Universal features of complex $n$-block copolymers

K Haydukivska and V Blavatska

Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 79011 Lviv, Ukraine

E-mail: viktoria@icmp.lviv.ua

Received 24 January 2019, revised 17 May 2019
Accepted for publication 3 June 2019
Published 19 November 2019

Abstract

We study the conformational properties of complex polymer macromolecules, consisting in general of $n$ subsequently connected chains (blocks) of different lengths and distinct chemical structure. Depending on the solvent conditions, the inter- or intra-chain interactions of some blocks may vanish, causing rich conformational behavior. Our main attention is focused on the universal conformational properties of such molecules. Applying the direct polymer renormalization group approach, we derive the analytical expressions for the scaling exponent $\gamma(n)$, governing the number of possible conformations of $n$-block copolymer, and analyze the effective linear size measures of individual blocks. In particular, the degree of extension of the block sizes as functions of $n$ and position of blocks in sequence is quantitatively estimated. The numerical simulations of the simplest $n = 2$-block copolymer chain on a cubic lattice are also performed to give an illustration of the conformational behavior of such molecules.

Keywords: polymers, conformational properties, renormalization group, computer simulations

(Some figures may appear in colour only in the online journal)

1. Introduction

Block copolymers are the specific class of polymer macromolecules, containing the subsequent blocks of chemically distinct monomers [1]. The ubiquitous feature of block-copolymer melts is their ability to microphase separation and self-assembling into lamellae, micelles and more complex structures [2–4], which provides potential or practical applications in many fields. In particular, block copolymers are used for developing dense and nanoporous membranes for gas separation and ultrafiltration [5–7], in targeted drug delivery [8], lithography [9], development of novel plastic materials [10], nanotechnology [11] etc.
The most basic system is the diblock copolymer (so called AB-copolymer): the molecule composed of just two chemically distinct linear blocks denoted A and B. Such systems have been investigated most extensively. Extension to the multiblock copolymers with \( n \) blocks of \( k \) chemically distinct types as well as to more complex branched architectures can produce much richer self-assembling behavior. The modern synthesis strategies and techniques, e.g. controlled polymerization technique, allow one to produce copolymers with controlled molecular weights and architectures [12]. For recent reviews on complex copolymers see e.g. [13, 14].

Note that whereas mainly the melts of copolymer molecules attract interest from a technological point of view, in our study we are concentrated on the statistical conformational properties of individual molecules in a very dilute regime. This allows one, for example, to determine the length scale of the block copolymer and relate it to the length scale of aggregates in more concentrated solutions or in the membranes [6]. The conformational properties of diblock AB copolymers in dilute regime served as a subject of intensive analytical [15–17] and numerical [18–22] studies. More complex triblock and multiblock copolymers were analyzed in [23–26].

It is established, that in the statistical description of long flexible polymer chains one finds a number of characteristics which are universal, i.e. not dependent on any details of chemical microstructure. In particular, the averaged end-to-end distance of a chain of total length (molecular weight) \( L \) scales according to [27, 28]

\[
\langle R^2 \rangle \sim L^{2\nu},
\]

(1)

where \( \langle \ldots \rangle \) denotes averaging over an ensemble of all possible conformations which attains the molecule in space, and \( \nu \) is the universal scaling exponent. For the case, when a polymer is in solution at the \( \theta \)-temperature regime when attractive and repulsive interactions between monomers are balanced, the scaling (1) holds with \( \nu_\theta = 4/7 \) in \( d = 2 \) dimensions [29]. At \( d = 3 \), which is an upper critical dimension of \( \Theta \)-transition, one observes the mean-field behavior \( \nu_\theta(d = 3) = 1/2 \) except for the logarithmic corrections [30, 31]. In the \( \Theta \)-regime, the polymer chains are fairly adequately described by a model of a freely jointed chain, similar to that of a diffusing particle executing a random flight. Here, each the skeletal bond of the chain resembles a step in the random walk (RW) trajectory, whose averaged end-to-end distance scales with \( \nu_{RW} = 1/2 \). This corresponds to the regime of the ideal Gaussian polymer in a continuous chain description of a macromolecule [28]. The model of random walk is widely exploited in studying the conformational properties of polymers in \( \Theta \)-regime in \( d = 3 \) [27, 32, 33]. For a chain in a regime of good solvent (with repulsive excluded volume interactions between monomers playing the role), the polymer chain behaves as a trajectory of self-avoiding random walk (SAW), which is not allowed to cross itself. In particular, a good approximation is given by the empirical Flory formula: \( \nu_{SAW}(d) = 3/(d + 2) \) [27], which is a nice agreement with results of more refined studies: \( \nu_{SAW}(d = 2) = 3/4 \) [34], \( \nu_{SAW}(d = 3) = 0.58759700(40) \) [35].

The number of possible conformations (partition function) of polymer chain is given by:

\[
Z(L) \sim \mu^L L^{\gamma-1},
\]

(2)

here \( \mu \) is a non-universal connectivity constant and \( \gamma \) is another universal scaling exponent. At the \( \theta \)-temperature regime, one has \( \gamma_{RW} = 1 \), whereas for a chain in a regime of good solvent: \( \gamma_{SAW}(d = 2) = 43/32 \) [36], \( \gamma_{SAW}(d = 3) = 1.15695300(95) \) [37].

Linking together two linear polymer chains of distinct chemical structure A and B, we receive the simplest diblock copolymer. Depending on the temperature, a situation may occur
when interaction within one block vanishes. Such a block can effectively be described as a RW (Gaussian chain), whereas the other behaves as a SAW at the same temperature. On the other hand, also the intra-chain interactions between monomers of different blocks can be taken into account. For example, one can have only the mutual excluded-volume interactions between blocks, whereas each block can intersect itself. Such a situation is closely related to the case of so-called ternary solutions [38, 39], containing chains of two different chemical structures at various temperatures, which can be at or above the θ-temperatures for both or only one type of polymer chains. It is established [15, 16, 18] that there are actually three characteristic length scales in such systems. One should distinguish between the end-to-end distances of two blocks A and B, which scale according to (1) with exponents ν_A and ν_B correspondingly, where ν_A and ν_B are given by either ν_{SAW} or ν_{RW}. The total mean-squared end-to-end distance of diblock copolymer chain as given by $\langle R^2 \rangle = \langle (\vec{R}_A + \vec{R}_B)^2 \rangle$, displays non-trivial behaviour when mutual interactions between blocks A and B are present.

Partition sum of the copolymer chain consisting of blocks with lengths $L_1$ and $L_2$ scales as:

$$Z(L_1, L_2) \sim \mu_1^{L_1} \mu_2^{L_2} (L_1 + L_2)^{\gamma - 1},$$

where $\mu_1$, $\mu_2$ are connectivity constants of corresponding blocks. The universality class (set of scaling exponents) $\gamma$ of diblock copolymers is actually given by that of polymer chains in ternary solutions [38–40]. The estimates of scaling exponents $\gamma$ governing the scaling (3) can be derived e.g. on the basis of results for more general branched copolymer structures obtained within the field-theory renormalization group technique in [40]. On the other hand, the scaling exponent $\gamma$ governing the scaling of a set of mutually avoiding Gaussian chains have been estimated in a number of works dedicated to probability of intersection of Brownian paths [41–45].

Generalizing expression (3) for the case of n-block copolymer with segments of different lengths $L_i$ we have:

$$Z(L_1, \ldots, L_n) \sim \prod_{i=1}^{n} \mu_i^{L_i} \left( \sum_{i=1}^{n} L_i \right)^{\gamma(n) - 1}.$$

Partition function depends on $\mu_i$ of each block, which can differ from that of individual polymer chains due to the crowdedness effect, caused by presence of other blocks. Note, that in the limit of large n, one can in principle replace each $\mu_i$ with the averaged value $\mu_{av} = 1/n \sum_i \mu_i$ and restore equation (1) with $L = \sum L_i$ and $\mu = \mu_{av}$.

The aim of the present work is to analyze the conformational properties of complex copolymers consisting of n blocks of different lengths $L_i$, $i = 1, \ldots, n$ (figure 1) in $d = 3$, applying an analytical approach of direct polymer renormalization. The layout of the paper is as follows. In section 2.1 we present the continuous chain model of n-block copolymer macromolecule. In section 2.2 we derive the analytical description of properties of the diblock copolymer (with $n = 2$), and generalize it to the n-block case in section 2.3. In section 3, we present some results of numerical simulations of diblock copolymer chain on a simple cubic lattice using the algorithm of a growing chain. We conclude with discussions in section 4.

2. Analytical studies of n-block copolymer

2.1. Continuous chain model

Within the continuous chain model, each block of the copolymer chain is considered as a trajectory parameterized by radius vector $\vec{R}(s)$ with $s$ changing from 0 to $L_i$, $i = 1, \ldots, n$. The
n-block copolymer can be thus presented as a set of \( n \) trajectories, consequently connected by their end points. The partition sum of the system is thus given by

\[
Z(L_1, \ldots, L_n) = \int D\mathbf{r} \prod_{i=1}^{n-1} \delta(\mathbf{r}_i(L_i) - \mathbf{r}_{i+1}(0)) e^{-H},
\]

(5)

here \( \int D\mathbf{r} \) denotes functional integration over \( n \) trajectories and \( H \) is an effective Hamiltonian of the system:

\[
H = \frac{1}{2} \sum_{i=1}^{n} \int_0^{L_i} ds \left( \frac{d\mathbf{r}_i(s)}{ds} \right)^2 + \sum_{i=1}^{n} u_i \int_0^{L_i} ds_1 \int_0^{L_i} ds_2 \delta(\mathbf{r}_i(s_2) - \mathbf{r}_i(s_1))
\]

\[
+ \sum_{i<j} w_{ij} \int_0^{L_i} ds_1 \int_0^{L_j} ds_2 \delta(\mathbf{r}_i(s_2) - \mathbf{r}_j(s_1)).
\]

(6)

Here, \( u_i \) are the coupling constants of excluded volume interactions between monomers of the same block and \( w_{ij} \) correspond to interactions between different blocks. Note that in the absence of interactions (\( u_i = w_{ij} = 0 \)) we just restore the case of the idealized Gaussian chain.

Evaluating the perturbation theory expansion in coupling constants \( u_i \) and \( w_{ij} \), and limiting ourselves only to the first order approximation, we obtain an expression

\[
Z(L_1, \ldots, L_n) = 1 + \sum_{i=1}^{n} \frac{u_i}{(2\pi)^{d/2}} \int_0^{L_i} ds_1 \int_0^{L_i} ds_2 (s_2 - s_1)^{-\frac{d}{2}}
\]

\[
+ \sum_{i<j} \frac{w_{ij}}{(2\pi)^{d/2}} \int_0^{L_i} ds_1 \int_0^{L_j} ds_2 (s_1 + s_2 + l_{ij})^{-\frac{d}{2}},
\]

(7)

where \( l_{ij} = \sum_{l=i+1}^{n-1} L_l \). Performing the integration, we have:

\[
Z(L_1, \ldots, L_n) = 1 - \sum_{i=1}^{n} \frac{u_i}{(2\pi)^{d/2}} \frac{L_i^{2-d/2}}{(1-d/2)(2-d/2)}
\]

\[
- \sum_{i<j} \frac{w_{ij}}{(2\pi)^{d/2}} \left( \frac{(l_{ij})^{2-d/2} - (L_i + L_j)^{2-d/2}}{(1-d/2)(2-d/2)} \right)
\]

\[
+ \left( L_i + L_j + l_{ij} \right)^{2-d/2} \left( L_i + L_j \right)^{2-d/2} \right) \left( (1-d/2)(2-d/2) \right).
\]

(8)
The generalized form of the scaling behavior of partition sum of $n$-block copolymer is given by equation (4).

Let us note, that performing the dimensional analysis of couplings, we find that $[u_i] = [L_1]^{(4-d)/2}$, $[v_{ij}] = [(L_i + L_j)]^{(4-d)/2}$. The ‘upper critical’ value of space dimension $d_c = 4$, at which the coupling becomes dimensionless, plays the role in the following application of the renormalization group scheme. It is important to stress, that though all the analytical expressions in the rest of this section are derived in a form of series in deviation from the upper-critical dimension $\epsilon = 4 - d$, which is standard in the renormalization group approach, we are interested only in the case $d = 3$ (evaluating the final results for quantities of interest at $\epsilon = 1$).

Within our approach, the value of scaling exponent $\gamma$ can be found according to [28]:

$$\gamma(n) = \frac{\epsilon}{2} \left( \sum_{i=1}^{n} \frac{\partial \ln Z(L_1, \ldots, L_n)}{\partial \ln \tilde{u}_i} + \sum_{i<j=1}^{n} \frac{\partial \ln Z(L_1, \ldots, L_n)}{\partial \ln \tilde{w}_{ij}} \right)$$  \hspace{1cm} (9)

where $\tilde{u}_i$ and $\tilde{w}_{ij}$ are dimensionless coupling constants:

$$\tilde{u}_i = \frac{u_i}{(2\pi)^{d/2} L_i^{2-d/2}},$$  \hspace{1cm} (10)

$$\tilde{w}_{ij} = \frac{w_{ij}}{(2\pi)^{d/2} (L_i + L_j)^{2-d/2}}.$$

2.2. Diblock copolymer chain

2.2.1. Partition sum. Let us start with the most simple case, when the system consists of only two connected block chains of lengths $L_1$ and $L_2$. For the partition function, we have:

$$Z(L_1, L_2) = 1 - \frac{u_1}{(2\pi)^{d/2}} \frac{L_1^{2-d/2}}{(1-d/2)(2-d/2)} - \frac{u_2}{(2\pi)^{d/2}} \frac{L_2^{2-d/2}}{(1-d/2)(2-d/2)} - \frac{w_{1,2}}{(2\pi)^{d/2}} \frac{(L_1 + L_2)^{2-d/2} - (L_1)^{2-d/2} - (L_2)^{2-d/2}}{(1-d/2)(2-d/2)}.$$  \hspace{1cm} (11)

Presenting the partition function in a form of series in $\epsilon$ and passing to the dimensionless coupling constants according to (10), we receive:

$$Z(L_1, L_2) = 1 + \left( \tilde{u}_1 + \tilde{u}_2 - \tilde{w}_{1,2} \right) \frac{2}{\epsilon} + \tilde{u}_1 + \tilde{u}_2 - \tilde{w}_{1,2} \left( 1 + \ln \left( \frac{L_1 L_2}{[L_1 + L_2]^2} \right) \right).$$  \hspace{1cm} (12)

2.2.2. End-to end distance. There are two characteristic length scales in the diblock copolymer, given by end-to-end distances:

$$\langle R_1^2 \rangle = \langle (\vec{r}_1(L_1) - \vec{r}_1(0))^2 \rangle$$  \hspace{1cm} (13)

$$\langle R_2^2 \rangle = \langle (\vec{r}_2(L_2) - \vec{r}_2(0))^2 \rangle.$$  \hspace{1cm} (14)
where indexes 1 and 2 indicate blocks of copolymer chain. Performing the perturbation theory expansion in coupling constants, we receive:

\[
\langle R_1^2 \rangle = dL_1 \left( 1 + \frac{u_1}{(2\pi)^{d/2}} \frac{L_1^{2-d/2}}{(3-d/2)(2-d/2)} + \frac{4w_{1,2}}{(2\pi)^{d/2}} \left( \frac{(L_1 + L_2)^{-d/2}}{L_1} \right) \frac{dL_1^2 + d^2L_1^2L_2 - 6dL_1^3}{d(d-6)(d-4)(d-2)} + \frac{(L_1 + L_2)^{-d/2}}{L_1} \frac{4dL_1L_2^2 - 2dL_1^2L_2 + 8(L_1^3 + L_2^3)}{d(d-6)(d-4)(d-2)} \right) + \frac{1}{L_1} \frac{d(6-d)L_1^{3-d/2} - 8(L_1^{3-d/2} + L_2^{3-d/2})}{d(d-6)(d-4)(d-2)} \right)
\]

\[
\langle R_2^2 \rangle = dL_2 \left( 1 + \frac{u_2}{(2\pi)^{d/2}} \frac{L_2^{2-d/2}}{(3-d/2)(2-d/2)} + \frac{4w_{1,2}}{(2\pi)^{d/2}} \left( \frac{(L_1 + L_2)^{-d/2}}{L_2} \right) \frac{dL_2^2 + d^2L_2^2L_1 - 6dL_2^3}{d(d-6)(d-4)(d-2)} + \frac{(L_1 + L_2)^{-d/2}}{L_2} \frac{4dL_2L_1^2 - 2dL_2^2L_1 + 8(L_1^3 + L_2^3)}{d(d-6)(d-4)(d-2)} \right) + \frac{1}{L_2} \frac{d(6-d)L_2^{3-d/2} - 8(L_1^{3-d/2} + L_2^{3-d/2})}{d(d-6)(d-4)(d-2)} \right)
\]

As for the case of partition function, we pass here to the dimensionless coupling constants and perform the series expansions in \( \epsilon \):

\[
\langle \tilde{R}_1^2 \rangle = \frac{L_1}{L_2} \left( \frac{\tilde{u}_1}{2} - \frac{\tilde{w}_{1,2}}{2(L_1 + L_2)} \right) \left( 2(L_1 + L_2) \ln \left( \frac{L_2}{L_1 + L_2} \right) + L_1 \right)
\]

\[
\langle \tilde{R}_2^2 \rangle = \frac{L_1}{L_2} \left( \frac{\tilde{u}_2}{2} - \frac{\tilde{w}_{1,2}}{2(L_1 + L_2)} \right) \left( 2(L_1 + L_2) \ln \left( \frac{L_2}{L_1 + L_2} \right) + L_2 \right)
\]

Note, that our expressions for \( \langle \tilde{R}_1^2 \rangle, \langle \tilde{R}_2^2 \rangle \) restore corresponding results obtained previously in [15, 16].

2.2.3. Fixed points, scaling exponents and size ratios. Applying the direct polymer renormalization scheme, briefly given in the appendix, we obtain the values of FPs governing the behaviour of different types of block copolymers as common zeros of functions (A.12), (A.13). We found six sets of FPs, which are usually distinguished in studies concerning the diblock copolymers [38–40]:

\[
(1) \tilde{u}_{1,R} = 0, \quad \tilde{u}_{2,R} = 0, \quad \tilde{w}_{1,2,R} = 0,
\]

\( (A.13) \)
(2) $\tilde{u}_{1,R} = 0, \quad \tilde{u}_{2,R} = 0, \quad \tilde{w}_{1,2,R} = \frac{\epsilon L_1 L_2}{(L_1 + L_2)^2}$.

(3) $\tilde{u}_{1,R} = 0, \quad \tilde{u}_{2,R} = \frac{\epsilon}{8}, \quad \tilde{w}_{1,2,R} = 0$.

(4) $\tilde{u}_{1,R} = 0, \quad \tilde{u}_{2,R} = \frac{\epsilon}{8}, \quad \tilde{w}_{1,2,R} = \frac{3\epsilon L_1 L_2}{4(L_1 + L_2)^2}$.

(5) $\tilde{u}_{1,R} = \frac{\epsilon}{8}, \quad \tilde{u}_{2,R} = \frac{\epsilon}{8}, \quad \tilde{w}_{1,2,R} = 0$.

(6) $\tilde{u}_{1,R} = \frac{\epsilon}{8}, \quad \tilde{u}_{2,R} = \frac{\epsilon}{8}, \quad \tilde{w}_{1,2,R} = \frac{\epsilon L_1 L_2}{2(L_1 + L_2)^2}$.

Case (1) corresponds to the most trivial situation of two idealized Gaussian chains, whereas case (2) includes mutual avoidance between them. Similarly, (3) and (4) describe the situation, when one block is a Gaussian chain and the other block feels the excluded volume effect, with and without mutual interactions, correspondingly. Finally, (4) and (5) describe two blocks with an excluded volume effect, again with and without mutual interactions. Note, that cases (3) and (4) are ‘degenerate’ in the sense, that we should also take into account the sets with symmetrical change of values $\tilde{u}_{1,R}$ and $\tilde{u}_{2,R}$.

The expression for $\gamma$ as given by equation (9) in the case of diblock copolymer reads:

$$
\gamma = 1 + (\tilde{u}_1 + \tilde{u}_2 - \tilde{w}_{1,2}) + \epsilon \left( \tilde{u}_1 + \tilde{u}_2 - \tilde{w}_{1,2} \right)
- \epsilon \tilde{w}_{1,2} \ln \left( \frac{L_1 L_2}{(L_1 + L_2)^2} \right). \tag{24}
$$

Substituting the values of FPs for the cases (1)–(6) into equation (24) and keeping terms only up to the linear order in $\epsilon$, we obtain the corresponding values of scaling exponents $\gamma$ given in table (1).

Let us consider the situation when $L_1 = L_2$. In this case, we can restore the first-order expansion for $\gamma$ from the set of star copolymer exponents $\eta_{f_i}$ obtained in [40]. We can make use of the scaling relation, which takes place for the diblock copolymer chain: $\gamma^{(i)} = 1 + \nu^{(i)} (\eta_{i,1} - \eta_{i,0}) - \eta_{i,2}^{(SAW)}$, where $\eta_{i,0}^{(SAW)} = \eta_{i,0}^{(SAW)} = (1 - \gamma_{SAW})/\nu_{SAW} = -\epsilon/4$, $\eta_{i,2}^{(RW)} = \eta_{i,2}^{(RW)} = 0$. Taking the values $\eta_{i,1}^{(3)} = -\epsilon/2, \eta_{i,4}^{(4)} = -3\epsilon/8$ from [40], we restore the values of $\gamma^{(2)}, \gamma^{(4)}$ obtained by us.

Aiming to find the quantitative estimates in this case for $d = 3$, we put $\epsilon = 1$ in corresponding expressions in table 1. Thus, we have:

$$
\gamma^{(1)} = 1, \tag{25}
$$

$$
\gamma^{(2)} = \frac{3}{4}, \tag{26}
$$

$$
\gamma^{(3)} = \frac{9}{8}, \tag{27}
$$

$$
\gamma^{(4)} = \frac{15}{16}. \tag{28}
$$
\[ \gamma^{(5)} = \frac{5}{4}, \quad (29) \]

\[ \gamma^{(6)} = \frac{9}{8}, \quad (30) \]

For comparison, we present the corresponding values obtained on the basis of the 3rd order of \( \epsilon \) expansion given in [40] for the set of star copolymer exponents \( \eta_{i,j} \). Again, making use of the scaling relation mentioned above and taking \( \eta_{SAW}^{(i)} = \eta_{RW}^{(i)} \) for the set of star copolymer exponents \( \eta_{f_1}, \eta_{f_2} \). Again, making use of the scaling relation mentioned above and taking \( \eta_{SAW}^{(2)} = 0 \), \( \eta_{SAW}^{(3)} = 0.2671 \), \( \eta_{SAW}^{(4)} = 0 \) (at \( \epsilon = 1 \)) we obtain: \( \gamma^{(2)} = 0.770 \), \( \gamma^{(4)} = 0.992 \).

We can also estimate the values of exponents \( \nu_i \), governing correspondingly the scaling behavior of the end-to-end distances \( \langle R_{1}^2 \rangle \) and \( \langle R_{2}^2 \rangle \) of two blocks. We receive [28]

\[ \nu_i = \frac{1}{2} \sum_{i=1}^{2} \tilde{u}_i \frac{d \ln \langle R_{i}^2 \rangle}{d \ln \tilde{u}_i} + \tilde{w}_{12} \frac{d \ln \langle R_{1}^2 \rangle}{d \ln \tilde{w}_{12}} \quad (31) \]

Substituting the expressions (16) and (17) into this relation, we obtain:

\[ \nu_1 = \frac{1}{2} \left( 1 + \tilde{u}_1 - \epsilon \tilde{w}_{12} + \frac{\epsilon \tilde{w}_{12}}{2(\tilde{L}_1 + \tilde{L}_2)} \right) \times \frac{\tilde{L}_2}{\tilde{L}_1} \left( 2(\tilde{L}_1 + \tilde{L}_2) \ln \left( \frac{\tilde{L}_2}{\tilde{L}_1 + \tilde{L}_2} + L_1 \right) \right). \quad (32) \]

\[ \nu_2 = \frac{1}{2} \left( 1 + \tilde{u}_2 - \epsilon \tilde{w}_{12} + \frac{\epsilon \tilde{w}_{12}}{2(\tilde{L}_1 + \tilde{L}_2)} \right) \times \frac{\tilde{L}_1}{\tilde{L}_2} \left( 2(\tilde{L}_1 + \tilde{L}_2) \ln \left( \frac{\tilde{L}_1}{\tilde{L}_1 + \tilde{L}_2} + L_2 \right) \right). \quad (33) \]

Substituting the values of FPs for the cases (1)–(6) into equations (32) and (33) and keeping again terms only up to the linear order in \( \epsilon \), we obtain the corresponding values of scaling exponents \( \nu_1, \nu_2 \) given in table 1. Note that the values of these exponents do not depend on \( L_1, L_2 \) and, mostly important, they are not modified by the presence of mutual avoidance with the other block chain.

However, the presence of interaction with the other block modifies the values of \( \langle R_{1}^2 \rangle \) and \( \langle R_{2}^2 \rangle \) as compared with that of a free chain. This can be easily seen by introducing the ratios:
\[ g_i = \frac{\langle R^2 \rangle_{\text{chain}}}{\langle R^2 \rangle_i} , \] (34)

where \( \langle R^2 \rangle_{\text{chain}} \) is the end-to-end distance of a single chain of a length \( L \):

\[ \langle R^2 \rangle_{\text{chain}} = dL \left( 1 + \tilde{u}_1 \frac{2}{\epsilon} - \tilde{u}_1 \right) . \] (35)

Thus, we have:

\[ g_1 = 1 + \frac{\tilde{w}_{1,2}}{2(L_1 + L_2)} \frac{L_2}{L_1} \left( L_1 + 2(L_1 + L_2) \ln \left( \frac{L_2}{L_1 + L_2} \right) \right) ; \] (36)

\[ g_2 = 1 + \frac{\tilde{w}_{1,2}}{2(L_1 + L_2)} \frac{L_1}{L_2} \left( L_2 + 2(L_1 + L_2) \ln \left( \frac{L_1}{L_1 + L_2} \right) \right) ; \] (37)

Again, considering the case when \( L_1 = L_2 \) we have:

\[ g_i = 1 - \tilde{w}_{1,2} (\ln(2) - 1/4). \] (38)

Substituting the FP value of \( w_{12} \) for cases (1)–(6), one can easily see that in the presence of mutual avoidance between blocks the ratio is always smaller than 1 and thus the effective size of a block is more extended in space.

2.3. \( n \)-block copolymer chain

2.3.1. End-to-end distances. The previous description can be easily generalized to a more complicated polymer consisting of \( n \) subsequently connected blocks. So, we come to the problem with the set of \( n \) coupling constants governing the excluded volume interactions within the same block (\( u_i \) with \( i = 1, \ldots, n \)) and \( n(n-1)/2 \) coupling constants governing the mutual interactions between any pair of blocks (\( w_{ij} \) with \( i < j = 1, \ldots, n \)). Correspondingly, there are \( n \) characteristic lengths in a system, given by:

\[ \langle R^2 \rangle_i = dL_i \left( 1 + \tilde{u}_i \left( \frac{2}{\epsilon} - 1 \right) + \sum_{j \neq i=1}^n \tilde{w}_{ij} \left[ \frac{l_{ij}}{L_{ij}} \ln \left( \frac{l_{ij}}{L_{ij}} \right) - \frac{L_iL_j}{L_{ij}} \ln \left( \frac{l_{ij} + L_i + L_j}{L_{ij}} \right) - \frac{L_iL_j}{2(L_i + l_{ij} + L_j)(L_i + l_{ij})} \right] \right. \] (39)

\[ + \left. \sum_{k=1}^{i-1} \sum_{m=i+1}^n \tilde{w}_{km}L_kL_m \frac{2(L_{km} + L_k + L_m)}{(L_{km} + l_{km} + L_k)(L_k + l_{km})(l_{km} + L_m)} \right) , \]

with \( l_{ij} = \sum_{t=i+1}^{j-1} L_t \), and it is important to note that \( l_{km} \) depends on \( L_i \) by containing it in the sum.

Again, we can consider the size ratio (34) to compare the effective size of \( i \)th block in the \( n \)-block copolymer chain with that of a single chain of the same length \( L_i \). The result reads:
2.3.2. Fixed points, scaling exponents and size ratios. Generalizing the direct polymer renormalization group scheme to the system of \( n \) blocks, we come to the system of \( n + n(n-1)/2 \) flow equations:

\[
\beta_{u_R} = \epsilon \tilde{u}_R - 8 \tilde{u}^2_R = 0, \tag{41}
\]

\[
\beta_{\tilde{u}_{i,R}} = \epsilon \tilde{w}_{i,R} - \frac{(L_i + L_j)^2}{L_i L_j} \tilde{w}^2_{i,R} - 2 \tilde{w}_{i,R} (u_{i,R} + u_{j,R}) = 0. \tag{42}
\]

Analyzing the set of FPs, which are the common zeros of functions (41), (42), we find that \( \tilde{u}_i \) can take the two possible values:

\[
\tilde{u}_{i,R} = 0, \quad \tilde{u}_{i,R} = \frac{\epsilon}{8}, \tag{43}
\]

so that the size scaling exponents \( \nu_n \), governing the scaling of the end-to-end distances \( \langle R^2 \rangle \) again take on the values of either 1/2 or 1/2 + \( \epsilon/16 \), correspondingly.

For the \( \tilde{w}_{i,j} \) we have:

\[
\tilde{w}_{i,j,R} = 0, \quad \forall \tilde{u}_i, \tilde{u}_j, \tag{44}
\]

\[
\tilde{w}_{i,j,R} = \frac{\epsilon L_i L_j}{(L_i + L_j)^2}, \quad \tilde{u}_i = \tilde{u}_j = 0, \tag{45}
\]

\[
\tilde{w}_{i,j,R} = \frac{3 \epsilon L_i^2}{4 (L_i + L_j)^3}, \quad \tilde{u}_i \neq \tilde{u}_j, \tag{46}
\]

\[
\tilde{w}_{i,j,R} = \frac{\epsilon L_i L_j}{2 (L_i + L_j)^2}, \quad \tilde{u}_i = \tilde{u}_j = \frac{\epsilon}{8}. \tag{47}
\]

Applying formula (9) to the expression for the partition function of \( n \)-block copolymer (8) and expanding the result into series over \( \epsilon \) with keeping only the terms that are linear in coupling constants we receive:

\[
\gamma(n) = 1 + \sum_{i=1}^n \tilde{u}_i - \sum_{i=1}^{n-1} \tilde{w}_{i,i+1}. \tag{48}
\]

It is interesting to note that in the one-loop approximation \( \gamma(n) \) depends only on interactions between neighboring segments, whereas the partition function depends on all \( \tilde{w}_{i,j} \).

For an illustration, let us consider the alternating sequence of the type ABABA..., where A and B are correspondingly blocks of SAW type (with \( w_{2i+1} = \epsilon/8, i = 0, \ldots, n/2 - 1 \)) and RW type (with \( w_{2i} = 0, i = 1, \ldots, n/2 \)), all of equal length. In the case, when there are no mutual interactions between blocks (\( w_{ij} = 0 \)), we have:
\[ \gamma(n) = 1 + \frac{n\epsilon}{16}. \]  
(49)

When mutual interactions are present between all pairs of blocks \((w_{ij} = 3\epsilon/16)\) we obtain:

\[ \gamma(n) = 1 + \frac{n\epsilon}{16} - (n-1)\frac{3\epsilon}{16}. \]  
(50)

Let us recall, that aiming to describe the 3-dimensional system, we should put \(\epsilon = 1\) in this expression.

For the size ratio (40) in this situation we have:

\[ g_i = 1 - \frac{3\epsilon}{16} \left[ \sum_{j \neq i=1}^{n} \left( \frac{|j-i| - 1}{|j-i|} \right) \ln \left( \frac{|j-i| - 1}{|j-i|} \right) \right] \]
\[ - |j - i| \ln \left( \frac{|j-i|}{1+|j-i|} \right) - \frac{1}{2(1+|j-i|)|j-i|} \]
\[ - \sum_{k=1}^{j-1} \sum_{m=i+1}^{n} \frac{1}{(m-k+1)(m-k)}. \]  
(51)

It is important to note, that the effective linear size measures of blocks depend not only on the overall number of blocks \(n\), but also on the position \(i\) of the block along the sequence.

On figure 2(a), we present the results for the end block (with \(i = 1\), which coincide with the case \(i = n\)). At \(n = 2\), we restore the size ratio (38) of the diblock copolymer for case (6). We note, that \(g_1\) slightly decreases with growing of \(n\), so that the block becomes more extended in space as compared with the size of single polymer chain of the same length, due to presence of other blocks. This effect becomes much more pronounced, when we analyze the size ratio for the central block (with \(i = n/2\), presented on figure 2(b). Due to a large amount of contacts with neighboring blocks, the effective size of the central block is more extended in space as compared with that of end blocks, and continuously grows with an increasing total number of blocks \(n\).

3. Numerical simulations of diblock copolymer chain

To provide some illustrations of our analytical results of the previous section, we present here some results of the lattice simulations of the diblock copolymer chain on a cubic lattice. We assume, that each block consists of \(N\) monomers (conjugated to the continuous length \(L\) in equations (1), (2)). The following six possibilities are considered, directly corresponding to the cases (18)–(23) introduced in the previous section:

(1) Both blocks are RW trajectories without mutual avoiding, so we restore the RW trajectory of total length \(2N\)
(2) Both are RW trajectories, but avoiding each other: each trajectory can cross itself, but cannot cross the other trajectory
(3) One block is SAW, the other is RW, without mutual avoiding
(4) One block is SAW, the other is RW, avoiding each other
(5) Both are SAW trajectories without mutual avoiding
(6) Both are SAW trajectories avoiding each other, so we restore the SAW trajectory of total length \(2N\)
In our simulations we apply the Rosenbluth–Rosenbluth growing chain algorithm [46]. Two chains are growing simultaneously from the same starting point, so that the $n$th monomer of each chain is placed at a randomly chosen neighboring site of the $(n-1)$th monomer ($n \leq N$). Note that some amount of nearest neighbor sites can be forbidden for placing a new monomer, if they are already visited (depending on conditions (1)–(6)). The weight $W_n = \prod_{l=1}^{n} m_1^l m_2^l$ is given to each sample configuration at the $n$th step, where $m_1^l$ and $m_2^l$ are the numbers of free lattice sites to place the $l$th monomer of the first and second chains, correspondingly. The growth is stopped, when the total length $N$ of each the block chain is reached. Then the next

\textbf{Figure 2.} The size ratios (51) for the end block (a) and central block (b) as functions of the number of blocks $n$. 

In our simulations we apply the Rosenbluth–Rosenbluth growing chain algorithm [46]. Two chains are growing simultaneously from the same starting point, so that the $n$th monomer of each chain is placed at a randomly chosen neighboring site of the $(n-1)$th monomer ($n \leq N$). Note that some amount of nearest neighbor sites can be forbidden for placing a new monomer, if they are already visited (depending on conditions (1)–(6)). The weight $W_n = \prod_{l=1}^{n} m_1^l m_2^l$ is given to each sample configuration at the $n$th step, where $m_1^l$ and $m_2^l$ are the numbers of free lattice sites to place the $l$th monomer of the first and second chains, correspondingly. The growth is stopped, when the total length $N$ of each the block chain is reached. Then the next
configuration is started to grow from the same starting point. The configurational averaging of any observable is thus given by:

$$\langle \ldots \rangle = \frac{\sum_{t=1}^{\text{conf}} W_t \ldots}{\sum_{t=1}^{\text{conf}} W_t},$$

where $\text{conf}$ is the number of different configurations constructed. The partition sum $Z_N$ is thus estimated as an averaged weight:

$$Z_N = \frac{1}{\text{conf}} \sum_{t=1}^{\text{conf}} W_t.$$

We constructed chains with $N$ up to 150 and performed 100 tours with building $10^6$ configurations in each of the tour.

We start with an effective size measure of the two-block copolymer chain. In the problem under consideration, we have two characteristic length scales of two blocks A and B: $\langle R^2 \rangle_A^{(i)}$ and $\langle R^2 \rangle_B^{(i)}$, with $i = 1, \ldots, 6$. Both of them scale according to equation (1) with exponents $\nu_A$ and $\nu_B$ correspondingly, which are given either by $\nu_{\text{SAW}}$ or $\nu_{\text{RW}}$, and the scaling is not modified by an avoidance with another block. Note however, than in experiments one mainly investigates the total effective length of a block copolymer chain

$$\langle R^2 \rangle^{(i)} = \langle R^2 \rangle_A^{(i)} + \langle R^2 \rangle_B^{(i)} + 2\langle \vec{R}_A^{(i)} \vec{R}_B^{(i)} \rangle.$$

Note, that when the mutual interaction between two blocks is absent (cases (1), (3), (5)), the last term in (54) vanishes, since there is no correlations between vectors $\vec{R}_A^{(i)}$ and $\vec{R}_B^{(i)}$ in this case.
In figure 3, we present simulation results for the characteristic lengths for case (4): \(\langle R^2 \rangle_{SAW}^{(4)}\), \(\langle R^2 \rangle_{RW}^{(4)}\), and also for the corresponding correlation term \(\langle \vec{R}^{(4)}_{SAW} \cdot \vec{R}^{(4)}_{RW} \rangle\).

To estimate the critical exponents, we use the linear least-square fits in the form

\[
\ln \langle R^2 \rangle_i \sim A + 2\nu (i) \ln N,
\]

with varying the lower cutoff for the number of steps \(N_{\text{min}}\). The \(\chi^2\) values (sums of squares of normalized deviation from the regression line) divided by the number of degrees of freedom DF serves as a test of the goodness of fit (see tables 2–4). Results of least square fitting give: \(\nu_{SAW} = 0.593 \pm 0.001\), \(\nu_{RW} = 0.499 \pm 0.001\). The error bars in tables 2–4 are observed to typically not overlap the known precise values. This is due to the fact that our numerical study involves only relatively short walks, and data for longer walks would be needed to reduce the influence of unfitted corrections to scaling. In addition, the values of the reduced \(\chi^2\) are undoubtedly too small, and this is because we do not explicitly take into account the correlations between estimates at different values of \(N\) which are introduced by the Rosenbluth–Rosenbluth sampling method.

When the mutual avoidance is present between the block chains, they become more extended in space. To describe this effect quantitatively, we introduce the ratios:

\[
\gamma_{RW}^{(i)} = \frac{\langle R^2 \rangle_{RW,\text{free}}^{(i)}}{\langle R^2 \rangle_{RW}^{(i)}},
\]
Here, by ‘free’ we denote the averaged end-to-end distances of the single individual chain of length \( N \). On figure 4, we give our results for the ratios \( g^{(i)}_{\text{SAW}} \) and \( g^{(i)}_{\text{RW}} \). We can see, that both values are smaller than 1, so that the effective lengths of both block chains are modified and become more extended in space due to mutual avoidance between them. This effect was described also in previous studies [18, 22].

![Figure 4](image)

**Figure 4.** The size ratios \( g^{(i)}_{\text{SAW}} \) (black squares) and \( g^{(i)}_{\text{RW}} \) (open circles) as functions of \( N \).

![Figure 5](image)

**Figure 5.** The connectivity constants of the RW chains (a) and SAW chains (b) considered as blocks of copolymer chain, as functions of length \( N \).

Here, by ‘free’ we denote the averaged end-to-end distances of the single individual chain of length \( N \). On figure 4, we give our results for the ratios \( g^{(i)}_{\text{SAW}} \) and \( g^{(i)}_{\text{RW}} \). We can see, that both values are smaller than 1, so that the effective lengths of both block chains are modified and become more extended in space due to mutual avoidance between them. This effect was described also in previous studies [18, 22].

Such an extension of the effective linear size of the individual block of copolymer chain caused by interactions with another block is also confirmed by analyzing the local connectivity constant for each block. The data for averaged connectivity constants of both building block chains for cases (1)–(6) are presented on figure 5. For case (1), when we have two RWs without avoidance, we restore \( \mu_{\text{RW}} = 6 \); the same holds for individual RW block in
the case (3), $\mu_{RW}^{(3)} = 6$. Similarly, for case (3) and (5), for the SAW block without mutual interaction with another block we approach the connectivity constant value of single SAW trajectory $\mu_{SAW}^{(3)} = \mu_{SAW}^{(5)} = \mu_{SAW}$, the most accurate result of which was obtained in the [47]: $\mu_{SAW} = 4.684039931(27)$.

In all other cases, when mutual interactions between blocks is taken into account, the values of connectivity constants are slightly modified as compared with corresponding values of free trajectories. This effect becomes less pronounced with increasing the length of both blocks. These (even very slight) modifications in the connectivity constants caused by presence of mutual avoidance with another block are actually leading to extension of the effective linear size of individual blocks, analyzed in previous paragraph.

Finally, we consider the partition sum of the diblock copolymer. We rewrite the expression (3) in the form:

$$\frac{\ln(Z_N)}{N} = a + \ln(\mu_1) + \ln(\mu_2) + (\gamma - 1)\ln(N)/N. \quad (58)$$

Corresponding results for cases (1)–(6) are given in figure 6. As expected, the largest number of configurations corresponds to case (1) of two independent random walk trajectories. Taking into account the avoidance of monomers within the block and mutual avoidance of different blocks (according to rules (2)–(6)) leads to decreasing of the possible number of configurations.

4. Discussions

The aim of the present paper was to analyze the universal conformational properties of complex macromolecules, consisting of $n$ sequential blocks of various chemical structure. In general, we consider all the blocks to be of different lengths $L_i$. Of particular interest is the set of scaling exponents $\gamma(n)$ governing behavior of the partition sum (number of possible conformations) as given by equation (4), and the effective sizes of blocks within the sequence.

Depending on the quality of a solvent, a situation may occur when some blocks are at the $\theta$-temperature regime, when attractive and repulsive interactions between monomers...
compensate each other. These chains in \( d = 3 \)-dimensional case, which is of most interest in the real polymer systems, can be considered as RW trajectories. The blocks in a regime of good solvent (with repulsive excluded volume interactions between monomers) behave as trajectories of SAW, which are not allowed to cross itself. Also, the interactions between monomers of different blocks can vanish or be present at some temperatures. Such a situation is closely related to the case of so-called ternary solutions \([38, 39]\).

As a first step in our analysis, we reconsider the simplest case of the diblock copolymer chain (so-called AB-copolymer), consisting of only two blocks. We studied all possible cases, considering blocks as RW or SAW trajectories with and without mutual avoiding between them. In accordance with previous studies \([15, 16, 18, 22]\), we observed in particular, that the values of scaling exponents governing the effective lengths \( \langle R^2_A \rangle \) and \( \langle R^2_B \rangle \) of blocks A and B are not modified by presence of another block. However, when mutual interaction between blocks is taken into account, the chains become more extended in space. We can propose the following explanation to this fact: the presence of other blocks plays the role of spatial hinderness to the given block and can be related to the case of a single polymer chain in an environment with structural defects. The last problem attracts considerable attention of researchers (see e.g. \([48]\) for a review and references therein). The main consequence is that the presence of structural defects causes the elongation of polymer chain, but does not impact the value of exponent \( \nu_{\text{SAW}}(d) \), unless the concentration of defects is above the percolation threshold and the percolation cluster of fractal dimension \( d_f \) emerges in the system. When one turns attention to the empirical Flory formula given below equation (1), one can intuitively explain this fact. Really, exponent \( \nu_{\text{SAW}}(d) \) is defined only by the space dimension \( d \). The presence of structural hinderness does not change the dimension of space, unless one has percolation cluster or any other underlying fractal structure with fractal dimension \( d_f \). Indeed, simply substituting \( d \) by fractal dimension of the percolation cluster gives a reliable estimate for corresponding \( \nu_{\text{SAW}}(d_f) \) \([49]\). However, the local crowdedness caused by presence of other blocks does not lead to the formation of a fractal environment. Thus, their presence leads to spatial elongation of an individual chain, as can be seen e.g. by analyzing the size ratios (shown on figures 5 and 6) but does not modify the values of size exponents.

This degree of extension can be quantitatively measured by introducing the size ratio (56), which allows us to compare the linear size of a block with that of single polymer chain of the same length. We found the analytical estimates for the set of scaling exponents \( \gamma \), governing the system of two subsequently connected blocks of different lengths.

Generalizing the direct polymer renormalization group scheme to the system of \( n \) subsequently connected blocks of different lengths \( L_i \) in section 2.3, we obtained the analytical expressions for scaling exponents \( \gamma(n) \) and size ratios \( g_i(n) \) of individual blocks as functions of both the number of blocks and their position along the sequence. For an illustration, we analyzed in more details the alternating sequence ABABA..., where A and B are correspondingly blocks of the SAW type and RW type, all of equal length. Due to inter-chain contacts with neighboring chains, the effective size measures of blocks are much more extended in space as compared with single polymer chains, and this effect becomes more and more pronounced with increasing the total number of blocks \( n \).

**Appendix**

Here, we give some details of direct polymer renormalization group scheme, as developed by des Cloiseaux \([28]\) and generalized by us to the case of diblock copolymers. The main idea of the method is to eliminate the divergences of observable quantities, arising in the asymptotic
limit of an infinite linear measure, by introducing corresponding renormalization factors, directly connected with physical quantities. The quantitative values of these observables are evaluated at the stable fixed point (FP) of the renormalization group transformation.

The renormalized coupling constants are determined in this process as:

\[ u_{i,R}(\tilde{u}_1, \tilde{u}_2, \tilde{w}_{1,2}) = -[Z(\tilde{u}_1, \tilde{u}_2, \tilde{w}_{1,2}, L_1, L_2)]^{-2} \times \left[ 2\pi L_i \chi_u(\tilde{u}_1, \tilde{w}_{1,2}) \right]^{-2-\epsilon/2} \]

\[ w_{1,2,R}(\tilde{u}_1, \tilde{u}_2, \tilde{w}_{1,2}) = -[Z(\tilde{u}_1, \tilde{u}_2, \tilde{w}_{1,2}, L_1, L_2)]^{-2} \times \left[ 2\pi (L_1 \chi_u(\tilde{u}_1, \tilde{w}_{1,2}) + L_2 \chi_u(\tilde{u}_2, \tilde{w}_{1,2})) \right]^{-2-\epsilon/2} \]  

(A.1)

\[ Z_{u_{1,2}}(L_1, L_2, L_1, L_2). \]  

(A.2)

Here, \( \chi_u(\tilde{u}_i, \tilde{w}_{1,2}) \) are the swelling factors for the corresponding end-to-end distances:

\[ \langle R_i^2 \rangle = dL_i \chi_u, i = 1, 2, \]  

(A.3)

and \( Z_{u_1}, Z_{u_2}, Z_{u_{1,2}} \) are so-called two-polymer partition functions.

We need to calculate additionally a two-polymer partition function, that can be presented as:

\[ Z(L_1, L_2, L_1, L_2) = -u_1 Z^2 - u_2 Z^2 - w_{1,2} Z^2 + \tilde{Z}(L_1, L_2, L_1, L_2) \]  

(A.4)

where \( \tilde{Z}(L_1, L_2, L_1, L_2) \) is given by a sum of all contributions, presented diagrammatically on figure A1. The analytical expressions, corresponding to presented diagrams, read:

\[ D1 = u_1 L_2^2 \tilde{u}_i \left( \frac{2}{\epsilon} - 2 \ln(2) + 1/2 \right), \]  

(A.5)

\[ D2 = w_{1,2} L_1 L_2 \tilde{w}_{1,2} \left( \frac{2}{\epsilon} + \frac{1}{2} - \frac{L_1}{2L_2} \ln \left( \frac{L_1 + L_2}{L_1} \right) \right), \]  

(A.6)

\[ D3(D3') = \frac{u_i w_{1,2}}{(2\pi)^{d/2}} \left( \frac{(2L_1 + L_2)^2}{2} \ln (2L_1 + L_2) \right) + \ln (L_1 + L_2) (L_1 + L_2) (2L_1 + L_2) - \frac{L_2^2}{2} \ln (L_2) - L_1 L_2 \ln (L_2) + 2 L_1^2 \ln (2) \]  

(A.7)

\[ D4 = \frac{w_{1,2}^2}{(2\pi)^{d/2}} \left( (L_1 + 2L_2)^3 \ln (L_1 + 2L_2) - L_1^3 \ln (L_1) + (2L_1 + L_2)^3 \ln (2L_1 + L_2) - 4 (L_1 + L_2)^2 \ln (L_1 + L_2) - 4 \ln (2) (L_1^2 + L_1 L_2 + L_2^2) - L_2^2 \ln (L_2) \right), \]  

(A.8)
The diagrams $D_1$ and $D_3$ have a pre-factor $2$, diagram $D_2$ has a pre-factor $4$ and the $D_4$ and $D_5$ are accounted for only once. Note also, that we need to take into account only the terms containing the poles $\epsilon^{-1}$.

The flows of the renormalized coupling constants are governed by $\beta$ functions defined according to

$$\beta_{u_i,R} = 2L_i \frac{\partial u_i,R}{\partial L_i},$$

$$\beta_{w_{1,2},R} = 2 \sum_{i=1}^{2} L_i \frac{\partial w_{1,2},R}{\partial L_i}. \quad (A.10)$$

We receive:

$$\beta_{u_i,R} = \epsilon u_i,R - 8u_i^2,R = 0, \quad (A.12)$$

$$\beta_{w_{1,2},R} = \epsilon w_{1,2},R - \frac{(L_1 + L_2)^2}{L_1 L_2} w_{1,2}^2,R - 2w_{1,2},R(u_1,R + u_2,R). \quad (A.13)$$

The FPs of the renormalization group transformations, allowing us to obtain the quantitative values of scaling exponents (9), (31), are defined as common zeros of functions (A.12), (A.13).

**ORCID iDs**

V Blavatska  [https://orcid.org/0000-0001-6158-1636](https://orcid.org/0000-0001-6158-1636)

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