

Correlated disorder in random block copolymers

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We study the effect of a random Flory-Huggins parameter in a symmetric diblock copolymer melt which is expected to occur in a copolymer where one block is near its structural glass transition. In the clean limit the microphase segregation between the two blocks causes a weak, fluctuation induced first order transition to a lamellar state. Using a renormalization group approach combined with the replica trick to treat the quenched disorder, we show that beyond a critical disorder strength, which depends on the length of the polymer chain, the character of the transition is changed. The system becomes dominated by strong randomness and a glassy rather than an ordered lamellar state occurs. A renormalization of the effective disorder distribution leads to nonlocal disorder correlations that reflect strong compositional fluctuation on the scale of the radius of gyration of the polymer chains. The reason for this behavior is shown to be the chain length dependent role of critical fluctuations, which are less important for shorter chains and become increasingly more relevant as the polymer length increases and the clean first order transition becomes weaker.

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I. INTRODUCTION

Copolymer systems, i.e., macromolecules built of sequences of chemically distinct repeat units, are of particular interest due to the phenomenon of microphase separation and the resulting formation of complex ordered structures changing their macroscopic, mechanical properties [1–7]. For example, a diblock copolymer melt consisting of blocks of *A* and *B* monomers is chiefly characterized by the Flory-Huggins parameter

$$\chi = \nu_{AB} - \frac{1}{2}(\nu_{AA} + \nu_{BB}) \quad (1)$$

which characterizes the segregation strength between *A* and *B* monomers. Here, $\nu_{ss'}$ is a measure for the short distance repulsion between *s* and *s'* monomers (*s, s' = A or B*) in units of $k_B T$. For large enough χ phase separation into *A*-rich and *B*-rich regions occurs [2]. These regions are limited in size due to the covalent bond between the blocks resulting in microphase separation. In case of equal length of the *A* and *B* blocks the transition between the disordered, i.e., mixed phase, and a microphase separated state is via a fluctuation induced first order transition [4], originally proposed by Brazovskii [8,9]. At low temperature the system develops lamellar order with a period determined by the radius of gyration of the polymer. The observation of this transition in poly(ethylene-propylene)-poly(ethylene) diblock copolymers of approximately equal block volume is probably the most convincing experimental verification of the Brazovskii scenario of weak crystallization [10].

The role of disorder in copolymers has been the subject of a number of theoretical studies. In many cases the disorder is caused by fluctuations in the sequence length of the blocks [11–15]. It was shown that fluctuation effects beyond mean field theory are crucial to stabilize microphase separation for disordered sequences [16–18]. In the limit where the typical segment length is small compared to the total length of the

polymer, recent numerical simulations found strong deviations from theories based upon an effective Ginzburg-Landau theory, while the latter is applicable if the block length, even though random, remains large with high probability [19]. Using a replica theory to analyze the quenched random segments, only replica symmetric solutions were found, indicating that disorder does not result in subtle aging and nonergodicity behavior as found for example in spin glasses. A much stronger impact of quenched randomness is caused by “random field” disorder. This can be realized in case of a copolymer melt in a gel matrix [20] with preferential adsorption of one of the monomers on the gel and was studied by Stepanow *et al.* [21] who found a glassy state for intermediate values of χ while a lamellar state only occurs for larger χ .

The dramatic impact of random field disorder becomes also evident from the results of Refs. [22–24] where it was shown for a model in the same universality class that infinitesimal random field disorder leads to a state with one-step replica symmetry breaking, i.e., a *self-generated glass* with nonergodic aging behavior. This result has been confirmed in dynamical, mode coupling calculations by Grousson *et al.* (Ref. [25]) where, in a similar spirit to the early work of Kirkpatrick and Thirumalai [26], it has been shown that this model, if supercooled below the first order transition to a lamellar state, becomes dynamically arrested within a mean field description of the dynamics. A detailed analysis of the theory put forward in Refs. [22–24] in the context of diblock copolymers was recently performed by Zhang and Wang [28]. They demonstrated that self-generated glassiness occurs if the equilibrium order-disorder transition is avoided, via supercooling. In the present paper we focus on the effects of quenched disorder alone, assuming that these further complications of the clean model can be avoided if the system is cooled down slowly enough to enter the equilibrium phase. Recent Monte Carlo and Langevin simulations performed by Geissler and Reichman [27] support this assumption, at least for weak coupling, showing that in a clean system it is in-

deed possible to nucleate the ordered, lamellar phase, in rather large spatial regions.

An interesting realization of quenched disorder, intermediate between random sequences and random field disorder of a gel matrix, occurs in case of fluctuating interaction strength between the monomers, i.e., $\nu_{ss'} \rightarrow \nu_{ss'}(\mathbf{x})$ which leads to a random, spatially varying Flory-Huggins parameter

$$\chi \rightarrow \chi(\mathbf{x}) = \bar{\chi} + \delta\chi(\mathbf{x}). \quad (2)$$

In Ref. [29] it was argued that this is the case in a copolymer where one block is near its structural glass transition. The decreased mobility of the monomers of this block implies a partial annealing and leads to slow nonthermal compositional fluctuations which can be described by Eq. (2). Systems where one of the two blocks is close to a glass transition were studied for example in Refs. [30,31]. Using a variational approach an ordered and a glasslike state with strong compositional fluctuations were identified, depending on the strength of the fluctuations [29].

In this paper we analyze symmetric block copolymers with random Flory-Huggins parameter, Eq. (2), using a renormalization group approach. In agreement with Ref. [29] we find that a critical strength of the fluctuations $\delta\chi(\mathbf{x})$ is needed to destroy the fluctuation induced first order Brazovskii transition to a lamellar state. In addition, in the glassy state we find, at low energies, a strong renormalization of the distribution function $P(\delta\chi(\mathbf{x}))$, characterized by nonlocal fluctuations and determine a phase diagram for variable polymer length N , mean Flory-Huggins parameter $\bar{\chi}$, and fluctuation strength g of $\delta\chi(\mathbf{x})$. We demonstrate that for sufficiently large chains a glassy behavior becomes inevitable, caused by the very different chain length dependence of thermal and disorder related fluctuations. The renormalization group technique used in this paper is a generalization of the approach of Hohenberg and Swift [32] to the case of systems with quenched randomness.

Our results demonstrate how disorder affects a first order transition and are thus of relevance beyond the specifics of random copolymer systems. The fluctuation induced first order transition studied in this paper is weak. An excess entropy is generated by a large phase space of fluctuations, rendering the system unable to reach a critical point while stabilizing an ordered structure at a finite but rather large correlation length [8,33]. In the opposite case of a strong first order transitions the influence of quenched disorder of the type discussed here was studied in Ref. [34]. In this and subsequent studies [35,36] it was shown that for $d=2$ disorder leads to a vanishing latent heat, a result obtained via mapping the two coexisting phases with sharp interfaces onto a random field Ising model. For $d>2$ the first order transition survives below a certain disorder strength. The extension of the above mapping to $d>2$ [37,38] demonstrates that the behavior for larger disorder is again in the same universality class as the random field Ising model. The situation is different in the present model. Due to the large interface width between distinct ordered regions at the weak first order transition, the mapping onto the random field Ising model cannot be justified anymore. Even though it is not

possible for us to specify the precise nature of the corresponding transition in our case, our results strongly suggest that the transition between a regime with effectively weak disorder to a disorder dominated behavior is not of the random field Ising type. On the other hand, the fact that the resulting first order transition is weak allows us to obtain a qualitative understanding of our results using a modified Harris criterion [39], typically used to analyze the role of quenched disorder at continuous phase transitions.

The remainder of the paper is organized as follows. In the next section we introduce the model and summarize the main steps of the replica trick to perform the disorder average. We introduce the renormalization group approach in Sec. III, where we also summarize the main results of this calculation, while the details of the derivation and solution of the flow equations are given in Appendixes. The results of our calculation and a generalized Harris criterion are given in Sec. IV and we briefly summarize our findings and their implications in Sec. V.

II. MODEL AND REPLICA TRICK

We consider N_p polymer chains ($n=1, \dots, N_p$), each consisting of N statistical segments ($s=1, \dots, N$). The A block on each molecule contains Nf statistical segments and the B block has $N(1-f)$ segments. We restrict the discussion to the case $f=1/2$. The relevant degrees of freedom of the polymer are the positions of the segments $\mathbf{R}_{n,s}$. The system is characterized by a Gaussian statistical weight and additional excluded volume pseudopotential:

$$H = \frac{d}{2} \sum_{n,s} \left(\frac{\mathbf{R}_{n,s+1} - \mathbf{R}_{n,s}}{a} \right)^2 + \frac{1}{2\rho_0} \sum_{s,s';n,n'} \nu_{s,s'}(\mathbf{R}_{n,s}) \times \delta(\mathbf{R}_{n,s} - \mathbf{R}_{n',s'}), \quad (3)$$

where a is the characteristic persistence length of the polymer and $\rho_0 = NN_p/V$ is the monomer density. In the spirit of Flory-Huggins lattice theory the monomer density for a dense polymer melt is roughly given by $\rho_0 \approx a^{-3}$. $\nu_{s,s'}$ is dimensionless and characterizes the excluded volume interaction. We consider a symmetric block copolymer with

$$\nu_{s,s'} = \begin{cases} \nu_{AA}, & s, s' \leq N/2, \\ \nu_{BB}, & N/2 < s, s', \\ \nu_{AB}, & s \leq N/2 < s' \text{ or } s' \leq N/2 < s \end{cases}$$

which are assumed to vary in space. The mean repulsion between different blocks, $\bar{\nu}_{AB}$, is taken to be larger than $\bar{\nu}_{AA}$ and $\bar{\nu}_{BB}$ such that for the mean Flory-Huggins parameter $\bar{\chi} > 0$ holds, i.e., A and B monomers segregate on the average. Following the procedure first outlined by Leibler [2] (for a recent review see Ref. [6]), one introduces monomer number density fields $\rho_A(\mathbf{r}) = \sum_{n,s \leq N/2}^A \delta(\mathbf{r} - \mathbf{R}_{n,s})$ and $\rho_B(\mathbf{r}) = \sum_{n,s > N/2}^B \delta(\mathbf{r} - \mathbf{R}_{n,s})$. Using the incompressibility assumption of a dense melt,

$$\rho_A(\mathbf{r}) + \rho_B(\mathbf{r}) = \rho_0,$$

one obtains a theory for a collective field $\phi(\mathbf{r})$ that describes the microscopic fluctuations of A and B monomers:

$$\phi(\mathbf{r}) = \frac{c}{\sqrt{a}} \left(\frac{\rho_A(\mathbf{r})}{\rho_0} - \frac{1}{2} \right) = - \frac{c}{\sqrt{a}} \left(\frac{\rho_B(\mathbf{r})}{\rho_0} - \frac{1}{2} \right),$$

with $c=1.1019$ [2]. The effective action of the problem is the Brazovskii model [8] for a scalar order parameter ϕ but with random mass term:

$$S[\phi] = \frac{1}{2} \int d^3x \left([\tau_0 - t(\mathbf{x})] \phi^2 + \frac{([\nabla^2 + q_0^2] \phi)^2}{4q_0^2} \right) + \frac{\Gamma_0}{4} \int d^3x \phi^4. \quad (4)$$

Following Refs. [4,10], τ_0, Γ_0 , and q_0 can be expressed in terms of the parameters of the polymer Hamiltonian Eq. (3):

$$\tau_0 = \frac{2}{c^2 a^2} (\chi_s - \bar{\chi}), \quad (5)$$

$$q_0 = \frac{1.945}{R_g}, \quad (6)$$

$$\Gamma_0 = \frac{156.56}{c^4 a N} \quad (7)$$

with $\chi_s = 10.49/N$. $R_g = a\sqrt{N/6}$ is the radius of gyration of a Gaussian chain. A natural dimensionless bare constant of the problem is $\Gamma_0/q_0 = \sqrt{495}/N$, putting the system in the weak coupling regime for $N \gtrsim 10^4$, similar to the conclusion obtained within in the self-consistent Hartree approach [4,8,10].

For the probability distribution of $t(\mathbf{x}) \equiv (2/c^2 a^2) \delta\chi(\mathbf{x})$ we assume a Gaussian form

$$P(t) \propto \exp - \left(\frac{1}{4} \int d^d x d^d x' t(\mathbf{x}) \Delta^{-1}(\mathbf{x} - \mathbf{x}') t(\mathbf{x}') \right), \quad (8)$$

with $\overline{t(\mathbf{x})t(\mathbf{x}')} = 2\Delta(\mathbf{x} - \mathbf{x}')$. In what follows we will assume uncorrelated disorder with correlation function

$$\Delta(\mathbf{x} - \mathbf{x}') = \Delta_0 \delta(\mathbf{x} - \mathbf{x}').$$

Δ_0 can be expressed in terms of the mean square fluctuations of the Flory-Huggins parameter $\sqrt{\overline{\Delta\chi^2}}$ as

$$\Delta_0 = \frac{23.14 \overline{\Delta\chi^2}}{a\sqrt{N} \chi_s^2}. \quad (9)$$

Here, $\overline{\Delta\chi^2} \equiv (1/V_0) \int_{V_0} d^d \mathbf{x} \overline{\delta\chi(\mathbf{x}) \delta\chi(\mathbf{0})}$ characterizes the spatial fluctuations of the Flory-Huggins parameter within the volume of a single chain $V_0 \approx (4\pi/3)R_g^3$. The corresponding dimensionless strength of the disorder is $\Delta_0/q_0 = 4.85 \overline{\Delta\chi^2}/\chi_s^2$ and, for fixed $\overline{\Delta\chi^2}/\chi_s^2$, does not decrease with N . The important ratio

$$\Delta_0/\Gamma_0 = 0.218 \frac{\overline{\Delta\chi^2}}{\chi_s^2} N^{1/2} \quad (10)$$

therefore grows for larger chain length N . The relative strength of the disorder becomes larger for longer chains.

We determine the averaged free energy via the replica trick

$$\bar{F} = -T \overline{\ln Z} = -T \lim_{m \rightarrow 0} \frac{1}{m} (\overline{Z^m} - 1)$$

and obtain

$$\begin{aligned} \overline{Z^m} &= \int D t P(t) \int D^m \phi \exp \left(-\beta \sum_{a=1}^m S[\phi_a] \right) \\ &= \int D^m \phi \exp(-\beta S^{(m)}[\phi]), \end{aligned}$$

with replicated Hamiltonian

$$S^{(m)}[\phi] = \sum_{a=1}^m H[\phi_a] - \frac{\Delta_0}{4} \sum_{a,b} \int d^d x \phi_a^2(\mathbf{x}) \phi_b^2(\mathbf{x}). \quad (11)$$

In the remainder of this paper we will analyze this replicated action using a renormalization group approach.

III. RENORMALIZATION GROUP APPROACH

The crucial difference between the Brazovskii model Eq. (4), and an ordinary ϕ^4 model of Ising-type ferromagnets is the nonlocal term $([\nabla^2 + q_0^2] \phi)^2$, which strongly prefers momenta \mathbf{q} with $|\mathbf{q}| = q_0$ as opposed to the state $\mathbf{q} = \mathbf{0}$. It is this enhancement in the phase space of low energy fluctuations that causes the mentioned fluctuation induced first order transition [8]. In case of ordinary n -vector ϕ^4 theories with quenched disorder a renormalization group approach was developed in Refs. [40–43]. However, the dramatic change in the low energy phase space of the Brazovskii model requires a different formulation.

The low energy modes of the problem are momentum states on a sphere with radius q_0 and one must adapt the usual decimation of high energy states in the momentum shell renormalization group accordingly. Instead of the conventional shell integration [44], where momenta with $\Lambda e^{-l} < |\mathbf{q}| < \Lambda$ are eliminated, one has to eliminate states in a shell with distance Λ from the sphere with radius q_0 . This procedure requires $\Lambda \ll q_0$. This decimation approach is sketched in Fig. 1 and was used in Ref. [32] to study the clean Brazovskii model. Here we generalize the approach to the replicated model Eq. (11), allowing us to study the role of quenched disorder. There is a close similarity of this approach to the renormalization group developed for many body fermion systems, where the low energy modes are also located on a sphere of finite momentum, the Fermi surface [45–49]. The distinct arrangements of the scattering momenta lead in the case of fermions to BCS, forward, and exchange scattering. This similarity supports the idea that the Brazovskii model will be characterized not only by one four-point vertex, but by an effective interaction with generic angle between incoming and scattered momenta and an interaction where all interactions are parallel.

The most general form of the quartic interaction in Eq. (11) is expressed in terms of two vertex functions Γ and Δ :

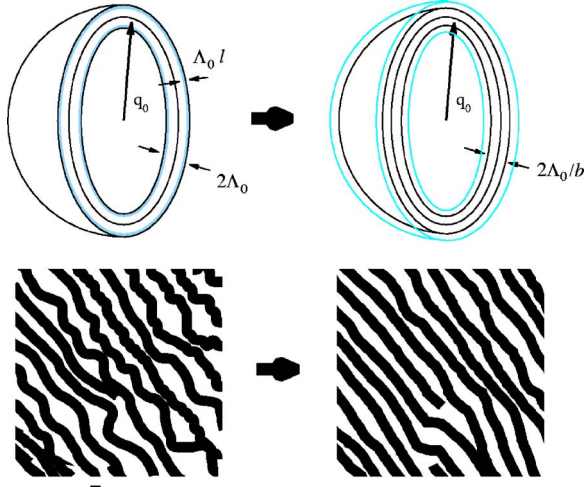


FIG. 1. (Color online) Momentum shell integration procedure. The configurations with higher wavelength modulations are integrated out, reducing the low energy degrees of freedom to configurations closer to the perfect lamellar arrangement (as illustrated in the lower panel).

$$S_{\text{int}}^{(m)}[\phi] = \frac{1}{4} \sum_a \int_{q_i} \Gamma_{\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4} \phi_{a, \mathbf{q}_1} \phi_{a, \mathbf{q}_2} \phi_{a, \mathbf{q}_3} \phi_{a, \mathbf{q}_4} \\ + \frac{1}{4} \sum_{a, b} \int_{q_i} \Delta_{\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4} \phi_{a, \mathbf{q}_1} \phi_{a, \mathbf{q}_2} \phi_{b, \mathbf{q}_3} \phi_{b, \mathbf{q}_4}$$

with shorthand $\int_{q_i} \cdots = \int [d^d q_1 \cdots d^d q_4 / (2\pi)^{4d}] \cdots$. The initial value of the inter-replica coupling is given as

$$\Delta_{\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4} = -\Delta_0 \delta(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 + \mathbf{q}_4).$$

The vertex $\Gamma_{\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4}$ has been determined by Leibler [2]. Considering $|\mathbf{q}_i| = q_0$, it only depends on two independent angles θ_{12} , between vectors \mathbf{q}_1 and \mathbf{q}_2 , and θ_{14} between vectors \mathbf{q}_1 and \mathbf{q}_4 , respectively. In the notation of Ref. [2], we can write $\Gamma_{\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4} \equiv \Gamma_4(h_1, h_2)$, where $h_1 = 2 + 2 \cos(\theta_{12})$ and $h_2 = 2 + 2 \cos(\theta_{14})$. The most relevant vertices are those where all momenta lie in the same plane. This only happens if either $h_1 = 0$ or $h_2 = 0$ (equivalent to $\theta_{12(4)} = \pi$ and $\theta_{14(2)}$ generic) or $h_1 + h_2 = 4$ (equivalent to $\theta_{12} = \theta_{14} \pm \pi$). We find that

$$\Gamma_4(\cos(\theta)) = \frac{1}{N} \sum_l a_l P_l(\cos(\theta)), \quad (12)$$

where P_l are Legendre polynomials and the coefficients of the first three angular momentum channel are $a_0 = 176.92$, $a_1 = 14.34$, $a_2 = 2.30$, and $a_3 = 8.33$. The angle θ stands for $\theta = \theta_{12}$ or θ_{14} . In the course of the renormalization, these vertices may change differently depending on the specific momentum dependence. The vertex Γ , which does not couple distinct replicas, leads at low energies to the two coupling constants

$$\bar{\Gamma}_0 = \Gamma_{\mathbf{p}, -\mathbf{p}, \mathbf{q}, -\mathbf{q}},$$

$$\Gamma_{0\parallel} = \Gamma_{\mathbf{p}, -\mathbf{p}, \mathbf{p}, -\mathbf{p}},$$

where $\bar{\Gamma}_0$ refers to a generic angle between the momenta \mathbf{p} and \mathbf{q} ($\theta_{12} = \pi$ and generic θ_{14}) with $|\mathbf{p}| = |\mathbf{q}| = q_0$, while $\Gamma_{0\parallel}$ determines the renormalized interaction of the special case $\mathbf{p} = \mathbf{q}$ ($\theta_{12} = \theta_{14} = \pi$). As first shown in Ref. [8], $\bar{\Gamma}_0$ and $\Gamma_{0\parallel}$ renormalize differently. Using Eq. (12) one can determine the initial values of these two coupling constants:

$$\Gamma_{0\parallel} = \frac{106.20}{Na_0 c^4}, \quad (13)$$

$$\bar{\Gamma}_0 = \frac{120.00}{Na_0 c^4}. \quad (14)$$

The fact that we restrict ourselves to these two coupling constants is consistent with the fact that the equilibrium structure of the clean system is lamellar. More complex ordered states are possible if the system is quenched rapidly below the order-disorder transition [22–24], effects that will be ignored in this paper, i.e., we assume that the system is cooled slowly enough to avoid self-generated randomness and vitrification.

The analysis of the allowed coupling constants becomes more subtle in case of the vertex Δ which couples distinct replicas. The symmetry of this interaction allows for altogether four distinct vertices:

$$\bar{\Delta} = \Delta_{\mathbf{p}, -\mathbf{p}, \mathbf{q}, -\mathbf{q}},$$

$$\Delta_{\parallel} = \Delta_{\mathbf{p}, -\mathbf{p}, \mathbf{p}, -\mathbf{p}},$$

$$\bar{\Omega} = \Delta_{\mathbf{p}, \mathbf{q}, -\mathbf{p}, -\mathbf{q}},$$

$$\Omega_{\parallel} = \Delta_{\mathbf{p}, \mathbf{p}, -\mathbf{p}, -\mathbf{p}}. \quad (15)$$

The coupling constants $\bar{\Delta}$ and $\bar{\Omega}$ refer to generic angles between the two scattered momenta, whereas they are parallel in the cases of Δ_{\parallel} and Ω_{\parallel} , respectively. While $\bar{\Gamma}$ and Γ_{\parallel} characterize the interactions of the system, the coupling constants $\bar{\Delta}$, Δ_{\parallel} , $\bar{\Omega}$, and Ω_{\parallel} determine the evolution of the disorder distribution function. $\bar{\Delta}$ and Δ_{\parallel} correspond to local disorder, as characterized by the bare distribution function Eq. (8), $t(\mathbf{x})t(\mathbf{x}') \propto \delta(\mathbf{x} - \mathbf{x}')$. On the other hand, $\bar{\Omega}$ and Ω_{\parallel} stand for nonlocal randomness generated as one considers the effective low energy properties of the system. This last aspect becomes most evident by undoing the replica trick. Introducing

$$G_{\mathbf{p}, \mathbf{q}} = \Delta_{\mathbf{p}, \mathbf{q}, -\mathbf{p}, -\mathbf{q}}, \quad (16)$$

the corresponding part of the replicated action is

$$S_{\Delta} = \frac{1}{4!} \sum_{a, b} \int_{x, x', y, y'} G(\mathbf{x} + \mathbf{x}', \mathbf{y} + \mathbf{y}') \phi_{a, \mathbf{x}} \phi_{a, \mathbf{x}'} \phi_{b, \mathbf{y}} \phi_{b, \mathbf{y}'},$$

with real space Fourier transform $G(\mathbf{x}, \mathbf{x}') = \int [d^d p d^d q / (2\pi)^{2d}] \exp(i(\mathbf{p}\mathbf{x} + \mathbf{q}\mathbf{x}')) G_{\mathbf{p}, \mathbf{q}}$. This can be considered as the result of a replica calculation where the initial disordered Hamiltonian was

$$S_{\text{dis}}[\phi] = \frac{1}{2} \int d^d x d^d y T(\mathbf{x}, \mathbf{y}) \phi(\mathbf{x}) \phi(\mathbf{y}). \quad (17)$$

The nonlocal random function $T(\mathbf{x}, \mathbf{y})$ has a distribution function

$$P(T) \sim \exp\left(-\frac{1}{4} \int d^d x d^d x' d^d y d^d y' \right. \\ \left. \times T(\mathbf{x}, \mathbf{y}) G^{-1}(\mathbf{x} - \mathbf{y}, \mathbf{x}' - \mathbf{y}') T(\mathbf{x}', \mathbf{y}')\right), \quad (18)$$

with correlation function $G(\mathbf{x} - \mathbf{y}, \mathbf{x}' - \mathbf{y}') = \frac{1}{2} \overline{T(\mathbf{x}, \mathbf{y}) T(\mathbf{x}', \mathbf{y}')}$.

Thus, in case $\bar{\Omega}$ or Ω_{\parallel} flows to large values, the system acquires a nonlocal randomness with typical length scale $|\mathbf{x} - \mathbf{y}|, |\mathbf{x}' - \mathbf{y}'| \sim 2\pi/q_0$. In this sense we obtain a renormalization of the distribution function of the problem. The initial distribution

$$G_0(\mathbf{x} - \mathbf{y}, \mathbf{x}' - \mathbf{y}') = 2\Delta_0 \delta(\mathbf{x} - \mathbf{y}) \delta(\mathbf{x}' - \mathbf{y}') \quad (19)$$

becomes broadened such that

$$\delta(|\mathbf{x} - \mathbf{y}|) \rightarrow f(q_0 |\mathbf{x} - \mathbf{y}|). \quad (20)$$

and the disorder correlations become nonlocal.

A. The clean case: Brazovskii transition

Before we analyze the disordered case with altogether six distinct coupling constants we summarize the renormalization group approach to the clean case, $\Delta_0=0$. The derivation of the corresponding flow equations was given in Ref. [32] and we repeat the main steps in Appendix I for completeness and in order to make the description of the replicated theory more transparent. In addition we determine the actual phase boundary from the flow equations and compare the result with Brazovskii's original calculation [50]. As shown in Appendix I, the flow equations of the clean model and after rescaling the coupling constants and mass term according to $\bar{\gamma} \equiv (q_0^2/\pi^2 \Lambda_0^3) \bar{\Gamma}$, $\gamma_{\parallel} \equiv (q_0^2/\pi^2 \Lambda_0^3) \Gamma_{\parallel}$, and $r \equiv \tau_0/\Lambda_0^2$ are

$$\begin{aligned} \frac{dr}{dl} &= 2r + 3\bar{\gamma}, \\ \frac{d\bar{\gamma}}{dl} &= 3\gamma_{\parallel} - 3\bar{\gamma}^2, \\ \frac{d\gamma_{\parallel}}{dl} &= 3\gamma_{\parallel} - 6\bar{\gamma}^2. \end{aligned} \quad (21)$$

This set of equations has a closed solution:

$$r(l) = e^{2l} \left(r_0 + 3 \int_0^l dx \bar{\gamma}(x) e^{-2x} \right), \\ \bar{\gamma}(l) = \frac{\bar{\gamma}_0 e^{3l}}{1 + \bar{\gamma}_0 (e^{3l} - 1)},$$

$$\gamma_{\parallel}(l) = \frac{2\gamma_{0\parallel} e^{3l}}{1 + \gamma_{0\parallel} (e^{3l} - 1)} - \gamma_{0\parallel} e^{3l}, \quad (22)$$

where $\bar{\gamma}(0) = \bar{\gamma}_0 \equiv (q_0^2/\pi^2 \Lambda_0^3) \bar{\Gamma}_0$, $\gamma_{0\parallel} = \gamma_{\parallel}(0) \equiv (q_0^2/\pi^2 \Lambda_0^3) \bar{\Gamma}_0$, and $r(0) = r_0 = \tau_0/\Lambda_0^2$. Note that $\bar{\gamma}(l)$ is always positive and approaches a fixed value $\bar{\gamma}(l \rightarrow \infty) \rightarrow 1$. However, $\gamma_{\parallel}(l)$ changes sign for $l = l^*$, where l^* is given by

$$l^* = \frac{1}{3} \ln \left(1 + \frac{1}{\gamma_0} \right). \quad (23)$$

If the system establishes a modulated order

$$\phi(\mathbf{x}) = \phi_0(\mathbf{x}) \exp(-i\mathbf{q}_m \cdot \mathbf{x}), \quad (24)$$

where $|\mathbf{q}_0| = q_0$ and $\phi_0(\mathbf{x})$ is a smoothly varying function on the scale q_0^{-1} , the driving interaction is the one where all interacting momenta are either parallel or antiparallel, i.e., γ_{\parallel} . A flow toward negative γ_{\parallel} indicates therefore a fluctuation induced first order transition to a modulated state, just as in Ref. [8]. Since the scaling dimension of the interaction is 3, we have, in distinction to a recent application to a quantum version of the Brazovskii model [51], no controlled ε expansion. Thus, we have to limit our analysis to the case of small $\bar{\gamma}_0$ and $\gamma_{0\parallel}$. The renormalization group (RG) flow will proceed until scaling stops at a scale l_0 with $r(l_0) = 1$, i.e., $\tau_0(l_0) = \Lambda_0^2$. If $l_0 < l^*$ scaling stops before the interaction changes sign. Then there is no first order transition. On the other hand, if $l_0 > l^*$ the system changes character before scaling stops and we cannot determine the bare parameters without introducing a term of order ϕ^6 . Thus we are in the ordered state or at least have local minima as in an overheated system. The transition happens for $l_0 = l^*$ and we are right at the first order transition (more precisely at the spinodal point where metastable ordered states emerge). From Eqs. (22) and (23) the condition $l_0 = l^*$ is obeyed if

$$r_0 = e^{-2l^*} - 3 \int_0^{l^*} dy \frac{1}{[(1 - \bar{\gamma}_0)/\bar{\gamma}_0] + y^3}. \quad (25)$$

We assume for simplicity $\bar{\gamma}_0 = \gamma_{0\parallel} = \gamma_0$. In the limit $\gamma_0 \ll 1$ holds $e^{l^*} \rightarrow \gamma_0^{-1/3}$ and we obtain to leading order in γ_0

$$l_0^* = \left(1 - \frac{\pi}{\sqrt{3}} - \ln 2 \right) \gamma_0^{2/3} + O(\gamma_0) \simeq -1.507 \gamma_0^{2/3}. \quad (26)$$

Returning to the unscaled variables and using the definition Eq. (5) for τ_0 , we obtain that the stability limit (i.e., the spinodal) of the lamellar phase is given by

$$(\bar{\chi}N)_s \simeq 10.50 + \frac{\alpha}{N^{1/3}}, \quad (27)$$

with $\alpha = 35.69$. The value for α is comparable to the result $\alpha = 41$, obtained in Refs. [4,10] using the self-consistent Hartree theory of Ref. [8]. If we further assume the initial vertices according to Eq. (14), instead of $\bar{\gamma}_0 = \gamma_{0\parallel}$, we obtain $r_0^* = -1.783 \gamma_0^{2/3}$, leading to $\alpha = 42.22$. The remaining small difference is likely caused by the fact that our flow equations are only approximately valid for $r(l_0) \simeq 1$, no matter how small the coupling constant. Still the deviation in the numerical prefactor is very small and we will continue our analysis

for the disordered case along similar lines. In addition we will, for the rest of the paper, assume $\gamma_0 = \bar{\gamma}_0 = \gamma_{0\parallel}$, with Γ_0 given by Eq. (7).

B. The disordered case: Flow equations

Since all the six coupling constants listed above are allowed by symmetry, we have to start our calculation with a model where all those terms are included. We use the same rescaling of the coupling constants as in the clean case, i.e., $\bar{\delta} = (q_0^2 / \pi^2 \Lambda_0^3) \bar{\Delta}$, $\bar{\omega} = (q_0^2 / \pi^2 \Lambda_0^3) \bar{\Omega}$, etc. The initial values of the flow are then $\bar{\delta}(0) = \delta_{\parallel}(0) = \bar{\omega}(0) = \omega_{\parallel}(0) = -g$, with

$$g \equiv \frac{q_0^2}{\pi^2 \Lambda_0^3} \Delta_0. \quad (28)$$

Generalizing the steps which led to the flow equations in the clean case to the replicated model Eq. (11) leads to the following flow equations up to one loop:

$$\begin{aligned} \frac{dr}{dl} &= 2r + 3\bar{\gamma} + 2\bar{\omega}, \\ \frac{d\bar{\gamma}}{dl} &= 3\bar{\gamma} - (3\bar{\gamma}^2 + 4\bar{\gamma}\bar{\omega}), \\ \frac{d\gamma_{\parallel}}{dl} &= 3\gamma_{\parallel} - 2(3\bar{\gamma}^2 + 4\bar{\gamma}\bar{\omega}), \\ \frac{d\bar{\delta}}{dl} &= 3\bar{\delta} - (6\bar{\gamma}\bar{\delta} + 4\bar{\omega}\bar{\delta}), \\ \frac{d\delta_{\parallel}}{dl} &= 3\delta_{\parallel} - (6\bar{\gamma}\bar{\delta} + 4\bar{\omega}\bar{\delta} + 2\bar{\omega}^2), \\ \frac{d\bar{\omega}}{dl} &= 3\bar{\omega} - 2\bar{\omega}^2, \\ \frac{d\omega_{\parallel}}{dl} &= 3\omega_{\parallel} - 4\bar{\omega}^2. \end{aligned} \quad (29)$$

Here the limit $m \rightarrow 0$ of the numbers of replicas was taken. This system of coupled flow equations can be solved in a closed fashion. The details of the solution are summarized in Appendix II. The main results of this calculation are as follows. For $g < g_c$ with

$$g_c = \frac{3\sqrt{2}(\sqrt{2}-1)}{8} \gamma_0 \approx 0.22 \gamma_0, \quad (30)$$

disorder does not change significantly the fluctuation induced first order transition, whereas for $g > g_c$ the system is dominated by strong, nonlocal disorder fluctuations and no ordered lamellar state forms. Since $g/\gamma_0 = \Delta_0/\Gamma_0$, this criterion can be expressed in terms of a critical value for the fluctuations of the Flory-Huggins parameter $\sqrt{\Delta\chi^2}$, and is given by

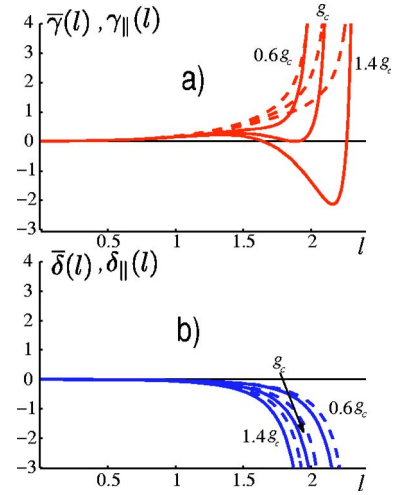


FIG. 2. (Color online) RG flow of the coupling constants as derived from Eq. (29) for $\gamma_0=0.01$ and $g=0.6g_c, g_c, 1.4g_c$. Dashed (full) curve refers to (a) $\bar{\gamma}(\gamma_{\parallel})$ and (b) $\bar{\delta}(\delta_{\parallel})$.

$$\left(\frac{\sqrt{\Delta\chi^2}}{\chi_s} \right)_c \approx \frac{1}{N^{1/4}}. \quad (31)$$

Disorder affects long polymer chains stronger than short chains, a consequence of the relation between the interaction and disorder strength given in Eq. (10).

If $g < g_c$, the coupling constant $\gamma_{\parallel}(l)$ changes sign [see Fig. 2(a)] at a scale

$$l^* = \frac{1}{3} \ln \left(1 + \frac{\phi(2g/3\gamma_0)}{\gamma_0} \right), \quad (32)$$

with

$$\phi(x) = \frac{2}{1 - 2x + \sqrt{1 + 8x^2 - 8x}}. \quad (33)$$

No other coupling constant diverges or changes sign for $l < l^*$. The behavior is similar to that of the clean Brazovskii transition and for $g/\gamma_0 \rightarrow 0$ we recover the clean limit Eq. (23). On the other hand, for $g > g_c$ all coupling constants diverge at the scale

$$l_g = \frac{1}{3} \ln \left(1 + \frac{3}{2g} \right). \quad (34)$$

From the solution of Eq. (29) it further follows that these divergencies are “driven” by the divergence of the coupling constant $\bar{\omega}$. As discussed in detail above, a large value of $\bar{\omega}$ implies a strong renormalization of the distribution function of the randomness. Nonlocal disorder correlations, which are clearly tied to strong random compositional fluctuations on the scale $2\pi/q_0$ occur instead of an ordered lamellar state. In Fig. 2 we show the flow of the various coupling constants, demonstrating that for $g < g_c$ the coupling constant γ_{\parallel} changes sign well before all other coupling constants diverge. On the other hand, for $g > g_c$ the systems flows to a behavior with strong randomness and nonlocal disorder correlations while γ_{\parallel} remains positive [see Fig. 2(a)].

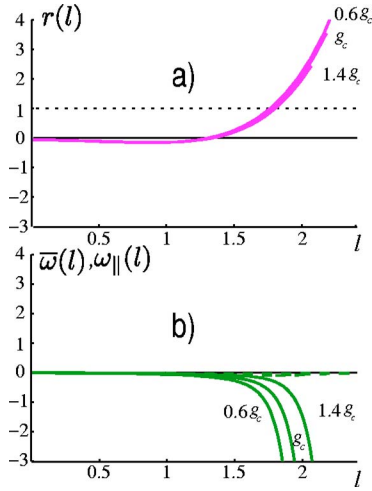


FIG. 3. (Color online) RG flows as derived from Eq. (29) for $\gamma_0=0.01$ and $g=0.6g_c, g_c, 1.4g_c$. (a) $r(l)$ for $r_0=r_0^*$ [see Eq. (26)]. The dotted line defines the scaling limit $\tau_0=\Lambda_0^2$, i.e. $r=1$. (b) Dashed (full) curve refers to $\bar{\omega}(\omega_{\parallel})$.

The details of the phase boundaries between the various states are determined by the flow behavior of the mass parameter $r(l)$. The solution for the mass flow equation is [see also Fig. 3(a)]

$$\begin{aligned} r(l) &= e^{2l} \left(r_0 + \int_0^l e^{-2l'} [2\bar{\omega}(l') + 3\bar{\gamma}(l')] dl' \right) \\ &= e^{2l} \left[r_0 + 3 \left(\gamma_0 - \frac{2g}{3} \right) \right. \\ &\quad \left. \times \int_0^l \frac{e^{l'}}{1 + (\gamma_0 - (2g/3))(e^{3l'} - 1)} dl' \right]. \end{aligned} \quad (35)$$

Here, the divergencies of $\bar{\gamma}$ and $\bar{\omega}$ at l_g are all canceled and the result for $r(l)$ is precisely the same as for the clean system but with

$$\gamma_0 \rightarrow \gamma_0 - \frac{2g}{3}. \quad (36)$$

As in the clean system, scaling stops at $r(l_0)=1$ which leads to a boundary

$$r_0 = e^{-2l_0} - 3 \int_0^{e^{l_0}} dy \frac{1}{\frac{1 - (\gamma_0 - (2g/3))}{(\gamma_0 - (2g/3))} + y^3}. \quad (37)$$

If $g < g_c = [3(2 - \sqrt{2})/8]\gamma_0$ there is a fluctuation induced first order transition with finite randomness at $l_0=l^*$, with l^* defined by Eq. (32). On the other hand, for $g > g_c$ up to the leading order in g and γ_0 the boundary between the liquid and glassy phases is given by

$$r_0 = \frac{5}{2} \left(\frac{2g}{3} \right)^{2/3} - \frac{2\pi}{\sqrt{3}} \left(\gamma_0 - \frac{2g}{3} \right)^{2/3}. \quad (38)$$

In Fig. 4 we show the phase boundary lines in the r_0, γ_0 , and g parameter space.

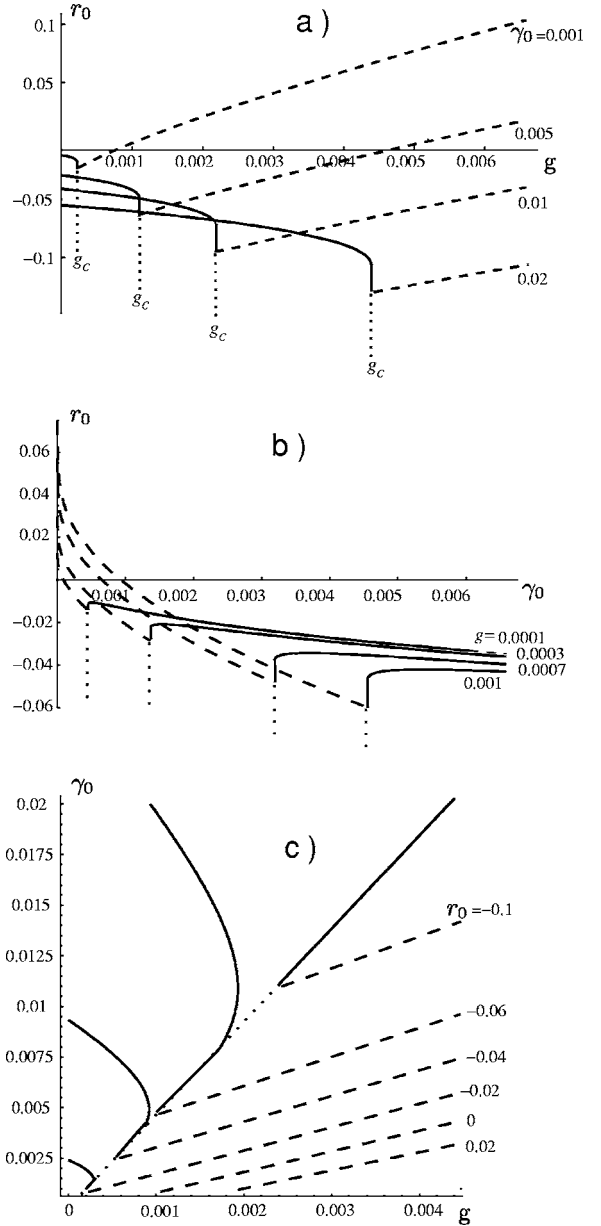


FIG. 4. Phase boundaries of the model Eq. (4) determined from the solution of the flow equations Eqs. (29). In the three graphics the solid lines represent the boundary between the liquid and lamellar phases, the dashed lines the boundary between the liquid and glassy phases, and the dotted line the boundary between the lamellar and glassy phases.

A qualitative understanding of these results can be obtained by combining simple droplet arguments with a criterion similar in spirit to the one developed by Harris [39] for disordered second order phase transitions. We consider the equation of state of the lamellar phase in the clean system [8], using the dimensionless variables of this paper:

$$-r_0 = \xi^{-2} + \gamma_0 \xi. \quad (39)$$

Here, ξ is the dimensionless correlation length (the correlation length measured in units of q_0^{-1}). This gives a value $r_0^* = -3\gamma_0^{2/3}/2^{2/3}$ where for the first time a nontrivial solution

becomes possible (spinodal line). The value of the correlation length at the transition is $\xi^* = 2^{2/3} \gamma_0^{-1/3}$. In the presence of disorder, the equation of state is given as

$$-r_0 - t(\mathbf{x}) = r + \gamma_0 \langle \phi_{\mathbf{x}}^2 \rangle, \quad (40)$$

where $\langle \phi_{\mathbf{x}}^2 \rangle$ is the (appropriately rescaled) mean square deviation of $\phi_{\mathbf{x}}$ in the presence of disorder. $t(\mathbf{x})$ is the random mass and has also been rescaled to be dimensionless. We consider a solution with fixed modulation direction \mathbf{q}_0 (with $|\mathbf{q}_0| = q_0$) along the x_{\parallel} axis: $\phi(x_{\parallel}, \mathbf{x}_{\perp}) = A(x_{\parallel}, \mathbf{x}_{\perp}) e^{i\mathbf{q}_0 \cdot \mathbf{x}_{\parallel}}$. As shown in Ref. [32], domain walls where $\mathbf{q}_0 \parallel \mathbf{n}$, with domain wall normal vector \mathbf{n} , are governed by $(\partial_{\parallel} A)^2$ and decay on the length scale of the correlation length ξ . On the other hand, domain walls with $\mathbf{q}_0 \perp \mathbf{n}$ are determined by $(1/4q_0)(\nabla_{\perp}^2 A)^2$ and decay on the scale $\sqrt{\xi q_0^{-1}}$. For weak coupling $\xi q_0 \gg 1$, and the transverse domain walls ($\mathbf{q}_0 \perp \mathbf{n}$) of a droplet are much less costly than the longitudinal ones. Droplets will therefore be ellipsoidal (cigarlike). Disorder fluctuations along \mathbf{q}_0 will predominantly affect droplet formation and are determined by $t_{\parallel}(\mathbf{x}_{\parallel}) = \int d^{d-1} \mathbf{x}_{\perp} t(x_{\parallel}, \mathbf{x}_{\perp})$, independent of the disorder variation perpendicular to \mathbf{q}_0 . Its distribution function is $t(x_{\parallel}) t(x'_{\parallel}) = 2g \delta(x_{\parallel} - x'_{\parallel})$. The typical value of the disorder in a regime of linear dimension L is then

$$t_L = \frac{1}{L} \int_{x_{\parallel} \in L} t(x_{\parallel}) dx_{\parallel}. \quad (41)$$

The typical value $\Delta t_L = \sqrt{t_L^2}$ is then given as $\overline{t_L^2} = 2g/L$. Disorder is not changing the equation of state dramatically if $\Delta t \xi \ll \xi^{-2}$ which gives $g \ll \xi^{-3}$. Due to the first order character of the transition the correlation length ξ never exceeds $\xi^* \sim \gamma_0^{-1/3}$. Thus, there is a regime at small disorder strength where the equation of state is not dramatically changed. The resulting criterion is $g < \gamma$ in agreement with our renormalization group results. The finite correlation length at the first order transition protects the ordered state from disorder fluctuations. If the first order transition becomes too weak, the correlation length at the transition becomes arbitrarily large and the system becomes effectively critical. In this case the disorder starts dominating the low energy physics and the system changes character. This conclusion is fully consistent with our renormalization group analysis presented above. It is the flow toward negative γ_{\parallel} and the related first order transition that avoids the otherwise inevitable disorder driven divergence of the coupling constants.

To summarize our results we show in Fig. 5 a phase diagram for the diblock copolymer system as a function of the mean phase segregation strength $\bar{\chi}$ and disorder strength $\Delta\chi \equiv \sqrt{\Delta\chi^2}$ for a fixed number of monomers ($N=10^4$). The boundary between the glassy state defined by Eqs. (27) and (30) appears at $\Delta\chi/\chi_s \sim 0.1$.

IV. CONCLUSION

In summary, we have investigated the effect of a random Flory-Huggins parameter $\chi(\mathbf{x})$ in a symmetric diblock copolymer melt. Such fluctuations occur in a copolymer where

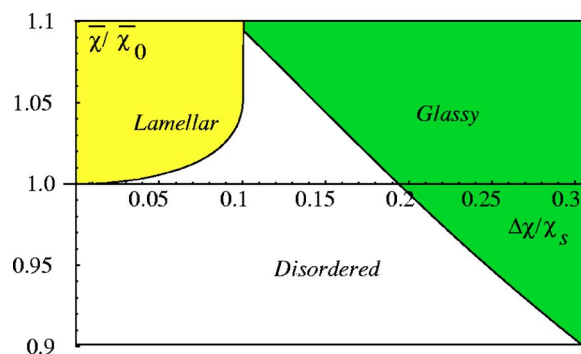


FIG. 5. (Color online) Phase boundaries between lamellar, glassy (nonlocal disorder correlations), and disordered states for a disordered symmetric copolymer with $N=10^4$ monomers as function of the average Flory-Huggins parameter $\bar{\chi}/\bar{\chi}_0$ and its fluctuation $\Delta\chi/\chi_s = \sqrt{\Delta\chi^2}/\chi_s$. The reference units are, respectively, $\bar{\chi}_0$, the critical Flory-Huggins parameter for the clean case ($\Delta_0=0$) as given by Eq. (27), and $\chi_s N = 10.50$.

one block is near its structural glass transition [30,31]. The decreased mobility of the monomers of this block implies a partial annealing and leads to slow nonthermal compositional fluctuations [29]. In the clean limit the microphase segregation between the two blocks causes a weak, fluctuation induced first order transition to a lamellar state. Using a renormalization group approach combined with the replica trick to treat the quenched disorder, we showed that in case of small fluctuations of $\chi(\mathbf{x})$ the first order transition to a lamellar state is unchanged by disorder. Once the strength of the spatial fluctuations of the Flory-Huggins parameter exceeds a critical value that depends on the length of the polymer chains, the character of the transition changes. The system becomes dominated by strong randomness. Very likely a glassy rather than ordered lamellar state occurs. In this disorder dominated regime a strong renormalization of the effective disorder correlations occur. Nonlocal disorder correlations emerge that reflect strong compositional fluctuation on the scale of the radius of gyration of the polymer chains. If nonthermal statistical fluctuation of the Flory-Huggins parameter within the volume occupied by a copolymer chain exceeds a fraction of the order of $N^{-1/4}$ of the critical coupling ($\approx \chi_s = 10.49/N$) the lamellar state is unstable. Instead it leads to a state with no long range order and a renormalized distribution of the Flory-Huggins constant. The strength of the first order transition depends on the chain length N and is more pronounced for shorter chains. In this case the correlation length of the system at the clean phase transition is comparatively short and critical fluctuations are unimportant. The first order transition is then unaffected by weak disorder. On the other hand, longer chains imply a much weaker first order transition and critical fluctuations with large characteristic correlation length come into play. These critical fluctuations are extremely susceptible with respect to disorder, which is reflected in a flow toward infinite disorder strength. The same result was obtained using a modified Harris criterion [39]. It is important to note that the RG and replica scheme employed here does not privilege particular configurations from either a specific wave vector [8] or superposi-

tions of randomly picked wave vectors, as in Refs. [52,53], but rather, expresses the entropy that can be extracted from the phase space of a spherical shell (of radius q_0) of wave vectors. Such a large phase space of the microphase separation transition in symmetric copolymers is therefore a very interesting example for the unique role that disorder can play at a first order phase transition.

ACKNOWLEDGMENTS

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APPENDIX A: THE CLEAN BRAZOVSKII MODEL WITHIN THE RENORMALIZATION GROUP APPROACH

In this appendix we summarize the main steps of the renormalization group approach to the clean Brazovskii model of Ref. [32]. The bare action of this problem is

$$S_0 = \frac{1}{2} \int \frac{d^d q}{(2\pi)^d} \phi_{\mathbf{q}} ((|\mathbf{q}| - q_0)^2 + \tau) \phi_{-\mathbf{q}}.$$

We introduce $k = |\mathbf{q}| - q_0$ and can write $\int [d^d q / (2\pi)^d] \cdots \rightarrow q_0^{d-1} \int_{-\Lambda_0}^{\Lambda_0} dk d\Omega \cdots$, where $d\Omega$ is the measure for the solid angle integration.

A tree level analysis with $k' = k/b$ and $\phi'_{k'} = b^{-\xi} \phi_k$ gives

$$S_0 = \frac{1}{2} b^{2\xi-3} \int_{-\Lambda_0}^{\Lambda_0} dk' d\Omega \phi'_{k',\Omega} (k'^2 + b^2\tau) \phi'_{-k',\Omega},$$

yielding $\tau' = b^2\tau$ and $\xi = \frac{3}{2}$ for the scaling dimension of ϕ , independent of dimension d .

In our treatment of the interaction term we also follow closely the approach of Ref. [45]. The interaction term is given as

$$\begin{aligned} S_{\text{int}} &= \frac{1}{4} \int_{p_1, p_2, p_3} \Gamma_{\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3, -(\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3)} \\ &\times \theta(\Lambda - |\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3|) \phi_{\mathbf{p}_1} \phi_{\mathbf{p}_2} \phi_{\mathbf{p}_3} \phi_{-(\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3)}, \end{aligned}$$

where the θ function ensures that $\mathbf{p}_4 = -(\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3)$ falls indeed into the small shell around the $(d-1)$ -dimensional surface of low energy excitations. In order to make the theory renormalizable the θ function is softened via $\theta(\Lambda_0 - |\mathbf{p}_4|) \rightarrow \exp(-|\mathbf{p}_4|/\Lambda_0)$. At the tree level it follows that

$$\Gamma'_{k'_i} = e^{-(b-1)q_0(|\Delta|-1)/\Lambda_0} b^3 \Gamma_{k'_i/b},$$

with $\Delta = \mathbf{n}_1 + \mathbf{n}_2 - \mathbf{n}_3$, where \mathbf{n}_i are the unit vectors of the momenta \mathbf{p}_i . The constraint $|\Delta| - 1$ is a consequence of the fact that the momentum \mathbf{p}_4 lies within a shell $[q_0 - \Lambda_0, q_0 + \Lambda_0]$. This implies that the four wave vectors \mathbf{p}_i are equal and opposite in pairs when their magnitude equals q_0 . Thus, only $\Gamma_{\mathbf{q}_1, -\mathbf{q}_1, \mathbf{q}_2, -\mathbf{q}_2}$ survives and satisfies

$$\Gamma'_{\mathbf{q}_1, -\mathbf{q}_1, \mathbf{q}_2, -\mathbf{q}_2} = b^3 (\Gamma_{\mathbf{q}_1, -\mathbf{q}_1, \mathbf{q}_2, -\mathbf{q}_2} + \delta\Gamma_{\mathbf{q}_1, \mathbf{q}_2}).$$

For a scalar field it holds generally that

$$\begin{aligned} \delta\Gamma_{\mathbf{q}_1, \mathbf{q}_2} &= -3 \int_{\mathbf{q}}^> u_{\mathbf{q}, -\mathbf{q}, \mathbf{q}_1, -\mathbf{q}_1} u_{\mathbf{q}, -\mathbf{q}, \mathbf{q}_2, -\mathbf{q}_2} G_{\mathbf{q}} G_{\mathbf{q}} \\ &- 3 \int_{\mathbf{q}}^> u_{\mathbf{q}, -\mathbf{q}', \mathbf{q}_1, \mathbf{q}_2} u_{\mathbf{q}', -\mathbf{q}, -\mathbf{q}_1, -\mathbf{q}_2} G_{\mathbf{q}} G_{\mathbf{q}'} \\ &- 3 \int_{\mathbf{q}}^> u_{\mathbf{q}, -\mathbf{q}'', \mathbf{q}_1, -\mathbf{q}_2} u_{\mathbf{q}'', -\mathbf{q}, \mathbf{q}_2, -\mathbf{q}_1} G_{\mathbf{q}} G_{\mathbf{q}''} \end{aligned}$$

with $\mathbf{q}' = \mathbf{q} + \mathbf{q}_1 + \mathbf{q}_2$ and $\mathbf{q}'' = \mathbf{q} + \mathbf{q}_1 - \mathbf{q}_2$. In distinction to the usual ϕ^4 theory we need to consider these three different terms separately. There are two distinct ways to arrange the angle of the unit vectors \mathbf{n}_1 and \mathbf{n}_2 , leading to $\bar{\Gamma}$ and Γ_{\parallel} . For a generic angle between \mathbf{q}_1 and \mathbf{q}_2 only one of the above three terms has propagating lines which are always on the low energy surface, yielding

$$\delta\Gamma_{\mathbf{q}_1, -\mathbf{q}_1, \mathbf{q}_2, -\mathbf{q}_2} = -3\bar{\Gamma}^2 \int_{\mathbf{q}}^> G_{\mathbf{q}}^2,$$

while in the case of $\mathbf{q}_1 = \mathbf{q}_2$ two of the three terms contribute and it follows that

$$\delta\Gamma_{\mathbf{q}_1, -\mathbf{q}_1, \mathbf{q}_1, -\mathbf{q}_1} = -6\bar{\Gamma}^2 \int_{\mathbf{q}}^> G_{\mathbf{q}}^2.$$

In both cases the coupling constant in the interaction is that for a generic angle, i.e., $\bar{\Gamma}$. It holds that

$$\int_{\mathbf{q}}^> G_{\mathbf{q}}^2 = 2q_m^{d-1} K_d \int_{\Lambda_0/b}^{\Lambda_0} dp \frac{1}{(r+p^2)^2} = \frac{1}{3} \alpha \frac{\Lambda_0 l}{(r + \Lambda_0^2)^2},$$

where $\alpha = 6q_m^{d-1} K_d$. Thus we find the following flow equations:

$$\frac{d\bar{\Gamma}}{dl} = 3\bar{\Gamma} - \frac{\alpha\Lambda_0\bar{\Gamma}^2}{(r + \Lambda_0^2)^2},$$

$$\frac{d\Gamma_{\parallel}}{dl} = 3\Gamma_{\parallel} - \frac{2\alpha\Lambda_0\bar{\Gamma}^2}{(r + \Lambda_0^2)^2}.$$

Similarly, it follows for the mass term that $\tau' = b^2(\tau + \Sigma)$, where

$$\Sigma_{\mathbf{q}'} = 3 \int_{\mathbf{q}}^> \Gamma_{\mathbf{q}', -\mathbf{q}', \mathbf{q}, -\mathbf{q}} G_{\mathbf{q}},$$

which is only weakly momentum dependent and it holds that

$$\frac{d\tau}{dl} = 2\tau + \alpha\Lambda_0 \frac{\bar{\Gamma}}{\tau + \Lambda_0^2}.$$

Considering a weak first order transition we neglect τ in the various denominators, i.e., $\tau + \Lambda_0^2 \approx \Lambda_0^2$. We verified by numerically solving the full flow equations of the problem that this approximation only causes very minor changes in the

final results. Rescaling $\bar{\gamma} = \alpha \bar{\Gamma} / 3 \Lambda_0^3$ and similarly for all the other coupling constants as well as $r = \tau / \Lambda_0^2$ yields the equations given in Eq. (21).

APPENDIX B: DETAILS OF THE SOLUTION OF THE FLOW EQUATIONS

In this appendix we give the full flow equation for the disordered Brazovskii model and summarize in detail its solution. A one-loop calculation along the lines of the clean model, but taking into account all six coupling constants, yields

$$\begin{aligned} \frac{d\tau}{dl} &= 2\tau + K(\tau)(3\bar{\Gamma} + m\bar{\Delta} + 2\bar{\Omega}), \\ \frac{d\bar{\Gamma}}{dl} &= 3\bar{\Gamma} - \Pi(\tau)(3\bar{\Gamma}^2 + 4\bar{\Gamma}\bar{\Omega}), \\ \frac{d\Gamma_{\parallel}}{dl} &= 3\Gamma_{\parallel} - 2\Pi(\tau)(3\bar{\Gamma}^2 + 4\bar{\Gamma}\bar{\Omega}), \\ \frac{d\bar{\Delta}}{dl} &= 3\bar{\Delta} - \Pi(\tau)(6\bar{\Gamma}\bar{\Delta} + m\bar{\Delta}^2 + 4\bar{\Omega}\bar{\Delta}), \\ \frac{d\Delta_{\parallel}}{dl} &= 3\Delta_{\parallel} - \Pi(\tau)(6\bar{\Gamma}\bar{\Delta} + m\bar{\Delta}^2 + 4\bar{\Delta}\bar{\Omega} + 2\bar{\Omega}^2), \\ \frac{d\bar{\Omega}}{dl} &= 3\bar{\Omega} - 2\Pi(\tau)\bar{\Omega}^2, \\ \frac{d\Omega_{\parallel}}{dl} &= 3\Omega_{\parallel} - 4\Pi(\tau)\bar{\Omega}^2. \end{aligned} \quad (\text{B1})$$

Here

$$\begin{aligned} K(\tau) &= \frac{d}{dl} \int_{\mathbf{q}} G_{\mathbf{q}} = \frac{1}{3} \alpha \frac{\Lambda_0}{\tau + \Lambda_0^2}, \\ \Pi(\tau) &= \frac{d}{dl} \int_{\mathbf{q}} G_{\mathbf{q}}^2 = \frac{1}{3} \alpha \frac{\Lambda_0}{(\tau + \Lambda_0^2)^2}, \end{aligned}$$

with $\alpha = 3q_0^2/\pi^2$. We first approximate $\Pi(\tau) \simeq \Pi(0)$ and $K(\tau) \simeq K(0)$ which gives $K(0) = \alpha/3\Lambda_0$ and $\Pi(0) = \alpha/3\Lambda_0^3$. We have solved numerically the flow equations without this simplification and only found very minor differences. Further we introduce dimensionless coupling constants $\bar{\gamma} = \Pi(0)\bar{\Gamma}$ and similarly for all other the coupling constants as well as $r = \tau/\Lambda_0^2$. Performing the $m \rightarrow 0$ limit of the numbers of replicas finally yields the flow equations given in Eq. (29).

Before we give the solution of this set of equations we discuss the fixed points and demonstrate that no additional disorder fixed point occurs. There are altogether four different fixed points. At the Gaussian fixed point all coupling constants together with r^* vanish. Next, we find the clean

fixed point where all disorder coupling constants vanish, but $\bar{\gamma}^* = 1$, $\gamma_{\parallel}^* = 2$, $\tau^* = -\frac{3}{2}$. This fixed point corresponds to a tricritical point and was discussed in detail in Ref. [51]. Furthermore, there are two more, unphysical fixed points where some of the ω 's and δ 's are positive, or the γ 's negative, which are in both cases signs that render the theory unstable. Note, all the disorder variables have a bare value $-g$ and are negative. Thus, there are no additional disorder related fixed points.

Next we summarize the solution of the flow equations. The above set of flow equations, Eq. (29), can be solved in a closed fashion. It is useful to first solve the flow equation for $\bar{\omega}(l)$:

$$\bar{\omega}(l) = \frac{-e^{3l}g}{1 - (2g/3)(e^{3l} - 1)}.$$

Since $\bar{\omega}(l=0) = -g < 0$, $\bar{\omega}(l)$ diverges at a value

$$l_g = \frac{1}{3} \log \left(1 + \frac{3}{2g} \right).$$

The important issue is whether the flow will ever reach l_g , i.e., whether there will be a divergence of other coupling constants, an instability of the system ($\gamma_{\parallel} < 0$), or whether scaling stops for some l smaller than l_g .

Considering next $\omega_{\parallel}(l)$ leads to the solution $\omega_{\parallel}(l) = 2\bar{\omega}(l) + g e^{3l}$ and $\nu_{\parallel}(l)$ diverges together with $\bar{\nu}(l)$ and will not change sign for $l < l_g$.

We next find the solution for $\bar{\gamma}(l)$:

$$\bar{\gamma}(l) = - \frac{\gamma_0 \bar{\omega}(l)/g}{1 + (\gamma_0 - (2g/3))(e^{3l} - 1)},$$

which diverges if $\bar{\omega}(l)$ does. If $g > \frac{3}{2}\gamma_0$, $\bar{\gamma}(l)$ also diverges at the scale

$$l_u = \frac{1}{3} \ln \left(1 + \frac{1}{(2g/3) - \gamma_0} \right).$$

However, for $g > 0$ it always holds that $l_g < l_u$, i.e., $\bar{\gamma}(l)$ does not diverge before $\bar{\omega}(l)$.

Next we consider the solution for $\gamma_{\parallel}(l)$ which signals the fluctuation induced first order transition in the clean case. It holds that

$$\gamma_{\parallel}(l) = 2\bar{\gamma}(l) - \gamma_0 e^{3l}.$$

γ_{\parallel} changes sign at the scale l^* where $\bar{\gamma}(l^*) = (\gamma_0/2)e^{3l^*}$. Using the above solution for $\bar{\gamma}(l)$ it follows that

$$l_{\pm}^* = \frac{1}{3} \ln \left[1 + \frac{1}{\gamma_0} \left(\frac{2}{1 - (4g/3)\gamma_0 \pm \chi(2g/3)\gamma_0} \right) \right]$$

with $\chi(x) = \sqrt{1 + 8x^2 - 8x}$. As can be seen in Fig. 2, there are two l values where $\bar{\gamma}(l)$ changes sign. We have to look for the smaller value (the first sign change). The first time where this gives a real solution for l^* happens when the argument of the square root in $\chi(x)$ vanishes. This yields the g value where γ_{\parallel} changes sign first:

$$g_c = \frac{3\sqrt{2}(\sqrt{2}-1)}{8} \gamma_0.$$

Finally we discuss the solutions for $\bar{\delta}(l)$ and $\delta_{\parallel}(l)$. It holds that

$$\bar{\delta}(l) = -\frac{g^3 e^{3l}}{\gamma_0^2} \left(\frac{\bar{\gamma}(l)}{\bar{\omega}(l)} \right)^2.$$

The solution $\bar{\delta}(l)$ will, for the same reason as $\bar{\gamma}(l)$, not diverge before $\bar{\omega}(l)$. Considering $\delta_{\parallel}(l)$,

$$\delta_{\parallel}(l) = \frac{g e^{3l} [1 + (2g/3)(e^{3l} - 1)^2 ((2g/3) - \gamma_0) y(l)]}{[1 - (2g/3)(e^{3l} - 1)][1 + y(l)]}$$

with $y(l) = (e^{3l} - 1)((2g/3) - \gamma_0) - 2$. δ_{\parallel} diverges at the scale l_g . However for $g > 27/2\gamma_0$ the coupling constant $\omega_{\parallel}(l)$ changes sign. Restricting ourselves to $g < 27/2\gamma_0$ we do not need to specify whether this sign change ever takes place before $\bar{\omega}(l)$ diverges.

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