

Multiscale modeling of diluted CNTs suspensions electrical properties

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Abstract: Reinforced polymers are more and more considered in structural applications. In particular, CNTs have remarkable electrical and mechanical properties and their use in nanocomposites has opened new perspectives for functional materials. The objective of this work is to model and control the electrical conductivity of diluted suspensions of CNTs described within the kinetic theory framework. Kinetic theory is a useful micro-to-macro approach which allows one to address the system at the mesoscale while keeping the fine physics through a number of conformational coordinates introduced to describe the microstructure and its evolution. As the conductivity depends on the contact between the CNTs, in the considered materials the conduction phenomena depends on two descriptors: the orientation distribution and the local particles concentration. Indeed, from them we can calculate, at each position, the density of contacts distribution as a function of the orientation. Finally, the proposed model establishes a natural bridge between the different scales of descriptions. After evaluating induced conductivity properties of the microstructure, we are able to identify preferential electric paths in the domain of interest.

Keywords: Suspensions, Electrical properties, CNTs, Kinetic theory models

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1. Introduction

The addition of fibrous fillers to polymer matrices gives rise to a change in the rheological and electrical properties of these composite materials. A challenge is then to be able to predict the properties of the modified fluid that depends on the particles type, their concentration and the flow induced microstructure evolution.

Kinetic theory approaches [1, 2] 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.

ximations whose impact in the results is unpredictable.

In this work a model is defined at the mesoscale, but based at the microscale, in order to obtain a local directional percolation based in the contact between the fibers.

2. Electric field induced orientation

In this section, it is first proposed the equation governing the orientation of a rod immersed in a Newtonian fluid of viscosity η when considering the combination of an electrical field $\mathbf{e}(\mathbf{x}, t)$ and the flow velocity $\mathbf{v}(\mathbf{x}, t)$. Then, this model will be introduced in coarser descriptions of the rods population within the kinetic theory framework.

2.1 Microscopic description

It is considered a suspending medium consisting of a Newtonian fluid in which there are suspended N rigid slender rods (e.g. CNTs) of length $2L$. As first approximation, it is assumed that the fibers presence and orientation do not affect the flow kinematics. A

3D domain is considered and the associated three-dimensional orientation configurations.

The microstructure can be described at the microscopic scale by given the unit vector defining the orientation of each rod, i.e. \mathbf{p}_i , $i=1, \dots, N$. We assume that \mathbf{p} points from the negative bead to the positive one.

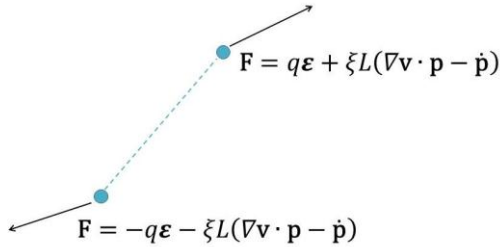


Figure 1. Forces applying on a rod

One could consider the system illustrated in Figure 1 consisting of a dumbbell immersed into a fluid flow with the beads having electrical charges $+q$ and $-q$ respectively, induced by the electrical field. The resulting force reads:

$$\mathbf{F}(\mathbf{p}L) = \mathbf{E} + \xi L(\nabla \mathbf{v} \cdot \mathbf{p} - \dot{\mathbf{p}}) \quad (1)$$

being ξ the friction coefficient and noting $\mathbf{E} = q \cdot \boldsymbol{\varepsilon}$. Both beads having an electrical charge of opposite sign, the linear momentum balance is ensured.

As the resulting torque must also vanish, the only possibility is that force \mathbf{F} acts along direction \mathbf{p} and finally, proceeding as in reference [4], we obtain:

$$\dot{\mathbf{p}} = \frac{1}{\xi L} (\mathbf{I} - \mathbf{p} \otimes \mathbf{p}) \cdot \mathbf{E} + (\nabla \mathbf{v} \cdot \mathbf{p} - (\mathbf{p}^T \cdot \nabla \mathbf{v} \cdot \mathbf{p}) \cdot \mathbf{p}) \quad (2)$$

where the first component corresponds to the rotary velocity due to the electrostatic forces and the second one represents the hydrodynamic contribution that, in the dilute regime, is described by the Jeffery's equation [5].

2.2 Mesoscopic description

Because the rods population is too large, the description that we just proposed fails to address the situations usually encountered in practice. For this reason, coarser descriptions are preferred. The first plausible coarser description applies a zoom-out, in which the rods individuality is lost in favor of probability distribution functions based descriptions.

In the case of rods, one could describe the microstructure at a certain point \mathbf{x} and time t from the orientation distribution function $\Psi(\mathbf{x}, t, \mathbf{p})$ given the fraction of rods that at position \mathbf{x} and time t are oriented in direction \mathbf{p} .

Obviously, function Ψ verifies the normality condition:

$$\int_{S(0,1)} \Psi(\mathbf{x}, t, \mathbf{p}) d\mathbf{p} = 1, \quad \forall \mathbf{x}, \forall t \quad (3)$$

where $S(0,1)$ represents the surface of the unit ball that defines all possible rod orientations.

However, in order to use it, one needs to derive the equation governing the evolution of this orientation distribution function. The rods balance leads to the so-called Fokker-Planck equation:

$$\frac{\partial \Psi}{\partial t} + \frac{\partial}{\partial \mathbf{x}} (\dot{\mathbf{x}} \Psi) + \frac{\partial}{\partial \mathbf{p}} (\dot{\mathbf{p}} \Psi) = \frac{\partial}{\partial \mathbf{p}} \left(D_r \frac{\partial \Psi}{\partial \mathbf{p}} \right) \quad (4)$$

where for inertialess rods in first gradient flows $\dot{\mathbf{x}} = \mathbf{v}$ and D_r quantifies the isotropic diffusion taking into account randomizing events coming from both, the rods hydrodynamic interactions and Brownian mechanisms. The rotary velocity $\dot{\mathbf{p}}$ is given by Eq. (2).

2.3 Macroscopic description

Fokker-Planck based descriptions are rarely considered precisely because the curse of dimensionality that the introduction of conformational coordinates entails. For this reason, mesoscopic models were coarsened one step further to derive macroscopic models defined in standard physical domains, involving space and time.

At the macroscopic scale the orientation distribution function is substituted by its moments for describing the microstructure as proposed in [1].

The first orientation moments are defined as

$$\mathbf{a}^{(1)} = \int_{S(0,1)} \mathbf{p} \Psi d\mathbf{p} \quad (5)$$

$$\mathbf{a}^{(2)} = \int_{S(0,1)} \mathbf{p} \otimes \mathbf{p} \Psi d\mathbf{p} \quad (6)$$

$$\mathbf{a}^{(3)} = \int_{S(0,1)} \mathbf{p} \otimes \mathbf{p} \otimes \mathbf{p} \Psi d\mathbf{p} \quad (7)$$

Note that because of the non-symmetry of Ψ the odd moments of the distribution function Ψ do not vanish.

The time derivative of $\mathbf{a}^{(1)}$ reads:

$$\dot{\mathbf{a}}^{(1)} = \int_{S(0,1)} \dot{\mathbf{p}} \Psi d\mathbf{p} \quad (8)$$

Taking into account Eq. (2) and proceeding as in reference [4], it results:

$$\dot{\mathbf{a}}^{(1)} = \frac{1}{\xi L} (\mathbf{I} - \mathbf{a}^{(2)}) \cdot \mathbf{E} + \nabla \mathbf{v} \cdot \mathbf{a}^{(1)} - \mathbf{a}^{(3)} : \nabla \mathbf{v} \quad (9)$$

In the previous expression, a closure issue appears because the presence of $\mathbf{a}^{(2)}$ and $\mathbf{a}^{(3)}$. A closure relation is needed in order to express the second and third order moments as a function of the lower order moments.

The simplest choice could be considering the quadratic closure relation, which becomes exact when rods fully align in a certain direction. For extending its validity when representing isotropic orientation distribution, the quadratic closure is modified, leading to the so-called hybrid closure:

$$\mathbf{a}^{(2)hyb} \approx \chi \mathbf{I} + \gamma \frac{\mathbf{a}^{(1)} \otimes \mathbf{a}^{(1)}}{\text{tr}(\mathbf{a}^{(1)} \otimes \mathbf{a}^{(1)})} \quad (10)$$

$$\text{with: } \chi = 0.5 \cdot \left(1 - (\mathbf{a}^{(1)} \cdot \mathbf{a}^{(1)})^2\right) \quad (11)$$

$$\gamma = (\mathbf{a}^{(1)} \cdot \mathbf{a}^{(1)})^2 \quad (12)$$

$$\mathbf{a}^{(3)hyb} \approx \mathbf{a}^{(2)hyb} \otimes \mathbf{a}^{(1)} \quad (13)$$

The second order hybrid closure proposal (Eq. (10)) do not result from a mathematical derivation, it consists in the simplest quadratic closure enriched with an isotropic term. Then, both terms are affected by a coefficient, both of them calculated in order to ensure the unit trace of the resulting second order tensor, that it exactly describes a fully alignment (the quadratic closure is exact in that case) as well as a 2D isotropic orientation. It is easy to verify that proposal (10-13) guarantee all these consistency conditions.

Many others possible and more accurate closure relations could be elaborated but in the present work we consider the above simple proposal.

3. Electrical properties

The electric and velocity fields induced microstructure has just been described. This section focuses on the prediction of the electric properties.

3.1 Evaluating the electric field

Although the electric field depends on the microstructure itself, that is on the CNTs distribution, in first approximation one could consider the electric field unperturbed by the CNTs presence and orientation. When it is not the case, homogenization techniques allow considering their effects. By assuming an isotropic and homogeneous medium, the electrostatic potential $V(\mathbf{x}, t)$ results from:

$$\nabla^2 V(\mathbf{x}, t) = 0 \quad (14)$$

where boundary conditions are prescribed on the domain boundary $\Gamma \equiv \partial\Omega$ that is composed of two parts, Γ_N where the normal derivative of the potential V vanishes and Γ_D on which the potential is prescribed.

As soon as the electric potential $V(\mathbf{x}, t)$ is known, the electric field $\mathbf{E}(\mathbf{x}, t)$ results from its gradient:

$$\mathbf{E}(\mathbf{x}, t) = -\nabla V(\mathbf{x}, t) \quad (15)$$

3.2 Evaluating the electric properties

For quantifying the electrical properties, we introduce the density of rods contacts $C(\mathbf{x}, t, \mathbf{p})$ depending on the two main microstructure descriptors: (i) the CNTs concentration $\phi(\mathbf{x}, t)$, assumed constant, and (ii) the orientation distribution $\Psi(\mathbf{x}, t, \mathbf{p})$.

For calculating the density of contacts, there is no difference between \mathbf{p} and $-\mathbf{p}$, and then it should be calculated from the symmetrized orientation distribution function $\Psi^S(\mathbf{x}, t, \mathbf{p}) = 0.5 (\Psi(\mathbf{x}, t, \mathbf{p}) + \Psi(\mathbf{x}, t, -\mathbf{p}))$.

For the sake of clarity we also omit all dependences on the space \mathbf{x} and time t . The fraction of rods oriented in direction \mathbf{p} is $\phi \Psi^S(\mathbf{p})$. We assume the center of gravity of all them located at position P . All the rods having their centers of gravity at position Q inside the sphere of radius $2L$ centered at point P could interact the former ones.

Due to the small size of the considered rods (e.g. CNTs), we can assume that the orientation distribution Ψ and concentration ϕ at positions P and Q coincide.

In fact, because electronic tunneling effect, the contact between the fibers is not necessarily needed. There is a minimum distance δ , from which the electrical conduction occurs. The interaction between rods aligned in directions \mathbf{p} and \mathbf{p}' whose centers are closer than $2L$ can be evaluated by a simple geometrical construction as shown in Figure 2.

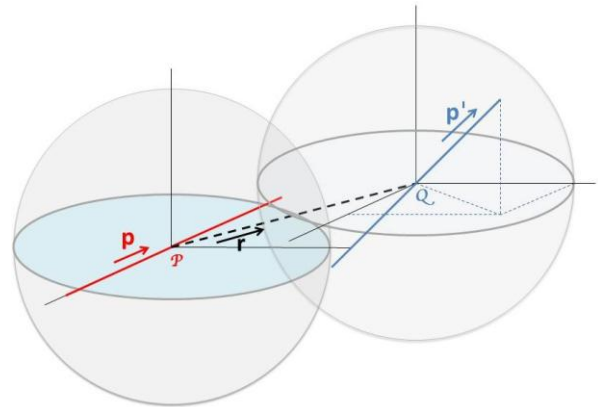


Figure 2. Evaluating the density of rod contacts

The derivation of the expression of the density of contacts $C(\mathbf{p})$, when its dependence on the space and time coordinates is omitted for the sake of notational simplicity, writes

$$C(\mathbf{p}) = \varphi^2 \oint_{B(\mathbf{p}, 2L)} \int_{S(\mathbf{p}, L)} \int_{S(\mathbf{p}, L)} \chi(\mathbf{r}, \mathbf{p}, \mathbf{p}') \Psi^S(\mathbf{p}) \Psi^S(\mathbf{p}') d\mathbf{p}' d\mathbf{p} d\mathbf{r} \quad (16)$$

being $\chi(\mathbf{r}, \mathbf{p}, \mathbf{p}')$ a function that is one if the distance between the fibers is lower than δ and null if it is not the case.

A local (at position \mathbf{x} and time t) and directional (along direction \mathbf{p}) percolation is expected occurring when the density of contacts $C(\mathbf{x}, t, \mathbf{p})$ is higher than a threshold value C^{th} . Lower values imply an infinite local directional electrical resistivity. Thus, percolation could be considered local and directional.

3.3 Determining electrical paths

In order to evaluate macroscopic quantities we must operate at the macroscopic scale, the one related to the domain of interest. In this section, we illustrate the derivation of macroscopic electrical properties from the just obtained density of contacts.

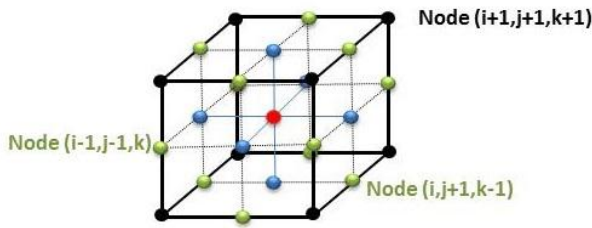


Figure 3. Cell related to node (i, j, k)

We consider for the sake of simplicity and without loss of generality a hexahedral domain equipped with a grid \mathcal{G} . Even if within the kinetic theory approach the current could have any direction \mathbf{p} , we consider the 26 directions at each position depicted in Figure 3.

Knowing the local directional resistivity at each node scaling with $C(\mathbf{x}, t, \mathbf{p})$, the electrical resistances between this node and each one of its neighbor nodes (illustrated in Fig. 3) can be calculated.

Now, an electrical circuit associated to the grid \mathcal{G} becomes perfectly defined and, when applying a potential difference between two regions of the domain boundary, the current through each segment of the circuit can be calculated by using the Kirchoff's first law that states that the total current entering a junction (a node) must equal the total current leaving it.

So, as each current in a segment depends on both the voltage difference between the two nodes defining it and on its resistance according to the Ohm's law, the

last depending on the density of contact at that position and orientation of the segment joining both neighbor nodes, we obtain a linear system that allows calculating the voltage at each node and then the current circulating in each segment.

In this manner it is very easy to identify preferential electrical paths as well as to evaluate the current reconfiguration by removing in a deterministic or stochastic manner some segments of the network.

4. Numerical results

The first step is to solve the electrostatic problem for obtaining $\mathbf{E}(\mathbf{x})$. We consider the hexahedral domain $\Omega = \Omega_x \times \Omega_y \times \Omega_z = (0, W) \times (0, L) \times (0, H)$ with $W = 2$, $L = 1$ and $H = 1$, where the Laplace problem defined in Eq. (14) is solved by using second order finite differences. The following potentials are prescribed on the indicated regions of the domain boundary:

$$V(0, 0 < y < L, \frac{H}{2} \leq z < H) = 0,$$

$$V(W, 0 < y < L, 0 \leq z < \frac{H}{2}) = 1$$

and a null normal derivative is prescribed on the remaining part of the domain boundary.

We selected $11 \times 6 \times 6$ nodes for depicting the solutions. In the present case, the nodes considered for visualizing the solution coincide with the ones employed in the finite differences grid, but in general they could be chosen independently. The potential $V(\mathbf{x})$ solution of Eq. (14) with the just indicated boundary conditions is shown in Figure 4.

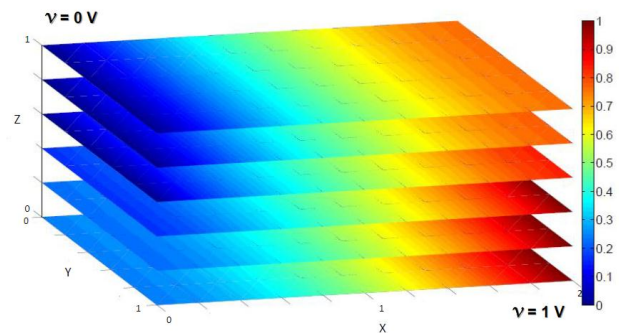


Figure 4. Potential V

Figure 5 depicts at those nodal positions the electric field $\mathbf{E}(\mathbf{x})$ obtained from Eq. (15). Once the electric field has been computed at each point of the mesh, the distribution function $\Psi(\mathbf{x}, t, \mathbf{p})$ is calculated by solving the associated Fokker-Planck equation (4). The rods were assumed immersed in a simple shear flow characterized by an homogeneous velocity field $\mathbf{v} = (\dot{\gamma}y, 0, 0)$ with $\dot{\gamma} = 1$, and it was assumed $\xi L = 1$.

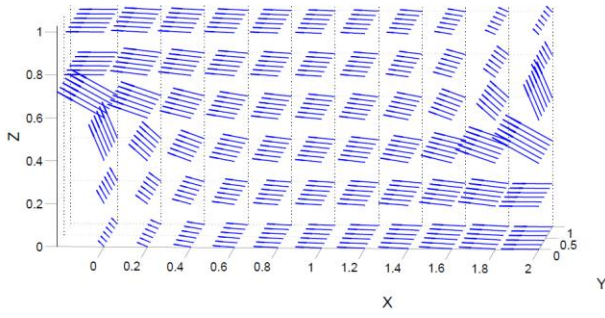


Figure 5. Electric field $\mathbf{E}(\mathbf{x})$

The last choice was arbitrary in the present numerical analysis in order to balance both contributions, the hydrodynamic and the electrical ones. In practical applications, as beads have not a real physical sense, an inverse identification should be performed before applying the simulation to situations of real interest. The time evolution of the orientation \mathbf{p} was computed as previously described, with \mathbf{p} expressed from (Fig. 6):

$$\mathbf{p} = \begin{pmatrix} \sin \theta \cos \varphi \\ \sin \theta \sin \varphi \\ \cos \theta \end{pmatrix} \quad (17)$$

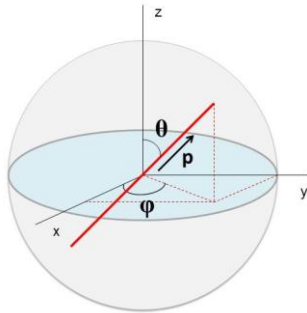


Figure 6. Orientation of a fiber

To solve the Fokker-Planck equation, we considered a spherical coordinates system. This choice essentially simplifies the application of discretization techniques, such as finite differences and finite elements, and allows for a computation with higher accuracy.

We consider its solution for different values of the diffusion coefficient, with the rotary velocity given by Eq. (2) and an initial isotropic orientation distribution $\Psi(\varphi, \theta, t=0) = \frac{1}{4\pi}$.

Results depicted in Figure 7 show the time evolution of the orientation distribution for one point x of the mesh, that becomes more and more localized as the diffusion decreases.

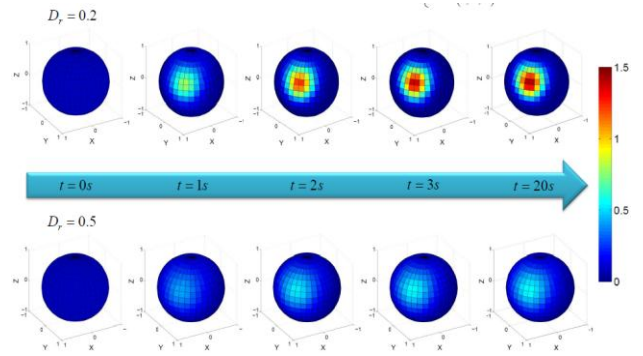


Figure 7. Evolution of the orientation distribution function Ψ defined on the unit surface for different values of D_r

Once the steady orientation distribution function Ψ is obtained, it is symmetrized at each point x according to:

$$\Psi^S(\mathbf{x}, \varphi, \theta) = \frac{\Psi(\mathbf{x}, \varphi, \theta) + \Psi(\mathbf{x}, -\varphi, -\theta)}{2} \quad (18)$$

Now, at each node of the grid \mathcal{G} , the density of contacts $C(\mathbf{x}, \varphi, \theta)$ is calculated. Figure 8 depicts $C(\mathbf{x}, \varphi, \theta)$ for a value of the diffusion coefficient (that describe the randomizing effects) $D_r=0.5$ when applying the electric field previously obtained.

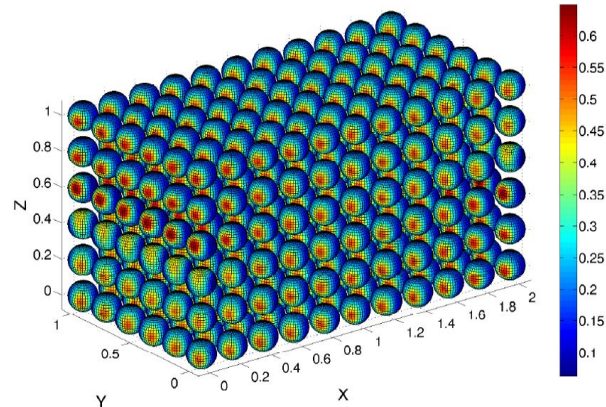


Figure 8: Contacts density $C(\mathbf{x}, \mathbf{p})$

Finally, after solving the linear system related to the Kirchoff's first law, we obtain the current circulating in each segment joining neighboring nodes of the grid \mathcal{G} as Figure 3 depicts.

Figure 9 plots the outgoing current at each nodal position. Figure 10 depicts the outgoing current of a given node located at $(x, y, z)=(1.6, 1, 0.4)$.

5. Conclusion

A first step towards a multi-scale description of electrical conduction in perfectly dispersed CNTs nanocomposites has been presented in this work.

The modeling approach consists of a microscopic description of the rod kinematics that takes into ac-

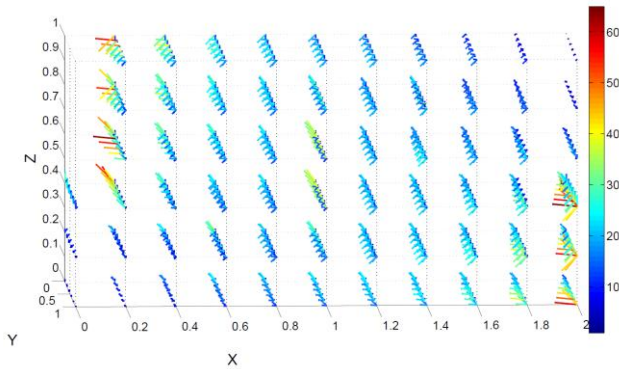


Figure 9. Current distribution

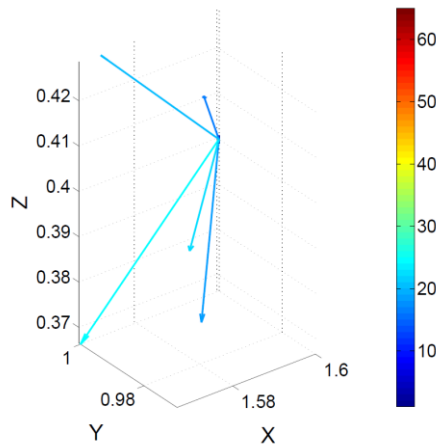


Figure 10. Outgoing current at a given node

count both, the contribution related to the electrical field, and the flow induced orientation.

Then, the orientation distribution is calculated by solving the resulting Fokker-Planck equation that constitutes a nice compromise between the microscopic scale in which the rods kinematics is defined and the macroscopic scale, the one of the part.

The orientation distribution allows calculating the local and directional density of contacts from which a sort of local and directional percolation can be defined. It allows defining a discrete electrical network at the part scale from which we evaluate the macroscopic electrical properties.

6. References

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[Version abrégée en Français]

Modélisation multi-échelle des propriétés électriques de suspensions diluées de nanotubes de carbone

Les matériaux composites à matrice polymère sont une famille de matériaux importante dans l'industrie, les propriétés de la matrice polymère pouvant être améliorées par l'introduction de particules. En particulier, les nanotubes de carbone ont des propriétés électriques et mécaniques remarquables et leur adjonction dans les nanocomposites a ouvert de nouvelles perspectives pour les matériaux fonctionnels.

L'objectif de ce travail est de modéliser la conductivité électrique des suspensions diluées de nanotubes de carbone en utilisant une méthode basée sur la théorie cinétique. La théorie cinétique est une approche micro-macro qui permet de considérer le système à la méso-échelle tout en conservant la physique fine nécessaire à la description de la microstructure et de son évolution. Cela est possible grâce à l'introduction d'un certain nombre de coordonnées de conformation. Dans les matériaux considérés, la conductivité dépend du contact entre les fibres. Les phénomènes de conduction dépendent alors de deux descripteurs: la distribution de l'orientation des fibres et la concentration locale des particules. En effet, à partir de celles-ci, il est possible de calculer, pour chaque position, la densité de répartition des contacts en fonction de l'orientation des nanotubes. Enfin, le modèle proposé établit un pont naturel entre les différentes échelles de description. Après l'évaluation des propriétés de conductivité induites par la microstructure, nous sommes en mesure d'identifier des chemins électriques préférentiels dans le domaine d'intérêt.