Numerical simulation of spin coating processes with carbon nanotubes suspensions

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ABSTRACT: In this paper we address the problem of simulating the behaviour of Carbon nanotubes (CNTs) suspensions in spin coating processes. Spin coating is a procedure used to apply uniform thin films to flat substrates by means of a high rotating velocity and the subsequent centrifugal force.

In this work we assume a suspension of chemically treated CNTs, such that they do not aggregate. In such a suspension, CNTs can be treated as rigid fibres whose orientation is dictated by the flow of the solvent. In order to treat the associated free-surface problem and to avoid the numerical problems associated to their FE solution, we have implemented a Natural Element strategy in an updated Lagrangian framework.

The resulting model is thus composed by a description of the micro scale, related to the orientation of the carbon nanotubes and the assumption of a quadratic closure relation, together with the natural element approximation for the Navier-Stokes problem governing the macroscopic suspension kinematics.

KEYWORDS: Spin coating, carbon nanotubes, numerical simulation, meshless methods.

1 INTRODUCTION

Carbon nanotubes have generated a tremendous interest in the scientific community after their discovering by Iijima in 1991 [4]. A single-walled carbon nanotube (SWNT) is a one-atom thick sheet of graphite (called graphene) rolled up into a seamless cylinder with diameter on the order of a nanometer. They posses impressive mechanical and electrical properties:

- Young's modulus: 1 to 5 TPa
- Tensile Strength: 13-53 GPa
- Elastic strain up to 5%.
- Density 2160 kg/m^3.

This, together with their low price (in the order of $50\$/kg$) suggest their use as reinforcements in composites. In addition, nanotube based transistors have been made that operate at room temperature and that are capable of digital switching using a single electron. To this end, it is extremely important to know their behaviour in suspension. Although several studies have focused on producing polymer nanotube composites, many practical challenges remain before their potential can be fully realized. Dispersing the nanotubes individually and uniformly into the matrix seems to be fundamental in producing composites with reproducible and optimal properties.

In this work we establish a method for the numerical simulation of carbon nanotubes suspensions forming processes. We focus our attention to spin coating processes, although we believe that the tech-

nique is general enough to be applied to other forming processes as well.

2 SPIN COATING PROCESSES

Spin coating is a procedure used to apply uniform thin films to flat substrates. In essence, an excess amount of a solution is placed on the substrate, which is then rotated at high speed in order to spread the fluid by centrifugal force, see Fig. 1.

Figure 1: An example of a spinning machine (Cf. `wikipedia.org`)

The difficulties in the numerical simulation of spin coating processes arise from the tremendous deformation of the domain, on one side (note that films of around $30 - 50\mu m$ are produced after a drop of liquid) and to the multiscale nature of the problem on the other.

The numerical strategy employed is composed by two main ingredient in order to cope with these difficulties. First, meshless methods (in particular, the natural element method, NEM) were employed to avoid the remeshing efforts characteristic of FE simulations, which are linked, as is well known, with numerical diffusion on the results and subsequent loss of accuracy.

In order to cope with the second difficulty mentioned before, we have implemented a kinetic theory model to simulate the behaviour of the carbon nanotubes in suspension. This model considers the carbon nanotubes as rigid fibers and allows for the tracking of their orientation during the process.

3 BASICS OF THE NATURAL ELEMENT METHOD

Consider a model composed by a cloud of points $\mathbf{N} = \{n_1, n_2, \ldots, n_m\} \subset \mathbb{R}^d$, for which there is a unique decomposition of the space into regions such that each point within these regions is closer to the node to which the region is associated than to any other in the cloud. This kind of space decomposition is called a Voronoi diagram (also Dirichlet tessellation) of the cloud of points and each Voronoi cell is formally defined as (see figure 2):

$$T_I = \{\mathbf{x} \in \mathbb{R}^d : d(\mathbf{x}, \mathbf{x}_I) < d(\mathbf{x}, \mathbf{x}_J) \; \forall \; J \neq I\}, \quad (1)$$

where $d(\cdot, \cdot)$ is the Euclidean distance function.

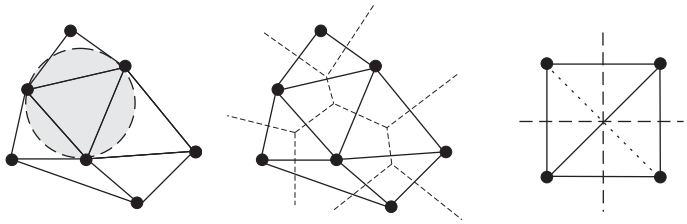

Figure 2: Delaunay triangulation and Voronoi diagram of a cloud of points.

The dual structure of the Voronoi diagram is the Delaunay triangulation, obtained by connecting nodes that share a common $(d-1)$-dimensional facet. While the Voronoi structure is unique, the Delaunay triangulation is not, there being some so-called *degenerate* cases in which there are two or more possible Delaunay triangulations (consider, for example, the case of triangulating a square in 2D, as depicted in Fig. 2 (right)). Another way to define the Delaunay triangulation of a set of nodes is by invoking the *empty circumcircle* property, which means that no node of the cloud lies within the circle covering a Delaunay triangle. Two nodes sharing a facet of their Voronoi cell are called *natural neighbours* and hence the name of the technique.

Equivalently, the second-order Voronoi diagram of the cloud is defined as

$$T_{IJ} = \{\mathbf{x} \in \mathbb{R}^d : d(\mathbf{x}, \mathbf{x}_I) < d(\mathbf{x}, \mathbf{x}_J) < d(\mathbf{x}, \mathbf{x}_K) \; \forall \; J \neq I \neq K\}. \quad (2)$$

The most extended natural neighbour interpolation method is the Sibson interpolant [7] [8]. Consider the introduction of the point $\mathbf{x}$ in the cloud of

nodes. Due to this introduction, the Voronoi diagram will be altered, affecting the Voronoi cells of the natural neighbours of $\mathbf{x}$. Sibson [7] defined the natural neighbour coordinates of a point $\mathbf{x}$ with respect to one of its neighbours I as the ratio of the cell T_I that is transferred to T_x when adding $\mathbf{x}$ to the initial cloud of points to the total volume of T_x. In other words, if $\kappa(\mathbf{x})$ and $\kappa_I(\mathbf{x})$ are the Lebesgue measures of T_x and T_{xI} respectively, the natural neighbour coordinates of $\mathbf{x}$ with respect to the node I is defined as

$$\phi_I(\mathbf{x}) = \frac{\kappa_I(\mathbf{x})}{\kappa(\mathbf{x})}. \tag{3}$$

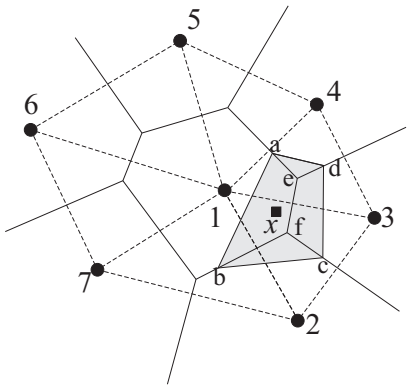

Figure 3: Definition of the Natural Neighbour coordinates of a point $\mathbf{x}$.

In Fig. 3 the shape function associated to node 1 at point $\mathbf{x}$ may be expressed as

$$\phi_1(\mathbf{x}) = \frac{A_{abfe}}{A_{abcd}}. \tag{4}$$

Sibson's interpolation scheme possesses the usual reproducing properties for this class of problems, i.e., verifies the *partition of unity* property (constant consistency), linear consistency (and therefore are suitable for the solution of second-order PDE). Other interesting properties such as the Kronecker delta property [9] and linear interpolation on the boundary [2] are also verified by the NEM. This is especially important for problems involving friction or, in general, in which the compatibility along the boundary is important.

This kind of interpolation scheme is then used in a Galerkin framework, exactly like in the finite element method. The advantages that this method provides, if compared to the Finite Element Method, is that no lack of accuracy is obtained due to mesh distortion [1]. This allows us to employ an updated Lagrangian strategy for simulating the free surface flows arising in the problem, which notably simplifies the formulation and practical implementation of the code. For more details on the method, the interested reader can consult [5].

4 CONSTITUTIVE MODELLING

The flow model of carbon nanotubes (CNT) considered as short fibers suspensions is defined by the following equations (see [6] and references therein)

- The balance of momentum equations, where we only consider, following [3], the centrifugal forces

$$\text{Div}\boldsymbol{\sigma} = -\boldsymbol{\omega} \times (\boldsymbol{\omega} \times \boldsymbol{r}) \tag{5}$$

  where $\boldsymbol{\sigma}$ is the stress tensor and ω the rotating speed of the machine.

- The incompressibility condition

$$\text{Div}\boldsymbol{v} = 0 \tag{6}$$

  where $\boldsymbol{v}$ represents the velocity field.

- The constitutive equation, with a quadratic closure relation for the fourth order orientation tensor and other simplifying assumptions, results

$$\boldsymbol{\sigma} = -p\boldsymbol{I} + 2\mu\{\boldsymbol{D} + N_p \text{Tr}(\boldsymbol{a}\,\boldsymbol{D})\,\boldsymbol{a}\} \tag{7}$$

  where p denotes the pressure, $\boldsymbol{I}$ the unit tensor, μ the equivalent suspension viscosity, $\boldsymbol{D}$ the strain rate tensor, N_p a scalar parameter depending on both the tube concentration and its aspect ratio, and $\boldsymbol{a}$ the second order orientation tensor defined by

$$\boldsymbol{a} = \oint \boldsymbol{\rho} \otimes \boldsymbol{\rho}\, \Psi(\boldsymbol{\rho})\, d\boldsymbol{\rho} \tag{8}$$

  where $\boldsymbol{\rho}$ is the unit vector defining the CNT axis direction, and $\Psi(\boldsymbol{\rho})$ is the orientation distribution function.

  From a physical point of view, we can consider that the eigenvalues of the second order orientation tensor ($\boldsymbol{a}$) represent the probability of finding the CNT in the direction of the corresponding eigenvectors.

- With a quadratic closure relation the orientation equation is expressed as

$$\frac{d\boldsymbol{a}}{dt} = \boldsymbol{\Omega}\,\boldsymbol{a} - \boldsymbol{a}\,\boldsymbol{\Omega} + \\ + k\,(\boldsymbol{D}\,\boldsymbol{a} + \boldsymbol{a}\,\boldsymbol{D} - 2\,\mathrm{Tr}(\boldsymbol{a}\,\boldsymbol{D})\,\boldsymbol{a}) \quad (9)$$

$\boldsymbol{D}$ and $\boldsymbol{\Omega}$ are the symmetric and skew-symmetric components of Grad$\boldsymbol{v}$, k is a constant that depends on the nanotube aspect ratio r (fiber length to fiber diameter ratio): $k = (r^2-1)/(r^2+1)$.

This model is solved on the domain defined by the nodes as they evolve. More details on a similar formulations can be found at [6] and references therein.

5 NUMERICAL RESULTS

The before presented model was applied to the simulation of spinning a drop of CNT suspension, with initial Gaussian geometry. The model was composed of 977 nodes under axisymmetric assumptions for the flow (but not for the orientation field, assumed 3-d). The results on the orientation field for the carbon nanotubes are shown in Fig. 4.

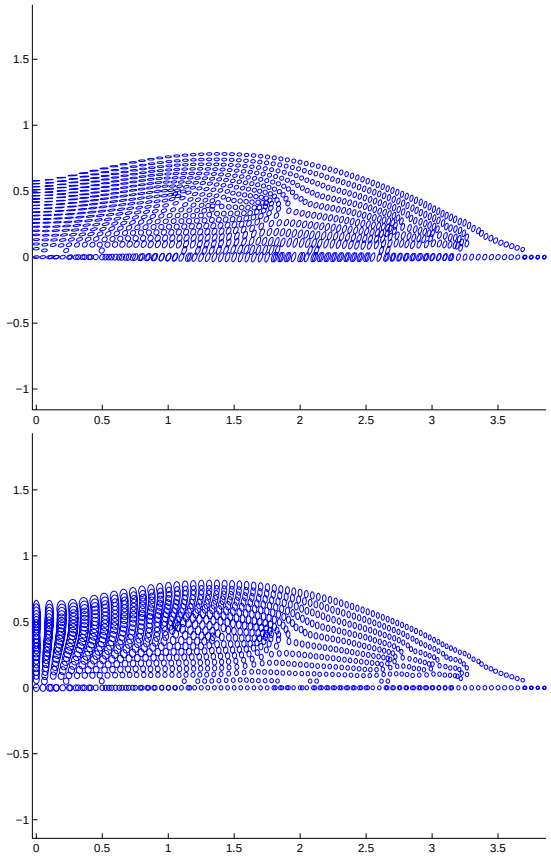

Figure 4: Orientation field for the CNT suspension at an intermediate step of the simulation (top: $r-z$ orientation field. Bottom: $r-\theta$ plane).

6 CONCLUSIONS

A model has been presented for the numerical simulation of spin coating of carbon nanotubes suspensions. The model is composed of a meshless (natural element) strategy for the flow that allows for a proper description of the free-surface flow and a micro-macro description of the nanotube scale that allows for a suitable description of their orientation field. Other possibilities, such as the kinetic description derived from the Fokker-Planck equation or its equivalent stochastic (Itô) counterpart could also be applied in this same framework. They constitute our current effort of research.

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