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The universal limit in dynamics of dilute polymeric solutions

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Abstract

The method of invariant manifold is developed for a derivation of reduced description in kinetic equations of dilute polymeric solutions. It is demonstrated that this reduced description becomes universal in the limit of small Deborah and Weissenberg numbers, and it is represented by the (revised) Oldroyd 8 constants constitutive equation for the polymeric stress tensor. Coefficients of this constitutive equation are expressed in terms of the microscopic parameters. A systematic procedure of corrections to the revised Oldroyd 8 constants equations is developed. Results are tested with simple flows. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Kinetic equations arising in the theory of polymer dynamics constitute a wide class of microscopic models of complex fluids. Same as in any branch of kinetic theory, the problem of reduced description becomes actual as soon as the kinetic equation is established. However, in spite of an enormous amount of work in the field of polymer dynamics [1–4], this problem remains less studied as compared to other classical kinetic equations.

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It is the purpose of this paper to suggest a systematic approach to the problem of reduced description for kinetic models of polymeric fluids. First, we would like to specify our motivation by comparing the problem of the reduced description for that case with a similar problem in the familiar case of the rarefied gas obeying the classical Boltzmann kinetic equation [5,6].

The problem of reduced description begins with establishing a set of slow variables. For the Boltzmann equation, this set is represented by five hydrodynamic fields (density, momentum and energy) which are low-order moments of the distribution function, and which are conserved quantities of the dissipation process due to particle's collisions. The reduced description is a closed system of equations for these fields. One starts with the manifold of local equilibrium distribution functions (local Maxwellians), and finds a correction by the Chapman–Enskog method [6]. The resulting reduced description (the Navier–Stokes hydrodynamic equations) is universal in the sense that the form of equations does not depend on details of particle's interaction whereas the latter shows up explicitly only in the transport coefficients (viscosity, temperature conductivity, etc.).

Coming back to the complex fluids, we shall consider the simplest case of dilute polymer solutions represented by dumbbell models studied below. Two obstacles preclude an application of the traditional techniques. First, the question which variables should be regarded as slow is at least less evident because the dissipative dynamics in the dumbbell models has no nontrivial conservation laws compared to the Boltzmann case. Consequently, a priori, there are no distinguished manifolds of distribution functions like the local equilibria which can be regarded as a starting point. Second, while the Boltzmann kinetic equation provides a self-contained description, the dumbbell kinetic equations are coupled to the hydrodynamic equations. This coupling manifests itself as an external flux in the kinetic equation.

The well-known distinguished macroscopic variable associated with the dumbbell kinetic equations is the polymeric stress tensor [1]. This variable is not the conserved quantity but, nevertheless, it should be treated as a relevant slow variable because it actually contributes to the macroscopic (hydrodynamic) equations. Equations for the stress tensor are known as the constitutive equations, and the problem of reduced description for the dumbbell models consists in deriving such equations from the kinetic equation.

Our approach is based on the method of invariant manifold [7], modified for systems coupled with external fields. This method suggests constructing invariant sets (or manifolds) of distribution functions that represent the asymptotic states of slow evolution of the kinetic system. In the case of dumbbell models, the reduced description is produced by equations which constitute stress–strain relations, and two physical requirements are met by our approach: The first is the principle of *frame-indifference* with respect to any time-dependent reference frame. This principle requires that the resulting equations for the stresses contain only frame-indifferent quantities. For example, the frame-dependent vorticity tensor should not show up in these equations unless being presented in frame-indifferent combinations with another tensors. The second

principle is the *thermodynamic stability*: In the absence of the flow, the constitutive model should be purely dissipative, in other words, it should describe the relaxation of stresses to their equilibrium values.

The physical picture addressed below takes into account two assumptions: (i) In the absence of the flow, deviations from the equilibrium are small. Then the invariant manifold is represented by eigenvectors corresponding to the slowest relaxation modes. (ii) When the external flow is taken into account, it is assumed to cause a small deformation of the invariant manifolds of the purely dissipative dynamics. Two characteristic parameters are necessary to describe this deformation. The first is the characteristic time variation of the external field. The second is the characteristic intensity of the external field. For dumbbell models, the first parameter is associated with the conventional Deborah number while the second one is usually called the Weissenberg number. An iteration approach which involves these parameters is developed.

Two main results of the analysis are as follows: First, the lowest-order constitutive equations with respect to the characteristic parameters mentioned above has the form of the revised phenomenological *Oldroyd 8 constants model*. This result is interpreted as the macroscopic limit of the microscopic dumbbell dynamics whenever the rate of the strain is low, and the Deborah number is small. This limit is valid generically, in the absence or in the presence of the hydrodynamic interaction, and for the arbitrary nonlinear elastic force. The phenomenological constants of the Oldroyd model are expressed in a closed form in terms of the microscopic parameters of the model. The universality of this limit is similar to that of the Navier–Stokes equations which are the macroscopic limit of the Boltzmann equation at small Knudsen numbers for arbitrary hard-core molecular interactions. The test calculation for the nonlinear FENE force demonstrates a good quantitative agreement of the constitutive equations with solutions to the microscopic kinetic equation within the domain of their validity.

The second result is a regular procedure of finding corrections to the zero-order model. These corrections extend the model into the domain of higher rates of the strain, and to flows which alternate faster in time. Same as in the zero-order approximation, the higher-order corrections are linear in the stresses, while their dependence on the gradients of the flow velocity and its time derivatives becomes highly nonlinear. These corrections have a similar meaning as the higher-order (Burnett) corrections in the Chapman–Enskog method though, again, the actual form of equations is different.

The paper is organized as follows: For the sake of completeness, we present the nonlinear dumbbell kinetic models in the next section. In Section 3, we describe in details our approach to the derivation of macroscopic equations for an abstract kinetic equation coupled to external fields. This derivation is applied to the dumbbell models in Section 4. The zero-order constitutive equation is derived and discussed in detail in this section, as well as the structure of the first correction. Tests of the zero-order constitutive equation for simple flow problems are given in Section 5.

2. The problem of reduced description in polymer dynamics

2.1. Elastic dumbbell models

The elastic dumbbell model is the simplest microscopic model of polymer solutions [1]. The dumbbell model reflects the two features of real-world macromolecules to be orientable and stretchable by a flowing solvent. The polymeric solution is represented by a set of identical elastic dumbbells placed in an isothermal incompressible liquid. Let $\mathbf{Q}$ be the connector vector between the beads of a dumbbell, and $\Psi(\mathbf{x},\mathbf{Q},t)$ be the configuration distribution function which depends on the location in the space $\mathbf{x}$ at time t. We assume that dumbbells are distributed uniformly, and consider the normalization, $\int \Psi(\mathbf{x},\mathbf{Q},t)\,\mathrm{d}\mathbf{Q} = 1$. The Brownian motion of beads in the physical space causes a diffusion in the phase space described by the Fokker–Planck equation (FPE) [1]:

$$\frac{D\Psi}{Dt} = -\frac{\partial}{\partial \mathbf{Q}} \cdot \mathbf{k} \cdot \mathbf{Q}\Psi + \frac{2k_{\mathrm{B}}T}{\xi}\frac{\partial}{\partial \mathbf{Q}} \cdot \mathbf{D} \cdot \left(\frac{\partial}{\partial \mathbf{Q}}\Psi + \frac{\mathbf{F}}{k_{\mathrm{B}}T}\Psi\right). \tag{1}$$

Here $D/Dt = \partial/\partial t + \mathbf{v}\cdot\nabla$ is the material derivative, ∇ is the spatial gradient, $\mathbf{k}(\mathbf{x},t) = (\nabla\mathbf{v})^{\dagger}$ is the gradient of the velocity of the solvent $\mathbf{v}$, $\dagger$ denotes transposition of tensors, $\mathbf{D}$ is the dimensionless diffusion matrix, k_{B} is the Boltzmann constant, T is the temperature, ξ is the dimensional coefficient characterizing a friction exerted by beads moving through solvent media (friction coefficient [1,2]), and $\mathbf{F} = -\nabla\phi$ is the elastic spring force defined by the potential well ϕ. We consider forces of the form $\mathbf{F} = Hf(Q^2)\mathbf{Q}$, where $f(Q^2)$ is a dimensionless function of the variable $Q^2 = \mathbf{Q}\cdot\mathbf{Q}$, and H is the dimensional constant. Incompressibility of solvent implies $\sum_i k_{ii} = 0$.

Let us introduce a time dimensional constant

$$\lambda_{\mathrm{r}} = \frac{\xi}{4H},$$

which coincides with a characteristic relaxation time of dumbbell configuration in the case when the force $\mathbf{F}$ is linear: $f(Q^2) = 1$. It proves convenient to rewrite the FPE (1) in the dimensionless form

$$\frac{D\Psi}{D\hat{t}} = -\frac{\partial}{\partial \hat{\mathbf{Q}}} \cdot \hat{\mathbf{k}} \cdot \hat{\mathbf{Q}}\Psi + \frac{\partial}{\partial \hat{\mathbf{Q}}} \cdot \mathbf{D} \cdot \left(\frac{\partial}{\partial \hat{\mathbf{Q}}}\Psi + \hat{\mathbf{F}}\Psi\right). \tag{2}$$

Various dimensionless quantities used are: $\hat{\mathbf{Q}} = (H/k_{\mathrm{B}}T)^{1/2}\mathbf{Q}$, $D/D\hat{t} = \partial/\partial\hat{t} + \mathbf{v}\cdot\overline{\nabla}$, $\hat{t} = t/\lambda_{\mathrm{r}}$ is the dimensionless time, $\overline{\nabla} = \nabla\lambda_{\mathrm{r}}$ is the reduced space gradient and $\hat{\mathbf{k}} = \mathbf{k}\lambda_{\mathrm{r}} = (\overline{\nabla}\mathbf{v})^{\dagger}$ is the dimensionless tensor of the gradients of the velocity. In the sequel, only dimensionless quantities $\hat{\mathbf{Q}}$ and $\hat{\mathbf{F}}$ are used, and we keep notations $\mathbf{Q}$ and $\mathbf{F}$ for them for the sake of simplicity.

The quantity of interest is the stress tensor introduced by Kramers [1]:

$$\boldsymbol{\tau} = -v_{\mathrm{s}}\dot{\boldsymbol{\gamma}} + nk_{\mathrm{B}}T(\mathbf{1} - \langle\mathbf{FQ}\rangle), \tag{3}$$

where v_s is the viscosity of the solvent, $\dot{\gamma} = \mathbf{k} + \mathbf{k}^{\dagger}$ is the rate-of-strain tensor, n is the concentration of polymer molecules, and the angle brackets stand for the averaging with the distribution function $\Psi : \langle \bullet \rangle \equiv \int \bullet \Psi(\mathbf{Q})\, d\mathbf{Q}$. The tensor

$$\boldsymbol{\tau}_p = nk_B T(\mathbf{1} - \langle \mathbf{FQ} \rangle) \tag{4}$$

gives a contribution to stresses caused by the presence of polymer molecules.

The stress tensor is required in order to write down a closed system of hydrodynamic equations

$$\frac{D\mathbf{v}}{Dt} = -\rho^{-1} \nabla p - \nabla \cdot \boldsymbol{\tau}[\Psi] \,. \tag{5}$$

Here p is the pressure, and $\rho = \rho_s + \rho_p$ is the mass density of the solution where ρ_s is the solvent, and ρ_p is the polymeric contributions.

Several models of the elastic force are known in the literature. The Hookean law is relevant to small perturbations of the equilibrium configuration of the macromolecule:

$$\mathbf{F} = \mathbf{Q} \,. \tag{6}$$

In that case, the differential equation for $\boldsymbol{\tau}$ is easily derived from the kinetic equation, and is the well known *Oldroyd-B* constitutive model [1].

The second model, the FENE force law [8], was derived as an approximation to the inverse Langevin force law [1] for a more realistic description of the elongation of a polymeric molecule in a solvent:

$$\mathbf{F} = \frac{\mathbf{Q}}{1 - \mathbf{Q}^2/\mathbf{Q}_0^2} \,. \tag{7}$$

This force law takes into account the nonlinear stiffness and the finite extendibility of dumbbells, where $\mathbf{Q}_0$ is the maximal extendibility.

The features of the diffusion matrix are important for both the microscopic and the macroscopic behavior. The isotropic diffusion is represented by the simplest diffusion matrix

$$\mathbf{D}_I = \tfrac{1}{2}\mathbf{1} \,. \tag{8}$$

Here $\mathbf{1}$ is the unit matrix. When the hydrodynamic interaction between the beads is taken into account, this results in an anisotropic contribution to the diffusion matrix (8). The original form of this contribution is the Oseen–Burgers tensor $\mathbf{D}_H$ [9,10]:

$$\mathbf{D} = \mathbf{D}_I - \kappa \mathbf{D}_H, \qquad \mathbf{D}_H = \frac{1}{Q}\left(\mathbf{1} + \frac{\mathbf{QQ}}{Q^2}\right) \,, \tag{9}$$

where

$$\kappa = \left(\frac{H}{k_B T}\right)^{1/2} \frac{\xi}{16\pi v_s} \,.$$

Several modifications of the Oseen–Burgers tensor can be found in the literature [11,12] [2] but here we consider only the classical version.

[2] More general than the Oseen–Burgers tensor, the *Rotne-Prager–Yamakawa* tensor was developed in Refs. [11,12].

2.2. Properties of the Fokker–Planck operator

Let us review some of the properties of the Fokker–Planck operator J in the right-hand side of the Eq. (2) relevant to what will follow. This operator can be written as $J = J_d + J_h$, and it represents two processes.

The first term, J_d, is the dissipative part,

$$J_d = \frac{\partial}{\partial \mathbf{Q}} \cdot \mathbf{D} \cdot \left(\frac{\partial}{\partial \mathbf{Q}} + \mathbf{F} \right). \tag{10}$$

This part is responsible for the diffusion and friction which affect internal configurations of dumbbells, and it drives the system to the unique equilibrium state,

$$\Psi_{eq} = c^{-1} \exp(-\phi(Q^2)),$$

where $c = \int \exp(-\phi)\, d\mathbf{Q}$ is the normalization constant.

The second part, J_h, describes the hydrodynamic drag of the beads in the flowing solvent:

$$J_h = -\frac{\partial}{\partial \mathbf{Q}} \cdot \hat{\mathbf{k}} \cdot \mathbf{Q}. \tag{11}$$

The dissipative nature of the operator J_d is reflected by its spectrum. We assume that this spectrum consists of real-valued nonpositive eigenvalues, and that the zero eigenvalue is not degenerated. In the sequel, the following scalar product will be useful:

$$\langle g, h \rangle_s = \int \Psi_{eq}^{-1} g h \, d\mathbf{Q}.$$

The operator J_d is symmetric and nonpositive definite in this scalar product:

$$\begin{aligned} &\langle J_d g, h \rangle_s = \langle g, J_d h \rangle_s, \\ &\langle J_d g, g \rangle_s \leqslant 0. \end{aligned} \tag{12}$$

Since $\langle J_d g, g \rangle_s = -\int \Psi_{eq}^{-1} (\partial g/\partial \mathbf{Q}) \cdot \Psi_{eq} \mathbf{D} \cdot (\partial g/\partial \mathbf{Q})\, d\mathbf{Q}$, the above inequality is valid if the diffusion matrix $\mathbf{D}$ is positive semidefinite. This happens if $\mathbf{D} = \mathbf{D}_I$ (8) but is not generally valid in the presence of the hydrodynamic interaction (9). Let us split the operator J_d in accord with the splitting of the diffusion matrix $\mathbf{D}$: $J_d = J_d^I - \kappa J_d^H$, where $J_d^{I,H} = \partial/\partial \mathbf{Q} \cdot \mathbf{D}_{I,H} \cdot (\partial/\partial \mathbf{Q} + \mathbf{F})$. Both the operators J_d^I and J_d^H have nondegenerated eigenvalue 0 which corresponds to their common eigenfunction Ψ_{eq}: $J_d^{I,H} \Psi_{eq} = 0$, while the rest of the spectrum of both operators belongs to the nonpositive real semi-axis. Then the spectrum of the operator $J_d = J_d^I - \kappa J_d^H$ remains nonpositive for sufficiently small values of the parameter κ. The spectral properties of both operators $J_d^{I,H}$ depend only on the choice of spring force $\mathbf{F}$. Thus, in the sequel, we assume that the hydrodynamic interaction parameter κ is sufficiently small so that the *thermodynamic stability* property (12) holds.

We note that the scalar product $\langle \bullet, \bullet \rangle_s$ coincides with the second differential $D^2 S|_{\Psi_{eq}}$ of an entropy functional $S[\Psi]$: $\langle \bullet, \bullet \rangle_s = -D^2 S|_{\Psi_{eq}}[\bullet, \bullet]$, where the entropy has the

form

$$S[\Psi] = -\int \Psi \ln\left(\frac{\Psi}{\Psi_{\rm eq}}\right) \mathrm{d}\mathbf{Q} = \left\langle \ln\left(\frac{\Psi}{\Psi_{\rm eq}}\right)\right\rangle . \tag{13}$$

The entropy S grows in the course of dissipation

$$DS[J_{\rm d}\Psi] \geqslant 0 .$$

This inequality similar to inequality (12) is satisfied for sufficiently small κ. Symmetry and nonpositiveness of operator $J_{\rm d}$ in the scalar product defined by the second differential of the entropy is a common property of linear dissipative systems.

2.3. Statement of the problem

Given the kinetic equation (1), we aim at deriving differential equations for the stress tensor τ (3). The latter includes the moments $\langle \mathbf{FQ}\rangle = \int \mathbf{FQ}\Psi \,\mathrm{d}\mathbf{Q}$.

In general, when the diffusion matrix is nonisotropic and/or the spring force is nonlinear, closed equations for these moments are not available, and approximations are required. With this, any derivation should be consistent with the three requirements:

(i) *Dissipativity or thermodynamic stability*: The macroscopic dynamics should be dissipative in the absence of the flow.

(ii) *Slowness*: The macroscopic equations should represent slow degrees of freedom of the kinetic equation.

(iii) *Material frame indifference*: The form of equations for the stresses should be invariant with respect to the Euclidian, time dependent transformations of the reference frame [1,13].

While these three requirements should be met by any approximate derivation, the validity of our approach will be restricted by two additional assumptions:

(a) Let us denote θ_1 the inertial time of the flow, which we define via characteristic value of the gradient of the flow velocity: $\theta_1 = |\nabla \mathbf{v}|^{-1}$, and θ_2 the characteristic time of the variation of the flow velocity. We assume that the characteristic relaxation time of the molecular configuration $\theta_{\rm r}$ is small as compared to both the characteristic times θ_1 and θ_2:

$$\theta_{\rm r} \ll \theta_1 \quad \text{and} \quad \theta_{\rm r} \ll \theta_2 . \tag{14}$$

(b) In the absence of the flow, the initial deviation of the distribution function from the equilibrium is small so that the linear approximation is valid.

While assumption (b) is merely of a technical nature, and it is intended to simplify the treatment of the dissipative part of the Fokker–Planck operator (10) for elastic forces of a complicated form, assumption (a) is crucial for taking into account the flow in an adequate way. We have assumed that the two parameters characterizing the composed system 'relaxing polymer configuration + flowing solvent' should be small: These two parameters are

$$\varepsilon_1 = \theta_{\rm r}/\theta_1, \quad \varepsilon_2 = \theta_{\rm r}/\theta_2 . \tag{15}$$

The characteristic relaxation time of the polymeric configuration is defined via the coefficient λ_r: $\theta_r = c\lambda_r$, where c is some positive dimensionless constant which is estimated by the absolute value of the lowest nonzero eigenvalue of the operator J_d. The first parameter ε_1 is usually termed the *Weissenberg number* while the second one ε_2 is the *Deborah number* (cf. Ref. [14], Sections 7–2).

3. The method of invariant manifold for weakly driven systems

3.1. The Newton iteration scheme

In this section we introduce an extension of the method of invariant manifold [7] onto systems coupled with external fields. We consider a class of dynamic systems of the form

$$\frac{d\Psi}{dt} = J_d\Psi + J_{ex}(\alpha)\Psi\,, \tag{16}$$

where J_d is a linear operator representing the dissipative part of the dynamic vector field, while $J_{ex}(\alpha)$ is a linear operator which represents an external flux and depends on a set of external fields $\alpha = \{\alpha_1, \ldots, \alpha_k\}$. Parameters α are either known functions of the time, $\alpha = \alpha(t)$, or they obey a set of equations,

$$\frac{d\alpha}{dt} = \Phi(\Psi, \alpha)\,. \tag{17}$$

Without any restriction, parameters α are adjusted in such a way that $J_{ex}(\alpha = 0) \equiv 0$. Kinetic equation (2) has the form (16), and general results of this section will be applied to the dumbbell models below in a straightforward way.

We assume that the vector field $J_d\Psi$ has the same dissipative properties as the Fokker–Planck operator (10). Namely, there exists the globally convex entropy function S which obeys: $DS[J_d\Psi] \geqslant 0$, and the operator J_d is symmetric and nonpositive in the scalar product $\langle \bullet, \bullet \rangle_s$ defined by the second differential of the entropy: $\langle g, h \rangle_s = -D^2S[g, h]$. Thus, the vector field $J_d\Psi$ drives the system irreversibly to the unique equilibrium state Ψ_{eq}.

We consider a set of n real-valued functionals, $M_i^*[\Psi]$ (macroscopic variables), in the phase space $\mathscr{F}$ of system (16). A macroscopic description is obtained once we have derived a closed set of equations for the variables M_i^*.

Our approach is based on constructing a relevant invariant manifold in phase space $\mathscr{F}$. This manifold is thought as a finite-parametric set of solutions $\Psi(M)$ to Eq. (16) which depends on time implicitly via the n variables $M_i[\Psi]$. The latter may differ from the macroscopic variables M_i^*. For systems with external fluxes (16), we assume that the invariant manifold depends also on the parameters α, and on their time derivatives taken to arbitrary order: $\Psi(M, \mathscr{A})$, where $\mathscr{A} = \{\alpha, \alpha^{(1)}, \ldots\}$ is the set of time derivatives $\alpha^{(k)} = d\alpha^k/dt^k$. It is convenient to consider time derivatives of α as independent parameters. This assumption is important because then we do not need an explicit form of Eq. (17) in the course of construction of the invariant manifold.

By a definition, the dynamic invariance postulates the equality of the "macroscopic" and the "microscopic" time derivatives:

$$J\Psi(M,\mathscr{A}) = \sum_{i=1}^{n} \frac{\partial \Psi(M,\mathscr{A})}{\partial M_i} \frac{\mathrm{d}M_i}{\mathrm{d}t} + \sum_{n=0}^{\infty} \sum_{j=1}^{k} \frac{\partial \Psi(M,\mathscr{A})}{\partial \alpha_j^{(n)}} \alpha_j^{(n+1)} , \tag{18}$$

where $J = J_\mathrm{d} + J_\mathrm{ex}(\alpha)$. The time derivatives of the macroscopic variables, $\mathrm{d}M_i/\mathrm{d}t$, are calculated as follows:

$$\frac{\mathrm{d}M_i}{\mathrm{d}t} = DM_i[J\Psi(M,\mathscr{A})] , \tag{19}$$

where DM_i stands for differentials of the functionals M_i.

Let us introduce the projector operator associated with the parameterization of the manifold $\Psi(M,\mathscr{A})$ by the values of the functionals $M_i[\Psi]$:

$$P_M = \sum_{i=1}^{n} \frac{\partial \Psi(M,\mathscr{A})}{\partial M_i} DM_i[\,\bullet\,] . \tag{20}$$

It projects vector fields from the phase space $\mathscr{F}$ onto tangent bundle $T\Psi(M,\mathscr{A})$ of the manifold $\Psi(M,\mathscr{A})$. Then Eq. (18) is rewritten as the *invariance equation*:

$$(1 - P_M)J\Psi(M,\mathscr{A}) = \sum_{n=0}^{\infty} \sum_{j=1}^{k} \frac{\partial \Psi}{\partial \alpha_j^{(n)}} \alpha^{(i+1)} , \tag{21}$$

which has the invariant manifolds as its solutions.

Furthermore, we assume the following: (i) The external flux $J_\mathrm{ex}(\alpha)\Psi$ is small in comparison to the dissipative part $J_\mathrm{d}\Psi$, i.e. with respect to some norm we require: $|J_\mathrm{ex}(\alpha)\Psi| \ll |J_\mathrm{d}\Psi|$. This allows us to introduce a small parameter ε_1, and to replace the operator J_ex with $\varepsilon_1 J_\mathrm{ex}$ in the Eq. (16). Parameter ε_1 is proportional to the characteristic value of the external variables α. (ii) The characteristic time θ_α of the variation of the external fields α is large in comparison to the characteristic relaxation time θ_r, and the second small parameter is $\varepsilon_2 = \theta_\mathrm{r}/\theta_\alpha \ll 1$. The parameter ε_2 does not enter the vector field J explicitly but it shows up in the invariance equation. Indeed, with a substitution, $\alpha^{(i)} \to \varepsilon_2^i \alpha^{(i)}$, the invariance equation (18) is rewritten in a form which incorporates both the parameters ε_1 and ε_2:

$$(1 - P_M)\{J_\mathrm{d} + \varepsilon_1 J_\mathrm{ex}\}\Psi = \varepsilon_2 \sum_{i} \sum_{j=1}^{k} \frac{\partial \Psi}{\partial \alpha_j^{(i)}} \alpha_j^{(i+1)} . \tag{22}$$

We develop a modified Newton scheme for solution of this equation. Let us assume that we have some initial approximation to desired manifold $\Psi_{(0)}$. We seek the correction of the form $\Psi_{(1)} = \Psi_{(0)} + \Psi_1$. Substituting this expression into Eq. (22), we derive

$$\begin{aligned} &(1 - P_M^{(0)})\{J_\mathrm{d} + \varepsilon_1 J_\mathrm{ex}\}\Psi_1 - \varepsilon_2 \sum_{i} \sum_{j=1}^{k} \frac{\partial \Psi_1}{\partial \alpha_j^{(i)}} \alpha_j^{(i+1)} \\ &\quad = -(1 - P_M^{(0)})J\Psi_{(0)} + \varepsilon_2 \sum_{i} \sum_{j=1}^{k} \frac{\partial \Psi_{(0)}}{\partial \alpha_j^{(i)}} \alpha_j^{(i+1)} . \end{aligned} \tag{23}$$

Here $P_M^{(0)}$ is a projector onto tangent bundle of the manifold $\Psi_{(0)}$. Further, we neglect two terms on the left-hand side of this equation, which are multiplied by parameters ε_1 and ε_2, regarding them small in comparison to the first term. In the result we arrive at the equation

$$(1 - P_M^{(0)})J_{\mathrm{d}}\Psi_1 = -(1 - P_M^{(0)})J\Psi_{(0)} + \varepsilon_2 \sum_i \sum_{j=1}^{k} \frac{\partial \Psi_{(0)}}{\partial \alpha_j^{(i)}} \alpha_j^{(i+1)} . \tag{24}$$

For $(n+1)$th iteration we obtain

$$(1 - P_M^{(n)})J_{\mathrm{d}}\Psi_{n+1} = -(1 - P_M^{(0)})J\Psi_{(n)} + \varepsilon_2 \sum_i \sum_{j=1}^{k} \frac{\partial \Psi_{(n)}}{\partial \alpha_j^{(i)}} \alpha_j^{(i+1)} , \tag{25}$$

where $\Psi_{(n)} = \sum_{i=0}^{n} \Psi_i$ is the approximation of nth order and $P_M^{(n)}$ is the projector onto its tangent bundle.

It should be noted that deriving equations (24) and (25) we have not varied the projector P_M with respect to yet unknown term Ψ_{n+1}, i.e., we have kept $P_M = P_M^{(n)}$ and have neglected the contribution from the term Ψ_{n+1}. The motivation for this action comes from the original paper [7], where it was shown that such modification generates iteration schemes properly converging to slow invariant manifold.

In order to gain the solvability of Eq. (25) an additional condition is required:

$$P_M^{(n)}\Psi_{n+1} = 0 . \tag{26}$$

This condition is sufficient to provide the existence of the solution to linear system (25), while the additional restriction onto the choice of the projector is required in order to guarantee the uniqueness of the solution. This condition is

$$\ker[(1 - P_M^{(n)})J_{\mathrm{d}}] \cap \ker P_M^{(n)} = \mathbf{0} . \tag{27}$$

Here ker denotes a null space of the corresponding operator. How this condition can be met is discussed in the next subsection.

It is natural to begin the iteration procedure (25) starting from the invariant manifold of the nondriven system. In other words, we choose the initial approximation $\Psi_{(0)}$ as the solution of the invariance equation (22) corresponding to $\varepsilon_1 = 0$ and $\varepsilon_2 = 0$:

$$(1 - P_M^{(0)})J_{\mathrm{d}}\Psi_{(0)} = 0 . \tag{28}$$

We shall return to the question how to construct solutions to this equation in Section 3.3.

The above recurrent equations (25), (26) are simplified Newton method for the solution of invariance equation (22), which involves the small parameters. A similar procedure for Grad equations of the Boltzmann kinetic theory was used recently in Ref. [15]. When these parameters are not small, one should proceed directly with Eq. (23).

Above, we have focused our attention on how to organize the iterations to construct invariant manifolds of weakly driven systems. The only question we have not yet answered is how to choose projectors in iterative equations in a consistent way. In the next subsection we discuss the problem of derivation of the reduced dynamics and its relation to the problem of the choice of projector.

3.2. Projector and reduced dynamics

Below we suggest the projector which is equally applicable for constructing invariant manifolds by the iteration method (25), (26) and for generating macroscopic equations based on given manifold.

Let us discuss the problem of constructing closed equations for macroparameters. Having some approximation to the invariant manifold, we nevertheless deal with a noninvariant manifold and we face the problem how to construct the dynamics on it. If the n-dimensional manifold $\tilde{\Psi}$ is found the macroscopic dynamics is induced by any projector P onto the tangent bundle of $\tilde{\Psi}$ as follows [7]:

$$\frac{\mathrm{d}M_i^*}{\mathrm{d}t} = DM_i^*|_{\tilde{\Psi}}[PJ\tilde{\Psi}]\,. \tag{29}$$

To specify the projector we involve the two above-mentioned principles: dissipativity and slowness. The dissipativity is required to have the unique and stable equilibrium solution for macroscopic equations, when the external fields are absent ($\alpha = 0$). The slowness condition requires the *induced* vector field $PJ\Psi$ to match the slow modes of the original vector field $J\Psi$.

Let us consider the parameterization of the manifold $\tilde{\Psi}(M)$ by the parameters $M_i[\Psi]$. This parameterization generates associated projector $P = P_M$ by Eq. (20). This leads us to look for the admissible parameterization of this manifold, where by admissibility we understand the concordance with the dissipativity and the slowness requirements. We solve the problem of the admissible parameterization in the following way. Let us define the functionals M_i, $i = 1,\ldots,n$ by the set of the lowest eigenvectors φ_i of the operator J_d:

$$M_i[\tilde{\Psi}] = \langle \varphi_i, \tilde{\Psi}\rangle_\mathrm{s}\,,$$

where $J_\mathrm{d}\varphi_i = \lambda_i\varphi_i$. The lowest eigenvectors $\varphi_1,\ldots,\varphi_n$ are taken as a join of basises in the eigenspaces of the eigenvalues with smallest absolute values: $0 < |\lambda_1| \leqslant |\lambda_2| \leqslant \cdots \leqslant |\lambda_n|$. For simplicity, we shall work with the orthonormal set of eigenvectors: $\langle \varphi_i, \varphi_j\rangle_\mathrm{s} = \delta_{ij}$ with δ_{ij} the Kronecker symbol. Since the function Ψ_eq is the eigenvector of the zero eigenvalue we have: $M_i[\Psi_\mathrm{eq}] = \langle \varphi_i, \Psi_\mathrm{eq}\rangle_\mathrm{s} = 0$.

Then the associated projector P_M, written as

$$P_M = \sum_{i=1}^{n} \frac{\partial\tilde{\Psi}}{\partial M_i}\langle \varphi_i, \bullet\rangle_\mathrm{s}\,, \tag{30}$$

will generate the equations in terms of the parameters M_i as follows: $\mathrm{d}M_i/\mathrm{d}t = \langle \varphi_i P_M J\tilde{\Psi}\rangle_\mathrm{s} = \langle \varphi_i J\tilde{\Psi}\rangle_\mathrm{s}$. Their explicit form is

$$\frac{\mathrm{d}M_i}{\mathrm{d}t} = \lambda_i M_i + \langle J_\mathrm{ex}^+(\alpha)g_i, \tilde{\Psi}(M)\rangle_\mathrm{s}\,, \tag{31}$$

where the J_ex^+ is the adjoint to operator J_ex with respect to the scalar product $\langle \bullet, \bullet\rangle_\mathrm{s}$.

Apparently, in the absence of forcing ($\alpha \equiv 0$) the macroscopic equations $\mathrm{d}M_i/\mathrm{d}t = \lambda_i M_i$ are thermodynamically stable. They represent the dynamics of slowest eigenmodes

of equations $d\Psi/dt = J_d\Psi$. Thus, projector (30) complies with the above stated requirements of dissipativity and slowness in the absence external flux.

To rewrite the macroscopic equations (31) in terms of the required set of macroparameters, $M_i^*[\Psi] = \langle m_i^*, \Psi\rangle_s$, we use formula (29) which is equivalent to the change of variables $\{M\} \to \{M^*(M)\}$, $M_i^* = \langle m_i^*, \tilde{\Psi}(M)\rangle_s$ in Eq. (31). Indeed, this is seen from the relation

$$DM_i^*|_{\tilde{\Psi}}[P_M J\tilde{\Psi}] = \sum_j \frac{\partial M_i^*}{\partial M_j} DM_j|_{\tilde{\Psi}}[J\tilde{\Psi}] .$$

We have constructed the dynamics with the help of the projector P_M associated with the lowest eigenvectors of the operator J_d. It is directly verified that such projector (30) fulfills condition (26) for arbitrary manifold $\Psi_{(n)} = \tilde{\Psi}$. For this reason it is natural to use projector (30) for both procedures, constructing the invariant manifold, and deriving the macroscopic equations.

We have to note that the above-described approach to defining the dynamics via the projector is different from the concept of "thermodynamic parameterization" proposed in the Refs. [7,16]. The latter was applicable for arbitrary dissipative systems including nonlinear ones, whereas the present derivations are applied solely for linear systems.

3.3. Linear zero-order equations

In this section we focus our attention on the solution of the zero-order invariance equation (28). We seek the *linear* invariant manifold of the form

$$\Psi_{(0)}(a) = \Psi_{eq} + \sum_{i=1}^{n} a_i m_i , \tag{32}$$

where a_i are coordinates on this manifold. This manifold can be considered as an expansion of the relevant slow manifold near the equilibrium state. This limits the domain of validity of manifolds (32) because they are not generally positively definite. This remark indicates that nonlinear invariant manifolds should be considered for large deviations from the equilibrium but this goes beyond the scope of this paper.

The linear n-dimensional manifold representing the slow motion for the linear dissipative system (16) is associated with n slowest eigenmodes. This manifold should be built up as the linear hull of the eigenvectors φ_i of the operator J_d, corresponding to the lower part of its spectrum. Thus we choose $m_i = \varphi_i$.

Dynamic equations for the macroscopic variables M^* are derived in two steps. First, following Section 3.2, we parameterize the linear manifold $\Psi_{(0)}$ with the values of the moments $M_i[\Psi] = \langle \varphi_i, \Psi\rangle_s$. We obtain that the parameterization of manifold (32) is given by $a_i = M_i$, or

$$\Psi_{(0)}(M) = \Psi_{eq} + \sum_{i=1}^{n} M_i \varphi_i .$$

Then the reduced dynamics in terms of variables M_i reads

$$\frac{\mathrm{d}M_i}{\mathrm{d}t} = \lambda_i M_i + \sum_j \langle J_{\mathrm{ex}}^{+}\varphi_i, \varphi_j\rangle_{\mathrm{s}} M_j + \langle J_{\mathrm{ex}}^{+}\varphi_i, \Psi_{\mathrm{eq}}\rangle_{\mathrm{s}} , \tag{33}$$

where $\lambda_i = \langle \varphi_i, J_{\mathrm{d}}\varphi_i\rangle_{\mathrm{s}}$ are eigenvalues which correspond to eigenfunctions φ_i.

Second, we switch from the variables M_i to the variables $M_i^*(M) = \langle m_i^*, \Psi_{(0)}(M)\rangle_{\mathrm{s}}$ in Eq. (33). Resulting equations for the variables M^* are also linear:

$$\begin{aligned}\frac{\mathrm{d}M_i^*}{\mathrm{d}t} &= \sum_{jkl} (B^{-1})_{ij}\Lambda_{jk}B_{kl}\Delta M_l^* + \sum_{jk} (B^{-1})_{ij}\langle J_{\mathrm{ex}}^{+}\varphi_j, \varphi_k\rangle_{\mathrm{s}}\Delta M_k^* \\ &\quad + \sum_j (B^{-1})_{ij}\langle J_{\mathrm{ex}}^{+}\varphi_j, \Psi_{\mathrm{eq}}\rangle_{\mathrm{s}} .\end{aligned} \tag{34}$$

Here $\Delta M_i^* = M_i^* - M_{\mathrm{eq}|i}^*$ is the deviation of the variable M_i^* from its equilibrium value $M_{\mathrm{eq}|i}^*$, and $B_{ij} = \langle m_i^*, \varphi_j\rangle$ and $\Lambda_{ij} = \lambda_i\delta_{ij}$.

4. Constitutive equations

4.1. Iteration scheme

In this section we apply the above developed formalism to the elastic dumbbell model (2). External field variables α are the components of the tensor $\hat{\mathbf{k}}$.

Since we aim at constructing a closed description for the stress tensor $\boldsymbol{\tau}$ (3) with the six independent components, the relevant manifold in our problem should be six dimensional. Moreover, we allow a dependence of the manifold on the material derivatives of the tensor $\hat{\mathbf{k}}$: $\hat{\mathbf{k}}^{(i)} = D^i\mathbf{k}/Dt^i$. Let $\Psi^*(M,\mathscr{K})\mathscr{K} = \{\hat{\mathbf{k}},\hat{\mathbf{k}}^{(1)},\ldots\}$ be the desired manifold parameterized by the six variables M_i $i = 1,\ldots,6$ and the independent components (maximum eight for each $\hat{\mathbf{k}}^{(l)}$) of the tensors $\hat{\mathbf{k}}^{(l)}$. Small parameters ε_1 and ε_2, introduced in Section 3, are established by Eq. (15). Then we define the invariance equation

$$(1 - P_M)(J_{\mathrm{d}} + \varepsilon_1 J_{\mathrm{h}})\Psi = \varepsilon_2 \sum_{i=0}^{\infty}\sum_{lm} \frac{\partial\Psi}{\partial\hat{k}_{lm}^{(i)}}\hat{k}_{lm}^{(i+1)} , \tag{35}$$

where $P_M = \partial\Psi/\partial M_i DM_i[\,\bullet\,]$ is the projector associated with chosen parameterization and summation indexes l,m run only eight independent components of tensor $\hat{\mathbf{k}}$.

Following the further procedure we straightforwardly obtain the recurrent equations:

$$\begin{aligned}(1 - P_M^{(n)})J_{\mathrm{d}}\Psi_{n+1} &= -(1 - P_M^{(n)})[J_{\mathrm{d}} + \varepsilon_1 J_{\mathrm{h}}]\Psi_{(n)} \\ &\quad + \varepsilon_2 \sum_i \sum_{lm} \frac{\partial\Psi_{(n)}}{\partial\hat{k}_{lm}^{(i)}}\hat{k}_{lm}^{(i+1)} ,\end{aligned} \tag{36}$$

$$P_M^{(n)}\Psi_{n+1} = 0 , \tag{37}$$

where Ψ_{n+1} is the correction to the manifold $\Psi_{(n)} = \sum_{i=0}^{n}\Psi_i$.

The zero-order manifold is found as the relevant solution to equation:

$$(1 - P_M^{(0)}) J_\mathrm{d} \Psi_{(0)} = 0 \,. \tag{38}$$

We construct zero-order manifold $\Psi_{(0)}$ in Section 4.3.

4.2. The dynamics in general form

Let us assume that some approximation to invariant manifold $\tilde{\Psi}(a, \mathscr{K})$ is found (here $a = \{a_1, \ldots, a_6\}$ are some coordinates on this manifold). The next step is constructing the macroscopic dynamic equations.

In order to comply with dissipativity and slowness by means of the recipe from the previous section we need to find six lowest eigenvectors of the operator J_d. We shall always assume in a sequel that the hydrodynamic interaction parameter κ is small enough that the dissipativity of J_d (12) is not violated.

Let us consider two classes of functions: $\mathscr{C}_1 = \{w_0(Q^2)\}$ and $\mathscr{C}_2 = \{w_1(Q^2)\mathring{\mathbf{Q}}\mathbf{Q}\}$, where $w_{0,1}$ are functions of Q^2 and the notation $\circ$ indicates traceless parts of tensor or matrix, e.g. for the dyad $\mathbf{QQ}$: $(\mathring{\mathbf{QQ}})_{ij} = Q_i Q_j - \frac{1}{3}\delta_{ij} Q^2$. Since the sets $\mathscr{C}_1$ and $\mathscr{C}_2$ are invariant with respect to operator J_d, i.e., $J_\mathrm{d}\mathscr{C}_1 \subset \mathscr{C}_1$ and $J_\mathrm{d}\mathscr{C}_2 \subset \mathscr{C}_2$, and densities $\mathbf{FQ} = f\mathring{\mathbf{Q}}\mathbf{Q} + (\frac{1}{3})\mathbf{1}fQ^2$ of the moments comprising the stress tensor $\boldsymbol{\tau}_p$ (4) belong to the space $\mathscr{C}_1 + \mathscr{C}_2$, we shall seek the desired eigenvectors in the classes $\mathscr{C}_1$ and $\mathscr{C}_2$. Namely, we intend to find one lowest isotropic eigenvector $\Psi_\mathrm{eq} m_0(Q^2)$ of eigenvalue $-\lambda_0$ ($\lambda_0 > 0$) and five nonisotropic eigenvectors $m_{ij} = \Psi_\mathrm{eq} m_1(Q^2)(\mathring{\mathbf{Q}}\mathbf{Q})_{ij}$ of another eigenvalue $-\lambda_1$ ($\lambda_1 > 0$). The method of derivation and analytic evaluation of these eigenvalues are discussed in Appendix A. For a while we assume that these eigenvectors are known.

In the next step we parameterize given manifold $\tilde{\Psi}$ by the values of the functionals:

$$\begin{aligned} M_0 &= \langle \Psi_\mathrm{eq} m_0, \tilde{\Psi} \rangle_\mathrm{s} = \int m_0 \tilde{\Psi} \, \mathrm{d}\mathbf{Q} \,, \\ \mathring{\mathbf{M}} &= \langle \Psi_\mathrm{eq} m_1 \mathring{\mathbf{Q}}\mathbf{Q}, \tilde{\Psi} \rangle_\mathrm{s} = \int m_1 \mathring{\mathbf{Q}}\mathbf{Q} \tilde{\Psi} \, \mathrm{d}\mathbf{Q} \,. \end{aligned} \tag{39}$$

Once a desired parameterization $\tilde{\Psi}(M_0, \mathring{\mathbf{M}}, \mathscr{K})$ is obtained, the dynamic equations are found as

$$\begin{aligned} &\frac{DM_0}{D\hat{t}} + \lambda_0 M_0 = \langle (\hat{\dot{\gamma}} : \mathring{\mathbf{Q}}\mathbf{Q}) m_0' \rangle \,, \\ &\mathring{\mathbf{M}}_{[1]} + \lambda_1 \mathring{\mathbf{M}} = -\tfrac{1}{3}\mathbf{1}\hat{\dot{\gamma}} : \mathring{\mathbf{M}} - \frac{1}{3}\hat{\dot{\gamma}} \langle m_1 Q^2 \rangle + \langle \mathring{\mathbf{Q}}\mathbf{Q} \, (\hat{\dot{\gamma}} : \mathring{\mathbf{Q}}\mathbf{Q}) m_1' \rangle \,, \end{aligned} \tag{40}$$

where all averages are calculated with the d.f. $\tilde{\Psi}$, i.e., $\langle \bullet \rangle = \int \bullet \tilde{\Psi} \, \mathrm{d}\mathbf{Q}$, $m_{0,1}' = \partial m_{0,1}(Q^2)/\partial(Q^2)$ and subscript [1] represents the upper convective derivative of tensor:

$$\Lambda_{[1]} = \frac{D\Lambda}{D\hat{t}} - \{\hat{\mathbf{k}} \cdot \Lambda + \Lambda \cdot \hat{\mathbf{k}}^\dagger\} \,.$$

The parameters $\lambda_{0,1}$, which are absolute values of eigenvalues of operator J_d, are calculated by formulas (for definition of operators G_1 and G_2 see Appendix A):

$$\lambda_0 = -\frac{\langle m_0 G_0 m_0 \rangle_e}{\langle m_0 m_0 \rangle_e} > 0\,, \tag{41}$$

$$\lambda_1 = -\frac{\langle Q^4 m_1 G_1 m_1 \rangle_e}{\langle m_1 m_1 Q^4 \rangle_e} > 0\,, \tag{42}$$

where we have introduced the notation of the equilibrium average:

$$\langle y \rangle_e = \int \Psi_{eq}\, y \, d\mathbf{Q}\,. \tag{43}$$

Equations on components of the polymeric stress tensor $\boldsymbol{\tau}_p$ (4) are constructed as a change of variables $\{M_0, \mathring{\mathbf{M}}\} \to \boldsymbol{\tau}_p$. The use of the projector $\tilde{P}$ makes this operation straightforward:

$$\frac{D\boldsymbol{\tau}_p}{D\hat{t}} = -nk_B T \int \mathbf{FQ}\tilde{P}J\tilde{\Psi}(M_0(\boldsymbol{\tau}_p, \mathscr{K}), \mathring{\mathbf{M}}(\boldsymbol{\tau}_p, \mathscr{K}), \mathscr{K})\, d\mathbf{Q}\,. \tag{44}$$

Here, the projector $\tilde{P}$ is associated with the parameterization by the variables M_0 and $\mathring{\mathbf{M}}$:

$$\tilde{P} = \frac{\partial \tilde{\Psi}}{\partial M_0}\langle \Psi_{eq} m_0, \bullet \rangle_s + \sum_{kl} \frac{\partial \tilde{\Psi}}{\partial \mathring{\mathbf{M}}_{kl}} \langle \Psi_{eq} m_1 (\mathbf{Q}\mathring{\mathbf{Q}})_{kl}, \bullet \rangle_s\,. \tag{45}$$

We note that sometimes it is easier to make transition to the variables $\boldsymbol{\tau}_p$ after solving Eq. (40) rather than to construct explicitly and solve equations in terms of $\boldsymbol{\tau}_p$. It allows to avoid reverting the functions $\boldsymbol{\tau}_p(M_0, \mathring{\mathbf{M}})$ and to deal with generally more simple equations.

4.3. Zero-order constitutive equation

In this subsection we derive the closure based on the zero-order manifold $\Psi_{(0)}$ found as appropriate solution to Eq. (38). Following the approach described in Section 3.3 we construct such a solution as the linear expansion near the equilibrium state Ψ_{eq} (32). After parameterization by the values of the variables M_0 and $\mathring{\mathbf{M}}$ associated with the eigenvectors $\Psi_{eq} m_0$ and $\Psi_{eq} m_1 \mathbf{Q}\mathring{\mathbf{Q}}$ we find

$$\Psi_{(0)} = \Psi_{eq}\left(1 + M_0 \frac{m_0}{\langle m_0 m_0 \rangle_e} + \frac{15}{2}\mathring{\mathbf{M}} : \mathbf{Q}\mathring{\mathbf{Q}} \frac{m_1}{\langle m_1 m_1 Q^4 \rangle_e}\right)\,. \tag{46}$$

Then with the help of projector (45):

$$P_M^{(0)} = \Psi_{eq}\left\{\frac{m_0}{\langle m_0 m_0 \rangle_e}\langle m_0, \bullet \rangle_e + \frac{15}{2}\frac{m_1}{\langle m_1 m_1 Q^4 \rangle_e}\mathbf{Q}\mathring{\mathbf{Q}} : \langle m_1 \mathbf{Q}\mathring{\mathbf{Q}}, \bullet \rangle\right\} \tag{47}$$

by formula (44) we obtain

$$\frac{D\,\mathrm{tr}\,\boldsymbol{\tau}_p}{D\hat{t}} + \lambda_0 \mathrm{tr}\,\boldsymbol{\tau}_p = a_0(\mathring{\boldsymbol{\tau}}_p : \hat{\dot{\boldsymbol{\gamma}}})\,,$$

$$\mathring{\boldsymbol{\tau}}_{p[1]} + \lambda_0 \mathring{\boldsymbol{\tau}}_{\mathrm{p}} = b_0[\mathring{\boldsymbol{\tau}}_{\mathrm{p}} \cdot \hat{\dot{\boldsymbol{\gamma}}} + \hat{\dot{\boldsymbol{\gamma}}} \cdot \mathring{\boldsymbol{\tau}}_{\mathrm{p}}] - \tfrac{1}{3}\mathbf{1}(\mathring{\boldsymbol{\tau}}_{\mathrm{p}} : \hat{\dot{\boldsymbol{\gamma}}}) + (b_1 \mathrm{tr}\,\boldsymbol{\tau}_{\mathrm{p}} - b_2 n k_{\mathrm{B}} T)\hat{\dot{\boldsymbol{\gamma}}}\,, \tag{48}$$

where the constants b_i, a_0 are

$$\begin{aligned}
a_0 &= \frac{\langle f m_0 Q^2\rangle_{\mathrm{e}} \langle m_0 m_1 Q^4 m_1'\rangle_{\mathrm{e}}}{\langle f m_0 Q^4\rangle_{\mathrm{e}} \langle m_0^2\rangle_{\mathrm{e}}}\,,\\
b_0 &= \frac{2}{7}\frac{\langle m_1 m_2' Q^6\rangle_{\mathrm{e}}}{\langle m_1^2 Q^4\rangle_{\mathrm{e}}}\,,\\
b_1 &= \frac{1}{15}\frac{\langle f m_1 Q^4\rangle_{\mathrm{e}}}{\langle f m_0 Q^2\rangle_{\mathrm{e}}}\left\{2\frac{\langle m_0 m_2' Q^4\rangle_{\mathrm{e}}}{\langle m_1^2 Q^4\rangle_{\mathrm{e}}} + 5\frac{\langle m_0 m_1 Q^2\rangle_{\mathrm{e}}}{\langle m_1 m_1 Q^4\rangle_{\mathrm{e}}}\right\}\,,\\
b_2 &= \frac{1}{15}\frac{\langle f m_1 Q^4\rangle_{\mathrm{e}}}{\langle m_1 m_1 Q^4\rangle_{\mathrm{e}}}\{2\langle m_2' Q^4\rangle_{\mathrm{e}} + 5\langle m_1 Q^2\rangle_{\mathrm{e}}\}\,.
\end{aligned} \tag{49}$$

We remind that $m_{0,1}' = \partial m_{0,1}/\partial(Q^2)$. These formulas were obtained by the use of the formulas from Appendix B.

It is remarkable that being rewritten in terms of the full stresses $\boldsymbol{\tau} = -v_{\mathrm{s}}\dot{\boldsymbol{\gamma}} + \boldsymbol{\tau}_{\mathrm{p}}$ the dynamic system (48) takes a form:

$$\begin{aligned}
&\boldsymbol{\tau} + c_1\boldsymbol{\tau}_{[1]} + c_3\{\dot{\boldsymbol{\gamma}}\cdot\boldsymbol{\tau} + \boldsymbol{\tau}\cdot\dot{\boldsymbol{\gamma}}\} + c_5(\mathrm{tr}\,\boldsymbol{\tau})\dot{\boldsymbol{\gamma}} + \mathbf{1}(c_6\boldsymbol{\tau} : \dot{\boldsymbol{\gamma}} + c_8\mathrm{tr}\,\boldsymbol{\tau})\\
&\quad = -v\{\dot{\boldsymbol{\gamma}} + c_2\dot{\boldsymbol{\gamma}}_{[1]} + c_4\dot{\boldsymbol{\gamma}}\cdot\dot{\boldsymbol{\gamma}} + c_7(\dot{\boldsymbol{\gamma}} : \dot{\boldsymbol{\gamma}})\mathbf{1}\}\,,
\end{aligned} \tag{50}$$

where the constants v, c_i are given by the following relationships:

$$\begin{aligned}
&v = \lambda_{\mathrm{r}} v_{\mathrm{s}}\mu, \qquad \mu = 1 + n k_{\mathrm{B}} T\lambda_1 b_2/v_{\mathrm{s}}\,,\\
&c_1 = \lambda_{\mathrm{r}}/\lambda_1, \qquad c_2 = \lambda_{\mathrm{r}}/(\mu\lambda_1)\,,\\
&c_3 = -b_0\lambda_{\mathrm{r}}/\lambda_0, \qquad c_4 = -2b_0\lambda_{\mathrm{r}}/(\mu\lambda_1)\,,\\
&c_5 = \frac{\lambda_{\mathrm{r}}}{3\lambda_1}(2b_0 - 3b_1 - 1), \qquad c_6 = \frac{\lambda_{\mathrm{r}}}{\lambda_1}(2b_0 + 1 - a_0)\,,\\
&c_7 = \frac{\lambda_{\mathrm{r}}}{\lambda_1\mu}(2b_0 + 1 - a_0), \qquad c_8 = \tfrac{1}{3}(\lambda_0/\lambda_1 - 1)\,.
\end{aligned} \tag{51}$$

In the last two formulas we returned to the original dimensional quantities: time t and gradient of velocity tensor $\mathbf{k} = \nabla\mathbf{v}$, and at the same time we kept the old notations for the dimensional convective derivative $\Lambda_{[1]} = D\Lambda/Dt - \mathbf{k}\cdot\Lambda - \Lambda\cdot\mathbf{k}^{\dagger}$.

If the constant c_8 were equal to zero, then the form of Eq. (50) would be recognized as *the Oldroyd 8 constant* model [17], proposed by Oldroyd about 40 years ago on a phenomenological basis. Nonzero c_8 indicates a presence of difference between $\lambda_{\mathrm{r}}/\lambda_0$ and $\lambda_{\mathrm{r}}/\lambda_1$ which are relaxation times of trace $\mathrm{tr}\,\boldsymbol{\tau}$ and traceless components $\mathring{\boldsymbol{\tau}}$ of the stress tensor $\boldsymbol{\tau}$.

4.4. Corrections

In this subsection we discuss the properties of corrections to the zero-order model (50). Let $P_M^{(0)}$ (46) be the projector onto the zero-order manifold $\Psi_{(0)}$ (46). The

invariance equation (36) for the first-order correction $\Psi_{(1)} = \Psi_{(0)} + \Psi_1$ takes a form

$$L\Psi_1 = -(1 - P_M^{(0)})(J_d + J_h)\Psi_{(0)}\,,$$
$$P_M^{(0)}\Psi_1 = 0\,, \tag{52}$$

where $L = (1 - P_M^{(0)})J_d(1 - P_M^{(0)})$ is the symmetric operator. If the manifold $\Psi_{(0)}$ is parameterized by the functionals $M_0 = \int g_0\Psi_{(0)}\,d\mathbf{Q}$ and $\mathring{\mathbf{M}} = \int m_1\mathbf{Q}\mathring{\mathbf{Q}}\Psi_{(0)}\,d\mathbf{Q}$, where $\Psi_{eq}m_0$ and $\Psi_{eq}\mathbf{Q}\mathring{\mathbf{Q}}m_1$ are lowest eigenvectors of J_d, then the general form of the solution is given by

$$\Psi_1 = \Psi_{eq}\{z_0M_0(\dot{\boldsymbol{\gamma}} : \mathbf{Q}\mathring{\mathbf{Q}}) + z_1(\mathring{\mathbf{M}} : \mathbf{Q}\mathring{\mathbf{Q}})(\dot{\boldsymbol{\gamma}} : \mathbf{Q}\mathring{\mathbf{Q}})$$
$$+ z_2\{\dot{\boldsymbol{\gamma}}\cdot\mathring{\mathbf{M}} + \mathring{\mathbf{M}}\cdot\dot{\boldsymbol{\gamma}}\} : \mathbf{Q}\mathring{\mathbf{Q}} + z_3\dot{\boldsymbol{\gamma}} : \mathring{\mathbf{M}} + \tfrac{1}{2}\dot{\boldsymbol{\gamma}} : \mathbf{Q}\mathring{\mathbf{Q}}\}\,. \tag{53}$$

The terms z_0 through z_3 are the functions of Q^2 found as the solutions to some linear differential equations.

We observe two features of the new manifold: first, it remains *linear* in variables M_0 and $\mathring{\mathbf{M}}$ and second it contains the dependence on the rate of strain tensor $\dot{\boldsymbol{\gamma}}$. As the consequence, the transition to variables $\boldsymbol{\tau}$ is given by the linear relations:

$$-\frac{\mathring{\boldsymbol{\tau}}_p}{nk_BT} = r_0\mathring{\mathbf{M}} + r_1M_0\dot{\boldsymbol{\gamma}} + r_2\{\dot{\boldsymbol{\gamma}}\cdot\mathring{\mathbf{M}} + \mathring{\mathbf{M}}\cdot\dot{\boldsymbol{\gamma}}\} + r_3\,\dot{\boldsymbol{\gamma}}\,\mathring{\cdot}\,\dot{\boldsymbol{\gamma}}\,,$$
$$-\frac{\operatorname{tr}\boldsymbol{\tau}_p}{nk_BT} = p_0M_0 + p_1\dot{\boldsymbol{\gamma}} : \mathring{\mathbf{M}}\,, \tag{54}$$

where r_i and p_i are some constants. Finally, the equations in terms of $\boldsymbol{\tau}$ should be also linear. Analysis shows that the first-order correction to the modified Oldroyd 8 constants model (50) will be transformed into the equations of the following general structure:

$$\boldsymbol{\tau} + c_1\boldsymbol{\tau}_{[1]} + \{\boldsymbol{\Gamma}_1\cdot\boldsymbol{\tau}\cdot\boldsymbol{\Gamma}_2 + \boldsymbol{\Gamma}_2^{\dagger}\cdot\boldsymbol{\tau}\cdot\boldsymbol{\Gamma}_1^{\dagger}\} + \boldsymbol{\Gamma}_3(\operatorname{tr}\boldsymbol{\tau}) + \boldsymbol{\Gamma}_4(\boldsymbol{\Gamma}_5 : \boldsymbol{\tau}) = -v_0\boldsymbol{\Gamma}_6\,, \tag{55}$$

where $\boldsymbol{\Gamma}_1$ through $\boldsymbol{\Gamma}_6$ are tensors dependent on the rate-of-strain tensor $\dot{\boldsymbol{\gamma}}$ and its first convective derivative $\dot{\boldsymbol{\gamma}}_{[1]}$, constant c_1 is the same as in Eq. (51) and v_0 is a positive constant.

Because the explicit form of the tensors $\boldsymbol{\Gamma}_i$ is quite extensive we do not present them in this paper. Instead, we give several general remarks about the structure of the first- and higher-order corrections:

(1) Since manifold (53) does not depend on the vorticity tensor $\omega = \mathbf{k} - \mathbf{k}^{\dagger}$ the latter enters Eq. (55) only via convective derivatives of $\boldsymbol{\tau}$ and $\dot{\boldsymbol{\gamma}}$. This is sufficient to acquire the frame indifference feature, since all the tensorial quantities in dynamic equations are indifferent in any time dependent reference frame [14].

(2) When $\mathbf{k} = 0$ the first-order equations (55) as well as equations for any order reduce to linear relaxation dynamics of slow modes:

$$\frac{D\mathring{\boldsymbol{\tau}}}{Dt} + \frac{\lambda_1}{\lambda_r}\mathring{\boldsymbol{\tau}} = 0\,,$$

$$\frac{D\mathrm{tr}\,\boldsymbol{\tau}}{Dt} + \frac{\lambda_0}{\lambda_r}\mathrm{tr}\,\boldsymbol{\tau} = 0\,,$$

which is obviously concordant with the dissipativity and the slowness requirements.

(3) In all higher-order corrections one will be always left with linear manifolds if the projector associated with functionals $M_0[\Psi]$ and $\mathring{\mathbf{M}}[\boldsymbol{\Psi}]$ is used in every step. It follows that the resulting constitutive equations will always take a linear form (55), where all tensors $\boldsymbol{\Gamma}_i$ depend on higher order convective derivatives of $\dot{\gamma}$ (the highest possible order is limited by the order of the correction). Similarly to the first and zero orders the frame indifference is guaranteed if the manifold does not depend on the vorticity tensor unless the latter is incorporated in any frame invariant time derivatives. It is reasonable to eliminate the dependence on vorticity (if any) at the stage of constructing the solution to iteration equations (36).

(4) When the force $\mathbf{F}$ is linear $\mathbf{F} = \mathbf{Q}$ our approach is proven to be also correct since it leads the Oldroyd-B model (Eq. (50) with $c_i = 0$ for $i = 3,\ldots,8$). This follows from the fact that the spectrum of the corresponding operator J_d is more degenerated, in particular $\lambda_0 = \lambda_1 = 1$ and the corresponding lowest eigenvectors comprise a simple dyad $\Psi_{eq}\mathbf{QQ}$.

5. Tests on the fene dumbbell model

In this section we specify the choice of the force law as the FENE springs (7) and present results of test calculations for the revised Oldroyd 8 constants (48) equations on the examples of two simple viscometric flows.

We introduce the extensibility parameter of FENE dumbbell model b:

$$b = \mathbf{Q}_0^2 = \frac{H\mathbf{Q}_0^2}{k_B T}\,. \tag{56}$$

It was estimated [1] that b is proportional to the length of polymeric molecule and has a meaningful variation interval 50–1000. The limit $b \to \infty$ corresponds to the Hookean case and therefore to the Oldroyd-B constitutive relation.

In our test calculations we will compare our results with the Brownian dynamic (BD) simulation data made on FENE dumbbell equations [18], and also with one popular approximation to the FENE model known as *FENE-P* (FENE-Peterelin) model [1,19]. The latter is obtained by selfconsistent approximation to FENE force

$$\mathbf{F} = \frac{1}{1 - \langle\mathbf{Q}^2\rangle/b}\mathbf{Q}\,. \tag{57}$$

This force law like Hookean case allows for the exact moment closure leading to nonlinear constitutive equations [1,19]. Specifically, we will use the modified variant of FENE-P model, which matches the dynamics of original FENE in near equilibrium region better than the classical variant. This modification is achieved by a slight modification of Kramers definition of the stress tensor:

$$\boldsymbol{\tau}_p = nk_B T(1 - \theta b)\mathbf{1} - \langle\mathbf{FQ}\rangle\,. \tag{58}$$

Table 1
Values of constants to the revised Oldroyd 8 constants model computed on the base of the FENE dumbbells model

b	λ_0	λ_1	b_0	b_1	b_2	a_0
20	1.498	1.329	−0.0742	0.221	1.019	0.927
50	1.198	1.135	−0.0326	0.279	1.024	0.982
100	1.099	1.068	−0.0179	0.303	1.015	0.990
200	1.050	1.035	0.000053	0.328	1.0097	1.014
∞	1	1	0	1/3	1	1

Table 2
Corrections due to hydrodynamic interaction to the constants of the revised Oldroyd 8 constants model based on FENE force

b	$\delta\lambda_0$	$\delta\lambda_1$	δb_0	δb_1	δb_2	δa_0
20	−0.076	−0.101	0.257	−0.080	−0.0487	−0.0664
50	−0.0618	−0.109	−0.365	0.0885	−0.0205	−0.0691
100	−0.0574	−0.111	−1.020	0.109	−0.020	−0.0603

The case $\theta=0$ gives the classical definition of FENE-P, while more thorough estimation [19,3] is $\theta=(b(b+2))^{-1}$.

5.1. Constants

The specific feature of the FENE model is that the length of dumbbells $\mathbf{Q}$ can vary only in a bounded domain of $\mathbb{R}^3$, namely inside a sphere $S_b=\{Q^2\leqslant b\}$. The sphere S_b defines the domain of integration for averages $\langle\bullet\rangle_e=\int_{S_b}\Psi_{eq}\bullet\,d\mathbf{Q}$, where the equilibrium distribution reads $\Psi_{eq}=c^{-1}(1-Q^2/b)^{b/2}$, $c=\int_{S_b}(1-Q^2/b)^{b/2}\,d\mathbf{Q}$.

In order to find constants for the zero-order model (48) we do the following: First, we analytically compute the lowest eigenfunctions of operator J_d: $g_1(Q^2)\mathbf{Q}\mathring{\mathbf{Q}}$ and $g_0(Q^2)$ without account of the hydrodynamic interaction ($\kappa=0$). The functions g_0 and g_1 are computed by a procedure presented in Appendix A with the help of the symbolic manipulation software *Maple V.3* [20]. Then we calculate the perturbations terms $h_{0,1}$ by formulas (A6) introducing the account of hydrodynamic interaction. Table 1 presents the constants $\lambda_{0,1}$, a_i, b_i (42) (49) of the zero-order model (48) without inclusion of hydrodynamic interaction $\kappa=0$ for several values of extensibility parameter b. The relative error $\delta_{0,1}$ (see Appendix A) of approximation for these calculations did not exceed the value 0.02. Table 2 shows the linear correction terms for constants from Table 1 which account a hydrodynamic interaction effect: $\lambda^h_{0,1}=\lambda_{0,1}(1+\kappa(\delta\lambda_{0,1}))$, $a^h_i=a_i(1+\kappa(\delta a_i))$, $b^h_i=b_i(1+\kappa(\delta b_i))$. The latter are calculated by substituting the perturbed functions $m_{0,1}=g_{0,1}+\kappa h_{0,1}$ into (42) and (49), and expanding them up to first order in κ. One can observe, since $\kappa>0$, the effect of hydrodynamic interaction results in the reduction of the relaxation times.

5.2. Dynamic problems

The rest of this section concerns the computations for two particular flows. The shear flow is defined by

$$\mathbf{k}(t) = \dot{\gamma}(t) \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} , \tag{59}$$

where $\dot{\gamma}(t)$ is the shear rate, and the elongation flow corresponds to the choice:

$$\mathbf{k}(t) = \dot{\varepsilon}(t) \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & -1/2 \end{bmatrix} , \tag{60}$$

where $\dot{\varepsilon}(t)$ is the elongation rate.

In test computations we will look at the so-called viscometric material functions defined through the components of the polymeric part of the stress tensor $\boldsymbol{\tau}_{\mathrm{p}}$. Namely, for shear flow they are the shear viscosity v, the first and the second normal stress coefficients ψ_1, ψ_2, and for elongation flow the only function is the elongation viscosity $\bar{v}$. In dimensionless form they are written as

$$\hat{v} = \frac{v - v_{\mathrm{s}}}{nk_{\mathrm{B}}T\lambda_{\mathrm{r}}} = -\frac{\boldsymbol{\tau}_{\mathrm{p},12}}{\bar{\gamma} nk_{\mathrm{B}}T} , \tag{61}$$

$$\hat{\psi}_1 = \frac{\psi_1}{nk_{\mathrm{B}}T\lambda_{\mathrm{r}}^2} = \frac{\boldsymbol{\tau}_{\mathrm{p},22} - \boldsymbol{\tau}_{\mathrm{p},11}}{\bar{\gamma}^2 nk_{\mathrm{B}}T} , \tag{62}$$

$$\hat{\psi}_2 = \frac{\psi_2}{nk_{\mathrm{B}}T\lambda_{\mathrm{r}}^2} = \frac{\boldsymbol{\tau}_{p,33} - \boldsymbol{\tau}_{p,22}}{\bar{\gamma}^2 nk_{\mathrm{B}}T} , \tag{63}$$

$$\vartheta = \frac{\bar{v} - 3v_{\mathrm{s}}}{nk_{\mathrm{B}}T\lambda_{\mathrm{r}}} = \frac{\boldsymbol{\tau}_{\mathrm{p},22} - \boldsymbol{\tau}_{\mathrm{p},11}}{\bar{\varepsilon} nk_{\mathrm{B}}T} , \tag{64}$$

where $\bar{\gamma} = \dot{\gamma}\lambda_{\mathrm{r}}$ and $\bar{\varepsilon} = \dot{\varepsilon}\lambda_{\mathrm{r}}$ are dimensionless shear and elongation rates. Characteristic values of latter parameters $\bar{\gamma}$ and $\bar{\varepsilon}$ allow to estimate the parameter ε_1 (15). For all flows considered below the second flow parameter (Deborah number) ε_2 is equal to zero.

Let us consider the steady-state values of viscometric functions in steady shear and elongation flows: $\dot{\gamma} = \mathrm{const}, \dot{\varepsilon} = \mathrm{const}$. For the shear flow the steady values of these functions are found from Eqs. (48) as follows:

$$\hat{v} = b_2/(\lambda_1 - c\bar{\gamma}^2), \qquad \hat{\psi}_1 = 2\hat{v}/\lambda_1, \qquad \hat{\psi}_2 = 2b_0\hat{v}/\lambda_1 ,$$

where $c = \frac{2}{3}(2b_0^2 + 2b_0 - 1)/\lambda_1 + 2b_1a_0/\lambda_0$. Estimations for the constants (see Table 1) shows that $c \leqslant 0$ for all values of b (case $c = 0$ corresponds to $b = \infty$), thus all three functions are monotonically decreasing in absolute value with increase of quantity $\bar{\gamma}$, besides the case when $b = \infty$. Although they qualitatively correctly predict the shear thinning for large shear rates due to power law, but the exponent -2 of power dependence in the limit of large $\bar{\gamma}$ from the values -0.66 for parameter $\hat{v}$ and -1.33 for $\hat{\psi}_1$

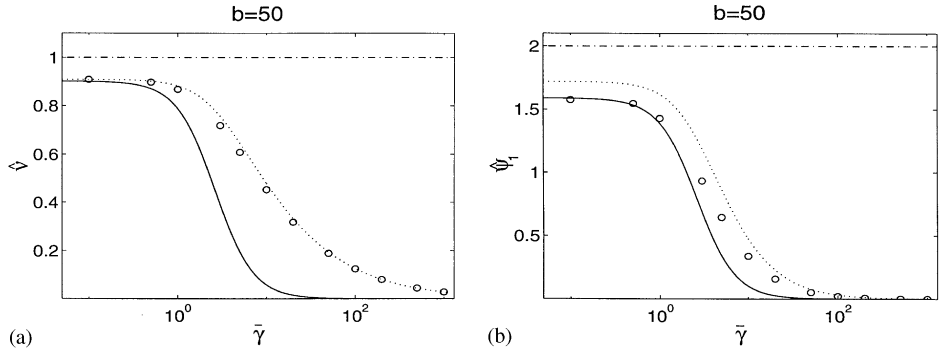

Fig. 1. Dimensionless shear viscosity and first normal stress coefficient vs. shear rate: (——) revised Oldroyd 8 constants model; (· · · · · ·) FENE-P model; (○○○) BD simulations on the FENE model; (— · — · —) Hookean dumbbell model.

observed in Brownian dynamic simulations [18]. It is explained by the fact that slopes of shear thinning lie out of the applicability domain of our model.

The predictions for the second normal stress coefficient indicate one more difference between revised Oldroyd 8 constant equation and FENE-P model (see Fig. 1). FENE-P model shows identically zero values for $\hat{\psi}_2$ in any shear flow, either steady or time dependent, while model (48), as well as BD simulations (see Fig. 9 in Ref. [18]) predict small, but nonvanishing values for this quantity. Namely, due to model (48) in shear flows the following relation $\hat{\psi}_2 = b_0\hat{\psi}_1$ is always valid, with proportionality coefficient b_0 small and mostly negative, what leads to small and mostly negative values of $\hat{\psi}_2$.

In the elongation flow the steady state value to ϑ is found as

$$\vartheta = \frac{3b_2}{\lambda_1 - (5/6)(2b_0+1)\bar{\varepsilon} - 7b_1a_0\bar{\varepsilon}^2/\lambda_0} \,. \tag{65}$$

The denominator has one root on positive semi-axis

$$\bar{\varepsilon}_* = -\frac{5\lambda_0(2b_0+1)}{84b_1a_0} + \left(\left(\frac{5\lambda_0(2b_0+1)}{84b_1a_0}\right)^2 + \frac{\lambda_1\lambda_0}{7b_1a_0}\right)^{1/2} \,, \tag{66}$$

which defines a singularity point for the dependence $\vartheta(\bar{\varepsilon})$. The BD simulation experiments [18] on the FENE dumbbell models shows that there is no divergence of elongation viscosity for all values of elongation rate (see Fig. 2). For Hookean springs $\bar{\varepsilon}_* = \frac{1}{2}$ while in our model (48) the singularity point shifts to higher values with respect to decreasing values of b as it is demonstrated in Table 3.

Fig. 3 gives an example of dynamic behavior for elongation viscosity in the instant start-up of the elongational flow. Namely, it shows the evolution of initially vanishing polymeric stresses after instant jump of elongation rate at the time moment $t = 0$ from the value $\bar{\varepsilon} = 0$ to the value $\bar{\varepsilon} = 0.3$.

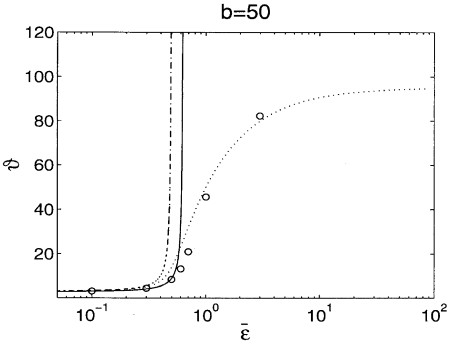

Fig. 2. Dimensionless elongation viscosity vs. elongation rate: (——) revised Oldroyd 8 constants model, (· · · · · ·) FENE-P model, (○ ○ ○) BD simulations on the FENE model; (— · — · —) Hookean dumbbell model.

Table 3
Singular values of elongation rate

b	20	50	100	120	200	∞
$\bar{\varepsilon}^*$	0.864	0.632	0.566	0.555	0.520	0.5

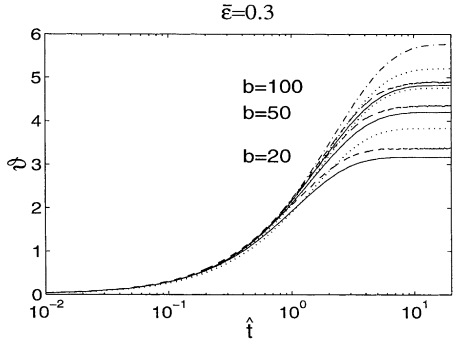

Fig. 3. Time evolution of elongation viscosity after inception of the elongation flow with elongation rate $\bar{\varepsilon} = 0.3$: (——) revised Oldroyd 8 constants model, (· · · · · ·) FENE-P model, (— — —) BD simulations on FENE model; (— · — · —) Hookean dumbbell model.

It is possible to conclude that the revised Oldroyd 8 constants model (48) with estimations given by (49) for small and moderate rates of strain up to $\varepsilon_1 = \lambda_r|\dot{\gamma}|/(2\lambda_1) \sim 0.5$ yields a good approximation to original FENE dynamics. The quality of the approximation in this interval is the same or better than the one of the nonlinear FENE-P model.

6. Conclusion

The main results of this paper are as follows:

(i) We have developed a systematic method of constructing constitutive equations from the kinetic dumbbell models for the polymeric solutions. The method is free from

a priori assumptions about the form of the spring force and is consistent with basic physical requirements: frame invariance and dissipativity of internal motions of fluid. The method extends the so-called method of invariant manifold onto equations coupled with external fields. Two characteristic parameters of fluid flow were distinguished in order to account for the effect of the presence of external fields. The iterative Newton scheme for obtaining a slow invariant manifold of the system driven by the flow with relatively low values of both characteristic parameters was developed.

(ii) We demonstrated that the revised phenomenological Oldroyd 8 constants constitutive equations represent the slow dynamics of microscopic elastic dumbbell model with any nonlinear spring force in the limit when the rate of strain and frequency of time variation of the flow are sufficiently small and microscopic states at initial time of evolution are taken not far from the equilibrium.

(iii) The corrections to the zero-order manifold lead generally to linear in stresses equations but with highly nonlinear dependence on the rate of strain tensor and its convective derivatives.

(iv) The zero-order constitutive equation is compared to the direct Brownian dynamics simulation for FENE dumbbell model as well as to predictions of FENE-P model. This comparison shows that the zero-order constitutive equation gives the correct predictions in the domain of its validity, but does not exclude qualitative discrepancy occurring out of this domain, particularly in elongation flows.

This discrepancy calls for a further development, in particular, the use of nonlinear manifolds for derivation of zero-order model. The reason is in the necessity to provide concordance with the requirement of the positivity of distribution function. It may lead to nonlinear constitutive equation on any order of correction. These issues are currently under consideration and results will be reported separately.

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Appendix A. Approximations to eigenfunctions of the Fokker–Planck operator J_d

In this appendix we discuss the question how to find the lowest eigenvectors $\Psi_{eq}m_0(Q^2)$ and $\Psi_{eq}m_1(Q^2)\mathbf{Q}\mathring{\mathbf{Q}}$ of the operator J_d (10) in the classes of functions having a form: $w_0(Q)$ and $w_1(Q)\mathbf{Q}\mathring{\mathbf{Q}}$. The results presented in this appendix were used in the Sections 4 and 5. It is directly verified that

$$J_d\Psi_{eq}m_0 = \Psi_{eq}G_0^h m_0 ,$$

$$J_d\Psi_{eq}m_1\mathbf{Q}\mathring{\mathbf{Q}} = \Psi_{eq}(G_1^h m_1)\mathbf{Q}\mathring{\mathbf{Q}} ,$$

where the operators G_0^h and G_1^h are given by

$$G_0^h = G_0 - \kappa H_0, \qquad G_1^h = G_1 - \kappa H_1 \ . \tag{A.1}$$

The operators $G_{0,1}$ and $H_{0,1}$ act in the space of isotropic functions (i.e., dependent only on $Q = (\mathbf{Q}\cdot\mathbf{Q})^{1/2}$) as follows:

$$G_0 = \frac{1}{2}\left(\frac{\partial^2}{\partial Q^2} - fQ\frac{\partial}{\partial Q} + \frac{2}{Q}\frac{\partial}{\partial Q}\right) , \tag{A.2}$$

$$G_1 = \frac{1}{2}\left(\frac{\partial^2}{\partial Q^2} - fQ\frac{\partial}{\partial Q} + \frac{6}{Q}\frac{\partial}{\partial Q} - 2f\right) , \tag{A.3}$$

$$H_0 = \frac{2}{Q}\left(\frac{\partial^2}{\partial Q^2} - fQ\frac{\partial}{\partial Q} + \frac{2}{Q}\frac{\partial}{\partial Q}\right) , \tag{A.4}$$

$$H_1 = \frac{2}{Q}\left(\frac{\partial^2}{\partial Q^2} - fQ\frac{\partial}{\partial Q} + \frac{5}{Q}\frac{\partial}{\partial Q} - 2f + \frac{1}{Q^2}\right) . \tag{A.5}$$

The following two properties of the operators $G_{0,1}^h$ are important for our analysis: Let us define two scalar products $\langle\bullet,\bullet\rangle_0$ and $\langle\bullet,\bullet\rangle_1$:

$$\langle y,x\rangle_0 = \langle xy\rangle_e, \qquad \langle y,x\rangle_1 = \langle xyQ^4\rangle_e \ .$$

Here $\langle\bullet\rangle_e$ is the equilibrium average as defined in (43). Then we state that for sufficiently small κ the operators G_0^h and G_1^h are symmetric and nonpositive in the scalar products $\langle\bullet,\bullet\rangle_0$ and $\langle\bullet,\bullet\rangle_1$, respectively. Thus for obtaining the desired eigenvectors of the operator J_d we need to find the eigenfunctions m_0 and m_1 related to the lowest nonzero eigenvalues of the operators $G_{0,1}^h$.

Since we regard the parameter κ small it is convenient, first, to find lowest eigenfunctions $g_{0,1}$ of the operators $G_{0,1}$ and, then, to use standard perturbation technique in order to obtain $m_{0,1}$. For the perturbation of the first order one finds [21]:

$$\begin{aligned} m_0 &= g_0 + \kappa h_0, \quad h_0 = -g_0\frac{\langle g_0 H_0 G_0 g_0\rangle_0}{\langle g_0, g_0\rangle_0} - G_0 H_0 g_0 \ , \\ m_1 &= g_1 + \kappa h_1, \quad h_1 = -g_1\frac{\langle g_1 H_1 G_1 g_1\rangle_1}{\langle g_1, g_1\rangle_1} - G_1 H_1 g_1 \ . \end{aligned} \tag{A.6}$$

For the rest of this appendix we describe one recurrent procedure for obtaining the functions m_0 and m_1 in a constructive way. Let us solve this problem by minimizing the functionals $\Lambda_{0,1}$:

$$\Lambda_{0,1}[m_{0,1}] = -\frac{\langle m_{0,1}, G_{0,1}^h m_{0,1}\rangle_{0,1}}{\langle m_{0,1}, m_{0,1}\rangle_{0,1}} \to \min \ , \tag{A.7}$$

by means of the *gradient descent method.*

Let us denote $e_{0,1}$ the eigenfunctions of the zero eigenvalues of the operators $G_{0,1}^h$. Their explicite values are $e_0 = 1$ and $e_1 = 0$. Let the initial approximations $m_{0,1}^{(0)}$ to the

lowest eigenfunctions $m_{0,1}$ be chosen so that $\langle m_{0,1}^{(0)}, e_{0,1}\rangle_{0,1}=0$. We define the variation derivative $\delta\Lambda_{0,1}/\delta m_{0,1}$ and look for the correction in the form

$$m_{0,1}^{(1)}=m_{0,1}^{(0)}+\delta m_{0,1}^{(0)}, \qquad \delta m_{0,1}^{(0)}=\alpha\frac{\delta\Lambda_{0,1}}{\delta m_{0,1}}\ , \tag{A.8}$$

where scalar parameter $\alpha<0$ is found from the condition

$$\frac{\partial\Lambda_{0,1}[m_{0,1}^{(1)}(\alpha)]}{\partial\alpha}=0\ .$$

In the explicit form the result reads

$$\delta m_{0,1}^{(0)}=\alpha_{0,1}^{(0)}\Delta_{0,1}^{(0)}\ ,$$

where

$$\begin{aligned}
\Delta_{0,1}^{(0)}&=\frac{2}{\langle m_{0,1}^{(0)}, m_{0,1}^{(0)}\rangle_{0,1}}(m_{0,1}^{(0)}\lambda_{0,1}^{(0)}-G_{0,1}^{\mathrm{h}}m_{0,1}^{(0)})\ ,\\
\lambda_{0,1}^{(0)}&=\frac{\langle m_{0,1}^{(0)}, G_{0,1}^{\mathrm{h}}m_{0,1}^{(0)}\rangle_{0,1}}{\langle m_{0,1}^{(0)}, m_{0,1}^{(0)}\rangle_{0,1}}\ ,\\
\alpha_{0,1}^{(0)}&=q_{0,1}-\sqrt{q_{0,1}^2+\frac{\langle m_{0,1}^{(0)}, m_{0,1}^{(0)}\rangle_{0,1}}{\langle\Delta_{0,1}^{(0)}, \Delta_{0,1}^{(0)}\rangle_{0,1}}}\ ,\\
q_{0,1}&=\frac{1}{\langle\Delta_{0,1}^{(0)}, \Delta_{0,1}^{(0)}\rangle_{0,1}}\left(\frac{\langle m_{0,1}^{(0)}, G_{0,1}^{\mathrm{h}}m_{0,1}^{(0)}\rangle_{0,1}}{\langle m_{0,1}^{(0)}, m_{0,1}^{(0)}\rangle_{0,1}}-\frac{\langle\Delta_{0,1}^{(0)}, G_{0,1}^{\mathrm{h}}\Delta_{0,1}^{(0)}\rangle_{0,1}}{\langle\Delta_{0,1}^{(0)}, \Delta_{0,1}^{(0)}\rangle_{0,1}}\right)\ .
\end{aligned} \tag{A.9}$$

Having the new correction $m_{0,1}^{(1)}$ we can repeat the procedure and eventually generate the recurrence scheme. Since by the construction all iterative approximations $m_{0,1}^{(n)}$ remain orthogonal to zero eigenfunctions $e_{0,1}$: $\langle m_{0,1}^{(n)}, e_{0,1}\rangle_{0,1}=0$ we avoid the convergence of this recurrence procedure to the eigenfunctions $e_{0,1}$.

The quantities $\delta_{0,1}^{(n)}$

$$\delta_{0,1}^{(n)}=\frac{\langle\Delta_{0,1}^{(n)}, \Delta_{0,1}^{(n)}\rangle_{0,1}}{\langle m_{0,1}^{(n)}, m_{0,1}^{(n)}\rangle_{0,1}}$$

can serve as relative error parameters for controlling the convergence of the iteration procedure (A.8).

Appendix B. Integration formulas

Let Ω be a sphere in $\mathbb{R}^3$ with the center at the origin of the coordinate system or be the entire space $\mathbb{R}^3$. For any function $s(x^2)$, where $x^2=\mathbf{x}\cdot\mathbf{x}$, $\mathbf{x}\in\mathbb{R}^3$, and any matrices $\mathbf{A}$, $\mathbf{B}$, $\mathbf{C}$ independent of $\mathbf{x}$ the following integral relations are valid:

$$\int_\Omega s(x^2)\mathbf{x}\mathring{\mathbf{x}}(\mathbf{x}\mathring{\mathbf{x}}:\ \mathbf{A})\,\mathrm{d}x=\frac{2}{15}\mathring{\mathbf{A}}\int_\Omega sx^4\,\mathrm{d}x\ ,$$

$$\int_\Omega s(x^2)\mathbf{x}\mathring{\mathbf{x}}(\mathring{\mathbf{x}}\mathbf{x}:\ \mathbf{A})(\mathring{\mathbf{x}}\mathbf{x}:\ \mathbf{B})\,\mathrm{d}x = \frac{4}{105}(\mathbf{A}\cdot\mathbf{B}\mathring{+}\mathbf{B}\cdot\mathbf{A})\int_\Omega sx^6\,\mathrm{d}x\ ,$$

$$\int_\Omega s(x^2)\mathbf{x}\mathring{\mathbf{x}}(\mathring{\mathbf{x}}\mathbf{x}:\ \mathbf{A})(\mathring{\mathbf{x}}\mathbf{x}:\ \mathbf{B})(\mathring{\mathbf{x}}\mathbf{x}:\ \mathbf{C})\,\mathrm{d}x$$
$$= \frac{4}{315}\{\mathring{\mathbf{A}}(\mathbf{B}:\ \mathbf{C}) + \mathring{\mathbf{B}}(\mathbf{A}:\ \mathbf{C}) + \mathring{\mathbf{C}}(\mathbf{A}:\ \mathbf{B})\}\int_\Omega sx^8\,\mathrm{d}x\ .$$

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