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

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ONE OF UNUSUAL FEATURES of macroscopically small three-dimensional nanocrystalline clusters is the dependence of their properties on the grain size as well as on the cluster size. Consequently, such clusters are ensembles of atoms or particles where the size effect becomes apparent. A phenomenological model of the description of thermomechanical properties of macroscopically small nanomaterial clusters is proposed. The model is based on the concept of size-effect bodies, the thermomechanical properties, dynamics and thermodynamics of which are referred to one whole body, not an infinite system of subbodies. It is pointed out that the proposed model of the size effect leads to an analogy with the theory of capillarity. A class of size-effect bodies generalizing this analogy is introduced and discussed. Particularly, it is stated that the heat capacity reveals not only the size effect but, contrary to the elastic properties, should depend also on the topological invariant of the compact and connected cluster.

1. Introduction

THE MACROSCOPIC PROPERTIES and effects of usual materials (e.g. moduli of elasticity and their temperature-sensitivity) are essentially the same on the micrometer (1 $\mu m = 10^4$ Å $= 10^{-3}$ mm) and on the millimeter observation level scale. So, from the macroscopic point of view, both observation level scales are physically equivalent [1]. It can be continued for various mesoscale observation levels, say down to the order 100 nm (1 nm $= 10$ Å $= 10^{-6}$ mm); the atomic-size observation level scale is taken equal to 1Å – diameter of the hydrogen atom in the ground state. Grains of usual polycrystalline materials have diameters of the order of 1 μm to 1 mm, and thus they reach the macroscopic observation level scale. It is known that in the case of usual well-annealed pure metals, the mean distance between dislocations is of the order of 1 μm [2]. Thus, the crystal with many dislocations can be considered, on a mesoscale observation level that lies in the range of 10 – 100 nm, as a part of an ideal crystal [2]. If the macroscopic properties of a crystalline solid body with many dislocations are considered, then a continuous limit approximation can be defined by means of the condition that,

at each point of the body, a characteristic mesoscale length, say of the order of 10 nm, can be approximately replaced with the local infinitesimal length [3, 4]. Consequently, according to such phenomenological approximation, the crystal with many dislocations can be identified with a locally homogeneous crystalline solid body. Thereby, the macroscopic physical equivalence of various observation level scales enables to introduce the local approximation of macroscopic material properties of crystalline bodies (homogeneous as well as with defects) that is independent of the body shape and size. For example, in this approximation, rotational symmetries of a crystalline structure are preserved (at least locally) but its translational symmetries are lost [3].

However, there exist nanocrystalline solids, both metallic and ceramic, that are built up by the same atoms as their commonly occurring counterparts, but with the grain size of the order of $1 - 10$ nm [5, 6]. For example, usual pure metals are used to produce almost spherical clusters of nanostructured metals, and size of these clusters varies from 1 nm to 100 nm according to the production process and the initial metal that has been used [5]. It is observed that if the nanostructure size becomes smaller than the critical length associated with a certain physical property, then this property changes [5, 6]. For example, it is known that nanocrystalline grains as well as clusters do not contain dislocations or they are not numerous and unstable [5]. Consequently, nanocrystalline metals reveal higher strength than their usual counterparts, and the strength increases if the size of the nanocrystalline ensemble of atoms decreases [5, 6]. Most of the unique features of three-dimensional nanostructures arise, owing to their macroscopically small size, from the very high ratio of the number of surface atoms to the total number of atoms in the cluster [7]. The fullerene C_{60} particles with all carbon atoms located in vertices of a truncated icosahedron [8, 9] provides an extreme example of such atomic structures. These particles are approximately spherical with the diameter slightly greater than 1 nm [9]. C_{60} particles crystallize, at room temperature, in solid clusters with close-packed face-centered-cubic structure [8]. The molecular dynamics simulations indicate that for some particular sizes of small C_{60} clusters these would exhibit a coexistence of solid and liquid states within a finite range of temperature. It concerns also small clusters that consist of nanometer-sized small particles built up by some other chemical elements [8]. This makes small clusters different from the bulk systems whose solid and liquid phases coexist only at a single point of temperature, the melting point [8]. Note that generally, in the nanometer regime, we have to deal with chemical bonds and no longer with bulk properties. Forces are extremely small - down to 10^{-12} N, yet strains and pressures can be very high, e.g. pressures up to 10^{12} Pa [1]. For example, computations have shown that C_{60} crystals would reveal elasticity in compression, and compressed to 70 percent of the initial volume would be harder than diamond [9].

It is observed that the production process of nanocrystalline materials can lead to clusters of a fractal structure built up by particles of the diameter 35Å [10]. In this case, the total mass m of a three-dimensional cluster of the size L_0 depends on this size according to the following formula [10]:

$$(1.1) \qquad m = m_p(L_0/l_p)^D,$$

where $D < 3$ is the mass fractal dimension, m_p is the mass of particles constituting the cluster, and l_p is the size of these particles. The mass density ρ_0 of the cluster depends also on L_0 according to a power law of the fractal type:

$$(1.2) \qquad \rho_0 = \rho_p(L_0/l_p)^{D-3},$$

where ρ_p is the mass density of particles constituting the cluster. In the case of close-packed particles $D = 3$. The fractal materials differ from the general case of nanomaterials because fractals are objects that exhibit similar structures over the range of length-scales for which one can define a noninteger dimension. Consequently, if l is the size of a part of the three-dimensional fractal cluster, then it follows from the self-similarity that the elastic modulus $E(l)$ of this part should reveal the following property [10]:

$$(1.3) \qquad E(\lambda l) = \lambda^{-d}E(l),$$

if l and λl belong to the self-similarity interval. The exponent d depends on the fractal structure of the cluster as well as on the forces acting between elements of this structure.

If macroscopically small clusters are considered, then their deformation and temperature can be treated as these approximated to uniform state variables of the cluster. It means, from the microscopic point of view, that the collective modes are considered [11]. Thus, owing to this phenomenological approximation, we are in the framework of classical thermodynamics which refers to one whole system, not an infinite family of subsystems [12]. Consequently, the dynamics of a macroscopically small cluster should have also a global character referable to one whole body only. It suggests us to formulate a description of macroscopically small nanomaterial clusters in the framework of the phenomenological theory of size effect that has been originally formulated as a theory which is not associated with an observation level scale [13, 14, 15]. The paper extends the contents of this theory, especially from the point of view of nanostructures revealing the existence of relations between the shape and size of a cluster and the observed properties of the condensed material of this cluster.

2. Size-effect body

Continuum mechanics is a phenomenological theory dealing with the macroscopic properties of material deformable bodies and based on an assumption that

these properties have essentially a local character independent of the change of the observation level scale (see Sec. 1). It concerns the notion of material (formalized in the framework of the theory of simple materials [16]) as well as the dynamics (the reduction of dynamics to local balance laws [16]). The same approach is applied to the description of thermodynamic processes [16] and to the description of the material structure evolution (e.g. the plasticity theory [17]). Unfortunately, in the case of nanomaterials the concept of localization can not be applied to the description of thermomechanical properties of these materials because of their sensibility to the size of nanostructures (Sec. 1). Moreover, the concept of local equilibrium states (dynamical or thermodynamical) of a body neglects the size and shape effects occurring in the case of macroscopically small bodies (cf. Sec. 1). However, the macroscopically small size of nanostructures offers a possibility for treating nanomaterial clusters, in the sense of phenomenological approximation used here (Sec. 1), as macroscopically small "*affinely rigid bodies*" with dynamics being a generalization of the rigid body dynamics which is not associated with an observation level scale [11].

If the equations of dynamics of these homogeneously deformed bodies are considered as balance laws [11, 15], then they can be extended to the balance laws of *classical thermodynamics* [13] dealing with the so-called *homogeneous thermodynamic processes* [12, 16] considered as being dependent on the body size and shape [13].

Therefore, we will deal with a homogeneous nanomaterial body of immovable center of mass, homogeneously deformed and endowed with an uniform absolute temperature. Spatial configurations of such a body can be identified with the subsets $\mathcal{B}$ of the three-dimensional Euclidean vector space E^3 (the physical space in this case) that have the form $\mathcal{B} = l(\mathbf{F})(\mathcal{B}_0)$, where $\mathcal{B}_0 \subset E^3$ is a distinguished spatial configuration and $l(\mathbf{F})$ denotes the following linear mapping in E^3:

$$l(\mathbf{F})(\mathbf{X}) = \mathbf{FX}, \qquad \mathbf{F} \in GL^+(E^3), \quad \mathbf{X} \in E^3,$$

(2.1)

$$GL^+(E^3) = \{\mathbf{F} \in L(E^3) : \det \mathbf{F} > 0\}, \qquad L(E^3) = E^3 \otimes E^3.$$

This distinguished spatial configuration of the body is called its *reference configuration* and can be identified with the body itself. The spatial configurations $\mathcal{B}$ are called *deformed configurations* of $\mathcal{B}_0$. Further on, we will consider three-dimensional compact and connected bodies $\mathcal{B}_0$. The uniform state variables of the body $\mathcal{B}_0$ (Sec. 1) are defined by the finite number of parameters $\mu = (\mathbf{F}, \theta) \in GL^+(E^3) \times I$, where $I \subset R^+$ is a certain interval of absolute temperature, and constitute a *thermodynamic configuration* of the body. The mass m of the body $\mathcal{B}_0$ is the same for all its deformed spatial configurations $\mathcal{B}$, and the volumetric mass density ρ of these configurations is defined by:

$$m = \rho_0 V(\mathcal{B}_0) = \rho V(\mathcal{B}),$$

(2.2)

$$V(\mathcal{B}) = J(\mathbf{F})V(\mathcal{B}_0), \qquad J(\mathbf{F}) = \det \mathbf{F},$$

where $V(\mathcal{B})$ denotes the volume of $\mathcal{B}$. Note that if the particles constituting a cluster $\mathcal{B}_0$ are close-packed, then the mass density ρ_0 of the body $\mathcal{B}_0$ is approximated by the mass density ρ_p of these particles. Further on, we restrict the considered cluster dynamics to the case of close-packed nanomaterial clusters the total mass of which admits the approximate representation of the size effect by Eq. (2.2). It can be e.g. the case of fullerene C_{60} clusters (Sec. 1) but, according to Eqs. (1.1) and (1.2), it is not the case of fractal clusters.

Let $\Psi = \Psi(\mathcal{B}_0; \mu)$, $E = E(\mathcal{B}_0; \mu)$, and $S = S(\mathcal{B}_0, \mu)$ denote the total Helmholtz free energy, the total internal energy, and the total entropy, respectively. The dependence of these functions on the figure $\mathcal{B}_0$ represents the shape and size effects that reveal macroscopically small nanomaterial clusters. This can be presented, for instance, by the dependence of these functions on such global geometrical characteristics as: the volume of $\mathcal{B}_0$, the surface field and (or) the total mean curvature of the boundary surface $\partial\mathcal{B}_0$, and also by the dependence on topological invariants of $\mathcal{B}_0$ as well as $\partial\mathcal{B}_0$ (e.g. the Euler characteristic). Consequently, the way in which these functions depend on homogeneous deformations can be dependent on the considered geometrical characteristics of $\mathcal{B}_0$ (see Sec. 4). To simplify latter statements, we will call a body $\mathcal{B}_0$ endowed with the above defined thermodynamic functions, the *size-effect body*.

The thermodynamic functions are related by the Legendre transformation:

(2.3)
$$\Psi = E - \theta S$$

and, as the functions describing physical properties of a nanomaterial body, would by the so-called *objective scalars*, that is functions $f = f(\mathcal{B}_0; \cdot)$ of class C^k, $k \geq 2$, such that for each $(\mathbf{F}, \theta) \in GL^+(E^3) \times I$, the following condition is fulfilled:

(2.4) $$\forall \mathbf{Q} \in SO(E^3), \qquad f(\mathcal{B}_0; \mathbf{QF}, \theta) = f(\mathcal{B}_0; \mathbf{F}, \theta),$$

where $SO(E^3) \subset GL^+(E^3)$ denotes the proper orthogonal group on E^3.

Thermomechanical properties of the size-effect body $\mathcal{B}_0$ are represented, at each instant $\tau \in R^+$, by the net working $W = W(\mathcal{B}_0; \tau)$ such that for each curve $\tau \to \mu(\tau) = (\mathbf{F}(\tau), \theta(\tau))$ in the space $GL^+(E^3) \times I$ of thermodynamic configurations, the following relation holds:

(2.5) $$\forall \tau \in R^+ \ \exists \mathbf{N}(\mathcal{B}_0; \tau) \in L(E^3), \quad W(\mathcal{B}_0; \tau) = -\mathbf{N}(\mathcal{B}_0; \tau) \cdot \dot{\mathbf{F}}(\tau),$$

where $\mathbf{A} \cdot \mathbf{B} = \mathrm{tr}(\mathbf{AB}^T)$ for $\mathbf{AB} \in L(E^3)$, $\mathbf{B}^T$ denotes a transpose of $\mathbf{B}$, and $\dot{\mathbf{F}}(\tau) = d\mathbf{F}(\tau)/d\tau$. $\mathbf{N}(\mathcal{B}_0; \tau)$ is a *generalized force* representing a thermomechanical response of the size-effect body $\mathcal{B}_0$ at the instant $\tau \in R^+$. The balance

equation of the total internal energy is given by:

$$(2.6) \qquad \forall \tau \in R^+, \quad \dot{E}(\mathcal{B}_0; \mu(\tau)) = W(\mathcal{B}_0; \tau) + Q(\mathcal{B}_0; \tau),$$

where $Q(\mathcal{B}_0; \tau)$ is the heat production at the instant $\tau \in R^+$, and $\dot{E}$ denotes the time-derivative of E taken along the curve $\tau \to \mu(\tau)$ of thermodynamic configurations. Moreover, the following Planck's dissipation inequality should be fulfilled [16]:

$$(2.7) \qquad \forall \tau \in R^+, \quad \delta(\mathcal{B}_0; \tau) = \theta(\tau)\dot{S}(\mathcal{B}_0; \mu(\tau)) - Q(\mathcal{B}_0; \tau) \geq 0.$$

Let us assume that for each curve $\tau \to \mu(\tau)$ of thermodynamic configurations:

$$(2.8) \qquad \mathbf{N}(\mathcal{B}_0; \tau) = \mathbf{N}(\mathcal{B}_0; \mu(\tau), \dot{\mu}(\tau))$$

where $\dot{\mu}(\tau) = d\mu(\tau)/d\tau$, and let us denote:

$$(2.9) \qquad \begin{aligned} \hat{\mathbf{T}} &= V(\mathcal{B}_0)^{-1}\partial_{\mathbf{F}}\Psi, \qquad \mathbf{T} = J(\mathbf{F})^{-1}\hat{\mathbf{T}}\mathbf{F}^T, \\[2mm] \mathbf{T}_D &= -V(\mathcal{B})^{-1}\mathbf{N}\mathbf{F}^T, \qquad J(\mathbf{F}) = \det\mathbf{F}, \end{aligned}$$

where Eq. (2.2) was taken into account. It can be shown [16] that *thermodynamically admissible* are e.g. such thermodynamic configurations $\mu \in GL^+(E^3) \times I$ for which

$$(2.10) \qquad S = -\partial_\theta\Psi,$$

and the mapping $(\mu, \dot{\mu}) \to \mathbf{T}_D(\mathcal{B}_0; \mu, \dot{\mu})$, where $\dot{\mu} \in L(E^3) \times R$ is a tangent element to the space of thermodynamic configurations $GL^+(E^3) \times I$ at the point μ, is a symmetric and objective tensor field of the form:

$$\mathbf{T}_D(\mathcal{B}_0; \mu, \dot{\mu}) = \mathbf{T}_D(\mathcal{B}_0; \mathbf{F}, \theta, \mathbf{L}), \quad \mathbf{L} = \dot{\mathbf{F}}\mathbf{F}^{-1} \in L(E^3),$$

$$(2.11) \qquad \mathbf{T}_D(\mathcal{B}_0; \mathbf{F}, \theta, \mathbf{L}) = \mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta) + \mathbf{h}_D(\mathcal{B}_0; \mathbf{F}, \theta, \mathbf{L}), \quad \mathbf{T}_D = \mathbf{T}_D^T,$$

$$\forall \mathbf{Q} \in SO(E^3), \quad \mathbf{T}_D(\mathcal{B}_0; \mathbf{QF}, \theta, \mathbf{QLQ}^T) = \mathbf{QT}_D(\mathcal{B}_0; \mathbf{F}, \theta, \mathbf{L})\mathbf{Q}^T,$$

and the Planck's dissipation inequality reduces to the following condition:

$$(2.12) \qquad \operatorname{tr}(\mathbf{h}_D\mathbf{D}) \geq 0, \quad h_D(\mathcal{B}_0; F, \theta, \mathbf{O}) = \mathbf{O}, \quad \mathbf{D} = \frac{1}{2}\left(\mathbf{L} + \mathbf{L}^T\right).$$

Moreover, it follows from the objectivity condition (2.4) and from the notations of Eq. (2.9) that the mapping $\mathbf{F} \to \mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta)$ should be, at each temperature

$\theta \in I$, a symmetric and objective tensor function that can be written in the following form:

$$\mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta) = \mathbf{R}\mathbf{h}(\mathcal{B}_0; \mathbf{U}, \theta)\mathbf{R}^T,$$

(2.13) $$\mathbf{h}(\mathcal{B}_0; \mathbf{U}, \theta) = V(\mathcal{B})^{-1}\partial_{\mathbf{U}}\Psi(\mathcal{B}_0; \mathbf{U}, \theta)\mathbf{U},$$

$$\mathbf{F} = \mathbf{R}\mathbf{U}, \quad \mathbf{R} \in SO(E^3), \quad \mathbf{U} = \mathbf{U}^T, \quad V(\mathcal{B}) = V(\mathcal{B}_0)\det\mathbf{U}.$$

The symmetric tensor fields $\mathbf{T}$ and $\mathbf{h}_D$ of Eq. (2.11) are isothermal counterparts, assigned to one whole body $\mathcal{B}_0$, of the Cauchy stress tensor for simple materials: thermoelastic and differential of complexity 1, respectively [16]. Note that, contrary to thermoelastic simple materials for which the dissipation coming from heat conduction appears, for a *thermoelastic size-effect body* the only thermodynamically admissible processes are the reversible ones ($\delta = 0$ in Eq.(2.7)). Therefore, thermoelastic size-effect bodies can be treated as these being *elastic within a certain range of temperature*. Let us introduce, imitating the theory of simple elastic materials, the *response insensibility group* $G_\theta(\mathcal{B}_0)$ at the temperature $\theta \in I$ of an (thermo)elastic size-effect body $\mathcal{B}_0$:

$$G_\theta(\mathcal{B}_0) = \{\mathbf{H} \in SL(E^3) : \forall \mathbf{F} \in GL^+(E^3), \ \mathbf{T}(\mathcal{B}_0; \mathbf{F}\mathbf{H}, \theta),$$

(2.14) $$= \mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta)\}$$

$$SL(E^3) = \{\mathbf{F} \in GL^+(E^3) : \det\mathbf{F} = 1\},$$

where $SL(E^3)$ is the so-called unimodular group defining, according to Eqs. (2.1) and (2.2), all deformed spatial configurations of $\mathcal{B}_0$ of the same volume equal to $V(\mathcal{B}_0)$. So, $G_\theta(\mathcal{B}_0)$ is the group of homogeneous deformations of $\mathcal{B}_0$ preserving, at the temperature $\theta \in I$, the volumetric mass density ρ_0 and the generalized Cauchy stress tensor $\mathbf{T}$ of the size-effect body $\mathcal{B}_0$. It follows from Eqs. (2.9) and (2.14) that $\mathbf{H} \in G_\theta(\mathcal{B}_0)$ iff [16]:

(2.15) $$\forall \mathbf{F} \in GL^+(E^3), \quad \Psi(\mathcal{B}_0; \mathbf{F}, \theta) = \Psi(\mathcal{B}_0; \mathbf{F}\mathbf{H}, \theta) + \Psi(\mathcal{B}_0; \mathbf{I}, \theta)$$

$$-\Psi(\mathcal{B}_0; \mathbf{H}, \theta),$$

where $\mathbf{I} \in GL^+(E^3)$ is the unit tensor. Let us consider the set $g_\theta(\mathcal{B}_0) \subset GL^+(E^3)$ of homogeneous deformations of $\mathcal{B}_0$ describing the *size-effect insensibility* of the free energy at the temperature $\theta \in I$:

$$g_\theta(\mathcal{B}_0) = \{\mathbf{P} \in GL^+(E^3) : \forall \mathbf{F} \in GL^+(E^3),$$

(2.16) $$\Psi(\mathcal{B}_{\mathbf{P}}; \mathbf{F}, \theta) = \Psi(\mathcal{B}_0; \mathbf{F}, \theta)\}$$

$$\mathcal{B}_{\mathbf{P}} = l(\mathbf{P})(\mathcal{B}_0),$$

where the linear mapping $l(\mathbf{P})$ is defined by Eq. (2.1). It easy to see that for each $\mathbf{P} \in g_\theta(\mathcal{B}_0)$:

$$(2.17) \qquad \mathbf{T}(\mathcal{B}_\mathbf{P}; \mathbf{F}, \theta) = J(\mathbf{P})^{-1} \mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta)$$

and thus

$$(2.18) \qquad \forall \mathbf{P} \in g_\theta(\mathcal{B}_0), \qquad G_\theta(\mathcal{B}_\mathbf{P}) = G_\theta(\mathcal{B}_0).$$

Moreover, it follows from Eq. (2.17) that for $\mathbf{P} \in g_\theta(\mathcal{B}_0) \cap SL(E^3)$ the elastic response of the size-effect body $\mathcal{B}_0$ (represented by the generalized Cauchy stress) is preserved. Therefore, let us consider the *size-effect insensibility group* $g_\theta(\mathcal{B}_0) \subset SL(E^3)$ at the temperature $\theta \in I$. If $g_\theta(\mathcal{B}_0) = SL(E^3)$ for each $\theta \in I$, then the size effect can be reduced to the dependence of elastic response and thermodynamic functions on the body volume $V(\mathcal{B}_0)$. If $g_\theta(\mathcal{B}_0) = SO(E^3)$ for each $\theta \in I$, then the size effect is independent of the body orientation.

Let us assume the existence of a homogeneous deformation $\mathbf{P} \in GL^+(E^3)$ such that the following formula, analogous to the local one appearing in the theory of simple materials, is valid (cf. [16]):

$$(2.19) \qquad \forall \mathbf{F} \in GL^+(E^3), \quad \mathbf{T}(\mathcal{B}_\mathbf{P}; \mathbf{F}, \theta) = \mathbf{T}(\mathcal{B}_0; \mathbf{F}\mathbf{P}, \theta).$$

Then [16]

$$(2.20) \qquad G_\theta(\mathcal{B}_\mathbf{P}) = \mathbf{P} G_\theta(\mathcal{B}_0) \mathbf{P}^{-1}.$$

For example, if

$$(2.21) \qquad \forall \theta \in I, \qquad g_\theta(\mathcal{B}_0) = G_\theta(\mathcal{B}_0),$$

then for each $\mathbf{P} \in g_\theta(\mathcal{B}_0)$ the conditions (2.19) and (2.20) become identities (see Eqs. (2.17) and (2.18)), and the elastic size-effect body will be called *quasi-simple* (within the range I of temperature).

In ordinary experience we commonly think of a body as being "solid" if, within a certain range of temperature, after changing its form (under a nonorthogonal transformation), we can observe a difference in the way it responds to further deformation [16]. If the elastic size-effect body $\mathcal{B}_0$ is quasi-simple, then the above observation can be expressed, according to Eq. (2.19), by the following counterpart of the definition of simple elastic solid materials (cf. [16]):

$$(2.22) \qquad \forall \theta \in I, \qquad G_\theta(\mathcal{B}_0) \subset SO(E^3).$$

The quasi-simple elastic size-effect body will then be called *elastic quasi-solid*. If $\mathcal{B}_0$ is an elastic size-effect body fulfilling the condition (2.22), then we will say that this body reveals the *quasi-solid response* within the range I of temperature. The spatial configuration $\mathcal{B}_0$ will then be called *undistorted*. Since from the objectivity condition (2.4) it follows that for each $\theta \in I$:

$$(2.23) \qquad \forall \mathbf{Q} \in SO(E^3), \qquad \Psi(\mathcal{B}_0; \mathbf{Q}, \theta) = \Psi(\mathcal{B}_0; \mathbf{I}, \theta),$$

we obtain from Eq. (2.15) that in the case (2.22) it should be:

(2.24) $G_\theta(\mathcal{B}_0) = \{\mathbf{Q} \in SO(E^3) : \forall \mathbf{F} \in GL^+(E^3), \quad \Psi(\mathcal{B}_0; [\mathbf{FQ}, \theta)$

$$= \Psi(\mathcal{B}_0; \mathbf{F}, \theta)\}.$$

If

(2.25) $\forall \theta \in I, \qquad G_\theta(\mathcal{B}_0) = SO(E^3),$

then the quasi-solid response is called *isotropic*.

In practical applications concerning solid bodies, the existence of an unstressed spatial configuration of the body [16] is usually assumed. In our case such configurations should exist within the range I of temperature, that is it should be:

$$\forall \theta \in I \quad \exists \mathbf{P}_\theta \in GL^+(E^3), \quad \mathbf{T}(\mathcal{B}_0(\theta); \mathbf{1}, \theta) = \mathbf{O},$$

(2.26)

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

where $\mathcal{B}_0$ is an elastic size-effect body. Let us consider, in order to intrinsically relate the size-effect body $\mathcal{B}_0$ with its deformed unstressed spatial configurations $\mathcal{B}_0(\theta)$ of Eq. (2.26), the following condition (cf. Eq. (2.20) and (2.22)):

(2.27) $\forall \theta \in I, \quad G_\theta(\mathcal{B}_0(\theta)) = \mathbf{P}_\theta G_\theta(\mathcal{B}_0)\mathbf{P}_\theta^{-1} \subset SO(E^3).$

The elastic size-effect body $\mathcal{B}_0$ fulfilling the conditions (2.26) and (2.27) will be called *solid within the range I of temperature*. Further on, we will restrict ourselves to the case of nanomaterial clusters being solid bodies in the above sense. The undistorted and unstressed spatial configurations $\mathcal{B}_0(\theta)$, $\theta \in I$, will be called then *natural* configurations of the elastic size-effect solid body $\mathcal{B}_0$. If, additionally, the spatial configuration $\mathcal{B}_0$ is undistorted, then it follows from Eqs. (2.22) and (2.27) that should be [16]:

$$\forall \theta \in I, \quad G_\theta(\mathcal{B}_0(\theta)) = \mathbf{R}(\theta)G_\theta(\mathcal{B}_0)\mathbf{R}(\theta)^T,$$

(2.28) $\mathbf{P}_\theta = \mathbf{R}(\theta)\mathbf{U}(\theta), \quad \mathbf{R}(\theta) \in SO(E^3), \quad \mathbf{U}(\theta) = \mathbf{U}(\theta)^T,$

$$\forall \mathbf{Q} \in G_\theta(\mathcal{B}_0), \quad \mathbf{Q}^T\mathbf{U}(\theta)\mathbf{Q} = \mathbf{U}(\theta).$$

If the quasi-solid response is isotropic, then the size-effect solid body $\mathcal{B}_0$ will be called an *isotropic solid*.

The formulae of Eq. (2.28) reduce then to:

$$\forall \theta \in I, \quad G_\theta(\mathcal{B}_0(\theta)) = G_\theta(\mathcal{B}_0) = SO(E^3),$$

(2.29)

$$\mathbf{P}_\theta = \eta(\theta)\mathbf{R}(\theta), \quad \eta(\theta) > 0, \quad \mathbf{R}(\theta) \in SO(E^3).$$

Thus, in this case, each natural configuration $\mathcal{B}_0(\theta)$ of $\mathcal{B}_0$ takes its shape.

If

(2.30) $\forall \theta \in I, \qquad G_\theta(\mathcal{B}_0) = SL(E^3),$

then the generalized Cauchy stress tensor $\mathbf{T}$ reduces to [16]:

$$\mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta) = -p(\mathcal{B}_0; J(\mathbf{F}), \theta)\mathbf{1},$$

(2.31)

$$J(\mathbf{F}) = \det \mathbf{F}.$$

We will say then that the elastic size-effect body $\mathcal{B}_0$ reveals the *quasi-fluid response* within the range I of temperature. The quasi-fluid response has, for an elastic quasi-simple size-effect body $\mathcal{B}_0$, the following form:

(2.32) $p(\mathcal{B}_0; J(\mathbf{F}), \theta) = p(V(\mathcal{B}_0); J(\mathbf{F}), \theta).$

Note that a fluid is commonly regarded as a material having "no preferred configuration" [16], what means that should be:

$$p(V(\mathcal{B}_0; J(\mathbf{F}), \theta) = p(V(\mathcal{B}), \theta),$$

(2.33)

$$V(\mathcal{B}) = J(\mathbf{F})V(\mathcal{B}_0).$$

However, since the response function $p = p(V, \theta)$ can describe not only a fluid but also a solid or gas, in hydrodynamics it is customary to impose the condition $p = p(V, \theta) > 0$ for $V > 0, \theta \in I$, [16].

3. Dynamics of size-effect bodies

Let $\mathcal{B}_0 \subset E^3$ be the spatial configuration of a size-effect body identified with the body itself, and let $\mathbf{F} : R^+ \to GL^+(E^3)$ be a homogeneous deformation process. Let us assume that on the body act, at each instant $\tau \in R^+$, external force fields: the body force field $\mathbf{b}(\mathbf{X}, \tau)$, $\mathbf{X} \in \mathrm{Int}\mathcal{B}_0$, and the surface force field $\mathbf{s}(\mathbf{X}, \tau), \mathbf{X} \in \partial \mathcal{B}_0$, where $\mathrm{Int}\mathcal{B}_0$ and $\partial \mathcal{B}_0$ denote the body $\mathcal{B}_0$ interior and its boundary, respectively. The volumetric kinetic energy $K(\mathcal{B}_0; \tau)$ of the body (cf. the approximate representation of the mass size-effect by Eq. (2.2)) and the power $P(\mathcal{B}_0; \tau)$ of external forces acting on the body are given by

$$K(\mathcal{B}_0; \tau) = \frac{1}{2} \int_{\mathcal{B}_0} |\mathbf{v}(\mathbf{X}, \tau)|^2 dm(\mathbf{X}),$$

(3.1)

$$P(\mathcal{B}_0; \tau) = \int_{\mathcal{B}_0} \mathbf{b}(\mathbf{X}, \tau) \cdot \mathbf{v}(\mathbf{X}) dV(\mathbf{X}) + \int_{\partial \mathcal{B}_0} \mathbf{s}(\mathbf{X}, \tau) \cdot \mathbf{v}(\mathbf{X}, \tau) dF(\mathbf{X}),$$

where we have denoted

$$v(\mathbf{X}, \tau) = \frac{d}{d\tau} l(\mathbf{F}(\tau)(\mathbf{X}) = \dot{\mathbf{F}}(\tau)\mathbf{X}, \quad |\mathbf{v}|^2 = \mathbf{v} \cdot \mathbf{v},$$

(3.2)

$$dm(\mathbf{X}) = \rho_0 dV(\mathbf{X}), \quad \rho_0 = m/V(\mathcal{B}_0).$$

The volumetric net working $W(\mathcal{B}_0; \tau)$ at the instant $\tau \in R^+$ has in an inertial frame of reference the following form [16]:

(3.3)
$$W(\mathcal{B}_0; \tau) = P(\mathcal{B}_0; \tau) - \dot{K}(\mathcal{B}_0; \tau).$$

It follows from Eqs. (3.1) – (3.3) that for the net working of Eq. (2.5) should be:

(3.4)
$$\left[\mathbf{M}_{\text{ext}}(\mathcal{B}_0; \tau)^T - \ddot{\mathbf{F}}(\tau)\mathbf{J}(\mathcal{B}_0) + \mathbf{N}(\mathcal{B}_0; \tau)\right] \cdot \dot{\mathbf{F}}(\tau) = 0,$$

where $\mathbf{M}_{\text{ext}}(\mathcal{B}_0; \tau)$ denotes the dipole moment of external forces:

(3.5)
$$\mathbf{M}_{\text{ext}}(\mathcal{B}_0; \tau) = \int_{\mathcal{B}_0} \mathbf{X} \otimes \mathbf{b}(\mathbf{X}, \tau) dV(\mathbf{X}) + \int_{\partial\mathcal{B}_0} \mathbf{X} \otimes \mathbf{s}(\mathbf{X}, \tau) dF(\mathbf{X}),$$

and $\mathbf{J}(\mathcal{B}_0)$ is the body inertia tensor determined with respect to its mass center $\mathbf{X} = \mathbf{O}$:

(3.6)
$$\mathbf{J}(\mathcal{B}_0) = \int_{\mathcal{B}_0} \mathbf{X} \otimes \mathbf{X} dm(\mathbf{X}).$$

The equation (3.4) will be fulfilled by a class of homogeneous thermodynamic processes such that

(3.7)
$$\mathbf{J}(\mathcal{B}_0)\ddot{\mathbf{F}}(\tau)^T = \mathbf{N}(\mathcal{B}_0; \tau)^T + \mathbf{M}_{\text{ext}}(\mathcal{B}_0; \tau).$$

The equation (3.7) generalizes the equation of dynamics of affinely rigid bodies. Particularly, for thermodynamically admissible processes defined by Eqs. (2.8) – (2.12), where $\mu = (\mathbf{F}, \theta) \in GL^+(E^3) \times I$, we have:

$$\mathbf{N}(\mathcal{B}_0; \tau)^T = -V(\mathcal{B}_0)J(\mathbf{F})(\tau)\mathbf{F}(\tau)^{-1}\mathbf{T}_D(\mathcal{B}_0; \mathbf{F}, \theta, \mathbf{L})(\tau),$$

(3.8)

$$\mathbf{L}(\tau) = \dot{\mathbf{F}}(\tau)\mathbf{F}(\tau)^{-1}.$$

Note that introducing the dipole moment $\mathbf{M}_{\text{int}}(\mathcal{B}_0; \tau)$ of internal surface forces acting on the body boundary $\partial\mathcal{B}_0$:

$$\mathbf{M}_{\text{int}}(\mathcal{B}_0; \tau) = \int_{\partial\mathcal{B}_0} \mathbf{X} \otimes \mathbf{t}_D(\mathcal{B}_0; \mathbf{X}, \tau) dF(\mathbf{X})$$

(3.9)
$$\mathbf{t}_D(\mathcal{B}_0; \mathbf{X}, \tau) = -\hat{\mathbf{T}}_D(\mathcal{B}_0; \tau)\mathbf{n}(\mathbf{X})$$

$$\hat{\mathbf{T}}_D(\mathcal{B}_0; \tau) = J(\mathbf{F})(\tau)\mathbf{T}_D(\mathcal{B}_0; \mathbf{F}, \theta, \mathbf{L})(\tau)\mathbf{F}^*(\tau), \quad \mathbf{F}^* = (\mathbf{F}^{-1})^T,$$

where $\hat{\mathbf{T}}_D(\mathcal{B}_0;\tau)$ is the counterpart of the Piola-Kirchhoff stress tensor (cf. [16]) and $\mathbf{n}$ is the outward normal versor, we obtain the following interpretation rule of the generalized force $\mathbf{N}(\mathcal{B}_0;\tau)$ [13]:

$$(3.10) \qquad \mathbf{N}(\mathcal{B}_0;\tau)^T = \mathbf{M}_{\mathrm{int}}(\mathcal{B}_0;\tau).$$

The condition of immobility of the mass center means that the total external force acting on the body $\mathcal{B}_0$ should vanish:

$$(3.11) \qquad \forall \tau \in R^+, \quad \int_{\mathcal{B}_0} \mathbf{b}(\mathbf{X},\tau)dV(\mathbf{X}) + \int_{\partial\mathcal{B}_0} \mathbf{s}(\mathbf{X},\tau)dF(\mathbf{X}) = \mathbf{O}.$$

If the considered size-effect body is thermoelastic, then the generaized Cauchy stress tensor $\mathbf{T}_D$ of Eq. (2.11) reduces to its part $\mathbf{T}$ (represented in the form (2.13)), and the thermodynamic processes become reversible ($\delta = 0$ in Eq. (2.7)). In this case, Eq. (2.6) can be written in the form of the following temperature evolution equation [13]:

$$(3.12) \qquad \begin{aligned} K_{\mathbf{F}}\dot{\theta} &= V(\mathcal{B}_0)\theta\partial_\theta\hat{\mathbf{T}}\cdot\dot{\mathbf{F}} + Q, \\ \hat{\mathbf{T}} &= V(\mathcal{B}_0)^{-1}\partial_{\mathbf{F}}\Psi, \quad \theta \in I, \end{aligned}$$

where $K_{\mathbf{F}} = K_{\mathbf{F}}(\mathcal{B}_0;\theta)$ is the heat capacity at a constant deformation $\mathbf{F}$ deined by:

$$(3.13) \qquad K_{\mathbf{F}} = \partial_\theta E = \theta\partial_\theta S = -\theta(\partial^2\Psi/\partial\theta^2)_{\mathbf{F}},$$

and the heating $Q = Q(\mathcal{B}_0;\theta)$ is given by:

$$(3.14) \qquad \begin{aligned} Q(\mathcal{B}_0;\theta) &= \theta(\tau)\dot{S}(\mathcal{B}_0;\theta), \quad S = -\partial_\theta\Psi, \\ \dot{S}(\mathcal{B}_0;\theta) &= \frac{d}{d\tau}S(\mathcal{B}_0;\mathbf{F}(\tau),\theta(\tau)). \end{aligned}$$

Note that the following relation holds [13]:

$$(3.15) \qquad V(\mathcal{B}_0)\partial_\theta\hat{\mathbf{T}}\cdot\dot{\mathbf{F}} = V(\mathcal{B})\partial_\theta\mathbf{T}\cdot\mathbf{D}, \quad V(\mathcal{B}) = J(\mathbf{F})V(\mathcal{B}_0),$$

$$\mathbf{D} = \frac{1}{2}\left(\mathbf{L} + \mathbf{L}^T\right), \quad \mathbf{L} = \dot{\mathbf{F}}\mathbf{F}^{-1}.$$

We see that the above formulated dynamics as well as the considered thermodynamics refer to only one whole body, not to an infinite system of subbodies as it occurs in a field theory (local or nonlocal) or in a thermodynamics of local (equilibrium or nonequilibrium) body states.

4. Liquid-like response

The notions discussed in Sec. 2 concerning materials of size-effect bodies are inspired by the continuum mechanics approach represented by the theory of simple materials [16]. Let us consider, in order to introduce a class of (homogeneous and elastic) size-effect bodies based on a different approach, the theory of capillarity. In this theory, a finite free energy density is attributed not only to the volume but also to the surface measure, and the body should be defined in such a way that in the limiting case of a thin film (infinitely thin in the sense of phenomenological approximation used in the theory of capillarity) should be also considered as a body [18]. Thus, in line with the classical capillarity theory, we can endow a body $\mathcal{B}_0$ with the total free energy of the form [18]:

$$\Psi(\mathcal{B}_0; \mathbf{F}, \theta) = \varepsilon(\theta)V(\mathcal{B}) + \gamma(\theta)F(\mathcal{B}),$$

(4.1)

$$\mathcal{B} = l(\mathbf{F})(\mathcal{B}_0), \quad \mathbf{F} \in GL^+(E^3), \quad \theta \in I,$$

where θ is uniform temperature, $V(\mathcal{B})$ and $F(\mathcal{B})$ denote the volume of the deformed body and the surface field of its boundary, respectively. The constants (at the given temperature $\theta \in I$) $\varepsilon(\theta)$ and $\gamma(\theta)$ denote the free energy densities needed to change the body volume unit and the boundary surface field unit, respectively. The formula (4.1) means that the capillarity theory enables us to define a particular case of the size-effect body endowed with the such total free energy function that can be transformed into a form independent of the choice of a preferred spatial configuration of the body. Note that Eqs. (2.31) – (2.33) can be considered as these corresponding to a total free energy of the same property but represented in the form

(4.2)
$$\Psi(\mathcal{B}_0; \mathbf{F}, \theta) = \varphi(V(\mathcal{B}), \theta),$$

where $\mathcal{B}$ is defined by Eq. (4.1). We will say, generalizing the formulae (4.1) and (4.2) and taking into account the analogy with fluids regarded as materials having no preferred spatial configuration, that an elastic size-effect body $\mathcal{B}_0$ has the *liquid-like response* if its total free energy function Ψ fulfills the following condition:

$$\Psi(\mathcal{B}_0; \mathbf{F}, \theta) = \Phi_\theta(l(\mathbf{F})(\mathcal{B}_0)), \quad \theta \in I,$$

(4.3)

$$\forall \mathbf{Q} \in SO(E^3), \qquad \Phi_\theta(l(\mathbf{Q})(\mathcal{B})) = \Phi_\theta(\mathcal{B}),$$

where the objectivity condition (2.4) was taken into account.

It can be shown (basing on the Hadwiger integral theorem – [14, 19]) that an additive (in the sense $\Phi(\mathcal{B}_1 \cup \mathcal{B}_2) = \Phi(\mathcal{B}_1) + \Phi(\mathcal{B}_2) - \Phi(\mathcal{B}_1 \cap \mathcal{B}_2)$), continuous

and invariant with respect to the action of isometry group in E^3, functional $\mathcal{B} \to \Phi_\theta(\mathcal{B})$ defined on the set of all compact and convex three-dimensional bodies in E^3 endowed with the Hausdorff metric for sets, can be represented in the following general form:

$$(4.4) \qquad \Phi_\theta(\mathcal{B}) = a(\theta)V(\mathcal{B}) + b(\theta)F(\mathcal{B}) + c(\theta)M(\mathcal{B}) + d(\theta)\chi(\mathcal{B}),$$

where $a(\theta), b(\theta), c(\theta), d(\theta)$ are arbitrary constants assumed here to be functions of class C^2 of the temperature parameter $\theta \in I$. $V(\mathcal{B})$, $F(\mathcal{B})$, $M(\mathcal{B})$, and $\chi(\mathcal{B})$ denote the volume of the domain $\mathcal{B}$, the surface field of its boundary $\partial\mathcal{B}$, the total mean curvature of $\partial\mathcal{B}$, and the Euler characteristic of $\mathcal{B}$, respectively. The formula (4.4) admits the case of convex bodies with a piecewise smooth boundaries, i.e. containing some edges and cornes [19, 20]. Note that it can hardly be supposed that the free energy functional of Eq. (4.4) suffers drastic changes on the transition from convex bodies to other shapes. It enables us to generalize the formula (4.4) by the extension of functionals Φ_θ, $\theta \in I$, of this form to all compact and connected spatial sets $\mathcal{B} \subset E^3$ with oriented regular boundary surface of class C^2 [18]. For compact and connected bodies [21]:

$$(4.5) \qquad \chi(\mathcal{B}) = 1 - n,$$

where n is the number of holes inside the body $\mathcal{B}$. Particularly, $\chi(\mathcal{B}) = 1$ for convex bodies. The geometric functionals of Eq. (4.4) have, for the assumed class of boundary surfaces, the following representations [20, 22]:

$$(4.6) \qquad V(\mathcal{B}) = \int_{\mathcal{B}} dV, \qquad F(\mathcal{B}) = \int_{\partial\mathcal{B}} dF, \qquad M(\mathcal{B}) = \int_{\partial\mathcal{B}} H\,dF,$$

$$\chi(\mathcal{B}) = \frac{1}{4\pi} \int_{\partial\mathcal{B}} K\,dF,$$

where H and K denote the mean and Gaussian curvatures of $\partial\mathcal{B}$, respectively. If R_1 and R_2 are principal radii of curvature of $\partial\mathcal{B}$, then

$$(4.7) \qquad H = \frac{1}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right), \qquad K = \frac{1}{R_1 R_2}.$$

It follows from Eq. (4.5) that

$$\forall \mathbf{P} \in GL^+(E^3), \qquad \chi(\mathcal{B}_\mathbf{P}) = \chi(\mathcal{B}_0),$$

$$(4.8)$$

$$\mathcal{B}_\mathbf{P} = l(\mathbf{P})(\mathcal{B}_0).$$

Thus, the last term of the total free energy function Ψ defined by Eqs. (4.3) – (4.6) is equal to $d(\theta)\chi(\mathcal{B}_0)$. Consequently, this term does not influence elastic properties of the size-effect body $\mathcal{B}_0$ but influences, according to Eq. (3.13), its heat capacity. Moreover, it follows from Eqs. (4.3), (4.4) and (4.8) that the change of topological connection of the size-effect body $\mathcal{B}_0$ needs a finite discontinuous jump of the total free energy term $d(\theta)\chi(\mathcal{B}_0)$. It means that this term is conditioned by the mathematical as well as the physical connectedness of the body. Therefore, we can recognize the coefficient $d(\theta)$ as the one conditioned by forces of connectedness of nanomaterial clusters.

Let us write Eqs. (4.4) and (4.6) in the form:

(4.9)
$$\Phi_\theta(\mathcal{B}) = a(\theta)V(\mathcal{B}) + \Phi_{s,\theta}(\mathcal{B}),$$

$$\Phi_{s,\theta}(\mathcal{B}) = \int_{\partial\mathcal{B}} w_\theta(H,K)dF,$$

where it has been denoted

(4.10)
$$w_\theta(H,K) = b(\theta) + c(\theta)H + (d(\theta)/4\pi)K.$$

The total surface free energy density $w_\theta(H,K)$ of Eq. (4.10) depends on the definition of the boundary surface $\partial\mathcal{B}$. In the case of solid bodies for which their size is much greater than the effective size of the boundary layer, the influence of both curvatures on the total surface free energy $\Phi_{s,\theta}(\mathcal{B})$ of Eq. (4.9) can be neglected [2] (that is $c(\theta) = 0$ and $d(\theta) = 0$ in Eq. (4.10)) and Eq. (4.9) reduces then to Eq. (4.1). Therefore, the constant $b(\theta)$ of Eq. (4.10) can be identified, up to its sign, with the so-called *surface tension* $\gamma(\theta)$ [2, 23] being the free energy density needed to change the boundary surface field unit. The density $\gamma(\theta)$ is conditioned by the interactions of atoms located on the boundary solid surface [2, 23] and it is a positive quantity at the considered temperature lower than the melting temperature [23]. However, we consider macroscopically small bodies and consequently, taking into account that the term $d(\theta)\chi(\theta)$ of Eq. (4.4) characterizes the physical connectedness of these bodies, we assume that the constant $d(\theta)$ of Eq. (4.10) is a nonvanishing quantity. Thus, we obtain

(4.11) $\varepsilon(\theta) = |a(\theta)| \geq 0, \quad \gamma(\theta) = |b(\theta)| > 0, \quad \omega(\theta) = |c(\theta)| \geq 0,$

$$\delta(\theta) = |d(\theta)|/4\pi > 0.$$

The quantity $M(\mathcal{B})/2\pi$, known in rock analysis and in stereographic metallography, is interpreted as the mean grain width [18, 20]. Therefore, according to Eqs. (4.3), (4.4) and (4.11), $\omega(\theta)/2\pi$ can be interpreted as the free energy density

needed to change the body mean width $M(\mathcal{B})/2\pi$ unit. On the other hand, the mean curvature H of Eqs. (4.9) – (4.11) is a relative geometric quantity depending on the Euclidean geometry of the ambient physical space in which the boundary surface is embedded. Consequently, the quantity $\omega(\theta)$ should be considered as the one conditioned by interactions between the boundary surface atoms and the bulk atoms located in a boundary layer. For the sake of simplicity we will call $\gamma(\theta)$ as well as $\omega(\theta)$ the *surface free energy densities*.

The generalized Cauchy stress $\mathbf{T}$ defined by Eqs. (2.9), (2.13), (4.3) – (4.5), and (4.8) – (4.11) takes the following form:

$$\mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta) = a(\theta)\mathbf{1} + \mathbf{T}_s(\mathcal{B}_0; \mathbf{F}, \theta),$$

$$\mathbf{T}_s(\mathcal{B}_0; \mathbf{F}, \theta) = \mathbf{R}\mathbf{T}_s(\mathcal{B}_0; \mathbf{U}, \theta)\mathbf{R}^T,$$

$$\mathbf{T}_s(\mathcal{B}_0; \mathbf{U}, \theta) = V(\mathcal{B}_\mathbf{U})^{-1}\partial_\mathbf{U}\Phi_{s,\theta}(\mathcal{B}_\mathbf{U})\mathbf{U},$$

(4.12)

$$\mathbf{F} = \mathbf{R}\mathbf{U}, \ \mathbf{R} \in SO(E^3), \ \mathbf{U} = \mathbf{U}^T,$$

$$\Phi_{s,\theta}(\mathcal{B}_\mathbf{U}) = b(\theta)F(\mathcal{B}_\mathbf{U}) + c(\theta)M(\mathcal{B}_\mathbf{U}) + d(\theta)\chi(\mathcal{B}_\mathbf{U}),$$

$$\mathcal{B}_\mathbf{U} = l(\mathbf{U})(\mathcal{B}_0), \ \ V(\mathcal{B}_\mathbf{U}) = V(\mathcal{B}_0)\det \mathbf{U}.$$

Further on we assume that, within the range I of temperature, the surface free energy density ω is either positive or vanishes identically. It follows from Eqs. (2.24), (4.3) – (4.5) and (4.8) that if the elastic generalized stress response of Eq. (4.12) is quasi-solid within the range I of temperature (Sec. 2), then its insensibility groups $G_\theta(\mathcal{B}_0)$, $\theta \in I$, are given by

(4.13) $$G_\theta(\mathcal{B}_0) = g_\theta(\mathcal{B}_0) \cap SO(E^3)$$

where, in the considered case, the size-effect insensibility group $g_\theta(\mathcal{B}_0)$ (Sec. 2) has the following representation:

(4.14) $$g_\theta(\mathcal{B}_0) = \{\mathbf{P} \in SL(E^3) : \forall \mathbf{F} \in GL^+(E^3), \ \ \Phi_{s,\theta}(\mathcal{B}_{\mathbf{FP}}) = \Phi_{s,\theta}(\mathcal{B}_\mathbf{F})\}.$$

It follows from Eqs. (4.12) – (4.14) that would be:

$$\forall \theta \in I, \ \ g_\theta(\mathcal{B}_0) = g(\mathcal{B}_0), \ \ G_\theta(\mathcal{B}_0) = G(\mathcal{B}_0),$$

(4.15) $$G(\mathcal{B}_0) = g(\mathcal{B}_0) \cap SO(E^3) = h(\mathcal{B}_0),$$

$$h(\mathcal{B}_0) = \{\mathbf{Q} \in SO(E^3) : l(\mathbf{Q})(\mathcal{B}_0) = \mathcal{B}_0\},$$

where $g(\mathcal{B}_0)$ is a subgroup of the unimodular group $SL(E^3)$, and $h(\mathcal{B}_0)$ denotes the group of rotational symmetries of $\mathcal{B}_0$; if the body $\mathcal{B}_0$ has no rotational symmetries, then $h(\mathcal{B}_0) = \{\mathbf{1}\}$. The condition (2.26) defining the unstressed spatial configurations $\mathcal{B}_0(\theta)$, $\theta \in I$, takes, according to Eq. (4.12), the following form:

$$a(\theta)V_0(\theta)\mathbf{1} + \partial_{\mathbf{U}}\Phi_{s,\theta}(\mathcal{B}_{\mathbf{U}}(\theta))|_{\mathbf{U}=\mathbf{1}} = \mathbf{0},$$

(4.16)

$$\mathcal{B}_{\mathbf{U}}(\theta) = l(\mathbf{U})(\mathcal{B}_0(\theta)), \quad \mathcal{B}_0(\theta) = l(\mathbf{P}_\theta)(\mathcal{B}_0), \quad V_0(\theta) = V(\mathcal{B}_0(\theta)).$$

The considered elastic size-effect body $\mathcal{B}_0$ with the quasi-solid liquid-like response is, within the range I of temperature, an elastic size-effect solid body (Sec. 2) if the conditions (2.28) and (4.16) are fulfilled. The condition (2.28) is, according to Eqs. (2.24) and (4.13) – (4.15), fulfilled and takes the form:

(4.17)
$$\forall \theta \in I, \quad G_\theta(\mathcal{B}_0(\theta)) = G(\mathcal{B}_0(\theta)) = \mathbf{R}(\theta)G(\mathcal{B}_0)\mathbf{R}(\theta)^T,$$
$$\mathbf{P}_\theta = \mathbf{R}(\theta)\mathbf{U}(\theta), \quad \mathbf{R}(\theta) \in SO(E^3), \quad \mathbf{U}(\theta) = \mathbf{U}(\theta)^T,$$
$$\forall \mathbf{Q} \in G(\mathcal{B}_0), \quad \mathbf{Q}^T\mathbf{U}(\theta)\mathbf{Q} = \mathbf{U}(\theta).$$

It is an isotropic elastic size-effect solid body iff $G(\mathcal{B}_0) = SO(E^3)$. In this case $\mathbf{P} \in GL^+(E^3)$ has the form given by Eq. (2.29) and $\mathcal{B}_0$ is a *ball*. Conversely, if $\mathcal{B}_0$ is a ball then $h(\mathcal{B}_0) = SO(E^3)$ and, according to Eq. (4.15), the elastic spherical size-effect solid body with the liquid-like response should be *isotropic*. The spatial natural configurations $\mathcal{B}_0(\theta)$ of Eq. (4.16) are then spherical of the radius $R_0(\theta)$, $\theta \in I$ and (cf. Eq. (2.29)):

(4.18) $\qquad R_0(\theta) = \eta(\theta)R_0, \quad V_0(\theta) = \eta(\theta)^3 V(\mathcal{B}_0), \quad V(\mathcal{B}_0) = (4/3)\pi R_0^3.$

Let us take as $\mathcal{B}_0$ an *oblong ellipsoid of revolution* with the axis of revolution parallel to a versor $\mathbf{n}$, and let R_0 and r_0, $R_0 > r_0$, denote the length of ellipsoid semiaxes in the $\mathbf{n}$-direction and in the directions perpendicular to this direction, respectively. The group $G(\mathbf{n})$ of all rotations about the axis of revolution describes rotational symmetries of the body $\mathcal{B}_0$ and

(4.19) $\qquad\qquad\qquad\qquad h(\mathcal{B}_0) = G(\mathcal{B}_0) = G(\mathbf{n}).$

Then, the condition (4.17) with

$$G(\mathcal{B}_0(\theta)) = G(\mathbf{n}_\theta), \quad \mathbf{n}_\theta = \mathbf{R}(\theta)\mathbf{n},$$

(4.20)

$$\mathbf{U}(\theta) = \eta(\theta)\mathbf{1} + \eta_n(\theta)\mathbf{n} \otimes \mathbf{n}, \quad \eta(\theta) > 0, \quad \eta_n(\theta) \geq 0,$$

is fulfilled. Thus, $\mathcal{B}_0(\theta)$, $\theta \in I$, is then the oblong ellipsoid of revolution with the axis of revolution parallel to the versor $\mathbf{n}_\theta$ of Eq. (4.20), and with the semiaxes

$R_0(\theta)$ and $r_0(\theta)$ in the $\mathbf{n}_\theta$-direction and in the directions perpendicular to $\mathbf{n}_\theta$, respectively, where:

$$R_0(\theta) = \eta_1(\theta)R_0, \quad r_0(\theta) = \eta(\theta)r_0, \quad R_0(\theta) > r_0(\theta),$$

(4.21) $$V_0(\theta) = \eta_1(\theta)\eta(\theta)^2 V(\mathcal{B}_0), \quad \eta_1(\theta) = \eta(\theta) + \eta_n(\theta),$$

$$V(\mathcal{B}_0) = (4/3)\pi R_0 r_0^2.$$

So, we have defined, within the range I of temperature, the *transversally isotropic* elastic oblong size-effect solid body $\mathcal{B}_0$ with the liquid-like response.

We see that, for the considered size-effect solid body with the liquid-like response, rotational symmetries of an undistorted spatial configuration $\mathcal{B}_0$ of the size-effect body define its *material symmetries* described by the response insensibility group $G(\mathcal{B}_0)$. Particularly, the spherical shape means that the size-effect solid body with the liquid-like response should be isotropic, and the oblong spheroidal shape means that this size-effect body should reveal transverse isotropy (cf. Eq. (4.15)). It is consistent with the essential feature of macroscopically small nanomaterial clusters: properties of these clusters (particularly - their thermomechanical properties) can not be separated from their size as well as the shape. The sphericity and oblongness of the cage shape of fullerene particles C_{60} and C_{70}, respectively [8], provide, on the nanometer observation scale, significant examples of particles whose total mass as well as shape are their intrinsic and correlated properties. Therefore, let $\mathcal{B}_0$ be an undistorted spatial configuration, and $\mathbf{P} \in GL^+(E^3)$ such that (cf. Eqs. (4.15) and (4.17)):

$$G(\mathcal{B}_\mathbf{P}) = \mathbf{P}G(\mathcal{B}_0)\mathbf{P}^{-1} \subset SO(E^3),$$

(4.22)

$$\mathcal{B}_\mathbf{P} = l(\mathbf{P})(\mathcal{B}_0), \quad G(\mathcal{B}_0) \subset SO(E^3).$$

Then [16]:

$$\mathbf{P} = \mathbf{RU}, \quad \mathbf{R} \in SO(E^3), \quad \mathbf{U} = \mathbf{U}^T,$$

(4.23)

$$\forall \mathbf{Q} \in G(\mathcal{B}_0), \quad \mathbf{Q}^T \mathbf{U}\mathbf{Q} = \mathbf{U},$$

and

(4.24) $$G(\mathcal{B}_\mathbf{P}) = \mathbf{R}G(\mathcal{B}_0)\mathbf{R}^T.$$

It follows from Eqs. (4.15), (4.23), and (4.24) that

(4.25) $$G(\mathcal{B}_\mathbf{U}) = G(\mathcal{B}_0)$$

and the right stretch tensors $\mathbf{U}$ of Eq. (4.23) constitute a subgroup $U(\mathcal{B}_0) \subset GL^+(E^3)$. Note that if $G(\mathcal{B}_0)$ is a Lie group, then $G(\mathcal{B}_0) = SO(E^3)$ or $G(\mathcal{B}_0) = G(\mathbf{n})$, and the property

$$(4.26) \qquad\qquad h(\mathcal{B}_0) = G(\mathcal{B}_0)$$

means then that the body boundary $\partial\mathcal{B}_0$ should be a sphere or a surface of revolution with the axis of revolution parallel to the versor $\mathbf{n}$. If $\mathcal{B}_0$ is a compact convex body and $G(\mathcal{B}_0)$ is a finite group of rotations, then Eq. (4.26) means that $\partial\mathcal{B}_0$ should be a piecewise smooth surface (see remarks following Eq. (4.4)). Therefore, since the group $U(\mathcal{B}_0)$ of right stretches of $\mathcal{B}_0$ defines undistorted spatial configurations of the same shape and of the same response insensibility group, deformations $\mathbf{U} \in U(\mathcal{B}_0)$ enable us to separate the shape variation effect from the size effect, and thus to describe the latter effect in a more clear manner. Particularly, the homothetic deformation

$$(4.27) \qquad\qquad \mathbf{U} = \lambda\mathbf{1}, \quad \lambda > 0$$

appears as the universal homogeneous deformation preserving the body shape and the body material symmetries. In a second part of the paper, an isotropic elastic spherical size-effect solid body for which homothetic deformations are the general ones preserving its shape, will be considered. For these deformations:

$$(4.28) \qquad\qquad \mathbf{T}_\infty(\theta) = \lim_{\lambda\to\infty} \mathbf{T}(\mathcal{B}_0; \lambda\mathbf{1}, \theta) = a(\theta)\mathbf{1}$$

and $\mathbf{T}_\infty(\theta)$ defines an asymptotic uniform tension if (cf. (4.11)):

$$(4.29) \qquad\qquad \varepsilon(\theta) = a(\theta) \geq 0.$$

The constant $a(\theta)$, $\theta \in I$, can be interpreted then as a quantity depending on the bulk interatomic interactions.

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