Phase diagram of disordered systems described by a generalized weak-crystallization Hamiltonian

A. V. Dobrynin and I. Ya. Erukhimovich

Institute of Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements, Russian Academy of Sciences, Moscow, 121357, ul. Veresaeva, 15; "Sightsoft" Individual Private Enterprise, Moscow, 127543, ul. Korneĭchuka, 32, kv. 3

(Submitted 2 April 1993)
Zh. Eksp. Teor. Fiz. **104**, 2838–2852 (August 1993)

The paper considers the behavior of disordered three-dimensional systems with quenched structural disorder, in which the loss of stability of the uniform state occurs by the Landau "soft mode" mechanism. By means of a variational principle based on a second Legendre transformation the conditions for the existence of glass phases with broken replica symmetry are analyzed and the free energy of the systems under consideration is calculated with allowance for the appearance of glass phases. Phase diagrams for this class of systems are constructed numerically and analyzed.

1. INTRODUCTION

Many physical systems exhibit phase transitions associated with instability of their spatially uniform state against arbitrarily small fluctuations of the order parameter with a certain finite wave number q_0. (Besides ordinary crystallization,[1,2] this class of phase transitions also includes a number of structural phase transitions in liquid crystals[3–5] and polymers.[6–14]) If such a system is characterized by some quenched structural disorder, the observable quantities are determined by averaging the free energy and the appropriate derivatives of it over a specified distribution of this disorder. (For a mixture of molecules with different geometric and energetic characteristics such disorder is described by the set of concentrations of molecules of all the types represented in the system.)

An important place amongst investigations of systems with quenched structural disorder is occupied by the analysis of phase transitions in polymer systems,[15–17] in which the onset of quenched topological disorder in the arrangement of links of different kinds along a polymer chain is dictated by the statistical nature of the polymerization process.[18] A remarkable distinctive feature of polymer systems is the fact that the coefficients of the Landau expansion of the free energy in powers of the order parameter are uniquely related to the topological structure of the macromolecules and can be calculated explicitly. (The latter possibility is based on the fundamental circumstance that, over the larger scales that are typical of polymers in comparison with those for low-molecular-weight systems, their correlation properties are determined principally by the very fact of the connectivity of the links in the macromolecules, and this has made it possible to develop analytical and numerical methods to calculate these coefficients.[7,11,19]) This feature of polymer systems makes it possible to standardize the procedure for averaging the free energy and observable quantities of statistical polymer systems. In particular, this is achieved through the replica formalism by introducing a perturbation associated with the interaction of fluctuations of the order parameter in different replicas (for more detail, see below). Here, the magnitude of this perturbation is related to the dispersion of the properties of the molecules composing the system, and can be calculated explicitly for any given distribution.[16,20]

In Refs. 15–17 such a procedure was used to investigate structural phase transitions of the weak-crystallization type in statistical polymer systems. However, as was first noted in Ref. 21, because of a special degeneracy of the Hamiltonian describing the statistical polymer systems considered in Refs. 15 and 17 the free energy of the ordered state in them does not depend on the symmetry type of the corresponding crystal (or quasicrystalline) lattice. In other words, the ground state of such systems is infinitely degenerate. In this sense, they behave below the transition point as a spin glass.[22,23] In fact, the authors have shown in Ref. 24 that this analogy is exact and that, for a broad class of systems that have quenched structural disorder and are described by a Hamiltonian of a rather general form, there is a phase transition associated with the appearance of nonzero inter-replica correlations—the formation of a glass phase. In this paper we construct the phase diagrams of such systems and discuss the physical meaning of the glass phases.

In Sec. 2 we obtain an expression for the free energy of the systems under consideration, using a variational principle based on a second Legendre transformation for the generalized weak-crystallization Hamiltonian describing the loss of stability of the uniform state of statistical polymer systems by a soft-mode mechanism. Typical phase diagrams, constructed both by analytical and by numerical investigation of this expression, are given in Sec. 3. The range of applicability and physical meaning of the results obtained are discussed in Sec. 4.

2. THE VARIATIONAL PRINCIPLE AND CALCULATION OF THE FREE ENERGY OF THE GLASS PHASE

We shall consider a system of (macro)molecules with a certain quenched structural disorder G (for a mixture of molecules with different geometric and energetic characteristics this disorder is described by the set of concentrations of molecules of all the types represented in the sys-

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tem). Let the probability that the system is in a state with a given configuration of structural disorder be $P(G)$. In this case, to calculate the thermodynamic characteristics of the system it is necessary to average the free energy of the system over all possible distributions of the structural disorder G:

$$F=\sum_G P(G)F(G) \tag{1}$$

where $F(G)$ is the free energy of the state with specified structural-disorder configuration G. For the average over configurations it is convenient to use the replica formalism, introducing n identical systems (replicas) and rewriting the expression (1) in the form

$$F=-T\lim_{n\to 0}\{1/n[\exp(-F_n/T)-1]\} \tag{2}$$

Here, the averaged (over all possible configurations of the structural disorder) n-replica free energy F_n of the system can be represented in general form as the functional integral

$$\exp(-F_n/T)=\int\prod_{\alpha=1}^{\alpha=n}\delta\psi_\alpha(\mathbf{x}_\alpha)\times\exp(-H(\{\psi_\alpha(\mathbf{x}_\alpha)\},T)/T) \tag{3}$$

where the Hamiltonian $H(\{\psi_\alpha(\mathbf{x}_\alpha)\},\mathrm{T})$ can be written in the form of a Landau expansion in the fluctuations of the order parameter:

$$\frac{H(\{\psi_\alpha(\mathbf{q}_\alpha)\},T)}{T}=\frac{1}{T}\sum_{\alpha=1}^{n}H_0(\{\psi_\alpha(\mathbf{q}_\alpha)\},T)-\frac{\varkappa}{8}\sum_{\alpha\neq\beta}\int\frac{d\mathbf{q}_\alpha}{(2\pi)^3}\frac{d\mathbf{q}_\beta}{(2\pi)^3}\psi_\alpha(\mathbf{q}_\alpha)\times\psi_\alpha(-\mathbf{q}_\alpha)\psi_\beta(\mathbf{q}_\beta)\psi_\beta(-\mathbf{q}_\beta)\,. \tag{4}$$

The summation in (4) is performed over the n replicas; the phenomenological parameter $\varkappa$ is positive, is related to the dispersion of the properties of the molecules, and vanishes for monodisperse systems, i.e., systems consisting of one kind of molecule.[16,20]

In the role of the one-replica Hamiltonian H_0 we shall consider here the weak-crystallization Hamiltonian[1-5]

$$\frac{H_0(\{\psi(\mathbf{q})\},T)}{T}=\frac{1}{2}\int\frac{d\mathbf{q}}{(2\pi)^3}g^{-1}(\mathbf{q})\psi(\mathbf{q})\psi(-\mathbf{q})-\frac{\gamma}{6}\times\int\delta\Big(\sum_{i=1}^{3}\mathbf{q}_i\Big)\prod_{i=1}^{3}\left[\psi(\mathbf{q}_i)\frac{d\mathbf{q}_i}{(2\pi)^3}\right]+\frac{\lambda}{24}\int\delta\Big(\sum_{i=1}^{4}\mathbf{q}_i\Big)\prod_{i=1}^{4}\left[\psi(\mathbf{q}_i)\frac{d\mathbf{q}_i}{(2\pi)^3}\right], \tag{5}$$

where the bare propagator has the characteristic form for weak crystallization:

$$g^{-1}(\mathbf{q})=(q-q_0)^2+\tau, \tag{6}$$

and the constants q_0, γ, and λ and the reduced temperature τ are related to the structural characteristics of the polymer (see Refs. 7, 11, and 19 and the references cited therein).

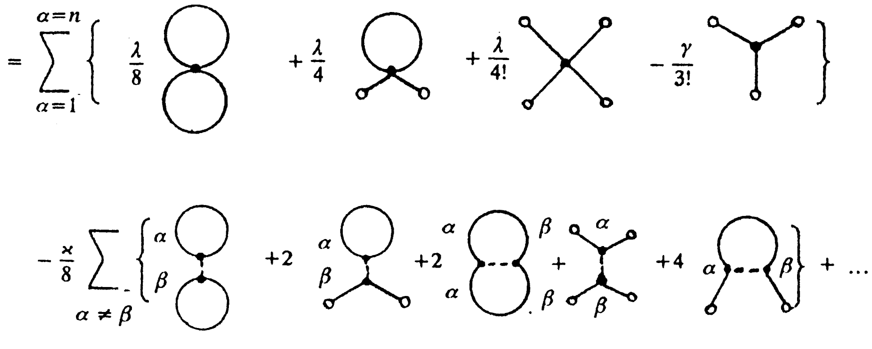
Following Ref. 19, to calculate F we shall use a variational principle based on a second Legendre transformation.[25] This principle makes it possible to represent the free energy in the following form:

$$F_n/T=\min H_n(\{\langle\psi_\alpha(\mathbf{q}_\alpha)\rangle\},\{G_{\alpha\beta}(\mathbf{q}_\alpha,\mathbf{q}_\beta)\}), \tag{7}$$

$$H_n=-\frac{1}{2}\,\mathrm{Sp}\ln G_{\alpha\beta}+\frac{1}{2}\sum_{\alpha=1}^{\alpha=n}\left\{\int\frac{d\mathbf{q}_\alpha}{(2\pi)^3}G_{\alpha\alpha}(\mathbf{q}_\alpha)g^{-1}(\mathbf{q}_\alpha)+\int\frac{d\mathbf{q}_\alpha}{(2\pi)^3}g^{-1}(\mathbf{q}_\alpha)\psi_\alpha(\mathbf{q}_\alpha)\psi_\alpha(-\mathbf{q}_\alpha)\right\}+\sigma(\{\langle\psi_\alpha(\mathbf{q}_\alpha)\rangle\},\{G_{\alpha\beta}(\mathbf{q}_\alpha,\mathbf{q}_\beta)\}), \tag{8}$$

where the minimum is sought on the class of all trial functions for $\langle\psi_\alpha(\mathbf{q}_\alpha)\rangle$ and $G_{\alpha\beta}(\mathbf{q}_\alpha,\mathbf{q}_\beta)$, and $\sigma(\{\langle\psi_\alpha(\mathbf{q}_\alpha)\rangle\},\{G_{\alpha\beta}(\mathbf{q}_\alpha,\mathbf{q}_\beta)\})$ is the sum of the contributions of all 2-irreducible skeleton diagrams. In the one-loop approximation we represent the functional σ in the form

$\sigma(\{\langle\psi_\alpha(\mathrm{q}_\alpha)\rangle\}, \{G_{\alpha\beta}(\mathrm{q}_\alpha, \mathrm{q}_\beta)\})$



(9)

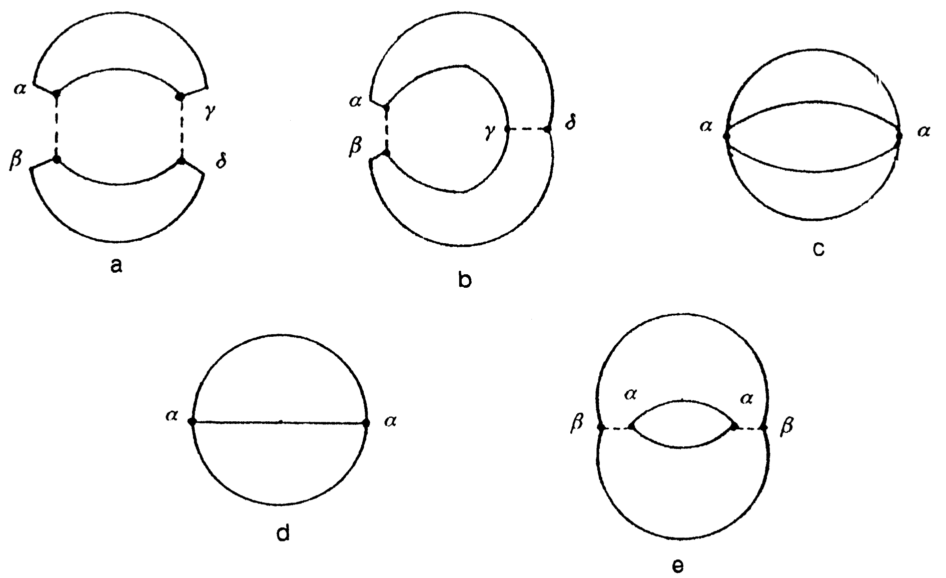


FIG. 1. Diagrams of second-order skeleton perturbation theory. The notation is the same as in Eq. (9). Diagrams (a) and (b) are diagrams that lead to instability of the Sherrington–Kirkpatrick solution; diagrams (c), (d), and (e) are diagrams determining the range of applicability of the phase diagrams constructed.

A solid line denotes the renormalized propagator $G_{\alpha\beta}(\mathbf{q}_\alpha,\mathbf{q}_\beta)=\langle\psi_\alpha(\mathbf{q}_\alpha)\psi_\beta(\mathbf{q}_\beta)\rangle-\langle\psi_\alpha(\mathbf{q}_\alpha)\rangle\langle\psi_\beta(\mathbf{q}_\beta)\rangle$, and the symbols

represent the average value $\langle\psi_\alpha(\mathbf{q}_\alpha)\rangle$ of the order parameter and vertices of the one-replica and inter-replica interaction, respectively.

We note that our variational principle is compatible with the approximation (9) for σ and coincides exactly with the Feynman variational principle used in the work of Mezard and Parisi,[26] which became known to us only after the publication of Ref. 24. We stress, however, that for a Hamiltonian of the form (4) the one-loop approximation leads to the conclusion that the Sherrington-Kirkpatrick replica-symmetric solution[27] corresponds to a stable extremum of the free energy. At the same time, allowance for the next diagrams in σ (given in Fig. 1) shows that the replica-nonsymmetric solution of Parisi[28,29] corresponds to this extremum (see below).

We shall seek an approximate value of F_n as the minimum of H_n on the class of trial functions of the following form:

$$\langle\psi_\alpha(\mathbf{r}_\alpha)\rangle=\frac{A_\alpha}{k^{1/2}}\sum\left[\exp\left(i\mathbf{q}_0\mathbf{r}_\alpha\right)+\text{c.c}\right], \qquad (10)$$

$$G_{\alpha\beta}(\mathbf{q}_\alpha,\mathbf{q}_\beta)=G^0_{\alpha\beta}(\mathbf{q}_\alpha,\mathbf{q}_\beta)+Q_{\alpha\beta}(\mathbf{q}_\alpha,\mathbf{q}_\beta)(1-\delta_{\alpha\beta}), \qquad (11)$$

where $\delta_{\alpha\beta}$ is the Kronecker symbol. The summation in (10) is performed over all vectors of the reciprocal lattice conjugate to the corresponding Bravais lattice that have length q_0, and k is the number of basis vectors of the reciprocal lattice. As regards the trial function $G_{\alpha\beta}(\mathbf{q}_\alpha,\mathbf{q}_\beta)$, it can be represented in the form of the sum of the one-replica trial function $G^0_{\alpha\beta}(\mathbf{q}_\alpha,\mathbf{q}_\beta)$, which has the usual form for the theory of weak crystallization:

$$G^0_{\alpha\beta}(\mathbf{q}_\alpha,\mathbf{q}_\beta)=\left(\left(|\mathbf{q}_\alpha|-q_0\right)^2+r\right)^{-1}\delta(\mathbf{q}_\alpha-\mathbf{q}_\beta)\delta_{\alpha\beta} \qquad (12)$$

and the two-replica trial function $Q_{\alpha\beta}(\mathbf{q}_\alpha,\mathbf{q}_\beta)$, which describes the onset of inter-replica correlations (the glass order parameter).

The choice of the form of the trial function $Q_{\alpha\beta}(\mathbf{q}_\alpha,\mathbf{q}_\beta)$ is determined by the following considerations. The very possibility of the appearance of a glass order parameter is related to the infinite degeneracy of the ordered state of the systems under consideration for $\gamma=0$ and $\lambda=0$ (Ref. 21). Here, in the framework of weak-crystallization theory, the main contribution to the free energy of the system is made by nonuniformities with wave numbers of magnitude q_0. It is natural, therefore, to seek $Q_{\alpha\beta}(\mathbf{q}_\alpha,\mathbf{q}_\beta)$ in the form of a function that, first, would be nonzero only for $|q_\alpha-q_0|,|q_\beta-q_0|\ll q_0$, and, second, is convenient for the calculation of the corresponding integrals in (9). These conditions are satisfied by a function of the form

$$Q_{\alpha\beta}(q_\alpha,q_\beta)=(\pi Q_{\alpha\beta}/sr)\left(\delta(q_\alpha-q_0)\delta(q_\beta-q_0)\right)^{1/2}, \qquad (13)$$

where $s=q_0^2/2\pi$, $Q_{\alpha\beta}$ is a certain numerical matrix, and the symbol $[\delta(x)]^{1/2}$ denotes the generalized function

$$\lim_{\varepsilon\to 0}\exp\left[\left(-x^2/2\varepsilon^2\right)/\left(\pi^{1/4}\varepsilon^{1/2}\right)\right].$$

The corresponding calculations of the free energy of the system to terms of order Q^5 lead to an expression

$$F=\min\left[F(0)+F_{gl}(Q)\right], \qquad (14)$$

in which the free energy of the system for zero value of the glass order parameter Q is given by the expression that is obtained as a result of substituting the trial functions (10) and (12) into (7) and then taking the limit $n\to 0$ (see Refs. 19 and 21):

$$F(0)=\tfrac{1}{2}sr^{1/2}+\tfrac{1}{2}s\tau r^{-1/2}+\tfrac{1}{8}(\lambda+\varkappa)s^2r^{-1}$$
$$+\tfrac{1}{2}(\lambda+\varkappa)sA^2r^{-1/2}\tau A^2-\alpha_k\gamma A^3\,\tfrac{1}{2}\varkappa A^4+B_k\lambda A^4. \tag{15}$$

The factors α_k and B_k in (15) depend on the number k and the symmetry of the lattice;[4] for the principal lattice types observed in weak crystallization they take the following values:

a) For a lamellar lattice,

$\alpha_1=0,\quad B_1=1/4;$

b) for a triangular lattice,

$\alpha_3=2/3^{3/2},\quad B_3=5/12;$

c) for a body-centered lattice,

$\alpha_6=(2/3)^{3/2},\quad B_6=15/24.$

The quantity $F_{gl}(Q_{\alpha\beta})$ describes the free-energy contribution associated with the onset of a nonzero glass order parameter $Q_{\alpha\beta}$, and is given by the expression

$$F_{gl}=\lim_{n\Rightarrow 0}\frac{1}{n}\left\{\frac{1}{2}\Delta\,\mathrm{Sp}\,Q^2_{\alpha\beta}-\frac{1}{6}\,\mathrm{Sp}\,Q^3_{\alpha\beta}\right.$$
$$+\frac{1}{8}\,\mathrm{Sp}\,Q^4_{\alpha\beta}-\frac{(1-2\Delta)^2}{8}\sum_{\substack{\alpha\neq\gamma\\ \beta\neq\delta}}\left(Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\delta}Q_{\delta\alpha}\right.$$
$$\left.\left.+\frac{1}{2}\,Q^2_{\alpha\beta}Q^2_{\gamma\delta}\right)+\ldots\right\}, \tag{16}$$

where

$$\Delta=(1-\varkappa/r^2)/2. \tag{17}$$

We note that the terms in the second line of (16), which are the ones that lead to loss of stability of the replica-symmetric solution, are obtained from the diagrams of the next (after the one-loop) approximation for σ, which are given in Fig. 1. Furthermore, the linear term in the expansion of the quantity $\mathrm{Tr}\ln G$ in $Q_{\alpha\beta}$ is identically equal to zero by virtue of the definition (11). As regards the contributions of the remaining diagrams of order not higher than $Q^4_{\alpha\beta}$ that did not appear in (16), they vanish by virtue of the definition (13) and the identity

$$\lim_{\varepsilon\to 0}\int_{-\infty}^{+\infty}dx\exp(-x^2/2\varepsilon^2)\Big/(\pi^{1/4}\varepsilon^{1/2})=0. \tag{18}$$

It seems useful to note here the following two facts. First, the coefficients of the expansion of the free energy F_{gl}(16) in powers of the order parameter $Q_{\alpha\beta}$ are (starting from the third power) numerical factors, in analogy with the situation in the theory of spin glasses.[22,23,28,29] Therefore, this expansion (which, generally speaking, is asymptotic in view of the factorial increase of its numerical coefficients) is applicable only for small values of the order parameter ($Q_{\alpha\beta}\ll 1$), or, what is the same thing, for $|\Delta|\ll 1$. Second, the contributions of diagrams of the type represented in Figs. 1a and 1b also contain terms of lower orders in powers of $Q_{\alpha\beta}$, which lead, in particular, to the following redefinition (renormalization) of the quantity Δ:

$$\Delta=1-\frac{\varkappa}{r^2}-\sum_{l=2}^{l=\infty}a_l\left(\frac{\varkappa}{r^2}\right)^l \tag{17a}$$

[and also to an analogous renormalization of the numerical coefficients of other powers of $Q_{\alpha\beta}$ in the expansion (16)]. All the coefficients a_1 of the series (17a) are then positive, in contrast to the situation typical for the usual theory of critical phenomena,[30] in which the perturbation-theory series have terms of alternating sign. Therefore, this renormalization can lead only to a numerical shift of the boundary of the region in which the solution corresponding to a zero matrix $Q_{\alpha\beta}$ is stable against perturbations of the form (13). However, rigorous allowance for this renormalization [e.g., by direct Borel summation of the series (17a)] lies outside the scope of this paper. Henceforth, therefore, we shall use here the approximate expressions (17) for Δ and (16) for F_{gl}.

As follows from (16), the solution corresponding to a zero matrix $Q_{\alpha\beta}$ becomes unstable against perturbations of the form (13) in the region $\Delta<0$. In this region we introduce the Parisi order parameter $q(x)$—a function defined on the interval [0,1] and related to $Q_{\alpha\beta}$ by

$$\int_0^1 q(x)^k dx=\lim_{n\to 0}\frac{1}{n(n-1)}\sum_{\alpha\neq\beta}Q^k_{\alpha\beta},\quad\forall k. \tag{19}$$

In terms of the new order parameter $q(x)$ the free energy (16) can be written, as in Refs. 22, 28, and 29, in the form

$$F_\lambda=\tfrac{1}{2}\max\left\{\int_0^1 dx\left[\left|\Delta\right|q^2(x)+\frac{3}{8}q^4(x)-\frac{x}{3}q^3(x)\right.\right.$$
$$\left.\left.-q(x)\int_0^x q^2(y)dy\right]-\frac{3}{4}\left(\int_0^1 q^2(x)dx\right)^2\right\}. \tag{20}$$

The functional (20) differs by the presence of the last term from the standard expression for the free energy of spin glasses, but one can easily convince oneself that its stable extremum, corresponding to a replica-nonsymmetric order parameter $Q_{\alpha\beta}$, is achieved for a function of the standard form[22,28,29]

$$q(x)=\begin{cases}2x/9, & x\leqslant x_1=9q_1/2,\\ q_1, & x_1\leqslant x\leqslant 1,\end{cases} \tag{21}$$

where $q_1=|\Delta|[1+15|\Delta|/4+O(|\Delta|^2)]$. Substituting (21) into (20) and (14), we obtain the final expression for the total free energy of the system:

$$F=\min\left\{\frac{1}{2}sr^{1/2}+\frac{1}{2}s\tau r^{-1/2}+\frac{1}{8}(\lambda+\varkappa)s^2r^{-1}\right.$$
$$+\frac{1}{2}(\lambda+\varkappa)sA^2r^{-1/2}\tau A^2+\frac{1}{2}\varkappa A^4-\alpha_k\gamma A^3+B_k\lambda A^4$$
$$\left.-\frac{\theta(-\Delta)\Delta^3}{6}\left(1+27\frac{|\Delta|}{8}+O(\Delta^2)\right)\right\}, \tag{22}$$

where $\theta(x)$ is the step function [$\theta(x)=0$ for $x<0$, and $\theta(x)=1$ for $x>0$], and the parameter Δ as a function of r is defined in (17). The minimum in (22) is sought with respect to the parameters A and r, the equilibrium values of which are found as solutions of the equations of the extremals:

$$\partial F/\partial r=\partial F/\partial A=0. \tag{23}$$

We shall analyze these equations while constructing typical phase diagrams in the next section.

3. THE PHASE DIAGRAMS

We begin by classifying the phases. As follows from the preceding section, each phase is characterized by the symmetry type of the order parameter (10) and by the presence or absence of inter-replica correlations (the parameter $Q_{\alpha\beta}$, $\alpha\neq\beta$). To refer to phases with zero value of the parameter $Q_{\alpha\beta}$ we shall use henceforth the established terminology of the theory of weak crystallization, without stipulating each time that in such a phase $Q_{\alpha\beta}=0$ for $\alpha\neq\beta$. We shall call all phases with a nonzero value of the parameter $Q_{\alpha\beta}$ glass phases, indicating where necessary the characteristic symmetry type of the order parameter (10) for this phase.

We first consider the simpler case of systems for which the parameter γ determining the magnitude of the cubic vertex in the expression (22) for the free energy is equal to zero. We recall that, in the absence of quenched structural disorder ($\varkappa=0$), as the temperature is lowered in such systems a first-order phase transition occurs from the spatially uniform (disordered) phase to a supercrystalline phase with a lamellar type of symmetry.[3,4] (In the following we shall denote these phases by DIS and LAM, respectively.)

For the phase (which we shall call G_{DIS}) with zero value of the order parameter $\langle\psi_\alpha(\mathbf{r}_\alpha)\rangle$ and a nonzero value of the glass order parameter $Q_{\alpha\beta}(\alpha\neq\beta)$, from Eqs. (23) there remains only the equation for r; to leading order in Δ this equation has the form

$$\tau=r-\frac{\varkappa+\lambda}{2}sr^{-1/2}-2\frac{\varkappa\Delta^2}{sr^{3/2}}. \tag{24}$$

For the phase (which we shall call G_{LAM}) with nonzero values of both order parameters $\langle\psi_\alpha(\mathbf{r}_\alpha)\rangle$ and $Q_{\alpha\beta}(\alpha\neq\beta)$, Eqs. (23), to leading order in Δ, can be brought to the form

$$\tau=-\frac{(2B_k\lambda+\varkappa)}{\lambda(1-2B_k)}\left(r-2\frac{\varkappa\Delta^2}{sr^{3/2}}\right)-\frac{(\varkappa+\lambda)}{2}sr^{-1/2}, \tag{25a}$$

$$A^2=\frac{1}{\lambda(1-2B_k)}\varkappa^{1/2}\left(1-\left|\Delta\right|-\frac{2|\Delta|^2}{s\varkappa^{1/4}}\right). \tag{25b}$$

We note that in Eqs. (24) and (25) we have neglected terms of order $O(\Delta^2)$ but kept terms of order $O(\Delta(\Delta/s\varkappa^{1/4}))$, which can be large for systems with a small degree of structural disorder ($\varkappa\ll 1$). Therefore, as follows from Eq. (25b), the amplitude of the order parameter for the phase G_{LAM} can vanish for small values of $|\Delta|$ satisfying the equation

$$1-|\Delta|-\frac{2|\Delta|^2}{s\varkappa^{1/4}}=0. \tag{26}$$

The line (26) is obviously a line of second-order phase transitions between the phases G_{DIS} and G_{LAM}.

The expression (22) for the free energy and Eqs. (24) and (25) for the extremals permit us to construct the phase diagram of the systems under consideration. The surface $\tau_1(\varkappa,\lambda)$ of the third-order phase transition from the uniform (disordered) phase to G_{DIS} is determined by the equation

$$\tau_{\mathrm{DIS}\text{-}gl}=\varkappa^{1/2}-\frac{(\varkappa+\lambda)}{2\varkappa^{1/4}}s, \tag{27}$$

which is obtained by substituting

$$\Delta=0 \tag{28}$$

or equivalently,

$$r=\varkappa^{1/2}, \tag{28a}$$

into Eq. (24). The same substitution into Eq. (25a) gives the surface $\tau_2(\varkappa,\lambda)$ of the third-order phase transition from the ordered (lamellar) phase to G_{LAM}:

$$\tau_{gl\text{-cryst}}=-\frac{\lambda+2\varkappa}{\lambda}\varkappa^{1/2}-\frac{(\varkappa+\lambda)}{2\varkappa^{1/4}}s. \tag{29}$$

In the latter case, however, we must bear in mind that part of this surface corresponds to nonphysical (unstable) values of the amplitude A of the order parameter characterizing the phase G_{LAM}. Further analysis shows that for that part of the surface $\tau_2(\varkappa,\lambda)$ which corresponds to a stable (or at least metastable) solution of Eq. (25a) the condition

$$\varkappa^{1/2}\geqslant\left(\frac{\lambda s(1-2B_k)(\varkappa+\lambda)}{4(\varkappa+2B_k\lambda)}\right)^{2/3} \tag{30}$$

is fulfilled.

In the plane $(\tau/\lambda^{1/2},\varkappa/\lambda)$ Fig. 2 gives the phase diagram for the system described by the Hamiltonian (4), for the values $\lambda=0.01$ and $q_0=1$). It can be seen that for lower values of τ a direct first-order phase transition from the disordered phase (DIS) to the lamellar phase (LAM) occurs only at very small values of $\varkappa/\lambda$. In this region, the pattern of the phase transitions is analogous to that for phase transitions in ordinary weak crystallization.[3,4] At the point A the temperature of the phase transition from the uniform phase to the supercrystalline phase is comparable to the temperature at which a nonzero glass order parameter $Q_{\alpha\beta}$ appears in the uniform phase. Further increase of $\varkappa/\lambda$ causes a region in which the glass phase G_{DIS} exists to appear in the system. Finally, for $\varkappa/\lambda\geqslant(\varkappa/\lambda)_B$, the following sequence of phase transitions is established in the system: DIS–G_{DIS}–G_{LAM}–LAM, where the transition G_{DIS}–G_{LAM} is a first-order phase transition.

Another section of the phase-transition surfaces in the variables (τ,λ), for $\varkappa=0.01$ and $q_0=1$, is shown in Fig. 3,

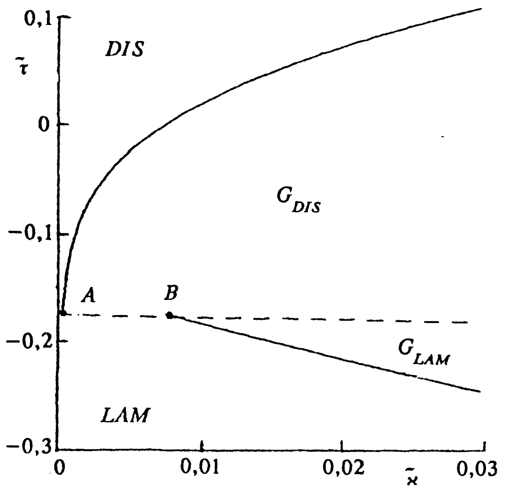


FIG. 2. The $\lambda=0.01$ section of the phase-transition surfaces in the variables $\tilde{\varkappa}=\varkappa/\lambda$, $\tilde{\tau}=\tau/\lambda^{1/2}$. The solid lines denote lines of third-order phase transitions, and the dashed line is a line of first-order phase transitions. The points A and B are points of intersection of lines of first-order and third-order phase transitions.

in which the left branch of the line of first-order phase transitions G_{DIS}–G_{LAM} is constructed on the basis of the following qualitative considerations. As noted in Ref. 24, for $\varkappa\neq0$ and $\lambda\to0$ the temperature of the first-order phase transition DIS-LAM tends to $-\infty$. The same follows from Eq. (25a) for the line of the third-order phase transition LAM–G_{LAM}. In addition, for $\lambda=0$ the system cannot be in any definite ordered state, since its free energy does not depend on its crystal-symmetry type (the ground state is infinitely degenerate).

As regards the line (26) of second-order phase transitions, numerical analysis shows that it always lies inside the phase G_{DIS} (where the phase G_{LAM} is already metastable), and, therefore, it is not shown in the figures. Nevertheless, this phase transition can also be observed when the system is heated sufficiently rapidly.

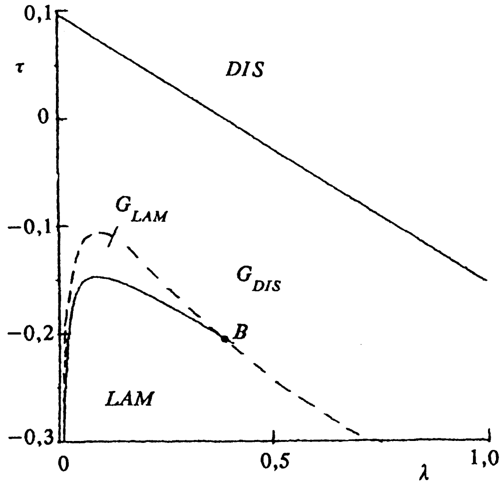


FIG. 3. The $\varkappa=0.01$ section of the phase-transition surfaces in the variables λ, τ. The notation is the same as in Fig. 2.

We now consider how the phase diagrams represented in Figs. 2 and 3 change with the appearance of a nonzero cubic vertex γ. As is well known,[2,4,7] in the absence of quenched structural disorder ($\varkappa=0$) the inclusion of a cubic vertex implies that, depending on the magnitude of the cubic vertex γ, lowering of the temperature in the disordered phase induces a transition first into a phase with a body-centered cubic (BCC) lattice, then into a two-dimensional structure with triangular symmetry (Δ), and only then into a one-dimensional lamellar structure. Here, allowance for fluctuation effects shows that, depending on the magnitude of the fourth-order vertex λ, either the whole sequence of phase transitions DIS–BCC–Δ–LAM or the reduced sequences DIS–Δ–LAM and DIS–LAM can occur.

It is obvious that the appearance of quenched structural disorder ($\varkappa\neq0$) can give rise to glass phases inside each of the regions corresponding to the indicated symmetries. It is natural to consider the corresponding change of the phase diagram first in the mean-field approximation, i.e., to terms of order $O(\lambda s/r^{3/2})$.

In this case the equations (25) of the extremals take the form

$$r-\tau-(\lambda+\varkappa)A^2=2\frac{\varkappa\Delta^2}{sr^{3/2}}, \tag{31a}$$

$$\tau-3\alpha_k\gamma A/2+(2B_k\lambda+\varkappa)A^2=0. \tag{31b}$$

Solving Eqs. (31) gives the equilibrium values of r and A, in the region where both the supercrystalline phases and the glass phases with the corresponding symmetry type of the order parameter (10) exist. However, as follows from numerical analysis of Eqs. (31), the right-hand side of (31a) near the line of the phase transition to the supercrystalline phases is small in comparison with any of the terms in the left-hand side, and so can be set equal to zero. Therefore, to construct the phase diagrams it is sufficient (with a high degree of accuracy) to construct first the usual weak-crystallization phase diagram, and then to plot on it the line (28) of the third-order phase transition between the supercrystalline phases and the glass phases. The results of numerical calculations for the case $q_0=1$ and two values of the parameter $\tilde{\varkappa}=\varkappa/\lambda$ are presented in Fig. 4.

As can be seen from comparison of the phase diagrams presented in Figs. 4a and 4b decreasing the parameter $\tilde{\varkappa}$ leads, as we should expect, to narrowing of the region of existence of the glass phases. In fact, according to (28), glass phases exist only for values $r^2<\varkappa$, or, in other words, in regions of strongly developed spatial fluctuations of the order parameter, which are possible only in the immediate vicinity of the point $\tau=0$, $\gamma=0$, corresponding, in the mean-field approximation, to a second-order phase-transition point. This circumstance makes it possible to understand immediately the character of the fluctuation corrections to the phase diagrams of Fig. 4 constructed in the mean-field approximation. Since, for $\varkappa=0$, fluctuation

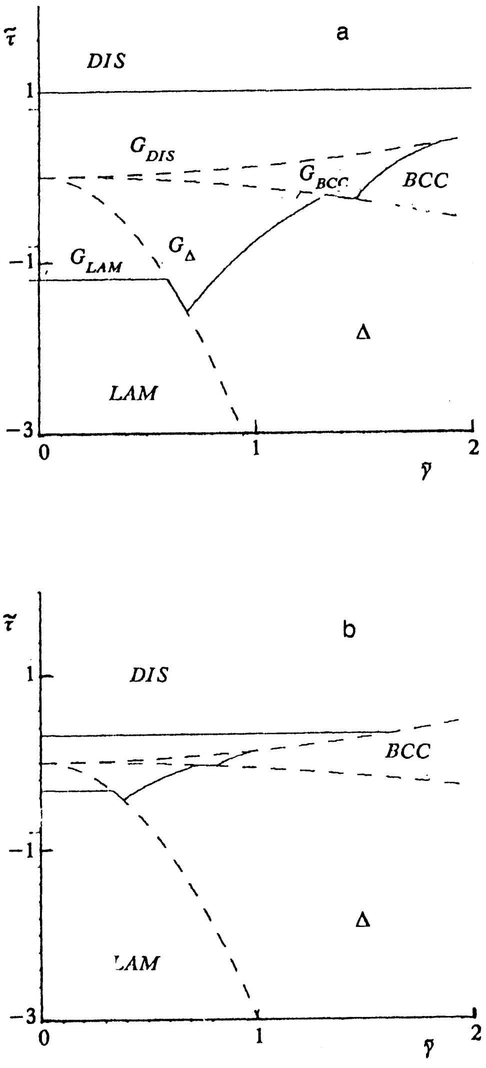


FIG. 4. The $\tilde{\varkappa}=\varkappa/\lambda=0.01$ section (a) and $\tilde{\varkappa}=0.01$ section (b) of the phase-transition surface in the variables $\tilde{\gamma}=\gamma/\lambda$, $\tilde{\tau}=\tau/\lambda$ for $\lambda=0.01$ and $q_0=1$. The notation is the same as in Fig. 2. The topology of the arrangement of the glass phases in Fig. 4b is the same as is indicated explicitly in Fig. 4a.

corrections cause a second-order phase transition to be replaced by a fluctuation-induced first-order phase transition, as a result of which the region in which the disordered phase exists expands at the expense of a narrowing (or even the disappearance) of the region of the supercrystalline phases,[3,4,9] for $\varkappa \neq 0$ these corrections will cause expansion of the region in which the phase $G_{\rm DIS}$ exists at the expense of a narrowing (and, for sufficiently large values of λ, the disappearance) of the supercrystalline glass phases. Thus, for sufficiently small values of the parameter γ the disordered glass phase should exist for all values of the fluctuation corrections, as is demonstrated by Fig. 3: For values $\lambda > \lambda_B \approx 0.4$ the line of first-order phase transitions $G_{\rm DIS}$–$G_{\rm LAM}$ goes over into the line of first-order phase transitions $G_{\rm DIS}$–LAM.

It is remarkable that the region of existence of the glass phases remains significant even for extremely small values of the parameter $\tilde{\varkappa}$ characterizing the relative magnitude of the inter-replica interaction in comparison with the one-replica interaction. We shall discuss this circumstance in more detail in the next section.

4. CONCLUSION

In the preceding sections we have shown that the presence of molecules with a distribution of structures in a system gives rise to a region of glass phases for the phase diagram. Up to now, however, we have not written out the conditions for applicability of our analysis of the phase transitions in disordered systems. We now discuss this question in more detail.

In the explicit calculation of the functional series (9) appearing in the expression (7) for the free energy, diagrams of order $O(\lambda^n)$ and $O(\gamma^n)$ $(n>1)$ were omitted (see Figs. 1c and 1d). These diagrams make the following contribution to the free energy of the system:

$$W_b \approx \lambda^2 q_0^5/r^2, \quad W_g \approx \gamma^2 q_0^3/r^{3/2}. \tag{32}$$

It is obvious that the contribution of these diagrams can be neglected in comparison with the contribution of the diagrams taken into account explicitly in (9) when the following conditions are fulfilled in the region of the phase transitions:

$$\lambda q_0/r \ll 1, \quad \gamma^2/\lambda q_0 r^{1/2} \ll 1. \tag{33}$$

As was shown in Refs. 3 and 4, in a region of first-order transitions to crystalline phases we have $r \approx (\lambda q_0^2)^{2/3}$, which is also true in our case for small values of the vertex of the inter-replica interaction $(\varkappa \ll \lambda)$. Then the relations (33) can be rewritten in the form

$$\lambda/q_0 \ll 1, \quad \gamma^2/\lambda^{4/3} q_0^{5/3} \ll 1. \tag{34}$$

Thus, the phase diagrams given in Figs. 4a and 4b, which were calculated, as noted above, for $q_0=1$, are valid only in the region $\gamma^2/\lambda^{4/3} \ll 1$. In the opposite limit our constructions are valid only qualitatively, because for these values of the parameters renormalization of the critical momentum q_0 (mode softening) becomes important[31] as a consequence of the contribution of certain diagrams, the first of which is shown in Fig. 1d.

To estimate the lower boundary of the range of the quantity $\varkappa$ for which the contribution of the diagrams of Figs. 1c and 1d can be neglected in the region of the glass phase transition it is sufficient to substitute for the parameter r in (33) its value $\varkappa^{1/2}$ on the line of this phase transition. This leads to the following inequalities:

$$(\lambda q_0)^2 \ll \varkappa, \quad (\gamma^2/\lambda q_0)^4 \ll \varkappa. \tag{35}$$

We note that for $\varkappa \gg \lambda$ the first of the conditions (35) for $q_0=1$ is fulfilled automatically, although in this case it is necessary to take into account diagrams like Fig. 1e. The expansion in this case is performed in the parameter

$$W_d \approx \varkappa q_0^2/r^{3/2}, \tag{36}$$

and in the region of the glass phase transition $(r \approx \varkappa^{1/2})$ these diagrams can be neglected when the following condition is fulfilled:

$$\varkappa^{1/4} q_0^2 \ll 1, \qquad (37)$$

which, for $q_0 = 1$, is equivalent to the condition $\varkappa \ll 1$.

We shall summarize the results. In our paper, for the first time, we have constructed phase diagrams of realistic three-dimensional disordered systems capable of forming phases with broken replica symmetry. As is known from the theory of spin glasses,[23,32,33] the existence of a solution with broken replica symmetry for the matrix $Q_{\alpha\beta}$ is related to the splitting of the phase space of the systems under consideration into an infinite number of disconnected regions (equivalent states), Gibbsian averaging over each of which leads to one and the same (in the thermodynamic limit) value of the free energy, while the matrix $Q_{\alpha\beta}$ describes the metric properties of the space of these states. It may be expected that in our case too the existence of a solution with broken replica symmetry is also related to the appearance of a hierarchical space of valleys in the Hilbert space of the order-parameter functions in the region $r < \varkappa^{1/2}$, leading, as shown in Ref. 26, to the appearance of statistical fluctuations (nonvanishing even in the thermodynamic limit) of the experimentally measured quantities. However, the feature of the case considered in our work that distinguishes it from the description of the glass phase in the theory of spin glasses is that in our case the principal contribution to the inter-replica susceptibility is made by fluctuations with finite wavelength $L = 1/2\pi q_0$.

Experimental verification of these phase diagrams is extremely urgent from a general theoretical point of view, since the possibility arises of checking the results of spin-glass theory on real three-dimensional systems in which all the parameters can be specified with a sufficiently high degree of accuracy at the stage of synthesis of the polymer. It appears that the most promising way to carry out this check is to measure the above-mentioned statistical fluctuations of the correlation functions of the order parameter by the methods of small-angle x-ray and neutron scattering.

The authors express their deep gratitude to the participants in the polymer-physics seminar founded by I. M. Lifshits in the Physics Faculty at Moscow State University for a discussion of the results obtained.

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Translated by P. J. Shepherd