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ABSTRACT

The smaller the scales on which complex fluids are studied, the more fluctuations become relevant, e.g. in microrheology and nanofluidics. In this paper, a general approach is presented for including fluctuations in conformation-tensor based models for viscoelasticity, in accordance with the fluctuation-dissipation theorem. It is advocated to do this not for the conformation tensor itself, but rather for its so-called contravariant decomposition, in order to circumvent two major numerical complications. These are potential violation of the positive semi-definiteness of the conformation tensor, and numerical instabilities that occur even in the absence of fluctuations. Using the general procedure, fluctuating versions are derived for the upper-convected Maxwell model, the FENE-P model, and the Giesekus model. Finally, it is shown that the fluctuating viscoelasticity proposed here naturally reduces to the fluctuating Newtonian fluid dynamics of Landau and Lifshitz [L. D. Landau and E. M. Lifshitz, Fluid Mechanics, Vol. 6 of Course of Theoretical Physics, Pergamon Press, Oxford, 1959], in the limit of vanishingly small relaxation time.

1. Introduction

The focus of this paper is on modeling the rheological behavior of complex, primarily polymeric, fluids on small scales. What is meant by small scales must be specified in relation to a typical length-scale or volume in polymers. For example, in melts of entangled polymer chains, a volume of relevance for the mechanical behavior is related to the plateau modulus G_N^0. Particularly, the ratio of the thermal energy $k_B T$ to G_N^0 gives an approximation of the volume occupied by an entanglement strand, which for typical polymer melts is between $2\,\text{nm}^3$ and $40\,\text{nm}^3$ [1,2]. Upon dilution, the characteristic volume can increase by several orders of magnitude. For entangled solutions, the characteristic volume depends on the volume fraction ϕ of polymer through an inverse power-law relation, $\phi^{-\beta}$ with $\beta \geq 1$ [3]. In general, it is to be expected that fluctuations become relevant if these complex fluids are confined on scales comparable to the above characteristic volumes, or the corresponding length scales, respectively.

A prominent example, where fluctuations are relevant due to the smallness of the involved length scales, is microrheology [4–6]. The fluctuating motion of a small tracer particle immersed in a fluid originates from the fluctuations in the surrounding fluid. Since the fluid fluctuations on the particle surface average out as the particle size increases, it is crucial for microrheology that the tracer particle is sufficiently small, in order to pick up the fluctuations of the fluid. For a Newtonian fluid, the Sutherland-Einstein-Smoluchowski relation links the diffusive behavior of the small tracer particle with the fluid

viscosity [7–9], which in turn is a measure for the fluctuating stress in the fluid. To derive such a relation, one can use a continuum formulation of Newtonian fluid dynamics with fluctuations, according to the approach of Landau and Lifshitz [10], and study its effect on an immersed particle [11,12]. The question arises how the dynamics of a tracer particle can be used to assess the rheology of the suspending fluid if the fluid is non-Newtonian, i.e., viscoelastic. This issue has been addressed by Mason and Weitz [4], based on a Langevin equation for the tracer particle [13,14] that is generalized by including a memory kernel, i.e. colored noise [15–18], which leads to a generalization of the Sutherland–Einstein–Smoluchowski relation. In order to arrive at such a relation not by postulating a certain particle dynamics, but rather by including fluctuations in the surrounding fluid, a theory of fluctuating viscoelasticity is needed. In [19,20], this has been done by relating the rate-of-strain tensor to the stress tensor through a memory kernel and by introducing colored noise on the stress tensor. However, it can be desirable to adopt an approach that, first, avoids the use of memory kernels, and second, that can more easily be extended to truly non-linear flows. While the latter is believed to be irrelevant for passive microrheology, it is likely of importance for active microrheology, where the particle is forced through the fluid by external influences. An approach that is devoid of memory kernels and coloured noise for describing fluctuating viscoelasticity has been proposed [21] and applied to microrheology [22]. This approach is based on smoothed-particle hydrodynamics, i.e., on discrete interacting particles mimicking the fluid behavior, which can be regarded as a discretized numerical

approximation to a continuum model.

In addition to microrheology, it is desirable to have a theory of fluctuating viscoelasticity at hand also in the context of microfluidics and particularly nanofluidics [23,24], where the fluid is confined to structures with characteristic dimensions of order micrometer or as small as a few nanometers.

The literature on modeling fluctuating viscoelasticity, on a level coarser than that of discrete microscopic particles, is scarce. For example, Langevin equations for concentration and stress variables with memory have been formulated for a collection of non-interacting Rouse polymers [25]. Furthermore, the Newtonian fluid model has been extended in order to capture elastic effects that are said to emerge on nanometer scales [26,27]. Memory-effects have been introduced in the relation between the stress and the rate-of-strain [19,20]. And a quite elaborate approach is the one in [21], where a smoothed-particle hydrodynamic model for viscoelastic fluids is developed. However, to the best of the authors' knowledge, there is no general procedure in the literature for including fluctuations in a non-linear and non-isothermal viscoelastic model on the continuum level.

In this paper, the formulation of fluctuating viscoelasticity is based on rheological models that make use of microstructural dynamic variables [28], specifically conformation tensors, e.g. the upper-convected Maxwell model [29,30], the FENE-P model [30,31], and the Giesekus model [30,32,33]. Using conformation-tensor based models, not only the memory kernel in the relation between stress and strain-rate is obsolete. There is also a variety of different models and substantial expertise in the literature about how to incorporate non-linearities depending on the material at hand, based on physical insight on the microstructural level. In order to incorporate fluctuations in this class of rheological models, this paper will use a nonequilibrium-thermodynamics formulation of the deterministic models [34,35], which is then extended by adding fluctuations in agreement with the fluctuation-dissipation theorem [36–38], according to [35,39,40].

The paper is organized as follows. After outlining the thermodynamic procedure in Section 2, the general form of a dynamic model for the conformation tensor c is formulated including fluctuations in Section 3. Motivated by numerical intricacies of that latter setting, in Section 4 fluctuating viscoelasticity is developed for a multiplicative decomposition of the conformation tensor, namely for the quantity b in $c = b \cdot b^T$, and the relation between the b- and c-formulations is established. Both b- and c-formulations of some specific well-known models are then discussed in Section 5. In Section 6, it is demonstrated that in the limit of a vanishingly small relaxation time, the developed approach reduces to the case of fluctuating Newtonian fluid dynamics studied by Landau and Lifshitz [10]. The paper is concluded with a summary and discussion, Section 7.

2. Thermodynamic procedure

2.1. Taking fluctuations into account

For formulating dynamic models, nonequilibrium thermodynamics is used as a guideline, in order to comply with fundamental thermodynamic principles. Particularly, fluctuations have to be included in a dynamic model in a thermodynamically consistent manner, i.e., the fluctuation-dissipation theorem [36–38] needs to be respected. While various nonequilibrium thermodynamic procedures have been developed, the General Equation for the Non-Equilibrium Reversible-Irreversible Coupling (GENERIC) framework [35,39,41] is going to be used in this paper. The main reason for this choice is that this framework, being derived by way of systematic coarse-graining [35,40], offers the concrete tools for adding fluctuations to an otherwise deterministic model.

In the following, the main aspects of the GENERIC with fluctuations are highlighted; the reader is referred to [35,39,40] for further detail. Let us consider the (non-redundant) set of variables x that describes the

system of interest to the desired detail. According to [35,39,40], the corresponding evolution equations can be written in the following form, in the absence of fluctuations,

$$\dot{\mathsf{x}} = \mathsf{L} \cdot \frac{\delta E}{\delta \mathsf{x}} + \mathsf{M} \cdot \frac{\delta S}{\delta \mathsf{x}}, \tag{1}$$

with energy E, entropy S, Poisson operator L, and friction operator M. The first term on the right-hand side (r.h.s.) of (1) is called reversible, while the second term is irreversible in nature. In the case that fluctuations of the variables x are included in the dynamic model, the Fokker–Planck equation for the (transition) probability p of x is given by [35,39,40],

$$\frac{\partial}{\partial t} p(\mathsf{x}) = -\frac{\delta}{\delta \mathsf{x}} \cdot \left[\left(\mathsf{L} \cdot \frac{\delta E}{\delta \mathsf{x}} + \mathsf{M} \cdot \frac{\delta S}{\delta \mathsf{x}} \right) p(\mathsf{x}) - k_B \mathsf{M} \cdot \frac{\delta}{\delta \mathsf{x}} p(\mathsf{x}) \right], \tag{2}$$

with Boltzmann constant k_B, and time t. Equivalently, this dynamics can be expressed in terms of the corresponding stochastic differential equation, using the Itô interpretation of stochastic calculus [42,43],

$$d\mathsf{x} = \mathsf{L} \cdot \frac{\delta E}{\delta \mathsf{x}} dt + \mathsf{M} \cdot \frac{\delta S}{\delta \mathsf{x}} dt + k_B \frac{\delta}{\delta \mathsf{x}} \cdot \mathsf{M} dt + \mathsf{B} \cdot d\mathsf{W}, \tag{3}$$

where $d\mathsf{W}$ stands for multicomponent white noise, more precisely, for the increment of a multicomponent Wiener process [42,43]. The fluctuating contribution in (3) is related to the irreversible dynamics by way of

$$\mathsf{B} \cdot \mathsf{B}^T = 2 k_B \mathsf{M}, \tag{4}$$

thereby respecting the fluctuation-dissipation theorem. It is noted that the fluctuations in (2) and (3) can be eliminated by letting the Boltzmann constant k_B go to zero, while leaving the building blocks E, S, L, and M unchanged.

2.2. Comment about local-field theories

There are some intricacies related to applying the above procedure with fluctuations to field theories. In general, stochastic partial differential equations are a difficult topic. In the following, some issues of relevance for this paper are discussed briefly. For a more general perspective on the subtleties of stochastic partial differential equations, the reader is referred to [44–46].

For simplicity, consider a local-field theory, by which we mean the following two properties: First, the operators L and M are not generalized functions depending on two positions r and r', but rather they are local operators depending on a single position only (see [35] for details on this difference). And second, the functionals E and S are volume integrals of the corresponding densities (e and s), which in turn depend locally on the fields of interest x, i.e. $E[\mathsf{x}] = \int e(\mathsf{x}) d^3 r$ and $S[\mathsf{x}] = \int s(\mathsf{x}) d^3 r$, respectively. In this setting, the functional derivatives of E and S are equal to the corresponding partial derivatives of the respective density. For the terms on the r.h.s. of (2), this implies that $(\delta S / \delta \mathsf{x}) p$ has the physical units of $[S][V]^{-1}[x]^{-1}[p]$, which must therefore also hold for $k_B(\delta p / \delta \mathsf{x})$. The units of that latter term can be rationalized as follows. Consider a quantity a that is a local function of the fields x. For this case, one can show that the functional derivative of the function a is proportional to the Dirac δ-function,

$$\frac{\delta}{\delta \mathsf{x}_{i,r}} a(\mathsf{x}_{r'}) = \delta(r - r') \frac{\partial}{\partial \mathsf{x}_{i,r}} a(\mathsf{x}_r). \tag{5}$$

Throughout the entire paper, the dependence of fields on position r and time t is omitted whenever all quantities in a relation are evaluated at the same position and time. Only if different positions and/or times are involved in a relation, as is the case in (5), the respective arguments are given explicitly, by subscripts. To proceed, we interpret the Dirac function as follows. In addition to the function being zero for $r \neq r'$, the height of the function at $r = r'$ is given by the inverse of the size of the volume element $\mathscr{V} \equiv d^3 r$, due to the normalization condition for the

Dirac function. Therefore, for $\boldsymbol{r} = \boldsymbol{r}'$,

$$\frac{\delta}{\delta \mathsf{x}_{i,\boldsymbol{r}}} a(\mathsf{x}_{\boldsymbol{r}}) = \mathscr{V}^{-1} \frac{\partial}{\partial \mathsf{x}_{i,\boldsymbol{r}}} a(\mathsf{x}_{\boldsymbol{r}}). \tag{6}$$

In other words, the spatial resolution of the field theory, as quantified by $\mathscr{V}$, plays an important role when taking functional derivatives of functions. The relation (6) not only explains that all M-related terms have proper, i.e., compatible, physical units in (2). It can also be shown that the second and third terms on the r.h.s. of (3) have the same physical units.

Finally, we comment on the noise term in (3), i.e., the last term on the r.h.s. of (3). It is straightforward to show that the physical units of $k_{\mathrm{B}}\mathsf{M}$ are $[x]^2[V][t]^{-1}$. By way of (4), the physical units of B are therefore $[x][V]^{1/2}[t]^{-1/2}$. From all this and from the last term on the r.h.s. of (3), one concludes that the physical units of $d\mathsf{W}$ must be $[V]^{-1/2}[t]^{1/2}$. This is in agreement with the usual form for the spatio-temporal expectations and covariances of white noise for field theories,

$$\langle d\mathsf{W}_{\boldsymbol{r},t} \rangle = 0, \tag{7}$$

$$\langle\!\langle d\mathsf{W}_{\boldsymbol{r},t} ; d\mathsf{W}_{\boldsymbol{r}',t'} \rangle\!\rangle = \delta(\boldsymbol{r} - \boldsymbol{r}')\delta(t - t')\,dt\,dt'\,\mathbf{1}, \tag{8}$$

i.e., with vanishing mean, and where the covariance of two quantities A and B is denoted by $\langle\!\langle A; B \rangle\!\rangle \equiv \langle AB \rangle - \langle A \rangle \langle B \rangle$. Using the same argumentation as earlier in this subsection, one can rewrite (8) in the form

$$\langle\!\langle d\mathsf{W}_{\boldsymbol{r},t} ; d\mathsf{W}_{\boldsymbol{r}',t'} \rangle\!\rangle \simeq \mathscr{V}^{-1}\delta_{\boldsymbol{r},\boldsymbol{r}'}\,\delta_{t,t'}\,dt\,\mathbf{1}, \tag{9}$$

which is useful for numerical implementations. Here, $\delta_{\boldsymbol{r},\boldsymbol{r}'}$ and $\delta_{t,t'}$ denote Kronecker delta's, rather than Dirac functions, i.e., they can assume values 0 and 1.

As it will turn out further below (Section 4.3), the quantity $\mathscr{V}$ also affects the relation between the free energy densities in different formulations.

3. Fluctuating viscoelasticity in terms of a conformation tensor c

3.1. Model development

For the Eulerian description of complex fluids, we consider the set of variables $\mathsf{x} = (\rho, \boldsymbol{m}, \vartheta, \boldsymbol{c})$, with mass density ρ, momentum density $\boldsymbol{m}$, conformation tensor $\boldsymbol{c}$, and where ϑ denotes a thermal variable (e.g. see [34,35,47]). In [35], ϑ has been chosen as the density of internal energy, for technical convenience in relation to the thermodynamics model development. In contrast, in this paper, we prefer to use as thermal variable the absolute temperature T for summarizing the results of [35], for two reasons: First, in the literature, most often the Helmholtz free energy is chosen as the preferred thermodynamic potential describing polymeric fluids, which implies using T in the set of variables. Also, this choice is particularly convenient for distinguishing between energy elasticity and entropy elasticity. And second, the temperature features prominently in the amplitude of fluctuations, which is the main topic of this paper.

In the sequel, the following assumptions are made, in order to keep the procedure for including fluctuations as transparent and compact as possible. First, it is assumed that there is no $\boldsymbol{c}$-related contribution to the energy, i.e., entropy elasticity is considered, which is the most relevant case for polymeric fluids. And second, in the absence of fluctuations, the relaxation of the conformation tensor $\boldsymbol{c}$ is the only irreversible dynamics accounted for, i.e., heat conduction and Newtonian viscous effects are not included. However, the latter two can be included in a straightforward way [35]. Under these conditions, the evolution equation for $\boldsymbol{c}$ in the absence of fluctuations, and the constitutive relation for the total stress tensor can be expressed as (see p.110ff. in [35])

$$\boldsymbol{c}_{(1)} = -\boldsymbol{\Lambda}^{(4)} \odot \frac{\partial \psi}{\partial \boldsymbol{c}}, \tag{10}$$

$$\boldsymbol{\sigma} = \left(a - \rho \frac{\partial a}{\partial \rho}\bigg|_{T,\boldsymbol{c}}\right)\mathbf{1} + \boldsymbol{\tau}_{\mathrm{p}}, \tag{11}$$

$$\boldsymbol{\tau}_{\mathrm{p}} = 2\boldsymbol{c}\cdot\frac{\partial \psi}{\partial \boldsymbol{c}}, \tag{12}$$

with the upper-convected time derivative defined by [29,48,49]

$$\boldsymbol{c}_{(1)} \equiv \partial_t \boldsymbol{c} + \boldsymbol{v}\cdot\nabla\boldsymbol{c} - \boldsymbol{\kappa}\cdot\boldsymbol{c} - \boldsymbol{c}\cdot\boldsymbol{\kappa}^{\mathrm{T}}, \tag{13}$$

with velocity field $\boldsymbol{v}\,(=\boldsymbol{m}/\rho)$ and its gradient $\boldsymbol{\kappa} = (\nabla\boldsymbol{v})^{\mathrm{T}}$. In the stress tensor (11), a stands for the total Helmholtz free energy density per unit volume, excl. the kinetic energy of the fluid. The (additive) $\boldsymbol{c}$-dependent contribution to a is denoted by ψ, and gives rise to both the relaxation of the conformation (10) and to the polymer contribution to the stress (12). Note that the derivatives of ψ could be expressed exclusively in terms of derivatives of its entropic contribution, since we restrict ourselves to the entropy-elastic case. However, for later convenience and for comparing with the literature, we use nevertheless ψ, keeping in mind that the entire treatment is applicable to entropy elasticity only. In the relaxation dynamics (10), $\boldsymbol{\Lambda}^{(4)}$ denotes a fourth-rank tensor, and the notation

$$\left[\boldsymbol{\Lambda}^{(4)} \odot \frac{\partial \psi}{\partial \boldsymbol{c}}\right]_{ij} = \Lambda_{ijkl}^{(4)}\frac{\partial \psi}{\partial c_{kl}} \tag{14}$$

is used, which differs slightly from the usual double-contraction denoted by ":", but is more convenient in the current context. Throughout the entire paper, the Einstein summation convention is used for all indices that occur twice, unless otherwise indicated. The tensor $\boldsymbol{\Lambda}^{(4)}$ must be positive semi-definite,

$$A_{ij}\Lambda_{ijkl}^{(4)}A_{kl} \geq 0, \quad \forall\, A_{mn}, \tag{15}$$

and possess the following symmetry properties,

$$\Lambda_{ijkl}^{(4)} = \Lambda_{klij}^{(4)}, \tag{16}$$

$$\Lambda_{jikl}^{(4)} = \Lambda_{ijkl}^{(4)}, \tag{17}$$

where (17) is needed to ensure that the conformation tensor stays symmetric. Note that $\Lambda_{ijlk}^{(4)} = \Lambda_{ijkl}^{(4)}$ follows from (16) and (17).

In view of the evolution equations without and with fluctuations, (1) and (3), it is mentioned that under the above assumptions, the friction matrix takes the form,

$$\mathsf{M} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & T\boldsymbol{\Lambda}^{(4)} \end{pmatrix}. \tag{18}$$

This implies that, when studying $\frac{\delta}{\delta \mathsf{x}}\cdot\mathsf{M}$ in (3) and the decomposition (4), one can therefore concentrate on the calculation of

$$[\mathrm{div}_{\boldsymbol{c}}\boldsymbol{\Lambda}^{(4)}]_{kl} = \frac{\partial}{\partial c_{ij}}\Lambda_{ijkl}^{(4)}, \tag{19}$$

$$B_{ijmn}^{(4)}B_{klmn}^{(4)} = 2k_{\mathrm{B}}T\Lambda_{ijkl}^{(4)}. \tag{20}$$

Obviously, the existence of a decomposition (20) automatically guarantees the positive semi-definiteness (15), as well as the symmetry property (16). In order to ensure the symmetry property (17), one needs to require $B_{jimn}^{(4)} = B_{ijmn}^{(4)}$. With this and in view of the general evolution Eq. (3), the stochastic differential equation for the conformation tensor, using the Itô interpretation, assumes the form

$$d\boldsymbol{c} = \left(-\boldsymbol{v}\cdot\nabla\boldsymbol{c} + \boldsymbol{\kappa}\cdot\boldsymbol{c} + \boldsymbol{c}\cdot\boldsymbol{\kappa}^{\mathrm{T}} - \boldsymbol{\Lambda}^{(4)} \odot \frac{\partial \psi}{\partial \boldsymbol{c}}\right)dt$$
$$+ \frac{k_{\mathrm{B}}T}{\mathscr{V}}\mathrm{div}_{\boldsymbol{c}}\boldsymbol{\Lambda}^{(4)}\,dt + \frac{1}{\sqrt{\mathscr{V}}}\boldsymbol{B}^{(4)} \odot d\widehat{\boldsymbol{W}}, \tag{21}$$

which is the main result about the formulation of fluctuating viscoelasticity in terms of a conformation tensor c. In (21), we have used the notation

$$[\boldsymbol{B}^{(4)} \odot d\widehat{\boldsymbol{W}}]_{ij} = B^{(4)}_{ijkl} d\widehat{W}_{kl} \,. \tag{22}$$

The increment $d\widehat{\boldsymbol{W}}$ (which can be represented by a 3×3-matrix in 3D space) of the Wiener processes is specified by the spatio-temporal expectations and covariances

$$\langle d\widehat{\boldsymbol{W}}_{\boldsymbol{r},t} \rangle \;=\; 0 \,, \tag{23}$$

$$\langle\langle d\widehat{\boldsymbol{W}}_{\boldsymbol{r},t} ; d\widehat{\boldsymbol{W}}_{\boldsymbol{r}',t'} \rangle\rangle \;=\; \delta_{\boldsymbol{r},\boldsymbol{r}'} \, \delta_{t,t'} \, dt \, \mathbf{1} \,, \tag{24}$$

where, in comparison to (7) and (9), a factor $\sqrt{\mathscr{V}}$ has been split off for later convenience. In matrix notation, the components of $\mathbf{1}$ are given by $[\mathbf{1}]_{ijkl} = \delta_{ik}\delta_{jl}$. Eq. (24) implies that any two of the (nine) components of $d\widehat{\boldsymbol{W}}$ are independent from each other.

At this point, it becomes clear that neglecting energy-elastic effects is not only reasonable for polymeric fluids and in agreement with literature. Rather, it is also convenient from a technical perspective, when studying fluctuations. Particularly, when applying the form (18) of the friction matrix to the general procedure (2)–(4), it is evident that only the c-dynamics is affected by the fluctuations, see (21). If, in contrast, energy-elastic effects were accounted for, also the third row and column of (18) would have non-vanishing contributions, which would eventually lead to fluctuations also in the thermal variable.

To finalize the general formulation of c-based fluctuating viscoelasticity, the equilibrium distribution p_{eq} of c is briefly discussed. Using the Fokker-Planck Eq. (2) with (18), one finds that the equilibrium distribution of the conformation tensor can be written in the form

$$p_{\mathrm{eq}}(\boldsymbol{c}) = \frac{1}{Z} \exp\!\left(-\frac{\mathscr{V} \, \psi(\boldsymbol{c})}{k_{\mathrm{B}} T} \right) , \tag{25}$$

with Z a normalization constant. Note that the volume of spatial resolution, $\mathscr{V}$, plays an important role in this distribution. Namely, it is the free energy in a volume element of size $\mathscr{V}$ that is compared to the thermal energy, which finally determines the magnitude of fluctuations of the conformation tensor c.

3.2. Complications in a numerical implementation

Two aspects of stochastic differential Eq. (21) require special attention, especially when it comes to its numerical implementation.

First, exceptional fluctuations in a finite time-step might lead to a violation of the positive semi-definiteness of the conformation tensor. To illustrate that, consider the evolution Eq. (21) in the absence of imposed flow, and use a relaxation tensor that is independent of conformation, for simplicity. Assume that, at some moment in time, the system is in the state that minimizes the Helmholtz free energy density, $\partial \psi / \partial \boldsymbol{c} = \boldsymbol{0}$, which implies $\boldsymbol{c} \propto \mathbf{1}$ (see Section 5), and typically one has $B^{(4)}_{ijkl} = (B/2)(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$ (see Section 5, in the limit of $\boldsymbol{c} \propto \mathbf{1}$). Therefore, in the subsequent time-step, the increment in an Euler-forward scheme [43] is given by $d\boldsymbol{c} = (B/2)(d\widehat{\boldsymbol{W}} + d\widehat{\boldsymbol{W}}^{\mathrm{T}})/\sqrt{\mathscr{V}}$. For a finite time-step, this increment of the conformation tensor can result in a violation of its positive semi-definiteness after the step, because the Gaussian-distributed increments of the Wiener process can in principle become arbitrarily large.

And second, in [50] it has been shown that the formulation in terms of the conformation tensor c suffers from a numerical instability that originates from an imbalance between the convection and the deformation terms on an Eulerian grid. The instability puts a severe requirement on spatial mesh resolution and manifests itself near stagnation points where exponential profiles in the conformation are present. Note, that the numerical instability exists even in the absence of fluctuations. The solution to this problem put forward in [50] is a formulation in terms of $\log c$. However, formulation of fluctuations in

terms of $\log c$ would be complicated and doesn't seem like an attractive way forward. In [51] it has been argued that the method of Brownian configuration fields (BCF) [52] does not suffer from the numerical instability. The reason being that in BCF the constitutive model, in addition to relaxation and stochastic forcing terms, has been formulated in terms of convection and deformation of (contravariant) vectors instead of tensors.

Both of the above mentioned issues will be addressed again at the end of Section 4.3.

4. Fluctuating viscoelasticity in terms of b (in $c = b \cdot b^{\mathrm{T}}$)

4.1. Motivation

Taking a step back, one can try to address the two issues mentioned at the end of the previous section not simply by numerical manipulations, but rather by reformulating the entire viscoelastic model. In this section, we propose to formulate fluctuating viscoelastic models not in terms of the conformation tensor c, but rather in terms of a quantity b obeying the decomposition

$$\boldsymbol{c} = \boldsymbol{b} \cdot \boldsymbol{b}^{\mathrm{T}} \,. \tag{26}$$

If one was successful with this, one would have addressed both issues mentioned at the end of the previous section: First, the positivity of c would be guaranteed, because one can, at any moment in time, calculate c for the current state b. And second, if convection and deformation of b would be similar to a contravariant vector, the evolution equation has close similarities with BCF regarding convection/deformation and is also expected to show similar numerical stability. For these reasons, this section formulates rheological models in terms of b.

A motivation for using the quantity b in the decomposition $c = b \cdot b^{\mathrm{T}}$ as a fundamental variable can be given as follows. The majority of the most popular conformation-tensor based models in the literature root in a more microscopic interpretation in terms of vectors [28], e.g. the end-to-end vector of the entire chain or of a segment of the chain. If the vector in the undeformed state is denoted by $\boldsymbol{l}_0$, affine deformation will result in $\boldsymbol{l}_t = \boldsymbol{F}_t \cdot \boldsymbol{l}_0$, where $\boldsymbol{F}_t$ denotes the deformation gradient [53,54]. Since the latter obeys $D_t \boldsymbol{F}_t = \boldsymbol{\kappa} \cdot \boldsymbol{F}_t$ with material (substantial) derivative $D_t = \partial_t + \boldsymbol{v} \cdot \nabla$, one finds for the dyadic product $D_t(\boldsymbol{l}_t \boldsymbol{l}_t) = \boldsymbol{\kappa} \cdot (\boldsymbol{l}_t \boldsymbol{l}_t) + (\boldsymbol{l}_t \boldsymbol{l}_t) \cdot \boldsymbol{\kappa}^{\mathrm{T}}$, which represents upper-convected behavior. In turn, the conformation tensor defined as the average of $\boldsymbol{l}_t \boldsymbol{l}_t$ over the initial vector $\boldsymbol{l}_0$ with suitable normalization, $\boldsymbol{c}_t = 3\langle \boldsymbol{l}_t \boldsymbol{l}_t \rangle_{\boldsymbol{l}_0} / \langle \boldsymbol{l}_0 \cdot \boldsymbol{l}_0 \rangle_{\boldsymbol{l}_0}$, is thus upper-convected as well. For an isotropically distributed initial vector, $\langle \boldsymbol{l}_0 \boldsymbol{l}_0 \rangle_{\boldsymbol{l}_0} \propto \mathbf{1}$, the conformation tensor becomes $\boldsymbol{c}_t = \boldsymbol{F}_t \cdot \boldsymbol{F}_t^{\mathrm{T}}$. In summary, therefore, the upper-convected behavior, the symmetry, and the positive definiteness of the conformation tensor all emerge naturally when resorting to the underlying vector, i.e., the deformation gradient. In this sense it is more fundamental to consider the deformation gradient, rather than the conformation tensor. In the current context, we are of course not only interested in affine deformation, but the relaxation and related fluctuations of the conformation are of particular interest. The above relation between F and c can be generalized in this direction, by using the concept of the elastic part of the deformation gradient [55,56], where the irreversible dynamics occurs in the current rather than the intermediate state [56–58]. The conclusion is that the quantity b in $c = b \cdot b^{\mathrm{T}}$ is to be interpreted as the elastic, i.e., recoverable, part of the deformation gradient.

In solid mechanics, one often deals with anisotropic materials. When attempting an Eulerian formulation of such materials, one notices the following, even when discussing the reversible, hyperelastic effects only [59]. On the one hand, the material anisotropy can not be captured in the thermodynamic potential only in terms of the left Cauchy-Green strain tensor $\boldsymbol{F} \cdot \boldsymbol{F}^{\mathrm{T}}$. On the other hand, the affine deformation can not be captured in closed form only in terms of the right Cauchy-Green strain tensor $\boldsymbol{F}^{\mathrm{T}} \cdot \boldsymbol{F}$. The conclusion is that, in order to describe anisotropic materials in an Eulerian setting, the deformation gradient itself is the

preferred quantity. Since also the models for complex fluids are most often formulated in an Eulerian setting, the same conclusion also applies to these materials, i.e., $\boldsymbol{b}$ is preferred over $\boldsymbol{c}$. For example, $\boldsymbol{b}$ can be a useful variable in relation to modeling the mechanical behavior of liquid crystals [60].

Before formulating viscoelasticity in terms of $\boldsymbol{b}$ with the interpretation elaborated above, it is mentioned that [61] has advocated using the square root of $\boldsymbol{c}$, i.e., $\boldsymbol{b}$ that is symmetric. However, it appears that the corresponding dynamics does not assume a very compact and transparent form for general flow situations, and also in [62] it has been argued on thermodynamic grounds that the square root of $\boldsymbol{c}$ is not a suitable structural variable. Furthermore, it does not respect the close ties discussed above between the conformation tensor and the underlying vectors.

4.2. Proper thermodynamic formulation of the $\boldsymbol{b}$-dynamics

The complete set of variables for formulating viscoelasticity is $\tilde{\mathsf{x}} = (\rho, \boldsymbol{m}, T, \boldsymbol{b})$, with mass density ρ, momentum density $\boldsymbol{m}$, absolute temperature T, and the quantity $\boldsymbol{b}$, the latter in line with the above discussion.

For the formulation of the evolution equations for $\tilde{\mathsf{x}}$, we start by writing the total energy and entropy in the form

$$E = \int \left[\frac{m^2}{2\rho} + \tilde{\varepsilon}(\rho, T) \right] d^3r , \tag{27}$$

$$S = \int \tilde{s}(\rho, T, \boldsymbol{b}) \, d^3r , \tag{28}$$

with the volumetric densities of internal energy $\tilde{\varepsilon}$ and entropy $\tilde{s}$, from which the functional derivatives $\delta E/\delta\tilde{\mathsf{x}}$ and $\delta S/\delta\tilde{\mathsf{x}}$ follow. Note that, in line with the focus on entropy elasticity mentioned earlier, it is assumed that the internal energy density $\tilde{\varepsilon}$ does not depend on the conformation $\boldsymbol{b}$.

For the determination of the Poisson operator $\tilde{\mathsf{L}}$, we make the choice that the advection behavior of $\boldsymbol{b}$ is identical to that of the total deformation gradient, in line with the motivation given in Section 4.1. This is the case studied in [59], where the deformation gradient was included in the formulation, and the corresponding Poisson operator was determined. It is noted that, in order to relate to [59], the addition of the mass density ρ is needed, which is straightforward. The resulting reversible contributions to the evolution equations are then given by

$$\partial_t \rho|_{\mathrm{rev}} = -\nabla \cdot (\boldsymbol{v}\rho) , \tag{29}$$

$$\partial_t \boldsymbol{m}|_{\mathrm{rev}} = -\nabla \cdot (\boldsymbol{v}\boldsymbol{m}) + \nabla \cdot \tilde{\boldsymbol{\sigma}} , \tag{30}$$

$$\partial_t \boldsymbol{b}|_{\mathrm{rev}} = -\boldsymbol{v} \cdot \nabla \boldsymbol{b} + \boldsymbol{\kappa} \cdot \boldsymbol{b} , \tag{31}$$

with velocity $\boldsymbol{v} = \boldsymbol{m}/\rho$, and the total stress tensor $\tilde{\boldsymbol{\sigma}}$ and its polymer contribution $\tilde{\tau}_{\mathrm{p}}$,

$$\tilde{\boldsymbol{\sigma}} = \left(\tilde{a} - \rho \frac{\partial \tilde{a}}{\partial \rho}\bigg|_{T,\boldsymbol{b}} \right) \boldsymbol{1} + \tilde{\tau}_{\mathrm{p}} , \tag{32}$$

$$\tilde{\tau}_{\mathrm{p}} = \frac{\partial \tilde{\psi}}{\partial \boldsymbol{b}}\bigg|_{\rho,T} \cdot \boldsymbol{b}^{\mathrm{T}} , \tag{33}$$

with total Helmholtz free energy density per unit volume $\tilde{a} = \tilde{\varepsilon} - T\tilde{s}$, and its $\boldsymbol{b}$-dependent contribution denoted by $\tilde{\psi}$. For showing that this stress tensor is indeed symmetric, the reader is referred to [59], where this issue has been discussed for general anisotropic materials. The reversible contribution to the evolution of $\boldsymbol{b}$, (31), is identical to the affine deformation behavior of the deformation gradient, in line with the discussion in Section 4.1. The temperature equation is not written explicitly here for simplicity, but it can be obtained in a straightforward way from $\partial \tilde{s}/\partial t = -\nabla \cdot (\tilde{s}\boldsymbol{v})$, and using the chain rule for the

differentiation of $\tilde{s} = \tilde{s}(\rho, T, \boldsymbol{b})$.

Because the evolution of $\boldsymbol{b}$ described by (31) is identical to that of a contravariant vector [48], for the remainder of this paper we will call $\boldsymbol{b}$ the "contravariant deformation", while the relation $\boldsymbol{c} = \boldsymbol{b} \cdot \boldsymbol{b}^{\mathrm{T}}$, (26), will be referred to as the "contravariant decomposition".

With respect to the irreversible dynamics, the friction operator $\tilde{\mathsf{M}}$ needs to be determined. Neglecting any other irreversible contribution than what is related to the conformational relaxation, we make the ansatz, in analogy to Section 3.1 and [35],

$$\tilde{\mathsf{M}} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & T\tilde{\boldsymbol{\Lambda}}^{(4)} \end{pmatrix} . \tag{34}$$

By construction, it is clear that (34) satisfies the degeneracy condition $\tilde{\mathsf{M}} \cdot \delta E/\delta \tilde{\mathsf{x}} = 0$. Furthermore, (34) is symmetric and positive semi-definite if these properties hold for $\tilde{\boldsymbol{\Lambda}}^{(4)}$, particularly

$$A_{ij} \tilde{\Lambda}^{(4)}_{ijkl} A_{kl} \geq 0 , \qquad \forall A_{mn} , \tag{35}$$

$$\tilde{\Lambda}^{(4)}_{ijkl} = \tilde{\Lambda}^{(4)}_{klij} . \tag{36}$$

Using (34), the only irreversible contribution to the evolution equations of $\tilde{\mathsf{x}}$ is given by

$$\partial_t b_{ij}|_{\mathrm{irr}} = -\tilde{\Lambda}^{(4)}_{ijkl} \frac{\partial \tilde{\psi}}{\partial b_{kl}}\bigg|_{\rho,T} , \tag{37}$$

where, in passing, we note the analogy between (37) and (10).

Due to the specific form of the friction operator $\tilde{\mathsf{M}}$, the calculation of $\frac{\delta}{\delta \tilde{\mathsf{x}}} \cdot \tilde{\mathsf{M}}$ in (3) and the decomposition (4) reduces to the calculation of

$$[\mathrm{div}_{\boldsymbol{b}} \tilde{\boldsymbol{\Lambda}}^{(4)}]_{kl} = \frac{\partial}{\partial b_{ij}} \tilde{\Lambda}^{(4)}_{ijkl} , \tag{38}$$

$$\tilde{B}^{(4)}_{ijmn} \tilde{B}^{(4)}_{klmn} = 2k_{\mathrm{B}} T \tilde{\Lambda}^{(4)}_{ijkl} . \tag{39}$$

Obviously, the existence of a decomposition (39) automatically guarantees the positive semi-definiteness (35), as well as the symmetry property (36). It is pointed out that for the $\boldsymbol{b}$-formulation the symmetry property (17) is not required. With this, and in view of the general evolution Eq. (3), the stochastic differential equation for the contravariant deformation $\boldsymbol{b}$, using the Itô interpretation, assumes the form

$$d\boldsymbol{b} = \left(-\boldsymbol{v} \cdot \nabla \boldsymbol{b} + \boldsymbol{\kappa} \cdot \boldsymbol{b} - \tilde{\boldsymbol{\Lambda}}^{(4)} \odot \frac{\partial \tilde{\psi}}{\partial \boldsymbol{b}} \right) dt$$
$$+ \frac{k_{\mathrm{B}} T}{\mathcal{V}} \mathrm{div}_{\boldsymbol{b}} \tilde{\boldsymbol{\Lambda}}^{(4)} dt + \frac{1}{\sqrt{\mathcal{V}}} \tilde{\boldsymbol{B}}^{(4)} \odot d\widehat{\boldsymbol{W}} . \tag{40}$$

This, together with the polymer contribution to the stress, (33), is the main result about the formulation of fluctuating viscoelasticity in terms of the contravariant deformation $\boldsymbol{b}$. In (40), we have used the notation (14) and (22), and the increment $d\widehat{\boldsymbol{W}}$ of the Wiener processes is specified by the expectations (23) and covariances (24).

To finalize the general formulation of $\boldsymbol{b}$-based fluctuating viscoelasticity, the equilibrium distribution $\tilde{p}_{\mathrm{eq}}$ of $\boldsymbol{b}$ is given. With a calculation analogous to the $\boldsymbol{c}$-based model, one finds that the equilibrium distribution can be written in the form

$$\tilde{p}_{\mathrm{eq}}(\boldsymbol{b}) = \frac{1}{\tilde{Z}} \exp\left(-\frac{\mathcal{V}\tilde{\psi}(\boldsymbol{b})}{k_{\mathrm{B}} T} \right) , \tag{41}$$

with $\tilde{Z}$ a normalization constant.

4.3. General relation between $\boldsymbol{b}$-based and $\boldsymbol{c}$-based models

In order to identify the proper choice for the conformation-

dependent free energy contribution $\widetilde{\psi}$ and the relaxation tensor $\widetilde{\boldsymbol{\Lambda}}^{(4)}$ for a known rheological model (e.g. Maxwell, Giesekus, FENE-P, see Section 5), the following two issues can be discussed in general terms.

It is known that a change of variables brings about an additional contribution to the entropy (e.g. see p.29 in [35]), and thus the free energy gets an additional contribution as well. To put this in practice for the subject at hand, it is noted that both $\boldsymbol{c}$ and $\boldsymbol{b}$ can be diagonalized simultaneously by an appropriate rotation, leading to $\boldsymbol{c} = \mathrm{diag}(\lambda_1^2, \lambda_2^2, \lambda_3^2)$ and $\boldsymbol{b} = \mathrm{diag}(\lambda_1, \lambda_2, \lambda_3)$, with λ_i the eigenvalues of $\boldsymbol{b}$. Therefore, for the change of variables, we can concentrate on the change in the eigenvalues. Based on the transformation rule specified on p.29 in [35], one finds that the additional entropy contribution due to this change of variables is $k_{\mathrm{B}}(\ln \det \boldsymbol{b} + \ln 8)$ in each volume element. Omitting the additive constant, $k_{\mathrm{B}}\ln 8$, and translating this to the difference of the Helmholtz free energy densities, one obtains

$$\widetilde{\psi}(\boldsymbol{b}) = \psi(\boldsymbol{c})|_{\boldsymbol{c}=\boldsymbol{b}\cdot\boldsymbol{b}^{\mathrm{T}}} - \frac{k_{\mathrm{B}}T}{\mathscr{V}} \ln \det \boldsymbol{b} , \tag{42}$$

with the volume element size $\mathscr{V}$ introduced earlier. It is noted that the additional term in the free energy, the second term on the r.h.s. of (42), leads to a modification of the stress tensor. Comparing the stress tensor in the $\boldsymbol{c}$-model, (11) with (12), to the stress tensor in the $\boldsymbol{b}$-model, (32) with (33), one finds

$$\widetilde{\boldsymbol{\sigma}} - \boldsymbol{\sigma} = -\frac{k_{\mathrm{B}}T}{\mathscr{V}}(\ln \det \boldsymbol{b} + 1)\boldsymbol{1} , \tag{43}$$

where we have made use of $\partial(\ln \det \boldsymbol{b})/\partial\boldsymbol{b} = \boldsymbol{b}^{-\mathrm{T}}$, with $\boldsymbol{b}^{-\mathrm{T}} = (\boldsymbol{b}^{-1})^{\mathrm{T}}$, and the general relation

$$\frac{\partial f}{\partial \boldsymbol{b}} = 2\frac{\partial f}{\partial \boldsymbol{c}}\cdot\boldsymbol{b} , \tag{44}$$

for an arbitrary function f that depends on $\boldsymbol{b}$ by way of $\boldsymbol{c}$. The issue of the difference in stress, (43), will be addressed again in Section 4.5.

For the specification of the relaxation tensor $\widetilde{\boldsymbol{\Lambda}}^{(4)}$, we make use of the equivalence of the brackets [35,60]

$$\frac{\partial f}{\partial c_{ij}}\Lambda^{(4)}_{ijkl}\frac{\partial g}{\partial c_{kl}} = \frac{\partial f}{\partial b_{ij}}\widetilde{\Lambda}^{(4)}_{ijkl}\frac{\partial g}{\partial b_{kl}} , \tag{45}$$

for two arbitrary functions f and g. By employing (44) and explicit symmetrization with respect to $i \leftrightarrow j$ and $k \leftrightarrow l$, one obtains

$$\Lambda^{(4)}_{ijkl} = \widetilde{\Lambda}^{(4)}_{irks}b_{jr}b_{ls} + \widetilde{\Lambda}^{(4)}_{jrks}b_{ir}b_{ls} + \widetilde{\Lambda}^{(4)}_{irls}b_{jr}b_{ks} + \widetilde{\Lambda}^{(4)}_{jrls}b_{ir}b_{ks} , \tag{46}$$

since (45) must hold for any two functions f and g.

It remains to be shown whether the general $\boldsymbol{c}$-based model (21) and the general $\boldsymbol{b}$-based model (40) are compatible when using the relations (42) for the Helmholtz free energy density and (46) for the relaxation tensor, respectively. In order to relate the two models, we refer to a result from stochastic calculus, from which it follows (see [63], and p. 99 in [43]) that, since $\boldsymbol{b}$ is an Itô process, also $\boldsymbol{c}$ is an Itô process, given by

$$d\boldsymbol{c} = d\boldsymbol{b}\cdot\boldsymbol{b}^{\mathrm{T}} + \boldsymbol{b}\cdot d\boldsymbol{b}^{\mathrm{T}} + d\boldsymbol{b}\cdot d\boldsymbol{b}^{\mathrm{T}} , \tag{47}$$

where in $d\boldsymbol{b}\cdot d\boldsymbol{b}^{\mathrm{T}}$ only terms involving $d\widehat{\boldsymbol{W}}d\widehat{\boldsymbol{W}}$ are kept, which are subsequently reduced according to the rule (see Table 3.1 in [43])

$$d\widehat{W}_{\boldsymbol{r},t,ij}d\widehat{W}_{\boldsymbol{r}',t',kl} \rightarrow \delta_{\boldsymbol{r},\boldsymbol{r}'}\,\delta_{t,t'}\,\delta_{ik}\,\delta_{jl}\,dt . \tag{48}$$

Applying this scheme for deriving the dynamics of $\boldsymbol{c}$ based on that of $\boldsymbol{b}$ (40), and making use of (42) and (46), one indeed recovers (21) if the following two relations hold,

$$\frac{\partial \Lambda^{(4)}_{klij}}{\partial c_{kl}} = \left(\widetilde{\Lambda}^{(4)}_{ikmn}b_{jk} + \widetilde{\Lambda}^{(4)}_{jkmn}b_{ik}\right)b_{nm}^{-1} + 2\widetilde{\Lambda}^{(4)}_{ikjk}$$
$$+ \left(\frac{\partial \widetilde{\Lambda}^{(4)}_{ikmn}}{\partial b_{mn}}b_{jk} + \frac{\partial \widetilde{\Lambda}^{(4)}_{jkmn}}{\partial b_{mn}}b_{ik}\right) , \tag{49}$$

$$B^{(4)}_{ijkl} = \widetilde{B}^{(4)}_{irkl}b_{jr} + \widetilde{B}^{(4)}_{jrkl}b_{ir} . \tag{50}$$

As far as the verification of (49) is concerned, one can use the explicit expression for $\boldsymbol{\Lambda}^{(4)}$ given by (46), take its derivative with respect to $\boldsymbol{c}$, and compare the result with the r.h.s. of (49). The $\boldsymbol{c}$-derivative can be calculated using (44), which reads in component notation $\partial(\cdot)/\partial c_{kl} = \frac{1}{2}b_{ql}^{-1}\partial(\cdot)/\partial b_{kq}$ or, by virtue of the symmetry of $\boldsymbol{c}$, $\partial(\cdot)/\partial c_{kl} = \frac{1}{2}b_{qk}^{-1}\partial(\cdot)/\partial b_{lq}$. It proves to be most convenient to apply $\frac{1}{2}b_{ql}^{-1}\partial(\cdot)/\partial b_{kq}$ to the first two terms in (46) and $\frac{1}{2}b_{qk}^{-1}\partial(\cdot)/\partial b_{lq}$ to the last two terms in (46). So doing, one finds that (49) is indeed satisfied. With regards to verifying the condition (50), it can be shown that the r.h.s. of (50) satisfies (20) with $\boldsymbol{\Lambda}^{(4)}$ according to (46), given that $\widetilde{\boldsymbol{B}}^{(4)}$ satisfies (39). In other words, the condition (50) is automatically fulfilled.

In summary, it has been established that the $\boldsymbol{b}$-formulation reduces to the $\boldsymbol{c}$-formulation, using the transformation rules (42) and (46) for the Helmholtz free energy density and the relaxation tensor, respectively. Therefore, in the sequel, we will refer to these two formulations as "representations" in order to underline that they are equivalent representations of one and the same model, i.e., the $\boldsymbol{c}$-representation and the $\boldsymbol{b}$-representation.

Having established the relation between the two representations, one finds that the fluctuating $\boldsymbol{c}$-dynamics, (21), actually preserves the positive definiteness of the conformation tensor, for an infinitesimally small time step. Knowing of the existence of the corresponding $\boldsymbol{b}$-representation, this is obvious, while it is not evident in the $\boldsymbol{c}$-representation, i.e., (21). In contrast, for a finite time-step, the positive definiteness of the conformation tensor $\boldsymbol{c}$ is only guaranteed when using the $\boldsymbol{b}$-representation.

Coming back to the issues discussed in Section 3.2, one can conclude the following. For any given model of fluctuating viscoelasticity in terms of the conformation tensor $\boldsymbol{c}$, there is an equivalent representation in terms of the contravariant deformation $\boldsymbol{b}$. Using the latter for a numerical implementation, both issues raised in Section 3.2 are thus alleviated, as discussed at the beginning of Section 4.1.

4.4. Non-uniqueness of $\boldsymbol{b}$

The expression for $\boldsymbol{b}$ as obtained from the decomposition (26) is not unique, since any modification of $\boldsymbol{b}$ to $\boldsymbol{b}' = \boldsymbol{b}\cdot\boldsymbol{R}$ for an arbitrary rotation $\boldsymbol{R}$ leaves the conformation tensor $\boldsymbol{c}$ unchanged. Requiring contravariant reversible dynamics (31) for $\boldsymbol{b}$ does not eliminate that non-uniqueness, as can be shown for the case that the material derivative of the rotation vanishes. However, the non-uniqueness of the contravariant deformation $\boldsymbol{b}$ is without any further consequence, as explained in the following.

In the procedure described in Section 4.3, the relation between the $\boldsymbol{b}$- and $\boldsymbol{c}$-representations of one and the same model has been established. For a known $\boldsymbol{c}$-based model, the corresponding building blocks in the $\boldsymbol{b}$-based approach have been determined as to represent that same model. The corresponding stochastic differential equation in the $\boldsymbol{c}$-representation, (21), may explicitly depend on $\boldsymbol{b}$, by way of the noise term, see (50). However, it can be seen from the corresponding Fokker–Planck equation of the $\boldsymbol{c}$-representation that the statistical properties of the process depend only on $\boldsymbol{c}$, rather than on $\boldsymbol{b}$ itself. This proves that the non-uniqueness of the contravariant deformation $\boldsymbol{b}$ has no physical consequence. For the special case of equilibrium, the irrelevance of the additional rotations on $\boldsymbol{b}$ is manifest in the equilibrium distribution (41), since the Helmholtz free energy density (42) is

rotation invariant.

As a word of caution, it is mentioned that there is a situation in which the non-uniqueness needs to be treated with care. Namely, this is the case when studying the steady state in the absence of fluctuations (note that, in the presence of fluctuations, there is no true steady state). The physical meaning of steady state is that the conformation tensor c and the quantities based on it, e.g. the stress tensor, do not depend on time. Using $b' = b \cdot R$, it is obvious that arbitrary time-dependent rotations R have no effect on requiring c to be time-independent. Therefore, when studying a steady state, one must not assume that b is constant. Rather, its dynamics is restricted to be rotary in nature, in terms of a time-dependent R.

4.5. Procedure for adding fluctuations to known rheological models

The literature provides a wealth of rheological models, formulated in terms of a conformation tensor c. In the following, a concrete step-by-step procedure is given for the identification of the building blocks in the corresponding b-representation of such models, $\widetilde{\psi}$ and $\widetilde{\boldsymbol{\Lambda}}^{(4)}$, based on which the entire b-representation, (33) and (40), can be derived. The concrete steps, in this order, are as follows:

1. For the known (deterministic) model in its c-representation, determine ψ and $\boldsymbol{\Lambda}^{(4)}$.
2. Determine $\widetilde{\psi}$ according to (42).
3. Determine $\widetilde{\boldsymbol{\Lambda}}^{(4)}$ according to (46).
4. Calculate $\mathrm{div}_b \widetilde{\boldsymbol{\Lambda}}^{(4)}$, (38).
5. Determine $\widetilde{\boldsymbol{B}}^{(4)}$ according to (39).
6. Compose all of the above, in order to arrive at the stochastic differential equation (in the Itô interpretation) of b, (40).
7. For determining the mechanical response of a certain fluctuating rheological model, there are two viewpoints, as discussed in the following. Based on the equivalence of representations discussed further above, one can take the viewpoint that the b-representation is chosen for the numerical implementation only for practical convenience. Having this viewpoint in mind when solving the dynamic model in the b-representation, c can be calculated at any moment in time, and the stress tensor σ is then given by (11) and (12). Contrary, if the b-formulation is viewed as a fundamental model, the stress tensor is given by $\widetilde{\sigma}$, (32) and (33).

5. Applications

In this section, the general procedure developed in the previous sections is applied to some concrete viscoelastic models. As prototypical examples, we consider the Maxwell model, the FENE-P model, and the Giesekus model. The reason for choosing these three models is that the FENE-P model differs from the Maxwell model by introducing nonlinearity via the Helmholtz free energy, while the Giesekus model differs from the Maxwell model by introducing nonlinearity via anisotropic relaxation. The concretion consists in identifying ψ and $\boldsymbol{\Lambda}^{(4)}$, and specifying the fluctuating model in the c-representation, which is followed by the determination of $\widetilde{\psi}$ and $\widetilde{\boldsymbol{\Lambda}}^{(4)}$, and the specification of the fluctuating model in the b-representation.

5.1. Maxwell model

Representation in terms of c: The conformation-tensor based upper-convected Maxwell model is given by [29,30]

$$c_{(1)} = -\frac{1}{\lambda}(c - 1),\tag{51}$$

$$\tau_{\mathrm{p}} = G(c - 1),\tag{52}$$

with relaxation time λ and shear modulus G. The corresponding

Helmholtz free energy density and the relaxation tensor have the form [30,47,60] (for $\boldsymbol{\Lambda}^{(4)}$, see also [29] without explicit symmetrization)

$$\psi = \frac{G}{2}(\mathrm{tr}\, c - \ln(\det c) - 3),\tag{53}$$

$$\Lambda_{ijkl}^{(4)} = \Lambda(c_{ik}\delta_{jl} + c_{il}\delta_{jk} + c_{jk}\delta_{il} + c_{jl}\delta_{ik}).\tag{54}$$

Indeed, using these expressions in the general evolution Eq. (10) and the stress tensor (12), one recovers (51) and (52), with the identification $1/\lambda = 2\Lambda G$.

It can be shown that (54) possesses the required symmetry properties (16) and (17). Its positive semi-definiteness is proven by the existence of the decomposition (20), assuming $\Lambda \geq 0$, with

$$B_{ijmn}^{(4)} = \sqrt{2k_{\mathrm{B}}T\Lambda}\,(b_{im}\delta_{jn} + b_{jm}\delta_{in}),\tag{55}$$

which satisfies the symmetry condition (17). For completeness, it is mentioned that, at this point, the only condition on the quantity b in (55) is that it satisfies (26). However, for the formulation of the b-representation further below, b will be identified with the contravariant deformation b introduced earlier, i.e., the reversible dynamics of b is given by (31).

For the divergence (19), one obtains (the reader is referred to Appendix A for the careful calculation)

$$\mathrm{div}_c(T\boldsymbol{\Lambda}^{(4)}) = 2(D + 1)T\Lambda \mathbf{1},\tag{56}$$

assuming, for simplicity, that $T\Lambda$ does not depend on c, and D denotes the dimensionality of the model (e.g. $D = 3$).

In summary, the stochastic differential equation for the Maxwell model becomes

$$\begin{aligned}
d_{\mathrm{m}}c = {} & \left[(\kappa \cdot c + c \cdot \kappa^{\mathrm{T}}) - \frac{1}{\lambda}(c - \mathbf{1})\right]dt \\
& + (D + 1)\frac{\Theta}{\lambda}\mathbf{1}\,dt \\
& + \sqrt{\frac{\Theta}{\lambda}}\,[b \cdot d\widehat{\boldsymbol{W}} + d\widehat{\boldsymbol{W}}^{\mathrm{T}} \cdot b^{\mathrm{T}}],
\end{aligned}\tag{57}$$

where d_{m} denotes the material (substantial) increment,

$$d_{\mathrm{m}}(\ldots) = d(\ldots) + v \cdot \nabla(\ldots)\,dt,\tag{58}$$

and the increments of the Wiener processes, $d\widehat{\boldsymbol{W}}$, have expectations (23) and covariances (24), respectively. With respect to the fluctuations, the crucial parameter in (57) is

$$\Theta \equiv \frac{k_{\mathrm{B}}T}{G\,\mathscr{V}},\tag{59}$$

which is a dimensionless measure for the importance of thermal fluctuations relative to the characteristic elastic energy. Particularly, if the shear modulus G is kept constant, Θ is linear in the absolute temperature T. However, in view of our focus on entropy elasticity, the shear modulus is proportional to the absolute temperature, particularly, $G = nk_{\mathrm{B}}T$, with n the number density of segments [28]. Therefore,

$$\Theta \equiv \frac{1}{n\,\mathscr{V}}.\tag{60}$$

In other words, the magnitude of fluctuations is inversely proportional to the number of segments contained in a volume element of size $\mathscr{V}$. As a word of caution, the reader is reminded of the statement at the end of Section 2.1, that the fluctuations can be eliminated from the model by letting the Boltzmann constant k_{B} go to zero, while leaving the building blocks E, S, L, and M unchanged. This implies that, for taking this limit, one should use (59), rather than (60), because the shear modulus G must be kept constant.

It is noted that b is involved in the determination of the fluctuations, see (55). This is not only the case for the Maxwell model, but also for the other models studied in the sequel. Therefore, in order to make

these models closed in terms of c, one needs an expression for b. This is another reason for preferring the b-representation over the c-representation of fluctuating viscoelasticity.

The fluctuating Maxwell model can be compared in detail with the one presented in the context of smoothed-particle hydrodynamics [21]. There, each fluid particle has a certain volume and contains a certain number of polymers. Furthermore, each fluid particle is equipped with a conformation tensor to describe the conformation of the polymer chains. In our current approach, the role of a fluid particle is taken over by that of a volume element of the fluid, with volume $\mathscr{V}$ and number of polymers $n\mathscr{V}$. The stochastic differential equation for the conformation tensor derived in [21] agrees with the one in this paper, (57), with one exception. The spurious drift term, associated with the Itô interpretation, i.e. $(D + 1)(\Theta/\lambda)\mathbf{1}\,dt$ in (57), is in [21] too small by a factor of two. This difference is related to whether the symmetry of the conformation tensor is or is not taken into account properly when calculating the divergence of the fourth-rank relaxation tensor, see Appendix A. Finally, it is noted that in [21,64] the fluctuations of the conformation tensor are related to the fluctuations of the (end-to-end) vector of the polymer chains, that is a contravariant vector. This further supports our approach of using the contravariant deformation b as a fundamental variable when formulating fluctuating viscoelasticity.

Representation in terms of b: To derive the b-representation of the Maxwell model, one first needs to calculate the Helmholtz free energy density $\widetilde{\psi}$ (42) with (53). And second, the relaxation tensor $\widetilde{\Lambda}^{(4)}$ must be determined. It can be shown that the condition obtained by inserting the expression (54) in (46) can be satisfied by

$$\widetilde{\Lambda}^{(4)}_{ijkl} = \Lambda \delta_{ik} \delta_{jl}, \tag{61}$$

which is positive semi-definite for $\Lambda \geq 0$, and satisfies the symmetry condition (36). Immediately, one notices that (38) vanishes, and for the decomposition (39) one obtains

$$\widetilde{B}^{(4)}_{ijkl} = \sqrt{2k_B T \Lambda}\, \delta_{ik} \delta_{jl}. \tag{62}$$

With this, one obtains the stochastic differential Eq. (40) for the b-representation of the Maxwell model,

$$d_m b = \left[\kappa \cdot b - \frac{1}{2\lambda}(b - b^{-T}) \right] dt + \frac{\Theta}{2\lambda} b^{-T} dt + \sqrt{\frac{\Theta}{\lambda}}\, d\widehat{W}. \tag{63}$$

where the second last term on the r.h.s. originates from the difference in Helmholtz free energy densities described by (42). Applying the scheme (47), (48) to (63), one can verify by explicit calculation that the stochastic differential equation for b, (63), is compatible with the one for c, (57).

It is noted that the b-representation of the Maxwell model requires b^{-T}, which will also be the case for the FENE-P model (Section 5.2) and the Giesekus model (Section 5.3) studied below. Since typical expressions for the Helmholtz free energy density, as (53), contain a contribution of the form $\ln(\det c)$ with a negative prefactor, $\det b \to 0$ is naturally avoided by the continuous dynamics, since that would lead to $\psi \to \infty$. It is mentioned that, in the absence of fluctuations, the conditions for maintaining the positive definiteness of the conformation tensor c were studied for a large class of differential models [65]. This implies that, for these same models, also the contravariant deformation b is known to remain positive definite, and hence its inverse is always well defined.

The issue is more subtle in the time-discreted case. A possible procedure forward is as follows. Technically speaking, the positive definiteness of c is lost only if one or more of the eigenvalues of b become zero. If this occurs in a certain iteration-step, one can re-calculate the corresponding b-increment with an adapted time-increment but using the same realization of noise. The specific adaptation of the time step is

chosen as to avoid vanishing eigenvalues of b at the end of the iteration step. In more physical terms, one might want to maintain also the positive definiteness of b, i.e., also not allowing negative eigenvalues of b. Also in this case, the procedure of adapting the time-step can be employed, as soon one or more eigenvalues of b are on the verge of becoming negative.

5.2. FENE-P model

Representation in terms of c: The conformation-tensor based FENE-P model is given by [30,31]

$$c_{(1)} = -\frac{1}{\lambda}(f\,c - \mathbf{1}), \tag{64}$$

$$\tau_p = G(f\,c - \mathbf{1}), \tag{65}$$

$$f = \frac{b}{b + 3 - \mathrm{tr}\,c}, \tag{66}$$

where f is a dimensionless measure of the non-linearity. The corresponding Helmholtz free energy density per unit volume has the form [30]

$$\psi = \frac{G}{2}(b\ln(f) - \ln(\det c)), \tag{67}$$

while the relaxation tensor is equal to (54) for the Maxwell model. Indeed, using these expressions in the general evolution Eq. (10) and stress tensor (12), one recovers (64) and (65), with the identification $1/\lambda = 2\Lambda G$. Along the same lines as for the Maxwell model above, one can derive the stochastic differential equation for the FENE-P model,

$$d_m c = \left[(\kappa \cdot c + c \cdot \kappa^T) - \frac{1}{\lambda}(f\,c - \mathbf{1}) \right] dt$$
$$+ (D + 1)\frac{\Theta}{\lambda}\mathbf{1}\,dt$$
$$+ \sqrt{\frac{\Theta}{\lambda}} [b \cdot d\widehat{W} + d\widehat{W}^T \cdot b^T], \tag{68}$$

which is identical to the Maxwell case (57), except for the factor f in the relaxation term.

Representation in terms of b: Since, the FENE-P model differs from the Maxwell model only in terms of the expression for the Helmholtz free energy density, the treatment is completely analogous to the Maxwell model above. The resulting stochastic differential Eq. (40) for the b-representation of the FENE-P model is

$$d_m b = \left[\kappa \cdot b - \frac{1}{2\lambda}(f\,b - b^{-T}) \right] dt + \frac{\Theta}{2\lambda} b^{-T} dt + \sqrt{\frac{\Theta}{\lambda}}\, d\widehat{W}, \tag{69}$$

with f given by (66). Applying the scheme (47), (48) to (69), one can verify by explicit calculation that the stochastic differential equation for b, (69), is compatible with the one for c, (68).

5.3. Giesekus model

Representation in terms of c: The conformation-tensor based Giesekus model is given by [30,32,33]

$$c_{(1)} = \frac{1}{\lambda}[(1 - \alpha)\mathbf{1} - (1 - 2\alpha)c - \alpha c^2], \tag{70}$$

$$\tau_p = G(c - \mathbf{1}), \tag{71}$$

with $0 \leq \alpha < 1$. It should be noted that the Giesekus model reduces to the upper-convected Maxwell model for $\alpha = 0$. While the corresponding Helmholtz free energy density is given by (53) [30,47], the relaxation tensor assumes the form [47] (see also [29] without explicit

symmetrization)

$$\Lambda_{ijkl}^{(4)} = (1 - \alpha)\Lambda(c_{ik}\delta_{jl} + c_{il}\delta_{jk} + c_{jk}\delta_{il} + c_{jl}\delta_{ik})$$
$$+ 2\alpha\Lambda(c_{ik}c_{jl} + c_{il}c_{jk}). \tag{72}$$

Indeed, using these expressions in the general evolution Eq. (10) and stress tensor (12), one recovers (70) and (71), again with the identification $1/\lambda = 2\Lambda G$.

It can be shown that (72) possesses the required symmetry properties (16) and (17). Its positive semi-definiteness is proven by the existence of the decomposition (20), assuming $\Lambda \geq 0$, with[1]

$$B_{ijmn}^{(4)} = \sqrt{2k_{\mathrm{B}}T\Lambda}\,[\sqrt{1 - \alpha}\,(b_{im}\delta_{jn} + b_{jm}\delta_{in}),$$
$$\sqrt{\alpha}\,(b_{im}b_{jn} + b_{jm}b_{in})], \tag{73}$$

which satisfies the symmetry condition (17). For the divergence (19), one obtains (the reader is referred to Appendix A for the careful calculation)

$$\mathrm{div}_{\boldsymbol{c}}(T\Lambda^{(4)}) = 2(D + 1)T\Lambda[(1 - \alpha)\boldsymbol{1} + 2\alpha\boldsymbol{c}], \tag{74}$$

assuming, for simplicity, that $(1 - \alpha)T\Lambda$ and $\alpha T\Lambda$ do not depend on $\boldsymbol{c}$.

In summary, the stochastic differential equation for the Giesekus model becomes

$$d_{\mathrm{m}}\boldsymbol{c} = [(\boldsymbol{\kappa}\cdot\boldsymbol{c} + \boldsymbol{c}\cdot\boldsymbol{\kappa}^{\mathrm{T}})$$
$$+ \frac{1}{\lambda}\{(1 - \alpha)\boldsymbol{1} - (1 - 2\alpha)\boldsymbol{c} - \alpha\boldsymbol{c}^2\}\Big]dt$$
$$+ (D + 1)\frac{\Theta}{\lambda}[(1 - \alpha)\boldsymbol{1} + 2\alpha\boldsymbol{c}]dt$$
$$+ \sqrt{\frac{\Theta}{\lambda}}\,[\sqrt{1 - \alpha}\,(\boldsymbol{b}\cdot d\widehat{\boldsymbol{W}}_{(1)} + d\widehat{\boldsymbol{W}}_{(1)}^{\mathrm{T}}\cdot\boldsymbol{b}^{\mathrm{T}})$$
$$+ \sqrt{\alpha}\,\boldsymbol{b}\cdot(d\widehat{\boldsymbol{W}}_{(2)} + d\widehat{\boldsymbol{W}}_{(2)}^{\mathrm{T}})\cdot\boldsymbol{b}^{\mathrm{T}}]. \tag{75}$$

The quantities $d\widehat{\boldsymbol{W}}_{(1)}$ and $d\widehat{\boldsymbol{W}}_{(2)}$ are statistically independent matrices of Wiener process increments, where each of them has the properties (23) and (24).

Representation in terms of $\boldsymbol{b}$: For deriving the $\boldsymbol{b}$-representation of the fluctuating Giesekus model, one can focus on the relaxation tensor, since the Helmholtz free energy density is identical to the Maxwell model. It can be shown that the condition obtained by inserting the expression (72) in (46) can be satisfied by

$$\widetilde{\Lambda}_{ijkl}^{(4)} = \Lambda[(1 - \alpha)\delta_{ik}\delta_{jl} + \alpha c_{ik}\delta_{jl}], \tag{76}$$

which is positive semi-definite for $\Lambda \geq 0$, and satisfies the symmetry condition (36). For the divergence (38) one obtains

$$\mathrm{div}_{\boldsymbol{b}}(T\widetilde{\Lambda}^{(4)}) = (D + 1)T\Lambda\alpha\boldsymbol{b}, \tag{77}$$

and the tensor $\widetilde{B}_{ijkl}^{(4)}$ in (39) is given by

$$\widetilde{B}_{ijkl}^{(4)} = \sqrt{2k_{\mathrm{B}}T\Lambda}\,[\sqrt{1 - \alpha}\,\delta_{ik}\delta_{jl},\ \sqrt{\alpha}\,b_{ik}\delta_{jl}]. \tag{78}$$

With this, one obtains the stochastic differential equation for the $\boldsymbol{b}$-representation of the Giesekus model,

$$d_{\mathrm{m}}\boldsymbol{b} = \Big[\boldsymbol{\kappa}\cdot\boldsymbol{b} + \frac{1}{2\lambda}\{(1 - \alpha)\boldsymbol{1} - (1 - 2\alpha)\boldsymbol{c} - \alpha\boldsymbol{c}^2\}\cdot\boldsymbol{b}^{-\mathrm{T}}\Big]dt$$
$$+ \frac{\Theta}{2\lambda}[\alpha(D + 2)\boldsymbol{c} + (1 - \alpha)\boldsymbol{1}]\cdot\boldsymbol{b}^{-\mathrm{T}}dt$$
$$+ \sqrt{\frac{\Theta}{\lambda}}\,(\sqrt{1 - \alpha}\,d\widehat{\boldsymbol{W}}_{(1)} + \sqrt{\alpha}\,\boldsymbol{b}\cdot d\widehat{\boldsymbol{W}}_{(2)}). \tag{79}$$

This entire treatment of the fluctuating $\boldsymbol{b}$-representation of the Giesekus model reduces to the fluctuating $\boldsymbol{b}$-representation of the Maxwell model

discussed in the previous section upon setting $\alpha = 0$.

Applying the scheme (47), (48) to (79), one can verify by explicit calculation that the stochastic differential equation for $\boldsymbol{b}$, (79), is compatible with the one for $\boldsymbol{c}$, (75).

6. Limit of Newtonian fluids

This section concentrates on recovering fluctuating Newtonian fluid dynamics as a limiting case of the general fluctuating viscoelasticity discussed above. Regarding the approach described in this paper as representative of a polymer melt, the limit discussed in this section can be imagined as decreasing the characteristic relaxation time by having ever shorter polymer chains, eventually leading to a low-molecular Newtonian fluid. Since the $\boldsymbol{c}$- and $\boldsymbol{b}$-representations discussed in Sections 3 and 4, respectively, are equivalent as shown above, one can choose either of them for discussing the limit to Newtonian fluids. Here, we depart from the $\boldsymbol{c}$-representation outlined in Section 3, for convenience.

In the sequel, it is assumed that the imposed flow and the thermal fluctuations result in only small deviations of the conformation tensor $\boldsymbol{c}$ from its equilibrium value, $\boldsymbol{c}_{\mathrm{eq}} = c_{\mathrm{eq}}\boldsymbol{1}$. This implies that we examine the general approach in Section 3, particularly the evolution Eq. (21), in terms of a linear-perturbation analysis. The following steps are taken. As a first step, the driving force for the conformational relaxation can be approximated by

$$\frac{\partial\psi}{\partial\boldsymbol{c}} = \boldsymbol{\Psi}_{\mathrm{eq}}^{(4)} \odot (\boldsymbol{c} - \boldsymbol{c}_{\mathrm{eq}}), \tag{80}$$

with

$$\boldsymbol{\Psi}_{\mathrm{eq}}^{(4)} = \frac{\partial^2\psi}{\partial\boldsymbol{c}\,\partial\boldsymbol{c}}\bigg|_{\boldsymbol{c}_{\mathrm{eq}}}. \tag{81}$$

The zeroth-order term in (80) vanishes because the equilibrium conformation $\boldsymbol{c}_{\mathrm{eq}}$ is determined by minimizing the Helmholtz free energy density ψ, and for the same reason the fourth-rank tensor $\boldsymbol{\Psi}_{\mathrm{eq}}^{(4)}$ is positive definite. As a second step, to arrive at a linear model, it is sufficient to evaluate the fourth-rank relaxation tensor at $\boldsymbol{c}_{\mathrm{eq}}$, . If this is done from the start when formulating the model, the fifth term on the r.h.s. of (21) vanishes identically, because the relaxation tensor does not depend on the conformation. And as a third step, in the flow-related terms, one can replace $\boldsymbol{c}$ by $\boldsymbol{c}_{\mathrm{eq}}$. As a result of all these steps, the evolution of the deviation in the conformation tensor, $\Delta\boldsymbol{c} = \boldsymbol{c} - \boldsymbol{c}_{\mathrm{eq}}$, can be written as

$$d\Delta\boldsymbol{c}_{\boldsymbol{r},t} = c_{\mathrm{eq}}(\boldsymbol{\kappa}_{\boldsymbol{r},t} + \boldsymbol{\kappa}_{\boldsymbol{r},t}^{\mathrm{T}})dt$$
$$- \boldsymbol{\Lambda}_{\mathrm{eq},\boldsymbol{r}}^{(4)} \odot \boldsymbol{\Psi}_{\mathrm{eq},\boldsymbol{r}}^{(4)} \odot \Delta\boldsymbol{c}_{\boldsymbol{r},t}dt$$
$$+ \boldsymbol{B}_{\mathrm{eq},\boldsymbol{r}}^{(4)} \odot d\boldsymbol{W}_{\boldsymbol{r},t}, \tag{82}$$

with

$$B_{\mathrm{eq},\boldsymbol{r},ijmn}^{(4)}B_{\mathrm{eq},\boldsymbol{r},klmn}^{(4)} = 2k_{\mathrm{B}}T_{\boldsymbol{r}}\Lambda_{\mathrm{eq},\boldsymbol{r},ijkl}^{(4)}, \tag{83}$$

and the increments $d\boldsymbol{W}_{\boldsymbol{r},\ t}$ are specified by the expectations (7) and covariances (8).

In the evolution Eq. (82), all position and time dependencies have been made explicit by using subscripts $\boldsymbol{r}$ and t, respectively, according to the following guidelines, in order to keep the further steps transparent. First, inspection of the examples studied in Section 5 suggests that it is reasonable to assume that c_{eq} is independent of both position and time. Second, again according to the examples studied in Section 5, the quantity $\boldsymbol{\Psi}_{\mathrm{eq}}^{(4)}$ depends on both c_{eq} and the shear modulus G. In the case of rubber elasticity, which we study in this paper, the latter is related to the number density of (effective) cross-links and to the absolute temperature. As a first approximation, it is reasonable to assume that neither the cross-link density nor the absolute temperature evolve in time, since the number density is not part of the dynamic model, and entropy elasticity leaves the temperature practically unchanged for

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[1] Note that $B = (\sqrt{y}, y)$ is a solution to $B\cdot B^{\mathrm{T}} = y + y^2$, while usually one would think of $B = \sqrt{y + y^2}$ only. This fact is helpful in finding the decomposition of $\Lambda^{(4)}$ for the Giesekus model.

deformations in the linear regime. Therefore, it is assumed that $\boldsymbol{\Psi}_{\mathrm{eq}}^{(4)}$ is independent of time. Third, a similar argument as for $\boldsymbol{\Psi}_{\mathrm{eq}}^{(4)}$ can be used for $\boldsymbol{\Lambda}_{\mathrm{eq}}^{(4)}$. Specifically, the combination $\boldsymbol{\Lambda}_{\mathrm{eq}}^{(4)} \odot \boldsymbol{\Psi}_{\mathrm{eq}}^{(4)}$ essentially represents the inverse of the relaxation time for the conformation tensor. Therefore, the position and time dependencies of $\boldsymbol{\Lambda}_{\mathrm{eq}}^{(4)}$ are due to those of $\boldsymbol{\Psi}_{\mathrm{eq}}^{(4)}$ and the time scales. The latter are usually assumed to be temperature dependent. However, for the reasons discussed above, temperature evolution is not considered in this section, and therefore one may regard $\boldsymbol{\Lambda}_{\mathrm{eq}}^{(4)}$, as well as $\boldsymbol{B}_{\mathrm{eq}}^{(4)}$ (see (83)), as not depending on time, but only on position.

Before proceeding, a note about the form of the fourth-rank tensors $\boldsymbol{\Lambda}_{\mathrm{eq}}^{(4)}$ and $\boldsymbol{\Psi}_{\mathrm{eq}}^{(4)}$ is in place. By its very definition (81), $\boldsymbol{\Psi}_{\mathrm{eq}}^{(4)}$ obeys the same symmetry properties as $\boldsymbol{\Lambda}_{\mathrm{eq}}^{(4)}$, (16) and (17). The only tensors available for constructing a fourth-rank tensor are the unity tensor $\boldsymbol{1}$ and the conformation tensor, which at equilibrium is also proportional to the unity tensor. Therefore, the most general fourth-rank tensor that can be constructed at equilibrium, that satisfies the symmetry property (17), is of the form

$$Z_{ijkl}^{(4)} = z_1(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + z_2\delta_{ij}\delta_{kl}. \tag{84}$$

It is noted that this tensor also satisfies the symmetry property (16) automatically. Furthermore, it can be shown that multiplication of two tensors of the form (84) with coefficients $(z_1, z_2) = (a_1, a_2)$ and $(z_1, z_2) = (b_1, b_2)$ leads again to a tensor of the form (84) with coefficients $(z_1, z_2) = (c_1, c_2)$, given by $c_1 = 2a_1b_1$ and $c_2 = 2(a_1b_2 + a_2b_1) + Da_2b_2$, where D denotes the dimensionality of the formulation. Since the expressions for c_1 and c_2 are symmetric with respect to $(a_1, a_2) \leftrightarrow (b_1, b_2)$, it is obvious that any two tensors of the form (84) commute. With respect to solving (82) along the lines of Appendix B, it is evident that the symmetry condition (B.6) and the commutativity condition in (B.8) are satisfied at equilibrium. Finally, it can be shown that, since both $\boldsymbol{\Lambda}_{\mathrm{eq}}^{(4)}$ and $\boldsymbol{\Psi}_{\mathrm{eq}}^{(4)}$ are positive definite, the combination $\boldsymbol{\Lambda}_{\mathrm{eq}}^{(4)} \odot \boldsymbol{\Psi}_{\mathrm{eq}}^{(4)}$ is positive definite as well.[2]

In order to recover fluctuating Newtonian fluid dynamics, the evolution Eq. (82) is studied in the limit that the conformational relaxation occurs "very rapidly", or, equivalently, one is interested in the behavior on time scales significantly longer than the characteristic time-scales of the material. More precisely, in the limit that even the longest relaxation time τ_{long} in $\boldsymbol{\Lambda}_{\mathrm{eq}}^{(4)} \odot \boldsymbol{\Psi}_{\mathrm{eq}}^{(4)}$ tends to zero, it can be shown that the expectations and covariances of the solution to the narrow-sense linear stochastic differential Eq. (82) for times $t \gg \tau_{\mathrm{long}}$ are given by (see Appendix B for details)

$$\langle \Delta \boldsymbol{c}_{\boldsymbol{r},t} \rangle = c_{\mathrm{eq}} \boldsymbol{\Psi}_{\mathrm{eq},\boldsymbol{r}}^{(4),-1} \odot \boldsymbol{\Lambda}_{\mathrm{eq},\boldsymbol{r}}^{(4),-1} \odot (\boldsymbol{\kappa}_{\boldsymbol{r},t} + \boldsymbol{\kappa}_{\boldsymbol{r},t}^{\mathrm{T}}), \tag{85}$$

$$\begin{aligned}\langle\langle \Delta \boldsymbol{c}_{\boldsymbol{r},t}; \Delta \boldsymbol{c}_{\boldsymbol{r}',t'} \rangle\rangle &= 2k_{\mathrm{B}}T_{\boldsymbol{r}}\delta(t-t')\delta(\boldsymbol{r}-\boldsymbol{r}') \\ &\times \boldsymbol{\Psi}_{\mathrm{eq},\boldsymbol{r}}^{(4),-1} \odot \boldsymbol{\Lambda}_{\mathrm{eq},\boldsymbol{r}}^{(4),-1} \odot \boldsymbol{\Psi}_{\mathrm{eq},\boldsymbol{r}}^{(4),-1}. \end{aligned} \tag{86}$$

This result can be used to determine the expectations and covariances of the polymer contribution to the stress. By virtue of (12), the polymer contribution to the stress in the linear approximation is given by $\boldsymbol{\tau}_{\mathrm{p}} = 2c_{\mathrm{eq}} \boldsymbol{\Psi}_{\mathrm{eq}}^{(4)} \odot \Delta \boldsymbol{c}$. Therefore,

$$\langle \boldsymbol{\tau}_{\mathrm{p},\boldsymbol{r},t} \rangle = \boldsymbol{\eta}_{0,\boldsymbol{r}}^{(4)} \odot \boldsymbol{\kappa}_{\boldsymbol{r},t}, \tag{87}$$

$$\langle\langle \boldsymbol{\tau}_{\mathrm{p},\boldsymbol{r},t}; \boldsymbol{\tau}_{\mathrm{p},\boldsymbol{r}',t'} \rangle\rangle = 2k_{\mathrm{B}}T_{\boldsymbol{r}}\delta(t-t')\delta(\boldsymbol{r}-\boldsymbol{r}')\boldsymbol{\eta}_{0,\boldsymbol{r}}^{(4)}, \tag{88}$$

where we have used the symmetry property of $\boldsymbol{\Lambda}_{\mathrm{eq}}^{(4),-1}$ in the expression for the expectations, and with the definition

$$\boldsymbol{\eta}_{0,\boldsymbol{r}}^{(4)} = 4c_{\mathrm{eq}}^2 \boldsymbol{\Lambda}_{\mathrm{eq},\boldsymbol{r}}^{(4),-1}, \tag{89}$$

which according to (87) represents the viscosity tensor for small deformations, i.e., in the linear Newtonian regime.

As a final step toward the limit of fluctuating Newtonian fluid dynamics, we put the quantity $\boldsymbol{\eta}_0^{(4)}$ in (87) and (88) in a more concrete form. For that purpose, one can choose $\boldsymbol{\eta}_0^{(4)}$ in (87) such that one recovers the usual expression of Newton (e.g. see p. 49 in [35], p. 187 in [60]) for the stress tensor in terms of the shear viscosity $\eta_{\mathrm{s}} > 0$ and dilational viscosity $\eta_{\mathrm{d}} > 0$. Bearing in mind that $\boldsymbol{\eta}_0^{(4)}$ must be of the form (84) by virtue of (89), the usual expression of Newton is obtained if one chooses the coefficients $(z_1, z_2) = (\eta_1, \eta_2)$ as (see also p. 49 in [35], p. 187 in [60])

$$\eta_1 = \eta_{\mathrm{s}}, \tag{90}$$

$$\eta_2 = \eta_{\mathrm{d}} - \tfrac{2}{3}\eta_{\mathrm{s}}. \tag{91}$$

Using these expressions for (η_1, η_2) and the therefrom resulting $\boldsymbol{\eta}_0^{(4)}$, the covariances of the stress tensor given by (88) are identical to the well-known result of Landau and Lifshitz, see Ch. XVII in [10].

The limit of infinitely rapid relaxation eliminates the conformation tensor from the set of independent dynamic variables. As a consequence, the elasticity-type relation between the stress and the conformation (12) becomes viscous in nature, see (87), with fluctuations. While for the full conformation tensor model, the energy balance contains a work term related to the polymer stress, $\dot{w} = \boldsymbol{\tau}_{\mathrm{p}} \odot \boldsymbol{\kappa}$, associated with the reversible dynamics [35], by way of (87) and (88) this becomes manifestly dissipative.

For the purpose of determining the fluctuations on the stress tensor explicitly, it may be desirable to calculate the decomposition for this expression for $\boldsymbol{\eta}_0^{(4)}$, $\boldsymbol{\eta}_0^{(4)} = \boldsymbol{\epsilon}_0^{(4)} \odot \boldsymbol{\epsilon}_0^{(4),\mathrm{T}}$, with $\boldsymbol{\epsilon}_0^{(4)}$ being again of the form (84) with coefficients $(z_1, z_2) = (\epsilon_1, \epsilon_2)$ given by

$$\epsilon_1 = \sqrt{\frac{\eta_{\mathrm{s}}}{2}}, \tag{92}$$

$$\epsilon_2 = \sqrt{\frac{\eta_{\mathrm{d}}}{3}} - \sqrt{\frac{2\eta_{\mathrm{s}}}{9}}. \tag{93}$$

Therefore, $\boldsymbol{\epsilon}_0^{(4)}$ exists for any $\eta_{\mathrm{s}} > 0$ and $\eta_{\mathrm{d}} > 0$, as expected. It is noted that $\eta_{\mathrm{s}} = 0$ and $\eta_{\mathrm{d}} = 0$ are explicitly excluded, since in these cases $\boldsymbol{\eta}_0^{(4)}$ can not be inverted, and hence a proper mapping to $\boldsymbol{\Lambda}_{\mathrm{eq}}^{(4)}$ in the conformation tensor model is not possible.

7. Summary and discussion

A general approach has been presented for including fluctuations in conformation-tensor based models for viscoelasticity. After actually achieving a formulation in terms of the conformation tensor $\boldsymbol{c}$ itself, it has been advocated that it is beneficial, for numerical reasons, to formulate viscoelastic models rather for the so-called contravariant decomposition of the conformation tensor, namely for the contravariant deformation $\boldsymbol{b}$. One of the reasons concerns the immunity of this formulation to a well-known numerical instability that occurs in the formulation in terms of the conformation tensor $\boldsymbol{c}$. It should be pointed out that this is an issue that occurs even in the absence of fluctuations, i.e., it is beneficial to use the contravariant deformation $\boldsymbol{b}$ even for the currently available deterministic models. Another reason for formulating models in terms of the contravariant deformation $\boldsymbol{b}$ is that the corresponding conformation tensor $\boldsymbol{c}$ can not become negative, even for finite time-steps, by virtue of (26). And finally, the $\boldsymbol{b}$-representation of fluctuating viscoelasticity is closed in terms of $\boldsymbol{b}$, while the $\boldsymbol{c}$-representation requires the calculation of a decomposition (26), since $\boldsymbol{b}$ enters via the fluctuations.

Using the general procedure described above, three of the most popular models have been extended to include fluctuations, namely the upper-convected Maxwell model, the FENE-P model, and the Giesekus model.

It has been shown that the fluctuating viscoelasticity proposed in

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[2] This can be shown as follows. In the decomposition (83) of $\boldsymbol{\Lambda}_{\mathrm{eq}}^{(4)}$, each of the two parts of that decomposition is again of the form (84), and thus it commutes with $\boldsymbol{\Psi}_{\mathrm{eq}}^{(4)}$. Therefore, one can write $\boldsymbol{\Lambda}_{\mathrm{eq}}^{(4)} \odot \boldsymbol{\Psi}_{\mathrm{eq}}^{(4)} = \boldsymbol{B}_{\mathrm{eq}}^{(4)} \odot \boldsymbol{\Psi}_{\mathrm{eq}}^{(4)} \odot \boldsymbol{B}_{\mathrm{eq}}^{(4),\mathrm{T}}$, which is thus positive definite by virtue of the positive definiteness of $\boldsymbol{\Psi}_{\mathrm{eq}}^{(4)}$.

this paper naturally reduces to the fluctuating Newtonian fluid dynamics of Landau and Lifshitz [10], in the limit of vanishingly small relaxation time. This supports the approach taken, however, it can also be used to go a step further in the following sense. The developments in this paper can be extended to several (N) conformation tensors in a straightforward way. Doing so, and then letting the smallest of all relaxation times approach zero, one ends up with a viscoelastic model in terms of $N - 1$ conformation tensors, embedded in a Newtonian (background) fluid.

The direct influence of flow on the conformation tensor c is captured, in this paper, by the upper-convected derivative [29,35,49], also known as the contravariant convected derivative [48]. Other choices could be of interest in certain rheological models, for example the lower-convected derivative [35], also known as the covariant convected derivative [48]. This alternative choice, however, is also covered by the procedure in this paper, since the inverse c^{-1} of an upper-convected tensor c is lower-convected, the latter being used e.g. in the Oldroyd-A model [66]. In addition to the variation in terms of upper- versus lower-convected derivatives, a significant number of rheological models make use of constrained tensors. Particularly, it is widespread to consider conformation tensors with trace equal to unity or zero, where the condition on the trace derives from a microscopic interpretation of the conformation tensor in terms of a second moment of a unit-vector distribution. For example, the pom-pom model for branched polymers [67,68], which has upper-convected characteristics, is of this type. Another example is the Doi-Ohta model for concentrated mixtures of immiscible fluids [69], which has lower-convected characteristics, both when formulated in terms of the interface tensor [69] and when expressed in terms of the area tensor [70]. As a final example of conformation tensor models with a constrained trace, models for suspensions of anisotropic particles are mentioned, with upper-convected characteristics for thin rods, and lower-convected characteristics for thin disks [71–73]. To describe rheological models with a constrained trace by using the procedure outlined in this paper, one can proceed as follows. First, one determines the evolution equation for an auxiliary tensor c. Second, if the final model possesses lower-convected characteristics, one writes the model in terms of $c' = c^{-1}$, which is lower convected. Finally, one defines the final quantity of interest by way of either $c'' = c'/\text{tr}c'$ or $c'' = (c'/\text{tr}c') - \frac{1}{3}\mathbf{1}$, respectively, depending on whether the trace is constrained to unity or zero [35,60]. In general, whatever the transformation from c to another tensor, the proper rules of stochastic calculus must be used for the transformation of the stochastic differential equation (see [63], and p. 99 in [43]), which involves not only the first-order derivatives of the transformation, but also the second-order derivatives.

Acknowledgment

Appendix A. Divergence of the relaxation tensor in the c-representation

A1. Maxwell model (and FENE-P model)

In this section, the divergence of the relaxation tensor (54),

$$\Lambda_{ijkl}^{(4)} = \Lambda \left(c_{ik}\delta_{jl} + c_{il}\delta_{jk} + c_{jk}\delta_{il} + c_{jl}\delta_{ik} \right), \tag{A.1}$$

is calculated.

Procedure 1: Without using the symmetry of c: One notices that (17) is satisfied even if one does not use the symmetry of c. However, it can be shown that (16) is satisfied only if the symmetry of c is employed. In other words, if the relaxation tensor is needed in a form that is also applicable to possibly non-symmetric c, one should write

$$\Lambda_{ijkl}^{(4),\text{sym}} = \Lambda \left(\frac{c_{ik} + c_{ki}}{2}\delta_{jl} + \frac{c_{il} + c_{li}}{2}\delta_{jk} \right.$$
$$\left. + \frac{c_{jk} + c_{kj}}{2}\delta_{il} + \frac{c_{jl} + c_{lj}}{2}\delta_{ik} \right). \tag{A.2}$$

The logics behind not enforcing the symmetry of c is as follows. One can argue that the dynamic model should be formulated in a way that, while being defined for all (potentially non-symmetric) c, the increments dc are always symmetric. If this model is then solved with a conformation tensor that is symmetric initially, it will remain symmetric in the course of time. In other words, the subset of symmetric tensors is invariant with respect to the dynamics. Calculating the c-divergence of the relaxation tensor (A.2), using Einstein summation convention, one obtains

$$\frac{\partial \Lambda_{ijkl}^{(4),\text{sym}}}{\partial c_{ij}} = 2(D + 1)\Lambda\delta_{kl}. \tag{A.3}$$

Procedure 2: Voigt notation: In this part, the divergence of the relaxation tensor is calculated by enforcing that c is symmetric, i.e., that there are only six independent degrees of freedom. For that purpose, the Voigt notation $[c_I] = (c_{11}, c_{22}, c_{33}, c_{23}, c_{13}, c_{12})$ is used. In turn, the fourth-rank relaxation tensor $\Lambda^{(4)}$ becomes a second-rank relaxation tensor $\Lambda^{(2)}$, with components $\Lambda_{IK}^{(2)}$. Calculating the divergence, $\sum_{I=1}^{6} \partial \Lambda_{IK}^{(2)}/\partial c_I$, and re-writing the resulting expression into a symmetric 3×3-tensor, the divergence can be expressed in the form (for $D = 3$)

$$\frac{\partial \Lambda_{ijkl}^{(4)}}{\partial c_{ij}} = 2(D + 1)\Lambda\delta_{kl}, \tag{A.4}$$

which is identical to the expression (A.3).

A2. Giesekus model

In this section, the Giesekus model is examined. Since the calculation of the (c-)divergence is a linear mapping, and since the main difference between the relaxation tensor of the Giesekus model (72) and the Maxwell model (54) (see A.1) is given by the additive contribution

$$\Delta\Lambda_{ijkl}^{(4)} = 2\alpha\Lambda(c_{ik}c_{jl} + c_{il}c_{jk}),$$
(A.5)

one can concentrate on this contribution in the sequel.

Procedure 1: Without using the symmetry of c: One notices that (17) is satisfied even if one does not use the symmetry of c. However, it can be shown that (16) is satisfied only if the symmetry of c is employed. In other words, if the relaxation tensor is needed in a form that is also applicable to possibly non-symmetric c, one should write

$$\Delta\Lambda_{ijkl}^{(4),\text{sym}} = 2\alpha\Lambda\left(\frac{c_{ik} + c_{ki}}{2}\frac{c_{jl} + c_{lj}}{2} + \frac{c_{il} + c_{li}}{2}\frac{c_{jk} + c_{kj}}{2}\right).$$
(A.6)

Calculating the c-divergence of this relaxation tensor, using Einstein summation convention, one obtains

$$\frac{\partial(\Delta\Lambda_{ijkl}^{(4),\text{sym}})}{\partial c_{ij}} = 4(D+1)\alpha\Lambda\frac{c_{kl} + c_{lk}}{2}.$$
(A.7)

Procedure 2: Voigt notation: In this part, the divergence of $\Delta\Lambda^{(4)}$ is calculated by enforcing that c is symmetric, i.e., that there are only six independent degrees of freedom. For that purpose, we use again the Voigt notation, and so $\Delta\Lambda^{(4)}$ becomes a second-rank tensor $\Delta\Lambda^{(2)}$, with components denoted by $\Delta\Lambda_{IK}^{(2)}$. Calculating the divergence, $\sum_{I=1}^{6}\partial(\Delta\Lambda_{IK}^{(2)})/\partial c_I$, and re-writing the resulting expression into a symmetric 3×3-tensor, the divergence can be expressed in the form (for $D=3$)

$$\frac{\partial(\Delta\Lambda_{ijkl}^{(4)})}{\partial c_{ij}} = 4(D+1)\alpha\Lambda c_{kl},$$
(A.8)

which is identical to the expression (A.7).

Appendix B. Limit of narrow-sense linear stochastic differential equations

B1. Introduction

A significant fraction of this section is based on Sec. 3.3.2 (p. 104 ff.) of [43]. All references to equations of the form (3.xx) refer to equations in that section of [43].

Consider the narrow-sense linear stochastic differential Eq. (3.54),

$$d\boldsymbol{X}_{\boldsymbol{r},t} = [\boldsymbol{a}_{\boldsymbol{r},t} + \boldsymbol{A}_{\boldsymbol{r}}\cdot\boldsymbol{X}_{\boldsymbol{r},t}]dt + \boldsymbol{B}_{\boldsymbol{r}}\cdot d\boldsymbol{W}_{\boldsymbol{r},t}.$$
(B.1)

Note that, in contrast to (3.54) in the book, we assume in all that follows that there is no time-dependence in $\boldsymbol{A}_{\boldsymbol{r}}$ and $\boldsymbol{B}_{\boldsymbol{r}}$, however, we include a spatial dependence in all of the quantities $\boldsymbol{a}_{\boldsymbol{r},t}$, $\boldsymbol{A}_{\boldsymbol{r}}$, and $\boldsymbol{B}_{\boldsymbol{r}}$. These dependencies are indicated by the subscripts $\boldsymbol{r}$ and t, respectively. The increments $d\boldsymbol{W}_{\boldsymbol{r},t}$ are specified by the expectations (7) and covariances (8).

It has been shown that the solution to (B.1) can be written as, (3.55),

$$\boldsymbol{X}_{\boldsymbol{r},t} = \boldsymbol{\Phi}_{\boldsymbol{r},t}\cdot\left[\boldsymbol{X}_{\boldsymbol{r},0} + \int_0^t \boldsymbol{\Phi}_{\boldsymbol{r},t'}^{-1}\cdot\boldsymbol{a}_{\boldsymbol{r},t'}\,dt' \right.$$
$$\left. + \int_0^t \boldsymbol{\Phi}_{\boldsymbol{r},t'}^{-1}\cdot\boldsymbol{B}_{\boldsymbol{r}}\cdot d\boldsymbol{W}_{\boldsymbol{r},t'}\right],$$
(B.2)

where $\boldsymbol{\Phi}_{\boldsymbol{r},t}$ is given by the time-ordered exponential (3.56), which for time-independent $\boldsymbol{A}_{\boldsymbol{r}}$ assumes the form

$$\boldsymbol{\Phi}_{\boldsymbol{r},t} = \sum_{n=0}^{\infty}\frac{1}{n!}t^n\boldsymbol{A}_{\boldsymbol{r}}^n = \exp\{t\boldsymbol{A}_{\boldsymbol{r}}\}.$$
(B.3)

Finally, it has been noted that, if the initial state $\boldsymbol{X}_{\boldsymbol{r},0}$ is Gaussian, the solution $\boldsymbol{X}_{\boldsymbol{r},t}$ is Gaussian, with expectations and covariances given by (see (3.57) and (3.58))

$$\langle\boldsymbol{X}_{\boldsymbol{r},t}\rangle = \boldsymbol{\Phi}_{\boldsymbol{r},t}\cdot\left[\langle\boldsymbol{X}_{\boldsymbol{r},0}\rangle + \int_0^t \boldsymbol{\Phi}_{\boldsymbol{r},t'}^{-1}\cdot\boldsymbol{a}_{\boldsymbol{r},t'}\,dt'\right],$$
(B.4)

$$\langle\langle\boldsymbol{X}_{\boldsymbol{r},t}; \boldsymbol{X}_{\boldsymbol{r}',t'}\rangle\rangle = \boldsymbol{\Phi}_{\boldsymbol{r},t}\cdot[\langle\langle\boldsymbol{X}_{\boldsymbol{r},0}; \boldsymbol{X}_{\boldsymbol{r}',0}\rangle\rangle$$
$$+ \delta(\boldsymbol{r}-\boldsymbol{r}')\int_0^{\min(t,t')}\boldsymbol{\Phi}_{\boldsymbol{r},t''}^{-1}\cdot\boldsymbol{B}_{\boldsymbol{r}}\cdot\boldsymbol{B}_{\boldsymbol{r}}^{\text{T}}\cdot\boldsymbol{\Phi}_{\boldsymbol{r}',t''}^{-1,\text{T}}dt'']\cdot\boldsymbol{\Phi}_{\boldsymbol{r}',t'}^{\text{T}},$$
(B.5)

where we have generalized the results from [43] by accounting for the spatial correlations quantified by (8).

For the sequel, we make the following assumptions,

$$\boldsymbol{A}_{\boldsymbol{r}}^{\text{T}} = \boldsymbol{A}_{\boldsymbol{r}},$$
(B.6)

$$\boldsymbol{A}_{\boldsymbol{r}} \ll \boldsymbol{0},$$
(B.7)

$$\boldsymbol{B}_{\boldsymbol{r}}\cdot\boldsymbol{B}_{\boldsymbol{r}}^{\text{T}} = -\boldsymbol{C}_{\boldsymbol{r}}\cdot\boldsymbol{A}_{\boldsymbol{r}}, \text{ with } \boldsymbol{C}_{\boldsymbol{r}}\cdot\boldsymbol{A}_{\boldsymbol{r}} = \boldsymbol{A}_{\boldsymbol{r}}\cdot\boldsymbol{C}_{\boldsymbol{r}},$$
(B.8)

with positive $\boldsymbol{C}_{\boldsymbol{r}}$. In other words, $-\boldsymbol{A}_{\boldsymbol{r}}$ plays the role of a relaxation matrix, where (B.7) states that all eigenvalues of $\boldsymbol{A}_{\boldsymbol{r}}$ are strongly negative. The condition (B.8) is introduced for later convenience. It is noted that the commutativity of $\boldsymbol{C}_{\boldsymbol{r}}$ with $\boldsymbol{A}_{\boldsymbol{r}}$, (B.8)$_2$, implies, first, that the r.h.s. of (B.8)$_1$ is

indeed symmetric and, second, that C_r also commutes with A_r^{-1}. For the further steps it is also useful to denote the longest relaxation time of the entire system by

$$\tau_{\text{long}} = \frac{1}{\min_{\Omega,i}(|\alpha_{r,i}|)},$$
(B.9)

where $\alpha_{r,\,i}$ denote the eigenvalues of A_r, and the minimum is taken over all eigenvalues i at all positions r in the entire domain Ω.

The goal of this appendix is to study all of the above in the limit $\tau_{\text{long}} \to 0$.

B2. Naive approach

Eq. (B.1) can formally be re-written as

$$\mathrm{d}\boldsymbol{X}_{r,t} = \boldsymbol{A}_r \cdot \left(\boldsymbol{A}_r^{-1} \cdot \boldsymbol{a}_{r,t} + \boldsymbol{X}_{r,t} + \boldsymbol{A}_r^{-1} \cdot \boldsymbol{B}_r \cdot \frac{\mathrm{d}\boldsymbol{W}_{r,t}}{\mathrm{d}t} \right) \mathrm{d}t,$$
(B.10)

and since the relaxation occurs "very rapidly", (B.7), one finds in the limit $\tau_{\text{long}} \to 0$, i.e., for $t \gg \tau_{\text{long}}$,

$$\boldsymbol{X}_{r,t} = -\boldsymbol{A}_r^{-1} \cdot \boldsymbol{a}_{r,t} - \boldsymbol{A}_r^{-1} \cdot \boldsymbol{B}_r \cdot \frac{\mathrm{d}\boldsymbol{W}_{r,t}}{\mathrm{d}t}.$$
(B.11)

This result is, of course, the same as setting $\mathrm{d}\boldsymbol{X}_{r,t} = \boldsymbol{0}$ on the r.h.s. of (B.1) right away. From (B.11) it follows that, in this limit, the expectations and the covariances are given by

$$\langle \boldsymbol{X}_{r,t} \rangle = -\boldsymbol{A}_r^{-1} \cdot \boldsymbol{a}_{r,t},$$
(B.12)

$$\langle\langle \boldsymbol{X}_{r,t}; \boldsymbol{X}_{r',t'} \rangle\rangle = -\delta(t-t')\delta(r-r')\boldsymbol{C}_r \cdot \boldsymbol{A}_r^{-1},$$
(B.13)

where we have used the symmetry of A_r (B.6), the relation (B.8), and the covariance (8).

B3. More careful approach

One can take the limit $\tau_{\text{long}} \to 0$ on the solution (B.2), and on the full expressions for the expectations (B.4) and covariances (B.5). As far as the solution (B.2) is concerned, one can show that, in the limit $\tau_{\text{long}} \to 0$, i.e., $t \gg \tau_{\text{long}}$,

$$\boldsymbol{\Phi}_{r,t} \cdot \boldsymbol{X}_{r,0} \to \boldsymbol{0},$$
(B.14)

$$\boldsymbol{\Phi}_{r,t} \cdot \int_0^t \boldsymbol{\Phi}_{r,t'}^{-1} \cdot \boldsymbol{a}_{r,t'} \, \mathrm{d}t' = \int_0^t \boldsymbol{\Phi}_{r,t-t'} \cdot \boldsymbol{a}_{r,t'} \, \mathrm{d}t'$$
$$\to -\boldsymbol{A}_r^{-1} \cdot \boldsymbol{a}_{r,t}.$$
(B.15)

Therefore, relations (B.14) and (B.15) of the more careful treatment agree with the deterministic contribution to the naive solution, (B.11). The third contribution on the r.h.s. of (B.2) is a fluctuating one, i.e., has vanishing mean, which should still be the case after taking the limit $\tau_{\text{long}} \to 0$. One thus concludes that the more careful approach confirms the expectation result (B.12) of the naive approach.

As far as taking the limit $\tau_{\text{long}} \to 0$ of the fluctuating contribution in (B.2) is concerned (third term on the r.h.s. of (B.2)), the situation is more complicated. It seems most appropriate to discuss the fluctuating contribution to the solution by studying the covariances (B.5) in the limit $\tau_{\text{long}} \to 0$. Assuming for simplicity $t \geq t'$, one obtains from (B.5)

$$\langle\langle \boldsymbol{X}_{r,t}; \boldsymbol{X}_{r',t'} \rangle\rangle = \frac{1}{2}\delta(r-r')\boldsymbol{C}_r \cdot \exp\{(t-t')\boldsymbol{A}_r\},$$
(B.16)

where (B.6) and (B.8) have been used. In turn, one gets for arbitrary $t \gg \tau_{\text{long}}$ and $t' \gg \tau_{\text{long}}$,

$$\langle\langle \boldsymbol{X}_{r,t}; \boldsymbol{X}_{r',t'} \rangle\rangle = \frac{1}{2}\delta(r-r')\boldsymbol{C}_r \cdot \exp\{|t-t'|\boldsymbol{A}_r\}.$$
(B.17)

To proceed, one notices that the following is an approximation of the Dirac delta-function,

$$\delta(t-t') = \lim_{\theta \to 0} f_\theta(t-t'),$$
(B.18)

with

$$f_\theta(t-t') = \frac{1}{2\theta} \exp\{-|t-t'|/\theta\}.$$
(B.19)

Not only is the function narrowly peaked around $t = t'$, but it can also be shown that $\int_{-\infty}^{\infty} f_\theta(t-t')dt' = 1$. Generalizing this result to higher dimensions, e.g. after diagonalizing A_r, one can show that (B.17) can be written in the form

$$\langle\langle \boldsymbol{X}_{r,t}; \boldsymbol{X}_{r',t'} \rangle\rangle = -\delta(t-t')\delta(r-r')\boldsymbol{C}_r \cdot \boldsymbol{A}_r^{-1}.$$
(B.20)

This result agrees with the one of the naive treatment (B.13). In conclusion, the naive treatment leads to the same result as the more careful approach.

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