

# Conditions for the existence of a glass phase in disordered systems described by a weak-crystallization Hamiltonian of a general type

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The behavior of disordered systems described by a generalized weak-crystallization Hamiltonian is examined. Systems of this sort contain a region with a phase of the spin-glass type. An expression is derived for the surface which bounds the region. This is a surface of third-order phase transitions. The free energy of the glass phase near the surface is calculated in the leading approximation.

The behavior of systems with a frozen structural disorder has recently attracted considerable interest.<sup>1–3</sup> Structural phase transitions of the weak-crystallization type have received most of the attention.<sup>4</sup> As was pointed out in Ref. 5, however, the free energy of the disordered state in the systems studied in Refs. 1–3 is independent of the symmetry of the corresponding crystal lattice (or quasicrystal lattice) because of a special degeneracy of the Hamiltonian describing these systems. In other words, the ground state of such systems is infinitely degenerate. In this sense, these systems behave like a spin glass below the transition point.<sup>6,7</sup> In the present letter we show that this analogy is exact and that a phase transition associated with the appearance of nonzero interreplica correlations, i.e., the formation of a glass phase, occurs for a wide family of systems with a frozen structural disorder which are described by a Hamiltonian of a fairly general type.

The behavior of many polymer systems consisting of identical macromolecules is described by the Hamiltonian

$$H_0(\{\psi(q)\}, T)/T = \int \frac{dq}{(2\pi)^3} g^{-1}(q) \psi(q) \psi(-q) / 2 \\ + \lambda \int \delta \left( \sum_{i=1}^{i=4} q_i \right) \prod_{i=1}^{i=4} \psi(q_i) \frac{dq_i}{(2\pi)^3} / 24, \quad (1)$$

where the seed propagator has the form typical of the case of weak crystallization,

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

and the constants  $q_0$  and  $\lambda$  and the reduced temperature  $\tau$  are related to structural characteristics of the polymer (see Refs. 8, 9, and 11 and the paper cited there).

In real polymer systems, there is always some distribution of macromolecules with respect to structure simply because of the statistical nature of the polymer syn-

thesis process. These systems must accordingly be regarded as systems with a frozen structural disorder, in which observable quantities are determined by averaging the free energy over a given distribution of the structural disorder. In the replica formalism<sup>2</sup> this is done by analyzing the general Hamiltonian

$$H[\{\psi_\alpha(q_\alpha)\}, T]/T = \sum_{\alpha=1}^{\alpha=n} H_0[\{\psi_\alpha(q_\alpha)\}, T]/T - \kappa \sum_{\alpha \neq \beta} \int \frac{dq_\alpha}{(2\pi)^3} \frac{dq_\beta}{(2\pi)^3} \psi_\alpha(q_\alpha) \psi_\alpha(-q_\alpha) \psi_\beta(q_\beta) \psi_\beta(-q_\beta) / 8, \quad (3)$$

where the parameter  $\kappa$ , always positive, is related to the dispersion of the structural distribution of the macromolecules. The free energy of this family of systems is

$$F = -T \lim_{n \rightarrow 0} \{1/n \{\exp(-F_n/T) - 1\}\}, \quad (4)$$

where  $\exp(-F_n/T) = \int \prod_{\alpha=1}^n \delta\psi_\alpha(x_\alpha) \exp(-H[\{\psi_\alpha(x_\alpha)\}, T]/T)$ .

Following Refs. 5 and 9, we calculate  $F$  by means of a variational principle based on a second Legendre transformation.<sup>10</sup> This principle makes it possible to express the free energy as the sum of contributions from skeleton diagrams. In the one-loop approximation,<sup>4,5,9</sup> we can thus write the free energy as

$$F_n/T = -\frac{1}{2} \text{Tr Ln } G_{\alpha\beta} + \sum_{\alpha=1}^n \left\{ \int \frac{dq_\alpha}{(2\pi)^3} G_{\alpha\alpha}(q_\alpha) g^{-1}(q_\alpha) / 2 + \frac{\lambda}{4!} \text{diagram 1} + \frac{\lambda}{8} \text{diagram 2} + \frac{\lambda}{4} \text{diagram 3} + \int \frac{dq_\alpha}{(2\pi)^3} g^{-1}(q_\alpha) \psi_\alpha(q_\alpha) \psi_\alpha(-q_\alpha) / 2 \right\} - \frac{\kappa}{8} \sum_{\alpha \neq \beta} \left\{ \text{diagram 4} + 2 \text{diagram 5} + 2 \text{diagram 6} + \text{diagram 7} + 4 \text{diagram 8} \right\}, \quad (5)$$

where a solid line represents the renormalized propagator  $G_{\alpha\beta}(q_\alpha)$ , and a small open circle, a small filled circle, and a dashed line represent the field  $\psi_\alpha(q_\alpha)$  and the vertices of the one-replica and interreplica interactions, respectively. We seek a minimum of  $F_n$  on the class of trial functions

$$G_{\alpha\beta}^0(q_\alpha, q_\beta) = [(|q_\alpha| - q_0)^2 + r]^{-1} \delta(q_\alpha - q_\beta) \delta_{\alpha\beta} \quad (6a)$$

$$\psi_\alpha(r_\alpha) = \frac{A_\alpha}{k^{1/2}} \sum (\exp i q_0 r_\alpha + \text{c.c.}). \quad (6b)$$

The summation in (6b) is over all the reciprocal-lattice vectors of the corresponding conjugate Bravais lattice which are equal in magnitude to  $q_0$ ; here  $k$  is the number of basis vectors of the reciprocal lattice. Substituting (6) into (5), and taking the limit  $n \rightarrow 0$ , we find an expression for the free energy  $F$  of the system:

$$F/T = \min \left\{ \frac{1}{2} sr^{1/2} + \frac{1}{2} s\tau r^{-1/2} + \frac{1}{8} (\lambda + \kappa) s^2 r^{-1} + \frac{1}{2} (\lambda + \kappa) s A^2 r^{-1/2} + \tau A^2 + \frac{1}{2} \kappa A^4 + B_n \lambda A^4 \right\}. \quad (7)$$

Here  $s = q_0^2/2\pi$ , and the factor  $B_n$  is determined by the number of vectors and the symmetry of the reciprocal lattice. The equilibrium values of  $r$  and  $A$  are found as the solutions of the extremal equations

$$\partial F/\partial r = \partial F/\partial A = 0 \quad (8)$$

which take the form

$$\tau = r - \frac{(\kappa + \lambda)}{2} sr^{-1/2}; \quad A = 0, \quad (9)$$

for the homogeneous phase and

$$\tau = -\frac{(2B_n\lambda + \kappa)}{\lambda(1 - 2B_n)} r - \frac{(\kappa + \lambda)}{2} sr^{-1/2}; \quad A^2 = \frac{r}{\lambda(1 - 2B_n)}, \quad (10)$$

for the ordered phase. Solution (10) exists only under the condition  $\lambda(1 - 2B_n) > 0$ .

It follows from the functional dependence  $\tau(r)$  that a solution for the ordered phase arises only under the condition

$$\tau < \tau_c = -\frac{3}{2^{4/3}} s^{2/3} (\kappa + \lambda)^{2/3} \left( \frac{(2B_n\lambda + \kappa)}{\lambda(1 - 2B_n)} \right)^{1/3}. \quad (11)$$

As the single-replica vertex  $\lambda$  approaches zero, as it may for systems with an uncorrelated alternation of units along the chain<sup>1-3</sup> and for copolymer systems which exhibit a tricritical behavior,<sup>9,11</sup> we find  $\tau_c \rightarrow -\infty$ . In this case the region  $\tau > \tau_c$ —the region in which solution (9), corresponding to a disordered phase, exists—expands to fill the entire axis,  $-\infty < \tau < \infty$ .

Significantly, however, this solution loses its stability with respect to nondiagonal (in multireplica space) perturbations of the correlation function of the type in (6a) at finite values of  $\tau$ . To see this, we write the trial function  $G_{\alpha\beta}(q_\alpha, q_\beta)$ , which is to be substituted into variational principle (5), as the sum of a single-replica trial function (6a) and a new trial function, which describes the appearance of interreplica correlations (a glass order parameter):

$$G_{\alpha\beta}(q_\alpha, q_\beta) = G_{\alpha\beta}^0(q_\alpha, q_\beta) + Q_{\alpha\beta}(q_\alpha, q_\beta)(1 - \delta_{\alpha\beta}). \quad (12)$$

The choice of the trial function  $Q_{\alpha\beta}(q_\alpha, q_\beta)$  is governed by the following considerations. The very possibility that a glass order parameter will arise stems from the fact, mentioned above, that the ordered state of these systems is infinitely degenerate in the case  $\lambda = 0$ . According to the theory of weak crystallization, the free energy of the system is determined primarily by inhomogeneities with wave numbers equal in mag-

nitude to  $q_0$ . It is thus natural to seek  $Q_{\alpha\beta}(q_\alpha, q_\beta)$  as a function which is nonzero only at  $|q_\alpha - q_0|, |q_\beta - q_0| \ll q_0$  and which is convenient for evaluating the corresponding integrals in (5). These conditions are satisfied by a function

$$Q_{\alpha\beta}(q_\alpha, q_\beta) = (Q_{\alpha\beta}/r) [\delta(q_\alpha - q_0)\delta(q_\beta - q_0)]^{1/2}, \quad (13)$$

where  $Q_{\alpha\beta}$  is a number matrix, and  $[\delta(x)]^{1/2}$  represents the generalized function  $\lim_{\epsilon \rightarrow 0} \exp(-x^2/2\epsilon^2)/(\pi^{1/4}\epsilon^{1/2})$ .

Substituting (12) and (13) into variational principle (5), we find

$$F_n(Q_{\alpha\beta})/T = F_n(0)/T + \frac{1}{4} \left( \frac{q_0^2}{2\pi^2} \right)^2 \left( 1 - \frac{\kappa}{r^2} \right) \text{Tr } Q^2 - \frac{1}{6} \left( \frac{q_0^2}{2\pi^2} \right)^3 \text{Tr } Q^3 + O(Q^4), \quad (14)$$

where  $F_n(0)$  is the free energy of the system in the case  $Q_{\alpha\beta} = 0$ . It is described by expression (5). Here we are using the convention of a summation over a repeated index. [The linear term of the expansion of  $\text{Tr } \ln G$  in  $Q_{\alpha\beta}$  is identically zero by virtue of definition (12). Because of definition (13) and the identity

$$\lim_{\epsilon \rightarrow 0} \int_{-\infty}^{+\infty} dx \exp(-x^2/2\epsilon^2)/(\pi^{1/4}\epsilon^{1/2}) = 0, \quad (15)$$

the contributions of the other diagrams of order no higher than  $O(Q^3)$  which are not written out in (14) vanish.]

It follows from (14) that for integer values  $n \geq 1$  a solution of the type in (6a) corresponding to a vanishing matrix  $Q_{\alpha\beta}$  becomes unstable with respect to perturbations of the type in (13) in the region

$$\Delta = 1 - (\kappa/r^2) < 0. \quad (16)$$

The equilibrium value of the parameter  $Q_{\alpha\beta}$ , corresponding to a replica-symmetry solution which is stable in this region, and the free energy of the system corresponding to the solution for integer values  $n > 2$  and small values of  $|\Delta|$  are given by

$$Q_{\alpha\beta} = \frac{\Delta}{n-2} \frac{2\pi^2}{q_0^2}; \quad (17)$$

$$\frac{F_n(Q_{\alpha\beta})}{T} = \frac{F_n(0)}{T} + n \frac{\Delta^3}{12} \frac{n-2}{(n-2)^2}. \quad (18)$$

Taking the limit  $n \rightarrow 0$  in (18), we finally find

$$F/T = F_0/T - \theta(-\Delta) \Delta^3/48, \quad (19)$$

where the functions  $F_0$  and  $\Delta$  are given by (7) and (16), respectively.

It follows from (17)–(19) that there is an exact analogy between the region  $\Delta < 0, |\Delta| \ll 1$  and the Sherrington–Kirkpatrick replica-symmetry glass phase.<sup>6,12</sup> We are thus justified in calling this region a “glass phase.”

In summary, we have shown that a region of a glass phase exists for three-dimensional systems which are described by the generalized weak-crystallization

Hamiltonian in (3). A detailed analysis of the phase diagrams of systems of this sort lies outside the scope of this letter, as does a consideration of the non-replica-symmetry corrections by means of the Parisi solution. We will simply reproduce the expressions for the surfaces of the third-order phase transitions, which bound the glass-phase region on the sides of the disordered and supercritical states, respectively [these expressions are found by substituting  $r = \kappa^{1/2}$  into Eqs. (9) and (10)]:

$$\tau_{\text{dis-gl}} = \kappa^{1/2} - \frac{(\kappa + \lambda)}{2\kappa^{1/4}} s; \quad (20)$$

$$\tau_{\text{gl-cryst}} = -\frac{(2B_n\lambda + \kappa)}{\lambda(1 - 2B_n)} \kappa^{1/2} - \frac{(\kappa + \lambda)}{2\kappa^{1/4}} s. \quad (21)$$

We would like to stress that Hamiltonian (3) and its obvious generalizations may be useful for a phenomenological description of the glass transition process not only in polymers but also in other real disordered systems, primarily mixtures of smectic liquid crystals.

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