13 Slow Invariant Manifolds for Open Systems

13.1 Slow Invariant Manifold for a Closed System Has Been Found. What Next?

Suppose that the slow invariant manifold is found for a dissipative system. What have we constructed it for? First of all, for solving the Cauchy problem, in order to separate motions. This means that the Cauchy problem is divided in the following two subproblems:

- Reconstruct the "fast" motion from the initial conditions to the slow invariant manifold (*the initial layer problem*).
- Solve the Cauchy problem for the "slow" motions on the manifold.

Thus, solving the Cauchy problem becomes easier (and in some complicated cases it just becomes possible).

Let us stress here that for any sufficiently reliable solution of the Cauchy problem one must solve not only the reduced Cauchy problem for the slow motion, but also the initial layer problem for fast motions.

While solving the latter problem it was found to be surprisingly effective to use piece-wise linear approximations with smoothing or even without it [26, 27]. This method was used for the Boltzman equation.

There exists a different way to model the initial layer in kinetics problems: it is the route of model equations. For example, the Bhatnagar–Gross–Krook (BGK) equation [116] is the simplest model for the Boltzmann equation. It describes relaxation into a small neighborhood of the local Maxwell distribution. There are many types and hierarchies of the model equations [22, 112, 116, 117, 166]. The principal idea of any model equation is to replace the fast processes by a simple relaxation term. As a rule, it has a form $\mathrm{d}x/\mathrm{d}t = \ldots - (x - x_{sl}(x))/\tau$, where $x_{sl}(x)$ is a point of the approximate slow manifold. Such form is used in the BGK-equation, or in the quasi-equilibrium models [117]. It also can take a gradient form, like in the gradient models [22, 166]. These simplifications not only allows to study the fast motions separately but it also allows to zoom in the details of the interaction of fast and slow motions in the vicinity of the slow manifold.

What concerns solving the Cauchy problem for the "slow" motions, this is the basic problem of the hydrodynamics, of the gas dynamics (if the initial "big" systems describes kinetics of a gas or a fluid), etc. Here invariant

Alexander N. Gorban and Iliya V. Karlin: *Invariant Manifolds for Physical and Chemical Kinetics*, Lect. Notes Phys. **660**, 367–417 (2005)
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manifold methods provide equations for a further study. However, even a preliminary consideration of the practical aspects of these studies shows a definite shortcoming. In practice, obtained equations are exploited not only for "closed" systems. The initial equations (3.1) describe a dissipative system that approaches the equilibrium. The equations of slow motion describe dissipative system too. Then these equations are supplied with various forces and flows, and after that they describe systems with more or less complex dynamics.

Because of this, there is a different answer to our question, what have we constructed the invariant manifold for? *First of all, in order to construct models of open system dynamics in the neighborhood of the slow manifold.* Various approaches to this modeling are described in the following subsections.

13.2 Slow Dynamics in Open Systems. Zero-Order Approximation and the Thermodynamic Projector

Let the initial dissipative system (3.1),

$$\frac{\mathrm{d}x}{\mathrm{d}t} = J(x),\ x \in U\ ,$$

be "spoiled" by an additional term ("external vector field" $J_{ex}(x,t)$):

$$\frac{\mathrm{d}x}{\mathrm{d}t} = J(x) + J_{ex}(x,t), x \subset U\ . \tag{13.1}$$

For this driven system the entropy does not increase everywhere. In the system (13.1) various nontrivial dynamic effects become possible, such as a non-uniqueness of stationary states, auto-oscillations, etc. The "inertial manifold" effect is well-known: solutions of (13.1) approach some relatively low-dimensional manifold on which all the non-trivial dynamics takes place [173, 317, 318]. This "inertial manifold" can have a finite dimension even for infinite-dimensional systems, for example, for the "reaction+diffusion" systems [334].

In the theory of nonlinear control of partial differential equations systems a strategy based on the approximate inertial manifolds [342] is suggested to facilitate the construction of finite-dimensional systems of ordinary differential equations (ODE), whose solutions can be arbitrarily close to the solutions of the infinite-dimensional system [344].

It is natural to expect that the inertial manifold of the system (13.1) is located somewhere close to the slow manifold of the initial dissipative system (3.1). This hypothesis has the following motivation. Suppose that the vector field $J_{ex}(x,t)$ is sufficiently small. Let us introduce, for example, a small

parameter $\varepsilon > 0$, and consider $\varepsilon J_{ex}(x,t)$ instead of $J_{ex}(x,t)$. Let us assume that for the system (3.1) a separation of motions into "slow" and "fast" takes place. In that case, there exists such an interval of positive ε that $\varepsilon J_{ex}(x,t)$ is comparable to J only in a small neighborhood of the given slow manifold of the system (3.1). Outside this neighborhood, $\varepsilon J_{ex}(x,t)$ is negligibly small in comparison with J and its influence on the motion is negligible. For this statement to be true, it is important that the system (3.1) is dissipative and every solution comes in finite time to a small neighborhood of the given slow manifold.

Precisely this perspective on the system (13.1) allows to exploit slow invariant manifolds constructed for the dissipative system (3.1) as the ansatz and the zero-order approximation in a construction of the inertial manifold of the open system (13.1). In the zero-order approximation, the right part of the equation (13.1) is simply projected onto the tangent space of the slow manifold.

The choice of the projector is determined by the motion separation which was described above, because the fast component of the vector field (13.1) is taken from the dissipative system (3.1). A projector which is suitable for all dissipative systems with the given entropy function is unique. It is constructed in the following way (detailed consideration was given above in Chap. 5 and in [10]). Let a point $x \in U$ be defined and some vector space T, on which one needs to construct a projection (T is the tangent space to the slow manifold at the point x). We introduce the entropic scalar product $\langle|\rangle_x$:

$$\langle a \mid b\rangle_x = -(a, D_x^2 S(b)) \, . \tag{13.2}$$

Let us consider T_0, a subspace of T, which is annulled by the differential of S at the point x

$$T_0 = \{a \in T | D_x S(a) = 0\} \, . \tag{13.3}$$

Suppose[1] that $T_0 \neq T$. Let $e_g \in T$, $e_g \perp T_0$ with respect to the entropic scalar product $\langle|\rangle_x$, and $D_x S(e_g) = 1$. These conditions uniquely define vector the e_g.

The projector onto T is defined by the formula

$$P(J) = P_0(J) + e_g D_x S(J) \tag{13.4}$$

where P_0 is the orthogonal projector onto T_0 with respect to the entropic scalar product $\langle|\rangle_x$. For example, if T is a finite-dimensional space, then the projector (13.4) is constructed in the following way. Let $e_1, \ldots, e_n$ be a basis in T, and for definiteness, $D_x S(e_1) \neq 0$.

(1) Let us construct a system of vectors

$$b_i = e_{i+1} - \lambda_i e_1, (i = 1, \ldots, n-1) \, , \tag{13.5}$$

[1] If $T_0 = T$, then the thermodynamic projector is the orthogonal projector on T with respect to the entropic scalar product $\langle|\rangle_x$.

where $\lambda_i = D_x S(e_{i+1})/D_x S(e_1)$, and hence $D_x S(b_i) = 0$. Thus, $\{b_i\}_1^{n-1}$ is a basis in T_0.

(2) Let us orthogonalize $\{b_i\}_1^{n-1}$ with respect to the entropic scalar product $\langle|\rangle_x$ (3.1). We thus derived an orthonormal with respect to $\langle|\rangle_x$ basis $\{g_i\}_1^{n-1}$ in T_0.

(3) We find $e_g \in T$ from the conditions:

$$\langle e_g \mid g_i\rangle_x = 0, (i = 1, \dots, n-1), D_x S(e_g) = 1 \,. \tag{13.6}$$

and, finally we get

$$P(J) = \sum_{i=1}^{n-1} g_i \langle g_i \mid J\rangle_x + e_g D_x S(J) \,. \tag{13.7}$$

If $D_x S(T) = 0$, then the projector P is simply the orthogonal projector with respect to the $\langle|\rangle_x$ scalar product. This happens if x is the point of the global maximum of entropy (equilibrium). Then

$$P(J) = \sum_{i=1}^{n} g_i \langle g_i|J\rangle_x, \langle g_i|g_j\rangle = \delta_{ij} \,. \tag{13.8}$$

Remark. In applications, equation (3.1) often has additional linear balance constraints (conservation laws) such as numbers of particles, momentum, energy, etc. When solving the closed dissipative system (3.1), we simply fix the balance values and consider the dynamics of (3.1) on the corresponding affine balance subspace.

For driven system (13.1) the conservation laws can be violated by external flows and fields. Because of this, for the open system (13.1) the natural balance subspace includes the balance subspace of (3.1) with different balance values. For every set of balance values there is a corresponding equilibrium. Slow invariant manifold of the dissipative systems that is applied to the description of the driven systems (13.1) is usually the *union* of slow manifolds for all possible balance values. The equilibrium of the dissipative closed system corresponds to the entropy maximum *given the balance values are fixed*. In the phase space of the driven system (13.1) the entropy gradient in the equilibrium points of the system (3.1) is not necessarily equal to zero.

In particular, for the Boltzmann entropy in the local finite-dimensional case one gets the thermodynamic projector in the following form.

$$\begin{aligned}
S &= -\int f(v)(\ln(f(v)) - 1)\,\mathrm{d}v \,, \\
D_f S(J) &= -\int J(v) \ln f(v)\,\mathrm{d}v \,, \\
\langle \psi \mid \varphi\rangle_f &= -(\psi, D_f^2 S(\varphi)) = \int \frac{\psi(v)\varphi(v)}{f(v)}\,\mathrm{d}v \\
P(J) &= \sum_{i=1}^{n-1} g_i(v) \int \frac{g_i(v)J(v)}{f(v)}\,\mathrm{d}v - e_g(v) \int J(v) \ln f(v)\,\mathrm{d}v,
\end{aligned} \tag{13.9}$$

where $g_i(v)$ and $e_g(v)$ are constructed according to the scheme described above,

$$\int \frac{g_i(v)g_j(v)}{f(v)}\,\mathrm{d}v = \delta_{ij}\ , \tag{13.10}$$

$$\int g_i(v)\ln f(v)\,\mathrm{d}v = 0\ , \tag{13.11}$$

$$\int g_i(v)e_g(v)\,\mathrm{d}v = 0\ , \tag{13.12}$$

$$\int e_g(v)\ln f(v)\,\mathrm{d}v = 1\ . \tag{13.13}$$

If for all $g \in T$ we have $\int g(v)\ln f(v)\,\mathrm{d}v = 0$, then the projector P is defined as the orthogonal projector with respect to the $\langle|\rangle_f$ scalar product.

13.3 Slow Dynamics in Open Systems. First-Order Approximation

The thermodynamic projector (13.4) defines the duality of slow and fast motions: if T is the tangent space of the slow manifold, then $T = \mathrm{im}P$, and $\ker P$ is the plane of fast motions. Let us denote by P_x the projector at a point x of a given slow manifold.

The vector field $J_{ex}(x,t)$ can be decomposed in two components:

$$J_{ex}(x,t) = P_x J_{ex}(x,t) + (1-P_x)J_{ex}(x,t)\ . \tag{13.14}$$

Let us denote $J_{ex\,s} = P_x J_{ex}$, $J_{ex\,f} = (1-P_x)J_{ex}$. The slow component $J_{ex\,s}$ gives a correction to the motion along the slow manifold. This is a zero-order approximation. The "fast" component shifts the slow manifold in the fast motions plane. This shift changes $P_x J_{ex}$ accordingly. Consideration of this effect gives a first-order approximation. In order to find it, let us rewrite the invariance equation taking J_{ex} into account:

$$\begin{cases} (1-P_x)(J(x+\delta x)+\varepsilon J_{ex}(x,t)) = 0\ ; \\ P_x\delta x = 0\ . \end{cases} \tag{13.15}$$

The first iteration of the Newton method subject to incomplete linearization gives:

$$\begin{cases} (1-P_x)(D_x J(\delta x)+\varepsilon J_{ex}(x,t)) = 0\ ; \\ P_x\delta x = 0\ . \end{cases} \tag{13.16}$$

$$(1-P_x)D_x J(1-P_x)J(\delta x) = -\varepsilon J_{ex}(x,t)\ . \tag{13.17}$$

Thus, we have derived a linear equation in the space $\ker P_x$. The operator $(1-P_x)D_x J(1-P_x)$ is defined in this space.

Taking into account of the self-adjoint linearization instead of the operator $D_x J$ (see Chap. 7) considerably simplifies solving and studying equation (13.17). It is necessary to take into account here that the projector P_x is a sum of the orthogonal projector with respect to the entropic scalar product $\langle|\rangle_x$ and a projector of rank one.

Assume that the first-order approximation equation (13.17) has been solved and the following function is found:

$$\delta_1 x(x, \varepsilon J_{ex\,f}) = -[(1 - P_x) D_x J (1 - P_x)]^{-1} \varepsilon J_{ex\,f} \ , \tag{13.18}$$

where $D_x J$ is either the differential of J or symmetrized differential of J (7.17).

Let x be a point on the initial slow manifold. At the point $x + \delta x(x, \varepsilon J_{ex\,f})$ the right-hand side of equation (13.1) in the first-order approximation is given by

$$J(x) + \varepsilon J_{ex}(x, t) + D_x J(\delta x(x, \varepsilon J_{ex\,f})) \ . \tag{13.19}$$

Due to the first-order approximation (13.19), the motion projected onto the manifold is given by the following equation

$$\frac{\mathrm{d}x}{\mathrm{d}t} = P_x(J(x) + \varepsilon J_{ex}(x, t) + D_x J(\delta x(x, \varepsilon J_{ex\,f}(x, t)))) \ . \tag{13.20}$$

Note that in equation (13.20), the vector field $J(x)$ enters only in the form of projection, $P_x J(x)$. For the invariant slow manifold it holds $P_x J(x) = J(x)$, but actually we always deal with approximately invariant manifolds, hence, it is necessarily to use the projection $P_x J$ instead of J in (13.20).

Remark. The notion "projection of a point onto the manifold" needs to be specified. For every point x of the slow invariant manifold Ω there are defined both the thermodynamic projector P_x (13.4) and the fast motions plane $\ker P_x$. Let us define a projector Π of some neighborhood of *motion* onto *motion* in the following way:

$$\Pi(z) = x, \quad \text{if } P_x(z - x) = 0 \ . \tag{13.21}$$

Qualitatively, it means that z, after all fast motions were completed, comes into a small neighborhood of x. The operation (13.4) is defined uniquely in some small neighborhood of the manifold *motion*.

A derivation of slow motion equations requires not only an assumption that εJ_{ex} is small but it must be slow as well: $\frac{\mathrm{d}}{\mathrm{d}t}(\varepsilon J_{ex})$ must be small too.

One can get further approximations for slow motions of the system (13.1), taking into account the time derivatives of J_{ex}. This approach is considered in a more detail in the following Example for a particularly interesting driven system of dilute polymeric solutions. A short description of the scheme is given in the next section. That is an alternative to the using the projection operators methods [194].

13.4 Beyond the First-Order Approximation: Higher-Order Dynamic Corrections, Stability Loss and Invariant Manifold Explosion

Let us pose formally the invariance problem for the driven system (13.1) in the neighborhood of the slow manifold Ω of the initial (dissipative) system.

Let for a given neighborhood of Ω an operator Π (13.21) be defined. One needs to define the function $\delta x(x,\ldots) = \delta x(x, J_{ex}, \dot{J}_{ex}, \ddot{J}_{ex}, \ldots)$, $x \in \Omega$, with the following properties:

$$\begin{aligned} &P_x(\delta x(x,\ldots)) = 0\ , \\ &J(x+\delta x(x,\ldots)) + J_{ex}(x+\delta x(x,\ldots),t) \\ &= \dot{x}_{sl} + D_x \delta x(x,\ldots)\dot{x}_{sl} + \sum_{n=0}^{\infty} D_{J_{ex}^{(n)}} \delta x(x,\ldots) J_{ex}^{(n+1)}\ , \end{aligned} \tag{13.22}$$

where

$$\dot{x}_{sl} = P_x(J(x+\delta x(x,\ldots)) + J_{ex}(x+\delta x(x,\ldots),t)),\ J_{ex}^{(n)} = \frac{d^n J_{ex}}{\mathrm{d}t^n}\ ,$$

$D_{J_{ex}^{(n)}} \delta x(x,\ldots)$ is a partial differential of the function

$$\delta x(x, J_{ex}, \dot{J}_{ex}, \ddot{J}_{ex}, \ldots, J_{ex}^{(n)}, \ldots)$$

with respect to the variable $J_{ex}^{(n)}$. One can rewrite equations (13.22) in the following form:

$$\begin{aligned} &(1 - P_x - D_x \delta x(x,\ldots))(J(x+\delta x(x,\ldots)) + J_{ex}(x+\delta x(x,\ldots),t)) \\ &= \sum_{n=0}^{\infty} D_{J_{ex}^{(n)}} \delta x(x,\ldots) J_{ex}^{(n+1)}. \end{aligned} \tag{13.23}$$

For solving (13.23) one can use iterations method and also take into account smallness considerations. The series in the right hand side of equation (13.23) can be rewritten as

$$\text{R.H.S.} = \sum_{n=0}^{k-1} \varepsilon^{n+1} D_{J_{ex}^{(n)}} \delta x(x,\ldots) J_{ex}^{(n+1)} \tag{13.24}$$

at the kth iteration, considering the terms only to order less than k. The first iteration equation was solved in the previous section. On the second iteration one gets the following equation:

$$\begin{aligned} &(1 - P_x - D_x \delta_1 x(x, J_{ex}))(J(x + \delta_1 x(x, J_{ex})) \\ &+ D_z J(z)|_{z=x+\delta_1 x(x,J_{ex})} \cdot (\delta_2 x - \delta_1 x(x, J_{ex})) + J_{ex}) \\ &= D_{J_{ex}} \delta_1 x(x, J_{ex}) \dot{J}_{ex}\ . \end{aligned} \tag{13.25}$$

This is a linear equation with respect to $\delta_2 x$. The solution $\delta_2 x(x, J_{ex}, \dot{J}_{ex})$ depends linearly on $\dot{J}_{ex}$, but non-linearly on J_{ex}. Let us remind that the first iteration equation solution depends linearly on J_{ex}.

In all these iteration equations the field J_{ex} and its derivatives are included in the formulas as if they were functions of time t only. Indeed, for any solution $x(t)$ of the equations (13.1) $J_{ex}(x,t)$ can be substituted for $J_{ex}(x(t),t)$. The function $x(t)$ will be a solution of the system (13.1) in which $J_{ex}(x,t)$ is substituted for $J_{ex}(t)$ in this way.

However, in order to obtain the macroscopic equations (13.20) one must return to $J_{ex}(x,t)$. For the first iteration such return is quite simple as one can see from (13.19). There $J_{ex}(x,t)$ is calculated in points of the initial slow manifold. In the general case, suppose that $\delta x = \delta x(x, J_{ex}, \dot{J}_{ex}, \ldots, J_{ex}^{(k)})$ has been found. The equations for x (13.20) have the following form:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = P_x(J(x+\delta x) + J_{ex}(x+\delta x, t)) \,. \tag{13.26}$$

In these equations the shift δx must be a function of x and t (or a function of x, t, α, where α are external fields, see example below. One calculates the shift $\delta x(x,t)$ using the following equation:

$$J_{ex} = J_{ex}(x + \delta x(x, J_{ex}, \dot{J}_{ex}, \ldots, J_{ex}^{(k)}), t) \,. \tag{13.27}$$

It can be solved, for example, by the iterative method, taking $J_{ex0} = J_{ex}(x,t)$:

$$J_{ex(n+1)} = J_{ex}(x + \delta x(x, J_{ex(n)}, \dot{J}_{ex(n)}, \ldots, J_{ex(n)}^{(k)}), t) \,. \tag{13.28}$$

We hope that using J_{ex} in the equations (13.27) and (13.28) both as a variable and as a symbol of an unknown function $J_{ex}(x,t)$ will not lead to a confusion.

In all the constructions introduced above it was assumed that δx is sufficiently small and the driven system (13.1) will not deviate too far from the slow invariant manifold of the initial system. However, a stability loss is possible: solutions of the equation (13.1) can deviate arbitrarily far if the strength of the perturbations exceeds a certain level. The invariant manifold can loose it's stability. Qualitatively, this effect of *invariant manifold explosion* can be represented as follows.

Suppose that J_{ex} includes the parameter ε: one has εJ_{ex} in the equation (13.1). When ε is small, the system's motions are located in a small neighborhood of the initial manifold. This neighborhood grows monotonically with increase of ε, but after some ε_0 a sudden change happens ("explosion") and the neighborhood, in which the motion takes place, becomes significantly wider at $\varepsilon > \varepsilon_0$ than at $\varepsilon < \varepsilon_0$. The stability loss is not necessarily associated with the invariance loss. In the last example to this chapter it is shown how the invariant manifold (which is at the same time the quasiequilibrium manifold in this example) can loose its stability. This "explosion" of the invariant manifold leads to essential physical consequences.

13.5 Example: The Universal Limit in Dynamics of Dilute Polymeric Solutions

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 flow situations.

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 [151–153, 354, 364], this problem remains less studied as compared to other classical kinetic equations.

It is the purpose of this section 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 [70, 112].

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 [70]. The resulting reduced description (the compressible 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 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 as 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-consistend closed description, the dumbbell

kinetic equations are coupled to the hydrodynamic equations. This coupling manifests itself as an external flux in the kinetic equation.

The distinguished macroscopic variable associated with the polymer kinetic equations is the polymeric stress tensor [151, 364]. This variable is not a 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 [11], modified for systems coupled with external fields. This method suggests constructing invariant sets (or manifolds) of distribution functions that represent the asymptotic states of the 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 the 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 the 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.

The two main results of the study 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 strain rates, 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.

The section is organized as follows: For the sake of completeness, we present the nonlinear dumbbell kinetic models in the next subsection, "The problem of reduced description in polymer dynamics". In the section, "The method of invariant manifold for weakly driven systems", 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 the section, "Constitutive equations". 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 the section, "Tests on the FENE dumbbell model".

13.5.1 The Problem of Reduced Description in Polymer Dynamics

Elastic Dumbbell Models

The elastic dumbbell model is the simplest microscopic model of polymer solutions [151]. It dumbbell reflects the two basic features of the 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 fluid. In this example we adopt notations used in kinetic theory of polymer dynamics [151]. Let $\boldsymbol{Q}$ be the connector vector between the beads of a dumbbell, and $\Psi(\boldsymbol{x}, \boldsymbol{Q}, t)$ be the configuration distribution function which depends on the location in the space $\boldsymbol{x}$ at time t. We assume that dumbbells are distributed uniformly, and consider the normalization, $\int \Psi(\boldsymbol{x}, \boldsymbol{Q}, t)\, \mathrm{d}\boldsymbol{Q} = 1$. The Brownian motion of beads in the physical space causes a diffusion in the phase space described by the Fokker–Planck equation (FPE) [151]:

$$\frac{\mathrm{D}\Psi}{\mathrm{D}t} = -\frac{\partial}{\partial \boldsymbol{Q}} \cdot \boldsymbol{k} \cdot \boldsymbol{Q}\Psi + \frac{2k_{\mathrm{B}}T}{\xi} \frac{\partial}{\partial \boldsymbol{Q}} \cdot \boldsymbol{D} \cdot \left(\frac{\partial}{\partial \boldsymbol{Q}}\Psi + \frac{\boldsymbol{F}}{k_{\mathrm{B}}T}\Psi \right) . \qquad (13.29)$$

Here, $\mathrm{D}/\mathrm{D}t = \partial/\partial t + \boldsymbol{v} \cdot \nabla$ is the substantional derivative, ∇ is the spatial gradient, $\boldsymbol{k}(\boldsymbol{x}, t) = (\nabla \boldsymbol{v})^{\dagger}$ is the gradient of the velocity of the solvent $\boldsymbol{v}$, $\dagger$

denotes transposition of tensors, $\boldsymbol{D}$ is the dimensionless diffusion matrix, k_B is the Boltzmann constant, T is the temperature, ξ is the dimensional coefficient characterizing a friction exerted on beads moving through solvent media (the friction coefficient [151, 152]), and $\boldsymbol{F} = \partial\phi/\partial\boldsymbol{Q}$ is the elastic spring force defined by the potential ϕ. We consider forces of the form $\boldsymbol{F} = Hf(Q^2)\boldsymbol{Q}$, where $f(Q^2)$ is a dimensionless function of the variable $Q^2 = \boldsymbol{Q}\cdot\boldsymbol{Q}$, 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 $\boldsymbol{F}$ is linear: $f(Q^2) = 1$. It proves convenient to rewrite the FPE (13.29) in the dimensionless form:

$$\frac{D\Psi}{D\widehat{t}} = -\frac{\partial}{\partial\widehat{\mathbf{Q}}}\cdot\widehat{\mathbf{k}}\cdot\widehat{\mathbf{Q}}\Psi + \frac{\partial}{\partial\widehat{\mathbf{Q}}}\cdot\boldsymbol{D}\cdot\left(\frac{\partial}{\partial\widehat{\mathbf{Q}}}\Psi + \widehat{\mathbf{F}}\Psi\right) . \tag{13.30}$$

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

The quantity of interest is the stress tensor introduced by Kramers [151]:

$$\boldsymbol{\tau} = -\nu_\mathrm{s}\dot{\boldsymbol{\gamma}} + nk_\mathrm{B}T(\mathbf{1} - \langle\boldsymbol{FQ}\rangle) , \tag{13.31}$$

where ν_s is the viscosity of the solvent, $\dot{\boldsymbol{\gamma}} = \boldsymbol{k} + \boldsymbol{k}^\dagger$ 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 Ψ: $\langle\bullet\rangle \equiv \int \bullet\Psi(\boldsymbol{Q})\,\mathrm{d}\boldsymbol{Q}$. The tensor

$$\boldsymbol{\tau}_\mathrm{p} = nk_\mathrm{B}T(\mathbf{1} - \langle\boldsymbol{FQ}\rangle) \tag{13.32}$$

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

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

$$\frac{\mathrm{D}\boldsymbol{v}}{\mathrm{D}t} = -\rho^{-1}\nabla p - \nabla\cdot\boldsymbol{\tau}[\Psi] . \tag{13.33}$$

Here p is the pressure, and $\rho = \rho_\mathrm{s} + \rho_\mathrm{p}$ 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:

$$\boldsymbol{F} = \boldsymbol{Q} \,. \tag{13.34}$$

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 [151].

Another model, the Finitely Extendible Nonlinear Elastic (FENE) force law [355], was derived as an approximation to the inverse Langevin force law [151] for a more realistic description of the elongation of a polymeric molecule in a solvent:

$$\boldsymbol{F} = \frac{\boldsymbol{Q}}{1 - \boldsymbol{Q}^2/\boldsymbol{Q}_0^2} \,. \tag{13.35}$$

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

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

$$\boldsymbol{D}_\mathrm{I} = \frac{1}{2}\mathbf{1} \,. \tag{13.36}$$

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 (13.36). The original form of this contribution is the Oseen-Burgers tensor $\boldsymbol{D}_\mathrm{H}$ [356, 357]:

$$\boldsymbol{D} = \boldsymbol{D}_\mathrm{I} - \kappa \boldsymbol{D}_\mathrm{H} \,, \qquad \boldsymbol{D}_\mathrm{H} = \frac{1}{Q}\left(\mathbf{1} + \frac{\boldsymbol{Q}\boldsymbol{Q}}{Q^2}\right) \,, \tag{13.37}$$

where

$$\kappa = \left(\frac{H}{k_\mathrm{B}T}\right)^{1/2} \frac{\xi}{16\pi\nu_\mathrm{s}} \,.$$

Several modifications of the Oseen-Burgers tensor can be found in the literature (the *Rotne-Prager-Yamakawa* tensor [358, 359]), but here we consider only the classical version.

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 (13.30) relevant to what will follow. This operator can be written as $J = J_\mathrm{d} + J_\mathrm{h}$, and it represents two processes.

The first term, J_d, is the dissipative part,

$$J_\mathrm{d} = \frac{\partial}{\partial \boldsymbol{Q}} \cdot \boldsymbol{D} \cdot \left(\frac{\partial}{\partial \boldsymbol{Q}} + \boldsymbol{F}\right) \,. \tag{13.38}$$

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,

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

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

The second part, J_{h}, describes the hydrodynamic drag of the beads in the flowing solvent:

$$J_{\mathrm{h}} = -\frac{\partial}{\partial \boldsymbol{Q}} \cdot \widehat{\mathbf{k}} \cdot \boldsymbol{Q} \ . \tag{13.39}$$

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:

$$\langle g, h \rangle_{\mathrm{s}} = \int \Psi_{\mathrm{eq}}^{-1} g h \, \mathrm{d}\boldsymbol{Q} \ .$$

The operator J_{d} is symmetric and nonpositive definite in this scalar product:

$$\langle J_{\mathrm{d}} g, h \rangle_{\mathrm{s}} = \langle g, J_{\mathrm{d}} h \rangle_{\mathrm{s}}, \quad \text{and} \quad \langle J_{\mathrm{d}} g, g \rangle_{\mathrm{s}} \leq 0 \ . \tag{13.40}$$

Since

$$\langle J_{\mathrm{d}} g, g \rangle_{\mathrm{s}} = -\int \Psi_{\mathrm{eq}}^{-1} (\partial g / \partial \boldsymbol{Q}) \cdot \Psi_{\mathrm{eq}} \boldsymbol{D} \cdot (\partial g / \partial \boldsymbol{Q}) \, \mathrm{d}\boldsymbol{Q} \ ,$$

the above inequality is valid if the diffusion matrix $\boldsymbol{D}$ is positive semidefinite. This happens if $\boldsymbol{D} = \boldsymbol{D}_{\mathrm{I}}$ (13.36) but is not generally valid in the presence of the hydrodynamic interaction (13.37). Let us split the operator J_{d} according to the splitting of the diffusion matrix $\boldsymbol{D}$:

$$J_{\mathrm{d}} = J_{\mathrm{d}}^{\mathrm{I}} - \kappa J_{\mathrm{d}}^{\mathrm{H}}, \text{ where } J_{\mathrm{d}}^{\mathrm{I,H}} = \partial / \partial \boldsymbol{Q} \cdot \boldsymbol{D}_{\mathrm{I,H}} \cdot (\partial / \partial \boldsymbol{Q} + \boldsymbol{F}) \ .$$

Both the operators $J_{\mathrm{d}}^{\mathrm{I}}$ and $J_{\mathrm{d}}^{\mathrm{H}}$ have nondegenerated eigenvalue 0 which corresponds to their common eigenfunction Ψ_{eq}: $J_{\mathrm{d}}^{\mathrm{I,H}} \Psi_{\mathrm{eq}} = 0$, while the rest of the spectrum of both operators belongs to the nonpositive real semi-axis. Then the spectrum of the operator $J_{\mathrm{d}} = J_{\mathrm{d}}^{\mathrm{I}} - \kappa J_{\mathrm{d}}^{\mathrm{H}}$ remains nonpositive for sufficiently small values of the parameter κ. The spectral properties of both operators $J_{\mathrm{d}}^{\mathrm{I,H}}$ depend only on the choice of the spring force $\boldsymbol{F}$. Thus, in the sequel we assume that the hydrodynamic interaction parameter κ is sufficiently small so that the *thermodynamic stability* property (13.40) holds.

We note that the scalar product $\langle \bullet, \bullet \rangle_{\mathrm{s}}$ coincides with the second differential $D_{\Psi}^2 S\big|_{\Psi_{\mathrm{eq}}}$ of an entropy functional $S[\Psi]$:

$$\langle \bullet, \bullet \rangle_{\mathrm{s}} = -D_{\Psi}^2 S\big|_{\Psi_{\mathrm{eq}}} [\bullet, \bullet] \ ,$$

where the entropy has the form:

$$S[\Psi] = -\int \Psi \ln \left(\frac{\Psi}{\Psi_{\mathrm{eq}}} \right) \mathrm{d}\boldsymbol{Q} = -\left\langle \ln \left(\frac{\Psi}{\Psi_{\mathrm{eq}}} \right) \right\rangle \ . \tag{13.41}$$

The entropy S grows in the course of dissipation:

$$D_\Psi S[J_\mathrm{d}\Psi] \geq 0 \,.$$

This inequality, similar to inequality (13.40), is satisfied for sufficiently small κ. Symmetry and nonpositiveness of operator J_d in the scalar product defined by the second differential of the entropy is a common property of linear dissipative systems.

Statement of the Problem

Given the kinetic equation (13.29), we aim at deriving differential equations for the stress tensor $\boldsymbol{\tau}$ (13.31). The latter includes the moments $\langle \boldsymbol{FQ} \rangle = \int \boldsymbol{FQ}\Psi \, \mathrm{d}\boldsymbol{Q}$.

In general, when the diffusion matrix is non-isotropic 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 the 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 Eucluidian, time dependent transformations of the reference frame [151, 360].

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 the characteristic value of the gradient of the flow velocity: $\theta_1 = |\nabla \boldsymbol{v}|^{-1}$, and θ_2 the characteristic time of the variation of the flow velocity. We assume that the characteristic relaxation time of the molecular configuration θ_r is small as compared to both the characteristic times θ_1 and θ_2:

$$\theta_\mathrm{r} \ll \theta_1 \text{ and } \theta_\mathrm{r} \ll \theta_2 \,. \tag{13.42}$$

(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 the 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 (13.38) for elastic forces of a complicated form, the 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:

$$\varepsilon_1 = \theta_\mathrm{r}/\theta_1 \ll 1 \ , \quad \varepsilon_2 = \theta_\mathrm{r}/\theta_2 \ll 1 \ . \tag{13.43}$$

The characteristic relaxation time of the polymeric configuration is defined via the coefficient λ_r: $\theta_\mathrm{r} = c\lambda_\mathrm{r}$, 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* ([361], Sect. 7.2).

13.5.2 The Method of Invariant Manifold for Weakly Driven Systems

The Newton Iteration Scheme

In this section we introduce an extension of the method of invariant manifold [11] onto systems coupled with external fields. We consider a class of dynamic systems of the form

$$\frac{\mathrm{d}\Psi}{\mathrm{d}t} = J_\mathrm{d}\Psi + J_\mathrm{ex}(\alpha)\Psi \ , \tag{13.44}$$

where J_d is a linear operator representing the dissipative part of the dynamic vector field, while $J_\mathrm{ex}(\alpha)$ 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,

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \Phi(\Psi, \alpha) \ . \tag{13.45}$$

Without any restriction, parameters α are adjusted in such a way that $J_\mathrm{ex}(\alpha = 0) \equiv 0$. Kinetic equation (13.30) has the form (13.44), and general results of this section will be applied to the dumbbell models below in a straightforward way.

We assume that the vector field $J_\mathrm{d}\Psi$ has the same dissipative properties as the Fokker–Planck operator (13.38). Namely there exists the globally convex entropy function S which obeys: $D_\Psi S[J_\mathrm{d}\Psi] \geq 0$, and the operator J_d is symmetric and nonpositive in the scalar product $\langle \bullet, \bullet \rangle_\mathrm{s}$ defined by the second differential of the entropy: $\langle g, h \rangle_\mathrm{s} = -D^2_\Psi S[g, h]$. Thus, the vector field $J_\mathrm{d}\Psi$ 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 $\mathcal{F}$ of the system (13.44). 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 the phase space $\mathcal{F}$. This manifold is thought as a finite-parametric set of

solutions $\Psi(M)$ to equations (13.44) 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 (13.44), we assume that the invariant manifold depends also on the parameters α, and on their time derivatives taken to arbitrary order: $\Psi(M, \mathcal{A})$, where $\mathcal{A} = \{\alpha, \alpha^{(1)}, \ldots\}$ is the set of time derivatives $\alpha^{(k)} = \mathrm{d}^k\alpha/\mathrm{d}t^k$. 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 (13.45) in the course of construction of the invariant manifold.

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

$$J\Psi(M, \mathcal{A}) = \sum_{i=1}^{n} \frac{\partial \Psi(M, \mathcal{A})}{\partial M_i} \frac{\mathrm{d}M_i}{\mathrm{d}t} + \sum_{n=0}^{\infty} \sum_{j=1}^{k} \frac{\partial \Psi(M, \mathcal{A})}{\partial \alpha_j^{(n)}} \alpha_j^{(n+1)} , \tag{13.46}$$

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:

$$\frac{\mathrm{d}M_i}{\mathrm{d}t} = D_\Psi M_i[J\Psi(M, \mathcal{A})] , \tag{13.47}$$

where $D_\Psi M_i$ stands for differentials of the functionals M_i.

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

$$P_M = \sum_{i=1}^{n} \frac{\partial \Psi(M, \mathcal{A})}{\partial M_i} D_\Psi M_i[\bullet] \tag{13.48}$$

It projects vector fields from the phase space $\mathcal{F}$ onto the tangent space $T\Psi(M, \mathcal{A})$ of the manifold $\Psi(M, \mathcal{A})$. Then (13.46) is rewritten as the *invariance equation*:

$$(1 - P_M)J\Psi(M, \mathcal{A}) = \sum_{n=0}^{\infty} \sum_{j=1}^{k} \frac{\partial \Psi}{\partial \alpha_j^{(n)}} \alpha_j^{(n+1)} , \tag{13.49}$$

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 (13.44). 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 (13.46) is rewritten in a form which incorporates both the parameters ε_1 and ε_2:

$$(1 - P_M)\{J_{\rm d} + \varepsilon_1 J_{\rm ex}\}\Psi = \varepsilon_2 \sum_i \sum_{j=1}^{k} \frac{\partial \Psi}{\partial \alpha_j^{(i)}} \alpha_j^{(i+1)} \tag{13.50}$$

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 (13.50), we derive:

$$\begin{aligned}(1 - P_M^{(0)})\{J_{\rm d} + \varepsilon_1 J_{\rm ex}\}\Psi_1 - \varepsilon_2 \sum_i \sum_{j=1}^{k} \frac{\partial \Psi_1}{\partial \alpha_j^{(i)}} \alpha_j^{(i+1)} = \\ -(1 - P_M^{(0)})J\Psi_{(0)} + \varepsilon_2 \sum_i \sum_{j=1}^{k} \frac{\partial \Psi_{(0)}}{\partial \alpha_j^{(i)}} \alpha_j^{(i+1)}.\end{aligned} \tag{13.51}$$

Here $P_M^{(0)}$ is a projector onto tangent bundle of the manifold $\Psi_{(0)}$. Further, we neglect two terms in 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,

$$(1 - P_M^{(0)})J_{\rm d}\Psi_1 = -(1 - P_M^{(0)})J\Psi_{(0)} + \varepsilon_2 \sum_i \sum_{j=1}^{k} \frac{\partial \Psi_{(0)}}{\partial \alpha_j^{(i)}} \alpha_j^{(i+1)} \ . \tag{13.52}$$

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

$$(1 - P_M^{(n)})J_{\rm d}\Psi_{n+1} = -(1 - P_M^{(0)})J\Psi_{(n)} + \varepsilon_2 \sum_i \sum_{j=1}^{k} \frac{\partial \Psi_{(n)}}{\partial \alpha_j^{(i)}} \alpha_j^{(i+1)} \ , \tag{13.53}$$

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

It should be noted that deriving equations (13.52) and (13.53) 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 [11], where it was shown that such modification generates iteration schemes properly converging to slow invariant manifold.

In order to gain the solvability of (13.53) an additional condition is required:

$$P_M^{(n)}\Psi_{n+1} = 0 \ . \tag{13.54}$$

This condition is sufficient to provide the existence of the solution to linear system (13.53), while the additional restriction onto the choice of the projector is required in order to guarantee the uniqueness of the solution. This condition is

$$\ker[(1 - P_M^{(n)})J_{\rm d}] \cap \ker P_M^{(n)} = \mathbf{0} \; . \tag{13.55}$$

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 (13.53) starting from the invariant manifold of the non-driven system. In other words, we choose the initial approximation $\Psi_{(0)}$ as the solution of the invariance equation (13.50) corresponding to $\varepsilon_1 = 0$ and $\varepsilon_2 = 0$:

$$(1 - P_M^{(0)})J_{\rm d}\Psi_{(0)} = 0 \; . \tag{13.56}$$

We shall return to the question how to construct solutions to this equation in the subsection "Linear zero-order equations".

The above recurrent equations (13.53), (13.54) present the Newton method for the solution of invariance equation (13.50), which involves the small parameters. A similar procedure for the Grad equations of the Boltzmann kinetic theory was used recently in [21]. When these parameters are not small, one should proceed directly with equations (13.51).

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 the 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 the projector.

Projector and Reduced Dynamics

Below we suggest the projector which is equally applicable for constructing invariant manifolds by the iteration method (13.53), (13.54) and for generating macroscopic equations on a 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 non-invariant manifold and we face the problem how to construct the dynamics on it. If the n-dimensional manifold $\widetilde{\Psi}$ is found then the macroscopic dynamics is induced by a projector P onto the tangent bundle of $\widetilde{\Psi}$ as follows [11]:

$$\frac{{\rm d}M_i^*}{{\rm d}t} = D_\Psi M_i^*\big|_{\tilde{\Psi}} \left[P J\widetilde{\Psi}\right] \; . \tag{13.57}$$

In order to specify the projector we apply 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 $\widetilde{\Psi}(M)$ by the parameters $M_i[\Psi]$. This parameterization generates associated projector $P = P_M$ by (13.48). 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 eigenvectors φ_i of the operator $J_{\rm d}$:

$$M_i[\widetilde{\Psi}] = \langle \varphi_i, \widetilde{\Psi} \rangle_{\rm s} \ ,$$

where $J_{\rm d}\varphi_i = \lambda_i \varphi_i$. The eigenvectors $\varphi_1, \ldots, \varphi_n$ are taken as a union of orthonormal basises in the eigenspaces corresponding to the eigenvalues with smallest absolute values: $0 < |\lambda_1| \leq |\lambda_2| \leq \ldots \leq |\lambda_n|$, $\langle \varphi_i, \varphi_j \rangle_{\rm s} = \delta_{ij}$. Since the function $\Psi_{\rm eq}$ is the eigenvector corresponding to the eigenvalue zero, we have: $M_i[\Psi_{\rm eq}] = \langle \varphi_i, \Psi_{\rm eq} \rangle_{\rm s} = 0$.

The associated projector P_M,

$$P_M = \sum_{i=1}^{n} \frac{\partial \widetilde{\Psi}}{\partial M_i} \langle \varphi_i, \bullet \rangle_{\rm s} \ , \tag{13.58}$$

generates the equations of the macroscopic dynamics in terms of the parameters M_i:

$$\mathrm{d}M_i/\mathrm{d}t = \langle \varphi_i P_M J\widetilde{\Psi} \rangle_{\rm s} = \langle \varphi_i J\widetilde{\Psi} \rangle_{\rm s} \ .$$

Their explicit form is

$$\frac{\mathrm{d}M_i}{\mathrm{d}t} = \lambda_i M_i + \langle J_{\rm ex}^{+}(\alpha) g_i, \widetilde{\Psi}(M) \rangle_{\rm s} \ , \tag{13.59}$$

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

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 the slowest eigenmodes the of the equation $\mathrm{d}\Psi/\mathrm{d}t = J_{\rm d}\Psi$. Thus, the projector (13.58) complies with the requirements of dissipativity and slowness in the absence the external flow.

In order to rewrite the macroscopic equations (13.59) in terms of the required set of macroparameters, $M_i^*[\Psi] = \langle m_i^*, \Psi \rangle_{\rm s}$, we use the formula (13.57) which is equivalent to the change of variables $\{M\} \to \{M^*(M)\}$, $M_i^* = \langle m_i^*, \widetilde{\Psi}(M) \rangle_{\rm s}$ in the equations (13.59). Indeed, this is seen from the relation:

$$D_\Psi M_i^*\big|_{\tilde{\Psi}} \left[P_M J\widetilde{\Psi} \right] = \sum_j \frac{\partial M_i^*}{\partial M_j} D_\Psi M_j\big|_{\tilde{\Psi}} [J\widetilde{\Psi}] \ .$$

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 (13.58) fulfills the condition (13.54) for arbitrary manifold $\Psi_{(n)} = \widetilde{\Psi}$. For this reason it is natural to use the projector (13.58) for both procedures, constructing the invariant manifold, and deriving the macroscopic equations.

We note that the above approach to defining the dynamics via the spectral projector is a specification of the concept of "thermodynamic parameterization" proposed in [9, 11].

13.5.3 Linear Zero-Order Equations

In this section we focus our attention on the solution of the zero-order invariance equation (13.56). We seek the linear invariant manifold of the form

$$\Psi_{(0)}(a) = \Psi_\mathrm{eq} + \sum_{i=1}^{n} a_i m_i \ , \tag{13.60}$$

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 the manifolds (13.60) because they may be not 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 Example.

The linear n-dimensional manifold representing the slow motion for the linear dissipative system (13.44) is associated with the 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 the subsection, "Projector and reduced dynamics", we parameterize the linear manifold $\Psi_{(0)}$ with the values of the moments $M_i[\Psi] = \langle \varphi_i, \Psi \rangle_\mathrm{s}$. We obtain the parameterization of the manifold (13.60) in terms of $a_i = M_i$,

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

The reduced dynamics in terms of variables M_i reads:

$$\frac{\mathrm{d}M_i}{\mathrm{d}t} = \lambda_i M_i + \sum_j \langle J_\mathrm{ex}^+ \varphi_i, \varphi_j \rangle_\mathrm{s} M_j + \langle J_\mathrm{ex}^+ \varphi_i, \Psi_\mathrm{eq} \rangle_\mathrm{s} \ , \tag{13.61}$$

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 $M_i^*(M) = \langle m_i^*, \Psi_{(0)}(M)\rangle_{\rm s}$ in (13.61). Resulting equations for the variables M^* are also linear:

$$\frac{{\rm d}M_i^*}{{\rm d}t} = \sum_{jkl}(B^{-1})_{ij}\Lambda_{jk}B_{kl}\Delta M_l^* + \sum_{jk}(B^{-1})_{ij}\langle J_{\rm ex}^+\varphi_j, \varphi_k\rangle_{\rm s}\Delta M_k^* + \sum_{j}(B^{-1})_{ij}\langle J_{\rm ex}^+\varphi_j, \Psi_{\rm eq}\rangle_{\rm s}\,. \tag{13.62}$$

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

13.5.4 Auxiliary Formulas. 1. Approximations to Eigenfunctions of the Fokker–Planck Operator

In this subsection we discuss the question how to find the lowest eigenvectors $\Psi_{\rm eq}m_0(Q^2)$ and $\Psi_{\rm eq}m_1(Q^2)\,\mathring{\mathbf{Q}}\mathbf{Q}$ of the operator $J_{\rm d}$ (13.38) in the classes of functions of the form: $w_0(Q)$ and $w_1(Q)\,\mathring{\mathbf{Q}}\mathbf{Q}$. The results presented in this subsection will be used below in the subsections: "Constitutive equations" and "Tests on the FENE dumbbell model".

It is directly verified that:

$$J_{\rm d}w_0 = G_0^{\rm h}w_0\,,$$
$$J_{\rm d}w_1\,\mathring{\mathbf{Q}}\mathbf{Q} = \left(G_1^{\rm h}w_1\right)\mathring{\mathbf{Q}}\mathbf{Q}\,,$$

where the operators $G_0^{\rm h}$ and $G_1^{\rm h}$ are given by:

$$G_0^{\rm h} = G_0 - \kappa H_0\,, \qquad G_1^{\rm h} = G_1 - \kappa H_1\,. \tag{13.63}$$

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

$$G_0 = \frac{1}{2}\left(\frac{\partial^2}{\partial Q^2} - fQ\frac{\partial}{\partial Q} + \frac{2}{Q}\frac{\partial}{\partial Q}\right)\,, \tag{13.64}$$

$$G_1 = \frac{1}{2}\left(\frac{\partial^2}{\partial Q^2} - fQ\frac{\partial}{\partial Q} + \frac{6}{Q}\frac{\partial}{\partial Q} - 2f\right)\,, \tag{13.65}$$

$$H_0 = \frac{2}{Q}\left(\frac{\partial^2}{\partial Q^2} - fQ\frac{\partial}{\partial Q} + \frac{2}{Q}\frac{\partial}{\partial Q}\right)\,, \tag{13.66}$$

$$H_1 = \frac{2}{Q}\left(\frac{\partial^2}{\partial Q^2} - fQ\frac{\partial}{\partial Q} + \frac{5}{Q}\frac{\partial}{\partial Q} - 2f + \frac{1}{Q^2}\right)\,. \tag{13.67}$$

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

$$\langle y, x\rangle_0 = \langle xy\rangle_{\rm e} \ ,$$

$$\langle y, x\rangle_1 = \langle xyQ^4\rangle_{\rm e} \ .$$

Here, $\langle\bullet\rangle_{\rm e}$ is the equilibrium average as defined in (13.80). For sufficiently small κ the operators $G_0^{\rm h}$ and $G_1^{\rm h}$ 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 $J_{\rm d}$ we need to find the eigenfunctions m_0 and m_1 related to the lowest nonzero eigenvalues of the operators $G_{0,1}^{\rm h}$.

Since we regard the parameter κ small it is convenient, first, to find the lowest eigenfunctions $g_{0,1}$ of the operators $G_{0,1}$ and, second, to use the standard perturbation technique in order to obtain $m_{0,1}$. For the first-order perturbation one finds [367]:

$$\begin{aligned} m_0 &= g_0 + \kappa h_0 \ , \quad h_0 = -g_0 \frac{\langle g_0 H_0 G_0 g_0\rangle_0}{\langle g_0, g_0\rangle_0} - G_0 H_0 g_0 \ ; \\ m_1 &= g_1 + \kappa h_1 \ , \quad h_1 = -g_1 \frac{\langle g_1 H_1 G_1 g_1\rangle_1}{\langle g_1, g_1\rangle_1} - G_1 H_1 g_1 \ . \end{aligned} \tag{13.68}$$

For the rest of this subsection 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 $Lambda_{0,1}$:

$$\Lambda_{0,1}[m_{0,1}] = -\frac{\langle m_{0,1}, G_{0,1}^{\rm h} m_{0,1}\rangle_{0,1}}{\langle m_{0,1}, m_{0,1}\rangle_{0,1}} \longrightarrow \min \ , \tag{13.69}$$

by means of the *gradient descent method*.

Let us denote $e_{0,1}$ the eigenfunctions of the zero eigenvalues of the operators $G_{0,1}^{\rm h}$, $e_0 = 1$ and $e_1 = 0$. Let the initial approximations $m_{0,1}^{(0)}$ to the lowest eigenfunctions $m_{0,1}$ be so chosen that $\langle m_{0,1}^{(0)}, e_{0,1}\rangle_{0,1} = 0$. We define the variational derivative $\delta\Lambda_{0,1}/\delta m_{0,1}$ and look for the correction in the form:

$$m_{0,1}^{(1)} = m_{0,1}^{(0)} + \delta m_{0,1}^{(0)} \ , \qquad \delta m_{0,1}^{(0)} = \alpha \frac{\delta\Lambda_{0,1}}{\delta m_{0,1}} \ , \tag{13.70}$$

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

$$\Delta_{0,1}^{(0)} = \frac{2}{\langle m_{0,1}^{(0)}, m_{0,1}^{(0)}\rangle_{0,1}} \left(m_{0,1}^{(0)}\lambda_{0,1}^{(0)} - G_{0,1}^{\mathrm{h}} m_{0,1}^{(0)}\right) , \tag{13.71}$$

$$\lambda_{0,1}^{(0)} = \frac{\langle m_{0,1}^{(0)}, G_{0,1}^{\mathrm{h}} m_{0,1}^{(0)}\rangle_{0,1}}{\langle m_{0,1}^{(0)}, m_{0,1}^{(0)}\rangle_{0,1}} ,$$

$$\alpha_{0,1}^{(0)} = q_{0,1} - \sqrt{q_{0,1}^2 + \frac{\langle m_{0,1}^{(0)}, m_{0,1}^{(0)}\rangle_{0,1}}{\langle \Delta_{0,1}^{(0)}, \Delta_{0,1}^{(0)}\rangle_{0,1}}} ,$$

$$q_{0,1} = \frac{1}{\langle \Delta_{0,1}^{(0)}, \Delta_{0,1}^{(0)}\rangle_{0,1}} \left(\frac{\langle m_{0,1}^{(0)}, G_{0,1}^{\mathrm{h}} m_{0,1}^{(0)}\rangle_{0,1}}{\langle m_{0,1}^{(0)}, m_{0,1}^{(0)}\rangle_{0,1}} - \frac{\langle \Delta_{0,1}^{(0)}, G_{0,1}^{\mathrm{h}} \Delta_{0,1}^{(0)}\rangle_{0,1}}{\langle \Delta_{0,1}^{(0)}, \Delta_{0,1}^{(0)}\rangle_{0,1}} \right) .$$

With the new correction $m_{0,1}^{(1)}$, we can repeat the procedure and eventually generate recurrence scheme. Since by the construction all iterative approximations $m_{0,1}^{(n)}$ remain orthogonal to the 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 $e_{0,1}$. (Note that this method resembles the relaxation method, Chap. 9.)

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 a relative error for controlling the convergence of the iteration procedure (13.70).

13.5.5 Auxiliary Formulas. 2. Integral Relations

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

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

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

$$\int_\Omega s(x^2)\,\mathring{\mathbf{x}}\mathring{\mathbf{x}}\,(\mathring{\mathbf{x}}\mathring{\mathbf{x}} : \mathbf{A})(\mathring{\mathbf{x}}\mathring{\mathbf{x}} : \boldsymbol{B})(\mathring{\mathbf{x}}\mathring{\mathbf{x}} : \boldsymbol{C})\,\mathrm{d}\boldsymbol{x} =$$

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

13.5.6 Microscopic Derivation of Constitutive Equations

Iteration Scheme

In this section we apply the above developed formalism to the elastic dumbbell model (13.30). External field variables α are the components of the tensor $\widehat{\mathbf{k}}$.

Since we aim at constructing a closed description for the stress tensor $\boldsymbol{\tau}$ (13.31) with the six independent components, the relevant manifold in the problem should be six-dimensional. Moreover, we allow a dependence of the manifold on the material derivatives of the tensor $\widehat{\mathbf{k}}$: $\widehat{\mathbf{k}}^{(i)} = D^i\boldsymbol{k}/Dt^i$. Let $\Psi^*(M,\mathcal{K})\quad \mathcal{K} = \{\widehat{\mathbf{k}}, \widehat{\mathbf{k}}^{(1)}, \ldots\}$ be the desired manifold parameterized by the six variables $M_i\quad i = 1,\ldots,6$ and the independent components (maximum eight for each $\widehat{\mathbf{k}}^{(l)}$) of the tensors $\widehat{\mathbf{k}}^{(l)}$. Small parameters ε_1 and ε_2, introduced in the section: "The problem of reduced description in polymer dynamics", are established by (13.43). We then write the invariance equation:

$$(1 - P_M)(J_\mathrm{d} + \varepsilon_1 J_\mathrm{h})\Psi = \varepsilon_2 \sum_{i=0}^{\infty} \sum_{lm} \frac{\partial \Psi}{\partial \widehat{k}_{lm}^{(i)}} \widehat{k}_{lm}^{(i+1)} \,, \tag{13.72}$$

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

Following the further steps of the procedure we obtain the recurrent equations:

$$(1 - P_M^{(n)})J_\mathrm{d}\Psi_{n+1} = -(1 - P_M^{(n)})[J_\mathrm{d} + \varepsilon_1 J_\mathrm{h}]\Psi_{(n)} + \varepsilon_2 \sum_{i} \sum_{lm} \frac{\partial \Psi_{(n)}}{\partial \widehat{k}_{lm}^{(i)}} \widehat{k}_{lm}^{(i+1)} \,, \tag{13.73}$$

$$P_M^{(n)}\Psi_{n+1} = 0 \,, \tag{13.74}$$

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 the equation:

$$(1 - P_M^{(0)})J_\mathrm{d}\Psi_{(0)} = 0 \tag{13.75}$$

We construct zero-order manifold $\Psi_{(0)}$ in the subsection, "Zero-order constitutive equation".

The Dynamics in the General Form

Let us assume that some approximation to invariant manifold $\widetilde{\Psi}(a,\mathcal{K})$ is found (here $a = \{a_1,\ldots,a_6\}$ are some coordinates on this manifold). The next step is the constructing of 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 $J_{\rm d}$. We shall always assume in the sequel that the hydrodynamic interaction parameter κ is small enough so that the dissipativity of $J_{\rm d}$ (13.40) is not violated.

Let us consider two classes of functions: $\mathcal{C}_1 = \{w_0(Q^2)\}$ and $\mathcal{C}_2 = \{w_1(Q^2)\ \overset{\circ}{\mathbf{QQ}}\}$, where $w_{0,1}$ are functions of Q^2 and the notation $\circ$ indicates the traceless part, e.g. for the dyad $\boldsymbol{QQ}$:

$$(\overset{\circ}{\mathbf{QQ}})_{ij} = Q_i Q_j - \frac{1}{3}\delta_{ij} Q^2 \ .$$

Since the sets $\mathcal{C}_1$ and $\mathcal{C}_2$ are invariant with respect to operator $J_{\rm d}$, i.e. $J_{\rm d}\mathcal{C}_1 \subset \mathcal{C}_1$ and $J_{\rm d}\mathcal{C}_2 \subset \mathcal{C}_2$, and densities $\boldsymbol{FQ} = f\ \overset{\circ}{\mathbf{QQ}} + (1/3)\mathbf{1} f Q^2$ of the moments comprising the stress tensor $\boldsymbol{\tau}_p$ (13.32) belong to the space $\mathcal{C}_1 \oplus \mathcal{C}_2$, we shall seek the desired eigenvectors in the classes $\mathcal{C}_1$ and $\mathcal{C}_2$. Namely, we intend to find one lowest isotropic eigenvector $\Psi_{\rm eq} m_0(Q^2)$ of the eigenvalue $-\lambda_0$ ($\lambda_0 > 0$) and five nonisotropic eigenvectors $m_{ij} = \Psi_{\rm eq} m_1(Q^2)(\overset{\circ}{\mathbf{QQ}})_{ij}$ corresponding to another eigenvalue $-\lambda_1$ ($\lambda_1 > 0$). The method of derivation and analytic evaluation of these eigenvalues were discussed in the subsection "Auxiliary formulas, 1". For now we assume that these eigenvectors are known.

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

$$\begin{aligned} M_0 &= \langle \Psi_{\rm eq} m_0, \widetilde{\Psi} \rangle_{\rm s} = \int m_0 \widetilde{\Psi}\, {\rm d}\boldsymbol{Q} \ , \\ \overset{\circ}{\mathbf{M}} &= \langle \Psi_{\rm eq} m_1\ \overset{\circ}{\mathbf{QQ}}, \widetilde{\Psi} \rangle_{\rm s} = \int m_1\ \overset{\circ}{\mathbf{QQ}}\ \widetilde{\Psi}\, {\rm d}\boldsymbol{Q} \ . \end{aligned} \tag{13.76}$$

Once the desired parameterization $\widetilde{\Psi}(M_0, \overset{\circ}{\mathbf{M}}, \mathcal{K})$ is obtained, the dynamic equations are found as:

$$\begin{aligned} &\frac{DM_0}{D\widehat{t}} + \lambda_0 M_0 = \left\langle (\hat{\dot{\boldsymbol{\gamma}}} : \overset{\circ}{\mathbf{QQ}}) m_0' \right\rangle \\ &\overset{\circ}{\mathbf{M}}_{[1]} + \lambda_1\ \overset{\circ}{\mathbf{M}} = -\frac{1}{3}\mathbf{1}\hat{\dot{\boldsymbol{\gamma}}} : \overset{\circ}{\mathbf{M}} - \frac{1}{3}\hat{\dot{\boldsymbol{\gamma}}}\, \langle m_1 Q^2 \rangle + \left\langle \overset{\circ}{\mathbf{QQ}}\ (\hat{\dot{\boldsymbol{\gamma}}} : \overset{\circ}{\mathbf{QQ}}) m_1' \right\rangle \ , \end{aligned} \tag{13.77}$$

where all averages are calculated with the distribution function $\widetilde{\Psi}$, i.e. $\langle \bullet \rangle = \int \bullet \widetilde{\Psi}\, {\rm d}\boldsymbol{Q}$, $m_{0,1}' = {\rm d}m_{0,1}(Q^2)/{\rm d}(Q^2)$ and the subscript [1] represents the upper convective derivative of a tensor:

$$\boldsymbol{\Lambda}_{[1]} = \frac{D\boldsymbol{\Lambda}}{D\widehat{t}} - \left\{ \widehat{\mathbf{k}} \cdot \boldsymbol{\Lambda} + \boldsymbol{\Lambda} \cdot \widehat{\mathbf{k}}^{\dagger} \right\} \ .$$

The parameters $\lambda_{0,1}$, which are the absolute values of eigenvalues of the operator $J_{\rm d}$, are calculated from the formulas (for the definition of operators G_1 and G_2 see subsection "Auxiliary formulas, 1"):

$$\lambda_0 = -\frac{\langle m_0 G_0 m_0 \rangle_{\rm e}}{\langle m_0 m_0 \rangle_{\rm e}} > 0 \,, \tag{13.78}$$

$$\lambda_1 = -\frac{\langle Q^4 m_1 G_1 m_1 \rangle_{\rm e}}{\langle m_1 m_1 Q^4 \rangle_{\rm e}} > 0 \,, \tag{13.79}$$

where we have introduced the notation for the equilibrium average:

$$\langle y \rangle_{\rm e} = \int \Psi_{\rm eq} y \, {\rm d}\boldsymbol{Q} \,. \tag{13.80}$$

Equations for the components of the polymeric stress tensor $\boldsymbol{\tau}_{\rm p}$ (13.32) are constructed as a change of variables $\{M_0, \overset{\circ}{\mathbf{M}}\} \to \boldsymbol{\tau}_{\rm p}$. The use of the projector $\widetilde{P}$ makes this operation straightforward:

$$\frac{D\boldsymbol{\tau}_{\rm p}}{D\widehat{t}} = -nk_{\rm B}T \int \boldsymbol{F}\boldsymbol{Q}\widetilde{P}J\widetilde{\Psi}(M_0(\boldsymbol{\tau}_{\rm p}, \mathcal{K}), \overset{\circ}{\mathbf{M}}(\boldsymbol{\tau}_{\rm p}, \mathcal{K}), \mathcal{K}) \, {\rm d}\boldsymbol{Q} \,. \tag{13.81}$$

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

$$\widetilde{P} = \frac{\partial \widetilde{\Psi}}{\partial M_0} \langle \Psi_{\rm eq} m_0, \bullet \rangle_{\rm s} + \sum_{kl} \frac{\partial \widetilde{\Psi}}{\partial \, \overset{\circ}{\mathbf{M}}_{kl}} \langle \Psi_{\rm eq} m_1 (\overset{\circ}{\mathbf{Q}}\mathbf{Q})_{kl}, \bullet \rangle_{\rm s} \,. \tag{13.82}$$

We note that sometimes it is easier to make a transition to the variables $\boldsymbol{\tau}_{\rm p}$ after solving the equations (13.77) rather than to construct explicitly and solve equations in terms of $\boldsymbol{\tau}_{\rm p}$. This allows to avoid inverting the functions $\boldsymbol{\tau}_{\rm p}(M_0, \overset{\circ}{\mathbf{M}})$ and to deal with simpler equations.

Zero-Order Constitutive Equation

In this subsection we derive the closed constitutive equations based on the zero-order manifold $\Psi_{(0)}$ found as the appropriate solution to (13.75). Following the approach described in subsection, "Linear zero-order equations", we construct such a solution as the linear expansion near the equilibrium state $\Psi_{\rm eq}$ (13.60). After parameterization by the values of the variables M_0 and $\overset{\circ}{\mathbf{M}}$ associated with the eigenvectors $\Psi_{\rm eq} m_0$ and $\Psi_{\rm eq} m_1 \, \overset{\circ}{\mathbf{Q}}\mathbf{Q}$ we find:

$$\Psi_{(0)} = \Psi_{\rm eq} \left(1 + M_0 \frac{m_0}{\langle m_0 m_0 \rangle_{\rm e}} + \frac{15}{2} \, \overset{\circ}{\mathbf{M}} \colon \overset{\circ}{\mathbf{Q}}\mathbf{Q} \, \frac{m_1}{\langle m_1 m_1 Q^4 \rangle_{\rm e}} \right) \,. \tag{13.83}$$

With the help of the projector (13.82):

$$P^{(0)}_M = \Psi_{\rm eq} \left\{ \frac{m_0}{\langle m_0 m_0 \rangle_{\rm e}} \langle m_0, \bullet \rangle_{\rm e} + \frac{15}{2} \frac{m_1}{\langle m_1 m_1 Q^4 \rangle_{\rm e}} \, \overset{\circ}{\mathbf{Q}}\mathbf{Q} : \langle m_1 \, \overset{\circ}{\mathbf{Q}}\mathbf{Q}, \bullet \rangle_{\rm e} \right\} \tag{13.84}$$

and using the formula (13.81) we obtain:

$$\frac{D\mathrm{tr}\boldsymbol{\tau}_{\mathrm{p}}}{D\widehat{t}} + \lambda_0 \mathrm{tr}\boldsymbol{\tau}_{\mathrm{p}} = a_0 \left(\overset{\circ}{\boldsymbol{\tau}}_{\mathrm{p}} : \hat{\dot{\boldsymbol{\gamma}}}\right), \tag{13.85}$$

$$\overset{\circ}{\boldsymbol{\tau}}_{p[1]} + \lambda_0 \overset{\circ}{\boldsymbol{\tau}}_{\mathrm{p}} = b_0 \left[\overset{\circ}{\boldsymbol{\tau}}_{\mathrm{p}} \cdot \hat{\dot{\boldsymbol{\gamma}}} + \hat{\dot{\boldsymbol{\gamma}}} \cdot \overset{\circ}{\boldsymbol{\tau}}_{\mathrm{p}}\right] - \frac{1}{3}\mathbf{1}(\overset{\circ}{\boldsymbol{\tau}}_{\mathrm{p}} : \hat{\dot{\boldsymbol{\gamma}}}) + (b_1 \mathrm{tr}\boldsymbol{\tau}_{\mathrm{p}} - b_2 n k_{\mathrm{B}} T)\hat{\dot{\boldsymbol{\gamma}}} ,$$

where the constants b_i, a_0 are defined by the following equilibrium averages:

$$\begin{aligned}
a_0 &= \frac{\langle f m_0 Q^2\rangle_{\mathrm{e}} \langle m_0 m_1 Q^4 m_1'\rangle_{\mathrm{e}}}{\langle f m_0 Q^4\rangle_{\mathrm{e}} \langle m_0^2\rangle_{\mathrm{e}}} , \\
b_0 &= \frac{2}{7}\frac{\langle m_1 m_2' Q^6\rangle_{\mathrm{e}}}{\langle m_1^2 Q^4\rangle_{\mathrm{e}}} , \\
b_1 &= \frac{1}{15}\frac{\langle f m_1 Q^4\rangle_{\mathrm{e}}}{\langle f m_0 Q^2\rangle_{\mathrm{e}}} \left\{ 2\frac{\langle m_0 m_2' Q^4\rangle_{\mathrm{e}}}{\langle m_1^2 Q^4\rangle_{\mathrm{e}}} + 5\frac{\langle m_0 m_1 Q^2\rangle_{\mathrm{e}}}{\langle m_1 m_1 Q^4\rangle_{\mathrm{e}}} \right\} , \\
b_2 &= \frac{1}{15}\frac{\langle f m_1 Q^4\rangle_{\mathrm{e}}}{\langle m_1 m_1 Q^4\rangle_{\mathrm{e}}} \left\{ 2\langle m_2' Q^4\rangle_{\mathrm{e}} + 5\langle m_1 Q^2\rangle_{\mathrm{e}} \right\} .
\end{aligned} \tag{13.86}$$

We remind that $m_{0,1}' = \partial m_{0,1}/\partial(Q^2)$. These formulas were obtained using the auxiliary results from subsection "Auxiliary formulas, 2".

Revised Oldroyd 8 Constant Constitutive Equation for the Stress

It is remarkable that when rewritten in terms of the full stresses, $\boldsymbol{\tau} = -\nu_{\mathrm{s}}\dot{\boldsymbol{\gamma}} + \boldsymbol{\tau}_{\mathrm{p}}$, the dynamic system (13.85) takes the form:

$$\begin{aligned}
\boldsymbol{\tau} + c_1\boldsymbol{\tau}_{[1]} + c_3\{\dot{\boldsymbol{\gamma}}\cdot\boldsymbol{\tau} + \boldsymbol{\tau}\cdot\dot{\boldsymbol{\gamma}}\} + c_5(\mathrm{tr}\boldsymbol{\tau})\dot{\boldsymbol{\gamma}} + \mathbf{1}\,(c_6\boldsymbol{\tau} : \dot{\boldsymbol{\gamma}} + c_8\mathrm{tr}\boldsymbol{\tau}) \\
= -\nu\left\{\dot{\boldsymbol{\gamma}} + c_2\dot{\boldsymbol{\gamma}}_{[1]} + c_4\dot{\boldsymbol{\gamma}}\cdot\dot{\boldsymbol{\gamma}} + c_7(\dot{\boldsymbol{\gamma}} : \dot{\boldsymbol{\gamma}})\mathbf{1}\right\} ,
\end{aligned} \tag{13.87}$$

where the parameters ν, c_i are given by the following relationships:

$$\begin{aligned}
&\nu = \lambda_{\mathrm{r}}\nu_{\mathrm{s}}\mu , \qquad \mu = 1 + nk_{\mathrm{B}}T\lambda_1 b_2/\nu_{\mathrm{s}} , \\
&c_1 = \lambda_{\mathrm{r}}/\lambda_1 , \qquad c_2 = \lambda_{\mathrm{r}}/(\mu\lambda_1) , \\
&c_3 = -b_0\lambda_{\mathrm{r}}/\lambda_0 , \qquad c_4 = -2b_0\lambda_{\mathrm{r}}/(\mu\lambda_1) , \\
&c_5 = \frac{\lambda_{\mathrm{r}}}{3\lambda_1}(2b_0 - 3b_1 - 1) , \qquad c_6 = \frac{\lambda_{\mathrm{r}}}{\lambda_1}(2b_0 + 1 - a_0) , \\
&c_7 = \frac{\lambda_{\mathrm{r}}}{\lambda_1\mu}(2b_0 + 1 - a_0) , \qquad c_8 = \frac{1}{3}(\lambda_0/\lambda_1 - 1) .
\end{aligned} \tag{13.88}$$

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

Note that all the parameters (13.88) are related to the entropic spring law f due to (13.86). Thus, the constitutive relation for the stress $\boldsymbol{\tau}$ (13.87) is fully derived from the microscopic kinetic model.

If the constant c_8 were equal to zero, then (13.87) would be recognized as *the Oldroyd 8 constant* model [362], proposed by Oldroyd about 40 years ago on a phenomenological basis. Nonzero value of c_8 indicates a difference between $\lambda_{\mathrm{r}}/\lambda_0$ and $\lambda_{\mathrm{r}}/\lambda_1$ which are the relaxation times of trace $\mathrm{tr}\,\boldsymbol{\tau}$ and of the traceless components $\overset{\circ}{\boldsymbol{\tau}}$ of the stress tensor $\boldsymbol{\tau}$.

Higher-Order Constitutive Equations

In this subsection we discuss some properties of corrections to the revised Oldroyd 8 constant constitutive equation (that is, the zero-order model) (13.87). Let $P_M^{(0)}$ (13.84) be the projector onto the zero-order manifold $\Psi_{(0)}$ (13.83). The invariance equation (13.73) for the first-order correction $\Psi_{(1)} = \Psi_{(0)} + \Psi_1$ takes the form:

$$\begin{aligned} L\Psi_1 &= -\left(1 - P_M^{(0)}\right)(J_{\mathrm{d}} + J_{\mathrm{h}})\Psi_{(0)} \\ P_M^{(0)}\Psi_1 &= 0 \end{aligned} \tag{13.89}$$

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

$$\begin{aligned} \Psi_1 = \Psi_{\mathrm{eq}}\Big\{ & z_0 M_0(\dot{\boldsymbol{\gamma}} : \overset{\circ}{\mathbf{Q}}\overset{\circ}{\mathbf{Q}}) + z_1(\overset{\circ}{\mathbf{M}}{:}\overset{\circ}{\mathbf{Q}}\overset{\circ}{\mathbf{Q}})(\dot{\boldsymbol{\gamma}} : \overset{\circ}{\mathbf{Q}}\overset{\circ}{\mathbf{Q}}) \\ & + z_2\{\dot{\boldsymbol{\gamma}}\cdot\overset{\circ}{\mathbf{M}} + \overset{\circ}{\mathbf{M}}\cdot\dot{\boldsymbol{\gamma}}\} : \overset{\circ}{\mathbf{Q}}\overset{\circ}{\mathbf{Q}} + z_3\dot{\boldsymbol{\gamma}} : \overset{\circ}{\mathbf{M}} + \frac{1}{2}\dot{\boldsymbol{\gamma}} : \overset{\circ}{\mathbf{Q}}\overset{\circ}{\mathbf{Q}}\Big\}\ . \end{aligned} \tag{13.90}$$

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 $\overset{\circ}{\mathbf{M}}$;
- 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:

$$\begin{aligned} -\frac{\overset{\circ}{\boldsymbol{\tau}}_{\mathrm{p}}}{nk_{\mathrm{B}}T} &= r_0\,\overset{\circ}{\mathbf{M}} + r_1 M_0\dot{\boldsymbol{\gamma}} + r_2\{\dot{\boldsymbol{\gamma}}\cdot\overset{\circ}{\mathbf{M}} + \overset{\circ}{\mathbf{M}}\cdot\dot{\boldsymbol{\gamma}}\} + r_3\,\dot{\boldsymbol{\gamma}}\cdot\overset{\circ}{\dot{\boldsymbol{\gamma}}}\ , \\ -\frac{\mathrm{tr}\boldsymbol{\tau}_{\mathrm{p}}}{nk_{\mathrm{B}}T} &= p_0 M_0 + p_1\dot{\boldsymbol{\gamma}} : \overset{\circ}{\mathbf{M}}\ , \end{aligned} \tag{13.91}$$

where r_i and p_i are some constants. Finally, the equations in terms of $\boldsymbol{\tau}$ should be also linear. It can be shown that the first-order correction to the modified Oldroyd 8 constants model (13.87) will be transformed into the equations of the following general structure:

$$\boldsymbol{\tau} + c_1\boldsymbol{\tau}_{[1]} + \left\{\boldsymbol{\Gamma}_1 \cdot \boldsymbol{\tau} \cdot \boldsymbol{\Gamma}_2 + \boldsymbol{\Gamma}_2^{\dagger} \cdot \boldsymbol{\tau} \cdot \boldsymbol{\Gamma}_1^{\dagger}\right\} + \boldsymbol{\Gamma}_3(\mathrm{tr}\boldsymbol{\tau}) + \boldsymbol{\Gamma}_4(\boldsymbol{\Gamma}_5 : \boldsymbol{\tau}) = -\nu_0\boldsymbol{\Gamma}_6 \,, \tag{13.92}$$

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 (13.88) and ν_0 is a positive constant.

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

1. Since the manifold (13.90) does not depend on the vorticity tensor $\omega = \boldsymbol{k} - \boldsymbol{k}^{\dagger}$, the latter enters the equations (13.92) only via convective derivatives of $\boldsymbol{\tau}$ and $\dot{\boldsymbol{\gamma}}$. This is sufficient to acquire the frame indifference, since all the tensorial quantities in dynamic equations are indifferent in any time dependent reference frame [361].
2. When $\boldsymbol{k} = 0$, the first order equations (13.92) as well as equations for any order reduce to linear relaxation dynamics of slow modes:

$$\frac{D\overset{\circ}{\boldsymbol{\tau}}}{Dt} + \frac{\lambda_1}{\lambda_{\mathrm{r}}}\overset{\circ}{\boldsymbol{\tau}} = 0 \,,$$
$$\frac{D\mathrm{tr}\boldsymbol{\tau}}{Dt} + \frac{\lambda_0}{\lambda_{\mathrm{r}}}\mathrm{tr}\boldsymbol{\tau} = 0,$$

   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 $\overset{\circ}{\mathbf{M}}[\Psi]$ is used in every step. It follows that the resulting constitutive equations will always take a linear form (13.92), where all tensors $\boldsymbol{\Gamma}_i$ depend on higher order convective derivatives of $\dot{\boldsymbol{\gamma}}$ (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 (13.73).
4. When the force $\boldsymbol{F}$ is linear, $\boldsymbol{F} = \boldsymbol{Q}$, we are led to Oldroyd-B model ((13.87) 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 correspond to the simple dyad $\Psi_{\mathrm{eq}}\boldsymbol{QQ}$.

13.5.7 Tests on the FENE Dumbbell Model

In this section we specify the choice of the force law as the FENE spring (13.35), and present results of test calculations for the revised Oldroyd 8 constants (13.85) equations on the examples of two simple viscometric flows.

We introduce the extensibility parameter of FENE dumbbell model b:

$$b = \widehat{\mathbf{Q}}_0^{\,2} = \frac{H\boldsymbol{Q}_0^2}{k_{\mathrm{B}}T} \,. \tag{13.93}$$

It was estimated [151] 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 equation.

In our test calculations we compare our results with the Brownian dynamic (BD) simulation data made on FENE dumbbell equations [363], and also with one popular approximation to the FENE model known as *FENE-P* (FENE-Peterelin) model [151, 364, 365]. The latter is obtained by selfconsistent approximation to the FENE force:

$$\boldsymbol{F} = \frac{1}{1 - \langle \boldsymbol{Q}^2 \rangle / b} \boldsymbol{Q} \,. \tag{13.94}$$

This force law, like the Hookean case, allows the exact moment closure leading to nonlinear constitutive equations [151,365]. Specifically, we use the modified variant of the FENE-P model, which matches the dynamics of the original FENE near equilibrium better than the classical variant. This is achieved by a slight modification of Kramers definition of the stress tensor:

$$\boldsymbol{\tau}_{\mathrm{p}} = nk_{\mathrm{B}}T(1 - \theta b)\mathbf{1} - \langle \boldsymbol{F}\boldsymbol{Q} \rangle \,. \tag{13.95}$$

The case $\theta = 0$ gives the classical definition of FENE-P, while a more thorough estimation [354, 365] is $\theta = (b(b+2))^{-1}$.

Constants

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

In order to find constants for the zero-order model (13.85) we do the following: First, we analytically compute the lowest eigenfunctions of operator J_{d}: $g_1(Q^2)\ \overset{\circ}{\mathbf{Q}\mathbf{Q}}$ and $g_0(Q^2)$ without hydrodynamic interaction ($\kappa = 0$). The functions g_0 and g_1 were computed by a procedure presented in Subsect. "Auxiliary formulas, 1" with the help of the *Maple V.3* [366]. Second, we

calculate the perturbations terms $h_{0,1}$ by formulas (13.68) introducing the account of hydrodynamic interaction. Table 13.1 presents the constants $\lambda_{0,1}$, a_i, b_i (13.79) (13.86) of the zero-order model (13.85) without hydrodynamic interaction ($\kappa = 0$) for several values of extensibility parameter b. The relative error $\delta_{0,1}$ (see Subsect. "Auxiliary formulas, 1") of approximation for these calculations did not exceed the value 0.02. Table 13.2 shows the linear correction terms for constants from Table 13.1 which take into account the hydrodynamic interaction: $\lambda^{\rm h}_{0,1} = \lambda_{0,1}(1 + \kappa(\delta\lambda_{0,1}))$, $a^{\rm h}_i = a_i(1 + \kappa(\delta a_i))$, $b^{\rm h}_i = b_i(1 + \kappa(\delta b_i))$. The latter are calculated by substituting the perturbed functions $m_{0,1} = g_{0,1} + \kappa h_{0,1}$ into (13.79) and (13.86), 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.

Table 13.1. 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 13.2. 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

Dynamic Problems

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

$$\boldsymbol{k}(t) = \dot\gamma(t) \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \tag{13.96}$$

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

$$\boldsymbol{k}(t) = \dot{\varepsilon}(t) \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & -1/2 \end{bmatrix} , \tag{13.97}$$

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

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

$$\widehat{\nu} = \frac{\nu - \nu_{\rm s}}{nk_{\rm B}T\lambda_{\rm r}} = -\frac{\boldsymbol{\tau}_{\rm p,12}}{\overline{\gamma} nk_{\rm B}T}, \tag{13.98}$$

$$\widehat{\psi}_1 = \frac{\psi_1}{nk_{\rm B}T\lambda_{\rm r}^2} = \frac{\boldsymbol{\tau}_{\rm p,22} - \boldsymbol{\tau}_{\rm p,11}}{\overline{\gamma}^2 nk_{\rm B}T} , \tag{13.99}$$

$$\widehat{\psi}_2 = \frac{\psi_2}{nk_{\rm B}T\lambda_{\rm r}^2} = \frac{\boldsymbol{\tau}_{p,33} - \boldsymbol{\tau}_{p,22}}{\overline{\gamma}^2 nk_{\rm B}T} , \tag{13.100}$$

$$\vartheta = \frac{\bar{\nu} - 3\nu_{\rm s}}{nk_{\rm B}T\lambda_{\rm r}} = \frac{\boldsymbol{\tau}_{\rm p,22} - \boldsymbol{\tau}_{\rm p,11}}{\bar{\varepsilon} nk_{\rm B}T} , \tag{13.101}$$

where $\overline{\gamma} = \dot{\gamma}\lambda_{\rm r}$ and $\bar{\varepsilon} = \dot{\varepsilon}\lambda_{\rm r}$ are dimensionless shear and elongation rates. Characteristic values of the latter parameters $\overline{\gamma}$ and $\bar{\varepsilon}$ allow to estimate the parameter ε_1 (13.43). 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: $\dot{\gamma} = const$, $\dot{\varepsilon} = const$. For the shear flow the steady values of these functions are found from (13.85) as follows:

$$\widehat{\nu} = b_2/(\lambda_1 - c\overline{\gamma}^2) , \qquad \widehat{\psi}_1 = 2\widehat{\nu}/\lambda_1 , \qquad \widehat{\psi}_2 = 2b_0\widehat{\nu}/\lambda_1 ,$$

where $c = 2/3(2b_0^2 + 2b_0 - 1)/\lambda_1 + 2b_1a_0/\lambda_0$. Estimations for the constants (see Table I) show that $c \le 0$ for all values of b (case $c = 0$ corresponds to $b = \infty$), thus all three functions are monotonically decreasing in absolute value with the increase of $\overline{\gamma}$, besides the case $b = \infty$. Although they qualitatively correctly predict the shear thinning for large shear rates due to a power law, but the exponent -2 in the limit of large $\overline{\gamma}$ deviations from the values -0.66 for $\widehat{\nu}$ and -1.33 for $\widehat{\psi}_1$ observed in Brownian dynamic simulations [363]. It is explained by the fact that slopes of shear thining lie out of the applicability domain of our model. A comparison with BD simulations and modified FENE-P model is shown in Fig. 13.1.

The predictions for the second normal stress coefficient indicate one more difference between the revised Oldroyd 8 constant equation and FENE-P model. FENE-P model shows zero values for $\widehat{\psi}_2$ in any shear flow, either steady or time dependent, while the model (13.85), as well as BD simulations (see Fig. 9 in [363]) predict small, but nonvanishing values for this quantity. Namely, due to the model (13.85) in shear flows the following relation $\widehat{\psi}_2 =$

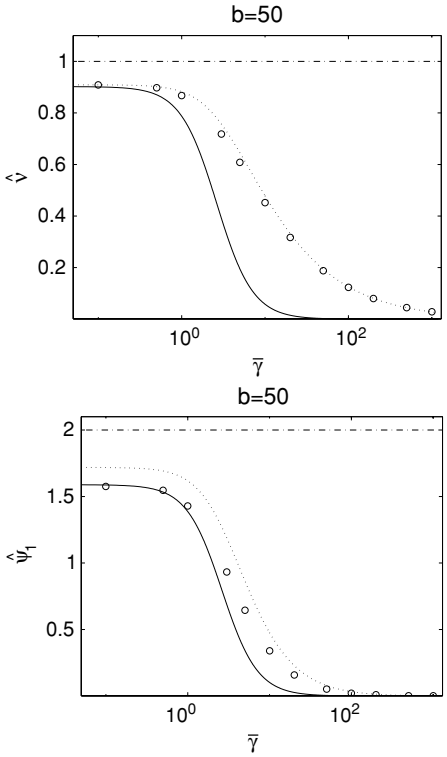

Fig. 13.1. Dimensionless shear viscosity $\widehat{\nu}$ and first normal stress coefficient $\widehat{\psi}_1$ vs. shear rate: (———) revised Oldroyd 8 constant model; (· · · · · ·) FENE-P model; (∘ ∘ ∘) BD simulations on the FENE model; (– · – · –) Hookean dumbbell model

$b_0\widehat{\psi}_1$ is always valid, with proportionality coefficient b_0 small and mostly negative, which leads to small and mostly negative values of $\widehat{\psi}_2$.

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

$$\vartheta = \frac{3b_2}{\lambda_1 - \frac{5}{6}(2b_0+1)\bar{\varepsilon} - 7b_1a_0\bar{\varepsilon}^2/\lambda_0} \,. \tag{13.102}$$

The denominator has one root on positive semi-axis

$$\bar{\varepsilon}_* = -\frac{5\lambda_0(2b_0+1)}{84b_1a_0} + \left(\left(\frac{5\lambda_0(2b_0+1)}{84b_1a_0}\right)^2 + \frac{\lambda_1\lambda_0}{7b_1a_0}\right)^{1/2} , \tag{13.103}$$

which defines a singularity point for the dependence $\vartheta(\bar{\varepsilon})$. The BD simulations [363] on the FENE dumbbell models shows that there is no divergence of elongation viscosity for all values of elongation rate (see Fig. 13.2). For the Hookean spring, $\bar{\varepsilon}_* = 1/2$ while in our model (13.85) the singularity

Table 13.3. Singular values of elongation rate

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

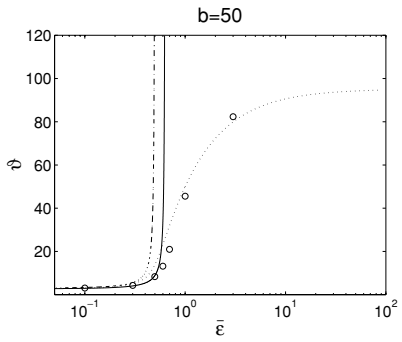

Fig. 13.2. Dimensionless elongation viscosity vs. elongation rate: (———) revised Oldroyd 8 constant model, (· · · · · ·) FENE-P model, (∘ ∘ ∘) BD simulations on the FENE model; (– · – · –) Hookean dumbbell model

point shifts to higher values with respect to decreasing values of b as it is demonstrated in Table 13.3.

The Fig. 13.3 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 $\overline{\varepsilon} = 0$ to the value $\overline{\varepsilon} = 0.3$.

It is possible to conclude that the revised Oldroyd 8 constants model (13.85) with estimations given by (13.86) for small and moderate rates of strain up to $\varepsilon_1 = \lambda_r|\dot{\boldsymbol{\gamma}}|/(2\lambda_1) \sim 0.5$ yields a good approximation to the 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.

13.5.8 The Main Results of this Example are as Follows:

(i) We have developed a systematic method of constructing constitutive equations from the kinetic models of polymeric solutions. The method is free from a'priori assumptions about the form of the spring force and is consistent with the basic physical requirements: frame invariance and dissipativity of the internal motions of the fluid. The method extends the method of invariant manifold onto equations coupled with external fields. Two characteristic parameters of fluid flows were distinguished in order to account for the effect of the presence of external fields. The

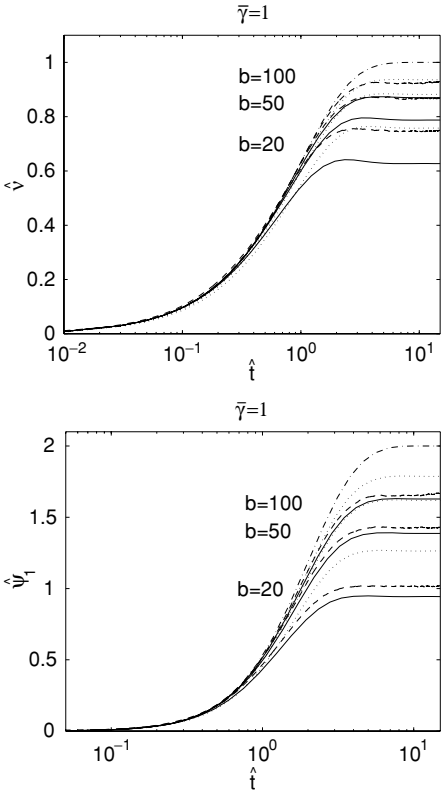

Fig. 13.3. Time evolution of elongation viscosity after inception of the elongation flow with elongation rate $\bar{\varepsilon} = 0.3$: (———) revised Oldroyd 8 constant model, (· · · · · ·) FENE-P model, (– – –) BD simulations on FENE model; (– · – · –) Hookean dumbbell model

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 models 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 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.

13.6 Example: Explosion of Invariant Manifold, Limits of Macroscopic Description for Polymer Molecules, Molecular Individualism, and Multimodal Distributions

Derivation of macroscopic equations from the simplest dumbbell models is revisited [109]. It is demonstrated that the onset of the macroscopic description is sensitive to the flows. For the FENE-P model, small deviations from the Gaussian solution undergo a slow relaxation before the macroscopic description sets on. Some consequences of these observations are discussed. A new class of closures is discussed, the *kinetic multipeak polyhedra.* Distributions of this type are expected in kinetic models with a multidimensional instability as universally, as the Gaussian distribution appears for stable systems. The number of possible relatively stable states of a nonequilibrium system grows as 2^m, and the number of macroscopic parameters is in order mn, where n is the dimension of configuration space, and m is the number of independent unstable directions in this space. The elaborated class of closures and equations describes effects of "molecular individualism".

13.6.1 Dumbbell Models and the Problem of the Classical Gaussian Solution Stability

We shall again consider the simplest case of dilute polymer solutions represented by dumbbell models. The dumbbell model reflects the two features of real-world macromolecules to be orientable and stretchable by a flowing solvent [151].

Let us consider the simplest one-dimensional kinetic equation for the configuration distribution function $\Psi(q,t)$, where q is the reduced vector connecting the beads of the dumbbell. This equation is slightly different from the usual Fokker–Planck equation. It is nonlinear, because of the dependence of potential energy U on the moment $M_2[\Psi] = \int q^2\Psi(q)\,\mathrm{d}q$. This dependence allows us to get the exact quasiequilibrium equations on M_2, but these equations are not always solving the problem: this quasiequilibrium manifold may become unstable when the flow is present [109]. Here is this model:

$$\partial_t \Psi = -\partial_q \{\alpha(t) q \Psi\} + \frac{1}{2}\partial_q^2 \Psi \ . \tag{13.104}$$

Here

$$\alpha(t) = \kappa(t) - \frac{1}{2} f(M_2(t)) \ , \tag{13.105}$$

$\kappa(t)$ is the given time-dependent velocity gradient, t is the reduced time, and the function $-fq$ is the reduced spring force. Function f may depend on the second moment of the distribution function $M_2 = \int q^2 \Psi(q,t)\,\mathrm{d}q$. In particular, the case $f \equiv 1$ corresponds to the linear Hookean spring, while $f = [1 - M_2(t)/b]^{-1}$ corresponds to the self-consistent finite extension nonlinear elastic spring (the FENE-P model [365]). The second moment M_2 occurs in the FENE-P force f as the result of the pre-averaging approximation to the original FENE model (with nonlinear spring force $f = [1 - q^2/b]^{-1}$). The parameter b changes the characteristics of the force law from Hookean at small extensions to a confining force for $q^2 \to b$. Parameter b is roughly equal to the number of monomer units represented by the dumbell and should therefore be a large number. In the limit $b \to \infty$, the Hookean spring is recovered. Recently, it has been demonstrated that FENE-P model appears as first approximation within a systematic self-confident expansion of nonlinear forces [29].

Equation (13.104) describes an ensemble of non-interacting dumbells subject to a pseudo-elongational flow with fixed kinematics. As is well known, the Gaussian distribution function,

$$\Psi^G(M_2) = \frac{1}{\sqrt{2\pi M_2}} \exp\left[-\frac{q^2}{2M_2}\right] \ , \tag{13.106}$$

solves equation (13.104) provided the second moment M_2 satisfies

$$\frac{\mathrm{d}M_2}{\mathrm{d}t} = 1 + 2\alpha(t) M_2 \ . \tag{13.107}$$

Solution (13.106) and (13.107) is the valid macroscopic description if all other solutions of the equation (13.104) are rapidly attracted to the family of Gaussian distributions (13.106). In other words [11], the special solution (13.106) and (13.107) is the macroscopic description if equation (13.106) is the stable invariant manifold of the kinetic equation (13.104). If not, then the Gaussian solution is just a member of the family of solutions, and equation (13.107) has no meaning of the macroscopic equation. Thus, the complete answer to the question of validity of the equation (13.107) as the macroscopic equation requires a study of dynamics in the neighborhood of the manifold (13.106). Because of the simplicity of the model (13.104), this is possible to a satisfactory level even for M_2-dependent spring forces.

13.6.2 Dynamics of the Moments and Explosion of the Gaussian Manifold

In [109] it was shown, that there is a possibility of "explosion" of the Gaussian manifold: with the small initial deviation from it, the solutions of the equation (13.104) are fast going far from the manifold, and then slowly come back to the stationary point which is located on the Gaussian manifold. The distribution function Ψ is stretched fast, but looses the Gaussian form, and after that the Gaussian form recovers slowly with the new value of M_2. Let us describe briefly the results of [109].

Let $M_{2n} = \int q^{2n}\Psi \, \mathrm{d}q$ denote the even moments (odd moments vanish by symmetry). We consider deviations $\mu_{2n} = M_{2n} - M_{2n}^{\mathrm{G}}$, where $M_{2n}^{\mathrm{G}} = \int q^{2n}\Psi^{\mathrm{G}} \, \mathrm{d}q$ are moments of the Gaussian distribution function (13.106). Let $\Psi(q, t_0)$ be the initial condition to (13.104) at time $t = t_0$. Introducing functions,

$$p_{2n}(t, t_0) = \exp\left[4n \int_{t_0}^{t} \alpha(t') \, \mathrm{d}t'\right] , \tag{13.108}$$

where $t \geq t_0$, and $2n \geq 4$, the exact time evolution of the deviations μ_{2n} for $2n \geq 4$ reads

$$\mu_4(t) = p_4(t, t_0)\mu_4(t_0) , \tag{13.109}$$

and

$$\mu_{2n}(t) = \left[\mu_{2n}(t_0) + 2n(4n-1) \int_{t_0}^{t} \mu_{2n-2}(t') p_{2n}^{-1}(t', t_0) \, \mathrm{d}t'\right] p_{2n}(t, t_0) , \tag{13.110}$$

for $2n \geq 6$. Equations (13.108), (13.109) and (13.110) describe evolution near the Gaussian solution for arbitrary initial condition $\Psi(q, t_0)$. Notice that explicit evaluation of the integral in (13.108) requires solution to the moment equation (13.107) which is not available in the analytical form for the FENE-P model.

It is straightforward to conclude that any solution with a non-Gaussian initial condition converges to the Gaussian solution asymptotically as $t \to \infty$ if

$$\lim_{t \to \infty} \int_{t_0}^{t} \alpha(t') \, \mathrm{d}t' < 0 . \tag{13.111}$$

However, even if this asymptotic condition is met, deviations from the Gaussian solution may survive for considerable *finite* times. For example, if for some finite time T, the integral in (13.108) is estimated as $\int_{t_0}^{t} \alpha(t') \, \mathrm{d}t' > \alpha(t - t_0)$, $\alpha > 0$, $t \leq T$, then the Gaussian solution becomes exponentially unstable during this time interval. If this is the case, the moment equation (13.107) cannot be regarded as the macroscopic equation. Let us consider specific examples.

For the Hookean spring ($f \equiv 1$) under constant elongation ($\kappa = \mathrm{const}$), the Gaussian solution is exponentially stable for $\kappa < 0.5$, and it becomes

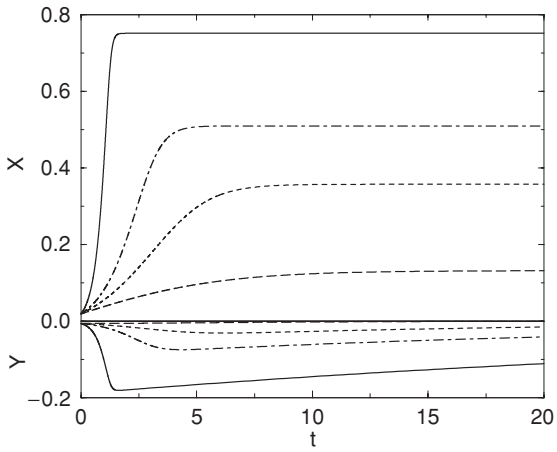

Fig. 13.4. Deviations of reduced moments from the Gaussian solution as a function of reduced time t in pseudo-elongation flow for the FENE-P model. *Upper* part: Reduced second moment $X = M_2/b$. *Lower* part: Reduced deviation of fourth moment from Gaussian solution $Y = -\mu_4^{1/2}/b$. *Solid*: $\kappa = 2$, *dash-dot*: $\kappa = 1$, *dash*: $\kappa = 0.75$, *long dash*: $\kappa = 0.5$. (The figure from the paper [109], computed by P. Ilg.)

exponentially unstable for $\kappa > 0.5$. The exponential instability in this case is accompanied by the well known breakdown of the solution to (13.107) due to the infinite stretching of the dumbbell. The situation is much more interesting for the FENE-P model because this nonlinear spring force does not allow the infinite stretching of the dumbbell [412, 413].

Euations (13.107) and (13.109) were integrated by the 5-th order Runge-Kutta method with adaptive time step. The FENE-P parameter b was set equal to 50. The initial condition was $\Psi(q, 0) = C(1 - q^2/b)^{b/2}$, where C is the normalization (the equilibrium of the FENE model, notoriously close to the FENE-P equilibrium [363]). For this initial condition, in particular, $\mu_4(0) = -6b^2/[(b+3)^2(b+5)]$ which is about 4% off the value of M_4 in the Gaussian equilibrium for $b = 50$. In Fig. 13.4 we demonstrate deviation $\mu_4(t)$ as a function of time for several values of the flow. Function $M_2(t)$ is also given for comparison. For small enough κ we find an adiabatic regime, that is μ_4 relaxes exponentially to zero. For stronger flows, we observe an initial *fast runaway* from the invariant manifold with $|\mu_4|$ growing over three orders of magnitude as compared to its initial value. After the maximum deviation is reached, μ_4 relaxes to zero. This relaxation is exponential as soon as the solution to (13.107) approaches the steady state. However, the time constant of this exponential relaxation $|\alpha_\infty|$ is very small. Specifically, for large κ,

$$\alpha_\infty = \lim_{t\to\infty} \alpha(t) = -\frac{1}{2b} + O(\kappa^{-1}) \,. \tag{13.112}$$

Thus, the steady state solution is unique and Gaussian but the stronger is the flow, the larger is the initial runaway from the Gaussian solution, while the return to it thereafter becomes flow-independent. Our observation demonstrates that, though the stability condition (13.111) is met, *significant deviations from the Gaussian solution persist over the times when the solution of* (13.107) *is already reasonably close to the stationary state.* If we accept the usually quoted physically reasonable minimal value of parameter b of the order 20 then the minimal relaxation time is of order 40 in the reduced time units of Fig. 13.4. We should also stress that the two limits, $\kappa \to \infty$ and $b \to \infty$, are not commutative, thus it is not surprising that the estimation (13.112) does not reduce to the above mentioned Hookean result as $b \to \infty$. Finally, peculiarities of convergence to the Gaussian solution are even furthered if we consider more complicated (in particular, oscillating) flows $\kappa(t)$. Further numerical experiments are presented in [110]. The statistics of FENE-P solutions with random strains was studied recently [368]

13.6.3 Two-Peak Approximation for Polymer Stretching in Flow and Explosion of the Gaussian Manifold

In accordance with [369], the ansatz for Ψ can be suggested in the following form:

$$\Psi^{An}(\{\sigma,\varsigma\},q) = \frac{1}{2\sigma\sqrt{2\pi}}\left(e^{-\frac{(q+\varsigma)^2}{2\sigma^2}} + e^{-\frac{(q-\varsigma)^2}{2\sigma^2}}\right) . \tag{13.113}$$

Natural inner coordinates on this manifold are σ and ς. Note, that now $\sigma^2 \neq M_2$. The value σ^2 is a dispersion of one of the Gaussian summands in (13.113),

$$M_2(\Psi^{An}(\{\sigma,\varsigma\},q)) = \sigma^2 + \varsigma^2 .$$

To build the thermodynamic projector on the manifold (13.113), the thermodynamic Lyapunov function is necessary. It is necessary to emphasize that equations (13.104) are nonlinear. For such equations, the arbitrarity in the choice of the thermodynamic Lyapunov function is much smaller than for the linear Fokker–Planck equation. Nevertheless, such a thermodynamic Lyapunov function exists. It is the free energy

$$F = U(M_2[\Psi]) - TS[\Psi] , \tag{13.114}$$

where

$$S[\Psi] = -\int \Psi(\ln\Psi - 1)\,\mathrm{d}q ,$$

$U(M_2[\Psi])$ is the potential energy in the mean field approximation, T is the temperature (below we assume $T = 1$).

Note that the Kullback–form entropy [156] $S_k = -\int \Psi \ln\left(\frac{\Psi}{\Psi^*}\right) \mathrm{d}q$ also has the form $S_k = -F/T$:

$$\Psi^* = \exp(-U) \,,$$
$$S_k[\Psi] = -\langle U\rangle - \int \Psi \ln \Psi \,\mathrm{d}q \,.$$

If $U(M_2[\Psi])$ in the mean field approximation is the convex function of M_2, then the free energy (13.114) is the convex functional too.

For the FENE-P model $U = -\ln[1 - M_2/b]$.

In accordance with thermodynamics the vector I of the flow of Ψ must be proportional to the gradient of the corresponding chemical potential μ:

$$I = -B(\Psi)\nabla_q \mu \,, \tag{13.115}$$

where $\mu = \frac{\delta F}{\delta \Psi}$, $B \geq 0$. From (13.114) it follows that

$$\mu = \frac{dU(M_2)}{dM_2} \cdot q^2 + \ln \Psi \,;$$
$$I = -B(\Psi)\left[2\frac{dU}{dM_2} \cdot q + \Psi^{-1}\nabla_q \Psi\right] \,. \tag{13.116}$$

If we assume here $B = \frac{D}{2}\Psi$, then we get

$$I = -D\left[\frac{dU}{dM_2} \cdot q\Psi + \frac{1}{2}\nabla_q \Psi\right];$$
$$\frac{\partial \Psi}{\partial t} = \mathrm{div}_q I = D\frac{dU(M_2)}{dM_2}\partial_q(q\Psi) + \frac{D}{2}\partial^2 q\Psi \,, \tag{13.117}$$

When $D = 1$ this equation coincides with (13.104) in the absence of the flow, and $\mathrm{d}F/\mathrm{d}t \leq 0$ due to (13.117).

Let us construct the thermodynamic projector with the help of the thermodynamic Lyapunov function F (13.114). Corresponding entropic scalar product at the point Ψ has the form

$$\langle f|g\rangle_\Psi = \left.\frac{d^2U}{dM_2^2}\right|_{M_2=M_2[\Psi]} \cdot \int q^2 f(q) dq \cdot \int q^2 g(q)\,\mathrm{d}q + \int \frac{f(q)g(q)}{\Psi(q)}\,\mathrm{d}q \,. \tag{13.118}$$

When stuying the ansatz (13.113), the scalar product (13.118) constructed for the corresponding point of the Gaussian manifold with $M_2 = \sigma^2$ will be used. This will allow us to investigate the neighborhood of the Gaussian manifold (and to get all the results analytically):

$$\langle f|g\rangle_{\sigma^2} = \left.\frac{d^2U}{dM_2^2}\right|_{M_2=\sigma^2} \cdot \int q^2 f(q)\,\mathrm{d}q \cdot \int q^2 g(q)\,\mathrm{d}q$$
$$+\sigma\sqrt{2\pi}\int e^{\frac{q^2}{2\sigma^2}} f(q)g(q)\,\mathrm{d}q \,. \tag{13.119}$$

Also we need to know the functional $D_f F$ at the point of Gaussian manifold:

$$D_f F_{\sigma^2}(f) = \left(\left. \frac{dU(M_2)}{dM_2} \right|_{M_2=\sigma^2} - \frac{1}{2\sigma^2} \right) \int q^2 f(q)\, \mathrm{d}q \,, \tag{13.120}$$

(subject to the condition $\int f(q)\, \mathrm{d}q = 0$). The point

$$\left. \frac{dU(M_2)}{dM_2} \right|_{M_2=\sigma^2} = \frac{1}{2\sigma^2} \,,$$

corresponds to the equilibrium.

The tangent space to the manifold (13.113) is spanned by the vectors

$$\begin{aligned} f_\sigma &= \frac{\partial \Psi^{An}}{\partial(\sigma^2)}; \; f_\varsigma = \frac{\partial \Psi^{An}}{\partial(\varsigma^2)} \,; \\ f_\sigma &= \frac{1}{4\sigma^3\sqrt{2\pi}} \left[e^{-\frac{(q+\varsigma)^2}{2\sigma^2}} \frac{(q+\varsigma)^2 - \sigma^2}{\sigma^2} + e^{-\frac{(q-\varsigma)^2}{2\sigma^2}} \frac{(q-\varsigma)^2 - \sigma^2}{\sigma^2} \right] \,; \\ f_\varsigma &= \frac{1}{4\sigma^2\varsigma\sqrt{2\pi}} \left[-e^{-\frac{(q+\varsigma)^2}{2\sigma^2}} \frac{q+\varsigma}{\sigma} + e^{-\frac{(q-\varsigma)^2}{2\sigma^2}} \frac{(q-\varsigma)}{\sigma} \right] ; \end{aligned} \tag{13.121}$$

The Gaussian entropy (free energy) production in the directions f_σ and f_ς (13.120) has a very simple form:

$$DF_{\sigma^2}(f_\varsigma) = DF_{\sigma^2}(f_\sigma) = \left. \frac{dU(M_2)}{dM_2} \right|_{M_2=\sigma^2} - \frac{1}{2\sigma^2} \,. \tag{13.122}$$

The linear subspace $\ker DF_{\sigma^2}$ in $\mathrm{lin}\{f_\sigma, f_\varsigma\}$ is spanned by the vector $f_\varsigma - f_\sigma$.

Let us consider the given vector field $\mathrm{d}\Psi/\mathrm{d}t = J(\Psi)$ at the point $\Psi(\{\sigma, \varsigma\})$. We need to build the projection of J onto the tangent space $T_{\sigma,\varsigma}$ at the point $\Psi(\{\sigma, \varsigma\})$:

$$P^{th}_{\sigma,\varsigma}(J) = \varphi_\sigma f_\sigma + \varphi_\varsigma f_\varsigma \,. \tag{13.123}$$

This equation means that the equations for σ^2 and ς^2 will have the form

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}t} = \varphi_\sigma \,; \quad \frac{\mathrm{d}\varsigma^2}{\mathrm{d}t} = \varphi_\varsigma \,. \tag{13.124}$$

Projection $(\varphi_\sigma, \varphi_\varsigma)$ can be found from the following two equations:

$$\begin{aligned} \varphi_\sigma + \varphi_\varsigma &= \int q^2 J(\Psi)(q)\, \mathrm{d}q \,; \\ \langle \varphi_\sigma f_\sigma + \varphi_\varsigma f_\varsigma | f_\sigma - f_\varsigma \rangle_{\sigma^2} &= \langle J(\Psi) | f_\sigma - f_\varsigma \rangle_{\sigma^2} \,, \end{aligned} \tag{13.125}$$

where $\langle f|g\rangle_{\sigma^2} = \langle J(\Psi)|f_\sigma - f_\varsigma\rangle_{\sigma^2}$, (13.118). First equation of (13.125) means, that the time derivative $\mathrm{d}M_2/\mathrm{d}t$ is the same for the initial and the reduced equations. Due to the formula for the dissipation of the free energy

(13.120), this equality is equivalent to the persistence of the dissipation in the neighborhood of the Gaussian manifold. Indeed, in according to (13.120) $\mathrm{d}F/\mathrm{d}t = A(\sigma^2)\int q^2 J(\Psi)(q)\,\mathrm{d}q = A(\sigma^2)\mathrm{d}M_2/\mathrm{d}t$, where $A(\sigma^2)$ does not depend of J. On the other hand, the time derivative of M_2 due to projected equation (13.124) is $\varphi_\sigma + \varphi_\varsigma$, because $M_2 = \sigma^2 + \varsigma^2$.

The second equation in (13.125) means, that J is projected orthogonally on $\ker D_f S \bigcap T_{\sigma,\varsigma}$. Let us use the orthogonality with respect to the entropic scalar product (13.119). The solution of equations (13.125) has the form

$$\begin{aligned}\frac{\mathrm{d}\sigma^2}{\mathrm{d}t} &= \varphi_\sigma = \frac{\langle J|f_\sigma - f_\varsigma\rangle_{\sigma^2} + M_2(J)(\langle f_\varsigma|f_\varsigma\rangle_{\sigma^2} - \langle f_\sigma|f_\varsigma\rangle_{\sigma^2})}{\langle f_\sigma - f_\varsigma|f_\sigma - f_\varsigma\rangle_{\sigma^2}}\,,\\ \frac{\mathrm{d}\varsigma^2}{\mathrm{d}t} &= \varphi_\varsigma = \frac{-\langle J|f_\sigma - f_\varsigma\rangle_{\sigma^2} + M_2(J)(\langle f_\sigma|f_\sigma\rangle_{\sigma^2} - \langle f_\sigma|f_\varsigma\rangle_{\sigma^2})}{\langle f_\sigma - f_\varsigma|f_\sigma - f_\varsigma\rangle_{\sigma^2}}\,,\end{aligned} \tag{13.126}$$

where $J = J(\Psi)$, $M_2(J) = \int q^2 J(\Psi)\,\mathrm{d}q$.

It is easy to check, that the formulas (13.126) are indeed defining the projector: if f_σ (or f_ς) is substituted instead of the function J, then we get $\varphi_\sigma = 1, \varphi_\varsigma = 0$ (or $\varphi_\sigma = 0, \varphi_\varsigma = 1$, respectively). Let us substitute the right part of the initial kinetic equations (13.104), calculated at the point $\Psi(q) = \Psi(\{\sigma,\varsigma\},q)$ (see (13.113)) in (13.126) instead of J. We shall get the closed system of equations on σ^2, ς^2 in the neighborhood of the Gaussian manifold.

This system describes the dynamics of the distribution function Ψ. The distribution function is represented as the half-sum of two Gaussian distributions with the averages of distribution $\pm\varsigma$ and mean-square deviations σ. All integrals in the right-hand part of (13.126) are possible to calculate analytically.

The basis (f_σ, f_ς) is convenient to use everywhere except for the points on the Gaussian manifold, $\varsigma = 0$, because if $\varsigma \to 0$, then

$$f_\sigma - f_\varsigma = O\left(\frac{\varsigma^2}{\sigma^2}\right) \to 0\,.$$

Let us analyze the stability of the Gaussian manifold with respect to the "dissociation" of the Gaussian peak in two peaks (13.113). In order to do this, it is necessary to find the first nonvanishing term in the Taylor series expansion in ς^2 of the right-hand side of the second equation in the system (13.126). The denominator has the order of ς^4, the numerator has, as it is easy to see, the order not less, than ς^6 (because the Gaussian manifold is invariant with respect to the initial system).

With the accuracy up to ς^4:

$$\frac{1}{\sigma^2}\frac{\mathrm{d}\varsigma^2}{\mathrm{d}t} = 2\alpha\frac{\varsigma^2}{\sigma^2} + o\left(\frac{\varsigma^4}{\sigma^4}\right)\,, \tag{13.127}$$

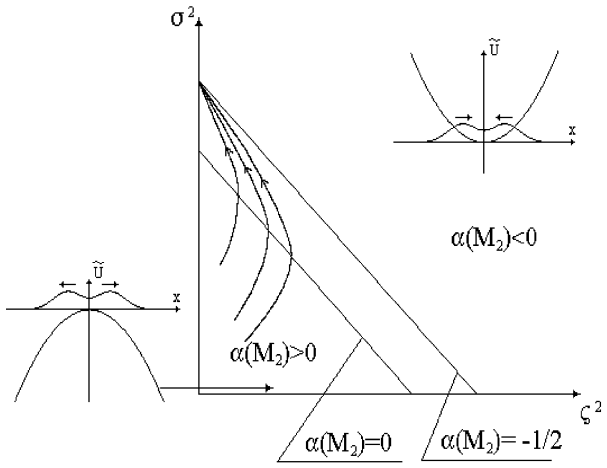

Fig. 13.5. Phase trajectories for the two-peak approximation, FENE-P model. The vertical axis ($\varsigma = 0$) corresponds to the Gaussian manifold. The triangle with $\alpha(M_2) > 0$ is the domain of exponential instability

where

$$\alpha = \kappa - \left.\frac{dU(M_2)}{dM_2}\right|_{M_2=\sigma^2} .$$

Thus, if $\alpha > 0$, then ς^2 grows exponentially ($\varsigma \sim e^{\alpha t}$) and the Gaussian manifold is unstable; if $\alpha < 0$, then ς^2 decreases exponentially and the Gaussian manifold is stable.

Near the vertical axis $\mathrm{d}\sigma^2/\mathrm{d}t = 1 + 2\alpha\sigma^2$. The form of the phase trajectories is shown qualitative on Fig. 13.5. Note that this result completely agrees with equation (13.109).[2]

For the linear Fokker–Planck equation with a non-linear force law (for example, with the FENE force) the motion in the presence of the flow can be represented as the motion in the effective potential well $\tilde{U}(q) = U(q) - \frac{1}{2}\kappa q^2$. Different variants of the phase portrait for the FENE potential are present on Fig. 13.6. Instability and dissociation of the unimodal distribution functions ("peaks") for the FPE is the general effect when the flow is present. The instability occurs when the matrix $\partial^2\tilde{U}/\partial q_i \partial q_j$ starts to have negative eigenvalues ($\tilde{U}$ is the effective potential energy, $\tilde{U}(q) = U(q) - \frac{1}{2}\sum_{i,j}\kappa_{i,j}q_i q_j$).

13.6.4 Polymodal Polyhedron and Molecular Individualism

What are the possible physical consequences of the instability of the Gaussian manifolds? The discovery of the molecular individualism for dilute polymers

[2] Pavel Gorban calculated the projector (13.126) analytically without Taylor expansion and with the same, but exact result: $\mathrm{d}\varsigma^2/\mathrm{d}t = 2\alpha\varsigma^2$, $\mathrm{d}\sigma^2/\mathrm{d}t = 1 + 2\alpha\sigma^2$.

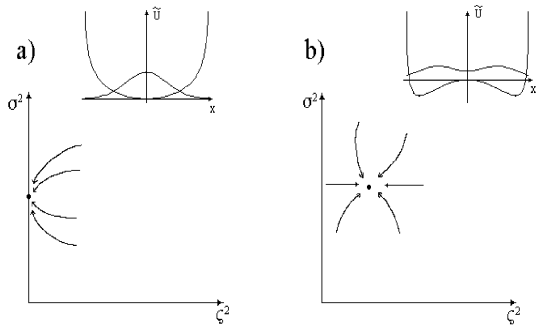

Fig. 13.6. Phase trajectories for the two-peak approximation, FENE model: (**a**) A stable equilibrium on the vertical axis, one stable peak; (**b**) A stable equilibrium with $\varsigma > 0$, stable two-peak configuration

in the elongational flow [370] was the challenge to theory from the very beginning. "Our data should serve as a guide in developing improved microscopic theories for polymer dynamics"... was the concluding sentence of the paper [370]. P.G. de Gennes invented the notion "molecular individualism" [371]. He stressed that in this case the usual averaging procedures are not applicable. At the highest strain rates distinct conformation shapes with different dynamics were observed [370]. Further works for the shear flow demonstrated not only shape differences, but large temporal fluctuations [372].

Equation for the molecules in a flow are known. These are the Fokker–Planck equations with external force. The theory of the molecular individualism is hidden inside these equations. Following the logic of model reduction we should solve two problems: to construct the slow manifold, and to project the equation on this manifold. The second problem is solved: the thermodynamic projector is necessary for this projection.

How to solve the first problem? We can find a hint in previous subsections. The Gaussian distributions form the invariant manifold for the FENE-P model of polymer dynamics, but this manifold can become unstable in the presence of a flow. We propose to model this instability as dissociation of the Gaussian peak into two peaks. This dissociation describes appearance of an unstable direction in the configuration space.

In the one-dimensional FENE-P model of the preceding section the polymer molecule is represented by one coordinate: the stretching of the molecule (the connector vector between the beads). There is a simple mean field generalized models for multidimensional configuration spaces of molecules. In these models, dynamics of distribution functions is described by the Fokker–Planck equation in a quadratic potential well. The matrix of coefficients of this quadratic potential depends on the matrix of the second order moments of the distribution function. The Gaussian distributions form the invariant

manifold for these models, and the first dissociation of the Gaussian peak after the emergence of the unstable direction in the configuration space has the same nature and the same description, as for the one-dimensional models of molecules considered below.

At a higher strain, new unstable directions can appear, and corresponding dissociations of Gaussian peaks form a *cascade* of dissociation. For m unstable directions we get the Gaussian parallelepiped: The distribution function is represented as a sum of 2^m Gaussian peaks located in the vertices of parallelepiped:

$$\Psi(q) = \frac{1}{2^m(2\pi)^{n/2}\sqrt{\det \Sigma}} \times \sum_{\varepsilon_i=\pm 1,\,(i=1,\ldots,m)} \exp\left(-\frac{1}{2}\left(\Sigma^{-1}\left(q+\sum_{i=1}^{m}\varepsilon_i\varsigma_i\right),\, q+\sum_{i=1}^{m}\varepsilon_i\varsigma_i\right)\right), \tag{13.128}$$

where n is the dimension of the configurational space, $2\varsigma_i$ is the vector of the ith edge of the parallelepiped, Σ is the one-peak covariance matrix (in this model, Σ is the same for all peaks). The macroscopic variables for this model are:

1. The covariance matrix Σ for a peak;
2. The set of vectors ς_i (or the parallelepiped edges).

The stationary polymodal distribution for the Fokker–Planck equation corresponds to the persistence of several local minima of the function $\tilde{U}(q)$. The multidimensional case is different from one-dimensional because it has the huge amount of possible configurations. An attempt to describe this picture quantitative meet the following obstacle: we do not know the details of the potential U, on the other hand, the effect of molecular individualism [370–372] seems to be universal in its essence, that is, independent of details of interactions.

We should find a mechanism that is as general, as the effect. The simplest dumbbell model which we have discussed in the previous subsection does not explain the effect, but it gives us a hint: the flow can violate the stability of unimodal distributions. If we assume that the whole picture is hidden inside a multidimensional Fokker–Planck equation for a large molecule in a flow, then we can use this hint in such a way: when the flow strain grows, there appears a sequence of bifurcations, and for each of them a new unstable direction arises. For the qualitative description of such a picture we can apply a language of normal forms [373], subject to a certain modification.

The bifurcation in dimension one with appearance of two point of minima from one point has the simplest polynomial representation: $U(q,\alpha) = q^4 + \alpha q^2$. If $\alpha \geq 0$, then this potential has one minimum, if $\alpha < 0$, then there are two points of minima. The normal form of degenerated singularity is $U(q) = q^4$. Such polynomial forms as $q^4 + \alpha q^2$ are very simple, but they have

inconvenient asymptotic at $q \to \infty$. For our goals it is more appropriate to use logarithms of convex combinations of Gaussian distributions instead of polynomials. It is the same class of jets near the bifurcation, but with given quadratic asymptotic $q \to \infty$. If one needs another class of asymptotic, it is possible just to change the choice of the basic peak. All normal forms of the critical form of functions, and families of versal deformations are well investigated and known [373].

Let us represent the deformation of the probability distribution under the strain in multidimensional case as a cascade of peak dissociation. The number of peaks will duplicate on the each step. The possible cascade of peaks dissociation is presented qualitatively on Fig. 13.7. The important property of this qualitative picture is the linear complexity of dynamical description with exponential complexity of geometrical picture. Let m be the number of bifurcation steps in the cascade. Then

- For description of parallelepiped it is sufficient to describe m edges;
- There are 2^{m-1} geometrically different conformations associated with 2^m vertex of parallelepiped (central symmetry halved this number).

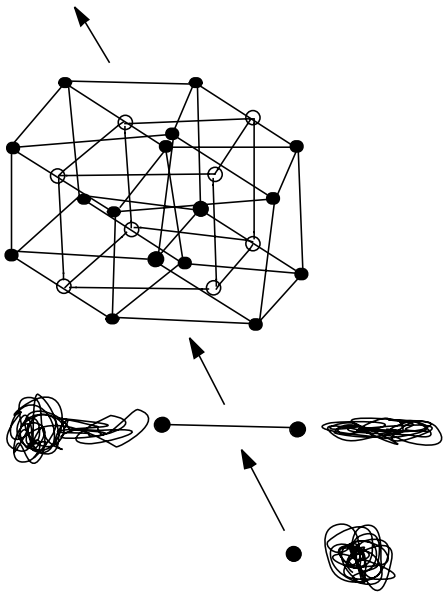

Fig. 13.7. Cartoon representing the steps of molecular individualism. Black dots are vertices of Gaussian parallelepiped. Zero, one, and four-dimensional polyhedrons are drawn. Presented is also the three-dimensional polyhedron used to draw the four-dimensional object. Each new dimension of the polyhedron adds as soon as the corresponding bifurcation occurs. Quasi-stable polymeric conformations are associated with each vertex. First bifurcation pertinent to the instability of a dumbbell model in elongational flow is described in the text

Another important property is the *threshold* nature of each dissociation: It appears in points of stability loss for new directions, in these points the dimension of unstable direction increases.

Positions of peaks correspond to parallelepiped vertices. Different vertices in configuration space present different geometric forms. So, it seems *plausible*[3] that observed different forms ("dumbbels", "half-dumbbels", "kinked", "folded" and other, not classified forms) correspond to these vertices of parallelepiped. Each vertex is a metastable state of a molecule and has its own basin of attraction. A molecule goes to the vertex which depends strongly on details of initial conditions.

The simplest multidimensional dynamic model is the Fokker–Planck equation with quadratic mean field potential. This is direct generalization of the FENE-P model: the quadratic potential $U(q)$ depends on the tensor of second moments $\boldsymbol{M}_2 = \langle q_i q_j \rangle$ (here the angle brackets denote the averaging). This dependence should provide the finite extensibility. This may be, for example, a simple matrix generalization of the FENE-P energy:

$$U(q) = \sum_{ij} K_{ij} q_i q_j,\ \mathbf{K} = \mathbf{K}^0 + \phi(\boldsymbol{M}_2/b),\ \langle U(q) \rangle = \mathrm{tr}(\mathbf{K}\boldsymbol{M}_2/b)$$

where b is a constant (the limit of extensibility), $\mathbf{K}^0$ is a constant matrix, $\boldsymbol{M}_2$ is the matrix of second moments, and ϕ is a positive analytical monotone increasing function of one variable on the interval $(0, 1)$, $\phi(x) \to \infty$ for $x \to 1$ (for example, $\phi(x) = -\ln(1-x)/x$, or $\phi(x) = (1-x)^{-1}$).

For quadratic multidimensional mean field models persists the qualitative picture of Fig. 13.5: there is *non-stationary moleqular individualism for stationary "molecular collectivism"*. The stationary distribution is the Gaussian distribution, and on the way to this stationary point there exists an unstable region, where the distribution dissociates onto 2^m peaks (m is the number of unstable degrees of freedom).

Dispersion of individual peak in unstable region increases too. This effect can deform the observed situation: If some of the peaks have significant intersection, then these peaks join into new extended classes of observed molecules. The stochastic walk of molecules between connected peaks can be observed as "large non-periodical fluctuations". This walk can be unexpected fast, because it can be effectively a *motion in a low-dimensional space*, for example, in one-dimensional space (in a neighborhood of a part of one-dimensional skeleton of the polyhedron).

[3] We can not *prove* it now, and it is necessary to determine the status of proposed qualitative picture: it is much more general than a specific model, it is the mechanism which acts in a wide class of models. The cascade of instabilities can appear and, no doubt, it appears for the Fokker–Planck equation for a large molecule in a flow. But it is not proven yet that the effects observed in well-known experiments have exactly this mechanism. This proof requires quantitative verification of a specific model. And now we talk not about a proven, but about the plausible mechanism which typically appears for systems with instabilities.

We discussed the important example of ansatz: the multipeak models. Two examples of these type of models demonstrated high efficiency during decades: the Tamm–Mott-Smith bimodal ansatz for shock waves, and the the Langer–Bar-on–Miller [374–376] approximation for spinodal decomposition.

The multimodal polyhedron appears every time as an appropriate approximation for distribution functions for systems with instabilities. We create such an approximation for the Fokker–Planck equation for polymer molecules in a flow. Distributions of this type are expected to appear in each kinetic model with multidimensional instability as universally, as Gaussian distribution appears for stable systems. This statement needs a clarification: everybody knows that the Gaussian distribution is stable with respect to convolutions, and the appearance of this distribution is supported by central limit theorem. Gaussian polyhedra form a stable class: convolution of two Gaussian polyhedra is a Gaussian polyhedron, convolution of a Gaussian polyhedron with a Gaussian distribution is a Gaussian polyhedron with the same number of vertices. On the other hand, a Gaussian distribution in a potential well appears as an exponent of a quadratic form which represents the simplest stable potential (a normal form of a nondegenerated critical point). Families of Gaussian parallelepipeds appear as versal deformations with given asymptotic for systems with cascade of simplest bifurcations.

The usual point of view is: The shape of the polymers in a flow is either a coiled ball, or a stretched ellipsoid, and the Fokker–Planck equation describes the stretching from the ball to the ellipsoid. It is not the whole truth, even for the FENE-P equation, as it was shown in [109, 369]. The Fokker–Planck equation describes the shape of a probability cloud in the space of conformations. In the flow with increasing strain this shape changes from the ball to the ellipsoid, but, after some thresholds, this ellipsoid transforms into a multimodal distribution which can be modeled as the peak parallelepiped. The peaks describe the finite number of possible molecule conformations. The number of this distinct conformations grows for a parallelepiped as 2^m with the number m of independent unstable direction. Each vertex has its own basin of attraction. A molecule goes to the vertex which depends strongly on details of initial conditions.

These models pretend to be the kinetic basis for the theory of molecular individualism. The detailed computations will be presented in following works, but some of the qualitative features of the models are in agreement with some of qualitative features of the picture observed in experiment [370–372]: effect has the threshold character, different observed conformations depend significantly on the initial conformation and orientation.

Some general questions remain open:

– Of course, appearance of 2^m peaks in the Gaussian parallelepiped is possible, but some of these peaks can join in following dynamics, hence the first question is: what is the typical number of significantly different peaks for a $m-$dimensional instability?

– How can we decide what scenario is more realistic from the experimental point of view: the proposed universal kinetic mechanism, or the scenario with long living metastable states (for example, the relaxation of knoted molecules in the flow can give an other picture than the relaxation of unknoted molecules)?
– The analysis of random walk of molecules from peak to peak should be done, and results of this analysis should be compared with observed large fluctuations.

The systematic discussion of the difference between the Gaussian elipsoid (and its generalizations) and the Gaussian multipeak polyhedron (and its generalizations) seems to be necessary. This polyhedron appears generically as the effective ansatz for kinetic systems with instabilities.