

STRUCTURAL-PHENOMENOLOGICAL THEORY OF STRESSED STATE IN GRADIENT FLOWS OF DILUTE POLYMER SOLUTIONS WITH DEFORMABLE CHAIN MACROMOLECULES

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A general rheological equation of dilute solutions of deformable chain macromolecules in low-molecular solvents is obtained. As a hydrodynamic model of macromolecules, we used a necklace of beads connected with Gaussian subchains. The constitutive equations of stressed state in solutions were derived using the structural-phenomenological approach. The obtained results are verified with the help of the rheological simulation of a solution of Zimm chain macromolecules with allowance for the elasticity of molecular chains and the micro-Brownian motion of their constituent atoms.

is explained by the easiness to derive very accurate experimental viscosimetric data [1]. Essential difficulties arise in the process of theoretical interpretation of the obtained experimental data. First of all, this is caused by a complicated structure of chain macromolecules of polymers and the infinite manifold of their possible conformations formed in the solution under the action of hydrodynamic forces arising in gradient flows, effective forces of Brownian diffusion, as well as intramolecular forces. Objectively, the latter are determined by structural peculiarities of a molecular chain of polymer macromolecules. In addition, they depend on the subjective viewpoint of a researcher (the author of the corresponding theory) on the dynamic model of macromolecules.

1. Introduction

In the present work, we have obtained the constitutive equations of stressed state in the gradient flows of deformable chain macromolecules in low-molecular solvents. A keen interest in such solutions arose when high-molecular compounds had been involved into the research field of molecular physics. In the condensed (block) state of polymers, the interaction between their macromolecules intertwined into a continuous net is so strong that structural features of macromolecules of a polymer cannot be judged by its measured physical properties. That's why, one of the necessary conditions for the investigation of the structure and properties of polymer macromolecules is their remoteness from one another by a distance sufficient for neglecting the intermolecular interaction. As polymer macromolecules cannot be converted to a gaseous phase without their destruction, the only way allowing to remote them by a sufficient distance from one another is the resolution of a polymer in low-molecular solvents [1, 2].

One of the methods used for the investigation of the structure and properties of macromolecules in dilute solutions is the research of the gradient flows of the latter [1, 2]. The essence of the method lies in the comparison of the characteristic viscosity of the solution that can be determined both theoretically and by means of viscosimetric experiments. A popularity of this method

A common feature for the majority of the theories of the characteristic viscosity of dilute solutions of deformable chain macromolecules [1,2] is the use of the same hydrodynamic model of macromolecules, namely a necklace whose beads are connected with Gaussian subchains. Another common point is the assumption that such a model of macromolecules interacts with a low-molecular solvent only through the beads. In the present paper, the use of the necklace-based model of macromolecules under the stated assumptions together with the structural-phenomenological approach [3–6] as a research method allows us to develop a general model of stressed state in the dilute solutions of deformable chain macromolecules in low-molecular solvents.

2. Structural Simulation of a Dilute Solution of Deformable Chain Macromolecules in Gradient Flows

In the present paper, we consider the dilute solutions of deformable polymer macromolecules in low-molecular solvents. The proposed theory restricts itself to studying the solutions of chain macromolecules, i.e. of

macromolecules, whose atoms are connected with one another by simple individual bonds [1, 2].

2.1. Hydrodynamic model of deformable chain macromolecules in solutions

The characteristic dimensions of polymer macromolecules having a high molecular weight and those of molecules of low-molecular solvents relate in such a way that the interaction between the solvent and macromolecules suspended in it can be considered hydrodynamic [1, 2]. The deformability of polymer macromolecules and a great number of constituent elements of their molecular chains give enough freedom for the formation of the infinite manifold of possible ball-like conformations in the process of micro-Brownian (thermal) motion of the constituent elements of such macromolecules. The most perfect hydrodynamic model of such macromolecules is the model of necklace which was used by many authors [1, 2] when studying the polymer solutions and, according to the results of investigations, provides a good description of the behavior of real chain macromolecules in the gradient flows of solutions. Like [7], we suppose that the necklace which simulates a macromolecule consists of n similar free-bound segments connected sequentially, and each of them represents a flexible subchain, the distance l between its ends being distributed by the Gaussian law.

The segments of real chain macromolecules have such characteristic dimensions that, on the one hand, their interaction with a solvent can be considered hydrodynamic and, on the other hand, the dynamics of segments depends on the thermal motion of atoms forming a polymer chain. In the necklace that simulates macromolecules in the present paper, the hydrodynamic interaction with a solvent is realized by the beads which are located at the ends of segments and are characterized with a coefficient of translational friction ξ in a low-molecular (Newton) solvent. The total number of beads that form a model chain amounts to $n + 1$ and they are numbered from 0 to n .

Studying the dynamics of a separate macromolecule, we use a rectangular coordinate system whose origin coincides with the center of masses of a macromolecule. It is supposed that, within a macromolecule, the velocity of the solvent can be presented in the form $v_i = (d_{ij} + \omega_{ij})r_j$; $d_{ij}, \omega_{ij} = \text{const}$, where d_{ij} is the strain rate tensor, $d_{ij} = (1/2)(v_{i,j} + v_{j,i})$; ω_{ij} is the velocity vortex tensor, $\omega_{ij} = (1/2)(v_{i,j} - v_{j,i})$; and r_j is the radius-vector of a point in space.

In the tensor notations used in the present paper, the Latin letters i, j, k, \dots denote lower indices that can take values 1, 2, 3 which correspond to the coordinate axes Ox_1, Ox_2 , and Ox_3 . The Greek letters $\alpha, \beta, \gamma, \dots$ denote the numbers of the beads of a macromolecular chain. They are upper indices and can take values from 0 to n . The comma in lower indices signifies the differentiation in the direction of a coordinate axis which is marked by the index following the comma; over similar indices of the given term, one carries out the summation within the limits of variation of the repeating index.

2.2. Dynamics of deformable chain macromolecules in the gradient flows of the dilute solutions of polymers

The derivation of the dynamic equation for a necklace that simulates a macromolecule in the gradient flows of a solution is based on the assumption that the interaction of the chosen hydrodynamic model of a macromolecule with a solvent is realized only through the beads. In this case, the bead α in the gradient flow of a solution is exposed to the force of hydrodynamic friction

$$g_i^\alpha = \xi[(d_{ij} + \omega_{ij})r_j^\alpha - \dot{r}_i^\alpha] = \xi(d_{ij}r_j^\alpha - \dot{r}_i^\alpha), \quad (1)$$

where r_i^α is the radius-vector that determines the position of the bead; the point over r_i^α signifies the differentiation with respect to time t ; \dot{r}_i^α is the Yaumann derivative of the vector r_i^α , $\dot{r}_i^\alpha = \dot{r}_i^\alpha - \omega_{ik}r_k^\alpha$; and the expression $(d_{ij} + \omega_{ij})r_j^\alpha$ determines the velocity the solvent would have at the place of the bead with number α in the absence of the latter.

The micro-Brownian motion of the atoms that constitute a chain of real polymer macromolecules with a large molecular weight manifests itself in their rotation about the directions of valence bonds [1]. In the absence of other forces, it results in the coagulation of the chain into a ball. According to [7], the micro-Brownian motion in the necklace that simulates such macromolecules takes place under the action of the effective forces of Brownian diffusion \bar{f}_i^α that are determined by the relation

$$\bar{f}_i^\alpha = -\frac{kT}{F} \frac{\partial F}{\partial r_i^\alpha}. \quad (2)$$

In (2), k is the Boltzmann constant, T is the absolute temperature, and F is the distribution function of the beads over the volume that satisfies the continuity equation

$$\frac{\partial F}{\partial t} + \frac{\partial}{\partial r_i^\alpha} (\dot{r}_i^\alpha F) = 0 \quad (3)$$

in the phase space of the coordinates of all the beads of a model macromolecule.

The chosen model of macromolecules also allows one to take into account the intramolecular forces that influence the dynamics of macromolecules as a whole. As in [7], it is assumed here that every bead is exposed to the forces acting from the side of neighboring segments — the so-called internal elastic forces. According to [7], the internal elastic force \bar{f}_i^α is proportional to the difference of the vectors that connect the beads $\alpha - 1$, α , and $\alpha + 1$. In the accepted notations, we have

$$\begin{aligned} \bar{f}_i^\alpha &= 2kT\bar{\alpha}[(r_i^{\alpha+1} - r_i^\alpha) - (r_i^\alpha - r_i^{\alpha-1})] = \\ &= 2kT\bar{\alpha}(r_i^{\alpha-1} - 2r_i^\alpha + r_i^{\alpha+1}). \end{aligned} \quad (4)$$

In (4), $\bar{\alpha}$ stands for the coefficient of internal elasticity, being a phenomenological parameter characterizing the simulated molecules. According to (4), the larger the bend of the necklace in the bead α , the higher the force \bar{f}_i^α .

In the accepted model of macromolecules, the sum of the nonhydrodynamic forces $f_i^\alpha = \bar{f}_i^\alpha + \bar{f}_i^\alpha$ influencing the bead is obviously equal to the force $-g_i^\alpha$ acting on the surrounding solvent from the side of the bead, i.e.

$$f_i^\alpha = -g_i^\alpha. \quad (5)$$

Substituting formula (1) for g_j^α in (5), we obtain a general dynamic equation for a separate bead of a model macromolecule under the action of the above-mentioned forces

$$\dot{r}_i^\alpha = (d_{ij} + \omega_{ij})r_j^\alpha + \frac{1}{\xi}f_i^\alpha. \quad (6)$$

The chosen model of necklace for polymer macromolecules suspended in a low-molecular solvent together with Eqs. (3) and (6) that determine its dynamics and conformation allow one to take into account also other forces (both intra-molecular and external ones) that influence the dynamics of the beads of the molecular chain and, therefore, its conformation. For example, in addition to the internal elastic force \bar{f}_i^α , one can consider the force of internal viscosity of macromolecules [8].

Among the external forces acting on the beads, one can take into account the forces arising from external force fields such as electric or magnetic fields in cases where macromolecules are sensitive to their influence.

2.3. Dissipation rate of the mechanical energy in the unit volume of a dilute solution of deformable chain macromolecules

The hydrodynamic simulation of macromolecules of a polymer with the help of a necklace allows us to calculate the dissipation rate of the mechanical energy in the process of interaction of a suspended macromolecule with a solvent in an arbitrary gradient flow of the solution:

$$\begin{aligned} W_1 &= \langle g_i^\alpha (d_{ij}r_j^\alpha - \hat{r}_i^\alpha) \rangle = \\ &= \xi(d_{ij}d_{ik}\langle r_j^\alpha r_k^\alpha \rangle - 2d_{ij}\langle \hat{r}_i^\alpha r_j^\alpha \rangle + \langle \hat{r}_i^\alpha \hat{r}_i^\alpha \rangle). \end{aligned} \quad (7)$$

The angle parentheses $\langle \rangle$ in (7) signify the averaging in the phase space of coordinates of the beads of a model macromolecule with the help of the distribution function F determined by Eq. (3).

The quite high dilution of the solution allows one to neglect the interaction of suspended macromolecules with one another and, taking into account (7), to calculate the dissipation rate of the mechanical energy per unit volume of a dilute solution of macromolecules in its arbitrary gradient flow in the following form:

$$\begin{aligned} W &= W_0 + N_0W_1 = W_0 + N_0\xi(d_{ij}d_{ik}\langle r_j^\alpha r_k^\alpha \rangle - \\ &- 2d_{ij}\langle \hat{r}_i^\alpha r_j^\alpha \rangle + \langle \hat{r}_i^\alpha \hat{r}_i^\alpha \rangle). \end{aligned} \quad (8)$$

In (8), W_0 stands for the dissipation rate of the mechanical energy per unit volume of a solvent in the absence of suspended macromolecules, and N_0 is the number of suspended macromolecules in the unit volume of the solution.

3. Structural-phenomenological Simulation of the Rheological Behavior of Dilute Solutions of Deformable Chain Macromolecules

The simulation of the gradient flows of the dilute solutions of the deformable chain macromolecules of polymers which is carried out in the present paper is *two-scale*. The study of the dynamics of a separate macromolecule in the framework of the *structural theory*, which allowed us to calculate the dissipation rate of the mechanical energy in the process of its interaction with the solvent in Section 2, is *microscale*, as it is carried out on the scale of a suspended macromolecule. In contrast, the simulation of the rheological behavior of the solution of macromolecules described in this section is *macroscale*, as it is performed on the scale of the

characteristic dimension of a macroflow of the solution which is assumed here to be much larger than that of the molecular balls of a dilute polymer.

The simulation of polymer solutions by the classical continuum and the derivation of their rheological equations with the use of the methods of continuum mechanics don't allow one to take into account the influence of a separate macromolecule on the rheological behavior of the solution. This fact represents an essential drawback of this — *phenomenological* — method of studying the rheological behavior of macromolecule solutions, because it is just the peculiarities of suspended macromolecules that influence the rheological properties of the solution on the whole.

Carrying out the simulation of the rheological behavior of the dilute solutions of deformable chain macromolecules, we avoid such a drawback deriving the constitutive rheological equations with the help of the *structural-phenomenological method* [3–6] that combines the advantages of the structural and phenomenological methods of studying such solutions. According to this technique, the macromolecule solutions are simulated by a *structural continuum* (instead of a classical one) with internal microparameters that must describe the spatial conformation and the kinematics of microstructural elements of the solution — suspended macromolecules — in the laboratory system of coordinates. The results of the microscale simulation of the dilute solutions of deformable chain macromolecules give a possibility to choose these microparameters as the vectors r_i^α and \hat{r}_i^α that characterize the conformation and the kinematics of model chain macromolecules in the gradient flows of the solution.

According to the technique of the structural-phenomenological investigation of polymer solutions [3–6], the constitutive equation for the stress tensor T_{ij} in the gradient flows of dilute solutions of deformable chain macromolecules should be searched in the following form

$$T_{ij} = t_{ij} + N_0 \bar{t}_{ij}. \quad (9)$$

In (9), t_{ij} stands for the stress in a Newton solvent in the absence of suspended macromolecules in it, $t_{ij} = -p_0 \delta_{ij} + 2\mu d_{ij}$, where p_0 is the pressure in the solvent in the absence of suspended macromolecules, μ is the dynamic viscosity of the solvent, δ_{ij} is the Kronecker symbol; and $N_0 \bar{t}_{ij}$ is the stress arising due to the presence of N_0 macromolecules in the unit volume of the solution. Such a choice of the expression for the stress T_{ij} in the solution is indicated by the structure of expression (8) for the dissipation rate of the mechanical energy in

the unit volume of the solution that was obtained in the process of structural simulation of the solution.

If the stress tensor T_{ij} is known, the dissipation rate of the mechanical energy per unit volume of the macromolecule solution is determined by the relation

$$W = t_{ij} d_{ij} + N_0 \bar{t}_{ij} d_{ij} - N_0 \langle \hat{r}_i^\alpha g_i^\alpha \rangle. \quad (10)$$

The comparison of expression (8) obtained within the framework of the structural theory with expression (10) allows us to conclude that the tensor \bar{t}_{ij} must be a polynomial function of the variables d_{ij} , r_i^α , and \hat{r}_i^α which is linear in d_{ij} and \hat{r}_i^α . According to [3–6], the most general form of this function can be accepted as

$$\begin{aligned} \bar{t}_{ij} = & (a_0 + a_1 d_{km} \langle r_k^\alpha r_m^\alpha \rangle + a_2 \langle \hat{r}_k^\alpha r_k^\alpha \rangle) \delta_{ij} + a_3 \langle r_i^\alpha r_j^\alpha \rangle + \\ & + a_4 d_{km} \sum_{\alpha=0}^n \langle r_k^\alpha r_m^\alpha r_i^\alpha r_j^\alpha \rangle + a_5 \sum_{\alpha=0}^n \langle \hat{r}_k^\alpha r_k^\alpha r_i^\alpha r_j^\alpha \rangle + a_6 d_{ij} + \\ & + a_7 d_{ik} \langle r_k^\alpha r_j^\alpha \rangle + a_8 d_{jk} \langle r_k^\alpha r_i^\alpha \rangle + a_9 \langle r_i^\alpha \hat{r}_j^\alpha \rangle + a_{10} \langle \hat{r}_i^\alpha r_j^\alpha \rangle, \end{aligned} \quad (11)$$

where $a_i (i = \overline{0, 10})$ are phenomenological rheological constants.

The peculiarity of the structural-phenomenological method of derivation of the rheological constitutive equation of a dilute solution lies in the possibility of the theoretical determination of the rheological constants $a_i (i = \overline{0, 10})$ in the constitutive equation for the stress T_{ij} arising in the dilute solution of deformable chain macromolecules with the help of the results of its microscale study.

For this purpose, we compare termwise expressions (8) and (10) for the dissipation rate of the mechanical energy per unit volume of such a solution obtained on different scales using the structural and phenomenological approaches, respectively. In this case, the account of the relation $W_0 = t_{ij} d_{ij}$ in (8) and expressions (1) and (11) for g_i^α and \bar{t}_{ij} in (10), as well as the use of the relation $\bar{t}_{ij} - \bar{t}_{ji} = \langle r_j^\alpha g_i^\alpha \rangle - \langle r_i^\alpha g_j^\alpha \rangle$, that results from the skew-symmetry of the stress tensor T_{ij} in the simulated solution, allows us to get the following values for the rheological constants $a_i (i = \overline{3, 10})$:

$$a_3 = a_4 = a_5 = a_6 = a_8 = a_9 = 0; a_7 = \xi, a_{10} = -\xi. \quad (12)$$

The rheological constants a_0, a_1 , and a_2 that enter into expression (11) and therefore into the constitutive

equation (9) for the stress T_{ij} in the solution cannot be obtained from such a comparison. But this cannot be considered as a drawback of the discussed method, because the first term in expression (11) for the tensor \bar{t}_{ij} , that contains these indefinite rheological constants, together with p_0 enter into the expression for the isotropic pressure p in the solution of macromolecules:

$$p = p_0 + N_0(a_0 + a_1 d_{km} \langle r_k^\alpha r_m^\alpha \rangle + a_2 \langle \hat{r}_k^\alpha r_k^\alpha \rangle). \quad (13)$$

Relation (9) together with the definitions of t_{ij} and \bar{t}_{ij} , values (12) for a_i ($i = \bar{3}, \bar{10}$), and relation (13) yield the final form of the stress tensor in an arbitrary gradient flow of the dilute solution of deformable chain macromolecules as

$$T_{ij} = -p\delta_{ij} + 2\mu d_{ij} + N_0 \xi (d_{ik} \langle r_k^\alpha r_j^\alpha \rangle - \langle \hat{r}_i^\alpha r_j^\alpha \rangle). \quad (14)$$

The rheological equation (14) together with Eqs. (3) and (6), that specify the conformation and the dynamics of suspended macromolecules in gradient flows of a dilute solution, constitute the variational mathematical model of a stressed state in the dilute solutions of deformable chain macromolecules with low-molecular solvents. It can be used for various versions of the determination of both intramolecular and external forces f_i^α that influence the conformation and the dynamics of suspended macromolecules and, as a result, the stressed state in the solution.

4. Stressed State in a Dilute Solution of Zimm Chain Macromolecules

Let's apply the obtained equations (6) and (14) to searching for the stress tensor in a dilute solution of Zimm elastic chain macromolecules [7].

In the dynamic equation of molecular beads (6), we account the explicit form of the forces of Brownian diffusion (2) as well as intramolecular elastic forces (4). According to the assumption made by Zimm [7], the latter together with hydrodynamic forces influence the conformation and the dynamics of suspended macromolecules and form a stressed state in the solution in this way.

For this purpose, the elastic forces \bar{f}_i^α must be preliminarily presented as $\bar{f}_i^\alpha = -2kT \mathfrak{A} A_{\alpha\beta} r_i^\beta$, where $A_{\alpha\beta}$ is the matrix of the following form:

$$A_{\alpha\beta} = \begin{bmatrix} 1 & -1 & 0 & 0 & \dots & 0 \\ -1 & 2 & -1 & 0 & \dots & 0 \\ 0 & -1 & 2 & -1 & \dots & 0 \\ 0 & 0 & -1 & 2 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & 0 & \dots & 1 \end{bmatrix}.$$

In this case, Eq. (6) describing the dynamics of the molecular necklace takes the form

$$\dot{r}_i^\alpha = (d_{ij} + \omega_{ij}) r_j^\alpha - \frac{2kT}{\xi} \mathfrak{A} A_{\alpha\beta} r_i^\beta - \frac{kT}{\xi F} \frac{\partial F}{\partial r_i^\alpha}. \quad (15)$$

Relations (14) and (15) yield the explicit form of the stress tensor in arbitrary gradient flows of a dilute solution of Zimm elastic chain macromolecules:

$$T_{ij} = -p\delta_{ij} + 2\mu d_{ij} + N_0 kT (2\mathfrak{A} A_{\alpha\beta} \langle r_i^\alpha r_j^\beta \rangle - n\delta_{ij}). \quad (16)$$

In (16), the averaging is performed with the help of the distribution function which represents, according to (3) and (15), the solution of the equation

$$\frac{\partial F}{\partial t} - \left\{ \frac{kT}{\xi} \frac{\partial^2 F}{\partial r_l^\alpha \partial r_l^\alpha} - \left[(d_{lk} + \omega_{lk}) r_k^\alpha - \frac{2kT}{\xi} \mathfrak{A} A_{\alpha\beta} r_l^\beta \right] \frac{\partial F}{\partial r_l^\alpha} + \frac{12kTn}{\xi} \mathfrak{A} F \right\} = 0. \quad (17)$$

Let's make sure that the obtained equation (16) for the stress in the dilute solution of Zimm elastic chain macromolecules coincides with the rheological equation obtained for the same solution in [9] in another way with the use of the structural approach.

The matrix $A_{\alpha\beta}$ is symmetric. That's why, there exists an orthogonal transformation of the coordinates r_i^α into η_i^α that reduces the matrix to the diagonal form with principal values λ_α . In this case, $\lambda_0 = 0$, because the determinant of the matrix $A_{\alpha\beta}$ equals zero; $\sum_{\alpha=1}^n \lambda_\alpha = 2n$ as a linear invariant of the matrix $A_{\alpha\beta}$; and $r_i^\alpha r_j^\alpha = \eta_i^\alpha \eta_j^\alpha$ due to the orthogonality of the transformation of coordinates. After this orthogonal transformation of coordinates, the rheological equation (16) takes the form

$$T_{ij} = -p\delta_{ij} + 2\mu d_{ij} + N_0 kT (2\mathfrak{A} \sum_{\alpha=0}^n \lambda_\alpha \langle \eta_i^\alpha \eta_j^\alpha \rangle - n\delta_{ij}). \quad (18)$$

For the further transformation of (18), we use Eq. (17) for the distribution function F of the beads that, in the new coordinates η_i^α , has the form

$$\frac{\partial F}{\partial t} - \sum_{\alpha=0}^n \left\{ \frac{kT}{\xi} \frac{\partial^2 F}{\partial \eta_l^\alpha \partial \eta_l^\alpha} - \left[(d_{lk} + \omega_{lk}) \eta_k^\alpha - \right. \right.$$

$$-\frac{2kT}{\xi} \left[\lambda_\alpha \eta_i^\alpha \right] \frac{\partial F}{\partial \eta_i^\alpha} + \frac{6kT}{\xi} \lambda_\alpha \alpha F \Big\} = 0. \quad (19)$$

Let's multiply Eq.(19) by $\eta_i^\alpha \eta_j^\alpha$, integrate it over the whole phase space of the arguments of the distribution function and, without summing over the index α , we obtain

$$\begin{aligned} \frac{d\langle \eta_i^\alpha \eta_j^\alpha \rangle}{dt} &= 2 \frac{kT}{\xi} \delta_{ij} + (d_{ik} + \omega_{ik}) \langle \eta_k^\alpha \eta_j^\alpha \rangle + (d_{jk} + \\ &+ \omega_{jk}) \langle \eta_k^\alpha \eta_i^\alpha \rangle - \frac{4kT}{\xi} \lambda_\alpha \langle \eta_i^\alpha \eta_j^\alpha \rangle. \end{aligned} \quad (20)$$

Carrying out the summation over α in (20), we obtain, in the stationary case,

$$\begin{aligned} 2kT \lambda_\alpha \sum_{\alpha=0}^n \langle \eta_i^\alpha \eta_j^\alpha \rangle - kT n \delta_{ij} &= \\ = \frac{\xi}{2} (d_{ik} + \omega_{ik}) \sum_{\alpha=0}^n \langle \eta_k^\alpha \eta_j^\alpha \rangle + \frac{\xi}{2} (d_{jk} + \omega_{jk}) \sum_{\alpha=0}^n \langle \eta_k^\alpha \eta_i^\alpha \rangle. \end{aligned} \quad (21)$$

The use of (21) in (18) gives the expression

$$\begin{aligned} T_{ij} &= -p \delta_{ij} + 2\mu d_{ij} + \frac{1}{2} N_0 \xi \times \\ &\times [(d_{ik} + \omega_{ik}) \langle \eta_k^\alpha \eta_j^\alpha \rangle + (d_{jk} + \omega_{jk}) \langle \eta_k^\alpha \eta_i^\alpha \rangle]. \end{aligned} \quad (22)$$

Returning to the old variables r_i^α in (22), we finally derive

$$\begin{aligned} T_{ij} &= -p \delta_{ij} + 2\mu d_{ij} + \frac{1}{2} N_0 \xi \times \\ &\times [(d_{ik} + \omega_{ik}) \langle r_k^\alpha r_j^\alpha \rangle + (d_{jk} + \omega_{jk}) \langle r_k^\alpha r_i^\alpha \rangle]. \end{aligned} \quad (23)$$

Taking into account that $\langle r_i^\alpha r_j^\alpha \rangle$ represents the inertia tensor of a model macromolecule normalized to unit mass, one can see that expression (23) obtained for the stress tensor in a dilute solution of Zimm macromolecules coincides with the expression obtained for such a tensor in [9] using another technique to within notations. Such a coincidence testifies to the correctness of the rheological equation (16) and, consequently, the constitutive equations (6) and (14) obtained in the present work.

5. Conclusions

The use of the structural-phenomenological method allowed us to obtain a general maximally variative model of the stressed state in a dilute solution of the deformable chain macromolecules of polymers in low-molecular solvents. In the obtained constitutive equations for the stress in the solution (3), (6), and (14), only the hydrodynamic forces acting on the molecular beads of a necklace are considered explicitly. The rest of the forces both internal and external, that also deform the molecular chain, determine its dynamics in gradient flows of the solution and, consequently, also influence the stressed state in it, is allowed for in total with the help of the resulting vectors. Therefore, Eqs. (3), (6), and (14) are the general constitutive equations for stresses in the dilute solutions of the deformable chain macromolecules of polymers and are able to describe a stressed state in gradient flows of these solutions in various cases of the determination and the allowance for external and intramolecular forces. For example, considering both the effective forces of Brownian diffusion (2), the forces related to the internal elasticity (4), and Eqs. (3), (6), (14), we have deduced the constitutive equation (16) for a dilute solution of Zimm macromolecules [7] which coincides with that obtained in another way in [9] to within notations.

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СТРУКТУРНО-ФЕНОМЕНОЛОГІЧНА ТЕОРІЯ
НАПРУЖЕНОГО СТАНУ У ГРАДІЄНТНИХ
ТЕЧІЯХ РОЗВЕДЕНИХ РОЗЧИНІВ ПОЛІМЕРІВ
З ДЕФОРМІВНИМИ ЛАНЦЮГОВИМИ
МАКРОМОЛЕКУЛАМИ

Ю.В. Придатченко, Є.Ю. Таран, Р.Я. Кондрат

Резюме

Одержано загальне реологічне рівняння розведених розчинів деформівних ланцюгових макромолекул у низькомо-

лекулярних розчинниках. Як гідродинамічна модель макромолекул використовується намисто, бусинки якого з'єднані гауссовими субланцюгами. Для виведення визначальних рівнянь напруженого стану у розчинах використано структурно-феноменологічний підхід. Перевірку одержаних результатів здійснено шляхом реологічного моделювання розчину ланцюгових макромолекул Зімма з врахуванням пружності молекулярних ланцюгів і мікроброунівського руху атомів, з яких вони складаються.