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ON NEW PHASE INTERMEDIATE LAYERS IN NANOCOMPOSITES AS A SOURCE OF INCREASING THE ELASTIC MODULI

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We study an opportunity to increase elastic moduli of a nanocomposite due to stress-induced phase transformations which lead to the formation of intermediate new phase layers around nanoparticles. These layers enlarge the effective size of the particles which from now become inclusions made up of kernels (the initial nanoparticles) enclosed by new phase layers shells. Increasing the volume fraction of the inclusions can change the effective elastic moduli of the composite much more than one could expect in a case of the composite with a small volume fraction of initial nanoparticles. As an example we consider an isotropic composite with spherical particles under hydrostatic loading. We begin with considering the new phase formation around an isolated inclusion including the interface stability analysis. We show that stable two-phase states are impossible if both elastic moduli of the matrix increase due to phase transition and possible if the bulk modulus increases and the shear module decreases. Then, basing on a self-consistent approach, we describe the new phase formation around spatially distributed particles and study how external strains effects the new phase areas growth. Finally we demonstrate that the new phase layers formation can lead to increasing the effective bulk modulus of the composite.

Keywords: nanocomposites, intermediate layers, effective elastic moduli, phase transformations, stability.

1. Introduction

Carbon nanotube and fulleren reinforced nanocomposites have received increased attention in recent years because of their mechanical, electrical, optical and magnetoelectrical properties [4,15,16]. One of the surprising facts is that a small volume fraction of nano-inclusions may lead to significant effects which cannot be predicted by common mathematical model of composite materials made of a matrix and uniform inclusions. In a number of papers (see, e.g., [1,4]) it was suggested that these effects may be related to the quality of the boundaries which separate the inclusions and matrix. But the theories of composite material usually imply ideal contacts at the inclusions boundaries and even in this case cannot give the effects declared.

To explain how a small volume fraction of particles may lead to disproportionately significant changes of mechanical properties of nanocomposites we suppose that this may be a result of the formation of intermediate layers surrounding the particles. The major hypothesis is that these layers appear as a result of phase transformation in matrix around the particles and the phase interfaces must satisfy thermodynamic equilibrium conditions. The formations of new phase layers increases the “effective” sizes of the particles. As a result the effective volume concentration of inclusions increases and, thus, effective elastic moduli change.

To simplify the derivations we consider a composite with isotropic spherical inclusions in isotropic matrix. This gives us a foreseeable script of general consideration and analytical basement for further verifications of numerical simulations.

Note that stress-induced phase transformations can be induced by external all-round compression/tension as well as by thermal stresses appeared because of the difference between thermal expansion coefficients of the inclusions and surrounding material. In fact, new phase areas can be formed under combined thermo-mechanical actions at the stage of the composite manufacturing. Since from the mathematical point of view thermal stresses can be reduced to stresses produced by mechanical loading, we consider further only external all-round tension/compression.

The following questions are being discussed within the above formulated elementary problem:

1. Is it possible to form the stable intermediate layers of a new phase if at least some of elastic moduli increase?

Given average strain and temperature, equilibrium and stable two-phase states are the microstructures which correspond to minimal value of the Helmholtz free energy of a body that differs from the strain energy only by a term related with free energies of the phases in stress free states and proportional to the new phase volume. The strain energy cannot decrease if all elastic moduli of the matrix increase due to phase transformation around the particles. Thus, we have to examine the case when some elastic moduli increase but the others decrease. From the mechanical point of view this means that we have to deal with a case for which the jump of the elasticity tensor due to phase transition is a non-signdefinite tensor, and in any case we need a stability analysis that is carried out in the present paper.

2. Is it possible to provide the controlled growth of the effective elastic moduli?

This question arises because, generally speaking, the stability of the two-phase state of the matrix can be lost and the instability may lead, particularly, to a spontaneous phase transformation of the whole matrix. That is why we find the interval of external strains at which two-phase states adjust to external strains and remain stable.

3. Is it possible to reduce stress concentration in the matrix due to the formation of new phase transition layers?

To answer this question we examine how the phase transformation effects the strain energy density spatial distribution. We demonstrate that in a case of the stable interface the phase transformation leads to the energy density decrease in the particle itself and in the matrix on the side of the parent phase. We also show the opportunity to reduce the energy density in all areas of the body. The intensity of the shear stresses also decreases.

2. Constitutive equations

We consider stress-induced phase transformations of martensite type accompanied by the transformation strain and changes of elastic moduli. Two-phase deformation of an elastic body is studied by a small strain approach.

Let new phase areas V_+ be bounded by interfaces Γ. A problem on the equilibrium two-phase configurations of an elastic body is reduced to finding position of unknown interfaces Γ and displacement $\mathbf{u}(\mathbf{x})$ sufficiently smooth at material points $\mathbf{x} \notin \Gamma$, continuous across Γ, and satisfying equilibrium and boundary conditions including conditions on the interface:

$$\mathbf{x} \notin \Gamma \quad : \qquad \nabla \cdot \boldsymbol{\sigma} = 0, \quad \theta = \text{const}, \tag{1}$$

$$\mathbf{x} \in \Gamma \quad : \qquad [\mathbf{u}] = 0, \quad [\boldsymbol{\sigma}] \cdot \mathbf{n} = 0, \tag{2}$$

$$[f] - \langle \boldsymbol{\sigma} \rangle : [\boldsymbol{\varepsilon}] = 0, \quad \langle \boldsymbol{\sigma} \rangle = \frac{1}{2}(\boldsymbol{\sigma}_+ + \boldsymbol{\sigma}_-) \tag{3}$$

where $\boldsymbol{\varepsilon}$ and $\boldsymbol{\sigma}$ are strain and stress tensors, θ is the temperature, $f = f(\boldsymbol{\varepsilon}, \theta)$ is the Helmholtz free energy volume density, $\mathbf{n}$ is the unit normal to the interface Γ, super- or subscripts "$-$" and "$+$" identify the values being taken for a material in the "$-$" and "$+$" phase states, respectively, the brackets $[\,\cdot\,] = (\cdot)_+ - (\cdot)_-$ denote the jump across Γ. Body forces, thermoelastic effects and surface energy are not taken into account. Note that from the displacement and traction continuity it follows that $\langle\boldsymbol{\sigma}\rangle : [\boldsymbol{\varepsilon}] = \boldsymbol{\sigma}_\pm : [\boldsymbol{\varepsilon}]$.

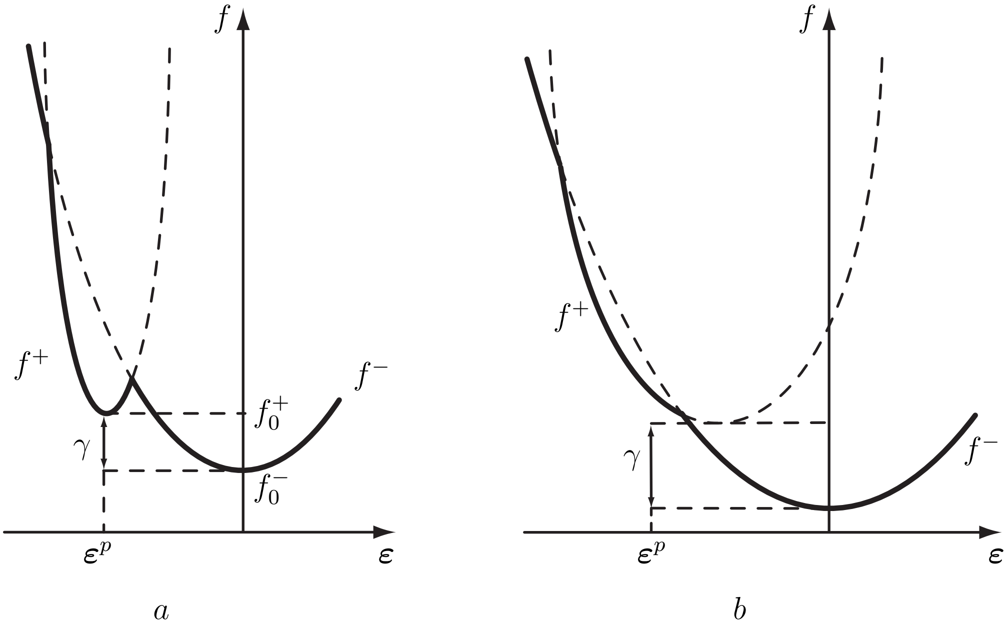
The conditions (2) are common contact conditions and can be satisfied on any contact surfaces in a body, as it is in composite materials. The additional thermodynamic condition (3) (known as the Maxwell relation) is related to an additional degree of freedom caused by an unknown phase boundary. This condition is the necessary (but not sufficient) condition for the energy minimization with respect to the position of the interface. Namely the thermodynamic equilibrium condition (3) imposes the restrictions on the existence and geometry of new phase areas (see, e.g., [9, 10]).

We consider a two-well strain-energy function:

$$f(\boldsymbol{\varepsilon},\theta) = \min_{-,+}\left\{f^-(\boldsymbol{\varepsilon},\theta), f^+(\boldsymbol{\varepsilon},\theta)\right\}, \tag{4}$$

$$f^\pm(\boldsymbol{\varepsilon},\theta) = f_0^\pm(\theta) + \frac{1}{2}(\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}^p_\pm) : \mathbf{C}_\pm : (\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}^p_\pm).$$

Upper and lower scripts "+" and "−" in relationships correspond to each other. 1D-sketch of the free energy density dependence is shown in Fig. 1



a *b*

Fig. 1. Free energy volume density: a – case 1, b – case 2

By (4), the constitutive equations take the form:

$$\boldsymbol{\sigma}_\pm(\boldsymbol{\varepsilon}) = \mathbf{C}_\pm : (\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}^p_\pm), \quad \boldsymbol{\varepsilon} \in \mathcal{E}_\pm \tag{5}$$

where $\mathcal{E}_\mp$

$$\mathcal{E}_- = \{\boldsymbol{\varepsilon} :\ \varphi(\boldsymbol{\varepsilon}) > 0\}, \quad \mathcal{E}_+ = \{\boldsymbol{\varepsilon} :\ \varphi(\boldsymbol{\varepsilon}) < 0\}, \quad \varphi(\boldsymbol{\varepsilon}) = f^+(\boldsymbol{\varepsilon}) - f^-(\boldsymbol{\varepsilon})$$

are the domains of definition of the phases "−" and "+" in strain space.

The parameters $\mathbf{C}_\pm$, $f_0^\pm$ and $\boldsymbol{\varepsilon}^p_\pm$ are the elasticity tensors, free energy densities and strain tensors in unstressed phases "±", respectively. If $\boldsymbol{\varepsilon}^p_+ = 0$ or $\boldsymbol{\varepsilon}^p_- = 0$, then $[\boldsymbol{\varepsilon}^p] \equiv \boldsymbol{\varepsilon}^p$ is the transformation eigenstrain.

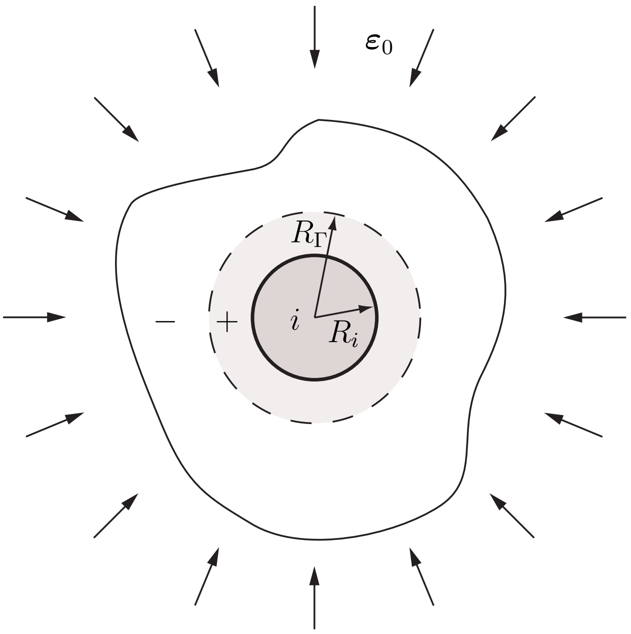


Fig. 2. A particle enclosed by a new phase intermediate layer

We emphasize that one of the unstressed states can be only hypothetical. The strain $\varepsilon = \varepsilon^p_+$ may belong to the domain of the phase "$-$", not to the phase "$+$", if $f^+(\varepsilon^p_+) > f^-(\varepsilon^p_+)$. Further we say that we are dealing with the case 1, if $f^+(\varepsilon^p_+) < f^-(\varepsilon^p_+)$ (Fig. 1 a) and with the case 2, if $f^+(\varepsilon^p_+) > f^-(\varepsilon^p_+)$ (Fig. 1 b).

The thermodynamic condition can be rewritten in the form that relates the strain on one side of the interface and the normal to the interface (see [7] or [2] and reference therein):

$$\chi(\boldsymbol{\varepsilon}_\pm, \gamma, \mathbf{n}) \triangleq \gamma + \frac{1}{2}\,[\boldsymbol{\varepsilon}^p : \mathbf{C} : \boldsymbol{\varepsilon}^p] + \frac{1}{2}\,\boldsymbol{\varepsilon}_\pm : \mathbf{C}_1 : \boldsymbol{\varepsilon}_\pm - \boldsymbol{\varepsilon}_\pm : [\mathbf{C} : \boldsymbol{\varepsilon}^p] \pm \frac{1}{2}\,\mathbf{q}_\pm : \mathbf{K}_\mp(\mathbf{n}) : \mathbf{q}_\pm = 0, \tag{6}$$

where

$$\mathbf{q}_\pm = \mathbf{C}_1 : \boldsymbol{\varepsilon}_\pm - [\mathbf{C} : \boldsymbol{\varepsilon}^p], \quad \mathbf{K}_\mp(\mathbf{n}) = \{\mathbf{n} \otimes \mathbf{G}_\mp(\mathbf{n}) \otimes \mathbf{n}\}^s, \quad \mathbf{G}_\mp(\mathbf{n}) = (\mathbf{n} \cdot \mathbf{C}_\mp \cdot \mathbf{n})^{-1},$$
$$\mathbf{C}_1 = \mathbf{C}_+ - \mathbf{C}_-, \quad \mathbf{B}_1 = \mathbf{C}_+^{-1} - \mathbf{C}_-^{-1}, \quad \gamma = [f_0].$$

The parameter γ acts as the temperature.

If the inverse tensor $\mathbf{C}_1^{-1}$ exists then (3) can be rewritten in terms of the tensor $\mathbf{q}$ taken on one side of the interface [14]:

$$\chi(\mathbf{q}_\pm, \gamma_*, \mathbf{n}) \triangleq \gamma_* + \frac{1}{2}\,\mathbf{q}_\pm : \left(\mathbf{C}_1^{-1} \pm \mathbf{K}_\mp(\mathbf{n})\right) : \mathbf{q}_\pm = 0, \quad \gamma_* \triangleq \gamma + \frac{1}{2}\,[\boldsymbol{\varepsilon}^p] : \mathbf{B}_1^{-1} : [\boldsymbol{\varepsilon}^p] \tag{7}$$

Thermodynamic condition (6) cannot be satisfied for all strains. This leads to the concept of phase transitions zones (PTZs) [9, 11, 12], which are the areas formed in strain space by all strains that may exist in the body at the equilibrium phase boundaries. In other words, PTZ is formed by the strains, for which the equation (6) can be solved with respect to the unit normal $\mathbf{n}$. Given material parameters and the parameter γ, the PTZ presents all possible local orientations of the equilibrium phase boundaries and strain jumps across the interfaces. Thus, the PTZ is the passport of a material which undergoes phase transformation (see, e.g., [3, 9]). In this paper, the construction of PTZs is used to reject the equilibrium but unstable solutions.

Further we consider a matrix that can undergo phase transformations and inclusions, which act as stress concentrators and induce phase transformation. The material of the matrix is piece-wise linear elastic described by the constitutive equations (4), (5). Material of the inclusion is also linear-elastic, its elasticity tensor is $\mathbf{C}_i$ and the free energy density is given by the dependence

$$f_i\left(\boldsymbol{\varepsilon}\right) = \frac{1}{2}\boldsymbol{\varepsilon} : \mathbf{C}_i : \boldsymbol{\varepsilon}. \tag{8}$$

3. Spherically-symmetric two-phase deformations induced by a spherical inclusion

We consider an unbounded medium with a spherical inclusion V_i of the radius R_i under all-round tension/compression. Let $\boldsymbol{\varepsilon}^p_- = 0,\ \boldsymbol{\varepsilon}^p_+ = \boldsymbol{\varepsilon}^p = (\vartheta^p/3)\mathbf{E}$, and $\boldsymbol{\varepsilon}_0 = (\vartheta_0/3)\mathbf{E}$ be the external strain. Suppose that there exists a two-phase deformation with one spherical interface (Fig. 2) and find the equilibrium interface radius R_Γ in dependence of external strain and material parameters.

Radial displacement u in areas $V_i,\ V_+,\ V_-$ is given by the formula

$$u = Ar + \frac{D}{r^2} \tag{9}$$

where dependencies of the integration constants $A = \{A_i, A_+, A_-\}$ and $D = \{D_i, D_+, D_-\}$ on ε_0 and the inverse of the relative interface radius

$$\rho = \frac{R_i}{R_\Gamma}, \quad \rho \in [0,1]$$

can be found from the contact conditions at the particle boundary and the interface, the condition at the vicinity, and the boundedness of the displacement in the center:

$$r = R_i,\ r = R_\Gamma : \quad [u] = 0, \quad [\sigma_r] = 0$$

$$\varepsilon_r \,|_{r\to\infty} = \vartheta_0/3 \equiv \varepsilon_0, \quad u \,|_{r=0} < \infty,$$

and $\sigma_r,\ \varepsilon_r,\ \varepsilon_\varphi$ are stress and strains in spherical coordinates.

It can be found that the integration constants are given by the following relationships

$$\begin{aligned}
&A_i = A_i^\varepsilon \varepsilon_0 + A_i^\vartheta, \quad D_i = 0, \quad A_i^\varepsilon = \frac{d_+^+\, d_-^-}{Z}, \quad A_i^\vartheta = \frac{4\mu_1(1-z)t}{Z}\\
&A_- = \varepsilon_0, \quad \frac{D_-}{R_\Gamma^3} \equiv \widehat{D}_- = D_-^\varepsilon \varepsilon_0 + D_-^\vartheta\\
&D_-^\varepsilon = \frac{3(d_-^+ k_{1i}^+ z - d_i^+ k_1)}{Z}, \quad D_-^\vartheta = \frac{d_i^+(1-z)t}{Z}\\
&A_+ = A_+^\varepsilon \varepsilon_0 + A_+^\vartheta, \quad A_+^\varepsilon = \frac{d_i^+\, d_-^-}{Z}, \quad A_+^\vartheta = \frac{(d_i^+ - 4\mu_1\, z)t}{Z}\\
&\frac{D_+}{R_i^3} \equiv \widehat{D}_+ = D_+^\varepsilon \varepsilon_0 + D_+^\vartheta, \quad D_+^\varepsilon = \frac{3d_-^- k_{1i}^+}{Z}, \quad D_+^\vartheta = -\frac{d_i^- t}{Z}
\end{aligned} \tag{10}$$

where

$$\begin{aligned}
&Z = d_i^+\, d_+^- - 12\mu_1\, k_{1i}^+\, z\\
&z = \rho^3,\ k_1 = k_+ - k_-,\ k_{1i}^+ = k_+ - k_i,\ \mu_1 = \mu_+ - \mu_-,\ t = k_+\vartheta^p\\
&d_\pm^+ = 3k_\pm + 4\mu_+,\ d_\pm^- = 3k_\pm + 4\mu_-,\ d_i^\pm = 3k_i + 4\mu_\pm
\end{aligned}$$

The mechanical equilibrium equation $(1)_1$ and contact conditions (2) are satisfied at any interface radius ρ if the solution is taken in the form (9) with integration constants given by formulae (10). The dependence of the thermodynamically equilibrium inverse interface radius

ρ_* on external strain ε_0 is determined by the thermodynamic condition (7) that, after substituting strains obtained by the differentiation of the displacement (9), takes the form of the algebraic equation

$$2\gamma_* + \frac{3\left(t - 3k_1A_+ + 4\mu_1 z\widehat{D}_+\right)^2}{d_-^-} + \frac{(t - 3k_1A_+)^2}{k_1} + 12\mu_1 z^2 \widehat{D}_+^2 = 0 \tag{11}$$

$$\gamma_* = \gamma - \frac{k_-k_+(\vartheta^p)^2}{2k_1}$$

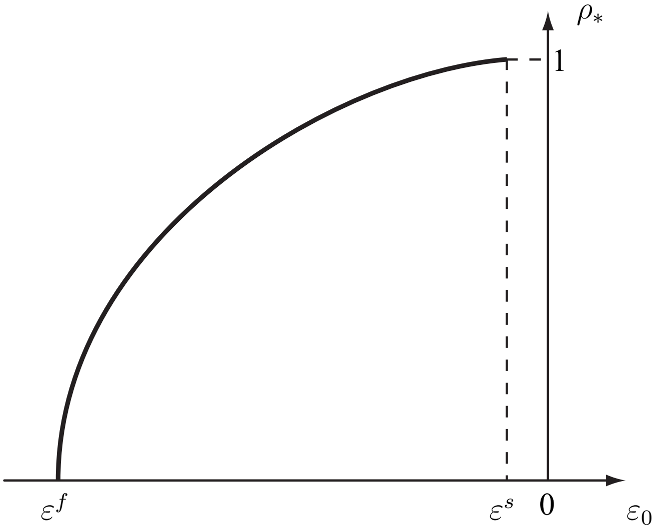


Fig. 3. The inverse relative equilibrium interface radius ρ in dependence on ε_0, $\mu_- > \mu_+$.

The dependence of the inverse relative equilibrium interface radius ρ_* on ε_0 is shown in Fig. 3 for the case $k_1 > 0$, $\mu_1 < 0$. New phase nucleation starts at the particle boundary at $\varepsilon_0 = \varepsilon^s$. The value ε^s can be found from (11) if substitute $\rho = 1$ into the formulae for D_+ and A_+.

The whole matrix transforms into the phase state "+" at $\varepsilon_0 = \varepsilon^f$. Substituting $\rho = 0$ into (11) leads to to the formula

$$\varepsilon^f = \frac{1}{3k_1}\left(t \pm \sqrt{-2\,\frac{d_+^-}{d_-^-}\,k_1\,\gamma_*}\right) \tag{12}$$

If $\vartheta^p < 0, k_1 > 0$ then the sign "–" is to be taken in (12).

4. Energy changes due to new phase areas growth and the interface stability

The interaction energy is determined as

$$E_\rho = \Pi_\rho - \Pi_- \tag{13}$$

where Π_ρ is the Gibbs free energy of a body with an inclusion that has the interface inverse radius ρ embedded into two-phase matrix, Π_- is the Gibbs free energy of a body with an inclusion embedded into one-phase matrix in the phase state "–" at the same boundary conditions as Π_ρ is calculated.

In the case under consideration

$$E_\rho = \int_{V_i} (f_i(\boldsymbol{\varepsilon}) - f_i(\boldsymbol{\varepsilon}_0^i))\,dV + \int_{V_+} (f_+(\boldsymbol{\varepsilon}) - f_-(\boldsymbol{\varepsilon}_0^-))\,dV + \int_{V_-} (f_-(\boldsymbol{\varepsilon}) - f_-(\boldsymbol{\varepsilon}_0^-))\,dV$$

where $\boldsymbol{\varepsilon}$ is a current strain field in a case of two-phase matrix with the interface inverse radius ρ, $\boldsymbol{\varepsilon}_0^i$ is a strain inside the inclusion when the matrix is in the phase state "$-$", $\boldsymbol{\varepsilon}_0^-$ is a strain in one-phase matrix in the "$-$" phase state.

Following [2] we derive from (4) and (8) that in a case of an arbitrary interface radius

$$\frac{E_\rho}{4\pi R_i^3} = \left(\gamma + \frac{1}{2}t(\vartheta^p - 3\boldsymbol{\varepsilon}_0) + \frac{3}{2}(3k_1\boldsymbol{\varepsilon}_0 - t)A_+\right)\frac{1-z}{3z} + 2\mu_1\widehat{D}_+\widehat{D}^0_-(1-z),$$

$$\widehat{D}^0_- = \frac{D^0_-}{R_i^3}, \quad D^0_- = \frac{3\varepsilon_0(k_- - k_i)R_i^3}{3k_i + 4\mu_-}$$

The equilibrium interface radius ρ_*, i.e. the radius satisfying the thermodynamic condition, corresponds to the extremum point on the dependence $E_\rho(\rho \,|\, \varepsilon_0)$.

Examples of the dependencies of the interaction energy on the interface radius are given in Fig. 4 b_1 (case 1) and Fig. 4 b_2(case 2) ($\mu_- > \mu_+$). The results for two values of the external strains $\varepsilon_0 = \varepsilon_{01}$ (solid lines) and $\varepsilon_0 = \varepsilon_{02}$ (dotted lines) are shown, $\varepsilon_{02} < \varepsilon_{01} < 0$. Minimum points in Fig. 4 b_1, b_2 demonstrate that the equilibrium solutions are stable with respect to interface radius perturbations if $\mu_- > \mu_+$. If $\mu_- < \mu_+$ then similar calculations show that the dependence of the interaction energy has a maximum at the new phase spherical layer equilibrium radius, and this means instability of the interface. That is why further we discuss in detail phase transformation, resulting in decreasing the shear modulus but the increasing the bulk modulus.

So, if the bulk modulus increases, while the shear modulus decreases due to phase transformation, i.e. $k_1 > 1$, $\mu_1 < 0$, then the interface is stable with respect to perturbations of the interface radius. However, when certain radius is reached, the interface becomes unstable with respect to axisymmetric perturbations. This instability can be detected with making use of an additional stability analysis basing on the procedure developed in [10,13]. The instability of equilibrium two-phase deformations have not been detected if the strain at the interface corresponded to the outer boundaries of the PTZs. The fact that strains at the stable interface must belong to the PTZ boundaries also follows from the recent paper [17].

Fig. 4 a_1, a_2 shows how strains at the interface are related with the PTZ at different external strains. Black dots denote to the local strains which take place at the equilibrium interface at the external strain ε_{01}. These strains are located at the external boundaries of PTZ. Crosses mark the local strains at the external strain ε_{02} ($\varepsilon_{02} < \varepsilon_{01} < 0$). One of these strains is located at the internal boundaries of PTZ.

In the case under consideration the strains belong to the outer PTZ boundaries if

$$(\varepsilon_\theta^- - \varepsilon_r^-)\,|_\Gamma > 0 \tag{14}$$

This inequality allows us to estimate the interval of external strains at which two-phase states remain stable. Straightforward calculations show that the transformation interval $|\varepsilon^f - \varepsilon^s|$ is larger in the case 2 that is if the value $\gamma(\theta)$ is chosen so that $f^+(\boldsymbol{\varepsilon}^p) > f^-(\boldsymbol{\varepsilon}^p)$.

Note that the stable homogeneous spherical new phase areas can exist in a uniform media under external all-round tension/compresion only if $\mu_+ > \mu_-$ [2,5,10,13]. Therefore, depending on the relationship between shear moduli of the phases, two types of new phase nucleation are possible. If $\mu_+ < \mu_-$ then inhomogeneities (stress concentrators) are the points of the new phase growth. If $\mu_+ > \mu_-$ then new phase areas can appear in the domains of homogeneity of the material.

5. Free energy density spatial re-distribution and energy release due to phase transformations

Two-phase deformations are always accompanied with some stress concentration at the interface. To clarify why two-phase deformations can be preferential from the energy minimization point of view we study how the free energy density is redistributed in a body if the phase transformation takes place around the particles.

Fig. 4 c_1 and c_2 shows the spatial distributions of the difference

$$\psi(r) = \begin{cases} f_i(\boldsymbol{\varepsilon}^\rho) - f_i(\boldsymbol{\varepsilon}_i^0), & 0 < r < R_i \\ f_-(\boldsymbol{\varepsilon}^\rho) - f_-(\boldsymbol{\varepsilon}_-^0), & R_i < r < R_\Gamma \\ f_+(\boldsymbol{\varepsilon}^\rho) - f_-(\boldsymbol{\varepsilon}_-^0), & r > R_\Gamma \end{cases}$$

between the free energy density in the case of the equilibrium two-phase state of a matrix with embedded inclusion and the free energy density in the case of one-phase state of the matrix with embedded inclusion at the same boundary conditions for the cases 1 and 2. As in the previous section, solid lines and dotted lines in Fig. 4 c_1 and c_2 correspond to external strains ε_{01} and ε_{02}, $\varepsilon_{02} < \varepsilon_{01} < 0$.

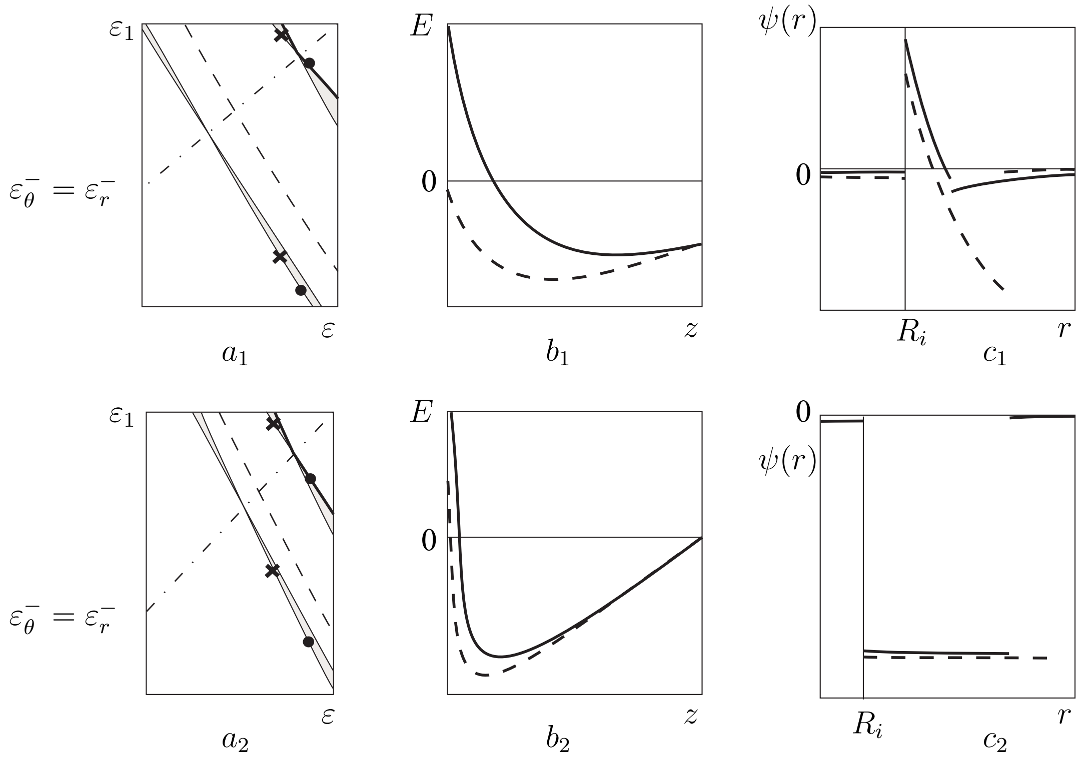


Fig. 4. a_1 and a_2 – the PTZ and local strains at the interfaces, b_1 and b_2 – the dependencies of the interaction energy E on $z = \rho^3$ (the cube of the inverse interface radius), c_1 and c_2 – the spatial redistribution of the free energy density in the cases 1 and 2, correspondingly.

Negative values of $\psi(r)$ mean that the local energy release takes place due to equilibrium new phase zone formation around the inclusion. In cases 1 and 2 the free energy density decreases both in initial inclusion and outside the coated one. In case 2 the free energy density is also decreased in intermediate layer and the relative contribution of this decreasing in body energy is very significant.

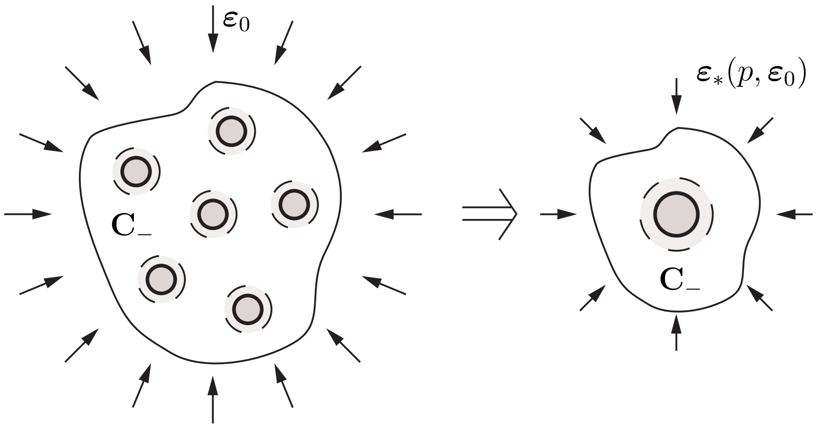


Fig. 5. The effective field method.

Note that if the strain energy density decreases in the vicinity of the inclusion then the stress concentration decreases. In this case the phase transformation acts as a reinforcing factor.

6. Composites with a matrix undergoing phase transformations

We consider a composite material with spherical inclusions. As in the previous sections the material of matrix can undergo phase transformations. The constitutive relationships of the material of the matrix and the particles are the same as in the case of the isolated inclusion, (4) and (8), correspondingly.

Following a self-consistent method [6, 8] we can consider every inclusion as an isolated one embedded into the homogeneous medium with elasticity tensor $\mathbf{C}_-$. The influence of other inclusions is taken into account by introducing the effective field $\boldsymbol{\varepsilon}_*$ that is the sum of the external field $\boldsymbol{\varepsilon}_0$ and the field induced by surrounding inclusions (Fig. 5). The main hypothesis of the method is that the field $\boldsymbol{\varepsilon}_*$ is constant and the same for all the inclusions. We also assume statistical independence of the inclusion properties from their spatial locations and use ergodic properties of the functions considered.

The following equation for the effective field can be obtained [18]:

$$\boldsymbol{\varepsilon}_* = \boldsymbol{\varepsilon}_0 + p\mathbf{A} : (\mathbf{P}_0 : \boldsymbol{\varepsilon}_* - \mathbf{P}_0^p) \tag{15}$$

where p is a volume fraction of coated inclusions, $p = p_0 + p_+$, p_0 is a volume fraction of the particles (initial inclusions), p_+ is a new phase volume fraction, the tensor $\mathbf{A}$ take the form [6]

$$\mathbf{A} = \frac{1 - æ_-}{9\mu_-}\mathbf{EE} + \frac{5 - 2æ_-}{15\mu_-}(\mathbf{I} - \frac{1}{3}\mathbf{EE}), \quad æ_- = \frac{3k_- + \mu_-}{3k_- + 4\mu_-}$$

where $\mathbf{I}$ is the isotropic unity fourth-range tensor, $I_{ijkl} = 1/2(\delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il})$.

The effective field must be spherical for hydrostatic loads $\boldsymbol{\varepsilon}_* = \varepsilon_*\mathbf{E}$. We have

$$\varepsilon_* = \frac{\varepsilon_0 d_-^- - P_0^p}{d_-^- - 3P_0}, \quad P_0 = (k_1 A_+^\varepsilon p_+ - k_{1i}^- A_i^\varepsilon p_0), \quad P_0^p = \left(\frac{tp_+}{3} + k_{1i}^- A_i^\vartheta p_0 - k_1 A_+^\vartheta p_+\right)\vartheta^p \tag{16}$$

A_i^ε, A_+^ε,A_i^ϑ, A_+^ϑ are determined by (10) at $z = p_0/p_+$.

If $p \to 0$ then the solution of a composite problem becomes the solution for the isolated inclusion given in previous sections.

After averaging the expression for the stresses and strains we derive the formula for the effective elastic moduli of the composite. The tensor of effective elastic moduli takes the form:

$$\mathbf{C}_* = k_*\mathbf{EE} + 2\mu_* \left(\mathbf{I} - \frac{1}{3}\mathbf{EE}\right)$$

where the dependencies of effective bulk and shear moduli on volume fractions of the particles and the thickness of the new phase layers is given by formulae

$$k_* = k_- - \frac{d_-^- P_0}{d_-^- - 3P_0}, \quad \mu_* = \mu_- - \frac{3d_-^- P_0}{2(d_-^- - 3P_0)}$$

The dependencies of relative effective bulk modulus k_*/k_*^0, shear modulus μ_*/μ_*^0 and Young's modulus E_*/E_*^0 on the volume fraction of layered inclusions are shown in Fig. 6. Here k_*^0, μ_*^0, and E_*^0 are the bulk, shear and Young's moduli of the initial composite without intermediate new phase layers. Fig. 7 shows the dependence of the equilibrium inclusions volume fraction p_* on the external strain. Both figures are pictured for the case 2, $k_- = 20$, $\mu_- = 9$, $k_+ = 140$, $\mu_+ = 6$, $k_i = 500$, $\mu_i = 170$, $\vartheta^p = -0.08$, $\gamma = 0.07$, the initial volume fraction of the particles 0.02.

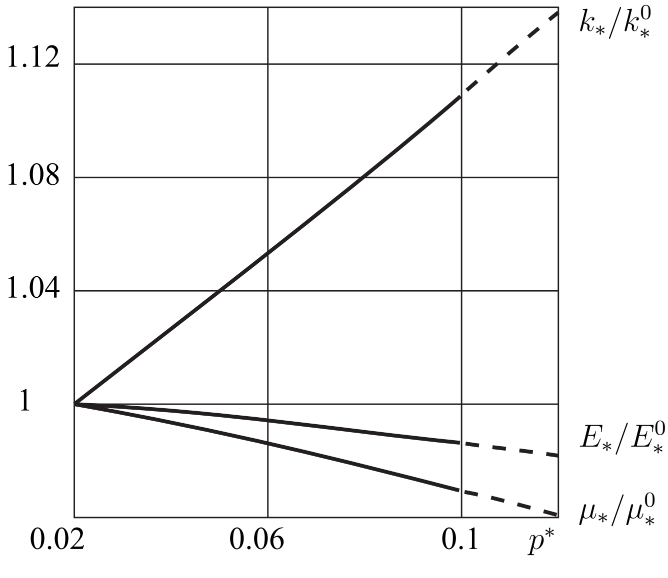


Fig. 6. The dependencies of the relative effective bulk modulus k_*/k_*^0, shear modulus μ_*/μ_*^0 and Young's modulus E_*/E_*^0 on the volume fraction of the layered inclusions.

The solid parts of the lines correspond to the equilibrium volume fraction of layered inclusions and corresponding external strains at which the local strains at the interface of the effective inclusion belong to the external PTZ-boundaries. We assume that corresponding interfaces are stable. The dotted parts of the lines correspond to external strain and volume fractions for which at least one of the strains at the effective interface does not belong to the external PTZ-boundary. The stability of the effective interface is lost in this case. Chosen parameters $k_\pm$, k_i, $\mu_\pm$, γ and volume fraction of the particle $p_0 = 0.02$, two-phase structure remains stable until the equilibrium volume fraction p_* of the layered inclusions reaches 0.1. The effective bulk modulus of the composite demonstrates 10 percent growth. Both Young's modulus and shear moduli decrease.

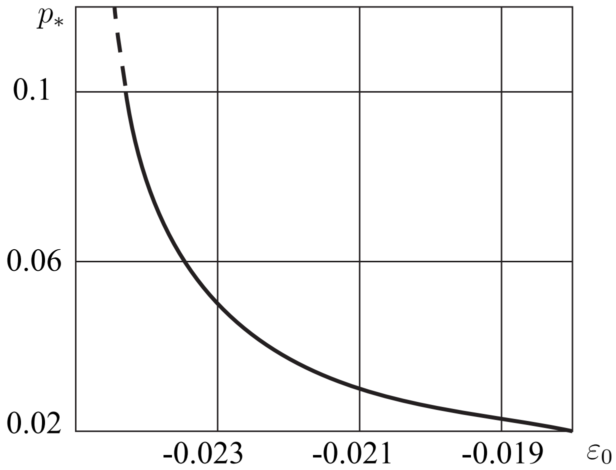


Fig. 7. The dependencies of the equilibrium volume fraction p_* on the external field ε_0

7. Conclusion

We developed a model to describe intermediate layers in composite materials as new phase areas. Phase transformation around spherical isolated inclusion was analyzed in detail. Then the growth of new phase areas around the particles in composite materials was described using the self-consistent approach.

Due to the fact that phase transformations lead to the total energy decrease and stability reasons, simultaneous increasing of all elastic moduli is impossible but it is possible to increase some of the moduli. We demonstrated that if materials of the components are isotropic and inclusions are spherical then the new phase formation under all-round compression can lead to increasing the bulk modulus. In this case the shear modulus is to decrease. We also demonstrated that due to the energy release the phase transformation can act as a reinforcing factor.

We developed a procedure for the interface stability analysis and showed that the desirable process of the new phase intermediate layers formation may be very sensitive with respect to the temperature and loading conditions. This in turn may result in experimental data scattering and misunderstending.

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