Elastic properties of inhomogeneous media with chaotic structure

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The elastic properties of an inhomogeneous medium with chaotic structure were derived within the framework of a fractal model using the iterative averaging approach. The predicted values of a critical index for the bulk elastic modulus and of the Poisson ratio in the vicinity of a percolation threshold were in fair agreement with the available experimental data for inhomogeneous composites.

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I. INTRODUCTION

The elastic properties of inhomogeneous media (IHM's) with chaotic structure and large differences in the properties of components have been studied mainly on percolating networks by numerical methods [1–9], a particular point of concern being the transition of a nonbonded ensemble (NBE) of bonds or junctions into a bonded ensemble (BE), and vice versa [10–14]. At the critical point (i.e., at the percolation threshold p_c), a linking ensemble proved to form a percolation cluster [12–16] with properties of a self-similar ensemble (i.e., a fractal), while the bulk elastic modulus scaled with distance to p_c as

$$K \sim \begin{cases} (p-p_c)^{\tau} & (p>p_c) \quad (1) \\ (p-p_c)^{-s} & (p<p_c), \quad (2) \end{cases}$$

where the critical indices τ and s depend only on the space dimensionality d. Equation (1) is expected to apply for a percolation system in the elastic regime assuming a fraction p of the bonds to have a finite elastic constant and the rest to have a zero elastic constant, while Eq. (2) is for a percolation system in the high elastic regime in which p is a fraction of the totally rigid bonds with infinite elastic constants, whereas the rest have a finite elastic constant. In this context, polymers, colloid systems, and composites may be cited as the relevant examples of IHM's.

It is pertinent to recall at this point that the problem of determination of the elastic properties of a percolating network may be considered as completely specified, should a Hamiltonian for a given ensemble of junctions and bonds be known. Moreover, the geometrical parameters of the ensemble (such as the numbers of bonds and junctions, the distances to the most remote elements, the tortuosity, etc.) are assumed to be statistically specified. In this case, the Hamiltonian describing the elastic properties of a percolation system, must meet the following requirements: (1) elastic connectivity, i.e., the elasticity micromoduli of the lattice should be finite at $p>p_c$, and should vanish as $p \to p_c+0$; (2) correct representation of the tensor properties of elasticity of the long chains forming a percolating cluster; (3) rotational invariance of the Hamiltonian free states.

The Born model [10] meets the first but not the second requirement. This model yields a set of equations similar to Kirchhoff's equations for electric currents in a resistance network; as a result, the corresponding critical index τ is identical to the critical index of conductivity t.

In contrast, the Kantor-Webman (KW) Hamiltonian [3] correctly predicts the elastic properties of percolating systems [4–8] in so far as it takes into account the energy changes concomitant to variations of lattice bond angles and thus meets all the above three requirements. Using scaling analysis, KW estimated that in two dimensions (2D) $\tau \cong 3.55$. This turns out to be close to the lower bound to τ that they had estimated, $1+\nu d$ which in 2D, with $d=2$ and $\nu = \frac{4}{3}$, yields $\tau = \frac{11}{3} \cong 3.66$ (ν is the critical index for the correlation length).

One more efficient approach to the description of physical properties of fractal structures is the position-space renormalization group (PSRG) method [12,13], which has been applied to problems of conductivity [1] and of the elastic moduli [2] of a percolating cluster. Calculations of the probability of formation of the percolating cluster at the $(n-1)$ st step, $p_n = R(p_{n-1})$, and of the bulk elastic modulus of a renormalized lattice were used to evaluate the critical index of the elasticity modulus τ,

$$\tau = \frac{\ln \lambda_k}{\ln \lambda_p}, \quad (3)$$

where

$$\lambda_p = \left. \frac{dR(p)}{dp} \right|_{p=p_c}, \quad (4)$$

$$\lambda_k = \left. \frac{dK^*}{dK} \right|_{p=p_c}, \quad (5)$$

and K^* is the bulk modulus of the renormalized lattice.

In 2D and with a 2×2 self-dual PSRG cell, one obtains $\nu \cong 1.43$ [1] and $\lambda_k \cong 0.1617$ [2], which then yield [2] τ

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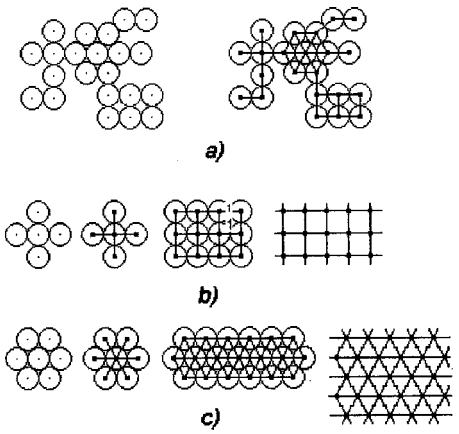

FIG. 1. Structural models of a composite: (a) a disordered cluster of particles; (b) a cluster of particles with coordination number 4; (c) a similar cluster with coordination number 6.

≅3.26. Further information on the elastic properties of percolation systems can be found in the review paper by Sahimi [10].

In this paper, we develop the method of iterative averaging for numerical calculations of the elastic properties of chaotic media making use of both *fractal geometry* and *renormalization group transformation* results. To account for the intrinsic tensor nature of elastic properties, we have chosen a continuum, ''blob'' model, rather than a discrete percolating network. This method of averaging proved highly successful in problems of the physical properties of composites [15,17–21].

II. STRUCTURAL MODEL

A lattice with a random distribution of its parameters was chosen as an appropriate model of the chaotic structure of an IHM. Spatial microinhomogeneities (i.e., system components) were modeled by the lattice junctions, and the interjunction bonds simulated their contacts with neighbors (Fig. 1). Thus, in view of the dominant contribution of contact conditions between the components to the macroscopic properties of an IHM, the general problem was reduced to a problem of bonds.

The main ensemble of bonds Ω was derived by an iteration process in which the initial step ($k=0$) involved treatment of a finite lattice in a space of dimension $d=2$ or 3 and a probability p_0 for a bond between neighboring lattice junctions to be unbroken (or ''colored'' with a definite color, so that bonds of the same color were assumed to have identical properties). At the next step ($k=1,2,\ldots,n$), each bond of the lattice was replaced by a lattice generated at the previous step (Fig. 2). The eventual independence of lattice properties of the iteration number n was recognized as the end of the iteration process. Lattices with linear dimensions L_n (assumed to exceed by far the correlation length) generated in this way were used to calculate the effective physical properties. It is clear that the ensemble of bonds $\Omega_n(l_0,p_0)$ derived by the iteration process is a function of both the size of the starting lattice l_0 and the probability p_0 [17–21].

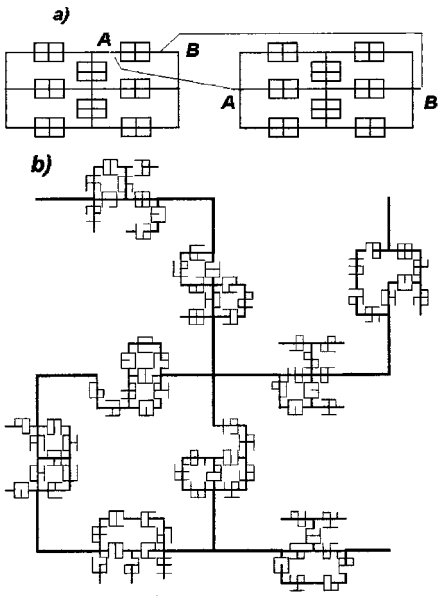

FIG. 2. The idea of the PSRG on a square lattice with $l_0=2$: $p_0=$(a)1 and (b) 0.75 at the fourth iteration step.

The formation probability $R(l_0,p_0)$ of a BE on the initial lattice at a given concentration of unbroken bonds $p=p_0$ depends only on geometry and on the linear lattice dimension l_0. This probability can be calculated as the ratio of the number of BE's to the total number of unbroken bonds on the initial lattice at given p_0 and l_0 [17].

Let $P_1=R(l_0,P_0)$ be the formation probability of the BE at the first iteration step; then, the formation probability of the BE at the second step of transformation of a lattice of the size $l_1=l_0^2$ along the rib, with P_1 as the probability of a bond to be unbroken (colored), would be

$$P_2=R(l_1,P_1), \tag{6}$$

the formation probability of the BE at the third step of transformation would be

$$P_3=R(l_2,P_2), \tag{7}$$

and so on, up to that for the nth step,

$$P_n=R(l_{n-1},P_{n-1}), \tag{8}$$

The trajectory of the iteration process at the nth step ends at a fixed point 0 or 1 (Fig. 3),

$$P_n=\begin{cases}1 & \text{if } R(l_0,P_0)>P^*\\ 0 & \text{if } R(l_0,P_0)<P^*.\end{cases} \tag{9}$$

The nontrivial fixed point P^* is defined by the equation [22]

$$P^*=R(l_0,P^*). \tag{10}$$

In the vicinity of the critical (fixed) point P^* cluster properties such as, e.g., the correlation length ξ or density P, exhibit singular dependencies on $\Delta p=p_0-p^*$,

$$\xi(p)\sim|\Delta p|^{\nu}, \tag{11}$$

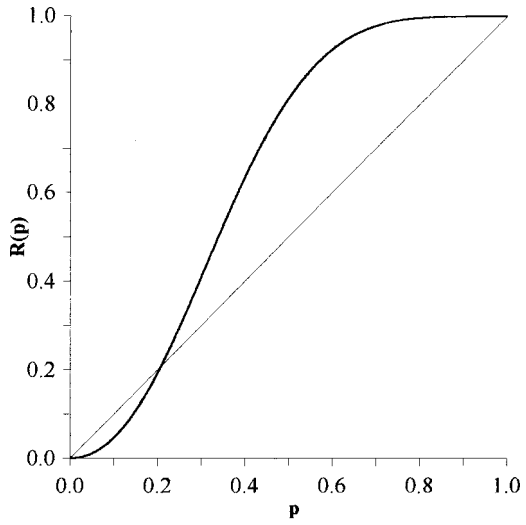

FIG. 3. Probability of BE formation as a function of concentration of nonbroken bonds ($l_0=3$, $d=3$).

$$P(p_0)\sim\Delta p^{\beta}. \tag{12}$$

The corresponding critical indices for a percolating cluster are [10,12] $\nu=\frac{4}{3}$ and $\beta=\frac{5}{36}$ $(d=2)$, and $\nu\cong 0.88$ and $\beta\cong 0.4(d=3)$.

The percolating cluster density $P(p_0)$ scales with size L as

$$P(p_0)\approx L^{\alpha},$$

$$\alpha=d-d_f. \tag{13}$$

Percolation thresholds p_c, critical indices ν, β, and α, fractal dimensionalities d_f were evaluated [17] for FG models of IHM's built on various initial rectangular lattices 2×2, 3×3, 4×4, 5×5, 6×6, 9×8, and 9×9 $(d=2)$, and $3\times 3\times 3$ $(d=3)$. The geometrical parameters of the derived fractal ensembles at the percolation threshold p_c proved to be identical to those for a percolating cluster, provided the dimension of the starting lattice was $l_0>8(d=2)$ and $l_0>3(d=3)$.

The effective elastic properties of an IHM $(d=3)$ were calculated making use of the function $R(p)$ for a $3\times 3\times 3$ lattice of size $l_0=3$ (Fig. 3).

III. ELASTIC PROPERTIES

Let a two-phase system be characterized by the partition function

$$P_0(C)=(1-p_0)\,\delta(C-C_2^{(0)})+p_0\,\delta(C-C_1^{(0)}), \tag{14}$$

where $\delta(x)$ is the Dirac function, p_0 is the probability for a given local region to have a property $C_1^{(0)}$, and $1-p_0$ is the probability to have a property $C_2^{(0)}$. The density function after k steps of the RG theory would be

$$P_k(C)=(1-p_k)\,\delta(C-C_2^{(k)})+p_k\,\delta(C-C_1^{(k)}), \tag{15}$$

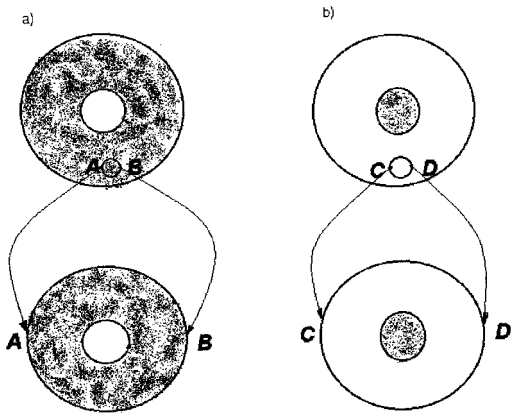

FIG. 4. Blob models of the BE (a) and NBE (b).

where $P_k=R(p_{k-1},L_{k-1})$ is the BE number density defined as the ratio of the number of BE's to the total number of random choices (''colors'') on a square lattice.

Generally speaking, the effective properties of a structural model can be calculated with the following scheme: evaluation of properties of different configurations→averaging out→transfer to the next step [17,18]. The rather cumbersome calculations above in the starting step may be avoided by use of an appropriate approximate method. The basic idea of the latter is that, of all configurations that are generated by random choices of bonds on a lattice, only two types of ensemble of bond configurations are selected, namely, BE and NBE. The other approximation is to switch over from a discrete model (on a lattice) to a continuous model, assuming that BE's and NBE's behave as a continuum within the context of the ''blob'' model (Fig. 4).

Thus, at each iteration step the structures of BE's and NBE's are modeled by composite ''blobs'' in which the BE is treated as a continuous medium of an ''elastic'' phase with an embedded sphere (blob) of a ''soft'' phase [Fig. 4(a)], whereas the NBE is represented by a continuous medium of a ''soft'' phase with an embedded sphere (blob) of an ''elastic'' phase [Fig. 4(b)]. The effective properties (i.e., the bulk modulus K and the shear modulus μ) of the BE and NBE may be calculated by standard formulas of the physics of composite materials [15] accounting for the tensor nature of elastic properties according to the following scheme: (i) definition of the function $R(p,l)$ for the fractal model (on a lattice); (2) calculation of the BE concentration and of the elastic properties of the ''blob'' model at the kth iteration step by the following formulas, respectively:

$$p_k=R(p_{k-1},l), \tag{16}$$

$$C_c^{(k)}=f_1(C_c^{(k-1)},C_n^{(k)},p_{k-1}) \quad \text{for the BE,} \tag{17}$$

$$C_c^{(k)}=f_2(C_c^{(k-1)},C_n^{(k)},p_{k-1}), \quad \text{for the NBE,} \tag{18}$$

where functions f_1,f_2 depend on the structural model and on the elastic properties $C_c^{(k-1)},C_n^{(k-1)}$ of the BE and NBE at the $(k-1)$st step. Thus, the effective properties of an IHM should conform to the following conditions:

$$C_c^{(k)} > C_{\text{eff}} > C_n^{(k)}, \quad \lim_{k\to\infty} C_c^{(k)} = \lim_{k\to\infty} C_n^{(k)} = C_{\text{eff}}. \quad (19)$$

Calculation of the elastic properties of fractal structures by the above scheme implies that the function $R(p)$ is specified analytically. This can be done, provided that fractal ensembles are built from initial (''nucleating'') lattices of a small size ($l_0<5$ for $d=2$), whereas for larger sizes ($l_0>5$ for $d=2$, and $l_0>3$ for $d=3$) the analytical solution for $R(p)$ is too cumbersome, and it can be solved only numerically [13].

Approximate numerical solutions of the function $R(p)$ for a $2\times2\times2$ lattice proved to be compatible with the function

$$R(p) = p^2(4+8p-14p^2-40p^3+16p^4+288p^5-655p^6 + 672p^7-376p^8+112p^9-14p^{10}), \quad (20)$$

which was derived elsewhere [1]. According to Eq. (20), the NBE→BE crossover should occur at the percolation threshold (i.e., critical point) $p_c \cong 0.2085$.

The elastic properties of a percolating system were calculated by our method of step-by-step (iterative) averaging out [15], substituting p for the volume fraction of a stiff, elastic component φ into the Hashin-Shtrikman formulas [25,26] for the structural model of a sphere embedded in a homogeneous continuum (Fig. 4). In this case, the bulk and shear elastic moduli for the BE at the $(i+1)$st iteration step may be calculated as

$$K_c^{(i+1)} = K_c^{(i)} + \frac{(1-p_i)(K_n^{(i)}-K_c^{(i)})}{1+p_i a_c^{(i)}(K_n^{(i)}-K_c^{(i)})}, \quad (21)$$

$$\mu_c^{(i+1)} = \mu_c^{(i+1)} + \frac{(1-p_i)(\mu_n^{(i)}-\mu_c^{(i)})}{1+p_i b_c^{(i)}(\mu_n^{(i)}-\mu_c^{(i)})}, \quad (22)$$

where

$$a_c^{(i)} = \frac{3}{3K_c^{(i)}+4\mu_c^{(i)}}, \quad b_c^{(i)} = \frac{6(K_c^{(i)}+2\mu_c^{(i)})}{5\mu_c^{(i)}(3K_c^{(i)}+4\mu_c^{(i)})}; \quad (23)$$

$K_c^0=K_1$, $\mu_c^0=\mu_1$, and $K_n^0=K_2$, $\mu_n^0=\mu_2$ are the bulk and shear elastic moduli of elastic and soft phases, respectively.

The elastic moduli $K_n^{(i+1)}$ and $\mu_n^{(i+1)}$ for the NBE may be calculated from the above formulas (21)–(23) by making the substitutions $c\leftrightarrow n$ and $p_i\leftrightarrow(1-p_i)$.

IV. RESULTS

As can be seen from the plots of $\log_{10}\mu$ [Fig. 5(a)] and $\log_{10}K$ [Fig. 5(b)] of the fractal ensemble versus the iteration step number n, all these elastic properties behave like fractals before an eventual leveling off. The latter is obviously associated with the upper limit to a fractal-like asymptotics, above which the elastic properties of a system are no longer dependent on the scale (i.e., on the iteration number).

Plots of $\log_{10}K$ vs p (i.e., the concentration of a stiff component) shown in Fig. 6 can be used to estimate critical indices τ (for the elastic regime) and s (for the high elastic regime) defined by Eqs. (1) and (2). The corresponding logarithmic derivatives

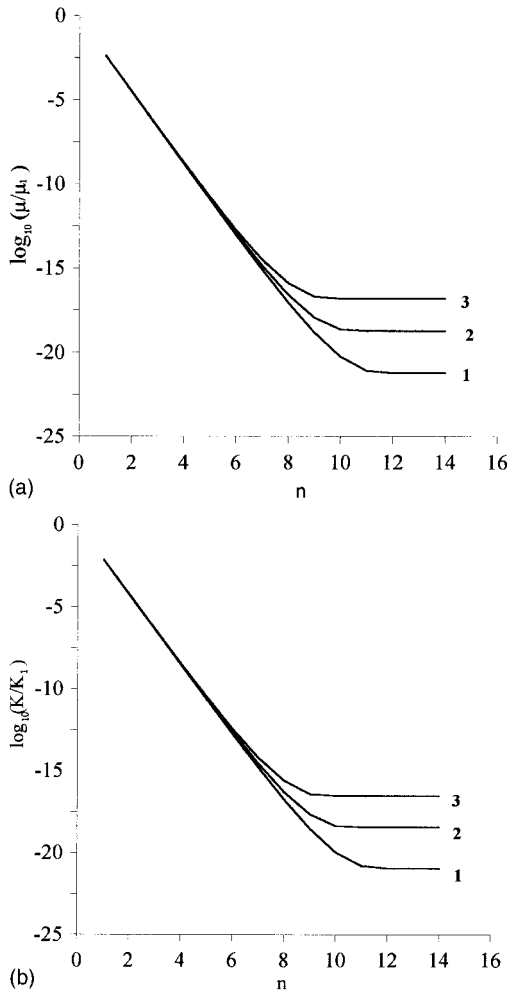

FIG. 5. Semilogarithmic dependencies of shear elasticity modulus (a) and bulk elasticity modulus (b) on the iteration number n for $p=0.2088$ (1), 0.2092 (2), and 0.2098 (3).

$$\tau = \lim_{p\to p_c+0} z(p), \quad (24)$$

$$s = \lim_{p\to p_c-0} z(p), \quad (25)$$

where

$$z(p) = \lim_{\Delta P\to 0} \frac{\Delta(\log_{10}K)}{\Delta[\log_{10}(p_c-p)]},$$

are plotted as functions of the concentration p for some $K_1/\mu_1 = K_2/\mu_2$ and for a few values of the logarithm of the ratio of the bulk elastic moduli of constituent phases, $a = \log_{10}(K_1/K_2)$, in Figs. 7(a) and 7(b). It can be seen there that when the ratio K_1/μ_1 is far from unity then to obtain correct values for the indices τ and s one needs to use materials whose elastic properties differ by more than ten orders of magnitude.

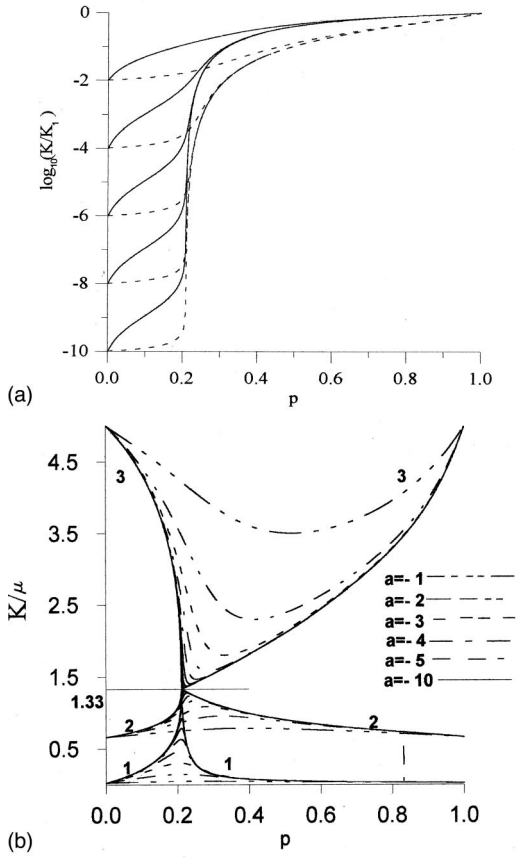

FIG. 6. Dependencies on p of (a) $\log_{10} K$ for $K_1/\mu_1 = K_2/\mu_2 = 5$ (1) and 0.025 (2), and (b) the ratio K/μ for $K_1/\mu_1 = K_2/\mu_2 = 0.025$ (1), 0.75 (2), and 5 (3); $a = \log_{10}(K_2/K_1)$.

The value 3.200 ± 0.002 obtained for the critical index τ that describes the singular behavior of the bulk modulus K in the vicinity of the critical point $p_c + 0$ is by about 15% smaller than that obtained for $d = 3$ by Sahimi and Arbabi [8], $\tau = 3.75 \pm 0.11$. We should add that for $d = 2$ Zabolitzky, Bergman, and Stauffer [27] obtained $\tau = 3.96 \pm 0.04$; the results obtained in Refs. [8], [27] are in good agreement with the relation proposed by Sahimi [28], $\tau = t + 2\nu$, where t is the critical exponent of the conductivity of percolation networks.

The values of the critical index s for the superelastic regime ($p < p_c$) were determined by using very accurate arithmetic (of a few hundred digits of accuracy) for various ratios of K_1/μ_1 and K_2/μ_2 with the requirement that $K_2/K_1 \to 0$ and $\mu_2/\mu_1 \to 0$; in all cases we obtained $s = 0.629\,62 \pm 0.000\,02$, which is in excellent agreement with the result obtained for $d = 3$ by Sahimi and Arbabi [8,29] ($s = 0.65 \pm 0.03$); for $d = 2$, the most reliable estimate of s is 1.24 ± 0.03 [8,29].

In the vicinity of the percolation threshold p_c the ratio of bulk modulus to shear modulus, K/μ, tends to a limiting value of $\frac{4}{3}$ [Fig. 6(b)]; this result was verified with accuracy better than 20 digits. This is consistent with the Bergman and Kantor result $K/\mu = 4/d$ at $p \to p_c$ [4].

As can be seen from plots of the effective Poisson ratio ν_P vs ''stiff'' phase concentration p at different values of the

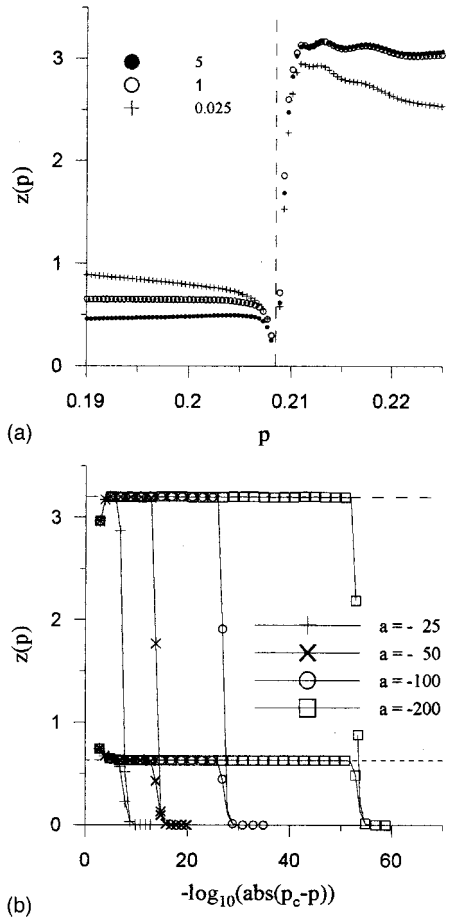

FIG. 7. (a) Logarithmic derivative $z(p)$ plotted as a function of the concentration p for a few values of the ratio $K_1/\mu_1 = K_2/\mu_2 = 5$ (dots), 1 (open circles), and 1/40 (crosses). The dashed line indicates the percolation threshold p_c. (b) $z(p)$ as a function of the logarithm of the distance from the percolation threshold for $K_1/\mu_1 = K_2/\mu_2 = 1/40$ and for very small values of the ratio of the bulk elasticity moduli $a = \log_{10}(K_2/K_1) = -25, -50, -100, -200$; the dashed lines correspond to the estimated values of τ and s, respectively.

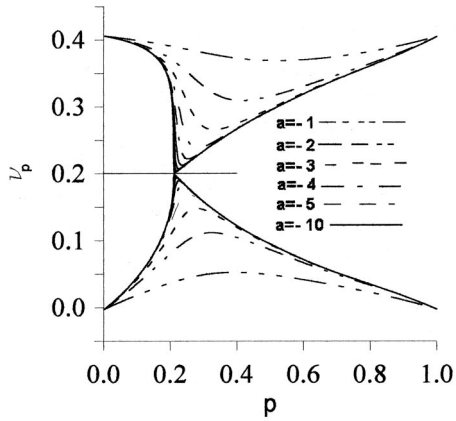

FIG. 8. Dependence of the effective Poisson ratio ν_P on the volume concentration of the ''stiff'' component p for different values of $a = \log_{10}(K_2/K_1)$ for the Poisson ratios of the components $\nu_{P1} = \nu_{P2} = 0$ (curves below $\nu = 0.2$), and $\nu_{P1} = \nu_{P2} = 0.4$ (curves above $\nu = 0.2$).

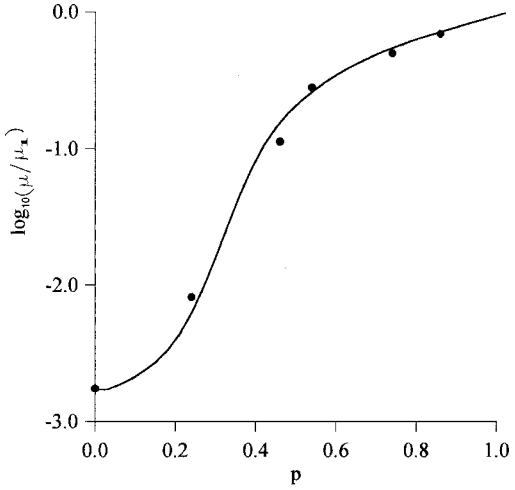

FIG. 9. Dependence of shear elastic modulus on the volume concentration of styrene for the butadiene-styrene block copolymer.

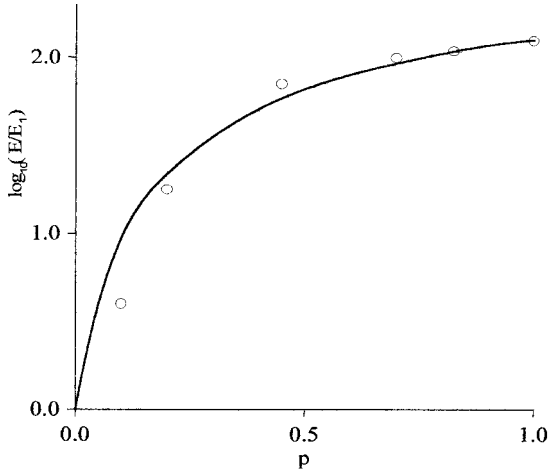

FIG. 10. Dependence of Young's modulus on the volume concentration of poly vinyl chloride (PVC) for the PVC–ethyl acrylate rubber binary blend.

ratio $a=\log_{10}(K_2/K_1)$ and for the values of Poisson ratios of each phase spanning the interval from 0 to 0.4 (Fig. 8), $\nu_P=\frac{1}{5}$ (with accuracy better than 20 digits) at the percolation threshold (in the limit $K_2/K_1\to 0$).

It should be emphasized that our method of calculation of the effective elastic properties of IHM's with chaotic structures can be applied for the analysis of structure-property relationships of both model and real composites, provided the difference between the intrinsic properties of constituent phases is finite (i.e., $a=0$). The quality of fits of the relevant experimental data [30] to theoretical predictions can be assessed from two representative plots, shear modulus vs composition for butadiene-styrene block copolymers (Fig. 9), and relative Young's modulus vs composition for a polyvinyl chloride–ethylacrylate rubber binary blend [15] (Fig. 10).

V. CONCLUSIONS

(1) The proposed method of construction of a structural model of a chaotic medium and the step-by-step (iterative) approach to calculation of elastic properties derived therefrom proved consistent with the results of numerical modeling of elastic properties of percolating systems. Thus, this method can be used to predict the elastic properties of both percolating systems and real composites, provided the difference between the properties of constituent phases is finite.

(2) The critical index for the bulk elasticity modulus in the elastic regime ($p>p_c$) was calculated as $\tau=3.200\pm0.002$. The corresponding critical index in the high elastic regime ($p<p_c$) was $s=0.629\,62\pm0.000\,02$. The ratio of bulk modulus to shear modulus was calculated as $K/\mu=\frac{4}{3}$ on the approach to the percolation threshold p_c, whereas the Poisson ratio of a percolating system in the vicinity of p_c proved independent of the elastic properties of constituent phases and was calculated as $\nu_P=\frac{1}{5}$ at p_c.

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