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SELF–AVOIDING RANDOM WALKS STATISTICS

Key words: self–avoiding random walks statistics, polymeric stars, diluted and concentrated solutions, viscosity.

It was proposed the self–avoiding random walks statistics for polymeric similar stars in diluted and concentrated solutions. On a basis of the proposed statistics the equilibrium thermodynamical properties (namely, volume, pressure, free energy) of the conformational state of polymeric stars and their transformation under the action of external forces have been described. It were determined the elastic properties (Yung's modulus and modulus of shearing) of the conformational volume of polymeric stars and also obtained the expressions for the main forces and for the deformation work. The dynamical properties of polymeric stars, in particular their characteristic times of translational and rotational motions, on a basis of which the coefficients of diffusion and elastic component of a viscosity determined have been studied. In concentrated solutions the all thermodynamic and dynamical properties expressed not only as the functions on a length and on a number of rays, but also on the concentration of the polymeric stars.

Ключевые слова: статистика случайных блужданий без самопересечения, полимерные звезды, разбавленные и концентрированные растворы, вязкость.

Предложена статистика случайных блужданий без самопересечения для полимераналогичных звезд в разбавленных и концентрированных растворах. На основе предложенной статистики были описаны равновесные термодинамические свойства (а именно, объем, давление, свободная энергия) конформационного состояния полимерных звезд и их трансформация под действием внешних сил. Определены упругие свойства (модуль Юнга и модуль сдвига) конформационного объема полимерных звезд, а также получены выражения для основных сил и для работы деформации. Изучены динамические свойства полимерных звезд, в частности, их характерные времена поступательного и вращательного движения, на основании которых определены коэффициенты диффузии и упругий компонент вязкости. В концентрированных растворах все термодинамические и динамические свойства выражаются не только в качестве функции длины и количества лучей, но также концентрации полимерных звезд.

1. Introduction

Polymeric stars attract the attention not only due to the own technological properties [1–3], which can be varied by a length N of the rays and by their number s, but also as the complicated and interesting object of the statistical physics of polymers.

Experimental data concerning to the properties of the polymeric stars are not numerous [4–7] and doesn't give the sufficient well–defined picture. In particular, an investigation of the low–angle scattering of the neutrons [**5**, **6**] for the diluted solutions of the star–like polybutadienes with 3, 4, 8 and 12 rays, one among which is deuterated, points on the fact, that the gyration radius of the tagged ray is increased at the number of the rays growing, but at this in diluted solutions the gyration radius is more, than in a melt.

Rheological investigations [7] of the regular polystyrene starts which are differed by a number of the rays (6, 12 and 22) and by the structure of the branching center (one or two covalently connected molecules of fullerene) also give the contradictory results: the characteristic viscosity of their solutions in chloroform is weakly increased at the molar mass of the star growing (with index α = 0,2 in *MKH* equation $[\eta] = M^{\alpha}$), whereas it is decreased in tetrahydrofurane, in other words, has the negative index $\alpha = -0.06$.

Theoretical analysis of the polymeric stars in *Daud–Cotton's* model [8], which considered them as spherical polymeric brushes in quasi–plate approximation [9–12] leads to the dependence of the conformational radius R_s of polymeric star on a number of rays s and their length N in a form (d – is dimensionality of a space):

$$R_s = aN^{3/(d+2)}s^{1/(d+2)}, \tag{1}$$

The expression (1) has an essential lack: at $s = 2$, that is, under condition of the polymeric star degeneracy into the linear chain by $2N$ length, it wrongly illustrates of this situation.

Besides, the experimental value of the so–called branching index g_R, determining by ratio

$$g_R = R_s^2 / R_{fs}^2, \tag{2}$$

in which R_{fs} is the conformational radius of the linear polymeric chain containing as same as the star of sN links,

$$R_{fs} = a(sN)^{3/(d+2)}, \tag{3}$$

is disagreed with the theoretical values g_R, calculated accordingly to (1)–(3).

In statistical physics like to the linear chains for polymeric stars two main tasks are solved. First is the estimation of a number of allowed configurations L with the calculation of indexes γ and γ_s in the scaling expressions by following type [13]:

$$L \approx z^N N^{\gamma-1} \tag{4}$$

for linear chain and

$$L_s \approx z^{sN} N^{\gamma_s - 1} \tag{5}$$

for the star.

In expressions (4) and (5) z is not strictly determined; at the scaling approach the effective coordination number of d–measured lattice, parameters γ and γ_s are assumed as universal scaling indexes.

For linear chain at $d = 3$ the value $\gamma = 1,1596 \pm 0,002$ was obtained [14] using the method of a group of the field theory renormalization. Index γ_s for polymeric star calculating by several methods including the groups of the field theory renormalization [15–18], methods of molecular dynamics [19–20] and *Monte–Carlo's* method [21–23] is sharply decreased at the s growing, taking more negative values even at $s > 8$ (for example, at $s = 32$ an estimation with the use of *Monte–Carlo's* method [23] gives the value $\gamma_s = -29$); this prejudices the universality of this scaling index.

Theoretical calculation of the L and L_s in statistics of the self–avoiding random walks *(SARW)* is represented in the next paper of this collection book. Here let's consider the second main task, which consists in the estimation of the distribution function of the end of a chain from its beginning.

More often the distribution function *P(N)* of the distance r between the ends of the linear chain by the N length is written in the scaling form [24–25]:

$$P(N) = R_f^{-d}\varphi(r/R_f), \tag{6}$$

In which R_f is the conformational radius of *Flory*

$$R_f = aN^{3/(d+2)} \tag{7}$$

Function $\varphi(r/R_f)$ represented by two asymptotes:

$$\varphi(x) \approx x^\theta \qquad \text{at x << 1} \tag{8}$$

$$\varphi(x) \approx \exp\{-x^\delta\} \qquad \text{at x>>1} \tag{9}$$

with indexes, for example, $\theta = 0,273$ [26] and $\delta = 2,5$ [27].

The same scaling ratios (6), (8) and (9) are used for the polymeric starts, but the indexes θ and δ are function on the number of rays.

Let's note, finally, that the scaling approach to the description of the distribution function in a form (6) in spite of its universality is approximate and limited. In particular, it not covers the most important field of the parameter x in (8) and (9) between $x << 1$ and $x >> 1$ change, in which *P(N)* takes the maximal values corresponding to the most probable conformational state of the polymeric chain. That is why, even the calculation of the indexes θ and δ doesn't give the possibility to describe the thermodynamical properties of the conformational state of polymeric chains and their transformation, for example at the deformation; this is not allow strictly to estimate the elastic properties of the conformational volume.

Exact form of the distribution function and following from it thermodynamical properties of linear polymeric chain conformation are strictly determined in the *SARW* statistics for ideal diluted [28] and concentrated [**29**] solutions. Here this approach is spread on the regular polymeric stars in diluted and concentrated solutions with the description of their thermodynamical and dynamical properties.

2. Diluted solution of polymeric stars

2.1. Self–avoiding random walk statistics

Let polymeric star with the s rays by the same length N is inserted into d–measured lattice space with the parameter of a cubic cell equal to the statistical length of a monomeric link of the rays of star, and let Z is the number of cells of the lattice space, in which there are the all sN links of a star. We will be neglect by the effects of interactions, assuming that the all possible configurations of polymeric star are energetically equal.

Let mark any undefined pair of rays and will be considered it as the linear polymeric chain by length of $2N$. Let fix its one end as the referenced position of the Gaussian phantom walks of the second end. Let define via n_i steps of walks the end of the marked chain relatively its beginning along the i directions of d–measured lattice space, limited by the condition of the normalization

$$\sum_i n_i = 2N \tag{10}$$

The number of methods for the realization of walks along the i direction is equal to $n_i!/n_i^+!n_i^-!$, where the numbers of the steps into positive n_i^+ and into negative n_i^- directions connected via the ratio $n_i^+ + n_i^- = n_i$. Since the a priori probability of a choice of the positive or negative direction for every step is the same and is equal to 1/2, the probability of $\omega(n_i)$ that under given n_i will be done of n_i^+ positive and n_i^- negative steps, will be determined by the *Bernoulli's* equation:

$$\omega(n_i) = \left(\frac{1}{2}\right)^{n_i} n_i!/n_i^+!n_i^-! \tag{11}$$

Inputting the numbers of the resulting steps via the ratio $s_i = n_i^+ + n_i^-$, we have $n_i^+ = (n_i + s_i)/2$, $n_i^- = (n_i - s_i)/2$. Then the (11) can be rewritten as follow:

$$\omega(n_i) = (1/2)^{n_i} n_i!/((n_i + s_i)/2)!((n_i - s_i)/2)! \tag{12}$$

For the walks along the all directions of the d–measured space we have

$$\omega(n) = (1/2)^N \prod_i n_i!/((n_i + s_i)/2)!((n_i - s_i)/2)! \tag{13}$$

The condition of the absence of self–intersection trajectories of walks requires from the point of view of the links of star per cells distribution that in every cell of the lattice space should be exist not more than one link of a star. The links of a polymeric chain are continuous; they cannot be separated one from other and located upon the cells into the undefined order. Therefore, the number of a links in a chain is its essential distinctive feature. The links of the different rays are also distinguishable. That is why the number of different methods location of sN distinguishable links of a star per Z similar cells under condition that in every cell cannot be more than one link is equal to $Z!/(Z - sN)!$. Due to the identity of the cells, a priori probability of fact that the presented cell will be occupied by a link is equal to $1/Z$, will be not occupied – $(1 - 1/Z)$. Therefore, the probability $\omega(z)$ of sN distribution of the distinguishable links of a star per Z identical cells under condition, that in every cell can be not more than one link, will be determined by the *Bernoulli's* distribution:

$$\omega(z) = \frac{Z!}{(Z - sN)!} \left(\frac{1}{Z}\right)^{sN} \left(1 - \frac{1}{Z}\right)^{Z - sN} \quad (14)$$

Distribution (13) describes the trajectory of the walks of undefined marked linear chain by the length $2N$, whereas the expression (14) determines the distribution of the all sN links of a star upon the Z identical cells. That is why the probability $\omega(2N)$ of the common fact consisting in that the trajectory of the random walk for the chosen chain by the $2N$ length is the trajectory without the self–avoiding is equal

$$\omega(2N) = (\omega(Z))^{2/s} \omega(n) \quad (15)$$

Here the index $2/s$ is the result of the division of $2N$ on sN,

Using the *Stirling's* formula by the following type $\ln N! \cong N \ln N - N$ at N >> 1, $Z >> sN$, $N >> 1$, $n_i >> 1$ and decomposition $\ln(1 - 1/Z) \cong -1/Z$, $\ln(1 - sN/2Z) \cong -sN/2Z$, $\ln(1 \pm s_i/n_i) \cong \pm s_i/n_i - (s_i/n_i)^2/2$ in accordance with the condition $s_i << n_i$, and assuming $N(N-1) = N^2$, we will obtained the asymptotic form (15) with the accuracy to the constant multiplier neared to the one:

$$\omega(2N) = \exp\left\{-\frac{(s/2)(2N)^2}{Z} - \frac{1}{2}\sum_i \frac{s_i^2}{n_i}\right\} \quad (16)$$

The transition to the metric d–measured space is possible via the introduction of the variable of the displacement x_i along the i direction of the end of a chain from its beginning,

$$x_i = a |s_i| d^{1/2}, \quad (17)$$

and also of the standard deviation σ_i of the Gaussian part in (16)

$$\sigma_i^2 = a^2 n_i d \quad (18)$$

Accordingly to the condition of the normalization (10) the following relationship is superposed on the value σ_i:

$$\sum_i \sigma_i^2 = a^2 2Nd \quad (19)$$

The expression (16) is true for any undefined chosen pair of the rays representing by itself the linear chain by the length $2N$. Therefore, for the all of them Z is general parameter characterizing in metric space the conformational volume of polymeric star:

$$Z = \prod_i x_i / a^d \quad (20)$$

So, taking into account the (17)–(20), a distribution (16) can be rewritten as follow:

$$\omega(2N) = \exp\left\{-a^d (s/2)(2N)^2 / \prod_i x_i - (1/2)\sum_i x_i^2 / \sigma_i^2\right\} \quad (21)$$

Distribution (21) in metric space determines the probability $\omega(2N) \prod_i dx_i$ of fact that the trajectory of the self–avoiding walk of any undefined pair of rays representing by itself the linear chain by $2N$ length, under the given values of s, N and σ_i will be finished into elementary volume $\prod_i dx_i$, locating on the surface of ellipsoid with the semi–axes x_i, $i = 1, d$.

2.2. *Thermodynamics of conformation and deformation of polymeric stars*

Without taking into account of the energetic effects of the interactions, the main factor determining the thermodynamic properties of the conformational state of polymeric star is the entropy of the self–avoiding random walks, which accordingly to the *Boltzmann* is determined by the thermodynamical probability of a state, that is by the number of methods of its realization; such methods are the trajectories of the self–avoiding random walks or configurations.

A connectedness of the links in polymeric chain imposes the first and essential limitation on the trajectories of walks – an inhibition of the step backwards. Consequently, the number of variants of a step of walk trajectory cannot be more than $2d-1$. Only the first step has $2d$ variants of the motion. This means, that the maximal number L_{max} of the trajectories of walk for undefined pair of rays will be equal

$$L_{max} = (2d/(2d-1))(2d-1)^{2N} \quad (22)$$

If the presented state is realized by L methods, then its probability is equal to L/L_{max}, that is why let

determine the number $L(2N)$ of configurations for the undefined chosen pair of the rays via expression:

$$\omega(2N) = L(2N)/L_{max} \qquad (23)$$

It's follow from this:

$$L(2N) = (2d/(2d-1))(2d-1)^{2N}\omega(2N) \qquad (24)$$

For polymeric star the number of independent pairs from s rays is equal to $s(s-1)/2$. That is why, the number of methods $L(sN)$ for the realization of conformational state of polymeric star will be equal:

$$L(sN) = (L(2N))^{s(s-1)/2} \qquad (25)$$

Therefore, in accordance with *Boltzmann*, the general entropy $S_0 = k \ln L(sN)$ of the conformational state of polymeric star can be represented as two components:

$$S_0 = k\frac{s(s-1)}{2}\ln\frac{2d}{2d-1}(2d-1)^{2N} + k\frac{s(s-1)}{2}\ln\omega(2N) \quad (26)$$

The first term is positive and is more than the second one; it takes into account the all trajectories of walk with imposed on them singular limitation of the connectedness of the links into a chain, and doesn't accept the reverse step. The second term is negative ($\omega(2N) < 1$); it takes into account the additional limitations on the trajectories of walk by requirement of their self−intersection absence. At this, the first term at given data s, N, d is the constant value, whereas the second term via $\omega(2N)$ is the function on the conformational state. That is why let assume only the second term in (26) as the entropy S of the conformational state of a polymeric star:

$$S = k(s(s-1)/2)\ln\omega(2N) \qquad (27)$$

Negative value of determined in such a way entropy of the conformation permits to consider the conformation as the statistical form of the self−organization of polymeric stars, and the numerical measure of this self−organization is entropy accordingly to (27).

Free energy of the conformational state without taking into account of the energetic effects is equal to $F(x) = -TS$. By combining of (21) and (27), we will obtain:

$$F(x) = kT\frac{s(s-1)}{2}\left[\frac{a^d(s/2)(2N)^2}{\prod_i x_i} + \frac{1}{2}\sum_i\frac{x_i^2}{\sigma_i^2}\right] \qquad (28)$$

Next, among the all possible conformational states let mark the most probable or thermodynamically equilibrium conformational states, to which the maximum S and the minimum F correspond in accordance with the condition $\partial F(x)/\partial x_i = 0$ at $x_i = X_i$. By differing of (28), we have

$$\partial F(x)/\partial x_i = kT\frac{s(s-1)}{2}\left[-\frac{a^d(s/2)(2N)^2}{x_i\prod_i x_i} + \frac{x_i}{\sigma_i^2}\right] \qquad (29)$$

By equaling of the right part to zero and solving the system consisting of the algebraic equations for the all i, we will find the most probable or equilibrium values of X_i, which are the semi−axes of the equilibrium conformational ellipsoid:

$$X_i = \sigma_i\left(a^d(s/2)(2N)^2/\prod_i\sigma_i\right)^{1/(d+2)} \qquad (30)$$

Under the absence of the external forces and into the ideal solution the all directions of the walk are equiprobable accordingly to condition $n_i = 2N/d$; that is why parameters σ_i in accordance with the (18) take the same value equal to:

$$\sigma_0^2 = a^2 2N \qquad (31)$$

The substitution of values $\sigma_i = \sigma_0$ in (30) based on (31) makes the semi−axes of the equilibrium conformational ellipsoid the same and equal to the conformational radius of the polymeric star:

$$R_s = a(2N)^{3/(d+2)}(s/2)^{1/(d+2)} \qquad (32)$$

Let's estimate the branching index g_R determined by the ratio (2) with the use of the expressions (3) for R_{fs} and (32) for R_s:

$$g_R = (s/2)^{-4/(d+2)} \qquad (33)$$

Calculations accordingly to (33) for variant $d = 3$ at $s = 3$ and $s = 12$ give the values equal to 0,73 and 0,24 respectively, which are good agreed with the experimental data 0,78 and 0,24 [31].

Under the action of external forces along the axes of d−measured space appearing in particular at the transition of polymeric star from the ideal solution into the real one, $\sigma_i \neq \sigma_0$ and spherical conformational space of the polymeric star is deformed into the ellipsoid with the semi−axes X_i accordingly to (30), equilibrium as to σ_i. We assume the following variables as a measure of the conformational volume deformation:

$$\lambda_i = X_i/R_s \qquad (34)$$

$$\lambda_v = \prod_i X_i/R_s^d = \prod_i\lambda_i, \qquad (35)$$

which represent by themselves the multiplicities of linear and volumetric deformation respectively.

In accordance with the condition of normalization (10) the values of λ_i cannot accept the undefined values. Let's determine the relationship between them by introducing the secondary parameters:

$$\varphi_i = \sigma_i / \sigma_0 \qquad (36)$$

It is follows from the determinations of σ_i from (18) and of σ_0 from (31):

$$\sum_i \varphi_i^2 = d \qquad (37)$$

Bu substitution of the values $\sigma_i = \varphi_i \sigma_0$ in (30) and taking into account (34) we will find

$$\lambda_i = \varphi_i \Big/ \left(\prod_i \varphi_i \right)^{1/(d+2)} \qquad (38)$$

Therefore,

$$\lambda_v = \prod_i \lambda_i = \left(\prod_i \varphi_i \right)^{2/(d+2)}, \qquad (39)$$

so

$$\varphi_i = \lambda_i \lambda_v^{1/2} \qquad (40)$$

Accordingly to (37) and (40) we have

$$\sum_i \lambda_i^2 = d / \lambda_v \qquad (41)$$

An analysis of (41) shows, that under any deformation of the spherical conformational volume of polymeric star, to which the values of $\lambda_i = 1, i = 1.d$ and $\lambda_v = 1$ correspond, into the conformational ellipsoid, the multiplicity of the volumetric deformation is decreased ($\lambda_v \le 1$);, that means the compaction of the conformational volume of polymeric star.

Next, let's determine a free energy $F(\lambda)$ of the equilibrium conformational ellipsoid by substitution in (28) of values $x_i = X_i = R_s \lambda_i$:

$$F(\lambda) = kT \frac{d+2}{2} \left(\frac{R_s}{\sigma_0} \right)^2 \frac{s(s-1)}{2} / \lambda_v \qquad (42)$$

Here

$$(R_s / \sigma_0)^2 = (2N)^{(4-d)/(d+2)} (s/2)^{2/(d+2)} \qquad (43)$$

That is why it can be also written:

$$F(\lambda) = kT((d+2)/2)(2N)^{(4-d)/(d+2)} (s/2)^{(d+4)/(d+2)} (s-1)/\lambda_v \quad (44)$$

For strainless state $\lambda_v = 1$, that is why a work of its transition into a deformed state in the system of the mechanics signs will be equal:

$$\Delta F_{def} = kT \frac{d+2}{2} \left(\frac{R_s}{\sigma_0} \right)^2 \frac{s(s-1)}{2} \left(\frac{1}{\lambda_v} - 1 \right) \quad (45)$$

Such work is positive, that is in the system of the mechanics signs it's realized under the system. If, however, the conformational volume is changed from the one deformed state with λ_v' into another deformed one with λ_v'', then the deformation work will be equal to:

$$\Delta F_{def} = kT \frac{d+2}{2} \left(\frac{R_s}{\sigma_0} \right)^2 \frac{s(s-1)}{2} \left(\frac{1}{\lambda_v''} - \frac{1}{\lambda_v'} \right), \quad (46)$$

and can be characterized by any sign.

Let's determine the pressure of conformation P of polymeric star via usual thermodynamic expression

$$\partial F(\lambda) / \partial V = -P \qquad (47)$$

as a measure of relationship between free energy and volume of conformation. Since the conformational volume is equal to $V = R_s^d \lambda_v$ we have

$$P = -(\partial F(\lambda) / \partial \lambda_v) / R_s^d \qquad (48)$$

By differing the (42) and (44) upon λ_v we will obtain respectively:

$$P = kT \frac{d+2}{2} \left(\frac{R_s}{\sigma_0} \right)^2 \frac{s(s-1)}{2} \Big/ R_s^d \lambda_v^2 , \quad (49)$$

$$P = \frac{kT}{a^d} \frac{d+2}{2} (2N)^{4(1-d)/(d+2)} (s/2)^{4/(d+2)} (s-1)/\lambda_v^2 \quad (50)$$

It's follows from the comparison of (42) and (49), that the pressure of conformation numerically is equal to density of free energy: $P = F(\lambda)/V$. Next, by multiplying of this expression on $V^2 = \left(R_s^d \lambda_v \right)^2$ and taking into account the (42) and (49), we will find the equation for the conformation state of the polymeric star in a form

$$PV^2 = FV = const \qquad (51)$$

where

$$const = kT \frac{d+2}{2} \left(\frac{R_s}{\sigma_0} \right)^2 \frac{s(s-1)}{2} R_s^d \qquad (52)$$

So, the values $PV^2 = FV$ are integrals of the process of equilibrium deformation of the conformational volume of polymeric star.

2.3. Modulus of elasticity

Under approximation of the isotropy of conformational volume of polymeric star its relative deformation $\partial x_i / x_i$ in i direction of d–measured space under the action of the all main forces f_i let's express via the differential form of the *Poisson's* equation:

$$Y \frac{\partial x_i}{x_i} = \frac{\partial f_i}{\prod\limits_{j \neq i} x_j} + \gamma \sum_{j \neq i} \frac{\partial f_j}{\prod\limits_{k \neq j} x_k} \qquad (53)$$

Here: Y is the *Young's* modulus, γ is the *Poisson's* coefficient, $Y \partial x_i / x_I$ is the tension in $(d-1)$–measured plate normal to the i direction; $\prod\limits_{j \neq i} x_j$

and $\prod_{k\neq j} x_k$ are values of the areas which are normal to the forces f_i and f_j respectively.

Let's rewrite (53) respectively to the *Young's* modulus:

$$Y = \frac{x_i^2}{\prod_i x_i}\frac{\partial f_i}{\partial x_i} + \gamma\sum_{j\neq i}\frac{x_i x_j}{\prod_i x_i}\frac{\partial f_j}{\partial x_i} \qquad (54)$$

In the system of the mechanics signs $f_i = \partial F(x)/\partial x_i$, that permits to use the expression (29). Under equilibrium values $x_i = X_i$ these forces (but not their derivatives) are equal to zero. That is why by differing of (29) upon x_i and x_j, and next by substituting of the equilibrium values $x_i = X_i = R_s\lambda_i$ we will obtain

$$\partial f_i/\partial x_i = 3kTs(s-1)/2\sigma_0^2\lambda_i^2\lambda_v, \qquad (55)$$

$$\partial f_i/\partial x_j = \partial f_j/\partial x_i = kTs(s-1)/2\sigma_0^2\lambda_i\lambda_j\lambda_v \quad (56)$$

By substituting of these derivatives in (54) with change of x_i on the equilibrium values X_i we will find

$$Y = kT\big(3+\gamma(d-1)\big)\big(R_s/\sigma_0\big)^2\frac{s(s-1)}{2}\Big/R_s^d\lambda_v^2 \quad (57)$$

Comparing the (57) and (49), we find the relationship between the *Young's* modulus and the pressure of conformation:

$$Y = 2\big(3+\gamma(d-1)\big)P/(d+2) \qquad (58)$$

From the other hand, in general case of the d–measured space the relationship between Y and P can be expressed via the volumetric modulus

$$E = -VdP/dV \qquad (59)$$

by the ratio

$$E = Y/d(1-\gamma(d-1)) \qquad (60)$$

It's follows from the determination of (59) and the equation of state (51):

$$E = 2P \qquad (61)$$

Substituting of (61) into (60) we will obtain another equation of relationship between Y and P:

$$Y = 2d(1-\gamma(d-1))P \qquad (62)$$

Comparing the (62) and (58) we find the expression for the *Poisson's* coefficient:

$$\gamma = (d+3)/(d+1)^2 \qquad (63)$$

Next, we determine the shear modulus via the *Young's* modulus and the *Poisson's* coefficient for d $\geq$ 2–measured space

$$\mu = Y/(d-1)(1+\gamma) \qquad (64)$$

which is also the function on the pressure of conformation:

$$\mu = \frac{2(3+\gamma(d-1))}{(d+2)(d-1)(1+\gamma)}P \qquad (65)$$

2.4. Main forces and the work of deformation

It follows from the determination of the main forces $f_i = \partial F(x)/\partial x_i$ in accordance with the (29) that at the equilibrium values $x_i = X_i$ these forces are equal to zero. That is why let's determine the main forces as those, which should be applied to the strainless conformational volume R_s^d, for which the conformational radius is equilibrium, with respect to σ_0, in order to transform it into the deformed state of the conformational ellipsoid with the semi–axes X_i, equilibrium with respect to σ_i. This determination means, that in expression (29) parameter σ_i should be replaced on σ_0, and values x_i should be replaced on X_i. Then we will obtain:

$$f_i = kT\frac{s(s-1)}{2}\left[-\frac{a^d(s/2)(2N)^2}{X_i\prod_i X_i}+\frac{X_i}{\sigma_0^2}\right] \qquad (66)$$

Substituting of $X_i = R_s\lambda_i$ in (66) we will obtain:

$$f_i = kT\frac{s(s-1)}{2}\frac{R_s}{\sigma_0^2}\frac{\lambda_i^2\lambda_v-1}{\lambda_i\lambda_v} \qquad (67)$$

It follows from this, that in the accepted system of the mechanics signs the positive forces correspond to the stretching along i axe ($\lambda_i^2\lambda_v > 1$), and the negative forces correspond to the compression ($\lambda_i^2\lambda_v < 1$). That is why the main forces of deformation cannot be undefined, but they are ordered to the equation of the relationship (as it is following from the (67) and (41)):

$$\sum_i f_i\lambda_i = 0 \qquad (68)$$

A work of the deformation under the action of the all main forces le's describe by the expression:

$$A_{def} = \sum_i \int_{R_s}^{R_s\lambda_i} f_i dx_i \qquad (69)$$

Using of the ratio (67) and

$$d\lambda_v/\lambda_v = \sum_i d\lambda_i/\lambda_i \qquad (70)$$

after the integration of (69) we will obtain the expression

$$A_{def} = kT \frac{d+2}{2} \left(\frac{R_s}{\sigma_0} \right)^2 \frac{s(s-1)}{2} \left(\frac{1}{\lambda_v} - 1 \right) \quad (71)$$

which is wholly identical to the obtained earlier (45). This proves the correctness of the determination of the main forces accordingly to (66) and (67).

2.5. Dynamical properties

2.5.1. Characteristic time of the transition and the coefficient of diffusion

Characteristic time of the translational motion t_t^* of the strainless polymeric star (here we will be specialized on the analysis only of this situation) let's determine as a time needed for the transfer of its equilibrium frozen conformation on the characteristic distance R_s. At the transfer of sN of the links on a distance R_s it is necessary to do $(R_s/a)sN$ steps, every of which is realized for a time τ, which can be called as the characteristic time of the segmental motion.

Thereby,

$$t_t^* = (R_s/a)sN\tau \quad (72)$$

Substituting the expression (32) for R_s in (72) we will obtain

$$t_t^* = (2N)^{(d+5)/(d+2)}(s/2)^{(d+3)/(d+2)}\tau \quad (73)$$

As it was shown in [32], the diffusion coefficient D at multivariate random transfer of the macromolecule is determined via expression:

$$D = \sigma_0^2 / 2t_t^* \quad (74)$$

which is the analog of the *Einstein's* equation $D = a^2/2\tau$ for low–molecular substances.

At the analysis of the directed transfer of macromolecule along i direction of the d–measured space, for example, under the action of gradient of chemical potential, it is necessary to use other determination of the diffusion coefficient:

$$D_i = \sigma_0^2 / 2dt_t^* \quad (75)$$

Substituting the expressions (73) and (31) in (75), finally we will obtain for the strainless polymeric star:

$$D_i = \frac{a^2}{2d\tau} \bigg/ (2N)^{3/(d+2)}(s/2)^{(d+3)/(d+2)} \quad (76)$$

2.5.2. Characteristic time of the rotational motion and the coefficient of the elastic component of viscosity

Viscous–elastic properties of the polymeric solutions suppose [32] the presence both of the frictional and elastic components of the measured effective viscosity. The elastic component of the viscosity is gradiently dependent value, depends also on a composition of the solution and on the coefficient of the elastic component of viscosity, which is determined via expression:

$$\eta_e^0 = \mu t_r^* \quad (77)$$

Here: μ is the determined earlier shear modulus; t_r^* is the characteristic time of the rotational motion.

As the characteristic time of the rotational motion let's assume a time during which the strainless polymeric star into the frozen equilibrium conformational state will be rotated around any axis on the characteristic angle, equal to the one radian. Accordingly to this determination, the links, allocated from the rotation axis on a distance r, pass a way r for r/a steps and for time $(r/a)\tau$. Since the allocation of the all sN links in d–measured space is unknown, we use the following approach [33] for the estimation of t_r^*.

Let's design on the $(d-1)$–measured rotation plate the all sN links of the polymeric star. Conformational radius of the rotation plate is equal to R_s, but the numbers of the projections should accept such acceptable values N' and s', that to provide the value R_s in $(d-1)$–measured space. Then substituting the values $d-1$, N' and s' in expression (32) for R_s instead of d, N and s correspondingly, we will obtain

$$R_s = a(2N')^{3/(d+1)}(s'/2)^{1/(d+1)} \quad (78)$$

From the comparison of (32) and (78) we will find the acceptable values of N' and s' in the rotation plate

$$2N' = (2N)^{(d+1)/(d+2)}, s'/2 = (s/2)^{(d+1)/(d+2)} \quad (79)$$

Let's select on the rotation plate the linear polymeric chain by $2N'$ length, consisting of the pair of rays from the s'. Let n is the number of the link of presented given undefined chain from the rotation axis. Let's assume, that the distance r_n of this link from the rotation axis is ordered to the same distribution (78), that is:

$$r_n = an^{3/(d+1)}(s'/2)^{1/(d+1)} \quad (80)$$

Although for the internal links of a chain this expression in not quite correct [*see the previous work in the presented collection book*], but the following integration shows, that the main endowment into characteristic time of the rotation has the links with the numbers neared to $2N'$.

Under the plane of rotation turn on the one radian, the links with the numbers of n tract a way r_n for r_n/a steps and for time $(r_n/a)\tau$. For all $s'N'$ links, distributed upon $s'/2$ linear chains, the rotation time will

be equal to $(s'/2)(r_n/a)\tau$. At the change of n on dn an increment of time consists of:

$$dt_r^* = (s'/2)(\tau/a)r_n dn \qquad (81)$$

After the integration of (81) via the limits from $n = 1$ till $n = 2N'$ with taking into account of (78) we will obtain

$$t_r^* = ((d+1)/(d+4))(2N')^{(d+4)/(d+1)}(s'/2)^{(d+2)/(d+1)}\tau \quad (82)$$

By change of N' on N and s' on s accordingly to (79), we finally find

$$t_r^* = \frac{d+1}{d+4}(2N)^{(d+4)/(d+2)}\frac{s}{2}\tau \qquad (83)$$

Next, using the expressions of (65) and (50) for shear modulus of unstrained polymeric star $\lambda_v = 1$, we have

$$\mu = \chi(kT/a^d)(2N)^{4(1-d)/(d+2)}(s/2)^{4/(d+2)}(s-1) \,(84)$$

Here $\chi = (3+\gamma(d-1))/(d-1)(1+\gamma)$

Combining the (83) and (84) for determination of the coefficient of elastic component of viscosity in (77) we finally find accurate within a multiplier neared to the one:

$$\eta_e^0 \cong (kT/a^d)(2N)^{(8-3d)/(d+2)}(s/2)^{(d+6)/(d+2)}(s-1)\tau \,(85)$$

Let's comment the obtained expressions (76) for D_i and (85) for η_e^0, comparing them with the same expressions for D_i and η_e^0 of linear polymeric chains, consisting the same number of sN links. For this purpose let introduce the branching indexes upon (2) type in form $g_D = D_i/D_{iL}$ and $g_\eta = \eta_e^0/\eta_{eL}^0$. For linear polymeric chains containing the sN links we have

$$D_{iL} = \frac{a^2}{2d\tau}\Big/(sN)^{3/(d+2)} \qquad (86)$$

$$\eta_{eL}^0 \cong \frac{kT}{a^d}(sN)^{(8-3d)/(d+2)}\tau \qquad (87)$$

Comparing the (87) and (85) and also (86) and (76) we have $g_D = (s/2)^{-d/(d+2)}$ and $g_\eta = (s/2)^{2(2d-1)/(d+2)}(s-1)$.

Thereby, at the same number of links, the polymeric stars are less mobile ($g_D < 1$), but have considerably more coefficient of the elastic component of viscosity $(g_\eta > 1)$, than the linear chains.

3. POLYMERIC STARS IN CONCENTRATED SOLUTION

3.1. Self–avoiding random walks statistics

In concentrated solution the conformational volumes of polymeric stars are overlapped in accordance with the condition $\rho > \rho^*$, in which ρ is a density of the solution upon polymer, ρ^* is the critical density corresponding to the start of the conformational volumes overlapping. Due to the polymeric star cannot be considered as an independent subsystem, it is necessary to consider the all set of the polymeric stars in conformational volume of the separated system.

Let's introduce the screen cubic d–measured space containing of m intertwining between themselves uniform polymeric stars. Let's separate from them any undefined star, and in it – any undefined pair of rays, forming the linear chain by $2N$ length. Its phantom *Gaussian* walks are ordered to the same distribution law (13) with the same normalization condition (10).

However, the probability $\omega(z)$ of the msN differed links distribution upon Z identical cells at the condition, that in every cell there is not more than one link, will be determined by a new expression:

$$\omega(z) = \frac{Z!}{(Z-msN)!}(\frac{1}{Z})^{msN}(1-\frac{1}{Z})^{Z-msN} \quad (88)$$

It follows from this, that the probability of the self–avoiding walks for undefined chosen pair of rays will be equal:

$$\omega(2N) = \big(\omega(Z)\big)^{2/ms}\omega(n) \qquad (89)$$

Here the index $2/ms$ was obtained as the ratio $2N/msN$. Combining the (13) and (88) into (89) and using as same principles as at the derivation of the (16) equation, we will obtain into the asymptotic limit from (89):

$$\omega(2N) = \exp\left\{-\frac{(ms/2)(2N)^2}{Z}-\frac{1}{2}\sum_i \frac{s_i^2}{n_i}\right\} \qquad (90)$$

The transition to the d–measured space is realizable with the use of the same previous expressions (17)–(20), accordingly to which

$$\omega(2N) = \exp\left\{-\frac{a^d(ms/2)(2N)^2}{\prod_i x_i}-\frac{1}{2}\sum_i \frac{x_i^2}{\sigma^2_i}\right\} \quad (91)$$

This distribution is true for any undefined pair of rays of any undefined star in general space $Z = \prod_i x_i/a^d$.

3.2. Thermodynamics of conformation and deformation of the intertwining polymeric stars

The numbers of configurations for pair of rays, polymeric star and m intertwined between themselves in m–ball polymeric stars let's determine, correspondingly, by the expressions:

$$L(2N) = L_{\max}(2N)\omega(2N) \qquad (92)$$

$$L(sN) = \big(L(2N)\big)^{s(s-1)/2} \qquad (93)$$

$$L(msN) = \left(L(2N)\right)^{ms(s-1)/2} \qquad (94)$$

Therefore, in accordance with *Boltzmann*, general entropy of the self–avoiding walks of the intertwined polymeric stars in *m*–ball will be equal:

$$S_0 = k\left(ms(s-1)/2\right)\ln L_{max}(2N) + k\left(ms(s-1)/2\right)\ln\omega(2N) \quad (95)$$

As same as earlier, only the second term in (95) we accept as the entropy of the conformation of *m*–ball of polymeric stars or as entropy of their self–organization:

$$S = k\left(ms(s-1)/2\right)\ln\omega(2N) \qquad (96)$$

At the absence of the energetic effects, a free energy of the conformation will be equal to:

$$F_m(x) = kT\frac{ms(s-1)}{2}\exp\left\{\frac{a^d(ms/2)(2N)^2}{\prod_i x_i} + \frac{1}{2}\sum_i\frac{x_i^2}{\sigma_i^2}\right\} \quad (97)$$

From the all possible states of the polymeric stars in *m*–ball let's choice the most probable or thermodynamically equilibrium states in accordance with the condition $\partial F_m(x)/\partial x_i = 0$. Differentiating of (98), we will obtain:

$$\partial F_m(x)/\partial x_i = kT\frac{ms(s-1)}{2}\exp\left\{-\frac{a^d(ms/2)(2N)^2}{x_i\prod_i x_i} + \frac{x_i}{\sigma_i^2}\right\} \quad (98)$$

Equaling the right parts of (98) to zero for all $i = 1,d$ and solving the obtained system of the algebraic equations, let's find the equilibrium semi–axes of the conformational ellipsoid, general for any pair of rays, any polymeric star and *m*–ball in the large:

$$X_i = \sigma_i\left[\frac{a^d(ms/2)(2N)^2}{\prod_i \sigma_i}\right]^{1/(d+2)} \qquad (99)$$

At the equiprobability of walks upon the all directions of *d*–measured space that is reflected by the condition of $\sigma_i = \sigma_0$ accordingly to (31), we have the spherical conformational volume with the radius:

$$R_m = a(2N)^{3/(d+2)}(ms/2)^{1/(d+2)} \qquad (100)$$

Deformation of the *m*–ball at its transition from the spherical (unstrained) conformational state into the ellipsoid with the semi–axes X_i let's express via the multiplicities of the linear λ_i and volumetric λ_v deformation via ratios:

$$\lambda_i = X_i/R_m, \quad \lambda_v = \prod_i X_i\Big/R_m^d = \prod_i \lambda_i \qquad (101)$$

which are also ordered to the equation of the relationship (41).

Next, substituting the equilibrium values $X_i = R_m\lambda_i$ in (97) we will find the equilibrium free energy of the strained *m*–ball:

$$F_m(\lambda) = kT\frac{d+2}{2}\left(\frac{R_m}{\sigma_0}\right)^2\frac{ms(s-1)}{2}\Big/\lambda_v \quad (102)$$

It follows from this, that in the system of the mechanics signs a work of the transition of the unstrained *m*–ball with $\lambda_v = 1$ into the deformed state of the conformational ellipsoid with $\lambda_v < 1$ will be equal to:

$$\Delta F_{def} = kT\frac{d+2}{2}\left(\frac{R_m}{\sigma_0}\right)^2\frac{ms(s-1)}{2}\left(\frac{1}{\lambda_v}-1\right) \qquad (103)$$

Next, determining the conformation pressure via the same thermodynamic ratio (47), in which the conformational volume of *m*–ball in general case is equal to $V = R_m^d\lambda_v$, we find

$$P = kT\frac{d+2}{2}\left(\frac{R_m}{\sigma_0}\right)^2\frac{ms(s-1)}{2}\Big/R_m^d\lambda_v^2 \qquad (104)$$

Again we have $P = F/V$ and the equation of the conformational state of *m*–ball for intertwined polymeric stars:

$$PV^2 = FV = const, \qquad (105)$$

$$const = kT\frac{d+2}{2}\left(\frac{R_m}{\sigma_0}\right)^2\frac{ms(s-1)}{2}R_m^d \quad (106)$$

3.3. Modulus of elasticity of m–ball for intertwining polymeric stars

An equation of the deformation for the *m*–ball of the intertwined polymeric stars we write in the same general differential form (53) and transform it relatively to the *Young's* modulus into the form (54). Corresponding derivatives we find via the differencing of (98) with the following substitution of the equilibrium values $x_i = X_i = R_m\lambda_i$:

$$\partial f_i/\partial x_i = 3kTms(s-1)/2\sigma_0^2\lambda_i^2\lambda_v, \qquad (107)$$

$$\partial f_i/\partial x_j = \partial f_j/\partial x_i = kTms(s-1)/2\sigma_0^2\lambda_i\lambda_j\lambda_v \quad (108)$$

Substituting of these expressions in (54), we will obtain:

$$Y = kT\left(3+\gamma(d-1)\right)\left(\frac{R_m}{\sigma_0}\right)^2\frac{ms(s-1)}{2}\Big/R_m^d\lambda_v^2 \quad (109)$$

Comparing of (109) with the expression (104) for *P*, we have the relationship between Y and *P*:

$$Y = 2\left(3+\gamma(d-1)\right)P/(d+2) \qquad (110)$$

From the other hand, determining of *Y* via the volumetric modulus $E = 2P$ by the ratio (60), we will again obtain the relationship by (62) type, comparing of which with the (110), we will obtain the expression for the *Poisson* coefficient in the well–known form (63). So, the *Poisson* coefficient both for the linear chains and for the polymeric stars in diluted and concentrated solutions is the universal function only on the *Euclidian* space.

Using the relationship (64), let's express the shear modulus μ of the m–ball of the intertwined polymeric stars via the conformation pressure in the known form:

$$\mu = \frac{2(3+\gamma(d-1))}{(d+2)(d-1)(1+\gamma)}P \qquad (111)$$

3.4. Main forces and a work of the deformation of m–ball of the intertwining polymeric star

The main forces of the deformation let's again determine as the forces, which should be applied to the m–ball, in order to transfer it from the unstrained state equilibrated with respect to the σ_0, into the deformated state, equilibrated with respect to the σ_i. That is why it is necessary again to substitute instead of σ_i the value σ_0 in the expression $f_i = \partial F_m / \partial x_i$ accordingly to (98), and x_i to change on X_i, that is

$$f_i = kTm\frac{s(s-1)}{2}\left[-\frac{a^d m(s/2)(2N)^2}{X_i\prod_i X_i}+\frac{X_i}{\sigma_0^2}\right] \qquad (112)$$

After the substitution $X_i = R_m\lambda_i$, we have

$$f_i = kT\frac{ms(s-1)}{2}\frac{R_m}{\sigma_0^2}\frac{\lambda_i^2\lambda_v-1}{\lambda_i\lambda_v} \qquad (113)$$

Describing the deformation work of the m–ball by the same equation of mechanics (69) with the use of the expression (113) for the main forces, we will obtain again the expression $A_{def} = \Delta F_{def}$ in accordance with the (103).

3.5. Determination of m, R_m, F_m and P as the explicit functions s, N and concentration ρ of polymeric stars in solution

Concentration (density of solution upon polymer) of polymeric stars in concentrated solution is equal to

$$\rho = M_0 msN/N_A R_m^d \qquad (114)$$

where M_0 is the molar mass of a link. At $m = 1$ we have the critical concentration, to which the beginning of the polymeric stars conformational volumes overlapping corresponds:

$$\rho^* = M_0 sN/N_A R_s^d \qquad (115)$$

From the comparison of (114) and (115) follows

$$m^{2/(d+2)} = \rho/\rho^* \qquad (116)$$

Determining the density in the volume of a link via expression

$$\rho_0 = M_0 / N_A a^d \qquad (117)$$

we find

$$\rho^* = \rho_0 (2N)^{2(1-d)/(d+2)}(s/2)^{2/(d+2)} \qquad (118)$$

This permits to write for m and R_m the expressions

$$m = (2N)^{d-1}(\rho/\rho_0)^{(d+2)/2}(s/2)^{-1}, \qquad (119)$$

$$R_m = a(2N)(\rho/\rho_0)^{1/2}. \qquad (120)$$

via substituting of which in (102) and (104), we will find

$$F_m(\lambda) = ((d+2)/2)kT(2N)^d(\rho/\rho_0)^{(d+4)/2}(s-1)/\lambda_v \qquad (121)$$

$$P = \frac{d+2}{2}\frac{kT}{a^d}\left(\frac{\rho}{\rho_0}\right)^2(s-1)/\lambda_v^2 \qquad (122)$$

We can easy find the explicit functions of the modulus of elasticity on N, s and ρ via P in accordance with (122).

3.6. A work of the intertwining of polymeric stars

A change of free conformation energy at the transition of the m polymeric stars from the diluted solution into the concentrated one is equal to $F_m - mF_s$. In calculation per one polymeric chain we have:

$$\Delta F_p = (F_m - mF_s)/m \qquad (123)$$

In a system of the mechanics signs this value determines a work of the polymeric stars intertwining as a work of the polymeric star transfer from the diluted solution in concentrated one. After the substitution in (123) of the expressions (42), (102) we will obtain:

$$\Delta F_p = \frac{d+2}{2}kT\frac{s(s-1)}{2}\left(\frac{R_s}{\sigma_0}\right)^2\left(m^{2/(d+2)}-1\right) \qquad (124)$$

where $m^{2/(d+2)} = \rho/\rho^*$. From the other hand, expressing the conformational volumes of polymeric chains in diluted solution $V_s = mR_s^d$, and in concentrated $V_m = R_m^d$, we have

$$\lambda_v = V_m/V_s = m^{-2/(d+2)} \qquad (125)$$

Therefore, a work of the polymeric stars overlapping into the m–ball represents by itself a work of the conformational volume compression at the transfer of the star from the diluted solution into the concentrated one:

$$\Delta F_p = \frac{d+2}{2}kT\frac{s(s-1)}{2}\left(\frac{R_s}{\sigma_0}\right)^2(1/\lambda_v-1) \qquad (126)$$

3.7. Dynamical properties of polymeric stars in concentrated solution

3.7.1. Characteristic time of the transition and a diffusion coefficient

Characteristic time of the translational motion of polymeric stars in concentrated solution let's determine as a time t_{mt}^*, for which the m–ball of the intertwined polymeric stars with the frozen equilibrium conformation will be displaced on the effective distance R_m consequently of the random walks upon the all d directions of space. The next expression corresponds to this determination:

$$t_{mt}^* = (R_m/a)msN\tau \qquad (127)$$

in which as before τ is the characteristic time of the segmental motion. Substituting in this expression the ratios (119) and (120), determining the m and R_m, we will obtain:

$$t_{mt}^* = (2N)^{d+1}(\rho/\rho_0)^{(d+3)/2}\tau \qquad (128)$$

A diffusion coefficient for the chosen direction, determined earlier by the ratio (75), will be described via expression:

$$D_i = \frac{a^2}{2d\tau}(2N)^{-d}(\rho/\rho_0)^{-(d+3)/2} \qquad (129)$$

3.7.2. Characteristic time of the rotational motion and the coefficient of the elastic component of viscosity

Characteristic time t_{mr}^* of the rotational motion of the m–ball of the intertwined polymeric stars let's determine as a time, needed for the turn of the frozen equilibrium conformation of m–ball on the elementary angle equal to the one radian.

Let's select the rotation plate by dimensionality d–1 with the same conformational radius R_m and blueprint on it the all msN links of the m–ball. Obtained projections N', s' and m' are ordered to the *SARW* statistics, that is why the conformation radius in d–1 plate can be write as follow:

$$R_m = (2N')^{3/(d+1)}((ms/2))^{1/(d+1)} \qquad (130)$$

Comparing the (130) and (100), we determine the relationships

$$(2N)' = (2N)^{(d+1)/(d+2)}, (ms)' = (ms)^{(d+1)/(d+2)} \qquad (131)$$

Let's select a chain by the $2N'$ length from the general numbers of the projections. Assuming that the internal links of this chain with the numbers of n from the rotation center are ordered to the same regularity (130), their rotation radius will be expressed via ratio:

$$r_n = an^{3/(d+1)}((ms)'/2)^{1/(d+1)} \qquad (132)$$

At the turn on an angle by the one radian these projections with the numbers n from the rotation center pass the distance r_n for r_n/a steps and for time $(r_n/a)\tau$. At the change of n on dn an increment of time consists of $dt_{1r}^* = (r_n/a)\tau dn$. By integrating of this expression from $n=1$ till $n=2N'$, we will obtain:

$$t_{1r}^* = \frac{d+1}{d+4}(2N')^{(d+4)/(d+1)}\left(\frac{(ms)'}{2}\right)^{1/(d+1)}\tau \qquad (133)$$

For the all $(ms)'/2$ chains we have $t_{mr}^* = t_{1r}^*(ms)'/2$. Taking into account the relationships (131) we finally find:

$$t_{mr}^* = \frac{d+1}{d+4}(2N)^{d+2/(d+2)}\left(\frac{\rho}{\rho_0}\right)^{(d+2)/2}\tau \qquad (134)$$

We determine the coefficient of the elastic component of viscosity of concentrated solution of polymeric stars $\eta_{me}^0 = \mu t_{mr}^*$ via the characteristic time t_{mr}^* and the shear modulus μ. Using the ratios (111) and (122) at λ_v=1 for μ and (134) for t_{mr}^*, we find:

$$\eta_{me}^0 = \chi\frac{kT}{a^d}(2N)^{d+2/(d+2)}\left(\frac{\rho}{\rho_0}\right)^{(d+6)/2}(s-1)\tau \qquad (135)$$

Here the value $\chi = (d+1)(3+\gamma(d-1))/(d+4)(d-1)(1+\gamma)$ for $d=3$ space neared to the one, that is why it can be written:

$$\eta_{me}^0 \cong \frac{kT}{a^3}(2N)^{3,4}(\frac{\rho}{\rho_0})^{4,5}(s-1)\tau \qquad (136)$$

4. Conclusion

Self–avoiding random walks statistics completely describes the thermodynamic and dynamic properties of the polymeric stars in diluted solutions as the function on a length and the number of rays; in concentrated solutions additionally as the function on the concentration of polymer.

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