TENSILITY AND COMPRESSIBILITY OF AXIALLY SYMMETRIC NANOCLUSTERS
PART I: SIMPLIFIED MODELLING

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A simplified method to model the temperature-dependent uniaxial tensility and volume compressibility of axially symmetric nanoclusters is proposed. Particularly, formulae for the isothermal generalized Young's and bulk moduli of nanoclusters being in the quasi-solid state are given and a model of isothermal uniaxial tension dynamics is proposed.

1. Introduction

Bulk nanostructured materials are defined as bulk solids with a nanoscale microstructure. The bulk nanostructured isolated clusters of the ultra-small size (≤ 100 nm), called further *nanoclusters* [1] are produced, as well as ultrafine-grained materials are synthesized by consolidation of such clusters. There exist only limited data on the mechanical behaviour – especially tensile properties – of bulk nanostructured materials [2]. Particularly, the dependence of elastic properties of nanoclusters upon their shape and size [1, 3, 4] has been observed. It means, that we should consider non-local counterparts of usual elastic moduli as well as introduce a global measure of internal surface forces consistent with these generalized elastic moduli. The latter notion can be defined e.g. in the following manner. Let us consider a homogeneous compact and connected elastic nanocluster $\mathcal{B}_0 \subset E^3$ of immovable center of mass, homogeneously deformed (with the gradient of deformation $\mathbf{F} \in GL^+(E^3)$) and endowed with the uniform absolute temperature $\theta \in I \subset R_+$; E^3 denotes a three-dimensional Euclidean vector space space [1, 3]. If $\Psi = \Psi(\mathcal{B}_0; \mathbf{F}, \theta)$ denotes the total Helmholtz free energy of this nanocluster, then corresponding generalized thermodynamic force $\mathbf{N} = \mathbf{N}(\mathcal{B}_0; \mathbf{F}, \theta)$ is defined by [1, 3]:

$$(1.1) \qquad \mathbf{N} = -\partial_{\mathbf{F}}\Psi.$$

Note that when the size and shape effects can be neglected, then the tensor $\hat{\mathbf{T}} \in E^3 \otimes E^3$ of the form:

$$(1.2) \qquad \hat{\mathbf{T}} = -V(\mathcal{B}_0)^{-1}\mathbf{N},$$

where $V(\mathcal{B}_0) = \mathrm{vol}\,\mathcal{B}_0$, reduces to the so-called Piola stress tensor for simple elastic bodies (see e.g. [5]). Thereby, we can consider $\hat{\mathbf{T}}$ as a *generalized Piola stress tensor* assigned to the one whole nanocluster. Consequently, the field of surface forces $\hat{\mathbf{t}}_\theta$, $\theta \in I$, of the form:

$$(1.3) \qquad \hat{\mathbf{t}}_\theta(\mathcal{B}_0; \mathbf{F}, \mathbf{X}) = -\hat{\mathbf{T}}(\mathcal{B}_0; \mathbf{F}, \theta)\mathbf{n}_0(\mathbf{X}),$$

where $\mathbf{n}_0(\mathbf{X})$, $\mathbf{X} \in \partial\mathcal{B}_0$, denotes the outward normal versor at a point $\mathbf{X}$ of the nanocluster boundary $\partial\mathcal{B}_0$, can be interpreted as a field of internal surface forces acting on the surface $\partial\mathcal{B}_0$.

Next, let us consider the dipole moment $\hat{\mathbf{M}}_{\mathrm{int}} = \hat{\mathbf{M}}_{\mathrm{int}}(\mathcal{B}_0; \mathbf{F}, \theta)$ of the surface forces defined as:

$$(1.4) \qquad \hat{\mathbf{M}}_{\mathrm{int}}(\mathcal{B}_0; \mathbf{F}, \theta) = \int_{\partial\mathcal{B}_0} \mathbf{X} \otimes \hat{\mathbf{t}}_\theta(\mathcal{B}_0; \mathbf{F}, \theta, \mathbf{X})dF(\mathbf{X}).$$

Since

$$(1.5) \qquad \hat{\mathbf{T}} = -V(\mathcal{B}_0)^{-1}\hat{\mathbf{M}}_{\mathrm{int}}^{T},$$

we can take the dipole moment $\hat{\mathbf{M}}_{\mathrm{int}}$ as a global measure of internal surface forces. We obtain then the following interpretation rule of the generalized thermodynamic force:

$$(1.6) \qquad \mathbf{N} = \hat{\mathbf{M}}_{\mathrm{int}}^{T}.$$

The symmetric *generalized Cauchy stress tensor* $\mathbf{T} = \mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta)$ can be defined as [1, 3, 5]:

$$(1.7) \qquad \begin{aligned} \mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta) &= J(\mathbf{F})^{-1}\hat{\mathbf{T}}(\mathcal{B}_0; \mathbf{F}, \theta)\mathbf{F}^{T}, \\ J(\mathbf{F}) &= \det \mathbf{F}. \end{aligned}$$

Introducing the field of internal surface forces $\mathbf{t}_\theta$, $\theta \in I$, acting on the boundary $\partial\mathcal{B}$ of the deformed spatial configuration $\mathcal{B} = l(\mathbf{F})(\mathcal{B}_0)$ of $\mathcal{B}_0$:

$$(1.8) \qquad \begin{aligned} \mathbf{t}_\theta(\mathcal{B}_0; \mathbf{F}, \mathbf{x}) &= -\mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta)\mathbf{n}(\mathbf{x}), \\ \mathbf{x} = l(\mathbf{F})\mathbf{X} &= \mathbf{F}\mathbf{X} \in \partial\mathcal{B}, \qquad \mathbf{X} \in \partial\mathcal{B}_0, \end{aligned}$$

where $\mathbf{n}$ is the outward normal versor, we obtain that the the dipole moment $\mathbf{M}_{\mathrm{int}} = \mathbf{M}_{\mathrm{int}}(\mathcal{B}_0; \mathbf{F}, \theta)$ of these forces:

$$(1.9) \qquad \mathbf{M}_{\mathrm{int}}(\mathcal{B}_0; \mathbf{F}, \theta) = \int_{\partial\mathcal{B}} \mathbf{x} \otimes \mathbf{t}_\theta(\mathcal{B}_0; \mathbf{F}, \mathbf{x})dF(\mathbf{x}),$$

has the following representation:

$$(1.10) \qquad \mathbf{M}_{\mathrm{int}}(\mathcal{B}_0; \mathbf{F}, \theta) = -V(\mathcal{B})\mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta),$$

where $V(\mathcal{B}) = \mathrm{vol}\,\mathcal{B}$.

Some of the unique features of solid nanoclusters make those clusters different from these of conventional size ($\geq 1\mu$m) and can be modeled, in the case of convex and compact clusters, on the basis of the phenomenological concept of the *quasi-solid state* of such nanoclusters [1]. Farther on, we will consider convex and compact axially symmetric nanoclusters $\mathcal{B}_0$ only. The boundary $\partial\mathcal{B}_0$ of these nanoclusters is assumed to be a surface of revolution or it consists of such a surface and flat circular bases normal to the axis of revolution. The quasi-solid state of a nanocluster $\mathcal{B}_0$ means that the total Helmholtz free energy Ψ of $\mathcal{B}_0$ has the form:

$$(1.11) \qquad \Psi(\mathcal{B}_0; \mathbf{F}, \theta) = \Phi_\theta(V, F, M),$$

where $V = V(\mathcal{B})$ is the volume of the figure $\mathcal{B} = l(\mathbf{F})(\mathcal{B}_0), \mathbf{F} \in GL^+(E^3)$, $F = F(\partial\mathcal{B})$ is the surface field of the boundary $\partial\mathcal{B}$ of $\mathcal{B}$, and $M = M(\partial\mathcal{B})$ is the total mean curvature of $\partial\mathcal{B}$. Moreover, if $\mathcal{B}_0$ is additionally an elastic undistorted solid nanocluster within the range I of the temperature [1], then its insensibility groups $G_\theta(\mathcal{B}_0)$, $\theta \in I$, [1, 3] would fulfill the following condition [1]:

$$(1.12) \qquad h(\mathcal{B}_0) = G(\mathbf{n}) \subset G_\theta(\mathcal{B}_0) \subset SO(E^3),$$

where $h(\mathcal{B}_0)$ is the group of rotational symmetries of $\mathcal{B}_0$ and $G(\mathbf{n})$ denotes the group of all rotations about the axis axis of revolution parallel to the versor $\mathbf{n}$. It follows from Eq. (1.12) that we are dealing here with transversally isotropic or isotropic homogeneous nanoclusters only.

We will deal also with the *shape-preserving* homogeneous deformations of nanoclusters under consideration. It follows from the polar decomposition theorem of deformation gradients $\mathbf{F} \in GL^+(E^3)$ [5] and from the geometry of nanoclusters that the deformation gradients under consideration can be written in the form:

$$(1.13) \qquad \mathbf{F} = \mathbf{RU}$$

where $\mathbf{R} \in SO(E^3)$ is the rotation tensor, $\mathbf{U}$ is the stretch tensor (a positive definite and symmetric tensor) of the form:

$$(1.14) \qquad \begin{aligned} \mathbf{U} &= \lambda_r \mathbf{E}_r + \lambda_n \mathbf{E}_n, \qquad \lambda_r > 0, \qquad \lambda_n > 0, \\ \mathbf{E}_r &= \mathbf{l} \otimes \mathbf{l} + \mathbf{m} \otimes \mathbf{m}, \qquad \mathbf{E}_n = \mathbf{n} \otimes \mathbf{n}, \end{aligned}$$

and $(\mathbf{l}, \mathbf{m}, \mathbf{n})$ is an orthonormal basis in the Euclidean vector space E^3; $\mathbf{n}$ is the versor parallel to the axis of symmetry.

For a solid (and elastic) nanocluster $\mathcal{B}_0$ being in the quasi-solid state, the generalized Cauchy stress tensor $\mathbf{T} = \mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta)$ defined by Eqs. (1.1), (1.2), (1.7), (1.11), (1.13) and (1.14) takes, in the interval I of absolute temperatures, the following form [1, 3]:

$$\mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta) = p_\theta(\mathcal{B}_0; \lambda_r, \lambda_n)\mathbf{1} + \mathbf{R}t_\theta(\mathcal{B}_0; \lambda_r, \lambda_n)\mathbf{R}^T,$$

$$(1.15) \qquad p_\theta = \frac{\partial\Phi_\theta}{\partial V}, \quad t_\theta = \frac{1}{V}\mathbf{S}_\theta\mathbf{U} \qquad \text{for} \qquad \mathbf{U} = \lambda_r\mathbf{E}_r + \lambda_n\mathbf{E}_n,$$

$$\mathbf{S}_\theta = \frac{\partial\Phi_\theta}{\partial F}\partial_{\mathbf{U}}F + \frac{\partial\Phi_\theta}{\partial M}\partial_{\mathbf{U}}M, \qquad \theta \in I,$$

where

(1.16) $$V = \lambda_r^2 \lambda_n V_0, \qquad V_0 = \text{vol}\,\mathcal{B}_0.$$

Let us consider nanoclusters $\mathcal{B}_\theta$, $\theta \in I$, of the form

(1.17)
$$\mathcal{B}_\theta = l(\mathbf{U}_\theta)(\mathcal{B}_0), \qquad \mathcal{B}_0 = \mathcal{B}_{\theta_0}, \qquad \theta_0 \in I,$$
$$\mathbf{U}_\theta = \lambda_r(\theta)\mathbf{E}_r + \lambda_n(\theta)\mathbf{E}_n, \qquad \lambda_r(\theta_0) = \lambda_n(\theta_0) = 1,$$

and being "unstressed" in this sense that

(1.18) $$\forall \theta \in I, \qquad \mathbf{T}(\mathcal{B}_\theta; \mathbf{1}, \theta) = \mathbf{0},$$

Since [1]

(1.19) $$\forall \theta \in I, \qquad G_\theta(\mathcal{B}_\theta) = G_\theta(\mathcal{B}_0),$$

we obtain, according to the condition (1.12), that

(1.20)
$$\mathbf{U}_\theta = \alpha(\theta)\mathbf{1} + \beta(\theta)\mathbf{n} \otimes \mathbf{n},$$
$$\alpha(\theta) > 0, \qquad \alpha(\theta) + \beta(\theta) > 0, \qquad \mathbf{n} \cdot \mathbf{n} = 1.$$

Comparing equations (1.17) and (1.20) we obtain that

(1.21) $$\lambda_r(\theta) = \alpha(\theta), \qquad \lambda_n(\theta_0) = \alpha(\theta) + \beta(\theta).$$

Therefore, the shape-preserving stretch tensors $\mathbf{U}_\theta$, $\theta \in I$, can be identified with *free thermal distortions* of the nanocluster $\mathcal{B}_0$. We will say then that the family $\mathcal{B}_I = \{\mathcal{B}_\theta, \theta \in I\}$ consists of *thermally equivalent solid nanoclusters* [1]. It seems physically reasonable to expect that the family $\mathcal{B}_I$ should be uniquely defined. Note that $\beta(\theta) = 0$ for isotropic nanoclusters $\mathcal{B}_\theta \in I$.

In this paper, a method of modelling the temperature-dependent mechanical properties of axially symmetric solid nanoclusters, based on the assumption that the quasi-solid state of these nanoclusters is associated with the shape-preserving stretches (1.14) only, is proposed (Sec. 2). It is a simplified approach to the description of dynamics (Sec. 3), uniaxial tensility (Sec. 4), and volume compressibility (Sec. 5) of nanoclusters. Nevertheless, as it has been presented in [3] (Part II), such an approach enables to draw some at least qualitative conclusions.

2. Simplified Model of Tensility

Let $\mathbf{n}$ denote the versor parallel to the axis of symmetry of a nanocluster $\mathcal{B}_0$ under consideration (Sec. 1) and let $e = (\mathbf{l}, \mathbf{m}, \mathbf{n})$ be an orthonormal base in the Euclidean vector space E^3. Let $G_e(\mathcal{B}_0)$ denote the set of all shape-preserving stretch tensors of $\mathcal{B}_0$ defined by e and the formula (1.14). Since for $\mathbf{U}, \mathbf{U}_1, \mathbf{U}_2 \in G_e(\mathcal{B}_0)$ we have:

(2.1)
$$\mathbf{U}_1\mathbf{U}_2 = \underset{1\ 2}{\lambda_r \lambda_r}\mathbf{E}_r + \underset{1\ 2}{\lambda_n \lambda_n}\mathbf{E}_n = \mathbf{U}_2\mathbf{U}_1 \,,$$
$$\mathbf{U}^{-1} = \lambda_r^{-1}\mathbf{E}_r + \lambda_n^{-1}\mathbf{E}_n, \qquad \mathbf{U}\mathbf{U}^{-1} = \mathbf{1} \,,$$

where $\mathbf{1} = \mathbf{E}_r + \mathbf{E}_n$ is the unit tensor, $G_e(\mathcal{B}_0)$ constitutes a two-dimensional Abelian Lie subgroup of the Lie group $GL^+(E^3)$ of all deformation tensors. The spaces tangent to this manifold can be identified with the two-dimensional linear space $T_e(\mathcal{B}_0) \subset E^3 \otimes E^3$ of all second order tensors of the form:

$$(2.2) \qquad \mathbf{T} = T_r\mathbf{E}_r + T_n\mathbf{E}_n, \qquad T_r, T_n \in R,$$

endowed with the following rules of addition and multiplication by real numbers:

$$(2.3) \qquad \mathbf{T}_1 + \mathbf{T}_2 = (\underset{1}{T}_r + \underset{2}{T}_r)\mathbf{E}_r + (\underset{1}{T}_n + \underset{2}{T}_n)\mathbf{E}_n,$$

$$\lambda\mathbf{T} = \lambda T_r\mathbf{E}_r + \lambda T_n\mathbf{E}_3.$$

The linear space $T_e(\mathcal{B}_0)$ can be also endowed with the standard scalar product induced from the Euclidan space $E^3 \otimes E^3$:

$$(2.4) \qquad \mathbf{A} \cdot \mathbf{B} = \mathrm{tr}(\mathbf{A}\mathbf{B}^T) = 2A_rB_r + A_nB_n.$$

Then

$$(2.5) \qquad ||\mathbf{E}_n|| = 1, \qquad ||\mathbf{E}_r|| = \sqrt{2}, \qquad \mathbf{E}_r \cdot \mathbf{E}_n = 0,$$

and the equation (2.2) can be rewritten in the following form:

$$(2.6) \qquad \mathbf{T} = \hat{T}_r\hat{\mathbf{E}}_r + T_n\mathbf{E}_n,$$

$$\hat{T}_r = \sqrt{2}T_r, \qquad \hat{\mathbf{E}}_r = \frac{1}{\sqrt{2}}\mathbf{E}_r, \qquad ||\hat{\mathbf{E}}_r|| = 1.$$

Since $G_e(\mathcal{B}_0) \subset T_e(\mathcal{B}_0)$ and $\dim G_e(\mathcal{B}_0) = \dim T_e(\mathcal{B}_0)$ we have for a scalar $f{:}G_e(\mathcal{B}_0) \to R$:

$$(2.7) \qquad \partial_{\mathbf{U}}f(\mathbf{U}) = \partial_{\hat{\lambda}_r}f(\hat{\lambda}_r\hat{\mathbf{E}}_r + \lambda_n\mathbf{E}_n)\hat{\mathbf{E}}_r + \partial_{\lambda_n}f(\hat{\lambda}_r\hat{\mathbf{E}}_r + \lambda_n\mathbf{E}_n)\mathbf{E}_n ,$$

where $(\hat{\lambda}_r, \lambda_n)$ are Cartesian coordinates in $T_e(\mathcal{B}_0)$ and

$$(2.8) \qquad \partial_{\hat{\lambda}_r}f(\hat{\lambda}_r\hat{\mathbf{E}}_r + \lambda_n\mathbf{E}_n) = \frac{1}{\sqrt{2}}\partial_{\lambda_r}f(\lambda_r\mathbf{E}_r + \lambda_n\mathbf{E}_n) .$$

Thus, identifying $f = f(\mathbf{U})$ with $f = f(\lambda_r, \lambda_n)$ we obtain that:

$$(2.9) \qquad \partial_{\mathbf{U}}f(\mathbf{U}) = \frac{1}{2}\partial_{\lambda_r}f(\lambda_r, \lambda_n)\mathbf{E}_r + \partial_{\lambda_n}f(\lambda_r, \lambda_n)\mathbf{E}_n .$$

We will consider an axially symmetric nanocluster $\mathcal{B}_0$ as a thermodynamic system with the admissible thermodynamic configurations $\lambda = (\mathbf{U}, \theta) \in G_e(\mathcal{B}_0) \times I$ and with the total Helmholtz free energy Ψ defined by the formula (1.11) and by the assumption that $\mathcal{B} = l(\mathbf{U})(\mathcal{B}_0)$, where $\mathbf{U}$ is given by Eq. (1.14). The volume V of $\mathcal{B}$ is given by Eq. (1.16). surface field F and the total mean curvature M of $\partial\mathcal{B}$ are then positive functions of variables λ_r and λ_n dependent on $\mathcal{B}_0$ as a parameter. It follows from Eqs. (1.1), (1.2), (1.7) and (1.13) with (1.13) with $\mathbf{R} = 1$ that

$$(2.10) \qquad \mathbf{N} = -V T \mathbf{U}^{-1},$$

where, according to the equations (1.11), (1.14), (1.15) and (2.9):

$$\mathbf{T} = p_\theta\,\mathbf{1} + \mathbf{t}_\theta = T_{\theta,r}\mathbf{E}_r + T_{\theta,n}\mathbf{E}_n,$$

(2.11) $$\mathbf{t}_\theta = t_{\theta,r}\mathbf{E}_r + t_{\theta,n}\mathbf{E}_n, \qquad \mathbf{1} = \mathbf{E}_r + \mathbf{E}_n,$$

$$T_{\theta,r} = p_\theta + t_{\theta,r}, \qquad T_{\theta,n} = p_\theta + t_{\theta,n},$$

and

$$p_\theta = \frac{\partial \Phi_\theta}{\partial V},$$

(2.12) $$t_{\theta,r} = \frac{\lambda_r}{2V}\left(\frac{\partial \Phi_\theta}{\partial F}\partial_{\lambda_r}F + \frac{\partial \Phi_\theta}{\partial M}\partial_{\lambda_r}M\right),$$

$$t_{\theta,n} = \frac{\lambda_n}{V}\left(\frac{\partial \Phi_\theta}{\partial F}\partial_{\lambda_n}F + \frac{\partial \Phi_\theta}{\partial M}\partial_{\lambda_n}M\right).$$

Moreover, according to Eqs. (1.11), (1.14), (1.17), (2.1) and (2.12), we have:

(2.13) $$\forall \mathbf{G} \in G_e(\mathcal{B}_\theta), \qquad \mathbf{T}(\mathcal{B}_\theta; \mathbf{G}, \theta) = \mathbf{T}(\mathcal{B}_0; \mathbf{G}\mathbf{U}_\theta, \theta).$$

Thus, the condition (1.18) is equivalent to

(2.14) $$\forall \theta \in I, \qquad \mathbf{T}(\mathcal{B}_0; \mathbf{U}_\theta, \theta) = \mathbf{0}.$$

It means that the stretches $\lambda_r(\theta)$ and $\lambda_n(\theta)$ of Eq. (1.17) are solutions, at the temperature $\theta \in I$, of the following system of equations:

(2.15) $$T_{\theta,r}(\mathcal{B}_0 : \lambda_r, \lambda_n, \theta) = 0,$$

$$T_{\theta,n}(\mathcal{B}_0 : \lambda_r, \lambda_n, \theta) = 0.$$

3. Simplified Model of Dynamics

Let us consider the method of derivation of an equation governing the dynamics of homogeneous thermodynamic processes [5] that has been proposed in order to describe size-effect bodies with the admissible thermodynamic configurations $\lambda = (\mathbf{F}, \theta) \in GL^+(E^3) \times I$ [3]. It is easy to see that this method of derivation can be adapted to the case of nanoclusters with thermodynamic configurations defined by the condition $\lambda = (\mathbf{U}, \theta) \in G_e(\mathcal{B}_0) \times I$ (Sec. 2). In this way we obtain the following equation describing the *dynamics of isothermal processes* (cf. [6, 7]):

(3.1) $$\mathbf{U}(\tau)\mathbf{J}(\mathcal{B}_0)\ddot{\mathbf{U}}(\tau) = -\mathbf{M}_{int}(\mathcal{B}_0; \tau) + \mathbf{M}_{ext}(\mathcal{B}_0; \tau)$$

where $\mathbf{M}_{int}(\mathcal{B}_0; \tau)$ and $\mathbf{M}_{ext}(\mathcal{B}_0; \tau)$ are actual (at the moment $\tau \geq 0$) dipole moments of internal (Sec. 1) and external [3] surface forces, respectively. The equation (3.1) is related to the actual spatial configurations $\mathcal{B}_\tau, \tau \geq 0$, of $\mathcal{B}_0$ and thus, according to Eqs. (1.10), (1.13) and (1.14) with $\mathbf{R} = \mathbf{1}$ and $\mathbf{U} = \mathbf{U}(\tau)$, we have:

(3.2) $$\mathbf{M}_{int}(\mathcal{B}_0; \tau) = -V(\tau)\mathbf{T}(\mathcal{B}_0; \mathbf{U}(\tau), \theta),$$

$$V(\tau) = \mathrm{vol}\,\mathcal{B}_\tau, \qquad \mathcal{B}_\tau = l(\mathbf{U}(\tau))(\mathcal{B}_0), \ \theta \in I,$$

where $\mathbf{T}(\mathcal{B}_0; \mathbf{U}, \theta)$ denotes the generalized Cauchy stress tensor defined by the equations (1.14), (2.11) and (2.12). Moreover, it is assumed that the actual dipole moment of external volume forces [3] can be neglected and the dipole moment of external surface forces defined as:

$$(3.3) \qquad \mathbf{M}_{\text{ext}}(\mathcal{B}_0; \tau) = \int_{\partial\mathcal{B}_\tau} \mathbf{x} \otimes \mathbf{s}(\mathbf{x}, \tau) dF(\mathbf{x}),$$

can be represented in the following form:

$$(3.4) \qquad \mathbf{M}_{\text{ext}}(\mathcal{B}_0; \tau) = M_r(\mathcal{B}_0; \tau)\mathbf{E}_r + M_n(\mathcal{B}_0; \tau)\mathbf{E}_n,$$

where Eqs. (1.9), (1.10) and (2.11) were taken into account. $\mathbf{J}(\mathcal{B}_0)$ is the inertia tensor of the considered homogeneous nanocluster $\mathcal{B}_0$ of mass m. It follows from Eqs. (1.12) and (1.14) that it should be:

$$(3.5) \qquad \mathbf{J}(\mathcal{B}_0) = J_r(\mathcal{B}_0)\mathbf{E}_r + J_n(\mathcal{B}_0)\mathbf{E}_n.$$

Thereby, we will deal with the following system of equations:

$$(3.6) \qquad \begin{aligned} \lambda_n J_n(\mathcal{B}_0)\ddot{\lambda}_n &= -VT_{\theta,n} + M_n, \\ \lambda_r J_r(\mathcal{B}_0)\ddot{\lambda}_r &= -VT_{\theta,r} + M_r, \end{aligned}$$

where the components $T_{\theta,n}$ and $T_{\theta,r}$ are defined by Eqs. (2.11) and (2.12).

It should be stressed that the simplified model of dynamics of axially symmetric nanoclusters is not a particular case of the model presented in [3]. This is because we consider here a different thermodynamic system: this one for which the only admissible thermodynamic configurations are those corresponding to the shape-preserving stretch tensors of Eq. (1.14) (Sec. 2), while in [1, 3] and Sec. 1 the admissible thermodynamic configurations correspond to general homogeneous deformations. However, the system of equations (3.6) can be considered as this one which defines a particular solution of equations governing the Newtonian dynamics of "affinely rigid bodies" [7] (see also [6]).

4. Generalized Simple Tension

We will consider isothermal uniaxial tension of axially symmetric nanoclusters only. The geometry of the problem suggests to consider the (isothermal) generalized simple tension (cf. [8]) of homogeneous axially symmetric nanoclusters being in the quasi-solid state. It can be defined, in the framework of the simplified model of tensility (Sec. 2), by the following condition:

$$(4.1) \qquad T_{\theta,r} = p_\theta + t_{\theta,r} = 0, \qquad \theta \in I.$$

In this case

$$(4.2) \qquad \begin{aligned} \mathbf{T}(\mathcal{B}_0; \mathbf{U}, \theta) &= T_{\theta,n}(\mathcal{B}_0; \lambda_r, \lambda_n)\mathbf{E}_n, \\ T_{\theta,n} &= p_\theta + t_{\theta,n} = t_{\theta,n} - t_{\theta,r}, \qquad \theta \in I. \end{aligned}$$

We will assume that the condition (4.1) is consistent with a relationship (in general dependent on the nanocluster geometry) between the axial (λ_n) and lateral (λ_r) stretches of the form:

$$(4.3) \qquad \lambda_r = h_\theta(\lambda_n), \qquad h_\theta(1) = 1, \qquad \theta \in I.$$

For example, in the case of isothermal incompressibility defined by:

$$(4.4) \qquad \begin{aligned} V_0 \lambda_n \lambda_r^2 &= V_0(\theta), \\ V_0 = V_0(\theta_0) &= \mathrm{vol}\,\mathcal{B}_0, \qquad \theta_0 \in I, \end{aligned}$$

h_θ, $\theta \in I$, are decreasing functions of the variable λ_n. Note that decreasing functions h_θ, $\theta \in I$, can appear also in the case of compressible elasticity [8].

It follows from Eqs. (1.11), (1.16)–(1.18), (2.12)–(2.14) that:

$$(4.5) \qquad \begin{aligned} T_{\theta,n}(\mathcal{B}_0; \lambda_r, \lambda_n) &= \hat{T}_\theta(\mathcal{B}_\theta; \mu_r, \mu_n), \\ \lambda_r &= \lambda_r(\theta)\mu_r, \qquad \lambda_n = \lambda_n(\theta)\mu_n, \end{aligned}$$

where, according to Eqs. (2.15), (4.1) and (4.3), the following conditions should be fulfilled:

$$(4.6) \qquad \begin{aligned} \lambda_r(\theta) &= h_\theta(\lambda_n(\theta)), \\ \mu_r &= \hat{h}_\theta(\mu_n) = h_\theta(\lambda_n(\theta)\mu_n)\lambda_r(\theta)^{-1}. \end{aligned}$$

Introducing the notations:

$$(4.7) \qquad \begin{aligned} \lambda_n &= \lambda, \qquad \mu_n = \mu, \\ T_\theta(\mathcal{B}_0; \lambda) &= T_{\theta,n}(\mathcal{B}_0; h_\theta(\lambda), \lambda), \\ \hat{T}_\theta(\mathcal{B}_\theta; \mu) &= \hat{T}_{\theta,n}(\mathcal{B}_\theta; \hat{h}_\theta(\mu), \mu), \end{aligned}$$

we can reduce Eqs. (1.18), (2.13) and (2.14) to the following form:

$$(4.8) \qquad T_\theta(\mathcal{B}_0; \lambda_n(\theta)\mu) = \hat{T}_\theta(\mathcal{B}_\theta; \mu)$$

where

$$(4.9) \qquad T_\theta(\mathcal{B}_0; \lambda_n(\theta)) = \hat{T}_\theta(\mathcal{B}_\theta; 1) = 0.$$

In the theory of simple elastic materials are considered the so-called "static inequalities" concerning the relationships between principal stretches and principal stresses [5]. We will take, as a nanoscale counterpart of such a relationship, the following *generalized postulate of tensility* of thermally equivalent solid nanoclusters $\mathcal{B}_\theta \in \mathcal{B}_I$ (Secs. 1 and 2):

$$(4.10) \qquad \forall \theta \in I, \qquad \hat{T}_\theta(\mathcal{B}_\theta; \mu)(\mu - 1) > 0 \qquad \text{for} \qquad \mu \neq 1$$

stating that axial elongations ($\mu > 1$) correspond to generalized tensile stresses ($\hat{T}_\theta > 0$) and axial contractions ($0 < \mu < 1$) correspond to generalized compressive stresses ($\hat{T}_\theta < 0$).

Let $l(\theta)$ denote the size of a nanocluster $\mathcal{B}_\theta \in \mathcal{B}_I$ in the direction of its axis of symmetry and let $l = \mu l(\theta)$, $\mu > 0$, be the actual size of the nanocluster in this direction. The elastic strain ϵ of $\mathcal{B}_\theta$ along its axis of symmetry is defined by:

$$d\epsilon = \frac{dl}{l} = \frac{d\mu}{\mu},$$
$$\epsilon = \epsilon(\mu), \qquad \epsilon(1) = 0,$$

(4.11)

and can be written as the so-called *natural strain*:

(4.12) $$\epsilon = \epsilon(\mu) = \ln\mu, \qquad \mu > 0.$$

Let us denote:

(4.13)
$$\sigma_\theta(\epsilon) = \hat{T}_\theta(\mathcal{B}_\theta; e^\epsilon),$$

$$\hat{E}_\theta(\epsilon) = \frac{d\sigma_\theta(\epsilon)}{d\epsilon}, \qquad E(\theta) = \hat{E}_\theta(0),$$

and

(4.14) $$E_\theta(\mathcal{B}_0; \lambda) = \lambda \frac{dT_\theta}{d\lambda}(\mathcal{B}_0; \lambda).$$

It follows from Eqs. (4.5)–(4.8) and (4.12)–(4.14) that

(4.15) $$E_\theta(\mathcal{B}_0; \lambda) = \hat{E}_\theta(\ln\mu)\Big|_{\mu=\lambda\lambda_n(\theta)-1},$$

and

(4.16) $$E(\theta) = E_\theta(\mathcal{B}_0; \lambda_n(\theta)).$$

The function $\lambda > 0 \to E_\theta(\mathcal{B}_0; \lambda)$ describes the *isothermal tensility* of a nanocluster $\mathcal{B}_0$ at the temperature $\theta \in I$.

Let δ be a small strain of the nanocluster $\mathcal{B}_\theta$ in the direction of its axis of symmetry:

(4.17) $$\delta = \frac{l - l(\theta)}{l(\theta)} = \mu - 1, \qquad |\delta| \ll 1.$$

Then

(4.18)
$$\sigma_\theta(\epsilon) = E(\theta)\epsilon + o(\epsilon),$$

$$\epsilon = \delta + o(\delta), \qquad E(\theta) > 0,$$

where $o(x)/x \to 0$ for $x \to 0$ and the generalized postulate of tensility was taken into account. Thus, if the family $\mathcal{B}_I$ of thermally equivalent solid nanoclusters is uniquely defined (Sec. 1), then the positive definite scalar $E(\theta)$ is a well-defined physical quantity and can be identified with the *generalized Young's modulus* of the nanocluster $\mathcal{B}_\theta \in \mathcal{B}_I$ in the direction of its axis of symmetry. The equation (4.16) suggests then that $E(\theta)$ can be interpreted as the *generalized isothermal Young's modulus* of a nanocluster $\mathcal{B}_0$ at the temperature $\theta \in I$.

We can observe, at least for some particular sizes of crystalline nanoclusters, the coexistence of solid and liquid states within a finite interval of temperatures [9]. The formulation of a phenomenological model of this phenomenon is an open question. In the case of uniaxial tensility of nanoclusters, such a model can be proposed on the basis of the following two assumptions [1, 3]: (i) the nanocluster is, within a certain range of temperature, in the quasi-solid state (Sec. 1 and [1]); (ii) the mechanical stability of the uniaxial tension of a nanocluster being in the quasi-solid state breaks down for some its critical sizes. So, let us consider the uniquely defined isothermal tensility function E_θ of Eq. (4.14). We will say, imitating the primary thermodynamic meaning of the notion of stability of bulk matter [10, 11], that the uniaxial tensility of a nanocluster $\mathcal{B}_0$ is *mechanically stable* in the range $I' \subset I$ of temperature if for each $\theta \in I'$ we have:

$$(4.19) \qquad\qquad \forall \lambda > 0, \qquad E_\theta(\mathcal{B}_0; \lambda) > 0,$$

or it is *mechanically stable of lower order* [12] if

$$(4.20) \qquad\qquad \forall \theta \in I', \qquad \exists \lambda_{cr}(\theta) > 0 : \ E_\theta(\mathcal{B}_0; \lambda_{cr}(\theta)) = 0,$$

and

$$(4.21) \qquad\qquad \forall \theta \in I', \qquad \frac{dE_\theta}{d\lambda}(\mathcal{B}_0; \lambda_{cr}(\theta)) \neq 0.$$

Note that the existence of a temperature $\theta_p \in I'$ such that the condition (4.20) is fulfilled for $\theta = \theta_p$ and

$$(4.22) \qquad\qquad \frac{dE_\theta}{d\lambda}(\mathcal{B}_0; \lambda_{cr}(\theta)) = 0 \qquad \text{for} \qquad \theta = \theta_p,$$

defines a phase transformation [12] (cf. [3], Part II, Sec. 2). The *critical configurations* $\mathcal{B}_{cr}(\theta), \theta \in I'$, of the nanocluster $\mathcal{B}_0$ defined by the conditions (4.20), (4.21) and by:

$$\mathcal{B}_{cr}(\theta) = l(\mathbf{U}_{cr}(\theta))(\mathcal{B}_0) \,,$$

$$(4.23) \qquad \mathbf{U}_{cr}(\theta) = \lambda_{cr,r}(\theta)\mathbf{E}_r + \lambda_{cr,n}(\theta)\mathbf{E}_n \,,$$

$$\lambda_{cr,n}(\theta) = \lambda_{cr}(\theta), \qquad \lambda_{cr,r}(\theta) = h_\theta(\lambda_{cr}(\theta)),$$

are supposed to be those for which the coexistence of solid and liquid states occurs within the range I' of temperature.

5. Generalized Uniform Pressure

Let us consider a generalized uniform pressure defined by the following condition:

$$\mathbf{T}(\mathcal{B}_0; \mathbf{U}, \theta) = T_\theta(\mathcal{B}_0; \lambda_r, \lambda_n)\mathbf{1},$$

$$(5.1)$$

$$T_\theta = T_{\theta,r} = T_{\theta,n},$$

where Eq. (2.11) was taken into account. Equivalently:

$$(5.2) \qquad\qquad \forall \theta \in I, \qquad t_{\theta,r}(\mathcal{B}_0; \lambda_r, \lambda_n) = t_{\theta,n}(\mathcal{B}_0; \lambda_r, \lambda_n),$$

where $t_{\theta,r}$ and $t_{\theta,n}$ are defined by Eq. (2.12). The "unstressed" nanoclusters $\mathcal{B}_\theta$, $\theta \in I$, of Eq. (1.17) are defined here, according to Eqs. (1.18), (2.13)–(2.15) and (5.1), by:

$$(5.3) \qquad T_\theta(\mathcal{B}_0; \lambda_r(\theta), \lambda_n(\theta)) = 0,$$

where the stretches $\lambda_r(\theta)$ and $\lambda_n(\theta)$ are constrained by the condition (5.2).

The modeling of compressibility of axially symmetric, homogeneous and elastic nanoclusters being in the quasi-solid state (Secs. 1 and 2) needs the assumption of a relationship between the generalized uniform pressure and the actual volume of these nanoclusters. It can be done if relationships (in general, dependent on the nanocluster geometry) between the stretches (λ_r-lateral and λ_n-axial) and the actual volume V can be formulated. These relationships would be constrained by Eqs. (1.16) and (5.2). Note that the "unstressed" nanoclusters $\mathcal{B}_\theta$, $\theta \in I$, defined by Eqs. (1.17), (4.1)–(4.3) and (4.9) are consistent with the conditions (5.2) and (5.3). So, let us assume that for each above mentioned and uniquely defined nanocluster $\mathcal{B}_\theta \in \mathcal{B}_I$, we have:

$$(5.4) \qquad \begin{aligned} \lambda_r &= \lambda_r(\theta)\mu_r, & \mu_r &= k_\theta(\xi), & \xi &= V/V_\theta > 0, \\ \lambda_n &= \lambda_n(\theta)\mu_n, & \mu_n &= \xi k_\theta(\xi)^{-2}, & k_\theta(1) &= 1, \\ V_\theta &= \mathrm{vol}\mathcal{B}_\theta = V_0\lambda_n(\theta)\lambda_r(\theta)^2, \end{aligned}$$

where Eq. (1.16) was taken into account. We obtain then the following representation of the generalized pressure T_θ of Eq. (5.1):

$$(5.5) \qquad \begin{aligned} T_\theta(\mathcal{B}_0; \lambda_r, \lambda_n) &= \hat{T}_\theta(\mathcal{B}_\theta; \mu_r, \mu_n) = \hat{\pi}_\theta(\xi), \\ \hat{\pi}_\theta(\xi) &= \hat{T}_\theta(\mathcal{B}_\theta; k_\theta(\xi), \xi k_\theta(\xi)^{-2}). \end{aligned}$$

The behaviour of real solid bodies implies the following *generalized postulate of compressibility* of thermally equivalent solid nanoclusters $\mathcal{B}_\theta \in \mathcal{B}_I$ (cf. [5] and [3], Part II): increasing of the volume V_θ requires generalized uniform tensile stresses and decreasing of this volume – generalized uniform compressive stresses. This postulate means that for each $\theta \in I$ it should be:

$$(5.6) \qquad \hat{\pi}_\theta(\xi)(\xi - 1) > 0, \qquad \xi \neq 1.$$

Let us denote

$$(5.7) \qquad d\kappa = \frac{dV}{V} = \frac{d\xi}{\xi},$$

$$\kappa = \kappa(\xi), \qquad \kappa(1) = 0,$$

or, equivalently:

$$(5.8) \qquad \kappa = \ln \xi.$$

If

$$(5.9) \qquad \hat{\sigma}_\theta(\kappa) = \hat{\pi}_\theta(e^\kappa),$$

and Δ is a small relative variation of the volume V_θ :

$$(5.10) \qquad \Delta = \frac{V - V_\theta}{V_\theta}, \qquad |\Delta| \ll 1,$$

then we obtain

$$\hat{\sigma}_\theta(\kappa) = K(\theta)\kappa + o(\kappa),$$

$$(5.11)$$

$$\kappa = \Delta + o(\Delta),$$

where, according to the condition (5.6), it should be:

$$(5.12) \qquad K(\theta) = \frac{d\hat{\sigma}_\theta}{d\kappa}(0) > 0.$$

Therefore, we can regard the scalar $K(\theta)$ as a *generalized bulk modulus* of the nanocluster $\mathcal{B}_\theta \in \mathcal{B}_I$.

Let us denote:

$$\zeta = \frac{V}{V_0} = \alpha(\theta)\xi,$$

$$\alpha(\theta) = \frac{V_\theta}{V_0} = \lambda_n(\theta)\lambda_r^2(\theta),$$

$$(5.13)$$

$$\lambda_r(\zeta, \theta) = \lambda_r(\theta)k_\theta(\zeta\alpha(\theta)^{-1}),$$

$$\lambda_n(\zeta, \theta) = \zeta\lambda_r(\zeta, \theta)^{-2},$$

and

$$(5.14) \qquad \pi_\theta(\mathcal{B}_0; \zeta) = T_\theta(\mathcal{B}_0; \lambda_r(\zeta, \theta), \lambda_n(\zeta, \theta)).$$

Then

$$(5.15) \qquad \hat{\sigma}_\theta(\kappa)|_{\kappa=\ln(\zeta/\alpha(\theta))} = \pi_\theta(\mathcal{B}_0; \zeta),$$

and

$$(5.16) \qquad \frac{d\hat{\sigma}_\theta}{d\kappa}(\kappa)\bigg|_{\kappa=\ln(\zeta/\alpha(\theta))} = K_\theta(\mathcal{B}_0; \zeta),$$

where

$$K_\theta(\mathcal{B}_0; \zeta) = \zeta\frac{d\pi_\theta}{d\zeta}(\mathcal{B}_0; \zeta),$$

$$(5.17)$$

$$K_\theta(\mathcal{B}_0; \alpha(\theta)) = K(\theta).$$

Therefore, the function $\zeta \to K_\theta(\mathcal{B}_0; \zeta)$ and the scalar $K(\theta)$ describe the *isothermal compressibility* and *generalized isothermal bulk modulus* of a nanocluster $\mathcal{B}_0$ at the temperature $\theta \in I$, respectively. Consequently, we are able to discuss the mechanical stability (or mechanical stability of lower order) of the volume compressibility of the axially symmetric nanocluster $\mathcal{B}_0$ in a manner analogous to that presented in Sec. 4. However, it is an open question whether the critical configurations of Eq. (4.23) will be identical with those defined by the state of generalized uniform pressure, or not.

6. Final Remarks

We see that the notion of thermally equivalent solid nanoclusters (Secs. 1 and 2) creates the possibility for a definition of such temperature-dependent *generalized elastic moduli* which can be interpreted as the isothermal mechanical characteristics of a solid nanocluster (Secs. 4 and 5). Note that these generalized elastic moduli are referred, contrary to the macroscopic elastic moduli, to one whole nanocluster, not an infinite family of subclusters. Thus, the existence of such defined generalized elastic moduli imposes conditions on the total free energy function. In the second part of this paper we will consider examples of such conditions.

In the second part of the paper we will also discuss an example of isothermal uniaxial tension dynamics of axially symmetric nanoclusters (Sec. 3).

Acknowledgment

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