Equivalence of quenched and annealed averaging in models of disordered polymers

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Abstract

The equivalence of the influence of quenched and annealed disorder on the scaling properties of long flexible polymer chains is proved by analyzing the $O(m)$-symmetric field theory in the polymer (de Gennes) limit $m \to 0$. Additional symmetry properties of the model in this limit are discussed.

In real physical processes, one is often interested in how structural obstacles (impurities) in the environment alter the behavior of a system. In polymer physics, of great importance is understanding the behavior of macromolecules in the presence of structural disorder, e.g., in colloidal solutions [1], in the vicinity of microporous membranes [2] or in a crowded environment of biological cells [3]. Structural obstacles strongly effect the protein folding and aggregation [4–7].

Dealing with systems that display randomness of structure, one usually encounters two types of ensemble averaging, treated as annealed and quenched disorder [8, 9]. In the former case, a characteristic time of impurities dynamics is comparable to relaxation times in the pure system and impurity variables are a part of the disordered system phase space, whereas in the latter case the impurities can be considered as fixed and thus one needs to perform configurational averaging over an ensemble of disordered systems with different realizations of the disorder. In principle, the critical behavior of systems with quenched and annealed disorder is quite different. For magnetic systems with annealed disorder it was proved long ago [10] that when a heat capacity critical exponent of an undiluted system $\alpha_{\text{pure}}$ is positive, then any critical index $\alpha_{\text{annealed}}$ of an annealed system is determined by those of the corresponding pure one $\alpha_{\text{pure}}$ by the simple relation (the so-called Fisher renormalization)

$$
\alpha_{\text{annealed}} = -\frac{\alpha_{\text{pure}}}{1 - \alpha_{\text{pure}}}.
$$

The quenched disorder causes changes in the critical indices also only if $\alpha_{\text{pure}}$ of the corresponding system is positive (this statement is known as the Harris criterion [11]); however, the quantitative influence is by far not as trivial as in the annealed case and has become a subject of intensive studies (for a review, see e.g. [12]).

It has been established that some conformational statistical properties of long flexible polymer chains in good solvent are governed by universal scaling exponents. As an example, the effective linear size such as averaged mean-squared end-to-end distance of a long flexible polymer chain scales with the number of monomers (mass) of the chain $N$ as

$$
\langle R^2 \rangle \sim N^{2\nu},
$$

with a universal exponent $\nu$ depending on space dimension $d$ only (e.g., the phenomenological Flory theory [13] gives $\nu(d) = 3/(d + 2)$). Note that at $d = 4$ the intrachain steric interactions are irrelevant, and the polymer behaves as an idealized Gaussian chain with $\nu_{\text{Gauss}} = 1/2$. The relation of the polymer size exponent to the correlation length critical index of the $m$-component spin vector model in the formal limit $m \to 0$ was provided by P-G de Gennes (the well-known de Gennes limit). This makes it possible to apply the advanced field theory approach developed to study the critical behavior of magnetic systems to analyze the scaling properties of polymers.

Analysis of the influence of annealed disorder on the polymer size exponent encounters some controversies. As...
pointed out in [14–16], an attempt to apply directly the Fisher renormalization (1) fails in this case. For example, in $d = 2$ for the polymer system $\theta_{\text{pure}} = 2 - d < 1/2$ is positive, and according to (1) one receives $v_{\text{annealed}} = 3/2$, which is unphysical: an extension of a chain beyond its total length ($\nu < 1$) is not possible. Note, however, that a similar misunderstanding arises when trying to apply the Harris criterion to analyze the influence of point-like uncorrelated quenched disorder on the scaling properties of polymers: though both in $d = 2$ and $d = 3$ the corresponding values of $\alpha$ are positive, such a type of disorder does not alter the value of scaling exponents (this has been proved analytically by Kim [17] and supported in numerous numerical studies [18–22]). Only correlated quenched disorder, leading to the appearance of pore-like structures of a fractal nature (e.g. percolation clusters) was shown to influence the conformational properties of polymer macromolecules in a non-trivial manner [23–26]. In a number of works [27–30] it is pointed out that the distinction between quenched and annealed models for an infinitely long single polymer chain is negligible. In the present study, we aim to confirm these suggestions by providing simple arguments based on a refined field-theoretical approach.

We start with the Edwards continuous chain model [31], considering a linear polymer chain in a solution in the presence of structural obstacles presented by a path $r(s)$, parameterized by $0 \leq s \leq S$ ($S$ is also called the Gaussian surface). The partition function of the system is given by the functional integral

$$Z(S) = \int D[r] \exp \left[ -\frac{1}{2} \int_0^S ds \left( \frac{d\bar{r}(s)}{ds} \right)^2 - \frac{u_0}{2} \int_0^S ds' \right]$$

$$\times \int_0^S ds'' \delta(\bar{r}(s'') - \bar{r}(s')) - \int_0^S ds V(\bar{r}(s)) \right]. \quad (3)$$

Here, an integration is performed over different polymer path $\bar{r}(s)$ configurations [32]. The first term in the exponent represents the chain connectivity, the second term describes the short-range excluded volume interaction with bare coupling constant $u_0$, and the last term contains random potential $V(\bar{r}(s))$ arising due to the presence of structural disorder. Let us denote by $\langle \cdots \rangle$ the average over different disorder and introduce notation for the second moment:

$$V(\bar{r}(s))V(\bar{r}(s')) = v_0 g(\bar{r}(s) - \bar{r}(s')) \quad (4)$$

with $v_0$ being some constant (the first moment of the distribution $V(\bar{r}(s)) = 0$). The case of structural disorder in the form of point-like uncorrelated defects corresponds to

$$r_{\text{uncor}}(\bar{r}(s) - \bar{r}(s')) = \delta(\bar{r}(s) - \bar{r}(s')) \quad (5)$$

(Kronecker delta function), whereas another interesting situation when structural obstacles are spatially correlated at large distances corresponds to [33]

$$g_{\text{cor}}(\bar{r}(s) - \bar{r}(s')) = |\bar{r}(s) - \bar{r}(s')|^{-a}, \quad a > 0. \quad (6)$$

In order to average the free energy $\mathcal{F}$ of the system over different configurations of quenched disorder, the usual replica method is used [9], which is based on the formal relation

$$\mathcal{F} = \ln Z = \lim_{n \to 0} \left( \frac{Z^n - 1}{n} \right). \quad (7)$$

For the replicated partition sum of continuous chain model $Z^n(S)$ one receives

$$Z^n(S) = \prod_{i=1}^n \int D[r_i] e^{-H_{\text{ann}}} \quad (8)$$

with an effective Hamiltonian

$$H_{\text{ann}} = \frac{1}{2} \int_0^S ds \left( \frac{d\bar{r}_a(s)}{ds} \right)^2 + \frac{u_0}{2} \sum_{a,b=1}^n \int_0^S ds' \delta(\bar{r}_a(s') - \bar{r}_b(s'))$$

$$\times \int_0^S ds'' \delta(\bar{r}_a(s'') - \bar{r}_b(s')) - \frac{v_0}{2} \int_0^S ds' \int_0^S ds'' g(\bar{r}_a(s'') - \bar{r}_b(s')). \quad (9)$$

Here, Greek indices denote replicas and the last term, describing the effective interaction between replicas, appears due to the presence of disorder in the environment.

To take into account the annealed disorder, one deals with the averaged partition sum in the form

$$\overline{Z(S)} = \int D[r] e^{-H_{\text{ann}}} \quad (10)$$

with an effective Hamiltonian

$$H_{\text{ann}} = \frac{1}{2} \int_0^S ds \left( \frac{d\bar{r}(s)}{ds} \right)^2$$

$$+ \frac{u_0}{2} \int_0^S ds' \int_0^S ds'' \delta(\bar{r}(s'') - \bar{r}(s'))$$

$$- \frac{v_0}{2} \int_0^S ds' \int_0^S ds'' g(\bar{r}(s'') - \bar{r}(s')). \quad (11)$$

We aim to show that models (9) and (11) are equivalent in the renormalization group sense.

Model (9) may be mapped to a field theory by a Laplace transform from the Gaussian surface $S$ to the conjugated chemical potential variable (mass) $\mu_0$ according to [31, 34]

$$\tilde{Z}^n(\mu_0) = \int dS \exp[-\mu_0 S] \overline{Z^n}(S). \quad (12)$$

Exploiting the analogy between the polymer problem and $O(m)$ symmetric field theory in the limit $m \to 0$ (de Gennes limit) [13], it can be shown [31] that the problem of the disordered polymer system is related to the $m = 0$ component field theory with an effective Lagrangian

$$\mathcal{L} = \frac{1}{2} \sum_{a=1}^n \int d^3x \left[ (\mu_0^a) \phi_0(x)^2 + |\nabla \phi_0(x)|^2 \right]$$

$$+ \frac{u_0}{4!} \left( \frac{\bar{\phi}_0^a(x)^2}{4!} \right)^2 - \frac{v_0}{4!} \sum_{a,b=1}^n \int d^3x \int d^3y \times g(x - y) \tilde{\phi}_0^a(x) \tilde{\phi}_0^b(y). \quad (13)$$
Here, each $\tilde{\phi}_a$ is an $m$-component vector field $\tilde{\phi}_a = (\phi_a^1, \ldots, \phi_a^m)$ and the last term describing replica coupling contains the correlation function in the form (5) or (6).

Usually, the effective Lagrangian (13) is studied in the limiting case $n \to 0$ which corresponds to quenched disorder. Let us note, however, that another limit $n \to \infty$ has physical interpretation, too. Indeed, as shown in [9], this limit corresponds to the annealed disorder. Therefore, the problem of analysis of the scaling properties of a polymer chain in different types of disorder is reduced to a study of the critical properties of the field theory (13) in the polymer limit $m = 0$ and two different limits $n \to 0$ (quenched disorder) and $n \to \infty$ (annealed disorder).

One of the ways of extracting the scaling behavior of the model (13) is to apply the field-theoretical renormalization group (RG) method [35] in the massive scheme, with Green’s function renormalization at non-zero mass and zero external momenta. The bare Green’s function $G^{(N)}(\vec{p})$ can be defined as an average of $N$ field components performed with the corresponding effective Lagrangian $\mathcal{L}$:

$$\delta \left( \sum \vec{p} \right) G^{(N)}_0(\vec{p}; \mu_0^N, \lambda_0) = \int_{\Lambda_0} \mathcal{P}(\vec{\phi}(r_1) \cdots \vec{\phi}(r_N)) \mathcal{D}d^d r_1 \cdots \mathcal{D}d^d r_N,$$

where $\mathcal{P}(\vec{p}) = (\vec{p}_1, \ldots, \vec{p}_N)$ is the set of external momenta, $\lambda_0 = (u_0, v_0)$ is the set of bare coupling constants and $\Lambda_0$ is a cut-off. Let us start by representing the two quartic potentials in (13) in the form of four-leg vertices according to so-called ‘faithful representation’ [35], as shown in figure 1. This allows convenient representation of the terms in perturbation theory expansions of the bare Green’s functions in coupling $u_0$ and $v_0$ by diagrams, as given in figure 2. The arguments given below are valid in any order of the perturbation theory. However, for simplicity, we restrict ourselves by the second-order expansion of a function $G^{2}_0(p)$ (so-called ‘two-loop’ approximation: in this case, only those diagrammatic contributions are taken into account which contain no more than two closed loops):

$$G^{2}_0(p) = \frac{1}{\mathcal{N}_0^N} \left( 2I^{(b)}_{u_0} + ml^{(e)}_{u_0} + \frac{v_0}{6} (2I^{(b)}_{v_0} + mm^{(e)}_{v_0}) \right)$$

$$+ \frac{\mu_0^N}{9} (2m^2I^{(d)}_{u_0} + 4ml^{(e)}_{u_0} + 4ml^{(f)}_{u_0})$$

$$+ 8l^{(e)}_{u_0} + 8l^{(f)}_{u_0} + 4ml^{(b)}_{u_0}$$

$$- \frac{2u_0v_0}{9} (2m^2I^{(d)}_{u_0v_0} + 2mm^{(e)}_{u_0v_0}).$$

Here, the following notation is used: $I^{(e)}_{u_0}$ denotes the loop integral, corresponding to diagram (e) in figure 2, containing $k$ vertices of type $u_0$ and $l$ vertices of type $v_0$. The loop integrals are dependent on the type of quartic interaction, e.g. in the case of point-like uncorrelated disorder (5), the integrals corresponding to diagram (e) read

$$I^{(e)}_{u_0} = I^{(e)}_{v_0} = \frac{1}{(p^2 + \mu_0^2)^2} \int \frac{d\vec{q}_1 d\vec{q}_2}{(q_1^2 + \mu_0^2)^2 (q_2^2 + \mu_0^2)},$$

whereas in the case of long-range correlated disorder, corresponding to (6), one has [26]

$$I^{(e)}_{u_0} = I^{(e)}_{v_0} = \frac{1}{(p^2 + \mu_0^2)^2} \int \frac{d\vec{q}_1 d\vec{q}_2}{(q_1^2 + \mu_0^2)^2 (q_2^2 + \mu_0^2)}.$$

The combinatorial prefactors corresponding to each loop integral in series (15) are defined, however, only by the topological type of the corresponding diagram. One may easily check that the diagrams, containing closed loops, produce combinatorial prefactors, proportional to $m$ or $mm$ [17]. It is crucial to note that $n$ appears only in combinations, where it is multiplied by $m$. The same feature

![Figure 1. Diagrammatic representation of quartic potentials in (13).](image)

![Figure 2. Contributions to the Green’s function $G^{2}_0$ up to two-loop approximation. Solid lines denote propagators $G^{(b)}_{u_0}$, dashed lines imply integration over internal momenta $\vec{q}$. Every interactive diagram appears twice, once with each of the two couplings $u_0$ and $v_0$.](image)
is observed also in analyzing any other Green’s function $G^N$ in any order of perturbation theory in coupling constants $u_0$, $v_0$. Thus, when the polymer limit $m \to 0$ is implied, all the renormalization group functions simultaneously become $n$-independent. Recalling the discussion below (13) concerning the dependence of the type of averaging on the choice of replica parameter $n$, this leads us to a straightforward conclusion: as long as the polymer problem is under interest, both quenched ($n \to 0$) and annealed ($n \to \infty$) averaging are equivalent.

Let us now recall once more the effective Hamiltonian, describing a continuous polymer chain in a disordered environment (9) and the corresponding field-theoretical model (13). The conclusion about $n$-independence in the polymer limit allows us to put $n = 1$ directly into these expressions, obtaining respectively

$$H_{\text{quen}} = \frac{1}{2} \int_0^S d\vec{r} (\frac{d\vec{r}(s)}{ds})^2$$

$$\frac{u_0}{2} \int_0^S ds \int_0^S ds' \delta(\vec{r}(s') - \vec{r}(s'))$$

$$- \frac{v_0}{2} \int_0^S ds \int_0^S ds' g(\vec{r}(s') - \vec{r}(s')); \quad (16)$$

$$L = \frac{1}{2} \int d^d x \left[ (\mu_0^2 \phi(x))^2 + |\nabla \phi(x)|^2 \right]$$

$$+ \frac{u_0}{4!} (\phi^2(x))^2 - \frac{v_0}{4!} \int d^d x d^d y g(x - y) \phi^2(x) \phi^2(y). \quad (17)$$

This immediately reveals the equivalence of (16) with the corresponding Hamiltonian of the system with annealed disorder (11). In performing analytical calculations one can thus restrict oneself to the simpler case of annealed averaging, which considerably simplifies the RG procedure. In particular, in the case of point-like uncorrelated defects (taking the correlation function in the form (5)) one then notices the equivalence of the last two terms in both (16) and (17), which in turn makes it possible to adsorb the third term (arising due to the presence of disorder) into the second term (describing the excluded volume effect) by simple redefinition of the coupling constant $u_0 \equiv u_0 - v_0$. Thus, in the RG sense the presence of uncorrelated point-like defects at low densities does not influence the scaling properties of polymers. This conclusion was obtained earlier for the case of polymers in quenched disorder by Kim [17] on the basis of a much more refined field-theoretical study.

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