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Abstract. *Suspensions involving nanoparticules - in particular nanofibers and nanotubes - are in much use in the development of functional materials. Thus in order to optimize the usage of these materials and their fabrication, it is essential to have a thorough knowledge of the microstructure and its evolution. In this work, the objective is to develop a two-scale kinetic theory description of concentrated suspensions including the modelling of nanotube aggregates and their evolution.*

Keywords: Kinetic theory; Carbon nanotubes; Concentrated suspension.

1 INTRODUCTION

In order to improve the mechanical and thermal performances of a fluid, a solution is to introduce micro/ nanoparticles that change its behaviour and properties. A challenge is then to be able to predict the macro properties of the modified fluid that depend on the particles type, their concentration and the flow induced microstructure evolution. In this work, the focus is made on the modelling of high concentrated suspensions.
Indeed, depending on the concentration, the suspensions involving rods present different morphologies. When the concentration is dilute enough, the microstructure can be described by tracking a population of rods that move with the suspending fluid and orient depending on the velocity gradient according to the Jeffery's equation [1]. In that case the motion and orientation of each fibre is assumed decoupled from the others. When the concentration increases, fibre-fibre interactions occur leading to the formation of clusters of entangled particles. The objective here is to derive a model that describes this microstructure and its evolution.
To do so, the model used is defined at the mesoscale, between (fine) micro and (fast) macro descriptions, and developed in the framework of kinetic theory [2]. The approach used to build it can be summed up in three points:

- The microstructure is defined at the microscale, via the introduction of different conformational coordinates (particle orientation, aspect ratio, disaggregation ratio...).
- Starting from this description, a distribution function ψ – and the associated conformation tensor $\mathbf{a}(\psi)$ – is defined at the mesoscale, representing the fraction of particles exhibiting a certain conformation present in the suspension at a certain position and a certain time.
- The conservation equation of ψ and $\mathbf{a}(\psi)$ are then written in order to describe the evolution of the microstructure during the suspension flow.

This approach allows then to address the system at the macroscale while keeping the fine physics through a number of conformational coordinates introduced to describe the microstructure and its time evolution.

In this work, the principle of the microstructure modelling is recalled. A focus is then made on the introduction of the relaxation in the conformation through an apporpriate term in the equation governing its time evolution.

2 TWO-SCALES MODELLING OF CONCENTRATED SUSPENSIONS

At the microscale, each nanotube is modelled as a rigid segment joining two opposite beads. Its orientation is defined by the unit vector $\mathbf{p}$ and all the forces applied on it are assumed acting on both beads.

When the concentration of the suspension is high enough, clusters composed of entangled rods are observed experimentally. In two dimensions, these clusters can be sketched as entangled aggregates of N rods.
In this structure, a rod is submitted to two kinds of forces: the hydrodynamic one due to the surrounding fluid, and one due to the rods entanglement. The latter is assumed scaling with the difference between the rigid motion velocity (the one that the rod would have if the cluster would be rigid) and the real one.

Finally the moment equilibrium of the cluster leads to the following rotary velocity for a rod involved in a cluster:

$$\dot{\mathbf{p}} = \frac{1}{1+\alpha}\dot{\mathbf{p}}^J + \frac{\alpha}{1+\alpha}\dot{\mathbf{p}}^R \tag{1}$$

where $\dot{\mathbf{p}}^J$ stands for the Jeffery's rotary velocity defined by:

$$\dot{\mathbf{p}}^J = \nabla\mathbf{v}\cdot\mathbf{p} - (\mathbf{p}^T\cdot\nabla\mathbf{v}\cdot\mathbf{p})\cdot\mathbf{p} \tag{2}$$

and $\dot{\mathbf{p}}^R$ stands for the rigid cluster rotary velocity defined by:

$$\dot{\mathbf{p}}^R = \mathbf{W}\cdot\mathbf{p} = (\mathbf{\Omega} + \mathbf{a}\cdot\mathbf{D} - \mathbf{D}\cdot\mathbf{a})\cdot\mathbf{p} \tag{3}$$

α is the "aggregation ratio" and represents the competition between the effect of the hydrodynamic force and the one due to the rod entanglement. Indeed, if $\alpha << 1$, the hydrodynamic forces effect is larger than the entanglement one, the cluster tends to disaggregate in the flow. A rod of the cluster tends then to behave as if it was alone (Jeffery's velocity). On the contrary, if $\alpha >> 1$, the entanglement effect is much larger than the one due to hydrodynamic forces, the cluster is completely aggregated and behaves as a rigid one.

Starting from this microscopic description, we can derive a mesoscopic description of the clusters characterised by the distribution function $\psi(\mathbf{x}, t, \mathbf{p})$, representing the rod distribution constituting the cluster. The second order moment time derivative of the associated conformation tensor $\mathbf{a}(\psi)$, which controls the microstructure evolution, writes:

$$\dot{\mathbf{a}} = \frac{1}{1+\alpha}\dot{\mathbf{a}}^J + \frac{\alpha}{1+\alpha}\dot{\mathbf{a}}^R \tag{4}$$

where

$$\dot{\mathbf{a}}^J = \nabla\mathbf{v}\cdot\mathbf{a} + \mathbf{a}\cdot(\nabla\mathbf{v})^T - 2\mathbf{a}^{(4)} : \nabla\mathbf{v} \quad \text{and} \quad \dot{\mathbf{a}}^R = \mathbf{W}\cdot\mathbf{a} + \mathbf{a}\cdot\mathbf{W}^T \tag{5}$$

This model allows to represent the kinematic of the aggregates during the suspension flow and gives good results when compared to direct mechanical simulations at the microscopic scale. However, in order to be able to compare it to real rheological experiments, we have to introduce the relaxation due to the clusters' elasticity, responsible to the noticed suspension elasticity.

3 RELAXATION: INTRODUCTION OF THE AGGREGATES' ELASTICITY

The experimental observations show that, during a simple shearing flow, the aggregates not only rotate with the flow but also undergo a stretching, and come back to an equilibrium conformation once the flow

stops. In order to take into account this "elasticity" of the aggregate, we introduce an extra term in the evolution equation that tends to bring the cluster back to an equilibrium conformation $\mathbf{a}^r$:

$$\dot{\mathbf{a}} = \frac{1}{1+\alpha}\dot{\mathbf{a}}^J + \frac{\alpha}{1+\alpha}\dot{\mathbf{a}}^R - K\left(\mathbf{a} - \mathbf{a}^r\right) \tag{6}$$

The equilibrium conformation is defined starting from the history of the cluster deformation. Indeed, one can easily understand that if the aggregate undergoes a short-time deformation, it comes back to its initial conformation. However, if the deformation state is prolonged, the cluster experiences internal reconfigurations and does not come back to its initial conformation but to one close to the deformed state. To model this behaviour, we introduce a stable conformation including fading memory function.

The objective then, is to compare this model to experimental tests in order to validate it and to begin the reflexion about its identification [3].

4 CONCLUSIONS

In this work, a model at the mesoscopic scale has been developed to model the aggregates observed in the case of concentrated CNTs suspension. This model is built using the kinetic theory that allows to include the microstructure characteristics at the mesoscale without a significant loss of information.
In order to take into account the elasticity of such structures, a relaxation term has been added including fading memory functions to mimic the internal reorganisation occurring during a prolonged deformed state.

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