On the Scale Dependence
of the Structural Models for Nanocomposite Materials

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In this paper the mechanical models for nanocomposites are discussed focussing on the main restrictions of the first order models. It is proposed, according to some results for the second order models, to include in the mechanical approach some geometrical parameters to handle the transition from to scale to scale, but also to refer the modelling to an expedient class of functions which naturally describe the scale transition.

Keywords: nanocomposites, first order models, second order models, wave propagation, wavelets

The mechanics of materials and nanostructures mainly deals with the analysis of problems of nanoformations connected with the properties of materials under deformations, from now on being named as nanomechanics of materials and structures.

Within this field one of the main problems is to take into account the physical processes in nanoformations, which can be fully described by the principles of quantum (or molecular) physics [1]. However, the most used methods for approaching the description of composite materials (in any scale) are based on continuum physics (and continuum mechanics). Thus the main hypotheses are:

- the real material body is replaced with a continuous distribution of matter within the same shape in a finite volume of space;
- in each point of this continuous distribution, the density of mass is a given function.

Together with the scalar field of density the mechanical approach requires some additional hypotheses on the behaviour of matter undergoing to some deformations due to mechanical sources. Therefore the third condition is that:
- in each point of the space domain (filled by the continuum) are given the;
  - vector field of displacements;
  - tensor field of stresses;
  - tensor field of strains.

If these fields are coupled linearly we have the linear theory on the contrary we have a nonlinear theory either of elasticity (if the deformations are reversible) or plasticity. The linear theory of elasticity for the description of composite materials is the most successful [2] for at least three reasons:

- the theoretical models enable to describe and characterize a wide range of materials, in as such way that the results of theoretical models well fit with the evolution of real materials;
- the linear theory of elasticity is the most investigated and developed so that many analytical and numerical methods are well known among the scientific community;
- this kind of materials have been deeply investigated especially from experimental point of view so that many results coming from fundamental experimental observations are available.

As a consequence, nanoparticles, nanofibers, nanofilms, etc at a first step are investigated by the methods of the linear theory of elasticity, despite the fact that they should

be handled by methods of nonlinear mechanics (and more in general quantum physics). Therefore the mechanical properties of nanoformations are usually summarized by a few parameters: the density, the Young elasticity modulus, the shear modulus, the Poisson ratio, so that the nanoformation objects are replaced by some models of continuum mechanics. For example, the discrete carbon nanotube-molecule is usually studied as a fictitious solid rod.

This approach has been proven to be very expedient in dealing with composite material when both the filler of composite and the representative volume with respect to matrix have a nanoscale size [3]. This method of replacing the discrete molecular structure with a corresponding theoretical continuum structure has been called continualization [4]

Theoretical background
Continualization in Composite materials

Let us consider a discrete composite material system made of a carbon nanotube and a polyethylene matrix. Specifically, a (10,10) zig-zag NT is embedded in a filler made of crystalline polymer matrix.

This system is made by nearly 23000 atoms, including an 880-C-atom NT, and 178 chains of 42 methylene units with hydrogen atoms.

According to the continualization principle the matrix is represented as a solid continuum while the nanotube as a solid beam [4-6].

Two fundamental problems

Against the continualization principle there are some experimental observations which suggest us to modify the mechanical approach. The first one is connected with the very high mechanical stability and strength of
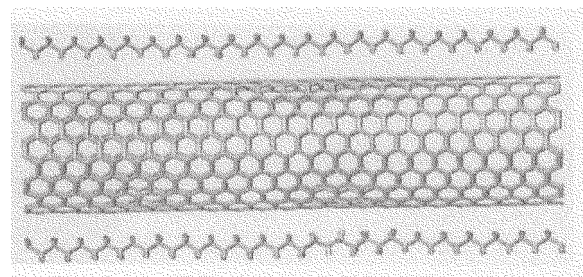

Fig. 1. (10,10) zig-zag carbon nanotube
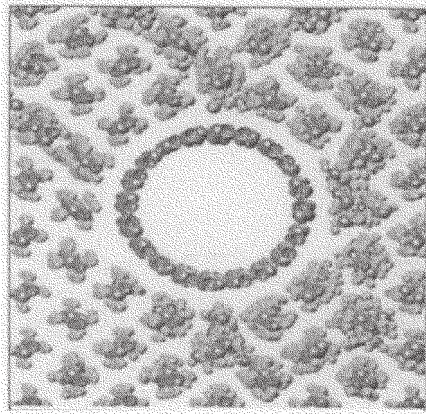
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Fig. 2. Carbon nanotube in a polyethylene matrix

nanocomposites, which cannot be explained by the theory of elasticity.

These mechanical properties are determined by the mechanical interaction between the matrix and the filler mostly at the interface. It has been observed that this interaction depends on the scale and differs from micro- to nanocomposites [7].

In order to explain this scale-dependent interaction there are two different approach. In the first one (e.g. [8-12]) the interaction depends on the Stress Intensity Factors at the interface. In the second one the forces are analysed at the molecular level at the interface between the filler (CNT – big molecule) and the matrix (polyethylene – supermolecular structure from small molecules). Indeed the last one implies the more general problem of the transition from the discrete model to the continuum one.

A second problem is associated with the dependence of the fundamental equations based on averaged mechanical properties, the average being computed not only on volume fractions of filler and matrix. When the mechanical properties are evaluated by some averages then there is no evidence of the scale (macro-, micro-, nano) on the resulting formulas.

There follows that approaching nanostructures with mechanical models one should add some additional parameters which reflect the influence of the scale on the evolution [11], or better one should modify the constants in a such a way to include the scale dependence.

First and second order microstructural models

The first order models for microstructured materials are due to Voigt who proposed (in 1887) to evaluate the physical parameters of nonhomogeneous material by averaging the components of material over the volume. In 1929, Reuss proposed to average the inverse tensors of physical properties of composites. In 1964, Hill showed that Voigt method gives the higher estimate whereas the Reuss one gives the lower estimate, so that the effective Young modulus is bounded by the so-called Voigt-Reuss brackets. Similar brackets were found for the shear modulus [12,13]but the common feature of all these formulas is the absence of a direct "geometrical" parameter related to the form of structure such as the layer thickness, and the fiber or granule diameters. In other words, in the first order models, there is only an indirect relation with the volume fraction, nothing else can directly characterize the geometrical constraints of the structure. In the first order model, the effective parameters are unable to take into account the changing of scales, which characterize the composite material (characteristic size of internal structure, filler sizes), thus showing its inadequacy for modeling nanocomposite materials.

Microstructural model of the second order proposed by Bolotin and Novichkov in 1980 [14] for layered composite materials includes, in the fundamental equations, a geometrical parameter which is strictly related to the thickness of the layers allowing thus the transition from micro- to nanolayers. Another example of second order microstructural model with a geometrical parameter is the model of elastic mixtures for the wave propagation in composite materials [15-18].

Wave propagation in composite materials

A two-component (or two phase) mixture is made by two interacting and interpenetrated continua. For each phase is defined the partial displacement vectors:

$$\vec{u}^{(\alpha)} = u_i^{(\alpha)}(x_1, x_2, x_3, t) \quad , \quad \left(\alpha = 1, 2; i, k, \dots = 1, 2, 3\right) \quad , \quad (1)$$

the vector of relative displacements $\bar{u}^{(1)}$- $\bar{u}^{(2)}$, two partial strain tensors $\varepsilon_{ik}^{(\alpha)}$ and two partial stress tensors $\sigma_{ik}^{(\alpha)}$. The fundamental equations are:

$$C_{iklm}^{(\alpha)} u_{l,mk}^{(\alpha)} + C_{iklm}^{(3)} u_{l,mk}^{(\delta)} + \beta_k \left(u_k^{(\delta)} - u_k^{(\alpha)}\right) = \left(\rho_{\alpha\alpha} + \rho_{12}^{(k)}\right) \ddot{u}_k^{(\alpha)} - \rho_{12}^{(k)} \ddot{u}_k^{(\delta)},$$
$$(2)$$

where $C_{iklm}^{(\alpha)}$, $C_{iklm}^{(3)}$, are three tensors of elastic constants, $\rho_{\alpha\alpha}$ the partial densities, and $\rho_{12}^{(k)}$ the vector of (constant) inertial interaction. In particular β_k the vector of (constant) force shear interaction depend inversely on the square characteristic length of internal structure of material, thus being a natural candidate as a geometric parameter.

In the case of an isotropic mixture, vector β_k has only one significant component, and from 9 constants of isotropic mixture $\rho_{\alpha\alpha}, \mu_k, \lambda_k, \beta$ $(\alpha = 1, 2; k = 1, 2, 3)$ only β owns this geometrical property. For instance, in the Bedford-Sutherland model [15] it is:

$$\beta = -\frac{\mu_m}{h^2 D}\left(1 - \frac{\delta^2}{h^2}\right), \qquad (3)$$

being δ the fiber radius, $h^2 = \frac{\sqrt{3}}{2\pi} s^2$, s the distance between fibers of fibrous periodic composite and

$$D = \lg \frac{h}{\delta} + \frac{1}{2}\frac{\delta^2}{h^2} - \frac{1}{8}\frac{\delta^4}{h^4} - \frac{3}{8} + \frac{1}{8}\frac{\mu_m}{\mu_f}\left(1 - \frac{\delta^2}{h^2}\right) \qquad (4)$$

the characteristic length of the microstructure. Therefore wave propagation in micro- and nanocomposites should show different phenomena. In the case of plane longitudinal waves the fundamental equations reduce to:

$$C_{3333}^{(\alpha)} u_{3,33}^{(\alpha)} + C_{3333}^{(3)} u_{3,33}^{(\delta)} + \beta_3 \left(u_3^{(\alpha)} - u_3^{(\delta)}\right) = \rho_{\alpha\alpha} \ddot{u}_3^{(\alpha)} \qquad (5)$$

$$k_3^2 = \frac{\omega^2}{2\Delta_c}\left[\left(C_{3333}^{(1)}\rho_{22} + C_{3333}^{(2)}\rho_{11} + B\sigma_c\right) \pm \right.$$

$$\left. \pm \sqrt{\left(C_{3333}^{(1)}\rho_{22} + C_{3333}^{(2)}\rho_{11} + B\sigma_c\right)^2 - 4\Delta_c W}\right] \qquad (6)$$

$$\Delta_c = C_{3333}^{(1)}C_{3333}^{(2)} - C_{3333}^{(3)}C_{3333}^{(3)}, \qquad B = \left(\beta_3/\omega^2\right), \qquad (7)$$

$$\sigma_c = C_{3333}^{(1)} + C_{3333}^{(2)} + 2C_{3333}^{(3)}, \quad W = \rho_{11}\rho_{22} - B\left(\rho_{11} + \rho_{22}\right).$$

Results and discussions

In particular, it can be shown [19] that:
-the mixture is a dispersive medium, since the phase velocities depend nonlinearly on frequency,;

-waves propagate with two modes, that is two waves are propagating simultaneously with different velocities $v_{ph}^{(\alpha)} = \left(\omega / k_3^{(\alpha)} \right)$,

-the solution has the form of superposition of harmonic waves:

$$u_3^{(\alpha)}(x_3,t) = u_3^{(\alpha)o} e^{-i\left(k_3^{(\alpha)}x_3 - \omega t\right)} + l\left(k_3^{(\delta)}, \omega\right) u_3^{(\delta)o} e^{-i\left(k_3^{(\delta)}x_3 - \omega t\right)} , \quad (8)$$

where

$$l\left(k_3^{(1)}, \omega\right) = -\frac{C_{3333}^{(3)}\left(k_3^{(1)}\right)^2 - \beta_3}{C_{3333}^{(1)}\left(k_3^{(1)}\right)^2 + \beta_3 - \rho_{11}\omega^2} ,$$

$$l\left(k_3^{(2)}, \omega\right) = -\frac{C_{3333}^{(2)}\left(k_3^{(1)}\right)^2 + \beta_3 - \rho_{22}\omega^2}{C_{3333}^{(3)}\left(k_3^{(1)}\right)^2 - \beta_3} . \quad (9)$$

Thus the geometrical parameter β_3 , interphase shear interaction, plays a fundamental role for the evolution of waves in the composites material and shows the distinctions in characteristic sizes, from micro- to nanostructured materials.

Scale dependence through the analytical representation

It has been recently observed [20-22] that in studying some propagation problem it is expedient to represent the solution (or better the evolution of the initial-boundary profile) as wavelet series [20-23]. Wavelets are some families of orthonormal functions, mostly defined in a short range domain, depending on 2 parameters: the scaling factor which compress or dilate the function and a translation parameters [23]. For instance the scaling and harmonic wavelets [20] are:

$$\varphi_k^n(x) \overset{\text{def}}{=} 2^{n/2} \frac{e^{2\pi i(2^n x - k)} - 1}{2\pi i(2^n x - k)} , \quad (10)$$

$$\psi_k^n(x) \overset{\text{def}}{=} 2^{n/2} \frac{e^{4\pi i(2^n x - k)} - e^{2\pi i(2^n x - k)}}{2\pi i(2^n x - k)} .$$

Due to their flexibility they can be used to represent any kind of localized function. In particular it is possible to solve the fundamental equations of the nanocomposites with respect to this basis by representing the solution (for longitudinal waves) as

$$u_3(x_3,t) = \sum_{k=0}^{\infty} \alpha_k \varphi_k^0(x) + \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \gamma_k^n \psi_k^n(x) , \quad (11)$$

where the wavelet coefficients α_k, γ_k^n, are computed by simple integrals (e.g. [20]).

The emergence from one scale to another can be realized through the scaling factor n. However, it can be seen that since γ_k^n represent the oscillations (and jumps) by using a scale parameter ≤ 0 $\varepsilon \leq 1$ the above equation can be written as

$$u_3(x_3,t) = \varepsilon \left(\sum_{k=0}^{\infty} \alpha_k \varphi_k^0(x) + \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \gamma_k^n \psi_k^n(x) \right) +$$

$$+ (1-\varepsilon) \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \gamma_k^n \psi_k^n(x) \quad (12)$$

so that according to the value of ε more details are added to the representation.

For instance if we consider the wavelet representation of the function $y = e^{-(16x)^2/2}$, we obtain figure 3.
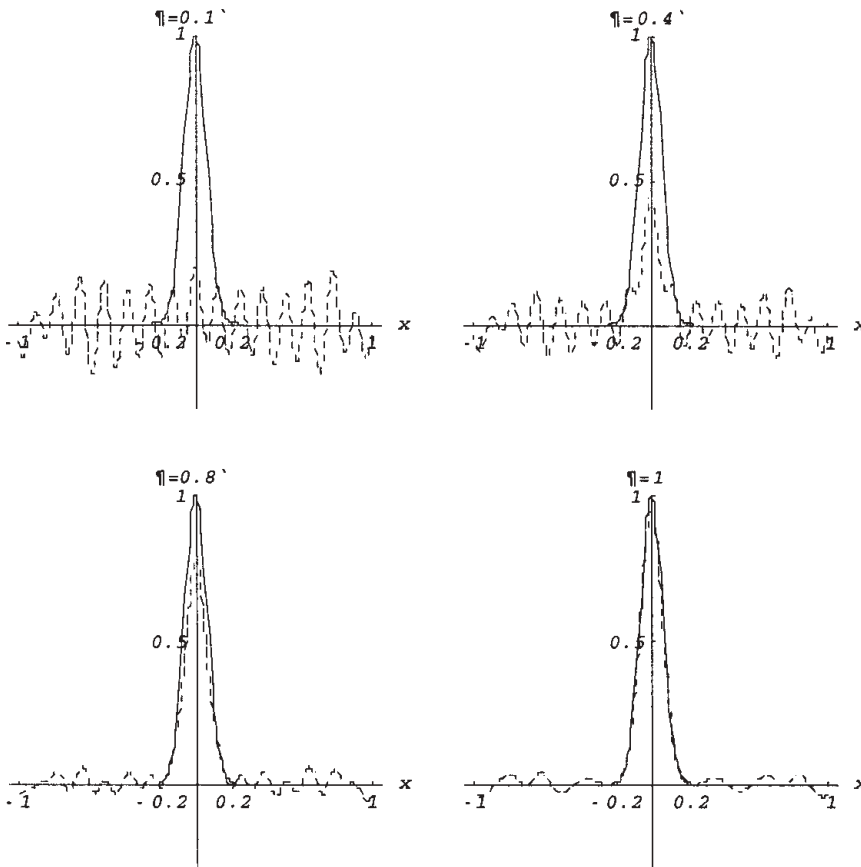

Fig. 3. Wavelet representation, with scale parameter, of the function $y = e^{-(16x)^2/2}$

Conclusions

Within the framework of micromechanics of composite material there exist the so called structural models of the second order which are sensitive to the structure change from micro-level [24-27] to nano-level. On an example of the structural model of elastic mixture, a geometrical parameter (interphase shear interaction) shows the distinction for composite materials of micro- and nano-level. In fact the wave propagation depending on this parameter gives different phenomena. Moreover, it has been shown that with a suitable representation of the solution, by using in particular the wavelets, it is possible to introduce an additional scale depending parameter for the transition from one scale to another.

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