\,sh\,2\bar{\beta}y + e^{2\bar{\beta}y}-\right.$$

$$\left.-e^{-2\bar{\beta}y}ch\,4\mathring{\beta}x\right\},\qquad (9c)$$

$$x = \frac{8}{27}\frac{1}{Z_o}e^{-\tilde{\beta}(\tilde{\alpha}+\tilde{\mu}\langle P\rangle)}\left\{2\,sh\,2\mathring{\beta}x + e^{-2\bar{\beta}y}sh\,4\mathring{\beta}x\right\},\qquad (9d)$$

$$\langle P\rangle = \left(\frac{4}{27}\right)^2\frac{28}{Z_o}e^{-\tilde{\beta}(\tilde{\alpha}+\tilde{\mu}\langle P\rangle)}\left\{6e^{4\bar{\beta}(\tilde{\alpha}+\tilde{\mu}\langle P\rangle)}ch\,2\bar{\beta}y - e^{2\bar{\beta}y}-\right.$$

$$\left.-e^{-2\bar{\beta}y}ch\,4\mathring{\beta}x - 4\,ch\,2\mathring{\beta}x\right\},\qquad (9e)$$

where $\mathring{\beta}=(J-\gamma)\tilde{\beta}$; index "o" denotes the orthogonal phase.

In what follows, some solutions of eqs. (7) and (9) will be found and the corresponding phase diagrams will be constructed in the space of the parameters of the theory $(\beta,J,\gamma,\alpha,\mu)$.

5. In this section the case when $\mu/J\gg 1$, $\mu/\gamma\gg 1$ will be studied. Then the $U(P)$ term in hamiltonian (2) becomes dominant and the solutions of eqs. (7) and (9) can be studied perturbatively. Physically, such a situation corresponds to a system where the surface tension of the structureless domain separating the two regions with different local structures (non-equal invariants) is large. This effect can be expected e.g. in systems with Coulomb forces.

5.1 Consider first the phase diagram of the liquid, i.e. when the crystal-order parameters vanish ($h=0$; $x=y=0$). Above the melting temperature of the crystal phases this phase diagram is exact, while below, the small corrections of relative order $(\mu/J)^{-1}\ll 1$ due to the non-zero values of the crys-

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tal-order parameters can be accounted for. The eqs (7d) and (9e) take the form

$$\left(\frac{27}{4}\right)^2 \frac{1}{42}\left\{\frac{V}{4\widetilde{\beta}\widetilde{\mu}} - \frac{\alpha}{\mu}\right\} = \frac{e^V - 1}{e^V + 3} \quad , \qquad (10)$$

where $V = 4\widetilde{\beta}\left(\widetilde{\alpha} + \widetilde{\mu}\langle p \rangle\right)$. Eq. (10) describes the PPT in the liquid phase. The graphical representation of eq. (10) and some characteristic cases are shown schematically in fig. 1. The character of the PPT depends on the value of $\frac{\alpha}{\mu}$. Consider first the case shown in fig. 1a, i.e. when $0 < \alpha/\mu < (\alpha/\mu)_{cr}$. The P.T. is the first order one, both the low-and high-temperature phases are the p -phases (the dashed line). When the value of α/μ is large enough, $\alpha/\mu > (\alpha/\mu)_{cr}$, there is no PPT. The local structure parameter changes continuously at all temperatures $T \equiv \widetilde{\beta}^{-1}$. When $14 \cdot \left(\frac{4}{27}\right)^2 > \alpha/\mu > (\alpha/\mu)_{cr}$ there exists the lower metastable branch, corresponding to the O -phase. When $\alpha/\mu > 14 \cdot \left(\frac{4}{27}\right)^2$ this branch disappears. This situation is shown in fig. 1,b. The value $\alpha/\mu = (\alpha/\mu)_{cr}$ corresponds to the critical point of the line of I-order PPT. This case is shown in fig. 1,c. At the critical temperature $\left(1/\widetilde{\beta}\widetilde{\mu}\right)_{cr}$ the tangent line to the plot is vertical (the dashed line). One finds

$$\left(\frac{\alpha}{\mu}\right)_{cr} = 14\left(\frac{4}{27}\right)^2 (\ln 3 - 1) \approx 3 \cdot 10^{-2} \qquad (11)$$

When $-14 \cdot \left(\frac{4}{27}\right)^2 < \alpha/\mu < 0$ there exist both upper and lower branches of V . At $T = 0$ the upper one is stable while at $T \to \infty$ there is only the lower one left. The PPT takes place between the low temperature p -phase and the high temperature O -phase of the liquid, as shown in fig. 1,d. For $-42\left(\frac{4}{27}\right)^2 < \alpha/\mu < -14\left(\frac{4}{27}\right)^2$ both the solutions exist but the p -phase turns out to be metastable. There is no PPT; the amorphous order parameter which describes the O -phase changes continuously at all temperatures T . Finally, when $\alpha/\mu < -42\left(\frac{4}{27}\right)^2$ there is only the O -phase left, as shown in fig. 1,e.

Let's study the phase diagram, corresponding to eqs (7a), (9a) and (10). The low-temperature expansion of the free ener-

gies (7a),(9a) yields

$$F_p^{(L)} = -63\left(\frac{4}{27}\right)^2 - 3\frac{\alpha}{\mu} \quad , \quad \left(\frac{\alpha}{\mu} > -42\left(\frac{4}{27}\right)^2\right), \qquad (12a)$$

$$F_0^{(L)} = -7\left(\frac{4}{27}\right)^2 + \frac{\alpha}{\mu} - \frac{\ln 3}{\widetilde{\beta}\widetilde{\mu}} \quad , \quad \left(\frac{\alpha}{\mu} < 14\left(\frac{4}{27}\right)^2 \text{ at } T = 0\right), \qquad (12b)$$

where $\left(\widetilde{\beta}\widetilde{\mu}\right)^{-1} \to 0$. The phase diagram at $T = 0$ is given in fig. 2. The line of the PPT $\left(F_p^{(L)} = F_0^{(L)}\right)$ is (at $\left(\widetilde{\beta}\widetilde{\mu}\right)^{-1} \to 0$)

$$\left(\frac{\alpha}{\mu}\right)_{PPT} = -14\left(\frac{4}{27}\right)^2 + \frac{\ln 3}{4\widetilde{\beta}\widetilde{\mu}} . \qquad (13)$$

The numerical analysis shows that relation (13) holds for all the points of the PPT line. This fact yields a very simple geometrical interpretation of the parameters of the PT in our generalised Potts model. Namely, the equation of the line given by the l.h.s. of eq. (10) and passing through the point $(\ln 3, 1/3)$ (see fig. 1,d) (where the second derivative of the r.h.s. of eq. (10) equals zero) is just that given by eq. (13), i.e. is the line of the PPT. Hence, for the given α/μ the PPT takes place at $\left(\widetilde{\beta}\widetilde{\mu}\right)^{-1}$ (eq. 13); the order parameter changes from V_0 to p_0 (see fig. 1,d).

The line of the I-order PPT terminates in the critical point

$$\left(\frac{\alpha}{\mu}\right)_{cr} = 14\left(\frac{4}{27}\right)^2 (\ln 3 - 1), \qquad (14a)$$

$$\left(\frac{1}{\widetilde{\beta}\widetilde{\mu}}\right)_{cr} = 54\left(\frac{4}{27}\right)^2 . \qquad (14b)$$

This point can be referred to, in analogy to that in the theory of the liquid-vapour P.T., as the critical point of the line of the "structural boiling".

Let's now find the equations of the lines of the instability (spinodals) of the p - and O - phases. At $T = 0$, the p -spinodal equation is $C \equiv -\left(\frac{27}{4}\right)^2 \frac{1}{42} \alpha/\mu = 1$ while for the O - spinodal one has $C = -1/3$ (see fig. 2). The simple treatment of eq. (10), namely constructing the tangent line to the

rhs of eq. (10) in point V_0 yields the following parametric representation of the spinodals

$$\left(\frac{\alpha}{\mu}\right)_{spin} = 42\left(\frac{4}{27}\right)^2 \left\{ 4V_0 \frac{e^{V_0}}{(e^{V_0}+3)^2} - \frac{e^{V_0}-1}{e^{V_0}+3} \right\} \qquad (15a)$$

$$\left(\frac{1}{\beta\tilde{\mu}}\right)_{spin} = 16*42\left(\frac{4}{27}\right)^2 \frac{e^{V_0}}{(e^{V_0}+3)^2} \qquad (15b)$$

For $-\infty < V_0 \leqslant 0$ one obtains the O-spinodal; for $1.64 \leqslant \leqslant V_0 < \infty$ - the p-spinodal. The values $O < V_0 < 1.64$ correspond to unphysical (unstable) solutions of eq. (10). At low temperatures one finds

$$\left(\frac{\alpha}{\mu}\right)_p^{spin} = -42\left(\frac{4}{27}\right)^2 + \frac{1}{4}\frac{1}{\beta\tilde{\mu}} \ln \tilde{\beta}\tilde{\mu} \qquad (16a)$$

$$\left(\frac{\alpha}{\mu}\right)_O^{spin} = 14\left(\frac{4}{27}\right)^2 - \frac{1}{4}\frac{1}{\beta\tilde{\mu}} \ln \tilde{\beta}\tilde{\mu} \qquad (16b)$$

(compare with fig. 2).

The phase diagram of our liquid is presented in fig. 3.

In close vincinity of the critical point, eq. (14a, b) the MFA treatment is inefficient (see, eg. in [8]). The two minima of the hamiltonian $H(\Psi)$ are well separated only when the correlation radius is small enough. Let L be the path in the space of the invariants Ψ_i joining the two minima, such that the values $H(\Psi)$, $\Psi \in L$, are as small as possible [3]. Then, the coordinate η along path L is the critical mode. Consider the long-wavelength slightly inhomogeneous fluctuations $\Psi(\vec{r})$. In the domain with linear dimension r_0, where r_0 denotes the radius of the orientational order, $\Psi(\vec{r})$ changes slowly. Then, the theory of the fluctuations of the field $\eta(\vec{r})$ is equivalent to that of the scalar field near its critical point and can be found, e.g. in [8].

5.2 At low temperatures $\tilde{T}_0 \sim \left(\frac{\mu}{J}\right)^{-1} \tilde{T}_{PPT} \ll \tilde{T}_{PPT}$ the crystal-

-liquid, i.e. the melting P.T. takes place. In the absence of the crystal phases (see sect. 5.1) at these temperatures the local structure parameter $\langle p \rangle$ changes very slowly with temperature ($\langle p \rangle (T) = \langle p \rangle (0) \pm \exp(-\frac{A}{T})$, $A \gg \tilde{T}_0$) and can be treated, with good accuracy, as the constant $\langle p \rangle (0)$, (see, eg. fig. 1). Then, in the first approximation, one can study the phase diagram of the system assuming that the interaction of the local structure- and crystal-order parameters do not change the value of the former. On the contrary, this interaction influences strongly the "free" crystal-order diagram, shown in fig. 8. Hence, in what follows we take $\langle p \rangle_p (T) = \langle p \rangle_p (0) = = 42\left(4/27\right)^2$ for the p-phase and $\langle p \rangle_O (T) = \langle p \rangle_O (0) = -14\left(4/27\right)^2$ for the O-phase.

5.2.1. Consider first the p-liquid - p-crystal P.T. From eq. (7a) one finds that the $h \neq 0$ solution of eqs. (7) is thermodynamically stable when

$$J + \gamma > 0 \qquad (17)$$

It's necessary to make some comments here. The MFA treatment of the spin hamiltonians of our type yields good results when the configurations giving the main contribution to the partition function Z do not differ too strongly. In the spinformalism language, they are the configurations of the ferromagnetic or antiferromagnetic types. On the contrary, when the typical configurations with approximately equal energies describe the strong fluctuations of some order parameter, the problem of the interpretation of the MFA results is difficult. For example, the MFA metastable phase at $T = 0$ in the theory of crystal order [5], constructed with the help of three energetically degenerated states, turns out to be unstable when the fluctuations are accounted for [9]. In the p-phase the analogous effects may take place for $\gamma \sim -J$. The "pure ferromagnetic" solutions correspond to

$$\gamma > 0 \qquad (17a)$$

instead of (17).

Eq. (7c) takes the standard form [5]

$$\frac{27}{32}\ \frac{1}{\beta} Z = \frac{e^z - 1}{e^z + 3} , \tag{18}$$

where $-8\bar{\beta}h = Z$. For the free energy F_p (eq. 7a) one obtains

$$F_p = F_p^{(L)} + \frac{J+\gamma}{\tilde{\mu}} F_p^{(c)}(h) , \tag{19}$$

where

$$F_p^{(c)}(h) = \frac{81}{4} h^2 + 6h - \frac{1}{\beta} \ln\left(1 + 3 e^{8\bar{\beta}h}\right) , \tag{19a}$$

and $F_p^{(L)}$ is given by formula (12a). The melting P.T., defined by

$$F_p^{(c)}\left(h(\bar{\beta}_c); \bar{\beta}_c\right) = F_p^{(c)}\left(0, \bar{\beta}_c\right) \tag{20}$$

is the I order P.T. One obtains

$$\bar{\beta}_c^{-1} = 0.360 \tag{21}$$

5.2.2. Let's now study the o -crystal- o -liquid P.T. The crystal-like solutions of eqs (9) are thermodynamically stable when

$$J+\gamma > 0 ; \quad J-\gamma > 0 \tag{22a,b}$$

(see eq. (9a)). The physical meaning of the latter inequality is quite analogous to that of (17). Namely, the $T = 0$ solutions of eqs. (9), $x_0 = y_0 = -4/27$, describe the case when the orientations $\hat{g}^{(1)}$, $\hat{g}^{(2)}$ of the two lattices do not coincide. When the strength of the ferromagnetic interaction increases and (22b) is violated these solutions do not correspond to the absolute minimum of energy. The inequality (22a) seems, at first look, somewhat strangely, since it imposes the lower bounding on the strength of the antiferromagnetic interaction in the system where the relative orientation of the two lattices is "antiferromagnetic" $\left(\hat{g}^{(1)} \neq \hat{g}^{(2)}, T=0\right)$. Note that there was no upper bounding in the ferromagnetic case. This is so

due to the somewhat different role which plays γ in p - and o - systems. Consider the case of $|\gamma| \to \infty$. In the p -phase, the γ -term in hamiltonian (4d) generates (at low temperatures) the crystal ordering in the two lattices. In the o -phase this term yields a metastable ordering of parameters $T^{(i)}_{\alpha\beta\gamma\delta}(\vec{r})$ studied in paper [5] which becomes unstable when the fluctuations are taken into account. The MFA inequalities (22) describe the case when the melting temperature of the "interlattice" ordering $T_i \sim \gamma$ is lower than that of the crystal ordering of each of the lattices, $T_c \sim J$. This rules out the $|\gamma| > J$ difficulties discussed above. Eq. (22a) guarantees that the $T = 0$ solution x_0 , y_0 yields the minimum of the energy. Namely, the fluctuation of the energy due to the variation of the $T = 0$ solution: $x_0 \to x_0$, $y_0 \to y_0 - |\delta|$ are favourable when $J+\gamma \leqslant 0$:

$$-\mathcal{H}'(T=0, \delta) = -\mathcal{H}(T=0, 0) - 4|\delta|(J+\gamma) . \tag{23}$$

In analogy with (17a) the "pure antiferromagnetic" ordering corresponds to

$$-J < \gamma < 0 , \tag{22,c}$$

instead of (22a, b).

The equations (9c, 9d) were solved numerically. For the thermodynamical potential (9a) one obtains

$$F_0 = F_0^{(L)} + \frac{J+\gamma}{\tilde{\mu}} F_0^{(c)}(x,y) , \tag{24}$$

where

$$F_0^{(c)}(x,y) = \frac{27}{2} \frac{J-\gamma}{J+\gamma} x^2 + \frac{27}{4} y^2 - \frac{1}{\beta} \ln\left\{ 2 e^{2\bar{\beta}y} + 4 e^{2\bar{\beta}x} + 4 e^{-2\bar{\beta}x} + e^{4\bar{\beta}x - 2\bar{\beta}y} + e^{-4\bar{\beta}x - 2\bar{\beta}y} \right\} , \tag{25}$$

and $F_0^{(L)}$ is given by (12b).

The two typical solutions of eqs. (9c, d) are shown schematically in fig. 4.

The solutions (x,y) and $(-x,y)$ are physically equivalent due to the $x \leftrightarrow -x$ symmetry of eqs. 8. We'll not deal here with other (metastable) solutions for the reasons discussed above. The character of the melting transition, taking place when

$$F_o^{(c)}\left(x(\bar{\beta}_c), y(\bar{\beta}_c); \bar{\beta}_c\right) = F_o^{(c)}\left(0, 0, \bar{\beta}_c\right) \tag{26}$$

depends on the ratio of constants J and γ. Let's introduce the parameter

$$W \equiv \frac{J - \gamma}{J + \gamma} \tag{27}$$

Then, there exists such a W_{tc} (tricritical) that for $W < W_{tc}$ the melting P.T. is of the first order (fig. 4,a), while for $W > W_{tc}$ it's the continuous one (fig. 4,b). One finds

$$W_{tc} = 1.49 \quad ; \quad \bar{\beta}_{tc}^{-1} = 0.234 \tag{28}$$

The dependence of $\bar{\beta}_c^{-1}$ on W is shown in fig. 5.

The phase diagram of the system with hamiltonian (4d), with $\mu/\gamma \gg 1$, $\mu/\beta \gg 1$ is shown in fig. 6. We have not shown there the small corrections (of relative order $\frac{\gamma}{\mu} \ll 1$) to the phase diagram of the liquid, which can be found from equation $F_P = F_o$ (eqs. (19), (24)). Note that we used $\bar{\beta}^{-1}$ instead of $\tilde{\beta}^{-1}$ for the temperature. As the result, the inclination of the surface of the PPT in liquid is no longer constant and depends on W.

6. In this section the case when $\mu/J \ll 1$, $\mu/\gamma \ll 1$ will be studied. The $U(p)$ term in hamiltonian (2) is small and the solutions of eqs (7) and (9) can be studied perturbatively. Physically, such a situation corresponds to a system where the surface tension of the structureless domain separating the two regions with different local structures (local invariants) is small.

We'll study the phase diagram in the first approximation, i.e. when $\mu = 0$. At $T=0$ $(\beta^{-1}=0)$ one finds, from eqs. (7c)

and (9c,d) the equations of the spinodals of the p- and 0-phase, respectively

$$\tilde{\alpha} = -\frac{4}{27}(J + \gamma) \quad ; \quad \tilde{\alpha} = \frac{4}{27}(J - \gamma) . \tag{29}$$

The free energies are given by

$$F_P\left(T=0, \mu=0, h=-\frac{4}{27}\right) = -\frac{4}{9}(J + \gamma) - 3\tilde{\alpha} \quad \left(\tilde{\alpha} > -\frac{4}{27}(J + \gamma)\right), \tag{30a}$$

$$F_0\left(T=0, \mu=0, x=y=-\frac{4}{27}\right) = -\frac{4}{27}(3J - \gamma) + \tilde{\alpha} \quad \left(\tilde{\alpha} < \frac{4}{27}(J - \gamma)\right) . \tag{30b}$$

The PPT $\left(F_P = F_0\right)$ takes place on the surface

$$\tilde{\alpha} = -\frac{4}{27}\gamma . \tag{31}$$

The $T=0$ phase diagram is shown in fig. 7.

The simple analytical treatment at $T \neq 0$ is available only in the vincinity of the line of the decoupling of the interaction between the two lattices: $\tilde{\alpha} = \gamma = 0$. Let's introduce

$$\delta F_{P,0} = F\left(d\tilde{\alpha}, d\gamma, \tilde{\beta} + d\tilde{\beta}; \langle p \rangle (d\tilde{\alpha}, d\gamma, \tilde{\beta} + d\tilde{\beta}); H_{P,0}(d\alpha, d\gamma, \tilde{\beta} + d\tilde{\beta})\right)$$
$$- F\left(0, 0, \tilde{\beta}; \langle p \rangle (0, 0, \tilde{\beta}); H_{P,0}(0, 0, \tilde{\beta})\right), \tag{32}$$

where $H_{P,0}$ denotes the crystal order parameter, i.e. $H_P = h$, $H_0 \equiv (x,y)$; $F\left(\ldots H_{P,0}\right) \equiv F_{P,0}$. One finds

$$\delta F_{P,0} = \frac{\partial F_{P,0}}{\partial \tilde{\alpha}}\bigg|_{(0)} d\tilde{\alpha} + \frac{\partial F_{P,0}}{\partial \gamma}\bigg|_{(0)} d\gamma + \frac{\partial F_{P,0}}{\partial \tilde{\beta}}\bigg|_{(0)} d\tilde{\beta} , \tag{33}$$

since

$$\frac{\partial F_0}{\partial x}\bigg|_{(0)} = \frac{\partial F_0}{\partial y}\bigg|_{(0)} = \frac{\partial F_P}{\partial h}\bigg|_{(0)} = \frac{\partial F_{P,0}}{\partial \langle p \rangle}\bigg|_{(0)} = 0 \tag{34}$$

16

17

in virtue of eqs. (5). The simple calculations yield

$$\frac{\partial F_P}{\partial \tilde{\alpha}}\bigg|_{(0)} = -3\left(\frac{27}{4}\right)^2 h_o^2 \quad ; \quad \frac{\partial F_P}{\partial \gamma}\bigg|_{(0)} = -3\left(\frac{27}{4}\right) h_o^2, \tag{35a}$$

$$\frac{\partial F_o}{\partial \tilde{\alpha}}\bigg|_{(0)} = \left(\frac{27}{4}\right)^2 h_o^2 \quad ; \quad \frac{\partial F_o}{\partial \gamma}\bigg|_{(0)} = \frac{27}{4} h_o^2, \tag{35b}$$

$$\frac{\partial F_{P,0}}{\partial \tilde{\beta}}\bigg|_{(0)} = -\frac{4}{\tilde{\beta}}\left\{ F_P(0) + \frac{81}{4} h_o^2 \right\}. \tag{35c}$$

In the above formulas the derivates are taken in point $(0) \equiv = (\tilde{\alpha} = \gamma = 0, \tilde{\beta})$.

The PPT takes place when

$$\delta F_P = \delta F_o , \tag{36}$$

which yields, with account of (33) and (35)

$$\frac{d\tilde{\alpha}}{d\gamma}\bigg|_{(0)}(\tilde{\beta}) = -\frac{4}{27} , \tag{37}$$

in agreement with (31).

The melting P.T. of the P- and O- phases takes place when

$$\delta F_{Liq} = \delta F_{P,O} , \tag{38}$$

where δF_{Liq} is given by (32) for $H_{P,O} = 0$. Accounting that $F(0,0,\tilde{\beta}_c, H_{P,0}(\tilde{\beta}_c), \langle P\rangle(\tilde{\beta}_c)) = F(0,0,\tilde{\beta}_c,0,0)$ one finds, for the P-phase melting

$$\frac{J}{\tilde{\beta}_c}(\tilde{\beta} - \tilde{\beta}_c) + \frac{27}{4}\tilde{\alpha} + \gamma = 0 , \tag{39}$$

and for the O- phase melting

$$-3\frac{J}{\tilde{\beta}_c}(\tilde{\beta} - \tilde{\beta}_c) + \frac{27}{4}\tilde{\alpha} + \gamma = 0 . \tag{40}$$

The phase diagram is shown in fig. 8. The structure of the liquid depends on the value of $\tilde{\alpha}$. For $\tilde{\alpha} > 0$ one has P -phase, for $\tilde{\alpha} < 0$ - O - phase of the liquid.

In the vicinity of the line $\tilde{\alpha} = \gamma = 0$ all the three P.T. are the first order ones. The melting of the P -phase is the I-order P.T. for $(\tilde{\alpha}/J+\gamma)^{-1} \neq 0$. This can be found by writting eq. (7a) in the form $h = f(h)$ and solving the equation $f''(0) = 0$. The only (real) solution is $(\frac{\tilde{\alpha}}{J+\gamma})^{-1} = 0$. The dependence of the melting temperature $\tilde{\beta}_c^{-1}$ on $\tilde{\alpha}/J+\gamma$ is shown in fig. 9. In order to obtain the full phase diagram it's necessary to solve numerically eqs. (9). We'll not deal with this task in this paper.

7. Let's discuss briefly some of the results. Consider first the case when there exists the critical point of the I-order P.T. in liquid, see fig. 3. The latent heat produced at the P.T. equals to the energy necessary to change the local structure of the liquid and depends on the distance from the critical point. When $\alpha/\mu \to (\alpha/\mu)_{cr}$, $1/\tilde{\beta}\tilde{\mu} \to (1/\tilde{\beta}\tilde{\mu})_{cr}$ then $Q \to 0$.

Away from the critical point where the local structures of the two phases differ strongly, $Q|_{dta} \gg kT$ since $\mu \gg 1$ and the P.T may be accompanied by strong energetic effects. Such a situation may take place in alkali halides, which undergo the B1 $\to$ B2 PPT at sufficiently high pressures [10]. The strong energetic effect in NaCl fluid observed by Alyoshin [11] may be the candidate for the I-order PPT in liquid. The strength of this effect decreases with temperature and vanishes near $T \approx 1000°C$.

When the energetic effect is small $(\mu \ll 1)$ there's no I-order P.P.T. in liquid. However, as can be seen from figs. 1, b; 3, on the formally continued line of the I-order P.P.T., not far from the critical point the value of the local structure parameter changes more strongly than for other values of parameters, see fig. 10. In these sense one may speak of

the "diffused" line of the continuous P.P.T. in the vicinity
of the critical point. Far away from this point the effect
vanishes. When $\mu \ll 1$ one has $\widetilde{\beta}_{cr} \gg \widetilde{\beta}_c$ and no effects of
the type described above can be expected in the liquid phase
near the melting point. The situation may, however, change
when $\mu \sim J \sim |\gamma|$. Namely, take $\mu < J \sim |\gamma|$; as the result
$\widetilde{\beta}_{cr} > \widetilde{\beta}_c$ but $\widetilde{\beta}_{cr} \approx \widetilde{\beta}_c$, i.e. the critical point is near the
melting point. Then, the noticeable fluctuations of physical
characteristics could be observed in the vicinity of the sur-
face (in the space of the parameters of the theory) of the
crystal PPT, formally continued into the liquid phase. One of
the candidates for such a "diffused" P.T. is the liquid near
the PPT cubic-hexagonal crystal, which reveals noticeable
change of density in this region.

    The next interesting problem is the P.T. between crystal
and liquid with different local structures. As can be seen
from the thermodynamical phase diagrams, figs 6,8, such the
phases can coexist for some values of parameters. From the
point of view of the thermodynamics, the corresponding P.T. is
equally well described as that between the phases with the sa-
me local invariants (structure). This is not so when the kine-
tics of the P.T. is studied. For example, there may appear an
extremaly large temperature interval of the supercooled liquid.
As the result, the thermodynamically stable phase cannot be
reached via an equilibrium P.T. Note that this effect exists
independently on the strength of the energetic effect due to
the local structure term (3) in hamiltonian (2). In such a ca-
se, an extra interaction is necessary to overcome the potenti-
al barrier. For example, the transition due to electron or
neutron interaction with the amorphous SiO_2 [12] might be an
example of such a "difficult" PPT in glassy phase.

Figure captions

Fig. 1. Graphical representation of eq. 10 and its solutions
for some values of $\frac{\alpha}{\mu}$.

Fig. 2. The phase diagram of liquid at $T = 0$. The continuous
and dashed lines represent, respectively, the stable
and metastable solutions. $(\mu \gg J, \gamma)$

Fig. 3. The phase diagram of the liquid for $\mu \gg J, \gamma$.

Fig. 4. The two typical solutions of eq. (9c,d).

Fig. 5. The dependence of the melting temperature $\overline{T}_c \equiv (\overline{\beta}_c)^{-1}$,
see fig. 4, on $W \equiv (J-\gamma)/(J+\gamma)$.

Fig. 6. The MFA phase diagram of the system with hamiltonian
(2), (3) for $\frac{\mu}{J} \gg 1$, $\frac{\mu}{\gamma} \gg 1$.

Fig. 7. The MFA phase diagram of the system with hamiltonian
(2), (3) for $\mu = 0$, at $T = 0$.

Fig. 8. The MFA phase diagram of the system with hamiltonian
(2), (3) for $\mu = 0$.

Fig. 9. The dependence of the melting temperature of p-pha-
se for $\mu = 0$ on $\frac{\widetilde{\alpha}}{J+\gamma}$

Fig.10. In the vicinity of the formally continued line of PPT
in liquid (fig. 3) beyond the critical point the or-
der parameter $\langle p \rangle$ changes rapidly with temperature;
when $\frac{\alpha}{\mu} \gg \left(\frac{\alpha}{\mu}\right)_{cr}$ the effect is small.

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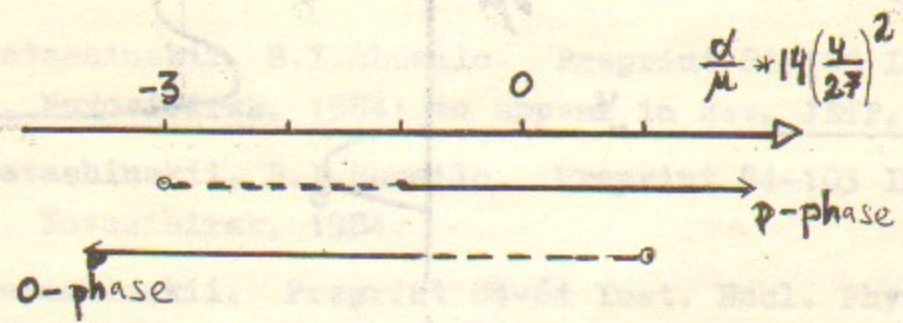[12] С.М.Бреховских, Ю.Н.Волкова, Л.В.Ланда. Радиационные эффекты в стеклах. М., Энергоиздат, 1982.
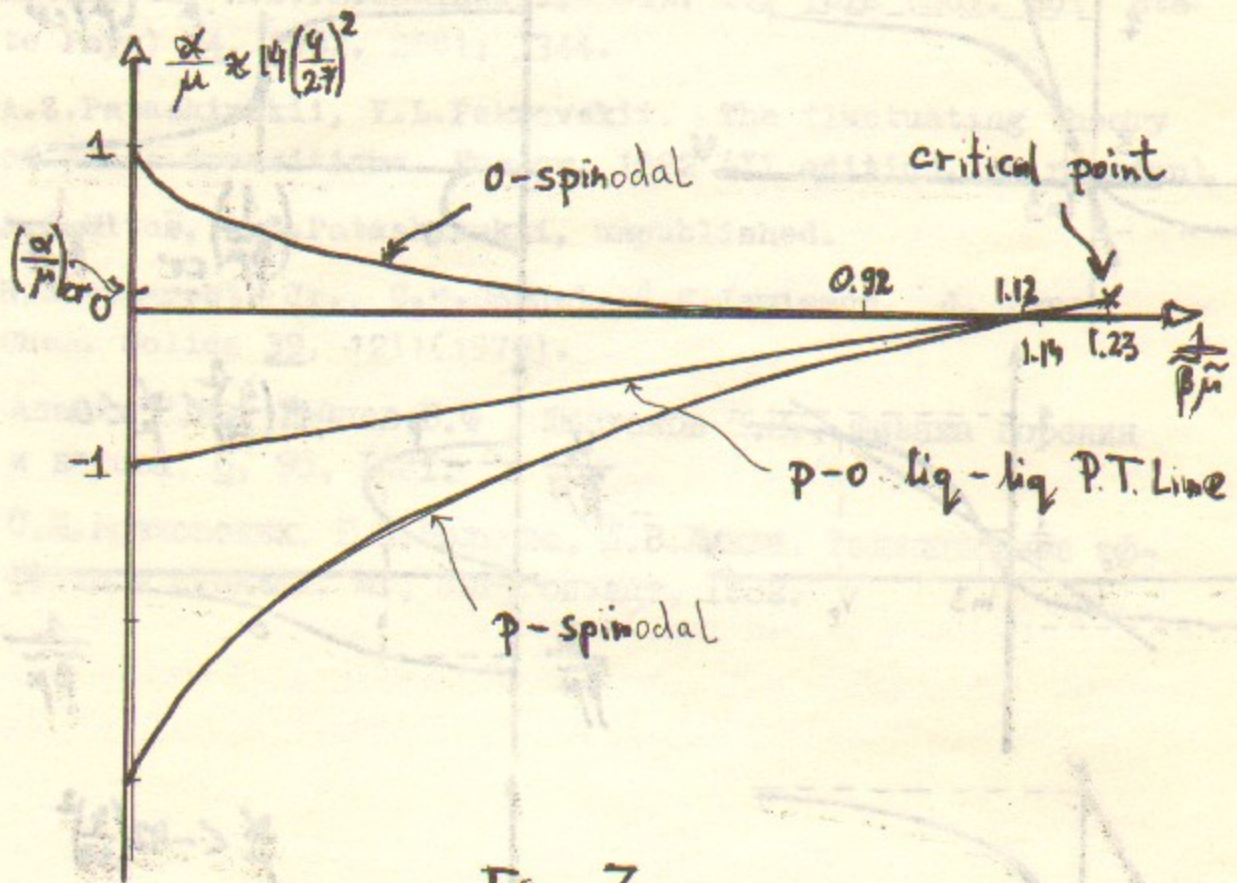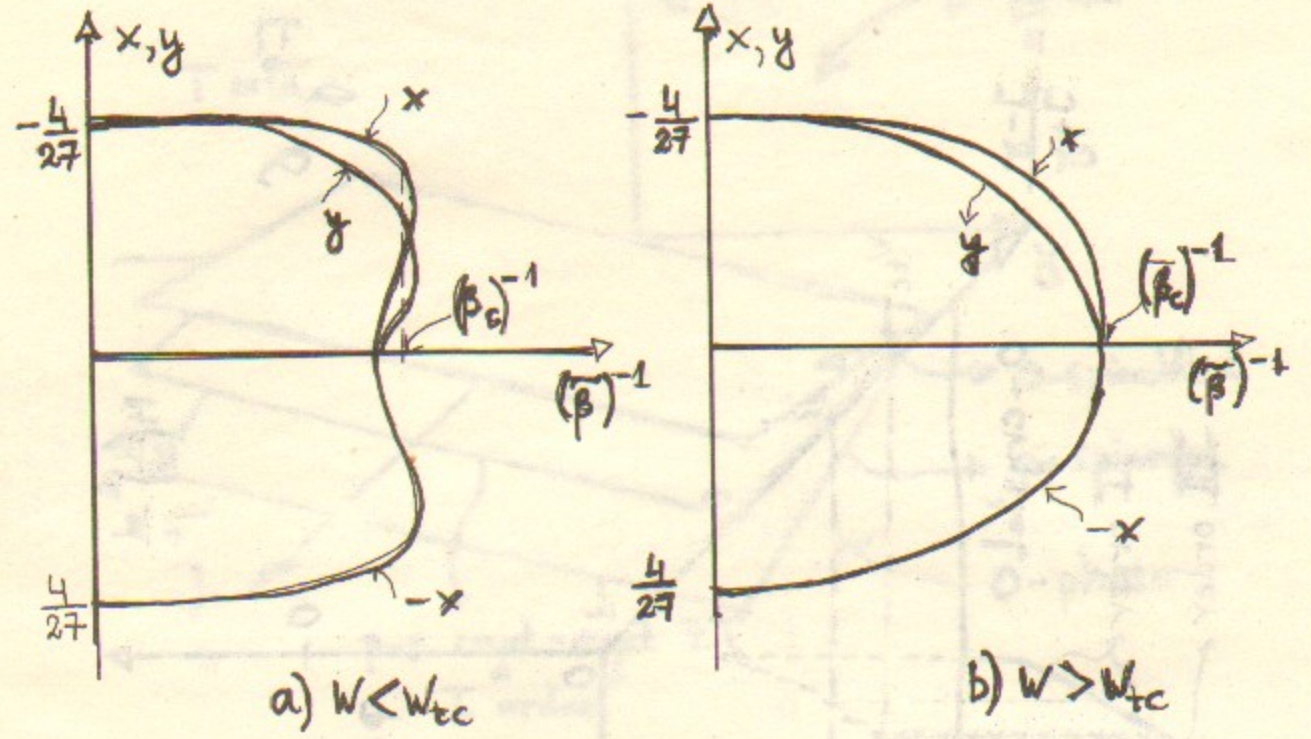
Fig. 1

Fig. 2

Fig. 3

a) $W < W_{tc}$ b) $W > W_{tc}$

Fig. 4

Fig. 5

Fig. 6

$W \equiv \frac{J - \chi}{J + \chi}$

$H\left(\frac{\mu}{2J}\right)^2 \frac{d}{\mu}$

W_{tc}

O-crystal

I order

I order

I order

× × × × × × × × × ×

Line of tricritical points

O-O liq-cryst P.T.

O-liquid

$(x, 0)$

$(\delta, 0)$

P-P P.T. I order

Liq-cryst P.T. I order

P-crystal

P-liquid

P-O liq-liq P.T. I order

P-O liq-cryst P.T. I order

$\frac{t}{\beta}$

P-phases

O-phases

-1

0

Fig. 7

T=0

$\tilde{\alpha}$

γ

p-phase

O-spinodal

p-spinodal

O-phase

J

P-O cryst-cryst P.T. I order

Fig. 8

$\tilde{\alpha}$

γ

p-crystal

o-crystal

liquid

(β)

(β)
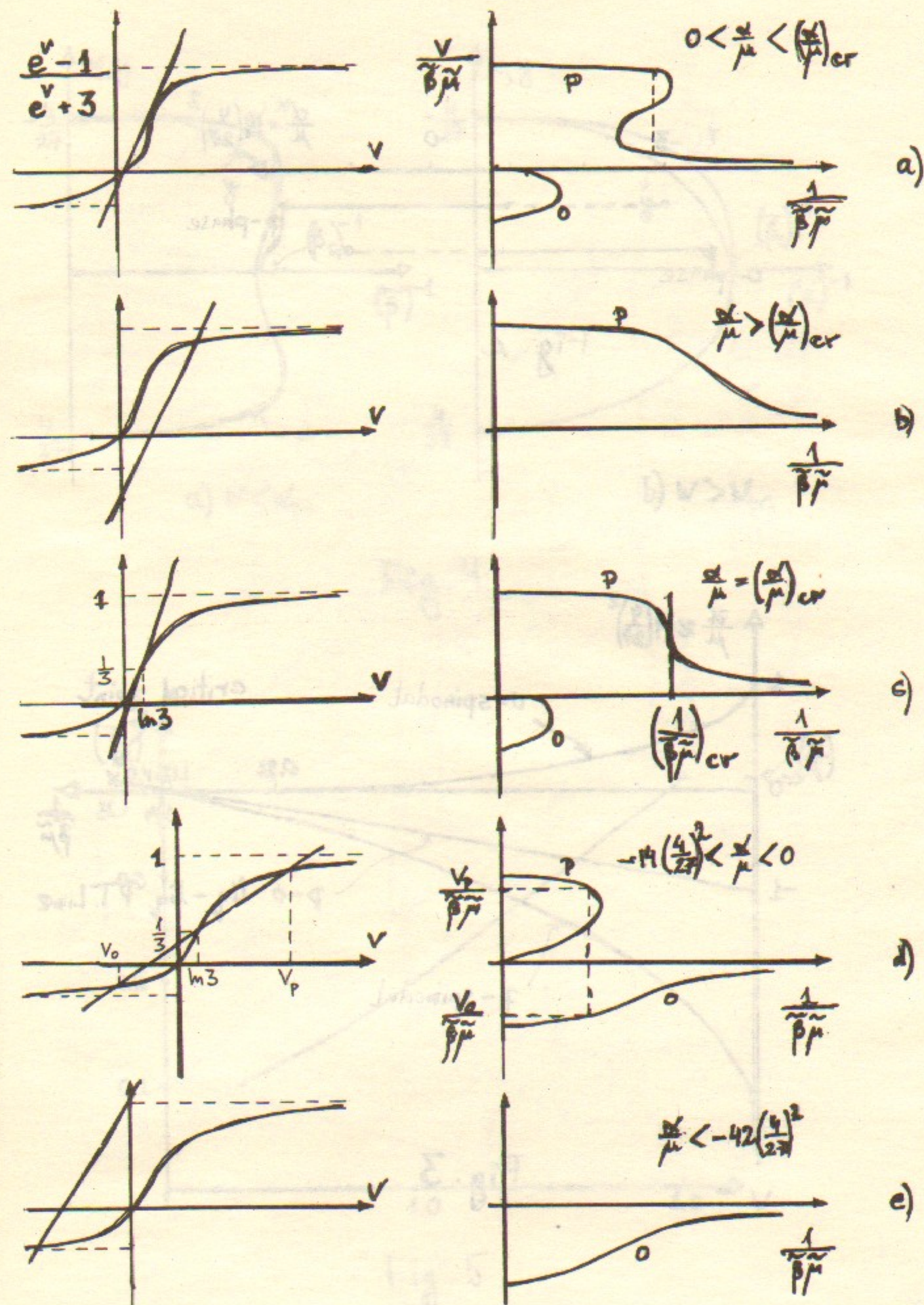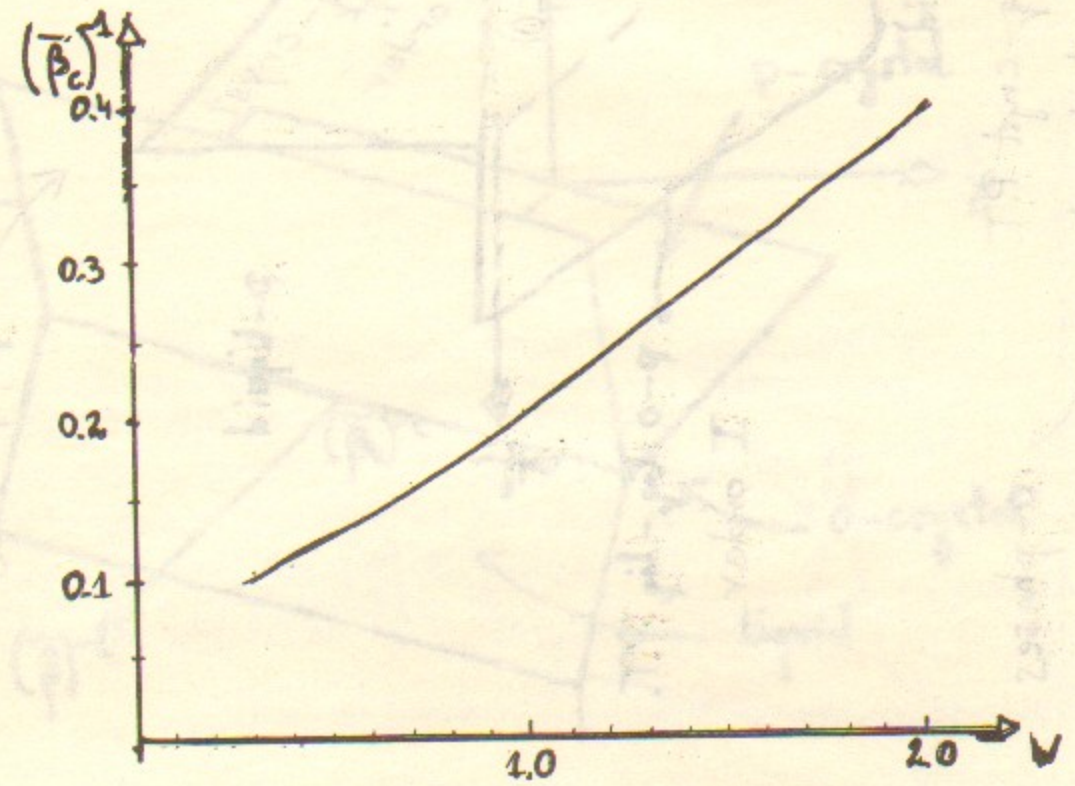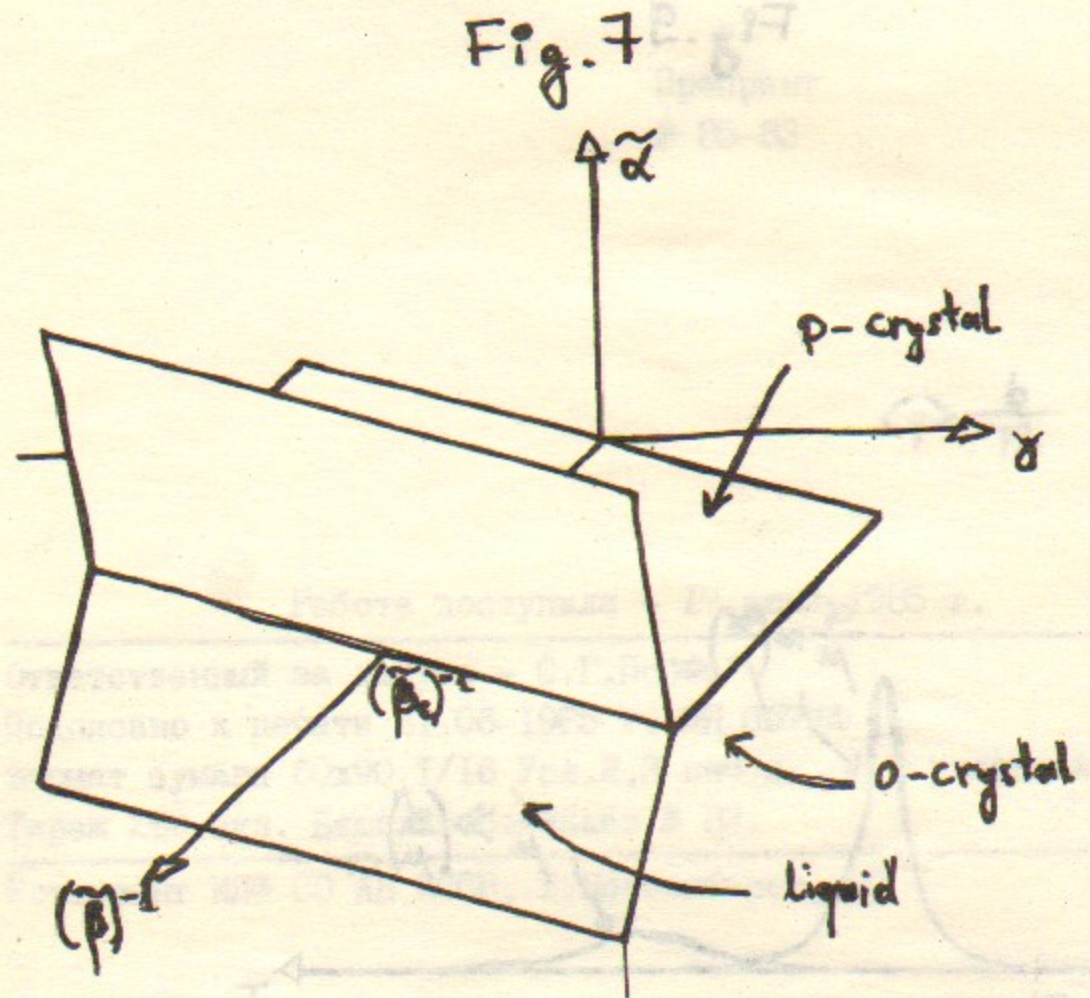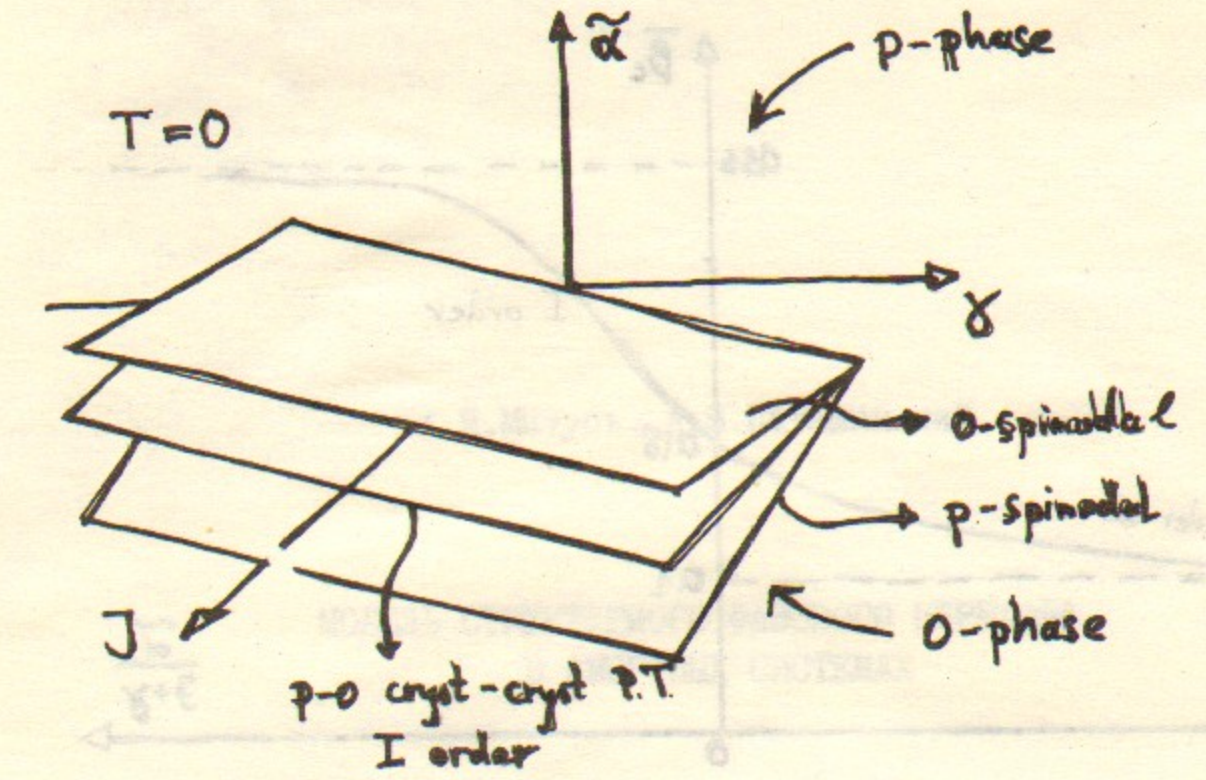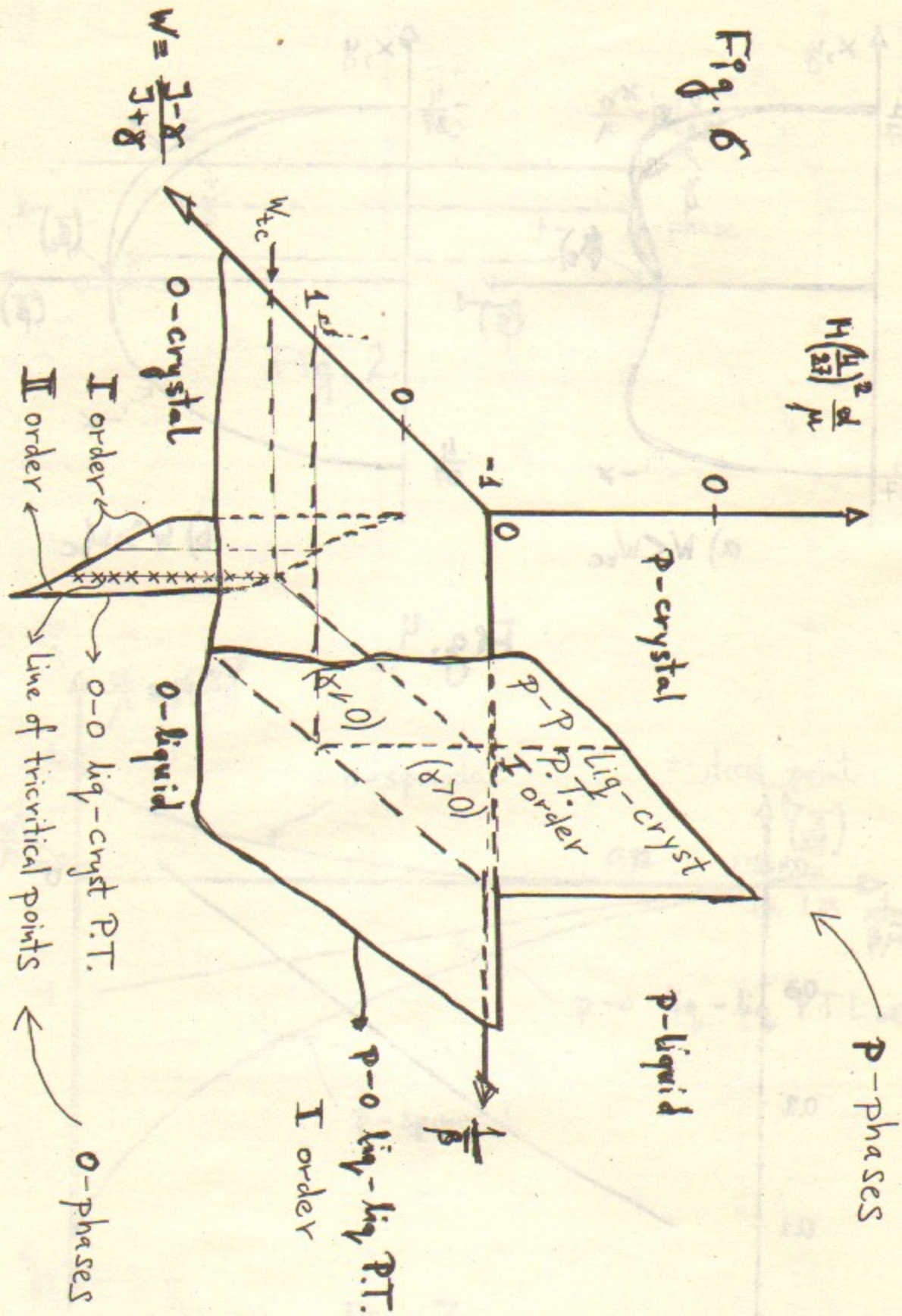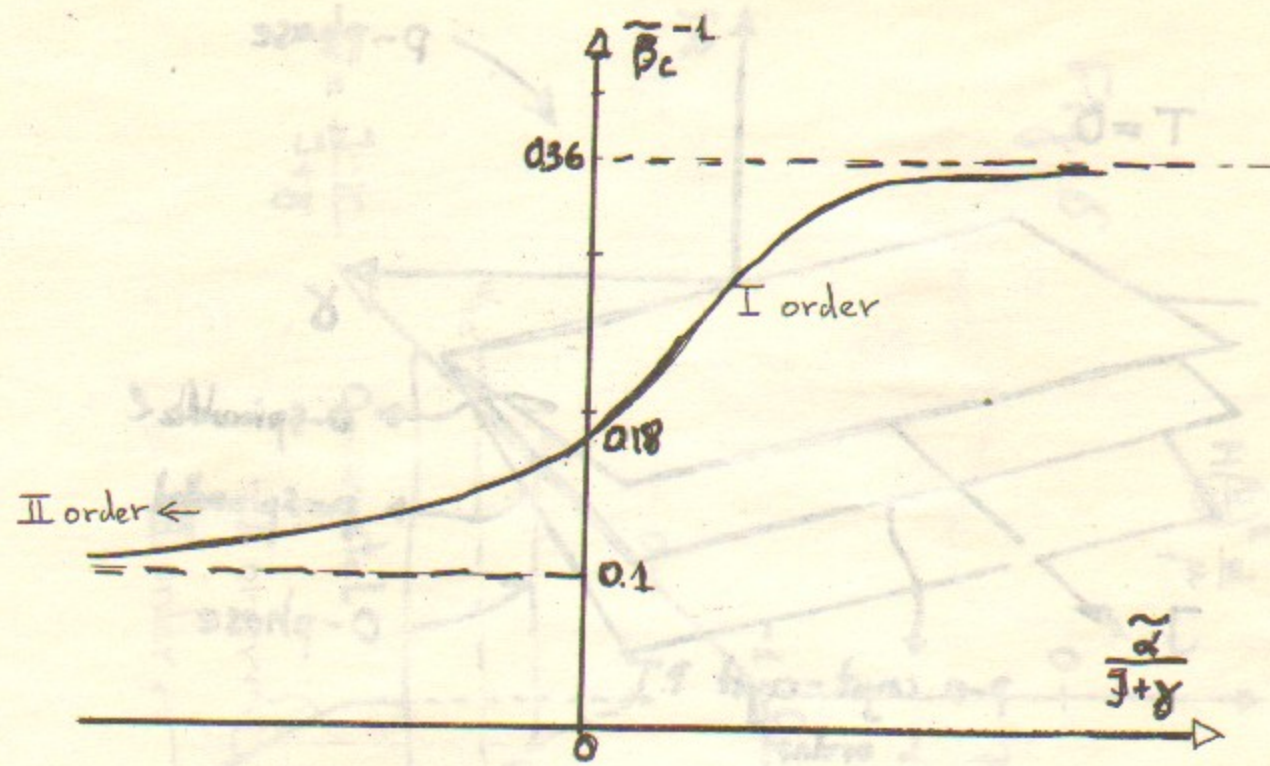
Fig. 9
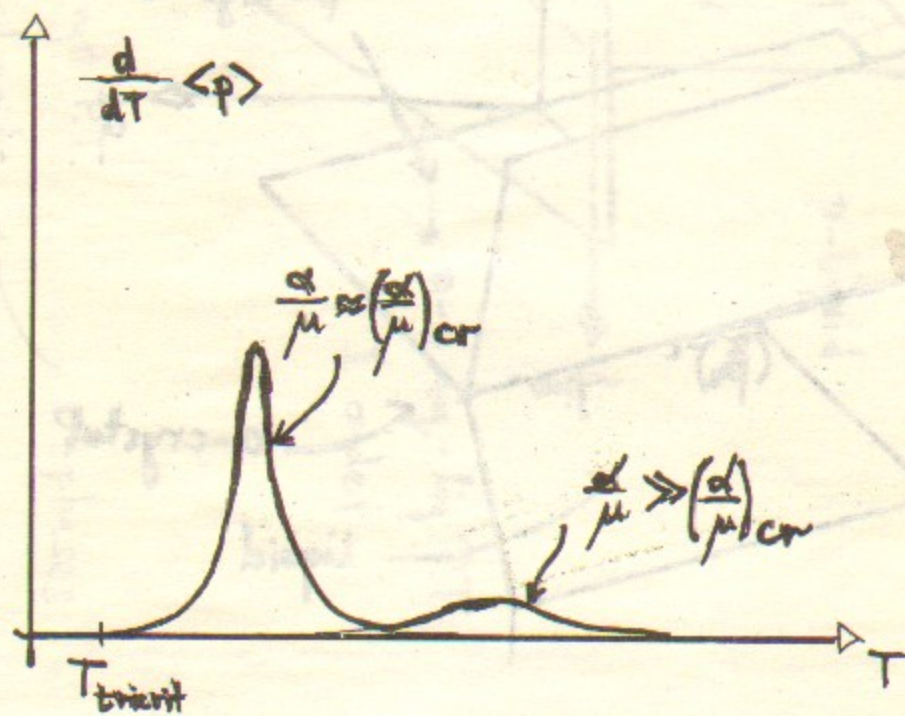
Fig. 10

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МОДЕЛЬ СТРУКТУРНОГО ФАЗОВОГО ПЕРЕХОДА
В АМОРФНЫХ СИСТЕМАХ