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Statistics of ideal randomly branched polymers in a semi-space

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Abstract. We investigate the statistical properties of a randomly branched 3-functional N-link polymer chain without excluded volume, whose one point is fixed at the distance d from the impenetrable surface in a 3-dimensional space. Exactly solving the Dyson-type equation for the partition function $Z(N,d) = N^{-\theta} e^{\gamma N}$ in 3D, we find the "surface" critical exponent $\theta = \frac{5}{2}$, as well as the density profiles of 3-functional units and of dead ends. Our approach enables to compute also the pairwise correlation function of a randomly branched polymer in a 3D semi-space.

PACS. 05.40.-a Fluctuation phenomena, random processes, noise, and Brownian motion – 82.35.Gh Polymers on surfaces; adhesion – 36.20.Ey Conformation (statistics and dynamics)

1 Introduction

The rapid development of statistical physics of macromolecules is indebted, in first turn, to the representation of linear polymers by Markov chains. The application of a theory of Markov processes for a description of conformational properties of linear polymer chains has become invaluable [1–3]. Besides the linear chains, the polymers of complex geometry, such as, for example, stars, brushes and branched chains, are of extreme importance in physical and chemical properties of macromolecular compounds [1,4,5].

Randomly branched macromolecules are one of the most interesting polymer systems with nonlinear structure. The possibility to form topologically different architectures leads to an extra contribution to the conformational entropy of samples constituted by randomly branched chains. There is a deep relation between the physics of randomly branched polymers and "lattice animals" appeared in percolation [6–8] and that of the gelation processes [9–16]. There are various methods for the statistical description of annealed randomly branched chains. On the one hand, we know successful attempts to compute various conformational properties of randomly branched polymers in terms of branched Markov processes [17–20].

Similarly to the theory of linear polymer chains (see, for example [3,21]), the problem of taking the volume interactions (*i.e.* interaction of particles situated topolgically far from each other) into account plays a central role in the construction of the proper theory for the randomly branched chains. Concerning this problem, one can imagine two most interesting limiting cases, corresponding to strong repulsive volume interactions and negligibly small ones, respectively (we discuss the applicability of these two limiting cases in the last section of this paper).

Speaking of the limit of strong repulsive volume interactions, special attention should be paid to the application of supersymmetry in the description of the thermodynamic characteristics of randomly branched chains. During last two decades since the seminal works [22–24] (see also the short self-reviews [25]), sypersymmetry becomes a powerful tool for the investigation of the statistics of randomly branched chains. In particular, one has to note the recent contributions [26,27] which have an impact on understanding the very origin of the supersymmetric dimensional reduction for randomly branched polymers. Speaking of the main objective of the present work —the influence of boundary conditions on statistical properties of randomly branched polymers, we know some recent successful attempts of calculating the critical exponents of the randomly branched chains with volume interactions near the impenetrable wall [28] and the thorough study of absorption of a randomly branched polymer [29]. The former of these works is based on a rather general lattice approximation (note that lattice theories always correspond to the presence of excluded volume); the latter is based on the supersimmetry technique. In the discussion section we

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will compare the results of [28,29] with ours obtained in the limit of no volume interactions.

In the no interaction (ideal) case, the basic question of the theory concerns the evaluation of the partition function $Z(N)$ of a non-self-interacting branched structure without loops. Briefly, the problem is formulated as follows. Take N elementary units (monomers) such that each monomer has no more than $f_{\max}$ branches (we call them $f_{\max}$-functional monomers) and compute all possible ways to arrange them in a *single-connected* loopless cluster. We call such a cluster "a $f_{\max}$-branching random tree". In what follows we shall consider, for simplicity, only the case $f_{\max} = 3$. The problem of calculating the partition function $Z(N)$ in the free space does not meet any difficulties and has been solved by various methods (see, for example, [30,31]). However, the influence of boundary conditions on statistical properties of randomly branched polymers is far from being as clear as the bulk properties. It seems to be instructive to compare this situation to the boundary behavior of linear phantom chains. The boundary effect for linear random walks can be easily taken into account by using the "image" principle which enables to represent the partition function of a linear polymer with, say, Dirichlet boundary conditions in terms of a linear combination of two shifted bulk partition functions [32, 33]. *A priori* the same "image" method seems to be inapplicable for randomly branched chains.

In the present work we generalize the technique developed in the earlier work [12,13] for a problem of thermoreversible gelation to compute a partition function, $Z(N, d)$, and calculate various thermodynamic characteristics of an annealed randomly branched loopless N-link polymer in a 3-dimensional space, whose one point is fixed at a distance d from the impenetrable wall. The approach used in our work is based on a diagram expansion of a partition function of a randomly branched polymer in a semi-space. Summing the diagrams we then construct and solve directly the Dyson-type equation for the aforementioned partition function. The developed method enables us also to compute the density profiles of the monomers having different numbers of neighbours as well as to derive an expression for the correlation function, $G(r_1, r_2, N)$, of the branched polymer in a semi-space.

The paper is organized as follows. In Section 2 we present the model of randomly branched polymers and discuss in detail the methods we are using. The resulting formalism is somewhat similar to that derived earlier in [34] and thus is not new, but we put it here to make the paper self-consistent. A brief review of the known main results concerning randomly branched polymers in the bulk is given in Section 3. Section 4 is devoted to the calculation of a generating function of branched random walk in a semi-space. That is the central part of our paper. In Sections 5-6, using the expression for the generating function, we compute, respectively: the partition function of an N-link random tree, the distribution of branchings in the tree, and the pairwise correlation function. In the last section we briefly summarize and discuss the obtained results.

2 The methods and the model

In order to make the paper self-consistent, it seems to be instructive to formulate the general thermodynamic language which has been elaborated for the description of the thermoreversible gelation process [12,13] and is very convenient for our needs. To begin with, let us consider a system of N identical 3-functional units capable to form reversible bonds between each other. The partition function $Z(N)$ of such a system can be written as a product of two terms:

$$Z(N) = Z_{\mathrm{str}}(N) Z_{\mathrm{int}}(N) , \tag{1}$$

where $Z_{\mathrm{str}}(N)$ and $Z_{\mathrm{int}}(N)$ denote, respectively, the "structural" and "interactional" parts of the partition function.

The structural contribution to the partition function, *i.e.* that due to the formation of clusters of specific structure, reads:

$$Z_{\mathrm{str}}(N) = \int \sum_{\{T\}} \frac{1}{r_T} \prod_{\{i,j\}\in T} \Big[\beta g(r_i, r_j)\Big] \mathrm{d}r_i, \tag{2}$$

where:

- the product is taken over all pairs of particles forming the manifold with topology T characterized by the symmetry index r_T;
- the external sum runs over all possible topological structures T of the system;
- the factor β is the weight of pairing;
- the function $g(r_i, r_j) = g(r_i - r_j)$ is the probability density to find two connected particles at the points r_i and r_j, respectively [3,12,13,35]. We assume this function to be the normalized Gaussian:

$$g(r) = \left(\frac{3}{2\pi a^2}\right)^{3/2} \exp\left(-\frac{3r^2}{2a^2}\right) , \tag{3}$$

where a is a mean-square length of the bond:

$$a^2 = \int r^2 g(r) \mathrm{d}r \, . \tag{4}$$

The partition function $Z_{\mathrm{int}}(N)$ is purely energetic and is due to the interactions among particles and between particles and an external field:

$$\begin{aligned} Z_{\mathrm{int}}(N) &= \int e^{-U(\{r_i\})/T} \prod \mathrm{d}r_i \, , \\ U(\{r_i\}) &= \sum_i \phi(r_i) + \sum_{i,j} V(r_i, r_j) \, , \end{aligned} \tag{5}$$

where:

- the potentials $\phi(r_i)$ and $V(r_i, r_j)$ are, respectively, an external field at the point r_i and a pairwise interaction energy in the system;
- T is the temperature measured in energetic units.

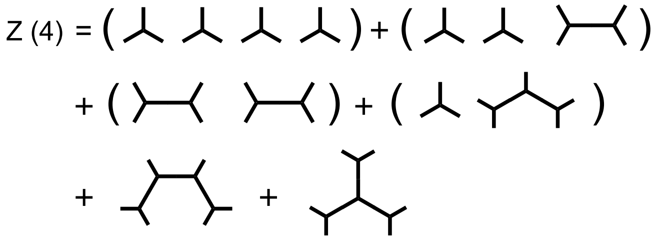

Fig. 1. The diagrammatic representation of the statistical sum $Z(N)$ for $N = 4$.

In what follows we neglect the volume interactions between particles and set therefore $V(r_i, r_j) = 0$.

In the present article we restrict ourselves to the investigation of randomly branched polymers only, *i.e.* we totally neglect the possibility of formation of any closed loops of bonds in the system. The calculation of the partition function $Z(N)$ can be described by the simple diagrammatic technique (see Fig. 1 as an example), the aforementioned absence of closed loops making the evaluation of this technique much simpler than in the case of reversible gels (see [13]). From our point of view, the diagrammatic technique suggested below, though physically similar, seems to be more transparent than the recurrent relations suggested for the same problem in [34].

Indeed, let us consider a system consisting of N 3-functional monomers bonded in such a way that no closed loops are present. In general, such a system consists of many disconnected trees. It is convenient to describe the structure of each tree by a diagram, where each monomer is represented by a vertex (with an assigned radius-vector r), the chemical bond between two monomers is represented by a line connecting the vertices corresponding to the bonded monomers and if a monomer has less than 3 bonds with other monomers, then each missing bond is represented by a short line. Next, let us attribute the weights $e^{-\phi(r)/T}$, $\beta g(r_i, r_j)$ and 1 to the vertices, long lines (connections), and short lines (missing bonds), respectively. Following the prescription (2), the weight of each diagram is given by a multiplication of all the weights, integration over all space coordinates and, finally, division by the symmetry index r_T. Now, the desired partition function $Z(N)$ is a sum running over all (connected and disconnected) weighted diagrams. To proceed further, let us introduce the generating function $\varXi(\lambda)$ of all diagrams (connected and disconnected) as follows:

$$\varXi(\lambda) = 1 + \sum_{N=1}^{\infty} Z(N)\lambda^N\,,$$

$$Z_{\text{all}}(N) = \frac{1}{2\pi i}\oint \frac{\varXi(\lambda)}{\lambda^{N+1}}\,\mathrm{d}\lambda\,.$$

The function $\varXi(\lambda)$ is just the partition function of the grand canonical ensemble with a fixed chemical potential $\mu = T\ln\lambda$. As follows from the so-called first Mayer theorem (see, for example, [36]), we can represent $\varXi(\lambda)$ in the following form:

$$\varXi(\lambda) = \exp\left[\chi(\lambda, \phi(r))\right], \tag{6}$$

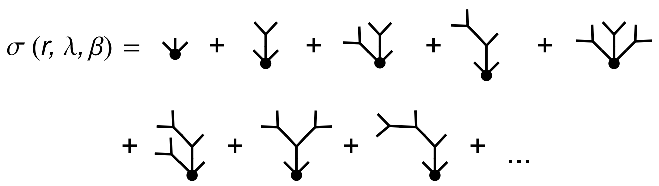

Fig. 2. The series of root diagrams for the function $\sigma(\lambda, \beta, r)$ up to 4 terms (see Eq. (8)).

where $\chi(\lambda, \phi(r))$ is the generating functional of all the *connected* diagrams (remember that in our approximation all connected diagrams are just trees). Accordingly, the partition function of all trees consisting of N monomers is

$$Z_{\text{con}}(N) = \frac{1}{2\pi i}\oint \frac{\chi(\lambda)}{\lambda^{N+1}}\,\mathrm{d}\lambda\,. \tag{7}$$

The simplest way to calculate $\chi(\lambda, \phi(r))$ is to define first the generating function of all the rooted diagrams (*i.e.* diagrams with one labelled vertex) $\sigma(\lambda, \beta, r) = -T\delta\chi(\lambda, \phi(r))/\delta\phi(r)$ as is shown in the equation below:

$$\begin{aligned}
\frac{\sigma(\lambda,\beta,r)}{\lambda e^{-\phi(r)/T}} &= \frac{1}{6} + \frac{\lambda\beta}{4}\int g(r,r_1)e^{-\phi(r_1)/T}\mathrm{d}r_1\\
&+\frac{\lambda^2\beta^2}{4}\int g(r,r_1)g(r_1,r_2)\prod_{i=1}^{2}e^{-\phi(r_i)/T}\mathrm{d}r_i\\
&+\frac{\lambda^2\beta^2}{8}\int g(r,r_1)g(r,r_2)\prod_{i=1}^{2}e^{-\phi(r_i)/T}\mathrm{d}r_i\\
&+\frac{\lambda^3\beta^3}{4}\int g(r,r_1)g(r_1,r_2)g(r_2,r_3)\prod_{i=1}^{3}e^{-\phi(r_i)/T}\mathrm{d}r_i\\
&+\frac{\lambda^3\beta^3}{4}\int g(r,r_1)g(r,r_2)g(r_2,r_3)\prod_{i=1}^{3}e^{-\phi(r_i)/T}\mathrm{d}r_i\\
&+\frac{\lambda^3\beta^3}{48}\int g(r,r_1)g(r,r_2)g(r,r_3)\prod_{i=1}^{3}e^{-\phi(r_i)/T}\mathrm{d}r_i\\
&+\frac{\lambda^3\beta^3}{16}\int g(r,r_1)g(r_1,r_2)g(r_1,r_3)\prod_{i=1}^{3}e^{-\phi(r_i)/T}\mathrm{d}r_i\\
&+\{\text{terms of higher orders in } \lambda \text{ and } \beta\}\,.
\end{aligned} \tag{8}$$

Equation (8) can be easily visualized. The corresponding diagrammatic expansion is displayed in Figure 2.

Note that $\lambda^{-1}e^{\phi(r)/T}\sigma(\lambda, \beta, r)$ is a functional of $\phi(r)$ and a function of $\lambda\beta$ only, which is due to the fact that the number of bonds in a tree-like cluster is always one less than the number of connected units: $N_{\text{bond}} = N - 1$. Therefore, in what follows we redefine

$$\epsilon = \lambda\beta$$

and rewrite $\sigma(\lambda, \beta, r)$ as

$$\sigma(\lambda, \epsilon, r) = \lambda e^{-\phi(r)/T}\sum_{N=1}^{\infty} C_N \epsilon^{N-1}\,. \tag{9}$$

It is noteworthy that the coefficient $\lambda e^{-\phi(r)/T} C_N \epsilon^{N-1}$ has a simple physical meaning —it is equal to the partition function of a randomly branched polymer consisting of $N+1$ links with one link fixed at the point r.

Now, it is easy to see that the following relationship holds:

$$\lambda\, \mathrm{d}\chi(\lambda, \beta, \phi(r))/\mathrm{d}\lambda = \int \sigma(\lambda, r) \mathrm{d}^3 r \,. \qquad (10)$$

Thus, to find the function $\chi(\epsilon)$ we should just integrate the generating function $\sigma(\lambda, \beta, r)$:

$$\chi(\lambda, \beta) = \beta^{-1} e^{-\phi(r)/T} \sum_{N=1}^{\infty} \frac{C_N}{N+1} \beta^N = z^{-1} \int_0^{\beta} \sigma(\lambda, \tau, r) \mathrm{d}\tau \,. \qquad (11)$$

Since the weights of the different branches of any tree are factorized under the assumption of the absence of closed loops and volume interactions in the system, the generating function ρ can be written in the factorized form:

$$\sigma(\lambda, \epsilon, r) = \frac{\lambda}{6}\, e^{-\phi(r)/T}\, t^3(\epsilon, r). \qquad (12)$$

Here $t(\epsilon, r)$ is a generating function of one branch, which has the following series expansion:

$$\begin{aligned} t(\epsilon, r) &= 1 + \frac{\epsilon}{2} \int g(r, r_1) e^{-\phi(r_1)/T} \mathrm{d}r_1 \\ &+ \frac{\epsilon^2}{2} \int g(r, r_1) g(r_1, r_2) \prod_{i=1}^{2} e^{-\phi(r_i)/T} \mathrm{d}r_i \\ &+ \frac{\epsilon^3}{2} \int g(r, r_1) g(r_1, r_2) g(r_2, r_3) \prod_{i=1}^{3} e^{-\phi(r_i)/T} \mathrm{d}r_i \\ &+ \frac{\epsilon^3}{8} \int g(r, r_1) g(r_1, r_2) g(r_1, r_3) \prod_{i=1}^{3} e^{-\phi(r_i)/T} \mathrm{d}r_i + \dots \,. \end{aligned} \qquad (13)$$

The diagrammatic form of this expansion is shown in Figure 3a.

The infinite series (13) could be easily evaluated taking into account the aforementioned statistical independence of different branches. Indeed, it is easy to see that all the terms in (13) are similar to that of the right-hand side of the diagrammatic equation presented in Figure 3b. Therefore, the generating function t satisfies the following exact non-perturbative equation:

$$t(\epsilon, r) = 1 + \frac{\epsilon}{2} \int g(r, r_1) e^{-\phi(r_1)/T} t^2(\epsilon, r_1) \mathrm{d}r_1. \qquad (14)$$

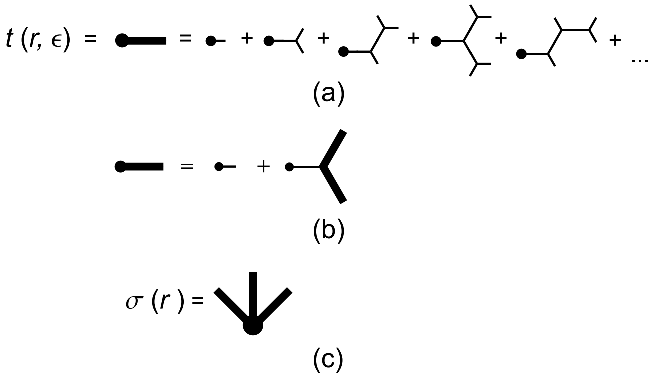

Fig. 3. Diagrammatic form of (a) equation (13), (b) equation (14), (c) equation (12).

Equation (14) plays a central role in our paper. Note that it is ideologically very similar to equation (2.4) in [34], the main difference being that we assume the equal reaction ability of the functional groups (the so-called Flory rule: the probability that a given group forms a bond does not depend on the state of the neighboring ones), and the fact that the external field does not distinguish the monomers with different number of reacted groups. This leads to some minor loss of generality but allows us to factorize the contributions of different branches.

Solving (14), one gets both "rooted" and "unrooted" generating functions ρ and χ and obtains the partition functions Ξ and Z. The method of generating functions enables also to compute easily the numbers ρ_f of the monomers having exactly f missing bonds (or $f_{\max} - f$ bonds with other monomers). (In what follows we refer to the monomers with $f = 0$ and $f = f_{\max} - 1$ as the junction monomers and dead ends, respectively.) The corresponding generation functions are, obviously,

$$\sigma_f(\lambda, r) = \frac{\lambda\, e^{-\phi(r_1)/T}}{f!(3-f)!} (t-1)^{3-f} = \lambda\, e^{-\phi(r_1)/T} \sum_{N=1}^{\infty} C_N^{(f)}(r) \epsilon^{N-1} \,. \qquad (15)$$

The N-th term $C_N^{(f)}(r)$ in the series expansion of ρ_f has a clear physical meaning. It is just a partition function of a randomly branched $(N+1)$-link polymer with: i) a root fixed at the given point r, and ii) exactly f branches starting from this root. Comparing this definition with that of C_N (see Eq. (9) and discussion below), we get the probability $p_f(r)$ for a vertex of a randomly branched $N+1$-link polymer situated at the point r to be f-functional, which equals

$$p_f(r) = \frac{C_N^{(f)}(r)}{C_N(r)} \,. \qquad (16)$$

Now, after the generating function t is calculated, one can also calculate readily the binary correlation function. Indeed, the correlation function $G(r_1, r_2)$ satisfies the following Dyson equation:

$$G(r_1, r_2) = g(r_1 - r_2) + \epsilon \int g(r_1 - r_3) t(r_3) \times e^{-\phi(r_3)/T} G(r_3, r_2) \mathrm{d}r_3 \,, \qquad (17)$$

which is represented in the diagrammatic form in Figure 4.

Note that equation (17) differs from that suggested earlier in [31], where $t(r_3)$ was improperly replaced by $\int G(r_3, r_4) \mathrm{d}r_4$.

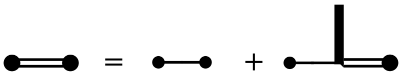

Fig. 4. Visualization of the Dyson equation (17). The correlation function G and the function g are shown by the double and ordinary solid lines, respectively.

3 The bulk properties of a randomly branched polymer

In this section we use the formalism introduced above to re-derive the well-known main characteristics of the randomly branched polymers in the infinite space, which will be useful to compare with the results in the semi-space to be obtained in the subsequent sections.

In the infinite homogenous space (*i.e.* for $\phi(r) \equiv 0$), the equation defining the generating function of branches t (14) has a unique solution which is invariant with respect to translations and approaches unity when $\epsilon \to 0$. This solution is easy to find as equation (14) becomes purely algebraic due to the aforementioned translation invariance:

$$t = \frac{1 - \sqrt{1 - 2\epsilon}}{\epsilon} , \tag{18}$$

where we took into account that $\int g(r)\mathrm{d}r = 1$. Note that all other solutions (in particular that approaching infinity when $\epsilon \to 0$) do not have any physical meaning and therefore in case of spatially inhomogeneous external field we will be interested only in solutions of equation (14), which approach the solution given by equation (18) when $r \to \infty$; $\phi(r) \to 0$.

The equilibrium densities of junctions and dead ends can be easily calculated in the way prescribed in the previous section. Indeed, we have

$$\rho = \lambda \frac{t^3}{3!} = \lambda \frac{(2 - 3\epsilon) - (2 - \epsilon)\sqrt{1 - 2\epsilon}}{3\epsilon^3} \tag{19}$$

for the generating function of all rooted randomly branched trees. The general expression for randomly branched trees with f missing bonds in the root (compare to (15)) reads

$$\sigma_f = \lambda \frac{(t - 1)^{(3-f)}}{f!(3 - f)!} . \tag{20}$$

Expanding equations (19, 20) into series with respect of ϵ and substituting the results into equation (16), one obtains finally the probabilities of junctions and dead ends:

$$p_0(N) = \frac{(N - 2)(N - 1)}{2(N + 1)(2N + 1)}; \;\; p_2(N) = \frac{(N + 5)}{2(2N + 1)} , \tag{21}$$

both values approaching 1/4 as N tends to infinity.

Now, to calculate the correlation function $G(r_1, r_2)$ in the bulk we substitute equation (18) into equation (17) and get

$$G(r) = g(r) + (1 - \sqrt{1 - 2\epsilon}) \int g(r')G(r - r')\mathrm{d}^3r' \tag{22}$$

(note that the correlation function in the bulk depends only on the distance between two roots $r = r_1 - r_2$).

There are various methods of solving (22); we will stick here to the one which seems to be the most suitable to be generalized in what follows to the case of the semi-space. As soon as we are interested mostly in the asymptotic characteristics of the trees when N is large, we can fully neglect all the short-range (*i.e.* on the scales of order $r \sim a$) peculiarities of a correlation function. We therefore replace the first term of the r.h.s. of (22) by a Dirac delta-function $\delta(r)$ (see Eqs. (3-4)) and expand the slowly changing function $G(r - r')$ into the series up to the second order in $(r - r')$ (see also [37]). After calculating the integrals we arrive at the following differential equation:

$$G(r) = \delta(r) + (1 - \xi) \left(G(r) + \frac{a^2}{6} \Delta G(r) \right) , \tag{23}$$

where we have introduced a new variable,

$$\xi = \sqrt{1 - 2\epsilon} .$$

As the function $G(r)$ depends on r only, we can rewrite the Laplace operator as $\Delta = r^{-2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right)$. Denoting $R = \frac{r\sqrt{6}}{a}\sqrt{\frac{\xi}{1-\xi}}$, we can rewrite equation (23) as follows (for $R > 0$):

$$G''(R) + 2R^{-1}G'(R) - G(R) = 0 . \tag{24}$$

Therefore, one gets finally the correlation function in the bulk

$$G(r) = A\frac{\exp(-R)}{R} , \tag{25}$$

which allows us to re-derive the well-known result (see [30, 31]) for the gyration radius of the tree:

$$\begin{aligned} \left\langle r^2(\epsilon) \right\rangle &= \frac{\int r^2 G(r)\mathrm{d}^3 r}{\int G(r)\mathrm{d}^3 r} \sim a^2 \left(\xi^{-1} - 1\right) ; \\ \left\langle r^2(N) \right\rangle &\sim a^2 N^{1/2}. \end{aligned} \tag{26}$$

It is worthwhile also to rewrite the result (25) in the cylindric coordinates:

$$\begin{aligned} G(Z, \rho) = A \,&\frac{\exp(-\sqrt{Z^2 + \rho^2})}{\sqrt{Z^2 + \rho^2}} = \\ &A \int_1^{+\infty} \exp(-c|Z|) J_0\left(\rho\sqrt{c^2 - 1}\right) \mathrm{d}c, \end{aligned} \tag{27}$$

where $J_0(x)$ is a Bessel function of 0-th order, and the variables (Z, $\rho = \sqrt{x^2 + y^2}$) are the usual cylindric coordinates renormalized by the factor $\frac{\sqrt{6}}{a}\sqrt{\frac{\xi}{(1-\xi)}}$.

4 Generating function t in a half-space

Assume now that our branched polymer is displaced in a semi-space $x \geq 0$. The presence of an impenetrable wall situated at $x = 0$ is described by the potential $\phi(r) \equiv \phi(x, y, z)$, where

$$\phi(x, y, z) = \begin{cases} 0 & \text{for } x \geq 0 \ , \\ \infty & \text{for } x < 0 \ . \end{cases} \tag{28}$$

In this case one can rewrite (14) as follows:

$$t(x, y, z, \epsilon) = 1 + \frac{\epsilon}{2} \int_0^\infty \mathrm{d}x \int_{-\infty}^\infty \mathrm{d}z \int_{-\infty}^\infty \mathrm{d}y \, g(x, y, z; x', y', z') \times t^2(x', y', z', \epsilon) \ . \tag{29}$$

To solve equation (29), we suggest the following procedure. First of all we represent (29) in the form:

$$\hat{g}^{-1}(t - 1) = \frac{\epsilon}{2} t^2 \ , \tag{30}$$

where $\hat{g}^{-1}$ is the inverse operator of $\hat{g}$, the latter being defined as

$$\hat{g} f(r) = \int g(r, r') f(r') \mathrm{d}r' \ .$$

Following [35] we expand $(t - 1)$ in (30) in the series up to the second order in $(x - x')$:

$$t(x', y', z') - 1 = t(x, y, z) - 1 + (x - x') \frac{\partial t}{\partial x} + \frac{(x - x')^2}{2} \frac{\partial^2 t}{\partial x^2} + \dots \ , \tag{31}$$

where we took into account that for obvious physical reasons t depends neither on y nor on z. This expansion is valid for a sufficiently smooth function $t(r)$. Therefore, in the case under consideration this substitution is acceptable if we are not too close to the surface (the wall). Substituting (31) into (30), we obtain finally

$$\hat{g}^{-1}(t - 1) \simeq t(x, \epsilon) - 1 + \frac{a^2}{6} \frac{\partial^2 t(x, \epsilon)}{\partial x^2}, \tag{32}$$

which results in the following differential equation instead of the integral one:

$$t(\widetilde{x}, \epsilon) - 1 - \frac{\partial^2 t(\widetilde{x}, \epsilon)}{\partial \widetilde{x}^2} = \frac{\epsilon}{2} t^2(\widetilde{x}, \epsilon) \ , \tag{33}$$

where

$$\widetilde{x} = \frac{x\sqrt{6}}{a}$$

is a reduced distance from the surface.

The differential equation (33) can be solved via the substitution $p(t) = \frac{\partial t}{\partial \widetilde{x}}$. We get, after some algebra,

$$\widetilde{x}(\epsilon, t) = \int_{t_0}^t \frac{\mathrm{d}y}{\sqrt{-\frac{2\epsilon}{3} y^3 + 2y^2 - 4y + \frac{4}{3} \frac{(1-2\epsilon)^{3/2} - 1 + 3\epsilon}{\epsilon^2}}} \ , \tag{34}$$

where $t_0 = t(0, \epsilon) \geq 1$ is a boundary value of t to be specified later (one could not define this boundary condition *a priori*, as the boundary $x = 0$ does not belong to the region where the substitution (31) is valid; see Section 6 for the discussion of the proper choice of t_0) and we have already used the boundary conditions at $+\infty$:

$$\begin{cases} \lim\limits_{x \to +\infty} t = \dfrac{1 - \sqrt{1 - 2\epsilon}}{\epsilon} \ , \\ \lim\limits_{x \to +\infty} \dfrac{\mathrm{d}t}{\mathrm{d}\widetilde{x}} = 0 \end{cases} \tag{35}$$

to define the last term in the denominator in (34).

Performing the substitution

$$\begin{aligned} \xi &= \sqrt{1 - 2\epsilon} \ , \\ s &= 1 + (\epsilon y - 1)\xi^{-1} \ , \end{aligned} \tag{36}$$

we arrive at the simple integral for the function $\widetilde{x}(\epsilon, t)$:

$$\widetilde{x}(\epsilon, t) = \sqrt{\frac{3}{2\xi}} \int\limits_{1 + (\epsilon t_0 - 1)/\xi}^{1 + (\epsilon t - 1)/\xi} \frac{\mathrm{d}s}{s\sqrt{3 - s}} \ , \tag{37}$$

which we can easily evaluate:

$$\widetilde{x}(\xi, t) = \frac{2}{\sqrt{\xi}} \left(\operatorname{arctanh} \frac{\sqrt{2 + 4\xi + t(\xi^2 - 1)}}{\sqrt{6\xi}} - \operatorname{arctanh} \frac{\sqrt{2 + 4\xi + t_0(\xi^2 - 1)}}{\sqrt{6\xi}} \right) . \tag{38}$$

Inverting (38) we obtain the desired partition function $t(\widetilde{x})$:

$$t(\widetilde{x}) = \frac{1}{\epsilon} \left[1 - \xi - 3\xi \sinh^{-2} \frac{\widetilde{x}\sqrt{\xi} + \ln g(\xi, t_0)}{2} \right] , \tag{39}$$

where the auxiliary function $g(\xi, t_0)$ reads

$$g(\xi, t_0) = \frac{\sqrt{2 + 4\xi + t_0(\xi^2 - 1)} + \sqrt{6\xi}}{\sqrt{2 + 4\xi + t_0(\xi^2 - 1)} - \sqrt{6\xi}} \ . \tag{40}$$

Note that as $\widetilde{x}$ tends to infinity, the function sinh(...) in (39) does too and, therefore, the function $t(x)$ approaches its bulk value (18).

5 Partition function of a randomly branched polymer near the surface

To compute the desired partition function $C_N(r)$ of a single randomly branched polymer, consisting of $N + 1$ links, one of which is fixed at a given point r, we should expand the generating function

$$\rho(\lambda, \epsilon, r) = \frac{\lambda \, t^3(\epsilon, r)}{6} \ , \tag{41}$$

where t is given by (39), in the power series in ϵ. We perform this expansion in two successive steps. First we expand t in the power series in ξ:

$$
\begin{aligned}
t = {} & 2(1-3x_0^{-2}) - 2\Bigg(1 - 3x_0^{-2} + \frac{x_0^2}{5} - \frac{3\sqrt{6}}{5}\,x_0^{-3} \\
& \times \frac{5t_0^2+12-10t_0}{(2-t_0)^{5/2}}\Bigg)(1-2\epsilon) + \frac{4}{63}x_0^{-3} \\
& \times \left(x_0^7 + 2\left(\frac{6}{2-t_0}\right)^{7/2}\right)(1-2\epsilon)^{3/2} + \mathrm{O}\left((1-2\epsilon)^2\right),
\end{aligned} \tag{42}
$$

where

$$
x_0 = \frac{\widetilde{x}}{2} + \frac{\sqrt{6}}{\sqrt{2-t_0}}\sqrt{6}\left(\frac{x}{2a} + \frac{1}{\sqrt{2-t_0}}\right) \tag{43}
$$

is a reduced coordinate, and we have used (36) to replace ξ by ϵ. Thus, the first singular (with respect to ϵ) term in the series expansion of $t(\epsilon, r)$ is proportional to $(1-2\epsilon)^{3/2}$ and not to $(1-2\epsilon)^{1/2}$ as in the bulk case. Now, the first singular term in the series for $\rho(\lambda, \epsilon, r)$ is equal to

$$
\begin{aligned}
\rho^{(1)}_{\mathrm{sing}} = {} & \frac{8x_0^{-3}}{63}\, z(1-3x_0^{-2})^2 \\
& \times \left(x_0^7 + 2\left(\frac{6}{2-t_0}\right)^{7/2}\right)(1-2\epsilon)^{3/2}.
\end{aligned} \tag{44}
$$

Now, taking into account that

$$
(1-2\epsilon)^{3/2} = 1 - 3\epsilon + \frac{3}{2}\epsilon^2 + 3\sum_{N=3}^{\infty}\frac{(2N-5)!!}{N!}\epsilon^N
$$

and allowing for the asymptotic behavior of the coefficients in the above sum:

$$
\frac{(2N-5)!!}{N!} = 2^N\, N^{-5/2}\left(1 + \mathrm{O}(N^{-1})\right),
$$

we obtain that the desired partition function $C_n(r)$ for $n \gg 1$ tends to

$$
C_N(x_0) = A(x_0)\, N^{-\theta}\, \epsilon^N, \tag{45}
$$

where the function $A(x)$ depends on the microscopic parameters of the model:

$$
A(x_0) = \frac{8}{7}\, x_0^{-3}\left(1-3x_0^{-2}\right)^2\left(x_0^7 + 2\left(\frac{6}{2-t_0}\right)^{7/2}\right) \tag{46}
$$

and the exponent $\theta = \frac{5}{2}$ is universal.

If x_0 is large enough (*i.e.* we are not too close to the surface), one can neglect all the sub-dominant contributions of x_0 and can rewrite (45)-(46) in a simpler form:

$$
C_N(r) \simeq \frac{2^N}{N^{3/2}}\left(\frac{x^4}{N\,a^4}\right). \tag{47}
$$

Note that the additional (in comparison with the bulk case) factor

$$
\frac{x^4}{N\,a^4} = \left(\frac{\langle x\rangle}{a\,N^{1/4}}\right)^4
$$

is just the 4-th power of the distance from the surface to the gyration radius of the randomly branched polymer (26). Thus, in contrast to the bulk behavior, the partition function of the randomly branched polymer near the surface carries the information about the spatial dimension of the branched polymer.

6 The probability of branching

Our next objective is to calculate the probabilities of f-functional branchings, $p_f(r, N)$ ($f = 1...3$) in a $N+1$-monomer tree. As we are mostly interested in the case of very large trees, we restrict ourselves here to the calculation of the limiting values $p_f(r) = \lim_{N\to\infty} p_f(r, N)$. To do that we should find, according to (16), the asymptotic form of the coefficients $C_N(r)$ and $C_N^{(f)}(r)$ in the series expansions of $t^3(r)$ for $C_N(r)$ and of $(t(r)-1)^3$, $3(t(r)-1)^2$, $3(t(r)-1)$ for $C_N^{(1)}(r)$, $C_N^{(2)}(r)$, $C_N^{(3)}(r)$, respectively. Thus, we find in particular for the probability of junctions ($f = 3$)

$$
\begin{aligned}
C_N(r) = {} & \frac{4}{7x_0^3}\left(2 - \frac{6}{x_0^2}\right)^2\left(x_0^7 + 2\left(\frac{6}{2-t_0}\right)^{7/2}\right) \\
& \times 2^N N^{-5/2}\left(1 + \mathrm{O}\left(N^{-1}\right)\right), \\
C_N^{(3)}(r) = {} & \frac{4}{7x_0^3}\left(1 - \frac{6}{x_0^2}\right)^2\left(x_0^7 + 2\left(\frac{6}{2-t_0}\right)^{7/2}\right) \\
& \times 2^N N^{-5/2}\left(1 + \mathrm{O}\left(N^{-1}\right)\right)
\end{aligned} \tag{48}
$$

and therefore

$$
p_3(r) = \left(\frac{x_0^2 - 6}{2x_0^2 - 6}\right)^2. \tag{49}
$$

Similarly, one easily finds for the probability of dead ends ($f = 1$):

$$
p_1(r) = \lim_{N\to\infty}\frac{C_N^{(1)}(r)}{C_N(r)} = \frac{x_0^4}{\left(2x_0^2 - 6\right)^2}. \tag{50}
$$

In Figure 5 we have plotted the dependencies $p_{1,3}(x_0)$. As $x_0 \to \infty$, these probabilities approach their bulk values given by equation (21).

On the other hand, if one chooses t_0, which is the boundary value of the function $t(x)$ to equal unity ($1 \le t(x) \le 2$ for $0 \le x < \infty$ (see Eq. (14)), the value of x_0 approaches $\sqrt{6}$ near the wall and the probabilities of dead ends and junctions tend to unity and zero, respectively. This result seems to be rather natural: as the wall is impenetrable at $x = 0$, there should be mostly dead ends. Therefore, we arrive at the conclusion that the choice of $t_0 = 1$ is at least the most natural one thus solving the problem of proper choice of the boundary conditions at $x = 0$ outlined in the discussion after equation (34). We restrict ourselves to this choice in what follows.

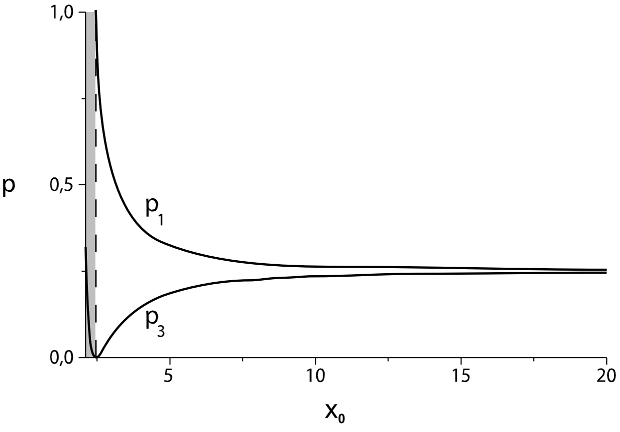

Fig. 5. Profiles of junction points, p_1, and of dead ends, p_3. The dashed line corresponds to $x_0 = \sqrt{6}$.

7 The correlation function in the semi-space

To find the correlation function $G(r_1, r_2)$ of a randomly branched polymer in a semi-space in 3D we have to solve equation (17), where the partition function $t(r)$ given by equation (39). To do that, let us multiply (17) by $\epsilon t(r_1)$ and define a new function

$$\Gamma(r_1, r_2) = \epsilon\, t(r_1) G(r_1, r_2).$$

After such substitution we get

$$\Gamma(r_1, r_2) = \epsilon\, t(r_1) \biggl(g\left(|r_1 - r_2|\right) + \int g\left(|r_1 - r_3|\right) \Gamma(r_3, r_2) \mathrm{d}^3 r_3 \biggr) . \quad (51)$$

Similarly to what we have done in the previous sections we substitute $g(|r_1 - r_2|) = \delta(r_1 - r_2)$ into the first term of the r.h.s. of (51) and expand $\Gamma(r_3, r_2)$ up to the second order in $(r_1 - r_3)$. Evaluating the integrals we arrive at the following differential equation:

$$\Gamma(u, v, \rho) = \epsilon\, t(u + v) \left(\Gamma(u, v, \rho) + \Delta_{u,\rho} \Gamma(u, v, \rho)\right) , \quad (52)$$

where

$$v = \frac{\sqrt{6} x_2}{a}; \qquad u = \frac{\sqrt{6}(x_1 - x_2)}{a}; \qquad \rho = \frac{\sqrt{6((y_1 - y_2)^2 + (z_1 - z_2)^2)}}{a} . \quad (53)$$

In what follows we assume $u > 0$. Such choice does not lead to any loss of generality due to the symmetry of the correlation function: $G(r_1, r_2) = G(r_2, r_1)$ and the case of $u = 0$ is to be taken into account via boundary conditions).

Now we seek for the solution of equation (52) in the form

$$\Gamma(u, v, \rho) = \int f(c, v) \Gamma_1(c, u) \Gamma_2(c, \rho) \mathrm{d}c , \quad (54)$$

where the arbitrary function $f(c, v)$ is to be determined later by the boundary conditions. The ansatz (54) allows us to separate the variables in (52). We thus obtain a simple equation for Γ_2

$$\rho^{-1} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial \Gamma_2}{\partial \rho} \right) = c^2 \Gamma_2 \quad (55)$$

the general solution of which is

$$\Gamma_2(c, \rho) = A\, J_0(c\rho) + B\, Y_0(c\rho) , \quad (56)$$

where J_0 and Y_0 are the Bessel functions of the first and second kind. Due to the boundary condition $\Gamma(c, 0) < \infty$, we set $B = 0$.

The equation for Γ_1 is as follows:

$$\frac{\partial^2 \Gamma_1}{\partial u^2} = \left(c^2 + \varphi(u, v)\right) \Gamma_1; \;\; \varphi(u, v) = \frac{1 - \epsilon\, t(u + v)}{\epsilon\, t(u + v)} . \quad (57)$$

If we plug the exact expression (39) for $t(u + v)$ into (57), the resulting equation seems to be not solvable. However, if we approximate the genuine function $\varphi(u, v)$ by its asymptotics in the most interesting regime $\xi \to 0$ (*i.e.* $N \to \infty$) and $a\xi^{-1/2} \gg x_1 \gg a$,

$$\varphi(u, v) \approx \frac{12}{(u + v + p)^2} , \quad (58)$$

where $p = 2\sqrt{6} = \lim_{\xi \to 0} \left(\xi^{-1/2} \ln g(\xi)\right)$, the resulting differential equation is solvable (by reduction to the Bessel one) precisely.

The corresponding solution is, however, not too accurate. To obtain an improved solution, which approximates the genuine one in the whole range of variables u, v, we are looking for the proper replacement of the genuine function $\varphi(u, v)$ defined in (57) in the form

$$\widetilde{\varphi}(u, v) = \frac{c_1(v)}{(u + c_2(v))^2} ,$$

thus preserving the limiting behavior of φ at $u \to \infty$, $\xi \to 0$. To preserve the limiting behavior of (57) at $u \to 0$ we now need to set

$$\begin{cases} \varphi(u = 0, v) = \widetilde{\varphi}(u = 0, v) , \\ \left.\dfrac{\partial \varphi(u, v)}{\partial u}\right|_{u=0} = \left.\dfrac{\partial \widetilde{\varphi}(u, v)}{\partial u}\right|_{u=0} , \end{cases}$$

which results into

$$\widetilde{\varphi}(u) \simeq \frac{12((p + v)^2 - 12)}{((p + v)(u + p + v) - 12)^2} . \quad (59)$$

At last, in the limit of $u \gg \xi^{-1/2}$ one should replace φ by its bulk value $\varphi = \xi/(1 - \xi)$ which does not depend on u and therefore does not affect the desired solubility of the differential equation (57). Thus, finally,

$$\widetilde{\varphi}(u) = \frac{\xi}{1 - \xi} + \frac{12((p + v)^2 - 12)}{((p + v)(u + p + v) - 12)^2} \quad (60)$$

seems to satisfy the desired conditions, both being a good approximation of φ in the whole range of parameters and

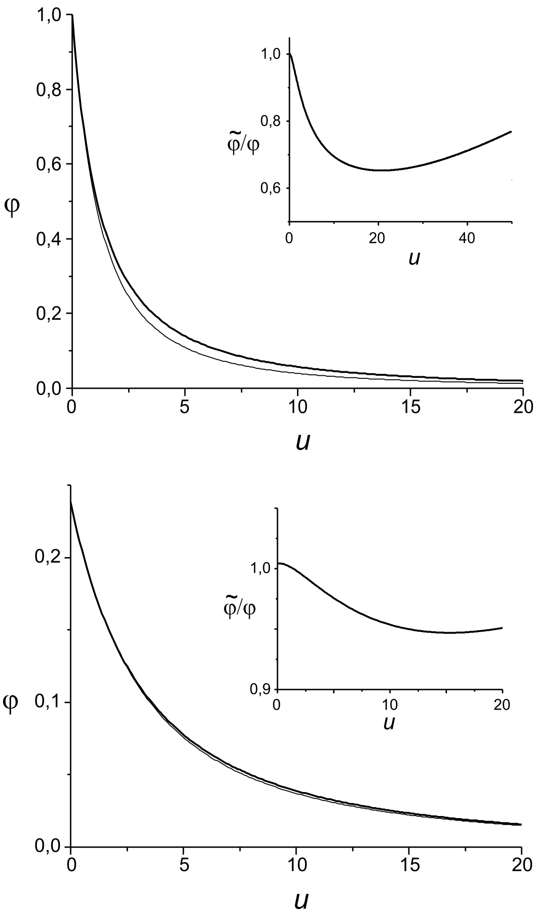

Fig. 6. Plots of the functions $\widetilde{\varphi}(u,v)$ (thin line) and $\varphi(u,v) = \frac{1-\beta t(u+v)}{\beta t(u+v)}$ (bold line) for $v=0$ (top) and for $v=3$ (bottom). The insertions in both plots show the ratio $\widetilde{\varphi}/\varphi$.

making equation (57) solvable. The comparison of the functions $\widetilde{\varphi}(u,v)$ and $\varphi(u,v) = \frac{1-\epsilon\, t(u+v)}{\epsilon\, t(u+v)}$ for two different values of the parameter v ($v=0$ and $v=3$) is shown in Figure 6.

As one sees, the approximation of the exact function $\varphi(u,v)$ by the function $\widetilde{\varphi}(u,v)$ is reasonable for $v=0$ and already very good for $v=3$. Let us recall that the distance from the wall $v=3$ in the non-renormalized (initial) coordinates according to (53) is $x_2 = 3a/\sqrt{6} \approx 1.22a$.

The resulting differential equation

$$\Gamma_1'' = (c^2 + \widetilde{\varphi}(u))\Gamma_1$$

is solved precisely via substitution $w = u + v + p - \frac{12}{v+p}$. Taking into account the boundary condition $\Gamma_1 \to 0$ at infinity, one obtains the final result in the following form:

$$\Gamma_1 = \sqrt{pw}\, K_\nu(c'w)\,, \tag{61}$$

where $K_\nu(c'v)$ is a modified Bessel function of 2nd kind of order ν, and the parameters are as follows:

$$\nu = \frac{\sqrt{49(v+p)^2 - 576}}{2(v+p)}, \quad c' = \sqrt{c^2 + \frac{\xi}{1-\xi}}\,. \tag{62}$$

Substituting (56), (61) into (54) we arrive at the desired solution of equation (52):

$$\Gamma(u,v,\rho) = \int f(c,v)\; J_0(c\rho)\; \sqrt{pw}\, K_\nu(c'w)\; \mathrm{d}c\,. \tag{63}$$

To make this equation comparable with that in the bulk case (27), let us introduce the new variables:

$$C = \sqrt{\frac{c^2(1-\xi)}{\xi} + 1}; \quad \left\{ \begin{matrix} R \\ U \\ V \\ W \\ P \end{matrix} \right\} = \sqrt{\frac{\xi}{1-\xi}} \left\{ \begin{matrix} \rho \\ u \\ v \\ w \\ p \end{matrix} \right\}. \tag{64}$$

After such a substitution, the correlation function acquires the form

$$\Gamma(U,V,R) = \int f(C,V)\; J_0(R\sqrt{C^2-1})\; \sqrt{W}\, K_\nu(CW)\, \mathrm{d}C. \tag{65}$$

The unknown function $f(C,V)$ is to be determined by the boundary conditions

$$\Gamma(U,V,R)\Big|_{U \gg 1 \text{ or } V \gg 1} \to \epsilon\, t_{\text{bulk}}\; G_{\text{bulk}}(\sqrt{U^2+R^2})\,. \tag{66}$$

One thus easily finds

$$f(C,V) \sim \sqrt{C} \exp\left[C\left(V + P - \frac{12}{V+P} \right) \right], \quad C > 1\,, \tag{67}$$

where we have omitted all terms which do not depend on c and v. Let us stress that the condition $C > 1$ ultimately defines the limits of integration in (67). Thus we finally arrive at the following expression for the correlation function:

$$\begin{aligned} G(u,v,\rho) = &\int_1^{+\infty} \sqrt{CW} e^{C(V+P-12(V+P)^{-1})} \\ &\times K_\nu(CW) J_0\left(R\sqrt{C^2-1}\right) \mathrm{d}C\,. \end{aligned} \tag{68}$$

Figure 7 shows the dependencies $G(U)$ for different values of V as compared with the bulk behavior. One sees easily how the presence of the wall affects the correlation function. In particular, it is interesting to note the increase of the polymer density in the vicinity of the wall, and also the smaller increase of the density in the outer region due to polymer-wall hardcore repulsion. The rapid decrease of the correlation function for $V = 0.05$ with the growth of U is due to the fact that in the system controlled by the fugacity ϵ, the mean size of clusters in the vicinity of the wall is much smaller than that in the bulk (this is clearly outlined by the fact that $t(x) \to 1$ as $x \to 0$).

8 Discussion

Summarizing, in this paper we presented a rigorous procedure to describe the behavior of the large ideal trees

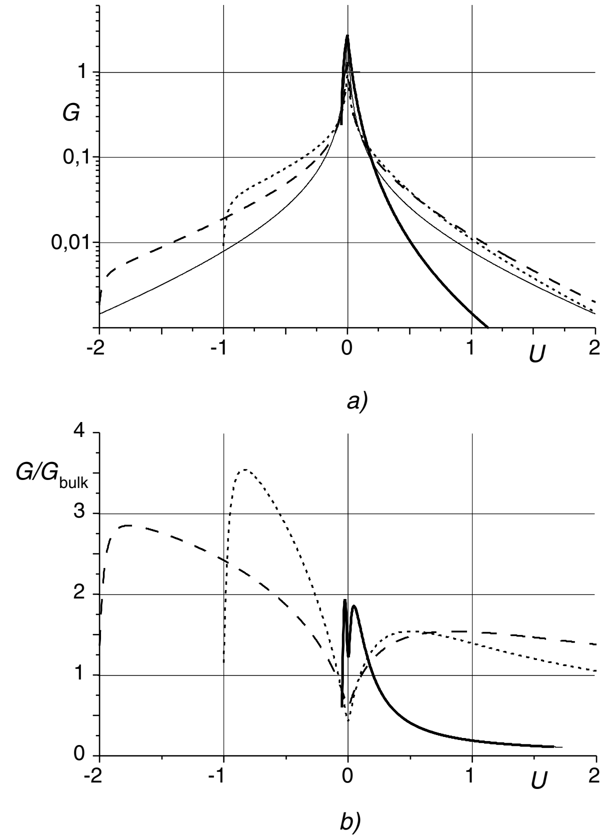

Fig. 7. a) The correlation functions $G(U,V,R)$ for $\xi = 10^{-4}$, $R = 0.01$ and $V = 0.05$ (dotted line), $V = 1$ (dashed line) and $V = 2$ (dot-dashed line) as compared to the bulk correlation function for similar R (bold line). All the curves are normalized by the condition $\int G(U,V,R)\mathrm{d}U = 1$; b) The ratios $G(U,V,R)/G_{\mathrm{bulk}}(U,R)$ for values of ξ, R and V similar to that in a).

near the impenetrable (non-adsorbing) wall and obtained rather accurate approximate expressions both for the partition function and 2-point correlation functions of the system.

For comparison of our results with those obtained earlier [28,29], we need a better understanding of the applicability of the original approximations of "large" and "no" excluded volume.

For simplicity, let us fully neglect the attractive interactions between the monomers. In this case, the only volume interactions in the system are those due to the excluded volume. To estimate how much these interactions disturb the original conformation of the non-interacting polymer one should (see [3]) calculate the mean number of pairwise contacts of the monomers. This value equals $n_2 = \rho N$, where ρ, which is the mean density of the polymer, can be calculated as $\rho = Nv/R_g^D \sim (v/a^3)N^{1/4}$, where v is the excluded volume per monomer. One can estimate that the theory presented above should be valid when the number of pairwise contacts (and therefore, as one can easily see, also the contacts of higher order, *i.e.* triple, etc.) is negligible, or, in other words, if $N \ll (a^3/v)^{4/5}$. On the contrary, if $N \gg (a^3/v)^{4/5}$, we expect the results of [29] to be valid. Note that the experimental value of the key parameter $Li = v/a^3$ (we refer to it as the Lifshitz parameter) can vary widely. *E.g.,* for the lattice models $Li \sim 1$ and, therefore, lattice trees almost never could be considered as ideal ones. On the contrary, for many real polymer systems $Li \ll 1$. Indeed, imagine, for example, a tree constructed of star-like monomers, whose arms are long polymer chains with associating groups at the end. For the polymers of such architecture, one can expect the Lifshitz parameter Li to be much less than unity. Thus, though in the limit of $N \to \infty$ the volume interactions are always important, there can be a rather wide range of polymer sizes $1 \ll N \ll Li^{-4/5}$, where the results obtained above are correct.

As is mentioned in the introduction, the statistics of randomly branched ideal polymer chain near the impenetrable boundary was studied by supersymmetric methods in the work [29], where the authors follow the general scheme of the supersymmetric "dimensional reduction" for branched random walks formulated for the first time in [22] and exploited later in [23,24]. The authors of the paper [29] have computed many thermodynamic properties of branched polymer chains near the repulsive and the adsorbing impenetrable surfaces in 3D. For our purposes, the most important are those of these results, which are related to the "non-adsorbing" (*i.e.* repulsive) regime.

In [29] the authors have got the following results below the adsorbing transition point for the quantities of our interest:

$$\begin{cases} \theta = \frac{5}{2}\,, \\ G_N(z,z') = \mathrm{erfc}(\zeta - \zeta') + \mathrm{erfc}(\zeta + \zeta') - 2\mathrm{erfc}(\zeta) \\ \qquad\qquad + 16\Gamma^2 \exp\left[\Gamma(\Gamma - 2\zeta - 2\zeta')\right]\,, \end{cases} \tag{69}$$

where

$$\zeta = z\sqrt{N}, \quad \zeta' = z'\sqrt{N}, \quad \Gamma = E\sqrt{N}$$

and E is some constant independent of N.

It can be seen that the surface critical exponent $\theta = \frac{5}{2}$ obtained in our work (Eqs. (45, 47)) coincides with the one of [29] (computed also in [28]). We can thus assume that this critical exponent seems to be independent of volume interactions, therefore being genuine for all $N \gg 1$ independently of the Lifshitz parameter Li.

Now, as far as the correlation function is concerned, its behaviour depends on the regime significantly. Indeed, (69) suggests the characteristic length scale of the problem to be of order $r \sim \sqrt{N}$ (this result being in compliance with the gyration radius for the randomly branched polymers with excluded volume as obtained in [22]). On the contrary, our approach results into $r \sim N^{1/4}$, as the integral in (68) is mostly defined by its lower limit (see also (47), where this characteristic scale is clearly outlined), in full coincidence with that obtained for the characteristic scale for the non-interacting randomly branched polymer in the bulk (compare to [31,30] and Eqs. (25, 26) in this paper).

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