The "critical limits for crystallinity" in nanoparticles of the elements: A combined thermodynamic and crystallographic critique

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A B S T R A C T

The theme of the present work is the procedure for evaluating the minimum size for the stability of a crystalline particle with respect to the same group of atoms but in the amorphous state. A key goal of the study is the critical analysis of an extensively quoted paper by F.G. Shi [J. Mater. Res. 9 (1994) 1307–1313], who presented a criterion for evaluating a "crystallinity distance" (h) through its relation with the "critical diameter" (d_C) of a particle, i.e., the diameter below which no particles with the crystalline structure are expected to exist at finite temperatures. Key assumptions of Shi's model are a direct proportionality relation between h and d_C, and a prescription for estimating h from crystallographic information. In the present work the accuracy of the Shi model is assessed with particular reference to nanoparticles of the elements. To this end, an alternative way to obtain h, that better realizes Shi's idea of this quantity as "the height of a monolayer of atoms on the bulk crystal surface", is explored. Moreover, a thermodynamic calculation of d_C, which involves a description of the bulk- and the surface contributions to the crystalline/amorphous relative phase stability for nanoparticles, is performed. It is shown that the Shi equation does not account for the key features of the h vs. d_C relation established in the current work. Consequently, it is concluded that the parameter h obtained only from information about the structure of the crystalline phase, does not provide an accurate route to estimate the quantity d_C. In fact, a key result of the current study is that d_C crucially depends on the relation between bulk- and surface contributions to the crystalline/ amorphous relative thermodynamic stability.

1. Introduction

There is ample evidence that the sintering and alloying ability, mechanical strength, critical temperatures for phase transitions, catalytic properties and other physicochemical properties of nanoparticles are strongly size-dependent [see, for example [1–6]]. More specifically, it is often hypothesized that the differences between the properties of the nanoparticles and the macroscopic material can be understood in terms of the surface-to-volume ratio, which is a measure of the amount of atoms located at the surface compared to that in the bulk [7,8]. A further, conceptually related issue, is that of the minimum size for a stable crystalline nanoparticle. Since crystallinity is a long-range characteristic of the material, when the fraction of the total number of atoms located at its surface is sufficiently large, a non-crystalline (in the following "an amorphous") phase might become more stable [9]. In a pioneering and extensively quoted paper, Shi [10] suggested that such critical condition

would be realized in a spherical nanoparticle of diameter d_C, for which all the atoms are accommodated as if they were located at the surface. This idea was quantitatively expressed by introducing the distance h, which was defined by Shi as "the height of a monolayer of atoms on the bulk crystal surface" [10]. By equating the volume of the spherical nanoparticle of diameter d_C with that of a thin spherical shell of the same diameter and width h, the following relation was established [10].

$$\frac{4}{3}\,\pi\left(\frac{d_C}{2}\right)^3 = 4\,\pi\left(\frac{d_C}{2}\right)^2 h \tag{1}$$

The so-determined critical diameter, which is directly related to the distance h through the relation

$$d_C = 6\,h \tag{2}$$

was adopted by Shi to represent a "crystallinity limit", i.e., the size below

which no particles with the crystalline structure are expected to exist at finite temperatures [10].

In order to apply eq. (2), Shi [10] assumed that h was related to the lattice parameter a of the crystalline material. Specifically, it was postulated without further arguments that $h = a/2$ and $h = a/4$ for the face centered cubic and diamond structures, respectively.

A survey of the standard citation databases indicates that the Shi paper has been extensively quoted (223 times according to Scopus). In particular, the concept of a critical distance has been included in theoretical analyses of the size-dependence of the melting temperature of nanoparticles [11–13], and Shi's values for h have been used to interpret experiments on the solid/liquid transition [14]. Contrasting with the ample use of this approach, it is noteworthy that a critical evaluation of its accuracy has not yet been reported. Such an assessment has been performed in the present work, which has been motivated by the following critical issues.

The first issue concerns the Shi prescription to estimate h. At first glance, one would have expected that the distance between close-packed planes in the face centered cubic structures ($\sqrt{3}\,a/3$) could be a better estimate for "the height of a monolayer of atoms on the bulk crystal surface". Such alternative crystallographic criterion would yield a new set of h values.

The second issue concerns the need for an independent method to determine d_C. Since this critical radius expresses the crystalline/amorphous relative stability, it is natural to expect that a thermodynamic approach would provide additional insight on the d_C values.

Both issues will be addressed in the following work by using information on the elements. Once the new, theoretically based h and d_C values had been determined, a critical discussion of the Shi [10] relation for the crystallinity limit, which is expressed by eq. (2) will be performed.

2. Thermodynamic relations

A "top-down" thermodynamic approach has recently been developed by the current authors to determine the relative stability between the crystalline and the amorphous phases of a nanoparticle as a function of the particle radius [15]. The most general formulation of the approach and its experimental test has been presented elsewhere [15]. In the following, only the relations of relevance for the present work are reviewed.

The Gibbs energy of formation (ΔG^ϕ) of a nanoparticle of an element in phase ϕ is expressed as the sum of two contributions:

$$\Delta G^\phi = \Delta^0 G^{\phi/st} + \Delta G^{\gamma,\phi} \tag{3}$$

where $\Delta^0 G^{\phi/st}$ is the "lattice-stability" of ϕ relative to the stable structure of the element [16] and $\Delta G^{\gamma,\phi}$ is the surface contribution to Gibbs energy. In the present work the focus is on the crystalline ("cr") and the amorphous ("am") phases, and the reference stable structure will be the crystalline one, i.e., $\Delta^0 G^{cr/st} = 0$. This implies that only the term $\Delta^0 G^{am/st} = \Delta^0 G^{am/cr}$ has to be determined at the temperature of interest (T_0), viz., at $T_0 = 300\,K$.

The second term in eq. (3) can be expressed as [15]:

$$\Delta G^{\gamma,\phi} = \left(\frac{\Sigma}{\Omega}\right) \gamma^\phi\, V^\phi = \left(\frac{6}{d}\right) \gamma^\phi\, V^\phi \tag{4}$$

where γ^ϕ and V^ϕ ($\phi = $ cr, am) are the surface energy per unit area and molar volume of the material, $\Sigma = \pi\, d^2$ the surface, $\Omega = \pi\, \frac{d^3}{6}$ the volume and d the diameter of the spherical particle. Eq. (4) was applied assuming that both phases have the same shape, viz., spherical. The molar volumes V^{cr} for the elements were taken from Ref. [17]. Lacking a consistent set of values for V^{am}, and taking into account a plausible expansion associated to the transition from the crystalline to the amorphous phase, the approximation $V^{am} = 1.01\, V^{cr}$ was adopted at 300 K.

In this equation the γ^ϕ parameter for the amorphous and the crystalline phase is a temperature dependent quantity. Furthermore, the γ^ϕ parameters are assumed to depend upon the curvature of the particle. This problem is the subject of an extensive literature, and various alternative equations have been presented to account for the effect of the diameter d of the particle upon γ^ϕ [18–20]. In particular, the equation by Tolman [18–20] was adopted

$$\gamma^\phi(T) = \left(\frac{d}{d + 4\,\delta^\phi}\right) \gamma_\infty^\phi(T) \tag{5}$$

In eq. (5), the surface energy parameter $\gamma_\infty^\phi(T)$ is a solely temperature-dependent quantity which is assessed in the next section, and δ^ϕ, which is the so-called Tolman parameter, characterizes the width of the interface [18–20]. In the present work, lacking more specific information, the Tolman parameter of both phases was related to the spacing h between the close-packed planes in the crystalline phase, by introducing the proportionality parameter α, viz.,

$$\delta^{am} = \delta^{cr} = \delta = \alpha\, h (0 \leq \alpha \leq 1) \tag{6}$$

By combining eqs. (3)–(6), the following expression was obtained for the diameter of the smallest crystalline particle which is stable with respect to the amorphous phase:

$$d_C + 4\,\delta = \frac{6\left(V^{cr}\gamma_\infty^{cr} - V^{am}\gamma_\infty^{am}\right)}{\Delta^0 G^{am/cr}(T_0)} \tag{7}$$

The assessment of the thermodynamic information involved in the application of eq. (7) to the elements of the Periodic Table is presented in the following sections.

3. Assessment of thermodynamic properties

The lattice-stability and surface Gibbs energy of the amorphous phases of the elements are poorly known from experiments. On the basis of the satisfactory results obtained in Ref. [15], these properties were modeled by identifying the amorphous with a liquid phase undercooled to very low temperatures, as follows.

3.1. Lattice-stability modeling and estimation methods

The lattice-stability term was modeled by assuming that: i) there will be a glass transition in the undercooled liquid ("ucl") at a temperature T_G usually located between one third and one half of the melting temperature (T_M); ii) below that point the heat capacity of the liquid would be similar to that of the crystalline phase; and, iii) at the glass transition the entropy of the liquid will be more or less approaching the entropy of the crystalline phase. Assuming these widely accepted ideas, and following [21], a qualitative curve for the temperature dependence of the entropy difference between the undercooled liquid and the crystalline phase ($\Delta^0 S^{ucl/cr}$) might be sketched as in Fig. 1a. The curve flattens below T_G and the entropy plateau has a negligible value due to assumption (iii).

The corresponding lattice-stability ($\Delta^0 G^{ucl/cr}$) function is presented in Fig. 1b using a thick black solid line. The current premises imply that the high temperature behavior of the liquid phase ("liq"), denoted as $\Delta^0 G^{liq/cr}$ (blue line in Fig. 1b), has to be extrapolated for temperatures below T_G as an approximately horizontal line to obtain the $\Delta^0 G^{ucl/cr}$ vs. T relation. This expectation is accounted for by the thick black solid line in Fig. 1b, which was drawn by assuming that $\Delta^0 S^{ucl/cr}$ diminishes gradually on cooling from the melting point down to T_G and then goes to zero.

On the basis of the thermodynamic behavior represented in Fig. 1, two alternative evaluations of $\Delta^0 G^{am/cr}(T_0)$ were performed. The first evaluation is based on directly identifying the amorphous phase with the undercooled liquid below T_G, and determining the lattice-stability value to be inserted in eq. (7) as: