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Fluctuating viscoelasticity

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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_BT to G_N^0 gives an approximation of the volume occupied by an entanglement strand, which for typical polymer melts is between $2\,\mathrm{nm}^3$ and $40\,\mathrm{nm}^3$ [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 nonlinear 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

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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 $\boldsymbol{c}$ 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 $\boldsymbol{b}$ in $\boldsymbol{c} = \boldsymbol{b}\cdot\boldsymbol{b}^{\mathrm{T}}$, and the relation between the $\boldsymbol{b}$- and $\boldsymbol{c}$-formulations is established. Both $\boldsymbol{b}$- and $\boldsymbol{c}$-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],

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

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],

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

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

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

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 $\boldsymbol{r}$ and $\boldsymbol{r}'$, 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. $E[\mathsf{x}] = \int e(\mathsf{x})d^3r$ and $S[\mathsf{x}] = \int s(\mathsf{x})d^3r$, 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 $k_{\mathrm{B}}(\delta p/\delta \mathsf{x})$. 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,

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

Throughout the entire paper, the dependence of fields on position $\boldsymbol{r}$ 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 $\boldsymbol{r} \neq \boldsymbol{r}'$, the height of the function at $\boldsymbol{r} = \boldsymbol{r}'$ is given by the inverse of the size of the volume element $\not{r} \equiv d^3r$, due to the normalization condition for the