Star copolymers in porous environments: scaling and its manifestations

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We consider star polymers, consisting of two different polymer species, in a solvent subject to quenched correlated structural obstacles. We assume that the disorder is correlated with a power-law decay of the pair correlation function $g(x) \sim x^{-a}$. Applying the field-theoretical renormalization group approach in $d$ dimensions, we analyze different scenarios of scaling behavior working to first order of a double $\varepsilon = 4 - d$, $\delta = 4 - a$ expansion. We discuss the influence of the correlated disorder on the resulting scaling laws and possible manifestations such as diffusion controlled reactions in the vicinity of absorbing traps placed on polymers as well as the effective short-distance interaction between star copolymers.

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I. INTRODUCTION

Understanding the behavior of polymer macromolecules in solutions in the presence of structural obstacles is of great interest in polymer physics. The presence of defects often leads to a large spatial inhomogeneity and may create pore spaces of fractal structure [1]. Such situations can be encountered in studying, e.g., polymer diffusion through microporous membranes [2] or within colloidal solutions [3].

Solutions of polymer macromolecules in disordered environment are subject to intensive studies. Numerous simulations [4–9] and analytical studies [7, 10–16] have focused on the case of uncorrelated structural defects at the percolation threshold of the remaining accessible sites, this situation is shown to alter significantly the universal behavior of polymer macromolecules. Recently, another special type of disorder has been brought to attention, which display correlations in mesoscopic scale. This case can be described within the frames of a model with long-range-correlated quenched defects, considered in Refs. [17–19] in the context of magnetic phase transitions. Here, structural defects are characterized by a pair correlation function $g(x)$, which in $d$ dimensions falls off at large distance $x$ according to a power law:

$$g(x) \sim x^{-a}. \quad (1)$$

In general, any value of $0 \leq a \leq d$ can be realized by defects that form clusters of fractal dimension $d_f = d - a$. For integer dimension $d_f$ these include the following special cases: uncorrelated point-like defects ($d_f = 0$), mutually uncorrelated straight lines of random orientation ($d_f = 1$), mutually uncorrelated planes of random orientation ($d_f = 2$). The influence of such long-range correlated defects on the universal properties of single polymer has been analyzed within the renormalization group approach in Refs. [20, 21].

To describe the universal properties of polymer chains in good solvents, one may due to universality in the long chain limit consider the model of self-avoiding walks (SAWs) on a regular lattice [22, 23]. In particular, the average square end-to-end distance $\langle R^2_e \rangle$ and the number of configurations $Z_N$ of SAWs with $N$ steps obey in the asymptotic limit $N \to \infty$ the following scaling laws:

$$\langle R^2_e \rangle \sim N^{2\nu}, \quad Z_N \sim R^{2-\eta-1/\nu}. \quad (2)$$

Here, the second equation shows the power law in terms of the effective polymer size $R \equiv \sqrt{\langle R^2_e \rangle} \sim N^\nu$, $\nu$ and $\eta$ are universal exponents that only depend on the space dimensionality $d$. For $d = 3$, high order renormalization group estimates are $\nu = 0.5882 \pm 0.0011$ and $\eta = 0.0284 \pm 0.0025$.

The theory can be generalized to describe star polymers, which consist of $f$ linear polymer chains or SAWs, linked together at their end-points. The study of star polymers is of great interest since they serve as building blocks of...
polymer networks [25, 26] and can be used to model complex polymer micellar systems and gels [27–29]. For a single star with $f$ arms of $N$ steps (monomers) each, the number of possible configurations obeys a power law in terms of the size $R$ of the isolated chain of $N$ monomers [25, 26]:

$$Z_{N,f} \sim R^{\eta f - f \eta}.$$  \hspace{1cm} \text{(3)}

Here, the exponents $\eta_f$ are universal star exponents, depending on the number of arms $f$ ($\eta_1 = 0, \eta_2 = 1/\nu - 2 - \eta$). Scaling properties of star polymers are well studied both numerically [30–35] and analytically [26, 36–42]. It has been shown that the presence of long-range-correlated disorder may have interesting consequences for the scaling properties of polymer stars such as entropic separation of polymers according to their architecture [43].

Linking together polymers of different species, we receive non-homogeneous star polymers with a much richer scaling behavior [44–47]. A particular case is the star copolymer, consisting of polymer chains of two different species. It has been shown [45], that the number of configurations $Z_{f_1 f_2}$ of a copolymer star with $f_1$ arms of species 1 and $f_2$ arms of species 2 scales as:

$$Z_{f_1 f_2} \sim (R)^{\eta_{f_1 f_2} - f_1 \eta_{f_1} - f_2 \eta_{f_2}},$$  \hspace{1cm} \text{(4)}

where $\eta_{f_1 f_2}$ constitutes a family of copolymer star exponents. These exponents are universal and depend only on space dimension $d$ and the number of chains $f_1, f_2$, as well as three different types of fixed points that govern the rich scaling behavior [44].

Depending on the temperature, a situation may occur, where one or more of the inter- or intrachain interactions vanishes. Indeed, for each polymer system one finds a so-called $\Theta$-temperature, at which attractive and repulsive interactions between monomers compensate each other (see, e.g., [22, 23]). Such a polymer chain can effectively be described by a simple random walk (RW). In this case, scaling laws (Eq. (2)) hold with exponents: $\nu = 1/2, \eta = 0$. As a result, for example, there may be only mutual excluded-volume interactions between chains of different species, while chains of the same species can freely intersect. That is, some species behave effectively like RWs. Within a copolymer star, the subset of chains of such species builds up a substar of random walks, possibly avoiding the second part of the star, which can be either of random walks or self-avoiding random walks (see Fig. 1). Cates and Witten [48] have shown, that this situation can also be interpreted as describing the absorption of diffusive particles on polymers.

Another example, where star exponents govern physical behavior concerns the short-range interaction between cores of star polymers in a good solvent [25, 49, 50]. The mean force $F_{fg}(r)$ acting on the centers of two stars with functionalities $f$ and $g$ is inversely proportional to the distance $r$ between their cores:

$$F_{fg}(r) = k_B T \frac{\Theta_{fg}}{r},$$  \hspace{1cm} \text{(5)}

with $k_B T$ denoting the thermal energy, $\Theta_{fg}$ the universal contact exponent, related to the family of exponents of star polymers by scaling relations:

$$\Theta_{fg} = \eta_f + \eta_g - \eta_{f+g}.$$  \hspace{1cm} \text{(6)}

FIG. 1: (color online) Schematic representation of copolymer stars consisting of two polymer species (denoted as red and blue). Solid lines present species behaving like SAWs, dashed lines present RWs. The two different sets in each example may further be either mutually avoiding or mutually “transparent”.

(a) \hspace{1cm} (b) \hspace{1cm} (c)
We are interested to generalize this relation to the case of copolymers, and to analyze the impact of disorder on mutual interactions between two star copolymers.

The questions of the influence of correlated disorder in the environment on the scaling behavior of star copolymers and the resulting consequences remain so far unresolved and are the subject of the present study. We will also analyze the spectrum of scaling exponents in particular for the above mentioned process of trapping diffusive particles in the vicinity of absorbing polymers in disordered environments.

The paper is organized as follows: in the next section we will give a field-theoretical representation of the model Lagrangean. The field-theoretical renormalization group method, which we use to find the qualitative characteristics of scaling behavior, is shortly described in Section 3. In Section 4 we discuss the results obtained. We finish by giving conclusions and an outlook.

II. THE MODEL

Let us consider a polymer star with \( f \) arms of different species in a solvent. We are working within the Edwards continuous chain model \([51, 52]\), representing each chain by a path \( r_i(s) \), parameterized by \( 0 \leq s \leq S_i, \ i = 1, 2, \ldots, f \). The central branching point of the star is fixed at \( r_1(0) \). The partition function of the system is then defined by the path integral \([26]\):

\[
Z_f(S_i) = \int D[r_1, \ldots, r_f] \times \exp[-\mathcal{H}_f] \prod_{i=2}^{f} \delta^d(r_i(0) - r_1(0)). \tag{7}
\]

Here, a multiple path integral is performed for the paths \( r_1, \ldots, r_f \), the product of \( \delta \)-functions reflects the star-like configuration of \( f \) chains, each starting at the point \( r_1(0) \), \( \mathcal{H}_f \) is the Hamiltonian, describing the system of \( f \) disconnected polymer chains:

\[
\mathcal{H}_f = \frac{1}{2} \sum_{i=1}^{f} \int_0^{S_i} ds \left( \frac{dr_i(s)}{ds} \right)^2 + \frac{1}{6} \sum_{i \leq j}^f \nu_{ij}^0 \int dr_i(r) \rho_j(r), \tag{8}
\]

where \( \rho_i(r) = \int_0^{S_i} ds \delta^d(r - r_i(s)) \) and \( \nu_{ij}^0 \) is a symmetric matrix of bare excluded-volume interactions between chains \( i \) and \( j \).

The continuous chain model \([7]\) can be mapped onto a corresponding field theory by a Laplace transform in the Gaussian surface \( S_i \) to the conjugated chemical potential variable (mass) \( \hat{\mu}_i \) \([22, 44]\):

\[
\tilde{Z}_f(\hat{\mu}_i) = \int \prod_b dS_j \exp[-\hat{\mu}_j S_j'] Z_f(S_i). \tag{9}
\]

One may then show that the Hamiltonian \( \mathcal{H} \) is related to an \( m \)-component field theory with a Lagrangean \( \mathcal{L} \) in the limit \( m \to 0 \):

\[
\mathcal{L}\{\varphi_j, \mu_j\} = \frac{1}{2} \sum_{i=1}^{f} \int d^d x \left( \mu_i^2 |\varphi_i(x)|^2 + |\nabla \varphi_i(x)|^2 \right) + \frac{1}{4!} \sum_{i \leq j}^f \nu_{ij}^0 \int d^d x \varphi_i^2(x) \varphi_j^2(x), \tag{10}
\]

where \( \varphi_i^m = \{\varphi_1^m, \ldots, \varphi_i^m\} \) and \( \mu_i \) are bare critical masses. On the base of the Lagrangean \([10]\) the one-particle irreducible vertex functions \( \Gamma^{(L)} \) of the theory can be obtained:

\[
\delta(\sum \Gamma_{i_1, \ldots, i_L}^L(q_i)) = \int e^{i q \cdot r_1 \cdots r_L} \left\langle \varphi_{i_1}(r_1) \ldots \varphi_{i_L}(r_L) \right\rangle_{1PI}, \tag{11}
\]
where only those contributions, that have non-vanishing tensor factors in the limit \( m \to 0 \) are kept.

The Laplace-transformed partition function \( \tilde{Z}_f(\tilde{\mu}_i) \) has a vertex part, which is defined by the insertion of the composite operator \( \prod_\nu \phi_i \):

\[
\delta(p + \sum_j q_j) \Gamma^f(p, q_1, \ldots, q_f) = \int e^{i(p \cdot \alpha + q_j r_j)} \, \text{d} r_0 \text{d} r_1 \ldots \text{d} r_f \, \phi_1(r_0) \cdots \phi_f(r_0) \phi_1(r_1) \cdots \phi_f(r_f) \mathcal{L}_{\Gamma f}.
\]

Let us note that we are interested in the case of a copolymer star, having \( f_1 \) chains of one species and \( f_2 \) of another, so that \( f_1 + f_2 = f \). To keep notations simple we will consider in the following discussion only two fields \( \phi_1 \) and \( \phi_2 \), corresponding to two different “species”. Thus, in (10) we have interactions \( u_{11}, u_{22} \) between the fields of the same “species” and \( u_{12} \) between different fields. The composite operator in (12) has the form of a product \( \langle \phi_1 \rangle f_1 \langle \phi_2 \rangle f_2 \).

We introduce disorder into the model (10), by redefining \( \hat{\mu}_i \) to \( \hat{\mu}_i = \mu_i + \delta\mu_i(x) \), where the local fluctuations \( \delta\mu_i(x) \) obey:

\[
\langle \langle \delta\mu_i(x) \rangle \rangle = 0,
\]

\[
\langle \langle \delta\mu_i(x) \delta\mu_j(y) \rangle \rangle = g_{ij}(|x - y|).
\]

Here, \( \langle \langle \cdots \rangle \rangle \) denotes the average over spatially homogeneous and isotropic quenched disorder. The form of the pair correlation function \( g(x) \) is chosen to decay with distance according to the power law (11).

In order to average the free energy over different configurations of the quenched disorder we apply the replica method to construct an effective Lagrangean:

\[
\mathcal{L}_{\text{eff}} = \int \text{d} x \frac{1}{2} \left[ \sum_{i=1}^2 \sum_{\alpha=1}^n \left[ \nabla^2 \phi_\alpha^i \right]^2 + \mu_i^2 (\phi_\alpha^i)^2 \right] + \sum_{i \leq j} \sum_{\alpha=1}^n \frac{u_{ij}^0}{4!} (\phi_\alpha^i)^2 (\phi_\alpha^j)^2 - \int \text{d} x \text{d} y \sum_{i \leq j} \sum_{\alpha, \beta=1}^n g_{ij}(|x - y|) (\phi_\alpha^i)^2 (\phi_\beta^j)^2.
\]

Here, the coupling of the replicas is given by the correlation function \( g(x) \) of Eq. (1), Greek indices denote replicas and the replica limit \( n \to 0 \) is implied.

For small \( k \), the Fourier-transform \( \tilde{g}_{ij}(k) \) of \( g_{ij}(x) \) (11) reads:

\[
\tilde{g}_{ij}(k) \sim \nu_{ij}^0 + w_{ij}^0 |k|^{a - d}.
\]

Thus, rewriting Eq. (13) in momentum space, one obtains an effective Lagrangean with 9 bare couplings: \( u_{11}^0, u_{22}^0, u_{12}^0, u_{11}^0, u_{22}^0, u_{12}^0, w_{12}^0, w_{11}^0, w_{22}^0 \). As it was pointed out in Ref. (14), once the limit \( m, n \to 0 \) has been taken, the \( u_{ij}^0 \) and \( v_{ij}^0 \) terms acquire the same symmetry, and an effective Lagrangean with couplings \( (u_{ij}^0 - v_{ij}^0) = O(\text{mn}) \) symmetry results. This leads to the conclusion that weak quenched uncorrelated disorder i.e. the case \( a = d \) is irrelevant for polymers. Taking this into account, we end up with only 6 couplings in an effective Lagrangean: \( u_{11}^0, u_{22}^0, u_{12}^0, u_{21}^0, w_{12}^0, w_{11}^0 \). For \( a < d \), the momentum-dependent coupling \( w_{ij}^0 k^{a-d} \) has to be taken into account. Note that \( \tilde{g}_{ij}(k) \) must be positively definite being the Fourier image of the correlation function. Thus, we have \( w_{ij}^0 > 0 \) for small \( k \). Note, that the couplings \( u_{ij}^0 \) should be positive, otherwise the pure system would undergo a 1st order transition.

The resulting Lagrangean in momentum space then reads:

\[
\mathcal{L}_{\text{eff}} = \frac{1}{2} \sum_{\alpha=1}^n \sum_{k} \left[ k^2 + \mu_i^2 \right] (\phi_\alpha^i(k))^2
\]

\[
+ \sum_{i \leq j} \sum_{k_1,k_2,k_3,k_4} \frac{u_{ij}^0}{4!} \sum_{\alpha=1}^n \delta(k_1+k_2+k_3+k_4) \phi_\alpha^i(k_1) \phi_\alpha^j(k_2) \phi_\alpha^j(k_3) \phi_\alpha^j(k_4)
\]

\[
- \frac{w_{ij}^0}{4!} \sum_{\alpha, \beta=1}^n |k_1+k_2|^{a-d} \delta(k_1+k_2-k_3-k_4) \phi_\alpha^i(k_1) \phi_\alpha^j(k_2) \phi_\beta^j(k_3) \phi_\beta^j(k_4).
\]
In the next section, we apply the field-theoretical renormalization group approach in order to extract the scaling behavior of the model \[15\].

### III. RENORMALIZATION GROUP APPROACH

We apply the renormalization group (RG) method \[53\] in the massive scheme renormalizing the one-particle irreducible vertex functions, in particular \(\Gamma^{(2)}, \Gamma^{(4)}\) and \(\Gamma^{2,1}\), as well as the vertex function \(\Gamma^{(f_1, f_2)}\), with a single \((\varphi_1)^{f_1}(\varphi_2)^{f_2}\) insertion. Note that the polymer limit of a zero component field leads to an essential simplification: each field \(\varphi_i\), mass \(\mu_i\) and coupling \(w_i^0\) renormalizes as if the other fields were absent. The renormalized couplings \(u_{ij}, w_{ij}\) are given by:

\[
\begin{align*}
  u_{ii}^0 &= \mu^\varepsilon Z_{\varphi_i}^{-2} Z_{ii} u_{ii}, & i = 1, 2 \\
  w_{ii}^0 &= \mu^\delta Z_{\varphi_i}^{-2} Z_{ii} w_{ii}, & i = 1, 2 \\
  u_{12}^0 &= \mu^\varepsilon Z_{\varphi_1}^{-1} Z_{\varphi_2}^{-1} Z_{12} u_{12}, \\
  w_{12}^0 &= \mu^\delta Z_{\varphi_1}^{-1} Z_{\varphi_2}^{-1} Z_{12} w_{12}.
\end{align*}
\]

Here, \(\mu\) is a scale parameter, equal to the renormalized mass, and parameters \(\varepsilon = 4 - d, \delta = 4 - a\). The renormalization factors \(Z\) have the form of power series, the coefficients of which are calculated perturbatively order by order.

The star vertex function \(\Gamma^{(f_1, f_2)}\) is renormalized by a factor \(Z_{f_1, f_2}\):

\[
Z_{\varphi_1}^{f_1/2} Z_{\varphi_2}^{f_2/2} Z_{f_1, f_2} \Gamma^{(f_1, f_2)} = \mu^{(f_1 + f_2)(\varepsilon/2 - 1) + 4 - \varepsilon}.
\]

The variation of the coupling constants under renormalization defines a flow in parametric space, governed by corresponding \(\beta\)-functions:

\[
\beta_{u_{ij}} (u_{ij}, w_{ij}) = \mu \frac{d}{d\mu} u_{ij}, \quad \beta_{w_{ij}} (u_{ij}, w_{ij}) = \mu \frac{d}{d\mu} w_{ij}, \quad i, j = 1, 2.
\]

The fixed points (FPs) of the RG transformation are given by the solution of the system of equations:

\[
\beta_{u_{ij}} (u_{ij}^*, w_{ij}^*) = 0, \quad \beta_{w_{ij}} (u_{ij}^*, w_{ij}^*) = 0, \quad i, j = 1, 2.
\]

The stable FP, corresponding to the critical point of the system, is defined as the fixed point where the stability matrix possesses eigenvalues \(\{\lambda_i\}\) with positive real parts.

The flow of the renormalizing factors \(Z\) in turn gives rise to RG functions \(\eta_{\varphi_i}\) and \(\eta_{f_1, f_2}\) as follows:

\[
\begin{align*}
  \mu \frac{d}{d\mu} \ln Z_{\varphi_i} &= \eta_{\varphi_i} (u_{ij}, w_{ij}), \\
  \mu \frac{d}{d\mu} \ln Z_{f_1, f_2} &= \eta_{f_1, f_2} (u_{ij}, w_{ij}).
\end{align*}
\]

At the FP of the renormalization group transformation, the function \(\eta_{\varphi_i}\) describes the pair correlation function critical exponent, while the functions \(\eta_{f_1, f_2}\) define the set of exponents for copolymer stars:

\[
\begin{align*}
  \eta &= \eta_{\varphi_i} (u_{ij}^*, w_{ij}^*) \\
  \eta_{f_1, f_2} &= \eta_{f_1, f_2} (u_{ij}^*, w_{ij}^*).
\end{align*}
\]

In the next section, we will present expressions for the \(\beta\) and \(\eta\) functions, together with a study of the RG flow and the fixed points of the theory.

### IV. THE RESULTS

#### A. Fixed points and scaling exponents

According to the renormalisation group prescriptions, we obtain the RG functions of the model \[15\] within a massive scheme up to the one-loop approximation:

\[
\beta_{u_{ii}} = -\varepsilon \left[ u_{ii} - \frac{4}{3} w_{ii}^2 I_1 \right] - \delta 2 u_{ii} w_{ii} \left[ I_2 + \frac{1}{3} I_3 \right] + (2\delta - \varepsilon) w_{ii}^2 I_3,
\]

where \(I_1, I_2, I_3\) are relevant integrals.
\[ \beta_{w_{ii}} = -\delta \left[ w_{ii} + \frac{2}{3} w_{ii}^2 I_2 + \frac{2}{3} w_{ii} I_4 \right] + \frac{2}{3} w_{ii} u_{ii} I_1, \quad i = 1, 2; \] (28)

\[ \beta_{u_{12}} = -\varepsilon \left[ u_{12} - \frac{2}{3} u_{12} I_1 - \frac{1}{3} u_{12}(u_{11} + u_{22}) I_2^2 \right] - \delta \left[ u_{12} w_{12} I_2 + \frac{1}{2} u_{12}(w_{11} + w_{22}) I_2 + \frac{1}{2} u_{12}(w_{11} + w_{22}) I_4 \right] \]

\[ + (2\delta - \varepsilon) \left[ \frac{1}{3} w_{12}^2 I_3 + \frac{1}{6} w_{12}(w_{11} + w_{22}) \right], \] (29)

\[ \beta_{w_{12}} = -\delta \left[ w_{12} + \frac{1}{3} w_{12}^2 I_2 + \frac{1}{3} w_{12}^2 I_4 \right] + \varepsilon \left[ \frac{1}{3} w_{12} u_{12} I_1 + \frac{1}{6} w_{12}(u_{11} + u_{22}) I_1 + \frac{1}{6} w_{12}(w_{11} + w_{12}) I_2 \right]. \] (30)

Note, that expressions for \( \beta_{u_{12}}, \beta_{w_{12}} \) restore the corresponding RG functions for a single polymer chain in long-range correlated disorder \[20, 21\]. Here, \( I_i \) are the loop-integrals:

\[
I_1 = \int \frac{d^d q}{(q^2 + 1)^2},
\]
\[
I_2 = \int \frac{d^d q q^{a-d}}{(q^2 + 1)^2},
\]
\[
I_3 = \int \frac{d^d q q^{2(a-d)}}{(q^2 + 1)^2},
\]
\[
I_4 = \frac{\partial}{\partial k^2} \left[ \int \frac{d^d q q^{a-d}}{(q + k)^2 + 1} \right]_{k^2 = 0}.
\] (31)

We make the couplings dimensionless by redefining \( u_{ij} = u_{ij} \mu^{d-4} \) and \( w_{ij} = w_{ij} \mu^{a-4} \), therefore, the loop integrals do not explicitly contain the mass. Besides, we absorb geometrical factors \( S_d \), resulting from angular integration into the couplings.

Additionally, we need the RG function \( \eta_{f_1 f_2}(u_{ij}, w_{ij}) \), which we find in the form:

\[
\eta_{f_1 f_2} = -\varepsilon \left( u_{11} \frac{f_1(f_1 - 1)}{6} I_1 + u_{22} \frac{f_2(f_2 - 1)}{6} I_1 + u_{12} \frac{f_1 f_2}{3} I_1 \right) +
+ \delta \left( w_{11} \frac{f_1(f_1 - 1)}{6} I_2 + w_{22} \frac{f_2(f_2 - 1)}{6} I_2 + w_{12} \frac{f_1 f_2}{3} I_2 \right). \] (32)

The perturbative expansions for RG functions may be analyzed by two complementary approaches: either by exploiting a double expansion in the parameters \( \varepsilon = 4 - d, \delta = 4 - a \) \[17, 20, 21\], or by fixing the values of the parameters \( d, a \) \[20\]. Let us note, that within the one-loop approximation the latter method cannot give reliable results \[20\], and we exploit the double expansion in \( \varepsilon = 4 - d, \delta = 4 - a \) for a qualitative analysis. The resulting expressions for \( \beta \)- and \( \eta \)-functions read:

\[
\beta_{u_{ii}} = -\varepsilon u_{ii} + \frac{4}{3} u_{ii}^2 - 2 u_{ii} w_{ii} + \frac{2}{3} w_{ii}^2 \] (33)

\[
\beta_{w_{ii}} = -\delta w_{ii} - \frac{2}{3} w_{ii}^2 + \frac{2}{3} u_{ii} w_{ii}, \quad i = 1, 2; \] (34)

\[
\beta_{u_{12}} = -\varepsilon u_{12} + \frac{2}{3} u_{12}^2 + \frac{1}{3} u_{12}(u_{11} + u_{22}) - \frac{1}{2} u_{12}(w_{11} + w_{22})
-u_{12} w_{12} + \frac{1}{3} w_{12}^2 + \frac{1}{6} w_{12}(w_{11} + w_{22}), \] (35)

\[
\beta_{w_{12}} = -\delta w_{12} - \frac{1}{3} w_{12}^2 + \frac{1}{3} u_{12} w_{12} + \frac{1}{6} w_{12}(u_{11} + u_{22}) - \frac{1}{6} w_{12}(w_{11} + w_{22}), \] (36)

\[
\eta_{f_1 f_2} = -\frac{f_1(f_1 - 1)}{6} (u_{11} - w_{11}) - \frac{f_2(f_2 - 1)}{6} (u_{22} - w_{22}) - \frac{f_1(f_1 - 1)}{3} u_{12} + \frac{f_2(f_2 - 1)}{3} w_{12}. \] (37)
Substituting Eqs. (33)–(36) into (22), we find a number of fixed points, corresponding to different scenarios of the scaling behavior of the model.

**Pure solution** First, let us consider the case, when disorder is absent \((w_{11} = w_{22} = w_{12} = 0)\) and we recover the problem of the so-called ternary solution of two polymer species in a good solvent \([44]\). Solving the equations \(\beta_{u_{ij}} = 0, i, j = 1, 2\), we find eight fixed points in correspondence with Refs. \([42][47]\). The trivial FPs: \(G_0(u_{11}^* = u_{22}^* = u_{12}^* = 0), U_0(u_{11}^* \neq 0, u_{22}^* = u_{12}^* = 0), U_0'(u_{22}^* \neq 0, u_{11}^* = u_{12}^* = 0)\) and \(S_0(u_{11}^* = u_{22}^* \neq 0, u_{12}^* = 0)\) describe sets of two mutually non-interacting polymer species. More interesting are the FPs denoted as \(G, U, U', S\), describing two mutually interacting species, their coordinates are given in the upper part of Table I. Corresponding values of the exponents \(\eta_{f_1,f_2}\) read:

\[
\eta_{f_1,f_2}^G = \frac{-(f_1 f_2)\varepsilon}{2},
\]

\[
\eta_{f_1,f_2}^U = \frac{u_{f_1,f_2}}{8},
\]

\[
\eta_{f_1,f_2}^S = \frac{-(f_1 + f_2)(f_1 + f_2 - 1)\varepsilon}{8}.
\]

Note, that \(\eta_{f_1,f_2}^S\) just recovers the exponent of a homogeneous polymer star with \(f = f_1 + f_2\) arms. The values of these exponents are known up to 4th order of the \(\varepsilon\)-expansion \([26][54]\) and in the fixed \(d\) approach \([45]\).

**Solution in the presence of long-range correlated disorder.** Next, let us turn on the disorder. Apart from the eight FPs listed above, now we have a whole set of new FPs describing two polymer species in the case, when one or both of the species feel the presence of long-range correlated disorder. Indeed, to find these FPs one has to solve the system of 6 second-order equations \((22)\) with the \(\beta\)-functions given by \([33]–[36]\). In principle, this may lead to \(2^6\) solutions \([55]\). In what follows we consider only four nontrivial points, corresponding to copolymer stars of mutually interacting species, both feeling the presence of disorder, which are of foremost interest (see Table I). These FPs describe particular situations of two mutually interacting sets of RWs \((G_L, S_L)\) and two interacting sets of RWs and SAWs \((U_L, U'_L)\). Note that due to the special form of the \(\beta\)-functions the fixed points with \(u_{11}^* = 0, w_{11}^* \neq 0\) do not exist, i.e. one cannot describe simple random walks in the media with long-range-correlated disorder.

We are interested in the points, which are stable in all coordinate directions. After analyzing the stability and physical accessibility of all the points, we come to the conclusion, that only the FPs \(S\) and \(S_L\) are stable in all directions and their stabilities are determined by the conditions:

- fixed point \(S\) is stable for \(\varepsilon > 2\delta\),
- fixed point \(S_L\) is stable for \(\delta < \varepsilon < 2\delta\).

Although the remaining FPs \((G_L, U, U_L\) from the Table 1) are unstable, they can be reached for \(\delta < \varepsilon < 2\delta\) under specific initial conditions. In particular, \(G_L\) is reachable from the initial condition \(u_{11} = u_{22} = u_{12} = 0\), \(U_L\) is reachable for \(u_{22} = w_{22} = 0\) and \(U'_L\) for \(u_{11} = u_{12} = 0\). Substitution of these FPs values into the expansion \([37]\) results in the following estimates for \(\eta_{f_1,f_2}\):

\[
\eta_{f_1,f_2}^{G_L} = -(f_1 f_2)\delta,
\]

\[
\eta_{f_1,f_2}^{U_L} = \frac{u_{f_1,f_2}}{4},
\]

\[
\eta_{f_1,f_2}^{S_L} = \frac{-(f_1 + f_2)(f_1 + f_2 - 1)\delta}{4}.
\]

**Table I:** Non-trivial fixed points of the model \([15]\).

| \(u_{11}^*\) | \(w_{22}^*\) | \(w_{12}^*\) | \(w_{11}^*\) | \(w_{22}^*\) | \(w_{12}^*\) |
|---|---|---|---|---|---|
| \(G\) | 0 | 0 | 0 | 0 | 0 |
| \(U\) | \(\frac{3\varepsilon}{4}\) | 0 | \(\frac{9\varepsilon}{4}\) | 0 | 0 |
| \(U'\) | 0 | \(\frac{3\varepsilon}{4}\) | 0 | 0 | 0 |
| \(S\) | \(\frac{3\varepsilon}{4}\) | \(\frac{3\varepsilon}{4}\) | 0 | 0 | 0 |
| \(G_L\) | 0 | 0 | \(\frac{9\varepsilon}{4}\) | 0 | 0 |
| \(U_L\) | \(\frac{3\varepsilon^2}{2(\varepsilon-\delta)}\) | 0 | \(\frac{3\varepsilon^2}{4(\varepsilon-\delta)}\) | \(\frac{3\varepsilon^2}{2(\varepsilon-\delta)}\) | 0 |
| \(U'_L\) | \(\frac{3\varepsilon^2}{2(\varepsilon-\delta)}\) | \(\frac{3\varepsilon^2}{4(\varepsilon-\delta)}\) | \(\frac{3\varepsilon^2}{2(\varepsilon-\delta)}\) | \(\frac{3\varepsilon^2}{4(\varepsilon-\delta)}\) | \(\frac{3\varepsilon^2}{2(\varepsilon-\delta)}\) |
| \(S_L\) | \(\frac{3\varepsilon^2}{2(\varepsilon-\delta)}\) | \(\frac{3\varepsilon^2}{4(\varepsilon-\delta)}\) | \(\frac{3\varepsilon^2}{2(\varepsilon-\delta)}\) | \(\frac{3\varepsilon^2}{4(\varepsilon-\delta)}\) | \(\frac{3\varepsilon^2}{2(\varepsilon-\delta)}\) |
This rate is proportional to the averaged moments of the concentration of particles simultaneously one needs to consider:

\[ \eta^{f_1 f_2}_{S_L} = \frac{-(f_1 + f_2)(f_1 + f_2 - 1)\delta}{4}. \]  

(39)

Here, \( \eta^{f_1 f_2}_{S_L} \) gives the exponent for the homogeneous star with \( f_1 + f_2 \) arms in solution in long-range-correlated disorder, \( \eta^{G_L}_{f_1 f_2} \) and \( \eta^{U_L}_{f_1 f_2} \) describe \( f_2 \) random walks, interacting with \( f_1 \) RWs and with \( f_1 \) SAWs respectively, in long-range-correlated disorder. All this leads to a variety of new scaling behavior for copolymer stars in a disordered medium.

B. Diffusion-limited reaction rates

Let us consider the \( f_1 \)-arm star polymer with arms of linear size \( R_s \) and absorbing sites all along these arms. At the center of the star a particular absorbing trap is placed. Free particles \( A \) which diffuse in solution are trapped or react at these sites. We are interested in the reaction rate \( k_{f_2} \) of simultaneously trapping \( f_2 \) randomly walking particles \( A \). This rate is proportional to the averaged moments of the concentration \( \rho \) of the particles near this trap and scales as

\[ k_{f_2} \sim \langle \rho^{f_2} \rangle \sim R_s^{-\lambda_{f_1 f_2}}. \]  

(40)

This process is an example of a so-called diffusion-limited reaction [56, 57], with the rate depending on the sum of the diffusion coefficients of the reactants [58]. As far as the presence of disorder lowers the diffusion coefficients [59, 60], it is predicted to lower rates of association in diffusion-limited circumstances. It is interesting to check this prediction calculating the partition function of a copolymer star with two species \( f_1, f_2 \). By means of the short-chain expansion of the set of exponents \( \eta_{f_1 f_2} \) in (41) can be related to the exponents \( \lambda_{f_1 f_2} \) in (40) [45, 47, 61]:

\[ \lambda^{RW}_{f_1 f_2} = -\eta^{G}_{f_1 f_2}, \]

\[ \lambda^{SAW}_{f_1 f_2} = -\eta^{U}_{f_1 f_2} + \eta^{U}_{f_1 0}. \]  

(41)

Based on these relations, the resulting values for the pure solution read [61]:

\[ \lambda^{RW}_{p u r e} = \frac{\varepsilon}{2} f_1 f_2, \]

\[ \lambda^{SAW}_{p u r e} = \frac{3\varepsilon}{8} f_1 f_2. \]  

(42)

Let us note, that the case \( f_1 = 2 \) corresponds to a trap located on the chain polymer, whereas \( f_1 = 1 \) corresponds to a trap attached at the polymer extremity.

Corresponding values for the exponents defining these processes in an environment with long-range correlated disorder can be obtained by substituting Eqs. (39) into (41):

\[ \lambda^{RW}_{f_1 f_2} = -\eta^{G}_{f_1 f_2} = \delta f_1 f_2, \]

\[ \lambda^{SAW}_{f_1 f_2} = -\eta^{U}_{f_1 f_2} + \eta^{U}_{f_1 0} = \frac{3\delta}{4} f_1 f_2. \]  

(43)

Comparing relations (42) and (43) at fixed values \( \varepsilon = 1 \) \((d = 3)\) and varying the parameter \( \delta \), one notes that the presence of correlated disorder results in an increase of the exponents \( \lambda \). Moreover, the stronger the correlation of defects, the larger is \( \lambda \). Recalling the definition (40), we immediately conclude that, as expected, the presence of long-range correlated disorder results in lowering the rates of diffusion-limited reactions. The crucial point is that while long-range correlated disorder apparently does not influence the RW itself (there is no new fixed point with \( u_{ii} = 0, u_{iii} \neq 0 \)), the fact that the absorbing polymer changes its conformation and fractal dimension in the LR background leads to a change of the diffusive behavior of particles being absorbed (or catalyzed) on the polymer.

Let us analyze several particular cases:

- For a given \( f_1 \)-star absorber i.e. a reactive site placed at one end of an otherwise absorbing polymer increasing the size \( R_s \) by a factor of \( l \) changes the reaction rate to \( k'_{f_1 f_2} \sim (l R_s)^{-\lambda_{f_1 f_2}} \), so that:

\[ k'_{f_1 f_2} / k_{f_1 f_2} \sim l^{-\lambda_{f_1 f_2}}. \]  

(44)
Increasing the size of the polymer thus leads to a reaction rate decrease by a factor of \( l^{-\lambda_{f_1/f_2}} \). Since \( \lambda_{f_1/f_2}^L \) is larger than \( \lambda_{f_1/f_2}^{\text{pure}} \), we conclude, that the presence of long-range correlated defects makes the reaction rate decreases more slowly as compared to the pure solution case.

- For a fixed number \( f_2 \) of particles to be trapped simultaneously the effect of attaching \( f'_1 \) additional arms to an \( f_1 \)-arm star absorber decreases the reaction rate:
  \[
  k_{f_1+f'_1/f_2}/k_{f_1/f_2} \sim R_{\lambda}^{-\left(\lambda_{f_1+f'_1/f_2}-\lambda_{f_1/f_2}\right)},
  \]
  as far as \( \lambda_{f_1+f'_1/f_2} > \lambda_{f_1/f_2} \). This decrease is suppressed to some extent in the presence of long-range correlated defects.

- For a given \( f_1 \)-star absorber an increase of the number of particles to be trapped simultaneously results in a decrease of the reaction rate:
  \[
  k_{f_1f_2+f'_2/f_2}/k_{f_1/f_2} \sim R_{\lambda}^{-\left(\lambda_{f_1f_2+f'_2}-\lambda_{f_1/f_2}\right)},
  \]
  since \( \lambda_{f_1f_2+f'_2} > \lambda_{f_1/f_2} \). Again, presence of disorder makes the reaction rate decrease more slowly as compared to pure case.

### C. Interaction between star copolymers

The effective interaction between two star copolymers at short distance \( r \) between their cores can be estimated following the scheme of Refs. [23, 40, 50], based on short distance expansion. The partition sum \( Z_{f_1f_2,g1g2}(r) \) of the two stars with \( f = f_1 + f_2 \) and \( g = g_1 + g_2 \) arms of species 1 and 2 at small center-to-center distances \( r \) factorizes into a function \( C_{f_1f_2,g1g2}(r) \) and the partition function \( Z_{f_1+g_1,f_2+g_2} \) of the star with \( f_1 + g_1 \) arms of species 1 and \( f_2 + g_2 \) arms of species 2 which is formed when the cores of the two stars coincide:

\[
Z_{f_1f_2,g1g2}(r) \simeq C_{f_1f_2,g1g2}(r)Z_{f_1+g_1,f_2+g_2}.
\]

For the function \( C_{f_1f_2,g1g2}(r) \) it was shown [23, 49] that power-law scaling for small \( r \) holds in the form:

\[
C_{f_1f_2,g1g2}(r) \simeq r^{\Theta_{f_1f_2,g1g2}}.
\]

To find the scaling relation for this power law, we take into account [41] and change the length scale in an invariant way by: \( r \to \ell r, R \to \ell R \). Eq. (47) then can be written as:

\[
\ell^{\eta_{f_1f_2}-f_1\eta_{20}-f_2\eta_{20}}\ell^{\eta_{g1g2}-g_1\eta_{20}-g_2\eta_{20}}Z_{f_1f_2,g1g2}(r) = \ell^{\Theta_{f_1f_2,g1g2}}\ell^{\eta_{f_1+g_1,f_2+g_2}-(f_1+g_1)\eta_{20}-(f_2+g_2)\eta_{20}}Z_{f_1+g_1,f_2+g_2}.
\]

Collecting powers of \( \ell \) provides the scaling relation for the contact exponent:

\[
\Theta_{f_1f_2,g1g2} = \eta_{f_1f_2} - f_1\eta_{20} - f_2\eta_{20} + \eta_{g1g2} - g_1\eta_{20} - g_2\eta_{20} - (f_1+g_1)\eta_{20} - (f_2+g_2)\eta_{20} = \eta_{f_1f_2} + \eta_{g1g2} - \eta_{f_1+g_1,f_2+g_2}.
\]

**FIG. 2:** (color online) Three non-trivial examples of copolymer stars where the interaction is governed by contact exponents \( \Theta_{f_1f_2,g1g2} \) (a), \( \Theta_{f_1f_2,g1g2} \) (b) and \( \Theta_{f_1f_2,g1g2} \) (c).
For two star copolymers at a distance \( r \) between their centers the mean force \( F_{f_1 f_2 g_1 g_2}(r) \) acting on the centers can be derived as the gradient of the effective potential \( V_{eff}(r) = -k_f T \log[Z_{f_1 f_2 g_1 g_2}(r)/(Z_{f_1 g_1} Z_{f_2 g_2})] \). For the force at short distances \( r \) this results in (52):

\[
F_{f_1 f_2 g_1 g_2}(r) = k_f T \frac{\Theta_{f_1 f_2 g_1 g_2}}{r}.
\]

For two mutually interacting star copolymers we have the three following nontrivial situations. First one may have two stars, each consisting of two species (with numbers of arms \( f_1, f_2 \) and \( g_1, g_2 \) respectively) all behaving as mutually avoiding SAWs (see Fig. 2a). This situation is equivalent to two SAW star polymers of the same species. A second possible situation is the interaction between two star copolymers, the first containing \( f_1 \) SAWs and \( f_2 \) RWs, another \( g_1 \) SAWs and \( g_2 \) RWs (Fig. 2b). Thirdly, one may have two stars, each consisting of two species (with \( f_1, f_2 \) and \( g_1, g_2 \) arms respectively) all behaving like RWs but with mutual avoidance between the species (Fig. 2c). It is easy to check, that any other case can be represented in terms of these three nontrivial examples. E.g., putting \( f_2 = 0 \) in the case corresponding to Fig. 2b, we obtain a homogeneous \( f_1 \)-arm star polymer interacting with a star copolymer, etc.

Taking into account Eqs. (53), (54) we find the following contact exponents corresponding to the three nontrivial situations described above.

1) Pure Solution

\[
\Theta_{f_1 f_2 g_1 g_2}^{S,S} = \eta_{f_1+f_2}^{S} + \eta_{g_1+g_2}^{S} - \eta_{f_1+f_2+g_1+g_2}^{S} = \frac{\varepsilon}{4}(f_1 + f_2)(g_1 + g_2)
\]

\[
\Theta_{f_1 f_2 g_1 g_2}^{U,U} = \eta_{f_1+f_2}^{U} + \eta_{g_1+g_2}^{U} - \eta_{f_1+f_2+g_1+g_2}^{U} = \frac{\varepsilon}{8}(2f_1 g_1 + 3f_1 g_2 + 3g_1 f_2)
\]

\[
\Theta_{f_1 f_2 g_1 g_2}^{G,G} = \eta_{f_1+f_2}^{G} + \eta_{g_1+g_2}^{G} - \eta_{f_1+f_2+g_1+g_2}^{G} = \frac{\varepsilon}{2}(f_1 g_2 + 2f_2 g_1).
\]

2) Presence of LR disorder

\[
\Theta_{f_1 f_2 g_1 g_2}^{(S,S)L} = \eta_{f_1+f_2}^{S} + \eta_{g_1+g_2}^{S} - \eta_{f_1+f_2+g_1+g_2}^{S} = \frac{\delta}{2}(f_1 + f_2)(g_1 + g_2)
\]

\[
\Theta_{f_1 f_2 g_1 g_2}^{(U,U)L} = \eta_{f_1+f_2}^{U} + \eta_{g_1+g_2}^{U} - \eta_{f_1+f_2+g_1+g_2}^{U} = \frac{\delta}{4}(2f_1 g_1 + 3f_1 g_2 + 3g_1 f_2)
\]

\[
\Theta_{f_1 f_2 g_1 g_2}^{(G,G)L} = \eta_{f_1+f_2}^{G} + \eta_{g_1+g_2}^{G} - \eta_{f_1+f_2+g_1+g_2}^{G} = \delta(f_1 g_2 + 2f_2 g_1).
\]

Qualitative estimates for the contact exponents in \( d = 3 \) can be found by direct substitution of \( \varepsilon = 1 \) in the above relations. To discuss the physical interpretation of these results, let us consider Fig. 3 comparing the cases of pure lattice and LR disorder with \( a = 2.2 \) and \( a = 2.7 \). Fig. 3a presents the contact exponent \( \Theta_{f_1 f_2 g_1 g_2}^{(S,S)L} \) governing the interaction between a star copolymer and a homogeneous star with \( g_2 \) arms of RWs. We fix \( g_2 = 8 \) and change \( f_1 \) and \( f_2 \) in such a way that \( f_1 + f_2 = 8 \). The case \( f_1 = 0 \), describing two stars of RWs, results in zero value contact exponents and thus the absence of interaction. Increasing the parameter \( f_1 \) (SAW component) leads to the gradual increase of the strength of the interaction. For \( f_1 = 8 \), we have a star of SAWs interacting with a star of RWs with maximal interaction strength. Fig. 3b depicts the situation of a star copolymer interacting with a star of \( g_1 = 1 \) SAWs. Again, we change \( f_1 \) and \( f_2 \) as above. The case \( f_1 = 0 \) describes a star of SAW interacting with a star of RWs and is a particular case of Fig. 3c described above. Increasing \( f_1 \) leads to a gradual decrease of the strength of the interaction. For \( f_1 = 8 \), we have two interacting stars of SAWs with minimal interaction strength. Fig. 3c depicts a situation of two interacting star copolymers with \( f_1, f_2 \) and \( g_1, g_2 \) arms correspondingly. We fixed \( g_1 = g_2 = 4 \) and again change \( f_1 \) and \( f_2 \) as described above. The case \( f_1 = 0 \) describes a copolymer star interacting with a star of RWs. Increasing the parameter \( f_1 \) leads to a gradual increase of the strength of the interaction, until it reaches its maximal value at \( f_1 = 8 \), corresponding to the interaction between a star copolymer and a star of SAWs. The case \( f_1 = f_2 = 4 \) describes the interaction between two identical copolymer stars.

Finally, we conclude, that in all situations considered above, the presence of correlated disorder leads to an increase of the contact exponent. The stronger the correlation (the smaller the value of correlation parameter \( a \)), the stronger is the interaction between polymers in such an environment. Let us recall, that the exponent \( \Theta_{f_1 f_2 g_1 g_2}^{(S,S)L} \) corresponds to the situations of two interacting homogeneous polymer stars of \( f = f_1 + f_2 \) and \( g = g_1 + g_2 \) arms in solution in the presence of long-range-correlated disorder. This problem has previously been analyzed (42) using a two-loop expansion series for \( G_{f_1 f_2}^{(S,S)L} \) in \( d = 3 \). The quantitative estimates obtained predict a decrease of the contact exponents with the strength of the disorder correlations in contrast to our present \( \varepsilon,\delta \)-expansion results. Revising the resummation as performed in (43) we conclude that the number of terms in the two-loop expansion is probably too small to rely on those quantitative results.
FIG. 3: Contact exponents of interaction between a copolymer star with $f_1$ SAWs and $f_2$ RWs and: an 8-armed star of RWs(a); an 8-armed star of SAWs(b); a copolymer star with 4 arms of SAWs and 4 arms of RWs in $d = 3$. Boxes: pure case ($a = 3$), circles: $a = 2.7$, triangles: $a = 2.2$

\[ \theta_{U}(f_1, f_2) \]

V. CONCLUSIONS

In the present paper, we have studied the scaling properties of copolymer stars, consisting of $f_1$ arms of polymer species 1 and $f_2$ arms of species 2 in a solution in which one or more of the intra- and interspecies interactions are found to be at their $\Theta$-point with the further complication of a disordered environment with correlated structural defects. We assume that the disorder is correlated with a power-law decay of the pair correlation function $g_2(x) \sim x^{-a}$ at large distance $x$. This type of disorder is known to be relevant for simple polymer chains [21, 21] and homogeneous
polymer stars, and we address the question of the scaling of copolymer stars in this situation.

Considering the $f_1$-arm absorbing star polymer with a special trap placed at the center of the star where $f_2$ free particles (RWs) are to be trapped simultaneously, the reaction rate of this diffusion-limited reaction is found to scale with exponents, connected to the spectrum of critical exponents $\eta_{f_1, f_2}$ of star copolymers. Such a process is an example of a so-called diffusion-limited reaction, with the rate depending on the sum of diffusion coefficients of the reactants. Another example, where star exponents govern physical behavior concerns the short-range interaction between the cores of star polymers in a good solvent. The present study aims to analyze the impact of structural disorder in the environment on these processes.

In the frames of the field-theoretical renormalization group approach, we obtain estimates for the critical exponents $\eta_{f_1, f_2}$ up to the first order of an $\varepsilon = 4 - d, \delta = 4 - a$-expansion, which belong to a new universality class. In particular, this enables us to conclude that the rates of diffusion-limited reactions are slowed down by the presence of long-range correlated disorder. The crucial point is that while long-range correlated disorder apparently does not influence the RWs and thus the universal behavior of diffusion itself, the fact that the absorbing polymer changes its conformation in the LR background leads to a change of the rate with which particles are absorbed (or catalyzed) on specific sites of the polymer.

The contact exponents, governing the repulsive interaction between two star copolymers in correlated disorder, are found to be larger than in the pure solution case. The stronger the correlation of the defects, the stronger is the interaction between polymers in such a disordered environment.

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