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INTERNAL LINKS OF THE POLYMER CHAIN IN THE SELF–AVOIDING RANDOM WALKS STATISTICS

Key words: macromolecule, internal link, conformation, distribution, solution.

Within the frame of the self–avoiding random walks statistics (SARWS), the derivation of the internal n–link (1<<n<<N) distribution of the polymer chain with respect to the chain ends is suggested. The analysis of the obtained expressions shows, that the structure of the conformational volume of the polymer chain is heterogeneous; the largest density of the number of links takes place in conformational volumes nearby the chain ends. It can create the effect of blockage of the active center of the growing macroradical and manifest itself as a linear chain termination. The equation for the most probable distance between two internal links of the polymer chain was obtained as well. The polymer chain sections, separated by fixing the internal links, are interactive subsystems. Their total conformational volume is smaller than the conformational volume of undeformed Flory coil. Therefore, total free energy of the chain sections conformation equals to free energy of the conformation of deformed (i. e. compressed down to the total volume of the chain sections) Flory coil.

Ключевые слова: макромолекула, внутренняя связь, конформация, распределение, решение.

В рамках статистики случайных блужданий без самопересечения (СБСС) предлагается вывод распределения внутренней n-связи (1<<n<<N) полимерной цепи относительно ее концов. Анализ полученных выражений показывает, что структура конформационного объема полимерной цепи является гетерогенной; наибольшее количество связей имеет место в конформационном объеме около концов цепи. Это может создать эффект блокирования активного центра растущего макрорадикала и проявляться в виде линейного обрыва цепи. Также было получено уравнение для наиболее вероятного расстояния между двумя внутренними связями полимерной цепи. Участки полимерной цепи, разделенные фиксированием внутренних связей, являются интерактивными подсистемами. Их общий конформационный объем меньше конформационного объема недеформированного клубка Флори. Таким образом, общая свободная энергия конформации участков цепи равна свободной энергии конформации деформированного (т. е. сжатого до общего объема участка цепи) клубка Флори.

Introduction

In *Gaussian* random walks statistics, the mean–square end–to–end distance R for a polymer chain, as well as mean–square distance between two not very closely located internal links obey general dependence[1]:

$$R = an^{1/2} \qquad n >> 1 \tag{1}$$

where a is the mean length of the chain link according to *Kuhn*[2]; n is the chain length or the length of a given chain section, expressed by the number of links in it.

Self–avoiding random walks statistics *(SARWS)* determines the conformational radius $R_{N,f}$ of the undeformed *Flory* coil as the most probable end–to–end distance of the polymer chain[3,4]:

$$R_{N,f} = aN^{3/(d+2)} \tag{2}$$

Here N is the total chain length, d is the *Euclidian* space dimension.

According to (2), *Flory* coil is a fractal, *i. e.* an object, possessing the property of the scale invariance in dimensionality space $d_f = (d+2)/3$.

At derivation[3] of (2), however, the distribution of the internal polymer chain links in its conformational space remains unknown, therefore, it can not be indicated in advance that the distances between the terminal and internal chain links or between the internal ones obey the same dependence (2) at the value of N as the length of the selected section of a polymer chain.

Study of the problem of internal polymer chain links' distribution is based mainly on the analysis [5,6] of the scale distribution function $P_{ij}(r)$ of distance r between two links with ordinal numbers i and j:

$$P_{ij}(r) = |i-j|^{-d\upsilon} f\left(r/|i-j|^{\upsilon}\right) \tag{3}$$

Function $f\left(r/|i-j|^{\upsilon}\right) = f(x)$ is usually written in the form of power or exponential dependence on the only variable x:

$$f(x) \sim x^{\theta} \qquad \text{at } x << 1,$$
$$f(x) \sim exp\{-x^{\delta}\} \qquad \text{at } x >> 1. \tag{4}$$

Studying the correlations between two arbitrary points i and j of a polymer chain, *Des Cloizeaux*[7] suggested dividing the scale function $P_{ij}(r)$ into three classes, that describe the distribution of distances between two terminal points of a polymer chain ($P^{(0)}_{ij}(r)$ with exponents θ_0 and δ_0 at $i = 1, j = N$), between the initial and internal points ($P^{(1)}_{ij}(r)$ with exponents θ_1 and δ_1 at $i = 1$, $1 << j << N$) and between two internal points ($P^{(2)}_{ij}(r)$ with exponents θ_2 and δ_2 at $1 << i << j << N$), respectively.

Using the method of the second order ε–expansion within the range $x << 1$ for the space $d = 3$, *Des Cloizeaux*[7] has obtained in particular: $\theta_o = 0,273$, $\theta_1 = 0,459$, $\theta_2 = 0,71$.

To evaluate the exponents θ_i and δ_i some other methods were used as well. Let us present some of the obtained results: [8]θ_o = 0,27; [8,9,10]θ_1 = 0,55, 0,61, 0,70; [8,9]θ_2 = 0,9, 0,67; [8,11]δ_o = 2,44, 2,5; [8]δ_1 = 2,6; [8]δ_2 = 2,48.

In spite of the spread in exponent values, they unambiguously indicate (especially when comparing the values of θ_o, θ_1 and θ_2), that distribution function $P_{ij}(r)$, retaining their scale universality, quantitatively significantly depends on whether we consider the distance between terminal points, a terminal and internal one or between two internal points of a polymer chain. Whereas the proposed methods of analysis establish this fact, they however do not reveal the reason of the above–mentioned difference. Reference to strengthening the effects of the volume interaction between the internal links of a polymer chain can not be absolutized, since these effects can not be taken into account at computer simulation of self–avoiding random walks, but the results of the calculations according to them give the same estimations of exponents θ_i and δ_i as the analytic methods that take into account the volume interaction.

The shortcoming of the proposed approaches is also the fact that the scale distribution function $P_{ij}(r)$ is approximate and does not enclose the most significant region of parameter x changing between $x << 1$ and $x >> 1$, where $P_{ij}(r)$ takes on maximal values. Finally, it should be noted that the role of the length of the second section of a polymer chain (at evaluating θ_1 and δ_1 the length of the second section is extrapolated to ∞) or the lengths of its two sections (at evaluating θ_2 and δ_2) is outside of the analysis.

Hence, the suggested approaches do not allow to solve the problem of the internal links distribution for a polymer chain completely. In the present work we propose its analytic solution in terms of *SARW* strict statistics, *i. e.* without taking into account of the so–called volume interaction.

Initial statements

Preliminary let us briefly introduce the main statements of *SARW* statistics, that are necessary for the subsequent analysis[3,4]. The *Gaussian* random walks in *N* steps are described by the density of the *Bernoulli* distribution:

$$\omega(N,s)=\left(\frac{1}{2}\right)^N\prod_i\frac{n_i!}{[(n_i+s_i)/2]![(n_i-s_i)/2]!},\qquad(5)$$

where n_i is a number of the random walk steps in i–direction of d–dimensional lattice space with the step length a, which is equal to the statistical length of *Kuhn* link; s_i is the number of effective steps in i–direction: $s_i = s_i^+ - s_i^-$, where s_i^+, s_i^- are numbers of positive and negative steps in i–direction. Numbers of n_i steps are limited by the following correlation:

$$\sum_i n_i = N\cdot\qquad(6)$$

The condition of self-avoidance of a random walk trajectory on d–dimensional lattice demands the step not to fall twice into the same cell. From the point of view of chain link distribution over cells it means that every cell can not contain more than one chain link. Chain links are inseparable. They can not be torn off one from another and placed to cells in random order. Consequently, the numbering of chain links corresponding to wandering steps is their significant distinction. That is why the quantity of different variants of N distinctive chain links placement in Z identical cells under the condition that one cell can not contain more than one chain link is equal to $Z!/(Z-N)!$

Considering the identity of cells, a priori probability that the given cell will be filled is equal to $1/Z$, and that it will not be filled is $(1-1/Z)$. Respectively, the probability $\omega(z)$ that N given cells will be filled and $Z - N$ cells will be empty, considering both the above mentioned condition of placement of N distinctive links in Z identical cells and the quantity of its realization variants will be determined by the following expression

$$\omega(Z)=\frac{Z!}{(Z-N)!}\left(\frac{1}{Z}\right)^N\left(1-\frac{1}{Z}\right)^{Z-N}.\qquad(7)$$

Probability density $\omega(N)$ of the fact that random walk trajectory is at the same time *SARW* statistics trajectory and at given Z, N, n_i will get the last step in one of the two equiprobable cells, which coordinates are set by vectors $s = (s_i)$, differentiated only by the signs of their components s_i, is equal to

$$\omega(N)=\omega(Z)\omega(N,s).\qquad(8)$$

Let us find the asymptotic limit (8) assuming $Z >> 1$, $N >> 1$, $n_i >> 1$ under the condition $s_i << n_i$, $N << Z$. Using the approximated *Stirling* formula $\ln x! \approx x \ln x - x + \ln (2\pi)^{1/2}$ for all $x >> 1$ and expansion $ln(1-1/Z) \approx -1/Z$, $ln(1-N/Z) \approx -N/Z$, $ln(1\pm s_i/n_i) \approx \pm s_i/n_i - (s_i/n_i)^2/2$, and assuming also $N(N-1)$ we will obtain[3,4]:

$$\omega(N)=exp\{-N^2/Z-(1/2)\sum_i s_i^2/n_i\}\cdot\qquad(9)$$

Transition to the metric space can be realized by introduction of the displacement variable

$$x_i = a|s_i|d^{1/2}.\qquad(10)$$

and also the parameter σ_i – the standard deviation of *Gaussian* part of distribution (9):

$$\sigma_i^2 = a^2 n_i d\,.\qquad(11)$$

Then

$$s_i^2 / n_i = x_i^2 / \sigma_i^2 \, , \qquad (12)$$

$$Z = \prod_i x_i / a^d \qquad (13)$$

and for the metric space expression (9) becomes:

$$\omega(N) = exp\left\{ -\frac{a^d N^2}{\prod_i x_i} - \frac{1}{2} \sum_i \frac{x_i^2}{\sigma_i^2} \right\} . \qquad (14)$$

Here $\prod_i x_i$ is the volume of conformational ellipsoid with the semiaxes of x_i, to the surface of which the states of the chain end belong.

A maximum of $\omega(N)$ at the set values of σ_i and N corresponds to the most probable, *i. e.* equilibrium state of the polymer chain. From the condition of $\omega(N) / \partial x_i = 0$ at $x_i = x_i^0$ we find semiaxes x_i^0 of the equilibrium conformational ellipsoid [3]:

$$x_i^0 = \sigma_i (a^d N^2 / \prod_i \sigma_i)^{1/(d+2)} . \qquad (15)$$

In the absence of external forces, all directions of random walks of the chain end are equiprobable, that allows to write:

$$n_i = N/d \, , \qquad (16)$$

$$\sigma_i^2 = \sigma_N^2 = a^2 N \, . \qquad (17)$$

The substitution of (17) into (15) makes the semiaxes of the equilibrium conformational ellipsoid identical and equal to the undeformed *Flory* coil radius: $x_i^0 = R_{N,f}$. Let us underline two important circumstances. First, *SARW* statistics leads to the same result, *i. e.* to formula (2), that *Flory* method, which takes into account the effect (repulsion) of the volume interaction between monomer links in the self−consistent field theory. However, as it was explained by *De Gennes*[6], accuracy of formula (2) in *Flory* method is provided by excellent cancellation of two mistakes: top−heavy value of repulsion energy as a result of neglecting of correlations and also top−heavy value of elastic energy, written for ideal polymer chain, that is in *Gaussian* statistics. Additionally, one must note, that formula (2) is only a special case of formula (15), which represents conformation of polymer chain in the form of ellipsoid with semiaxes $x_i^o \neq R_f$, allowing to consider this conformation as deformed state of *Flory* coil.

Second, obtained expression (14) for density of distribution of the end links of polymer chain is not only more detailed but also more general than scale dependencies (4) at θ_o and δ_o, which are approximately correct only at the limits $x_i / R_i << 1$ and $x_i / R_f >> 1$.

Free energy F_N of the equilibrium conformation is determined by the expression

$$F_N = -kT \ln \omega(N) \qquad \text{at } x_i = x_i^0 \qquad (18)$$

From here for undeformed *Flory* coil we have:

$$F_{N,f} = (1 + d/2) kT (R_{N,f} / \sigma_N)^2 \, . \qquad (19)$$

For the deformed one –

$$F_N = F_{N,f} / \lambda_v \, , \qquad (20)$$

where λ_v is the repetition factor of *Flory* coil's volume deformation:

$$\lambda_v = \prod_i x_i^0 / R_f^d = \prod_i \lambda_i \, , \qquad (21)$$

where λ_i is a repetition factor of linear deformation,

$$\lambda_i = x_i^o / R_f \, . \qquad (22)$$

At any deformations the conformational volume diminishes, therefore in general case $\lambda_v \leq 1$ [3].

Sarw statistics for the internal links of a chain

The internal n−link ($1<<n<<N$) divides polymer chain into two sections with the lengths of n and $N−n$ links, respectively. This situation is illustrated with high quality in *Figure* 1.

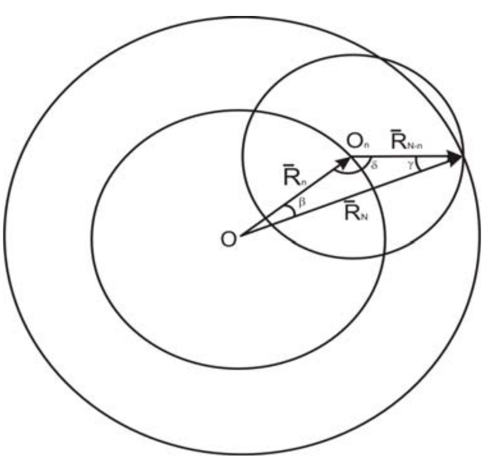

Fig. 1 - The scheme, explaining the necessity to enter new conformational volume Z' at fixing of the position of the polymer chain internal n−link

Let us assume, as it is shown in *Figure* 1, that the most probable position of n−link with respect to the chain end is the surface of sphere with radius R_n and chain's n−link accidentally appeared at point O_n on this sphere. Then with respect to this point N−link of the chain over $N−n$ steps with the highest probability should appear on the surface of sphere with radius R_{N-n}.

As it can be seen from *Figure* 1, $R_n^d + R_{N\ n}^d < R_N^d$. Consequently, fixing of n−link position diminishes the polymer chain's conformational volume regardless of where specifically point O_n is situated on the surface of sphere with radius R_n.

This means that for the analysis of *SARW* statistics of the chain's internal links in the lattice space, a new number of cells $Z' < Z$ needs to be introduced. Then the probability density of the random walk trajectory's self–avoiding for the polymer chain with fixed position of the internal link can be described by the *Bernoulli* distribution in the same form (7), but with a new value of cells number:

$$\omega(Z') = \frac{Z'!}{(Z'-N)!}\left(\frac{1}{Z'}\right)^{N}\left(1-\frac{1}{Z'}\right)^{Z'-N}. \qquad (23)$$

The *Gaussian* random walks in n and $N-n$ steps of the first and second chain sections can be described thereby by the *Bernoulli* distribution (5), but here in expressions for the distribution density $\omega(n, s)$ for the first chain section and $\omega(N-n, s)$ for the second one, respectively, the following conditions of normalization must be implemented:

$$\sum_i n_i = n, \qquad (24)$$

$$\sum_i n_i = N - n \qquad (25)$$

and in place of the factor $(1/2)^N$ factors $(1/2)^n$ and $(1/2)^{N-n}$ respectively should be used.

As $\omega(Z')$ applies to the whole polymer chain, the distribution densities $\omega(n)$ and $\omega(N-n)$ of the *SARW* statistics trajectories for the first and second chain sections can be determined by the following expressions:

$$\omega(n) = (\omega(Z'))^{n/N}\,\omega(n,s), \qquad (26)$$

$$\omega(N-n) = (\omega(Z'))^{(N-n)/N}\,\omega(N-n,s). \qquad (27)$$

In an asymptotic limit the expressions (26) and (27) can be written:

$$\omega(n) = exp\{-\alpha N^2/Z' - (1/2)\sum_i s_i^2/n_i\}, \qquad (28)$$

$$\omega(N-n) = exp\{-(1-\alpha)N^2/Z' - (1/2)\sum_j s_j^2/n_j\}. \qquad (29)$$

The lengths of every section fractions of the total chain length are introduced here as:

$$\alpha = n/N, \qquad 1-\alpha = (N-n)/N. \qquad (30)$$

Defining the variables of the metric displacement of x_i and y_i in the form (10) and standard deviations $\sigma_{n,i}$ and $\sigma_{N-n,i}$ of the *Gaussian* part of distribution (28) and (29) in the form (11), instead of (28) and (29) we obtain:

$$\omega(n) = exp\{-\alpha N^2/Z' - (1/2)\sum_i x_i^2/\sigma_{n,i}^2\}, \qquad (31)$$

$$\omega(N-n) = exp\{-(1-\alpha)N^2/Z' - (1/2)\sum_i y_i^2/\sigma_{N-n,i}^2\}. \qquad (32)$$

Owing to the normalization (24) and (25) we have:

$$\sum_i \sigma_{n,i}^2 = a^2 nd, \quad \sum_i \sigma_{N-n,i}^2 = a^2(N-n)d. \qquad (33)$$

The values $\prod_i x_i$ and $\prod_i y_i$ are the volumes of the conformational ellipsoids with the semiaxes x_i and y_i of the first and second sections of the polymer chain, respectively. Hence, as laid down earlier (13), it is possible to write:

$$Z' = (\prod_i x_i + \prod_i y_i)/a^d. \qquad (34)$$

Entering the volume fractions of the proper conformational ellipsoids

$$\beta = \prod_i x_i / \left(\prod_i x_i + \prod_i y_i\right),$$

$$1-\beta = \prod_i y_i / \left(\prod_i x_i + \prod_i y_i\right) \qquad (35)$$

we obtain:

$$\omega(n) = exp\{-a^d\alpha\beta N^2/\prod_i x_i - (1/2)\sum_i x_i^2/\sigma_{n,i}^2\}, \qquad (36)$$

$$\omega(N-n) = exp\{-a^d(1-\alpha)(1-\beta)N^2/\prod_i y_i - (1/2)\sum_i y_i^2/\sigma_{N-n,i}^2\} \qquad (37)$$

These expressions are sought densities of distribution of internal links of the chain from its ends. Parameter β will be determined later.

The most probable states of the polymer chain sections meet the conditions $\partial\omega(n)/\partial x_i = 0$ at $x_i = x_i^o$, $\partial\omega(N-n)/\partial y_i = 0$ at $y_i = y_i^o$. Using them and assuming that values β and $1-\beta$ do not depend on specific realizations of x_i and y_i, *i. e.* these are functions of n and $N-n$ only, we find

$$x_i^0 = \sigma_{n,i}(a^d\alpha\beta N^2/\prod_i \sigma_{n,i})^{1/(d+2)}, \qquad (38)$$

$$y_i^0 = \sigma_{N-n,i}(a^d(1-\alpha)(1-\beta)N^2/\prod_i \sigma_{N-n,i})^{1/(d+2)} \qquad (39)$$

In the absence of external forces, all directions of random walks are equiprobable, therefore according to (31) it is possible to write:

$$\sigma_{n,i}^2 = \sigma_n^2 = a^2 n = \sigma_N^2\alpha, \qquad (40)$$

$$\sigma_{N-n,i}^2 = \sigma_{N-n}^2 = a^2(N-n) = \sigma_N^2(1-\alpha). \qquad (41)$$

Using (40) and (41) in (38) and (39), we will obtain expressions for the equilibrium conformational radii of both polymer chain sections:

$$R_n = R_{N,f}\,\alpha^{2/(d+2)}\beta^{1/(d+2)}, \qquad (42)$$

$$R_{N-n} = R_{N,f}(1-\alpha)^{2/(d+2)}(1-\beta)^{1/(d+2)}. \qquad (43)$$

The conformational volumes here are equal to

$\prod\limits_i x_i = R_n^d$, $\prod\limits_i y_i = R_{N-n}^d$, therefore expression (35) may be rewritten in the form

$$\beta/\ (1-\beta) = R_n^d \,/\, R_{N-n}^d \tag{44}$$

From (42) − (44) it follows:

$$\beta = \alpha^d \,/\left[\alpha^d + (1-\alpha)^d\right],$$
$$1-\beta = (1-\alpha)^d \,/\left[\alpha^d + (1-\alpha)^d\right]. \tag{45}$$

Excepting β from (42) and (43), we get finally

$$R_n = R_{N,f}\,\alpha \,/\left[\alpha^d + (1-\alpha)^d\right]^{1/(d+2)}, \tag{46}$$
$$R_{N-n} = R_{N,f}(1-\alpha)\,/\left[\alpha^d + (1-\alpha)^d\right]^{1/(d+2)}. \tag{47}$$

Eqns. (46) and (47) together determine the most probable, that is the equilibrium distances of the internal link from the polymer chain ends.

As one can see, although between R_n and R_{N-n} a simple correlation $R_n/\ R_{N-n} = \alpha/(1-\alpha)$ is observed, each of these values depends by complicated way not only on its own section length but also on the length of another one.

Formulas (46) and (47) are correct at $d \leqslant 4$ [2], including at $d = 1$. For one–dimensional space from (46) and (47) follows physically expected result $R_n = an$, $R_{N-n} = a(N-n)$.

Structure of the polymer chain conformational space

From eqns. (46) and (47) follows that $R_n/\ R_{N,f} \geqslant \alpha$ and $R_{N-n}/R_{N,f} \geq 1-\alpha$, and signs of equality are achieved only on the chain ends, *i. e.* at $\alpha = 1$ and $\alpha = 0$, respectively. This gives evidence to heterogeneity of the polymer chain conformational volume. In addition, because of interconnection between R_n and R_{N-n}, both chain sections are not fractals. Let us comment both circumstances, confronting the values R_n and R_{N-n} from (46) and (47) with those values of $R_{n,f}$ and $R_{N-n,f}$, which these chain sections would have, if they were free and submitted to fractal correlation of the type (2):

$$R_{n,f} = an^{3/(d+2)} = R_{N,f}\,\alpha^{3/(d+2)}, \tag{48}$$
$$R_{N-n,f} = a(N-n)^{3/(d+2)} = R_{N,f}(1-\alpha)^{3/(d+2)}. \tag{49}$$

From comparison of (46) − (49) it follows:

$$R_n/\ R_{n,f} = \alpha^{(d-1)/(d+2)} \,/\left[\alpha^d + (1-\alpha)^d\right]^{1/(d+2)}, \tag{50}$$

$$R_{N-n}/\ R_{N-n,f} = (1-\alpha)^{(d-1)/(d+2)} \,/\left[\alpha^d + (1-\alpha)^d\right]^{1/(d+2)} \tag{51}$$

Dependencies (50), (51) are illustrated on *Figure* 2 for the option of $d = 3$.

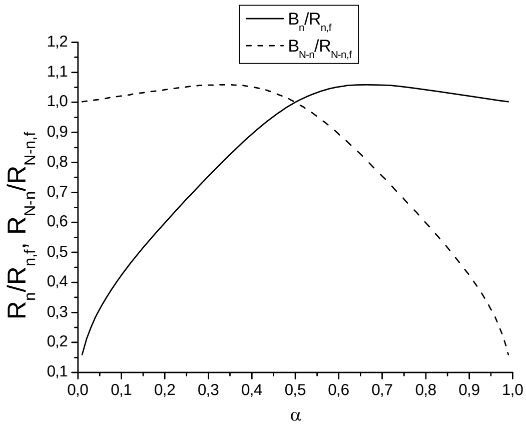

Fig. 2 - Ratios $R_n/\ R_{n,f}$ and $R_{N-n}/\ R_{N-n,f}$ calculated on the eqns. (50) and (51) depending on α and 1−α

As one can see, only in the area α >0.5 and correspondingly $1-\alpha$ >0,5, ratios $R_n/\ R_{n,f}$ and $R_{N-n}/\ R_{N-n,f}$, though are more than 1, but insignificantly. It allows to consider of these chain sections as the fractals objects with a small error and to describe them by fractal dependences (48) and (49). However, for short chain sections, *i. e.* at α <0,5 or $1-\alpha$ <0,5 ratios $R_n/\ R_{n,f}$ and $R_{N-n}/\ R_{N-n,f}$ become less than 1 and sharply diminish towards the chain ends, which indicates the compression of the conformational volume space nearby the ends of a chain.

Yet even more evidently heterogeneity of the structure of polymer chain's conformational volume becomes apparent at the analysis of volume density ρ, *i. e.* the numbers of links in the unit of conformational volume for given chain section. Let us be limited to considering only the first chain section *n* in length, for which

$$\rho_n = n \,/\, R_n^d. \tag{52}$$

Using (46), we get

$$\rho_n/\ \rho_N = \left[\alpha^d + (1-\alpha)^d\right]^{d/(d+2)} /\ \alpha^{d-1}, \tag{53}$$

where $\rho_N = N \,/\, R_{N,f}^d$ is an average links' density in conformational volume of the whole polymer chain.

The correlation between local and average density of the chain links is illustrated on *Figure* 3 at *d* = 3. Evidently, ratio $\rho_n/\ \rho_N$ in the range of α <0.2 at $\alpha \to 0$ sharply increases, and for example at α =0.01 achieves the value of 10^4 order. As the dependence of the ratio $\rho_{N\ n}/\ \rho_N$ is similar, but asymmetric, it can be concluded that the conformational volumes near the chain ends are strongly compressed, so that the density of links in them considerably exceeds the average one over the conformational volume of the whole chain. With some caution one can suppose that the conformational volumes near the chain ends have a globular structure.

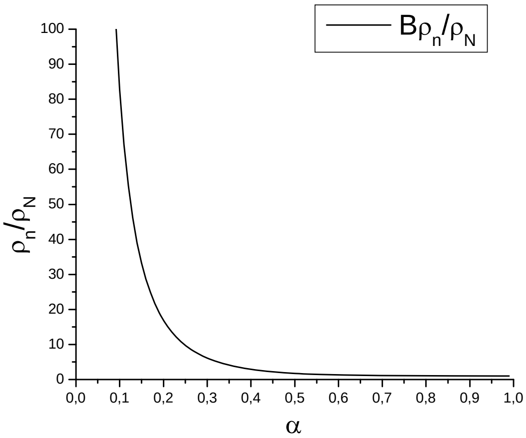

Fig. 3 - Ratio between local density of polymer chain link ρ_n and average one ρ_N depending on α calculated on (53)

To support this point, we propose also considerations based on experimental research of dymethacrylates postpolymerization kinetics, *i. e.* dark, after turning off *UV* irradiation, process of polymerization[4]. It was found, that the chain termination is linear, and its kinetics submits to the law of stretched *Kohlrausch* exponent:

$$\psi(t) = g\,exp\{-t/t_0\}^{\gamma}. \tag{54}$$

Here g and $0 < \gamma \leq 1$ are constants; t_0 is characteristic time of linear chain termination.

A theoretical derivation[12] was based on the idea, that linear chain termination is the act of «self–burial» of macroradical's active center and manifests itself as the act of chain propagation, leading into a trap. Taking into account the fractal properties of polymer chain and assuming that a set of traps in its conformational volume is a fractal as well, we obtain the expression similar to (54):

$$\psi(t) = g\,exp\{-t/\ \tau_p(\rho_m/\rho_0)^{\xi}\}^{1/\xi}, \tag{55}$$

where τ_p is characteristic time of chain propagation act, ρ_m and ρ_0 are monomer and traps concentrations in the macroradical's conformational volume, respectively.

According to the derivation of expression (55)

$$\xi = d_f/(d_f + d_L - d), \tag{56}$$

where $d_f = (d+2)/\ 3$ and d_L are fractal dimensions of the conformational volume of macroradical and a set of traps in it. From experimental data the value of $\gamma = 1/\xi = 0.6$, so we can accept $\xi = d_f$. Then for the dimension of the traps set fractal the expression (57) follows from (56):

$$d_L = \frac{d_f + d}{2} = \frac{2d+1}{3}, \tag{57}$$

which not only satisfactorily coincides with experimental value of d_L at $d = 3$, but also presents physically justified value of $d_L = 1$ at $d = 1$.

Correlation (57) shows that $d_f < d_L < d$. Therefore, in the reaction zone of growing macroradical, there are both «strange» traps formed by polymer chains, external for given macroradical, with fractal dimension close to d and «own» ones with fractal dimension of polymer chain $d_f = (d+2)/3$.

This derivation in[12] is based only on kinetic researches of dymethacrylates postpolyme-rization, but, apparently, it coordinates well with the results of present work, according to which «own» traps for a growing macroradical are caused by high density of links in the conformational volumes near the polymer chain ends, that can screen or even block up macroradical active center.

Free energy of conformation of polymer chain sections

Let us determine free energies F_n and F_{N-n} of the conformation of polymer chain sections, separated by fixing of internal n–link, on type (18) by expressions:

$$F_n = -kT\,ln\,\omega(n) \quad \text{at } x_i = x_i^o, \tag{58}$$

$$F_{N-n} = -kT\,ln\,\omega(N-n) \quad \text{at } y_j = y_j^o. \tag{59}$$

For the equilibrium state in the absence of external forces, *i. e.* at all $x_i^0 = R_n$ and $y_i^0 = R_{N-n}$, using (36), (37), (45)–(47) in (58) and (59), we get

$$F_n = F_{N,f}\,\alpha\Big/\left[\alpha^d + (1-\alpha)^d\right]^{2/(d+2)}, \tag{60}$$

$$F_{N-n} = F_{N,f}\,(1-\alpha)\Big/\left[\alpha^d + (1-\alpha)^d\right]^{2/(d+2)}. \tag{61}$$

From here it follows:

$$F_n + F_{N-n} = F_{N,f}\Big/\left[\alpha^d + (1-\alpha)^d\right]^{2/(d+2)}. \tag{62}$$

Hence, $F_n + F_{N\ n} \geqslant F_{N,f}$. It is related to the fact that two chain sections are thermodynamic subsystems, which interact with each other. Thus, fixing the position of a polymer chain internal link increases its negative entropy and positive free energy of conformation due to diminishment of the polymer chain conformational volume. Therefore the sum $F_n + F_{N-n}$ of free energies of the chain sections conformation must be compared not to $F_{N,f}$, representing free energy of undeformed *Flory* coil conformation with the volume of $R^d_{N,f}$, whereas for free energy of conformation F_N of the *Flory* coil deformed to the volume $R^d_n + R^d_{N-n}$, determined by the expression (20).

As the multiple (repetition factor) of the volume deformation λ_V here is equal to

$$\lambda_V = \left(R^d_n + R^d_{N-n}\right) / R^d_{N,f} = \left[\alpha^d + (1-\alpha)^d\right]^{2/(d+2)} \qquad (63)$$

we have identically

$$F_n + F_{N-n} = F_{N,f} / \lambda_V \,. \qquad (64)$$

It is now possible to accomplish the reverse transition and write the expression

$$[\omega(n)\omega(N-n)]^{\lambda_V} = \omega(N), \qquad (65)$$

which was not obvious in the beginning.

The most probable distance between two internal links of a polymer chain

If two internal links of a chain are selected according to the condition 1 << *k* << *n* << *N*, the polymer chain is divided into three sections with the lengths of *k, n*−*k* and *N*−*n*, to which the fractions of the total chain length $\alpha_k = k/N$, $\alpha_{n-k} = (n-k)/N$ and $\alpha_{N-n} = (N-n)/N$ correspond.

Let us suggest that $j = \overline{1,3}$ are numbers of sections with quantities of links *k*, *n* − *k* and *N* − *n*, to which fractions $\alpha_1 = k / N$, $\alpha_2 = (n-k) / N$ and $\alpha_3 = (n-k) / N$ from general number *N* of links in a chain are corresponded.

Extending the above−mentioned procedure of analysis of two chain sections to three sections, we get the general expression for the distribution density of the end of the given section regarding to its beginning:

$$\omega(j) = exp\{-a^d \alpha_j \beta_j N^2 \Big/ \prod_i x_{ji}{}^2 - (1/2) \sum_i x_{ji}{}^2 \Big/ \sigma^2_{ji}\},$$
$$j = \overline{1,3},\ i = \overline{1,d}\,. \qquad (66)$$

Here β_j is a fraction of conformational volume of the given section in the sum of conformational volumes of all sections; x_{ji} , $i = \overline{1,d}$ are semiaxes of conformational ellipsoid *j* with center in the beginning of the given section. The surfaces of this section involve the states of its end.

The square deviations σ_{ji} of *Gaussian* part of distribution (66) obey the normalization conditions of the form:

$$\sum_i \sigma^2_{ij} = a^2 \alpha_j N d\,. \qquad (67)$$

At equiprobability of walks in all directions of *d*–dimensional space we have:

$$\sigma^2_{ij} = \sigma^2_{j0} = a^2 \alpha_j N\,. \qquad (68)$$

In this case the most probable distance between the beginning and the end of the chain in the given section will be equal to:

$$R_j = \frac{R_{N,f}\alpha_j}{\sum_j (\alpha_j{}^d)^{1/(d+2)}}, \qquad (69)$$

and for β_j the following expression will be correct:

$$\beta_j = \frac{\alpha_j{}^d}{\sum_j \alpha_j{}^d}\,. \qquad (70)$$

According to (69) the value of R_j depends not only on the length of the given chain section but also on where this section has been chosen. Thus, we can note again that selected three sections of polymer chain are not independent, but are interactive subsystems. Therefore, total free energy of conformation of the chain three sections exceeds free energy of conformation of undeformed Flory coil. But the following equality holds identically:

$$F_k + F_{n-k} + F_{N-k} = F_{N,f} / \lambda_v\,, \qquad (71)$$

where the multiplicity of *Flory* coil's volume deformation at the division of the chain into three sections is determined by the expression:

$$\lambda_v = \left(R^d_k + R^d_{n-k} + R^d_{N-n}\right) / R^d_{N,f}\,. \qquad (72)$$

Conclusions

Fixation of the position of polymer chain internal links separates its conformational volume into interacting subsystems. Their total conformational volume is smaller, and free energy is larger than the conformational volume and free energy of *Flory* coil, respectively. From expressions, which determine the probable distance between the polymer chain's internal link and its ends, as well as between any internal links, it follows that the structure of the polymer chain conformational volume is heterogeneous: the largest density of the number of links is observed near the chain ends. This can result in blockage of the macroradical's active centre and appear as a linear chain termination.

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