Nanomaterial clusters as macroscopically small size-effect bodies. Part II

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AN ISOTROPIC ELASTIC SPHERICAL size-effect solid body is proposed as a phenomenological model for the description of thermomechanical properties of macroscopically small nanomaterial spherical clusters subjected to a uniform pressure. Nanomaterial clusters being mechanically stable as well as those being mechanically stable of lower order are investigated. It is shown, among others, that the isothermal bulk modulus reveals the size effect due to the influence of surface tension of the cluster boundary solid surface.

1. Introduction

INVESTIGATION OF COMPRESSIBILITY of crystalline solid bodies subjected to a uniform pressure is, independently of the grain size, of considerable importance for determining their elastic properties. This is connected with the fact that under conditions of uniform pressure, it is possible to determine experimentally the elastic response of the body to the homothetic deformation

$$(1.1) \qquad \mathbf{F} = \lambda\mathbf{1}, \quad \lambda > 0,$$

without producing any plastic deformations due to the lattice defects [1]. As a result, the body elastic response to the homothetic deformation, determined by measuring the volume variation due to pressure changes, is more closely connected with the elastic character of interatomic interactions in ideal crystals than the elastic response to the other types of deformations. This statement is confirmed, for example, by fairly good experimental verification of a formula for the macroscopic bulk modulus K of usual metals determined within the framework of free-electron approximation [2]. This approximation of bulk modulus is formulated for a macroscopic metal sample such that surface atoms have a negligible contribution to bulk properties of the crystal, and as a result we obtain [2]:

$$(1.2) \qquad K = \left(\frac{61.2}{r_e/a_0}\right)^5 \text{N/cm}^2,$$

where r_e is the effective radius of an electron gas and a_0 – Bohr's radius of a hydrogen atom.

We see that the macroscopic observation level scale of the free electron approximation enables a description of the macroscopic bulk modulus in terms of atomic-sized quantities (cf. [3], Sec. 1). However, for a macroscopically small sample, the influence of surface atoms makes impossible an approximation of bulk properties of a condensed material based on atomic-sized quantities only. It is observed e.g. as the dependence of elastic properties of nanostructures on the observation level scale. It suggests to consider the nanostructures as macroscopically small size-effect bodies [3]. A more detailed introduction to the topic is provided in [3], where also the general homogeneous deformations are considered. This part of the paper is a modification and extension, stimulated by properties of nanocrystalline clusters, of the paper [4] (Secs. 2 and 3). The phenomenological models introduced in Secs. 4, 5, idealizing the properties of metallic and fullerene C_{60} crystalline nanomaterials (see [3], Sec. 1), are discussed in Sec. 6.

2. Elastic compressibility of a spherical size-effect solid body

Let us consider a homogeneous and isotropic elastic size-effect spherical body $\mathcal{B}_0$ subjected to a uniform pressure ([3], Sec. 2). The body deformation has then the form (1.1). Since this deformation preserves the spherical shape of the spatial configuration $\mathcal{B}_0$, we will refer to a *spherical size-effect body* identified with its reference spatial configuration $\mathcal{B}_0$ (cf. remarks at the very end of [3], Sec. 4). The spherical body $\mathcal{B}_0$ can be treated, under these conditions, as a thermodynamic system described by thermodynamic configurations of the form $(\lambda, \theta) \in R^+ \times I$, thermodynamic functions Ψ (total free energy), E (total internal energy), S (total entropy), and the generalized force $\mathbf{N}$ depending on the radius R_0 of $\mathcal{B}_0$ as a parameter. The thermodynamic functions are related by formulae (2.3) and (2.10) of [3], and the generalized force has the form:

$$\mathbf{N}(\mathcal{B}_0; \mathbf{F}, \theta) = N(R_0; \lambda, \theta)\mathbf{1},$$

(2.1)

$$N(R_0; \lambda, \theta) = -\partial_\lambda \Psi(R_0; \lambda, \theta).$$

The corresponding generalized Cauchy stress tensor is given by:

$$\mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta) = -V(\mathcal{B})^{-1}\mathbf{N}(\mathcal{B}_0; \mathbf{F}, \theta)\mathbf{F}^T = t(R_0; \lambda, \theta)\mathbf{1},$$

(2.2) $$t(R_0; \lambda, \theta) = V(R_0)^{-1}\lambda^{-2}\partial_\lambda \Psi(R_0; \lambda, \theta),$$

$$V(\mathcal{B}) = V(R) = (4/3)\pi R^3 = \lambda^3 V(R_0), \quad R = \lambda R_0,$$

where R denotes the radius of a deformed spatial configuration $\mathcal{B}$ of $\mathcal{B}_0$. Since the natural spatial configurations $\mathcal{B}_0(\theta)$, $\theta \in I$, are here spherical of the radius $R_0(\theta)$, the condition (2.26) of [3] takes, according to Eq. (2.2), the following form:

$$(2.3) \qquad \forall \theta \in I \; \exists R_0(\theta) > 0, \quad t(R_0(\theta); 1, \theta) = 0,$$

defining the considered isotropic elastic spherical size-effect body as a solid body ([3], Sec. 2). Let us denote by $t_\theta(\lambda)$ the isothermal generalized stress due to the deformation λ of a natural spatial configuration $\mathcal{B}_0(\theta)$:

$$(2.4) \qquad t_\theta(\lambda) = t(R_0(\theta); \lambda, \theta), \quad t_\theta(1) = 0.$$

The behaviour of real solid bodies implies the following *postulate of compressibility* (cf. [5]): in the deformation process of Eq. (1.1) of a natural spatial configuration $\mathcal{B}_0(\theta)$, increasing of its volume $V_0(\theta)$ requires uniform tensile stresses, and decreasing of this volume - uniform compressive stresses. This postulate means that should be:

$$(2.5) \qquad \forall \theta \in I, \quad \forall 0 < \lambda \neq 1, \quad t_\theta(\lambda)(\lambda - 1) > 0.$$

Let $R = \lambda R_0$ be the radius of a deformed spatial configuration $\mathcal{B}$ of the body $\mathcal{B}_0$ of the radius R_0, and let $V = V(\lambda)$ and $V = V_0$ denote the volume of the deformed and undeformed configurations, respectively. Let us denote

$$(2.6) \qquad d\kappa = \frac{dV}{V}, \quad V(1) = V_0$$

or, equivalently

$$(2.7) \qquad \kappa = \ln(V/V_0) = 3\varepsilon, \quad \varepsilon = \ln \lambda.$$

Denoting

$$\sigma(R_0; \kappa, \theta) = t(R_0; e^{\kappa/3}, \theta),$$

$$(2.8)$$

$$K_\theta(R_0; \lambda) = \frac{\partial \sigma}{\partial \kappa} (R_0; \kappa, \theta)|_{\kappa = 3\ln \lambda},$$

we obtain:

$$(2.9) \qquad K_\theta(R_0; \lambda) = \frac{\lambda}{3} \partial_\lambda t(R_0; \lambda, \theta).$$

The function $\lambda \in R^+ \to K_\theta(R_0; \lambda)$ defines the *isothermal compressibility* at a constant temperature θ of the spatial configuration $\mathcal{B}_0$ of the isotropic elastic spherical size-effect solid body. If $\mathcal{B}_0 = \mathcal{B}_0(\theta)$ is a natural spatial configuration of

the body, $R_0 = R_0(\theta)$ – its radius, Δ is a small relative variation of the volume $V_0 = V_0(\theta)$ of this configuration:

$$\Delta = \frac{V(R) - V_0(\theta)}{V_0(\theta)}, \quad |\Delta| \ll 1,$$

(2.10)

$$R = \lambda R_0(\theta), \quad V_0(\theta) = V(R_0(\theta)),$$

and

(2.11)
$$\sigma_\theta(\kappa) = t_\theta(e^{\kappa/3}),$$

then we obtain, taking into account the postulate of compressibility (Eq. (25)), that

$$\sigma_\theta(\kappa) = K(\theta)\kappa + o(\kappa),$$

(2.12)

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

where $o(x)/x \to 0$ for $x \to 0$, and it was denoted:

(2.13)
$$K(\theta) = \partial_\kappa \sigma_\theta(\kappa)|_{\kappa=0} = K_\theta(R_0(\theta), 1) > 0.$$

Thus, the scalar $K(\theta)$, $\theta \in I$, can be identified with the isothermal bulk modulus of the natural spatial configuration $\mathcal{B}_0(\theta)$. If the natural configuration is uniquely defined at each temperature $\theta \in I$, then $K(\theta)$ is a well-defined physical quantity and can be considered as the *isothermal bulk modulus* of the spherical size-effect solid body. Thereby, the existence of such isothermal bulk modulus imposes a condition on the total free energy function (see e.g. Sec. 3).

Let $\mathcal{B}_0$ be an arbitrary reference configuration of the spherical size-effect solid body. The *heat capacity* function $\theta \in I \to K_\lambda(R_0; \theta)$ at the constant deformation λ is defined by

(2.14) $$K_\lambda = \partial_\theta E = \theta \partial_\theta S = -\theta(\partial^2 \Psi / \partial \theta^2)_\lambda.$$

The condition of *thermal stability* at the constant deformation λ:

(2.15) $$\forall \theta \in I, \qquad K_\lambda(R_0; \theta) > 0$$

and the condition of *mechanical stability* at the constant temperature θ:

(2.16) $$\forall \lambda > 0, \qquad K_\theta(R_0; \lambda) > 0,$$

define the *thermodynamical stability* of an undeformed spatial configuration I_0 of the radius R_0 of the spherical size-effect solid body. The state of matter is stable (in the spatial configuration $\mathcal{B}_0$) iff both the stability conditions are fulfilled [6, 7]. Otherwise, the mater becomes unstable and shows a tendency to break up

into separate phases [6]. Let us assume the existence of a curve $(\theta, \lambda_{cr}(\theta))$, $\theta \in I$, in R^2 along which the so-called *mechanical stability of lower order* [8] occurs, that is:

$$(2.17) \qquad \forall \theta \in I, \qquad K_\theta(R_0; \lambda_{cr}(\theta)) = 0.$$

According to this definition, the *critical thermodynamic configurations* separate the stable and unstable isothermal states of matter [6]. The critical deformations $\lambda_{cr}(\theta)$, $\theta \in I$, can be equivalently defined as stationary points of the isothermal generalized Cauchy stress function (see Eq. (2.9)):

$$(2.18) \qquad (\partial t / \partial \lambda)_\theta = 0 \quad \text{for} \quad \lambda = \lambda_{cr}(\theta).$$

If $t \in C^2$ and there exists a temperature $\theta_p \in I$ such that (see Eqs. (2.7) – (2.9) and (2.18)):

$$(2.19) \qquad (\partial^2 t / \partial \lambda^2)_\theta = 0 \quad \text{for} \quad \lambda = \lambda_{cr}(\theta_p),$$

then the conditions (2.18) (with $\theta = \theta_p$) and (2.19) define the so-called *critical point* $(\theta_p, t_p(R_0))$ of a phase transition, where

$$(2.20) \qquad t_p(R_0) = t(R_0; \lambda_{cr}(\theta_p), \theta_p).$$

The existence of critical points has been experimentally confirmed [8]. Further on (Secs. 3 and 5), we consider critical thermodynamic configurations within the range I of temperature, but such that the condition (2.19) of existence of a critical point is not fulfilled.

Let us consider the generalized force $\mathbf{N}$ of Eq. (2.1) defining an elastic response of the spherical size-effect solid body to homogeneous deformations of the form (1.1) of a distinguished spatial configuration $\mathcal{B}_0$ (identified with the body itself). Assuming that

$$\mathbf{s}(\mathbf{X}, \tau) = p_s(\tau)\mathbf{n}(\mathbf{X}), \quad \mathbf{n}(\mathbf{X}) \cdot \mathbf{n}(\mathbf{X}) = 1 \quad \text{for } \mathbf{X} \in \partial \mathcal{B}_0,$$

(2.21)

$$\mathbf{b}(\mathbf{X}, \tau) = 0 \quad \text{for } \mathbf{X} \in \text{Int}\mathcal{B}_0; \quad \mathbf{X} = R_0 \mathbf{n}(\mathbf{X}) \quad \text{for } \mathbf{X} \in \partial \mathcal{B}_0,$$

where $\mathbf{n}$ is the unit outward normal to the sphere $\partial \mathcal{B}_0$ of the radius R_0, and taking into account Eqs. (2.5) and (3.1) – (3.3) of [3], we obtain the following equation of the spherical size-effect body dynamics [4]:

$$J_0 \ddot{\lambda} = N(R_0; \lambda, \theta) + 3V_0 p_s,$$

$$(2.22) \qquad N(R_0; \lambda, \theta) = -\partial_\lambda \Psi(R_0; \lambda, \theta), \quad \lambda(0) = 1,$$

$$J_0 = (3/5)mR_0^2, \quad V_0 = V(R_0) = (4/3)\pi R_0^3,$$

where $\ddot{\lambda} = d^2\lambda/d\tau^2$, $J_0\mathbf{1}$ is the body $\mathcal{B}_0$ inertia tensor, and $p_s = p_s(\tau)$ is a uniform external pressure (tension or compression) acting on the body boundary at the instant $\tau \geq o$. If the radius R_0 is not dependent on the temperature (i.e. we exclude natural spatial configurations $\mathcal{B}_0(\theta)$), then nonisothermal reversible processes of time-dependent thermodynamic configurations of the body are described by the Eq. (2.22) and by the following temperature evolution equation [4] (cf. Eq. (3.12) of [3]):

$$K_\lambda(R_0; \theta)\dot{\theta} = -\theta\partial_\theta N(R_0; \lambda, \theta)\dot{\lambda} + Q(R_0; \tau),$$

(2.23)

$$Q(R_0; \tau) = \theta(\tau)\dot{S}(R_0; \lambda(\tau), \theta(\tau)), \quad S = -\partial_\theta\Psi,$$

where Q is the heat production, and $\dot{S}$ denotes the time derivative of the total entropy S along a curve of thermodynamic configurations.

If we deal with irreversible processes, then the generalized force $N(R_0; \lambda, \theta)$ of Eq. (2.22) should be replaced e.g. by (cf. Eqs. (2.9) – (2.12) of [3], and (2.1) – (2.3)):

$$N_D(R_0; \lambda, \dot{\lambda}, \theta) = -V_0\lambda^2 t_D(R_0; \lambda, \dot{\lambda}, \theta) = N(R_0; \lambda, \theta)$$

(2.24) $$+H_D(R_0; \lambda, \dot{\lambda}, \theta)$$

$$H_D(R_0; \lambda, \dot{\lambda}, \theta) = -V_0\lambda^2 h_D(R_0; \lambda, \dot{\lambda}, \theta),$$

where

$$\mathbf{T}_D(\mathcal{B}_0; \mathbf{F}, \theta, \mathbf{L}) = t_D(R_0; \lambda, \dot{\lambda}, \theta)\mathbf{1}, \quad \mathbf{L} = (\dot{\lambda}/\lambda)\mathbf{1},$$

(2.25)

$$t_D(R_0; \lambda, \dot{\lambda}, \theta) = t(R_0; \lambda, \theta) + h_D(R_0; \lambda, \dot{\lambda}, \theta),$$

is the generalized Cauchy stress tensor, and

(2.26) $\forall\theta \in I, \qquad h_D(R_0; \lambda, 0, \theta) = 0, \qquad h_D(R_0; \lambda, \dot{\lambda}, \theta)\dot{\lambda} \geq 0.$

It should be stressed that the description of a spherical size-effect body introduced in this section is not a particular case of the model introduced in [3]. It is because we consider here a different thermodynamic system: this one for which the only admissible thermodynamic configurations are these corresponding to homothetic deformations, while in [3] the admissible thermodynamic configurations correspond to general homogeneous deformations. Nevertheless, the notions and the approach presented in [3] are applicable to this simpler case.

3. Liquid-like response of a spherical size-effect solid body

The definition of liquid-like response introduced in [3], Sec. 4 (Eqs. (4.3) and (4.4)) takes, in the case of a spherical size-effect body $\mathcal{B}_0$ of the radius R_0

considered in Sec. 2, the following form:

$$(3.1) \qquad \Psi(R_0; \lambda, \theta) = \Phi_\theta(R_0 \lambda), \qquad \lambda > 0, \qquad \theta \in I$$

where

$$(3.2) \qquad \begin{aligned} \Phi_\theta(R) &= a(\theta)V(R) + b(\theta)F(R) + c(\theta)M(R) + d(\theta), \\ V(R) &= (4/3)\pi R^3, \qquad F(R) = 4\pi R^2, \quad M(R) = 4\pi R. \end{aligned}$$

The generalized Cauchy stress function $t(R_0; \lambda, \theta)$ of Eq. (2.2) takes then the form:

$$(3.3) \qquad t(R_0; \lambda, \theta) = T_\theta(R_0 \lambda),$$

where

$$(3.4) \qquad T_\theta(R) = 3\left[a(\theta) + 2b(\theta)R^{-1} + c(\theta)R^{-2}\right].$$

The isothermal compressibility $K_\theta(R_0; \lambda)$ defined by Eq. (2.8) can be written, according to Eqs. (2.9), (3.3), and (3.4), in the form:

$$(3.5) \qquad K_\theta(R_0; \lambda) = K_\theta(R_0 \lambda),$$

where

$$(3.6) \qquad K_\theta(R) = \frac{R}{3}\frac{dT_\theta(R)}{dR} = -2\left[b(\theta)R^{-1} + c(\theta)R^{-2}\right].$$

The heat capacity $K_\lambda(R_0; \theta)$ (Eq. (2.14)) takes the form:

$$(3.7) \qquad \begin{aligned} K_\lambda(R_0; \theta) &= -\theta\frac{d^2}{d\theta^2}C_{R_0\lambda}(\theta), \\ C_R(\theta) &= \Phi_\theta(R). \end{aligned}$$

It follows from Eqs. (2.3), (3.3), and (3.4) that the radius $R_0(\theta)$ of a natural spatial configuration $\mathcal{B}_0(\theta)$ of the spherical size-effect body is defined by the following equation:

$$(3.8) \qquad a(\theta)R^2 + 2b(\theta)R + c(\theta) = 0, \quad R > 0$$

that has a solution $R = R_0(\theta)$ iff

$$(3.9) \qquad \forall \theta \in I, \qquad B(\theta) = b(\theta)^2 - a(\theta)c(\theta) \geq 0.$$

If the condition (3.9) is fulfilled, then the generalized Cauchy stress function $t_\theta(\lambda)$ of Eq. (2.4) exists and, according to Eqs. (3.3) and (3.4), takes the form:

$$(3.10) \qquad t_\theta(\lambda) = T(R_0(\theta)\lambda) = 3\left[a(\theta) + 2b(\theta)h_0(\theta)\lambda^{-1} + c(\theta)k_0(\theta)\lambda^{-2}\right]$$

where $h_0(\theta)$ and $k_0(\theta)$ denote the mean and Gaussian curvatures of the boundary surface $\partial \mathcal{B}_0(\theta)$ of the natural spatial configuration $\mathcal{B}_0(\theta)$:

$$(3.11) \qquad h_0(\theta) = R_0(\theta)^{-1}, \quad k_0(\theta) = R_0(\theta)^{-2}.$$

The postulate of compressibility (2.5), applied to the generalized Cauchy stress function $t_\theta(\lambda)$ defined by Eqs. (3.9) – (3.11), leads to the following condition (cf. [3], Eq. (4.29)):

$$(3.12) \qquad \forall \theta \in I, \qquad a(\theta) \geq 0, \qquad c(\theta) \leq 0.$$

Consequently, the radius $R_0(\theta)$ is uniquely defined at each temperature $\theta \in I$ and given by

$$R_0(\theta) = \frac{1}{a(\theta)}\left[-b(\theta) + B(\theta)^{1/2}\right] \quad \text{if} \quad a(\theta) > 0, \ b(\theta) \leq 0,$$

$$(3.13) \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad c(\theta) < 0,$$

$$R_0(\theta) = -\frac{2b(\theta)}{a(\theta)} \quad \text{if} \quad a(\theta) > 0, \ b(\theta) < 0, \ c(\theta) = 0,$$

or

$$R_0(\theta) = \frac{1}{a(\theta)}\left[-b(\theta) + B(\theta)^{1/2}\right] \quad \text{if} \quad a(\theta) > 0, \ b(\theta) > 0,$$

$$(3.14) \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad c(\theta) < 0,$$

$$R_0(\theta) = -\frac{c(\theta)}{2b(\theta)} \quad \text{if} \quad a(\theta) = 0, \ b(\theta) > 0, \ c(\theta) < 0.$$

It follows from Eqs. (2.16), (2.17), (3.5), (3.6) and (3.12) – (3.14) that the spherical size-effect solid body is, at each temperature $\theta \in I$ and for each reference configuration $\mathcal{B}_0$ of the radius R_0, *mechanically stable* iff

$$(3.15) \qquad \forall \theta \in I, \quad a(\theta) > 0, \quad b(\theta) \leq 0, \quad b(\theta)^2 + c(\theta)^2 \neq 0$$

or *mechanically stable of lower order* iff

$$(3.16) \qquad \forall \theta \in I, \quad a(\theta) \geq 0, \quad b(\theta) > 0, \quad c(\theta) < 0.$$

The radius $R(\theta)$ of the mechanically stable of lower order spatial configuration $\mathcal{B}_{cr}(\theta)$ is given by:

$$(3.17) \qquad R(\theta) = -\frac{c(\theta)}{b(\theta)}, \quad \theta \in I.$$

It follows from Eqs. (3.4), (3.6) and (3.14) that, for the *critical spatial configuration* $\mathcal{B}_{\mathrm{cr}}(\theta)$ of the radius $R(\theta)$, the condition (2.19) of existence of a critical point of a phase transition, is not fulfilled within the range I of temperature. Since the unstressed natural spatial configurations $\mathcal{B}_0(\theta)$, $\theta \in I$, are preferred reference configurations of the spherical size-effect solid body, the *critical deformations* $\lambda_{\mathrm{cr}}(\theta)$ of Eq. (2.17) will be referred to these reference configurations:

$$\lambda_{\mathrm{cr}}(\theta) = \frac{R(\theta)}{R_0(\theta)} = \frac{e(\theta)}{[1 + e(\theta)]^{1/2} - 1} > 1 \quad \text{if} \quad a(\theta) > 0,$$

(3.18)

$$e(\theta) = -\frac{a(\theta)b(\theta)}{c(\theta)} > 0,$$

or

(3.19)
$$\lambda_{\mathrm{cr}}(\theta) = \frac{R(\theta)}{R_0(\theta)} = 2 \quad \text{if} \quad a(\theta) = 0.$$

The corresponding *critical generalized Cauchy stress* $t_{\mathrm{cr}}(\theta)$ is independent of the choice of a reference configuration and given by (see Eqs. (3.4), (3.10), and (3.17)):

(3.20)
$$t_{\mathrm{cr}}(\theta) = T_\theta(R(\theta)) = -\frac{B(\theta)}{c(\theta)} > 0,$$

where the conditions (3.9) and (3.16) were taken into account. It follows from Eq. (3.20) that $t_{\mathrm{cr}}(\theta)$ is the absolute maximum of the generalized stress function $T_\theta(R)$ defined by Eqs. (3.4) and (3.16). Thus, $t_{\mathrm{cr}}(\theta)$ defines a finite *upper elastic limit* of the mechanically stable of lower order elastic spherical size-effect solid body with the liquid-like response. The isothermal bulk modulus $K(\theta)$ of this size-effect body (Eq. (2.13)) has, according to Eqs. (3.5), (3.6) and (3.11), the following representation:

(3.21) $$K(\theta) = K_\theta(R_0(\theta)) = -2\left[b(\theta)h_0(\theta) + c(\theta)k_0(\theta)\right] > 0,$$

where $R_0(\theta)$ of Eq. (3.11) is given by Eq. (3.14). Note that if the considered spherical size-effect body is mechanically stable, then the isothermal bulk modulus is given also by Eq. (3.21) but with the radius of $R_0(\theta)$ Eq. (3.11) defined by Eq. (3.13).

It follows from Eqs. (3.2), (3.4), and (3.6) that the influence of the body boundary surface causes the dependence on the body size of the isothermal generalized Cauchy stress $T_\theta(R)$ as well as the isothermal compressibility $K_\theta(R)$. Thereby, it is a phenomenological model of the influence of surface atoms on thermomechanical properties of spherical nanomaterial clusters (see [3], Secs. 1 and 4). If the elastic spherical size-effect solid body is mechanically stable, then

its asymptotic uniform expansion defines the finite isothermal generalized Cauchy stress $t(\theta)$:

(3.22) $$t(\theta) = \lim_{R\to\infty} T_\theta(R) = 3a(\theta) > 0$$

being a finite *asymptotic upper elastic limit* of this size-effect body (cf. [3], Eqs. (4.28) and (4.29)). Denoting by $p_\theta(R) = -T_\theta(R)$ the uniform pressure compensating the generalized Cauchy stress $T_\theta(R)$, we obtain the following properties of the asymptotic uniform compression:

(3.23) $$\lim_{R\to 0} p_\theta(R) = \infty, \qquad \lim_{R\to 0} K_\theta(R) = \infty.$$

It means that, within the range I of temperature, the elastic spherical size-efect solid body of the very small size can carry a very high uniform pressure (compression). It agrees with the observation that macroscopically small nanocrystaline clusters can carry very high compressions ([3], Sec. 1). Moreover, it folbws from Eqs. (3.20), (3.22), and (3.23) that the considered size-effect solid body has unsymmetrical elastic properties under the conditions of uniform tension and compression. It agrees with elastic properties of crystalline materials.

4. Mechanically stable mesoscale clusters

Let us consider the mechanically stable, isotropic and elastic spherical size-effect solid body with the liquid-like response under the conditions of uniform pressure. It follows from Eqs. (2.4), (2.9), (2.16), (3.10) and (3.15) that the isothermal generalized stress function t_θ monotonically increases and has, according to Eqs. (3.22) and (3.23), the following asymptotic properties:

(4.1) $$\lim_{\lambda\to 0} t_\theta(\lambda) = -\infty, \qquad t_\theta(1) = 0,$$

$$t(\theta) = \lim_{\lambda\to\infty} t_\theta(\lambda) = 3a(\theta) > 0.$$

Moreover, we can identify the constant $a(\theta) > 0$ of the formula (3.2) with the free energy density $\varepsilon(\theta)$ needed to change the volume unit and conditioned by bulk interatomic interactions. Thus, taking into account the identification of constants $b(\theta)$ and $c(\theta)$ ([3], Sec. 4, remarks following Eqs. (4.10) and (4.11)), we obtain for the considered mechanically stable size-effect solid body the conditions see Eq. (3.15)):

(4.2) $$a(\theta) = \varepsilon(\theta) > 0, \quad b(\theta) = -\gamma(\theta) < 0, \quad c(\theta) = -\omega(\theta) \le 0,$$

where $\gamma(\theta)$ and $\omega(\theta)/2\pi$ are the free energy densities necessary to change the boundary surface field unit and to change the diameter $M(\mathcal{B})/2\pi = 2R$ unit of

the spherical body, respectively. The isothermal generalized stress function t_θ of Eq. (3.10) can be written then in the following form:

(4.3) $$t_\theta(\lambda) = T_\theta(R_0(\theta)\lambda),$$

where

(4.4)
$$T_\theta(R) = t(\theta) - 3\left[2\gamma(\theta)R^{-1} + \omega(\theta R^{-2}\right],$$

$$t(\theta) = 3\varepsilon(\theta) > 0,$$

and the isothermal bulk modulus $K(\theta)$ of Eq. (3.21) takes the form:

(4.5) $$K(\theta) = 2\left[\gamma(\theta)h_0(\theta) + \omega(\theta)k_0(\theta)\right] > 0,$$

where $h_0(\theta)$ and $k_0(\theta)$ denote the mean and Gaussian curvatures (given by Eq. (3.11)) of the boundary surface of the natural spatial configuration $\mathcal{B}_0(\theta)$ of radius $R_0(\theta)$. Thus, in accordance with the observed properties of nanocrystaline macroscopically small clusters ([3], Sec. 1), the bulk modulus increases if the body $\mathcal{B}_0(\theta)$ size decreases. Note that, according to Eqs. (3.13) and (4.1), the radius $R_0(\theta)$ decreases if the upper elastic limit t_θ increases.

Let us observe that the term $\omega(\theta)R^{-2}$ appearing in Eq. (4.4) can be interpreted as the one corresponding to the long-range interactions between the surface atoms and bulk atoms located in a boundary layer (see [3], remarks following Eq. (4.11)). Thereby, in the case

(4.6) $$\varepsilon(\theta) > 0, \qquad \gamma(\theta) > 0, \qquad \omega(\theta) = 0$$

these interactions are neglected. Since in this case Eq. (4.4) takes the form

(4.7) $$T_\theta(R) = 3\left[\varepsilon(\theta) - 2\gamma(\theta)R^{-1}\right],$$

the isothermal generalized Cauchy stress depends on interatomic bulk interactions ($\varepsilon(\theta) > 0$) as well as on interactions of the surface atoms located on the body boundary ($\gamma(\theta) > 0$). These interatomic interactions influence the radius $R_0(\theta)$ of a natural spatial configuration in the following manner (cf. Eqs. (3.13) and (4.7)):

(4.8) $$R_0(\theta) = \frac{2\gamma(\theta)}{\varepsilon(\theta)}.$$

Consequently, according to Eqs. (4.5), (4.6), and (4.8), the isothermal bulk modulus reduces to:

(4.9) $$K(\theta) = 2\gamma(\theta)R_0(\theta)^{-1} = \varepsilon(\theta),$$

and it follows from Eqs. (4.3), (4.7), and (4.9) that the isothermal generalized Cauchy stress $t_\theta(\lambda)$ (Eq. (3.10)), referred to the natural configuration of the radius $R_0(\theta)$ of Eq. (4.8), can be written in the form:

$$(4.10) \qquad t_\theta(\lambda) = t(\theta)(1 - \lambda^{-1}), \qquad \lambda > 0,$$

where the asymptotic upper elastic limit $t(\theta)$ is related to the bulk modulus $K(\theta)$ according to the following formula:

$$(4.11) \qquad t(\theta) = 3K(\theta).$$

The graph of this function t_θ is an equilateral hyperbola. Note that Eq. (4.9) means that the isothermal bulk modulus depends on interatomic bulk interactions only. It is a point of similarity between this bulk modulus and the macroscopic bulk modulus (see Sec. 1). On the other hand, the bulk modulus $K(\theta)$ of Eq. (4.9) is referred, contrary to the macroscopic bulk modulus, to the preferred spatial configuration of the body that is conditioned by the influence of surface atoms (Eq. (4.8)). It suggests that the spherical size-effect solid body defined by the conditions (4.2) and (4.6) can be considered as the one whose size lies in the upper range of the mesoscale observation levels (see [3], Sec. 1).

If

$$(4.12) \qquad \omega(\theta) > 0$$

then the radius $R_0(\theta)$, $\theta \in I$, of a natural spatial configuration (Eqs. (3.13) and (4.2)) becomes greater than that of the case (4.6) (Eq. (4.8)). The isothermal bulk modulus $K(\theta)$ reveals explicitly the size effect in a manner observed for macroscopically small nanomaterial clusters (see remarks following Eq. (4.5)) and the dependence of this modulus on interatomic bulk interactions is still preserved. Thus, the size of such natural configuration should lie also in the upper range of the mesoscale observation levels.

5. Fullerene-like response

Let us consider the mechanically stable of lower order, isotropic and elastic spherical size-effect solid body with the liquid-like response defined by Eqs. (3.1), (3.2) and by the conditions (3.16) written in the form (see [3], Eqs. (4.11), (4.19)):

$$(5.1) \qquad a(\theta) = \varepsilon(\theta) \geq o, \quad b(\theta) = \gamma(\theta) > 0, \quad c(\theta) = -\omega(\theta) < 0.$$

The radius $R_0(\theta)$ of a natural configuration is defined by Eq. (3.14), the radius $R(\theta)$ of a critical spatial configuration can be written in the form (see Eq. (3.7)):

$$(5.2) \qquad R(\theta) = \frac{\omega(\theta)}{\gamma(\theta)},$$

and the isothermal generalized Cauchy stress $T_\theta(R)$ of Eq. (3.4) can be rewritten as:

$$T_\theta(R) = t(\theta) + 3[2\gamma(\theta)R^{-1} - \omega(\theta)R^{-2}],$$

(5.3)

$$t(\theta) = 3\varepsilon(\theta) \geq 0.$$

The isothermal compressibility of Eq. (3.6) takes then the form:

$$K_\theta(R) = 2[-\gamma(\theta)R^{-1} + \omega(\theta)R^{-2}],$$

(5.4)

$$K_\theta(R(\theta)) = 0.$$

If $\lambda_{cr}(\theta)$ is the critical deformation of the spatial natural configuration $\mathcal{B}_0(\theta)$ defined by Eqs. (3.18) and (3.19), and $\delta_{cr}(\theta)$ denotes the critical relative variation of the radius $R_0(\theta)$ of this configuration

(5.5)
$$\delta_{cr}(\theta) = \frac{R(\theta) - R_0(\theta)}{R_0(\theta)} = \lambda_{cr}(\theta) - 1 > 0,$$

then the isothermal bulk modulus is given by:

(5.6)
$$K(\theta) = K_\theta(R_0(\theta)) = 2\lambda_{cr}(\theta)\delta_{cr}(\theta)\frac{\gamma(\theta)}{R(\theta)} > 0.$$

The isothermal generalized Cauchy stress function t_θ, describing the elastic response of the spherical size-effect solid body with respect to its natural configuration and defined by Eqs. (3.10), and (5.1) – (5.3), takes the form:

$$t_\theta(\lambda) = T_\theta(R_0(\theta)\lambda) = t(\theta) + s_\theta(\mu)|_{\mu=\lambda/\lambda_{cr}(\theta)},$$

(5.7)

$$s(\mu) = s_{cr}(\theta)(2\mu^{-1} - \mu^{-2}),$$

where it was denoted:

(5.8)
$$s_{cr}(\theta) = \frac{3\gamma(\theta)}{R(\theta)} = \frac{3\gamma(\theta)^2}{\omega(\theta)},$$

and takes its maximum value $t_{cr}(\theta)$ for $\lambda = \lambda_{cr}(\theta)$, that is in the critical spatial configuration $\mathcal{B}_{cr}(\theta)$ of the radius $R(\theta)$:

(5.9)
$$t_{cr}(\theta) = T_\theta(R(\theta)) = t(\theta) + s_{cr}(\theta).$$

It follows from Eqs. (5.1) – (5.9) that the case $\varepsilon(\theta) > 0$ means the existence of interatomic bulk interactions that influence the critical point $(\lambda_{cr}(\theta), t_{cr}(\theta))$.

However, the occurrence of size effect (Eqs. (5.6) and (5.8)) is independent of the existence of these interactions. This is why we restrict ourselves to the case

(5.10) $$\varepsilon(\theta) = 0,$$

at which

$$\lambda_{\mathrm{cr}}(\theta) = 2, \quad \text{i.e.} \quad \delta_{\mathrm{cr}}(\theta) = 1, \quad R(\theta) = 2R_0(\theta),$$

(5.11)

$$t(\theta) = 0, \quad \text{i.e.} \quad t_{\mathrm{cr}}(\theta) = s_{\mathrm{cr}}(\theta).$$

The isothermal bulk modulus $K(\theta)$ and the isothermal critical generalized Cauchy stress $t_{\mathrm{cr}}(\theta)$ reveal then the size effect of the form:

(5.12) $$K(\theta)R_0(\theta) = 2\gamma(\theta),$$

and
(5.13) $$t_{\mathrm{cr}}(\theta)R(\theta) = 3\gamma(\theta).$$

Note that the relation (5.12) is equivalent to the following representation of the bulk modulus:

(5.14) $$K(\theta) = \frac{4\gamma(\theta)^2}{\omega(\theta)},$$

and, according to Eqs. (5.11) and (5.13), we obtain:

(5.15) $$t_{\mathrm{cr}}(\theta) = \frac{3}{4}K(\theta).$$

It follows from Eqs. (5.14) and (5.15) that the size effect appearing in Eqs. (5.12) and (5.13) depends only on interactions between surface atoms ($\gamma(\theta) > 0$) and on their long-range interactions with bulk atoms located in a boundary layer ($\omega(\theta) > 0$) (see [3], Sec. 4). Thereby, this size effect has a physical meaning that corresponds to the properties of the very nanostructures (see [3], Sec. 1). Consequently, we can expect that the case (5.1), (5.10) concerns nanomaterial spherical clusters smaller than mesoscale clusters discussed in Sec. 4.

The isothermal generalized stress function t_θ (Eq. (5.7)) takes in the case (5.10) the following form:

(5.16) $$t_\theta(\lambda) = 4t_{\mathrm{cr}}(\theta)(\lambda^{-1} - \lambda^{-2}), \quad \lambda > 0.$$

The function t_θ of Eq. (5.16) monotonically increases (taking positive as well as negative values) in the interval $0 < \lambda < 2$ and for $\lambda = \lambda_{\mathrm{cr}}(\theta) = 2$ (being a critical deformation for which the isothermal compressibility vanishes) reaches the upper elastic limit $t_{\mathrm{cr}}(\theta)$ (see Sec. 3). For $\lambda > 2$ the stress function is positive

and decreases to zero if the uniform extension λ tends to infinity. It means that the elastic resistance to uniform tension decreases for $\lambda > \lambda_{cr}$ (and vanishes at infinity). We will call this process the (nonlinear) *elastic flow effect*. Note that the similar relation between a uniform pressure (compression or tension) and the deformation of Eq. (1.1) was found for usual crystals by means of numerical computations based on the analysis of bound energy changes in cubic crystal lattices (direct, body-centered, and face-centered) [9]. In these computations the central binary interactions with Morse-type potential (or with an arbitrary type potential but for the case of nearest neighbour interactions only) and the natural reference configuration temperature 0 K, were assumed. Particularly, the elastic flow effect has been computed. This effect is, in the framework of the considered liquid-like response of the spherical elastic size-effect solid body, a consequence of the mechanical stability of lower order.

The liquid-like response manifests itself in the dependence of the total free energy as well as the generalized Cauchy stress on the actual spatial configurations only (Eqs. (3.2) and (5.9)). Therefore, the considered size-effect solid body reacts in a manner similar to a fluid body regarded as a material body having no preferred configuration (see [3], Secs. 2 and 4). On the other hand, the condition (5.1), defining the mechanical stability of lower order, means the existence of preferred configurations (the natural spatial configurations) and the existence of critical spatial configurations (being configurations of the mechanical stability of lower order). Since the critical spatial configurations are not associated with the existence of a critical point of a phase transition (see remarks following Eq. (3.17)) and reveal the elastic flow effect, they can be considered to exhibit the existence of solid state with the liquid-like elastic behaviour within a finite range of temperature. It can be interpreted as an elastical analogue of properties of small spherical fullerene C_{60} clusters that exhibit a coexistence of solid and liquid states within a finite range of temperature and for some particular sizes of these clusters only (see [3], Sec. 1). If so, the uniquely defined diameter $2R(\theta)$ of a critical spatial configuration (Eq. (5.2)) can be considered as a counterpart, at the temperature $\theta \in I$, of the particular size of a small fullerene C_{60} cluster. The mechanically stable of lower order, isotropic and elastic spherical size-effect solid body with the liquid-like response will be called, coming into line with the above analogy, a spherical size-effect body with the *fullerene-like response*.

Note that if the fullerene-like response is interpreted as an elastical analogue of the coexistence of solid and liquid states within a finite range of temperature, then it seems reasonable to admit that a *viscosity effect* (cf. Eqs. (2.24) – (2.26)) occurs in the critical spatial configurations. Unfortunately, viscosity properties of small nanomaterial clusters are not satisfactorily recognized.

6. Conclusions and remarks

The analysis of a homogeneous isotropic and elastic spherical size-effect solid body (Sec. 2) with the liquid-like response (Secs. 3-5) subjected, within a certain range of temperature, to a uniform pressure, shows that if the body is mechanically stable, then it can be considered to be a model of nanocrystalline (e.g. metallic) clusters with a size which lies in the upper range of the mesoscale observation levels. It has been shown that a part of the total surface energy, representing the long-range interactions between the surface atoms and bulk atoms located in a boundary layer, is then responsible for the explicit occurrence of the size effect (Sec. 4). If the body is mechanically stable of lower order, then it reveals the fullerene-like response that can be interpreted as an elastic analogue of the properties of small C_{60} clusters of a size corresponding to the very nanometer observation level scale (Sec. 5). In both cases a finite upper elastic limit appears. If the spherical size-effect body is mechanically stable, then the upper elastic limit is an asymptotic elastic property. If the spherical size-effect body is mechanically stable of lower order, then the upper elastic limit corresponds to a critical spatial configuration of the body and reveals a size effect (Eq. (5.13)). Moreover, in both cases, the body can carry a high pressure (compression) with very small elastic deformations (Sec. 3). This asymmetry of elastic properties under a uniform tension and compression is a characteristic feature of crystalline solid clusters, of usual as well as nanostructured materials. In fact, the domain of physically admissible elastic homogeneous deformations of a nanomaterial cluster is bounded by a hypersurface defined by the elastic limit. The hypersurface is dependent on the body uniform temperature (cf. [10] and [11]) and can depend on the body itself (cf. Eqs. (2.17) and (2.18)).

The isothermal bulk modulus $K(\theta)$ of the spherical size-effect solid body with the liquid-like response increases if the radius $R_0(\theta)$ of its unstressed spatial configuration $\mathcal{B}_0(\theta)$ decreases (Eq. (3.21)). For the body being mechanically stable of lower order, the bulk modulus has the representation given by Eq. (5.6) from which it follows that if the critical deformation $\lambda_{\mathrm{cr}}(\theta)$ of $\mathcal{B}_0(\theta)$ (Eqs. (3.18) and (3.19)) is constant, then this bulk modulus is inversely proportional to the radius $R(\theta)$ of the critical spatial configuration $\mathcal{B}_{\mathrm{cr}}(\theta)$. Particularly, if the bulk interatomic interactions can be neglected (cf. [3], Secs. 1 and 4), then $\lambda_{\mathrm{cr}}(\theta) = 2$ for each $\theta \in I$ and this size effect reduces to (Sec. 5):

$$(6.1) \qquad\qquad K(\theta)R_0(\theta) = 2\gamma(\theta)$$

where
$$(6.2) \qquad\qquad R(\theta) = 2R_0(\theta) = \omega(\theta)/\gamma(\theta).$$

It follows from Eqs. (6.1) and (6.2) that the isothermal bulk modulus depends only on the interactions of the boundary surface atoms ($\gamma(\theta) > 0$) and on the

long-range interactions between these atoms and the bulk atoms located in a boundary layer ($\omega(\theta) > 0$ (Sec. 5). Note that if the body is mechanically stable and the long-range interactions between the surface atoms and bulk atoms of a boundary layer are neglected ($\omega(\theta) = 0$), then the formula (6.1) is also valid but in this case the radius $R_0(\theta)$ is given by

$$(6.3) \qquad R_0(\theta) = 2\gamma(\theta)/\varepsilon(\theta),$$

where $\varepsilon(\theta) > 0$ is the volumetric free energy density conditioned by the interatomic bulk interactions (Sec. 4). Let us denote by $\alpha(\theta)$ the coefficient of linear thermal expansion of an unstressed configuration $\mathcal{B}_0(\theta)$ of the spherical size-effect solid body, and by $\beta(\theta)$ – the temperature bulk compressibility coefficient of this configuration:

$$(6.4) \qquad \alpha(\theta) = \frac{1}{R_0(\theta)}\frac{dR_0(\theta)}{d\theta} = \frac{1}{3V_0(\theta)}\frac{dV_0(\theta)}{d\theta},$$

$$\beta(\theta) = \frac{1}{K(\theta)}\frac{dK(\theta)}{d\theta}, \quad V_0(\theta) = (4/3)\pi R_0(\theta)^3.$$

Differentiating the relation (6.1) with respect to the parameter θ, and taking into account that if the temperature increases from 0 K to $\theta \in I$, then the surface tension $\gamma(\theta)$ monotonically decreases [1] and $\alpha(\theta) > 0$ because almost all material bodies expand under heating, we obtain that the following conditions would be fulfilled:

$$(6.5) \qquad \alpha(\theta) > 0, \quad d\gamma(\theta)/d\theta < 0, \quad \beta(\theta) < 0,$$

$$|\beta(\theta)| > \alpha(\theta), \quad \theta \in I,$$

and

$$(6.6) \qquad d\varepsilon(\theta)/d\theta < 0 \quad \text{if} \quad \omega(\theta) = 0,$$

$$d\omega(\theta)/d\theta < 0 \quad \text{if} \quad \varepsilon(\theta) = 0.$$

It is known that the macroscopic bulk moduli of usual crystals decrease if the temperature increases [1]. We see that the mesoscale as well as the nanoscale bulk modulus has the same property. It agrees with the observation that the elevated temperatures have the effect of degrading the mechanical properties of nanomaterials [11]. The case of bulk modulus suggests that the phenomena of thermal expansion and decreasing of free energy densities (superficial as well as volumetric) have a contribution to this effect.

Note that the problem when a cluster can be treated as the macroscopic one, has as yet no accurate general solution. For example, a cluster of an inert gas can be considered as a macroscopic particle if it consists of more than 10^4 atoms under the condition that the cluster temperature is not too low [12]. This example, the properties of small fullerene clusters ([3], Sec. 1), and the effect of degrading mechanical properties of nanomaterials at elevated temperatures, lead to a conclusion that the size effect in macroscopically small nanomaterial clusters should be related to thermomechanical properties of these clusters rather than to their purely mechanical properties only.

The classical thermodynamic is applied in this paper to macroscopically small systems that can contain even less than 200 atoms [13]. Consequently, such systems may not be satisfactorily described, in a manner consistent with the classical thermodynamics, by means of the classical statistical physics. However, for example, a finite system of mutually interacting identical particles, the dynamical behaviour of which is random, can admit the thermodynamical interpretation of the Markovian-type evolution of the system [14]. Namely, the existence of thermodynamically permitted Markov processes can be shown that are consistent with the assumption of thermal character of the interaction of the system with the environment, with the first and second laws of thermodynamics, with the postulate of existence of the equilibrium state, and with the relaxation postulate (stating that the process relax, independently of the choice of the initial condition, towards the state of thermodynamical equilibrium). Moreover, if the environment of the system is a thermostat, then we can generalize, replacing the uniform temperature of the system with the (uniform) temperature of the thermostat, the equilibrium definition of the free energy to the nonequilibrium situation [14]. This example shows that the classical thermodynamics can be also consistent with the randomness of microstate dynamics of macroscopically small systems containing a small number of atoms.

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