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Mathematical modeling of near-surface non-homogeneity in nanoelements

Nahirnyj T. S.[1,2], Tchervinka K. A.[3]

[1] *Centre of Mathematical Modelling of IAPMM named after Ya.S.Pidstryhach*
15 Dudayev str., 79005, Lviv, Ukraine
[2] *Faculty of Mechanical Engineering, University of Zielona Góra*
4 Prof. Szafrana str., 65-516, Zielona Góra, Poland
[3] *Department of Mathematical Modeling, Ivan Franko National University of Lviv*
1 Universytetska str., 79000 Lviv, Ukraine

This paper is a further development of the local gradient approach in thermomechanics. The presented model allows us to study the stress-strain state of nanoelements under one-continuum approach. Thermoelastic body is considered as an open thermodynamical system where the mass fluxes and sources are connected with sudden occurrence of the structure of material and real surface of the body at the moment of body formation. The complete system of equations includes mass balance equation generalized for locally heterogeneous systems. As a model problem, there is considered an equilibrium state of a thin layer (film). The size effects of near-surface stress and effective Young's modulus have been studied.

1. Introduction

In recent years, there has been increasing interest in non-classical models of continuum mechanics. The advent of new materials and technologies are often connected with the effects that cannot be described within the framework of classical models [12,21,27]. Due to the recent technological developments in science and engineering and the achievements in fabrication and manufacturing, structures of nanometer dimensions are now present in many engineering devices. Thus, a need arises in extension of classical models, in particular, for taking into account such effects as near-surface and structural non-homogeneities, which are essential in bodies made of nanomaterial. In such materials the contributions of bulk and surface constituents into the energy are comparable. Experimental and theoretical study of size effects has been a subject of numerous works, e.g. [3] presents a review of studies of the size effect of tensile strength of quasibrittle materials, [10,28] review the mechanical properties of bulk nanostructured materials, in [6,12] the size effects of mechanic properties in nanowires and nanotubes are discussed, [2,14] and many others examine the size effects of thin films properties. Some theoretical concepts regarding the observed effects can be found in [1,8,28,29].

The set of models that employ the one-continuum approach to describe the structure of material include non-local and gradient models of mechanics. These models are based on the generalization of the classical Hooke's law, namely on the inclusion of spatial derivatives usually of the second order into the relation that links the stress and strain tensors [21,23], or on presentation of dependence between these tensors in the form of spatial functional dependence where the kernel depends on the distance from the point in question to traveling point [7,11,24]. The parameters that characterize spatial non-homogeneity are usually associated with microstructure of the solid. Comparison of models based

on gradient and integral formulations along with application of these models is discussed particularly in [15,21,25].

Another approach to description of structural and near-surface non-homogeneities is the local gradient approach in thermomechanics [4,5,18]. It is based on the general principles of irreversible thermodynamics and nonlinear mechanics. Within such approach, a deformable solid is considered as an open thermodynamic system whose mass changes relatively to the reference state of the solid. There have been suggested a number of linear models showing that they permit taking near-surface non-homogeneity into account and describing various size effects, including the ones of surface tension and tensile strength as well as the effect of different physical fields [17,19]. In formulating the boundary value problems with this approach the surface constraints on the chemical potential (conjugated to the density) were usually assigned. However, further studies have shown that there are no methods for direct determination of the chemical potential. In [16], Nahirnyj et al. have introduced a new interpretation of the local gradient approach proposing a formulation of the boundary conditions for density based on non-homogeneity of the surface geometry (surface roughness).

This paper rests upon the local gradient approach. We propose a model generalization aimed at correct description of the nanoelements by introducing the mass sources arising at the stage of body surface formation and taking into account dependences of the material properties (incl. elasticity moduli) on density. Distinctions arising from the expansion of the model are illustrated for a thin film. We also study the size effect of the effective Young's modulus and discuss the limits of applicability of linear models.

2. Principal model relations of the locally non-homogeneous thermoelastic solid

2.1. Basic assumptions of the model

Let us consider the processes of heat transfer, deformation and density change in a deformable solid. We assume that full energy E in arbitrary region (V) (bounded by surface (∂V)) may change due to mechanical work, supply of heat and mass and satisfies the energy balance equation in the integral form

$$\frac{d}{d\tau} \int\limits_{(V)} E\, dV = \int\limits_{(\partial V)} \mathbf{n} \cdot (\boldsymbol{\sigma} \cdot \mathbf{v} - T\mathbf{j}_s - H\mathbf{j}_m)\, d\Sigma + \int\limits_{(V)} \sigma_E\, dV. \tag{1}$$

Here τ is time, $\boldsymbol{\sigma}$ is the Cauchy stress tensor, $\mathbf{v}$ is the velocity vector, $\mathbf{j}_s$ and $\mathbf{j}_m$ are vectors of entropy and mass fluxes, T and H are the absolute temperature and chemical potential, σ_E is the energy sources, $\mathbf{n}$ is the outside normal to surface (∂V), the dot "·" denotes the inner product operation.

When constructing models with methods of irreversible thermodynamics the solid is usually considered as a closed thermodynamic system. For structurally invariable bodies the mass flow and energy sources in (1) are zero: $\mathbf{j}_m = 0, \sigma_E = 0$. We want to take into account the structure of the material and the structure of the surface that appear at the stage of the formation of the solid. So we assume that the mass flow and the energy production are zero for $\tau > 0$, while the structure of the material and the surface suddenly originate at the initial time $\tau = 0$ and do not change afterwards.

Neglecting the convective components of fluxes we write the equation (1) in the local form

$$\frac{\partial E}{\partial \tau} = \nabla \cdot (\boldsymbol{\sigma} \cdot \mathbf{v} - T\mathbf{j}_s - H\mathbf{j}_m) + \sigma_E, \tag{2}$$

where ∇ is the Hamilton gradient operator.

Along with equation (2) the following local form of balance equations for the mechanical translational motion momentum $\mathbf{k}_v$, the entropy S and the mass must hold

$$\frac{\partial \mathbf{k}_v}{\partial \tau} = \nabla \cdot \boldsymbol{\sigma}, \quad \frac{\partial S}{\partial \tau} = -\nabla \cdot \mathbf{j}_s + \sigma_s, \quad \frac{\partial \rho}{\partial \tau} = -\nabla \cdot \mathbf{j}_m + \sigma_m, \tag{3}$$

where ρ is the density of mass, σ_s and σ_m are the entropy and mass production. The entropy production σ_s is non-negative in each point for any time according to the second law of thermodynamics [9]. We also assume $\sigma_m = \sigma_E/H$.

Using (3) and the representation $E = U + K$ of total energy as a sum of internal U and kinetic K energies along with conventional expression for the increase of the latter $dK = \mathbf{v} \cdot d\mathbf{k}_v$ the equation (2) is transformed to

$$\frac{\partial U}{\partial \tau} = \boldsymbol{\sigma} : \frac{\partial \mathbf{e}}{\partial \tau} + H\frac{\partial \rho}{\partial \tau} + T\frac{\partial S}{\partial \tau} - T\sigma_s - \mathbf{j}_s \cdot \nabla T - \mathbf{j}_m \cdot \nabla H, \tag{4}$$

where $\mathbf{e}$ is the strain tensor, ":" denotes the double inner product.

This equation is called the equation of balance of internal energy and it is the key equation for formulating the constitutive equations (equations of state and kinetic equations) of the model.

2.2. Constitutive equations

The thermodynamic fluxes $\mathbf{j}_s, \mathbf{j}_m$ are caused by thermodynamic forces that are associated with field gradients $\nabla T, \nabla H$, i.e. $\mathbf{j}_s, \mathbf{j}_m$ are usually taken as functions of forces $\nabla T, \nabla H$,

$$\mathbf{j}_s = \mathbf{j}_s(\nabla T, \nabla H), \qquad \mathbf{j}_m = \mathbf{j}_m(\nabla T, \nabla H). \tag{5}$$

More general is the functional dependence

$$\mathbf{j}_s = \mathbf{j}_s^\tau(\nabla T, \nabla H), \qquad \mathbf{j}_m = \mathbf{j}_m^\tau(\nabla T, \nabla H), \tag{6}$$

where $\mathbf{j}_s^\tau(\bullet), \mathbf{j}_m^\tau(\bullet)$ are the functionals that transform the actual values of the forces $\nabla T(\tau), \nabla H(\tau)$ along with theirs histories $\nabla T(\zeta), \nabla H(\zeta)$ $(-\infty \leqslant \zeta < \tau)$ into the actual values of corresponding fluxes.

For an isotropic material, the relation (6) can be written in the following linear form:

$$\mathbf{j}_\alpha = G_{\alpha s} * \nabla T + G_{\alpha m} * \nabla H, \tag{7}$$

where $G_{\alpha\beta}$ is a functional over the history of the force changes,

$$G_{\alpha\beta} * f = \int\limits_{-\infty}^{\tau} g_{\alpha\beta}(\tau, \zeta)\frac{\partial f(\zeta)}{\partial \zeta}d\zeta, \quad \alpha, \beta = \{s, m\}, \tag{8}$$

where $g_{\alpha\beta}(\tau, \zeta)$ is the influence function (kernel).

By choosing the influence function we can specify the dependence of thermodynamic fluxes on forces. Taking into account the dependence of the influence function on the variable of its integration means taking into account the history; this dependence being not taken into account turns the functional dependence into the function dependence. If the influence function is proportional to the delta-function of $\tau - \zeta$, then one speaks of the non-fading memory of some event at the initial moment of time [22].

To describe thermal processes we use the approximation of classical thermoelasticity [20]. We assume also that at the initial moment of time the material structure has appeared suddenly. Its emergence is taken into account as the non-fading memory for the mass flux vector in (7). In this

regard we assume

$$g_{ss}(\tau,\zeta) = -\lambda_s/T(\tau), \quad g_{mm}(\tau,\zeta) = -g_{mm}\delta(\tau-\zeta), \quad g_{sm}(\tau,\zeta) = g_{ms}(\tau,\zeta) = 0. \tag{9}$$

Here λ_s, g_{mm} are constants.

Substituting (9) into (8) yields

$$\mathbf{j}_s = -\lambda_s \frac{\nabla T}{T}, \qquad \mathbf{j}_m = -g_{mm}\frac{\partial \nabla H}{\partial \tau}. \tag{10}$$

The relations (10) are common in the models of local gradient approach.

Formulae (10) modify the mass balance equation into the form

$$\frac{\partial}{\partial \tau}\left(\rho - g_{mm}\nabla^2 H\right) = \sigma_m. \tag{11}$$

Substituting (10) into (4) yields

$$\frac{\partial}{\partial \tau}\left(U - \frac{g_{mm}}{2}\nabla H \cdot \nabla H\right) = \boldsymbol{\sigma} : \frac{\partial \mathbf{e}}{\partial \tau} + T\frac{\partial S}{\partial \tau} + H\frac{\partial \rho}{\partial \tau} - T\sigma_s + \lambda_s \nabla T \cdot \frac{\nabla T}{T}. \tag{12}$$

We use the classical expression for the entropy production [9],

$$\sigma_s = \lambda_s \frac{\nabla T}{T} \cdot \frac{\nabla T}{T}. \tag{13}$$

By introducing the energy F through

$$F = U - TS - \frac{g_{mm}}{2}\nabla H \cdot \nabla H, \tag{14}$$

one can derive from (12) the expression for the energy F increase

$$dF = \boldsymbol{\sigma} : d\mathbf{e} - SdT + Hd\rho. \tag{15}$$

This relation indicates that the chemical potential is the energy required to transfer a beforehand chosen material point from infinity to the considered point of the solid (in general, to change the value of density by one unit). Given that the material point at infinity outside the body is free, while inside the body it is connected with other points forming the skeleton of the solid, it can be stated that the perturbation of the chemical potential is equal to the perturbation of the binding energy. Thus, the proposed model can be called a model of local non-homogeneous thermoelastic solid or a model of the thermoelastic solid with taking into account the binding energy.

The energy F is defined in the space of the strain $\mathbf{e}$, the temperature T, and the density ρ

$$F = F(\mathbf{e}, T, \rho). \tag{16}$$

Equation (15) implies the state equations

$$\boldsymbol{\sigma} = \frac{\partial F}{\partial \mathbf{e}}, \qquad S = -\frac{\partial F}{\partial T}, \qquad H = \frac{\partial F}{\partial \rho}. \tag{17}$$

The concept of the thermodynamic variables suggests that each of them can change regardless of the others. A natural question arises: how within the one-continuum approach the density can change when transferring from one arbitrarily chosen physically small element to another if its temperature and strain do not change? To illustrate this point, we focus more on an arbitrarily selected physically small element. In thermomechanics, this element is attributed with the temperature T and the strain

e, which may change in transition to another element. In classical thermomechanics density is usually taken the same within all physically small elements. Let us imagine that at the initial moment of time a structure originated in the solid such as pores or inclusions of some another material. Within the one-continuum approach the averaging operation leads to a homogeneous physically small element. In this case, one can claim that the density as well as the temperature and strain may change in transition from one local element to another. Thus the density may be used as the parameter corresponding to the structure of material in some way.

Further specification of the model is connected with concretization of state equations and with the reference state. As the reference state we choose the homogeneous isotropic medium free of loading with the parameters

$$T = T_*, \ S = S_*, \ H = H_*, \ \rho = \rho_*, \ \mathbf{e} = \mathbf{0}, \ \boldsymbol{\sigma} = \mathbf{0}. \tag{18}$$

We take the energy F as a quadratic function of the deflections of the state variables: temperature, mass density, and strain

$$\theta = T - T_*, \quad \rho - \rho_*, \quad \mathbf{e} - \mathbf{0}, \tag{19}$$

i.e.

$$F = F_* - S_*\theta - H_*(\rho - \rho_*) + \frac{1}{2}\lambda e^2 + \mu\mathbf{e} : \mathbf{e} - (3\lambda + 2\mu)a_t e\theta -$$

$$- (3\lambda + 2\mu)a_m e(\rho - \rho_*) + \alpha_{mt}(\rho - \rho_*)\theta + \frac{1}{2}\alpha_{mm}(\rho - \rho_*)^2 - \frac{c_v}{2T_*}\theta^2, \tag{20}$$

where $\lambda, \mu, a_t, a_m, \alpha_{mm}, \alpha_{mt}, c_v$ are material characteristics; $e = \mathbf{e} : \mathbf{I}$, $\mathbf{I}$ is the identity tensor.

It should be noted that the expression (20) corresponds to the first terms of series expansion for energy F with respect to small deflections relative to the reference state, therefore we assume that $|\theta|/T_* \ll 1$, $|\rho - \rho_*|/\rho_* \ll 1$ and the deformation is small.

In general, such density deflection can be large due to the change of microstructure of the material. It is known that many nanomaterials are highly porous. If the dependence on density is essential, in (18) one should take into account higher orders of the density deflection. Another modeling possibility could be selecting the proper dependence of coefficients in (20), such as $\lambda, \mu, a_t, a_m, \alpha_{mm}, \alpha_{mt}, c_v$, on the density.

The derived system of equations, consisting of the balance equations of momentum and entropy (first and second equations of (3)), the mass balance (11), expression for the entropy production (13) with the expression (18), the state equations (16), the formula for the momentum of mechanical translational motion

$$\mathbf{k}_v = \rho\mathbf{v}, \tag{21}$$

and the Cauchy relation for the strain tensor

$$\mathbf{e} = \frac{1}{2}\left(\nabla \otimes \mathbf{u} + (\nabla \otimes \mathbf{u})^T\right) \tag{22}$$

constitute the complete system of equations of the model of the locally non-homogeneous thermoelastic solid. Here **u** is the displacement vector, $\otimes$ denotes the tensor dyadic product and the symbol "T" denotes transposition.

2.3. Linearized systems of equations

Let us consider the approximation of the model when the density deflection relative to the reference state is small: $|\rho - \rho_*|/\rho_* \ll 1$. In this case we can assume that the parameters in (20) are constant. On the basis of (17), (20) the explicit form of the state equations is

$$\boldsymbol{\sigma} = 2\mu\mathbf{e} + \{\lambda e - (3\lambda + 2\mu)[a_m(\rho - \rho_*) + a_t\theta]\}\mathbf{I},$$

$$S = S_* + (3\lambda + 2\mu)a_t e - \alpha_{mt}(\rho - \rho_*) + \frac{c_v}{T_*}\theta,$$

$$H = H_* - (3\lambda + 2\mu)a_m e + \alpha_{mm}(\rho - \rho_*) + \alpha_{mt}\theta. \tag{23}$$

Considering the displacement vector, temperature, and density deflections to be the key functions we obtain the following linearized system of equations to describe the stationary state

$$\mu\nabla^2\mathbf{u} + (\lambda + \mu)\nabla(\nabla \cdot \mathbf{u}) - (3\lambda + 2\mu)[a_m\nabla(\rho - \rho_*) + a_t\nabla\theta] = 0,$$

$$\nabla^2\theta = 0, \qquad \nabla^2(\rho - \rho_*) - \kappa^2(\rho - \rho_*) + \kappa^2 d_{\sigma m} = 0, \tag{24}$$

where $\kappa^{-2} = g_{mm}[\alpha_{mm} - (3\lambda + 2\mu)^2 a_m^2/(\lambda + 2\mu)]$, $d_{\sigma m} = \int_{-\infty}^{\tau} \sigma_m d\tau$. It should be noted, that the third equation of (24) is obtained from the mass balance equation (11) taking into account the reference state, state equation for the chemical potential with the first two equations of (24).

If the stress tensor is the key function, then the key system of equations has the form

$$\nabla \times \left\{\nabla \times \left[\frac{\boldsymbol{\sigma}}{2\mu} - \left(\frac{\lambda\sigma}{2\mu(3\lambda + 2\mu)} - a_m(\rho - \rho_*) - a_t\theta\right)\mathbf{I}\right]\right\}^T = 0,$$

$$\nabla^2\theta = 0, \qquad \nabla^2(\rho - \rho_*) - \kappa^2(\rho - \rho_*) + \kappa^2 d_{\sigma m} = 0, \tag{25}$$

where $\sigma = \boldsymbol{\sigma} : \mathbf{I}$, "$\times$" denotes the vector product.

Formulating the boundary value problems we complement the system of equations with the appropriate boundary conditions:

$$\boldsymbol{\sigma} \cdot \mathbf{n}|_{\partial V_\sigma} = \boldsymbol{\sigma}_a, \quad \mathbf{u}|_{\partial V_u} = \mathbf{u}_a, \quad \theta|_{\partial V} = \theta_a, \quad \rho|_{\partial V} = \rho_a, \tag{26}$$

where (∂V_σ) and (∂V_u) are the parts of the body surface where the force load vector $\boldsymbol{\sigma}_a$ and the displacement vector $\mathbf{u}_a$ respectively are prescribed $((\partial V_\sigma) \cup (\partial V_u) = (\partial V))$, θ_a and ρ_a are the temperature and density values at the surface. Of course, any other applicable conditions for the temperature may be used [13]. Another form of boundary conditions for density may be also used.

Analyzing the systems (24), (25), it becomes obvious that within the model, the study of the thermoelastic state of a deformable solid in the connected system of equations is reduced to successive determination of the temperature and density, with further examination of the stress-strain state. Like in the classical thermoelasticity, the linear distribution of temperature does not cause stresses [20]. With our approximation, temperature has also no effect on the distribution of density. Therefore from now on, we assume temperature to be constant $T = T_*$ and consequently $\theta = 0$ excluding temperature from our further consideration.

3. Steady state of thin films

3.1. Near-surface density non-homogeneity and the "mass defect"

Neglecting the mass production in the third equation of (22) (i.e. $d_{\sigma m} = 0$) we write it in the form

$$\nabla^2(\rho - \rho_*) - \kappa^2(\rho - \rho_*) = 0. \tag{27}$$

Such homogeneous Helmholtz equation for the density deflection is the focal one in the models constructed under the local gradient approach [18].

The solution of this equation for a layer $|x| \leqslant l$, which satisfies the boundary condition (26), is

$$\rho = \rho_* + (\rho_a - \rho_*)\frac{\cosh(\kappa x)}{\cosh(\kappa l)}. \tag{28}$$

Figure 1, a shows the distribution of the density ρ/ρ_* in the layer for $\rho_a/\rho_* = 0.5$ and $\kappa l = 2, 6, 20$ (dashed, dotted and dash-dotted curves, respectively). The solid line $\rho/\rho_* = 1$ shows the density in the reference solid. Parameter κ^{-1} is the characteristic size of near-surface non-homogeneity region. If the thickness of the layer is comparable to the characteristic size of the near-surface non-homogeneity region, the density of the layer is noticeably different from the density of the reference solid at each point. Such layers are called "thin films". For "thick layers" (layer's thickness is much larger than the characteristic size of the near-surface non-homogeneity region) the density difference from the reference solid density is far from zero in narrow near-surface regions only.

One can see that the density of the solid at the actual moment of time differs from the corresponding density of the reference solid. The integral of density from $-l$ to l equals to the area limited by the solid line and each of dashed, dotted or dash-dotted curves in Figure 2, allows us to indicate near-surface "defect of mass". It is obvious that such "mass defect" is particularly important in modeling and study of behavior of thin films and other nanoelements for which the contribution of the surface energy compound in the total energy becomes essential.

We recall that the reference state parameters of the body were the density ρ_* and the phenomenological coefficients λ, μ (Lamé parameters). It is evident that the change in the density can cause significant change of the parameters λ, μ. This imposes restrictions on the applicability of the model presented in this section (constant characteristics of the material in the formula (20)) to the solids whose characteristic size is much greater than the size of near-surface non-homogeneity region, i.e. to solids that have the area where $\rho \approx \rho_*$ is much greater than the area where ρ differs considerably from ρ_*. A natural question arises: how to take into account the "mass defect" presented in Figure 1, a and how to extend the model to the correct description of solids whose characteristic sizes are comparable to the size of the near-surface non-homogeneity region such as nanoelements.

To consider and explain the "mass defect" presented in Figure 1, a we use the introduced sources of mass. We also assume that they satisfy the relation

$$\int\limits_{(V)} d_{\sigma m} d\mathbf{r} = \int\limits_{(V)} (\rho - \rho_*) d\mathbf{r}. \tag{29}$$

Another argument in favor of the mass sources is the surface geometric non-homogeneity of the real solids. According to the continuum approach, the real surface of the solid is modeled with a piecewise smooth geometrically ideal surface, ignoring numerous micro-nonhomogeneities known as surface roughness (see Figure 1, b, left). The size and nature of these irregularities depend primarily on the method of formation (or finishing) of the solid surface. Idealized solid surface (dashed line in Fig. 1,b, right) can be chosen between the highest and lowest points (dash-dotted lines) of the surface profile in Fig. 1, b). This yields such a region for the surface value of the density $0 < \rho_a < \rho_*$.
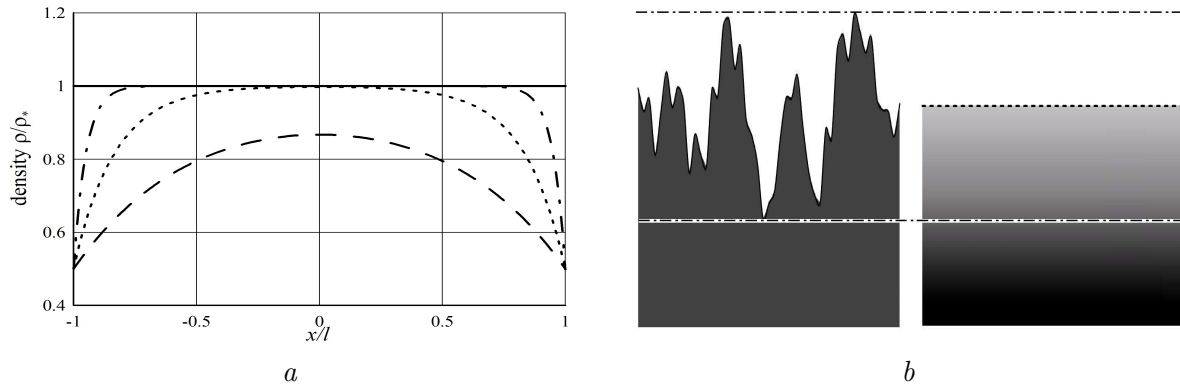
Fig. 1. Density distribution in a layer (a), and schematic presentation of the real and idealized body surface corresponding to the boundary condition $0 < \rho_a < \rho_*$ (b).

Geometrical irregularities of the surface of thin film surface can cover the whole region of the solid. Taking into account the homogeneous state of the reference, we conclude that geometrical non-homogeneity of the surface (surface microstructure) can be modeled by sources (sinks) of mass in the near-surface region of the body. In this case, the intensity of the sources must tend to zero with the bulk of the body. As we consider structurally invariable bodies, it is natural to assume that the mass defect arose at the initial moment of time when the solid (and its surface) was formed. Therefore,

$$\sigma_m(\tau, \mathbf{r}) = d_{\sigma m}(|\mathbf{r} - \mathbf{r}_s|)\delta(\tau), \tag{30}$$

where $\mathbf{r}$ is the radius vector of the arbitraryly chosen point in the solid, $\mathbf{r}_s$ is its projection onto the geometrically ideal surface of the solid, $d_{\sigma m}$ is some decreasing function.

3.2. Elasticity moduli dependent on density

Numerous results from literature indicate the presence of the size effect of mechanical properties of the solids, one of whose dimensions is of the nanometer range, including the size effect of the Young's modulus [10,28]. In the model relations above, namely (20), (23)–(24) we have used Lamé parameters λ, μ. These parameters are related to Young's modulus E and Poisson ratio ν through the relations [20]

$$\lambda = \frac{\nu E}{(1+\nu)(1-2\nu)}, \qquad \mu = \frac{E}{2(1+\nu)}. \tag{31}$$

Next we consider the dependence of the elasticity moduli on density:

$$E = E_0 f_E(\rho), \qquad \nu = \nu_0 f_N(\rho), \tag{32}$$

where E_0, ν_0 are elasticity moduli of the material in the reference state, $f_E(\rho), f_N(\rho)$ are some functions such that $f_E(\rho_*) = 1, f_N(\rho_*) = 1$. For numerical studies we use (32), where

$$f_E(\rho) = \left(\frac{\rho}{\rho_*}\right)^{\beta_E}, \qquad f_N(\rho) = \left(\frac{\rho}{\rho_*}\right)^{\beta_N}. \tag{33}$$

Depending on the signs of the coefficients β_E, β_N, we postulate the increase or decrease of Young's modulus and Poisson's ratio in the region where $\rho < \rho_*$. If $\beta_E = \beta_N = 1$ we arrive at the relations often used for porous materials [26]. Note that the surface roughness is compared with the porosity of nanomaterial in [29].

We use the above formulated system of equations to study the stress-strain state of the layer that occupies the domain $|x| \leqslant l$ in the Cartesian coordinate system $\{x, y, z\}$. We assume that the layer surfaces $x = \pm l$ are free of external forces with the assigned constant value of the density ρ_a. At

infinity $y \to \pm\infty$, the layer is stretched by the load σ_a. To simulate the distribution of mass sources in the solid, we take the distribution of density disturbance (28) in the model of layer where the mass sources are not taken into account.

Neglecting the effect of the deformation on density, the system of equations describing the steady state of the layer taking into account the structural non-homogeneity of the material and the geometrical non-homogeneity of the surface with the reference temperature ($\theta = 0$) can be written as

$$\frac{d^2}{dx^2}\left(\frac{1+\nu}{E}\sigma_{\gamma\gamma} - \frac{\nu\sigma}{E}\right) = -\frac{d^2}{dx^2}[a_m(\rho - \rho_*)], \quad \gamma = \{y, z\}$$

$$\frac{d\sigma_{xx}}{dx} = 0,$$

$$\frac{d^2(\rho - \rho_*)}{dx^2} - \xi^2(\rho - \rho_*) + \xi^2 d_{\sigma m} = 0,$$

$$\int_{-l}^{l} d_{\sigma m}dx = \int_{-l}^{l}(\rho - \rho_*)dx, \tag{34}$$

where

$$\xi^{-2} = g_{mm}\left(\alpha_{mm} - \frac{E_0(1 + \nu_0)a_m^2}{(1 - \nu_0)(1 - 2\nu_0)}\right),$$

$\sigma_{\alpha\alpha}(\alpha = \{x, y, z\})$ are the stress tensor components. Note that in the first equation of (34) E, ν depend on density, therefore this system is nonlinear..

In accordance with (28) we take

$$d_{\sigma m}(x) = d_m\frac{\cosh(\zeta x)}{\cosh(\zeta l)}. \tag{35}$$

The parameter ζ characterizes the mass sources distribution and can be associated with geometrical non-homogeneity of the real solid surface. Its value depends on the method of formation of the surface.

This system of equations is complemented with the boundary conditions

$$\sigma_{xx} = 0, \qquad \rho = \rho_a \tag{36}$$

at the layer surfaces $x = \pm l$ as well as the conditions

$$\int_{-l}^{l}\sigma_{yy}dx = 2l\sigma_a, \quad \int_{-l}^{l}\sigma_{zz}dx = 0, \quad \int_{-l}^{l}x\sigma_{yy}dx = 0, \quad \int_{-l}^{l}x\sigma_{zz}dx = 0 \tag{37}$$

in arbitrary cross-section of the layer.

The solution of the problem is

$$\rho = \rho_* + \frac{\rho_a - \rho_*}{1 - D}\left(\frac{\cosh(\xi x)}{\cosh(\xi l)} - D\frac{\cosh(\zeta x)}{\cosh(\zeta l)}\right),$$

$$\sigma_{xx} = 0,$$

$$\sigma_{yy} = \frac{f_E\sigma_a}{2(1+\nu)I_{n2}}\left(\frac{1+\nu}{1-\nu} + \frac{I_{n2}}{I_{n0}}\right) - \frac{f_E\sigma_0}{1-\nu}\left(\frac{\rho}{\rho_*} - 1 - \frac{I_{n1}}{I_{n0}}\right),$$

$$\sigma_{zz} = \frac{f_E\sigma_a}{2(1+\nu)I_{n2}}\left(\frac{1+\nu}{1-\nu} - \frac{I_{n2}}{I_{n0}}\right) - \frac{f_E\sigma_0}{1-\nu}\left(\frac{\rho}{\rho_*} - 1 - \frac{I_{n1}}{I_{n0}}\right), \tag{38}$$

where

$$I_{n0} = \frac{1}{2l} \int\limits_{-l}^{l} \frac{f_E}{1+\nu} dx, \quad I_{n1} = \frac{1}{2l} \int\limits_{-l}^{l} \frac{f_E}{1-\nu} \left(\frac{\rho}{\rho_*} - 1 \right) dx, \quad I_{n2} = \frac{1}{2l} \int\limits_{-l}^{l} \frac{f_E}{1-\nu} dx,$$

$$D = \frac{\xi \tanh(\xi l)}{\zeta \tanh(\zeta l)}, \quad \sigma_0 = E_0 a_m \rho_*.$$

In case of constant moduli, the expression for stresses can be simplified to the following form:

$$\sigma_{yy} - \sigma_a = \sigma_{zz} = \frac{\rho_a - \rho_*}{1-D} \frac{E_0 a_m}{1-\nu_0} \left[\frac{\cosh(\xi x)}{\cosh(\xi l)} - \frac{\tanh(\xi l)}{\xi l} - D \left(\frac{\cosh(\zeta x)}{\cosh(\zeta l)} - \frac{\tanh(\zeta l)}{\zeta l} \right) \right]. \qquad (39)$$

The solution analisys shows that in the layer free of load the stresses σ_{yy}, σ_{zz} differ from zero and their distribution is non-homogeneous. The density ρ and the stresses σ_{yy}, σ_{zz} feature two characteristic sizes. One of them is associated with the structural non-homogeneity of the solid material (ξ^{-1}) and the other one with the geometrical irregularity of the surface (ζ^{-1}).

Figure 2, a shows the distribution of density ρ/ρ_* in a free layer with $\rho_a = \rho_*/2$, $\xi l = 2, 4, 20$ (solid, dashed and dash-dotted curves, respectively) for $\zeta l = 10$. Comparing the graphs in Figures 1, a and 2, a we note the qualitative difference of the distributions in the vicinity of the external surfaces $x = \pm l$ of the solid. With the layer thickness (parameters $\xi l, \zeta l$) increasing the density at its median surface tends to the density ρ_* of the reference solid.

Nonzero stresses $\sigma_{yy} = \sigma_{zz}$ decrease monotonically with increase in distance from their maximum values $\sigma_{yy}(\pm l) = \sigma_{zz}(\pm l) \geqslant 0$ (tensions) reaching their minimum $\sigma_{yy}(0) = \sigma_{zz}(0) \leqslant 0$ (compressions) at the median surface $x = 0$. In a thin film the entire solid is stressed whereas in the case of a thick layer only narrow near-surface regions are stressed. The stresses σ_{yy}, σ_{zz} in the bulk of a thick layer are almost equal to zero. This is illustrated by graphs in Fig. 2, b which shows the distribution of the stresses $\sigma_{yy}/\sigma_0, \sigma_0 = E_0 a_m \rho_*$ in the layer. The graphs are plotted for $\zeta l = 10$, $\rho_a = \rho_*/2, \nu_0 = 0.33, \beta_E = -2, \beta_N = 0$. The solid curve in each graph corresponds to $\xi l = 2$, the dashed one to $\xi l = 4$ and the dash-dotted one to $\xi l = 20$. Taking into account the dependence of elasticity moduli on density does not practically change the character of the stress distribution, but it has considerable effect on its value.
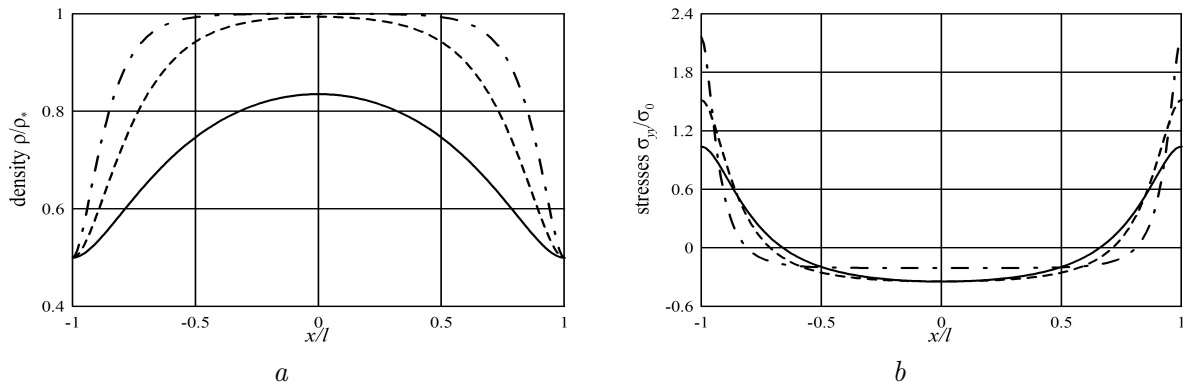
Fig. 2. Distributions of density (a), and stress (b) in the layer.

With the increase in the layer thickness, the surface stresses increase, tending to their constant value corresponding to the value of surface stresses in half-space, thus demonstrating their size effect. The stresses in the middle of the layer are compressive and tend to zero with the increase in the layer thickness.

3.3. Size effect of Young's modulus

It is of great interest to investigate the dependence of Young's modulus on the characteristic size of the body, i.e. its size effect. We shall use the obtained solution (38) of the problem (34)–(37) to study this dependence. The mechanical behavior of materials at the nanoscale is often different from that at macroscopic scale. To determine the Young's modulus of nanotubes, nanowires and ultrathin films the nanoindenter techniques, the electrostatic resonant-contact atomic force microscopy, and many others special methods are used [6]. However, taking advantage of theoretical consideration, let us use classical understanding of Young's modulus.

Young's modulus is an experimentally measurable characteristic of a solid, which is numerically equal to the ratio of the stress along the axis to the strain along that axis. In classical mechanics this experimentally measurable characteristic of a homogeneous solid is attributed to any point of the body, thus becoming the local characteristic of the solid (a property of the material). This local property is included in the energy representation (20) and the state equations (23) through the relations (31). If a solid is non-homogeneous, such experimentally measured characteristic is a property of the solid (effective Young's modulus). Since we assume that local elasticity moduli depend on density, one should expect to obtain a size effect of the effective elasticity moduli.

Using the relation (23) and the solution (38), we obtain the expression for the relative elongation in the direction of the applied stress

$$e_{yy} = \frac{\sigma_a}{2E_0 I_{n2}} \left(1 + \frac{I_{n2}}{I_{n0}}\right) + a_m \rho_* \frac{I_{n1}}{I_{n2}}. \tag{40}$$

The component of the strain e_{yy}, caused by the load σ_a is

$$e_{yy}^* = \frac{\sigma_a}{2E_0 I_{n2}} \left(1 + \frac{I_{n2}}{I_{n0}}\right). \tag{41}$$

Proceeding from this, we can write the expression for the effective Young's modulus

$$E_{ef} = \frac{2E_0 I_{n0} I_{n2}}{I_{n0} + I_{n2}}. \tag{42}$$

Figure 3, a illustrates the dependence of the effective Young's modulus E_{ef}/E_0 on the layer thickness (parameter ξl) for $\beta_E = 1, 0, -1.5, -3$ (curves 1–4) and $\zeta/\xi = 1.8, \beta_N = 0, \rho_a = \rho_*/2, \nu_0 = 0.33$. Thus, if local Young's modulus depends on the density as in a porous body ($\beta_E = 1$), then the effective modulus increases tending to E_0 with the layer thickness growth (curve 1). If the dependence of E on density ρ is not taken into account, then $E_{ef} = E_0$ (curve 2). Postulating the local modulus E increase with the density reduction ($\beta_E < 0$) leads to experimentally observed effective Young's modulus decrease with the thin film thickness increase [6,10,12,14] (line 3,4). Figure 3, b illustrates the dependence of Young's modulus E_{ef}/E_0 on the parameter β_E for $\beta_N = 0, r_a = 0.5, \nu_0 = 0.33, \xi l = 10$ if $\zeta/\xi = 0.5, 1.5, 5.0$ (solid, dashed and dash-dotted curves, respectively).

A similar scheme can be used to study the size effect of the Poisson's ratio.

4. Conclusions

Within the proposed model, the non-zero stress-strain state of a load-free solid is caused by the density deflection relative to the reference state. The density field in the equilibrium state is described by the non-homogeneous Helmholtz equation, which follows from the mass balance equation, equations of equilibrium and heat conduction. It is assumed that the mass flux and mass sources have an instant character and originate suddenly at the initial moment of time, as soon as the material structure and the surface of the solid are formed.
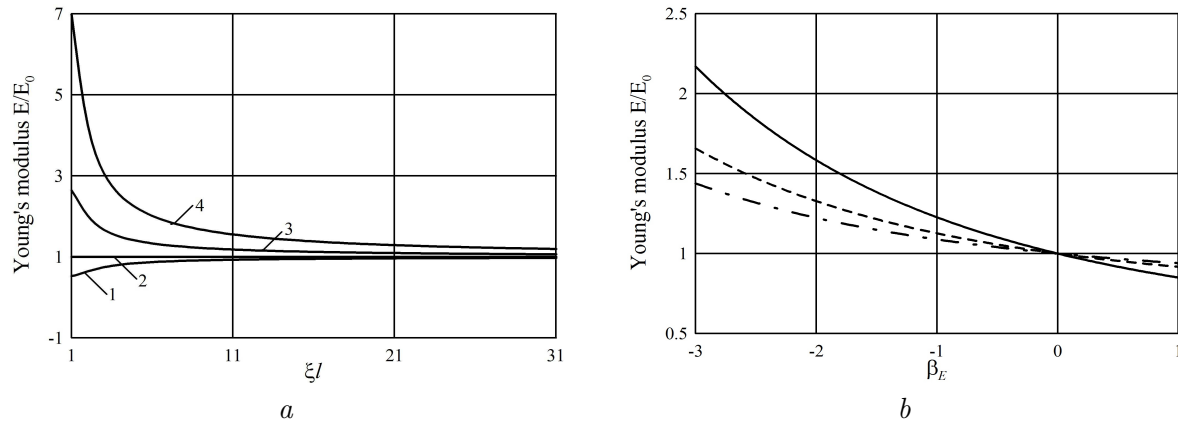
Fig. 3. Size effect of effective Young's modulus (*a*), and its dependence on β_E (*b*).

Distributions of density and stresses feature two characteristic sizes. The first size can be associated with the structural non-homogeneity of the material and the second one with geometric irregularities of the real surface of the solid.

The largest stress in a film (layer) is the tensile surface stress and it features size effect. Its value increases to the value of the surface stress in a half-space with the layer thickness increase. Taking into account the dependence of the elasticity moduli on density leads to the essential quantitative difference in the values of stresses and practically does not change the character of their distribution in the layer.

The solution of the boundary value problem for a stretched layer is used to study the size effect of the effective Young's modulus. We have established that in the model the size effect of the modulus is due to taking into account the dependence of phenomenological coefficients on the density in the state equation for the stress tensor.

Finally we note that taking into account the internal stresses is essential in predicting the functional properties of nanoelements, including their strength parameters.

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Математичне моделювання приповерхневої неоднорідності у наноелементах

Нагірний Т. С.[1,2], Червінка К. А.[3]

[1] *Центр математичного моделювання ІППММ ім.Я.С. Підстригача,*
вул. Дж. Дудаєва, 15, 79005, Львів, Україна
[2] *Механіко-машинобудівний факультет, Університет міста Зелена Гура*
вул. проф. Шафрана 4, 65-516, Зелена Гура, Польща
[3] *Львівський національний університет імені Івана Франка,*
вул. Університетська, 1, Львів 79000, Україна

Дана робота є подальшим розвитком локально градієнтного підходу в термомеханіці. Представлена у роботі модель дозволяє вивчати за одно-континуумного підходу напружено-деформований стан наноелементів. Термопружне тверде тіло розглядається як відкрита термодинамічна системи, у якій потоки та джерела маси пов'язано із раптовим виникненням структури матеріалу та реальної поверхні тіла в момент формування тіла. Повна система рівнянь включає рівняння балансу маси, узагальнене на локально неоднорідні системи. У якості модельної задачі розглянуто рівноважний стан тонкого шару (плівки). Вивчено розмірні ефекти приповерхневих напружень та ефективного модуля Юнга.

Ключові слова: *локально градієнтний підхід, приповерхнева неоднорідність, наноелементи, розмірні ефекти, ефективний модуль Юнга*

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