

ON THE QUASI-SOLID STATE OF SOLID NANOCCLUSERS

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The paper concerns the dependence of thermomechanical properties of three-dimensional nanoclusters on the cluster size as well as on its shape. The main topics discussed are: (i) a group-theoretical description of structurally stable solid nanoclusters; (ii) a phenomenological model of nanoclusters revealing the coexistence of solid and liquid states in a finite interval of absolute temperature.

1. Introduction

The science of nanoscale concerns the properties and behavior of aggregates of atoms and/or molecules, at a scale not yet large enough to be considered macroscopic but far beyond what can be called microscopic. The mesoscale objects are not so large as to be completely free of quantum effects; thus, they do not simply obey the classical physics governing the macroworld [1]. As we shrink the mesoscale to the *nanoscale*, physics becomes increasingly dominated by the surfaces. Namely, much of the foundations of solid state physics rests on the premise that the physical properties are dominated by the physics of the bulk (that is, surface atoms have a negligible contribution to bulk properties of solid bodies). Nanoscale aggregates, called further on *nanoclusters*, are so small that this assumption breaks down completely.

Nanotechnology deals with materials and systems having three key properties: they have at least one dimension not greater than 100 nm (the basic research of such structures is the subject of *nanoscience*), they are designed through processes that exhibit fundamental control over the physical and chemical attributes of molecular-scale structures. It is used, for example, in *self-assembly processes* to put together larger structures – atoms or molecules that make ordered arrangements spontaneously, given the right conditions [2]. The fullerene C_{60} molecules with all atoms located in vertices of a truncated icosahedron [3, 4] as well as three-dimensional compact nanoclusters with the mean size not greater than 100 nm are examples of *self-ensambled nanostructures* considered in the paper.

One particular phenomenon – the dependence of a cluster properties upon its size – occurs for clusters in the nanometer scale. For example, the strength of nanoclusters increases when the cluster size decreases [5]. The elastic moduli (Young's, bulk and shear) of such clusters reveal also the size effect [6]. These are *mechanical size effects*.

There exist also the *thermodynamic size effects*; for example, the reduction of the melting point of small gold aggregates as a function of decreasing particle size [7, 8].

The shape of nanostructures can depend on its size. Namely, it is observed that sodium clusters with a small number of atoms ($< 150 \sim 200$) crystallize in the form of icosahedra. The structure becomes unstable for a large number of atoms and transforms to cubo-octahedra (i.e. a cube with truncated corners) which is just a path of the face-centered cubic lattice [9, 10]. More generally, when a large number of metallic atoms aggregate in a slow manner at low temperature, then they take the shape of a regular polyhedron with the close packing structure [9]. Moreover, it is known that the structurally most stable are such symmetric crystalline nanoclusters that are invariant under the action of the point symmetry group of their crystal structure [11]. For example, the proper symmetry group of a cube (that covers the symmetry group of an octahedron) defines the (proper) point symmetry group of a face-centered cubic lattice [12].

Note also that, on the nanoscale level, the notion of the state of matter takes a new meaning. Namely, it follows from theoretical predictions, confirmed by the computer modelling and experimental observations, that at least for some particular sizes of the crystalline nanoclusters they would exhibit a coexistence of solid and liquid states within a finite range of temperature [3, 8]. This makes small clusters different from the bulk systems whose solid and liquid phases coexist only at a single temperature point, the melting point. Consequently, one may even attempt to identify the nanosystems as constituting a new phase of matter [10] – the *nanomatter*.

Most of the unique features of three-dimensional nanostructures arise from the very high ratio of the number of surface atoms to the total number of atoms in the cluster. Therefore, the surface energy substantially affects the properties of the bulk material [10]. Consequently, from the point of view of classical thermodynamics, we ought to consider a nanostructure as the one whole system, not an infinite family of subsystems (as it is admissible e.g. for bulk solids with nanoscale microstructure). Particularly, it means that surface effects that are not associated with the existence of boundary regions of nanoclusters, as it take place in the case of the above mentioned sodium nanostructures or fullerene molecules, can be then considered. Moreover, the thermodynamic generalized forces would have also a global character referable to one whole body only [13].

The main topics discussed in the paper are: (i) a group-theoretical analysis of such generalized thermodynamic forces that can be associated with the structurally stable elastic solid nanoclusters (see [13]) in a way consistent with the observed properties of such clusters (Secs. 2 and 3); (ii) the notion of quasi-solid state introduced in order to describe nanoclusters revealing the coexistence of solid and liquid states within a finite range of temperature (Secs. 4 and 5).

2. Generalized Thermodynamic Forces

The macroscopically small mean size of a nanocluster offers a possibility for treating its deformation and temperature as these approximated to uniform state variables of the cluster [13]. Thus, owing to this phenomenological approximation, we are in the framework of classical thermodynamics dealing with the so-called *homogeneous thermodynamic processes* [14, 15] considered as being dependent on the cluster size and shape [13]. Therefore, we will deal with homogeneous compact and connected nanoclus-

ters (called also *size-effect bodies* [13]) of immovable center of mass, homogeneously deformed and endowed with a uniform temperature. Spatial configurations of such a body can be identified with the subsets \mathcal{B} of the three-dimensional Euclidean vector space E^3 that have the form $\mathcal{B} = l(\mathbf{F})(\mathcal{B}_0)$ where $\mathcal{B}_0 \subset E^3$ is a distinguished spatial configuration of the body called its *reference configuration* and identified with the body itself, $l(\mathbf{F})$ denotes the following linear mapping in E^3 :

$$(2.1) \quad \begin{aligned} l(\mathbf{F})(\mathbf{X}) &= \mathbf{F}\mathbf{X}, & \mathbf{F} &\in GL^+(E^3), & \mathbf{X} &\in E^3, \\ GL^+(E^3) &= \{\mathbf{F} \in E^3 \otimes E^3 : \det \mathbf{F} > 0\}. \end{aligned}$$

Let $I \subset R_+$ be an interval of absolute temperatures and let $\Psi = \Psi(\mathcal{B}_0; \mathbf{F}, \theta)$, $\mathbf{F} \in GL^+(E^3)$, $\theta \in I$, denote the total *Helmholtz free energy* of the body \mathcal{B}_0 . We will assume that Ψ is of class C^k , $k \geq 2$, with respect to variables (\mathbf{F}, θ) . Moreover, the free energy function should be an objective scalar, that is for each pair $(\mathbf{F}, \theta) \in GL^+(E^3) \times I$ the following condition should be fulfilled:

$$(2.2) \quad \forall \mathbf{Q} \in SO(E^3), \quad \Psi(\mathcal{B}_0; \mathbf{Q}\mathbf{F}, \theta) = \Psi(\mathcal{B}_0; \mathbf{F}, \theta),$$

where $SO(E^3) \subset GL^+(E^3)$ denotes the proper orthogonal group on E^3 . The dependence of Ψ on the (compact and connected) geometrical figure \mathcal{B}_0 represents the dependence of thermomechanical properties of a nanocluster upon its size and shape [13].

In the classical thermodynamics, the mechanical influence on the body \mathcal{B}_0 can be introduced into the theory by what is called the Gibbs form on $GL^+(E^3) \times I$:

$$(2.3) \quad \Omega = dE - \theta dS + \mathbf{N} \cdot d\mathbf{F},$$

where E, S and \mathbf{N} denote the internal energy, entropy and the *generalized thermodynamic force*, respectively. The influence of mechanical action (i.e. the generalized thermodynamic force \mathbf{N}) and the temperature θ on the change of the internal energy is described by the following dissipation inequality:

$$(2.4) \quad \Omega(\mathcal{B}_0; \lambda) \leq 0.$$

for each *thermodynamic configuration* $\lambda = (\mathbf{F}, \theta)$ of \mathcal{B}_0 . If, according to the so-called effective principle of thermodynamic determinism [14], the following relations hold:

$$(2.5) \quad \mathbf{N} = \mathbf{N}(\mathcal{B}_0; \lambda), \quad S = S(\mathcal{B}_0; \lambda),$$

then the dissipation inequality is equivalent to the following formulae:

$$(2.6) \quad \mathbf{N} = -\frac{\partial \Psi}{\partial \mathbf{F}}, \quad S = -\frac{\partial \Psi}{\partial \theta},$$

stating that the free energy function is the so-called thermodynamic potential. Eq. (2.6) is then equivalent to the following condition:

$$(2.7) \quad -d\Psi = \mathbf{N} \cdot d\mathbf{F} + Sd\theta,$$

and the thermodynamic functions are related by the Legendre transformation:

$$(2.8) \quad \Psi = E - \theta S.$$

A *stationary state* of the nanocluster \mathcal{B}_0 is defined by the thermodynamic configuration $\lambda_0 = (\mathbf{F}_0, \theta_0)$ such that

$$(2.9) \quad d\Psi(\mathcal{B}_0; \lambda_0) = 0,$$

what is equivalent to the following conditions:

$$(2.10) \quad \mathbf{N}(\mathcal{B}_0; \lambda_0) = 0, \quad S(\mathcal{B}_0; \lambda_0) = 0.$$

The stationary states defined by $\lambda_0 = (\mathbf{1}, \theta_0)$ will be called *natural* at the temperature $\theta_0 \in I$. Note that, in general, the generalized thermodynamic force \mathbf{N} of Eqs. (2.3) and (2.4) may be dependent on the rate of change of the deformation tensor [13]. In this case, the free energy function is not a thermodynamic potential.

Let us consider, at each temperature $\theta \in I$, a symmetric and objective tensor function (e.g. [15]) $\mathbf{F} \rightarrow \mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta) \in E^3 \otimes E^3$ defined as [13]:

$$(2.11) \quad \begin{aligned} \mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta) &= -\frac{1}{V(\mathcal{B})} \mathbf{N}(\mathcal{B}_0; \mathbf{F}, \theta) \mathbf{F}^T, \\ V(\mathcal{B}) &= J(\mathbf{F})V(\mathcal{B}_0), \quad J(\mathbf{F}) = \det \mathbf{F}, \end{aligned}$$

where \mathbf{N} is the generalized thermodynamic force of Eq. (2.6) and $V(\mathcal{B})$ denotes the volume of \mathcal{B} . The tensor \mathbf{T} of Eq. (2.11), assigned to the one whole nanocluster, is a global counterpart of the Cauchy stress tensor for thermoelastic simple materials but it is not a measure of stress as normally understood. Nevertheless, \mathbf{N}^T can be interpreted as a dipole moment of internal surface forces acting on the nanocluster boundary [13]. Moreover, contrary to the thermoelastic simple materials for which the dissipation coming from the heat conduction appears, for the above defined *thermoelastic size-effect bodies* the only thermodynamically admissible processes are the reversible ones [13]. Consequently, a nanocluster can be treated as being *elastic within a certain range of temperature*. The objectivity of the tensor function of Eq. (2.11) means that should be [13]:

$$(2.12) \quad \begin{aligned} \mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta) &= \mathbf{R} \mathbf{h}(\mathcal{B}_0; \mathbf{U}, \theta) \mathbf{R}^T, \\ \mathbf{h}(\mathcal{B}_0; \mathbf{U}, \theta) &= V(\mathcal{B})^{-1} \partial_{\mathbf{U}} \Psi(\mathcal{B}_0; \mathbf{U}, \theta) \mathbf{U}, \end{aligned}$$

where the polar decomposition of \mathbf{F} was taken into account:

$$(2.13) \quad \mathbf{F} = \mathbf{R} \mathbf{U}, \quad \mathbf{R} \in SO(E^3), \quad \mathbf{U} = \mathbf{U}^T \in GL^+(E^3).$$

It should be stressed that the above model of homogeneous thermodynamic processes has been adapted to the description of macroscopically small clusters only. It is not the case of bulk nanomaterials for which the influence of inhomogeneity of nanostructure distortions seems to be the most interesting effect.

3. Insensibility Groups of Solid Nanoclusters

Let us consider the *insensibility group* $G_\theta(\mathcal{B}_0)$ of the elastic size-effect body \mathcal{B}_0 at the temperature $\theta \in I$ [13]:

$$(3.1) \quad \begin{aligned} G_\theta(\mathcal{B}_0) &= \{ \mathbf{H} \in SL(E^3) : \forall \mathbf{F} \in GL^+(E^3), \mathbf{T}(\mathcal{B}_0; \mathbf{F} \mathbf{H}, \theta) = \mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta) \}, \\ SL(E^3) &= \{ \mathbf{F} \in GL^+(E^3) : \det \mathbf{F} = 1 \}. \end{aligned}$$

It follows from Eqs. (2.6) and (2.11) that $\mathbf{H} \in G_\theta(\mathcal{B}_0)$ if and only if

$$(3.2) \quad \Psi(\mathcal{B}_0; \mathbf{F}, \theta) = \Psi(\mathcal{B}_0; \mathbf{F}\mathbf{H}, \theta) + \Psi(\mathcal{B}_0; \mathbf{1}, \theta) - \Psi(\mathcal{B}_0; \mathbf{H}, \theta)$$

for each $\mathbf{F} \in GL^+(E^3)$ [15]. We will say, imitating the concept of simple solid materials [15], that \mathcal{B}_0 is an (elastic) *undistorted solid nanocluster* (within the range I of temperatures – see Sec. 2) if

$$(3.3) \quad \forall \theta \in I, \quad G_\theta(\mathcal{B}_0) \subset SO(E^3).$$

Then, according to (3.2):

$$(3.4) \quad G_\theta(\mathcal{B}_0) = \{\mathbf{Q} \in SO(E^3) : \forall \mathbf{F} \in GL^+(E^3), \Psi(\mathcal{B}_0; \mathbf{F}\mathbf{Q}, \theta) = \Psi(\mathcal{B}_0; \mathbf{F}, \theta)\}.$$

Note that in particular applications concerning solid bodies, the existence of an *unstressed* spatial configuration of the body is usually assumed [15]. We will denote by $\mathcal{B}_0 = \mathcal{B}_{\theta_0}$ an undistorted solid nanocluster \mathcal{B}_0 such that

$$(3.5) \quad \exists \theta_0 \in I, \quad \mathbf{T}(\mathcal{B}_0; \mathbf{1}, \theta_0) = \mathbf{0}.$$

For example, it is the case of undistorted solid nanocluster \mathcal{B}_0 being in a natural stationary state (Sec. 2). Further on, we will restrict ourselves, taking into account remarks concerning the stability of nanoclusters (Sec. 1), to the case of undistorted solid nanoclusters being *structurally stable* in this sense that

$$(3.6) \quad \forall \theta \in I, \quad G_\theta(\mathcal{B}_0) \subset h(\mathcal{B}_0),$$

where $h(\mathcal{B}_0)$ is the group of rotational symmetries of \mathcal{B}_0 :

$$(3.7) \quad h(\mathcal{B}_0) = \{\mathbf{Q} \in SO(E^3) : l(\mathbf{Q})(\mathcal{B}_0) = \mathcal{B}_0\}.$$

Eqs. (2.11)–(2.13) and (3.1)–(3.7) define a nanoscale counterpart of the well-known phenomenological representation of macroscopic properties of the elastic solid bodies (see e.g. [15]) and we will assume that it describes the thermomechanical properties of the considered nanoclusters.

Let us $\mathcal{B}_I = \{\mathcal{B}_\theta, \theta \in I\}$ denote the family of structurally stable undistorted solid nanoclusters of the form $\mathcal{B}_\theta = l(\mathbf{P}_\theta)(\mathcal{B}_0)$, $\mathbf{P}_\theta \in GL^+(E^3)$, and let $g \subset SO(E^3)$ be a subgroup of rotations. If

$$(3.8) \quad \forall \theta \in I, \quad G_\theta(\mathcal{B}_\theta) = \mathbf{P}_\theta g \mathbf{P}_\theta^{-1} \subset h(\mathcal{B}_\theta),$$

then we will say that nanoclusters $\mathcal{B}_\theta \in \mathcal{B}_I$ belong to the same g – class. Particularly, if g is a (proper) point symmetry group of a Bravais lattice, we will say also that nanoclusters $\mathcal{B}_\theta, \theta \in I$, belong to the same *crystallographic class*. Let us consider the polar decomposition of \mathbf{P}_θ :

$$(3.9) \quad \begin{aligned} \mathbf{P}_\theta &= \mathbf{R}(\theta)\mathbf{U}(\theta), \\ \mathbf{R}(\theta) &\in SO(E^3), \quad \mathbf{U}(\theta) = \mathbf{U}(\theta)^T \in GL^+(E^3). \end{aligned}$$

It can be shown [15] that, at each temperature $\theta \in I$, Eqs. (3.8) and (3.9) are equivalent to the following two conditions:

$$(3.10) \quad G_\theta(\mathcal{B}_\theta) = \mathbf{R}(\theta)g\mathbf{R}(\theta)^T,$$

and

$$(3.11) \quad \forall \mathbf{Q} \in g, \quad \mathbf{Q}\mathbf{U}(\theta)\mathbf{Q}^T = \mathbf{U}(\theta).$$

It follows from Eqs. (3.8), (3.10) and (3.11) that it should be:

$$(3.12) \quad \forall \theta \in I, \quad \mathbf{R}(\theta) \in h(\mathcal{B}_\theta) \quad \text{and} \quad g \subset h(\mathcal{B}_\theta).$$

According to the well-known theorem concerning finite subgroups of the proper rotation group $SO(3)$, there exists a correspondence between symmetries of regular polyhedrons and these finite subgroups. Namely [12, 16]: symmetries of a *tetrahedron* defines the tetrahedron group T , symmetries of an *octahedron* defines the octahedron group O and symmetries of an *icosahedron* defines the icosahedron group I . Moreover, a *cube* has the same symmetry group as an octahedron and *dodecahedron* has the some symmetry group as an icosahedron [16]. It follows from Eq. (3.11) that if

$$(3.13) \quad g = O,$$

then

$$(3.14) \quad \mathbf{U}(\theta) = \alpha(\theta)\mathbf{1}, \quad \alpha(\theta) > 0,$$

and, according to Eqs. (3.6), (3.7), (3.10) and (3.11), Eq. (3.14) is also valid for $g = SO(E^3)$ and \mathcal{B}_θ being a *ball* of the radius $R(\theta)$. If

$$(3.15) \quad g = T \subset O,$$

then

$$(3.16) \quad \begin{aligned} \mathbf{U}(\theta) &= \alpha(\theta)\mathbf{1} + \beta(\theta)\mathbf{k} \otimes \mathbf{k}, \\ \alpha(\theta) &> 0, \quad \alpha(\theta) + \beta(\theta) > 0, \quad \mathbf{k} \cdot \mathbf{k} = 1. \end{aligned}$$

Eq. (3.16) is also valid for $g = G(\mathbf{k})$ – the group of all rotations about an axis parallel to the versor \mathbf{k} . In this case the nanocluster boundary $\partial\mathcal{B}_\theta$ should be e.g. a *surface of revolution* with the axis of revolution parallel to \mathbf{k} . The groups $SO(E^3)$ and $G(\mathbf{k})$ as well as the icosahedron group I are not crystallographic point groups [12, 15, 16]. However, the groups O and T are point groups corresponding to the *cubic* crystallographic system and to the *tetragonal* (and *hexagonal*) crystallographic system, respectively [12, 15, 16]. Therefore, according to (3.12), structurally stable are e.g. nanoclusters $\mathcal{B}_\theta, \theta \in I$, such that: (i) \mathcal{B}_0 is an isotropic ball or a ball with a cubic crystal lattice; (ii) \mathcal{B}_0 has the boundary $\partial\mathcal{B}_0$ being a surface of revolution and \mathcal{B}_0 is transversally isotropic or with a tetragonal or hexagonal crystal lattice. Note that in both above examples the corresponding tensors $\mathbf{U}(\theta)$ (of Eq. (3.14) in the case (i) or of Eq. (3.16) in the case (ii)) define *shape preserving transformations* $\mathcal{B}_0 \rightarrow \mathcal{B}_\theta, \theta \in I$. If additionally

$$(3.17) \quad \forall \theta \in I: \quad \mathbf{R}(\theta) = \mathbf{1}, \quad \mathbf{T}(\mathcal{B}_\theta; \mathbf{1}, \theta) = \mathbf{O},$$

then these shape preserving transformations can be identified with *free thermal distortions* of \mathcal{B}_0 and thus the family $\mathcal{B}_I = \{\mathcal{B}_\theta, \theta \in I\}$ consists of *thermally equivalent nanoclusters*.

It is observed that if the temperature of an equilibrium polyhedral nanocluster increases to the sufficiently high level, then in general, a nanocluster shape can be transformed into an equilibrium curvature shape [8]. So, we can consider e.g. the case when a dodecahedron or icosahedron takes, at a sufficiently high temperature, a spherical shape. It can be viewed as a kind of phase transition of nanoclusters. Although it is not an universal phenomenon (it is not observed e.g. for small gold particles - [8]), we assume that the temperatures under consideration are not too high.

4. Quasi-Solid State

It is known that nanoclusters can exhibit, as it was mentioned in Sec. 1, a coexistence of solid and liquid states in a finite interval of absolute temperature. It seems to be consistent with the fact that if the observation level is sufficiently low, then we can observe the same symmetry elements in the solid and fluid states. Namely, it is known that metallic clusters with small number of atoms crystallize in the form of icosahedra (Sec. 1). On the other hand, it is observed that the liquid state exhibits short-range order extending only a few atomic distances given by the liquid correlation length, which is typically 3–8 Å in a simple liquid; for example, an icosahedral (short-range) arrangement has been found in a liquid [17].

The above consistency suggests that the coexistence of solid and liquid states for nanoclusters should be also consistent with the nanoscale thermomechanical properties of solid nanoclusters discussed in Secs. 2 and 3. First of all, since in the framework of the macroscopic local approximation fluids are isotropic materials [15], let us consider the well-known isotropic invariants of the deformation tensor \mathbf{F} :

$$(4.1) \quad \begin{aligned} \text{I} &= \text{tr } \mathbf{U} = \lambda_1 + \lambda_2 + \lambda_3, \\ \text{II} &= \frac{1}{2}[(\text{tr } \mathbf{U})^2 - \text{tr } \mathbf{U}^2] = \lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_1\lambda_3, \\ \text{III} &= \det \mathbf{U} = \lambda_1\lambda_2\lambda_3, \end{aligned}$$

where Eq. (2.13) and the formulae:

$$(4.2) \quad \begin{aligned} \mathbf{U}\mathbf{e}_k &= \lambda_k\mathbf{e}_k, & k &= 1, 2, 3, \\ \mathbf{e}_k \cdot \mathbf{e}_l &= \delta_{kl}, & \lambda_k &> 0, \end{aligned}$$

were taken into account. If \mathcal{B}_0 is a cube with edges of length a directed along \mathbf{e}_k - directions of Eq. (4.2), then the deformation tensor of Eq. (2.13) defines the rectangular parallelepiped $\mathcal{B} = l(\mathbf{F})(\mathcal{B}_0)$ whose concurrent edges have directions $\mathbf{a}_k = \mathbf{R}\mathbf{e}_k$ and lengths $a_k = \lambda_k a$, $k = 1, 2, 3$. The volume $V = V(\mathcal{B})$ of \mathcal{B} , the surface field $F = F(\partial\mathcal{B})$ of the boundary $\partial\mathcal{B}$ of \mathcal{B} , and the total mean curvature $M = M(\partial\mathcal{B})$ of $\partial\mathcal{B}$ are given by [18]:

$$(4.3) \quad \begin{aligned} V &= a_1 a_2 a_3 = a^3 \text{III}, \\ F &= 2(a_1 a_2 + a_2 a_3 + a_1 a_3) = 2a^2 \text{II}, \\ M &= \pi(a_1 + a_2 + a_3) = \pi a \text{I}. \end{aligned}$$

A fluid is commonly regarded as a material having “no preferred configuration” [15]. It suggests to consider a nanoscale counterpart of such understood elastic isotropic materials defined by:

$$(4.4) \quad \Psi(\mathcal{B}_0; \mathbf{F}, \theta) = \Phi_\theta(V, F, M), \quad \theta \in I.$$

We will extend Eq. (4.4) on all compact and convex nanoclusters \mathcal{B}_0 . V, F and M are defined now as global geometrical characteristics of the corresponding sets $\mathcal{B} = l(\mathbf{F})(\mathcal{B}_0)$. Note that the formula

$$(4.5) \quad \Phi_\theta(V, F, M) = a(\theta)V + b(\theta)F + c(\theta)M + d(\theta),$$

has been introduced in [13] as a particular case of the free energy function of an elastic size-effect body with the *liquid-like response* defined by the following conditions:

$$(4.6) \quad \begin{aligned} \Psi(\mathcal{B}_0; \mathbf{F}, \theta) &= \Phi_\theta(l(\mathbf{F})(\mathcal{B}_0)), \\ \forall \mathbf{Q} \in SO(E^3), \quad \Phi_\theta(l(\mathbf{Q})(\mathcal{B})) &= \Phi_\theta(\mathcal{B}), \end{aligned}$$

where $\mathcal{B} = l(\mathbf{F})(\mathcal{B}_0)$ and the objectivity condition of Eq. (2.2) was taken into account.

It follows from Eq. (4.4) that (see Sec. 3):

$$(4.7) \quad \forall \theta \in I, \quad h(\mathcal{B}_0) \subset G_\theta(\mathcal{B}_0) \subset SL(E^3),$$

and

$$(4.8) \quad \forall \theta \in I, \quad G_\theta(\mathcal{B}_0) = SL(E^3),$$

iff

$$(4.9) \quad \forall \theta \in I, \quad \Psi(\mathcal{B}_0; \mathbf{F}, \theta) = \Phi_\theta(V).$$

The free energy function of Eq. (4.9) describes an elastic fluid or gas. So, if the free energy function of Eq. (4.4) does not reduce to its form of Eq. (4.9), then the general condition of Eq. (3.3) can be assumed. Consequently, \mathcal{B}_0 is then an (elastic) undistorted *solid nanocluster* (within the range I of temperatures) such that

$$(4.10) \quad \forall \theta \in I, \quad h(\mathcal{B}_0) \subset G_\theta(\mathcal{B}_0) \subset SO(E^3),$$

and thus these solid nanoclusters are structurally stable iff

$$(4.11) \quad \forall \theta \in I, \quad G_\theta(\mathcal{B}_0) = h(\mathcal{B}_0).$$

We see that the liquid-like response of a nanocluster \mathcal{B}_0 defined by Eq. (4.4) admits, in general, its solid state as well as gaseous or liquid states. We will say, taking into

account this statement, that the free energy function of Eq. (4.4) describes the *quasi-solid state* of the nanocluster \mathcal{B}_0 . Equation (4.10) means that it is a solid nanocluster (Sec. 3) being in the quasi-solid state. It follows from Eqs. (2.12), (2.13) and (4.4) that in the quasi-solid state:

$$(4.12) \quad \begin{aligned} \mathbf{T}(\mathcal{B}_0; \mathbf{F}, \theta) &= \frac{\partial \Phi_\theta}{\partial V}(V, F, M) \mathbf{1} + \mathbf{R}t(\mathcal{B}_0; \mathbf{U}, \theta) \mathbf{R}^T, \\ t(\mathcal{B}_0; \mathbf{U}, \theta) &= \frac{1}{V} \left(\frac{\partial \Phi_\theta}{\partial F} \partial_{\mathbf{U}} F + \frac{\partial \Phi_\theta}{\partial M} \partial_{\mathbf{U}} M \right) \mathbf{U}. \end{aligned}$$

If

$$(4.13) \quad T_\infty(\theta) = \lim_{V \rightarrow \infty} (\partial \Phi_\theta / \partial V) < \infty,$$

$$\lim_{V \rightarrow \infty} \frac{1}{V} (\partial \Phi_\theta / \partial F) = \lim_{V \rightarrow \infty} \frac{1}{V} (\partial \Phi_\theta / \partial M) = 0,$$

then $T_\infty(\theta)$ defines an asymptotic uniform tension dependent on bulk interatomic interactions only, and the tensor t is a measure of the influence of surface atoms on the bulk mechanical properties of nanoclusters. For example it is the case of Eq. (4.5).

If \mathcal{B}_0 and $\mathcal{B}_P = l(\mathbf{P})(\mathcal{B}_0)$, $\mathbf{P} \in GL^+(E^3)$, are elastic size-effect solid bodies with the liquid-like response, then it should be:

$$(4.14) \quad \begin{aligned} G_\theta(\mathcal{B}_P) &= \mathbf{P} G_\theta(\mathcal{B}_0) \mathbf{P}^{-1} \subset SO(E^3), \\ G_\theta(\mathcal{B}_0) &\subset SO(E^3), \quad \theta \in I, \end{aligned}$$

where Eqs. (3.4), (4.6) and (4.10) were taken into account. Thus, denoting

$$(4.15) \quad \mathbf{P} = \mathbf{R}(\mathbf{P}) \mathbf{U}(\mathbf{P}),$$

we obtain that

$$(4.16) \quad G_\theta(\mathcal{B}_P) = \mathbf{R}(\mathbf{P}) G_\theta(\mathcal{B}_0) \mathbf{R}(\mathbf{P})^{-1}$$

and

$$(4.17) \quad \forall \mathbf{Q} \in G_\theta(\mathcal{B}_0), \quad \mathbf{Q} \mathbf{U}(\mathbf{P}) \mathbf{Q}^T = \mathbf{U}(\mathbf{P})$$

where Eqs. (3.8)–(3.11) with $SO(E^3)$ in place of $h(\mathcal{B}_0)$ were taken into account. Moreover, we have:

$$(4.18) \quad h(\mathcal{B}_0) \subset G_\theta(\mathcal{B}_0), \quad h(\mathcal{B}_P) \subset G_\theta(\mathcal{B}_P).$$

For example, if

$$(4.19) \quad \begin{aligned} \mathbf{T}(\mathcal{B}_\theta; \mathbf{1}, \theta) &= \mathbf{0}, \\ \mathcal{B}_\theta &= l(\mathbf{P}_\theta)(\mathcal{B}_0), \quad \mathcal{B}_0 = \mathcal{B}_{\theta_0} \end{aligned}$$

then Eqs. (4.16)–(4.18) with $\mathbf{P} = \mathbf{P}_\theta$ describe the influence of temperature on the insensibility groups of undistorted and unstressed elastic size-effect bodies \mathcal{B}_θ , $\theta \in I$, with the liquid-like response (cf. Eqs. (3.8)–(3.11) and (3.13)–(3.16) with $G_\theta(\mathcal{B}_0)$ in place of g).

5. Final Remarks

It has been observed that the most stable small metallic clusters have an almost spherical shape. The oblate or prolate shape of such a cluster means that its structure is less stable [9]. Therefore, it is physically reasonable to consider also the influence of the degree of sphericity of compact and simply connected deformed nanoclusters on their properties. Let us define the following effective radii:

$$(5.1) \quad r_V = \left(\frac{3V}{4\pi}\right)^{1/3}, \quad r_F = \frac{1}{2} \left(\frac{F}{\pi}\right)^{1/2}, \quad r_M = \frac{M}{4\pi},$$

where V , F and M denote the volume of a cluster, the surface field and the total mean curvature of its boundary, respectively. Note that the quantity $2r_M$ is in the rock analysis and stereographic metallography interpreted as the mean grain width [13]. Note also that if we restrict ourselves to compact and convex three-dimensional bodies, then the following inequalities hold [19]:

$$(5.2) \quad r_V \geq r_F \geq r_M.$$

In each of these three relations equality is attained in the case of a ball, and in this case only. Next, let us introduce the following *shape coefficient*:

$$(5.3) \quad \kappa = \frac{r_V}{r_F}.$$

Since $\kappa = 1$ if the deformed nanocluster \mathcal{B} is a ball [19], the nondimensional quantity $\kappa = \kappa(\mathcal{B})$ can be taken as a measure of degree of sphericity of \mathcal{B} . In the literature is also considered, as a measure of the degree of sphericity, the following quantity [20]:

$$(5.4) \quad K = \frac{VF_V}{FV_F},$$

where it was denoted:

$$(5.5) \quad F_V = 4\pi r_V^2, \quad V_F = (4/3)\pi r_F^3.$$

Since

$$(5.6) \quad K = \kappa^5,$$

K and κ are equivalent measures. For example, for regular polyhedra $\mathcal{B} = \mathcal{B}_0$, an icosahedron has the highest shape coefficient κ ($K = 0.855 - [19]$). It is the case of metallic nanoclusters with a small number of atoms (Sec. 1). Consequently, we can expect that the regular polyhedra $\mathcal{B} = \mathcal{B}_0$ observed for a large number of atoms (Sec. 1) correspond to less stable shapes of nanoclusters than the icosahedral nanocluster is. Namely, we have [20]: $K = 0.791$ for a dodecahedron, $K = 0.657$ for an octahedron, $K = 0.583$ for a cube, and $K = 0.370$ for a tetrahedron.

The physical distinction of the spherical shape suggests also to consider such a class of functions Φ_θ of Eq. (4.4) that takes into account this shape effect as well as the observed size effect of nanoclusters. It can be realized e.g. in this manner. First of

all, let us observe that it is physically reasonable to restrict ourselves to functions Φ_θ symmetric with respect to their arguments V, F, M . So, let us introduce three elementary symmetric functions [21] $S_n, n = 1, 2, 3$, of arguments r_V, r_F and r_M , defined as:

$$(5.7) \quad \begin{aligned} S_1 &= r_V + r_F + r_M = l_0 I, & I &= \lambda_V + \lambda_F + \lambda_M, \\ S_2 &= r_V r_M + r_M r_F + r_F r_V = l_0^2 II, & II &= \lambda_V \lambda_M + \lambda_M \lambda_F + \lambda_F \lambda_V, \\ S_3 &= r_V r_F r_M = l_0^3 III, & III &= \lambda_V \lambda_F \lambda_M, \quad l_0 > 0, \end{aligned}$$

where l_0 is a characteristic length of the considered nanoclusters (e.g. the mean size of nanoclusters revealing the coexistence of solid and liquid states [3]; see Section 1) and

$$(5.8) \quad \lambda_V = r_V/l_0, \quad \lambda_F = r_F/l_0, \quad \lambda_M = r_M/l_0,$$

are nondimensional variables. Since we consider Eq. (4.4) for compact and convex nanoclusters only, the following inequalities would be fulfilled:

$$(5.9) \quad \lambda_V \leq \lambda_F \leq \lambda_M,$$

where Eq. (5.2) was taken into account. Moreover, introducing the new variables ξ and η by:

$$(5.10) \quad \xi = \frac{\lambda_F}{\lambda_M}, \quad \eta = \frac{\lambda_V}{\lambda_M},$$

we obtain that [19]:

$$(5.11) \quad 0 \leq \eta \leq \xi^{4/3} \leq 1, \quad 0 < \kappa = \eta/\xi \leq 1$$

and $\xi = 1$ or $\eta = 1$ iff the deformed nanocluster \mathcal{B} is a ball.

Now, assuming that (cf. Eqs. (4.1)–(4.4)):

$$(5.12) \quad \Phi_\theta(V, F, M) = \varphi_\theta(S_3, S_2, S_1) = \sigma_\theta(l_0; III, II, I)$$

we obtain an example of the considered class of functions Φ_θ . Another example of this function define the following symmetric functions [21]:

$$(5.13) \quad S_n = r_V^n + r_F^n + r_M^n = \left(\frac{d}{2}\right)^n (1 + \xi^n + \eta^n), \quad d = 2r_M, \quad n = 1, 2, 3,$$

where d can be interpreted as the actual mean nanocluster width (see the commentary following Eq. (5.1)). Therefore:

$$(5.14) \quad \Phi_\theta(V, F, M) = \sigma_\theta(d; \xi, \eta) = \sigma_\theta(d; \eta, \xi),$$

where the variables ξ and η are constrained by Eq. (5.11) and describe the shape effect while the variable d describes the size effect. Moreover, for physical reasons (see Sec. 1), it should be:

$$(5.15) \quad 0 < \frac{l_0}{d} \in \langle \alpha, \beta \rangle,$$

where l_0 is a characteristic length of the nanocluster (e.g. $l_0 = d_0$ – such a mean nanocluster width for which it exhibits a coexistence of solid and liquid states).

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