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Thermodynamically consistent fluid particle model for viscoelastic flows

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A recently proposed viscoelastic dissipative particle dynamics model is put into a thermodynamically consistent form that allows for nonisothermal situations. This model consists of fluid particles that have an additional elastic vector characterizing the state of elongation of the molecules within the fluid particle. Very simple physical mechanisms are proposed for the dynamics of the elastic vector that, with the help of the GENERIC formalism, allows us to derive the full set of dynamic equations for the model. The model is further generalized to include polymer diffusion. The connection of the present model with the CONNFFESSIT approach and the Brownian configuration field approach is discussed.

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I. INTRODUCTION

Dissipative particle dynamics (DPD), as originally invented by Hoogerbrugge and Koelman, is a stochastic particle model for the simulation of Newtonian fluids at mesoscopic scales [1,2]. In DPD, a Newtonian fluid is represented by a collection of points with prescribed stochastic interactions that conserve momentum and produce hydrodynamic behavior. DPD bears a strong resemblance with the smoothed particle hydrodynamics (SPH) method for solving the Navier-Stokes equations [3], except that DPD includes thermal fluctuations and it is thus applicable to mesoscopic scales where diffusive processes are important. The connection between SPH and DPD has been made clear in a recent paper [4] where it is shown that by including in the original DPD model two extra state variables, the internal energy and the volume of the particles, one can construct a SPH model which is thermodynamically consistent, has a well-defined physical scale, allows for input transport properties (without the need of kinetic theory to find out the transport coefficients), and allows for arbitrary thermodynamic behavior, thus solving the conceptual shortcomings of the original DPD model.

The primary objective of DPD research has been to use this stochastic fluid solver for the study of nonNewtonian fluids displaying interesting and complex rheological behavior, for example, colloidal suspensions and polymeric solutions. The simple Newtonian fluid of DPD has been made ''complex'' by introducing additional interactions between the dissipative particles. For example, the complex rheological behavior of colloidal suspensions has been simulated by freezing spheres (i.e., introducing a rigid interaction between particles) of DPD particles that behave like solid suspended objects [5–7]. Polymer solutions have been simulated by connecting some of the dissipative particles with springs [8,9]. Binary mixtures have been also modeled by considering two types of particles that interact with different interaction parameters [10–12]. In this respect, DPD turns out to be a versatile method for the simulation of complex fluids. A couple of recent reviews on applications of DPD to the simulation of complex fluids can be found in Refs. [13,14].

A very interesting generalization of the dissipative particle dynamics model has been recently introduced by ten Bosch in order to study polymer flows [15]. The idea is to capture the complex behavior of polymeric fluids by introducing an additional variable **Q** associated with each particle [15]. The vector **Q** collects the elastic information about the fluid at scales ''within'' the dissipative particles. The introduction of the additional internal variable **Q** is a radically different way of introducing complexity in the DPD model. It actually changes the scale of the technique with respect to those DPD simulations in which elasticity is modeled through springs connecting dissipative particles. A particle in the ten Bosch model would represent large portions of particles in previous DPD simulations of polymers. It represents, therefore, a serious computational advantage. Of course, the price to pay for this advantage is the required profound knowledge of the physics of the mesoscopic viscoelasticity in order to formulate the suitable equations of motion for **Q**. Because the ten Bosch model is a more coarse grained model than the usual DPD models for polymers, molecular details are hidden in the phenomenological parameters of the model. However, from the point of view of applications and computer time saving, this might be regarded in some cases as a benefit.

The ten Bosch model suffers from the same conceptual shortcomings of the original DPD model: it is not thermodynamically consistent, it cannot possibly specify arbitrary thermodynamic behavior, does not a have well-defined physical scale, and one needs to use kinetic theory to relate the transport coefficients of the fluid with the parameters of the model. The aim of this paper is to formulate in a thermodynamically consistent way a generalization of the ten Bosch model to nonisothermal situations. To this end we first for-

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mulate a model in which each fluid particle contains a fixed number of dumbbells. This model can be understood as a Lagrangian SPH version of the CONNFFESSIT approach [16,17]. Inspired by this model, in the second step we consider only one elongation variable per fluid particle, as in the ten Bosch model. This second model is much faster to simulate because of the large reduction of dumbbell variables in the system. In addition, the second model incorporates the number of dumbbells in the cell as an additional variable and allows one to study polymer diffusivity problems. The model is essentially a version of the smoothed particle hydrodynamic model such as the one presented in Ref. [4], with additional elastic variables. As a final remark, we note that the hydrodynamic equations for a viscoelastic fluid described by a suitable *constitutive equation* have been discretized by using smoothed particle hydrodynamics very recently [18].

II. FLUID PARTICLES OF POLYMER SOLUTIONS

A very convenient way to construct new discrete models for fluid dynamics which are consistent with thermodynamics is by using the GENERIC framework [19] which we summarize in Appendix A. This framework, introduced by Öttinger and Grmela, captures in a very synthetic way all the required constraints that a model should satisfy in order to comply with the first and second laws. It also describes how to introduce thermal fluctuations in a consistent way through the fluctuation-dissipation theorem. No additional physics is introduced in GENERIC further than the first and second Laws and the fluctuation-dissipation theorem. However, it facilitates enormously the task of constructing new models which are compatible with these physical laws. This approach has been successfully used in Refs. [4,20,21], where mesoscale fluid particle models for Newtonian fluids have been constructed.

In this paper, 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. Each thermodynamic subsystem is composed by N_i^s molecules of the solvent plus the N_i^d polymer molecules. We will assume initially that the numbers N_i^s and N_i^d are fixed, and, therefore, the mass of each fluid particle is constant. In Sec. VI we will relax the condition of constant number of dumbbells N_i^d per fluid particle. The simplest model for a polymer molecule is a dumbbell, where two beads are connected with a spring, and for the sake of presentation we will focus on this simple model. Every dumbbell in the fluid particle is characterized by its end-to-end vector or elongation $\mathbf{Q}_i^\alpha$, where $\alpha = 1, \ldots, N_i^d$ runs over the different dumbbells of the fluid particle i. We show schematically a fluid particle in Fig. 1.

Every fluid particle has two additional thermodynamic variables, which are the internal energy E_i and the volume $\mathcal{V}_i$. 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). The volume of a fluid particle is not an independent variable but rather depends on the positions of the given particle and its neighbors. In some recent works [22,21] the partitioning of the space occupied by the fluid has been done through the Voronoi tessellation. In this case, each particle has associated a cell around it with a given volume that depends on the location of the neighboring particles. In the DPD or SPH philosophy [4], one rather provides a volume $\mathcal{V}_i$ to each particle through the inverse of a density d_i, which is defined by

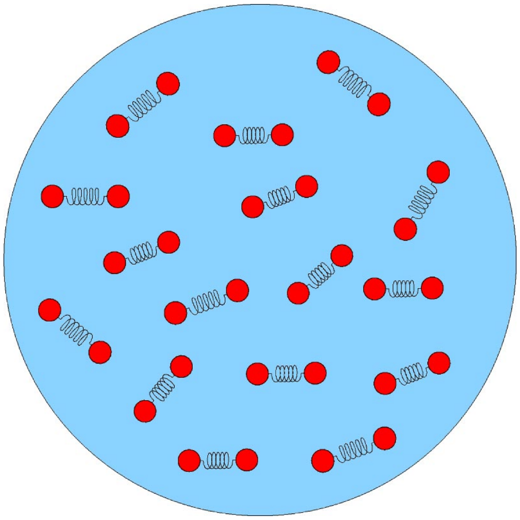

FIG. 1. A schematic representation of a fluid particle containing N_i^d dumbbells. The set of the elongations of the dumbbell within the fluid particle i is denoted by $\mathbf{Q}_i$.

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

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

$$\int d\mathbf{r} W(r) = 1. \tag{2}$$

Note that if particle i has many neighboring particles within r_c, then the density d_i in Eq. (1) will be large. Consistently, we associate a smaller volume $\mathcal{V}_i$ with it.

Finally, every fluid particle, that is, every thermodynamic subsystem, has associated an entropy function $S_i(E_i, \mathbf{Q}_i)$. The microscopic definition of this entropy function is given by the logarithm of the "number of microstates," which are compatible with the prescribed values of $E_i, \mathbf{Q}_i$ [23]. In more precise terms,

$$S(E_i, \mathbf{Q}_i) = k_B \ln \int dz\, \delta(H(z) - E_i)\, \delta(\mathbf{Q}_i(z) - \mathbf{Q}_i), \tag{3}$$

where z is the set of microscopic degrees of freedom (positions and velocities of the solvent molecules and beads) and $H(z)$ is the Hamiltonian of the fluid particle. If the Dirac δ functions containing $\mathbf{Q}_i$ were not present, Eq. (3) would be the equilibrium thermodynamic entropy of the fluid particle. The introduction of these δ functions arises from our requirement of describing the system at a more refined level of description through the **Q** variables.

We compute the entropy of a fluid particle through Eq. (3) in Appendix B under the basic assumption that the suspension is dilute (so we may neglect the interactions among the dumbbells and between the dumbbells and the solvent). The result is

$$S(E,\mathbf{Q})=S^s(E)-\frac{V(\mathbf{Q})}{T^s(E)}+k_BN^d(1+\ln n^d\lambda_d^D), \tag{4}$$

where the dumbbell density number is $n^d=N^d/\mathcal{V}$. In obtaining this equation, we have neglected terms that scale as the inverse $1/N^s$ of the number of solvent molecules. We have introduced the solvent entropy $S^s(E)$, which is assumed to be a known function of its arguments. The generalized entropy depends on the dumbbell potential

$$V(\mathbf{Q})=\sum_\alpha^{N^d} V^d(\mathbf{Q}^\alpha), \tag{5}$$

where $V^d(\mathbf{Q})$ is the spring potential of a single dumbbell. It is possible to show that for multi-bead-spring models, the entropy has a form identical to Eq. (4) except that an effective potential appears instead of $V^d(\mathbf{Q})$. The solvent temperature introduced in Eq. (4) is defined by

$$\frac{1}{T^s(E)}=\frac{\partial S^s(E)}{\partial E}, \tag{6}$$

whereas the thermal wavelength λ_d of the dumbbells is

$$\lambda_d=\left(\frac{h^2}{2\pi m_d k_B T^s(E)}\right)^{1/2}. \tag{7}$$

The constants k_B, h, m_d, and D are the Boltzmann constant, the Planck constant, the mass of one bead of the dumbbell, and the dimension of physical space, respectively.

III. GENERIC FORMULATION

We will denote by $x=\{\mathbf{r}_i,\mathbf{v}_i,E_i,\mathbf{Q}_i,\ \ i=1,\dots,M\}$, the full state of the system, where $\mathbf{Q}_i=\{\mathbf{Q}_i^\alpha,\alpha=1,\dots,N_i^d\}$ is the collection of the elongations of the dumbbells of particle i. The total energy of the system is given by

$$E(x)=\sum_i^M \frac{m}{2}\mathbf{v}_i^2+E_i. \tag{8}$$

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

$$S(x)=\sum_i S(E_i,\mathbf{Q}_i,\mathcal{V}_i). \tag{9}$$

Note that the entropy of the full system is defined as the sum of the entropies of each cell taken as thermodynamic subsystems, that is, by the sum of function (3) evaluated at E_i, $\mathbf{Q}_i$, $\mathcal{V}_i$. This is the well-known *local equilibrium assumption.*

For future reference we present here the derivatives of the energy and entropy functions (computed in Appendix B) with respect to the state variables,

$$\frac{\partial E}{\partial x}=\begin{pmatrix}\dfrac{\partial E}{\partial \mathbf{r}_i}\\[2mm] \dfrac{\partial E}{\partial \mathbf{v}_i}\\[2mm] \dfrac{\partial E}{\partial E_i}\\[2mm] \dfrac{\partial E}{\partial \mathbf{Q}_i^\beta}\end{pmatrix}=\begin{pmatrix}\mathbf{0}\\ m\mathbf{v}_i\\ 1\\ \mathbf{0}\end{pmatrix}, \tag{10}$$

$$\frac{\partial S}{\partial x}=\begin{pmatrix}\dfrac{\partial S}{\partial \mathbf{r}_i}\\[2mm] \dfrac{\partial S}{\partial \mathbf{v}_i}\\[2mm] \dfrac{\partial S}{\partial E_i}\\[2mm] \dfrac{\partial S}{\partial \mathbf{Q}_i^\beta}\end{pmatrix}=\begin{pmatrix}\displaystyle\sum_k \mathbf{\Omega}_{jk}\frac{P_k}{d_k^2T_k}\\ 0\\ \dfrac{1}{T_j}\\[2mm] \dfrac{\mathbf{F}_j^\beta}{T_j}\end{pmatrix}, \tag{11}$$

where we have introduced the following vector that depends only on the position of the particles:

$$\mathbf{\Omega}_{ij}=-\frac{\partial d_j}{\partial \mathbf{r}_i}=-\left[\omega_{ij}+\delta_{ij}\sum_k \omega_{ik}\right], \tag{12}$$

where

$$\omega_{ij}=-W'(r_{ij})\mathbf{e}_{ij}. \tag{13}$$

Here, the prime denotes the derivative and $\mathbf{e}_{ij}=\mathbf{r}_i-\mathbf{r}_j/|\mathbf{r}_i-\mathbf{r}_j|$ is the unit vector joining particles i,j.

The temperature appearing in Eq. (11) is given by the derivative of the entropy (4) with respect to energy, that is,

$$\frac{1}{T}=\frac{\partial S(E,\mathbf{Q})}{\partial E}=\frac{1}{T^s(E)}+O(1/N^s). \tag{14}$$

The temperature is given, therefore, by the solvent temperature, because we are neglecting terms that are inversely proportional to the size of the fluid particles.

The pressure P_k of the fluid particle k is given by the usual thermodynamic definition

$$\frac{P}{T}=\frac{\partial S(E,\mathbf{Q})}{\partial \mathcal{V}}. \tag{15}$$

By taking the volume derivative of Eq. (4) we obtain

$$P=P^s+k_BT^sn^d, \tag{16}$$

where P^s is the solvent pressure and the last term is the osmotic pressure of the dumbbells.

Finally, we have introduced in Eq. (11) the dumbbell force

$$\mathbf{F}_j^\beta=-\frac{\partial V^d(\mathbf{Q}_j^\beta)}{\partial\mathbf{Q}_j^\beta}. \tag{17}$$

The physics that we want to introduce in this model can be summarized in rather simple terms. The fluid solvent moves hydrodynamically and a fixed number of dumbbells N_i^d are transported by each fluid particle in its overall motion. If the fluid is in an extensional state, the elongation vector $\mathbf{Q}_i^\alpha$ of the dumbbell α within the ith fluid particle should increase, as if both ends of the dumbbell were "anchored" in the flow field. To this elongation due to the flow field there is an opposite relaxation effect due to the underlying spring that tries to reduce as much as possible the magnitude of $\mathbf{Q}_i$. Our aim in the following sections is to translate in mathematical terms this physical picture.

IV. 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 represents purely kinematic effects on the evolution of the variables, and it is given by [see Eq. (A1) in Appendix A]

$$\dot{x}|_{\text{rev}}=L\frac{\partial E}{\partial x}, \tag{18}$$

where L is an antisymmetric matrix. We wish that the reversible part of the dynamics produces the following equations of motion for the positions of the fluid particles:

$$\dot{\mathbf{r}}_i=\mathbf{v}_i. \tag{19}$$

The simplest nontrivial reversible part $L(\partial/\partial x)E$ that produces the above equaton (19) has the following form

$$\begin{pmatrix}\dot{\mathbf{r}}_i\\ \dot{\mathbf{v}}_i\\ \dot{E}_i\\ \dot{\mathbf{Q}}_i^\alpha\end{pmatrix}_{\text{rev}}=\sum_j\mathbf{L}_{ij}\begin{pmatrix}\mathbf{0}\\ m\mathbf{v}_j\\ 1\\ 0\end{pmatrix}, \tag{20}$$

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

$$\mathbf{L}_{ij}=\frac{1}{m}\begin{pmatrix}\mathbf{0} & \mathbf{1}\delta_{ij} & \mathbf{0} & \mathbf{0}\\ -\mathbf{1}\delta_{ij} & \mathbf{0} & \mathbf{\Delta}_{ij} & \mathbf{\Lambda}_{i\beta_j}\\ \mathbf{0} & -\mathbf{\Delta}_{ji} & 0 & \mathbf{0}\\ \mathbf{0} & -\mathbf{\Lambda}_{j\alpha_i}^T & \mathbf{0} & \mathbf{0}\end{pmatrix}. \tag{21}$$

Note that in order to have antisymmetry of L, we must have $\mathbf{L}_{ij}=\mathbf{L}_{ji}^T$, where the superscript T means matrix transposition. The first row of $\mathbf{L}_{ij}$ ensures the equation of motion (19). The first column is fixed by antisymmetry of L. We have set to zero the right lower block in order to satisfy the degeneracy condition $L(\partial/\partial x)S=0$ in Eq. (A2) in Appendix A. The only nontrivial part of this degeneracy condition becomes, after the matrix multiplication of Eq. (21) with Eq. (11),

$$-\sum_j\mathbf{\Omega}_{ij}\frac{P_j}{d_j^2T_j}+\mathbf{\Delta}_{ij}\frac{1}{T_j}+\sum_{\beta_j}\mathbf{\Lambda}_{i\beta_j}\cdot\frac{\mathbf{F}_j^\beta}{T_j}=0. \tag{22}$$

The simplest choice for $\mathbf{\Delta}_{ij}$ that satisfies Eq. (22) is

$$\mathbf{\Delta}_{ij}=\mathbf{\Omega}_{ij}\frac{P_j}{d_j^2}-\sum_\beta\mathbf{\Lambda}_{i\beta_j}\cdot\mathbf{F}_j^\beta. \tag{23}$$

The final reversible part of the dynamics will be

$$\begin{aligned}\dot{\mathbf{r}}_i|_{\text{rev}}&=\mathbf{v}_i,\\ m\dot{\mathbf{v}}_i|_{\text{rev}}&=\sum_j\mathbf{\Delta}_{ij},\\ \dot{E}_i|_{\text{rev}}&=-\sum_j\mathbf{\Delta}_{ji}\cdot\mathbf{v}_j,\\ \dot{\mathbf{Q}}_i^\alpha|_{\text{rev}}&=-\sum_j\mathbf{\Lambda}_{j\alpha_i}^T\cdot\mathbf{v}_j.\end{aligned} \tag{24}$$

Let us turn, now, to the specification of $\mathbf{\Lambda}_{ij}$ by requiring a particular motion for the vector $\mathbf{Q}_i$ due to the advection of the fluid. From a continuum point of view, an arbitrary vector $\mathbf{A}$ is advected under a velocity field $\mathbf{v}(\mathbf{r})$ according to

$$\dot{\mathbf{A}}=\mathbf{A}\cdot\nabla\mathbf{v}(\mathbf{r}), \tag{25}$$

where the dot stands for the substantial derivative [Eq. (E3) in Appendix E]. The physical picture is that the vector $\mathbf{A}$ has its both ends anchored in the fluid, as shown heuristically in Appendix C. We want that the elastic vector $\mathbf{Q}_i^\alpha$ evolves in a similar way. We need, therefore, the gradient of the velocity field at the point where particle i is. Following the SPH philosophy, we interpolate the velocity field according to

$$\mathbf{v}(\mathbf{r})=\frac{\sum_j W(\mathbf{r}-\mathbf{r}_j)\mathbf{v}_j}{\sum_j W(\mathbf{r}-\mathbf{r}_j)}. \tag{26}$$

By taking the gradient of this expression we obtain

$$\nabla\mathbf{v}(\mathbf{r})=\frac{\sum_j\nabla W(\mathbf{r}-\mathbf{r}_j)\mathbf{v}_j}{\sum_j W(\mathbf{r}-\mathbf{r}_j)}-\mathbf{v}(\mathbf{r})\frac{\sum_j\nabla W(\mathbf{r}-\mathbf{r}_j)}{\sum_j W(\mathbf{r}-\mathbf{r}_j)}. \tag{27}$$

Therefore, at particle i we have the approximate expression for the gradient of the velocity field,

$$\nabla \mathbf{v}(\mathbf{r}_i)=\frac{\sum_j \nabla W(\mathbf{r}_i-\mathbf{r}_j)\mathbf{v}_j}{d_i}-\mathbf{v}(\mathbf{r}_i)\frac{\sum_j \nabla W(\mathbf{r}_i-\mathbf{r}_j)}{d_i}$$

$$\approx \frac{1}{d_i}\sum_j \omega_{ij}\mathbf{v}_{ij}, \tag{28}$$

where $\mathbf{v}_{ij}=\mathbf{v}_i-\mathbf{v}_j$ and ω_{ij} is defined in Eq. (13). Therefore, the continuum advection equation (25) becomes the discrete equation for the kinematic motion of $\mathbf{Q}_i^\alpha$

$$\dot{\mathbf{Q}}_i^\alpha=\frac{\mathbf{Q}_i^\alpha}{d_i}\cdot\sum_j \omega_{ij}\mathbf{v}_{ij}. \tag{29}$$

By comparing Eq. (29) with the last equation in Eqs. (24) we obtain the explicit form for the matrix $-\mathbf{\Lambda}_{ji}^T$, i.e.,

$$-\mathbf{\Lambda}_{j\alpha_i}^T=\frac{\mathbf{Q}_i^\alpha}{d_i}\cdot\left[-\omega_{ij}+\delta_{ij}\sum_k \omega_{ik}\right]\mathbf{1}$$

$$\mathbf{\Lambda}_{i\beta_j}=-\frac{\mathbf{Q}_j^\beta}{d_j}\cdot\left[\omega_{ij}+\delta_{ij}\sum_k \omega_{ik}\right]\mathbf{1}=-\frac{\mathbf{Q}_j^\beta}{d_j}\cdot\mathbf{\Omega}_{ij}\mathbf{1}. \tag{30}$$

With this particular form of the matrix $\mathbf{\Lambda}_{ij}$ we can write the vector $\mathbf{\Delta}_{ij}$ in Eq. (23) as

$$\mathbf{\Delta}_{ij}=\frac{1}{d_j^2}\mathbf{\Omega}_{ij}\cdot\left[P_j\mathbf{1}+d_j\sum_\beta \mathbf{F}_j^\beta\mathbf{Q}_j^\beta\right]. \tag{31}$$

The term in brackets can be understood as the reversible part of the stress tensor of particle j, i.e.,

$$\mathbf{\Pi}_j=P_j\mathbf{1}+d_j\sum_\beta \mathbf{F}_j^\beta\mathbf{Q}_j^\beta. \tag{32}$$

This stress tensor includes an isotropic component given by pressure in Eq. (16) and a nondiagonal part. Substitution of (12) and (32) into Eqs. (24) leads to the final *reversible* part of the dynamics for the viscoelastic model:

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

$$m\dot{\mathbf{v}}_i|_{\rm rev}=\sum_j\left[\frac{\mathbf{\Pi}_i}{d_i^2}+\frac{\mathbf{\Pi}_j}{d_j^2}\right]\cdot\omega_{ij},$$

$$\dot{E}_i|_{\rm rev}=-\frac{\mathbf{\Pi}_i}{d_i^2}:\sum_j \omega_{ij}\mathbf{v}_{ij},$$

$$\dot{\mathbf{Q}}_i^\alpha|_{\rm rev}=\frac{\mathbf{Q}_i^\alpha}{d_i}\cdot\sum_j \omega_{ij}\mathbf{v}_{ij}. \tag{33}$$

These equations (33) conserve total energy (due to the antisymmetry of L) and leave the entropy unchanged (due to the degeneracy $L\partial S/\partial x=0$). They also conserve total momentum $\mathbf{P}(x)=\Sigma_i m\mathbf{v}_i$ due to the symmetries under exchange of the indices i, j in the momentum equation.

Let us summarize now the line of reasoning followed in this section. We have assumed a particular equation of motion for $\mathbf{Q}_i^\alpha$ in which this vector is anchored in the solvent. This implies a particular form for the matrix $\mathbf{\Lambda}_{i\beta_j}$ in Eq. (30). The conservation of energy implied by the antisymmetry of the matrix L imposes that this matrix $\mathbf{\Lambda}_{i\beta_j}$ should appear in an additional term in the momentum equation. The particular form of this term is dictated by the degeneracy condition $L\partial S/\partial x=0$, Eq. (23) which ensures that there is no entropy production due to the reversible part of the dynamics. As a result, we have been able to identify a reversible part of the stress tensor, which depends on the configuration $\mathbf{Q}_i^\alpha$ of the dumbbells. It is quite remarkable that the small physical input given by the anchoring of $\mathbf{Q}_i^\alpha$ translates, through the GENERIC formalism, into a very specific form for the stress tensor. Finally, the energy equation in Eqs. (33) describes how the mechanical work is transformed into internal energy in a reversible way.

V. IRREVERSIBLE PART OF THE DYNAMICS

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

$$M=\frac{d\tilde{x}d\tilde{x}^T}{2k_Bdt}. \tag{34}$$

This procedure ensures that M defined through Eq. (34) is automatically symmetric and positive semidefinite. We postulate the following form for the thermal noises $d\tilde{x}=\{\mathbf{0},d\tilde{\mathbf{v}}_i,d\tilde{E}_i,d\tilde{\mathbf{Q}}_i^\alpha\}$. Note that we do not assume any thermal noise for the position of the fluid particles, as we want to respect the equation of motion $\dot{\mathbf{r}}_i=\mathbf{v}_i$. In Ref. [4] we have discussed how to introduce the thermal noises $d\tilde{\mathbf{v}}_i,d\tilde{E}_i$ in order to recover a matrix M which produces an irreversible part of the dynamics that can be understood as a smoothed particle hydrodynamics discretization of the irreversible terms of the Navier-Stokes equations. We only have to postulate now the noise terms $d\tilde{\mathbf{Q}}_i^\alpha$. We discuss in Appendix D that a reasonable assumption for the stochastic force on $\mathbf{Q}_i^\alpha$ is given by

$$d\tilde{\mathbf{Q}}_i^\alpha=\left(4\frac{k_BT_i}{6\pi\eta a}\right)^{1/2}d\mathbf{U}_{\alpha_i}, \tag{35}$$

where $d\mathbf{U}_{\alpha_i}$ is an independent increment of the Wiener process, satisfying

$$d\mathbf{U}_{\alpha_i}d\mathbf{U}_{\beta_j}=\delta_{\alpha_i\beta_j}\mathbf{1}dt. \tag{36}$$

We recognize in the prefactor of Eq. (35) the diffusion coefficient of the beads of radius a given by the Stokes-Einstein relation. We will assume that the noise $d\tilde{\mathbf{Q}}_i^\alpha$ are statistically independent of $d\tilde{\mathbf{v}}_i, d\tilde{E}_i$.

According to Eq. (34), the matrix $M \rightarrow \mathbf{M}_{ij}$ is given by

$$\begin{pmatrix} \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \dfrac{d\tilde{\mathbf{v}}_i d\tilde{\mathbf{v}}_j^T}{2k_B dt} & \dfrac{d\tilde{\mathbf{v}}_i d\tilde{E}_j}{2k_B dt} & \mathbf{0} \\ \mathbf{0} & \dfrac{d\tilde{E}_i d\tilde{\mathbf{v}}_j^T}{2k_B dt} & \dfrac{d\tilde{E}_i d\tilde{E}_j}{2k_B dt} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \dfrac{d\tilde{\mathbf{Q}}_i^\alpha d\tilde{\mathbf{Q}}_j^\beta}{2k_B dt} \end{pmatrix}. \tag{37}$$

The central diagonal block has been computed in Ref. [4] and we have to compute only the last diagonal element, which is

$$\frac{d\tilde{\mathbf{Q}}_i^\alpha d\tilde{\mathbf{Q}}_j^\beta}{2k_B dt} = \frac{2T_i}{\zeta}\delta_{\alpha\beta}\delta_{ij}\mathbf{1}. \tag{38}$$

Now we are in position to write the deterministic irreversible part of the dynamics $\dot{x}|_{\mathrm{irr}} = M \cdot \partial S/\partial x$ which, after use of Eq. (11) for the derivative of the entropy, becomes

$$\begin{pmatrix} \dot{r}_i \\ \dot{\mathbf{v}}_i \\ \dot{E}_i \\ \dot{\mathbf{Q}}_i^\alpha \end{pmatrix}_{|\mathrm{irr}} = \sum_j \mathbf{M}_{ij} \begin{pmatrix} \sum_k \mathbf{\Omega}_{jk} P_k / d_k^2 T_k \\ 0 \\ \dfrac{1}{T_j} \\ \dfrac{\mathbf{F}_j^\beta}{T_j} \end{pmatrix}, \tag{39}$$

By collecting the results of Ref. [4] (once we neglect, for simplicity, the bulk viscosity) for the diagonal blocks of $\mathbf{M}_{ij}$ together with Eq. (38) we obtain the following irreversible part of the dynamics:

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

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

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

$$\dot{\mathbf{Q}}_i^\alpha|_{\mathrm{irr}} = \frac{2}{\zeta}\mathbf{F}_i^\alpha, \tag{40}$$

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

$$F_{ij} = -\frac{W'(r_{ij})}{r_{ij}}. \tag{41}$$

Note that concerning the irreversible part of the dynamics, the solvent and dumbbells are completely uncoupled and, therefore, the solvent irreversible dynamics is identical to that in Ref. [4].

By collecting the reversible part of the dynamics, Eqs. (33), and the irreversible part of the dynamics, Eqs. (40), we obtain the following set of *deterministic* equations, corresponding to Eq. (A1):

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

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

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

$$-2\kappa\sum_j \frac{F_{ij}}{d_i d_j}T_{ij},$$

$$\dot{\mathbf{Q}}_i^\alpha = \frac{\mathbf{Q}_i^\alpha}{d_i}\cdot\sum_j \omega_{ij}\mathbf{v}_{ij} + \frac{2}{\zeta}\mathbf{F}_i^\alpha. \tag{42}$$

This set of equations have the very appealing features of conserving energy and total momentum $\mathbf{P} = \Sigma_i m\mathbf{v}_i$, and leading to a positive production of entropy $\dot{S}(x) \geqslant 0$.

The evolution of $\mathbf{r}_i$, $\mathbf{v}_i$, and E_i is identical to that of a simple fluid without dumbbells, as given in Ref. [4], except for the additional dumbbell contribution to the stress tensor in Eq. (32). Apart from that, we recognize in these equations the different physical processes involved. In the momentum equation, viscous forces proportional to the viscosity try to reduce velocity differences between fluid particles. In the energy equation, a viscous heating term proportional to the shear viscosity describes how the kinetic energy which is dissipated by the friction forces leads to an increase of internal energy of the particles. Also in this energy equation, the heat conduction term, with overall magnitude given by the thermal conductivity of the solvent, tries to reduce temperature differences between fluid particles.

Finally, the last set of equations governs the dynamics of the elongation of every single dumbbell in the solution. Let us discuss in detail this set of equations for the simplest case of Hookean dumbbells. For Hookean dumbbells $\mathbf{F}_i^\alpha = -H\mathbf{Q}_i^\alpha$, where H is the spring constant, and the last irreversible term describes an exponential decay governed by a time scale given by $\zeta/2H$. Given an initial elongation of every dumbbell in each fluid particle, this terms relaxes it towards a zero elongation. The advective term cannot do anything against this relaxation and, actually, $\mathbf{Q}_i^\alpha = 0$ is the final solution of the equations for the dumbbell elongation.

Apparently, we have derived a model in which the dumbbells just relax towards zero elongations, the dumbbell contribution to the stress tensor vanish, and we are back to the model for a Newtonian fluid.

Of course, an essential element is lacking in the above set of equations, which is the presence of thermal fluctuations. Thermal fluctuations are the crucial bit that make the model sound and useful for the simulation of polymer solutions. The way to proceed is to formulate the GENERIC stochastic differential equations as shown in Appendix A. This has been done for the Newtonian model in Ref. [4] and leads to a proper thermodynamic version of the original dissipative particle dynamics model. A particularly interesting feature of this version of DPD is that thermal fluctuations depend on the size of the fluid particles, in accordance with usual concepts of equilibrium statistical mechanics. Therefore, for large enough fluid particles, the thermal fluctuations in the momentum and energy equation can be neglected. Of course, this is consistent with the fact that in order to simulate a basket ball in a swimming pool we do not introduce thermal fluctuations in the description whereas if we want to simulate a micron sized colloidal particle we will necessarily need to introduce thermal fluctuations. The essential physical reason for the dependence of the thermal fluctuations on the size of the fluid particle is that the momentum and energy are extensive quantities.

Whereas thermal fluctuations can be neglected in the final stochastic equations for the momentum and energy, they cannot be neglected at all for the dynamics of the dumbbell elongation. The dumbbell elongation is not an extensive variable, it is rather a mesoscopic variable for which the fluctuations are an important component of its full dynamics. The effect of the thermal fluctuations in the dynamics of the elongation variable is quite dramatic. Although the dumbbells want to relax towards zero elongation, the thermal noise guarantees a permanent kickoff of this state of zero elongation. This slight deviation from zero is sufficient for the convective term in the elongation equation in Eq. (42) to ‘‘drag’’ the ends of the dumbbell apart. In a steady shear flow, for example, the system will reach a stationary situation where, although the elongation of each dumbbell is zero on average, the resulting distribution is not isotropic, leading to a nonzero contribution to the stress tensor (see Sec. VII).

The final set of stochastic equations in this model are, therefore,

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

$$\begin{aligned}
m\,d\mathbf{v}_i = {} & \sum_j \left[\frac{\boldsymbol{\Pi}_i}{d_i^2} + \frac{\boldsymbol{\Pi}_j}{d_j^2}\right]\cdot \omega_{ij} dt \\
& - \frac{5\eta}{3}\sum_j \frac{F_{ij}}{d_i d_j}[\mathbf{v}_{ij} + (\mathbf{e}_{ij}\cdot\mathbf{v}_{ij})\mathbf{e}_{ij}]dt,
\end{aligned}$$

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

$$d\mathbf{Q}_i^\alpha = \frac{\mathbf{Q}_i^\alpha}{d_i}\cdot \sum_j \omega_{ij}\mathbf{v}_{ij} dt - \frac{2H}{\zeta}\mathbf{Q}_i^\alpha dt + d\tilde{\mathbf{Q}}_i^\alpha . \tag{43}$$

Of course, due to the coupling between equations, the full set of equations is stochastic even though there is only one noise source $d\tilde{\mathbf{Q}}_i^\alpha$. It may appear odd that having neglected thermal fluctuations in the momentum and energy equations, the equations for these variables still retain a stochastic character. However, we should remark that what we have neglected are spontaneous thermal fluctuations as they appear in the Landau-Lifshitz theory of fluctuating hydrodynamics. Its physical origin is the random interchange of solvent molecules between fluid particles, and these fluctuations are small as compared with the total amount of momentum or energy in the fluid particle. However, the fluctuations in the $\mathbf{Q}_i^\alpha$ variables have an *indirect* effect on the momentum and energy variables through the coupling via the stress tensor. The importance of this indirect coupling depends, of course, on the concentration of polymer molecules and the strength of the springs, and can make a crucial contribution to the dynamic behavior of the fluid.

VI. POLYMER DIFFUSIVITY

The model governed by Eqs. (43) describes the dynamics of every single dumbbell in the system. This approach is a similar to CONNFFESSIT [16,17], where a stochastic simulation of the dumbbells is coupled with a numerical solution of the fluid flows. Of course, having to keep track of the evolution of every single dumbbell in each fluid particle is an expensive task. Note that, according to the last equation in Eq. (43), all the dumbbells of a given fluid particle will display essentially the same behavior, at least in a statistical sense. The dynamics of different dumbbells of the same fluid particle differs only by the initial conditions and the actual sequence of random numbers used for the stochastic term. For this reason, we could focus on a given tagged dumbbell within each fluid particle and assume that the rest of dumbbells of that fluid particle ‘‘are doing the same thing.’’

In addition, the model presented above has a constant number of dumbbells in every fluid particle. This does not seem to be a very reasonable assumption. After all, if the beads of each dumbbell are subject to thermal fluctuations, then the center of mass of the dumbbell will suffer also from thermal fluctuations, leading to a diffusion of the center of mass of the dumbbells within the region of a fluid particle until they cross the fluid particle’s ‘‘boundary.’’ This, eventually, should lead to an interchange of dumbbells between fluid particles. The model in Eqs. (43) does not allow for a change in time of the number of dumbbells in a fluid particle.

In order to encompass the possibility of describing polymer diffusion and, at the same time, reduce the number of variables to simulate, we present in this section a new model that differs from the one presented in the previous sections in the variables used to describe the state of the system. Now, each fluid particle will be characterized by its position $\mathbf{r}_i$, its velocity $\mathbf{v}_i$, its internal energy E_i, a *unique* vector $\mathbf{Q}_i$ describing the elongation of a statistical representative of the dumbbells, and the number of dumbbells N_i^d within the fluid particle. By selecting a single elongation vector for every fluid particle we return to a version of the ten Bosch model which, in turn, is analogous to a Lagrangian version of the Brownian configuration field approach [24]. The Brownian configuration field approach is similar to the CONNFFESSIT approach except that only one suitably correlated elongation variable is kept for each fluid element. The connection between both approaches has been elucidated in Ref. [25] where it is shown that the Brownian configuration field approach can be understood as a variance reduction version of the CONNFFESSIT approach.

Let us proceed to formulate the equations of motion for this new set of variables by following the GENERIC strategy again. The total energy $E(x)$ of the system in the new variables is still given by Eq. (8) and the total entropy $S(x)$ has the same form as in Eq. (9), but now the entropy of a fluid particle is not given by Eq. (4) but rather it is postulated to be

$$S(E,\mathbf{Q})=S^s(E)-\frac{N^dV^d(\mathbf{Q})}{T^s(E)}+k_BN^d(1+\ln n^d\lambda_d^D). \tag{44}$$

Despite of its similar notation, the fluid particle entropy postulated in Eq. (44) depends on the energy, a *single* variable $\mathbf{Q}$, and the number of dumbbells N^d whereas the fluid particle entropy (4) depends on the energy and the N^d elongation variables of each dumbbell in the fluid particle.

The derivatives of the energy and entropy with respect to the new variables are

$$\frac{\partial E}{\partial x}=\begin{pmatrix}\mathbf{0}\\ m\mathbf{v}_i\\ 1\\ 0\\ 0\end{pmatrix}, \quad \frac{\partial S}{\partial x}=\begin{pmatrix}\sum_k \mathbf{\Omega}_{jk}\dfrac{P}{d_k^2T_k}\\ 0\\ \dfrac{1}{T_j}\\ \dfrac{\mathbf{F}_j}{T_j}\\ -\dfrac{\mu_j^d}{T_j}\end{pmatrix}, \tag{45}$$

where we have introduced the chemical potential through

$$\frac{\mu^d}{T}=-\frac{\partial S}{\partial N^d}=k_B\ln(n^d\lambda_d^D)+\frac{V^d(\mathbf{Q})}{T}. \tag{46}$$

Due to the dilute assumption, we expect that the variation of the number of dumbbells does not affect appreciably the mass m of the fluid particle, which is still assumed to be constant. However, it might strongly affect the elastic properties of the fluid particle and for this reason we retain N^d as a variable.

Concerning the dynamics of the new variables, we basically construct a system of GENERIC equations by proposing L and M matrices. As far as the reversible part of the dynamics is concerned we choose the following L matrix, to be compared with Eq. (21):

$$\mathbf{L}_{ij}=\frac{1}{m}\begin{pmatrix}\mathbf{0} & \mathbf{1}\delta_{ij} & \mathbf{0} & \mathbf{0} & \mathbf{0}\\ -\mathbf{1}\delta_{ij} & \mathbf{0} & \mathbf{\Delta}_{ij} & \mathbf{\Lambda}_{ij} & \mathbf{0}\\ \mathbf{0} & -\mathbf{\Delta}_{ji} & 0 & \mathbf{0} & 0\\ \mathbf{0} & -\mathbf{\Lambda}_{ji}^T & \mathbf{0} & \mathbf{0} & \mathbf{0}\\ \mathbf{0} & \mathbf{0} & 0 & \mathbf{0} & 0\end{pmatrix}. \tag{47}$$

This matrix ensures that $\dot{N}_i^d|_{\mathrm{rev}}=0$, that is, the reversible part of the dynamics does not change the number of dumbbells in each fluid particle. The dumbbells are simply transported by the reversible dynamics. From the argument in Appendix C concerning the advection of a vector, the $\mathbf{\Lambda}_{ij}$ element is given by

$$\mathbf{\Lambda}_{ij}=-\frac{\mathbf{Q}_j}{d_j}\cdot\mathbf{\Omega}_{ij}\mathbf{1}, \tag{48}$$

and the degeneracy condition $L\partial S/\partial x=0$ now leads to

$$\mathbf{\Delta}_{ij}=\frac{1}{d_j^2}\mathbf{\Omega}_{ij}\cdot\mathbf{\Pi}_j, \tag{49}$$

where the stress tensor of particle j now takes the form

$$\mathbf{\Pi}_j=P_j\mathbf{1}+d_jN_j^d\mathbf{F}_j\mathbf{Q}_j, \tag{50}$$

to be compared with Eq. (32).

For the irreversible matrix M we now select

$$\begin{pmatrix} \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \frac{d\tilde{\mathbf{v}}_i d\tilde{\mathbf{v}}_j^T}{2k_B dt} & \frac{d\tilde{\mathbf{v}}_i d\tilde{E}_j}{2k_B dt} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \frac{d\tilde{E}_i d\tilde{\mathbf{v}}_j^T}{2k_B dt} & \frac{d\tilde{E}_i d\tilde{E}_j}{2k_B dt} & 0 & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & 0 & \frac{d\tilde{\mathbf{Q}}_i d\tilde{\mathbf{Q}}_j}{2k_B dt} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \frac{d\tilde{N}_i^d d\tilde{N}_j^d}{2k_B dt} \end{pmatrix}, \tag{51}$$

where we have introduced a noise term $d\tilde{N}_i^d$, which is statistically independent of $d\tilde{\mathbf{v}}_i$, $d\tilde{E}_i$, and $d\tilde{\mathbf{Q}}_i$. In the discussion in Appendix D we see that the mechanism by which the center of mass of the dumbbells diffuses is essentially the same as the mechanism by which the elongation $\mathbf{Q}_i^\alpha$ of the dumbbells change, that is, the diffusion of each bead of the dumbbells. In that respect, one would expect certain correlation between the process by which the number of dumbbells in a region of the fluid changes and the process of change of $\mathbf{Q}$. However, note that the elementary process by which N_i^d changes is the diffusion of the center of mass for those dumbbells that are in the boundary between two fluid particles. The diffusion of these small numbers of particles near the boundary should not affect strongly the stochastic change of $\mathbf{Q}_j$ and, for this reason, we assume $d\tilde{N}_i^d$ to be uncorrelated with $d\tilde{\mathbf{Q}}_i$, i.e., $d\tilde{N}_i^d d\tilde{\mathbf{Q}}_j = 0$, leading to the block diagonal form of the matrix M.

Now, concerning the stochastic changes of the number of dumbbells, we identify the elementary stochastic process by which this number changes the random interchange of dumbbells between fluid particles due to the diffusive nature of the center of mass of the dumbbells within a fluid particle. The mechanism is essentially the same as that of heat conduction as considered in Ref. [4] and we postulate the matrix term

$$\frac{d\tilde{N}_i^d d\tilde{N}_j^d}{2k_B dt} = \frac{1}{2k_B}\left[\delta_{ij}\sum_k D_{ik}^2 - D_{ij}^2\right], \tag{52}$$

where $D_{ij} = D_{ji}$. The irreversible evolution of the number of dumbbells will be, therefore,

$$\dot{N}_i^d|_{\mathrm{irr}} = -\sum_j \frac{D_{ij}^2}{2k_B}\left[\frac{\mu_i^d}{T_i} - \frac{\mu_j^d}{T_j}\right]. \tag{53}$$

After the discussion in Appendix E, we find that a reasonable functional form for the coefficients D_{ij} is simply

$$D_{ij} = \left[\frac{F_{ij}}{d_i d_j}\frac{2}{\zeta}(T_i n_i^d + T_j n_j^d)\right]^{1/2}. \tag{54}$$

In this way, Eq. (53) becomes a smoothed particle hydrodynamics discretization of an advection-diffusion equation.

We have thus completed the formulation of this new model. The equations are simply Eqs. (43) with only one elongation variable per fluid particle, the stress tensor given by Eq. (50), coupled to the diffusion equation

$$dN_i^d = -\sum_j \left[\frac{F_{ij}}{d_i d_j}\frac{2}{\zeta}(T_i n_i^d + T_j n_j^d)\right]^{1/2}\left[\frac{\mu_i^d}{T_i} - \frac{\mu_j^d}{T_j}\right]dt. \tag{55}$$

This equation conserves the total number of dumbbells $\Sigma_i \dot{N}_i^d = 0$. The evolution of the number of dumbbells in each fluid particle is governed by the unbalance of dumbbell chemical potentials between neighboring fluid particles that will produce an exchange of dumbbells between fluid particles. This equation couples with the momentum and energy equations through the stress tensor. Note that the variable N_i^d is extensive and we do not consider additional stochastic forces in Eq. (55) that are assumed to be negligible. In this way, we are assuming that even though the suspension is dilute, every fluid particle contains a sufficiently large number of dumbbells for the fluctuations on the number of dumbbells to be negligible. It is of course possible to validate this assumption by explicitly including the thermal noise and to assess its effect. For the sake of simplicity, we neglect in this paper the stochastic forces on the number of dumbbells.

VII. SIMULATION RESULTS

In this section, we present simulation results in order to check and validate the present model. As a first step, we will assume that the number of dumbbells within each fluid particle is a constant equal to N_0^d, thus neglecting dumbbell diffusion between fluid particles. We will also assume that the thermal conductivity is very large in such a way that the temperature is already equilibrated to the same T_0 in all the fluid particles. A Hookean dumbbell spring will be assumed in this paper. Although the model permits to study more general situations, the isothermal and constant dumbbell density case allows for a comparison with analytically known predictions for Hookean dumbbells.

The simulated isothermal equations are

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

$$d\rho_i = -\rho_i \sum_j \frac{m}{\rho_j} \mathbf{v}_{ij} \cdot \omega_{ij} dt,$$

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

$$d\mathbf{Q}_i = \frac{\mathbf{Q}_i}{d_i} \cdot \sum_j \omega_{ij} \mathbf{v}_{ij} dt - \frac{2H}{\zeta} \mathbf{Q}_i dt + d\tilde{\mathbf{Q}}_i, \tag{56}$$

with

$$\mathbf{\Pi}_i = (P_i^s + k_B T_0 n_0^d) \mathbf{1} - H n_0^d \mathbf{Q}_i \mathbf{Q}_i, \tag{57}$$

where $\rho_i = m d_i$ is the solvent mass density and $n_0^d = N^d/\mathcal{V}$ is the constant dumbbells number density. Note that we solve explicitly the equation for the density, which is easily obtained from definition (1). We evolve the density rather than computing it from definition (1) because we foresee future applications where the presence of walls makes the evaluation of the density through (1) less accurate near the wall [3]. We select an ideal gas equation of state for the solvent pressure $P_i^s = c_p \rho_i T_0$, where c_p is the specific heat at constant pressure. For the weight function, we have chosen the Lucy function

$$W(r) = c_W (1 + 3r/r_c)(1 - r/r_c)^3, \tag{58}$$

where $c_W = 5/\pi r_c^2$ in two dimensions and $c_W = 105/16\pi r_c^3$ in three dimensions.

In order to make the previous equations dimensionless, we consider the following basic units: unit of mass m_s (mass of a solvent molecule), unit of length L_0 (box dimension), unit of time $\lambda_H = \xi/4H$ (viscoelastic decay time for Hookean dumbbell model), unit of temperature T_0. We define a reference velocity in terms of the primary variables as $v_0 = L_0/\lambda_H$. By using these units, we can make the above equations dimensionless (variables with an overline are dimensionless):

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

$$d\overline{\rho}_i = -\overline{\rho}_i \sum_j \frac{\overline{m}}{\overline{\rho}_j} \overline{\mathbf{v}}_{ij} \cdot \overline{\omega}_{ij} \overline{dt},$$

$$d\overline{\mathbf{v}}_i = \sum_j \overline{m} \left[\frac{\overline{\mathbf{\Pi}}_i}{\overline{\rho}_i^2} + \frac{\overline{\mathbf{\Pi}}_j}{\overline{\rho}_j^2} \right] \cdot \overline{\omega}_{ij} \overline{dt} - C_1 \sum_j \overline{m} \frac{\overline{F}_{ij}}{\overline{\rho}_i \overline{\rho}_j} [\overline{\mathbf{v}}_{ij} + (\mathbf{e}_{ij} \cdot \overline{\mathbf{v}}_{ij}) \mathbf{e}_{ij}] \overline{dt},$$

$$d\overline{\mathbf{Q}}_i = \frac{\overline{\mathbf{Q}}_i}{\rho_i} \cdot \sum_j \overline{m \omega_{ij}} \mathbf{v}_{ij} \overline{dt} - \frac{1}{2} \overline{\mathbf{Q}}_i \overline{dt} + d\overline{\tilde{\mathbf{Q}}}_i, \tag{59}$$

with

$$d\overline{\tilde{\mathbf{Q}}}_i = C_2 d\overline{\mathbf{U}}_i,$$

$$\overline{\mathbf{\Pi}}_i = (\overline{P}_i^s + C_3) \mathbf{1} - C_4 \overline{\mathbf{Q}}_i \overline{\mathbf{Q}}_i,$$

$$\overline{P}_i^s = C_5 \overline{\rho}_i. \tag{60}$$

Five nondimensional constants appear in Eqs. (59) and (60):

$$C_1 = \frac{5\eta_s}{3\rho_0 L_0 v_0}, \quad C_2 = \sqrt{\frac{k_B T_0}{H L_0^2}}, \tag{61}$$

$$C_3 = \frac{N^d k_B T_0}{\rho_0 v_0^5 \lambda_H^3}, \quad C_4 = \frac{N^d H}{\rho_0 v_0^3 \lambda_H}, \quad C_5 = \frac{c_p T_0}{v_0^2}. \tag{62}$$

The reference density is $\rho_0 = m_s N^s / L_0^3$. Here m_s represents the mass of a single-solvent molecule and N^s the total number of solvent molecules contained in the box. Note that we have the usual dimensions for density, pressure, viscosity, etc., corresponding to three-dimensional (3D) systems. On the other hand, we are performing 2D simulations, under the assumption of translationally invariant behavior in the z direction.

A. Theoretical results for Hookean dumbbells

Analytical results for an isothermal Couette flow for Hookean dumbbells are available in the literature [26], and give exact prescriptions for the dependence of the material functions and the stretching of the dumbbells $\langle Q^2 \rangle$ as a function of the shear rate in a steady shear flow. Let us assume a 2D steady shear flow. The Cartesian components of the velocity field are by definition

$$v_x = \dot{\gamma} y, \quad v_y = 0, \tag{63}$$

where $\dot{\gamma} = \partial v_x / \partial y$ is the shear rate. Let us consider now only the polymeric contribution to the pressure tensor. It can be written in tensorial notation as

$$\tau_{\alpha\beta}^p = k_B T_0 n_0^d \delta_{\alpha\beta} - H n_0^d \mathbf{Q}_\alpha \mathbf{Q}_\beta, \tag{64}$$

where the greek indices indicate the spatial coordinates. For Hookean dumbbells, it can be shown that the stress components and material functions in the final steady-state configuration are [26]

$$\tau_{xy}^p = -n_0^d k_B T_0 \lambda_H \dot{\gamma}, \tag{65}$$

$$\tau_{yy}^p - \tau_{xx}^p = 2 n_0^d k_B T_0 \lambda_H^2 \dot{\gamma}^2. \tag{66}$$

From Eqs. (65) and (66), we obtain the polymer contribution to the shear viscosity η_p and the first normal stress difference Ψ_1,

$$\eta_p = -\frac{\tau_{xy}^p}{\dot{\gamma}} = n_0^d k_B T_0 \lambda_H, \tag{67}$$

$$\Psi_1 = \frac{\tau^p_{yy} - \tau^p_{xx}}{\dot{\gamma}^2} = 2 n_0^d k_B T_0 \lambda_H^2 . \tag{68}$$

In this Hookean model, all material functions are constant, independent of the shear rate. It is also found that the global dumbbell stretching takes the form (2D)

$$\frac{\langle Q^2 \rangle}{\langle Q^2_{eq} \rangle} = 1 + (\lambda_H \dot{\gamma})^2 . \tag{69}$$

This shows that the Hookean dumbbells continue to stretch indefinitely as the shear rate is increased. This characteristic of the dynamics based on the Hookean model is inadequate for the description of realistic polymeric solutions. In fact, it is well known that the viscosity and the first normal stress coefficient should decrease for increasing shear rate instead of remaining constant. The failure of the model is related to the infinite extensibility which is shown in Eq. (69). Nevertheless, although this model does not provide an accurate description of a polymeric solution, it allows for exact comparisons with numerical results. More complex models such as the FENE (finitely extensible nonlinear elastic) spring model can be easily taken into account.

B. Setup of the numerical simulations

In order to produce a uniform stable shear flow, we apply the well-known Lees-Edwards boundary conditions [27]. The periodic image criterion is applied in both spatial directions in order to simulate an infinite periodic medium. In addition, a shear is imposed along the y axis simply by moving in opposite directions the periodic boxes at the top and the bottom of the central simulation box. Their respective velocities are $\pm v_{box} = \dot{\gamma} L_0$, where $\dot{\gamma}$ is the desired shear rate. Particles crossing the edge at the top of the simulation box are re-inserted at the bottom with the same y component of the velocity v_y but with opposite v_x. A linear stable velocity profile corresponding to Eq. (63) is therefore produced.

The numerical parameters of our simulations are: the reference temperature, chosen to be the typical room temperature $T_0 = 300$ K, the reference time $\lambda_H = 1.0 \times 10^{-6}$ s, and the reference length $L_0 = 1.0 \times 10^{-5}$ m, which corresponds to the length of the box. The reference velocity is therefore $v_0 = L_0/\lambda_H = 10 \mathrm{~m\,s^{-1}}$. We choose a value for m_s corresponding to the mass of a water molecule ($m_s = 2.98 \times 10^{-26}$ kg) and total number of solvent molecules $N^s = 3.35 \times 10^{13}$. This gives a solvent density $\rho_0 = 10^3 \mathrm{~kg\,m^{-3}}$ corresponding to typical values for water under standard conditions.

There are other input parameters which influence the dynamics. The solvent shear viscosity $\eta_s = 10^{-3} \mathrm{~kg\,m^{-1}\,s^{-1}}$. The reference dumbbell number density is defined as $n_0^d = N^d / L_0^3$, where N^d is an arbitrary number corresponding to the total number of dumbbells contained in the simulation box. The viscoelastic behavior is due to the last term in the stress tensor in Eq. (57). This term is proportional to N^d and controls the magnitude of the deviatoric non-Newtonian effects. Indeed, for $N^d = 0$ we recover the Newtonian fluid dynamics. The value of N^d is determined accordingly with all the other parameters in order to obtain a suitable polymeric viscosity consistent with Eq. (67). Here we assumed $N^d = 10^8$. With these parameters and by using formulas (67)–(68), we obtain the polymeric contribution to the viscosity $\eta_p = 4.142 \times 10^{-4} \mathrm{~kg\,m^{-1}\,s^{-1}}$ and the first normal stress coefficient $\Psi_1 = 8.284 \times 10^{-10} \mathrm{~kg\,m^{-1}}$ in SI units. Therefore, in our numerical framework, their dimensionless values are $\eta_p = 4.142 \times 10^{-3}$ and $\Psi_1 = 8.284 \times 10^{-3}$. As already noticed, these viscometric functions for a Hookean spring model should be independent of the shear rate. The spring constant H can be determined using the the Stokes-Einstein relation, so that $H = 6 \pi \eta_s a / 4 \lambda_H$, where a is the radius of a bead and λ_H the reference time. Here we chose $a = 4.0 \times 10^{-10}$ m, which gives a value of $H = 1.88 \times 10^{-6} \mathrm{~kg\,s^{-2}}$. In addition, the equilibrium value for $\langle Q^2_{eq} \rangle$ in Eq. (69) (averaged over all the box domain) for zero shear rate should be equal to $\langle Q^2_{x,eq} \rangle + \langle Q^2_{y,eq} \rangle = 2C^2 = 2 k_B T_0 / H L_0^2 = 4.4 \times 10^{-5}$ in dimensionless units.

In the equation of state c_p is chosen equal to $462 \mathrm{~J\,kg^{-1}\,K^{-1}}$. As the speed of sound is defined as $c_s = \sqrt{\partial p / \partial \rho} = \sqrt{c_p T_0}$, we obtain a value equal to $372.3 \mathrm{~m\,s^{-1}}$. Its value in reduced units is 37.2, which is almost ten times larger than the typical box velocity whose maximum value is 5 (corresponding to the highest shear rate simulated $\dot{\gamma} = 10$). This choice of c_s prevents compressibility effects and retains the divergence-free velocity conditions according to Monaghan [28].

The cutoff radius r_c for the "smoothed particle" is chosen 0.08 in reduced units. From a computational point of view, such a choice of r_c involves nearly 50 neighbors for each smoothed particle, which is a quite large but necessary number for an accurate estimate of the viscometric functions. Finally, the total number M of simulated fluid particle is 2500.

C. Numerical results

In this section we present the results of a Couette shear flow experiment. The polymeric viscosity η_p, first normal stress coefficient Ψ_1, and global stretching $\langle Q^2 \rangle$ are extracted from seven different runs corresponding to different values of the shear rate $\dot{\gamma}$. Finally, we compare the numerical results with the analytical ones coming from Eqs. (65)–(69).

Given the homogeneous flow field developed by the boundary conditions, we evaluate the global quantities which we are interested in by taking the average of their local values defined at the position of every fluid particle. For example,

$$\langle \tau_{\alpha\beta} \rangle = \frac{1}{M} \sum_{i=1}^{M} \tau^i_{\alpha\beta} , \tag{70}$$

where M is the number of the simulated SPH particles. In Figs. 2 and 3 we plot $\langle \tau_{xy} \rangle$ and $\langle \tau_{yy} - \tau_{xx} \rangle$, respectively, as functions of the shear rate. The symbols correspond to the results of the simulations while the solid lines are the theoretical previsions corresponding to Eqs. (65) and (66). As

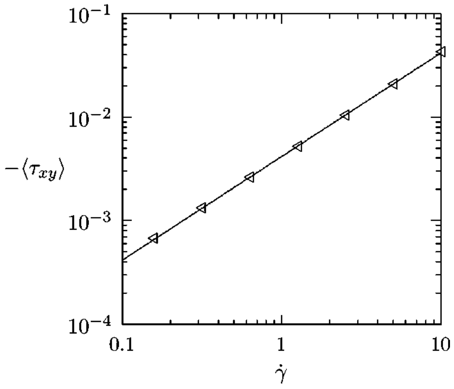

FIG. 2. Steady-state off-diagonal component of the polymeric dimensionless stress tensor τ_{xy} as a function of shear rate $\dot{\gamma}$. Triangles are the simulation results and the solid line is the theoretical prediction in Eq. (65). The numerical errors are comparable to symbol size.

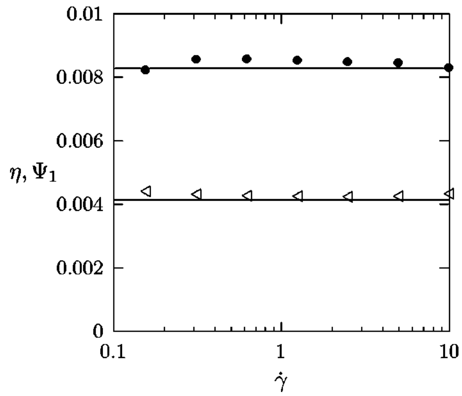

FIG. 4. Dimensionless polymeric viscosity η_p (◁) and the first normal stress coefficient ψ_1 (●) vs shear rate $\dot{\gamma}$. The numerical results are compared with the theoretical constant values predicted from Eqs. (67) and (68) in solid lines.

prescribed, their values increase respectively linearly and quadratically with $\dot{\gamma}$. The x and y-scale are both logarithmic and cover a range of $\dot{\gamma}$ from about 0.1 to 10 in reduced units.

As already pointed out, the components of the polymeric stress should increase with the shear rate in such a way that the viscosity and the first normal stress coefficient remain constant as prescribed by Eqs. (67) and (68). In Fig. 4 we plot η_p and Ψ_1 and compare them with their theoretical constant values. This shows that the agreement is also quantitatively good over all the range of $\dot{\gamma}$ simulated. It must be pointed out that no fit parameters have been used.

Equation (69) shows that the dumbbells continue to stretch as the shear is increased. This is a particular property of the Hookean dumbbell model. In Fig. 5 we plot the global molecular stretching $\langle Q^2\rangle$. Even in the global stretching we achieved a very good quantitative agreement with the analytical results. In addition, also the exact output equilibrium value for the average square elongation vector is recovered in the limiting case of small shear rate. In this regime a limiting value is obtained corresponding to the equilibrium (zero shear rate) stretching. This cannot be observed in the previous figure because of its smallness compared with the values corresponding to high $\dot{\gamma}$. In the next figure the temporal evolution of $\langle Q^2\rangle$ for a shear flow with $\dot{\gamma}=0.156$ is shown. The agreement with the theoretical prevision for $\langle Q^2_{eq}\rangle$ is clearly visible in Fig. 6.

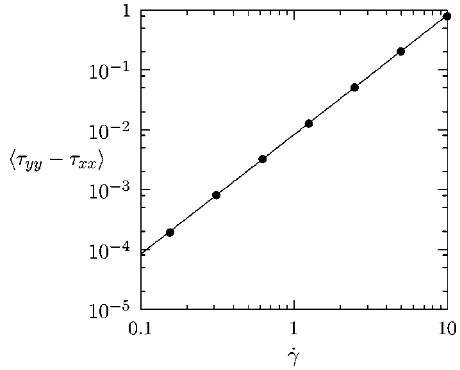

FIG. 3. Difference between the steady-state diagonal components of the polymeric dimensionless stress tensor $\tau_{yy}-\tau_{xx}$ as a function of shear rate $\dot{\gamma}$. Bullets are the simulation results and the solid line is the theoretical prediction in Eq. (66).

Finally, in Fig. 7 we present snapshots of the Q-vector configuration at different times and for a fixed shear rate $\dot{\gamma}=10$. The x and y axes represent, respectively the Q_x and Q_y components of the elongation of the dumbbell representative of every simulated fluid particle. The snapshots correspond to times $t=0.1$, 0.3, 0.6, 1.0, 2.0, and 4.0. As expected, we observe the stretching of Q_x component while in the y direction the configuration tends to that of equilibrium at zero shear rate. We notice also that at every time the stretching in the x direction increases, but always preserving the symmetry of the particle distribution around the origin in the Q plane, that is, on average over all the box the components of the Q vector are zero.

VIII. CONCLUSIONS

Inspired by a dissipative particle dynamics model formulated by ten Bosch [15], we have proposed a fluid particle

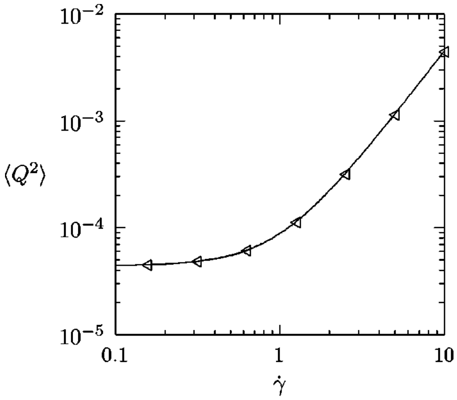

FIG. 5. Steady-state molecular dimensionless stretching $\langle Q^2\rangle$ vs shear rate. Triangles are the simulation results and the solid line is the theoretical prediction in Eq. (69).

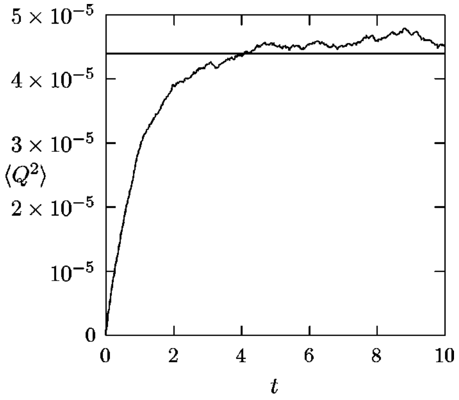

FIG. 6. Molecular dimensionless stretching growth curve corresponding to a shear rate $\dot{\gamma}=0.156$. It can be observed that the steady-state value of $\langle Q^2\rangle$ fluctuates around the equilibrium value corresponding to zero shear rate. This shows that the agreement with the theory is achieved quantitatively also in the small shear rate regime.

model for the simulation of dilute polymeric solutions. Special attention has been paid to the thermodynamic consistency of the model by writing it within the GENERIC framework. Actually, several basic differences between the model presented and that of ten Bosch [15] arise from the thermodynamic consistency of our model. First, our model includes a fluid particle volume variable and, therefore, the conservative forces in the momentum equation are replaced by actual pressure forces. As we have shown in Ref. [4], the conservative forces in the original classic DPD model are not very physical and do not allow us to study *arbitrary* equations of state. Second, our model includes an internal energy variable and it allows us to study nonisothermal processes. Again, this can be regarded as an improvement over the classic DPD model. Finally, we have introduced the number of dumbbells as an additional variable, which allows us to study diffusive processes of dumbbells which are absent in the ten Bosch model.

From a more technical point of view, we observe that our model has a smaller number of parameters and functions than the ten Bosch model. For example, the antisymmetry of L forces the α and β parameters of the ten Bosch model to be exactly the same. Also, the solvent parameters are the physical transport coefficients, which are directly given as an input. There is no need to perform a kinetic theory of the model in order to obtain the transport coefficients in terms of the model parameters, as it is done in Ref. [15].

Our approach also puts the ten Bosch model in a conceptual framework that highlights the validity and limitations of the model as a tool for simulating viscoelastic materials. From the microscopic calculation of the entropy and the physical arguments used to derive the equations of motion, it is apparent that this model should provide a good description for *dilute* polymeric solutions. Semidilute solutions could perhaps be treated by including excluded volume effects of the dumbbells and mean field interactions between dumbbells using similar ideas as those of van der Waals for simple fluids. Polymer melts cannot be described by our model. A continuum theory for polymer melts in nonisothermal situations has been presented in Ref. [29], which makes use of a conformation tensor for describing the microstructure of the melt. The continuum equations for polymer melts in Ref. [29] could also be discretized in terms of fluid particles with a well-defined underlying physical picture that respects the laws of thermodynamics.

In this paper, we have presented numerical simulations for isothermal homogeneous shear flow without polymer diffusivity. For reasons of simplicity, we have modeled the polymer molecules with Hookean dumbbells, although more realistic models for polymer molecules can also be considered. Finite extensibility and more complex bead-spring models [26] are easily implemented. The simulation results are preliminary but, nevertheless, reproduce the known theoretical predictions without fitting parameters. Of course, the potential of the method lies in the possibility of exploring more complex nonisothermal, nonhomogeneous, and non-Hookean situations.

A final comment on the connection between our model and the Brownian Configuration field (BCF) method is in order. In BCF, there is also only one elastic variable per (Eulerian) computational cell, and the goal is to reduce the noise inherent in the method by using the same sequence of random kicks for all the position over the domain. Then one has one realization of the vector field **Q** (and consequently one realization of the polymeric pressure tensor), which are completely correlated over all the space. When the divergence of the stress tensor is evaluated in the momentum equation, it is usually done by a two-point difference discretization, and, because of the total correlation between tensor fields in different points, the noise is dramatically reduced. In the SPH discretization of the momentum equation, the gradients are represented by a sum (in order to have an antisymmetric force in the particle index) and not by a difference. Therefore, our method is intrinsically noisy and the noise level cannot be reduced by the trick in BCF (or we would lose exact momentum conservation). In order to study nonhomogeneous flows, the two options are either to use a large number of dumbbells per fluid particle as in the CONNFFESSIT approach or to use a sufficiently large number of fluid particles in such a way that we can perform spatial averages over many particles underlying the same shear flow. More work deserves to be done in this respect.

ACKNOWLEDGMENTS

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APPENDIX A: REVIEW OF GENERIC

In this appendix, we present a summary of the GENERIC framework [19]. The state of a system at a given level of description is described by a set of variables that form a

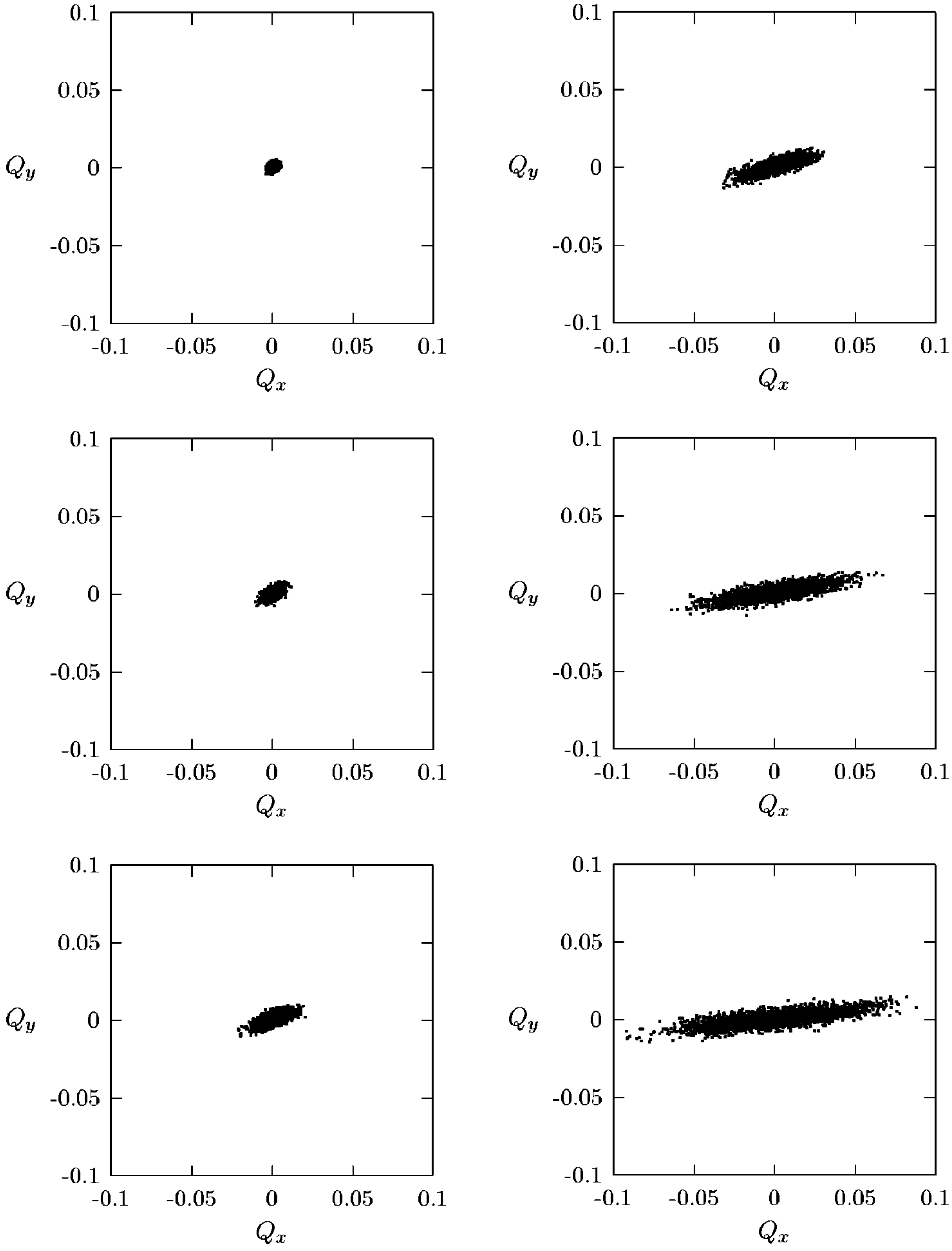

FIG. 7. The dimensionless elongation of the dumbbell representative of every fluid particle in a start up of the shear flow at times $t=0.1$, 0.3, 0.6, 1.0, 2.0, and 4.0. Initially the dumbbells distribute isotropically, but as time proceeds the distribution becomes more and more anisotropic.

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 then given by

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

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

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

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

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

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

The 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 [23]:

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

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

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

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 if one form) 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.

APPENDIX B: MICROSCOPIC CALCULATION OF THE ENTROPY OF A DUMBBELL SOLUTION

In this appendix we compute the entropy of a thermodynamic system composed of a set of N^s solvent molecules and N^d dumbbells. We understand this system as the portion of fluid that constitutes a fluid particle. The dumbbells are a highly simplified model of a real polymer molecule. The purpose of this calculation is to provide specific analytical expressions for the entropy which may have some resemblance with the actual entropy of a dilute polymer system. We denote by z the set of microscopic degrees of freedom of the system, which are $\mathbf{r}_i$, $\mathbf{p}_i$ for the position and momentum of the solvent molecules, $\mathbf{R}_i$, $\mathbf{Q}_i$ for the center of mass and relative position of the dumbbells, and $\mathbf{P}_i$ for the bead momentum. We will denote schematically $\mathbf{r} = \{\mathbf{r}_i, i = 1, \ldots, N^s\}$, $\mathbf{R} = \{\mathbf{R}_i, i = 1, \ldots, N^d\}$, and $\mathbf{Q} = \{\mathbf{Q}_i, i = 1, \ldots, N^d\}$. The Hamiltonian is given by

$$H(z) = \sum_i^{N^s} \frac{p_i^2}{2m_s} + \sum_i^{2N^d} \frac{P_i^2}{2m_d} + V^s(\mathbf{r}) + V^{sd}(\mathbf{r},\mathbf{R},\mathbf{Q}) + V^d(\mathbf{Q}). \tag{B1}$$

Here we have introduced the potential energy of the solvent molecules, $V^s(r)$, which depends only on the coordinates of the solvent molecules, the potential energy of interaction between solvent and beads, $V^{sd}(\mathbf{r},\mathbf{R},\mathbf{Q})$ of the dumbbells, and finally, the potential energy of interaction of the dumbbells, $V^d(\mathbf{R},\mathbf{Q})$. In order to be able to obtain analytical expressions, we will assume that the suspension is dilute in such a way that the potential energy of interaction between solvent and dumbbells can be neglected in front of the solvent potential energy, that is, $V^{sd}(\mathbf{r},\mathbf{R},\mathbf{Q}) = 0$. Also, we will assume that the interaction between different dumbbells is negligible and, therefore, the potential energy of the dumbbells does not depend on the center of mass variables, i.e., $V^d(\mathbf{R},\mathbf{Q}) = V^d(\mathbf{Q})$.

The entropy, defined as the logarithm of the number of microstates compatible with a given macrostate E, $\mathbf{Q}$ is given by the classic Boltzmann definition

$$S(E,\mathbf{Q}) = k_B \ln \int dz\, \delta(H(z) - E)\delta(\mathbf{Q}(z) - \mathbf{Q}). \tag{B2}$$

The measure dz is given by the product of solvent and dumbbell measures

$$dz = \frac{d^{N^s}\mathbf{p}\, d^{N^s}\mathbf{r}}{h^{DN^s} N^s!} \times \frac{d^{2N^d}\mathbf{P}\, d^{N^d}\mathbf{Q}\, d^{N^d}\mathbf{R}}{h^{D2N^d} N^d!}. \tag{B3}$$

Here, k_B is the Boltzmann constant and h is the Planck constant. The factorials $N^s!$ and $N^d!$ come from the quantum indistinguishability of the molecules and dumbbells. Note that the entropy $S(E,\mathbf{Q})$ depends implicitly on N^s, N^d, and V, where the volume V appears because the integrals over coordinate variables are defined over the physical volume.

Under the dilute assumption, it is possible to perform explicitly the integrals over the center of mass variables. In this case, the integrand of Eq. (B2) does not depend on the center of mass variable and each integral over the center of mass vector produces just a volume factor V. We can also perform the integral over the elongation variables in the δ functions in Eq. (B2), with the result

$$S(E,\mathbf{Q}) = k_B \ln \frac{V^{N^d}}{N^d!} \int \frac{d^{2N^d}\mathbf{P}}{h^{D2N^d}} \int \frac{d^{N^s}\mathbf{p}\, d^{N^s}\mathbf{r}}{h^{DN^s} N^s!} \times \delta\left(H^s(r,p) - \left[E - V^d(\mathbf{Q}) - \sum_i^{2N^d} \frac{P_i^2}{2m_d} \right] \right), \tag{B4}$$

where the solvent Hamiltonian is

$$H^s(\mathbf{r},\mathbf{p}) = \sum_i^{N^s} \frac{p_i^2}{2m_s} + V^s(\mathbf{r}). \tag{B5}$$

If we introduce the solvent entropy through the usual definition

$$S^s(\mathcal{E}) = k_B \ln \int \frac{d^{N^s}\mathbf{p}\, d^{N^s}\mathbf{r}}{h^{DN^s} N^s!}\,\delta(H^s(\mathbf{r},\mathbf{p})-\mathcal{E}), \tag{B6}$$

we can write Eq. (B4) in the following way:

$$S(E,\mathbf{Q}) = k_B \ln \frac{V^{N^d}}{N^d!}\int \frac{d^{2N^d}\mathbf{P}}{h^{D2N^d}} \times \exp\left\{ \frac{1}{k_B} S^s\left(E - V^d(\mathbf{Q}) - \sum_i^{2N^d} \frac{P_i^2}{2m_d}\right)\right\}. \tag{B7}$$

This equation is exact as far as the dilute assumption holds. Of course, we would like to have a more manageable expression not involving an integral over dumbbell momenta. For this reason, we will expand the solvent entropy in the following way:

$$S^s\left(\mathcal{E} - \sum_i^{2N^d} \frac{P_i^2}{2m_d}\right) = S^s(\mathcal{E}) - \frac{1}{T^s(\mathcal{E})} \sum_i^{2N^d} \frac{P_i^2}{2m_d} + \frac{1}{2C_V^s(\mathcal{E})}\left(\sum_i^{2N^d} \frac{P_i^2}{2m_d}\right)^2 - \cdots, \tag{B8}$$

where $\mathcal{E} = E - V^d(\mathbf{Q})$ and we have introduced the usual thermodynamic derivatives of the entropy with respect to the energy, that is, the temperature T^s and the heat capacity at constant volume C_V^s. Note that the solvent entropy is a first-order function of its variables, that is,

$$S^s(\mathcal{E}, N^s, V) = N^s s(e,n), \tag{B9}$$

where $e = \mathcal{E}/N^s$ is the energy per unit molecule and $n = N^s/V$ is the number density. Equation (B9) implies the following scaling on the number of solvent molecules N^s of the derivatives of the solvent entropy appearing in Eq. (B8):

$$\frac{1}{T^s(\mathcal{E})} = \frac{\partial}{\partial \mathcal{E}} S^s(\mathcal{E}, N^s) = s^{(1)}(e,n),$$

$$\frac{1}{C_V^s(\mathcal{E})} = \frac{\partial^2}{\partial \mathcal{E}^2} S^s(\mathcal{E}, N^s) = \frac{1}{N^s} s^{(2)}(e,n),$$

$$\frac{\partial^M}{\partial \mathcal{E}^M} S^s(\mathcal{E}, N^s) = \frac{1}{N^{s(M-1)}} s^{(M)}(e,n), \tag{B10}$$

where the superscript M denotes the Mth derivative with respect to e of the solvent entropy per molecule $s^s(e,n)$. Given the scaling in Eq. (B10), Eq. (B7) becomes

$$S(E,\mathbf{Q}) = k_B \ln \frac{V^{N^d}}{N^d!} \exp\left\{ \frac{1}{k_B} S^s(\mathcal{E})\right\} \int \frac{d^{2N^d}\mathbf{P}}{h^{D2N^d}} \times \exp\left\{ -\beta^s(\mathcal{E}) \sum_i^{2N^d} \frac{P_i^2}{2m_d}\right\} + \mathcal{O}\left(\frac{1}{N^s}\right), \tag{B11}$$

where we have introduced $\beta^s(\mathcal{E}) = 1/k_B T^s(\mathcal{E})$. The Gaussian integral is now trivially performed and we obtain

$$S(E,Q) = S^s(E - V(Q)) + k_B \ln \frac{V^{N^d}}{N^d!}\left(\frac{2\pi m_d}{h^2 \beta^s}\right)^{DN^d} + O\left(\frac{1}{N^s}\right). \tag{B12}$$

Of course, within the same approximation of neglecting terms that scale as the inverse of the number of solvent molecules, we can also write

$$S(E,\mathbf{Q}) = S^s(E) - \frac{V(\mathbf{Q})}{T^s(E)} + k_B \ln \frac{V^{N^d}}{N^d!}\left(\frac{2\pi m_d}{h^2 \beta^s}\right)^{DN^d} + \mathcal{O}\left(\frac{1}{N^s}\right). \tag{B13}$$

The last term corresponding to the integration over the center of mass of the dumbbells has the form of an ideal gas contribution. By using Stirling's approximation ($\ln N! \approx N \ln N - N$), this ideal gas term has the usual form

$$\ln \frac{V^{N^d}}{N^d!\,\lambda_d^{DN^d}} = N^d(1 + \ln n^d \lambda_d^D), \tag{B14}$$

where $n^d = N^d/V$ is the dumbbell density and we have introduced the thermal wavelength of the beads by

$$\lambda_d = \left(\frac{h^2}{2\pi m_d k_B T^s(\mathcal{E})}\right)^{1/2}, \tag{B15}$$

and our final result is

$$S(E,\mathbf{Q}) = S^s(E) - \frac{V(\mathbf{Q})}{T^s(E)} + k_B N^d(1 + \ln n^d \lambda_d^D) + O\left(\frac{1}{N^s}\right). \tag{B16}$$

APPENDIX C: ADVECTION OF A VECTOR

We present here an heuristic argument in order to motivate Eq. (25). Consider two neighboring points $\mathbf{r}_1, \mathbf{r}_2$ in a velocity field $\mathbf{v}(\mathbf{r})$. After a small time τ, these points have moved to positions $\mathbf{r}_1', \mathbf{r}_2'$ which are given by

$$\mathbf{r}_1' = \mathbf{r}_1 + \tau v(\mathbf{r}_1)$$

$$\mathbf{r}_2' = \mathbf{r}_2 + \tau v(\mathbf{r}_2). \tag{C1}$$

If we consider the vectors $\Delta\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ and $\Delta\mathbf{r}' = \mathbf{r}_2' - \mathbf{r}_1'$ we have

$$\Delta\mathbf{r}' = \Delta\mathbf{r} + \tau(v(\mathbf{r}_2) - v(\mathbf{r}_1)). \tag{C2}$$

By expanding the velocity field $v(\mathbf{r}_2)$ around $\mathbf{r}_1$ we obtain

$$\Delta\mathbf{r}' = \Delta\mathbf{r} + \tau\Delta\mathbf{r}\cdot\boldsymbol{\nabla}v(\mathbf{r}_1). \tag{C3}$$

Therefore,

$$\Delta\mathbf{r} = \frac{\Delta\mathbf{r}' - \Delta\mathbf{r}}{\tau} = \Delta\mathbf{r}\cdot\boldsymbol{\nabla}v(\mathbf{r}_1), \tag{C4}$$

which provides the time rate of change in a Lagrangian frame of a small vector $\Delta\mathbf{r}$ as it moves anchored with the flow.

APPENDIX D: DIFFUSION OF DUMBBELLS

Consider a dumbbell diffusing in a fluid at constant temperature. We understand that this fluid is that portion of the fluid which is contained in a fluid particle with respect to the reference frame of the fluid particle and with the temperature corresponding to that fluid particle. For the sake of the discussion, though, we assume the fluid as infinite and at rest. We assume that each bead of the dumbbell is describing a diffusive overdamped motion governed by the following stochastic equations

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

$$d\mathbf{r}^2 = \frac{\mathbf{F}(\mathbf{r}^2 - \mathbf{r}^1)}{\zeta} + (2D_0)^{1/2} d\mathbf{W}^2, \tag{D1}$$

where $\mathbf{r}^1, \mathbf{r}^2$ are the positions of the first and second beads of the microscopic dumbbell, $\mathbf{F}(\mathbf{r}^1 - \mathbf{r}^2)$ is the force that bead $\mathbf{r}^2$ exerts on $\mathbf{r}^1$, and D_0 is the diffusion coefficient of the beads, given by the Stokes-Einstein relation $D_0 = k_B T/6\pi\eta a$, where a is the bead of radius a and η is the solvent shear viscosity. The vectorial independent increments of the Wiener process satisfy

$$d\mathbf{W}^\alpha d\mathbf{W}^\beta = \delta^{\alpha\beta}\mathbf{1}dt. \tag{D2}$$

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

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

$$d\mathbf{Q} = \frac{\mathbf{F}(\mathbf{Q})}{\zeta} + (2D_0)^{1/2}(d\mathbf{W}^1 - d\mathbf{W}^2),$$

$$= \frac{\mathbf{F}(\mathbf{Q})}{\zeta} + d\tilde{\mathbf{Q}}. \tag{D3}$$

In order to compute the diffusive motion of the center of mass of the dumbbells, we need

$$d\mathbf{R}\cdot d\mathbf{R} = D_0 dt, \tag{D4}$$

which corresponds to a diffusion coefficient $D_0/2$. The physical meaning of this is that the dumbbell is subject to *two* friction forces (one for each bead), and therefore the center of mass diffuses with *half* the diffusion coefficient of each bead. We also need to compute

$$d\tilde{\mathbf{Q}}\cdot d\tilde{\mathbf{Q}} = 4D_0 dt. \tag{D5}$$

This means that the average dumbbell elongation $\mathbf{Q}$ is subject to a random walk with a diffusion coefficient given by $2D_0$.

APPENDIX E: SMOOTHED PARTICLE DISCRETIZATION OF THE ADVECTION-DIFFUSION EQUATION

Consider the advection-diffusion equation for the concentration of a passive density $n(\mathbf{r},t)$ in a velocity field $\mathbf{v}(\mathbf{r},t)$,

$$\frac{\partial n}{\partial t} = -\boldsymbol{\nabla}\cdot n\mathbf{v} + \boldsymbol{\nabla}\cdot\frac{Tn}{\zeta}\boldsymbol{\nabla}\frac{\mu}{T}, \tag{E1}$$

where $\mu = \mu(n(\mathbf{r},t))$ is the chemical potential field and $T = T(\mathbf{r})$ is the temperature field. For a very dilute system, one can use the ideal gas form for the chemical potential $k_B T \ln n$. If we further assume an isothermal system, the above equation becomes

$$\frac{\partial n}{\partial t} = -\boldsymbol{\nabla}\cdot n\mathbf{v} + D\nabla^2 n, \tag{E2}$$

where $D = k_B T/\zeta$ is the diffusion coefficient and $\zeta = 6\pi\eta a$ is the friction coefficient of the beads of radius a with the solvent of shear viscosity η.

We write Eq. (E1) in the Lagrangian form by using the usual substantial derivative

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v}\cdot\boldsymbol{\nabla}, \tag{E3}$$

so we obtain

$$\frac{dn}{dt} = -n(\boldsymbol{\nabla}\cdot\mathbf{v}) + \boldsymbol{\nabla}\cdot\frac{Tn}{\zeta}\boldsymbol{\nabla}\frac{\mu}{T}, \tag{E4}$$

which expresses the time rate of change of the concentration field as we move with the flow field.

Our aim is to discretize Eq. (E4) on the fluid particles following the smoothed particle hydrodynamics philosophy. A discrete version of Eq. (E4) would read

$$\dot{n}_i = -n_i^d(\boldsymbol{\nabla}\cdot\mathbf{v})_i + \left(\boldsymbol{\nabla}\cdot\frac{Tn}{\zeta}\boldsymbol{\nabla}\frac{\mu}{T}\right)_i. \tag{E5}$$

Instead of working with the density n_i^d we prefer to work with $N_i = n_i/d_i$, the actual number of suspended particles in the fluid particle of volume d_i^{-1}. This variable evolves according to

$$\dot{N}_i = -N_i\frac{\dot{d}_i}{d_i} - \frac{n_i}{d_i}(\boldsymbol{\nabla}\cdot\mathbf{v})_i + \frac{1}{d_i}\left(\boldsymbol{\nabla}\cdot\frac{Tn}{\zeta}\boldsymbol{\nabla}\frac{\mu}{T}\right)_i. \tag{E6}$$

This equation is still a meaningless collection of symbols until we specify how the derivatives in the parenthesis are computed. The divergence of the velocity field $(\boldsymbol{\nabla}\cdot\mathbf{v})_i$ at the location of the ith fluid particle can be computed from Eq. (28). The final result can be written as

$$(\nabla\cdot\mathbf{v})_i = \frac{\dot{\mathcal{V}}_i}{\mathcal{V}_i} = -\frac{\dot{d}_i}{d_i}. \tag{E7}$$

The physical meaning of this equation is clear, the divergence of the velocity field is associated to the relative rate of change of the volume of the fluid particles, as expected. After substitution of Eq. (E7) into Eq. (E6) one obtains

$$\dot{N}_i = \frac{1}{d_i}\left(\nabla\cdot\frac{Tn}{\zeta}\nabla\frac{\mu}{T}\right)_i, \tag{E8}$$

and we observe that if the dynamics is given by the advection-diffusion equation (E1), then the rate of change of the number of suspended particles as we follow the fluid is entirely due to irreversible processes (governed by the transport coefficient ζ). This is consistent with our requirement that the reversible part of the dynamics for $\dot{N}_i$ is zero, as expressed in Eqs. (33).

We still have to provide an expression for the derivatives appearing in Eq. (E8). We follow here the interpolant method first proposed by Cleary and Monaghan [31]. As a preliminary, we introduce the isotropic function $F(r)$ through

$$\nabla W(r) = -\mathbf{r}F(r), \tag{E9}$$

which satisfies

$$\int d\mathbf{r}\mathbf{r}\cdots\mathbf{r}F(r) = 0, \tag{E10}$$

if the number of **r**'s is odd by isotropy. It also satisfies

$$\int d\mathbf{r}\mathbf{r}\mathbf{r}F(r) = \mathbf{1}, \tag{E11}$$

as can be proved from

$$\int d\mathbf{r}\mathbf{r}\nabla W(r) = -\mathbf{1}. \tag{E12}$$

This equation is obtained from a partial integration and the normalization of the weight function $W(r)$.

Now, consider the following integral:

$$\int d\mathbf{r}[B(\mathbf{r}')+B(\mathbf{r})][A(\mathbf{r}')-A(\mathbf{r})]F(|\mathbf{r}-\mathbf{r}'|), \tag{E13}$$

where $A(\mathbf{r})$ and $B(\mathbf{r})$ are arbitrary functions that change slowly on the scale of the range of $W(r)$ and $F(r)$. By Taylor expanding $A(\mathbf{r}'),B(\mathbf{r}')$ around **r**, neglecting terms of order higher than the second, and using Eqs. (E10) and (E11) we obtain that the above integral is given by $\nabla\cdot[B(\mathbf{r})\nabla A(\mathbf{r})]$, up to terms involving higher-order derivatives. The next step in SPH is to discretize the integral on the locations of the particles

$$\int d\mathbf{r}[B(\mathbf{r}_i)+B(\mathbf{r})][A(\mathbf{r}_i)-A(\mathbf{r})]F(|\mathbf{r}-\mathbf{r}_i|)$$
$$\approx\sum_j \frac{1}{d_j}[B(\mathbf{r}_i)+B(\mathbf{r}_j)][A(\mathbf{r}_i)-A(\mathbf{r}_j)]F(|\mathbf{r}_j-\mathbf{r}_i|). \tag{E14}$$

So finally, we obtain the following interpolant for computing the second derivatives at a particle location, i.e.,

$$\{\nabla\cdot[B(\mathbf{r})\nabla A(\mathbf{r})]\}_i \approx \sum_j \frac{1}{d_j}(B_i+B_j)A_{ij}F_{ij}, \tag{E15}$$

where $B_i = B(\mathbf{r}_i)$, $A_{ij} = A(\mathbf{r}_i) - A(\mathbf{r}_j)$, and $F_{ij} = F(|\mathbf{r}_j - \mathbf{r}_i|)$.

With this result (E15) inserted into Eq. (E8), we can readily obtain a discretized version of Eq. (E1) on the Lagrangian grid of moving fluid particles in the form

$$\dot{N}_i = \frac{1}{d_i}\left(\nabla\cdot\frac{Tn}{\zeta}\nabla\frac{\mu}{T}\right)_i = \sum_j \frac{F_{ij}}{d_j d_i}\left(\frac{T_i n_i}{\zeta}+\frac{T_j n_j}{\zeta}\right)\left(\frac{\mu_i}{T_i}-\frac{\mu_j}{T_j}\right). \tag{E16}$$

Note that this equation conserves the total number of suspended particles, $\Sigma_i \dot{N}_i = 0$.

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