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The Effective Stiffness of a Nanoporous Rod

V. A. Eremeyev^{a, b} and Academician N. F. Morozov^c

Many nanomaterials have abnormal physical properties, which differ considerably from the properties of bulk materials. One of the explanations for these differences consists in the presence of surface effects, the role of which can be extremely large for nanodimensional structures in comparison with those in classical mechanics [1].

The purpose of this work is analysis of the influence of surface effects on the elastic characteristics of nanoporous materials. Two models are considered. The first one is based on taking into account the surface stresses [1–4]. The surface stresses τ are the generalization of the surface tension known in the theory of capillarity for the case of solids. As is shown in [1, 5], taking into account surface stresses results in increasing stiffness of nanoporous materials. This phenomenon is similar to increasing flexural stiffness of nanoplates in comparison with the plates of macroscopic sizes [6, 7]. The second model uses the approach of the theory of composite materials [8–10]. In this approach, the surface effects are taken into account due to the surface layer of finite thickness with elastic moduli differing from those of the basic material (the matrix). Here the increase or decrease in the rod stiffness depends on the relation between the elastic moduli of the surface layer and the matrix. The effective stiffness can both decrease and increase with decreasing pore radius. On the basis of these two approaches, we proposed a complex model combining both the presence of surface stresses and the surface layer with the properties that differ from those of the matrix.

PROBLEM FORMULATION

We consider the problem on the tension–compression of a linear elastic rectilinear rod. Let the rod have a circular cross section of radius R . We consider that n cylindrical pores with identical radii r (Fig. 1) are located in parallel to the rod axis. We designate the area occupied with pores in the rod cross section as $S = \pi nr^2$. We assume also that the rod cross section is symmetric so that it is not subjected to bending under tension. A regularly distributed load, which is statically equivalent to forces P , acts on the rod end faces.

We designate the Young's modulus of the rod material as E . For a large number ($n \gg 1$) of pores, the rod can be considered as a homogeneous cylinder made of transversally isotropic material. We designate the corresponding effective longitudinal Young's modulus

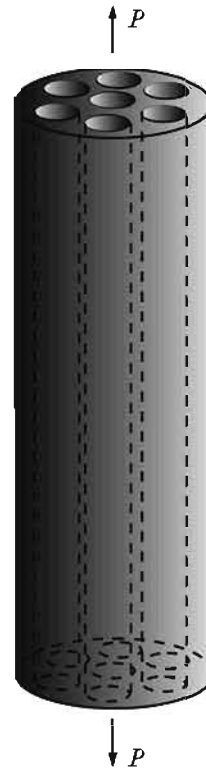


Fig. 1. Porous rod.

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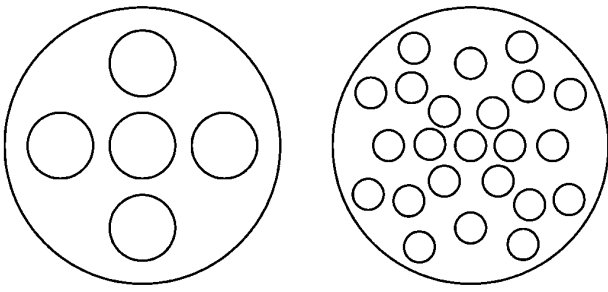


Fig. 2. Two cross sections of the rod with an identical pore area S .

with the asterisk superscript. Within the classical representation on the strength of materials (see, for example, [11]), it is given by the elementary formula

$$E_0^* = E(1 - \varphi), \quad (1)$$

where $\varphi = S/F$ is the porosity and $F = \pi R^2$ is the total rod cross-section area including the pore area. It is easy to understand that E_0^* depends only on the value of the matrix Young's modulus E and the porosity φ and is independent of the pore number n , it always being valid that $E_0^* < E$ for $\varphi \neq 0$.

For nanomaterials, the size effect is characteristic, and it is possible to expect the dependence of the effective Young's modulus also on the pore radius or their number. Further, assuming that the pore area S is set, we consider how the effective Young's modulus depends on the number n of pores if we take into account the surface effects. For example, we can determine for which cross sections shown in Fig. 2 the effective Young's modulus is higher.

SURFACE STRESSES

Using the relations of the theory of elasticity with taking into account the surface stresses [1–6], we consider the problem of the porous-rod tension if the surface stresses act on the boundaries of pores. The equilibrium equations and the boundary conditions on the rod lateral surface have the form

$$\begin{aligned} \nabla \cdot \boldsymbol{\sigma} &= \mathbf{0} \text{ in } V, \quad \mathbf{n} \cdot \boldsymbol{\sigma}|_{\Omega} = \mathbf{0}, \\ (\mathbf{n} \cdot \boldsymbol{\sigma} - \nabla_S \cdot \boldsymbol{\tau})|_{\Omega_k} &= \mathbf{0}, \quad k = 1, 2, \dots, n. \end{aligned} \quad (2)$$

Here $\boldsymbol{\sigma}$ is the stress tensor, ∇ is the three-dimensional gradient operator, \mathbf{n} is the vector of the normal to the body surface, $\partial V = \Omega \cup \Omega_1 \cup \dots \cup \Omega_n$, Ω is the lateral surface, while Ω_k are the pore surfaces on which the surface stresses $\boldsymbol{\tau}$ act, ∇_S is the surface gradient operator related with ∇ by the formula $\nabla_S = \nabla - \mathbf{n} \frac{\partial}{\partial r}$, and r

is the coordinate counted along the normal to Ω and Ω_k . On the lateral surface Ω , there are no loads and

surface stresses, and the boundary conditions are accepted on the end faces in the sense of the Saint-Venant conditions and consist in fulfilling the integral equations

$$\iint_{F \setminus S} \sigma_{zz} d\Omega + \sum_{k=1}^n \int_{\Gamma_k} \tau_{zz} ds = P, \quad (3)$$

where Γ_k are the contours of apertures of pores.

The single-axis stress state for the cylinder with pores is determined by the formulas

$$\boldsymbol{\sigma} = \sigma_{zz} \mathbf{e}_z \otimes \mathbf{e}_z, \quad \boldsymbol{\tau} = \tau_{zz} \mathbf{e}_z \otimes \mathbf{e}_z.$$

The remaining components of stress tensors are zero. Restricting ourselves to the case of an isotropic material, we can show that Hook's law and its surface analogue [1] result in the equalities

$$\sigma_{zz} = E \varepsilon_{zz}, \quad \tau_{zz} = E_S \epsilon_{zz},$$

where E_S is the surface analogue of the Young's modulus having the dimension of N/m, ε_{zz} and ϵ_{zz} are the longitudinal components of strain and surface strain. For this problem, they are identical: $\varepsilon_{zz}|_{\Omega_k} = \epsilon_{zz} = \varepsilon$.

Assuming the strain ε to be constant, we write the relation from Eq. (3)

$$P = [E(F - S) + 2\pi nr E_S] \varepsilon. \quad (4)$$

For a homogeneous rod with the effective modulus E_S^* , the elementary formula is fulfilled

$$P = E_S^* F \varepsilon,$$

Comparing it with Eq. (4), we obtain the value of E_S^*

$$E_S^* = E(1 - \varphi) + E_S \frac{2\pi rn}{F} = E_0^* + E_S \frac{2\pi rn}{F}.$$

Because the value of S is fixed, the pore radius r is related to their number n as

$$r = \sqrt{\frac{S}{\pi n}}. \quad (5)$$

Hence, the relation is fulfilled

$$E_S^* = E(1 - \varphi) + E_S \frac{2\sqrt{S}}{\sqrt{\pi} F} \sqrt{n} = E_0^* + E_S \frac{2\sqrt{S}}{\sqrt{\pi} F} \sqrt{n}. \quad (6)$$

The mathematically correct formulation of the problem of the theory of elasticity with the surface stresses requires that $E_S > 0$. Thus, E_S^* is an increasing function of n and $E_S^* > E_0^*$. In other words, the smaller the pore radius, the more stiff the rod with surface stresses becomes.

It is necessary to note that the surface stresses can result in the fact that the stiffness can prove to be even higher for a nanoporous rod than that for the solid one

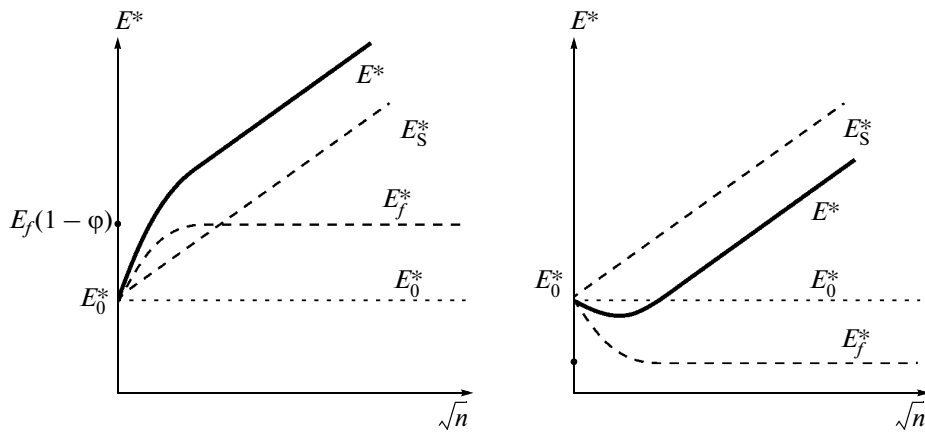


Fig. 3. Dependences of E^* , E_0^* , E_S^* , and E_f^* on \sqrt{n} for $E_f > E$ (on the left) and for $E_f < E$ (on the right).

with the same radius R . In fact, it follows from Eq. (6) that

$$E_S^* > E \text{ for } n > \frac{\pi}{4} S \left(\frac{E}{E_S} \right)^2.$$

The last condition can be transformed also to the form $r < 2E_S/E$. With taking into account the data for the surface elastic constants [1, 5], the inequality $E_S^* > E$ can be fulfilled for such materials as, for example, nanoporous anodic aluminum.

SURFACE LAYER

The variety of materials requires taking into account various factors affecting their mechanical properties. We consider another model of the surface phenomena, which enables us to take into account more precisely the surface effects for porous solids. The comparison carried out in [12] with the case of three-layer plates showed that taking into account surface stresses is equivalent to the presence of surface layers of a certain thickness, the surface elastic moduli being expressed through the Lamé constants of the surface-layer material multiplied by its thickness with the thickness tending to zero. At the same time, there are also differences—an elastic body with surface stresses is similar to an elastic body on the surface of which the elastic membrane [2, 3] is glued. Thus, the presence of surface stresses in the model always renders a reinforcing action. We assume now that there is a thin surface layer of thickness δ in a vicinity of each pore, whose elastic properties differ from those of the matrix. As an example of such a layer, the oxide film arising on the surface of the material can serve. We note that the elastic moduli of the surface layer, for example, the Young's modulus can be both higher (for example, in the Al–Al₂O₃ system) and lower (Si–SiO₂) than that of matrix. For a softer surface layer, it

is necessary to expect a decrease in the rod effective stiffness.

For this problem, it is possible to use the formulas of the theory of composites [8–10] representing the matrix reinforced with fibers. Each fiber represents a hollow cylinder of thickness δ and internal radius r . We designate the Young's modulus of the surface layer as E_f . For the effective longitudinal Young's modulus of the rod, the rule of mixtures [8–10] is fulfilled, which gives

$$E_f^* = E \left(1 - \frac{S + S_\delta}{F} \right) + E_f \frac{S_\delta}{F} = E_0^* + (E_f - E) \frac{S_\delta}{F}, \quad (7)$$

where $S_\delta = \pi n[(r + \delta)^2 - r^2]$ is the total cross-section area of surface layers if they are not intersected. From Eq. (7), it can be seen that an increase in stiffness occurs if the Young's modulus of the surface layer exceeds the matrix modulus ($E_f - E > 0$). Otherwise, a decrease in E_f^* takes place. Expressing r through n with the help of Eq. (5) and considering that $\delta \ll r$, we obtain

$$E_f^* = E_0^* + (E_f - E) \frac{2\delta\sqrt{\pi S}}{F} \sqrt{n}. \quad (8)$$

It should be noted that, contrary to Eq. (7), Eq. (8) is not applicable for all n because $S_\delta \leq F - S$. If n increases, the surface-layer area increases as \sqrt{n} until these layers begin to intersect; for $n \rightarrow \infty$, the entire cross section proves to be formed from the surface-layer material. Thus, $E_f^* \rightarrow E_f(1 - \phi)$ at $n \rightarrow \infty$.

COMBINED MODEL

The results of the two previous paragraphs enable us to propose a model including both the surface stresses acting on the boundaries of pores and the presence of a thin surface layer around the pores. In this

case, the effective Young's modulus of the rod is formed by the terms included in Eqs. (1), (6), and (7):

$$E^* = E_0^* + E_s \frac{2\sqrt{S}}{\sqrt{\pi F}} \sqrt{n} + (E_f - E) \frac{S_\delta(n)}{F}. \quad (9)$$

From Eqs. (8) and (9), it follows that E^* increases with n if the following relation is fulfilled

$$E_s \frac{2\sqrt{S}}{\sqrt{\pi F}} + (E_f - E) \frac{2\delta\sqrt{\pi S}}{F} > 0.$$

If this inequality is violated, which is possible if the surface layer is softer in comparison with that of the matrix, the dependence of E^* is nonmonotonic: E^* first decreases but again increases for certain n . The qualitative dependences of E^* on n are shown in Fig. 3 (solid lines). The dashed lines in Fig. 3 also show the dependences for E_0^* , E_s^* , and E_f^* .

Thus, in our work, we analyzed how the surface effects affected the effective longitudinal Young's modulus of a porous rod with the pores located in parallel to the rod axis. The combined formula (9), which coincides in special cases with the formulas proposed previously, enables us to take into account certain factors—the presence of surface stresses and the surface layer on the boundaries of pores. It makes it possible to take into account more exactly the presence of surface effects including those for nanoporous materials. It is shown that, depending on the problem parameters, the rod stiffness can decrease with an increasing number of pores with a subsequent increase, or a monotonic increase.

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