VISCOELASTIC PROPERTIES OF INHOMOGENEOUS NANOCOMPOSITES

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ABSTRACT

Hierarchic model of structure [V. V. Novikov, K. W. Wojciechowski, D. V. Belov and V. P. Privalko, Phys. Rev. E **63,** 036120 (2001)] is generalized and applied to study viscoelastic properties of a two-component inhomogeneous medium with chaotic, fractal structure and with one of the components exhibiting a negative shear modulus. It is shown that similarly to the results obtained recently in frames of the Hashin-Strikman model [R. S. Lakes, Phys. Rev. Let. **86**, 2897 (2001)], the present model predicts possibility to obtain composites of the effective shear and dumping coefficient much higher than those characterizing both the component phases. The viscoelastic properties of the fractal medium are, however, qualitatively different from the properties of the Hashin-Strikman medium.

1. INTRODUCTION

Recent studies of inhomogeneous materials with inclusions of negative stiffness indicated that such composites show very interesting properties, e.g. they can exhibit much higher stiffness and higher dumping coefficient than the phases constituting them [1-3].

Analysis of influence of inclusions with negative shear modulus on the effective shear modulus of a composite was performed on the basis of the Hashin-Strikman formulae [4, 5] which were obtained in approach that properties don't depend on scale.

Recently, however, increasing attention has been paid to physical properties of media which can be thought of as fractal structures in some size range. Examples of such structures are particle aggregates in colloids [6-8], polymer molecules, percolationg clusters, structures of some binary solutions and polymers [9-12], and structures produced in processes of diffusion-controlled aggregation (polymerization) [13-15]. One should add that media of fractal-like structures show qualitatively different properties than those characteristic for gases, liquids and solids.

Let us consider elastic properties of inhomogeneous medium of chaotic, fractal structure which one of the phases shows negative shear modulus. (One should stress here that any pure phase of such a property is, by definition, unstable. It can be stabilized, however, when inclusions of it are put into a stabilizing matrix composed of a phase exhibiting positive shear modulus [1-3].) The analysis is carried on by the method described in [16-20].

2. FRACTAL MODEL OF VISCOELASTIC PROPERTIES OF CHAOTIC STRUCTURE

The present analysis is performed on the basis of a hierarchical model of two-component structure and is a generalization of the method of elastic properties calculations described in detail in [18-20]. In the modeling of chaotic structures presented there, hierarchical lattices of random distribution of parameters are applied. The main set of bond configurations, Ω, is obtained by an iterative procedure. In the initial step of the procedure, a finite lattice is considered with bonds of length ℓ_0 and probability p_0 that a given bond belongs to the first phase. In the following steps (k = 1, 2, ...) each bond of the initial lattice is substituted by an example of a lattice obtained in the previous step. In contrast to the case considered in [20], where the bonds of the lattice represented purely elastic properties, the bonds considered in the present paper may represent more general, viscoelastic case (see Fig. 1). The limiting set of bonds, $\Omega(\ell_0, p_0)$, which depends on the size of the initial lattice and the probability p_0, is self-similar, i.e. it constitutes a fractal [16,18-20]. (In practical calculations, the iterative procedure is finished when the properties of the lattice become independent of the index *k*.)

Two ensembles of structures were introduced in [18-20]. The first one is the bonded ensemble (BE), being the set of all configurations in which bonds representing the first phase connect opposite surfaces of the lattice. The second one, the non-bonded ensemble (NBE) constitutes of the remaining configurations, for which bonds of the first phase do not connect the opposite surfaces of the lattice.

According to [20], in calculations of the elastic properties one exploits simple analytic formulae, in particular the probability function, $R(l,p)$, and dependencies of the elastic properties of the BE and NBE configurations on properties and concentrations of phases forming the considered inhomogeneous medium.

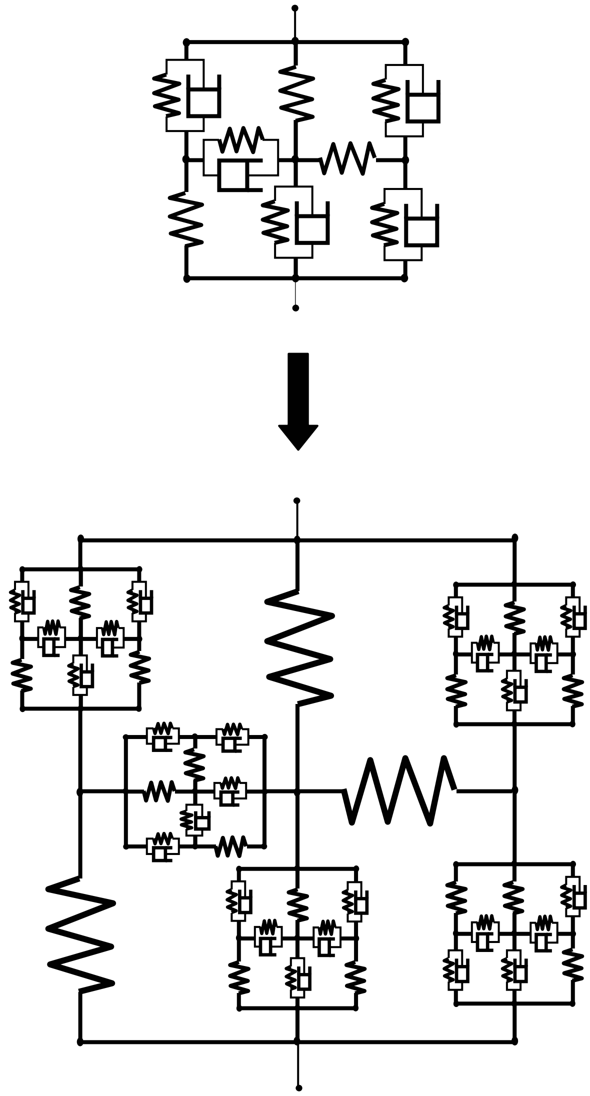

Figure 1. Illustration of the self-similarity of the fractal system $\Omega_n(L_0, p_0{=}3/8)$ (where $n\to\infty$) of viscoelastic bonds for $L_0 = 2$.

The probability function, $R(l,p)$, is defined as the ratio of the number of the BE configurations to the number of all configurations for a cubic initial lattice. The numerical analysis [20] of initial lattices of various sizes showed that good results can be obtained for the lattice as small as 2x2x2 for which [21]

$$R(p) = p^2(4+8p-14p^2-40p^3+16p^4+288p^5+655p^6+ \\ +672p^7-376p^8+112p^9-14p^{10}) \quad , (1)$$

According to (1) the percolation threshold, i.e. the transition from the NBE to the BE, occurs at $p_c = 0.2084626828...$.

The dependencies of the elastic properties of the BE and NBE configurations on properties and concentrations of phases forming the considered inhomogeneous medium were modeled by the “blob model” [18- 20]. In this approach each BE configuration is treated as a continuum of the first phase with a spherical inclusion of the second phase (see Fig.2a), and each NBE configuration is treated as a spherical inclusion of the first phase in a continuum of the second phase (see Fig.2b). The elastic properties of configurations corresponding to the BE and NBE were calculated by applying the Hashin-Shtrikman formulae [4,5,21,22][1)].

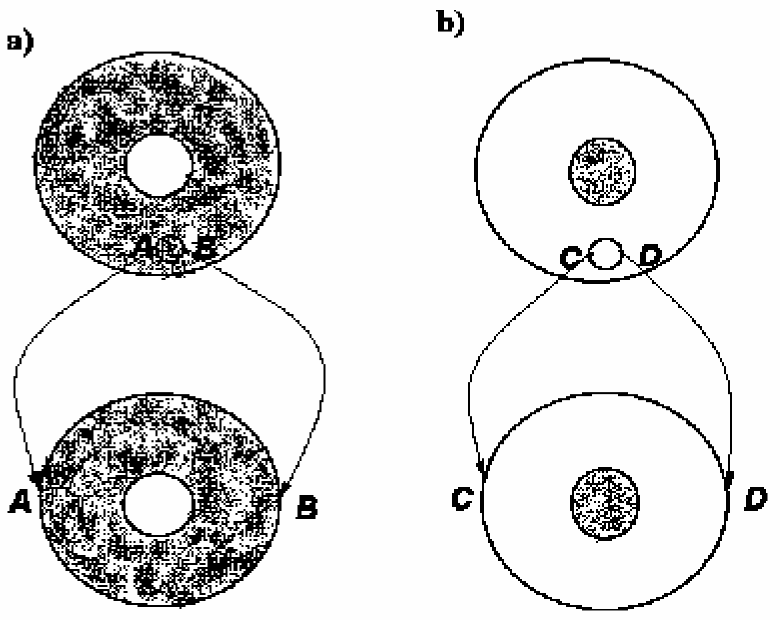

Fig.2. Simulation of (a) a connected and (b) a disconnected set

[1] Hashin-Strikman formulae were obtained on the basis of the principle of minimum of addition energy by using variational calculation method for an inhomogeneous medium [Z. Hashin , “The elastic moduli of heterogeneous materials”, J. Applied Mechanics,29,143-150 (1962).] to determine the upper K_c, μ_c and the lower K_n, μ_n bounds of effective elastic properties. The upper bound K_c, μ_c corresponds to the composite structure in which spherical inclusions of the elastic constants K_2, μ_2. are placed into a matrix of the elastic constants K_1, μ_1; in the following, it is assumed that $K_1 > K_2$, $\mu_1 > \mu_2$. The lower bound K_n, μ_n is obtained in the when the components are replaced, i.e. when the matrix is described by K_2, μ_2 and the spherical inclusions by K_1, μ_1.

From the “Hashin-Strikman spheres” (inside a sphere of one material a sphere of the other material is placed centrally) one can form a composite as follows [21, 22]: spheres of various sizes, down to infinitely small, are taken and the space V is filled by them without empty spaces. Only one condition is required: in each Hashin-Strikman sphere the volume concentrations of both components are the same, i.e. all the Hashin-Strikman spheres exhibit the same elastic properties [21]. Such a composite will be further referred to as the “Hashin-Strikman composite”. Elastic properties of the Hashin-Strikman composite are described by the formulae which are obtained basing on the exactly solvable model consisted of a single spherical inclusion of one phase in an infinite matrix of the second phase [21]. The elastic properties of the Hashin-Strikman composite depend only on the volume concentrations and elastic properties of the phases forming it; they do not depend on the scale. Inthis sense the Hashin-Strikman composite can be thought of as “uniform”. In contrast to the Hashin-Strikman composite real composites are not “uniform” in this sense as their properties *do* depend on the scale on which they are measured. One expects that the macroscopic properties of such non-uniform composites should be obtained from the microscopic ones by a proper averaging. In [18-20] a simple averaging scheme, based on the idea of the renormalization group and the blob model, was proposed. The non-uniform composites for which this scheme works will be further referred to as fractal composites.

Results obtained for static elastic properties correspond to results for viscoelastic properties (for arising harmonic vibrations) obtained by replacing the real elastic modules, (the bulk modulus) and (the shear modulus), by the complex modules K^*, μ^* [22-24]. Applying this correspondence one obtains the following formulae for the complex bulk modulus, K_c^*, and the complex shear modulus, μ_c^*, for configurations belonging to the BE at the (k+1)-th iteration step [4,5]:

$$K_c^{*(k+1)} = K*_c^{(k)} + \frac{(1-p_k)(K*_n^{(k)} - K*_c^{(k)})}{1+p_k a_c^{(k)}(K*_n^{(k)} - K*_c^{(k)})}, \quad (2)$$

$$\mu_c^{*(k+1)} = \mu*_c^{(i)} + \frac{(1-p_k)(\mu*_n^{(k)} - \mu*_c^{(k)})}{1+p_k b_c^{(k)}(\mu*_n^{(k)} - \mu*_c^{(k)})}, \quad (3)$$

where

$$a_c^{(k)} = \frac{3}{3K*_c^{(k)} + 4\mu*_c^{(k)}}; \quad b_c^{(k)} = \frac{6(K*_c^{(k)} + 2\mu*_c^{(k)})}{5K*_c^{(k)}(3K*_c^{(k)} + 4\mu*_c^{(k)})} \quad (4)$$

and $K*_c^{(0)} = K*_1$, $\mu*_c^{(0)} = \mu*_1$ denote the complex bulk modulus and the complex shear modulus of the first phase of the inhomogeneous medium, and $K*_n^{(0)} = K*_2$, $\mu*_n^{(0)} = \mu*_2$ denote the complex bulk modulus and the complex shear modulus of the second phase, respectively.

For non-bonded configurations the viscoelastic modules $K*_n^{(k+1)}$, $\mu*_n^{(k+1)}$ are described by the formulae which come from (2), (3) after the following replacements $c \leftrightarrow n$ and $p_k \leftrightarrow (1\text{-}\ p_k)$.

3. RESULTS & DISCUSSION

Calculations were performed for a two-component, inhomogeneous medium. For simplicity, it has been assumed that both the phases are isotropic and the first phase is purely elastic whereas the second phase is elastic from the point of view of volume deformations and viscoelastic from the point of view of shear deformations. The concentration of the purely elastic phase is denoted by p.

It is convenient to write the shear modulus of the second phase, $\mu*_2$, in the form

$$\mu*_2 = -x(1+iy)\mu'_1, \quad (5)$$

where $y = tg(\varphi_2) = \mu''_2/\mu'_2$, $\mu'_2/\mu'_1 = -x$, and $\mu*_1 = \mu'_1$ is the (real) shear modulus of the first phase.

As it has been mentioned before, fractal structures can show properties different from uniform structures. To illustrate the point let us compare the effective shear modulus and the dumping coefficient of an inhomogeneous medium with fractal structure (further referred to as a "fractal composite") with a composite material corresponding to the Hashin-Strikman formulae (further referred to as the "Hashin-Strikman composite").

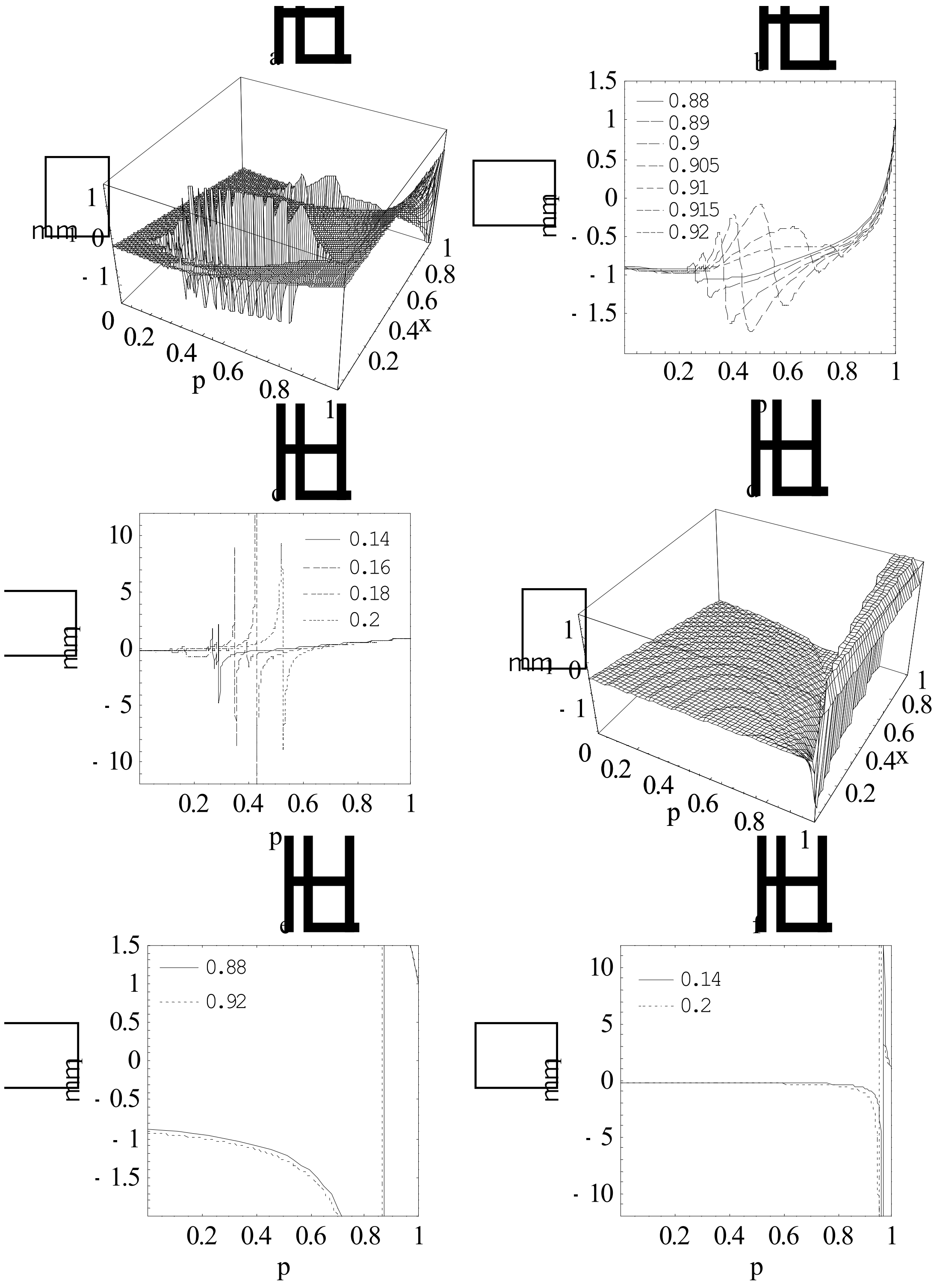

Figure 3. Comparison of the ratio of the effective shear modulus to the shear modulus of the elastic phase at y=0.001 as a function of the concentration of the elastic phase and x :in the fractal composite (a), (b), (c) and (d), (e), (f) in the Hashin-Strikman composite.

In Fig.3, the ratio of the effective shear modulus to the shear modulus of the elastic phase is shown as a function of the concentration of the elastic phase and x for $y=10^{-3}$. It is assumed that the viscoelestic phase in Fig. 4 has a negative shear modulus (i.e. negative real part of the complex shear modulus) and is characterized by $y=tg\varphi_2=0.001$ and the Poisson's ratios of both phases (calculated from real parts of the elastic moduli) are equal to 0.184... . (The latter assumption means that the ratio of the real part of the shear moduls to the bulk modulus is equal to $\mu'_i / K'_i = 0.8$, where $i = 1,2$ numerates the phases; in consequence the ratio of the bulk modulus of the second phase to the bulk modulus of the first phase is equal to $K_2' / K_1' = x$.) It can be seen there that for the inhomogeneous fractal medium the shear modulus shows in some *ranges* of concentration a resonance-like behavior similar to that discussed in [1-3] whereas in the Hashin-Strikman composite there exists only *one* such a resonance in the vicinity of the concentration p=1 .

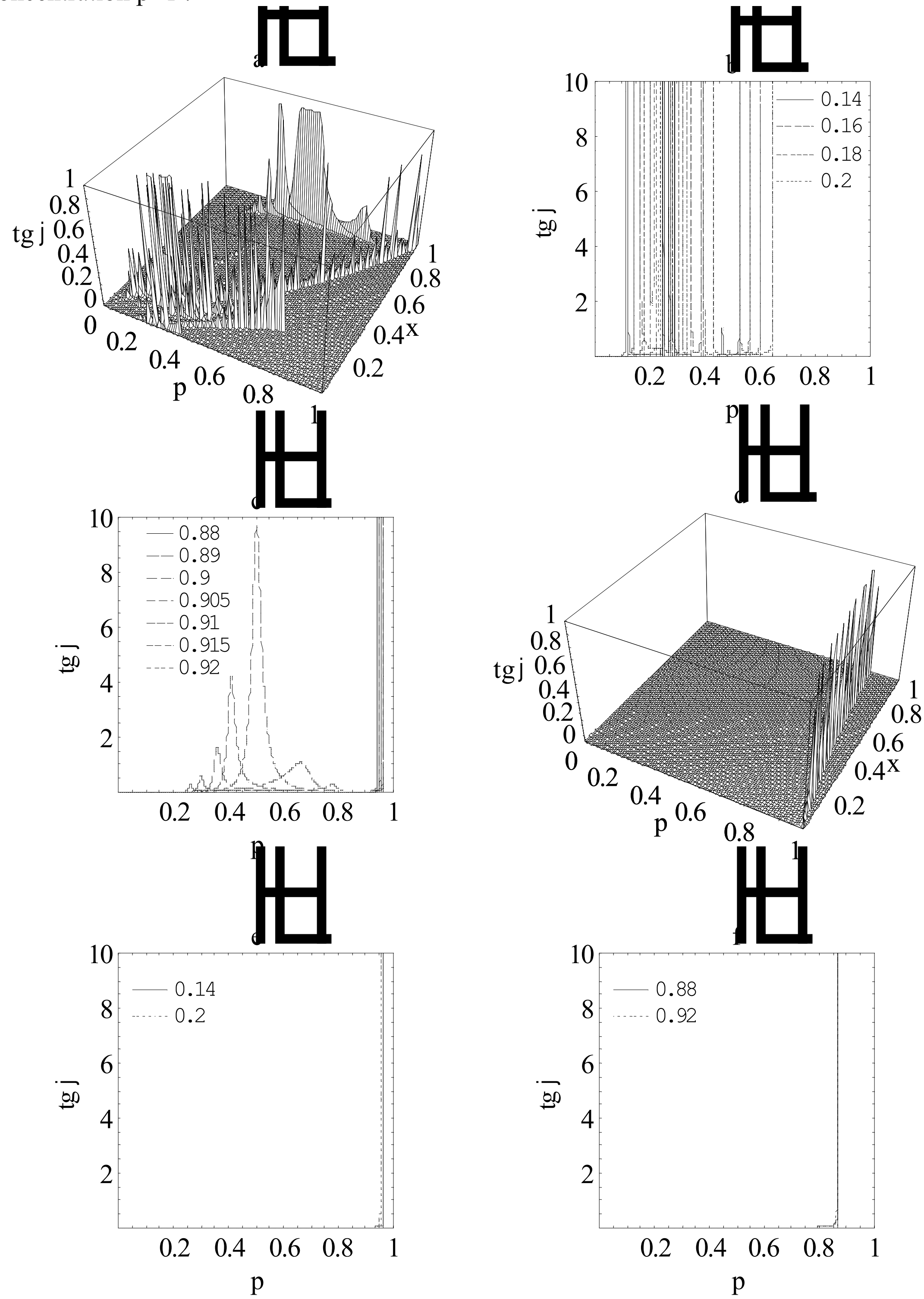

Figure 4. The ratio of the imaginary to the real part of the effective shear modulus (a), (b), (c) in the fractal composite and (d), (e), (f) in the Hashin-Strikman composite; the other details are the same as in Fig. 3.

As it has been mentioned before, fractal structures can show properties different from uniform structures. To illustrate the point let us compare the effective shear modulus and the dumping coefficient of an inhomogeneous medium with fractal structure (further referred to as a “fractal composite”) with a composite material corresponding to the Hashin-Strikman formulae (further referred to as the “Hashin-Strikman composite”).

In Fig.3, the ratio of the effective shear modulus to the shear modulus of the elastic phase is shown as a function of the concentration of the elastic phase and $x = \left|\mu_2' / \mu_1'\right|$ for y=10^{-3}. It is assumed that the viscoelestic phase in Fig. 3 has a negative shear modulus (i.e. negative real part of the complex shear modulus) and is characterized by $y = tg\varphi_2 = 10^{-3}$ and the Poisson’s ratios of both phases (calculated from real parts of the elastic moduli) are equal to 0.184... . (The latter assumption means that the ratio of the real part of the shear moduls to the bulk modulus is equal to μ'_i / K'_i = 0.8, where i =1,2 numerates the phases; in consequence the ratio of the bulk modulus of the second phase to the bulk modulus of the first phase is equal to $x = K_2' / K'_1$.) It can be seen there that for the inhomogeneous fractal medium the shear modulus shows in some *ranges* of concentration a resonance-like behavior similar to that discussed in [1-3] whereas in the Hashin-Strikman composite there exists only *one* such a resonance in the vicinity of the concentration p=1 .

In Fig.4 the ratio of the imaginary to real part of the effective shear modulus, i.e. the tangent of loses tg φ, is shown as a function of the concentration of the elastic phase and x for y=10^{-3}. The parameters of the phases are the same as in Fig.3. It can be seen again that, depending on x , tg φ of the fractal composite shows very large values in some *ranges* of concentration whereas the Hashin-Strikman composite exhibits only *one* large value, in the vicinity of the concentration p=1 , for x in the range considered.

The above comparisons show that the viscoelastic properties of the fractal composite differ qualitatively from the properties of the Hashin-Strikman composite. The observed differences can be understood taking into account that the hierarchical model considered takes into account clusters of various length scales and different parameters of their ‘resonances’ which are formed in the fractal composite whereas the Hashin-Strikman composite is ‘uniform’ in this aspect.

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It follows from the calculations of the viscoelastic properties (Figs.3, 4) that in a fractal composite peaks (“resonances”) are obtained in a broad range of concentrations of phases.

The nature of the peaks and the way in which they are formed depending on the effective shear modulus μ^* , the frequency ω, and the concentration p one can understand considering a single inclusion with the negative shear modulus ($\mu^*_1 = \mu'$ $(\mu' = -xK_1)$) which is immersed in a medium (stabilizing matrix) of the positive shear modulus $\mu^*_2 = \mu_2'$.

The shear modulus μ^* of the composite with a single inclusion can be determined by the formula [4, 5, 22]

$$\mu^* = \mu^*_2 + \frac{p(\mu^*_1 - \mu^*_2)}{1 + (1-p) b_2 (\mu^*_1 - \mu^*_2)} \quad , \tag{6}$$

where

$$b_2 = \frac{6(K^*_2 + 2\mu^*_2)}{5\mu^*_2 (3K^*_2 + 4\mu^*_2)}.$$

It follows from (6) that when $\mu^*_1 = \mu'$ $(\mu' = -xK_1)$, then

$$\mu^* = \mu'_2 - \frac{p(xK_1 + \mu'_2)}{1-(1-p)b_2(xK_1+\mu'_2)}. \tag{7}$$

From the equation

$$1-(1-p)b_2(xK_1+\mu'_2) = 0, \tag{8}$$

one can determine the “resonance” parameters of the composite for which the peaks arise, i.e. the parameters for which the external disturbance is in the “resonance” with the inclusion parameters (being equal to its “characteristic” frequency).

As the composite constitutes self-similar, chaotic system, composed of clusters of various sizes, on the *k*-th scale-level each cluster will have its own “resonance” parameters, i.e. its own “characteristic” frequency, which produces the system of peaks (characteristic frequencies) in the dependence of the effective shear modulus on the parameters of the composite.

At this point let us notice that a material of fractal structure which should show the viscoelastic properties similar to those obtained by solving the model described can be manufactured in reality by the following scheme. At the first step (the lowest size level) one produces “tablets”, e.g. of a polymer with required inclusions. At the next step, the tablets obtained at the preceding level are used as inclusions to larger tablets. The process is continued and a hierarchy shown in Fig.5 is obtained.

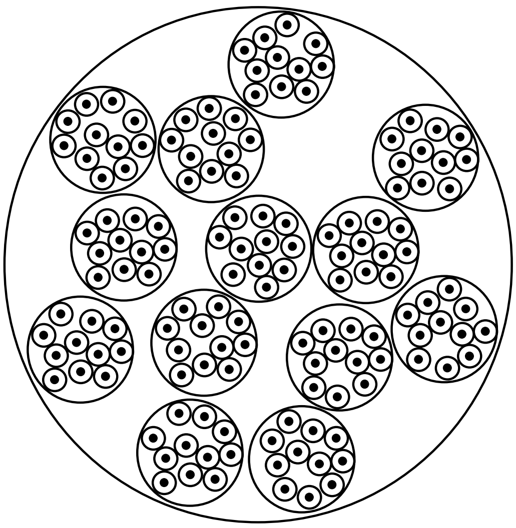

Figure 5. The idea of construction of a material with fractal structure.

It has been shown that a hierarchic ‘blob’ model used to study viscoelastic properties of an inhomogeneous fractal medium (the fractal composite) gives results, which differ qualitatively from the results obtained by applying to an inhomogeneous medium the Hashin-Shrikman approximation (the Hashin-Strikman composite). In particular, studies of the fractal model composed of an elastic phase (which can be seen as a stabilizing matrix) and a viscoelastic phase with a negative shear modulus proved that the effective shear modulus and the effective tangent of loses calculated in this model exhibit much more complex behavior (more ‘singularities’) than those predicted by the standard Hashin-Strikman model. The new ‘singularities’ observed in the fractal composite are interpreted as ‘resonances’ coming from (‘mesoscopic’) clusters of various length scales which are described by different (mesoscopic) parameters of ‘resonances’. Such clusters are taken into account by the hierarchical model whereas they are neglected completely in the standard Hashin-Strikman approximation.

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CONCLUSIONS

It has been shown that a hierarchic ‘blob’ model used to study viscoelastic properties of an inhomogeneous fractal medium (the fractal composite) gives results, which differ qualitatively from the results obtained by applying to an inhomogeneous medium the Hashin-Shrikman approximation (the Hashin-Strikman composite). In particular, studies of the fractal model composed of an elastic phase (which can be seen as a stabilizing matrix) and a viscoelastic phase with a negative shear modulus proved that the effective shear modulus and the effective tangent of loses calculated in this model exhibit much more complex behavior (more ‘singularities’) than those predicted by the standard Hashin-Strikman model. The new ‘singularities’ observed in the fractal composite are interpreted as ‘resonances’ coming from (‘mesoscopic’) clusters of various length scales which are described by different (mesoscopic) parameters of ‘resonances’. Such clusters are taken into account by the hierarchical model whereas they are neglected completely in the standard Hashin-Strikman approximation.

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