

Correlation between the Melting Point of a Nanosolid and the Cohesive Energy of a Surface Atom

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An atomistic model is presented for the melting behavior of a surface and a nanosolid, as well as their interdependence based on the recent “bond order–length–strength” (bond-OLS) correlation mechanism (*J. Phys. D* **2001**, 34, 3470). It is suggested that the coordination number (CN) of a surface atom reduces whereas the remaining bonds of the lower-coordinated surface atom relax spontaneously associated with the single bond energy rise. Hence, the atomic cohesive energy (a single bond energy multiplies the CN) or the heat required for loosening the atom at the surface differs from the bulk value. Such a difference is suggested to be responsible for the fall (depression) or rise (overheating) of the melting point of a surface and a nanosolid of which the portion of surface atoms varies with the particle size. Being with few assumptions or freely adjustable parameters, the current premise is in good accordance with existing models and is perhaps able to link the existing models to the fact of surface CN imperfection and its effect on surface atomic cohesive energy.

I. Introduction

The size and shape dependence of the melting behavior of a surface and a nanosolid has attracted tremendous interest of research both theoretically and experimentally for decades.^{1,2} A huge volume of data has been established,^{3–11} and a number of excellent models have been developed in terms of classical thermodynamics and modern molecular dynamics.^{12–30} A theory based on the surface Laplace equation and the Gibbs–Duhem equation¹⁷ derived that the melting temperature, T_m , of a nanosolid depresses, which follows the relation:^{12,18}

$$\frac{\Delta T_m(D)}{T_m(\infty)} \approx \frac{4}{H_m(\infty)} \frac{\alpha}{D} \quad (D \neq 0)$$

and

$$\alpha = \begin{cases} \sigma_{sv} - \sigma_{lv}(\rho_s/\rho_l)^{2/3} & \text{HGM} \\ \frac{\sigma_{sl}}{1 - \frac{r_0}{r}} + \sigma_{lv}\left(1 - \frac{\rho_s}{\rho_l}\right) \quad (r_0 < r) & \text{LSM} \\ \left[\sigma_{sl} \quad \frac{3}{2} \left(\sigma_{sv} - \sigma_{lv} \frac{\rho_s}{\rho_l} \right) \right] & \text{LNG} \end{cases} \quad (1)$$

Where H_m is the latent energy of fusion, D and ∞ represent the diameters of a spherical dot of finite and infinite sizes, and ρ and σ are the mass density and the interfacial energy, respectively. Subscripts s, l, and v represent the phases of solid, liquid,

and vapor. Expressions of the α correspond to three outstanding models in terms of classical thermodynamics: (1) The homogeneous melting and growth (HMG) model^{19,20} considers the equilibrium between the entire solid and the entire molten particle indicating that the melt proceeds throughout the solid simultaneously. (2) The liquid shell nucleation (LSN) model^{21–25} assumes that a liquid layer of r_0 thick is in equilibrium at the surface of a solid of radius r , which indicates that the surface melts in prior to the core of the solid. (3) The liquid nucleation and growth (LNG) model^{26–28} suggests that the melting starts by the nucleation of liquid layer at the surface and moves into the solid as a slow process with definite activation energy.

Besides, the Lindemann’s vibrational-lattice instability criterion³¹ has led to an advanced atomistic model that relates the melting behavior of a nanosolid to the ratio of the root mean square displacement (rmsd, δ^2) of an atom at the surface to the rmsd of an atom inside a spherical solid:^{30,32–36}

$$\frac{\Delta T_m(D)}{T_m(\infty)} = \exp\left(-\frac{\beta - 1}{\frac{N}{N_s} - 1}\right) - 1 \approx -\frac{\beta - 1}{\frac{N}{N_s} - 1} \quad (2)$$

where $\beta = \delta_s^2(D)/\delta_b^2(D) = \delta_s^2(\infty)/\delta_b^2(\infty)$ is an adjustable parameter. Fitting experimental measurements could obtain information on the rmsd ratio of atoms at the surface to that in the bulk. N_s is the number of atoms in the surface region, and N is the number of atoms of the entire solid. This model indicates that if $\beta > 1$, the surface melts below the bulk melting point, and vice versa. The rmsd model has been applied well to the size-dependent melting of compounds,³⁰ metals,³² polymers,³³ glasses,³⁴ inert gases,³⁵ and ice³⁶ nanoclusters.

The models of LSN, HMG, and LNG suit only for the cases of melting point suppression ($\Delta T_m < 0$), while the rmsd model

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covers both the fall and rise of the T_m of a nanosolid. For particles larger than several nanometers, all of the models work well in simulating the size-dependent trends of measurement despite the different mechanisms. However, a large number of independent parameters is involved in models summarized in eq 1, such as the latent energy of fusion, mass density, and interface energy of different phases are needed to be considered when evaluating the melting behavior of a nanosolid. These quantities often change with the particle size.

Questions may arise: Which one of the mechanisms dominates the melting of a nanosolid? Is there any relevance among the different models? Is there anything common behind them? Therefore, a consistent understanding of the melting mechanism for a surface and a nanosolid and the possible interrelationship among the various models is highly desirable. Furthermore, a description relating the thermal energy to the atomic adhesion is still lacking, which forms an interesting challenge. In this work, we attempt to present an atomistic insight into this matter from the perspective of equilibration between the thermal energy of melting and the cohesive energy of an atom at different sites. We also attempted to relate the proposed atomic bonding mechanism to the existing models of rmsd instability, LNG, the LSN nucleation, and the random fluctuation melting (RFM)³⁷ and attempt to link all of the quantities involved to the effect of surface coordination number (CN) imperfection.

II. Theory Model

The “bond order—length—strength” (bond-OLS) correlation mechanism³⁸ states that (i) a small particle has a higher proportion of surface atoms than larger particles, (ii) atomic radius relaxes spontaneously because of the reduced atomic CN at the surface, (iii) as a consequence of the spontaneous relaxation, the binding energy of the relaxed bond increases, (iv) the relaxation-enhanced bond strength and the reduced atomic CN vary the cohesive energy of the surface atom from the bulk value, and (v) the bond energy rise increases the energy density in the relaxed region because the number of bonds does not change between any two neighboring circumferential atomic layers. The variation of atomic cohesive energy relates to the processes of thermodynamics such as self-assembly, phase transition,³⁹ and thermal stability of the system.⁴⁰ The density rise of binding energy in the relaxed region contributes to the Hamiltonian of the solid that determines the entire band structure of a nanosolid.³⁸ Any physical properties of a solid are determined by either the atomic cohesive energy or the Hamiltonian of the solid.

The concept of CN-imperfection-induced bond contraction was initiated first by Goldschmidt⁴¹ in 1927 for ionic solids and by Pauling⁴² in 1945 for metallic solids. According to Goldschmidt, if the CN reduces from 12 to 8, 6, and 4, the corresponding ionic radius will shrink by 3%, 4%, and 12%. Except for some II-a (Be, Mg(0001) surface) and II-b (Zn, Cd, Hg dimmer bond) elements that are reported to expand, all of the elemental dimmer bonds contract by even as high as 30%–40% for Ti, Zr, V, and Mo, for example.⁴³ The first interlayer spacing of diamond (111) has been reported to contract by 30%.⁴⁴ A contraction by from 4% to 12% of the O–Cu bond has been found to form one of the four essential stages in the O–Cu(001) surface bonding kinetics.⁴⁵ A 12%–14% contraction of the N–Ti/Cr bond has been confirmed to enhance the surface stress by up to 100%.⁴⁶ Most encouragingly, a recent density functional theory calculation⁴⁷ reveals that for Au, Cu, Pt, Pd, Ni, and Ag single atomic chains, the binding energy per bond is (–3 to –1 eV) 2–3 times larger in the chains than the

single bond energy (–1 to –0.4 eV) of the bulk fcc structures, and the equilibrium atomic separation contracts by 10% (for Cu and Ag) to 15% (for Pt). These findings concur with the bond-OLS premise, though the extent of relaxation and the amount of energy rise differ from source to source. Efforts made so far have shown consistently that the bond contraction at a surface dictates the size and shape dependency of nanometric materials in many aspects, such as the mean lattice contraction,⁴⁸ blue shift in photoluminescence,⁴⁹ and dielectric suppression⁵⁰ of semiconductive nanosolids, as well as the transition behavior of ferro- and pyro-electrics of PbZrTi oxides.^{51,52} It has been shown that the CN-imperfection-enhanced bond strength matters for the entire band structure of a nanosolid including the band gap, core level shift, bandwidth, and band tails through the change of the crystal field.³⁸

The bond length, or the diameter of an atom, in the i th atomic layer can be defined as $d_i = c_i d$ by introducing the coefficient c_i that depends on the CN (z_i) of the specific atom. The d is the bond length of an atom without CN imperfection. The bond-OLS correlation is formulated as³⁸

$$\begin{cases} d_i &= c_i d \\ E_B(d_i) &= c_i^{-m} E_B(d) \\ c_i(z_i) &= 2/[1 + \exp[(12 - z_i)/(8z_i)]] \end{cases} \quad (3)$$

The $c_i(z_i)$ is formulated based on Goldschmidt’s premise⁴¹ and Feibelman’s finding on the dimer bond contraction of Ti, Zr, Mo, and V.⁴³ The c_i^{-m} describes the energy change of the relaxed single bond with the reduced bond length. The m is an adjustable, which varies with the nature of the bond. Progress^{38,46,49,50,53} so far reveals that for elemental solid, m is around unity; for compounds and alloys, m is around 4. Normally, for the outermost two atomic layers, the effective CNs take the value of $z_1 = 4$ and $z_2 = 6$. At the lower end of size limit of a spherical dot, z_1 takes 3 or smaller. It should be indicated that the bond-OLS premise contains no assumptions or freely adjustable parameters for data fitting.

It is known that the total energy of a pair of atoms can be expressed in a Taylor’s series:

$$E_{\text{total}} = \sum_{n=0}^{\infty} \left(\frac{d^n u(r)}{n! dr^n} \right)_{r=d} (r - d)^n \quad (4)$$

which can be simplified as

$$E_{\text{total}}(r, T) = E_B(r) + E_v(T) = \begin{cases} 0 & \text{evaporation} \\ E_m & \text{liquidization} \end{cases} \quad (5)$$

The term of $n = 0$ corresponds to the minimal binding energy, $E_B(d) < 0$, at equilibrium atomic separation. The term $n = 1$ is the force ($= 0$) at equilibrium atomic distance, and the terms $n \geq 2$ correspond to the thermal vibration energy.

The physical ground for the model is that if one wishes to peel or loosen an atom off the solid thermally, one must supply sufficient thermal energy to overcome the cohesion of the specific atom to its surrounding. The thermal energy required to loosen one bond is the separation between the E_m , or E_{eva} , and the minimal bond energy E_B , as illustrated in Figure 1. If the thermal vibration energy, $E_v(T)$, is sufficiently large, all of the bonds of the specific atom will break and this atom will get rid of the bulk. At the evaporating point of any kind of solid, $E_{\text{total}} = 0$; at the melting point, $E_{\text{total}} = E_m$. The E_m may vary from material to material but for a specific material, the separation between E_m and E_{eva} should be fixed, which means

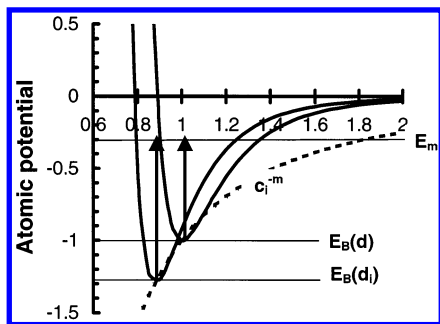


Figure 2 compares the measured size-dependent melting behavior of Sn and Al on SiN,^{61,62} Au on C⁸ and In embedded in Al matrix⁸ with the predictions using parameters given in Table 1. It is interesting to note that Al nanoparticles grown on SiN substrate are more platelike ($p = 1$) throughout the measured size but Sn on SiN and Au on C are more spherical-like ($p = 3$) at the particle size smaller than 10 nm. This may reflect the difference in the interfacial energy between the particles and the substrates. This also provides information about the fashion of epitaxial crystal growth and the bonding status of Al and Sn to SiN and Au to C. It is even interesting to note that the melting point of the In/Al system rises with reducing particle size. The current premise indicates that the rise of the melting point originates from the interfacial effect. It is understandable that an atom performs differently at a free surface from an atom at the interface. The unapparent change of the coordination ratio ($z_{ib} \approx 1$) in the interface and the formation of compound or alloy not only reduces the bond length but also

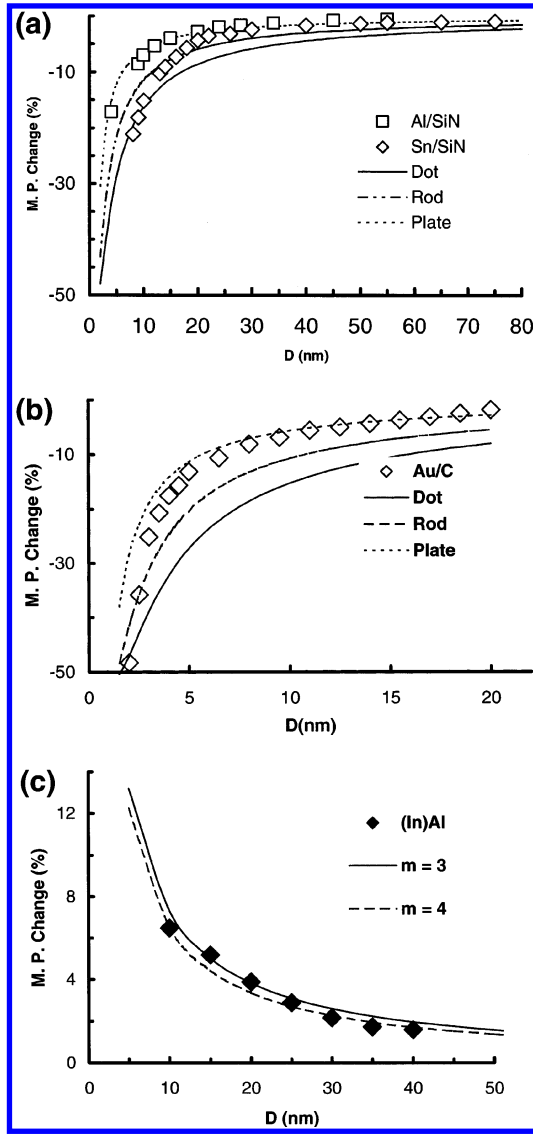


Figure 2. Agreement between predictions (solid lines) and experimental observations of the size and shape dependence of the melting points of (a) Sn and Al on Si_3N_4 substrate,^{55,62} (b) Au on C,²⁰ and (c) In embedded in Al matrix.⁸ Parameters are given in Table 1.

TABLE 1: Parameters Used in Simulation of Experimental Observations in Figure 2

parameter	media			
	In in Al	Au/C	Sn/SiN	Al/SiN
d_0 (nm)	0.330	0.288	0.309	0.286
$T_{\text{melt}}(\infty)$ (K)	698	1593	505	933
m	3/4	1	1	1
z_{1b}, c_1	0.9/0.825, 0.88	$1/3$, 0.88	$1/3$, 0.88	$1/3$, 0.88
z_{2b}, c_2	0.9/0.825, 0.96	$1/2$, 0.96	$1/2$, 0.96	$1/2$, 0.96
z_{3b}, c_3	0.9/0.825, 0.97	$2/3$, 0.97	$2/3$, 0.97	$2/3$, 0.97

alters the nature of the interatomic bond. It is known that an ionic bond or covalent bond is often stronger than the metallic bond. The higher $m \gg 1$ value represents the enhancement of the interatomic binding energy of compounds or alloys, as we confirmed recently.^{38,46,49,50} From the rmsd instability point of view, the interfacial binding constrains the rmsd of the interfacial atom to be smaller than that of a bulk atom.³⁰

It should be noted that with the particle size reduction the surface curvature increases and the surface atomic CN further decreases and the bond should contract further. With increase of the particle size, the area of interface between the particle

and the substrate increases. Atoms at the interface perform quite differently from atoms at a free surface, as we have compared. These factors may bring errors in the measurement that deviate from ideal modeling expectations. As we noted, the possible errors affect the accuracy of the m and the effective z_{ib} values in eq 10 but not the nature of the phenomenon or the general trend of change. Nevertheless, we should concern more about the physical origin and the general trends of the change than the precision of simulation because there exist possible errors in experiments and modeling approximations.

B. Model Comparison. First, we would like to indicate that all of the models are correct though they are based on different premises. Compared with the existing models, the current premise is simpler and straightforward without involving so many independent parameters. We relate the melting behavior directly to the strength of atomic bonding and quantize statistically the so-called “liquid shell” in other models as the contribution of individual atomic layers (eq 6) with different atomic CNs.

One may wonder that the pairwise potential may not correctly represent the multiatom interaction that involves the local charge density and high-order CN effects. Actually, we use the binding energy at equilibrium atomic separation, which is independent of the particular forms of the multiatomic potential. The atomic cohesive energy is the resultant effects of local charge density and the pairwise energy of different order CN. Actually, the effects of charge density and high-order CN can be treated as the background with a fluctuation caused by the CN imperfection. In considering the relative change of a quantity, the accuracy of the absolute intensity of interaction is not that meaningful because the background has been removed by the numerical treatment. The fluctuation may modify the value of m and the effective CN, as we discussed.

Second, the current bond-OLS premise involves almost no assumptions or freely adjustable variables. The model does not need to consider the latent energy of fusion, the mass density, and the surface/interface energy of different phases. Actually, the surface and interface energy and the local mass density of liquid and solid are functions of atomic separation and bond energy that are subject to the effect of CN imperfection.⁴⁶

The current premise supports the assumptions made in the models of LSN, LNG, and the rmsd for nanosolid. Only atoms in the outermost two or three atomic layers experience the CN imperfection, which modifies the energy binding the surface atoms to their coordinates. The thermal vibration (both frequency and amplitude) depends on the bond strength (for the first-order approximation, the force constant equals the second-order differentiation of the interatomic potential at equilibrium atomic separation) and the effective number of bonds. It is seen that in the present premise the $\Delta T_m(D)$ originates from $z_{ib}c_i^{-m} - 1$, compared with the rmsd one in which $-(\beta - 1)$ dominates. If $z_{ib}c_i^{-m} < 1$, then $\beta > 1$. It is seen that if the E_{coh} of a surface atom is weaker, its rmsd will be larger, and vice versa. For superheating, $z_{ib}c_i^{-m} > 1$, and $\beta < 1$. Therefore, the models of rmsd instability, LSN, LNG, and the current bond-OLS are in good accordance. All of the modeling variables relating to the melting can be related functionally to the E_{coh} , which should provide natural link between the various models.

IV. Conclusion

In summary, a cohesive-vibration energy-equilibrium mechanism has been developed for the size and shape dependence of the melting behavior of a surface and a nanosolid. It is suggested that the difference between the cohesive energy of

an atom at the surface and that of an atom inside the solid determines the fall or rise of the melting point of a surface and a nanosolid of which the portion of surface atoms varies with particle size. Therefore, by knowing the nature and trend of melting point change, it is possible to tune the melting point of a solid by simply controlling the shape and size of the constituent solids. Being with little assumptions or freely adjustable parameters, the current approach involves the essential facts happening at the surface: CN-imperfection-enhanced bond strength. Our approach is in good accordance with existing models based on classical and molecular thermodynamics. Combination of these models should provide deeper insight into the physical origin and the general trends of the melting behavior of an elemental, compound, and alloy nanosolid.

Note Added in Proof

While proofing this article, we have become aware of the liquid-drop model⁶³ and the surface-phonon instability model⁶⁴ for nano-solid melting and the measurement of silica-encapsulated Au nanoparticles.⁶⁵ All of these results show the 1/D dependence of the melting point, agreeing with the trend predicted by the current bond-OLS correlation.

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