

1. INTRODUCTION The number of configurations L of a polymeric chain is one among methods of its conformational state realization. Under this sense L is the statistical analogue of the important thermodynamical characteristic of the conformational state of a polymeric chain, namely its entropy S : $S = k \ln L$, where k is the Boltzmann's constant. The first results of the numerical estimation L for linear polymeric chain at little values of number of its links N with the use of the Monte–Carlo method were interpreted in a form of the scaling dependence [1, 2]: , (1) Parameter z was determined as un–universal constant or effective coordinating number of d -measured cubic lattice, in space of which the trajectory of self–avoiding random walks (SARW) of the polymeric chain is constructed; is the universal scaling index, depending only on the dimension d of the screen space. The first estimations of values $z = 4,68$ and $\nu = 1,16$ at $d = 3$ later were made more exact: $z = 4,6853$ [3], $\nu = 1,1596$ [4]. For polymeric star consisting of s rays by equal length N , the number of configurations is also postulated by the scaling expression of type (1) [5, 6]: , (2) With the use of the calculations performed by the methods of group renormalization of field theory [7] and by the Monte–Carlo method [8–10] it was shown, that the scaling index of the polymeric star very nontrivially depends on the number of the rays: under the s increasing the index firstly slowly is decreased to zero (at $s \sim 7$), and after that under $s > 7$ it's sharply decreased taking the negative values up to $\nu = -29$ at $s = 32$ [8]. Such values are badly agreed with the physical interpretation of the scaling index. Probably, this caused by the absence of numerical estimations of z parameter and its possible dependence on s and N . In connection with this fact let us note, that the both expressions (1) and (2) represent the number of the configurations of polymeric chain as two co-factors, absolutely different upon its «weight». Let us estimate of their weights accordingly to the expression (1) for linear polymeric chain using the presented above values $z = 4,68$ and $\nu = 1,16$ for the reference point. At $N = 50$ we will obtain: $L = 4,6850 \cdot 500,16 = (3,3 \cdot 10^{33})(1,9)$. So, the main factor determining the value L , is the co-factor z^N , against the background of which the co-factor has an insignificant role. This is visualized also under the comparison of their endowment into the entropy of conformation which is proportional to $N \ln z = 77,1$ and $\ln N = 0,6$ correspondingly. As we can see, these endowments are differed on two orders; under the N increasing the difference will be just only increased. That is why in the presented paper the all attention will be paid into the analysis of z parameter of linear chains and polymeric stars into diluted and concentrated, ideal and real solutions.

2. AN AVERAGE VARIANCE OF TRAJECTORIES STEP OF SARW AND THEIR NUMBER Any random configuration of the polymeric chain can be considered as the trajectory of SARW in N steps into the d -measured screen space with the size of the cubic cell, which is equal to the length of the monomeric link of a chain. The connectedness of the monomeric links into a polymeric chain makes the first and very important contingency on the trajectory of the SARW, namely the prohibition of step backwards [8]. That is why only the first step has the $2d$ methods or variants of transition into the neighboring cells;

the second and the following steps can have not more than $2d-1$ variants of the transition. If among $2d-1$ of the neighboring cells the n are occupied, then the number of the variants of transition on presented step is equal to the number of unoccupied or empty cells, that is $2d-1-n$. The number n can be changed via the limits from 0 to $2d-1$. The last means that the trajectory of SARW finds oneself into the trap with the absence of variants of the transition into the neighboring cells. This case is very interesting for the kinetics of the macroradical propagation at the polymerization, since represents by itself the monomolecular chain termination [11]. Under analysis of the number of configurations of polymeric chain the value n can be limited by a number of $2d-2$ which makes the following step by monovariant, and therefore, by possible. Let introduce the average probability p_n of that the n of the neighboring cells occupied. Then the average variance of step z_p for the all trajectories of SARW will be equal: , (3) Every step of the SARW trajectory represents by itself the $2d-1$ independent tests on occupancy of the neighboring cells and random transition into the one among free cells. Therefore, in accordance with the theorem about the repeated tests the average probability of that among of $2d-1$ of the neighboring cells exactly n will be occupied, and $2d-1-n$ will be vacant, is ordered to the binomial distribution law: , (4) Here the binomial coefficients are described by the expressions: (5) p is the mathematical expectation or the average upon the all SARW trajectories probability of the occupancy of the one cell. Combining the (3) and (4), we will obtain: (6) Due to the probabilistic or stochastic character of the SARW trajectories the expression (6) is true only at $d \geq 2$. For the one-dimensional space only the first step has the variance $2d$, the rest of $N-1$ steps determined, in other words are not stochastic, and that is why cannot be described by the expression (6). Since in accordance with the determination of (6) z_p is the average variance of the step of trajectories in $N-1$ steps, and the first step has the $2d$ variants, a general number L_p of different trajectories or configurations of polymeric chain upon the property of the multiplicativity will be equal to: , (7) The expression (6) permits to analyze the endowments of steps with the variance $2d-1-n$ into the average variance of step z_p of SARW trajectories. Let us illustrate of this fact on the example of $d = 3$ -space, for which the expression (6) takes the form: (8) Under two random values $p_1 = 0,1$ and $p_2 = 0,01$ we have correspondingly: Here the first terms give the endowment into z_p steps with $n = 0$, the second ones - with $n = 1$ and ect. As we can see, under the p decreasing the average variance of a step is increased at the expense of the sharp steps endowment decreasing with $n = 1$ and sharp increasing of the steps endowment with $n = 0$. However, if don't use of this detail information, but to be concentrated only on the value z_p , it can be find without taking into account of the binomial distribution law. Really, since the p is an average upon the all trajectories probability to discover the occupied cell, the mathematical expectation of the number of occupied cells at $2d-1$ independent tests will be equal to $(2d-1)p$. Correspondingly, the mathematical expectation of the number of empty cells under the same $2d-1$ independent tests will be equal to $(2d-1)(1-p)$. Exactly this number determines the

average variance of a step of the SARW trajectories: , (9) By substituting in this expression the previous undefined values $p_1 = 0,1$ and $p_2 = 0,01$, we will again obtain $z_{p1} = 4,5$ and $z_{p2} = 4,95$. At $p = 1$ the expression (9) can be written in the form (10) As we can see from the (9) and (10), at $p = 0$ the average variance of a step of the SARW trajectories takes its maximal value: $z_p = 2d-1$. Correspondingly, the maximal number of the SARW trajectories or the configurations of polymeric chain replies to a case $p = 0$: (11) Condition $p = 0$ points on the single contingencies, superposed on the SARW trajectories: any among their steps cannot be returned due to the connectedness of the monomeric links into the chain. The remaining contingencies of the self-avoiding random walks lead to the condition $p > 0$. Performed analysis shows, that the average variance of a step of the SARW trajectories is the universal function only on two parameters, namely d and p . However, into presented approach the parameter p is not determined. Evidently, it should be depending on the type of a polymeric chain (for example, linear or star-like), the length of a chain or the rays and their number, the concentration of a polymer into solution and its thermodynamical properties (ideal or real). An analysis of the influence of these factors on parameter p let's carried out within the strict SARW statistics [12, 13], which considers the conformation of a polymeric chain as the result of the statistical average upon the all possible configurations with taking into account the probability of their realization.

3. AN AVERAGE VARIANCE OF THE STEP IN THE SARW STATISTICS

3.1. Linear polymeric chains

3.1.1. Diluted solutions, ideal & real ones

The SARW statistics of linear polymeric chain into diluted solution determines [12] the density of distribution, to which corresponds the probability $i = 1, d$ of that the SARW trajectory by its last step hits into the volume of the elementary layer on the surface of the equilibrium conformational ellipsoid with the semiaxes $X_i = R_f$, in a form (12) Here: is the root-mean-square deviation of the Gaussian part (12); R_f is the most probable radius of the polymeric chain conformation into the ideal diluted solution or the radius of the undeformed Flory ball: (13) It follows from this (14) Parameters are the multiplication factors of a linear deformation of the Flory ball along the corresponding axes of d -measured space; is the multiplication factor of the volumetric deformation. For a polymeric chain into the ideal solution the all $= 1$ and $= 1$. Under any deformations of the Flory ball its conformational volume is decreased, that is why in the real solution 1. Parameters cannot take the unconditioned values, since they are connected via the ratio , (15) This permits to write the eq. (12) in more convenient form for the following analysis: (16) Since the density of distribution represents the result of the statistical average upon the all possible configurations of a polymeric chain with taking into account of the probability of their realization, it can be considered as the ratio of number of the SARW trajectories, realizing the presented conformational state, to the maximally possible number of the trajectories which limited only by the connectedness of the links into a chain: , (17) Taking into account the eq. (11), it follows from this: (18) By substituting of the expressions (14) and (16) into (18), we will obtain (19) This

permits to write , (20) where is an average variance of a step in the SARW statistics:

(21) Next let's introduce an average occupancy of a cell into the conformational volume of a polymeric chain via the ratio (22) from which with taking into account of (13) follows (23) Comparing the (21) and (23), we find (24) Definitionally on (22) is the probability to discover the cell occupied into conformational volume of linear polymeric chain, and under this sense it could be equated to p. However, such assumption doesn't take into account, that the expression (22) into the evident form supposes the uniform distribution of the links of a chain into its conformational volume. Any among SARW trajectories cannot be uniformly distributed upon the whole conformational volume and that is why due to the local character of the SARW trajectories the condition $p \gg 1$ should be performed. Comparing the expressions (9) and (24) and taking into account that the both of them should represent the same physical value , in general case we obtain the following relationship: (25) the partial case of which under $p \gg 1$ and $L \gg 1$ is the ratio (26) Let's note that although the SARW statistics is based on the indispensable condition $N \gg 1$, both conditions $p \gg 1$ and $L \gg 1$ can simultaneously and exactly don't perform. That is why more general expression (25) will be used into the following calculations. In accordance with the (7) and (20) under condition between d and the difference in co-factors $2d/zp$ and $2d/(2d-1)$ neared to 1 and having a little significance at the co-factor zN is kept. That is why without a great error it can be taken that $L_p = L$, and L can be expressed via the ratio (27) and finally the average variance of a step of trajectories of linear polymerization for a chain in the SARW statistics can be determined via expression (28) For illustration of the dependence of , p and z on N , d and in Table 1 there are their calculated values upon the expressions (23), (25) and (28). Table 1

N	$d=2$	$d=3$	$d=4$	p	z	$p z$
20	0,224	0,361	1,918	0,091	0,203	3,982
50	0,141	0,246	2,261	0,044	0,103	4,482
100	0,1	0,181	2,456	0,025	0,061	4,694
$N d = 3, d = 4$	0,032	0,061	2,816	0,004	0,010	4,951
20	0,182	0,367	3,172	0,05	0,139	6,025
50	0,087	0,197	4,018	0,02	0,058	6,592
100	0,05	0,118	4,402	0,01	0,029	6,793
- -	6,988	- -	6,988	- -	- -	- -

As a short comment to the Table 1, let's note, that at the chain length propagation an average variance of a step of the SARW trajectories is increased, in the limit N tending to the value $2-1$; deformation of the Flory ball for example, under converting of the polymeric chain of the ideal solution into the real one or under the action of the external forces, in particular of the shear ones under the gradient rate of the hydrodynamic flow, increases ϕ and p and decreases z , sharply decreasing the number of the configurations realizing the presented conformational state. As it was note earlier, an average probability p to discover of cell occupied due to local character of the SARW trajectories is more than the average occupation of the cell into the conformational space of a polymeric chain. This permits us like to the determination of accordingly to (22), to express of p via the average configurational volume V_c , which consists of a part of the conformational volume $V = :$ (29) Comparing the (29) and (22), we will obtain (30) In Table 2 there are calculated values of an

average part of the configurational volume on conformational one under different variants. As we can see, the configurational volume occupies a great part of the conformational volume, testifying to «smeared» SARW trajectory into the space of a walk. At the length of a chain propagation the part V_c/V is decreased and in a range N is stabilized by the ratio: (31) Table 2

N	V_c/V	p	$d=2$	$d=3$	$d=3$	$d=4$
20	0,620	0,448	0,496	0,359	0,574	0,424
50	0,574	0,424	0,444	0,344	0,551	0,413
100	0,551	0,413	0,425	0,339	0,516	0,402
1000	0,516	0,402	0,400	0,333	0,500	0,400
10000	0,500	0,400	0,400	0,333		

3.1.2. Concentrated solutions and melts In accordance with the conclusion done from the expression (9), which determines an average variance of a step of the SARW trajectories for the linear polymeric chain via average probability to discover the occupied cell, it kept true for any polymeric chain into the concentrated solutions and melts, but at this the p value should be additionally depended on the concentration of polymer. Let us show also, that the main expressions (25) and (28) for the concentrated solutions are kept in the previous form (for short the term «melt» will be used as the need arises). The SARW statistics [13] of the linear polymeric chains into the concentrated solutions is based on the notion of m -ball of the intertwined between themselves linear polymeric chains by the same length N with the conformational radius R_m : (32) Number m of the chains into the m -ball depends on the concentration of polymer in the solution: (33) Here: is the density, and is the critical density of the solution upon polymer, to which corresponds the start of the Flory balls conformational volumes overlapping. It is determined by the expression: (34) in which M_0 is the molar mass of the link of a chain; N_A is the Avogadro number. By introducing the density into a volume of the monomeric link ad via the ratio (35) the expression (34) can be rewritten in a form: (36) An average occupancy of the cell into the conformational volume of m -ball can be determined standardly (37) Here, as before, the parameter is the multiplicity of the volumetric deformation of the m -ball; into the ideal solution and melt = 1, into the real concentrated solutions 1. With taking into account of the previous expressions (32)-(36) It's follows from the (37) (38) So, an average occupancy of the cell into the concentrated solutions is the linear function of the concentration of polymer and should be weakly depend on the length of a chain only via parameter , which can slightly decreased in the real solutions at the N propagation [14]. The density of probability for any linear polymeric chain into m -ball is described by the expression like to (16), but via the conformational radius of the m -ball: (39) Here as same as earlier, ; that is why from the determination of R_m accordingly to (32) and following expressions (33)-(36) follows: (40) This permits to rewrite the expression (39) in the next form: (41) By substituting of the (41) into determination (18) the numbers L of the SARW trajectories for any linear polymeric chain into m -ball, we will obtain: (42) This implies the expression for average variance of the step of SARW trajectories of the linear polymeric chain into concentrated solutions and melts: (43) which in turn with taken into account of the (38) takes a form (44) So, the difference between z for diluted and concentrated solutions is determined by the expressions of numerical

estimation of \bar{V} . Therefore, the relationship between p and \bar{V} for concentrated solutions is kept in the previous form (25), which for more convenience can be rewritten as follows (45) Let us demonstrate as the illustration in Table 3 the numerical estimations of \bar{V} , p and z , and also the ratios in which V_m is the conformational volume, and V_c is the configurational volume of polymeric chain into m -ball, at different N and d . Calculated done for variant $d = 3$, $lv = 1$ on example of polystyrene for which $M_0 = 104,15$ g/mole, $a = 1,86 \cdot 10^{-10}$ m; that is why in accordance with (35) and (36) we have $\bar{V} = 26,9 \cdot 10^6$ g/mole and $\bar{V}_c = 0,6757$ and $\bar{V}_m = 0,1071$ g/mole at $N = 102$ and $N = 103$ respectively. The values $\bar{V}_c = 1,554$ and $\bar{V}_m = 9,804$ correspond to the polystyrene melts. As we can see from the Table 3, at the chosen values N the ratio \bar{V}_c/p is near to the limited one $2/(d + 2) = 0,4$. Thus, even into the concentrated solutions the configurational volume, which is an average volume of the SARW trajectories, consists of the great part of the conformational volume that assumes a strong interweaving of the polymeric chains into m -ball. At the polymer concentration increasing at >1 an average variance of the SARW trajectory is visibly decreased that corresponds to the sharp decreasing of the number of configurations L , realizing the conformational state of the polymeric chain into m -ball. An Independence of the presented calculated parameters on the length of a chain is good shown upon their similar values for the melts. Table 3

N	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
\bar{V}_c	1,554	0,025	0,028	0,030	0,033	0,039	p	0,061	0,067	0,073	0,078	0,093	z	4,696	4,666	4,638	4,608	4,535	\bar{V}_c/p	0,413	0,414	0,415	0,416	0,420	$N = 1000$	1	2	3	4	9,804	0,004	0,008	0,012	0,016	0,039	p	0,001	0,020	0,029	0,039	0,093	z	4,951	4,901	4,853	4,805	4,535	\bar{V}_c/p	0,402	0,404	0,406	0,408	0,420																																															

3.2. Polymeric stars 3.2.1. Diluted solutions Let the polymeric star consists from the s rays equal to N length. For any pair of rays forming the linear chain by $2N$ length, the SARW statistics [15] determines the density of distribution by the expression: (46) in which \bar{V}_c and R_s is the conformational radius of any undefined chosen pair of rays, determining also the general conformational volume of the polymeric star: (47) It follows from this (48) By substituting of this expression into determination of L accordingly to (18), we will obtain (49) that gives the possibility to express an average variance of a step of the SARW trajectories for any pair of rays of the polymeric star: (50) An average occupancy of a cell into conformational volume of the polymeric star we find from the expression: (51) which can be rewritten in a form (52) Comparing (50) and (52), we have again (53) Therefore, the relationship (24) is kept also for the polymeric star. The numbers of configurations for pair of rays forming the linear chain by $2N$ length, and for the whole polymeric star taking into account that the number of the independent pairs consisting of s rays equal to $s(s - 1)/2$, will be equal correspondingly: (54) For demonstration of the dependence of \bar{V} , p and z parameters on the number of rays s in polymeric star in Tabl. 4 presented their values at $2N = 100$, $d = 3$, $lv = 1$. Table 4

s	2	3	6	9	0,0251	0,0295	0,0390	0,0458	p	0,0608	0,0712	0,0929	0,1083	z	4,6956	4,6441	4,5357	4,4585	\bar{V}_c/p	0,413	0,415	0,420	0,423	s	12	15	18	21	0,0514	0,0562	0,0605	0,0643	p	0,1207	0,1312	0,1403	0,1486	z	4,3966	4,3442	4,2982	4,2571	\bar{V}_c/p	0,426	0,429	0,431
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0,433 3.2.2. Concentrated solutions and melts SARW statistics of the polymeric stars into the concentrated solutions, as same as the linear chains, is based on the conception of the m-ball of intertwining between themselves polymeric stars. For any pair of rays into undefined star of the m-ball the density of distribution is as follow: (55) Here r , and is the conformational radius of the m-ball of polymeric stars: (56) From the determination (57) with taking into account of the ratios r , it can be written (58) So, into the concentrated solutions of polymeric starts the value does not depend on the length and the number of rays, but only on the concentration of polymer into solution. Next, using the developed algorithm and the expressions (55)-(58), the standard expression for z type (24), (44) and (53) can be again obtained.

4. CONCLUSION

The number of configurations L for linear polymeric chain in d 2-measured lattice space accurate within multipliers $2d/z$ or $2d/(2d-1)$, neared to unit, is unambiguously determined via the average variance of the step z of the SARW trajectories: (59) The probabilistic analysis of the SARW trajectories determines z as the mathematical expectation of the number of free among $2d-1$ neighbouring cells via average upon the all SARW trajectories probability p to discover the occupied cell. It leads to the expression: (60) in which, however, the value p is kept indeterminate. SARW statistics which considers the conformation of polymeric chain as the result of the statistical average upon the all its possible configurations with taking into account of the probability of their realization leads to the ratio: (61) in which is an average upon the conformational volume occupancy of cell or probability to discover the cell occupied into the conformational volume. From the comparison of (60) and (61) the next relationship follows (62) On the basis of values p and it can be determined the ratio of the average local volume of configuration V_c to the conformational volume V of polymeric chain: (63) At the N increasing this ratio is tended to its limit при N (64) pointing on the great smeared upon the average of the SARW trajectory into conformational volume of the polymeric chain. The expressions (59)-(63) are universal in sense that they are true for any linear polymeric chain, including the superposed from undefined pair of rays of polymeric star, in diluted and concentrated, ideal and real solutions. Into diluted solutions p and z depend on the length of a chain, and correspondingly on length and number of rays in polymeric star; in concentrated solutions these parameters are function only on the concentration of polymer.