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LETTER TO THE EDITOR

Fluctuation effects on microphase separation in a random copolymer Hamiltonian

C D Sfatos, A M Gutin and E I Shakhnovich

Harvard University, Department of Chemistry, 12 Oxford Street, Cambridge MA 02138, USA

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Abstract. We investigate the effect of fluctuations in the effective Hamiltonian that describes the microphase separation in random copolymers. This Hamiltonian is previously studied on the level of mean-field theory where a phase transition to a phase with periodic microdomain structure was predicted. It is shown here that the one-loop treatment of fluctuations is exact in the thermodynamic limit and that the phase predicted by mean field is unstable within the framework of the studied Hamiltonian.

We study the effect of fluctuations in the effective Hamiltonian that describes a random copolymer sequence, where each monomer along the sequence can be randomly of kind *A* or *B* and similar kinds of monomers attract each other. The mean-field study of these systems showed [1-3] that they undergo a temperature induced phase separation transition to a non-uniform phase. The transition from the disordered to the ordered phase has been predicted to be third order. A first attempt to describe this transition beyond mean field [4] showed that, on the level of the one-loop approximation, fluctuations make the disordered phase locally stable at any temperature $T > 0$. It was then argued that the transition takes place through a first-order mechanism similar to the weak crystallization transition to a non-uniform phase investigated by Brazovskii [5-7].

We perform here an exact treatment of fluctuations for this effective Hamiltonian. We show that fluctuations not only make the disordered state locally stable at any temperature $T > 0$, but also destabilize the ordered phase. This result holds true in any dimension.

The microphase separation transition is described by the order parameter [8]

$$m(\mathbf{R}) = \rho_A(\mathbf{R}) - \rho_B(\mathbf{R}) \quad (1)$$

where $\rho_A(\mathbf{R})$, $\rho_B(\mathbf{R})$ are the densities of monomer kinds *A*, *B* respectively. The effective Hamiltonian for the random copolymer is [1]

$$\mathcal{H} = \frac{1}{2} \sum_{\mathbf{k} \neq 0} (\mathbf{k}^2 + \tau) m(\mathbf{k}) m(-\mathbf{k}) + V^{-1} \sum_{\mathbf{k}_1, \mathbf{k}_2 \neq 0} \frac{\lambda}{\mathbf{k}_1^2 + \mathbf{k}_2^2} m(\mathbf{k}_1) m(-\mathbf{k}_1) m(\mathbf{k}_2) m(-\mathbf{k}_2) \quad (2)$$

where V is the volume and the Fourier transform of the order parameter is defined as $m(\mathbf{k}) = (1/\sqrt{V}) \int m(\mathbf{R}) e^{i\mathbf{k} \cdot \mathbf{R}} d\mathbf{R}$. The Hamiltonian (2) refers to the polymeric chain with an equal amount of *A* and *B* kinds of monomers so that $\int m(\mathbf{R}) d\mathbf{R} = 0$. The fourth-order vertex is due entirely to the heteropolymeric entropy. The coefficient λ is inversely proportional to the square of the polymeric bond length.

We see that the important features of this vertex are the strong momentum dependence and the pairing of momenta. The polymeric fourth-order term suppresses phase separation with long wavelengths. On the other hand short wavelength modes are suppressed by the surface tension contribution to the second-order term. It was shown [1] that the mean-field solution can be taken in the form

$$m(\mathbf{k}) = m_0 \sqrt{V/2} (\Delta(\mathbf{k} - \mathbf{k}_0) + \Delta(\mathbf{k} + \mathbf{k}_0)) \quad (3)$$

where Δ is Kronecker's delta. This solution corresponds to the lamellar phase. The mean-field amplitude m_0 and the frequency k_0 can be determined by minimization of (2) to be

$$m_0 = -\frac{\tau}{3\sqrt{\lambda}} \quad k_0^2 = -\frac{\tau}{3} \quad \text{for } \tau < 0. \quad (4)$$

Therefore, the mean-field theory predicts a continuous phase transition at $\tau = 0$.

Shortly after the derivation of this Hamiltonian it was observed [4] that a renormalization of the Green function on the one-loop level changes its form qualitatively. The one-loop Dyson equation for the Green function $G(\mathbf{k})$ is

$$G^{-1}(\mathbf{k}) = (k^2 + \tau) + V^{-1} \sum_{\mathbf{k}_1} \frac{4\lambda}{k_1^2 + k^2} G(\mathbf{k}_1). \quad (5)$$

By substituting even the bare Green function into the integral of (5) for $\tau > 0$, the renormalized Green function in three dimensions becomes

$$G^{-1}(k) = k^2 + \tau + \frac{2\lambda/\pi}{\tau^{1/2} + k} \quad (6)$$

with $k = |\mathbf{k}|$. We see immediately that there is a minimum of $G^{-1}(\mathbf{k})$ at some $k_* \neq 0$. It was, therefore, proposed that the form of the renormalized Green function can be described by the form used in weak crystallization theory

$$G^{-1}(k) = C(k - k_*)^2 + r. \quad (7)$$

This approximation is good for $r \ll k_*^2$. By substitution of this into (5) it was found that

$$r = \tau + \frac{3\lambda}{2\pi(Cr)^{1/2}} \quad k_*^2 = \frac{\lambda}{2\pi(Cr)^{1/2}} \quad C = 2. \quad (8)$$

According to the first relation in (8), the renormalized mass r , cannot become zero except for $\tau = -\infty$ which corresponds to $T = 0$. Therefore the disordered phase never loses stability as in the Brazovskii theory. This result is quite general and is due to the fact that the integral corresponding to the one-loop correction,

$$\int \frac{d^d k_1}{(k^2 + k_1^2)[(k_1 - k_*)^2 + r]} \quad (9)$$

is divergent as $r \rightarrow 0$ for every dimensionality. On the basis of this evidence it was assumed [4] that this system will have a first-order transition of the Brazovskii type. A more careful study, however, is to be carried out in what follows.

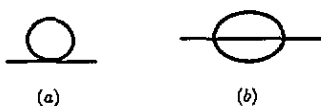


Figure 1. One-loop (a) and two-loop (b) Feynman diagram contribution to the self-energy.

Consider the diagrams that contribute to a perturbation expansion. The contribution of the one-loop diagram shown in figure 1(a) to the Dyson equation is of order

$$V^{-1} \sum_{k_1} \frac{\lambda G(k_1)}{k_1^2 + k^2} = V^{-1} \lambda \frac{V}{(2\pi)^3} \int dk_1 \frac{G(k_1)}{k_1^2 + k^2} \sim 1. \quad (10)$$

The two-loop diagram shown in figure 1(b) is of order

$$\lambda^2 V^{-2} G(k) \frac{V}{(2\pi)^3} \int dk_1 \frac{G^2(k_1)}{(k_1^2 + k^2)^2} \sim V^{-1} \quad (11)$$

and therefore should be neglected in the thermodynamic limit. We can easily see that all higher loops diagrams do not contribute for the same reasons.

From the above remarks we conclude that the one-loop Dyson equation given in (5) is exact and the lack of continuous transition for the effective Hamiltonian (2) is a general result that does not depend on the smallness of the parameter λ . This is a first important difference between the results of Hamiltonian (2) and the Brazovskii theory.

On the premises discussed above, we calculate here the stability of the ordered phase. If we assume that the symmetry is broken as described by (3) we need to write down the free energy functional $\mathcal{H}\{m_0, k_0; \psi\}$. The order parameter is

$$m(k) = \begin{cases} m_0 \sqrt{V/2} & \text{for } k = \pm k_0 \\ \psi(k) & \text{for } k \neq \pm k_0 \end{cases} \quad (12)$$

Fluctuations of the mode $k = k_0$ are of order 1 and are ignored compared to the mean-field $m(k) \sim \sqrt{V}$. Fluctuations to other modes are denoted by ψ . Then the free energy functional becomes

$$\begin{aligned} \mathcal{H}'\{m_0, k_0; \psi\} &= \mathcal{H}\{m_0, k_0\} + \frac{1}{2} \sum_{k \neq k_0} \left(k^2 + \tau + \frac{4\lambda m_0^2}{k_0^2 + k^2} \right) \psi(k) \psi(-k) \\ &+ \lambda V^{-1} \sum_{k_1, k_2 \neq k_0} \frac{\psi(k_1) \psi(-k_1) \psi(k_2) \psi(-k_2)}{k_1^2 + k_2^2} \end{aligned} \quad (13)$$

where $\mathcal{H}\{m_0, k_0\}$ is the value of the Hamiltonian (2) if we substitute the mean-field solution in the form given by (3).

The classical field values m_0, k_0 are found from the equation of state given by the thermodynamic relations

$$\left\langle \frac{\partial \mathcal{H}'\{m_0, k_0; \psi\}}{\partial m_0} \right\rangle = 0 \quad \text{and} \quad \left\langle \frac{\partial \mathcal{H}'\{m_0, k_0; \psi\}}{\partial k_0} \right\rangle = 0. \quad (14)$$

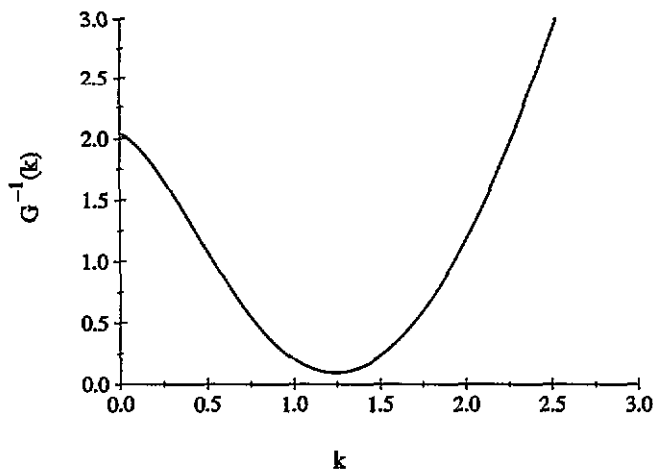


Figure 2. Numerical solution of the Dyson equation (5) for G^{-1} in the disordered phase.

The first equation reads

$$(k_0^2 + \tau)m_0 + \frac{2\lambda}{k_0^2}m_0^3 + 4\lambda m_0 V^{-1} \sum_{k \neq k_0} \frac{\langle \psi(k)\psi(-k) \rangle}{k_0^2 + k^2} = 0 \quad (15)$$

where $\langle \psi(k)\psi(-k) \rangle = G(k)$. The Dyson equation for the ordered phase for $k \neq k_0$ is

$$G^{-1}(k) = k^2 + \tau + \frac{4\lambda m_0^2}{k_0^2 + k^2} + 4\lambda V^{-1} \sum_{k_1 \neq k_0} \frac{G(k_1)}{k_1^2 + k^2}. \quad (16)$$

This equation is exact since higher-loop diagrams are subdominant in V due to the peculiar symmetry of our vertex.

Then, by comparison of (15) and (16) we see that $G(k)$ depends only on the modulus k and

$$G^{-1}(k_0)m_0 = 0. \quad (17)$$

The minimum value of $G^{-1}(k)$ is positive since, if $G^{-1} = 0$, the integral of (16) diverges. Then $G^{-1}(k_0) > 0$ and therefore, according to (17), $m_0 = 0$. We see that we cannot have a stable solution with $m_0 \neq 0$ and $k_0 \neq 0$, due to the divergence of the integral (9) in any dimension.

The Dyson equation (5) can be solved numerically. The solution for $G^{-1}(k)$ taking $\lambda = (2\pi)^3/4$ is shown in figure 2 at $\tau = -5.0$ and the dependence on τ of the minimum value r of G^{-1} and of the mode k_* that corresponds to this minimum is plotted in figure 3. We see from figure 2 that the approximation proposed in (7) is good around the minimum. The behaviour of the real space correlation function can be obtained with Fourier transform of (7), from which we get

$$\langle m(\mathbf{R})m(0) \rangle \sim \frac{e^{-\sqrt{r}R}}{\sqrt{r}R} k_* \sin(k_* R) \quad (18)$$

where R is the modulus of the distance vector. This is a decaying oscillation with period k_*^{-1} and relaxation length $r^{-1/2}$. We see from figure 3 that as τ becomes negative, r decreases towards zero where k_* increases and becomes larger than r . Then we can have several periods before the decay, signifying some local periodic structure.

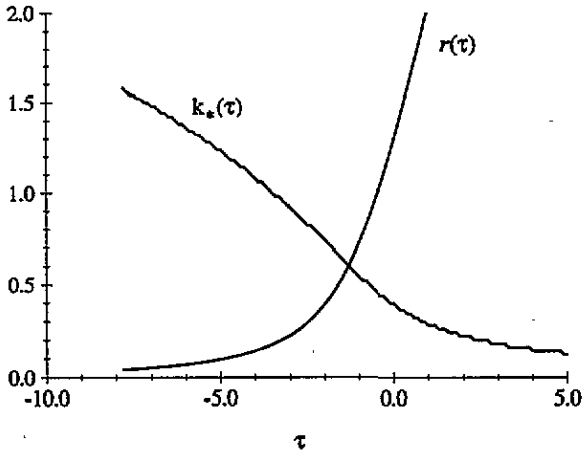


Figure 3. Dependence on τ of the minimum value r of G^{-1} and of the mode modulus k_* that corresponds to this minimum.

The peculiar symmetry of the fourth-order vertex of (2) with pairing of momenta allowed for the exact treatment of fluctuations on the one-loop level as opposed to the effect of fluctuations due to the Ising model interaction term. According to the above analysis we conclude that every effective Hamiltonian which has a fourth-order vertex with integration over pairs of momenta as in (2) will not allow the transition to a non-uniform ($k_0 \neq 0$) phase with spontaneously broken symmetry. Previous studies [9, 10] did not reveal the simplifications of the fluctuation treatment allowed by this pairing symmetry of the vertex in (2).

However, for the heteropolymer problem, the strong result given in (17) only implies that the mean-field conclusion based on the Hamiltonian (2) that predicts a microphase separation transition is wrong. The complete heteropolymer problem needs to be reconsidered in a different basis since other terms of the full Hamiltonian have been omitted because they are not important in the mean-field. More specifically, the regular Ising model fourth-order vertex

$$V^{-1} \sum_{k_1, k_2, k_3} \lambda_2 m(k_1) m(k_2) m(k_3) m(-k_1 - k_2 - k_3) \quad (19)$$

which appears in the entropy part of the Landau expansion for the phase separation of a non-polymeric binary system. This term has been neglected in mean-field because near transition k_0 is very small and, therefore, the heteropolymeric vertex considered in (2) dominates in mean-field. A thorough consideration of the full Hamiltonian will be given elsewhere [11].

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