Interphases in nano-reinforced materials: stochastic multiscale modeling

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Abstract—This paper analyzes nano-reinforced heterogeneous materials' stochastic multiscale interphases. Materials with surface effects are usually modeled using interface models in mean-field homogenization theories. Both experiments and numerical simulations show a disturbed area near the inclusion-matrix phase boundary. After modeling this area as an interphase, its elastic properties randomly fluctuate and must be probabilistically defined. Therefore, our goal is to build a probabilistic model for the matrix-valued random field that models the interphase's elastic features. A parametric investigation of the microstructure's apparent tensor is then performed using this model. Simulations characterize how the random interphase and interface models affect material properties. Assuming the interface model is physically consistent, the elastic surface properties are calculated by optimizing the random medium's effective properties.

Keywords—Mechanical properties; nano-reinforced materials; interphase - interface; probabilistic model; random field.

I. INTRODUCTION

A material consisting of at least two elementary phases is called a composite or composite material. This artificial assembly is achieved thanks to the capacity for adhesion between the constituents. Generally, there are two phases in a composite: one called matrix and the other called reinforcement (or filler). When one of the elementary phases has one, two or three dimensions of less than 100 nanometers, it is called nanocomposite. The assembly of these two phases makes it possible to improve the mechanical or physical properties of the matrix for a certain use. This explains the growing need for this type of material in different sectors of industry. However, understanding nanocomposites remains complex from a mechanical point of view due to the non-homogeneity of the material.

This research focuses on multi-scale modeling of heterogeneous materials with nanoparticle reinforcements. Surface effects of this type of material have been extensively established experimentally (see, for example, Berriot et al. [1]). Recent contributions utilizing molecular dynamics simulations [2] have revealed that the effect of strengthening in polymer matrices is primarily due to a local alteration of the chain distribution. In terms of modeling, this disturbed area can be compared to an interphase, the mechanical properties of which display spatial and random oscillations. As a result, it is reasonable to challenge the modeling of these qualities, as well as link between this model and interface models commonly employed in homogenization by mean fields approaches.

The heterogeneous material has a matrix, spherical particle, and interphase (Fig. 1). For simplicity, and based on Brown et al. results [2], the thickness of the interphase is considered to be constant.

II. PROBABILISTIC MODELING OF INTERPHASE PROPERTIES

The microstructure's geometric data are the nanoscopic reinforcement's radius $R_0$, inclusion's surface percentage $f_i$, interphase thickness $h$, and domain size $L$. In a cylindrical coordinate system, $(I)$ is the geometric domain occupied by the interphase.

$$(I) = \{(r \cos \theta, r \sin \theta) \mid r \in [R_0; R_0 + h], \theta \in [0; 2\pi]\}$$  (1)

In the next section, the construction of a probabilistic model for interphase properties is introduced.

Fig. 1. Microstructure considered
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As a result, we introduce the modeling of a random field \([C^w(x)]\), \(x \in (I)\) with values in space \(\mathbb{M}^+_1(\mathbb{R}^2)\) of matrices (3×3) real, symmetric positive-definite, exhibiting the interphase’s mechanical properties. For a specific point of the considered space, \([C^w(x)]\) is a random matrix defined by a probability density denoted by \(P_{[C^w(x)]}\). In the present study, the construction methods described in Guilleminot and Soize [3] have been applied:

- defining a family of marginal rules of order 1, each of which is built using the Maximum Entropy concept;
- establishing statistical dependencies (and functions of correlation) by the use of standardized Gaussian fields (stochastic germs).

The Shannon's entropy \(S(p)\) of \(p\) is defined as following:

\[
S(p) = - \int_{\mathbb{M}^+_1(\mathbb{R}^2)} p([C]) \ln(p([C])) d[C]
\]  

(2)

In Eq. (2), \(d[C]\) is a element on \(\mathbb{M}^+_1(\mathbb{R}^2)\). Next, it is supposed that \(\lambda\) algebraic constraints, expressed in the form of mathematical expectations and defining the available information on \([C^w(x)]\), are satisfied by \([C^w(x)]\). The probability density function \(P_{[C^w]}\) is then deduced:

\[
p_{[C^w]} = \arg \max_{p_{[C]} \in C} S(p)
\]  

(3)

In Eq. (3), \(C_{ad}\) is the space of admission in \(\mathbb{M}^+_1(\mathbb{R}^2)\) (of all the functions of \(\mathbb{M}^+_1(\mathbb{R}^2)\)). To be specific, the following constraints are considered [4]:

\[
\begin{align*}
\int_{\mathbb{M}^+_1(\mathbb{R}^2)} p_{[C^w]}([C]) d[C] &= 1, \\
\mathbb{E}([C^w(x)]) &= [C(x)] \in \mathbb{M}^+_1(\mathbb{R}^2), \\
\mathbb{E}([\ln(\det([C^w(x)]))] &= \nu, \quad |\nu| < +\infty.
\end{align*}
\]  

(4)

The following marginal law is obtained:

\[
p_{[C^w]}([C]) = \begin{cases} 
1_{\mathbb{M}^+_1(\mathbb{R}^2)}([C]) \times c \times \det([C])^\delta \exp\left(-\frac{B}{\delta^2} [C]^T [C]\right) 
\end{cases}
\]  

(5)

In Eq. (5), \(c\) is a constant, \(\delta\) is the parameter controlling the level of statistical fluctuations, and

\[
B = \frac{1}{2} + \frac{(tr[C])^2}{2tr[C]^T}
\]  

(6)

and \(\cdot\), \(\cdot\), \(\cdot\) stands for the sign of the dot product in \(\mathbb{M}^+_1(\mathbb{R}^2)\).

Furthermore, there is a measurable nonlinear transformation \(T\) such as [5]:

\[
[C^w(x)] = T(\xi_1(x), \ldots, \xi_n(x))
\]  

(7)

for every \(x\) of \((I)\), where \(\{\xi_1(x), x \in \mathbb{R}^2\}, \ldots, \{\xi_n(x), x \in \mathbb{R}^2\}\) are homogeneous and normalized real scalar Gaussian fields (stochastic germs). The model now needs the average function \(x \mapsto [C(x)]\), \(\delta\) and functions of correlation for the stochastic germs. We then denote \((r, \theta, r', \theta') \mapsto \rho^\varphi(r, \theta, r', \theta')\) the normal function of correlation of the germ \(\{\xi_n(x), x \in \mathbb{R}^2\}\). It is retained here a hypothesis of the variable separation such as:

\[
\rho^\varphi(r, \theta, r', \theta') = \rho^\varphi(r, \theta') \times \rho^\varphi(r', \theta)
\]  

(8)

Based on Brown et al. [2] and Le et al. [6], the orthoradial stationarity hypothesis can be provided such as:

\[
\rho^\varphi(r, \theta, r', \theta') = \rho^\varphi(\tau_\theta)\text{ with } \tau_\theta = |\theta - \theta'|
\]  

(9)

Assuming more homogeneity in the radial direction, the same hypothesis is written such as:

\[
\rho^\varphi(r, r') = \rho^\varphi(\tau_r)\text{ with } \tau_r = |r - r'|
\]  

(10)

In the present, the following correlation functions are considered:

\[
\begin{align*}
\rho^\varphi(\tau_\theta) &= \cos(2\tau_\theta) \frac{L_\theta}{L_o}, \\
\rho^\varphi(\tau_r) &= \frac{4L_r^2}{\pi^2 \tau_r^2} \sin^2\left(\frac{\pi \tau_r}{L_o}\right),
\end{align*}
\]  

(11)

where: \(L_r\) and \(L_\theta\) are the lengths of correlation in the radial and orthogonal directions, respectively. It is interesting to notice that these two correlation lengths are assumed to be identical - for simplicity - for the six stochastic germs.

### III. STOCHASTIC HOMOGENIZATION AND CORRESPONDING INTERFACE MODEL

#### A. Parametric analysis of apparent properties

By using geometry and random models, it is now possible to simulate the microstructure that was looked at. Specifically, surface fraction of nano reinforcement \(f_1 = 0.15\). Radial and orthogonal correlation lengths are discretized such as \(L_r \in \{0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5\}\) and \(L_\theta \in \{0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35\}\).

The finite element approach is used to solve the homogenization problem associated with Dirichlet boundary conditions. To divide the region, an adaptive mesh is employed (Fig. 2). The optimal number of triangular elements in the interphase along the radial direction was discovered in this study to be 20. This was done to ensure that the random field’s correlation structure was sampled at least three times per correlation length.
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In this study, different elastic properties of the matrix, interphase and nanoparticle are summarized below in Table 1:

<table>
<thead>
<tr>
<th>Constituent phase</th>
<th>Elasticity modulus (GPa)</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix (polyethylene)</td>
<td>1.1</td>
<td>0.4</td>
</tr>
<tr>
<td>Interphase: average model</td>
<td>1.65 ($3E_m$)</td>
<td>0.4</td>
</tr>
<tr>
<td>Nanoparticle (silica)</td>
<td>40</td>
<td>0.25</td>
</tr>
</tbody>
</table>

For a comparison and illustration purposes, in Figs. 3a, 3d and 3g, the component $C_{11}^{\text{int}}$ of the elasticity tensor of the interphase is depicted with three configurations of correlation lengths: $\{L_r = h, L_\theta = \pi / 5\}$, $\{L_r = h / 6, L_\theta = \pi / 5\}$, and $\{L_r = h / 6, L_\theta = \pi / 30\}$. Fig. 3 also presents the strain (3b, 3e, 3h) and stress (3c, 3f, 3i) fields when applying macroscopic strain in a tensile simulation.

**CONCLUSIONS**

The modeling of heterogeneous materials with surface effects is the focus of this work. We relied on probabilistic modeling of the interphase zone, the existence of which has been highlighted in the literature, to do this. First, we used a random field with matrix values to offer a probabilistic description of the elastic properties of the interphase. The uncertainty was then propagated in order to analyze the apparent elastic properties of the microstructure. The importance of radial and orthoradial correlation lengths in interphase property uniformity can be highlighted via parametric analysis.

**REFERENCES**


