A Physically-Based Fractional Diffusion Model for Semi-Dilute Suspensions of Rods in a Newtonian Fluid

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Abstract

The rheological behaviour of suspensions involving interacting (functionalized) rods remains nowadays incompletely understood, in particular with regard to the evolution of the elastic modulus with the applied frequency in small-amplitude oscillatory flows. In a previous work, we addressed this issue by assuming a fractional diffusion mechanism, however the approach followed was purely phenomenological. The present work revisits the topic from a physical viewpoint, with the aim of justifying the fractional nature of diffusion. After accomplishing this first objective, we explore by means of numerical experiments the consequences of the proposed fractional modelling approach in linear and non-linear rheology.

Keywords: Anomalous diffusion, Fractional diffusion, Fractional Brownian Motion, Fractional Fokker-Planck, Suspensions rheology

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1. Introduction

It is well known that the process-induced microstructure in short fibre composites and nano-composites determines the mechanical or functional properties of the final part. Thus, the development of accurate models and efficient computational solvers is crucial. Industrial applications usually involve semi-concentrated or concentrated short fibre suspensions in which inter-particle interactions occur. The latter have an additional impact on the development of fibre orientation.

We assume the suspension composed of rods (infinite aspect ratio ellipsoids) immersed into a Newtonian fluid. The kinematic of a single rod, whose orientation is defined by the unit vector $\mathbf{p}$, immersed in an unconfined flow assumed unperturbed by the rod presence and orientation, is given by the Jeffery's equation [13]

$$\dot{\mathbf{p}}^J = \nabla \mathbf{v} \cdot \mathbf{p} - \nabla \mathbf{v} : (\mathbf{p} \otimes \mathbf{p}) \mathbf{p}, \tag{1}$$

where $\nabla \mathbf{v}$ represents the velocity gradient assumed constant at the rod length scale.

For describing a suspension at the mesoscopic level, a probability density function – pdf – is introduced $\psi(\mathbf{p}, t)$, assumed in what follows and without loss of generality uniform in the physical space, justifying the fact of ignoring its dependence on the position $\mathbf{x}$. It represents the fraction of rods that at time t are oriented in direction $\mathbf{p}$ at each point $\mathbf{x}$. The pdf balance equation reads

$$\frac{\partial \psi}{\partial t} + \nabla_p (\dot{\mathbf{p}} \psi) = 0, \tag{2}$$

that when using Eq. (1) for expressing the rotary velocity $\dot{\mathbf{p}}$ results in the so-called Fokker-Planck equation.

In the case of dilute non-Brownian suspensions rods interaction can be neglected and the rod rotary velocity $\dot{\mathbf{p}}$ is given by Eq. (1), i.e. $\dot{\mathbf{p}} = \dot{\mathbf{p}}^J$. When Brownian effects are relevant, they can be described by introducing a diffusion mechanism, that results in

$$\dot{\mathbf{p}} = \dot{\mathbf{p}}^J + \dot{\mathbf{p}}^B, \tag{3}$$

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with the Brownian contribution $\dot{\mathbf{p}}^B$ given by

$$\dot{\mathbf{p}}^B = -\frac{D_r}{\psi}\nabla_p\psi. \tag{4}$$

For taking into account rods interaction in suspensions ranging from the semi-dilute to the semi-concentrated regimes, Folgar & Tucker assumed the diffusion coefficient scaling with the second invariant of the velocity gradient, $\dot{\gamma}$, according to $D_r = C_I\dot{\gamma}$, where C_I is the so-called interaction coefficient [10].

Macroscopic models result from considering the pdf moments [1, 2], most of them are based on the use of the second order one, the so-called orientation tensor $\mathbf{a}$, defined from

$$\mathbf{a} = \int \mathbf{p}\otimes\mathbf{p}\psi d\mathbf{p}, \tag{5}$$

that by taking its time derivative and substituting the expression of $\dot{\mathbf{p}}$ given by Eq. (3) results in the macroscopic orientation description

$$\dot{\mathbf{a}} = \nabla\mathbf{v}\cdot\mathbf{a} + \mathbf{a}\cdot(\nabla\mathbf{v})^T - 2\,\mathbf{A}^{clr} : \nabla\mathbf{v} - 6D_r\left(\mathbf{a} - \frac{\mathbf{I}}{3}\right), \tag{6}$$

where D_r is set to zero in absence of interactions and $\mathbf{A}^{clr}$ refers to an appropriate closure of the pdf fourth order moment [2] [8] [16] [21].

The Cauchy stress results

$$\boldsymbol{\sigma} = -P\mathbf{I} + \boldsymbol{\tau}, \tag{7}$$

where P is the isotropic pressure and $\boldsymbol{\tau}$ the extra-stress tensor given by [19]

$$\boldsymbol{\tau} = 2\eta\mathbf{D} + 2\eta N_p\,(\mathbf{D}:\mathbf{A}) + \beta D_r\left(\mathbf{a} - \frac{\mathbf{I}}{3}\right), \tag{8}$$

that involves the rheological parameters η, N_p and β.

Linear and nonlinear rheology of carbon nanotube suspensions was reported in many works, as for exemple [9, 22, 11, 4] to cite few. In [17] authors reported for functionalized CNTs suspensions a slope of around 0.6 in the storage modulus $G'(\omega)$ that they tried to justify from the standard modeling framework introduced in the previous section.

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As LVE involves small amplitude oscillations applied to an essentially isotropic suspension for which the linear closure relation of the fourth pdf moment becomes exact [2], in [17] authors derived the expressions of the shear rate of strain and stress, and from them, the storage and loss modules that write

$$G' = \beta D_r \frac{\lambda \mu \omega^2}{1 + \lambda^2 \omega^2}, \tag{9}$$

and

$$G'' = \omega \eta \left(1 + \frac{2}{15} N_p\right) + \beta D_r \frac{\mu \omega}{1 + \lambda^2 \omega^2}, \tag{10}$$

where $\lambda = \frac{1}{6D_r}$ and $\mu = \frac{1}{30D_r}$, and from with at low frequencies the storage modulus is expected scaling with the square of the frequency, showing a slope of two when using the usual logarithmic representation.

To recover the experimental behavior in [17] authors assumed that the diffusion coefficient scale with an adequate power of the frequency. This route is not really new, it was considered in dynamics for addressing the experimental findings from an adequate scaling of the damping with the frequency, however, as discussed by Crandall [5] such a route is not free of conceptual difficulties.

That purely phenomenological route does not allow to give a physical picture of the subjacent reality. In [17] authors advanced the possible existence of a sort of rod network induced by Van der Walls effects or by the CNTs functionalization. However these mechanics were totally speculative. Later, other mechanisms were postulated in order to explain this discrepancy between the predicted and measured storage modulus $G'(\omega)$, among them, the thermally-activated bending or the flow-induced bending in the case of non-straight CNTs [6][7].

Recently, in [3] authors adopted a more phenomenological viewpoint by considering a non-standard randomizing mechanism, i.e., an anomalous diffusion modelled using fractional derivatives. Despite the fact of surprisingly obtaining an excellent agreement between the predictions and the experimental measurements in linear viscoelasticity and the relaxation after a step strain, again, no physical mechanisms were proposed for justifying the considered anomalous diffusion.

The main aim of the present work is to revisit the framework related to the fractional diffusion, elaborating a physical picture able to justify the modeling choices, and then extend such framework to nonlinear viscoelasticity, never until now carried out.

2. Fractional modelling

Anomalous diffusion is often observed in complex fluids [12], and this justifies the use of non-integer or fractional derivatives in the associated mathematical models.

In semi-concentrated suspensions, the inter-particle interactions could be at the origin of anomalous diffusion and fractional modelling may thus be relevant as discussed below.

2.1. Fractional Brownian motion

As discussed in [14, 18] fractional diffusion models can be derived from continuous time random walks – CTRW –, that for long rests describe subdiffusion.

We consider an entangled suspension in which particles occupy the equilibrium position in absence of thermal effects, by only considering their interactions via a variety of possible potentials. Now, the thermal effects are reintroduced, a fact that results in the bombardement of the different particles from the molecules of the surrounding suspending fluid. Even if each particle tends to move because the impact they suffer, the surrounding particles tend to resist their displacement through a mean field potential $\mathcal{V}(\mathbf{x})$. Thus the forces balance for each particle i, $i = 1, \cdots, \mathcal{P}$, involves the force transmitted by the bombardement of the molecules composing the suspending fluid $\mathbf{f}_i^b$, the viscous drag $\mathbf{f}_i^d = -\xi \dot{\mathbf{x}}_i$ and the internal force that can derived from the gradient mean field potential $\mathcal{V}(\mathbf{x})$, $\mathbf{f}^e(\mathbf{x}) = -\nabla \mathcal{V}(\mathbf{x})$, that is assumed be modeled from a linear elastic spring in the limit of small system transformations, $\mathbf{f}_i^s = -\kappa(\mathbf{x}_i - \mathbf{x}_i^r)$, where $\mathbf{x}_i^r$ is the reference position that the particule should occupy for ensuring the equilibrium in absence of thermal effects because of the

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presence of the neighbor particles (here represented by a mean field). Thus, balance for each particle in absence of inertia effects, $\mathbf{f}_i^b + \mathbf{f}_i^d + \mathbf{f}_i^s = \mathbf{0}$, leads to the scholastic equation:

$$\xi \dot{\mathbf{x}}_i(t) + \kappa(\mathbf{x}_i(t) - \mathbf{x}_i^r(t)) = \mathbf{f}_b^s(t), \tag{11}$$

from which the particles position can be easily updated.

We consider a population of $\mathcal{P} = 2000$ particles, initially located at position $x = 0$ (for the sake of simplicity and without loss of generality we consider a one-dimensional system). All the parameters were set to a unit value (even the time step used for integrating Eq. (11)) for obtaining directly the evolution of the mean-squared displacement with the elapsed time. The bombardement was modeled from a normal distribution with zero mean and unit standard deviation. At each time t we compute the covariance of particles position and compare it with the expression giving the covariance of a fractional Brownian motion – fBm – $\mathbf{X}^H(t)$ ($H \in [0,1]$ refers to the Husrt index and $\mathbf{X}$ the vector with entries x_i, $i = 1, \cdots, \mathcal{P}$) generated by a continuous-time Gaussian process that has null expectation at any time:

$$E(t,s) = E(\mathbf{X}_H(t), \mathbf{X}_H(s)) = \frac{1}{2}\left(t^{2H} + s^{2H} - (t-s)^{2H}\right), \tag{12}$$

for $0 \leq s \leq t$. $H = 0.5$ corresponds with the standard Brownian motion, $H < 0.5$ with processes positively correlated and $H > 0.5$ with the ones negatively correlated. It can be seen that for $H = 0.5$, $E(t,s) = s$ and that $E(t,t) = t$ characterizing standard Brownian motion.

When considering $\kappa = 0$ or equivalently $\mathbf{x}_i^r(t) = \mathbf{x}_i(t)$, we obtain from our discrete simulation $E(t,s) = s$ and $T(t,t) = t$ proving that the system evolves from a standard Brownian motion. However, by keeping $\kappa = 1$ constant and considering $\mathbf{x}_i^r(t) = \mathbf{x}_i(t - \Delta t)$, we obtain $H = 0.4$. When introducing a larger "memory", e.g. $\mathbf{x}_i^r(t) = \mathbf{x}_i(t - 2\Delta t)$ the value of H was as expected lower, $H = 0.36$. Thus the diffusion process perfectly fits with a fractional Brownian motion independently of the considered times t and s involved in the covariance function and moreover as $E(t,t)$ reduced to t^{2H} we can associate the fractional

Brownian motion with a fractional diffusion characterized by $\alpha = 2H$.

Figure 1 compares the histograms at $t = 10$ when considering one million of particles, for $\kappa = 0$ (Brownian motion) and $\kappa = 1$ (fractional Brownian motion) related to a fBm with $H = 0.4$ ($\alpha = 0.8$). When considering fractional Brownian motion a net sub-diffusion is noticed, but more importantly, the fBm does not correspond with a Brownian one with a smaller diffusion coefficient.

2.2. Fractional diffusion

Within the standard modeling framework discussed in the previous section it was assumed that randomizing mechanisms are described by $\dot{\mathbf{p}}^B$ given in Eq. (4). Its fractional counterpart proposed in [3] reads

$$_{t_0}\mathbb{D}_t^\alpha \mathbf{p}^B = -D_r \frac{\frac{\partial \psi}{\partial \mathbf{p}}}{\psi}, \tag{13}$$

where the left Riemann-Liouville fractional time derivative $_{t_0}\mathbb{D}_t^\alpha$, defined from

$$_{t_0}\mathbb{D}_t^\alpha f(t) = \frac{d^m}{dt^m} \left\{ \frac{1}{\Gamma(m-\alpha)} \int_{t_0}^t (t-\tau)^{m-\alpha-1} f(\tau) d\tau \right\}, \tag{14}$$

involves the non-integer parameter α, with $m - 1 < \alpha < m$, and $\alpha \in (0,1)$. It is important to note that the left Riemann-Liouville fractional derivative of a constant is in general not zero. The interested reader can refer to [15] [20] for a complete description of fractional calculus.

In what follows, and without loss of generality, we consider only diffusive effects, i.e. the purely viscous flow induced contribution on the rotary velocity $\dot{\mathbf{p}}^J$ is not taken into account on the discussion that follows, being always expressed by the Jeffery equation. Thus, the rotary velocity be written taking into account (13) as

$$\dot{\mathbf{p}}^B \equiv \frac{d\mathbf{p}^B}{dt} =_{t_0} \mathbb{D}_t^{1-\alpha} \left(_{t_0}\mathbb{D}_t^\alpha \mathbf{p}^B \right) =_{t_0} \mathbb{D}_t^{1-\alpha} \left(-D_r \frac{\frac{\partial \psi}{\partial \mathbf{p}}}{\psi} \right), \tag{15}$$

in which it is assumed that the index-rule works for derivation composition, i.e.

$$_{t_0}\mathbb{D}_t^\alpha \left(_{t_0}\mathbb{D}_t^\beta f(t) \right) =_{t_0} \mathbb{D}_t^{\alpha+\beta} f(t), \tag{16}$$
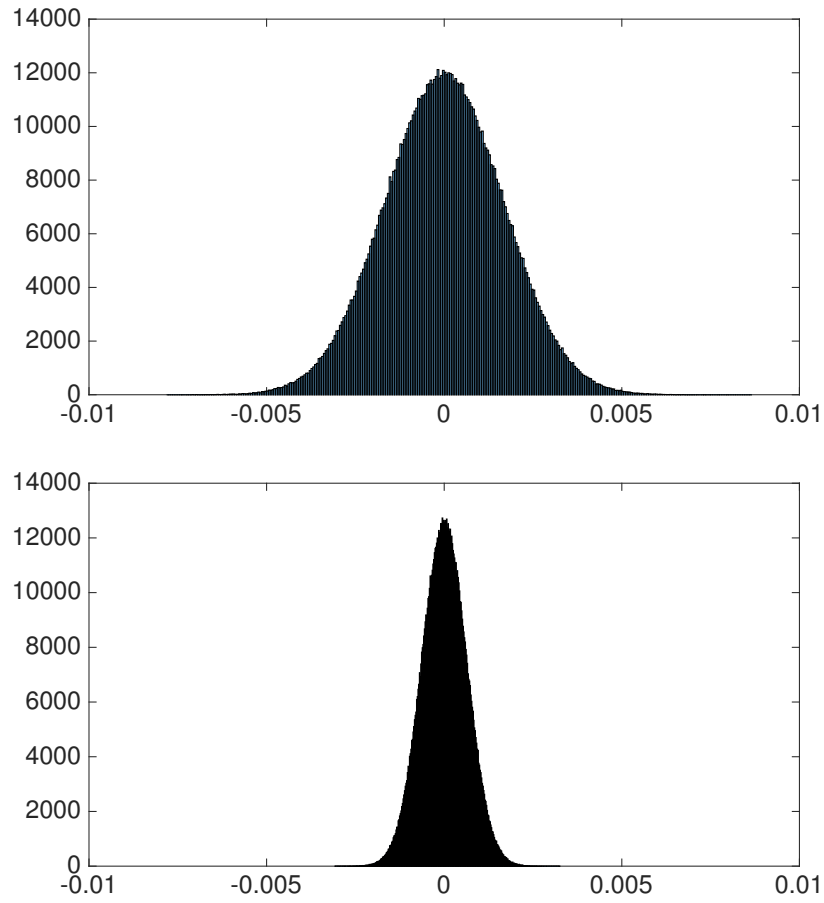
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Figure 1: Histograms (number of particles at the different positions) at $t = 10$ for $\kappa = 0$ (top) and $\kappa = 1$ (bottom).

with $\alpha, \beta \in (0,1)$ and $\alpha \neq \beta$. However the conditions ensuring that index-rule applies in derivation composition are quite particular [20, 15].

If we assume for a while that the conditions ensuring that the index-rule works are fulfilled, by introducing (13) into the Fokker-Planck equation (2) and taking the time derivative of order $\alpha - 1$ of both members results in the fractional Fokker-Planck equation

$$_{t_0}\mathbb{D}_t^\alpha \psi - \psi_0 \, {}_{t_0}\mathbb{D}_t^\alpha 1 = \nabla_p \left(D_r \nabla_p \psi \right), \tag{17}$$

where ψ_0 is the initial condition and where the facts that index rule applies and that the fractional derivative of a constant does not vanish have been taken into account.

In the micro mechanical model introduced in the previous section we considered a very short memory effect. In order to limit the incidence of the initial condition we consider the fractional time derivative with $t_0 = -\infty$, that leads from one side to $_{-\infty}\mathbb{D}_t^\alpha 1 = 0$ and from the other ensures that the index-rule of derivation compositions applies. The latter is a consequence of the fact that the extra-terms involved in the derivation composition involve $(t-t_0)^{-\alpha-m}$ [20, 15], with $0 < \alpha < 1$ and $m = 1$, then it vanishes as soon as $t_0 \to \infty$ (since $-\alpha - 1 < -1$), and the index-rule in the derivation composition applies.

Thus, the fractional Fokker-Planck equation (2) reduces to

$$_{-\infty}\mathbb{D}_t^\alpha \psi = \nabla_p \left(D_r \nabla_p \psi \right), \tag{18}$$

whose mean-squared angular displacement of the random process related to the pdf ψ scales with t^α, reducing to standard diffusion for $\alpha = 1$.

In order to prove the equivalence between the fractional Brownian motion and the fractional Fokker-Planck equation we compare in Fig. 2 the solution of models (11) and (18) for $\alpha = 0.72$ and $\alpha = 1$ at two time instants. It can be noticed that fractional Brownian motion related to the microscopic model and the solution of the fractional Fokker-Planck equation generate almost the same solution.
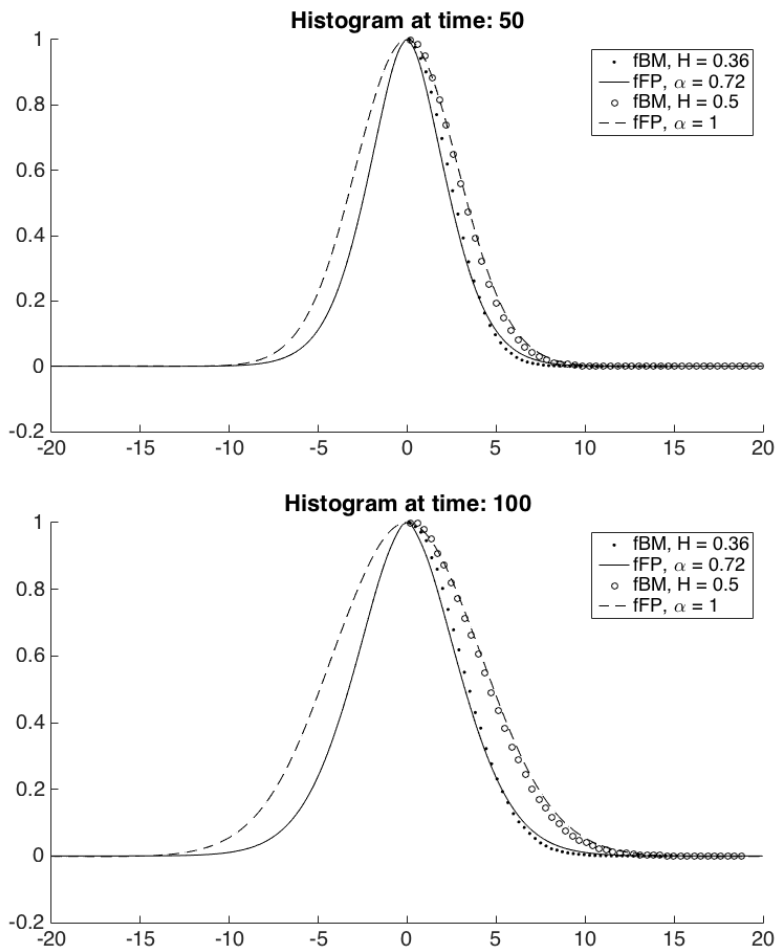
Figure 2: Comparing solutions of Eqs. (11) and (18) for $\alpha = 0.72$ and $\alpha = 1$ at times $t = 50$ (top) and $t = 100$ (bottom).

Now, once a physical picture has been associated to the fractional diffusion occurring in semi-concentrated suspensions of CNTs, and after having proved that such a mechanism allows explaining the frequency dependence of the storage modulus is small amplitude oscillatory flows or in the stress relation of a step strain [3], we consider in the next section the impact that such a fractional diffusion in nonlinear rheology.

3. Macroscopic modelling

As detailed in [3], taking the time derivative of the second order orientation tensor definition (5) and taking into account the expression of the rotary velocity $\dot{\mathbf{p}} = \dot{\mathbf{p}}^J + \dot{\mathbf{p}}^B$, a fractional evolution equation for the second-order orientation tensor results:

$$\frac{d\mathbf{a}}{dt} = \dot{\mathbf{a}}|^J - 6D_{r\ -\infty}\mathbb{D}_t^{1-\alpha}\left(\mathbf{a} - \frac{\mathbf{I}}{3}\right), \tag{19}$$

with $\dot{\mathbf{a}}|^J = \nabla\mathbf{v}\cdot\mathbf{a} + \mathbf{a}\cdot(\nabla\mathbf{v})^T - 2\,\mathbf{A}^{clr}:\nabla\mathbf{v}$.

3.1. Linear viscoelasticity

It was shown in [3] that the fractional orientation model (19) predicts the following expressions of the storage moduli:

$$G' = \beta D_r \frac{\lambda\mu\omega^2 + \mu\nu\omega^{2-\alpha}}{\chi^2\omega^{2(1-\alpha)} + (\omega\lambda + \nu\omega^{1-\alpha})^2}, \tag{20}$$

with $i^{1-\alpha} = \chi + i\nu$. At small frequencies, the predicted storage modulus G' scales as ω^α. Thus, it suffices to select $\alpha = 0.6$ to describe the experimental behaviour observed for suspensions of functionalized CNTs, reported in [17]. It was proved that this choice allows also a excelling fitting of the stress relaxation after a step strain.

3.2. Nonlinear viscoelasticity

In order to evaluate the effect of the derivative order α, we solved the same fractional model in a 2D simple shear flow (assuming without loss of generality

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planar orientation) expressed by the generic velocity gradient

$$\nabla \mathbf{v} = \begin{pmatrix} 0 & \dot{\gamma} \\ 0 & 0 \end{pmatrix}, \tag{21}$$

for $\dot{\gamma} = 1$.

For the numerical discretization of the fractional orientation equation (19), we proceed as follows. The discrete version of the Grünwald-Letnikov formula [15] [20] for the fractional derivative of order α of a function $f(t)$, $t \in [a, t]$, reads:

$$_a\mathbb{D}_t^\xi f(t) = \frac{1}{h^\xi} \sum_{m=0}^{\frac{t-a}{h}} (-1)^m g_m^\xi f(t - mh), \tag{22}$$

where h is the discrete time step and g_m^ξ is given by

$$g_m^\xi = \frac{\Gamma(\xi + 1)}{m!\, \Gamma(\xi + 1 - m)}. \tag{23}$$

Here, $\Gamma(\cdot)$ denotes the gamma function.

Expression (23) is not suitable for large values of m, for example when considering fine dicretizations, in view of the numerical issues related to the calculation of factorial and gamma functions. Thus, is is preferable to exploit the equivalent form

$$\begin{cases} \text{if } m = 0, \quad g_0^\xi = 1 \\ \text{if } m > 0, \quad g_m^\xi = g_{m-1}^\xi \dfrac{\xi - m + 1}{m} \end{cases} \tag{24}$$

With a semi-implicit quadratic closure, the evolution equation (19) reads at time step n using the Grünwald-Letnikov formula:

$$\frac{\mathbf{a}^n - \mathbf{a}^{n-1}}{h} = \nabla \mathbf{v} \cdot \mathbf{a}^n + \mathbf{a}^n \cdot (\nabla \mathbf{v})^T - 2(\mathbf{a}^{n-1} : \mathbf{D})\mathbf{a}^n -$$

$$6Dr \frac{1}{h^{1-\alpha}} \sum_{m=0}^{n} (-1)^m g_m^{1-\alpha} \left(\mathbf{a}^{n-m} - \frac{\mathbf{I}}{2} \right), \tag{25}$$

which accounts for the history of the orientation tensor $\mathbf{a}$ weighted by $g_m^{1-\alpha}$.
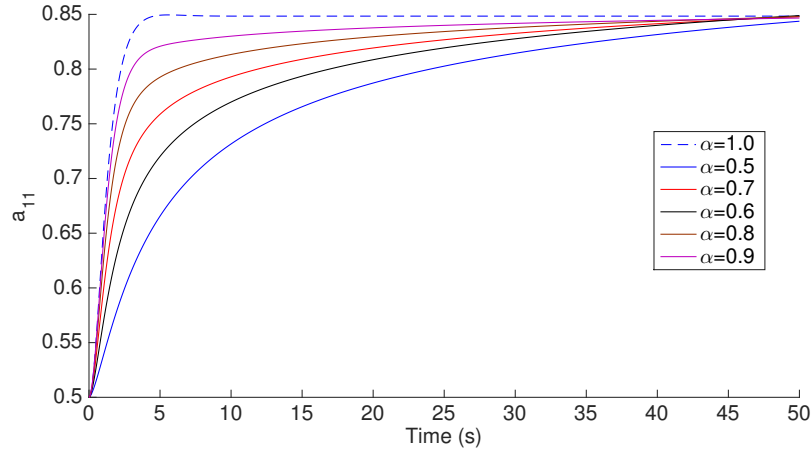
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Figure 3: Fractional model: evolution of $\mathbf{a}_{11}$ in simple shear flow for various values of α.

3.3. Numerical results

We consider the flow kinematics expressed by (21) with $\dot{\gamma} = 1$ and $\alpha = 1, 0.9, 0.8, 0.7, 0.6, 0.5$, while adjusting the value of the diffusion coefficient to reach almost the same solution at $t = 50$ in all cases. Figures 3 and 4 compare the time evolution $\mathbf{a}_{11}(t)$ and $\mathbf{a}_{12}(t)$, respectively (for the sake of clarity Figs. 5 and 6 show similar results that Figs. 3 and 4 but using a logarithmic scale). We note that the overshoot of $\mathbf{a}_{12}$ decreases when α decreases, being almost suppressed for $\alpha = 0.5$.

Figures 3 and 4 show that values of α near 0.7 induce a significant delay in the orientation process while the shear stress overshoot (related to $\mathbf{a}_{12}$) is significantly reduced but not totally suppressed. The same trends have been reported by Wang el al. [23], where the authors modified diffusion mechanisms using the RSC (Reduced Strain Closure) in order to delay the orientation process.
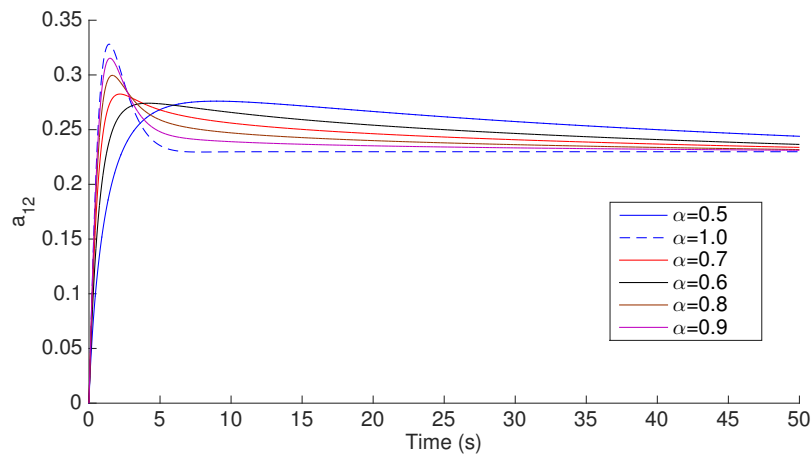
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Figure 4: Fractional model: evolution of $\mathbf{a}_{12}$ in simple shear flow for various values of α.
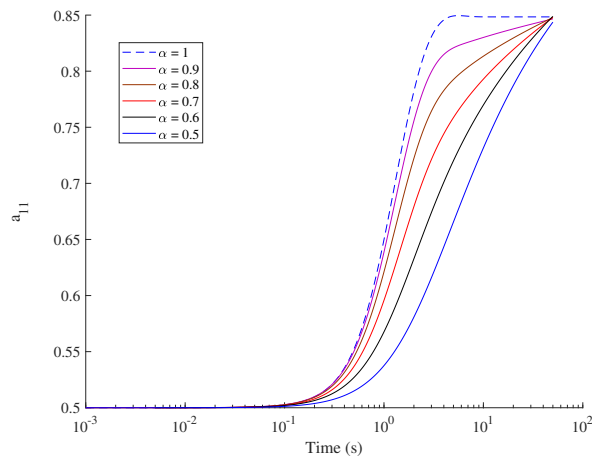

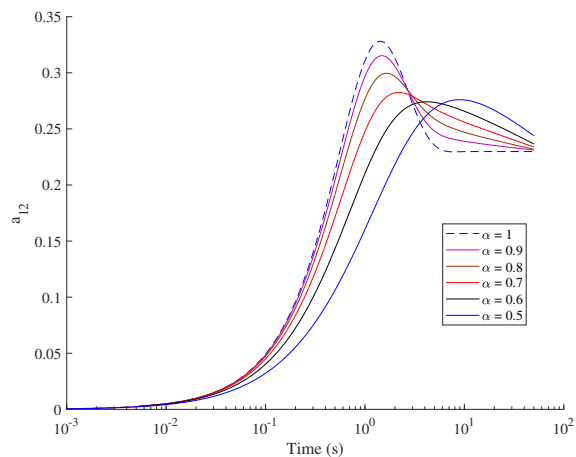Figure 5: Fractional model: evolution of $\mathbf{a}_{11}$ in simple shear flow for various values of α (log scale).

Figure 6: Fractional model: evolution of $\mathbf{a}_{12}$ in simple shear flow for various values of α (log scale).

4. Discussion and conclusions

In our former works we proved that the introduction of a fractional diffusion into the equation governing the evolution of the orientation of a suspension of CNTs allowed a perfect fitting of linear viscoelastic data. However at that time we did not propose any physical mechanisms associated to such a fractional behavior. In the present paper, to enhance the physical understanding, we started considering a suspension of particles, each of them subjected to the bombardement coming from the neighbor molecules of solvent, a viscous drag and an elastic term related to the interaction with neighboring particles.

The stochastic inertia-free simulation proved that the mean square displacement does not scale with the time, but with a power of it lower than one. The analysis of the covariance reveals that the motion can be assimilated to a fractional Brownian motion, that allowed us associating such a motion with the solution of a fractional Fokker-Planck diffusion equation. The numerical experiments confirm an excellent agreement between both solutions.

From this analysis, we finally concluded on the pertinence of using a frac-

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tional diffusion mechanism associated within the fractional Fokker-Planck equation, as successfully considered in our former works. Finally we extended the use of such a fractional diffusion in nonlinear flow regimes, and proved that when considering it, the kinematics of the orientation changes significantly, leading even to the suppression of the orientation overshoots characteristic of standard orientation models. Thus, fractional diffusion could offer a flexibility when modeling concentrated suspensions.

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