

Conformation and Deformation of Linear Macromolecules in Concentrated Solutions and Melts in the Self-Avoiding Random Walks Statistics

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ABSTRACT: A strict statistics of self-avoiding random walks in the d -measured lattice and continuous space for intertwining chains in the concentrated solutions and melts was proposed. On the basis of this statistics the thermodynamics of conformation and isothermal and adiabatic deformation of intertwining chains was described. The equation of conformational state has been obtained. It was shown that in the field of chains overlap they are stretched increasing its conformational volume. In this volume there are other chains with the formation of m -ball. Free energy of a chain conformation does not depend upon the fact, if the chains intertwined or they are isolated in the m -ball. Mixing entropy is responsible to the chains interweaving in the m -ball. Dependencies of the conformational radius, free energy, and conformation pressure on respective concentration of polymeric chains have been determined. Using the thermodynamics of intertwining polymeric chains of m -ball conformational state and also the laws of isotropic media deformation into linear differ-

ential form the theoretical expressions for elasticity modules (namely, volumetric volume, Young's module and shift's module) and for the main tensions appearing at the equilibrium deformation of the m -ball were obtained. Poisson's coefficient is a function only on the Euclidean's space and for the real three-dimensional space is equal to $3/8$. A simple model explaining the tensile strength of the m -ball by the chains intertwining effect and, thereafter by the loss of the mixing entropy, but not by the chemical bonds breaking was proposed. Calculations of the elastic properties, the main tensions, and tensile strength of natural rubber carried out without using the empirical adjusting parameters are in good agreement with the experimental data. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2472–2481, 2008

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INTRODUCTION

Self-avoiding random walks (SARW) statistics has been proposed¹ for single, that is noninteracting between themselves, ideal polymeric chains (free-articulated Kuhn's chains²) into ideal solvents, in which the all-possible configurations of the polymeric chain are energetically equal. From this statistics it is followed that under the absence of external forces the conformation of a polymeric chain takes the shape of the Flory ball, the most verisimilar radius R_f of which is described by known expression^{3,4}

$$R_f = aN^{3/(d+2)} \quad (1)$$

Here a is statistical length of the chain's link; N is number of the links in chain or its length; d is the dimension of the Euclidean's space.

Polymeric chains in the concentrated solutions and melts at molar-volumetric concentration c of the chains more than critical one $c^* = (N_A R_f^d)^{-1}$ are intertwined. As a result, from the author's point of view³ the chains are squeezed decreasing their conformational volume. Accordingly to the Flory theorem⁴ polymeric chains in the melts behave as the single ones with the size $R = aN^{1/2}$, which is the root-mean quadratic radius in the random walks (RW) Gaussian statistics.

SARW statistics leads to other result.

SARW STATISTICS FOR INTERTWINING CHAINS IN D -DIMENSIONAL LATTICE SPACE

Let us introduce the d -dimensional lattice with the cell's parameter equal to the statistical length a of the chain's link; let us notify, that Z is number of cells in a space and m chains are represented in it; every chain has the length N . As same as earlier,¹ we will disregard the energetic effects considering the all-possible configurations of the chains as equivalent.

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We appropriate the random chain and notify as n_i the numbers of steps of the end of chain random walk along i -directions of d -dimensional lattice. At this,

$$\sum_i n_i = N, \quad i = 1, d \quad (2)$$

The probability $\omega(n)$ that at given n_i the end of chain draws $s_i = n_i^+ - n_i^-$ efficient steps is subordinated to Bernoulli's distribution.¹

$$\omega(N) = \left(\frac{1}{2}\right)^N \prod_i \{n_i! / [(n_i + s_i)/2]! [(n - s_i)/2]!\} \quad (3)$$

Change of a sign s_i in eq. (3) does not change the value $\omega(n)$; hence this probability represents the probability of fact that the RW trajectory per n_i steps along i -directions of the d -dimensional space will be finished in one of the 2^d cells $M(s)$, position data of which are given by vectors $s = (s_i)$, $i = 1, d$ differing only by the signs of own components s_i .

Condition of the self-avoiding RW trajectories' absence on the d -dimensional lattice demands the circumstance at which more than one link of the chain cannot be stood in every cell. Links of the chain are inseparable; they cannot be divided from each other and located into the cells in random order. Thereby, number of different methods of mN differing links location per Z identical cells under condition that in every cell more than one link of the chain cannot be stood is equal to $Z! / (Z - mN)!$.

By identifying the cells the antecedent probability of fact that the cell will be occupied by presented link equal to $1/Z$, and when it will not be occupied—then $(1 - 1/Z)$. Consequently, probability $\omega(z)$ of mN differing links distribution per Z identical cells is determined by Bernoulli's distribution.

$$\omega(z) = \frac{Z!}{(Z - mN)!} \left(\frac{1}{Z}\right)^{mN} \left(1 - \frac{1}{Z}\right)^{Z - mN} \quad (4)$$

Distribution (3) describes the RW trajectory of one random chain whereas the expression (4) assigns the links distribution of all m chains. That is why, the probability $\omega(s)$ of common event consisting of the fact that the RW trajectory of random chain is also the SARW trajectory and at given Z , n , N , and n_i will turned out by its own last step in one among 2^d equiprobable cells $M(s)$ will be equal to

$$\omega(s) = (\omega(z))^{1/m} \omega(n) \quad (5)$$

Using the Stirling's formula under condition $Z > 1$, $N > 1$, $n_i > 1$ and factorizations $\ln(1 - 1/Z) \approx -1/Z$, $\ln(1 - mN/Z) \approx -mN/Z$, $\ln(1 \pm s_i/n_i) \approx \pm s_i/n_i - (s_i/n_i)^2/2$ accordingly to condition $s_i < n_i$, $mN <$

Z and also assuming $N(N-1) \approx N^2$, we find the asymptotic (5) with accuracy to the constant multiplier:

$$\omega(s) \approx \exp\left\{-\frac{mN^2}{Z} - \frac{1}{2} \sum_i s_i^2/n_i\right\}, \quad m \geq 1 \quad (6)$$

As same as earlier,¹ let us assume, that the fiducial cells $M(s)$ generally appertain to ellipsoid surface. Then we have¹

$$Z = d^{d/2} \prod_i |s_i| \quad (7)$$

Determination (7) means, that the d -dimensional space consisting of Z cells is disposable for any random chain; this demands of their full mixing.

Combining the expressions (6) and (7) we will obtain

$$\omega(s) = \exp\left\{-mN^2/d^{d/2} \prod_i |s_i| - \frac{1}{2} \sum_i s_i^2/n_i\right\} \quad (8)$$

Function $\omega(s)$ determines the probability that the RW trajectory of the random walk is simultaneously also by SARW trajectory and by its own last step realizes the state $M(s)$. Hence, it is numerically equal to part of these SARW trajectories among general number $(2d)^N$ of RW trajectories which realize the state $M(s)$. Number $L(s)$ of such SARW trajectories determines the thermodynamical probability of the realization $M(s)$:

$$L(s) = (2d)^N \omega(s) \quad (9)$$

By summing $L(s)$ upon the all set of possible state of the chain's end we find general number L of SARW trajectory:

$$L = (2d)^N c(s) \quad (10)$$

where

$$c(s) = \sum_s \exp\left\{-mN^2/d^{d/2} \prod_i |s_i| - \frac{1}{2} \sum_i s_i^2/n_i\right\} \quad (11)$$

Then function

$$w(s) = \frac{1}{c(s)} \exp\left\{-mN^2/d^{d/2} \prod_i |s_i| - \frac{1}{2} \sum_i s_i^2/n_i\right\} \quad (12)$$

normalized per unity and determines the end of chain distribution upon states $M(s)$ of d -dimensional lattice. It is equal to ratio of number $L(s)$ of SARW trajectories realizing the state $M(s)$ to general number L of SARW trajectories: $w(s) = L(s)/L$.

In turn, the ratio $L/(2d)^N$ equal to part of general number of SARW trajectories among general number of RW trajectories in accordance with the adopted terms³ is the fatigue function $g(N)$ of the SARW trajectories: $g(N) = L/(2d)^N = c(s)$.

SARW STATISTICS FOR INTERTWINING CHAINS IN CONTINUOUS D -DIMENSIONAL SPACE

Let us introduce the variable of displacement x_i , which is by semiaxis of conformational ellipsoid; the state $M(s)$ appertains to the surface of this ellipsoid¹

$$x_i = a|s_i|d^{1/2} \quad (13)$$

and parameter σ_i is a standard deviation of the Gaussian part of the distribution (12)

$$\sigma_i^2 = a^2 n_i d \quad (14)$$

In accordance with the expression (2) the following connection is imposed on the values σ_i

$$\sum_i \sigma_i^2 = a^2 N d \quad (15)$$

Since $S_i^2/n_i = x_i^2/\sigma_i^2$, $d^{d/2} \prod_i |s_i| = a^{-d} \prod_i x_i$ the eq. (12) can be re-written as

$$\omega(x) = \frac{1}{c(x)} \exp \left\{ -a^d m N^2 / \prod_i x_i - \frac{1}{2} \sum_i x_i^2 / \sigma_i^2 \right\} \quad (16)$$

$$c(x) = \int \exp \left\{ -a^d m N^2 / \prod_i x_i - \frac{1}{2} \sum_i x_i^2 / \sigma_i^2 \right\} dx \quad (17)$$

At this, $c(x)$ is d -multiple integral upon all possible values x_i , $dx = \prod dx_i$. Since $c(x) = a^d d^{d/2} c(s)$ we have $g(N) = c(x)/a^d d^{d/2}$.

Integral $c(x)$ can be taken with the adequate accuracy by saddle-point technique.^{1,5}

Change of (13) introduces an essential difference between $w(s)$ and $w(x)$: the last determines the probability $w(x)dx$ of fact that the SARW trajectory at given values m , N , and σ_i will finished in the elementary volume $dx = \prod_i dx_i$ lying on the surface of the ellipsoid with the semiaxes x_i , $i = 1, d$.

THERMODYNAMICS OF CONFORMATION AND DEFORMATION OF INTERTWINING CHAINS

Maximum $w(x)$ at given m , N , and σ_i determines the most expected or equilibrium state of the polymeric chain. Semiaxes x_i of equilibrium conformational ellipsoid will be found from the condition $\partial \ln w(x) / \partial x_i = 0$ at $x_i = X_i$:

$$X_i = \sigma_i \left(a^d m N^2 / \prod_i \sigma_i \right)^{1/(d+2)} \quad (18)$$

In the absence of external forces all the directions of the end of chain walking are equiprobable accordingly to condition $n_i = N/d$; so

$$\sigma_i^2 = \sigma_0^2 = a^2 N \quad (19)$$

Substitution of (19) into (18) makes the semiaxes X_i of equilibrium ellipsoid the same and equal to radius R_m of the conformational sphere; the same distribution density $\omega(x)$ corresponds to the surface of this conformational sphere:

$$R_m = a N^{3/(d+2)} m^{1/(d+2)} \quad (20)$$

Expression (20) determines not only the conformational radius of one random chain, but due to the chains intertwining effect it also determines the conformational radius of all m chains. Thereby R_m^d is the conformational volume of m -ball disposable for all the intertwining chains. As we can see, m -ball is a fractal with two fractal indexes: first is $3/(d+2)$ and it determines the dependence R_m on the chain N ; the second is $1/(d+2)$ and it determines the dependence on number of chain in m -ball.

We can see from the comparison of (20) and (1) that the conformational radius R_m of m -ball and, respectively, of any random chain in it is more than the conformational radius R_f of random chain: in m -ball the chains are stretched but are not twisted. The presence of other chains diminishes the number of free cells of d -dimensional lattice accessible for SARW trajectory of presented chains enforcing it to encroach more volume of the space.

In the presence of external forces acting along i -axes of the d -dimensional space, $\sigma_i \neq \sigma_0$ and m -ball is deformed into the ellipsoid with semiaxes X_i , according to (18). It is convenient to introduce the following variables as a measure of m -ball deformation

$$\Lambda_i = X_i / R_m \quad (21)$$

which characterize the multiplicity of the linear deformation of m -ball along i -direction of a space.

Next, let us determine the multiplicity Λ_v of volumetric deformation via expression

$$\Lambda_v = \prod_i X_i / R_m^d = \prod_i \Lambda_i \quad (22)$$

Because of eq. (2)¹ at any deformations of the m -ball its conformational volume is decreased: $\Lambda_v \leq 1$. The connection equation between Λ_i corresponds to connection eq. (2):

$$\sum_i \Lambda_i^2 = d / \prod_i \Lambda_i \tag{23}$$

In continuous space the thermodynamical probability $W(x)$ of the realization of state in which the end of chain is located on the surface of the ellipsoid with the semiaxes X_i is equal to

$$W(x) = L\omega(x) \tag{24}$$

As same as for the lattice space, general number L of SARW trajectories in continuous space let us determine in the form (10), that is $L \approx (2d)^N c(x)$. That is why

$$W(x) \approx (2d)^N \exp \left\{ -a^d m N^2 / \prod_i x_i - \frac{1}{2} \sum_i x_i^2 / \sigma_i^2 \right\} \tag{25}$$

Entropy S of presented conformational state is equal to $S = k \ln W(x)$, free energy $F = -TS$ or $F = -kT \ln W(x)$. From (25) follows $F = F_0 + F(x)$ where

$$F_0 \approx -kTN \ln 2d \approx -\frac{d}{2} kTN \tag{26}$$

$$F(x) = kT \left\{ a^d m N^2 / \prod_i x_i + \frac{1}{2} \sum_i x_i^2 / \sigma_i^2 \right\} \tag{27}$$

Thereby, F_0 represents by itself a free energy of random walks independent of the conformational state of a chain; $F(x)$ brings a positive contribution into F and the sense of this consists in a fact that the terms $F(x)$ and $S(x)$ represent the limitations imposed on the trajectories of random walk by request of the self-avoiding absence. These limitations form the self-organization effect of the polymeric chain; the conformation of polymeric chain is the statistical form of its self-organization.

Since F_0 doesn't depend on the conformational state of a chain we assume that the free energy of a polymeric chain conformation is equal to $F = F(x)$ accordingly to (27). Expression for the free energy of equilibrium conformation of polymeric chain will be obtained by substitution of the values $x_i = X_i$ in (27) in accordance with the (18):

$$F_m = \left(1 + \frac{d}{2} \right) kT \left(\frac{R_m}{\sigma_0} \right)^2 / \Lambda_v \tag{28}$$

For nondeformed m -ball we have $\Lambda_v = 1$ and

$$F_m^0 = \left(1 + \frac{d}{2} \right) kT \left(\frac{R_m}{\sigma_0} \right)^2 \tag{29}$$

From this the expression for the deformation work ($A = \Delta F_{\text{def}}$ in the system of the mechanics signs) of m -ball into ellipsoid in calculation per one chain follows

$$\Delta F_{\text{def}} = \left(1 + \frac{d}{2} \right) kT \left(\frac{R_m}{\sigma_0} \right)^2 \left(\frac{1}{\Lambda_v - 1} \right) \tag{30}$$

Since $\Lambda_v \leq 1$, a work of the deformation is positive $\Delta F_{\text{def}} \geq 0$, that is realized above the polymeric chain. Let us compare a free energy F_m^0 of the polymeric chain in nondeformed m -ball with a free energy F_f of single deformed polymeric chain¹

$$F_f = \left(1 + \frac{d}{2} \right) kT \left(\frac{R_f}{\sigma_0} \right)^2 / \lambda_v \tag{31}$$

Here λ_v is a multiplicity of the volumetric deformation of *Flory* ball.

Let us assume that the chains in m -ball aren't intertwined, each of them occupies the isolated volume equal to R_m^d/m . Then the multiplicity of the volumetric deformation of *Flory* ball into m -ball will be equal to

$$\lambda_v = R_m^d / m R_f^d = m^{-2/(d+2)} \tag{32}$$

We will obtain for the conformation free energy of isolated chain into m -ball

$$F_f = \left(1 + \frac{d}{2} \right) kT \left(\frac{R_f}{\sigma_0} \right)^2 m^{2/(d+2)} \tag{33}$$

that is equal to F_m^0 according to (29) with taking into account that $(R_m/\sigma_0)^2 = (R_f/\sigma_0)^2 m^{2/(d+2)}$.

Thereby, free energy of the conformation of single chain into m -ball for intertwining or isolated one from another chains is the same. Free energy of the conformation is not the factor, which facilitates or prohibits the chains intertwining.

In the absence of energetic interaction this factor is the entropy of mixing. It can be estimated via the numbers of displacement methods of all the chains links into m -ball with the exception of a displacement links in every chains: $(mN)!/(N!)^m$. From this, under the Stirling's approximation, we will obtain the expression for the entropy of mixing ΔS_c in calculation per one chain, $\Delta S_c = kN \ln m$, and, respectively, we will obtain for free energy ΔF_c of mixing

$$\Delta F_c = -kTN \ln m \tag{34}$$

The value $\Delta F_c < 0$ and can be sufficiently big per absolute value, for instance for melts, to provide the chains intertwining of their mixing in m -ball.

EQUATION FOR THE CONFORMATIONAL STATE OF M-BALL

Let us determine the pressure P of a conformation via the ordinal thermodynamic ratio $(\partial F / \partial V)_T = -P$

as a connection measure between the free energy and the volume of conformation. Taking into account all the chains into m -ball, we have $F = mF_m$, $V = R_m^d \Lambda_v$ that is why $P = -m \partial F_m / \partial \Lambda_v R_m^d$. By differing eq. (28) we have

$$P = \left(1 + \frac{d}{2}\right) kT \left(\frac{R_m}{\sigma_0}\right)^2 m / R_m^d \Lambda_v^2 \quad (35)$$

By multiplying eq. (35) to $V^2 = (R_m^d \Lambda_v)^2$ we will obtain the equation of the conformational state of m -ball:

$$PV^2 = mkT\beta \quad (36)$$

$$\beta = \left(1 + \frac{d}{2}\right) \left(\frac{R_m}{\sigma_0}\right)^2 R_m^d \quad (37)$$

By comparing eqs. (35) and (28) it follows that the pressure of the conformation numerically is equal to the density of free energy of the conformation of m -ball $P = mF_m/V$. That is why we have

$$F_m V = kT\beta \quad (38)$$

Thereby, the values PV^2 and $F_m V$ are integrals of the process of equilibrium deformation of m -ball.

ADIABATIC EQUATION FOR EQUILIBRIUM DEFORMATION OF M -BALL

It is well-known^{6,7} that at the adiabatic deformation of rubber its temperature is increased. The analysis of this phenomenon in the works^{6,7} is not quite correct. So let us consider the adiabatic deformation of the m -ball with the use of obtained thermodynamic ratios.

For elementary adiabatic process $C_v dT = -\delta A$, where C_v is the heat of the m -ball, δA is the elementary work in the systems of the thermodynamics signs. Because of determination of the conformation pressure we can write $\delta A = PdV$ and, thereby

$$C_v dT = -PdV \quad (39)$$

Using the equation of the conformational state (36) let us divide the variables in eq. (39)

$$C_v dT/T - mk\beta dV/V^2 \quad (40)$$

Integration of eq. (40) at $C_v = \text{const}$ for low-temperature interval in a ranges from $V = R_m^d$ and $V = R_m^d \Lambda_v$ and from T_0 till T corresponding to the temperatures of the start and the finish of the adiabatic process gives

$$C_v \ln \frac{T}{T_0} = \frac{mk\beta}{R_m^d} (1/\Lambda_v - 1) \quad (41)$$

We can see from this, that the adiabatic equation is as follow

$$T \exp\{-mk\beta/C_v R_m^d \Lambda_v\} = \text{const} \quad (42)$$

In accordance with the experimental data the temperature change at the adiabatic deformation of rubber is slight, hence it can be assumed that $\Delta T = T - T_0 \ll T_0$; this permits to rewrite eq. (41) with taking into account the expression (37) for β in following form

$$\Delta T \approx \left(1 + \frac{d}{2}\right) \frac{kT_0}{c_v} \left(\frac{R_m}{\sigma_0}\right)^2 (1/\Lambda_v - 1) \quad (43)$$

Here it was assumed that $C_v = mc_v$, where c_v is a heat of one chain.

EXPRESSION OF THE THERMODYNAMIC FUNCTIONS VIA RELATIVE CONCENTRATION OF MACROMOLECULES

In the field of the chains overlapping at $c \geq c^* = (N_A R_m^d)^{-1}$ their molar-volumetric concentration into m -ball and in all volume of the solution or melt is the same: $c = m/N_A R_m^d$.

It is more convenient for the melts to use the other determination of concentration since $\rho = mM/N_A R_m^d$, where M is a molar mass of the chain and is experimentally determined by a specific density of the melt. Speculative critical density $\rho^* = M/N_A R_m^d$ corresponds to it.

From this follows

$$\rho/\rho^* = c/c^* = m^{2/(d+2)} \quad (44)$$

The ratio (44) permits to determine the following dependencies, which with the aim of the shortness can be represented in the form of the commensurability: $R_m \sim (c/c^*)^{1/2}$, $F_m \sim c/c^*$, and $P \sim (c/c^*)^2$.

FORCES AND WORK OF THE DEFORMATION

Let us introduce one more parameter for characteristics of m -ball deformation with the aim of convenient description of elastic properties of the intertwining chains

$$\psi_i = \sigma_i/\sigma_0 \quad (45)$$

Because of the ratio (15) the following connection exists between ψ_i

$$\sum_i \psi_i^2 = d \quad (46)$$

We determine from the analysis of eqs. (18) and (20), and also from the determinations (21) and (22)

$$\psi_i = \Lambda_i \Lambda_v^{1/2} \tag{47}$$

In the system of the mechanics signs the deformation forces acting on the random chain into m -ball along i -axes of the d -dimensional space are equal to $f_i = \partial F(x)/\partial x_i$. By differing (27) we will obtain

$$f_i = kT \left(-a^d m N^2 / x_i \prod_i x_i + x_i / \sigma_i^2 \right) \tag{48}$$

However, under the equilibrium deformation in every current conformational state the forces should be equal to zero; just this is expressed via the equilibrium condition $\partial F(x)/\partial x_i = 0$ at $x_i = X_i$. Thereby, the substitution of the values $x_i = X_i$ into (48) draws f_i into zero. Let us determine as the force the external deformation force along i -direction, which should be imposed on the nondeformed m -ball with the conformation radius R_m , which is equilibrium with respect to the values $\sigma_i = \sigma_0$ to transform it into the deformed state of the ellipsoid with the semiaxes X_i equilibrium with respect to the values $\sigma_i \neq \sigma_0$, $i = 1, d$. In accordance with this determination in the expression (48) in the second term it is necessary to put $\sigma_i = \sigma_0$ but the values x_i to change on X_i accordingly to (18) at $\sigma_i \neq \sigma_0$. Making the corresponding substitution we will obtain the following expression for the external main forces of a deformation

$$f_i = kT \left(\frac{R_m}{\sigma_0^2} \right) (\psi_i^2 - 1) / \psi_i \left(\prod_i \psi_i \right)^{1/(d+2)} \tag{49}$$

In the adopted systems of signs $f_i > 0$ at the stretching ($\psi_i > 1$) and $f_i < 0$ at the contraction ($\psi_i < 1$).

With taking into account the connection (47) the force can be determined via the multiplicities of linear and volumetric deformation of m -ball.

$$f_i = kT \left(\frac{R_m}{\sigma_0^2} \right) (\Lambda_i^2 \Lambda_v - 1) / \Lambda_i \Lambda_v \tag{50}$$

The work of the deformation A in calculation per one chain into m -ball along the all main directions can be written in accordance with the mechanics rules in form:

$$A = \sum_i \int_{R_m}^{x_i} f_i dx_i \tag{51}$$

Substitution of (49) in (51) with taking into account the connection (47) leads to the expression for A , which is identical to the expression (30) for F_{def} : $A = \Delta F_{\text{def}}$ in the systems of the mechanics signs. The agreement confirms the truth of the deter-

mination of external forces of deformation according to (49).

ELASTICITY MODULES OF M-BALL

Taking into account the big sizes of polymeric chains deformation and their nonlinear relation with the tension let us express the relative linear deformation dx_i/x_i along i -direction of d -dimensional space under the action of all main forces f_i , $i = 1, d$ under the approximation of m -ball isotropy via the differential form⁸

$$Y \partial x_i / x_i = \partial f_i / \prod_{j \neq i} x_j + \gamma \sum_{j \neq i} \frac{\partial f_j}{\prod_{k \neq j} x_k} \tag{52}$$

Here: Y is Young's module; γ is Poisson's coefficient; $\prod_{j \neq i} x_j$ and $\prod_{k \neq j} x_k$ are the values of the sites in d -dimensional space normal to the forces f_i and f_j , respectively.

Let us rewrite the (52) relative to Young's module

$$Y = \frac{x_i^2}{\prod_i x} \frac{\partial f_i}{\partial x_i} + \gamma \sum_{j \neq i} \frac{x_i x_j}{\prod_i x_i} \frac{\partial f_j}{\partial x_i} \tag{53}$$

At equilibrium deformation the forces f_i are equal to zero, but not their derivatives $\partial f_i / \partial x_i$ and $\partial f_j / \partial x_j$. That is why by differing (48) upon x_i and x_j and by substituting the equilibrium values $x_i = X_i$ into obtained expressions we will obtain

$$\partial f_i / \partial x_i = 3kT / \sigma_0^2 \psi_i^2 \tag{54}$$

$$\partial f_i / \partial x_j = \partial f_j / \partial x_i = kT / \sigma_0^2 \psi_i \psi_j \tag{55}$$

Derivatives in (54) and (55) have been written in accordance with the determination (48) for one random chain. However, as same as the conformation pressure the elastic properties of the intertwining chains in m -ball need to take into account all the m chains. That is why by multiplying the right terms of (54) and (55) on m and by substituting the result in (53) we will find

$$Y = mkT [3 + \gamma(d - 1)] \left(\frac{R_m}{\sigma_0} \right)^2 / R_m^d \Lambda_v^2 \tag{56}$$

From the comparison of eqs. (35) and (56) follows, that the Young's module of m -ball and the conformation pressure are differed only by the coefficient and

$$Y = \frac{2[3 + \gamma(d - 1)]}{d + 2} P \tag{57}$$

In general case of the d -dimensional space the connection between the Young's module and the pres-

sure is expressed via the volumetric module $E = -VdP/dV$ by ratio⁸

$$E = Y/d[1 - \gamma(d - 1)] \quad (58)$$

From the equation of a state (12) follows

$$E = 2P \quad (59)$$

By comparing the eqs. (57)–(59) we will obtain the expression for Poisson's coefficient

$$\gamma = (d + 3)/(d + 1)^2 \quad (60)$$

Thereby, as same as for the random chain,¹ the Poisson's coefficient for intertwining chains is determined only by the dimensionality d of the Euclidean's space and at $d = 3$ is equal to $\gamma = 3/8$.

Via the Young's module and the Poisson's coefficient we find the shift module μ^2 :

$$\mu = Y/2(1 + \gamma) \quad \text{at } d \geq 2 \quad (61)$$

which is also easy expressed via the conformation pressure

$$\mu = \frac{3 + \gamma(d - 1)}{(d + 2)(1 + \gamma)} P \quad (62)$$

MAIN TENSIONS AND THE TENSILE STRENGTH

Connection between the tension G_i in planar surface normal to i -direction of the deformation and between its relative value $\partial x_i/x_i$ also let us write in differential form

$$\partial G_i = Y \partial x_i/x_i \quad (63)$$

In general case this equation hasn't a simple analytical solution, but permits with the use of (23) and (46) to obtain easily the constraint equation between G_i . By acting analogously to the developed algorithm,¹ we will obtain

$$\sum_i G_i = -\frac{1}{2} Y^0 (1/\Lambda_v^2 - 1) \quad (64)$$

where $Y^0 = Y$ at $\Lambda_v = 1$, that is for nondeformed m -ball.

The sign "minus" signifies, that a sum of the main tensions is subzero (that is negative) at any deformations of m -ball through its volume decreasing.

For analytical demonstration of G_i at equilibrium deformation, that is at $x_i = X_i$ let us rewrite the eq. (63) by taking into account the ratio $Y = Y^0/\Lambda_v^2$ and

substitute in it the expression $\partial \ln x_i = \partial \ln \psi_i - 1/2 d \ln \Lambda_v$ which follows from the connection (47). Then we will obtain

$$\partial G_i = Y^0 \left[\partial \psi_i / \psi_i \left(\prod_i \psi_i \right)^{4/d+2} - \frac{1}{2} \partial \Lambda_v / \Lambda_v^3 \right] \quad (65)$$

In the starting nondeformed state of m -ball the all $\psi_i = 1$, $\Lambda_v = 1$, and $G_i = 0$. By integrating (65) accordingly to these conditions we will find

$$G_i = Y^0 \left[\frac{1}{4} (1/\Lambda_v^2 - 1) + I_i \right] \quad (66)$$

$$I_i = \int_1^{\psi_i} \partial \psi_i / \psi_i \left(\prod_i \psi_i \right)^{4/(d+2)} \quad (67)$$

From this follows, that for the calculation of I_i and G_i , respectively, the constraint eq. (46) between ψ_i is insufficient; additional information about the character of deformation is needed to determinate the additional connection between ψ_i . One among the variants of the G_i calculation is considered in the next chapter.

At the m -ball stretching along the i -direction such critical tension is beginning at which m -ball is broken into two parts. Such critical tension G_{icr} is the numerical estimation of m -ball tensile stretch. Its mechanism is sufficiently complicated, but we will propose a simple model for the G_{icr} calculation. Accordingly to this model we assume that the break of m -ball into two parts at G_{icr} proceeds at the expense of the chains fraying, that is at the expense of the process inverse to their intertwining the physical network of the linkings is destroyed. Crosslinking of the chains at rubber vulcanization blocks the chains intertwining and so increases the stability of the vulcanized rubber. The chains intertwining in m -ball decreases the entropy of mixing. For nondeformed m -ball the entropy of mixing ΔS_c for all m chains is determined as

$$\Delta S_c = k Nm \ln m \quad (68)$$

Let in the deformed m -ball at a moment of break the part of the residual intertwining chains is equal to α . Then the entropy of mixing will be equal to

$$\Delta S_c = k Nm \alpha \ln(m\alpha), \quad m\alpha > 1 \quad (69)$$

The break of m -ball we consider as such equilibrium transition at which m -ball with the intertwining parameter α is divided by the plane of fracture into two $m/2$ -balls with the same intertwining parameter. The entropy of mixing into two $m/2$ -balls will be equal to

$$\Delta S'_c = kN\alpha m \ln(\alpha m/2), \quad \frac{\alpha m}{2} > 1 \quad (70)$$

The loss of the entropy of mixing at the m -ball braking will be $\Delta(\Delta S_c) = \Delta S'_c - \Delta S_c$; thereafter the work of a break $\Delta F_{br} = -T\Delta(\Delta S_c)$ will be

$$\Delta F_{br} = kTN\alpha m \ln 2 \quad (71)$$

At breaking the m -ball into two parts it can be assumed that $\alpha = 1/2$. Then

$$\Delta F_{br} = (1/2)kTNm \ln 2 \quad (72)$$

This work of the break is created by the work of the m -ball deformation at some critical value of the multiplicity of volumetric deformation $\Lambda_{v_{cr}}$. That is why by equating a work of the deformation ΔF_{def} according to (30) multiplied on m - in calculation per all m -ball at some critical value $\Lambda_{v_{cr}}$ to the work of a break ΔF_{br} accordingly to (72), we will find $\Lambda_{v_{cr}}$:

$$\Lambda_{v_{cr}} = \left[1 + \frac{1}{d+2} \left(\frac{\sigma_0}{R_m} \right)^2 N \ln 2 \right]^{-1} \quad (73)$$

Knowing the $\Lambda_{v_{cr}}$ we can calculate the tensile strength $G_{i_{cr}}$ at the m -ball stretching along the i -direction.

CALCULATIONS AND ILLUSTRATIONS

For calculations let us consider the real $d =$ three-dimensional space assuming that among three main tensions $f_x, f_y,$ and f_z only one, for example f_z is independent variable, that is external force, and $f_x,$ and f_y are reaction forces on f_z . At the isotropy of m -ball the forces and multiplicities of linear deformations along the x and y axes will be equal: $f_x = f_y, \Lambda_x = \Lambda_y$. In this case the conformational volume of the m -ball shapes the elongated ($f_z > 0, \Lambda_z > 1$) or strangulated ($f_z < 0, \Lambda_z < 1$) along z -axis on the ellipsoid of rotation.

For the ellipsoid of rotation the general constraint eqs. (23) and (46) take on the particular form

$$2\Lambda_v^2 + \Lambda_z^3 \Lambda_v - 3\Lambda_z = 0 \quad (74)$$

$$2\psi_x^2 + \psi_z^2 = 3 \quad (75)$$

By assigning the values Λ_z as to singular independent variable the values Λ_v have been calculated and further $\Lambda_x = \Lambda_y = (\Lambda_v/\Lambda_z)^{1/2}$.

For the shortness let us confine to the numerical analysis of the isothermal and adiabatic deformation of natural rubber, which at comparatively low chains crosslinking can be described as a melt.

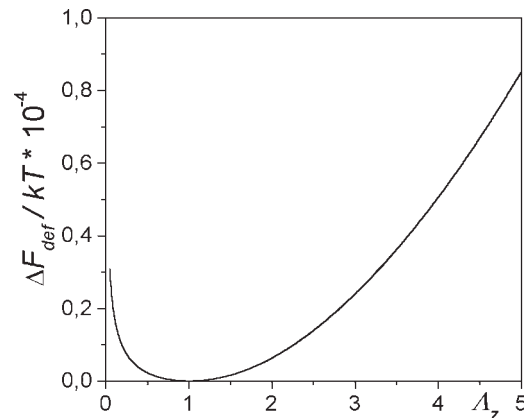


Figure 1 The work of the natural rubber deformation at its stretching ($\Lambda'_z > 1$) and squeezing ($\Lambda'_z < 1$) along z axis. Calculation has been done in accordance with the eq. (76).

For natural rubber—polyisoprene (C_5H_8) $_N$ —the following parameters have been chosen: number-average molar mass of the chain $M = 2 \cdot 10^6$ g/mol and average length of the chain $N = 2.9 \cdot 10^4$; $\rho = 0.91 \cdot 10^6$ g/m³, $a = 0.125$ nm. On the basis of these parameters $\rho^* = 1.54 \cdot 10^4$ g/m³ and $\rho/\rho^* = 59.1$ were determined.

The work of the isothermal deformation in units kT has been calculated in accordance with the eq. (30) converted to a form

$$\Delta F_{def}/kT = \frac{5}{2} N^{1/5} \left(\frac{\rho}{\rho^*} \right) (1/\Lambda_v - 1) \quad (76)$$

Results of the calculations are represented on Figure 1.

Dependence of $\Delta F_{def}/kT$ for one chain of the natural rubber on Λ_z is the same as for the Flory's ball,¹ but numerically exceeds the last in ρ/ρ^* times. Let us notify also, that in spite of the "very much" value $\Delta F_{def}/kT$ for one chain in calculation per one link, this magnitude has an order equal to 1.

Temperature change at adiabatic deformation of natural rubber was calculated accordingly to eq. (43), which under assumption $c_v = c_v^0 N$, where $c_v^0 = c_p^0$ is molar heat of the isoprene carries to

$$\Delta T = 5/2 \frac{RT_0}{c_p^0} N^{-4/5} \left(\frac{\rho}{\rho^*} \right) (1/\Lambda_v - 1) \quad (77)$$

where R is universal gaseous constant. At the calculation accordingly to (77) it was assumed in accordance with the reference data for the isoprene $c_p^0 = 152.3$ J/moleK, $T_0 = 300$ K.

Results of the calculations are represented on Figure 2. They are in good agreement with the experimental data.^{6,7}

Young's module has been calculated in accordance with the eq. (56) by taking into account (44) and $\gamma = 3/8$:

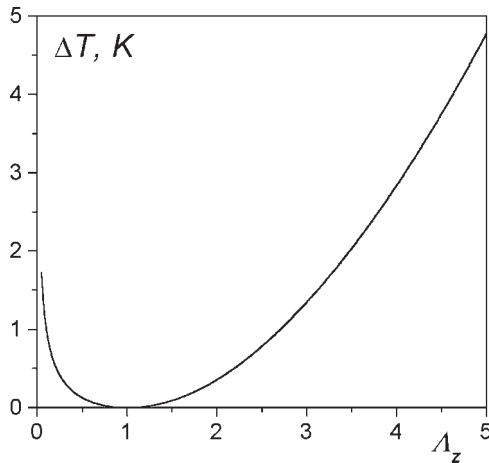


Figure 2 Temperature increasing at adiabatic deformation of natural rubber at its stretching ($\Lambda_z > 1$) and squeezing ($\Lambda_z < 1$) along z axis. Calculation has been done in accordance with the eq. (77).

$$Y = 3,75 \frac{kT}{a^3} N^{-8/5} \left(\frac{\rho}{\rho^*}\right)^2 / \Lambda_v^2 = Y^0 / \Lambda_v^2 \quad (78)$$

where $Y^0 = 1,97$ MPa is Young’s module of nondeformed rubber at $T = 300$ K. Results of the calculations are represented on Figure 3.

For the ellipsoid of rotation $G_x = G_y$, that is why we can write in accordance with (66)

$$G_x = Y^0 \left[\frac{1}{4} (1/\Lambda_v^2 - 1) + I_x \right] \quad (79)$$

$$G_z = Y^0 \left[\frac{1}{4} (1/\Lambda_v^2 - 1) + I_z \right] \quad (80)$$

Because of connection (75) every from integrals I_x and I_z can be balanced to one own variable. In accordance with the (67) and (75) we have

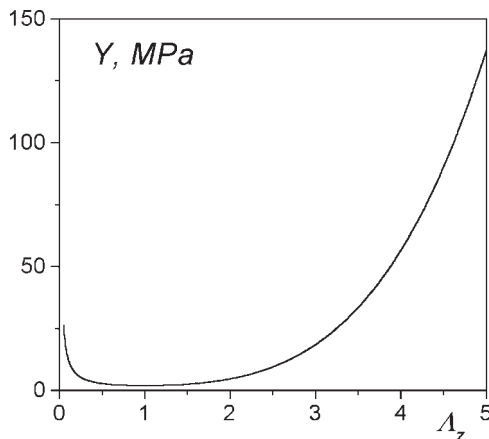


Figure 3 Dependence of the Young’s module on the multiplicity of linear deformation Λ_z at stretching and squeezing of natural rubber along z axis. Calculation has been done in accordance with the eq. (78).

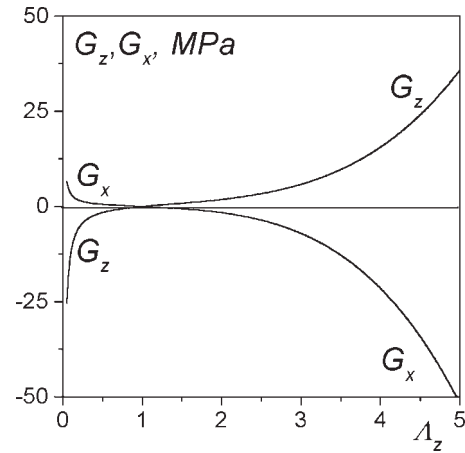


Figure 4 Dependence of the main tensions G_z and G_x on the multiplicity of linear deformation Λ_z at stretching and squeezing of natural rubber along z axis. Calculation has been done in accordance with the eqs. (79)–(82).

$$I_x = \int_1^{\psi_x} d\psi_x / \psi_x^{13/5} (3 - 2\psi_x^2)^{2/5} \quad (81)$$

$$I_z = 2^{4/5} \int_1^{\psi_z} d\psi_z / \psi_z^{9/5} (3 - \psi_z^2)^{4/5} \quad (82)$$

At this, superior limits of the integration are given by the ratios $\psi_x = \Lambda_x \Lambda_v^{1/2}$ and $\psi_z = \Lambda_z \Lambda_v^{1/2}$ following from (47).

Results of the calculations accordingly to eqs. (79)–(82) at $Y^0 = 1,97$ MPa are represented on Figure 4.

Needed for the estimation of $G_{z_{cr}}$ value of critical multiplicity of volumetric deformation $\Lambda_{v_{cr}}$ was calculated accordingly to eq. (73) by transforming it to a form

$$\Lambda_{v_{cr}} = \left[1 + \frac{1}{5} N^{4/5} \left(\frac{\rho^*}{\rho}\right) \ln 2 \right]^{-1} \quad (83)$$

As a result, we have obtained $\Lambda_{v_{cr}} = 0,103$, respectively, $\Lambda_{z_{cr}} = 5,39$, $\Lambda_{x_{cr}} = 0,138$. $G_{z_{cr}} = 48$ MPa corresponds to these values.

As we can see from the Figure 4, calculated dependence of the tension G_z on the multiplicity of natural rubber stretch is in good agreement with the experimental data.^{6,7,9} However, the numerical values G_z and $G_{z_{cr}}$ are in whole rather higher than the experimental ones. It is connected with the fact, that the last represented by themselves was not faithful, but conventional tensions and tensile strengths, which were estimated by not taking into account the volumetric deformation of the rubber.^{6,7,9}

CONCLUSIONS

Accordingly to the self-avoiding random walks statistics in the field of the chains intertwining that is in concentrated solutions and melts the polymeric chains are stretched increasing its conformational volume. In this volume other chains are also represented forming the m -ball. Free energy of the chain conformation doesn't depend on a fact if chains are intertwined or they are isolated in m -ball. The entropy of mixing is responsible for the chains intertwining in m -ball, but not free energy of the chains conformation. Dependencies of the conformational radius, free energy, and conformation pressure on relative concentration of the polymeric chains into solution or melt have been determined. Thermodynamical analysis of the isothermal and adiabatic deformation of m -ball has been done.

Self-avoiding random walks statistics for intertwining polymeric chains and based on it thermodynamics of their conformational state in m -ball permitted to obtain the theoretical expressions for elasticity modules and main tensions appearing at the

equilibrium deformation of m -ball. Calculations on the basis of these theoretical expressions without empirical adjusting parameters are in good agreement with the experimental data.

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