Smoothed particle hydrodynamic model for viscoelastic fluids with thermal fluctuations

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We present a fluid-particle model for a polymer solution in nonisothermal situations. The state of the fluid particles is characterized by the thermodynamic variables and a configuration tensor that describes the underlying molecular orientation of the polymer molecules. The specification of very simple physical mechanisms inspired by the dynamics of single polymer molecules allows one, with the help of the general equation for nonequilibrium reversible-irreversible coupling (GENERIC) formalism, to derive the equations of motion for a set of fluid particles carrying polymer molecules in suspension. In the simplest case of Hookean dumbbells we recover a fluid-particle version of the Oldroyd-B model in which thermal fluctuations are included consistently. Generalization to more complex viscoelastic models, such as finitely extensible nonlinear elastic Peterlin (FENE-P) model, with the proper introduction of thermal fluctuations is straightforward.

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I. INTRODUCTION

Microrheology is an experimental optical technique that probes the viscoelastic response of a fluid by optically measuring the Brownian motion of suspended colloidal particles [1,2]. In these experiments, the mean-square displacement during the diffusion of tracer colloidal particles is recorded and, through a generalized Stokes-Einstein relation, the viscoelastic properties of the medium are inferred. The technique allows one to probe local viscoelasticity in tiny (picoliter) quantities of fluids [3]. This has opened up the extensive use of microrheological techniques in the study of the mechanical response of biological fluids and living cells [4,5].

There are a number of questions to address in the technique, starting from the very initial assumption about the generalized Stokes-Einstein relation [6]. Simulations of viscoelastic fluids with well-known rheological behavior with colloidal particles immersed may give insight and further support to this relation. Note that the generalized Stokes-Einstein relation assumes the fluid to behave in the linear viscoelastic regime, and it may be interesting to probe the nonlinear regime also. Also, because the size of the samples used is very small (in the micron scale), viscoelastic hydrodynamic interactions with container walls are expected to play a role that should be appropriately quantified. Finally, questions on the effect of other probe colloidal particles on the measurement of a single colloidal particle may arise also.

A simulation technique for these types of problems (i.e., colloidal particles immersed in a confined viscoelastic fluid) requires the consideration of thermal fluctuations which are the ultimately responsible for the diffusion of the colloidal particles. There are not many simulation techniques that have considered the introduction of thermal fluctuations in viscoelastic fluids. Lattice Boltzmann, which has been generalized to include thermal fluctuations in the Newtonian case [7], has also been generalized to describe viscoelastic behavior [8], but without thermal fluctuations. Dissipative particle dynamics (DPD) [9,10] is a natural method for dealing with the simulation of polymers in which thermal fluctuations are naturally incorporated. DPD is closely related to the smoothed particle hydrodynamic (SPH) technique [11]. In these particle methods, a polymer may be modeled by joining fluid particles with springs [12,13]. The resulting fluid displays nontrivial rheological behavior [14]. One may want to model the polymeric fluid at a more coarse-grained scale by introducing for each fluid particle a vector describing the average end-to-end vector of polymer molecules that are *within* the fluid particle [15,16]. The resulting model is closely related to the Brownian configuration-field approach [17], and is the discrete counterpart of a continuum theory using the hydrodynamic fields and the space-dependent distribution function for the end-to-end distance of polymer molecules as relevant variables [18]. The Brownian configuration-field approach, like the calculation of non-Newtonian flow: finite elements & stochastic simulation techniques (CONNFFESSIT) approach [19], is intrinsically stochastic and requires the averaging of many configurations in order to obtain smooth macroscopic results, thus increasing the computational resources required.

In the present paper, we formulate an even more coarse-grained fluid-particle model, in which the state of the polymer molecules within a fluid particle is represented by a conformation tensor [18]. The conformation tensor may be thought of as the second moment of the end-to-end distance distribution function. The motivation to consider the conformation tensor is that we will obtain a model in which thermal fluctuations may be controlled by the specific selection of the size of the fluid particles [20]. Also, rather than using constitutive equations for the extra elastic stress, the use of the conformation tensor, which is directly connected to microscopic quantities, allows for a natural introduction of thermal fluctuations in the model. In the model presented in this paper, when the underlying polymer molecules can be modeled by Hookean dumbbells, the resulting fluid-particle model corresponds to a smoothed particle hydrodynamic discretization of the well-known Oldroyd-B model for viscoelastic fluids. Note, however, that more realistic models can be encompassed in the present formulation just by appropriate
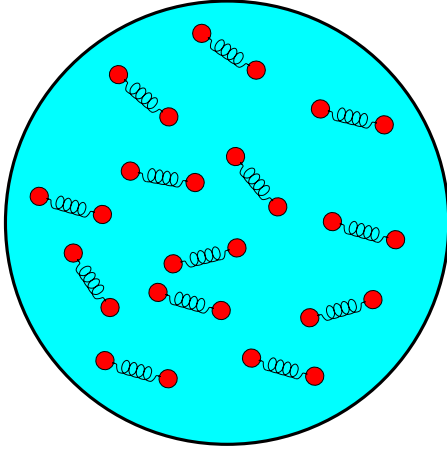
FIG. 1. (Color online) A fluid particle contains N^p polymer molecules and has a conformation tensor **c**.

definition of the conformation-tensor-dependent entropy of the fluid particles. Oldroyd-B model of viscoelasticity is perhaps the simplest model describing nonlinear rheological behavior. It can be derived either from kinetic theory [21] or from more phenomenological approaches [18]. The model has also been simulated with a number of different computational fluid dynamics techniques [22], including SPH [23,24]. Being one of the simplest nontrivial model for nonlinear rheology, with known rheological behavior, it seems the most appropriate for studying the microrheology issues described above. Also, the modelization of the Oldroyd-B model in terms of fluid particles instead of simply discretizing the well-known continuum equations with, for example, finite-difference or spectral methods, allows for a simple introduction of thermal noise with clear physical meaning. The formulation of a general fluid-particle viscoelastic solver valid for dilute polymer solutions with thermal fluctuations included consistently is a first step toward computational microrheology.

II. NONISOTHERMAL PARTICLE MODEL FOR DILUTE POLYMER SOLUTIONS

We model a polymeric solution through a collection of M *fluid particles* with positions $\mathbf{r}_i$ and velocities $\mathbf{v}_i$ which are understood as representing real portions of the material. They are regarded actually as small thermodynamic subsystems that move following the flow. The fluid particle labeled i contains N_i^p polymer molecules as schematically shown in Fig. 1. We will characterize the state of the elongation of the polymer molecules within the fluid particle with a dimensionless conformation tensor defined by

$$\mathbf{c}_i = \frac{1}{N^p q_0^2} \sum_a^{N^p} \mathbf{q}_a \mathbf{q}_a, \tag{1}$$

where $\mathbf{q}_a$ is the end-to-end distance of the ath polymer molecules within the fluid particle i. The tensor has been normalized with q_0 in such a way that the equilibrium value of the conformation tensor is $\mathbf{c}_i = \mathbf{1}$.

In order to formulate the dynamics of the conformation tensor we may resort to the more refined level of description in which the dynamics of the polymer molecules is resolved. For simplicity, the polymer molecules will be represented by dumbbells. The positions of the first and second beads of dumbbell a are $\mathbf{r}_a^1$ and $\mathbf{r}_a^2$, respectively. In the overdamped limit, its evolution is given by the Langevin equations

$$d\mathbf{r}_a^1 = \mathbf{V}(\mathbf{r}_a^1)dt + \frac{1}{\gamma}\mathbf{F}(\mathbf{r}_a^1 - \mathbf{r}_a^2)dt + (2D_0)^{1/2}d\mathbf{W}_a^1,$$

$$d\mathbf{r}_a^2 = \mathbf{V}(\mathbf{r}_a^2)dt + \frac{1}{\gamma}\mathbf{F}(\mathbf{r}_a^2 - \mathbf{r}_a^1)dt + (2D_0)^{1/2}d\mathbf{W}_a^2. \tag{2}$$

Here, $\mathbf{V}(\mathbf{r})$ is the flow velocity field. We assume that *within* the fluid particle we have a homogeneous flow field given by $\mathbf{V}(\mathbf{r}) = \mathbf{v}_i + \boldsymbol{\kappa}_i \cdot \mathbf{r}$, where $\mathbf{v}_i$ is the velocity of the fluid particle and $\boldsymbol{\kappa}_i = (\nabla\mathbf{v})_i$ is the velocity gradient tensor within the fluid particle. The force due to the spring connecting the two beads is $\mathbf{F}(\mathbf{r}_a^2 - \mathbf{r}_a^1)$. The friction coefficient is $\gamma = 6\pi\eta a$, with a as the bead radius and η as the solvent shear viscosity. The stochastic forces are proportional to the diffusion coefficient D_0 of the beads, given by the Stokes-Einstein relation $D_0 = k_B T/\gamma$, while $d\mathbf{W}$ is a vector independent increment of the Wiener process. Note that in Eq. (2) we assume that different polymer molecules do not interact with each other, which is true in the dilute limit.

By changing to center of mass $\mathbf{R}_a = (\mathbf{r}_a^1 + \mathbf{r}_a^2)/2$ and relative coordinate $\mathbf{q}_a = \mathbf{r}_a^1 - \mathbf{r}_a^2$ variables, we have

$$d\mathbf{R}_a = \tfrac{1}{2}[\mathbf{V}(\mathbf{r}_a^1) + \mathbf{V}(\mathbf{r}_a^2)]dt + d\widetilde{\mathbf{R}}_a,$$

$$d\mathbf{q}_a = \boldsymbol{\kappa}_i \cdot \mathbf{q}_a dt + \frac{2\mathbf{F}(\mathbf{q}_a)}{\gamma}dt + d\widetilde{\mathbf{q}}_a, \tag{3}$$

where the noise terms are defined by

$$d\widetilde{\mathbf{R}}_a = (2D_0)^{1/2}\frac{d\mathbf{W}_a^1 + d\mathbf{W}_a^2}{2},$$

$$d\widetilde{\mathbf{q}}_a = (2D_0)^{1/2}(d\mathbf{W}_a^1 - d\mathbf{W}_a^2), \tag{4}$$

and their variances are given by

$$d\widetilde{\mathbf{q}}_a d\widetilde{\mathbf{q}}_b = \delta_{ab}4D_0\mathbf{1}dt,$$

$$d\widetilde{\mathbf{R}}_a d\widetilde{\mathbf{R}}_b = \delta_{ab}D_0\mathbf{1}dt,$$

$$d\widetilde{\mathbf{q}}_a d\widetilde{\mathbf{R}}_b = 0. \tag{5}$$

We may now use the evolution of the dumbbells as described in Eq. (2) in order to obtain the evolution of the conformation tensor **c**. By using stochastic calculus (i.e., expanding to *second order* in $d\widetilde{\mathbf{q}}_a$) to obtain the stochastic variation in the configuration tensor defined in Eq. (1), we arrive at

$$d\mathbf{c} = \frac{1}{N^p q_0^2} \sum_a^{N^p} (\mathbf{q}_a d\mathbf{q}_a + d\mathbf{q}_a \mathbf{q}_a + d\mathbf{q}_a d\mathbf{q}_a), \tag{6}$$

where we have suppressed, for easiness of notation, the fluid-particle index.

By using the last equation in Eq. (3), we can write

$$d\mathbf{c} = (\mathbf{c} \cdot \boldsymbol{\kappa}^T + \boldsymbol{\kappa} \cdot \mathbf{c})dt + \frac{1}{N^p q_0^2} \sum_a^{N^p} \left(\mathbf{q}_a \frac{2\mathbf{F}(\mathbf{q}_a)}{\gamma} + \frac{2\mathbf{F}(\mathbf{q}_a)}{\gamma} \mathbf{q}_a \right.$$
$$\left. + 4D_0 \mathbf{1} \right) dt + d\tilde{\mathbf{c}}, \tag{7}$$

where the noise in the configuration tensor is defined by

$$d\tilde{\mathbf{c}} = \frac{1}{N^p q_0^2} \sum_a^{N^p} (\mathbf{q}_a d\tilde{\mathbf{q}}_a + d\tilde{\mathbf{q}}_a \mathbf{q}_a). \tag{8}$$

The stochastic properties of this noise $d\tilde{\mathbf{c}}$ are basically given by the second moments, which can be computed easily from Eqs. (8) and (4), with the result

$$d\tilde{\mathbf{c}}^{\mu\nu} d\tilde{\mathbf{c}}^{\mu'\nu'} = dt \frac{1}{N^p \tau} [\mathbf{c}^{\mu\mu'} \delta^{\nu\nu'} + \mathbf{c}^{\mu'\nu} \delta^{\mu\nu'}$$
$$+ \mathbf{c}^{\mu\nu'} \delta^{\nu\mu'} + \mathbf{c}^{\nu\nu'} \delta^{\mu\mu'}], \tag{9}$$

where the relaxation time is defined as $\tau \equiv q_0^2/4D_0$.

Dynamic equation (7) for the conformation tensor has three contributions. The first two terms involving the velocity gradient tensor $\boldsymbol{\kappa}$ describes how the tensor is advected and is a purely reversible process. It results in the well-known upper-convected evolution of the conformation tensor. The next term in Eq. (7), which involves the friction coefficient γ, is an irreversible contribution. This irreversible term is not expressed in terms of $\mathbf{c}$ and, therefore, Eq. (7) is not a *closed* stochastic differential equation for the configuration tensor. This is a general theme of coarse-graining a detailed level of description: given detailed dynamics of the fine degrees of freedom, the dynamics of a coarse-grained function of these fine degrees is not closed in general and a closure is necessary. For example, given Hamilton's equations, the kinetic equation for the distribution function is given in terms of the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy that must be closed with some approximation. The route we choose in the present paper in order to close the dynamic equation for the conformation tensor is to resort to the general equation for nonequilibrium reversible-irreversible coupling (GENERIC) framework, which is ultimately based on a closure through a Markovian approximation [25].

Nevertheless, note that for the Hookean dumbbell model, for which the spring law is linear, $\mathbf{F}(\mathbf{q}) = -H\mathbf{q}$, with H as the spring constant, we do have a closed equation for $\mathbf{c}$,

$$d\mathbf{c} = (\mathbf{c} \cdot \boldsymbol{\kappa}^T + \boldsymbol{\kappa} \cdot \mathbf{c})dt + \frac{1}{\tau}[\mathbf{1} - \mathbf{c}]dt + d\tilde{\mathbf{c}}. \tag{10}$$

For Hookean dumbbells, the equilibrium dumbbell length is $q_0 = \sqrt{k_B T/H}$ and the relaxation time is $\tau = \gamma/4H$.

III. GENERIC FORMULATION

In order to construct the fluid-particle model, we will resort to the GENERIC framework [18], which has proved to

be a very useful tool in order to formulate fluid-particle models in a thermodynamically consistent way [11,26].

The first step in the GENERIC formulation is the specification of the state variables. In the present model, to each of the M fluid particles that compose the system we associate the independent variables $\mathbf{r}_i$, $\mathbf{v}_i$, E_i, and $\mathbf{c}_i$ which will characterize the state of the fluid. The internal energy E_i represents the contributions of kinetic energy of the solvent and bead particles with respect to the center of mass of the fluid particle plus the potential energy of interaction (including solvent-solvent, solvent-bead, and bead-bead interactions). Note that we assume that each fluid particle has a *constant* number N^p of polymer molecules. A more general model can be constructed in which this number is also a variable, which may evolve due to diffusion of polymer molecules from one fluid particle to another [16]. However, in the present paper, and for the sake of simplicity, we assume that this diffusion can be neglected. Each fluid particle has also associated a volume, which is not an independent variable but rather depends on the positions of the given particle and its neighbors. In the SPH and smoothed dissipative particle dynamics (SDPD) philosophy [11], one provides a volume $\mathcal{V}_i$ to each particle through the inverse of a density d_i, which is defined by

$$\frac{1}{\mathcal{V}_i} = d_i = \sum_j W(r_{ij}). \tag{11}$$

Here, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and $W(r)$ is a bell-shaped function of finite support r_c and which is normalized to unity,

$$\int d\mathbf{r} W(r) = 1. \tag{12}$$

In this work a quintic spline kernel as in [24] was used,

$$W(s) = w_0 \begin{cases} (3-s)^5 - 6(2-s)^5 + 15(1-s)^5, & 0 \le s < 1 \\ (3-s)^5 - 6(2-s)^5, & 1 \le s < 2 \\ (3-s)^5, & 2 \le s < 3 \\ 0, & s \ge 3, \end{cases} \tag{13}$$

where $s = r/h$ and $w_0 = 7/478\pi h^2$ in two dimensions (2D). Note that if particle i has many neighboring particles within $r_c = 3h$, then the density d_i in Eq. (11) will be large. Consistently, we associate a smaller volume $\mathcal{V}_i$ to it.

Finally, every fluid particle (i.e., thermodynamic subsystem) has associated an entropy function $S_i(E_i, \mathbf{c}_i, \mathcal{V}_i)$. The microscopic definition of this entropy function is given by the logarithm of the "number of microstates" which are compatible with prescribed values of E_i and $\mathbf{c}_i$ [18]. In more precise terms,

$$S(E, \mathbf{c}, \mathcal{V}) = k_B \ln \int dz \delta[H(z) - E] \delta[\mathbf{c}(z) - \mathbf{c}], \tag{14}$$

where z is the set of microscopic degrees of freedom (positions and velocities of the solvent molecules and beads), $H(z)$ is the Hamiltonian of the system, and $\mathbf{c}(z)$ is given in Eq. (1). If the Dirac delta function on $\mathbf{c}$ was not present, Eq.

(14) would be the equilibrium thermodynamic entropy of the system. The introduction of this additional delta functionarises from our requirement of describing the system at a more refined level, through the conformation tensor **c**.

The full state of the system is thus characterized by the variables $x=\{\mathbf{r}_i,\mathbf{v}_i,E_i,\mathbf{c}_i, i=1,\dots,M\}$. The total energy of the system is given by

$$E(x) = \sum_i^M \frac{m}{2}\mathbf{v}_i^2 + E_i. \tag{15}$$

Here, E_i must be understood as the total internal energy of the fluid particle, including elastic contributions from the suspended polymer molecules. The total entropy of the system will be

$$S(x) = \sum_i S(E_i,\mathbf{c}_i,\mathcal{V}_i). \tag{16}$$

Note that the entropy of the full system is defined as the sum of the entropies of each fluid particle taken as thermodynamic subsystems, that is, by the sum of function (14) evaluated at E_i, $\mathbf{c}_i$, and $\mathcal{V}_i$. This is the well-known *local equilibrium assumption*. The particular functional form of $S(E_i,\mathbf{c}_i,\mathcal{V}_i)$ will be discussed later on.

For future reference we present here the derivatives of the energy and entropy functions with respect to the state variables,

$$\frac{\partial E}{\partial x} = \begin{pmatrix} \mathbf{0} \\ m\mathbf{v}_j^\nu \\ 1 \\ \mathbf{0}^{\nu\nu'} \end{pmatrix}, \quad \frac{\partial S}{\partial x} = \begin{pmatrix} \sum_k \mathbf{\Omega}_{jk}^\nu \dfrac{P_k}{d_k^2 T_k} \\ 0 \\ \dfrac{1}{T_j} \\ \dfrac{\boldsymbol{\sigma}_j^{\nu\nu'}}{T_j} \end{pmatrix}. \tag{17}$$

We have introduced the equations of state of the fluid particle as the derivatives of the entropy with respect to its variables, that is,

$$\frac{P}{T} = \frac{\partial S}{\partial \mathcal{V}},$$

$$\frac{1}{T} = \frac{\partial S}{\partial E},$$

$$\frac{\boldsymbol{\sigma}}{T} = \frac{\partial S}{\partial \mathbf{c}}. \tag{18}$$

Here, T is the temperature, P is the pressure, and $\boldsymbol{\sigma}$ is the tensorial variable thermodynamically conjugated of **c**. Note that, as a consequence of the dependence of the entropy on the conformation tensor **c**, the temperature and the pressure will also depend in general on the conformation tensor. In Eq. (17) we have introduced the vector

$$\mathbf{\Omega}_{ij} = -\frac{\partial d_j}{\partial \mathbf{r}_i} = \boldsymbol{\omega}_{ij} + \delta_{ij}\sum_k \boldsymbol{\omega}_{ik}, \tag{19}$$

where

$$\boldsymbol{\omega}_{ij} = -W'(r_{ij})\mathbf{e}_{ij}. \tag{20}$$

Here, the prime denotes derivative and $\mathbf{e}_{ij} = \frac{\mathbf{r}_i - \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|}$ is the unit vector joining particles i and j. The function $-W'(r) > 0$ is positive. The vector $\boldsymbol{\omega}_{ij}$ is a purely geometric object that depends only on the positions of the fluid particles.

A. Reversible part of the dynamics

In this section, we formulate the reversible part of the dynamics for the set of variables x. According to GENERIC, the reversible part of the dynamics is given by [see Eq. (A1) of Appendix A]

$$\dot{x}|_{\text{rev}} = L\frac{\partial E}{\partial x}, \tag{21}$$

The reversible part of the dynamics represents purely kinematic effects on the evolution of the variables. We wish that the reversible part of the dynamics produces the following equation of motion for the positions of the fluid particles:

$$\dot{\mathbf{r}}_i = \mathbf{v}_i. \tag{22}$$

A second requirement for L comes from our desire that it describe the reversible upper-convected dynamics we have encountered in Eq. (7), which we write in component form as

$$\dot{\mathbf{c}}_i^{\mu\mu'}|_{\text{rev}} = \mathbf{c}_i^{\mu\nu}(\nabla^\nu\mathbf{v}^{\mu'})_i + \mathbf{c}_i^{\mu'\nu}(\nabla^\nu\mathbf{v}^\mu)_i, \tag{23}$$

where Greek indices μ, ν, and μ' represent Cartesian coordinates and Einstein summation rule is applied over repeated indices.

We now obtain a form for $(\nabla\mathbf{v})_i$ by following the SPH philosophy. We interpolate the velocity field according to

$$\mathbf{v}(\mathbf{r}) = \frac{\sum_j W(\mathbf{r}-\mathbf{r}_j)\mathbf{v}_j}{\sum_j W(\mathbf{r}-\mathbf{r}_j)}. \tag{24}$$

By taking the gradient of this expression we obtain

$$\nabla\mathbf{v}(\mathbf{r}) = \frac{\sum_j \nabla W(\mathbf{r}-\mathbf{r}_j)\mathbf{v}_j}{\sum_j W(\mathbf{r}-\mathbf{r}_j)} - \mathbf{v}(\mathbf{r})\frac{\sum_j \nabla W(\mathbf{r}-\mathbf{r}_j)}{\sum_j W(\mathbf{r}-\mathbf{r}_j)}. \tag{25}$$

Therefore, at particle i we have the approximate expression

$$\nabla^\nu\mathbf{v}^\mu(\mathbf{r}_i) = \frac{1}{d_i}\left(\sum_j \nabla^\nu W(r_{ij})\mathbf{v}_j^\mu - \mathbf{v}^\mu(\mathbf{r}_i)\sum_j \nabla^\nu W(r_{ij})\right)$$

$$\approx \frac{1}{d_i}\sum_j \boldsymbol{\omega}_{ij}^\nu\mathbf{v}_{ij}^\mu = \frac{1}{d_i}\sum_j \mathbf{\Omega}_{ji}^\nu\mathbf{v}_j^\mu, \tag{26}$$

where $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$ and Ω_{ij} and $\boldsymbol{\omega}_{ij}$ are defined in Eqs. (19) and (20). By inserting this discrete form (26) into Eq. (23), we can write

$$\dot{\mathbf{c}}_i^{\mu\mu'}\big|_{\text{rev}} = \sum_j \Lambda_{ij}^{\mu\mu'\nu} \mathbf{v}_j^\nu, \tag{27}$$

where we have introduced the following third-order tensor for every pair i, j of particles:

$$\Lambda_{ij}^{\mu\mu'\nu} = \frac{1}{d_i} [\delta^{\mu\nu}\mathbf{c}_i^{\mu'\nu'} + \delta^{\mu'\nu}\mathbf{c}_i^{\mu\nu'}]\Omega_{ji}^{\nu'}. \tag{28}$$

This tensor is symmetric with respect to the first two indices μ and μ', and there is a sum over the repeated index ν'.

The simplest nontrivial reversible dynamics that produces the above Eqs. (22) and (27) has the following form:

$$\begin{pmatrix} \dot{\mathbf{r}}_i \\ \dot{\mathbf{v}}_i^\mu \\ \dot{E}_i \\ \dot{\mathbf{c}}_i^{\mu\mu'} \end{pmatrix}_{\Big|_{\text{rev}}} = \sum_j \mathbf{L}_{ij} \begin{pmatrix} \mathbf{0} \\ m\mathbf{v}_j^\nu \\ 1 \\ \mathbf{0}^{\nu\nu'} \end{pmatrix}, \tag{29}$$

where the block $\mathbf{L}_{ij}$ has the structure

$$\mathbf{L}_{ij} = \frac{1}{m} \begin{pmatrix} \mathbf{0} & \delta^{\mu\nu}\delta_{ij} & 0 & \mathbf{0} \\ -\delta^{\mu\nu}\delta_{ij} & \mathbf{0} & \boldsymbol{\Delta}_{ij}^\mu & -\Lambda_{ji}^{\nu\nu'\mu} \\ 0 & -\boldsymbol{\Delta}_{ji}^\nu & 0 & 0 \\ \mathbf{0} & \Lambda_{ij}^{\mu\mu'\nu} & 0 & \mathbf{0} \end{pmatrix}. \tag{30}$$

The first and fourth rows of $\mathbf{L}_{ij}$ ensure the equations of motion (22) and (27). The first and fourth columns are fixed by antisymmetry of L. The only term that remains to be specified in the matrix L is $\boldsymbol{\Delta}_{ij}^\mu$. This term is determined by the degeneracy requirement that $L\frac{\partial S}{\partial x}=0$, which physically ensures that the reversible part of the dynamics does not change the entropy of the system. This degeneracy condition takes the following form in the present case:

$$\begin{pmatrix} \mathbf{0} \\ \mathbf{0}_i^\mu \\ 0_i \\ \mathbf{0}_i^{\mu\mu'} \end{pmatrix} = \sum_j \mathbf{L}_{ij} \begin{pmatrix} \sum_k \Omega_{jk}^\nu \dfrac{P_k}{d_k^2 T_k} \\ 0 \\ \dfrac{1}{T_j} \\ \dfrac{\boldsymbol{\sigma}_j^{\nu\nu'}}{T_j} \end{pmatrix}. \tag{31}$$

The only nontrivial term comes from the second row of L, which leads to

$$\sum_j \left[-\Omega_{ij}^\mu \frac{P_j}{T_j d_j^2} + \boldsymbol{\Delta}_{ij}^\mu \frac{1}{T_j} - \frac{\boldsymbol{\sigma}_j^{\nu\nu'}}{T_j}\Lambda_{ji}^{\nu\nu'\mu} \right] = 0. \tag{32}$$

A simple selection for $\boldsymbol{\Delta}_{ij}^\mu$ that satisfies this equation is

$$\boldsymbol{\Delta}_{ij}^\mu = \Omega_{ij}^\mu \frac{P_j}{d_j^2} + \boldsymbol{\sigma}_j^{\nu\nu'}\Lambda_{ji}^{\nu\nu'\mu}. \tag{33}$$

By inserting into Eq. (33) expression (28) we arrive at

$$\boldsymbol{\Delta}_{ij}^\mu = \frac{1}{d_j^2}\Pi_j^{\mu\mu'}\Omega_{ij}^{\mu'}, \tag{34}$$

where the reversible part Π_j of the stress tensor of the fluid particle j is

$$\Pi_j = P_j\mathbf{1} + 2d_j\boldsymbol{\sigma}_j \cdot \mathbf{c}_j. \tag{35}$$

We show in Eq. (B4) of Appendix B that $\boldsymbol{\sigma}_j \cdot \mathbf{c}_j = \mathbf{c}_j \cdot \boldsymbol{\sigma}_j$ and, because $\boldsymbol{\sigma}_j$ and $\mathbf{c}_j$ are both symmetric tensors, it follows that the reversible stress tensor Π_j is itself symmetric.

Now that we have an explicit expression for all the elements of the matrix L, we can perform the matrix multiplication in Eq. (29) and obtain the reversible part of the equations of motion for the relevant variables. They are

$$\dot{\mathbf{r}}\big|_{\text{rev}} = \mathbf{v}_i,$$

$$m\dot{\mathbf{v}}_i^\mu\big|_{\text{rev}} = \sum_j \left[\frac{\Pi_i^{\mu\nu}}{d_i^2} + \frac{\Pi_j^{\mu\nu}}{d_j^2} \right] \boldsymbol{\omega}_{ij}^\nu,$$

$$\dot{E}_i\big|_{\text{rev}} = -\frac{\Pi_i^{\mu\nu}}{d_i^2}\sum_j \boldsymbol{\omega}_{ij}^\nu\mathbf{v}_{ij}^\mu,$$

$$\dot{\mathbf{c}}_i^{\mu\mu'}\big|_{\text{rev}} = \frac{\mathbf{c}_i^{\mu\nu}}{d_i}\sum_j \boldsymbol{\omega}_{ij}^\nu\mathbf{v}_{ij}^{\mu'} + \frac{\mathbf{c}_i^{\mu'\nu}}{d_i}\sum_j \boldsymbol{\omega}_{ij}^\nu\mathbf{v}_{ij}^\mu. \tag{36}$$

It is a simple exercise to check that total momentum is conserved (due to the symmetry $\boldsymbol{\omega}_{ij}=-\boldsymbol{\omega}_{ji}$). Total energy and entropy are conserved exactly by these equations, as a consequence of their GENERIC structure.

Let us summarize now the line of reasoning followed in this section. We have assumed a particular equation of motion for the conformation tensor $\mathbf{c}_i$ given in Eq. (23) or, more explicitly, in the last equation of Eq. (36), which is the SPH version of the upper-convected evolution for $\mathbf{c}_i$. In the reversible matrix L this dynamics is captured by the matrix elements $\Lambda_{ij}^{\mu\mu'\nu}$ in the last row of Eq. (30). The degeneracy condition $L\frac{\partial S}{\partial x}=0$ allows us to fix the remaining undetermined element $\boldsymbol{\Delta}_{ij}^\mu$ of L. As a result, we have been able to identify a reversible part of the stress tensor $\Pi_i^{\mu\nu}$, which depends on the configuration $\mathbf{c}_i$ of the polymer molecules. In other words, the requirement that the reversible part of the dynamics does not produce an increase in entropy enforces the form of the stress tensor.

B. Irreversible part of the dynamics

As shown in Appendix A, in order to derive the irreversible part of the dynamics of a system, a very useful route is to *first* postulate the thermal noises $d\tilde{x}$ and *afterward* compute the dissipative matrix M through the fluctuation-dissipation theorem,

$$M = \frac{d\tilde{x}d\tilde{x}^T}{2k_B dt}. \tag{37}$$

This procedure ensures that M defined through Eq. (37) is automatically symmetric and positive semidefinite, which are

two essential properties of the dissipative matrix M. One should note that, in principle, it would be easier to simply postulate the form of M in order to have a physically sensible set of equations. However, we would still have the problem of finding out the explicit form of thermal noises that fulfill fluctuation-dissipation theorem (37). This would involve computing the square root in matrix sense of M, which might be difficult to perform.

We postulate the following form for the thermal noises $d\widetilde{x} = \{\mathbf{0}, d\widetilde{\mathbf{v}}_i, d\widetilde{E}_i, d\widetilde{\mathbf{c}}_i\}$. Note that we do not assume any thermal noise for the position of the fluid particles, as we want to respect the kinematic equation of motion $\dot{\mathbf{r}}_i = \mathbf{v}_i$. In Ref. [11] we discussed how to introduce the thermal noises $d\widetilde{\mathbf{v}}_i$ and $d\widetilde{E}_i$ in order to recover a matrix M which produces an irreversible part of the dynamics that can be understood as a smoothed particle hydrodynamic discretization of the irreversible terms of the Navier-Stokes equations. We simply borrow from [11] the forms of these noises. Note that in [11] we used the entropy as independent variable, as opposed to the internal energy. This means that we have a stochastic term $d\widetilde{S}_i$, instead of a stochastic term $d\widetilde{E}_i$. The connection, however, is trivial, $d\widetilde{E}_i = T_i d\widetilde{S}_i$. In this way, we have

$$md\widetilde{\mathbf{v}}_i = \sum_j A_{ij} d\overline{\mathbf{W}}_{ij} \cdot \mathbf{e}_{ij},$$

$$d\widetilde{E}_i = \sum_j C_{ij} dV_{ij} - \sum_j \frac{A_{ij}}{2} d\overline{\mathbf{W}}_{ij} : \mathbf{e}_{ij} \mathbf{v}_{ij}, \qquad (38)$$

where

$$d\overline{\mathbf{W}}_{ij} = \tfrac{1}{2}[d\mathbf{W}_{ij} + d\mathbf{W}_{ij}^T]. \qquad (39)$$

In this expression we have introduced, for each pair i,j of particles, a matrix of independent increments of the Wiener process, $d\mathbf{W}_{ij}$. In Eq. (38) we have also introduced an independent increment of the Wiener process for each pair of particles, dV_{ij}. This last term will give rise to the heat conduction terms in the energy evolution [27]. We postulate the following symmetry properties:

$$d\mathbf{W}_{ij} = d\mathbf{W}_{ji},$$

$$dV_{ij} = -dV_{ji}. \qquad (40)$$

The independent increments of the Wiener processes satisfy the following Itô mnemotechnical rules:

$$dW_{ii'}^{\alpha\alpha'} dW_{jj'}^{\beta\beta'} = [\delta_{ij}\delta_{i'j'} + \delta_{ij'}\delta_{i'j}]\delta^{\alpha\beta}\delta^{\alpha'\beta'} dt,$$

$$dV_{ii'} dV_{jj'} = [\delta_{ij}\delta_{i'j'} - \delta_{ij'}\delta_{i'j}] dt,$$

$$dW_{ii'}^{\alpha\alpha'} dV_{ii'} = 0, \qquad (41)$$

which respect symmetries (40) under particle interchange. For the amplitudes A_{ij} and C_{ij} of the noises in Eq. (38), we select the very specific forms [11]

$$A_{ij} = \left[\frac{40\eta}{3} k_B \frac{T_i T_j}{T_i + T_j} \frac{F_{ij}}{d_i d_j}\right]^{1/2},$$

$$C_{ij} = \left[4\kappa k_B T_i T_j \frac{F_{ij}}{d_i d_j}\right]^{1/2}, \qquad (42)$$

where η is the shear viscosity of the solvent and κ is the thermal conductivity. The geometrical factor F_{ij} is given by

$$F_{ij} = -\frac{W'(r_{ij})}{r_{ij}}. \qquad (43)$$

This completes the definition of the thermal noises $d\widetilde{\mathbf{v}}_i$ and $d\widetilde{E}_i$, as proposed in Ref. [11]. Note that we have assumed for simplicity that the bulk viscosity of the solvent is zero [11]. As we showed in Ref. [11], the above noise terms produce dissipative dynamics that can be understood as a proper discretization of the irreversible part of the Navier-Stokes equation of a fluid with transport coefficients η and κ.

We still have to postulate the noise term $d\widetilde{\mathbf{c}}_i$. We assume that this noise term captures the elementary processes by which $\mathbf{c}_i$ changes irreversibly. We will assume that $d\widetilde{\mathbf{c}}_i$ is statistically independent of $d\widetilde{\mathbf{v}}_i$ and $d\widetilde{E}_i$. Concerning the stochastic changes in $\mathbf{c}_i$, we have discussed in Sec. II that a reasonable assumption for the stochastic properties of the term $d\widetilde{\mathbf{c}}_i$ is given by Eq. (9).

The total linear momentum $P(x) = \Sigma_i m\mathbf{v}_i$ is an additional dynamical invariant $I(x)$ in this model. Its derivatives with respect to the state variables are

$$\frac{\partial \mathbf{P}}{\partial x} \to \begin{pmatrix} 0 \\ m\mathbf{1} \\ 0 \\ \mathbf{0} \end{pmatrix}. \qquad (44)$$

Now, it is a trivial exercise to show that Eq. (A6) in Appendix A, which now takes the form

$$\sum_i m\mathbf{v}_i \cdot d\widetilde{\mathbf{v}}_i + d\widetilde{E}_i = 0,$$

$$\sum_i m d\widetilde{\mathbf{v}}_i = 0, \qquad (45)$$

is exactly satisfied by the noise terms in Eq. (38), due to symmetries (40). In this way, the postulated noises conserve exactly the energy and momentum. Consequently, the irreversible part of the dynamics will also conserve momentum and energy.

According to Eq. (37), the matrix $M \to \mathbf{M}_{ij}$ is given by

$$\begin{pmatrix} \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\[4pt] \mathbf{0} & \dfrac{d\widetilde{\mathbf{v}}_i d\widetilde{\mathbf{v}}_j^T}{2k_B dt} & \dfrac{d\widetilde{\mathbf{v}}_i d\widetilde{E}_j}{2k_B dt} & \mathbf{0} \\[10pt] \mathbf{0} & \dfrac{d\widetilde{E}_i d\widetilde{\mathbf{v}}_j^T}{2k_B dt} & \dfrac{d\widetilde{E}_i d\widetilde{E}_j}{2k_B dt} & \mathbf{0} \\[10pt] \mathbf{0} & \mathbf{0} & \mathbf{0} & \dfrac{d\widetilde{\mathbf{c}}_i d\widetilde{\mathbf{c}}_j}{2k_B dt} \end{pmatrix}. \qquad (46)$$

The central diagonal block was computed in Ref. [11] and the last diagonal element is given by Eq. (9).

Now we are in position to write the deterministic irreversible part of the dynamics $\dot{x}|_{irr} = M \cdot \frac{\partial S}{\partial x}$, which will be given by

$$\begin{pmatrix} \dot{r}_i \\ \dot{\mathbf{v}}_i \\ \dot{E}_i \\ \dot{\mathbf{c}}_i \end{pmatrix}_{\!\!|irr} = \sum_j \mathbf{M}_{ij} \begin{pmatrix} \sum_\sigma \mathbf{\Omega}_{jk} \dfrac{P_k}{d_k^2 T_k} \\[6pt] 0 \\[6pt] \dfrac{1}{T_j} \\[6pt] \dfrac{\boldsymbol{\sigma}_j}{T_j} \end{pmatrix}, \qquad (47)$$

where we have used Eq. (17). The matrix multiplication leads readily to the following equations:

$$\dot{\mathbf{r}}|_{irr} = 0,$$

$$m\dot{\mathbf{v}}_i|_{irr} = -\frac{5\eta}{3} \sum_j \frac{F_{ij}}{d_i d_j} [\mathbf{v}_{ij} + (\mathbf{e}_{ij} \cdot \mathbf{v}_{ij})\mathbf{e}_{ij}],$$

$$\dot{E}_i|_{irr} = \frac{1}{2} \frac{5\eta}{3} \sum_j \frac{F_{ij}}{d_i d_j} (\mathbf{v}_{ij}^2 + (\mathbf{v}_{ij} \cdot \mathbf{e}_{ij})^2) - 2\kappa \sum_j \frac{F_{ij}}{d_i d_j} T_{ij},$$

$$\dot{\mathbf{c}}_i|_{irr} = \frac{2}{k_B N^p T_i \tau} \mathbf{c}_i \cdot \boldsymbol{\sigma}_i, \qquad (48)$$

where we have used Eq. (B4) in Appendix B.

By collecting reversible part (36) and irreversible part (48), we end up with the final equations of motion for the viscoelastic fluid-particle model. They are

$$\dot{\mathbf{r}}_i = \mathbf{v}_i,$$

$$m\dot{\mathbf{v}}_i = \sum_j \left[\frac{\mathbf{\Pi}_i}{d_i^2} + \frac{\mathbf{\Pi}_j}{d_j^2} \right] \cdot \boldsymbol{\omega}_{ij} - \frac{5\eta}{3} \sum_j \frac{F_{ij}}{d_i d_j} [\mathbf{v}_{ij} + (\mathbf{e}_{ij} \cdot \mathbf{v}_{ij})\mathbf{e}_{ij}],$$

$$\dot{E}_i = -\frac{\mathbf{\Pi}_i}{d_i^2} : \sum_j \boldsymbol{\omega}_{ij} \mathbf{v}_{ij} + \frac{1}{2} \frac{5\eta}{3} \sum_j \frac{F_{ij}}{d_i d_j} [\mathbf{v}_{ij}^2 + (\mathbf{v}_{ij} \cdot \mathbf{e}_{ij})^2]$$
$$- 2\kappa \sum_j \frac{F_{ij}}{d_i d_j} T_{ij},$$

$$\dot{c}_i^{\mu\mu'} = \frac{c_i^{\mu\nu}}{d_i} \sum_j \omega_{ij}^\nu \mathbf{v}_{ij}^{\mu'} + \frac{c_i^{\mu'\nu}}{d_i} \sum_j \omega_{ij}^\nu \mathbf{v}_{ij}^\mu + \frac{2}{\tau N^d k_B T_i} c_i^{\mu\nu} \sigma_i^{\nu\mu'}, \qquad (49)$$

with the reversible stress tensor $\mathbf{\Pi}_i$ given in Eq. (35).

In order to close Eq. (49), we need to know the explicit functional forms of the thermodynamic conjugate variables P_i, T_i, and $\boldsymbol{\sigma}_i$ in terms of the state variables $\mathbf{r}_i$, E_i, and $\mathbf{c}_i$. (Note that the entropy and its derivatives do not depend on the velocity $\mathbf{v}_i$.) Because the thermodynamic conjugate variables are the derivatives of the entropy, we need the explicit form of the entropy function. Several forms based on a Gaussian form of the equilibrium probability distribution

function of the conformation tensor have been proposed in the literature for the entropy depending on the conformation tensor [18,28]. Another possible approach to obtain the functional form of the conformation-dependent entropy is to compute the phase-space integrals involved in Eq. (14), which can be analytically computed for the case of a dilute solution of dumbbells with a Hookean spring law. Note that, in general, the particular form of the "spring law" modeling the intradynamics of the polymer molecules appears in the present model only through the functional form of the entropy. For a dilute solution of Hookean dumbbells, the configuration-dependent entropy is given by [18]

$$S(E, \mathbf{c}, \mathcal{V}) = S_s(E, \mathcal{V}) + S_p(\mathbf{c}), \qquad (50)$$

where $S_s(E, \mathcal{V})$ is the entropy of the solvent and $S_p(\mathbf{c})$ is the contribution due to the polymers. The functional form for S_s has to be yet specified. Very simple models (such as the ideal gas) are used frequently in the SPH literature. For the Hookean dumbbell model, the functional form of S_p is given by

$$S_p(\mathbf{c}) = k_B \frac{N^p}{2} (\text{tr}[\mathbf{1} - \mathbf{c}] + \ln \det \mathbf{c}). \qquad (51)$$

The intensive parameters defined in Eq. (18) are given by

$$T = T_s,$$

$$\boldsymbol{\sigma} = \frac{N^p}{2} k_B T [\mathbf{c}^{-1} - \mathbf{1}],$$

$$P = P_s, \qquad (52)$$

where T_s and P_s are the solvent temperature and pressure, which depend only on the volume, mass, and internal energy of the fluid particle, and not on the polymer variables $\mathbf{c}$. In Eq. (52) the Jacobi formula

$$\frac{\partial \ln \det \mathbf{c}}{\partial \mathbf{c}} = \mathbf{c}^{-1} \qquad (53)$$

has been used to compute $\boldsymbol{\sigma}$. After using the expression of $\boldsymbol{\sigma}$ we obtain the expressions for the stress tensor

$$\mathbf{\Pi}_j = P_j^s \mathbf{1} - n_j^p k_B T \mathbf{c}_j, \qquad (54)$$

where $n_i^p = N^p d_i = N^p / \mathcal{V}_i$ is the number density of polymer molecules. Also, we have the following expression for the irreversible change in the configuration tensor in Eq. (48):

$$\dot{\mathbf{c}}_i|_{irr} = \frac{1}{\tau} [\mathbf{1} - \mathbf{c}_i], \qquad (55)$$

In order to describe finite extensibility of the polymer molecules, the term $\text{tr}[\mathbf{1} - \mathbf{c}]$ in the entropy function may be substituted by

$$\phi(\text{tr } \mathbf{c}) = b \ln\left(\frac{b+3}{3} - \frac{1}{b} \text{tr } \mathbf{c} \right), \qquad (56)$$

which leads to the widely used finitely extensible nonlinear elastic Peterlin (FENE-P) model [18]. In the limit very large

finite extensibility parameter $b \rightarrow \infty$, we recover Hookean model (50). For simplicity reasons only, we restrict ourselves in the present paper to the Hookean model.

C. Physical meaning of the equations

We discuss now the physical content of Eq. (49). The first three equations are very similar to the equations obtained for the fluid-particle model of a Newtonian fluid in Ref. [11], except for the only difference that now we have a more complex form for the reversible stress tensor, given in Eq. (35). In addition to the usual diagonal part involving the pressure of the solvent, we have now an additional term depending on the conformation tensor that accounts for the stress due to the nonisotropic distribution of elongations of the microscopic polymer molecules. The second term in the momentum equation is a purely frictional force that tries to reduce velocity differences between fluid particles. The overall magnitude of this force is governed by the shear viscosity. This force dissipates energy because it drives the particles toward the rest state. The kinetic energy of the fluid particles must be transformed, therefore, into internal energy. This effect is captured by the second term in the energy equation, which is a *viscous heating* term. The last term in the energy equation tries to reduce temperature differences between fluid particles. It is a *heat conduction* term with overall magnitude given by the thermal conductivity of the solvent. The first term in the energy equation is the reversible rate of change in the work made by the reversible forces in the momentum equation.

The new equation that appears when comparing Eq. (49) with the SDPD model for a Newtonian fluid [11] is for the conformation tensor $\mathbf{c}_i$. We observe that the first two reversible terms in the equation for $\mathbf{c}_i$ simply convect the configuration, as if the microscopic polymer molecules were anchored with the solvent. Extensions, shears, and compressions will produce reversible variations in the configuration tensor. Opposed to this effect is the relaxation of the configuration tensor to its isotropic equilibrium value, for which $\boldsymbol{\sigma} = 0$. The time scale of this relaxation is given by τ.

We observe, therefore, that the above equations are able to display complex phenomena in which the motion of the particles is coupled to the inner microstructure of the solution. Equation (49) conserves total mass, momentum, and energy, and also satisfies exactly the second law of thermodynamics [i.e., $\dot{S}(x) \geq 0$]. Therefore, it is thermodynamically consistent.

IV. CONTINUUM EQUATIONS

It is possible to show, by following steps similar to those in Ref. [11], that discrete equations (49) can be understood as a particular smoothed particle hydrodynamic discretization of the following continuum hydrodynamic equations:

$$\partial_t \rho = - \nabla \cdot \rho \mathbf{v},$$

$$\partial_t \rho \mathbf{v} = - \nabla \cdot \rho \mathbf{v} \mathbf{v} - \nabla \cdot \boldsymbol{\Pi} + \eta \nabla^2 \mathbf{v} + \frac{\eta}{3} \nabla (\nabla \cdot \mathbf{v}) + \rho \mathbf{g},$$

$$\partial_t \epsilon = - \nabla \cdot \rho \mathbf{v} \epsilon + \boldsymbol{\Pi} : \nabla \mathbf{v} + 2 \eta \overline{\nabla \mathbf{v}} : \overline{\nabla \mathbf{v}} + \kappa \nabla^2 T,$$

$$\partial_t \mathbf{c} = - \mathbf{v} \cdot \nabla \mathbf{c} + (\nabla \mathbf{v}) \cdot \mathbf{c} + \mathbf{c} \cdot \nabla \mathbf{v}^T + \frac{2}{\tau n k_B T} \mathbf{c} \cdot \boldsymbol{\sigma}, \quad (57)$$

where ρ is the mass density field, $\mathbf{v}$ is the velocity field, ϵ is the internal energy density field, and the conjugate variables are now defined as

$$\frac{1}{T} = \frac{\partial s(\epsilon, \mathbf{c})}{\partial \epsilon},$$

$$\frac{\boldsymbol{\sigma}}{T} = \frac{\partial s(\epsilon, \mathbf{c})}{\partial \mathbf{c}}, \quad (58)$$

where $s(\epsilon, \mathbf{c})$ is the entropy density (i.e., per unit volume). The reversible part of the stress tensor is given by

$$\boldsymbol{\Pi} = P \mathbf{1} + [\boldsymbol{\sigma} \cdot \mathbf{c} + \mathbf{c} \cdot \boldsymbol{\sigma}], \quad (59)$$

where P is the pressure field of the solvent and

$$\overline{\nabla \mathbf{v}} = \tfrac{1}{2} [\nabla \mathbf{v} + \nabla \mathbf{v}^T] - \tfrac{1}{3} \nabla \cdot \mathbf{v} \quad (60)$$

is the symmetric traceless part of the velocity gradient tensor.

The total energy and entropy are the continuum counterparts of Eqs. (15) and (16), that is,

$$E = \int d\mathbf{r} \left[\frac{\rho_\mathbf{r}}{2} \mathbf{v}_\mathbf{r}^2 + \epsilon_\mathbf{r} \right],$$

$$S = \int d\mathbf{r} s(\epsilon_\mathbf{r}, \mathbf{c}_\mathbf{r}). \quad (61)$$

The above Eq. (57) satisfies $\partial_t E = 0$ and $\partial_t S \geq 0$. For a Hookean model for the polymer molecules we have

$$\boldsymbol{\sigma} = \frac{n k_B T}{2} [\mathbf{c}^{-1} - \mathbf{1}],$$

$$\boldsymbol{\Pi} = P_s \mathbf{1} + n k_B T \mathbf{c},$$

$$\frac{2}{\tau n k_B T} \mathbf{c} \cdot \boldsymbol{\sigma} = \frac{1}{\tau} [\mathbf{1} - \mathbf{c}] \quad (62)$$

to be substituted into Eq. (57).

In order to check that the proposed discrete model produces sensible results, we will perform numerical simulation in the simplest of the nontrivial version of the viscoelastic model. In particular, we assume a Hookean entropy and constant temperature. This allows us to obtain simple analytical flow results. For example, in a stationary homogeneous shear flow $\mathbf{v} = (\dot{\gamma} y, 0)$ (in 2D), the following solution is obtained for the conformation tensor:

$$c_{xx} = 1,$$

$$c_{xy} = \tau \dot{\gamma},$$

$$c_{yy} = 1 + 2(\tau \dot{\gamma})^2. \quad (63)$$

Note that $c_{xx} - c_{yy} = 2(\tau \dot{\gamma})^2$ and, therefore, the model exhibits first normal stress differences.

We may also consider as a second example a stationary forcing of the fluid, producing the so-called Kolmogorov flow. We impose an external acceleration $\mathbf{g} = g_0(\sin(ky), 0)$. We assume a steady-state solution in which the density, pressure, and temperature are constant, the velocity field is modulated according to the forcing, that is, $\mathbf{v} = v_0(\sin(ky), 0)$, and $\mathbf{c} = \mathbf{c}(y)$. Then $\nabla \cdot \mathbf{v} = 0$ and the continuity equation is automatically satisfied. The convective terms also vanish: $\mathbf{v} \cdot \nabla \mathbf{v} = 0$ and $\mathbf{v} \cdot \nabla \mathbf{c} = 0$. In this way, the momentum equation leads to the following set of equations:

$$nk_B T \frac{\partial c_{xy}}{\partial y} - \eta v_0 k^2 \sin(ky) + \rho(y) g_0 \sin(ky) = 0,$$

$$n \frac{\partial c_{yy}}{\partial y} = 0. \tag{64}$$

By inserting the assumed form for the fields in the last equation in Eq. (57) leads to

$$c_{yy} = 1,$$

$$c_{xy} = \tau v_0 k \cos(ky),$$

$$c_{xx} = 1 + 2(\tau v_0 k)^2 \cos^2(ky). \tag{65}$$

By using Eq. (65) back in momentum equation (64) we obtain

$$v_0 = \frac{\rho g_0}{k^2(nk_B T \tau + \eta)}. \tag{66}$$

Note that the polymer contribution to the viscosity of the fluid is $nk_B T \tau$.

It is possible to obtain also a time-dependent solution for a sudden application of the external acceleration $\mathbf{g} = g_0(\sin(ky), 0)$ on the rest state. The solution of the form $\mathbf{v} = \tilde{v}(t)(\sin(ky), 0)$ and $\mathbf{c} = \tilde{\mathbf{c}}(t)\mathbf{c}(y)$ can be found by solving the linear system of coupled ordinary differential equations for $\tilde{v}(t)$, $\tilde{c}_{xy}(t)$, $\tilde{c}_{xx}(t)$, and $\tilde{c}_{yy}(t)$ for an initially assigned equilibrium flow field [i.e., $v(y,0)=0$, $c_{xy}(y,0)=0$, $c_{xx}(y,0)=1$, and $c_{yy}(y,0)=1$]. The result for the velocity component reads

$$\tilde{v}(t) = C_1 e^{\alpha_1 t} + C_2 e^{\alpha_2 t} + v_0, \tag{67}$$

where $C_1 = [2\tau \rho g_0 - v_0(\gamma + \sqrt{\Delta})]/(2\sqrt{\Delta})$, $C_2 = -C_1 - v_0$, and $\alpha_{1,2} = 1/(2\tau\rho)[-\gamma \pm \sqrt{\Delta}]$, with $\gamma = \tau \eta k^2 + \rho$, $\Delta = \gamma^2 - 4\rho\tau k^2(\eta + nk_B T\tau)$, and v_0 as the steady-state value given in Eq. (66). Note that, depending on the value assumed by Δ, $\alpha_{1,2}$ may be real or complex, leading to overdamped and underdamped solutions, respectively. However, due to the specific choice of $C_{1,2}$ which depends on the initial conditions, the final value assumed by $\tilde{v}(t)$ in Eq. (67) is always real.

The off-diagonal component of the conformation tensor $\tilde{c}_{xy}(t)$ can be easily obtained in terms of $\tilde{v}(t)$ and it reads

$$\tilde{c}_{xy}(t) = -C_1\left(\frac{\alpha_1 \rho + \eta k^2}{nk_B Tk}\right)e^{\alpha_1 t} - C_2\left(\frac{\alpha_2 \rho + \eta k^2}{nk_B Tk}\right)e^{\alpha_2 t}$$

$$+ \frac{\rho g_0 - \eta k^2 v_0}{nk_B Tk} \tag{68}$$

and $c_{xy}(y,t) = \tilde{c}_{xy}(t)\cos(ky)$. Concerning the diagonal parts, for the initial condition $c_{yy}(y,0)=1$, we have that $c_{yy}(y,t) = 1$ at every time.

V. SIMULATION OF THE MODEL

In this section we show that the discrete model in Eq. (49) does actually conform with the predictions of the continuum model in Eq. (57) with Eq. (62). We will compare simulation results with analytical expressions for the two benchmark tests discussed in Sec. IV, that is, uniform shear and Kolmogorov flow. We consider an isothermal equation of state for the solvent given by the expression for ideal gases, that is, $P(\rho_i) = c_s^2 \rho_i$, where $c_s = k_B T/m$ is the speed of sound for the solvent and $\rho_i = md_i$ is the solvent mass density. The only evolution equations for the isothermal fluid-particle variables in Eq. (49) are the particle-position, momentum, and conformation tensor equations.

The system is defined in a two-dimensional periodic square box of side $L=1$ and $N=400$ fluid particles are initially placed on a square lattice with zero velocities and separation distance $\Delta r = L/N_x$, where $N_x = N_y = 20$. A quintic spline interpolation kernel is used with $h = \Delta r$.

It is possible to define a number of dimensionless parameters which characterize uniquely the physics. For the problems considered here, the relevant ones are: (i) the Mach number $Ma = V/c_s$, where V is a typical flow velocity; (ii) the Reynolds number $Re = LV/\nu$, where $\nu = \eta/\rho$ is the kinematic fluid viscosity; and (iii) the Weissenberg number $We = \tau V/L$, which determines the relative importance of elastic effects over inertial ones.

A. Uniform shear flow

In order to produce a simple shear flow, the common Lees-Edwards boundary conditions are applied [29]. We choose units in which the fluid mass density $\rho = 1$, the sound speed $c_s = 1$, and kinematic viscosity $\nu = 1$. The relevant input parameters for this test case are the elastic relaxation time $\tau = 1$ and shear rates $\dot{\gamma}$ given by a range of box velocities V between 0.005 and 0.5. Accordingly to the previous definitions, Ma, Re, and We span a range of $[0.005:0.5]$ depending on the selected value of V.

In Fig. 2, the off-diagonal component of the conformation tensor c_{xy} is plotted versus the dimensionless shear rate $\tau\dot{\gamma}$ (Weissenberg number We). The global component c_{xy} was obtained by averaging the values assumed by $\mathbf{c}$ over all the particles, that is, $c_{xy} = (1/N)\Sigma_{i=1}^N c_{xy}^i$, where i is the particle index. Every point in Fig. 2 was extracted from the simulation once the system reached the steady state. The agreement with the dotted line representing the theoretical expression in Eq. (63) is excellent.

In Fig. 3 also the averaged normal stress difference coefficient has been plotted in log-log scale and compared with Eq. (63). Again, the agreement with the theory is very good, indicating the accuracy of the particle method for the discretization of the continuum Oldroyd-B model in a homogenous shear situation.
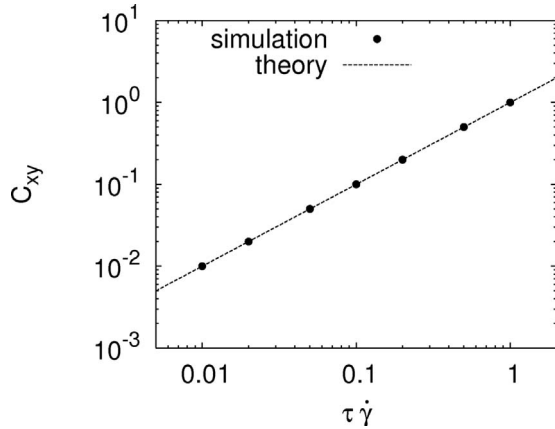
FIG. 2. Averaged steady-state off-diagonal component of the conformation tensor c_{xy} plotted versus the dimensionless applied shear rate $\dot{\gamma}\tau$ in log-log scale.

B. Kolmogorov flow

As mentioned in Sec. IV, another possible test is to impose a sinusoidal external forcing with an acceleration given by $\mathbf{g}=g_0(\sin(ky),0)$, where g_0 is the amplitude of the acceleration, and $k=2\pi/L$. The particles are accelerated by the external perturbation and eventually achieve a steady state characterized by the conformation tensor and velocity field given in Eqs. (65) and (66). For this specific case, we chose $\nu=0.02$ and $c_s=1$ and tested several values of the relaxation time $\tau=0.02,2,200$. g_0 was determined in such a way that $v_0=0.0002$ for all the simulations. Accordingly, the Reynolds number for this flow is Re=0.01, while the Weissenberg number assumes several values, i.e., We=0.000 004, 0.0004, 0.04. The resolution N_y corresponds here to 60 particles spanning the y direction.

Figure 4 shows the steady-state x component of the velocity field V_x as a function of the spatial variable y for We=0.04. Very good agreement is obtained with the theoretical solution (dotted line).

Concerning the conformation tensor **c**, comparisons of the numerical results with the theoretical ones in Eq. (65) for its
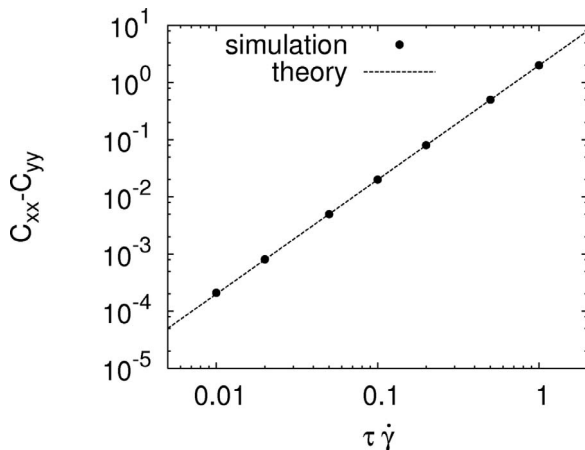
FIG. 3. Averaged steady-state normal stress difference coefficient $c_{xx}-c_{yy}$ plotted versus the dimensionless applied shear rate $\dot{\gamma}\tau$ in log-log scale.
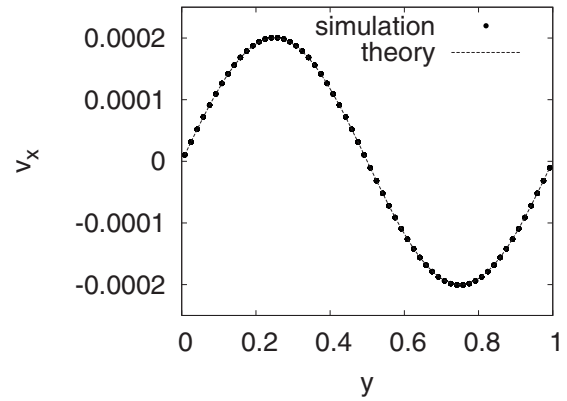

FIG. 4. Steady-state velocity field v_x plotted versus the y coordinate for We=0.04. Solid line: SDPD; dotted line: theory.

components c_{xx} and c_{xy} are shown, respectively, in Figs. 5 and 6. Again, good agreement is obtained.

In order to test the accuracy of the method for the description of an unsteady flow, comparisons of the SPH simulations have been performed with the time-dependent solutions reported in Eqs. (67) and (68). Figures 7–9 show the time-dependent behaviors of V_x and c_{xy} evaluated at specific points of the domain for different Weissenberg numbers. Note that at small We (i.e., We=4×10^{-6}), the coefficients $\alpha_{1,2}$ in the exponents of Eq. (67) are real and, consequently, the solution corresponds to an overdamped relaxation without oscillations; see Fig. 7. On the other hand, for larger values of the Weissenberg number, i.e., We=0.0004, 0.04, $\alpha_{1,2}$ have an imaginary part and therefore an underdamped solution is obtained; see Figs. 8 and 9.

VI. THERMAL FLUCTUATIONS IN THE CONFORMATION TENSOR

One of the benefits of a fluid-particle model in the GE-NERIC form, such as the one presented in this paper, is that it allows for the introduction of thermal fluctuations in a natural way. Actually, the noise to dissipation route we have proposed for the construction of the friction matrix postulates first the form of the noise terms and from these noise constructs the friction matrix, thus ensuring the symmetric
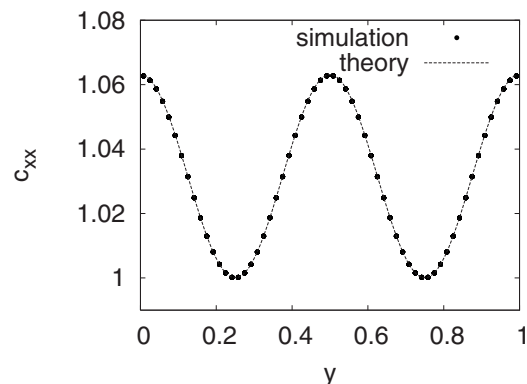

FIG. 5. Steady-state values of c_{xx} plotted versus the y coordinate for We=0.04. Solid line: SDPD; dotted line: theory.
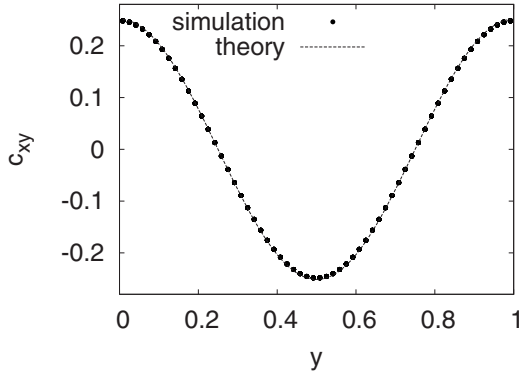
FIG. 6. Steady-state values of c_{xy} plotted versus the y coordinate for We=0.04. Solid line: SDPD; dotted line: theory.

and positive semidefinite character of the friction matrix M. While we have given explicit forms for the noise terms for $d\tilde{v}_i$ and $d\tilde{E}_i$ in terms of independent increments of the Wiener process in Eqs. (38), we still have to produce an explicit form of the random term for the conformation tensor $d\tilde{c}_i$. Note that expression (8), which motivated variance (9) required to construct the friction matrix, is not a proper stochastic term because the elongations of the polymer molecules $\mathbf{q}_a$ are not state variables. What we need is an expression of the random term $d\tilde{c}_i$ that, while still producing correct variances (9), is given entirely in terms of the state variable $\mathbf{c}_i$.

A first possibility for the formulation of the stochastic noise $d\tilde{c}_i$ is (we suppress the fluid-particle index i for clarity)

$$d\tilde{\mathbf{c}}^{\mu\nu} = \sum_\alpha \left(\frac{\lambda_\alpha}{\tau N^p} \right)^{1/2} [d\tilde{\mathbf{u}}_\alpha^\mu \mathbf{u}_\alpha^\nu + d\tilde{\mathbf{u}}_\alpha^\nu \mathbf{u}_\alpha^\mu], \qquad (69)$$

where λ_α are the eigenvalues of the tensor $\mathbf{c}$ and $\mathbf{u}_\alpha$ are the corresponding eigenvectors, that is,
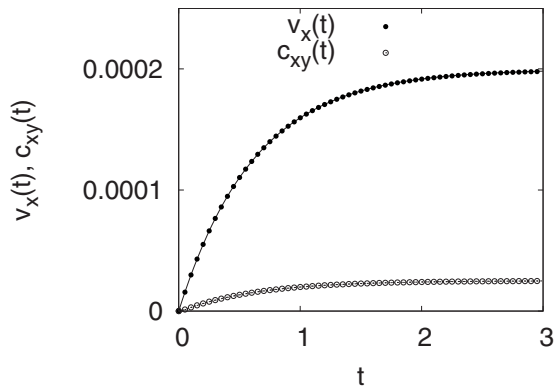

FIG. 7. Time-dependent evolutions of v_x and c_{xy} for a Weissenberg number We=4×10^{-6}. Circles (● and ○) correspond to the numerical results, whereas lines correspond to the theoretical solutions in Eqs. (67) and (68). For small values of We, an overdamped solution describes the evolutions of both velocity field and conformational stress tensor.
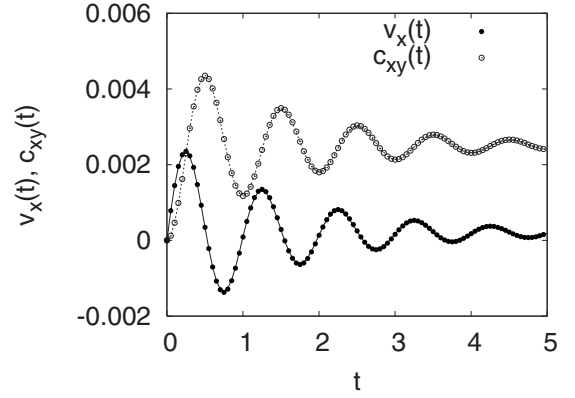

FIG. 8. Time-dependent evolutions of v_x and c_{xy} for a Weissenberg number We=4×10^{-4}. Circles (● and ○) correspond to the numerical results, whereas lines correspond to the theoretical solutions in Eqs. (67) and (68).

$$\mathbf{c}^{\mu\nu} \mathbf{u}_\alpha^\nu = \lambda_\alpha \mathbf{u}_\alpha^\mu, \qquad (70)$$

while $d\tilde{\mathbf{u}}_\alpha^\mu$ is a set of independent increments of the Wiener process with the following variances:

$$d\tilde{\mathbf{u}}_\alpha^\mu d\tilde{\mathbf{u}}_\beta^\nu = \delta_{\alpha\beta} \delta^{\mu\nu} dt. \qquad (71)$$

By using the eigenrepresentation of the conformation tensor

$$\mathbf{c}^{\mu\nu} = \sum_\alpha \lambda_\alpha \mathbf{u}_\alpha^\mu \mathbf{u}_\alpha^\nu, \qquad (72)$$

it is straightforward to show that the stochastic forces defined in Eq. (69) do actually have the correct variances as given in Eq. (9). Note that this formulation of the stochastic force in the conformation tensor requires the use of nine independent increments of the Wiener process for each fluid particle ($d\tilde{\mathbf{u}}_\alpha^\mu$ for $\alpha = 1, 2, 3$ and $\mu = 1, 2, 3$).

A second possible formulation for the noise is the following. Postulate (for each fluid particle) that
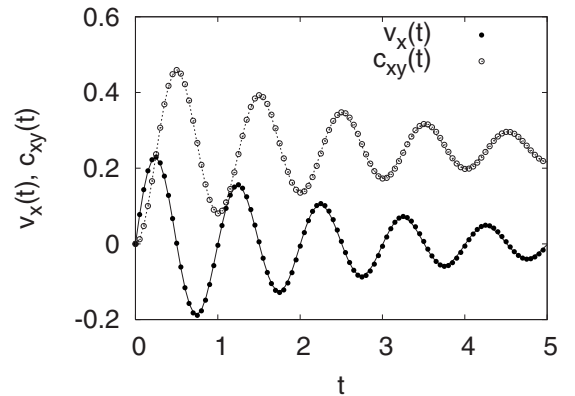

FIG. 9. Time-dependent evolutions of v_x and c_{xy} for a Weissenberg number We=4×10^{-2}. Circles (● and ○) correspond to the numerical results, whereas lines correspond to the theoretical solutions in Eqs. (67) and (68).

$$d\widetilde{\mathfrak{c}}^{\mu\nu} = \sum_\alpha \left(\frac{4\lambda_\alpha}{\tau N^p}\right)^{1/2} d\widetilde{\lambda}_\alpha \mathbf{u}_\alpha^\mu \mathbf{u}_\alpha^\nu, \tag{73}$$

where $d\widetilde{\lambda}_\alpha$ is an independent increment of the Wiener process that has the following variance:

$$d\widetilde{\lambda}_\alpha d\widetilde{\lambda}_\beta = \delta_{\alpha\beta} dt. \tag{74}$$

In this case the variance is given by

$$d\widetilde{\mathfrak{c}}^{\mu\nu} d\widetilde{\mathfrak{c}}^{\mu'\nu'} = \sum_\alpha \frac{4\lambda_\alpha}{\tau N^p} \mathbf{u}_\alpha^\mu \mathbf{u}_\alpha^\nu \mathbf{u}_\alpha^{\mu'} \mathbf{u}_\alpha^{\nu'} dt. \tag{75}$$

The friction matrix element corresponding to the conformation tensor is, therefore [see Eq. (46)],

$$M^{\mu\nu\mu'\nu'} = \frac{d\widetilde{\mathfrak{c}}^{\mu\nu} d\widetilde{\mathfrak{c}}^{\mu'\nu'}}{2k_B dt} = \sum_\alpha \frac{2\lambda_\alpha}{\tau N^p k_B} \mathbf{u}_\alpha^\mu \mathbf{u}_\alpha^\nu \mathbf{u}_\alpha^{\mu'} \mathbf{u}_\alpha^{\nu'}. \tag{76}$$

This element of the friction matrix is given, in fact, by

$$M^{\mu\nu\mu'\nu'} = \frac{1}{2\tau N^p k_B}[\mathbf{c}^{\mu\mu'}\delta^{\nu\nu'} + \mathbf{c}^{\mu'\nu}\delta^{\mu\nu'}$$
$$+ \mathbf{c}^{\mu\nu'}\delta^{\nu\mu'} + \mathbf{c}^{\nu\nu'}\delta^{\mu\mu'}]. \tag{77}$$

The proof is immediate when we contract Eqs. (76) and (77) with the eigenvectors $\mathbf{u}_a^\mu$, $\mathbf{u}_b^\nu$, $\mathbf{u}_{a'}^{\mu'}$, and $\mathbf{u}_{b'}^{\nu'}$ and observe that identical results are obtained in each case. Because the components of the fourth-order tensors $M^{\mu\nu\mu'\nu'}$ coincide in a particular basis, they are identical.

The fact that two different noise terms [in Eqs. (69) and (73)] lead to the same variance should not come as a surprise [30]. There are many different nonsquare matrices that when multiplied lead to the same square matrix. The second formulation in Eq. (73) is preferred computationally because it requires the generation of only three random numbers instead of nine for each fluid particle, and it is the one selected in the following.

A. Eigendynamics of the conformation tensor

In this subsection, we present the dynamics of the conformation tensor in terms of the dynamics of its eigenvalues and eigenvectors. Note that the construction of the random term $d\widetilde{\mathbf{c}}_i$ in the conformation tensor in Eq. (73) requires the knowledge of the eigenvectors, and we have to diagonalize the conformation tensor. This suggests that it may be profitable to formulate the dynamics directly in terms of the eigenvalues and eigenvectors of the conformation tensor. In fact, this strategy was followed in Refs. [31,32] in order to improve problems that may arise due to the loss of the positive character of the conformation tensor, due to purely numerical errors.

By taking the time derivative of eigenrepresentation (72) of the conformation tensor and left and right multiplying this time derivative with the eigenvectors, we obtain

$$\mathbf{u}_\alpha \cdot \dot{\mathbf{c}} \cdot \mathbf{u}_\beta = \delta_{\alpha\beta}\dot{\lambda}_\alpha + (\lambda_\alpha - \lambda_\beta)\dot{\mathbf{u}}_\alpha \cdot \mathbf{u}_\beta, \tag{78}$$

where we have used the orthogonality of the eigenvectors in the form $\frac{d}{dt}(\mathbf{u}_\alpha \cdot \mathbf{u}_\beta) = 0$.

We assume that the conformation tensor evolves according to the last equation in Eq. (49) (no particle index shown for simplicity)

$$\dot{\mathbf{c}} = \mathbf{c}\cdot\boldsymbol{\kappa} + \boldsymbol{\kappa}^T\cdot\mathbf{c} + \frac{2}{\tau N^p k_B T}\mathbf{c}\cdot\boldsymbol{\sigma}. \tag{79}$$

If we left and right multiply Eq. (79) with the eigenvectors, we obtain

$$\mathbf{u}_\alpha \cdot \dot{\mathbf{c}} \cdot \mathbf{u}_\beta = \lambda_\alpha \kappa_{\alpha\beta} + \lambda_\beta \kappa_{\beta\alpha} + \frac{2}{\tau N^p k_B T}\sigma_\alpha \lambda_\alpha \delta_{\alpha\beta}, \tag{80}$$

where we have introduced the matrix element of the velocity gradient tensor in the eigenbasis of the conformation tensor,

$$\kappa_{\alpha\beta} \equiv \mathbf{u}_\alpha \cdot \boldsymbol{\kappa} \cdot \mathbf{u}_\beta. \tag{81}$$

We have also introduced $\sigma_\alpha = \mathbf{u}_\alpha \cdot \boldsymbol{\sigma} \cdot \mathbf{u}_\alpha$, which are the eigenvalues of $\boldsymbol{\sigma}$. As shown in Appendix B, $\boldsymbol{\sigma}$ and $\mathbf{c}$ diagonalize in the same basis.

By equating Eqs. (78) and (80) we obtain the following evolution equations for the eigenvalues and eigenvectors:

$$\dot{\lambda}_\alpha = 2\lambda_\alpha \kappa_{\alpha\alpha} + \frac{2}{\tau N^p k_B T}\lambda_\alpha \sigma_\alpha,$$

$$\dot{\mathbf{u}}_\alpha = \sum_\beta H_{\alpha\beta}\mathbf{u}_\beta, \tag{82}$$

where the antisymmetric matrix $H_{\alpha\beta}$ is given by

$$H_{\alpha\beta} = \begin{cases} \dfrac{1}{\lambda_\alpha - \lambda_\beta}[\lambda_\alpha \kappa_{\alpha\beta} + \lambda_\beta \kappa_{\beta\alpha}] & \text{if } \lambda_\alpha \neq \lambda_\beta \\ \kappa_{\alpha\beta} & \text{if } \lambda_\alpha = \lambda_\beta. \end{cases} \tag{83}$$

For Hookean dumbbells the equation for the eigenvalues becomes

$$\dot{\lambda}_\alpha = 2\lambda_\alpha \kappa_{\alpha\alpha} + \frac{1}{\tau}[1 - \lambda_\alpha], \tag{84}$$

while the equation for the eigenvector remains the same.

Equations (79) and (82) are mathematically equivalent. Note that, apparently, from the 6 equations and unknowns involved in the symmetric tensor Eq. (79) in 3 dimensions (3D), we have now 12 equations and 12 unknowns in Eqs. (82) (3 eigenvalues and the 3 components of the three eigenvectors). However, we should note that the eigenvectors are orthogonal, which means that, in addition, $\mathbf{u}_\alpha \cdot \mathbf{u}_\beta = \delta_{\alpha\beta}$. These are 6 constraints that reduce the number of independent unknowns to 6, as it should. In the remaining of the paper, we solve the eigendynamics given by Eqs. (82)–(84) instead of Eq. (79) and observe a sufficient degree of orthonormality for the eigenvectors. We suggest a possible improvement in Appendix C.

B. Stochastic eigendynamics

Given a deterministic dynamic equation of the GENERIC form, we know how to construct a corresponding stochastic differential equations (SDE) that fulfils the fluctuation-

dissipation theorem, as shown in Appendix A. In order to construct the SDE that corresponds to the deterministic equations Eq. (49), we first consider the stochastic equations that would be obtained if the backcoupling between the conformation tensor and the fluid variables were neglected. In that case, the only equations to be considered would be Eq. (79) and (82), where $\kappa_{\alpha\beta}$ can be understood as an "external velocity gradient." By realizing that for the discussion of the introduction of thermal fluctuations only the irreversible part is required (through the fluctuation-dissipation theorem, there is noise only when there is dissipation), we consider the irreversible part of Eq. (82), which can be written as

$$\dot{\lambda}_\alpha|_{\mathrm{irr}} = \frac{2\lambda_\alpha}{\tau N^p k_B}\frac{\partial S}{\partial \lambda_\alpha}. \tag{85}$$

Note that this deterministic equation is of the form $\dot{x} = M(x)\frac{\partial S}{\partial x}$, with $M(x) \to \lambda_\alpha/\tau N^p k_B$. From Appendix A, we observe that the corresponding Itô stochastic equation is

$$dx|_{\mathrm{irr}} = M(x)\frac{\partial S}{\partial x}dt + k_B\frac{\partial M}{\partial x}dt + d\tilde{x}, \tag{86}$$

with $d\tilde{x}d\tilde{x} = 2k_B M(x)dt$. For the case of the dynamics of the eigenvalues, general SDE (86) corresponding to deterministic equation (85) is

$$d\lambda_\alpha|_{\mathrm{irr}} = \frac{2\lambda_\alpha}{\tau N^p k_B}\frac{\partial S}{\partial \lambda_\alpha}dt + \frac{2}{\tau N^p}dt + \left(\frac{4\lambda_\alpha}{\tau N^p}\right)^{1/2}d\tilde{\lambda}_\alpha, \tag{87}$$

where the independent increments of the Wiener process, $d\tilde{\lambda}_\alpha$, satisfy Eq. (74).

By adding the purely reversible part of the dynamics to the above irreversible dynamics, we obtain

$$d\lambda_\alpha = 2\lambda_\alpha\kappa_{\alpha\alpha}dt + \frac{2}{\tau N^p k_B}\lambda_\alpha\frac{\partial S}{\partial \lambda_\alpha}dt + \frac{2}{\tau N^p}dt + \left(\frac{4\lambda_\alpha}{\tau N^p}\right)^{1/2}d\tilde{\lambda}_\alpha,$$

$$d\mathbf{u}_\alpha = \sum_\beta H_{\alpha\beta}\mathbf{u}_\beta dt. \tag{88}$$

By using Eq. (72), it is straightforward to show that this Eq. (88) leads to the following SDE for the conformation tensor:

$$d\mathbf{c} = [\mathbf{c}\cdot\boldsymbol{\kappa} + \boldsymbol{\kappa}^T\cdot\mathbf{c}]dt + \frac{2}{\tau N^p k_B T}\mathbf{c}\cdot\boldsymbol{\sigma}dt + \frac{2}{\tau N^p}\mathbf{1}dt + d\tilde{\mathbf{c}}, \tag{89}$$

where $d\tilde{\mathbf{c}}$ is given by Eq. (73). This is the SDE equation that corresponds to the deterministic last equation in Eq. (49).

C. Complete stochastic equations

The final SDEs are obtained by adding the noise terms in Eqs. (38) and (73) to deterministic equations (49). Note that the usual Itô term of the form $k_B\frac{\partial M}{\partial x}$ that should be included in the GENERIC SDE (see Appendix A) produces negligible contributions on the order of $k_B/C_i = 1/N_s$ in the momentum and energy equations. C_i is the heat capacity of the fluid particle which, in turn, is on the order of $N_s k_B$, where N_s is the (very large) number of solvent atoms within the fluid

particle. However, the Itô term $k_B\frac{\partial M}{\partial x}$ does actually have a non-negligible contribution in the equation for the conformation tensor. This term can be computed from Eq. (77) with the simple result

$$k_B\frac{\partial M}{\partial x} \to \frac{2}{\tau N^p}\mathbf{1}, \tag{90}$$

which is clearly displayed in Eq. (89).

In summary, the stochastic model for viscoelastic fluid particles is given by the following set of SDEs:

$$d\mathbf{r}_i = \mathbf{v}_i dt,$$

$$md\mathbf{v}_i = \sum_j\left[\frac{\mathbf{\Pi}_i}{d_i^2} + \frac{\mathbf{\Pi}_j}{d_j^2}\right]\cdot\omega_{ij}dt - \frac{5\eta}{3}\sum_j\frac{F_{ij}}{d_i d_j}[\mathbf{v}_{ij}$$
$$+ (\mathbf{e}_{ij}\cdot\mathbf{v}_{ij})\mathbf{e}_{ij}]dt + md\tilde{\mathbf{v}}_i,$$

$$dE_i = -\frac{\mathbf{\Pi}_i}{d_i^2}:\sum_j\omega_{ij}\mathbf{v}_{ij}dt + \frac{1}{2}\frac{5\eta}{3}\sum_j\frac{F_{ij}}{d_i d_j}[\mathbf{v}_{ij}^2 + (\mathbf{v}_{ij}\cdot\mathbf{e}_{ij})^2]dt$$
$$- 2\kappa\sum_j\frac{F_{ij}}{d_i d_j}T_{ij}dt + d\tilde{E}_i,$$

$$d\lambda_\alpha = 2\lambda_\alpha\kappa_{\alpha\alpha}dt + \frac{2}{\tau N^p k_B}\lambda_\alpha\frac{\partial S}{\partial \lambda_\alpha}dt + \frac{2}{\tau N^p}dt + \left(\frac{4\lambda_\alpha}{\tau N^p}\right)^{1/2}d\tilde{\lambda}_\alpha,$$

$$d\mathbf{u}_\alpha = \sum_\beta H_{\alpha\beta}\mathbf{u}_\beta dt, \tag{91}$$

where $\mathbf{\Pi}$ is given by Eq. (35) and **c** is given by Eq. (72).

D. Equilibrium fluctuations

Associated to the above SDE there exists a mathematically equivalent Fokker-Planck equation (FPE), which in general has the structure shown in Eq. (A7) of Appendix A. The equilibrium solution of this FPE gives the Einstein equilibrium probability given in Eq. (A8). By integrating over all degrees of freedom, except one of the eigenvalues of the conformation tensor of a single fluid particle, we obtain the following marginal equilibrium distribution function:

$$P(\lambda) = \frac{1}{\mathcal{N}}\exp\left\{\frac{S_p(\lambda)}{k_B}\right\}, \tag{92}$$

where S_p is the entropy defined in Eq. (51) and $\mathcal{N}$ is a normalizing constant. It is apparent that the entropy in Eq. (51) should depend on the configuration tensor only through its eigenvalues. In fact, for the Hookean dumbbell model, Eq. (51) implies

$$S_p(\mathbf{c}) = k_B\frac{N^p}{2}\left(D - \sum_\alpha\lambda_\alpha + \sum_\alpha\ln\lambda_\alpha\right). \tag{93}$$

Therefore, the probability distribution in Eq. (92) for the eigenvalues is
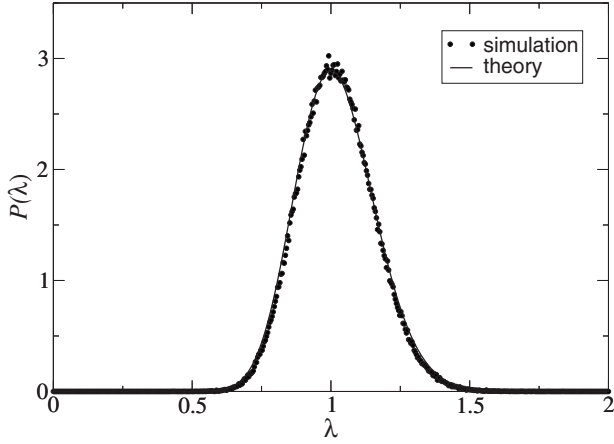
FIG. 10. Equilibrium histogram of eigenvalues of the conformation tensor compared with the theoretical result in Eq. (94).

$$P(\lambda_\alpha) = \frac{1}{\mathcal{N}} \lambda_\alpha^{N^p/2} \exp\left\{-\frac{N^p}{2}\lambda_\alpha\right\}. \qquad (94)$$

It is apparent that the width of this distribution function narrows with increasing number N^p of polymers within a fluid particle. In general, for a fixed *concentration* of polymers, the number N^p of polymer molecules will increase with the size of the fluid particles. As a consequence, the effect of thermal fluctuations in the configuration tensor (and, therefore, in the rest of the dynamics) will be reduced as the fluid particles are larger. This effect of switching off thermal fluctuations by using larger fluid particles has been discussed recently in the SDPD model for Newtonian fluids [20].

We have run a simulation of Eq. (91) in an equilibrium state (no forcing in a periodic box). We have binned the values of the eigenvalues realized during the simulation and computed the histogram in Fig. 10. The agreement with Eq. (94) is excellent. We also show in Fig. 11 the stochastic time evolutions of the component $\mathbf{c}^{xy}$ in a startup from rest of a Kolmogorov flow, for different numbers N^p of polymer molecules within the fluid particle (fluctuations on the momentum and energy are switched off for simplicity). We have explicitly checked that the error in the degree of orthonormality for the eigenvectors remains confined below a certain small level, i.e., 1% over all the run. We observe that as the number of polymer molecules is increased, the fluctuations in the configuration tensor decrease accordingly. This is what has to happen in order to respect the idea that as *the size* of the fluid particles increases, for constant concentration of polymers, the effect of thermal fluctuations must decrease, in accordance with a basic statistical-mechanics principle. However, in microscopic conditions as those represented by microrheology, such fluctuations may play a crucial role in the dynamics and they are consistently taken into account by the model.

VII. CONCLUSION

We have formulated a fluid-particle model for the simulation of dilute polymer solutions in which for each fluid
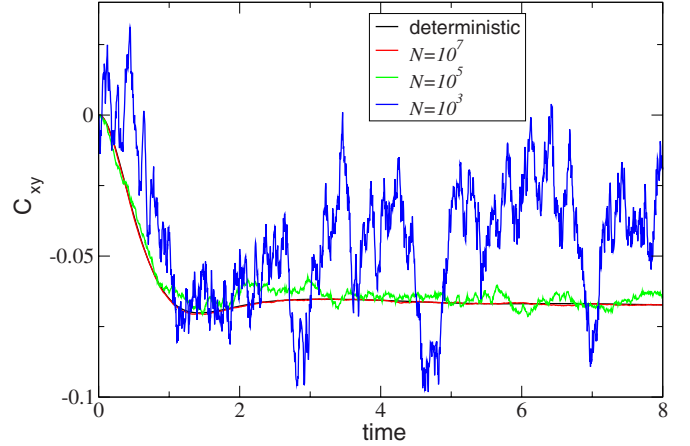

FIG. 11. (Color online) Time evolution of the off-diagonal component of the configuration tensor in a startup from rest of a Kolmogorov flow. For a given size of fluid particles, the evolution of the configuration tensor depends strongly on the number N^p of polymer molecules that are within the fluid particle. Few polymer molecules imply large fluctuations.

particle a conformation tensor variable is introduced. Thanks to the clear physical definition of the conformation tensor in "microscopic" terms in Eq. (1), the use of the conformation tensor, as opposed to other formulations of viscoelastic flow based on constitutive equations for the stress tensor, allows for a simple introduction of thermal fluctuations. The formulation of the model following the GENERIC framework ensures that the model is thermodynamically consistent. The model is based on a previous fluid-particle model valid for Newtonian fluids, to which it reduces in the limit of zero polymer concentration. The resulting model can be understood as a smoothed particle hydrodynamic discretization of the continuum equations for a viscoelastic fluid. Note, however, that there are many different ways of discretizing the equations by following the SPH philosophy. The GENERIC framework guides toward a proper discretization that respects the first and second laws of thermodynamics exactly. We have conducted simulations in simple fluid flows to check that the predictions of the continuum model are fulfilled in the simulations. Although we have considered in the simulations only isothermal situations, the model may deal with temperature gradients, viscous heating, and related thermal phenomena.

One of the main contributions of the present paper is the introduction of thermal fluctuations in the viscoelastic fluid-particle model. In the Newtonian fluid-particle model, momentum and energy fluctuations are introduced through the fluctuation-dissipation theorem, and they can be understood as the stochastic contributions introduced by Landau and Lifshitz [33] in fluctuating hydrodynamics. In a viscoelastic fluid, additional fluctuations in the conformation tensor may play an important role. The coupling of the present fluid viscoelastic fluid with colloidal particles in suspension is under consideration and will be the subject of a future publication.

APPENDIX A: REVIEW OF GENERIC

In this appendix, and for the sake of completeness, we review the GENERIC framework [18].

The state of a system at a given level of description is described by a set of variables that form a vector x. The energy and the entropy are two of the basic building blocks of the GENERIC formalism and they should be expressed as functions of the state variables at the given level of description. The GENERIC dynamic equations are given by

$$\frac{dx}{dt} = L \cdot \frac{\partial E}{\partial x} + M \cdot \frac{\partial S}{\partial x}. \tag{A1}$$

The first term in the right-hand side is named the *reversible* part of the dynamics and the second term is named the *irreversible* part. The predictive power of GENERIC relies on the fact that very strong requirements exist on the matrices L and M, leaving relatively small room for the physical input about the system. First, L is antisymmetric, whereas M is symmetric and positive semidefinite. Most importantly, the following *degeneracy* conditions should hold:

$$L \cdot \frac{\partial S}{\partial x} = 0, \quad M \cdot \frac{\partial E}{\partial x} = 0. \tag{A2}$$

These properties ensure that the energy is a dynamical invariant, $\dot{E}=0$, and that the entropy is a nondecreasing function of time, $\dot{S} \geq 0$, as can be proved by a simple application of the chain rule and equations of motion (A1). In the case that other dynamical invariants $I(x)$ exist in the system (such as, for example, linear or angular momentum), then further conditions must be satisfied by L and M. In particular,

$$\frac{\partial I}{\partial x} \cdot L \cdot \frac{\partial E}{\partial x} = 0, \quad \frac{\partial I}{\partial x} \cdot M \cdot \frac{\partial S}{\partial x} = 0, \tag{A3}$$

which ensure that $\dot{\mu}=0$.

Deterministic equations (A1) are, actually, an approximation in which thermal fluctuations are neglected. If thermal fluctuations are not neglected, the dynamics is described by the following stochastic differential equations [34]:

$$dx = \left[L \cdot \frac{\partial E}{\partial x} + M \cdot \frac{\partial S}{\partial x} + k_B \frac{\partial}{\partial x} \cdot M \right] dt + d\tilde{x}, \tag{A4}$$

to be compared with the deterministic equations (A1). The deterministic additional term involving the Boltzmann con-

stant k_B appears due to the stochastic interpretation of the equation which is taken to be the Itô interpretation. The stochastic term $d\tilde{x}$ in Eq. (A4) is a linear combination of independent increments of the Wiener process. It satisfies the mnemotechnical Itô rule

$$d\tilde{x}d\tilde{x}^T = 2k_B M dt, \tag{A5}$$

which means that $d\tilde{x}$ is an infinitesimal of order 1/2 [30]. Equation (A5) is a compact and formal statement of the fluctuation-dissipation theorem.

In order to guarantee that the total energy and dynamical invariants do not change in time, a strong requirement on the form of $d\tilde{x}$ holds,

$$\frac{\partial E}{\partial x} \cdot d\tilde{x} = 0, \quad \frac{\partial I}{\partial x} \cdot d\tilde{x} = 0, \tag{A6}$$

implying the last equations in Eqs. (A2) and (A3). The geometrical meaning of Eq. (A6) is clear. The random kicks produced by $d\tilde{x}$ on the state x are orthogonal to the gradients of E and I. These gradients are perpendicular vectors (strictly speaking they are one forms) to the hypersurface $E(x)=E_0, I(x)=I_0$. Therefore, the kicks let the state x always within the hypersurface of dynamical invariants.

The FPE that is mathematically equivalent to the GENERIC SDE is given by

$$\frac{\partial P(x,t)}{\partial t} = -\frac{\partial}{\partial x} \cdot \left[L(x) \cdot \frac{\partial E}{\partial x} P(x,t) + M(x) \cdot \frac{\partial S}{\partial x} P(x,t) \right]$$
$$+ k_B \frac{\partial}{\partial x} \cdot M(x) \cdot \frac{\partial}{\partial x} P(x,t). \tag{A7}$$

The equilibrium distribution function which is the solution of the Fokker-Planck equation (provided that the boundary conditions permit this solution) is given by the Einstein formula for fluctuations, suitably modified for the presence of dynamical invariants [35],

$$P(x)^{\text{eq}} = \frac{1}{\mathcal{N}} \delta[E(x) - E_0] \delta[I(x) - I_0] \exp\left\{ \frac{S(x)}{k_B} \right\}, \tag{A8}$$

where $\mathcal{N}$ is a normalization constant. The proof that Eq. (A8) is actually the equilibrium solution of Eq. (A7) makes use of the degeneracy conditions (in the form of Eq. (6.76) of Ref. [18]), and the antisymmetry of L.

APPENDIX B: PROPERTIES OF $\boldsymbol{\sigma}$

In this appendix we show several results concerning the intensive parameter $\boldsymbol{\sigma}$ defined as proportional to the derivative of the entropy with respect to the conformation tensor in Eq. (18).

First, consider the following remarkable identity:

$$\frac{\partial \lambda_\alpha}{\partial \mathbf{c}^{\mu\nu}} = \mathbf{u}_\alpha^\mu \mathbf{u}_\alpha^\nu, \tag{B1}$$

which relates the derivatives of the eigenvalue with respect to the components of the conformation tensor with the eigenvectors. This identity (B1) is easily demonstrated by taking

the derivative of eigenequation (70) with respect to each component $c^{\mu\nu}$ of the conformation tensor.

Next, consider a function such as the entropy that depends on the conformation tensor only through its eigenvalues. (Note that the invariants $\text{Tr } c = \Sigma_\alpha \lambda_\alpha$ and $\det c = \Pi_\alpha \lambda_\alpha$ are simple functions of the eigenvalues.) In this case, the derivative of the entropy with respect to the conformation tensor takes the form

$$\frac{\partial S}{\partial c^{\mu\nu}} = \sum_\alpha \frac{\partial S}{\partial \lambda_\alpha} u_\alpha^\mu u_\alpha^\nu, \tag{B2}$$

where we have used the chain rule and Eq. (B2). Equation (B2) implies that u_α is an eigenvector of the matrix $\frac{\sigma}{T} = \frac{\partial S}{\partial c}$ with eigenvalue $\frac{\partial S}{\partial \lambda_\alpha}$. Therefore, σ diagonalizes on the same basis as c and the eigenvalues σ_α of σ are given by

$$\frac{\sigma_\alpha}{T} = \frac{\partial S}{\partial \lambda_\alpha}. \tag{B3}$$

Equation (B2) also implies that

$$\sigma \cdot c = c \cdot \sigma. \tag{B4}$$

This is easily proved from

$$\frac{\partial S}{\partial c^{\mu\nu}} c^{\nu\nu'} = \sum_\alpha \frac{\partial S}{\partial \lambda_\alpha} \lambda_\alpha u_\alpha^\mu u_\alpha^{\nu'},$$

$$c^{\mu\nu} \frac{\partial S}{\partial c^{\nu\nu'}} = \sum_\alpha \frac{\partial S}{\partial \lambda_\alpha} \lambda_\alpha u_\alpha^\mu u_\alpha^{\nu'}, \tag{B5}$$

which are identical.

APPENDIX C: CAYLEY PARAMETRIZATION

Instead of solving nine of Eq. (82) that give the dynamics of the eigenvectors, we may reduce by a factor of 3 the number of equation to be solved, through the Cayley parametrization of orthogonal matrices. Any orthogonal matrix U which does not have -1 as eigenvalue can be expressed as $U = (1+A)(1-A)^{-1}$ for some suitable antisymmetric matrix A (which in 3D has only three independent elements). The matrix A is expressed in terms of U as $A = (U+1)^{-1}(U-1)$. If the orthogonal matrix U has as columns the eigenvectors of the conformation tensor c, then dynamic equation (82) for the eigenvectors translates into the following equation for the orthogonal matrix U:

$$\frac{dU}{dt} = HU, \tag{C1}$$

where the component of H are given in Eq. (83). Through the Cayley parametrization, the dynamic equation for the antisymmetric matrix A is

$$\frac{dA}{dt} = (1-A)H(1+A)(1-A)^{-1}(1+A), \tag{C2}$$

which despite its appearance is a simple set of three nonlinear differential equations, one for each component of A. Reconstructing the eigenvectors from the Cayley transformation ensures its orthogonality and allows to construct a well-defined (symmetric and positive definite) conformation tensor through Eq. (72). The formulation above using the antisymmetric matrix A differs from the formulation in Ref. [32] and it may be computationally more efficient because (in 3D) it solves three differential equations instead of the nine differential equations required for the eigenvalues.

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