DESCRIBING ELASTICITY IN CONCENTRATED SUSPENSIONS OF CNT INVOLVING AGGREGATES

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Abstract

Suspensions involving nanoparticles are widely used in the development of engineered materials. These particles allow changing both the properties and the behavior of these materials. CNTs suspensions present different behaviours depending on their concentrations. For dilute concentrations, microscopic, mesoscopic and macroscopic descriptions have been well applied to describe the rheology of these suspensions. When the suspensions become too concentrated, fiber-fiber interactions occur and richer microstructures can be observed. It is in this case when the difficulties appear. Kinetic theory is a useful micro-to-macro approach for solving the flow of such kind of suspensions as it allows including the microstructure characteristics at the macroscale without a significant loss of information. However, in order to represent well experimental data, numerous physics have still to be introduced in our model at the micro-scale.

In this work, we focus on the modeling of the aggregates elasticity in concentrated suspensions of CNTs. Establish a micro-mechanical approach taking into account the clusters elastic effects constitutes the main contribution of the present work.

1. Introduction

CNTs suspensions present different behaviours depending on their concentrations. For dilute concentrations, the motion and orientation of each CNT that moves with the suspending fluid is assumed decoupled from the others according to the Jefferys equation [9]. The representative population can involve too many fibers, and in that case the computational efforts to track the population is unaffordable. Thus, the simple and well-defined physics must be sacrificed in order to derive coarser descriptions.

Kinetic theory approaches [4] [10] describe such systems at the mesoscopic scale. Their main advantage is their capability to address macroscopic systems, while keeping the fine physics through a number of conformational coordinates introduced for describing the microstructure and its time evolution. At this mesoscopic scale, the microstructure is defined from a distribution function that depends on the physical space, the time and a number of conformational coordinates. The moments of this distribution constitutes a coarser description in general used in macroscopic modeling [3]. At the macroscopic scale the equations governing the time evolution of these moments usually involve closure approximations whose impact in the results is unpredictable [5] [7].

When the concentration increases, fiber-fiber interactions occur leading to the formation of clusters of entangled particles and appropriate models addressing these intense interactions must be considered, as for example the one proposed in [8]. In the extreme case, a sort of clusters composed of entangled rods are observed [11] [12]. When the suspension flows those clusters seem animated of almost rigid motions.

Clusters can be viewed as entangled aggregates of N rods, with these rods consisting of a rigid segment joining the two beads located at the segment ends where it is assumed that forces apply. In what follows, we consider the cluster idealization depicted in Fig.1

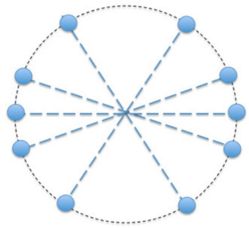

Figure 1. Star representation of a cluster composed of rigid rods.

The first force applied, $\mathbf{F}_i^H$, is the hydrodynamic force due to the flow, which is proportional to the difference of velocity between the fluid and the bead,

$$\mathbf{F}_i^H = \xi \left(\nabla \mathbf{v} \cdot \mathbf{p}_i \, L - \dot{\mathbf{p}}_i \, L \right) \tag{1}$$

where ξ is the friction coefficient and $\mathbf{v}$ the flow velocity field unperturbed by the cluster presence.

The second force considered, $\mathbf{F}_i^C$, is related to the rods entanglements. This force is assumed scaling with the difference between the rigid motion velocity, the one that the bead would have if the cluster would be rigid, and the real one [6] [2].

$$\mathbf{F}_i^C = \mu \left(\mathbf{W} \cdot \mathbf{p}_i \, L - \dot{\mathbf{p}}_i \, L \right) \tag{2}$$

with

$$\mathbf{W} = \mathbf{\Omega} + \mathbf{D} \cdot \mathbf{a} - \mathbf{a} \cdot \mathbf{D} \tag{3}$$

where $\mathbf{D}$ and $\mathbf{\Omega}$ are respectively the symmetric and skew-symmetric components of the velocity gradient $\nabla \mathbf{v}$ and $\mathbf{a}$ writes

$$\mathbf{a} = \frac{1}{N} \sum_{i=1}^{N} \mathbf{p}_i \otimes \mathbf{p}_i \tag{4}$$

By neglecting inertia effects [6] [2], the resulting moment for the whole cluster must vanish, so the rod rotary velocity results

$$\dot{\mathbf{p}}_i = \frac{\xi}{\xi + \mu} \nabla \mathbf{v} \cdot \mathbf{p}_i - \frac{\xi}{\xi + \mu} \left(\mathbf{D} : (\mathbf{p}_i \otimes \mathbf{p}_i) \right) \, \mathbf{p}_i + \frac{\mu}{\xi + \mu} \mathbf{W} \cdot \mathbf{p}_i =$$

$$= \frac{\xi}{\xi+\mu}\,\dot{\mathbf{p}}_i^J + \frac{\mu}{\xi+\mu}\,\mathbf{W}\cdot\mathbf{p}_i = \frac{\xi}{\xi+\mu}\,\dot{\mathbf{p}}_i^J + \frac{\mu}{\xi+\mu}\,\dot{\mathbf{p}}_i^C \tag{5}$$

where $\dot{\mathbf{p}}_i^J$ represents the hydrodynamic contribution in absence of rod-rod interactions (dilute regime described by the Jeffery's equation) and $\dot{\mathbf{p}}_i^C$ the one coming from the rods entanglements that results in a rigid-like cluster kinematics.

2. Introducing elastic effects

Clusters immersed in a flowing suspension experience two types of transformations, a rigid-like one associated with rigid motions and a second one implying the cluster stretching, both considered until now purely viscous. Therefore, it cannot account for the elastic component evidenced during classical rheological experiments on such suspensions [12]. To account for this elasticity, a first alternative is described in [2], where a elastic mechanism has been introduced at the aggregates scale. This phenomenological model is described below and will be compared with another model derived from micromechanics.

When the cluster conformation is described from the second order moment $\mathbf{a}$ of its orientation distribution ψ, the simplest way of quantifying stretching is by evaluating its eigenvalues change. In what follows we consider that clusters try to recover a configuration that combines the recent ones by a sort of fading-memory but only in what concerns the cluster stretching, that is, the memory does not concerns rigid motions.

It is assumed the orientation tensor $\mathbf{a}_\tau$ known at times $\tau \leq t$. Tensor $\mathbf{a}_\tau$ can be diagonalized according to

$$\mathbf{a}_\tau = \mathbf{R}_\tau^T \cdot \mathbf{\Lambda}_\tau \cdot \mathbf{R}_\tau \tag{6}$$

The reference configuration $\mathbf{\Lambda}_t^r$ that the cluster try to recover at time t reads

$$\mathbf{\Lambda}_t^r = \int_0^t m(t-\tau)\,\mathbf{\Lambda}_\tau\,d\tau \tag{7}$$

where the memory function $m(t-\tau)$ decreases as $t-\tau$ increases, with $m(t-\tau) = 0$ for $t-\tau \geq \theta$ and

$$\int_0^t m(t-\tau)\,d\tau = 1 \tag{8}$$

As soon as the reference configuration at time t, $\mathbf{\Lambda}_t^r$, is available, the reference second order moment at time t, $\mathbf{a}_t^r$, can be obtained by applying

$$\mathbf{a}_t^r = \mathbf{R}_t^T \cdot \mathbf{\Lambda}_t^r \cdot \mathbf{R}_t \tag{9}$$

If the characteristic time of the elastic recover is $\mathcal{T}$, then the equation governing the evolution of the second order tensor reads

$$\dot{\mathbf{a}} = \frac{\xi}{\xi+\mu}\,\dot{\mathbf{a}}^J + \frac{\mu}{\xi+\mu}\,\dot{\mathbf{a}}^C + \frac{\mathbf{a}^r - \mathbf{a}}{\mathcal{T}} \tag{10}$$

Memory effects disappear when θ vanishes. In this case the memory function approaches the Dirac's delta distribution $m(t-\tau) = \delta(t-\tau)$. Thus the reference configuration corresponds to the present one, i.e. $\mathbf{a}_t^r = \mathbf{a}_t$, implying the cancellation of the last term.

3. Towards a micro-mechanical approach

At the microscale, observations show that, during a simple shear flow, the cluster rotates with the flow and stretch. When the flow stops stretching relaxes a reference configuration is recovered and the reference conformation is built by considering a fading memory function, $m(t-\tau)$, that takes into account the deformation history experienced by the cluster. This relaxation mechanism depends on the stretching duration. Indeed, if the aggregate has undergone a short-time deformation, it will come back to its initial conformation. However, if the deformation state has been prolonged, the cluster will experience internal reconfigurations and will not come back to its initial conformation but to one close to the deformed state.

Based on the characteristics of the behaviour of the cluster, it seem suitable to propose an elasticity force applied at each bead of each rod of the cluster. This new force represents the elastic interaction forces like a sort of springs between the rods inside the cluster. The second order derivative is proposed in order to obtain a parabolic distribution of this interaction forces, so one rod could have compression applied in one side and traction applied in the other.

$$\mathbf{F}_i^E = \chi^E \cdot \mathbf{n}_i = \left(\int_0^t k \, \frac{\partial^2 \dot{\mathbf{p}}_i}{\partial \mathbf{p}_i^2} \, m(t-\tau) \, d\tau \right) \cdot \mathbf{n}_i \tag{11}$$

where k is the rigidity of the cluster and $\mathbf{n}_i$ is the unit vector perpendicular to the orientation $\mathbf{p}_i$ of each rod. Adding all the forces it results,

$$\mathbf{F}_i = \mathbf{F}_i^H + \mathbf{F}_i^C + \mathbf{F}_i^E = L\left((\xi \, \nabla\mathbf{v} + \mu \, \mathbf{W}) \cdot \mathbf{p}_i - (\xi + \mu) \, \dot{\mathbf{p}}_i\right) + \chi^E \cdot \mathbf{n}_i \tag{12}$$

By neglecting inertia effects, the resulting moment for the whole cluster must vanish, so the only possibility is that the resulting force $\mathbf{F}_i$ acts along $\mathbf{p}_i$, that is $\mathbf{F}_i = \lambda \mathbf{p}_i$. Thus proceeding as in [6] [2] we obtain,

$$\dot{\mathbf{p}}_i = \frac{\xi}{\xi+\mu} \, \nabla\mathbf{v} \cdot \mathbf{p}_i - \frac{\xi}{\xi+\mu} \left(\mathbf{D} : (\mathbf{p}_i \otimes \mathbf{p}_i)\right) \, \mathbf{p}_i + \frac{\mu}{\xi+\mu} \, \mathbf{W} \cdot \mathbf{p}_i + \frac{1}{\xi+\mu} \, \chi^E \cdot \mathbf{n}_i =$$

$$= \frac{\xi}{\xi+\mu} \, \dot{\mathbf{p}}_i^J + \frac{\mu}{\xi+\mu} \, \dot{\mathbf{p}}_i^C + \frac{1}{\xi+\mu} \, \dot{\mathbf{p}}_i^E \tag{13}$$

where $\dot{\mathbf{p}}_i^E$ is the contribution due to the deformation history experienced by the cluster. Notice that the elastic term will not depend on L because it is assumed that the rigidity constant k takes into account the length L of the road. Note that the second order partial derivative of the rotary velocity of the rod $\dot{\mathbf{p}}_i$ involves the fourth order partial derivative. In order to close the model we only consider the Jeffery contribution in the rotary velocity involved in the elastic effects.

Until now, we have defined the elasticity force applied perpendicular to the rod, in the direction named $\mathbf{n}$. In order to obtain an exact closure relation it seems suitable to express the elasticity term in the direction of the fibers $\mathbf{p}$.

$$\mathbf{F}_i^E = \chi^E \cdot \mathbf{n}_i = \left(\int_0^t k \, \frac{\partial^2 \dot{\mathbf{p}}_i}{\partial \mathbf{p}_i^2} \, m(t-\tau) \, d\tau \right) \cdot \mathbf{n}_i \tag{14}$$

with $\dot{\mathbf{p}}_i = \frac{\xi}{\xi+\mu}\,\dot{\mathbf{p}}_i{}^J$. If we multiply $\dot{\mathbf{p}}_i{}^J$ by $\mathbf{n}$ we obtain $\dot{\theta}_i^J$. Notice that the first term, which the skew-symmetric component of the gradient of velocity tensor, is also void. So we have:

$$\dot{\theta}_i = \frac{\xi}{\xi+\mu}\,\dot{\theta}_i^J = \frac{\xi}{\xi+\mu}\,(\mathbf{n}_i{}^T \cdot \mathbf{D} \cdot \mathbf{p}_i) = \frac{\xi}{\xi+\mu}\,\mathbf{D} : (\mathbf{p}_i \otimes \mathbf{n}_i) \tag{15}$$

and we proceed in order to obtain the second order partial derivative term from Eq. (14)

$$\frac{\partial \dot{\theta}_i}{\partial \theta_i} = \frac{\xi}{\xi+\mu}\,\mathbf{D} : (\mathbf{n}_i \otimes \mathbf{n}_i + \mathbf{p}_i \otimes \mathbf{p}_i) \tag{16}$$

$$\frac{\partial^2 \dot{\theta}_i}{\partial \theta_i^2} = \frac{\xi}{\xi+\mu}\,\mathbf{D} : (-\mathbf{p}_i \otimes \mathbf{n}_i - \mathbf{n}_i \otimes \mathbf{p}_i - \mathbf{n}_i \otimes \mathbf{p}_i - \mathbf{p}_i \otimes \mathbf{n}_i) = \frac{\xi}{\xi+\mu}\,\left(-2\mathbf{D} : (\mathbf{p}_i \otimes \mathbf{n}_i + \mathbf{n}_i \otimes \mathbf{p}_i)\right) \tag{17}$$

It has been obtained the elastic force expressed in the direction $\mathbf{p}$ as

$$\mathbf{F}_i^E = \frac{\xi}{\xi+\mu} \cdot k\,\left(-2\mathbf{D} : (\mathbf{p}_i \otimes \mathbf{n}_i + \mathbf{n}_i \otimes \mathbf{p}_i)\right) \cdot \mathbf{n}_i = -4k \cdot \frac{\xi}{\xi+\mu}\,((\mathbf{n}_i \otimes \mathbf{n}_i) \cdot \mathbf{D}) \cdot \mathbf{p}_i \tag{18}$$

Now, the next step is to express the deformation history, in the direction $\mathbf{p}$ of the present time. For this purpose we will multiply the elastic term with a rotation matrix. So we obtain,

$$\mathbf{F}_i^E = -4k \cdot \frac{\xi}{\xi+\mu}\,(\mathbf{n}_i \otimes \mathbf{n}_i)\left(\int_0^t \mathbf{Q}(\theta(\tau)) \cdot \mathbf{D} \cdot \mathbf{Q}^T(\theta(\tau))\, m(t-\tau)\, d\tau\right) \cdot \mathbf{p}_i \tag{19}$$

if we rename the term in brackets as $\widetilde{\mathbf{D}}$ and we proceed as in [6] [2] we finally obtain,

$$\dot{\mathbf{p}}_i = \frac{\xi}{\xi+\mu}\,\dot{\mathbf{p}}_i^J + \frac{\mu}{\xi+\mu}\,\dot{\mathbf{p}}_i^C - 4k \cdot \frac{\xi}{(\xi+\mu)^2}\,(\mathbf{I} - (\mathbf{p}_i \otimes \mathbf{p}_i)) \cdot \widetilde{\mathbf{D}} \cdot \mathbf{p}_i \tag{20}$$

Starting from the microscopic description obtained before, we can now derive a mesoscopic description characterized by the orientation distribution function $\psi(\mathbf{x}, t, \mathbf{p})$ and its associated tensor $\mathbf{a}$. The time derivative of the orientation tensor writes

$$\dot{\mathbf{a}} = \frac{\xi}{\xi+\mu}\,\dot{\mathbf{a}}^J + \frac{\mu}{\xi+\mu}\,\dot{\mathbf{a}}^C - 4k \cdot \frac{\xi}{(\xi+\mu)^2}\,\dot{\mathbf{a}}^E \tag{21}$$

with $\dot{\mathbf{a}}^J$, $\dot{\mathbf{a}}^C$ and $\dot{\mathbf{a}}^E$ the resulting expressions

$$\begin{cases} \dot{\mathbf{a}}^J = \mathbf{\Omega} \cdot \mathbf{a} - \mathbf{a} \cdot \mathbf{\Omega} + \mathbf{D} \cdot \mathbf{a} + \mathbf{a} \cdot \mathbf{D} - 2\,\mathbf{A} : \mathbf{D} \\ \dot{\mathbf{a}}^C = \mathbf{W} \cdot \mathbf{a} + \mathbf{a} \cdot \mathbf{W}^T \\ \dot{\mathbf{a}}^E = \widetilde{\mathbf{D}} \cdot \mathbf{a} + \mathbf{a} \cdot \widetilde{\mathbf{D}} - 2\,\mathbf{A} : \widetilde{\mathbf{D}} \end{cases} \tag{22}$$

A closure relation is needed in order to express the fourth order moment $\mathbf{A}$ as a function of the lower order moments. Eq.3 shows that the cluster rotates with a velocity which only depends on the second moment of its orientation distribution function $\mathbf{a}$, so in order to consider a closure relation as in [1], it seems suitable to propose obtaining $\widetilde{\mathbf{D}}$ just with the cluster rotatory velocity. Considering then the quadratic closure relation, that is only exact when all the rods are locally aligned in the same direction the fourth order moment results

$$\mathbf{A} \approx \mathbf{a} \otimes \mathbf{a} \tag{23}$$

4. Numerical results

We consider a rod oriented initially along the direction $\mathbf{p}^T = (\cos\theta, \sin\theta)$ immersed in a simple shear flow characterized by an homogeneous velocity $\mathbf{v}^T = (\dot{\gamma} \cdot y, 0)$ field, with $\dot{\gamma} = 1$. At time t the orientation of the rod will be given by θ and its rotational velocity by $\dot{\theta}$. The kinematics of the rod are given by:

$$\dot{\mathbf{p}} = \frac{\xi}{\xi+\mu}\,\dot{\mathbf{p}}^J + \frac{\mu}{\xi+\mu}\,\dot{\mathbf{p}}^C - 4k \cdot \frac{\xi}{(\xi+\mu)^2}\,\dot{\mathbf{p}}^E \tag{24}$$

then multiplying the first equation by $-\sin\theta$, the second one by $\cos\theta$ and then adding both, it results the rotary velocity of the rod $\dot{\theta}$

$$\dot{\theta} = \frac{\xi}{\xi+\mu}\,\dot{\theta}^J + \frac{\mu}{\xi+\mu}\,\dot{\theta}^C - 4k \cdot \frac{\xi}{(\xi+\mu)^2}\,\dot{\theta}^E \tag{25}$$

Starting from θ=90 and whit values of ξ=1 and μ=1, an introducing a memory function of duration=5s, the evolution of the angle θ of one fiber inside the cluster with the time with and without the elasticity term is represented on Fig.2. It is observed that introducing the elastic term slows down the rotatory velocity of the rod.

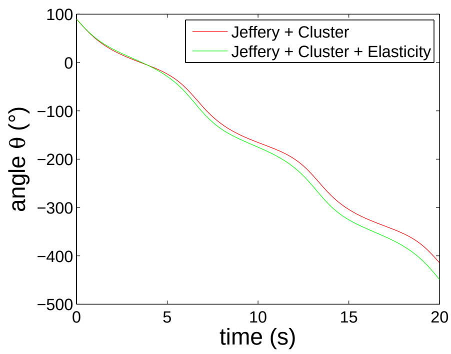

Figure 2. Angle variation of a fiber.

Fig.3 shows the angle variation of a fiber when the elastic term is expressed in the $\mathbf{n}$ direction (green line) and the $\mathbf{p}$ direction: first considering for the calculation of $\widetilde{\mathbf{D}}$ the global rotatory velocity $\dot{\theta}$ (blue line) and second, just the rotatory velocity of the cluster $\dot{\theta}^C$ (red line). It is shown that there is not a huge difference between the two ways of obtaining $\widetilde{\mathbf{D}}$, so the simplification introduced in order to consider a closure relation is not changing the result of the model.

Finally, we compare the model (named model 1) obtained in section 2 and the model 2, which is the one derived from the micromechanics. Now, an alternative step-shear is applied at $0.1s^{-1}$ and $1s^{-1}$. In Fig.4 it is observed that the time evolution of the components of the second order moment $\mathbf{a}$ fit in a correct way.

It is also shown the evolution of the viscosity η with the shear rate $\dot{\gamma}$ in both models. Being N_p the particle number, that only depends on the type and the concentration of particles considered, the viscosity due to the presence of the aggregates writes

$$\eta = 2N_p \left[\frac{\xi}{\xi+\mu}\, a_{12}^2 + \frac{\mu}{\xi+\mu}\, a_{11}(1-a_{11}) \right] \tag{26}$$

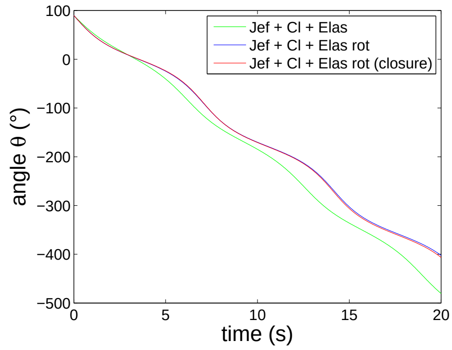

Figure 3. Angle variation of a fiber with elastic term in **p** and **n** direction

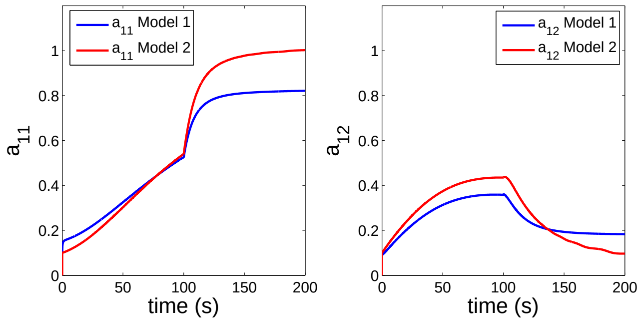

Figure 4. Evolution of the component 11 and 12 of tensor **a** comparing the phenomenological model of section 2 (model 1) and the one derived from the micromechanics (model 2)

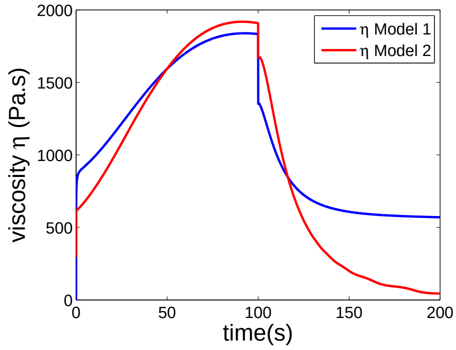

Figure 5. Evolution of the viscosity comparing the phenomenological model of section 2 (model 1) and the one derived from the micromechanics (model 2)

5. Conclusions

In this work we proposed a model derived from the microscale within the kinetic theory framework we introduced physical effects as clustering, hydrodynamic forces and clusters' elasticity. From a physical point of view when the shear rate increases, aggregates can break. So more complex scenarios should be considered in the model as the one implying aggregation mechanisms.

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