Direct Numerical Simulation of Carbon Nanofibre Composites

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ABSTRACT

Carbon nanofibers (CNFs) and carbon nanotubes (CNTs) are expected to yield very good mechanical properties and high thermal and electrical conductivities when embedded into polymeric matrices, especially if one can control fiber orientation and dispersion. Since it is difficult to monitor the behavior of CNF and CNT composites under flow fields, it is hoped that by realistic modeling a better insight into their structure and the consequent relations with macroscopic properties can be gained. We have thus developed a software based on the particle simulation method (PSM) considering van der Waals (VDW) and hydrodynamic (HD) interactions to analyze fiber orientation and dispersion kinetics and rheological properties under simple shear flow. The main results are the following: 1) flocculation in the flow direction is obtained when fibers are rigid; 2) flocculation in the vorticity direction is obtained when fibers are semi-flexible; 3) apparently large flocculation cannot be developed when fibers are flexible. The results of 1) and 2) match well with published experimental results.

Keywords: fiber simulation, coarse grained modeling, van der Waals interaction, hydrodynamic interaction, flocculation

1 INTRODUCTION

It is well known that carbon nanotube (CNT) and carbon nanofiber (CNF) have good mechanical, thermal, and electrical properties and are good candidates for the development of advanced composites with very good mechanical, electrical and thermal properties.

The present work details a direct fiber simulation software based on the particle simulation method (PSM) of Yamamoto et al. [1], that can treat flexible as well as rigid fibers extended in order to be applied to fiber dispersed systems by considering hydrodynamic (HD) interactions, which, to the authors best knowledge has not be developed. The software considers both effects in order to study flocculation of nano-scaled fiber dispersed systems under flow fields.

2 MODELING

This section explains the modeling of flexible fibers – intra-fiber interaction, inter-fiber interaction, HD interaction and dynamics.

2.1 Intra-fiber Interactions

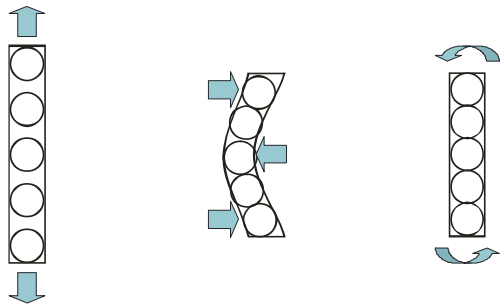
Each individual fiber is modeled by joining single segments and considering stretch, bending and torsion, each of which can be expressed by the following equations [1]:

Stretching force: $F^s = -k_s\left(r - r_0\right)$ (1)

Bending torque: $T^b = -k_b\left(\theta - \theta_0\right)$ (2)

Torsion torque: $T^t = -k_t\left(\theta_t - \theta_{t0}\right)$ (3)

where k_s is the stretching force constant, k_b the bending torque constant, k_t the torsion torque constant, r the segment center-to-center distance, θ the bending angle and θ_t the torsion angle. At equilibrium r_0 is the diameter of fiber and $\theta_0 = \theta_{to} = 0$.



(a) stretch (b) bending (c) torsion

Figure 1: Intra-fiber Interaction

2.2 Van der Waals Interactions

Particle size is of the nano-order and thus it is necessary to consider VDW interactions in the modeling. The VDW potential, V, is expressed by the following equation:

$$V = -\frac{A}{6}\left[\frac{2}{s^2-4} + \frac{2}{s^2} + \ln\frac{s^2-4}{s^2}\right], \quad (4)$$

where A is the Hamaker constant of the system, $s = r/a$, r is the particle center to center distance and a is the

radius of the particle. "A" depends on both medium and particles, and can be calculated the following equation,

$$A = \left(\sqrt{A_{11}} - \sqrt{A_{22}}\right)^2, \quad (5)$$

where A_{11} and A_{22} are the Hamaker constants for the particle and the medium, respectively. The VDW forces, $\boldsymbol{F}^{VDW}$, can be calculated by differentiating equation (4) in order to s.

2.3 Hydrodynamic Interactions

HD interaction has been studied before in colloidal dispersed systems. For calculating HD interactions, a $6N \times 6N$ sized system of equations, where N is the number of segments [2], needs to be solved for each time step. This method implies long calculation times, with PSM classifying the HD interaction into one between segments in the same fiber and one between different fibers. However, this treatment is not accurate for condensed systems. The authors [2] then introduced a different method, which does not need to solve system of equations as shown below:

$$\begin{pmatrix} \boldsymbol{F}^h \\ \boldsymbol{T}^h \end{pmatrix} = -\boldsymbol{R}\begin{pmatrix} \boldsymbol{v} - \boldsymbol{U} \\ \boldsymbol{\omega} - \boldsymbol{\Omega} \end{pmatrix}, \quad (6)$$

where $\boldsymbol{F}^h$ and $\boldsymbol{T}^h$ are the hydrodynamic force and torque, respectively, $\boldsymbol{v}$ and $\boldsymbol{\omega}$ are the velocity and the angular velocity of segments and $\boldsymbol{U}$ and $\boldsymbol{\Omega}$ are those of matrix. $\boldsymbol{R}$ is the resistance matrix. In the expression, it is not necessary to calculate the full system of equations, thereby reducing calculation time.

2.4 Collision Interaction

When VDW interaction is important collision effects should be considered and this paper follows the method PSM applied in [3]:

$$\boldsymbol{F}^c = -D_0 \exp\left[G_0\left(1 - \frac{|\boldsymbol{r}_{ij}|}{2a}\right)\right]\boldsymbol{n}_{ij}, \quad (7)$$

where a is the radius of the fiber, D_0 and G_0 are constants, and $\boldsymbol{n}_{ij} = \left(\boldsymbol{r}_j - \boldsymbol{r}_i\right) \Big/ \left|\boldsymbol{r}_j - \boldsymbol{r}_i\right|$.

2.5 Fiber Dynamics

The model considers translational and rotational behaviors of segments and a non-slip condition between segments; thus, the following equations must be solved:

$$m\frac{dv_i}{dt} = \sum_j F_{ij}^s + \sum_j f_{ij} + \sum_j F_j^{VDW} + F_i^h + \sum_j F_j^c \quad (8)$$

$$\frac{2}{5}ma^2\frac{d\boldsymbol{\omega}_i}{dt} = \sum_j \boldsymbol{T}_{ij}^b + \sum_j \boldsymbol{T}_{ij}^t + \sum_j \left(\boldsymbol{f}_{ij} \times a\boldsymbol{n}_{ij}\right) + \boldsymbol{T}_i^h \quad (9)$$

$$\boldsymbol{v}_i + a\boldsymbol{\omega}_i \times \boldsymbol{n}_{ij} = \boldsymbol{v}_j + a\boldsymbol{\omega}_j \times \boldsymbol{n}_{ji} \quad (10)$$

where $\boldsymbol{f}_{ij}$ is the tangential friction force which exerts at the constant point between paired segments in the fiber.

2.6 Fiber Orientation

The orientation of a singe fiber is characterized by the angles θ and ϕ and, the unit vector $\boldsymbol{p}$ directing along the fiber axis, as depicted in Figure 2 [4]. The components of $\boldsymbol{p}$ are given by:

$$\begin{aligned} p_1 &= \sin\theta\cos\phi \\ p_2 &= \sin\theta\sin\phi \\ p_3 &= \cos\theta \end{aligned} \quad (11)$$

The 1-axis is the flow direction, the 2-axis is perpendicular to the 1-axis in the shear plane and the 3-axis is perpendicular to the shear plane. Let ψ be a probability density function describing fiber orientation, being defined in such a way that the probability of a fiber lying within the range $\boldsymbol{p}$ and $\left(\boldsymbol{p} + d\boldsymbol{p}\right)$ is equal to $\psi(\boldsymbol{p})d\boldsymbol{p}$. In this work, a second order fiber orientation tensor, is used:

$$a_{ij} = \int p_i p_j \psi(\boldsymbol{p}) d\boldsymbol{p} = \left\langle p_i p_j \right\rangle, \quad (12)$$

where the bracket denotes the orientation averaging.

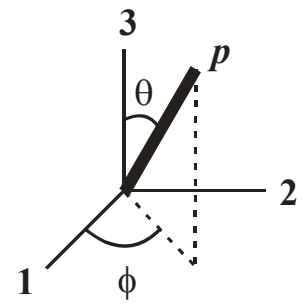


Figure 2: Definition of fiber angles

3 CALCULATION CONDITIONS

This work focuses on the flocculation structures that form under shear flows for different fiber flexibilities. Young moduli, *E*, of 6, 60, and 600 G Pa were selected for flexible, semi-flexible, and rigid fibers, respectively. Table 1 shows details of the model nano-fiber composites.

Volume fraction, ϕ	0.01
Radius of fiber, a	25 nm
Aspect ratio	20
Number of fiber	50
Shear rate, $\dot{\gamma}$	10
Viscosity of matrix, η_0	1000 $Pa \cdot s$
Young modulus, E	6, 60, 600GPa

Table 1: Materials parameters used for simulation.

4 RESULTS AND DISCUSSION

The randomly oriented, perfectly dispersed, no contact between fibers state shown in the figure 3 was used as an initial condition for the simulations. Figure 4 shows the snapshots of fiber structures of (a) *E*= 6 GPa, (b) *E*= 60 GPa, and (c) *E*= 600 GPa under simple shear flows. Figure 4a shows small round flocculation, consisting of a few fibers. There is not only flocculation but also isolated S-shaped fibers that tumble periodically along their axis. Figure 4b shows cylindrical flocculation from many fibers, with the bundles essentially aligned in the vorticity direction. Figure 4c shows flocculation parallel to the flow direction, with percolation conditions occurring. The percolation volume fraction threshold for rigid fibers of aspect ratio 20 is 0.0415 [6]. Although the present simulation is for a volume fraction 0.01, which is less than the threshold, it is conceivable that VDW interactions effectively decrease it, thus allowing percolation to occur. The behaviors shown in Figures 4b and 4c have also been observed experimentally [5].

Figure 5 shows the orientation of fibers under simple shear flows. At strain $\gamma = 0$, the components of orientation a_{xx}, a_{xx}, a_{xx} are 0.33, from which it is obvious that the initial state is an isotropically oriented one. After the application of the flow field, the maximum oriented state is achieved for every case at a strain γ around 20. After that, differences are observed, with both Figure 5a and 5b showing that a_{xx} decreases and a_{yy} and a_{zz} are gradually increasing (at strain 200 a_{yy} and a_{zz} are almost equal).

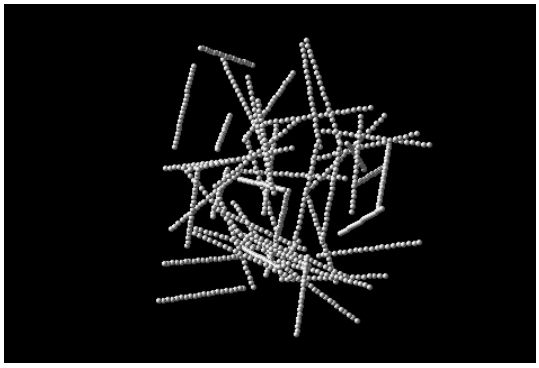
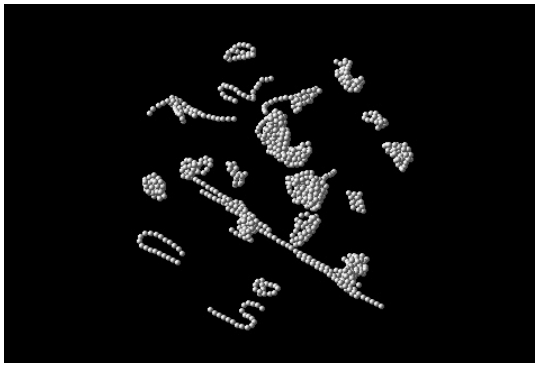
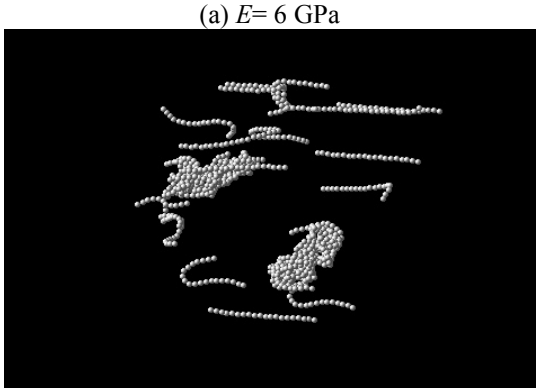


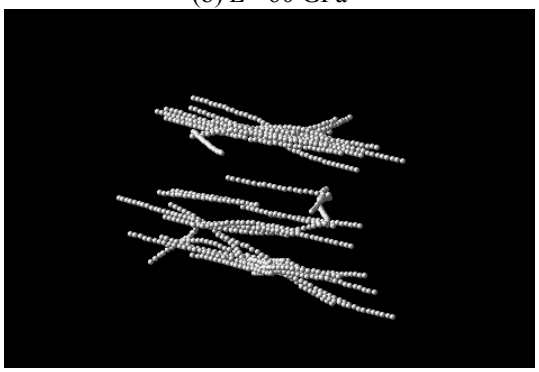
Figure 3: Initial condition of nano-fibers



(a) *E*= 6 GPa

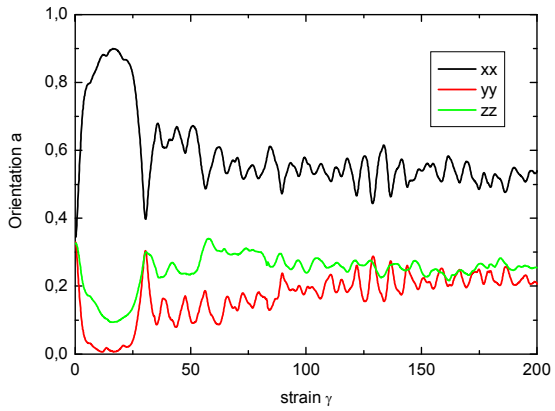


(b) *E*= 60 GPa

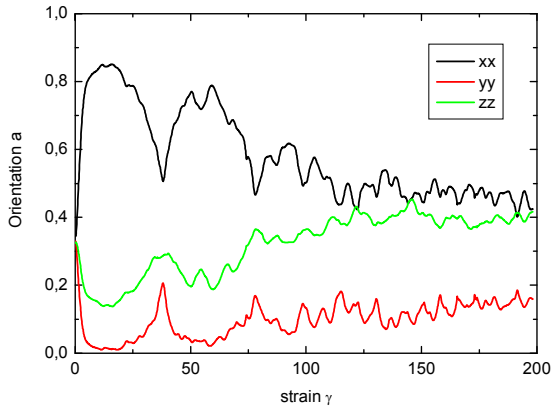


(c) *E*= 600 GPa

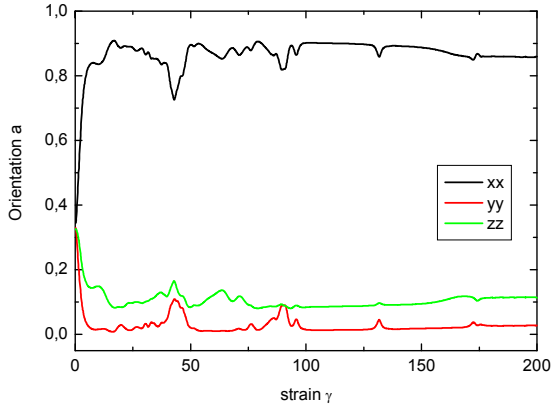
Figure 4: Aggregated structures of nano-fibers at γ=200 under simple shear flows.



(a) *E*= 6 GPa



(b) *E*= 60 GPa



(c) *E*= 600 GPa

Figure 5: Development of orientation of nano-fibers under simple shear flows.

On the other hand, a_{xx} and a_{zz} are almost same in Figure 5b. In the case of Figure 5c, at small strains orientation is wavy, but after strain of approximately 100 all the components of orientation are constant, meaning that steady state has been reached. Depending on the stiffness of the fibers, development of aggregated structures and orientation are different.

CONCLUSIONS

The main conclusions of the current work are the following: 1) flocculation in the flow direction is obtained when fibers are rigid; 2) flocculation in the vorticity direction is obtained when fibers are semi-flexible; 3) large flocculation cannot be developed when fibers are flexible. The results of 1) and 2) match very well with published experimental results.

Also, in general the results show that the model is useful for analyzing nanoscale fiber dispersed systems and that fiber stiffness is an important factor in determining the flocculation structures that are formed.

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