Fluctuation theory of weak crystallization in disordered heteropolymer systems

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The behavior of disordered heteropolymer systems in the region where they become unstable relative to the fluctuations which destroy the spatially homogeneous state has been studied. It is shown on the basis of the Brazovskiĭ approximation that the transition from the homogeneous state is a first-order phase transition. Some characteristic features of the behavior of the systems under consideration below the transition point are discussed.

The behavior of a system with a frozen structure disorder has recently been studied extensively. In particular, the behavior of heteropolymer systems, i.e., linear chains which are sufficiently long, uncorrelated sequences of two types of links which interact in such a way that these systems in the "unfrozen" state, i.e., thermodynamically equilibrium state, should undergo a phase transition.

On the basis of a replica formalism it was concluded if Refs. 2 and 3 that the loss of stability of the spatially uniform state of such a system with respect to fluctuations of its composition occurs in an unusual way: At temperatures below a certain critical temperature T_C the system undergoes a transition to a supercrystalline state with a period $L = 2\pi/q_0$, where $q_0 \sim (T_C - T)^{1/2}$. This transition is a third-order phase transition. This conclusion, however, seems to be a consequence of an incorrect extrapolation of a mean-field approximation, used in Refs. 2 and 3, to a region of substantial fluctuations, $T_C < T$. Allowance for the fluctuation effects in the framework of the approximation of Ref. 4 shows that this is a first-order phase transition.

According to Refs. 2 and 3, the free energy of the system under consideration is

$$F = -T \lim_{n \Rightarrow 0} \left\{ \frac{1}{n} \{ \exp(-F_n/T) - 1 \} \right\}, \tag{1}$$

where

$$\exp(-F_n/T) = \int \prod_{\alpha=1}^{\alpha=n} \delta\psi_\alpha(\vec{x}^\alpha) \exp(-H(\{\psi_\alpha(\vec{x}^\alpha)\}, T)/T),$$

$$H(\{\psi_\alpha(\vec{q}^\alpha)\}, T)/T = \sum_{\alpha=1}^{n} \int \frac{d\vec{q}^\alpha}{(2\pi)^3} g^{-1}(\vec{q}^\alpha) \psi_\alpha(\vec{q}^\alpha) \psi_\alpha(-\vec{q}^\alpha)/2$$

$$- \sum_{\alpha \neq \beta} \int \frac{d\vec{q}^\alpha}{(2\pi)^3} \frac{d\vec{q}^\beta}{(2\pi)^3} \lambda(\vec{q}^\alpha, \vec{q}^\beta) \psi_\alpha(\vec{q}^\alpha) \psi_\alpha(-\vec{q}^\alpha) \psi_\beta(\vec{q}^\beta) \psi_\beta(-\vec{q}^\beta)/4, \tag{2}$$

where $g^{-1}(\vec{q}^\alpha) = \epsilon q^2 + \tau$; $\lambda(\vec{q}^\alpha, \vec{q}^\beta) = \kappa/(q_\alpha^2 + q_\beta^2)$; τ is the reduced temperature,

and ϵ and κ are certain positive molecular parameters of the system (these are differ-ent parameters in Refs. 2 and 3). In a spatially uniform state the Dyson equation for $G_{\alpha\alpha}(\vec{q}^{\alpha})$— the renormalized Green's function—is written in the form

$$G_{\alpha\alpha}^{-1}(\vec{q}^{\alpha}) = \epsilon q^2 + \tau - \sum_{\alpha \neq \beta} \int \frac{d\vec{q}^{\beta}}{(2\pi)^3} \lambda(\vec{q}^{\alpha}, \vec{q}^{\beta}) G_{\beta\beta}(\vec{q}^{\beta}). \tag{3}$$

Although the bare Green's function becomes unstable at $\tau < 0$ near small values of q, the long-range nature of the vertex $\lambda(\vec{q}^{\alpha}, \vec{q}^{\beta})$, characteristic of the system under consi-deration, accounts for the fact that in the limit $n \to 0$ we are considering the minimum of the renormalized Green's function lies near the finite values of q. [This can be easily seen by substituting instead of $G_{\beta\beta}(\vec{q}^{\beta})$ its bare value $g(\vec{q}^{\beta}) = (\epsilon q^2 + \tau)^{-1}$ in the integral on the right side of Eq. (3)]. To determine the nature of the transition, therefore, we will make use of the approximation of the complete Green's function, which is usually used in the theory of weak crystallization:

$$G_{\alpha\alpha}^{-1}(\vec{q}^{\alpha}) = C(q - q_0)^2 + r. \tag{4}$$

Substituting (4) in (3) and setting $n = 0$, we easily see that approximation (4) is valid and that the parameters in (4) can be determined from the equation

$$r = \tau + 3\kappa/(8\pi(Cr)^{1/2}), \quad q_0^2 = \kappa/(8\pi\epsilon(Cr)^{1/2}); \quad C = 2\epsilon. \tag{5}$$

In particular, it can be seen from (5) that in the approximation used by us, as in the weak crystallization theory,[4,5] the system under consideration does not have a stability loss boundary relative to infinitesimal fluctuations of the order parameter. In contrast with the usual situation, however, the value of q_0 now is no longer an independent parameter of the system, but is determined by the parameter τ. In this sense, this situation is similar to that which occurs in the structural phase transitions in polyelec-trolytes.[6,7] To describe the system in the ordered phase, we will therefore use, as in Ref. 7, a variational principle[8] which is based on the second Legendre transform and which makes it possible to represent the free energy as a sum of the components of the block diagrams. In the approximation used by us this allows us to write the free energy in the form

$$F_n/T = \min \left\{ \frac{1}{2} n q_0^2 \xi r^{1/2} - \frac{1}{8} n(n-1)\kappa\xi^2 q_0^2 r^{-1} - \frac{1}{4} n(n-1)\kappa\xi^{-1/2} A \right.$$
$$\left. + \frac{1}{2} n\xi(\epsilon q_0^2 + \tau) q_0^2 r^{-1/2} + n(\epsilon q_0^2 + \tau) A - \frac{1}{2} n(n-1)\kappa(q_0^2)^{-1} A^2 \right\}, \tag{6}$$

where $\xi = 1/2\pi(2\epsilon)^{1/2}$, and the minimum can be found from the values of q_0^2, r and from the sum of the square amplitudes of the order parameter in the ordered phase $A = \Sigma a_i^2$, where the summation is over all vectors of the first coordination sphere of the corresponding reciprocal lattice. Substituting (6) in (1), we obtain the final expression for the free energy of the system

$$F/T = \min \left\{ \frac{1}{2}q_0^2 \xi r^{1/2} + \frac{1}{8}\kappa\xi^2 q_0^2 r^{-1} + \frac{1}{2}\kappa\xi r^{-1/2}A \right.$$

$$\left. + \frac{1}{2}\xi(\epsilon q_0^2 + r)q_0^2 r^{-1/2} + (\epsilon q_0^2 + r)A + \frac{1}{2}\kappa(q_0^2)^{-1}A^2 \right\}. \tag{7}$$

We will not carry out a numerical analysis but simply note that the value of q_0 is the same in order of magnitude, both in the disordered phase and the ordered phase. The conditions under which the transition occurs can therefore be qualitatively estimated by directly using the results of Refs. 4 and 5. According to these results, the first-order phase transition to an ordered state occurs at

$$r \approx (\kappa/4\pi)^{2/3}C^{-1/3}. \tag{8}$$

However, a remarkable feature of this class of disordered systems, which directly follows from Hamiltonian (2), is the fact that the minimum of the free energy (and hence the value of q_0) of the ordered phase does not depend on their symmetry or, more exactly, on the number k of the vectors of the first coordination sphere. In other words, below the transition temperature the system can be with equal probability in the state with any value of k, and not only in the states with a known crystal or quasicrystal symmetry. In this sense, this system behaves as a spin glass below the transition point. It should be noted that such a behavior is characteristic of certain branched (grid) systems and not only linear heteropolymer systems. This degeneracy is lifted, however, when an arbitrarily small, single-replica term, which describes the interaction between the fluctuations, is included in Hamiltonian (2). Further analysis of these features may prove to be useful in the understanding of the nature of glass transition.

In summary, we have shown that the fluctuation effects radically change the behavior of disordered heteropolymer systems in the region of the instability of the fluctuations which cause the destruction of spatially homogeneous state.

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