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Computational modeling of elastic properties of carbon nanotube/polymer composites with interphase regions. Part II: Mechanical modeling

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ABSTRACT

We present two modeling approaches for predicting the macroscopic elastic properties of carbon nanotubes/polymer composites with thick interphase regions at the nanotube/matrix frontier. The first model is based on local continuum mechanics; the second one is based on hybrid local/non-local continuum mechanics. The key computational issues, including the peculiar homogenization technique and treatment of periodical boundary conditions in the non-local continuum model, are clarified. Both models are implemented through a three-dimensional geometric representation of the carbon nanotubes network, which has been detailed in Part I. Numerical results are shown and compared for both models in order to test convergence and sensitivity toward input parameters. It is found that both approaches provide similar results in terms of homogenized quantities but locally can lead to very different microscopic fields.

1. Introduction

Following the first part, *"Computational modeling of elastic properties of carbon nanotube/polymer composites with interphase regions. Part I: micro-structural characterization and geometric modeling"* [1], we now assess the elastic mechanical properties of carbon nanotube (CNT)/polymer composites by large scale computational models.

CNT/polymer composites present peculiar micro-structural features. CNTs tend to create interwoven networks and to agglomerate together to form "clusters" due to the Van der Waals forces and Coulomb attractions [2–4]. These complex microstructures might result in strong heterogeneities in the nano-composites. Another feature of CNT/polymer composites are the thick (with respect to the CNT diameter) polymer interphase regions at the CNT/bulk polymer frontier. Polymer chains easily wrap, crystallize or agglomerate around a CNT [5–8] to form a thick polymer interphase region [5,9,10]. The mechanical properties of this interphase region are much higher compared to the properties of the amorphous phase [11,12]. Additionally, we proved in the first part [1] that, even at low CNT content, the volume fraction of these interphase regions can be quite high. Some experimental studies suggest that these interphase regions play, in fact, a major reinforcing role in nano-composites [11,13].

Multiple modeling and simulation strategies have been proposed to estimate the mechanical properties of CNT/polymer composites [14], such as, molecular dynamics [15–17], continuum mechanics [18,19] and multiscale approaches [20–24]. However, few simulations focus on both CNT networks and polymer interphase regions to study their effects on the mechanical behavior of nano-composites. The reason is that accounting for the CNT network and the surrounding interphase regions becomes quickly untraceable from the computational point of view at the scale of the representative volume element (RVE).

Here, we intend to present two possible modeling approaches: classical local continuum mechanics, involving contact forces, and hybrid local/non-local continuum mechanics that involves both local and non-local interactions. While the first class of model is classical, the second class is of interest for its future possible applications to failure simulation. It belongs to a more general framework known as "peridynamics". Peridynamics [25] has been recently proposed as a way to model the deformation of bodies, especially for discontinuity and fracture problems [26,27]. It has been proven to be an upscaling of molecular dynamics [28] and a limiting case of classical local models when the peridynamics length scale goes to zero [29–31]. The motivation for using a non-local continuum model is double: (1) it can be a way to simulate the macroscopic behavior while capturing some specific features at the very low scale (non-local forces and interactions), and (2) it defines a consistent framework for failure simulations in the future.

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Then, the objective of this paper is to simulate the RVE using both classical approaches and a hybrid local/non-local model, to compare their results in pure elasticity and to derive for each of them the homogenized elastic material parameters. We can observe that both models provide similar results on homogenized quantities despite the fact that they lead to very different microscopic fields.

The reminder of this paper is organized as follows. Section 2 reviews the modeling choices with respect to the geometry and physics modeling. The local, non-local and hybrid continuum mechanics models are introduced in Section 3. In Section 4, we discuss some specific technical points related to homogenization and periodical boundary conditions when the non-local continuum model is used. Numerical experiments and results are reported and discussed in Section 5.

2. Overview on modeling assumptions

2.1. Major geometrical assumptions

The assumptions about the geometrical modeling have been discussed in details in Part I [1]. They are listed as follows:

1. *Diameters of CNTs is neglected:* the diameter of CNTs is ignored in our model. Because the size of the RVE (in the order of 1 μm for such materials [32]) is much larger than the diameter of the CNTs (in the order of 10 nm), we model the CNTs by geometrical threads with zero volume.
2. *Existence of thick polymer interphase regions around the CNTs:* the presence of a CNT results in a modification of the surrounding resin (due to rearrangement of the polymer chains, wrapping around the CNT or locally higher degree of crystallinity) over an interphase that is thick with respect to the original diameter of the CNT [5,9,10].
3. *No void in the bulk polymer:* the bulk polymer is assumed free of bubbles, voids or cracks.

2.2. Mechanical assumptions

We adopt the following key assumptions concerning the mechanical properties of the different phases involved in a CNT/polymer nano-composite with thick interphase regions:

1. *Anisotropic behaviors for both the CNTs and the polymer interphase regions:* a CNT is regarded as transverse isotropic; the local transverse isotropy direction is given by the local tangent vector to the CNT thread [33]. In the same way, the behavior of the modified polymer in the surrounding interphase region is transverse isotropic in the same local basis, as the local direction of the CNT guides the polymer rearrangement [10,34].
2. *Progressive decrease of the properties of the polymer interphase region:* the properties of the surrounding polymer are assumed to decrease progressively when moving away from the CNT. This is supported by experimental evidence such as [10,35]. Barber et al. [35] revealed that the polymer phase around the CNT displays higher mechanical resistance than the bulk resin. Furthermore, Ding et al. [10] suggested the existence of multiple polymer layers coating multiwall CNTs with decreasing stress transfer from the inner to the outer layers; therefore, the mechanical properties of the polymer interphase region (here, the elastic parameters as we focus only on the elastic behavior for this first study) were modeled as progressively varying from the properties of the CNT to the modulus of the bulk polymer.

3. Two modeling propositions: A local continuum model and an hybrid local/non-local continuum model

3.1. A classical continuum model

Let us consider an elastic body occupying an open, bounded and regular domain Ω_1. This structure is subjected to body forces $\underline{b}$ and surface tractions $\overline{\underline{T}}$ over a portion $\Gamma_{\overline{T}}$ of the boundary $\partial\Omega_1$, $\underline{n}$ being the outward unit normal to $\Gamma_{\overline{T}}$. Over the complementary part $\Gamma_{\underline{u}}$ of the boundary, the displacement $\overline{\underline{u}}$ is prescribed (see Fig. 1).

$\underline{u}$, $\underline{\underline{\varepsilon}}$ and $\underline{\underline{\sigma}}$ are respectively the displacement vector field, the infinitesimal strain tensor field and the Cauchy stress tensor field. $\underline{\underline{\underline{\underline{K}}}}(\underline{x})$ is the 4th-order stiffness tensor at point $\underline{x}$. The governing equations for the local continuum model are:

- **Kinematic admissibility and compatibility**

$$\underline{\underline{\varepsilon}} = \frac{1}{2}\left(\underline{\underline{\nabla}} \cdot \underline{u}(\underline{x}) + {}^t\underline{\underline{\nabla}} \cdot \underline{u}(\underline{x})\right) \quad \forall \underline{x} \in \Omega_1 \tag{1}$$

$$\underline{u} = \overline{\underline{u}} \quad \forall \underline{x} \in \Gamma_{\overline{u}} \tag{2}$$

- **Static admissibility**

$$\underline{div}\,\underline{\underline{\sigma}} = -\underline{b} \quad \forall \underline{x} \in \Omega_1 \tag{3}$$

$$\underline{\underline{\sigma}} \cdot \underline{n} = \overline{\underline{T}} \quad \forall \underline{x} \in \Gamma_{\overline{T}} \tag{4}$$

- **Constitutive equation**

$$\underline{\underline{\sigma}} = \underline{\underline{\underline{\underline{K}}}}(\underline{x}) : \underline{\underline{\varepsilon}} \quad \forall \underline{x} \in \Omega_1 \tag{5}$$

The local stiffness operator $\underline{\underline{\underline{\underline{K}}}}(\underline{x})$ varies in space to define the complex network of CNTs and interphase regions.

Based on the mechanical assumptions we presented in Section 2.2, the stiffness parameters are assumed to vary continuously in space and the matrix surrounding a CNT displays a locally increased stiffness. The stiffness tensor $\underline{\underline{\underline{\underline{K}}}}(\underline{x})$ is defined by introducing a weighting scalar function α as follows:

$$\underline{\underline{\underline{\underline{K}}}}(\underline{x}) = \alpha(t_{\underline{x}})\underline{\underline{\underline{\underline{K}}}}^1 + (1 - \alpha(t_{\underline{x}}))\underline{\underline{\underline{\underline{K}}}}^0 \tag{6}$$

where $\underline{\underline{\underline{\underline{K}}}}^0$ is the stiffness tensor of the (isotropic) amorphous polymer matrix, and $\underline{\underline{\underline{\underline{K}}}}^1$ is the maximum stiffness of the ordered polymer phase when it becomes close to the CNT surface. $t_{\underline{x}}$ ($\geqslant 0$) denotes the closest distance of a point $\underline{x}$ to a CNT. The function α is a modeling choice but should meet at least the following criteria:

$$\begin{cases} \alpha(t_{\underline{x}}) = 1 & \text{for } t_{\underline{x}} = 0 \\ \alpha(t_{\underline{x}}) = 0 & \text{for } t_{\underline{x}} \geqslant t_p > 0 \\ 0 < \alpha(t_{\underline{x}}) < 1 & \text{for } 0 < t_{\underline{x}} < t_p \end{cases} \tag{7}$$

in which t_p is the maximum thickness of polymer interphase regions above which the matrix is assumed to be only the bulk matrix that is not affected by the CNTs (see Fig. 2).

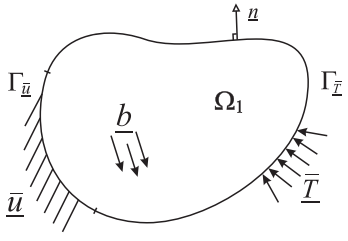

Fig. 1. The classical continuum domain Ω_1.