

Thermodynamic modelling of polymer solutions with molecular form birefringence

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Abstract

Thermodynamics of isotropic polymer solutions with anisotropic molecules modelled as extensible ellipsoids of revolutions is considered. Anisotropy of molecules is accounted for by introducing internal variables — structure and elongation tensors describing re-orientation of the molecules and their elongation. Decomposition of the thermodynamic fluxes into dissipative and elastic constituents is assumed. The thermodynamic analysis leads to a constitutive law for the stress tensor and evolution equations for the structure and elongation tensors. Study of elongational flow shows how different relations among elastic moduli lead to different extents of the re-orientation and elongation of the molecules. Modelling of simple flows shows that the coupling between the structure and elongation tensors can lead to an overshoot in one of them even in a start-up of elongational flow. The effect on the stress, however, is less pronounced. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Molecules of some polymers can take anisotropic configurations due to the interaction with the solvent, an effect called *form birefringence*. Examples of such polymers are polyelectrolytes (e.g. proteins, DNA, polyvinyl sulphonic acid, etc.), whose molecules due to the different extent of the ionisations in the pH solutions, take different conformations: from spherical, with features of coiled flexible macromolecules, via elliptic, with intermediate characteristics, to almost fully extended, with the behaviour of rigid rod-like molecules (Fig. 1). When a solution of molecules with elliptic conformation is subjected to a strain, two effects occur, which exhibit viscoelastic properties of the fluid: re-orientation of the molecules and their elongation. Therefore, in modelling such a process by continuum mechanics, corresponding *internal variables* describing both mechanisms of viscoelasticity pertaining to coiled flexible as well as rigid

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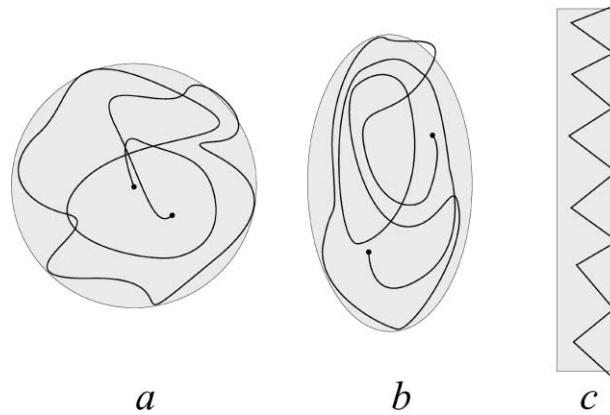


Fig. 1. Different forms of a polymer molecule in different solvents: isotropic coiled form (a), ellipsoidal (b), rod-like (c).

rod macromolecules can be introduced. One measure of deviation of the internal structure of flexible macromolecules from their equilibrium state is the *conformation tensor* [1,2], which has been also used in the study of thermodynamics of polyelectrolyte solutions [3,4]. In particular, some simple idealized forms of solutions, for example, dilute solutions of dumbbells, can be completely described by using the conformation tensor as the only internal variable [5], the result following from the kinetic theory. A similar approach, considering a dilute solution of charged dumbbells with a non-linear Warner spring as a model of a polyelectrolyte solution, was employed by Dunlap and Leal [6] to study strong flows, and recently by Valdez and Manero [7] to study effects of boundaries on polyelectrolyte dynamics. In the cited works, special assumptions have been used to make the problem tensorially linear in the conformation tensor, however, with a scalar coefficient, non-linear with regard to its first invariant. At the same time, for describing the rheology of rigid rod molecules, the *structure tensor*, showing the distribution of the molecules with regard to their orientation is used [8,9].

Because polymers with molecular form birefringence must exhibit simultaneously the features of flexible as well as rigid rod molecules due to the stiffening caused by the interaction with the solvent, we will generalize in this work the continuum approach of modelling polymer solutions proposed by Maugin and Drouot [1] by introducing an additional internal variable—the structure tensor, which, together with the conformation tensor, is capable of differentiating between re-orientation and elongation of anisotropic elastic molecules, which will be modelled as extensible ellipsoids of revolution. Our purpose is to develop a relatively simple constitutive theory of polymer solutions accounting for the molecular form birefringence by applying methods of continuum thermodynamics in order to gain more insight into the different mechanisms of elasticity—re-orientation and elongation of molecules. For simplicity, we will not consider any electromechanical effects are considered, which, of course, are also important in polyelectrolyte dynamics.

2. Thermodynamic analysis

2.1. Governing equations and internal variables

Cartesian tensor notation will be employed with the Einstein summation convention over doubly repeated indices. If C_{ij} (or \mathbf{C} in symbolic notation) is a second rank tensor, then $C_{(ij)}(\mathbf{C}_{\circ})$,

$C_{(ij)}(\mathbf{C}_{(})$) and $C_{[ij]}(\mathbf{C}_{[})$) will denote its symmetric, deviatoric and skew-symmetric parts, respectively.

The following notations are used: ρ is the density, \mathbf{v} the velocity vector, t the time, $\boldsymbol{\sigma}$ the symmetric dynamic stress tensor, $\boldsymbol{\tau}$ the stress deviator tensor, \mathbf{q} the heat flux vector, e the specific internal energy, p the pressure, s the specific entropy, $\theta := (\partial s / \partial e)^{-1}$ the absolute temperature, $\psi = e - \theta s$ the specific free energy, \mathbf{F} the specific body force vector, while $D_{ij} = \frac{1}{2}(\partial v_i / \partial x_j + \partial v_j / \partial x_i)$ and $W_{ij} = \frac{1}{2}(\partial v_i / \partial x_j - \partial v_j / \partial x_i)$ are the strain-rate and vorticity tensors, respectively.

We will assume that the solution is homogeneous with regard to the polymer concentration. The balance laws of mass, momentum and internal energy in the absence of internal energy supplies, referred to an inertial frame, are

$$\dot{\rho} + \rho \nabla \cdot \mathbf{v} = 0, \quad (1)$$

$$\rho \dot{\mathbf{v}} = \nabla \cdot (-p \mathbf{1} + \boldsymbol{\sigma}) + \rho \mathbf{F}, \quad (2)$$

$$\rho \dot{e} + \nabla \cdot \mathbf{q} = \text{tr}(\boldsymbol{\sigma} \mathbf{D}) - p \text{tr} \mathbf{D}, \quad (3)$$

and the second law of thermodynamics in the absence of entropy supplies is assumed to be

$$\rho \dot{s} + \nabla \cdot \left(\boldsymbol{\varphi} + \frac{\mathbf{q}}{\theta} \right) \geq 0, \quad (4)$$

an inequality requiring entropy production to be non-negative for all thermodynamic processes, where $\boldsymbol{\varphi}$ is the excess entropy flux. In the above

$$\dot{y} := \frac{\partial y}{\partial t} + \mathbf{v} \cdot \nabla y \quad (5)$$

is the total or material time derivative of the field quantity y .

In order to take into account the dependence of the polymer rheology on the internal structure of the fluid within the context of a phenomenological approach, internal variables are introduced. For polymers with anisotropic coiled molecules these variables must describe orientation as well as elongation of the molecules. Although polymers are long-chain molecules, and interaction among them is very complex, in this work we will assume that a state of such a molecule can be described only by a vector \mathbf{r} , whose beginning and end coincide with the extremely distant monomers of the polymer chain. Moreover, the usual head-tail symmetry will be considered, that is, \mathbf{r} and $-\mathbf{r}$ describe the same molecule. In particular, such a description is sufficient for a non-rigid ellipsoidal molecule, when its length completely determines its form and there is no transversal anisotropy. The state of an extensible rod-like molecule can be also described by the vector \mathbf{r} . The latter polymer model was used by Entov [10], who considered the dynamics of suspensions of extensible rods oriented strictly along the direction of elongational flow.

In one fluid particle there are many molecules, therefore one is interested in their distribution, described by variables in three-dimensional space. To this end a second-order moment describing the lowest harmonic departure from sphericity is introduced [1,2,5]

$$\mathbf{R} = \langle \mathbf{r} \otimes \mathbf{r} \rangle, \quad (6)$$

where the operation $\langle \cdot \rangle$ describes averaging over all molecules at a given point. The tensor \mathbf{R} is usually called the *conformation tensor*.

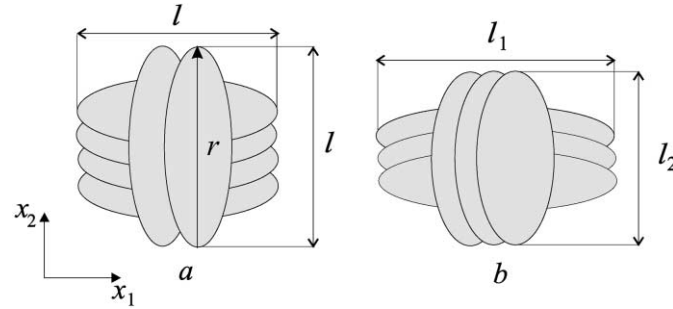


Fig. 2. Two cases of different internal structures.

In order to ascertain sufficiency of the conformation tensor alone to describe the distribution of the molecules at one point, let us consider two exemplary situations (Fig. 2), when the molecules are situated only along the x_1 - and x_2 -axes. In the first case (a), all molecules have the same length l , four of them lying along x_1 and two along x_2 . Averaging over the number of molecules yields the conformation tensor

$$\mathbf{R}_1 = \begin{pmatrix} \frac{2}{3}l^2 & 0 & 0 \\ 0 & \frac{1}{3}l^2 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (7)$$

In the second case (b) there are three molecules of length l_1 lying along x_1 , while the other three molecules of length l_2 lie parallel to x_2 . This determines the conformation tensor

$$\mathbf{R}_2 = \begin{pmatrix} \frac{1}{2}l_1^2 & 0 & 0 \\ 0 & \frac{1}{2}l_2^2 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (8)$$

Putting $l_1 = 2/\sqrt{3}l$, $l_2 = \sqrt{2/3}l$ yields $\mathbf{R}_1 = \mathbf{R}_2$, which also determines the same mean squared length of the molecules $\langle l^2 \rangle = \text{tr } \mathbf{R}$ in the two situations. This means that the second-rank conformation tensor alone does not distinguish between elongation and re-orientation of the molecules. However, these two arrangements can have different influences on the rheology. In order to overcome this problem one can use the forth-order moment tensor, which takes different values in the considered situations. However, calculations including a forth-rank tensor are very complex; we will use instead two second-rank tensors describing the internal structure — the *structure tensor* describing only the re-orientation of the molecules, and a tensor describing the mean elongation of the molecules in any direction. For the description of the elongation of the molecules with fixed orientation distribution, the tensor of elastic deformation [11] can, for example, be used. However, this approach is connected with some kinematic and physical inconsistency [12,13], associated with the decomposition of the deformation tensor into elastic and plastic parts, and therefore we will choose another measure.

The two tensors describing the internal structure of the polymers will be derived from the orientation–elongation distribution function $f^*(\mathbf{n}, l)$, where $\mathbf{n} = \mathbf{r}/l$, l being the length of the vector \mathbf{r} , and the dependence on t and \mathbf{x} being omitted for brevity. The function f^* is defined on the region $S^2 \otimes \mathbb{R}^+$, where S^2 is a sphere in \mathbb{R}^3 of unit radius; it represents the relative number of molecules of length l directed along

the vector \mathbf{n} , and obviously $f^*(\mathbf{n}, l) = f^*(-\mathbf{n}, l)$. The *orientation distribution function* f determining the fraction of molecules having direction \mathbf{n} at a given point can be defined as

$$f(\mathbf{n}) = \int_0^{+\infty} f^*(\mathbf{n}, l) dl, \quad \int_{S_2} f(\mathbf{n}) d\mathbf{n} = 1. \quad (9)$$

We can also introduce a measure describing the mean molecular length in different directions

$$l^{(m)}(\mathbf{n}) = \int_0^{+\infty} f^*(\mathbf{n}, l) l^m dl, \quad \int_{S_2} l^{(m)}(\mathbf{n}) d\mathbf{n} = \langle l^m \rangle, \quad (10)$$

where $l^{(m)}/f$ is the mean molecular length (taken in power m) in a particular direction, and $\langle l^m \rangle$ is the average molecular length (taken in the same power) at a point². $m > 0$ is an exponent, which can take different values for different models. Using tensorial expansion [14] these functions can be expressed in terms of an infinite number of *moment tensors* of even ranks. We will assume that the two second-rank symmetric tensors in the expansions of f and $l^{(m)}$, respectively, which we will denote as $\bar{\mathbf{A}}$, $\bar{\mathbf{B}}$ and call the *structure* and *elongation* tensors, are sufficient to describe the internal structure of some polymeric fluids. These symmetric tensors are determined by

$$\bar{A}_{ij} = \int_{S^2} f n_i n_j d^2 n, \quad \bar{B}_{ij} = \int_{S^2} l^{(m)} n_i n_j d^2 n. \quad (11)$$

Owing to (9)₂ and (10)₂, we have $\text{tr } \bar{\mathbf{A}} = 1$ and $\text{tr } \bar{\mathbf{B}} = \langle l^m \rangle$. Again, $m = 2$ yields $\bar{\mathbf{B}} = \mathbf{R}$, and $l^{(m)}/f$ is the mean squared molecular length. If $l_E^{(m)}$ is the mean molecular length in power m at *equilibrium*, which will be assumed to be a known function of θ and ρ , then at non-equilibrium, generally $\langle l^m \rangle \neq l_E^{(m)}$. In the following analysis, by \mathbf{A} , we will mean the deviatoric part of $\bar{\mathbf{A}}$ ($\mathbf{A} = \bar{\mathbf{A}}_{(\cdot)}$), and by \mathbf{B} the normalized non-equilibrium part $\mathbf{B} = 1/(l_E^{(m)})\bar{\mathbf{B}} - \frac{1}{3}\mathbf{1}$. We also define the invariants

$$I_B = \text{tr } \mathbf{B}, \quad II_A = \text{tr } \mathbf{A}_{(\cdot)}^2, \quad II_B = \text{tr } \mathbf{B}_{(\cdot)}^2, \quad II_{AB} = \text{tr}(\mathbf{A}_{(\cdot)}\mathbf{B}_{(\cdot)}).$$

Evidently, for fixed \mathbf{A} , a change of \mathbf{B} characterizes only elongation of molecules.

For the internal variables \mathbf{A} and \mathbf{B} we assume the evolution equations

$$\frac{\mathcal{D}\mathbf{A}}{\mathcal{D}t} = \Phi(\theta, \rho, \mathbf{A}, \mathbf{B}, \mathbf{D}, \nabla\theta), \quad (12)$$

$$\frac{\mathcal{D}\mathbf{B}}{\mathcal{D}t} = \Psi(\theta, \rho, \mathbf{A}, \mathbf{B}, \mathbf{D}, \nabla\theta), \quad (13)$$

where $\mathcal{D}\mathbf{A}/\mathcal{D}t = \dot{\mathbf{A}} + \mathbf{A}\mathbf{W} - \mathbf{W}\mathbf{A}$ is the Jaumann or co-rotational derivative. Such a form of constitutive equations has been adopted in [1,3,15]; and the use of the Jaumann derivative is suggested by Prager's kinetic theory of rigid dumbbells [16].

It should be noted that in (12) and (13) there are no flux terms, however, the distribution of molecules and their mean molecular length in a particle of a five-dimensional space will change also due to spatial

² An alternative measure of the mean molecular length can be chosen directly as $\hat{l} = l^{(m)}/f_1$ which will lead to independence of the corresponding elongation tensor \mathbf{B} or the structure tensor \mathbf{A} . The thermodynamic analysis in terms of \mathbf{B} will not, however, change.

molecular diffusion. This, in particular, can be seen by inspecting the exact evolution equation for the structure tensor, which includes the relative diffusive velocities [9]. On the other hand, the terms Φ and Ψ describe effects caused by the processes occurring in one material particle due to changes of its internal structure. These processes account for diffusion of molecules with regard to their orientation. Such a diffusion is characterized by the scale comparable with the molecular length, while the spatial diffusion is determined by the global scale of the flow which is much larger. This means that the terms describing spatial diffusive effects, which generally speaking, could enter the evolution equations (12) and (13), are negligible in comparison with the production terms Φ and Ψ describing processes in the internal space.

2.2. Entropy principle

Due to the principles of *objectivity* and *equi-presence* [17], we assume that the entropy s , internal energy e and fluxes $\boldsymbol{\varphi}$ and \boldsymbol{q} can generally depend on the variables $\theta, \rho, \mathbf{A}, \mathbf{B}, \mathbf{D}, \nabla\theta$.

In a closed system, the entropy inequality, constrained by the balance equations (1)–(3) and the evolution equations (12) and (13) through the introduction of Lagrange multipliers [18] takes the form

$$\begin{aligned} & \rho \frac{\partial s}{\partial \theta} \dot{\theta} + \rho \frac{\partial s}{\partial \rho} \dot{\rho} + \rho \operatorname{tr} \left(\frac{\partial s}{\partial \mathbf{A}} \frac{\mathcal{D}\mathbf{A}}{\mathcal{D}t} + \frac{\partial s}{\partial \mathbf{B}} \frac{\mathcal{D}\mathbf{B}}{\mathcal{D}t} + \frac{\partial s}{\partial \mathbf{D}} \dot{\mathbf{D}} \right) + \rho \frac{\partial s}{\partial \nabla\theta} \cdot \dot{\nabla}\theta - \lambda^\rho (\dot{\rho} + \rho \operatorname{tr} \mathbf{D}) \\ & - \boldsymbol{\lambda}^v \cdot [\rho \dot{\mathbf{v}} - \nabla \cdot (-p\mathbf{1} + \boldsymbol{\sigma})] + 2\rho \operatorname{tr} \left[\mathbf{W} \left(\frac{\partial s}{\partial \mathbf{A}} \mathbf{A} + \frac{\partial s}{\partial \mathbf{B}} \mathbf{B} \right) \right] \\ & - \lambda^e \left\{ \rho \frac{\partial e}{\partial \theta} \dot{\theta} + \rho \frac{\partial e}{\partial \rho} \dot{\rho} + \rho \operatorname{tr} \left(\frac{\partial e}{\partial \mathbf{A}} \frac{\mathcal{D}\mathbf{A}}{\mathcal{D}t} + \frac{\partial e}{\partial \mathbf{B}} \frac{\mathcal{D}\mathbf{B}}{\mathcal{D}t} + \frac{\partial e}{\partial \mathbf{D}} \dot{\mathbf{D}} \right) + \rho \frac{\partial e}{\partial \nabla\theta} \cdot \dot{\nabla}\theta \right. \\ & \left. + 2\rho \operatorname{tr} \left[\mathbf{W} \left(\frac{\partial e}{\partial \mathbf{A}} \mathbf{A} + \frac{\partial e}{\partial \mathbf{B}} \mathbf{B} \right) \right] + \nabla \cdot \boldsymbol{q} - \operatorname{tr}(\boldsymbol{\sigma} \mathbf{D}) + p \operatorname{tr} \mathbf{D} \right\} \\ & - \operatorname{tr} \left[\boldsymbol{\Lambda}^A \left(\frac{\mathcal{D}\mathbf{A}}{\mathcal{D}t} - \Phi \right) + \boldsymbol{\Lambda}^B \left(\frac{\mathcal{D}\mathbf{B}}{\mathcal{D}t} - \Psi \right) \right] + \nabla \cdot \left(\boldsymbol{\varphi} + \frac{\boldsymbol{q}}{\theta} \right) \geq 0, \end{aligned} \quad (14)$$

where by $p := -\theta\rho^2\partial s/\partial\rho$, we defined the non-equilibrium thermodynamic pressure. In the inequality above, λ^ρ, λ^e are scalar, $\boldsymbol{\lambda}^v$ vectorial, and $\boldsymbol{\Lambda}^A, \boldsymbol{\Lambda}^B$ tensorial Lagrange multipliers. The chain rule of differentiation can also be applied to $\boldsymbol{\varphi}$ and \boldsymbol{q} . In particular,

$$\frac{\partial \varphi_i}{\partial x_i} = \frac{\partial \varphi_i}{\partial \theta} \frac{\partial \theta}{\partial x_i} + \frac{\partial \varphi_i}{\partial \rho} \frac{\partial \rho}{\partial x_i} + \frac{\partial \varphi_i}{\partial A_{kl}} \frac{\partial A_{kl}}{\partial x_i} + \frac{\partial \varphi_i}{\partial B_{kl}} \frac{\partial B_{kl}}{\partial x_i} + \frac{\partial \varphi_{(i}}{\partial D_{kl}} \frac{\partial^2 v_l}{\partial x_i \partial x_k} + \frac{\partial \varphi_{(i}}{\partial \nabla\theta_j} \frac{\partial^2 \theta}{\partial x_i \partial x_j}. \quad (15)$$

Due to the linearity of the left-hand side of (14) with regard to $\dot{\theta}, \dot{\rho}, \dot{\mathbf{v}}, \mathbf{W}, \dot{\mathbf{D}}, \dot{\nabla}\theta, \mathcal{D}\mathbf{A}/\mathcal{D}t, \mathcal{D}\mathbf{B}/\mathcal{D}t, \nabla\rho, \nabla\mathbf{A}, \nabla\mathbf{B}, \nabla\mathbf{D}, \nabla^2\theta$, we derive

$$\boldsymbol{\lambda}^v = \mathbf{0}, \quad \lambda^e = \frac{1}{\theta}, \quad \lambda^\rho = -\frac{p}{\rho\theta}, \quad \boldsymbol{\Lambda}^A = -\frac{\rho}{\theta} \frac{\partial \psi}{\partial \mathbf{A}}, \quad \boldsymbol{\Lambda}^B = -\frac{\rho}{\theta} \frac{\partial \psi}{\partial \mathbf{B}}, \quad (16)$$

$$(\boldsymbol{\Lambda}^A \mathbf{A} + \boldsymbol{\Lambda}^B \mathbf{B})_{\square} = \mathbf{0}, \quad \frac{\partial \psi}{\partial \mathbf{D}} = \mathbf{0}, \quad \frac{\partial \psi}{\partial \nabla\theta} = \mathbf{0}, \quad (17)$$

$$\frac{\partial \boldsymbol{\varphi}}{\partial \rho} = \mathbf{0}, \quad \frac{\partial \varphi_i}{\partial A_{kl}} = \frac{\partial \varphi_i}{\partial B_{kl}} = \frac{\partial \varphi_{(i}}{\partial D_{kl}} = \frac{\partial \varphi_{(i}}{\partial \nabla\theta_j)} = 0, \quad (18)$$

where $\psi = e - \theta s$ is the free energy. From (17) it follows that the free energy does not depend on \mathbf{D} and $\nabla\theta$. Moreover, due to the definition of the free energy and absolute temperature, we have $s = -\partial\psi/\partial\theta$, which yields that the entropy and internal energy likewise do not depend on these variables. It can be also shown [19] that Eq. (18) determines $\boldsymbol{\varphi} = \mathbf{0}$.

The residual entropy inequality takes the form

$$\text{tr} \left(\boldsymbol{\Lambda}^A \boldsymbol{\Phi} + \boldsymbol{\Lambda}^B \boldsymbol{\Psi} + \frac{1}{\theta} \boldsymbol{\sigma} \mathbf{D} \right) - \frac{\mathbf{q} \cdot \nabla\theta}{\theta^2} \geq 0. \quad (19)$$

Developing a general model of viscoelastic media is a very complex problem, therefore, we will restrict ourselves by several simplifying assumptions making the problem more tractable. We assume that due to the viscoelasticity of the fluid, the functions $\boldsymbol{\Phi}$ and $\boldsymbol{\Psi}$ allow the decomposition

$$\boldsymbol{\Phi} = \boldsymbol{\Phi}^d + \boldsymbol{\Phi}^e, \quad \boldsymbol{\Psi} = \boldsymbol{\Psi}^d + \boldsymbol{\Psi}^e, \quad (20)$$

into the dissipative (viscous) $\boldsymbol{\Phi}^d, \boldsymbol{\Psi}^d$ and elastic contributions $\boldsymbol{\Phi}^e, \boldsymbol{\Psi}^e$, describing viscous and elastic mechanisms of changing of the internal variables.³ In particular, viscous effects are caused by movement of molecules of the polymer and solvent past each other due to Brownian motion, while elastic effects are determined by intermolecular forces. Moreover, the following equation determining zero entropy production is satisfied by the elastic constituents $\boldsymbol{\Phi}^e, \boldsymbol{\Psi}^e$

$$\text{tr} \left(\boldsymbol{\Phi}^e \boldsymbol{\Lambda}^A + \boldsymbol{\Psi}^e \boldsymbol{\Lambda}^B + \frac{1}{\theta} \boldsymbol{\sigma}^e \mathbf{D} \right) = 0. \quad (21)$$

The stress $\boldsymbol{\sigma}^e$ is called an elastic stress, since its work is reversible. It should be noted that (21) determines the elastic stress to within the order of an additive term $\Delta\boldsymbol{\sigma}^e$ such that $\text{tr}(\mathbf{D}\Delta\boldsymbol{\sigma}^e) = 0$. This means that such an additional stress does not perform work, and therefore will be discarded.

2.3. Viscous constitutive quantities

The entropy inequality can be rewritten only in terms of the dissipative constituents as

$$\text{tr} \left(\boldsymbol{\Lambda}^A \boldsymbol{\Phi}^d + \boldsymbol{\Lambda}^B \boldsymbol{\Psi}^d + \frac{1}{\theta} \boldsymbol{\tau}^d \mathbf{D}_{(\cdot)} \right) + \frac{1}{\theta} p^d \text{tr} \mathbf{D} - \frac{1}{\theta^2} \mathbf{q} \cdot \nabla\theta \geq 0, \quad (22)$$

where $\boldsymbol{\sigma}^d = \boldsymbol{\sigma} - \boldsymbol{\sigma}^e = p^d \mathbf{1} + \boldsymbol{\tau}^d$, and $p^d = \frac{1}{3} \text{tr} \boldsymbol{\sigma}^d$. This structure of the entropy production represents a sum of products of the thermodynamic forces $\boldsymbol{\Lambda}^A, \boldsymbol{\Lambda}^B, \mathbf{D}_{(\cdot)}, \text{tr} \mathbf{D}, \nabla\theta$ and corresponding fluxes $\boldsymbol{\Phi}^d, \boldsymbol{\Psi}^d, \boldsymbol{\tau}^d, p^d, \mathbf{q}$ that vanish in equilibrium. Evidently, the forces $\boldsymbol{\Lambda}^A, \boldsymbol{\Lambda}^B$ work in the subspace associated with the internal structure, and are caused by the non-equilibrium distribution of the molecules with regard to different directions and lengths at a point. As usually performed in irreversible thermodynamics we assume the constitutive relations relating the forces and fluxes in the general form

$$\boldsymbol{\Phi}^d = \boldsymbol{\Phi}^d(\theta, \rho; \boldsymbol{\Lambda}^A, \boldsymbol{\Lambda}^B, \mathbf{D}_{(\cdot)}, \text{tr} \mathbf{D}, \nabla\theta), \quad (23)$$

³ Existence of such entropy — non-producing (elastic) constituents together with the dissipative (viscous) ones is the usual assumption in thermodynamic modelling of viscoelastic materials, which is expressed through the existence of “elastic deformation” [11], “natural configuration” [20] or “orthogonal forces and fluxes” [1].

and similarly for Ψ^d , τ^d , p^d , \mathbf{q} . The general linear isotropic constitutive equations with regard to the forces satisfying the second law and including only entropy-producing terms can be written as

$$\Phi^d = \alpha \mathbf{\Lambda}_{(\cdot)}^A + \zeta \mathbf{\Lambda}_{(\cdot)}^B, \quad (24)$$

$$\Psi^d = \beta_1 \text{tr} \mathbf{\Lambda}^B \mathbf{1} + \zeta \mathbf{\Lambda}_{(\cdot)}^A + \beta_2 \mathbf{\Lambda}_{(\cdot)}^B, \quad (25)$$

$$\tau^d = 2\eta \mathbf{D}_{(\cdot)}, \quad p^d = \eta_b \text{tr} \mathbf{D}, \quad (26)$$

$$\mathbf{q} = -\lambda \nabla \theta, \quad (27)$$

where the coefficients in the expressions above are scalar functions of θ and ρ , such that

$$\alpha, \beta_1, \beta_2, \eta, \eta_b, \lambda \geq 0, \quad \zeta^2 \leq \alpha\beta_2. \quad (28)$$

In the derivation of the above equations we used Onsager's relations, which lead to symmetry or antisymmetry among the coefficients in (24)–(26). In particular, \mathbf{D} is odd in time, while $\mathbf{\Lambda}^A$ and $\mathbf{\Lambda}^B$ are even, therefore we neglected the dependence of the fluxes τ^d and p^d on the forces $\mathbf{\Lambda}^A$ and $\mathbf{\Lambda}^B$, as well as the dependence of the fluxes Φ^d and Ψ^d on the force \mathbf{D} , because the mentioned terms determine zero entropy production and are considered as elastic constituents. This means that these omitted terms enter the elastic stress and Φ^e , Ψ^e and the dissipative constituents Φ^d , Ψ^d do not depend on the strain-rate tensor. It was also taken into account that \mathbf{A} is traceless.

Assuming the linear dependence among the fluxes and forces, we have restricted ourselves to isotropic materials, because for anisotropic fluids, the effect of excluded volume can lead to the existence of nematic phases and to non-linear dependence of the fluxes on forces. For isotropic materials, however, such a linearity, still allows us to consider non-linear effects caused by non-linearity of the free energy with regard to the internal variables. The latter, in particular, makes it possible to model finite extensibility of the molecules [1].

2.4. Elastic constitutive quantities

Let us now consider the problem of the determination of the elastic constitutive behaviour. Evidently, the requirement that the viscous fluxes are small does not generally imply that the elastic constituents must also be small. Therefore, generally, non-linear relations for elastic constituents are admissible.

Because the elastic stress σ^e is caused by changing the internal structure and, in turn, the free energy, we assume it to be independent of the strain-rate tensor, as suggested by thermodynamics of elasticity [21]. This implies, in view of (17) and (21), linear dependence of Φ^e , Ψ^e on \mathbf{D} with $\Phi^e, \Psi^e \rightarrow \mathbf{0}$ as $\mathbf{D} \rightarrow \mathbf{0}$.

Further, we differentiate (21) with respect to D_{ij} to deduce

$$\sigma_{ij}^e = -\theta \left(\Lambda_{kl}^A \frac{\partial \Phi_{kl}^e}{\partial D_{ij}} + \Lambda_{kl}^B \frac{\partial \Psi_{kl}^e}{\partial D_{ij}} \right). \quad (29)$$

For the elastic constituents Φ^e , Ψ^e one can generally use isotropic tensorial functions linear in \mathbf{D} . However, in this work we restrict ourselves to neglecting all the terms which are higher than second order in the non-equilibrium variables to obtain

$$\Phi^e = (\mathbf{C}^\Phi \mathbf{D})_{(\cdot)} + \chi_4 \text{tr}(\mathbf{D}) \mathbf{A} + \chi_5 \text{tr}(\mathbf{D}) \mathbf{B}_{(\cdot)}, \quad (30)$$

$$\Psi^e = (\mathbf{C}^\Psi \mathbf{D})_{\langle \rangle} + \text{tr}(\mathbf{D} \mathbf{C}_0^\Psi) \mathbf{1} + \sigma_4 \text{tr}(\mathbf{D}) \mathbf{A} + \sigma_5 \text{tr}(\mathbf{D}) \mathbf{B}_{\langle \rangle}, \quad (31)$$

where

$$\begin{aligned} \mathbf{C}^\Phi &= (\chi_0 + \chi_1 I_B) \mathbf{1} + \chi_2 \mathbf{A} + \chi_3 \mathbf{B}_{\langle \rangle}, & \mathbf{C}^\Psi &= (\sigma_0 + \sigma_1 I_B) \mathbf{1} + \sigma_2 \mathbf{A} + \sigma_3 \mathbf{B}_{\langle \rangle}, \\ \mathbf{C}_0^\Psi &= (\sigma_0^0 + \sigma_1^0 I_B) \mathbf{1} + \sigma_2^0 \mathbf{A} + \sigma_3^0 \mathbf{B}_{\langle \rangle}. \end{aligned} \quad (32)$$

Owing to (29), Eqs. (30) and (31) yield

$$\begin{aligned} \sigma^e &= -\theta \{ [\chi_4 \text{tr}(\mathbf{\Lambda}^A \mathbf{A}) + \chi_5 \text{tr}(\mathbf{\Lambda}^A \mathbf{B}_{\langle \rangle}) + \sigma_4 \text{tr}(\mathbf{\Lambda}^B \mathbf{A}) + \sigma_5 \text{tr}(\mathbf{\Lambda}^B \mathbf{B}_{\langle \rangle})] \mathbf{1} \\ &\quad + \text{tr}(\mathbf{\Lambda}^B) \mathbf{C}_0^\Psi + (\mathbf{C}^\Phi \mathbf{\Lambda}^A)_{\langle \rangle} + (\mathbf{C}^\Psi \mathbf{\Lambda}^B)_{\langle \rangle} \}. \end{aligned} \quad (33)$$

Now it is necessary to discuss how the definition of the elastic stress (21) and the adopted assumptions correspond to the well-known results of Doi (e.g., [22]). We introduced relation (21) for the elastic stress only by requiring that it does not produce entropy. The same relation can be obtained from Doi's results, basing on the Kirkwood theory and leading to the principle of virtual work in the form [23]

$$\rho \delta \psi = \text{tr}(\sigma^e \mathbf{D}) \delta t, \quad (34)$$

where ψ was called the “dynamic free energy”. When the time scale is much larger than the relaxation time, the elastic properties overshadow viscous effects, and $\Phi \approx \Phi^e$, $\Psi \approx \Psi^e$. Evidently, substituting $\delta \psi = \text{tr}((\partial \psi / \partial \mathbf{A}) \delta \mathbf{A} + (\partial \psi / \partial \mathbf{B}) \delta \mathbf{B})$ into (34) and dividing by δt under isothermal conditions leads to (21). Again, the linearity of the evolution equation for the structure tensor with regard to the strain-rate tensor is also consistent with Doi's results. However, it should be noted that to guarantee the self-consistency of a model written in terms of the structure tensor when the elastic stress is derived from the principle of virtual work (34), it is necessary to satisfy relation (21) for some particular form of $\mathbf{\Lambda}^A$ (for rod-like molecules $\mathbf{\Lambda}^B \equiv 0$). However, due to successive simplifications in considering rod-like polymers, Doi [22] finally derived a model which does not satisfy (21) for any form of $\mathbf{\Lambda}^A$.

Returning to the problem of determining the elastic stress in explicit form, we expand the free energy in terms of non-equilibrium variables thereby neglecting the contributions of the terms higher than the second order in \mathbf{A} and \mathbf{B} to derive the neo-Hookean law

$$\begin{aligned} \psi &= \psi_E(\theta, \rho) + \frac{\theta}{2\rho} (\psi_1 I_B^2 + \psi_2 II_A + \psi_3 II_B + 2\psi_4 II_{AB}), \\ \psi_E &= \psi|_{\mathbf{A}, \mathbf{B}=\mathbf{0}}, \quad \psi_1, \psi_2, \psi_3 > 0, \quad \psi_4^2 < \psi_2 \psi_3, \end{aligned} \quad (35)$$

where the conditions imposed on the coefficients determine thermodynamic stability through concavity of the free energy and through the requirement that the free energy reaches its minimum at equilibrium; the coefficients ψ_i correspond to moduli of elasticity. By the very derivation, the expression for the free energy (35) can only be valid for small deviations from equilibrium. If the deviation is large, it is necessary to impose additional restrictions that the free energy does not depend on the structure tensor when the elliptic molecules are contracted to spheres, and the evolution equations for \mathbf{A} and \mathbf{B} must guarantee physically consistent values of these tensors (for example, the Maier–Saupe order parameter, whose definition will be given later, cannot be larger than unity). While the adopted neo-Hookean form of the free energy (35) does not suffice to model the effect of finite extensibility of the molecules, which is important in considering polymer dynamics, it allows us to focus on the effects caused only by the anisotropy of the molecules, thus distinguishing them from the effects of finite extensibility.

The constitutive law for the free energy (35) yields the expressions for the forces

$$\mathbf{\Lambda}^A = -(\psi_2 \mathbf{A} + \psi_4 \mathbf{B}_{\langle 1 \rangle}), \quad \mathbf{\Lambda}^B = -(\psi_1 I_B \mathbf{1} + \psi_3 \mathbf{B}_{\langle 1 \rangle} + \psi_4 \mathbf{A}), \quad (36)$$

which allow us to determine the specific form of the dissipative fluxes

$$\mathbf{\Phi}^d = -(\alpha \psi_2 + \zeta \psi_4) \mathbf{A} - (\alpha \psi_4 + \zeta \psi_3) \mathbf{B}_{\langle 1 \rangle}, \quad (37)$$

$$\mathbf{\Psi}^d = -3\beta_1 \psi_1 I_B \mathbf{1} - (\zeta \psi_2 + \beta_2 \psi_4) \mathbf{A} - (\zeta \psi_4 + \beta_2 \psi_3) \mathbf{B}_{\langle 1 \rangle}. \quad (38)$$

2.5. Extinction angles

Evidently, directions of the highest elongation and orientational density of molecules, determined, respectively, by the principal axes of \mathbf{B} and \mathbf{A} corresponding to the largest principal values, do not generally coincide. In case of volume preserving conformations, determined by $I_B \equiv 0$ [1], it is possible to find a relationship between these directions for steady simple shear as $\mathbf{D} \rightarrow \mathbf{0}$ ($\dot{\mathbf{A}} = \dot{\mathbf{B}} = \mathbf{0}$), in which case they are called extinction angles. Following [22], let us denote by $\mathbf{n}^{(k)}$, λ_k and $\mathbf{u}^{(k)}$, ν_k the principal vectors and values of \mathbf{A} and \mathbf{B} , respectively, where superscript (1) corresponds to the largest value. Then we can write

$$\mathbf{A} = \lambda_k \mathbf{n}^{(k)} \otimes \mathbf{n}^{(k)}, \quad \mathbf{B} = \nu_k \mathbf{u}^{(k)} \otimes \mathbf{u}^{(k)}. \quad (39)$$

Because $\mathbf{A} \rightarrow \mathbf{0}$, $\mathbf{B} \rightarrow \mathbf{0}$ as $\mathbf{D} \rightarrow \mathbf{0}$, we can omit the co-rotational derivatives in the evolution equations (12) and (13) as well as all the cross-products in formulas for $\mathbf{\Phi}^e$ and $\mathbf{\Psi}^e$ (30) and (31) as the higher order terms, whose effect becomes negligible as $\mathbf{D} \rightarrow \mathbf{0}$. In this case, we derive from the evolution equation for the structure and elongation tensors (12) and (13)

$$\vartheta_1 \lambda_k \mathbf{n}^{(k)} \otimes \mathbf{n}^{(k)} + \vartheta_2 \nu_k \mathbf{u}^{(k)} \otimes \mathbf{u}^{(k)} + \chi_0 \mathbf{D} = \mathbf{0}, \quad (40)$$

$$\varsigma_1 \lambda_k \mathbf{n}^{(k)} \otimes \mathbf{n}^{(k)} + \varsigma_2 \nu_k \mathbf{u}^{(k)} \otimes \mathbf{u}^{(k)} + \sigma_0 \mathbf{D} = \mathbf{0}, \quad (41)$$

where

$$\vartheta_1 = -(\alpha \psi_2 + \zeta \psi_4), \quad \vartheta_2 = -(\alpha \psi_4 + \zeta \psi_3), \quad \varsigma_1 = -(\zeta \psi_2 + \beta_2 \psi_4), \quad (42)$$

$$\varsigma_2 = -(\zeta \psi_4 + \beta_2 \psi_3). \quad (43)$$

Multiplying the first equation by $\mathbf{n}^{(1)}$, and the second by $\mathbf{u}^{(1)}$ and omitting the superscript (1), we obtain

$$\vartheta_1 \lambda \mathbf{n} + \vartheta_2 \nu (\mathbf{n} \cdot \mathbf{u}) \mathbf{u} + \chi_0 \mathbf{D} \mathbf{n} = \mathbf{0}, \quad (44)$$

$$\varsigma_1 \lambda (\mathbf{n} \cdot \mathbf{u}) \mathbf{n} + \varsigma_2 \nu \mathbf{u} + \sigma_0 \mathbf{D} \mathbf{u} = \mathbf{0}. \quad (45)$$

The parameters λ and ν can be eliminated from the above system to give four relations among four independent components of the principal vectors. For simple shear, where the only non-zero components of the strain-rate tensor are $D_{12} = D_{21} = \frac{1}{2} \dot{\gamma}$, Eqs. (43) and (44), after elimination of λ and ν , yield the relations among the principal vectors \mathbf{n} and \mathbf{u} as $\dot{\gamma} \rightarrow 0$

$$\frac{\chi_0 \varsigma_1 n_2^2 (\mathbf{n} \cdot \mathbf{u}) - \sigma_0 \vartheta_1 u_1 n_1}{\vartheta_1 \varsigma_2 n_1 u_2 - \vartheta_2 \varsigma_1 n_2 u_1 (\mathbf{n} \cdot \mathbf{u})^2} \left[u_2 - \frac{u_1 n_2}{n_1} \right] \vartheta_2 (\mathbf{n} \cdot \mathbf{u}) + \chi_0 n_1 = \chi_0 \frac{n_2^2}{n_1}, \quad (46)$$

$$\frac{\chi_0 \varsigma_1 n_2^2 (\mathbf{n} \cdot \mathbf{u}) - \sigma_0 \vartheta_1 u_1 n_1}{\vartheta_1 \varsigma_2 n_1 u_2 - \vartheta_2 \varsigma_1 n_2 u_1 (\mathbf{n} \cdot \mathbf{u})^2} \left[u_2 - \frac{\vartheta_2 \varsigma_1}{\vartheta_1 \varsigma_2} u_1 (\mathbf{n} \cdot \mathbf{u})^2 \right] \varsigma_2 + \sigma_0 u_2 = \chi_0 \frac{\varsigma_1}{\vartheta_1} n_2 (\mathbf{n} \cdot \mathbf{u}). \quad (46)$$

These relations are satisfied by $n_1 = n_2 = u_1 = u_2 = 2^{-1/2}$ for any values of the constitutive parameters, which gives the conventional value of the extinction angles between the direction of flow and the principal directions of orientation and elongation of the molecules equal to 45° .

2.6. Volume preserving flow

For volume preserving flow $\mathbf{D} \equiv \mathbf{D}_{(\cdot)}$, and (21) determines an elastic stress with arbitrary trace. Therefore, as usually performed in thermodynamics of volume preserving fluids, we assume the pressure to be an independent variable and the dynamic stress to be traceless $\boldsymbol{\sigma} = \boldsymbol{\sigma}_{(\cdot)} = \boldsymbol{\tau}$. In this case, in (30)–(32), we can put $\chi_4 = \chi_5 = \sigma_4 = \sigma_5 = \sigma_0^0 = \sigma_1^0 = 0$ and obtain

$$\boldsymbol{\tau}^e = -\theta [\text{tr}(\boldsymbol{\Lambda}^B) \mathbf{C}_0^\psi + (\mathbf{C}^\phi \boldsymbol{\Lambda}^A)_{(\cdot)} + (\mathbf{C}^\psi \boldsymbol{\Lambda}^B)_{(\cdot)}]. \quad (47)$$

For the dissipative constitutive quantities (26), (27) and (36)–(38), we have the same formulas with $\eta_b = 0$. This yields the constitutive law for the stress deviator

$$\boldsymbol{\tau} = 2\eta \mathbf{D} + (\kappa_1 + \kappa_2 I_B) \mathbf{A} + (\kappa_3 + \kappa_4 I_B) \mathbf{B}_{(\cdot)} + \kappa_5 (\mathbf{A} \mathbf{B}_{(\cdot)})_{(\cdot)} + \kappa_6 (\mathbf{A}^2)_{(\cdot)} + \kappa_7 (\mathbf{B}_{(\cdot)}^2)_{(\cdot)}, \quad (48)$$

and the evolution equations for the structure and elongation tensors

$$\frac{\mathcal{D}\mathbf{A}}{\mathcal{D}t} = \vartheta_1 \mathbf{A} + \vartheta_2 \mathbf{B}_{(\cdot)} + (\chi_0 + \chi_1 I_B) \mathbf{D} + \chi_2 (\mathbf{A} \mathbf{D})_{(\cdot)} + \chi_3 (\mathbf{B}_{(\cdot)} \mathbf{D})_{(\cdot)}, \quad (49)$$

$$\begin{aligned} \frac{\mathcal{D}\mathbf{B}}{\mathcal{D}t} = & \varsigma_0 I_B \mathbf{1} + \varsigma_1 \mathbf{A} + \varsigma_2 \mathbf{B}_{(\cdot)} + [\sigma_2^0 \text{tr}(\mathbf{A} \mathbf{D}) + \sigma_3^0 \text{tr}(\mathbf{B}_{(\cdot)} \mathbf{D})] \mathbf{1} \\ & + (\sigma_0 + \sigma_1 I_B) \mathbf{D} + \sigma_2 (\mathbf{A} \mathbf{D})_{(\cdot)} + \sigma_3 (\mathbf{B}_{(\cdot)} \mathbf{D})_{(\cdot)}, \end{aligned} \quad (50)$$

where

$$\begin{aligned} \varsigma_0 = & -3\beta_1 \psi_1, & \kappa_1 = & \theta(\chi_0 \psi_2 + \sigma_0 \psi_4), & \kappa_2 = & \theta(3\sigma_2^0 \psi_1 + \chi_1 \psi_2 + \sigma_1 \psi_4 + \sigma_2 \psi_1), \\ \kappa_3 = & \theta(\chi_0 \psi_4 + \sigma_0 \psi_3), & \kappa_4 = & \theta(3\sigma_3^0 \psi_1 + \chi_1 \psi_4 + \sigma_1 \psi_3 + \sigma_3 \psi_1), \\ \kappa_5 = & \theta(\chi_2 \psi_4 + \chi_3 \psi_2 + \sigma_2 \psi_3 + \sigma_3 \psi_4), & \kappa_6 = & \theta(\chi_2 \psi_2 + \sigma_2 \psi_4), \\ \kappa_7 = & \theta(\chi_3 \psi_4 + \sigma_3 \psi_3), \end{aligned} \quad (51)$$

and $\vartheta_1, \vartheta_2, \varsigma_1$ and ς_2 are defined in (42).

From (13), (31) and (38), we derive

$$\dot{I}_B = -9\beta_1 \psi_1 I_B + 3\sigma_2^0 \text{tr}(\mathbf{A} \mathbf{D}) + 3\sigma_3^0 \text{tr}(\mathbf{B}_{(\cdot)} \mathbf{D}) \quad (52)$$

from where it follows that generally, $I_B \neq 0$. The term $-9\beta_1 \psi_1 I_B$ describes irreversible conversion of the elastic energy of the elongated molecules into thermal energy. In particular, if $p = \text{const.}$, $\mathbf{q} = \mathbf{0}$, $\mathbf{A} = \mathbf{B}_{(\cdot)} = \mathbf{D} = \mathbf{0}$, then there is no macroscopic motion and $I_B = I_B|_{t=0} e^{-9\beta_1 \psi_1 t}$. Therefore, the energy balance yields $(\partial e / \partial \theta) \dot{\theta} = -(\partial e / \partial I_B) I_B|_{t=0} e^{-9\beta_1 \psi_1 t}$, which shows the rate at which the temperature rises due to the viscous relaxation. Evidently, volume preservation of the solution ($\text{tr} \mathbf{D} \equiv 0$) does not generally lead to volume preservation of conformations of the macromolecules ($I_B \equiv 0$).

Detailed comparison of a thermodynamically consistent model of polymers, which includes only the conformation tensor \mathbf{R} as an independent variable, with other models was performed by Maugin and Drouot [1]. Such a one-tensor model can be derived from the theory, developed here by putting $\mathbf{A} \equiv \mathbf{0}$, $\mathbf{B} := \mathbf{R}$; the latter being true for $m = 2$. Therefore, here we will mention only the main points of such an analysis in order to focus on the differences between the one-tensor and two-tensor models.

Considering the evolution equation for the conformation tensor (50), it can be seen that the kinetic theory determines $\sigma_3 = 2$ for dumbbells and rigid rods. However, for a model with $\zeta_{0,1} = \sigma_{2,3}^0 = \sigma_{1,2} = 0$, $\sigma_3 < 0.8$ was identified for a steady shear [1,24]. Moreover, a value of $\sigma_3 \neq 2$ can generally describe more complex interaction between the solvent and molecules than it is assumed in the kinetic theory.

In the derivation of the present model we restricted ourselves by considering the neo-Hookean model for the elasticity of the molecules, which is generally correct only for small deviation from the equilibrium configuration, or for infinitely extensible molecules without consideration of excluded volume effects. The finite extensibility can be taken into account by considering non-linear laws for the free energy. As a particular case, $\partial\psi/\partial\mathbf{B} = \hat{\zeta}(I_B)\mathbf{B}$ with $\hat{\zeta} \propto (1 - I_B/L)^{-1}$, where L is the maximum length of a dumbbell with Warner springs, yields the Chilcott–Rallison model [25]. For the model of Dunlap and Leal [6], the function $\hat{\zeta}(I_B)$ has more complex form. Therefore, such a non-linear behaviour is accounted for even with linear representation of the thermodynamic fluxes through forces. For study of anisotropic fluids, for example nematic liquid crystals, where excluded volume effects play a crucial role, non-linear relations among fluxes and forces are necessary, which should determine several stationary solutions of the evolution equation for the conformation or structure tensor. However, modelling of anisotropic fluids is out of scope of this study.

Another important point, also discussed in [1], is that the application of thermodynamics, which insists on the relation among the coefficients of the evolution equation (50) for the conformation tensor and the coefficients entering the expression (48) for the stress tensor, for $\psi_3 \neq 0$ leads to the necessary non-linearity of the stress tensor with regard to \mathbf{B} in order to guarantee irreversibility of the process. For the particular case considered here, when the deviation from equilibrium is small, these terms have no significant effect on the stress. For large deviations, however, they can play an important role which cannot be predicted by simple kinetic models.

Let us now consider new physical effects, which are accounted for by considering both structure and elongation tensors as internal variables. The evolution equation for the structure tensor (49) includes terms describing the influence of the non-equilibrium molecular length distribution. If we consider the situation when $\mathbf{A} = \mathbf{D} = \mathbf{0}$, then $\mathbf{B}_{(t)} \neq \mathbf{0}$ will lead to re-orientation of the molecules, whereas for purely rigid rods, the evolution equation for the structure tensor [22]⁴ determines such situation as stationary. We can distinguish between two mechanisms associated with two coefficients $\alpha\psi_4$ and $\zeta\psi_3$ in the expression for ϑ_2 in (42), which drive the re-orientation in this case. The presence of the coefficient $\alpha\psi_4$ is caused by the dependence of the free energy ψ on the term $\text{tr}(\mathbf{A}\mathbf{B}_{(t)})$, which determines the dependence of the driving force for the re-orientation $\partial\psi/\partial\mathbf{A}$ on $\mathbf{B}_{(t)}$. For a non-equilibrium elongational distribution this force is not zero, even when the orientational distribution of the molecules is at equilibrium ($\mathbf{A} = \mathbf{0}$). This effect can be illustrated by the following considerations.

Let us assume an equilibrium orientational distribution of the molecules, and that the direction of the highest elongation of the molecules, determined by the traceless part of \mathbf{B} , lays along the axis x_1 , while the direction of the highest compression along x_2 . An elongation of the molecules, which changes the free

⁴ The linearized version of this equation can be derived with the condition $\psi_1 = \psi_3 = \psi_4 = \chi_1 = \chi_3 = 0$.

energy, has the same effect as an increase of their orientational density: these processes give rise to an elastic stress. However, a compression of the molecules, as well as a decrease of their orientational density, determines an elastic stress with opposite sign. Therefore, if in the case under consideration the density of the molecules becomes larger along x_2 and lower along x_1 , then this leads to a decrease of the overall elastic stress through the balancing of the elastic stresses caused by the re-orientation and elongation of the molecules. The latter process leads to a decrease of the free energy, and therefore determines a driving force for the re-orientation of the molecules, even when $\mathbf{A} = \mathbf{0}$.

Mathematically such a mechanism can be seen through investigating the case when $\psi_4 \rightarrow \sqrt{\psi_2\psi_3}$. In this case $\psi \rightarrow \psi_E(\theta, \rho) + \theta(2\rho)^{-1}[\psi_1 I_B^2 + \text{tr}(\psi_2^{1/2} \mathbf{A} + \psi_3^{1/2} \mathbf{B}_{\langle \rangle})^2]$, and for $I_B = 0$, $\psi - \psi_E(\theta, \rho) \rightarrow 0$ not only when $\mathbf{A}, \mathbf{B} \rightarrow \mathbf{0}$, but also when $\mathbf{A} \rightarrow -(\psi_3/\psi_2)^{1/2} \mathbf{B}_{\langle \rangle}$. This mechanism driving the re-orientation, becomes weaker as $\psi_4 \rightarrow 0$.

If we consider a particular situation by putting $\psi_4 = 0$, then the above described effect drops out, however, the elongation tensor still governs the evolution of the structure tensor when $\mathbf{A} = \mathbf{D} = \mathbf{0}$. This is caused by the presence of the term $\zeta \psi_3$ in the expression for ϑ_2 , describing the dependence of the flux Ψ of the variable \mathbf{A} on the force Λ^B associated with the variable \mathbf{B} . This term can account for different degrees of mobility of the molecules of different length,⁵ because free energy of rigid dumbbells depends on the length of the molecules. Moreover, local hydrodynamic disturbances caused by a non-uniform change of the elongation of the molecules can exert an additional force driving the re-orientation of the molecules. This force can be also accounted for by this term, because $\mathcal{D}\mathbf{B}/Dt \propto \mathbf{B}$.

The terms in (49) proportional to the strain-rate tensor \mathbf{D} describe effects caused by the macroscopic motion. The terms at χ_0 and χ_2 enter the model of rigid rod dynamics, while the term $\chi_1 I_B$ describes the influence of the mean molecular length, and $\chi_3(\mathbf{B}_{\langle \rangle} \mathbf{D})_{\langle \rangle}$ accounts for the effect of non-uniform distribution of molecular lengths.

2.7. Flow birefringence in elongational flow

In studying rheometric flows let us for simplicity consider a volume preserving flow with volume preservation of conformations of macromolecules: $\text{tr} \mathbf{D} \equiv I_B \equiv 0$. We will consider a uniaxial stretching of the fluid along the x_1 -axis. In this case, the structure and elongation tensors can be expressed only through the corresponding scalar parameters a and b . If a unit vector \mathbf{u} , called director, describes the axis of symmetry, then we have $A_{ij} = a(u_i u_j - \frac{1}{3} \delta_{ij})$, which in our case yields

$$\mathbf{A} = a \begin{pmatrix} \frac{2}{3} & 0 & 0 \\ 0 & -\frac{1}{3} & 0 \\ 0 & 0 & -\frac{1}{3} \end{pmatrix}, \quad \mathbf{D} = \dot{\epsilon} \mathbf{\Gamma}, \quad \mathbf{\Gamma} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & -\frac{1}{2} \end{pmatrix}. \quad (53)$$

The scalar a is called the *order parameter* or *Maier–Saupe order parameter*, and in transition from equilibrium to complete alignment along \mathbf{u} , takes values from zero to unity. If all the molecules are directed perpendicular to the director \mathbf{u} , then $a = -\frac{1}{2}$, and generally $-\frac{1}{2} \leq a \leq 1$. In the same way, for the elongation tensor we can introduce the scalar parameter b , which for volume preserving molecular

⁵ This is similar to the situation, when the presence of a temperature gradient leads to a flux of concentration.

conformations, is bounded as $-\frac{1}{2} \leq b \leq 1$. Using these formulas, we can derive from (48)–(50)

$$\tau = 2\eta\dot{\epsilon} + \frac{2}{3}(\kappa_1 a + \kappa_3 b) + \frac{2}{9}(\kappa_5 ab + \kappa_6 a^2 + \kappa_7 b^2), \quad (54)$$

$$\frac{da}{dt} = \left(\vartheta_1 + \frac{\chi_2}{2}\dot{\epsilon}\right)a + \left(\vartheta_2 + \frac{\chi_3}{2}\dot{\epsilon}\right)b + \frac{3}{2}\chi_0\dot{\epsilon}, \quad (55)$$

$$\frac{db}{dt} = \left(\varsigma_1 + \frac{\sigma_2}{2}\dot{\epsilon}\right)a + \left(\varsigma_2 + \frac{\sigma_3}{2}\dot{\epsilon}\right)b + \frac{3}{2}\sigma_0\dot{\epsilon}. \quad (56)$$

For stationary flow (55) and (56) yield

$$a = \frac{3\dot{\epsilon}}{2Q} \left[\sigma_0 \left(\vartheta_2 + \frac{\chi_3}{2}\dot{\epsilon} \right) - \chi_0 \left(\varsigma_2 + \frac{\sigma_3}{2}\dot{\epsilon} \right) \right], \quad (57)$$

$$b = \frac{3\dot{\epsilon}}{2Q} \left[\chi_0 \left(\varsigma_1 + \frac{\sigma_2}{2}\dot{\epsilon} \right) - \sigma_0 \left(\vartheta_1 + \frac{\chi_2}{2}\dot{\epsilon} \right) \right], \quad (58)$$

$$Q = \left(\vartheta_1 + \frac{\chi_2}{2}\dot{\epsilon} \right) \left(\varsigma_2 + \frac{\sigma_3}{2}\dot{\epsilon} \right) - \left(\vartheta_2 + \frac{\chi_3}{2}\dot{\epsilon} \right) \left(\varsigma_1 + \frac{\sigma_2}{2}\dot{\epsilon} \right).$$

In this case the longitudinal stress deviator can be found in the form

$$\tau = 2 \left[\eta + \frac{\omega_0\dot{\epsilon}^3 + \omega_1\dot{\epsilon}^2 + \omega_2\dot{\epsilon} + \omega_3}{(\dot{\epsilon}^2 + \omega_4\dot{\epsilon} + \omega_5)^2} \right] \dot{\epsilon}, \quad (59)$$

where the coefficients ω_i are expressed through the parameters entering (54)–(56).

The stationary solution also determines

$$\frac{a}{b} = \frac{\sigma_0 \left[\frac{1}{2}(\chi_3)\dot{\epsilon} - (\alpha\psi_4 + \zeta\psi_3) \right] - \chi_0 \left[\frac{1}{2}(\sigma_3)\dot{\epsilon} - (\zeta\psi_4 + \beta_2\psi_3) \right]}{\chi_0 \left[\frac{1}{2}(\sigma_2)\dot{\epsilon} - (\zeta\psi_2 + \beta_2\psi_4) \right] - \sigma_0 \left[\frac{1}{2}(\chi_2)\dot{\epsilon} - (\alpha\psi_2 + \zeta\psi_4) \right]}. \quad (60)$$

Assuming mutual independence of the elastic moduli ψ_i , it can be found that $a/b \rightarrow 0$ as $\psi_2 \rightarrow \infty$, and $b/a \rightarrow 0$ as $\psi_3 \rightarrow \infty$, when the strain-rate is fixed. In the first case, where the “orientational” elastic modulus is large, the change of the internal structure is mainly due to the elongation of molecules, which is similar to the behaviour of isotropic coiled molecules. In the second case, where the “elongational” elastic modulus is large, the situation is reverse, which leads to weak changes of molecular length and significant changes in molecular orientation distribution. The latter situation resembles the behaviour of rigid rods. However, it should be noted that, for example in the first case ($\psi_2 \rightarrow \infty$), because of the linear dependence of κ_1 on ψ_2 , orientational effects will still play a significant role in the determination of the stresses; therefore the analogies with the behaviour of isotropic coiled molecules and rigid rods are purely geometrical.

2.8. Theoretical predictions for simple flows

Because experimental data on polyelectrolyte flows are scarce, and their dynamics is still not well understood, let us here compare the predictions of the presented thermodynamical theory with the predictions of the linearized model describing rigid dumbbells dynamics, in order to show which effects could be expected in flows of polymers, whose molecules can be roughly considered as extensible ellipsoids of revolution.

As before we will consider volume preserving flow with volume preservation of conformations of macromolecules: $\text{tr } \mathbf{D} \equiv I_B \equiv 0$. To make the model tractable we will neglect the effect of the cross-coupling between the thermodynamical fluxes ($\zeta = 0$), consider $\alpha = \beta_2$ and as proposed by kinetic models of elastic and rigid dumbbells, we put $\chi_0 = \sigma_0 = \frac{2}{3}$, $\chi_2 = \sigma_2 = 2$. We also assume the coefficients χ_3 and σ_2 , describing, in particular, the influence of the molecular length on their orientation in flow, to be negligibly small, because the coefficient in a one tensor model for rigid dumbbells do not depend on the dumbbell length.

Normalizing the time by $1/\dot{\epsilon}$ and dividing (49) and (50) by $\dot{\epsilon}$, we derive

$$\frac{\mathcal{D}\mathbf{A}}{\mathcal{D}t} = -\frac{1}{De_A}\mathbf{A} - \frac{1}{De_{AB}}\mathbf{B} + \frac{2}{3}\mathbf{\Gamma} + 2(\mathbf{A}\mathbf{\Gamma})_{\langle \rangle}, \quad (61)$$

$$\frac{\mathcal{D}\mathbf{B}}{\mathcal{D}t} = -\frac{1}{De_{AB}}\mathbf{A} - \frac{1}{De_B}\mathbf{B} + \frac{2}{3}\mathbf{\Gamma} + 2(\mathbf{B}\mathbf{\Gamma})_{\langle \rangle}, \quad (62)$$

where $De_A = -\dot{\epsilon}/\alpha\psi_2$, $De_B = -\dot{\epsilon}/\alpha\psi_3$, $De_{AB} = -\dot{\epsilon}/\alpha\psi_4$ are corresponding Debra numbers. For elongational flow the tensor $\mathbf{\Gamma}$ is given by (53), while for shear flow the only non-zero components are $\Gamma_{12} = \Gamma_{21} = \frac{1}{2}$. Let us also introduce the ratios $h_1 = De_A/De_B = \psi_3/\psi_2$ and $h_2 = De_{AB}/(De_B De_A)^{1/2}$. h_1 is a ratio between the orientational and elongational relaxation times, such a parameter is also used in considering FENE dumbbells [5]. The parameter h_2 shows the importance of the coupling between \mathbf{A} and \mathbf{B} : there is no coupling when $h_2 = 0$, and the coupling becomes stronger as $|h_2| \rightarrow 1$. Due to the relations of thermodynamic stability (35), $|h_2| < 1$. The values $h_1 = 1$, $h_2 = 0$ lead to symmetry and decoupling of (61) and (62), and therefore yield the linearized model for rigid dumbbells. Because the free energy of a suspension of neo-Hookean dumbbells is inversely proportional to their squared length, we will model increasing of the aspect ratios of the molecules by increasing of h_1 .

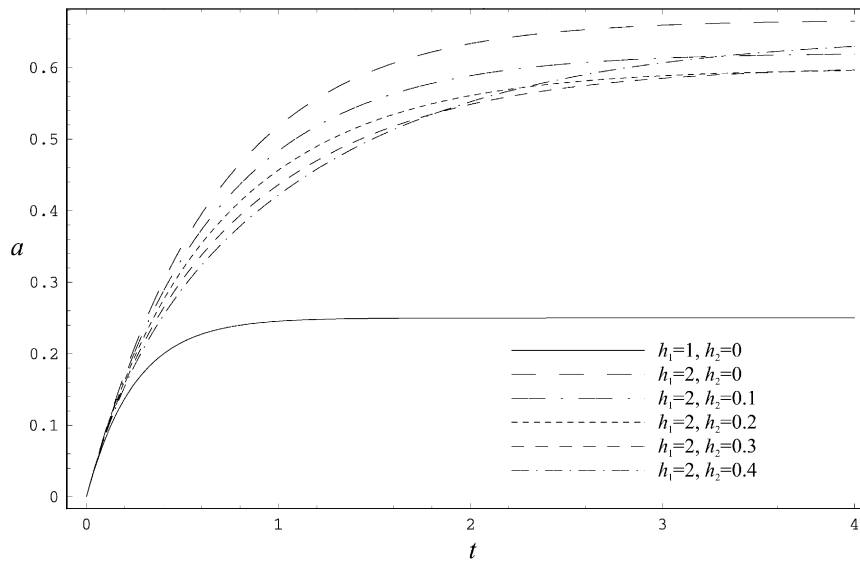


Fig. 3. The Maier–Saue parameter a for different values of the coupling efficiency h_2 at a start-up of elongational flow, $De_B = 0.2$, $h_1 = 2$. Case $h_1 = 1$, $h_2 = 0$ corresponds to rigid dumbbells.

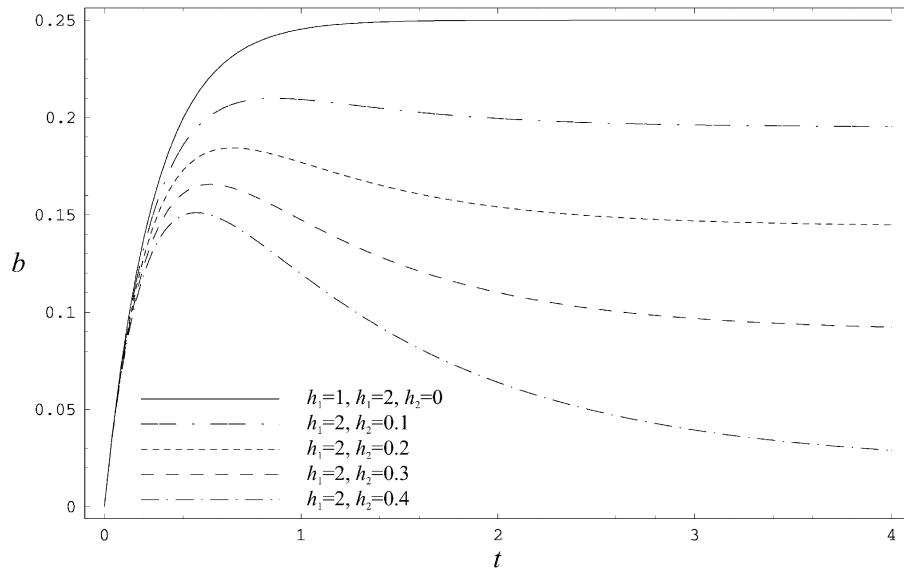


Fig. 4. The elongation parameter b for different values of the coupling efficiency h_2 at a start-up of elongational flow, $De_B = 0.2$, $h_1 = 2$. Case $h_1 = 1, h_2 = 0$ corresponds to rigid dumbbells.

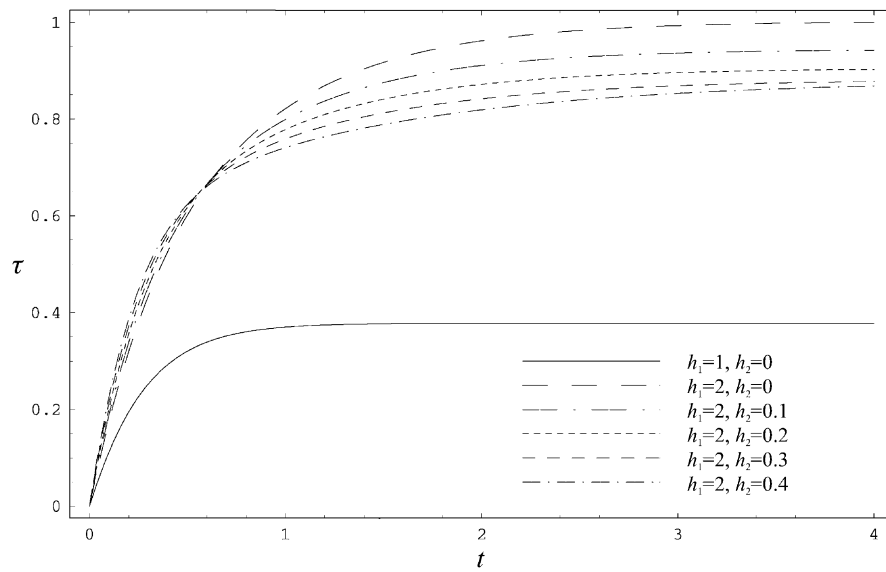


Fig. 5. The normalized normal stress for different values of the coupling efficiency h_2 at a start-up of elongational flow, $De_B = 0.2$, $h_1 = 2$. Case $h_1 = 1, h_2 = 0$ corresponds to rigid dumbbells.

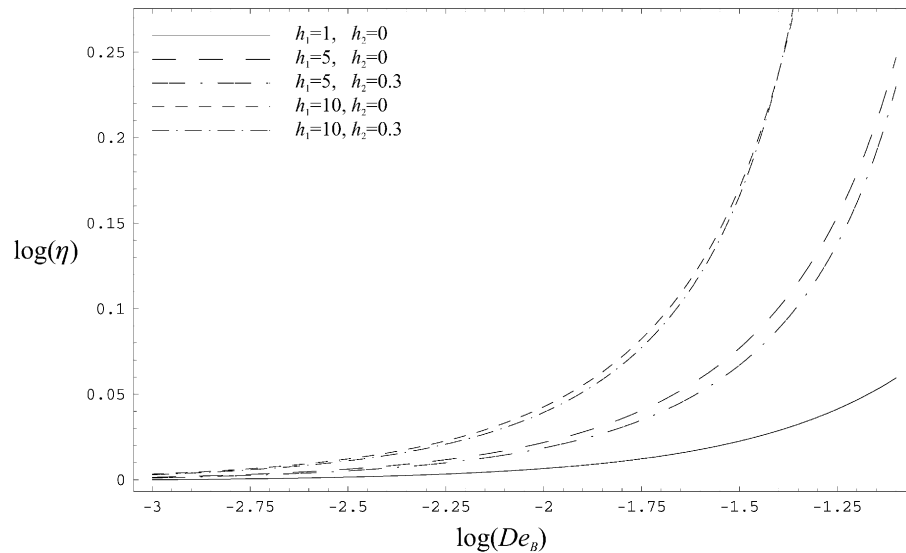


Fig. 6. The normalized elongational viscosity for different ratios h_1 between the orientational and elongational relaxation times and coupling efficiency h_2 at steady elongational flows. Case $h_1 = 1, h_2 = 0$ corresponds to rigid dumbbells.

Results of modelling of a start-up of elongational flow are presented in Figs. 3–5. It can be seen that an increase of h_2 leads to an overshoot of b . This is explained by the fact that for increasing h_1 , the orientational elastic modulus decreases, which leads to higher degree of orientation of the molecules along the direction of flow. The higher orientational density causes a force driving shrinking of the molecules in the direction of flow and elongation of the molecules in the perpendicular direction, as was explained before. Because the value of b is smaller than that of a , the coupling does not produce an overshoot in a . Moreover, because the gradient of a is high at the region of the maximum of b , there is no overshoot in the stress τ . At the beginning of the start-up the coupling has no effect, because \mathbf{A} and \mathbf{B} are small and their dynamics is governed mainly by the term $\frac{2}{3}\mathbf{\Gamma}$, describing elastic effects.

Values of the normalized elongational viscosity as a function of De_B are presented in Fig. 6. The range of change of the Debora number De_B is confined from above by $De_B = 0.1$ to insure validity of the linearized model. The shown behaviour is typical also for FENE dumbbells, because the non-linear effects are negligible for low Debora numbers. The increase of the viscosity for increasing h_1 is also qualitatively similar to the dynamics of FENE dumbbells [5]. Including coupling between the structure and elongation tensors does not have a qualitative effect as it was in modelling a start-up of elongational flow.

Results of modelling a start-up of simple shear are presented in Figs. 7–9. The coefficients A_{12} and B_{12} are chosen for the presentation as determining the shear stress. Due to the coupling described before, there is an overshoot in B_{12} , however, not so pronounced as in the case of elongation flow. This is because flow-induced anisotropy in simple shear is much weaker than in elongational flow. This overshoot does not lead to an overshoot in shear stress. However, because we operate with traceless tensors, even this linear model yields a stress overshoot for higher Debora numbers, which can be seen in Fig. 10. The presence of the coupling between \mathbf{A} and \mathbf{B} has no qualitative effect.

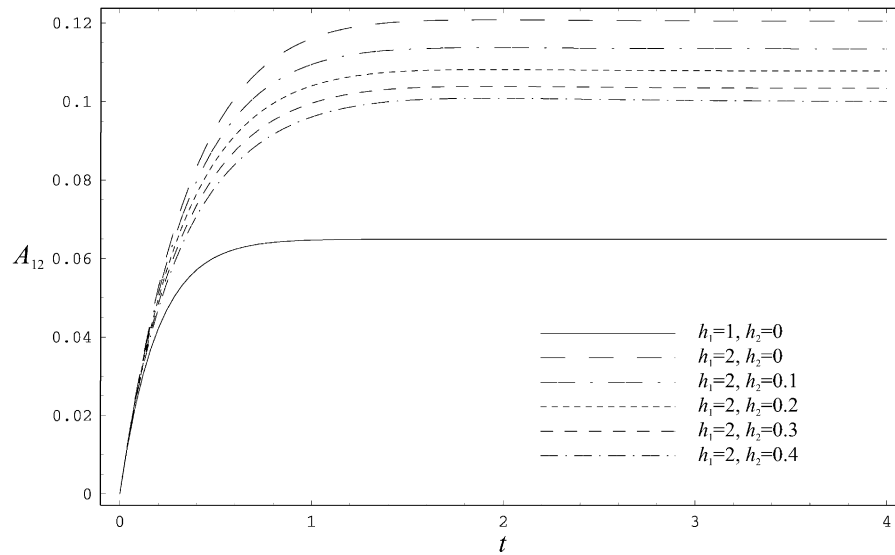


Fig. 7. The coefficient A_{12} of the structure tensor \mathbf{A} for different values of the coupling efficiency h_2 at a start-up of simple shear, $De_A = 0.2$, $h_1 = 2$. Case $h_1 = 1$, $h_2 = 0$ corresponds to rigid dumbbells.

Plot of the shear viscosity as a function of De_A at steady shear is shown in Fig. 11. Change of h_1 leads to a shift of the curve, which is qualitatively similar to the behaviour of the FENE dumbbells [5]. However, the two-tensor model yields an inflection of the curve, which is caused by a shift between the maxima of A_{12} and B_{12} for $h_1 \neq 1$ (Fig. 12). Including coupling yields skewing of the profiles of A_{12} and B_{12} .

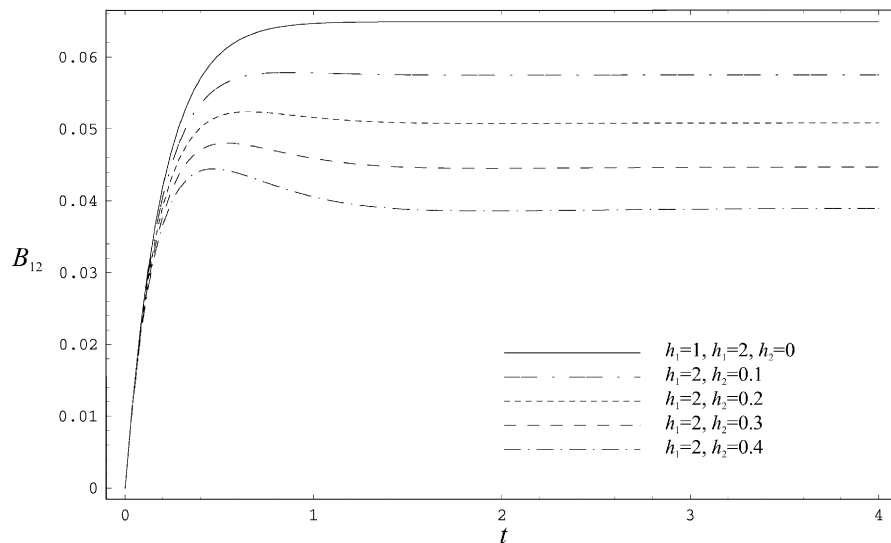


Fig. 8. The coefficient B_{12} of the elongation tensor \mathbf{B} for different values of the coupling efficiency h_2 at a start-up of simple shear, $De_A = 0.2$, $h_1 = 2$. Case $h_1 = 1$, $h_2 = 0$ corresponds to rigid dumbbells.

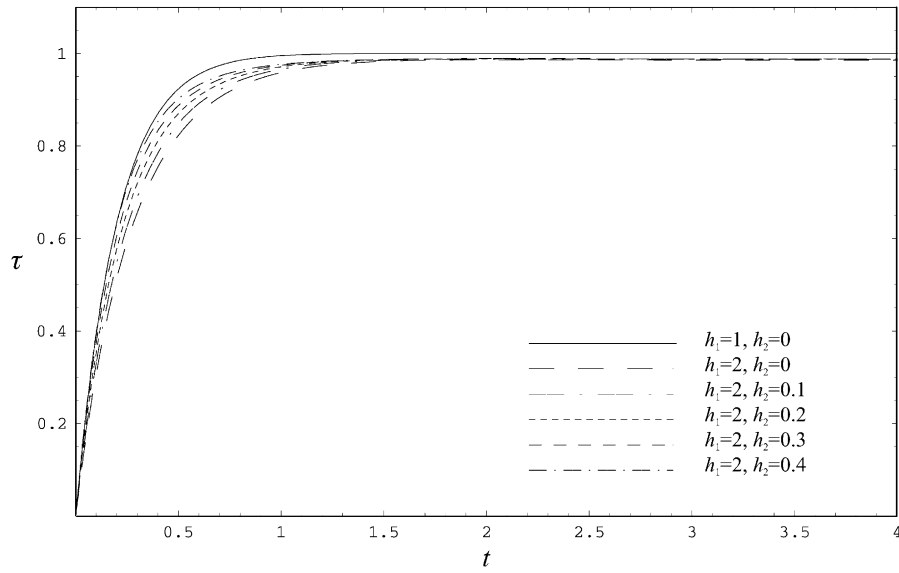


Fig. 9. The normalized shear stress for different values of the coupling efficiency h_2 at a start-up of simple shear, $De_A = 0.2$. Case $h_1 = 1, h_2 = 0$ corresponds to rigid dumbbells.

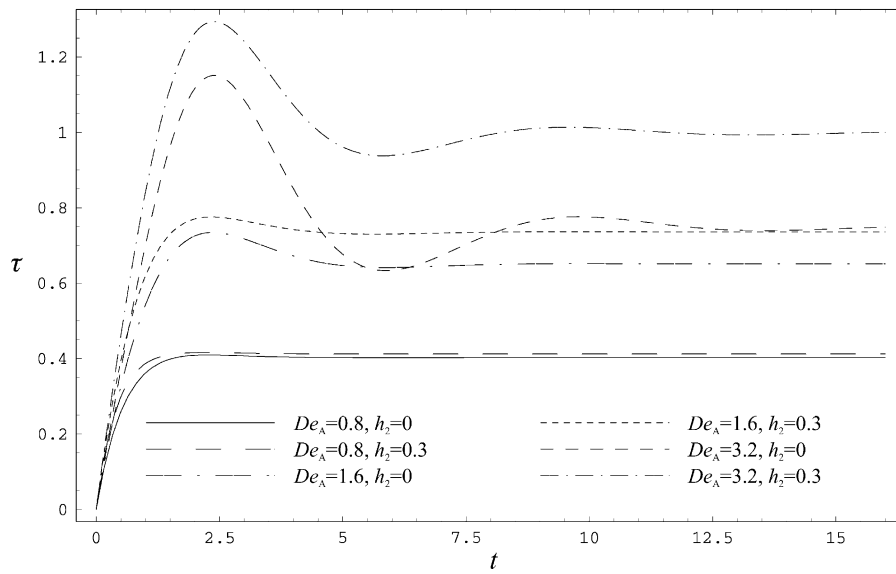


Fig. 10. The normalized shear stress for different Debora numbers De_A and elongational relaxation times and coupling efficiency h_2 at start-up of simple shear, $h_1 = 2$. Case $h_1 = 1, h_2 = 0$ corresponds to rigid dumbbells.

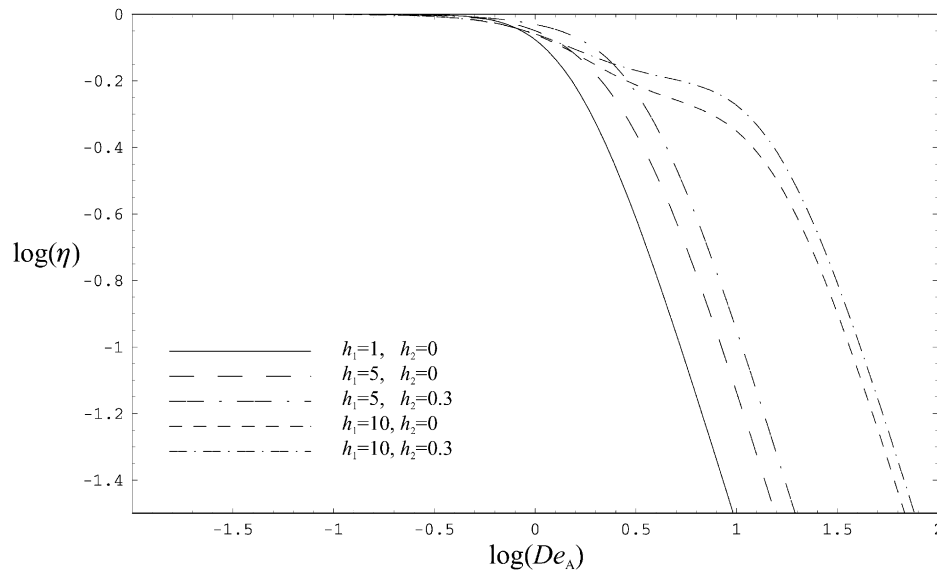


Fig. 11. The normalized shear viscosity for different ratios h_1 between the orientational and elongational relaxation times and coupling efficiency h_2 at steady simple shear. Case $h_1 = 1, h_2 = 0$ corresponds to rigid dumbbells.

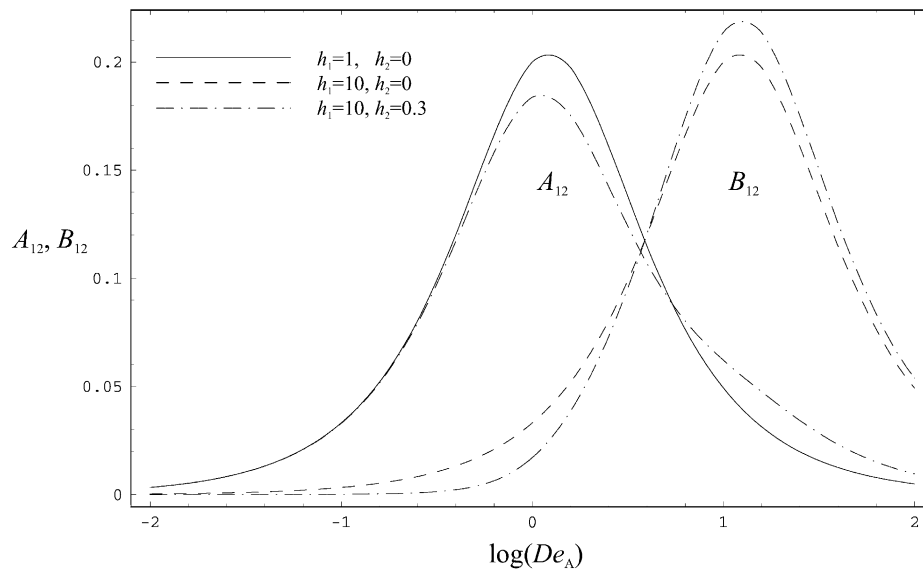


Fig. 12. The profiles of A_{12} and B_{12} for different ratios h_1 between the orientational and elongational relaxation times and coupling efficiency h_2 at steady simple shear. Case $h_1 = 1, h_2 = 0$ corresponds to rigid dumbbells.

3. Conclusion

Using the methods of irreversible thermodynamics a model of polymer solutions with molecular form birefringence was developed. The molecules are modelled as extensible ellipsoids, whose distribution with regard to orientation is described by the structure tensor, and their elongation by the corresponding elongation tensor. These characteristics are considered as internal variables determining the internal structure of this kind of fluids. The model is linear in the strain-rates and non-linear in the internal variables. Constitutive law for the stress deviator is presented, together with the evolution equation for the structure and elongation tensors. Analysis of elongational flows shows that the distribution of the molecules with regard to their orientation and elongation is determined by the corresponding elastic moduli, which can lead to such limiting situations as changing of internal structure mainly by re-orientation or elongation of molecules. Coupling between the structure and elongation tensors can lead to an overshoot of one of them in a start-up of simple flows. Qualitative effect of the coupling on the stress is much less pronounced.

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