



Atomistic investigations of melting characterization in metallic nanostructures

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ABSTRACT

Melting temperatures, for bulk materials at constant pressure, remain constant for given materials. In case of nanomaterials however, melting temperature is subject to changes in the shape and size of the material. In this work, the liquid shell nucleation and the liquid skin nucleation and growth models, along with empirical relations, are used to predict the melting temperatures of Pt, Au and Ag nanowires and nanofilms. The melting temperatures are calculated taking into account the phenomenon of surface melting and the criteria of stability of the surface liquid layer. For platinum and gold, which are susceptible to surface melting, the liquidus and solidus curves are built, that characterize nanowire melting.

1. Introduction

By the simplest definition, melting temperature of a substance is the temperature at which a solid changes its state to a liquid. For bulk materials, this temperature point remains constant. But as we keep on reducing the size of the material, something interesting happens. As we enter the nano regime, the melting temperature no longer remains a constancy of the material, but rather changes with the slightest change in the material dimensions. Nanomaterials have suppressed melting temperatures with respect to their bulk counterparts owing to the enlarged relative surface area at that small size. Hence, nanomaterials can be melted at temperatures lower than the material melting point [1-5]. Also, if small size nanoparticles are embedded in a matrix of a material with higher melting point, then due to superheating, the melting temperature of such nanoparticles can be increased beyond the conventional melting point of the material [6]. This is the reason the analysis of low dimensional materials has captivated the attention of many scientists. As the dimensions of a crystal decreases, its relative surface area increases. More and more atoms occupy the surface and hence, the surface area to volume ratio plays a significant role in determining the properties of the material. Nanomaterials don't just behave as fragments of bulk materials but rather, entirely different structures in themselves. As the reactivity of any substance depends on

its surface area, low dimensional materials have greater reactivities and hence, their properties are far different from their bulk counterparts. By controlling the size and shape of the crystal, the surface area can be modified and hence, different materials can be engineered according to our needs. For this, a detailed study of different properties of the material is needed to be done.

One such property, the melting temperature, is being studied intensively. Though seemingly simple, melting is a very complex phenomenon whose all mechanisms have not yet been understood fully. Scientists have been trying to understand the mechanism behind melting as far back as the 1890's. From the point of view of classical thermodynamics, melting is a first order phase transition, occurring at a temperature where the Gibbs free energy of a solid and liquid become equal [7]. However, this definition is a loose one and gives no information about the mechanism leading to melting. Many intensive and extensive studies have been carried out by scientists and a large number of models [2-6, 8-14] have been put forth as a way to theoretically predict the melting temperature of such nanomaterials. The first established attempt to predict the melting temperature of bulk crystalline materials was given by Sutherland [7, 15] in 1891, in his kinetic theory of solids, wherein he considered atoms as hard spheres vibrating against each other. The idea behind this theory was his observation that as the temperature of a material increases, the

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thermal vibrations of atoms in that material increase. Frederick Lindemann [7] advanced this theory and stated that melting should be expected when temperature becomes high enough so that direct collisions start occurring between neighboring vibrating atoms. Gilvarry [7] modified the Lindemann rule further and computed that melting is expected when the root mean square of the amplitude of vibrations of atoms exceeds a threshold value, i. e. when the amplitude reaches at least 10% of the nearest neighbor distance [1]. This is the form of Lindemann criterion [7] used widely now. This theory is a one phase theory and is not completely accurate as it does not take the free energy of the liquid state into account; however, it is still widely used as the basis of most melting theories.

By all these theories and experimental investigations [7, 16], we further came to the understanding that melting is a surface phenomenon. It initiates at the surface of the nanocrystal and moves inward toward the crystal core, thus undergoing a first order phase transition between solid and liquid phase. All types of melting models in the classical regime can usually be divided into 3 categories [17, 18]:

- 1 Homogeneous melting model
- 2 Liquid shell nucleation model
- 3 Liquid skin nucleation and growth model (with an unstable liquid skin)

A semi-infinite solid is a crystal containing free surfaces. As explained in [7, 19] consider such a solid to be in equilibrium with its own vapor at pressure P and temperature T . Now we know, at the bulk triple point (T_{mb}, P_{mb}) , the solid, liquid and gas phases coexist. As T and P are increased to approach (T_{mb}, P_{mb}) , the solid-liquid interface generally wets itself with a thin liquid film. This is called surface melting. Surface melting is essentially the wetting of a solid by its own melt (complete wetting). The surface acts as active centers for premelting as the surface atoms are more loosely bound compared to the atoms in the bulk of the crystal and hence can be activated thermally.

We know that when a solid crystal is wetted by its own melt [20], a liquid layer encompasses the solid at a temperature less than the bulk melting temperature T_{mb} . The degree up to which a liquid can wet the solid which it surrounds is determined by the internal cohesive forces and the adhesive force between solid and liquid. A contact angle $\theta < 90^\circ$ means wetting of the solid nanocrystal by its own melt is favorable and the fluid will spread over a large area. Likewise, $\theta > 90^\circ$ implies wetting is unfavorable and hence melt will try to minimize the contact with the solid.

In the liquid skin melting model [20], our basic assumption is that a thin melt layer is formed on the surface of the nanocrystal initially, and as the temperature increases, the melt thickness grows inward. As the temperature of the solid approaches the bulk melting point of the material, the thickness of the film keeps on increasing and diverges asymptotically at $T = T_{mb}$. This is known as surface induced melting or pre melting. In case of surface induced melting, the melting temperature of the bulk crystal depends on the size of the nanoparticle. We model this skin growth to be homogenous, i.e. formation of uniform liquid layers on top of each other. The number of such liquid layers increases with temperature until the particle core melts suddenly at its curvature dependent melting temperature point.

A very beautiful experiment carried out by [19, 21] gives a visual representation of surface melting in lead Pb(1 1 0). Scattering experiments were able to reveal the presence of a liquid skin formation on top of the solid nanocrystal surface, the thickness of which diverges asymptotically as T tends to T_{mb} .

In many substances, a phenomenon contrary to this occurs- which is called surface non-melting. In this phenomenon, the surface remains solid and crystalline till T_{mb} is approached. This is also known as partial wetting. Surprisingly, both these phenomenon can occur for the same substance too, but on different crystallographic planes. For example, Pb

(1 1 0) [19, 21] undergoes surface melting but Pb (1 1 1) [19, 22] undergoes surface non melting.

Hence, we see a clear [19] relationship between the contact angles and surface thermodynamic parameters. Surface non melting takes place when the solid-vapor interface is unable to lower its free energy by turning to a series of separate solid-liquid and liquid-vapor interfaces. Hence, $\gamma_{SV} < \gamma_{SL} + \gamma_{LV}$. Surface melting occurs when this inequality doesn't hold. It is clearly seen [19] the film remains thin till just a few degrees before T_{mb} . Hence, information readily crosses the thin liquid skin.

2. Theory

2.1. The surface melting models

There are models linking the melting temperature of nanoscale systems with the loss of thermodynamic stability of the surface layer [23-25], or with the instability of surface phonons [26]. In this paper, we restrict ourselves to consider the liquid shell nucleation (LSN) model [24] and the liquid skin nucleation and growth (LNG) model [25], both of which belong to the first type. Both theories suggest the formation of a quasi-liquid layer on the surface of a nanocrystal, which is in equilibrium with a solid core. The Gibbs free energy change due to formation of this layer has the form:

$$\Delta G = L \cdot N_L \cdot \left(1 - \frac{T}{T_{mb}}\right) + \gamma_{SL} A_C + \gamma_{LM} A_L - \gamma_{SM} A_S \quad (1)$$

Here, L (J/g) is the latent heat of fusion per molecule; A_C, A_L, A_S are the surface areas of the crystalline core under this layer, the liquid layer and the solid crystal correspondingly; $\gamma_{SL}, \gamma_{LM}, \gamma_{SM}$ (mJ/m²) are the Helmholtz free energies per unit surface at the interfaces between the solid "S", the liquid "L" and the encapsulating matrix "M", which can be either a vacuum or a solid; N_L is the number of molecules in the liquid layer; T is the temperature and T_{mb} (K) is the bulk melting temperature.

In LSN model, the coefficients $\gamma_{SL}, \gamma_{LM}, \gamma_{SM}$ are independent of the thickness of the liquid layer δ . Within this model, the thickness δ cannot be calculated, being used as a parameter. For each temperature T , there is a minimum surface curvature radius R at which the crystal remains stable. This critical radius is the size of the nanosystem at which the temperature T coincides with its melting temperature $T_{melting}$. In the case of a nanowire, the formula for calculating the melting temperature is given by:

$$T_{melting}(R, \delta) = T_{mb} \left(1 - \frac{1}{L \cdot n_s} \left(\frac{\gamma_{SL}}{R - \delta} + \frac{\gamma_{LM}}{R} \left(1 - \frac{n_s}{n_l}\right) \right) \right) \quad (2)$$

The magnitude of δ is considered to be a variable parameter of the LSN model. It can be expected that at temperatures significantly below T_{mb} the parameter δ will be of the order of the crystal lattice constant. For small enough values of δ , this equation simplifies to:

$$T_{melting}(R, \delta \ll R) = T_{mb} \left(1 - \frac{1}{L \cdot n_s \cdot R} \left(\gamma_{SL} + \gamma_{LM} \left(1 - \frac{n_s}{n_l}\right) \right) \right) \quad (3)$$

The parameters n_l and n_s are the numerical densities of particles in the liquid and solid phase respectively. They can be calculated by dividing the mass density of the melt by the molar mass of the substance and multiplying it by the Avogadro number, or as a value inverse to the specific volume of one particle ϑ_L . It is important to note that in the case of an ideal thin film, the surface areas of the solid state, the liquid layer and the crystalline core are equal regardless of the thickness of the film. As a result, the melt stability condition has the form:

$$\frac{d\Delta F(T, R)}{dN_L} = L \left(1 - \frac{T}{T_{mb}}\right) \geq 0 \quad (4)$$

which indicates at the coincidence of the melting points of a thin film and an infinite crystal, $T_{\text{melting}} = T_{\text{mb}}$.

In fact, the theory described above links the melting temperature of nanocrystals to the curvature of their surface. This is why, at infinite radius of curvature, the nanosystem melting temperature coincides with the melting temperature of the bulk. Thus, for thin films, the LSN model does not predict a depression in the melting temperature. This is a fundamental difference between this model and the empirical theories based on the specific cohesive energy of a crystal or change in surface energy with decreasing size. The theoretical absence of a significant melting point depression for thin films can hardly be consistent with practice. In practice, the melting of thin films can start at the boundaries or defects that have small radii of curvature- which is determined by the thickness of the film, and therefore, by the surface area to volume ratio.

Surface melting of nanocrystals with the formation of a liquid layer of variable thickness is described in this work using the Liquid Skin Nucleation and Growth model [25]. This model is relatively old; however, it considers the formation of surface melt in almost the same approximations as more modern models, such as [27]. Similar to newer models, the LNG theory predicts the formation of a quasi-molten layer on the surface of crystals at sufficiently high temperatures, the coexistence of molten and crystalline phases in a certain temperature range and melting of a nanocrystal due to propagation of the surface melt into the bulk with further increase in temperature.

A necessary condition for the formation of a surface melt is the dependence of the specific energy of its surfaces on the thickness of the liquid layer. The advantage of the LNG model is the presence of a physical mechanism that explains the decrease in the surface energy of the melt by its partial ordering. This makes the LNG model relatively easy to apply to freeform surfaces.

In the framework of the LNG model [25], the surface energies at the interfaces between the liquid layer, the crystalline core and the environment, depend on the thickness of the molten layer; since these energies include the effect of partial ordering of the melt under the influence of the boundary. It is assumed that the density of the free energy of the bulk of the molten layer $f(\vec{x})$ changes under the influence of a surface element dA according to the relation:

$$d(f(\vec{x})) = \text{const} \cdot \left(\frac{\exp\{-r/\xi_L\}}{r} \right) dA \quad (5)$$

where, ξ_L is a parameter characterizing the depth of penetration of the ordering effect into the melt and r is the distance from the point \vec{x} to the surface element dA . The proportionality coefficient can be associated with experimental data, based on the following considerations [25]:

- A molten layer "L" of macroscopic thickness adjacent to the crystalline core "C" and the surrounding medium "M" should have surface free energy:

$$F_{\text{surface}}[C|L|M] = \gamma_{SL}A_C + \gamma_{LM}A_L \quad (6)$$

where γ_{SL} and γ_{LM} are the experimental values of the surface free energy densities at the corresponding boundaries. It is assumed that these experimental data include the contribution (5);

- A molten layer of infinitely small thickness ($A_S = A_C$) should be equivalent to the solid crystalline surface "S" that has the free energy:

$$F_{\text{surface}}[S|M] = \gamma_{SM}A_S = \gamma_{SM}A_C \quad (7)$$

As shown in [25], the above limiting conditions are satisfied if the surface energy of the molten layer of finite thickness is expressed in the form:

$$F_{\text{surface}} = \gamma_{SL}A_C + \gamma_{LM}A_L + \alpha\Delta\gamma \cdot \left(A_L - \frac{1}{2\pi\xi_L^2} \int_{(V_L)} \int_{(A_L)} \frac{\exp\{-r/\xi_L\}}{r} dA_L dV_L \right) + (1-\alpha)\Delta\gamma \cdot \left(A_C - \frac{1}{2\pi\xi_L^2} \int_{(V_L)} \int_{(A_C)} \frac{\exp\{-r/\xi_L\}}{r} dA_C dV_L \right) \quad (8)$$

Here, $\Delta\gamma = \gamma_{SM} - (\gamma_{SL} + \gamma_{LM})$, and V_L is the volume of the molten layer. The additional parameter $\alpha \in [0, 1]$ characterizes the comparative contribution of the external and internal surfaces of the molten layer to the free energy of its bulk. In [25], for both platinum and lead, this parameter was taken to be $\alpha = 0.3$. We have kept this same value of the parameter in the present work as well.

Taking into account (26), the change in the Gibbs energy due to the formation of a surface liquid layer has the form:

$$\Delta G = L \cdot n_L \cdot V_L \cdot \left(1 - \frac{T}{T_{\text{mb}}} \right) + F_{\text{surface}} - \gamma_{SM}A_S \quad (9)$$

where A_S is the area of the crystal when it is completely solid.

Integration (8) can be carried out analytically for an infinite flat layer, and also for a spherical system consisting of a crystalline core and a molten shell. Taking into account (8), the excess Gibbs energy of a molten layer of thickness δ on the surface of a planar macrocrystal takes the form [25]:

$$\frac{\Delta G(\delta, T)}{A} = L \cdot n_L \cdot \delta \cdot \left(1 - \frac{T}{T_{\text{mb}}} \right) - \Delta\gamma \cdot \left(1 - \exp\left\{ -\frac{\delta}{\xi_L} \right\} \right) \quad (10)$$

where n_L is the particle density of the liquid layer, L is the latent heat of fusion per molecule and T_m (same as T_{mb}) is the macroscopic melting temperature. This form of the excess free energy completely coincides with the result from the newer work [28], where it was obtained using an alternative approach.

The equilibrium molten layer on a flat surface will exist under the condition:

$$\frac{d}{d\delta} \left(\frac{\Delta G(\delta, T)}{A} \right) = 0 \Rightarrow \delta(T) = -\xi_L \cdot \ln \left(\frac{L \cdot n_L \cdot \xi_L}{\Delta\gamma} \cdot \left(1 - \frac{T}{T_{\text{mb}}} \right) \right) \quad (11)$$

The corresponding dependence of the melting temperature T_m on the thickness of the molten layer takes the form:

$$T_m(\delta) = T_{\text{mb}} \cdot \left(1 - \frac{\Delta\gamma}{L \cdot n_L \cdot \xi_L} \exp\left\{ -\frac{\delta}{\xi_L} \right\} \right) \quad (12)$$

The same result has been obtained in [28]. Additionally, the equations [29-31] show that no liquid layer is formed on the surface given $\Delta\gamma < 0$. Condition $\Delta\gamma > 0$ is true for most metals, including Pt, Au, and Pb. However, $\Delta\gamma$ is less than zero for Ag (Table 2).

For a spherical nanocrystal, the integration (8) gives the result:

TABLE 1
N/n ratios [4] for different nanostructures. d = diameter of atom, l = diameter of nanowire and h = thickness of nanofilm.

Nanosolid	N/n
Nanowires	(8/3)d/l
Nanofilm	(4/3)d/h

$$\begin{aligned} \Delta G(R_L, \delta, T) = & L \cdot n_L \cdot V_L \cdot \left(1 - \frac{T}{T_{mb}}\right) + \gamma_{SL} A_C + \gamma_{LM} A_L - \gamma_{SM} A_S + \\ & + 4\pi R_L \cdot \alpha \Delta \gamma \cdot \left(\begin{aligned} & \xi_L + (R_C - \xi_L) \cdot \exp\{-\delta/\xi_L\} + \\ & + (R_C + \xi_L) \cdot \exp\{-(R_L + R_C)/\xi_L\} - (R_L + \xi_L) \cdot \exp\{-2R_L/\xi_L\} \end{aligned} \right) + \\ & + 4\pi R_C \cdot (1 - \alpha) \Delta \gamma \cdot \left(\begin{aligned} & -\xi_L + (R_L + \xi_L) \cdot \exp\{-\delta/\xi_L\} - \\ & - (R_L + \xi_L) \cdot \exp\{-(R_L + R_C)/\xi_L\} + (R_C + \xi_L) \cdot \exp\{-2R_C/\xi_L\} \end{aligned} \right) \end{aligned} \quad (13)$$

which has been obtained in the original work [25]. Here, R_C and R_L are the radius of the crystal core and the outer radius of the liquid layer; $\delta = R_L - R_C$ and A_S is the surface area of the crystal in the solid state.

Formulas (8) and (13) turn out to be applicable to describe melting in cases where the liquid layer cannot be formed on the surface of the nanocrystal. This situation takes place for silver ($\Delta\gamma < 0$), as well as for the smallest nanocrystals, the linear size of which does not exceed ξ_L . In this case, formula (13) gives the criterion for melting as:

$$\begin{aligned} \Delta G|_{\delta=R_L} = & L \cdot n_L \cdot V_L \cdot \left(1 - \frac{T_{melting}}{T_{mb}}\right) + \gamma_{LM} A_L - \gamma_{SM} A_S + \\ & + 4\pi R_L \cdot \alpha \Delta \gamma \cdot (\xi_L \cdot (1 - \exp\{-2R_L/\xi_L\}) - R_L \cdot \exp\{-2R_L/\xi_L\}) < 0 \end{aligned} \quad (14)$$

Using approximations $A_S \approx A_L$ and $R_L \gg \xi$, condition (14) takes the form:

$$T_{melting} = T_{mb} \cdot \left(1 - \frac{A_L \cdot \gamma_{SM} - \gamma_{LM}}{V_L \cdot L \cdot n_L}\right) = T_{mb} \cdot \left(1 - 3 \cdot \frac{\gamma_{SM} - \gamma_{LM}}{L \cdot n_L \cdot R_L}\right) \quad (15)$$

which coincides with the dependence proposed for the same case in the work [27].

Melting of nanowires has not been studied using the LNG model before. We were not able to carry out integration (8) analytically for this case, and therefore, the integration was carried out by a numerical procedure. The integration procedure was verified using spherical geometry, achieving practically full coincidence of the result with the calculation by formula (13).

In the general case, to predict the melting point according to formulas (8) and (13), it is necessary to analyze the shape of the curves at different temperatures. The methodology for this analysis is briefly discussed in the next section.

2.2. The empirical equations

The linear dependence of the melting temperature on the ratio of the nanocrystal area and volume is also a characteristic of the empirical formulas considered below. Research [1, 4, 11, 32, 33] reveals that the melting of low dimensional materials not only depends on the size of the material, but also on its shape. As we move towards the nanoscale, the relative surface area increases greatly and hence the effects due to the surface area to volume ratio or more importantly, ratio of number of surface atoms (N) and number of volume atoms (n) becomes more prominent. Properties like cohesive energy and melting temperature at nanoscale thus heavily depend on the N/n ratio and hence, different shaped nanoparticles of the same size exhibit different melting points.

Nanda et al. [2] uses the liquid drop model to explain the superheating phenomenon in low dimensional materials along with melting suppression. The expression relating the bulk (T_{mb}) and nano (T_{mp}) melting temperatures is as follows:

$$T_{mp} = T_{mb} \left(1 - \frac{\beta}{zd}\right) \quad (16)$$

Here,

$$\beta = \frac{6 \times v_0 \times \gamma}{0.0005736 \times T_{mb}} \quad (17)$$

Here, v_0 (cm^3) is the atomic volume per mole, γ (mJ/m^2) is the surface energy and d (nm) is the diameter for nanoparticle and nanowire and thickness for nanofilm. Also, $z = 1$ for nanoparticles, $3/2$ for nanowires and 3 for nanofilms. Here, the unit of the constant 0.0005736 is eV/K.

Qi et al. [4] provides a model taking into account the free surface and cohesive energy of the nanomaterial, which is modelled as follows:

$$E_p = E_b \left(1 - \frac{N}{2n}\right) \quad (18)$$

Here, E_p is the cohesive energy of the nanomaterial and E_b is that of its bulk counterpart. It has been deduced before [2,4,10] that cohesive energy and melting temperature have a linear relation. Hence, the relation between T_{mb} and T_{mp} can be similarly given as:

$$T_{mp} = T_{mb} \left(1 - \frac{N}{2n}\right) \quad (19)$$

Clearly, the value of N/n is different for different types of nanomaterials. These values are given in Table 1.

D. Xie et al. [5] has also made use of molar cohesive energy. By calculating the surface area to volume ratio as a function of particle size, a model for theoretical computation of cohesive energy has been developed and a relation for the melting temperature of nanosolids is thus deduced as follows:

$$T_{mp} = T_{mb} \left(1 - \frac{3\alpha}{4}\right) \quad (20)$$

Here, $\alpha = \frac{4r}{D} (3 - d)$, r is the atomic radius (nm), D is the wire diameter or film thickness (nm) and $d = 0$ for nanoparticles, 1 for nanowires and 2 for nanofilms.

The Eqs. (16), (19) and (20) are based on an empirical relationship between the melting temperature and the cohesive energy of macroscopic crystals [2, 34]. This relationship, which is very well justified by experimental data [35-36], consists of the fact that in the series of compounds with the same crystal lattice structure, the bulk melting temperature linearly depends on the cohesive energy per coordination (a bond between two atoms) [2]. In addition, the slope of these dependencies, which is a derivative of the melting temperature with respect to the cohesive energy, is almost constant for various types of crystal lattices. However, the use of the same or similar empirical dependence to describe the transition from a macroscopic crystal to a nanoscale system of the same chemical composition requires verification.

The transition from one material to another involves a change in the electronic structure of the particles and the interaction potentials, which determine both the melting temperature and the cohesive energy. Thus, the presence of a clear relationship between the changes in the melting

temperature and the cohesive energy of a crystal in this case is not surprising. However, when varying the sizes of one and the same crystal, the interaction potentials change only due to the influence of the surface, which may be insignificant. Molecular dynamic simulation of nanoparticles [37] has demonstrated a significant decrease in the melting temperature with a decrease in the crystal size using constant pair interaction potentials that did not change at the surface at all. Therefore, it is interesting and relevant to compare the melting temperatures predicted by the empirical expressions (16), (19) and (20) with other models that propose specific melting mechanisms of nanosystems.

2.3. Melting criteria for nanocrystals in the presence of a surface molten layer

As discussed above, in a certain temperature range, nanocrystals can be two-phase systems consisting of a crystalline core and a surface molten layer [16, 17, 19, 20, 38]. Thus, instead of a single melting point of a nanocrystal, it is necessary to consider a number of critical temperatures characterizing the appearance and stability of a surface melt. In this work, the following critical temperatures are considered:

- The solidus temperature at which a stable surface layer of extremely small thickness appears (in this work, the limiting thickness was assumed to coincide with the lattice constant of crystals; its refinement requires additional research).
- The liquidus temperature, which is the maximum temperature at which the surface melt is in stable equilibrium with the crystal core (such temperatures are denoted in this work as T_{m1}).
- A higher temperature at which the metastable equilibrium between the surface melt and the crystal core disappears (such temperatures are denoted in this work as T_{m3}).

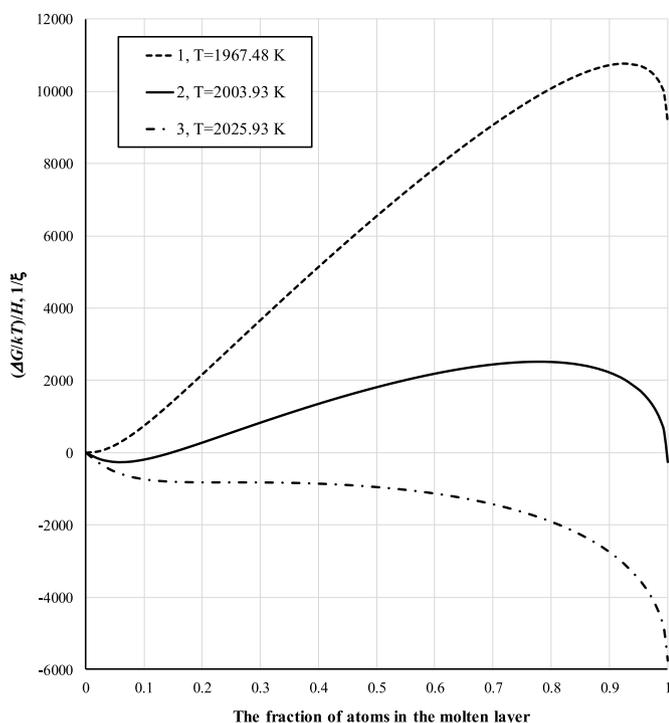


Fig. 1. The specific free energies $\Delta G/H$ of a platinum nanowire at critical temperatures. Curve 1 corresponds to the solidus temperature; curve 2 corresponds to the liquidus temperature (T_{m1}); curve 3 corresponds to the temperature, at which the crystalline core cannot exist in a metastable state (T_{m3}). Here, $\xi_L = 0.392$ nm, $R_S = 12.5$ nm.

- The temperature lying between temperatures T_{m1} and T_{m3} , at which nanocrystals will melt, overcoming the potential barrier between the metastable state of the <surface melt>/<crystal core> system and the completely molten state (such temperatures are denoted in this work as T_{m2}).

Fig. 1 demonstrates the characteristic dependences of the free energy of the <surface melt>/<crystal core> system on the fraction of atoms in the melt at the critical temperatures described above. In all cases, the liquid state of the whole system corresponds to the extreme right point. The liquidus temperature (T_{m1}) ensures equality of the free energies ΔG in a local minimum and in the molten state (curve 2 in Fig. 1).

At temperatures above T_{m1} , the molten state becomes the most stable; however, the <surface melt>/<crystal core> system can exist in a metastable state, since the potential barrier hinders the transition of the system to the molten state. In Fig. 1, the height of the potential barrier E is given by the difference between the energies ΔG at the local maximum and local minimum of the curve 2. Thermal activation is required to overcome this potential barrier. The probability of the thermal activation of melting per unit time is proportional to an exponential function $\exp\{-E/kT\}$. The value of E increases with crystal size fast enough to make the probabilities of melting of macroscopic crystals at the liquidus temperature negligible, even over macroscopic times [25].

In [25], the probabilities of melting of spherical platinum and lead nanocrystals during one second were estimated using formula (21), where V is the volume of the crystal. The melting was attributed to such temperatures T at which the value of J became greater than 1. In this work, we refer to the temperatures that satisfy this condition as critical temperatures of type 2 (T_{m2}).

$$J = (6.3 \times 10^{24} \text{ nm}^{-3} \text{ s}^{-1}) \cdot V \cdot \exp\left\{-\Delta \frac{F}{kT}\right\} \geq 1 \quad (21)$$

In the case of nanowires, the applicability of criterion (21) is doubtful since an ideal nanowire at any radius has an infinite length. Accordingly, the activation energy E becomes infinite. In practice, thermal activation of melting in a local region may be sufficient to melt the nanowire as a whole. Unfortunately, it was not possible to determine the sizes of such regions here. Therefore, we did not apply criterion (21) to nanowires. However, this criterion was used to compare the LNG model with other calculations and experimental data using the example of lead (Fig. 3).

As the temperature rises, the positions of the local minimum and maximum of ΔG move towards each other, while the potential barrier between these points decreases. At a certain temperature (the critical temperature of type 3, T_{m3}), the maximum and minimum merge,

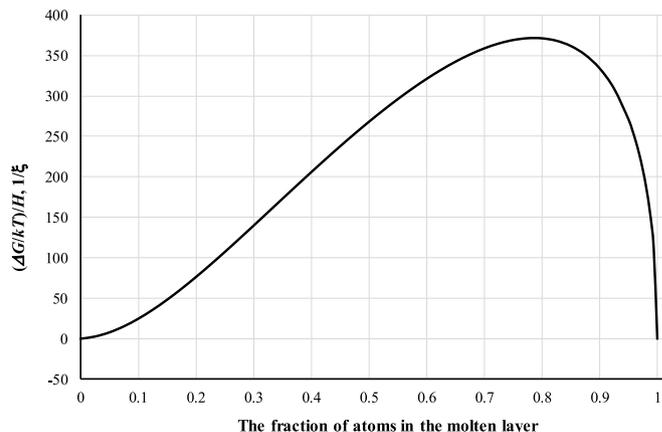


Fig. 2. A liquidus-type specific energy curve for a platinum nanowire with no liquid layer at the surface. Here, $\xi_L = 0.392$ nm, $R_S = 4.55$ nm, $T = T_{m1} = 1929.35$ K.

forming a step (curve 3 in Fig. 1). The potential barrier disappears, providing melting of the crystalline core without thermal activation. Type 3 critical temperature gives the upper bound for the melting point estimation within the LNG model.

For very small nanocrystals of Pt, Au and Pb (linear size less than 5 nm), the LNG model predicts the absence of the stable liquid layer at any temperature, since the free energy ΔG does not have a local minimum (as shown in Fig. 2), or the local minimum is always higher than the energy of the molten state. The same result has been obtained in [28]. For this case, the critical temperatures T_{m1} were assumed to be those temperatures at which the free energy of the molten nanocrystal became lower than the energy of the solid state. For Pt, Au, and Pb crystals, these temperatures continue the liquidus curve into the small size region. The same melting criterion is applicable for Ag nanocrystals of all sizes.

The applicability of the melting criteria discussed above must be verified by comparing the calculations with experimental data. Unfortunately, we do not know the necessary data for Pt, Au, or Ag. On the other hand, the melting of lead has been well studied experimentally and theoretically [19-21].

To find out the correspondence of the described melting criteria with the experiment, as well as to assess the quality of the LNG model as a whole, we compared the results of calculations within this model with the experimental data known for spherical lead crystals. The comparison is demonstrated in Fig. 3.

As can be seen from Fig. 3, the large scatter of experimental data does not allow unambiguous choosing of the best model and melting criterion. The following conclusions seem to be fair:

- The LNG model overestimates the melting temperatures of the smallest nanocrystals. However, in the limit of large sizes, it may turn out to be the best of those considered.
- Taking into account the activation melting by means of critical temperatures T_{m2} reproduces to some extent the nonlinearity of the experimental data of [30]; this does not change the model melting temperatures much.
- After crossing the liquidus curve, the solidus curve obtained in this work corresponds to the metastable liquid layer [39] on the surface of small nanocrystals;

- The empirical formula from [2] gives the best prediction of the melting points of small nanocrystals; the model [28] gives similar results.
- The melting temperatures of nanocrystals, diameter of which exceeds 10 nm, will most likely lie between the critical temperatures T_{m1} (liquidus) and T_{m3} calculated within the LNG model.

The choice of the parameter ξ_L is characterized by great uncertainty. In [26], a theory and a formula are given which estimate ξ_L in the form:

$$\xi_L = \frac{5.7 \times \gamma_{SL}}{\rho_l \times k_b \times T_m} \tag{22}$$

At that, work [26] overestimates the values of ξ_L by 2–3 times compared with works [25] and [28] (in the latter work, the parameter $\xi_L[\text{Pb}] = 0.47 \text{ nm}$ was estimated by comparing the melting model with experimental data; this value is very close to the value $\xi_L[\text{Pb}] = 0.495 \text{ nm}$ proposed in [25]).

In this work, we estimated the effect of the choice of ξ_L on the calculation of the melting temperature of nanocrystals. The values of ξ_L calculated using (13) are listed in Table 2. The calculation results for lead (Fig. 3) suggest that the value $\xi_L[\text{Pb}] = 1.37 \text{ nm}$ from Table 2 is less applicable to small nanocrystals.

3. Results and discussion

Figs 4, 5 and 6 show the dependences of the melting temperatures of gold, platinum and silver nanowires, calculated without direct consideration of surface melting. Calculations of the melting temperature of thin films are also presented there. It is seen that the LSN model yields a significantly smaller decrease in the melting temperature of nanocrystals than the empirical formulas. This can be explained by the need to take into account the surface liquid layer.

In the case of thin films, empirical formulas predict a significantly larger decrease in the melting point than the LNG theory. The discrepancy here is fundamental, since the surface melting is accounted for in this case. Further research is needed to find out which of these results is more accurate. Note that in practice, the melting temperatures of thin films can significantly decrease due to the imperfections of their surface.

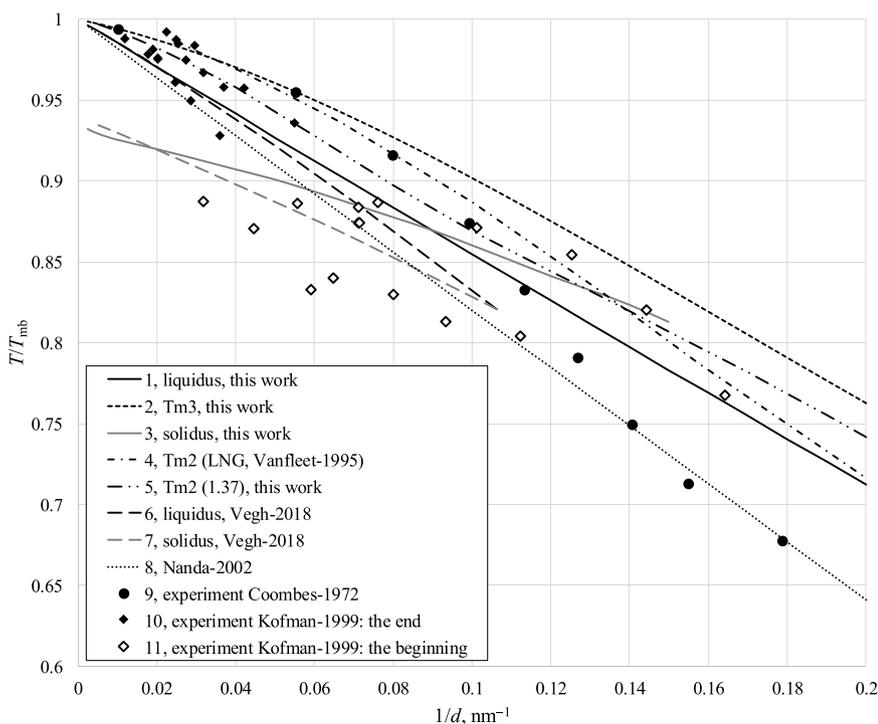


Fig. 3. A comparison of calculated and experimental melting temperatures of spherical Pb crystals. The calculations 1–4 were carried out using the parameter $\xi_L = 0.495 \text{ nm}$ (the same value as in [25]); the calculation 5 used an alternative value $\xi_L = 1.37 \text{ nm}$, calculated by formula (22); Nanda-2002 [2] is an empirical calculation using formula (17) suggested in that work; in the experimental work Kofman-1999 [39], the “beginning” of melting corresponded to the temperatures of formation of the liquid layer, when at the “end” temperatures the nanocrystals melted completely.

TABLE 2
Parameter values [7, 25-28, 40-41] required for LSN and LNG model.

Ele-ment	ξ_L (nm)	L (J/g)	γ_{SM} (mJ/m ²)	γ_{SL} (mJ/m ²)	γ_{LM} (mJ/m ²)	γ (mJ/m ²)	Molar mass(g/mol)	ρ_s (g/cm ³)	ρ_l (g/cm ³)	n_s (atom/nm ³)	n_l (atom/nm ³)
Ag	1.183	104.6	1065	184	910	-29	107.9	9.86	9.32	55.05	52.03
Au	1.177	63.72	1363	200	1130	33	197.0	18.27	17.17	55.86	52.50
Pt	1.138	113.6	2223	334	1860	29	195.1	20.52	19.2	63.34	59.27
Pb	0.495	23.0	544	62	460	22	207.2	11.4	10.7	33.1	31.1

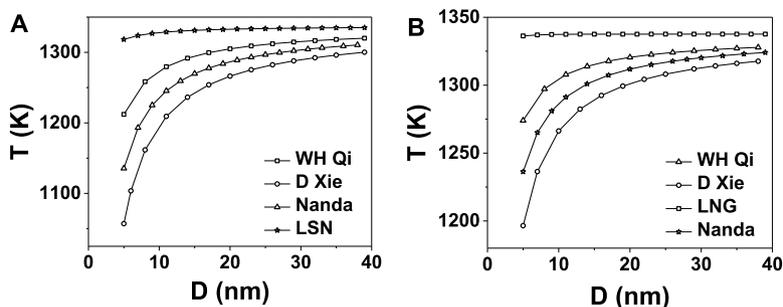


Fig. 4. Melting temperatures of gold. (A) Nanowire as a function of wire diameter (B) Nanofilm as a function of film thickness. The bulk melting temperature of gold is taken to be 1337.58 K and its atomic diameter is taken as 0.348 nm.

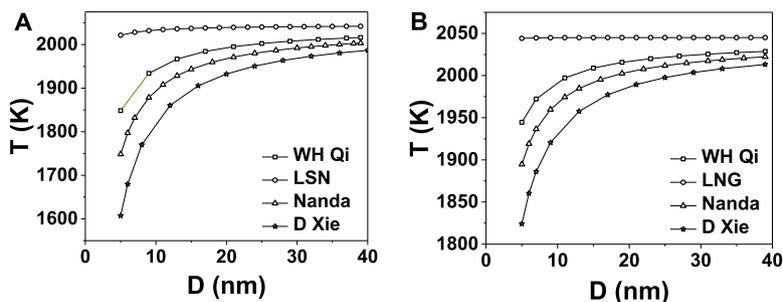


Fig. 5. Melting temperatures of platinum. (A) Nanowire as a function of wire diameter (B) Nanofilm as a function of film thickness. The bulk melting temperature of platinum is taken to be 2045 K and its atomic diameter is taken as 0.354 nm.

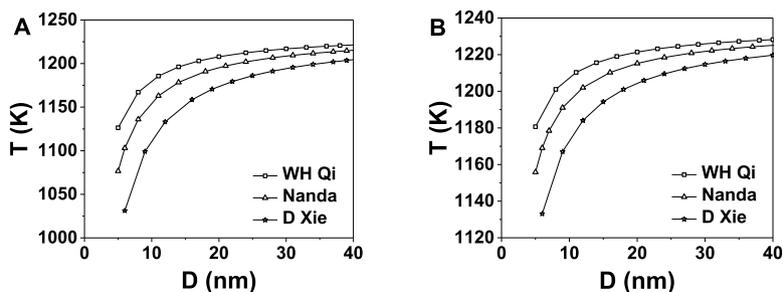


Fig. 6. Melting temperatures of silver. (A) Nanowire as a function of wire diameter (B) Nanofilm as a function of film thickness. The bulk melting temperature of silver is taken to be 1235.08 K and its atomic diameter is taken as 0.33 nm.

It is important to note that Ag, according to [26], is characterized by a negative $\Delta\gamma$ value at the nanocrystal–vacuum interface. This leads to the absence of a stable surface melt at all temperatures below the melting point. The unstable surface melt, according to our calculations, was formed only at nanocrystal radii within 3.5 nm and temperatures very close to the bulk melting point. At larger radii, the surface melt could form only at temperatures above the melting point of the bulk. This result may be of the same nature as the result of experiment [29]. Thus, it is possible that silver nanocrystals and nanowires are not subject to significant depression in the melting temperature, but instead, can be overheated relatively easily. This indicates a fundamental difference between the melting mechanisms of Ag nanocrystals and nanowires from Au and Pt.

The effect of changing the ξ_L value on the melting temperature of platinum and gold nanowires is shown in Figs. 7-8. Comparison of the calculated and the experimental data for lead showed that, within the LNG model, it is preferable to use the melting criterion (21). However, its application to nanowires is beyond the scope of this work. Thus, for platinum and gold, we limited ourselves to plotting the critical temperatures T_{m1} and T_{m3} , which set the lower and upper boundaries of the real melting temperature. The liquidus temperatures T_{m1} and the alternative critical temperatures T_{m3} for platinum were calculated using the values $\xi_L = 0.392$ nm and $\xi_L = 1.1382$ nm. Both critical temperatures are almost unaffected by choice of ξ_L . The significant dependence of the melting temperatures on ξ_L is obtained only for the crystals of the smallest sizes (less than 3 nm).

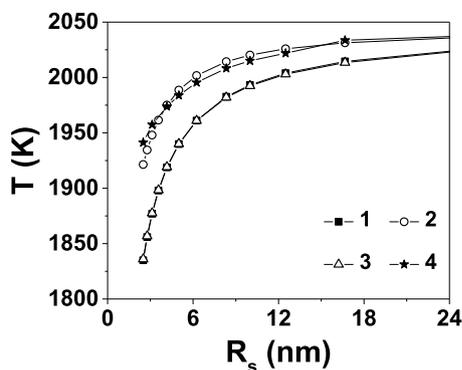


Fig. 7. The critical temperatures depending on the Pt nanowire radius: 1 is the dependence $T_{m1}(R)$ given $\xi_L = 0.392$ nm (the value from [25]); 2 is the dependence $T_{m3}(R)$ given $\xi_L = 0.392$ nm; 3 is the dependence $T_{m1}(R)$ given $\xi_L = 1.138$ nm (the value is calculated by formula (22)); 4 is the dependence $T_{m3}(R)$ given $\xi_L = 1.138$ nm.

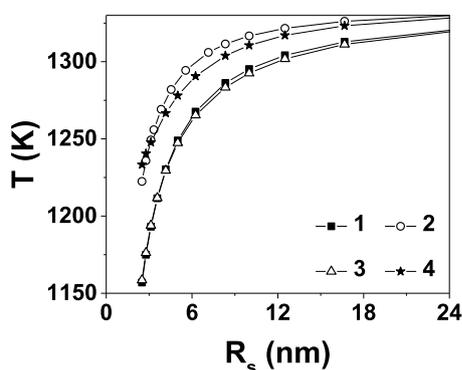


Fig. 8. The critical temperatures depending on the Au nanowire radius: 1 is the dependence $T_{m1}(R)$ given $\xi_L = 0.405$ nm (the value is estimated in this work); 2 is the dependence $T_{m3}(R)$ given $\xi_L = 0.405$ nm; 3 is the dependence $T_{m1}(R)$ given $\xi_L = 1.177$ nm (the value is calculated by formula (22)); 4 is the dependence $T_{m3}(R)$ given $\xi_L = 1.177$ nm.

It is also seen that formula (22) most likely overestimates the values of the parameter ξ_L . For platinum, there is an alternative value of 0.392 nm from [25]. The simplest way to obtain a similar value for gold is to

use formula (22) with an additional coefficient of 0.392/1.1382, where 1.1382 nm is the calculation by formula (22) for platinum. This modification gives an estimate of $\xi_L = 0.405$ nm. Plots corresponding to alternative ξ_L values are shown in Fig. 8. It can be seen that the lower estimates of the nanowire melting temperature $T_{m1}(R)$ are practically independent of ξ_L , while the upper estimates $T_{m3}(R)$ are sensitive to ξ_L in the region of medium nanowire radii.

Fig. 9 shows the temperatures of liquidus and solidus for platinum and gold, depending on the diameter of the nanowire. In the region of small diameters, the solidus temperatures turn out to be higher than the liquidus temperatures, which means the metastability of the surface melt at such sizes.

Fig. 10 demonstrates the result of calculating the melting temperature of an Ag nanowire given $\xi_L[\text{Ag}] = 1.183$ nm, using formula (8), under the assumption that the crystalline nanowire passes to the molten state without intermediate surface melting ($\delta = R_L$ always). Interestingly, the effect of lowering of the melting temperature of the nanowire still exists, and in magnitude (relative to the bulk melting point) it practically coincides with the melting temperature depression for platinum and gold. This also indicates the applicability of the empirical formulas for silver.

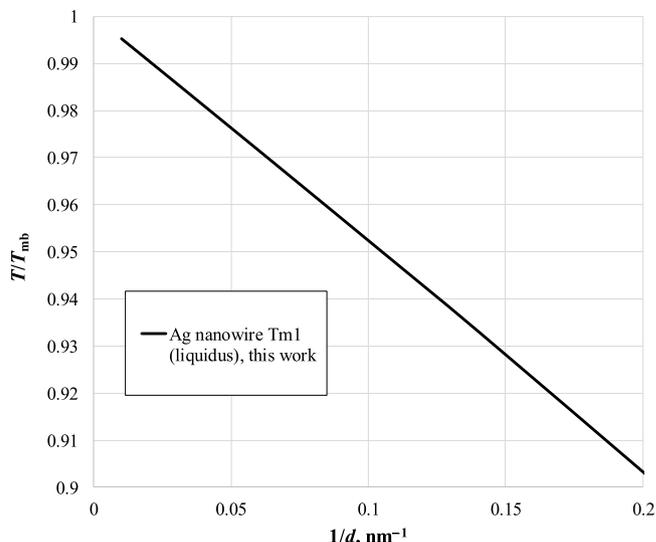
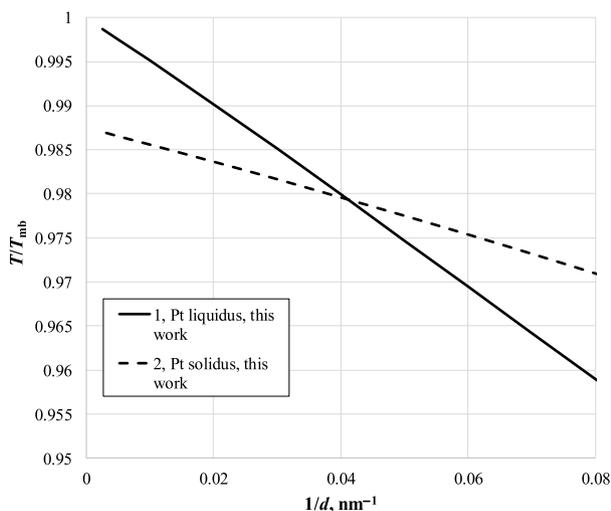
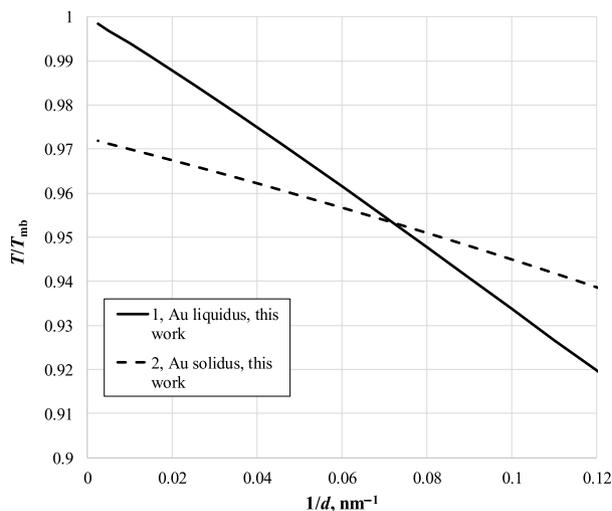


Fig. 10. The melting temperature T_{m1} (liquidus) for Ag. $\xi_L[\text{Ag}] = 1.183$ nm.



a)



b)

Fig. 9. The liquidus and solidus temperatures for Pt and Au. Here, $\xi_L[\text{Pt}] = 0.392$ nm and $\xi_L[\text{Au}] = 0.405$ nm.

4. Conclusion

In this work, the melting temperatures of platinum, gold and silver nanowires and nanofilms are calculated using the models liquidshell nucleation [24] and liquid skin nucleation and growth [25], as well as a number of empirical formulas, including the equation proposed by Nanda et al. in [2]. Both LSN and LNG models are based on the idea of surface induced melting wherein a liquid layer is formed on the surface of the solid material, which wets the solid, and grows while moving into the solid. The mechanism of such surface induced melting is studied in depth using the dependence of the Gibbs free energy on thickness of the liquid layer. A number of critical temperatures characterizing the stability of the surface liquid layer are considered, and the effect of differing the liquid ordering parameter ξ_L values on these critical temperatures is discussed. It was found that uncertainty in ξ_L values strongly affects the temperatures of formation of the surface liquid layer, but not the temperatures at which the melt loses stability. For the crystals of sizes less than 3 nm, the significant dependence of melting temperatures on ξ_L was observed. Comparison of the solidus and liquidus curves for platinum and gold suggests that the liquid layer on the nanowire surface will be metastable at radii less than 5 nm. For silver, it is shown that the effect of the nanoscale melting point depression exists despite the absence of a stable surface melt.

CRedit authorship contribution statement

Niyati Shah: Conceptualization, Methodology, Software, Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Visualization. **K.A. Nekrasov:** Conceptualization, Methodology, Software, Formal analysis, Investigation, Writing - review & editing, Visualization, Funding acquisition. **Sanjeev K. Gupta:** Conceptualization, Methodology, Writing - review & editing, Supervision, Funding acquisition. **P.N. Gajjar:** Supervision. **A.S. Boyarchenkov:** Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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