Melting and superheating of crystalline solids: From bulk to nanocrystals

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Abstract

Melting of solids is a common phenomenon in nature. It is also one of the most important phase transformations in materials science and engineering. In recent years, extensive experimental and theoretical investigations in conjunction with computer simulations on melting of solids, with various geometries ranging from bulk forms to nanometer-sized clusters, have greatly enhanced our understanding of the nature of melting. This paper reviewed the up-to-date research results on this classical and cutting-edge topic. Emphasis was made on melting and superheating of nano-sized particles and thin films including thermodynamic and kinetic analyses of the size effect and the interfacial structure effect on melting processes.

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Nomenclature

\( b \) Burgers vector
\( C_L \) Lindemann constant
\( C_m \) concentration of migrating atoms in solids
\( C_v \) concentration of vacancies in solids
\( C_m(T^*) \) concentration of migrating atoms at a critical temperature \( T^* \) in solids
\( d \) particle/cluster diameter
\( D \) film thickness
\( \delta \) surface liquid layer thickness
\( \delta_L \) Lindemann parameter
\( \Delta E \) free energy change associated with melting
\( \Delta G_v \) solid–liquid free energy difference per unit volume
\( \Delta H_m \) melting enthalpy
\( \Delta H_{m}(r) \) melting enthalpy of nanocrystals with a radius \( r \)
\( \Delta H_{m}(d) \) melting enthalpy of nanocrystals with a diameter \( d \)
\( \Delta H_{m} (\infty) \) melting enthalpy of bulk solids
\( \Delta \gamma_{\infty} \) surface free energy difference for non-interacting solid–liquid and liquid–vapour interfaces
\( \Delta \gamma(\delta) \) surface free energy difference for interacting solid–liquid and liquid–vapour interfaces with a distance \( \delta \)
\( \Delta T_{m}^I \) superheating limit for heterogeneous melt nucleation at misfit dislocations at the interface
\( \Delta T_{m}^L \) superheating limit for melt nucleation at lattice dislocations within the solid
\( \Delta T_{m}^K \) superheating limit for homogeneous nucleation catastrophe of melting in solids
\( \Delta V \) volume change upon melting
\( E_{m} \) vacancy migration energy
\( E_v \) vacancy formation energy
\( G \) shear modulus of solids
\( G_0 \) shear modulus of solids at 0 K
\( G_m \) shear modulus of the matrix
\( G_s \) shear modulus of the solid particle
\( \gamma_{sl} \) solid (s)–liquid (l) interfacial energy
\( \gamma_{sv} \) solid (s)–vapour (v) interfacial energy
\( \gamma_{lv} \) liquid (l)–vapour (v) interfacial energy
\( \gamma_{sm} \) solid (s)–matrix (m) interfacial energy
\( \gamma_{lm} \) liquid (l)–matrix (m) interfacial energy
\( h_M \) atomic diameter of the matrix
\( h_n \) atomic diameter of the nanocrystal
\( k \) Boltzmann’s constant
\( L_m \) latent heat of melting
\( \lambda \) ratio between the rmsd of atoms on the surface and of those inside the nanocrystals
\( M \) atomic mass
\( \mu_s \) chemical potential of solid
\( \mu_l \) chemical potential of liquid
\( v \) Poisson ratio
\( Q \) activation energy for atomic diffusion in the crystal lattice
\( r \) particle/cluster radius
\( r_s \) radius of solid particle
\( r_l \) radius of liquid particle
\( r_n \) nucleus radius of liquid
\( r_n^* \) critical nucleus radius of liquid
\( \rho \) density of solid or liquid
\( \rho_s \) density of solid
\( \rho_l \) density of liquid
\( S_m \) entropy change caused by vacancy migration
\( S_v \) entropy change caused by vacancy formation
\( \sigma_m^2(r) \) average rmsd of atoms of nanocrystals at \( T_m(r) \)
\( \sigma_m^2(\infty) \) average rmsd of atoms of bulk solids at \( T_0 \)
\( T \) temperature in K
\( T_0 \) equilibrium melting point of bulk solids
\( T_{0(n)} \) bulk melting point of the nanocrystal
\( T_{0(M)} \) bulk melting point of the matrix
\( T_g \) idea glass transition temperature (or Kauzmann temperature)
\( T_m \) melting temperature of solids
\( T_m(r) \) melting temperature of a nanocrystal of radius \( r \)
\( T_s \) isentropic temperature of solids (or inverse Kauzmann temperature or F-J temperature)
\( T_r \) rigidity instability point of solids
\( T_v \) isochoric temperature of solids
\( T^k_m \) critical temperature for homogeneous nucleation catastrophe of melting in solids
\( T^H_m \) critical temperature for heterogeneous nucleation catastrophe of melting on dislocations in solids
\( T_m^a(\varepsilon) \) melting temperature of solids under a strain of \( \varepsilon \)
\( T^* \) instability temperature caused by vacancy decomposition
\( T_w \) onset temperature of surface melting
\( \theta \) contact angle for melt nucleation on the matrix
\( \Theta \) characteristic temperature of the solid
1. Introduction

Melting, a phase transformation from a crystalline solid state (rigid and topologically long-range-ordered) into a liquid state (fluid and topologically long-range-disordered), is a common phenomenon in nature. Investigations on melting of solids have dated back to beginning of the last century for its scientific and technological importance. Melting is born to be a key subject in condensed matter physics. As one of the most important phase transformations in processing and applications of materials, melting is also a vital process in materials science and engineering. In addition, melting of solids is closely related to nature environment, biology, and many other fields [1]. Therefore, investigations on the nature of melting are of interdisciplinary interests covering a broad range of sampling from tiny clusters containing several tens of atoms to the inner core of the earth.

In the framework of classic thermodynamics, melting of a solid is known as a first-order discontinuous phase transformation occurring at a critical temperature at which Gibbs free energies of the solid and the liquid states are equal, i.e. $T_0$ of the solid. The melting process of a solid involves an abrupt change in latent heat and volume at $T_0$. Numerous experimental observations verified that melting is normally initiated at solid surfaces because of the vanishing nucleation barrier there [1,2]. In addition, investigations revealed that various kinds of defects in solids, such as interfaces, grain boundaries, voids, impurities and other defects, also facilitate melting.

Indeed, understanding of the melting process has been greatly improved after extensive and intensive studies in the past century and several models for melting of solids have been developed. Nevertheless, many aspects of melting are to be understood and the intrinsic mechanism of melting in solids is still a mystery.

Recent development of low-dimensional materials including nano-sized particles, nanometer-thick thin films, nano-wires, nano-tubes, and nano-grained polycrystalline solids, presented many novel properties and performance that are attractive to technological
applications. At the same time, these advanced materials provide us new venues for studying melting of solids because they all possess numerous amounts of surfaces or interfaces. Especially these low-dimensional materials brought unique opportunities to examine the role of surfaces and interfaces in melting as well as the size effect on melting kinetics.

Melting kinetics of low-dimensional materials, in which surfaces and/or interfaces play a dominant role, is much deviated from that for the conventional bulk solids. For example, the melting point of free-standing nanometer-sized particles is remarkably depressed relative to \( T_0 \) \([3]\). It is also observed that when the nanoparticles are properly coated by (or embedded in) a high-melting-point matrix, the melting point of the particles can be elevated above \( T_0 \) \([3]\), that rarely happens in bulk solids. These interesting phenomena make melting of low-dimensional solids to be an attractive topic which has drawn increasing attentions in both fields of condense matter physics and materials science in recent years.

With the increasing technological applications of low-dimensional materials in industries, thermal stability of the materials becomes one of the crucial issues to concern for their practical performance. Melting becomes one of the failure modes at elevated temperatures for low-dimensional materials. For example, owing to the size effect, catalysts of nano-sized metallic particles might melt and agglomerate at temperatures far below \( T_0 \), thus losing their functionality. Clearly, investigations on melting of low-dimensional materials, on the other hand, are of significance for the technological applications of this new materials family.

It is known that melting is normally nucleated at solid surfaces or interfaces. Once the heterogeneous nucleation of melt is somehow suppressed at the solid surfaces or interfaces, one may expect that the solid phase persists in its metastable solid form above \( T_0 \), which is known as superheating, or overheating \([4]\). Pioneering exploration of superheating in metals was performed by Daeges et al. \([5]\) in 1986 and they successfully achieved superheated Ag micro-sized particles coated by Au. Since then, numerous investigations on superheating of metallic particles in various systems have been reported and several models accounting for the superheating phenomenon have been proposed. Superheating of solids provides an interesting subject and a new territory for studies of melting. On one hand, studying superheating of solids greatly facilitates understanding of the nature of melting and the ultimate stability limit of crystalline solids. On the other hand, achieving superheated solids may provide effective approach for stabilization of low-dimensional materials exposed to elevated temperatures, which is of technological significance for materials.

In recent years, extensive experimental and theoretical investigations as well as computer simulations on melting and superheating of crystalline solids (especially on low-dimensional materials) have been carried out. Significant progresses have been made on this fascinating subject with a large body of publications appeared in the literature, including several review articles related to some aspects of melting \([1,3,4,6–16]\). The objective of the present paper is to provide a comprehensive summary of the up-to-date research results in recent years on this classical and interesting topic, including a considerable amount of new results from the authors’ group. Emphasis will be made on melting and superheating of nanostructured solids including thermodynamic and kinetic analyses of the size effect and the interfacial structure effect on melting processes.

In this review, we begin with a survey on various melting theories and analyses on the superheating limits of solids, with an emphasis on correlations among those models. Then surface melting is discussed, which is considered as a precursor of melting for “real” solids. Melting of small particles is discussed in the fourth section, including experimental studies
and theoretical models for the size-dependent melting point depression, the size-dependent melting enthalpy, effects of crystal shapes and surface coating, and the abnormal size effect. In the fifth and sixth sections, we concentrate on superheating of confined nano-sized particles and nanometer-thick thin films, including effects of interfacial structure and crystal dimensions on superheating, experimental observations and simulations on the melting process of superheated crystals, and thermodynamics and kinetics of superheating. In the seventh section, recent studies on melting of alloy particles are addressed. Finally, prospective and further developments on this topic are presented as concluding remarks.

2. Melting theories and superheating limits

2.1. Lindemann criterion

As early as in 1891, Sutherland [17], in his kinetic theory of solids, considered atoms as hard spheres vibrating against each other and speculated that melting would occur when distances between atoms reach a certain value relative to the atomic diameter. Further calculations based on Sutherland’s model revealed that the ratio of vibration amplitude to the atomic spacing is almost the same for all elements at their melting points [17]. In 1910, Lindemann [18] advanced Sutherland’s idea and assumed that melting would take place when the amplitude of thermal vibration of atoms becomes so great (i.e. it attains a critical fraction of the equilibrium spacing of neighbouring atoms) that direct collisions occur between neighbouring atoms, leading to the lattice instability. Applying the Einstein model for heat capacity of solids to calculate the Einstein frequency at the melting point, Lindemann obtained

$$T_0/M\Theta^2V_m^{\frac{3}{2}} = C_L,$$

where $C_L$ is assumed to be the same for crystals of a similar structure.

Ever since Lindemann proposed his melting hypotheses, theoretical modifications as well as experimental tests have been performed by various groups of scientists [19,20]. For example, Gilvarry [21] put forward Lindemann rule and stated that melting occurs when the root-mean-square amplitude of thermal vibrations of atoms reaches a critical fraction of the nearest-neighbour separation, which is the form of Lindemann criterion generally used now. Based on theoretical analysis and numerical calculations on various metals and rare gases, Cho [19] found that the Lindemann constant and the Lindemann parameter (the critical ratio of vibration amplitude over the interatomic distance) are structure-dependent, i.e. they are significantly different for bcc, fcc and hcp metals and Lindemann law holds for each structure separately.

As a one-phase theory, Lindemann criterion is not thermodynamically sound as it does not take the free energy of the liquid state into account [22]. Also, such an approach to understand melting does not explain the mechanism leading to melting. Nevertheless, Lindemann criterion is still widely used nowadays for its simplicity and capability in predicting melting points, especially for substances under extreme conditions [8].

2.2. Born criterion

As temperature rises, atomic distances in a solid increase and the restoring force decreases due to thermal expansion. It is therefore expected that the shear modulus of a
crystal solid decreases with an increasing temperature. Sutherland [17] studied the temperature-dependence of shear modulus \(G\) for various metals, and suggested that it follows

\[
G = G_0(1 - T/T_0)^2,
\]

(2)

The model indicates that the shear modulus of a solid sinks to zero at \(T_0\). Sutherland [17] emphasized that the melting point of a solid should be defined as the temperature at which its rigidity becomes zero. In 1938, in studying the elastic coefficients of solids, Brillouin [23] found that the macroscopic rigidity of a solid becomes zero while the microscopic rigidity remains finite as the melting point is approached. He also considered the anisotropy of solids and suggested that for a crystal, different rigidity coefficients would not become zero at the same temperature and that the whole crystal stability would be destroyed once one of the rigidity coefficients tends to zero.

One year later, Born [24] further stated that the difference between a solid and a liquid is that the solid has an elastic resistance against shearing stress while the liquid has not. Independently of Brillouin’s work, Born [24] conducted a more sophisticated thermodynamic treatment to investigate crystal lattices under shearing stress. Finally, Born criterion was developed as definition of melting in terms of mechanical instability of a crystal: melting of a crystal occurs when one of its shear modulus vanishes.

Similar to Lindemann melting criterion, Born’s model is also a one-phase theory that contains no distinct description of liquid, and thus fails to account for the discontinuous, first order character of the melting transition. Besides, Born’s theory was challenged by subsequent observations of elastic moduli of various solids that failed to vanish at the melting point [25,26]. Despite the numerous experimental results which seem to refute Born’s theory, the idea that melting and shear instability of a solid may be somehow correlated has remained alive, since a large body of experimental evidences does reveal a relationship between the two phenomena [9]. Quite later, Tallon et al. [27,28] tried to modify Born’s initial criterion to obtain a more physically sound theory of melting. They found the shear modulus of solid is a continuous function of dilatation through the melting expansion and falls to zero at the dilatation of the liquid. Thus, they suggested that Born’s criterion should be replaced by the following: melting occurs when a solid can transform isothermally to a state of zero shear modulus. According to Tallon et al., the modified theory becomes a two-phase theory capable of explaining the discontinuous character as well as the heat absorption of melting. However, their extrapolation seems not applicable for crystal with a negative volume change upon melting.

Recently, Yip and coauthors [29–32] performed computer simulations to re-examine Born criteria of lattice stability in cases of zero external stress and arbitrary external load. They showed that Born’s criteria are valid only under zero external stress. When heating an idea solid to melting at zero pressure, melting occurs as incipient lattice instability due to vanishing of tetragonal shear modulus, as predicted by the Born criteria. However, when a solid is subjected to pure dilatation under a negative pressure, the lattice instability is initiated by vanishing of bulk modulus as a result of lattice de-cohesion.

2.3. Thermoelastic instability criterion

In 1934, in a theoretical study of the equation of state of argon, Herzfeld and Goeppert-Mayer (HGM) [33] suggested that melting might be caused by a thermodynamic instability of a solid in which the isothermal compressibility diverges as \(T\) approaches \(T_0\). Five years
later, Kane [34] extended the work to include the rest rare gas solids except He. However, at that time, Born’s theory was more appealing (because it pointed out that the character of a liquid that makes it a liquid is its lack of resistance to shear stress) and gained much more acceptance than the HGM theory.

Until recently, Boyer [9] re-introduced the HGM theory, and showed that there is indeed a connection between Born’s idea and the work of HGM, i.e. the decrease in resistance to shear stress actually leads to the HGM instability. Based on experimental results and theoretical analyses of various melting theories, he gave a new thermoelastic instability theory of melting: the decrease of resistance to shear stress is characterized by divergence of thermal expansion and isothermal compressibility at $T_0$. Further, Boyer showed that various ideas to understand melting which seem to be very diverse can be included within the frame work of the thermoelastic theory. Boyer’s interpretation was later supported by computer simulations [31,32].

2.4. Defect-induced melting

2.4.1. Vacancies

In the hole theory of liquids, the elementary mechanism of melting is believed to be connected to the formation of vacancies in solids [35,36]. Gorecki [37] systematically studied the role that vacancies may play in melting of metals. He adduced extensive evidences to demonstrate existence of correlations between the parameters which characterize the vacancy formation in solids and the change of physical properties of metals across melting points. He found correlations between the vacancy formation energy and the bonding energy of metals. By calculating the equilibrium vacancy concentration at melting points, he showed that for many metals with different structures (fcc, bcc and hcp), the equilibrium vacancy concentration, which is a function of temperature, reaches a critical value of 0.37% at the onset of melting, followed immediately by a sudden creation of more vacancies to about 10% at the expense of latent heat. Further, Gorecki tried to rationalize the changes of various physical properties on melting based on the vacancy model [38]:

(a) The latent heat of melting is related to the vacancy formation energy of metals.
(b) The volume change on melting can be interpreted as the result of the volume increase caused by formation of additional vacancies on melting.
(c) The increase in electrical resistivity on melting is proportional to the resistivity increase caused by vacancies.
(d) The initial slope of the pressure effect on melting point can be quantitatively interpreted in terms of the pressure dependence of vacancy formation energy.

Generally, as Cahn pointed out [11], the vacancy model of melting is empirically self-consistent and watertight, in that it has built up a very wide range of distinct phenomenon which it can interpret. A possible weakness in Gorecki’s model is that he tacitly assumes that the holes in a molten metal are of the same size and have the same physical properties as vacancies in the corresponding solid. Despite some criticisms, there are also strong experimental evidences supporting the vacancy model. For example, studies on several metals showed that gamma irradiation (which creates point defects) lowers the melting point by an amount which is proportional to the dose (corresponding to the additional vacancy concentration). However, the vacancy model still did not explain the melting
mechanism, i.e. why and how the vacancy concentration increases during melting from 0.37% to about 10%.

An earlier computer simulation work by Fukushima and Ookawa [39] tried to understand the behaviour of vacancy on melting. They introduced the bubble raft model by setting it in a vibrating state in order to simulate the real crystal in thermal vibration. Their results suggested that vacancies become more diffusible as a crystal is heated. For instance, an isolated vacancy at room temperature will be shared by neighbouring atoms as temperature is raised close to the melting point, resulting in formation of a region of reduced atomic density. The simulation might provide a way to understand why a vacancy concentration of 0.37% can affect the stability of the whole crystal lattice: at a critical vacancy concentration, low density regions with locally high vibration amplitude formed by the merge of diffuse vacancy groups, might be able to trigger the destruction of the lattice order. However, the physical reason determining the increased vacancy concentration upon melting still remains unrevealed.

Recently, Wang et al. [40] re-examined the role of vacancy on melting, with a focus on vacancy migration rather than vacancy concentration. The basic idea is that, as a crystal is heated towards its melting point, intense atomic migrations near vacancies will be induced to such an extent that a single vacancy will be decomposed by neighbouring atoms—a phenomenon similar to the sharing of an isolated vacancy as described in the bubble raft model [39], leading to an onset of lattice disordering. Further, they found quantitatively that there is a correlation between the vacancy decomposition temperature and the kinetic instability temperature of crystals.

In the model, atoms having the ability to exchange positions with the neighbouring vacancies are defined as migrating atoms. Analogous to the thermal equilibrium vacancy concentration in the solid, the concentration of migrating atoms ($C_m$) can be expressed as

$$C_m = \exp \left( \frac{S_m}{kT} - \frac{E_m}{kT} \right).$$

According to the above equation, $C_m$ increases with increasing temperature, as shown in Fig. 1. It is supposed that when $C_m$ reaches a critical value $C_m(T^*) = 2/N_n$ (where $N_n$ is the number of first-coordination neighbouring atoms, e.g. 12 for fcc metals), vacancy decomposition happens because there are two neighbouring atoms near a vacancy possessing energies higher than $E_m$ and hence having an ability to migrate to the vacancy simultaneously. Such a kind of vacancy decomposition is believed to be able to induce destruction of the local lattice structure around the vacancy. The temperature at which the vacancy decomposition happens ($T^*$) is found to be approximately equal to $T_m^k$ of solids [41], as shown in Fig. 2. The coincidence between $T^*$ and $T_m^k$ is believed to be an implication of a possible correlation between vacancy decomposition and the onset of melting in solids.

2.4.2. Interstitials

Besides vacancies, another type of point defects, namely interstitials, were also considered for interpreting melting, known as the Lennard-Jones-Devonshire model [42]. In this model, melting is viewed as an order–disorder transition resulting from the change of relative atomic positions—positional melting, in which the interaction of normal lattice atoms and self-interstitial atoms plays an important role. Similar to vacancies, it is also found that on melting the interstitial atom reaches a critical value of $\sim 10^{-3}$ [43].
Although the approach of Lennard-Jones-Devonshire model is not strictly a two-phase theory of melting, it considered much more on the structure features of liquid than other melting theories at that time (e.g. Lindemann criterion and Born criterion). Also, despite the physical crudity, the theory is helpful to understand several important characteristic of melting, such as correlation between interatomic forces and melting, pre-melting of crystals, the origin of thermal expansion of melts, and structure of supercooled melts, etc. [8]. However, the theory has not gained much acceptance as Born criterion and HGM theory.

A recent simulation work dealt with the mechanism for a solid losing its crystalline order on the atomic scale [44]. By means of molecular dynamics modeling, it is possible...
to trace the position of every atom at each instant as melting happens. Detailed simulation results for superheated Al revealed that the thermal fluctuation initiating inner melting is an aggregate typically with 6–7 interstitials and 3–4 vacancies, a mechanism different from those proposed traditionally that involve many more atoms at the initial stage of melting. The simulation, on the other hand, inspired one to consider the cooperation of various kinds of point defects, such as vacancy–interstitial pairs, as basic elements to initiate melting. Interestingly, Kanigel et al. [45] showed that vacancies do not influence the elastic moduli of a solid, while interstitials cause a large reduction in them. The result indicates the different roles of point defects in inducing mechanical melting (Born criterion).

Reviewing the previous studies on the point defect effect on melting of crystals, it is conceivable that a new model for melting is to be advanced by considering both the concentration and the mobility of various types of point defects (i.e. vacancies and interstitials) in solids. A key point is to understand how these defects cooperate with each other to induce the local lattice instability. Meanwhile, different conditions should be taken into account: solids with free surfaces that perform normal melting (with heterogeneous nucleation at surfaces), and those without free surfaces exhibiting superheating (i.e. melting above $T_0$) when heterogeneous nucleation is suppressed. The role of point defects on melting should be different under these two conditions. For example, one may expect that the critical concentration of point defects needed to induce surface melting at $T_0$ might be similar to that for bulk melting at the superheating limit. Recent computer simulations [46,47] suggested that the homogeneous and heterogeneous melting processes are both mediated by atoms with defective coordination. Moreover, their concentration in the regions close to the surface at $T_0$ is found to be approximately the same as in the surface-free bulk at the limit of superheating.

2.5. Dislocations

Unlike point defects, lattice dislocations in solids are a kind of cooperate defects. The idea to understand melting on basis of dislocations was first propounded by Mott in 1952 [48], followed by Mizushima [49] and Ookawa [50]. Their point is that the total excess energy of dislocations depends on the dislocation density and temperature. Later, Kuhlmann-Wilsdorf [51] advanced a dislocation based theory to account for melting qualitatively and quantitatively, which is based on the contention that melting occurs when the free energy of glide dislocation cores becomes negative. Then, dislocation cores are generated freely to fill the crystal to capacity. Meanwhile, the solid absorbs the latent heat and loses resistance to shear stress. The melting point and latent heat of melting are related to the known properties of crystals, and the energy and dilatation of dislocation cores. The theory is successful in that it is in a good agreement with a considerable body of experimental data. Moreover, aside from the melting point and latent heat of melting, it derived some well-known relationships of metals, such as the Richard’s Law (the ratio of latent heat to melting point is close to the gas constant for many metals), the correlation between the entropy of melting and ductility of metals and the Lindemann Law. The volume expansion on melting can also be qualitatively explained except for metals with a negative volume expansion on melting. The success of the theory indicated that the liquid can be viewed as a crystal filled with capacity of glide dislocation cores, providing a useful model to understand many properties of liquids.
Computer simulation provides a powerful tool to study melting in that it makes possible to observe the system on atomic scale in very short time intervals. Cotterill et al. [52] performed extensive computer simulations investigating the role of dislocations on melting, revealing that melting proceeds through the spontaneous proliferation of dislocation dipoles. Also, the size-dependent melting point depression and surface melting were evidenced. Based on a series of studies, Cotterill et al. [52] deduced that melting might be caused by a bifurcation instability, and that a liquid should be regarded as resulting from a series of cascading bifurcations.

The dislocation theory of melting has gained much supports from computer simulations as well as experiments. It predicts successfully the features of a first-order transition: the latent heat and the volume change of melting, only that the melting temperature cannot be rationized exactly. Lund [53] correlated the dislocation melting model with Born’s theory, and showed that the thermally excited circular dislocation loops in a three-dimensional elastic solid will renormalized the shear modulus to zero at a temperature of the same magnitude of the melting point for most solids. Burakovsky and Preston [54], by modeling melting as a dislocation-mediated transition, obtained a constitutive equation relating the melting point to the crystal structure, atomic volume, and the shear modulus of a solid.

Besides the above melting theories, there are other theories, although less-known, dealing with the instability limits of solids (and even liquids) and their possible correlation with melting [55–62].

2.6. Limits of superheating

Solids usually melt at a temperature below their $T_0$ due to pre-melting at surfaces or interfaces that act as heterogeneous nucleation sites for melt. When heterogeneous nucleation of melt at surfaces is suppressed, e.g. by means of proper coating with a high-$T_0$ material, melting would occur well above $T_0$, which is normally referred as to superheating as we mentioned before. Experimental observations showed that superheating can be achieved in various systems including metals and inorganic solids and the degree of superheating is dependent on kinetic factors (such as the heating rate) and structural ones such as the particle sizes and the effectiveness of coating, etc. [3]. An interesting question to be answered is whether there is an ultimate limit for superheating of a solid, which is fundamentally correlated with the mechanism governing the melting of solids.

Fecht and Johnson [63] explored the limit of superheating in solids by examining the temperature dependence of entropy change for a superheated solid and liquid, respectively, which is analogous to the famous Kauzmann’s paradox in supercooled liquids. Kauzmann [64] noticed that the entropy difference of a crystal and a supercooled liquid may vanish at a temperature well above absolute zero, below which the supercooled liquid would have a lower entropy than the crystal. The condition, as Kauzmann termed it a paradox, determines the maximum a liquid can be supercooled while remaining in metastable equilibrium because the supercooled liquid would have to transform into a glass state to avoid the Kauzmann paradox. The temperature for such an isentropic condition is then called as the ideal glass transition temperature $T_g$ (or Kauzmann temperature).

In dealing with superheated solids, Fecht and Johnson [63] pointed out that a similar entropy paradox exists at a temperature well above the $T_0$, beyond which the entropy of the superheated crystal exceeds that of the liquid. This isentropic point determines the upper bound of superheating. They calculated the temperature dependences of entropy
for a crystalline and a liquid Al for both stable and metastable states. The isentropic temperature $T_m^s$, also termed as the inverse Kauzmann temperature or F-J temperature, was determined as $1.38T_0$ if the vacancy contribution is properly included.

Tallon [65] argued that the entropy catastrophe is an outer bound on the stability limit of solids, and a hierarchy of inner catastrophes occurs at lower superheatings. For crystal superheating, successions of catastrophe occur in the sequence of thermodynamic (equilibrium melting), elastic compressibility, elastic rigidity, isochoric and entropic points, as shown in Fig. 3. The isochoric temperature $T_v^m$ is the point at which the crystalline and the liquid phases have the same molar volume or density. Beyond $T_v^m$ the crystal would be less dense than its liquid phase at the same temperature, which is unreasonable for a close-packed crystal. Therefore, $T_v^m$ represents a catastrophe point for superheated solids. For Al, it was estimated as $1.28T_0$. The rigidity instability point, $T_r^m$, as Born’s idea should mean, indicates where the rigidity of the superheated solid equals that of the liquid at the $T_0$. It is $1.24T_0$ for Al, obviously lower than $T_v^m$ and $T_s^m$. Therefore, Tallon believed that $T_v^m$ and $T_s^m$ are not observable as they are preempted by the rigidity catastrophe.

On the other hand, superheating of solids, like supercooling, can be determined by kinetic factors. Actually, the maximum supercooling has been estimated by kinetic considerations that catastrophic homogeneous nucleation of crystals occurs (about $0.2T_0$ for most metals). With this idea, Lu and Li [41] performed a kinetic analysis of homogeneous nucleation of melt in superheated crystals.

For a bulk crystal, if heterogeneous nucleation of melting at defects (such as grain boundaries, dislocations or free surfaces) can be avoided, melting would proceed by homogeneous nucleation inside the crystal lattice. On this condition, the Gibbs free energy change ($\Delta G(T)$) required to form a liquid spherical nucleus of a radius $r_n$ will be

$$\Delta G(T) = \frac{4}{3}\pi r_n^3(\Delta G_v + \Delta E) + 4\pi r_n^2\gamma_{sl}$$  \hspace{1cm} (4)
in which $\Delta G_v$ can be approximated by $\Delta H_m(T_0 - T)/T_0$. By analogy with the classical homogeneous nucleation theory for solidification, a critical size of

$$r_n^*(T) = \frac{-2\gamma_{sl}}{(\Delta G_v + \Delta E)}$$

(5)

and a critical work of nucleation of

$$\Delta G^*(T) = \frac{16\pi\gamma_{sl}^3}{3(\Delta G_v + \Delta E)^2}$$

(6)

can be obtained for the homogeneous melt nucleation.

The homogeneous nucleation rate of liquid can be calculated via

$$I_{\text{hom}} = I_0 \exp\left(-\frac{\Delta G^*(T)}{kT}\right) \exp\left(-\frac{Q}{kT}\right)$$

(7)

where $I_0$ is a pre-factor related to vibration frequency of atoms and the surface area of the nuclei. Fig. 4 shows calculated results of the nucleation rate as a function of temperature for aluminum, compared with that of the nucleation rate of solidification. It is seen that the homogeneous nucleation rate for melting increases by orders of magnitude from essentially zero to very high values over a narrow temperature range, i.e. there is effectively a critical temperature, $T_{km}$, at which an “explosive” homogeneous nucleation of melting occurs inside the superheated crystal lattice. The critical superheating temperature required to give one nucleus per second per cm$^3$ under homogeneous nucleation of melting in Al was found to be 1127 K, about 1.21$T_0$. The critical superheating, $T_{km}$, is found to be around 0.20$T_0$ for many elements, comparable to the degree of undercooling in freezing.

From a kinetic point of view, the critical temperature ($T_{km}$) is considered as an upper limit for a superheated crystal, above which catastrophic melting will be initiated by

![Fig. 4. Calculated results of the homogeneous nucleation rates for melting and solidification in Al. The characteristic stability limits ($T_m^s$, $T_n^s$, and $T_m^s$) are indicated [41].](image-url)
massive homogeneous nucleation. For Al, $T^k_m = 1.21T_0$, is the lowest among various instability limits discussed previously, as shown in Fig. 4. In other words, with progressive superheating, a homogeneous nucleation catastrophe occurs before other catastrophes can intervene. It is also noted that the model deals with the metastable superheating limit induced by homogeneous nucleation catastrophe, while large transient superheating might be observed at very high heating rates, which may exceed the kinetic superheating limit, or even the isentropic temperature (see also Section 5). A density functional argument by Iwamastu [66] also yielded a similar result with the classic homogeneous nucleation theory of melting.

Since experimentally it is rather difficult to measure the melting process inside a crystal lattice without pre-melting at surfaces, MD simulation was applied to verify the homogeneous melting theory of melting [67]. In the simulation, in order to exclude any free surface effect and to mimic part of an infinite bulk single crystal, periodic boundary conditions are employed along the three-dimensional (3D) directions of a cubic box containing 500 Al atoms. The atomic volume ($\Omega$) and the potential energy ($E$) were recorded as a function of temperature. The resulting $\Omega$–$T$ and $E$–$T$ curves showed a sudden change of $\Omega$ and $E$ at 1137 K, indicating that the melting point of the surface free MD bulk Al crystal is 1137 K, or $1.22T_0$. From the recorded profiles of the atomic positions in the MD box, thermodynamic fluctuations can be observed just before melting, and the crystalline lattice was found to collapse abruptly and homogeneously into the liquid structure upon melting. Taking into account the size effect of the MD system, the melting point of the MD Al crystal is consistent with that predicted by the homogeneous nucleation theory.

Ma and Li considered the effect of dislocations on superheating in real crystals [68]. Following Lu and Li’s model, they examined the heterogeneous nucleation of melt at lattice dislocations and found that a massive heterogeneous nucleation catastrophe on dislocation will occur in superheated crystals at a critical temperature, $T_H^m$, typically $1.10T_0$ for metallic crystals, lower than $T^k_m (1.20T_0)$.

A recent computer simulation showed the close relation between homogeneous nucleation and superheating [69]. It was found that the solid/liquid density difference at melting and the interface disordering are two key factors determining the superheating limit, in that the former can cause a nucleation forbidden gap and the latter may reduce the nucleation barrier rising from the interface.

2.7. Correlations among various melting theories

As described above, different superheating limits were yielded from different melting mechanism, some of which were found to be correlated. However, a general agreement among these melting mechanisms is not available [70]. With MD simulations, Jin et al. [71] performed detailed investigation to explore the correlation between different melting theories in case of melting initiated at the surface at $T_0$, and inside the crystal lattice at the limit of superheating.

In the simulation, a model of 6912 Lennard-Jones (LJ) Ar particles in a fcc cubic box with 3D periodic boundary conditions was used to represent an initially surface-free and defect-free idea crystal. MD is performed by rescaling velocities of the particles using the explicit Verlet algorithm under the zero pressure condition. The first-order melting transition manifests itself at a reduced temperature $T_m = 0.79$ where the mean $\Omega$ undergoes a sudden upward jump, as indicated in Fig. 5a. The melting temperature is almost 20%
above $T_0$ ($T_0 = 0.66$), indicating the existence of a substantial metastable superheating since no signal for melting can be detected even after long runs at $T = 0.775$. Unstable superheating induced by rapid heating (melting kinetics) is insignificant in the present case considering the transient nature of melting at such a high degree of superheating.

The temperature dependence of the Lindemann parameter $\delta_L$, i.e. the rmsd of a particle from its equilibrium position divided by the averaged nearest-neighbour distance, is calculated as shown in Fig. 5b. The system average $\delta_L$ is about 0.12–0.13 at $T_0$, consistent with Lindemann’s original criterion for simple crystals. As the temperature rises upon superheating, $\delta_L$ continues to increase almost linearly up to about 0.2, followed by a divergence upon melting. It is interesting that the $\delta_L$ value at the melting temperature of the superheated crystal ($T_m \sim 0.22$) is similar to the value for heterogeneous melting at surfaces near $T_0$. This indicates that to initiate melting without free surfaces as heterogeneous melt nucleation sites, atoms inside the bulk have to rely on significant superheating to increase their rmsd (by enhanced thermal vibrations) to a level equivalent to that of surface atoms near $T_0$. The condition $\delta_L = 0.22$ therefore seems to have a physical significance in both bulk and surface melting.

The non-Gaussian parameter $\chi_2$ is introduced to characterize the highly displaced atoms near $T_m$, with larger $\chi_2$ values represent higher spatial or dynamic heterogeneities of the system. As shown in Fig. 6, calculated result of $\chi_2$ indicates a near-zero value and a very weak $T$ dependence until $T \sim 0.77$ is close to $T_m$. Afterwards, $\chi_2$ increases significantly until melting, indicating extensive atomic movements with corresponding strong deviation from the equilibrium lattice sites near the melting temperature, and then

Fig. 5. Melting within the LJ crystal: the $T$-dependence of the atomic volume (a) and the scaled rmsd (or the Lindemann ratio) (b, squares) and the percent of Lindemann atoms relative to atoms in the whole system (b, circles). The thin line in (b) shows the linear dependence of the low-$T$ data. Temperature and volume are in the reduced units [15].
followed by a quick drop to zero, corresponding to the complete loss of crystallinity in the random (homogeneous) liquid.

Another important finding comes from calculating the Born elastic moduli of the Lindemmann atoms. As shown in Fig. 6, the shear moduli difference $\Delta C_s = C' - C_{44}$ of the whole system is not zero right at the melting temperature, but goes to zero upon melting. However, it was found that $\Delta C_s$ can be nearly zero or below zero for a sufficiently large cluster formed by more cooperative Lindemann atoms. The “Lindemmann atoms” is then defined as those whose fractional rmsd exceeds the critical value $\delta_L^c = 0.22$. As shown in Fig. 5b, the number of Lindemmann atoms increases rapidly with temperature near the melting temperature. Also, the Lindemann atoms were found to appear cooperatively and form extended clusters just before melting (where $\kappa_2$ shows a peak), as displayed in Fig. 6 by the snapshots of the 3D atomic configuration taken at $T_m$. The structure inhomogeneity suggests that melting does not occur all at once throughout the
whole crystal but rather initiates via local instabilities. The interstitial point defects are believed to be responsible for the formation of these Lindemann atoms.

The results demonstrate a strong correlation between Lindemann criterion and Born criterion: melting is initiated by local instabilities governed by both. With $T$ increasing, the number of Lindemann atoms increases as the lattice continuously expands and softens. When the shear moduli become small enough (Born criterion), destabilization of the atoms becomes locally collective, promoting the formation of clusters locally satisfy $\Delta C_s = 0$. Alternatively, the coinciding violation of both the vibrational and the shear elastic criteria sets the stage for the emergence of local regions that play the role of surfaces in initiating the equilibrium melting, which is, as Cahn commented [72], one of the most surprising conclusion of the study.

The observed intrinsic heterogeneous dynamics also provide an atomic-level perspective to view melting of a superheated crystal as a process of homogeneous nucleation of the liquid. The liquid embryos are formed microscopically by those thermally destabilized Lindemann particles, which appear in a cooperative way spatially, time wise, and energetically. Such a process is believed to have the effect of converting a second-order phase transition into a first-order one. It was observed that at first such clusters are small, few and far between, and fluctuate in and out. As the superheating limit is approached, with Born and Lindemann instabilities prevailing over larger and larger distances, the clusters expand, accumulate, and coalesce to eventually become the critical nuclei. It is found that a liquid nucleus consisting of about 300 atoms at $T_m$ is found to be stable for continuous growth of the liquid phase, which is reasonable with that predicted by the homogeneous nucleation theory at the superheating limit. Therefore, it is evidenced by the simulation, that the various melting mechanisms, namely Linderann and Born criteria, and the homogeneous nucleation theory are tied together in inducing the melting of solids [72].

Following the above study, Zhou and Jin [73] performed a similar MD simulation for a further clarification of the related problems. Following the previous understanding of the behaviour of defects during melting, the role of interstitial was examined in detail with a physical analysis. It is found that, near the melting temperature, spherical domains of instability (SDIs) were nucleated by the collaboration of interstitial atoms, as a result of thermal fluctuation and relaxation. The SDIs satisfy Born and Lidemann criteria simultaneously and provide channels for particle flow within the solid phase, just as do surface boundaries in surface melting. The residual shear modulus of the whole crystal at $T_m$, which seems to contradict Born’s original criterion, can be attributed to the unoccupied space among the packed spheres.

3. Surface melting

3.1. Experimental observations

Atoms at solid surfaces are less coordinated than those within the lattice interior; hence, surfaces usually exhibit a lower thermal stability relative to the lattice. In fact, free surfaces of solids may act as heterogeneous nucleation sites of melt, allowing melt nucleation at surfaces below $T_0$. In other words, melting temperature of surface is lower than that of the bulk solids. Continuous melting is initiated by a liquid layer nucleated at surfaces which grows from the outside into the bulk interior at the $T_0$. 

Surface melting can be viewed as wetting of the solid–vapour interface by its liquid as temperature approaches the melting point. It is one of the surface phase transformations closely related to excess free energy contributions associated with specific modes of surface vibrations, fluctuations and changes of electronic structures [74]. It is now established that crystal surfaces display a variety of behaviours as temperature is approaching $T_0$ from far below [75]: surface relaxation, surface reconstruction, deconstruction, pre-roughening, roughening and wetting. Wetting is the early stage of surface melting and from the thermodynamic point of view, is equivalent to wetting of the solid by its own liquid. Hence the temperature at which a liquid layer is nucleated at the solid surface is referred to as “wetting temperature”. As temperature exceeds the wetting temperature, surface melting occurs with growing of the quasi-liquid layer at wetting and transform into a regular liquid when sufficiently thick. The thickness diverges as the melting point is reached.

As early as in the 19th century, Faraday [76] made the first observation of the surface melting of ice, which is the origin of the idea that a solid may have a liquid layer on its surface [77,78]. However, extensive experimental characterizations of surface melting started only recently when techniques became available to prepare well-ordered and purified crystal surfaces and to detect the ultrathin incipient liquid layers. Investigations on surface melting have been performed on simple substances, such as metals, rare gases, ice and semiconductors of which the solid structures are relatively simple. Experimental evidences obtained on surface melting of bulk single crystals include

(a) before melting, a disordered surface region is formed on the crystal surface, which can be viewed as a quasi-liquid exhibiting structural, dynamic, and transport properties that are intermediate between those of the solid and the liquid [79];
(b) the surface quasi-liquid layer thickness grows as temperature approaches $T_0$ [2,80];
(c) surface melting is crystal-face dependent [81].

The first direct evidence of surface melting was provided by Frenken et al. [82,83]. By iron shadowing and blocking measurements of the scattering of a medium energy proton beam, they studied microscopically the surface melting of Pb(110). Properly fitting the experimental data revealed a model for surface melting: a transition layer with the characteristics of a defected solid or a partially ordered liquid is formed at 500 K, then a surface liquid film is formed at 560 K on the transition layer. As temperature approaches $T_0$, thickness of the surface liquid layer increases dramatically, with an additional 20 surface layers formed at $T_0$ since the surface melting starts. Several years later, surface melting of Al(110) was observed by Denier van der Gon et al. [84] in a medium energy scattering experiment, in which a logarithmic growth of the thickness of surface liquid layer was identified as $T$ approached $T_0$.

Surface melting has been investigated extensively using different experimental techniques such as LEIS [82,84], ED [85,86], X-ray reflectivity [87], neutron scattering [88], as well as computer simulations [89]. A summary of the experimental works can be found in previous articles [6,75]. Basically, three types of surface melting behaviour were found:

(a) open (110) surfaces of fcc metals, e.g. Al [90], Au [91], Cu [92], In [93] and Ni [94] were observed to exhibit a complete surface pre-melting;
(b) close-packed (111) surfaces of some fcc metals (such as Pb, Al, Au, etc.) do not melt below $T_0$ (non-melting) [81,84,95–97].
(c) (100) surfaces of fcc metals such as Pb [98], Ni [99] and Au [100], with an intermediate packing density between (110) and (111), were found to exhibit incomplete surface melting, i.e. thickness of the surface liquid layer remains finite as $T_0$ is approached.

3.2. Phenomenological theory of surface melting

Surface melting can be understood from a thermodynamic point of view [75,101]. As shown in Fig. 7, two configurations are considered: solid surface and that with a surface liquid layer with a thickness of $\delta$. The free energy difference of the two configurations is

$$
\Delta F(\delta) = \rho L_m \delta \left(1 - \frac{T}{T_0}\right) + \Delta \gamma(\delta).
$$

For systems that are dominated by short-range forces, the expression of $\Delta \gamma(\delta)$ is

$$
\Delta \gamma(\delta) = \Delta \gamma_{\infty}(1 - e^{-\delta/\xi}),
$$

where $\xi$ is found to be about 1 monolayers for metals such as Pb and Al, and

$$
\Delta \gamma_{\infty} = \gamma_{sl} + \gamma_{lv} - \gamma_{sv}.
$$

It is seen from Eq. (8) that surface melting occurs for $\Delta \gamma_{\infty} = \gamma_{sl} + \gamma_{lv} - \gamma_{sv} < 0$. The equilibrium liquid thickness can then be obtained by minimizing the free energy with respect to $\delta$:

$$
\delta(T) = \xi \ln \left(\frac{T_0 \Delta \gamma_{\infty}}{L_m \rho \xi (T - T_0)}\right)
$$

or

$$
\delta(T) = \frac{\xi \ln \left(\frac{T_w - T_0}{T - T_0}\right)}{\xi}.
$$

where $T_w = T_0 \left(1 - \frac{\Delta \gamma_{\infty}}{L_m \rho \xi}\right)$ denotes the onset temperature of surface melting, which can be determined by $\delta(T = T_w) = 0$.

It can be deduced from the above analysis that:

1. surface melting occurs when $\Delta \gamma_{\infty} < 0$;
2. the solid surface is stable below $T_w$, without a surface liquid layer

Fig. 7. Schematic illustrations of (a) a solid surface in equilibrium with its vapour and a surface wetted by a quasi-liquid film; (b) $\delta$ as a function of temperature.
(3) when $T_w < T < T_0$, a surface liquid layer forms on the solid surface, of which the thickness is given by Eq. (11);

(4) thickness of the liquid layer diverges logarithmically as $T$ approaches $T_0$ for short-range force systems;

(5) the solid melts above $T_0$ with $\delta = \infty$.

For short-range force systems, it is anticipated that the surface liquid thickness diverges as $|\ln(T_0 - T)|$ tends to zero, which is consistent with experimental observations on metals as described above. For materials with Van der Walls interactions (e.g. ice), it diverges as $(T_0 - T)^{-m}$ tends to zero, where $m$ is typically 1/3 [102–104]. This relation can be obtained by modifying Eq. (9) for the long range force systems, as described in [105]:

$$\Delta \gamma(\delta) = \Delta \gamma(1 - \varepsilon^2/\delta^2).$$  \hspace{1cm} (13)

Following the similar process, a power law temperature dependence of the equilibrium thickness is deduced

$$\delta(T) = \omega \left(\frac{T_0 - T}{T_0}\right)^{-1/3},$$  \hspace{1cm} (14)

where $\omega$ is a parameter depending on the properties of the liquid.

Clearly, the value of $\Delta \gamma_\infty$ determines the melting behaviour of the system, surface melting occurs for $\Delta \gamma_\infty > 0$, as in most cases; however, for systems with $\Delta \gamma_\infty < 0$, non-melting behaviour can be observed. Alternatively, the value of $\Delta \gamma_\infty$ is determined by observation of the surface melting behaviour in some cases. In Table 1 the interfacial free energies of a number of elements are listed [106]. The melting or non-melting behaviour of those elements can be predicted from $\Delta \gamma_\infty$.

### 3.3. Strain effect on surface melting

For a strained surface with a small bulk strain $\varepsilon$ which is assumed to be parallel to the surface, the free energy change for forming a surface liquid layer is modified accordingly [107]

$$\Delta F(\delta) = \rho L_m \delta \left(1 - \frac{T}{T_0}\right) + \Delta \gamma(\delta) - \frac{1}{2} Y' \delta e^2 - \sigma^{(s)} e,$$  \hspace{1cm} (15)

where $\frac{1}{2} Y' \delta e^2$ represents the decrease of the elastic energy stored in the strained solid. $\sigma^{(s)} e$ is the surface free energy change caused by a non-zero surface stress.

Defining $T_m(\varepsilon)$ as

$$T_m(\varepsilon) = \left(1 - \frac{Y'}{2L_m \rho} \varepsilon^2\right) T_0,$$  \hspace{1cm} (16)

Eq. (15) can be rewritten as

$$\Delta F(\delta) = \rho L_m \delta \left(\frac{T_m(\varepsilon) - T}{T_0}\right) + \Delta \gamma(\delta) - \frac{1}{2} Y' \delta e^2 - \sigma^{(s)} e.$$  \hspace{1cm} (17)

As temperature reaches $T_m(\varepsilon)$, the thickness of the surface liquid layer diverges, i.e. $T_m(\varepsilon)$ is the melting temperature of the solid under strain. It is seen that the strain enhances free
energy of the solid phase without affecting that of the liquid; hence melting is favored by strain and \( T_m(e) < T_0 \). Fig. 8 demonstrates the calculation results for Al(110) from the model as well as MD simulation data. It can be seen that both negative and positive strains would lower the melting point of solids, with an increased surface liquid thickness at a given temperature, that is, a strained solid has a lower melting point than the strain-free one. The onset temperature of the surface melting, however, exhibits different behaviours. For a positive strain, the surface melting onset temperature decreases with an increasing strain, and the surface liquid layer increases continually with temperature (complete surface melting). However, for a negative strain, the pre-wetting (incomplete surface melting) occurs. Thereby, one can see that although complete surface melting is observed in many cases for a strain-free surface, incomplete surface melting or even non-melting may be observed for a strained surface. The study demonstrates the dramatic effect of strain on melting of solids, suggesting that for interpreting the experimental results on surface melting it is important to consider the different states of strain resulting from various surface treatments of the measured solids.
3.4. Atomistic mechanism of surface melting

Recent density-functional molecular dynamics (DFMD) simulations [15,108] provided more atomistic information concerning the origin of surface melting for Al(110). One important finding is the existence of two distinct ‘channels’, one is confined within the top surface layer, and the other is extended down to only one layer below the top surface layer. With these channels, atoms can vibrate more easily in a much larger space than otherwise.

In Fig. 9, the 3D-projected configurations of an ideally coordinated fcc solid with a (110) surface was shown as the reference state. The vibrational amplitudes measured by mean square displacements (MSD) along several characteristic orientations, layer-resolved, and their $T$-dependence, are shown in Fig. 10. Below the surface melting temperature (such as at 700 K, Fig. 10a), the in-plane MSDs in the [001] direction (or the $x$ component) are twice as large for the surface atoms as for those within other inner layers, also larger than the other in-plane component (namely, in the $\frac{1}{2}110$ direction) at the top layer, characterizing one easy channel for atomic vibrations at the surface. The MSDs in the [110] direction (or the $z$ component, perpendicular to the surface) are much larger in the second layer instead of the top one, indicating another easy channel. For inner layers starting from the third the MSDs converge and decay quickly to the ‘bulk’ value, i.e. the anisotropic oscillations only occur to the outermost two layers. The two channels are characterized by almost the same MSD values. Fig. 10b demonstrates that both of them can be further ‘softened’ with increasing $T$, competitively and anharmonically, since the $T$-dependence of MSD is exact linear if lattice atoms are treated as harmonic oscillators. In contrast, MSDs of other layers increase almost linearly, following closely the experimentally measured data for the bulk crystal.

The calculated MSDs are in an excellent agreement with the experimental data measured either by using synchrotron XRD [109] or LEIS [110]. As an example, the data...
measured by the later method is shown in Fig. 10c. Above 750 K, the $z$-component of MSD exhibits a strong deviation from the linear regression of low-$T$ ($<700$ K) data. This happens as a direct consequence of the nonlinear $T$-dependence as shown in Fig. 10b, a strong anharmonic effect of surface vibrations. The anisotropic behaviour of the surface dynamics, i.e. the enhancements of MSDs through those ‘easy’ channels, are due to the lower coordination and the modified nearly free-electron-gas bonding close to the surface.

The existence of ‘easy channels’ for atomic vibrations provides a microscopic description of the adatom-vacancy formation processes, which are necessary precursors in facilitating surface melting. The anomalous proliferation of adatoms on Al(110) becomes possible because atoms within the second layer ‘see’ less barrier in popping out of the surface; such an activity can be further enhanced if the atoms in the top layer vibrate cooperatively because of the existence of any other in-plane and out-plane channels for easier vibrations. When the number of those atoms, together with vacancies left behind in the second layer, becomes sufficiently large, significant percolations can occur locally and globally due to large thermal fluctuations at high temperatures. The surface lattice structure can be finally destabilized, resulting in the formation of a quasiliquid layer which grows laterally and inward at $T$ close to $T_0$.

Such a microscopic perspective for surface melting, though not shown explicitly by the above mentioned first principle simulations, is supported by other MD simulations and experimental measurements. It is demonstrated that, during the pre-melting process, the preferential bond breaking happens in the direction normal to the surface [111]. The quasi-liquid layer, once formed, contains segments with a residual short-range order along both [001] and [110] azimuths, which can be ascribed to the fact that along [110] direction atoms exhibit smaller and more consistent MSDs than others (Fig. 10b). Thus a stronger stability for coordination along this and other related closed-packing directions can survive to certain extent at the beginning of surface melting. As a result, the residual order
of the quasi-liquid during surface melting consists of intact \( [\overline{1} 1 0] \) rows or segments with liquid-like mobility, and there are considerable residual orders exist within the molten Al(110) surface layer [109,110,112]. Surface melting is a consequence of a poor stability of that surface. It can be viewed as a local area of the bulk material where a huge defect can be easily generated and percolated.

3.5. Pre-melting at defects

The physical origin of surface melting can be qualitatively understood if one considers the fact that, even in bulk, melting is favored by defects, and that the surface is a kind of defect where atoms are loosely bound to each other relative to the perfect 3-D crystal lat-
The amplitudes of thermal vibration of surface atoms are larger than the bulk ones; hence melting is initiated at surfaces since Lindemann criterion is firstly fulfilled there. Also, there are other kinds of defects in materials, such as dislocations and GBs in polycrystals. Pre-melting on those defects has been evidenced. For example, it was reported that Al GBs melt at 4 K below $T_0$ [113]. Efforts to investigate the pre-melting behaviour at defects have been made for understanding the underlying mechanism of melting. Various models for pre-melting at GBs [114,115] or at dislocations [116,117] have been proposed.

A recent investigation provided detail observations of pre-melting at GBs and dislocations within bulk colloidal crystals using real time video microscopy [118,119]. A common pre-melting behaviour at a GB is illustrated in Fig. 11, which shows bright-field images at different temperatures (i.e. particle volume fractions) of two crystallites separated by a GB (crystallites tilted at an angle $\theta \sim 13^\circ$ with respect to one another). In Fig. 11A, the solid and dashed lines show the GB and a partial dislocation, respectively. The GB cuts the two crystals along two different planes (the yellow line has two slopes). It is composed of an array of dislocations; the two extra planes are indicated by lines in the inset. As temperature increases, particles near the GB start to pre-melt (as in Fig. 11B) in order to minimize the free energy, and the nearby particles undergo liquid-like diffusion as seen in inset of Fig. 11B. In contrast, the partial dislocation which has a lower interfacial free energy than that of GBs, denoted by the dashed line, is not affected. As temperature is increased further but not much, abrupt melting occurs along the GB as shown in Fig. 11C. At this stage, the melted region has engulfed the partial dislocation. The width of the pre-melted region increases continuously as temperature is raised (Fig. 11B–D). In addition to GB pre-melting, pre-melting at partial dislocations in the colloidal crystals was also clearly observed. Pre-melting from a Shockley partial dislocation was observed at a temperature (28.2 °C) higher than the GB pre-melting temperature.

![Fig. 11. Pre-melting of the colloidal crystal at a grain boundary [118]. Scale bars, 5 µm. See text for details.](image-url)
The Lindermann parameter $d_L$ was measured as an indication of the particle fluctuations both nearby and far from these defects. It was found that Lindermann criterion still works for the present system. In Fig. 12, the local values of $d_L$ near various crystalline defects just before bulk melting (28.3 °C) were shown. It is found that the particle fluctuations in the proximity of these defect regions are evidently larger than those in the bulk crystal ($d_L \sim 0.085$). At the same temperature and same distance, regions near the pre-melt GB have the highest $d_L$, dislocation the medium, and vacancies the lowest, indicating their different free energies. Furthermore, the magnitude of these fluctuations decreases approximately exponentially away from the pre-melt region toward the interior of the bulk crystal. Extrapolation of the exponential fits of $d_L$ to zero distance suggests that $d_L$ is about 0.18 in the pre-melt GB region, twice that within the interior (0.085) at the same temperature.

Yip and co-authors studied by means of MD simulations the significant role of lattice defects in melting [120]. They found that an idea crystal without defects can be superheated substantially, while a crystal with grain boundaries, free surfaces or voids melt readily below $T_0$. The study again confirmed the understanding that lattice defects serve as the most favorable nucleation sites for liquid, which determines the melting behaviour of “real” crystals. However, although GBs catalyze melting in a similar manner as free surfaces, no GB pre-melting was evidenced in their studies [121,122].

3.6. Surface melting of small particles

For small particles, the finite curvature will be an important factor governing surface melting. Kofman et al. [123] studied the surface melting of Pb small particles (a few to 100 nm) embedded in SiO$_2$ and Al$_2$O$_3$ matrices, respectively. Experimental results from both optical measurements and direct electron microscopy observations revealed that melting of small Pb particles begins with a continuous and reversible process whose extension increases when the particle size decreases. Moreover, it is shown that the liquid layer thickness is larger for a curved surface than for the flat one at the same temperature. From a thermodynamic point of view, Kofman et al. [123] presented a formalism to account for the curvature effect temperature-dependence of the surface liquid shell thickness ($\delta$).
\[
\frac{T_0 - T}{T_0} = \frac{2\gamma_{sl}}{\rho L_m r^2} (1 - e^{-\delta/\xi}) + \frac{S'(r^2)}{L_m \xi r^2} e^{-\delta/\xi}
\]

(18)

with \(S' = \gamma_{sv} - \left[\gamma_{lv} + \gamma_{sl}(\frac{\xi}{r})\right]\), \(r' = r - \delta\).

The model indicates that surface melting will be enhanced by the finite size effect in small particles. Meanwhile, different melting behaviours are expected for positive and negative crystals [124]. For materials whose surface melting is governed by long-range interactions, the model is modified accordingly [105]. The capillary effect and the impurity effect on small particle surface melting were also addressed [125–127].

Experimental investigations of surface melting of nanoparticles are of great importance in understanding their melting mechanism. However, particular attention should be made in selecting proper experimental techniques to avoid possible spurious effects, since the surface liquid shell is very thin. A recent study by Peters et al. [128] explored the surface melting of Pb small particles by using carefully designed in situ XRD. They trickily utilized the phenomenon of supercooling of liquid particles without solidification to separate surface melting from size-dependent melting. Meanwhile, Fourier analysis of the XRD peak intensity and shape provided information of the diffraction volume, the average size, and the size distribution of crystallites. Surface melting induced a reversible change of XRD intensity when the sample was changed in a temperature excursion. The density change was then related geometrically to growth of the liquid skin as

\[
\frac{\Delta I}{I} = \left(\frac{(d) - 2\Delta \tau}{(d)^3} - 1\right) \approx -6\Delta \tau
\]

(19)

where \((d)\) is the mean particle size, \(\Delta \tau\) is the change of liquid layer thickness, and \(\Delta I/I\) is the relative intensity change.

The \(\Delta \tau\) values they measured for two different temperature excursions are significantly larger than the corresponding values for the flat surface. The authors also compared their results with the Baker–Dash theory [105], which, however, seems more proper for systems that are dominated by long-range interactions. Since the particle size distribution can be measured by peak shape analysis, it seems to be possible to obtain a relationship between \(d\) and \(\Delta \tau\) by modifying the above equation as

\[
\frac{\Delta I}{I} = \sum_d \Gamma(d) \left(\frac{(d) - 2\Delta \tau}{d^3} - 1\right) \approx \sum_d \Gamma(d) \left(\frac{-6\Delta \tau}{d}\right)
\]

(20)

with \(\sum_d \Gamma(d) = 1\) representing the particle size distribution.

A very recent study by Parravicini et al. [129] revealed by capacitance measurements the different stages of surface melting of small particles. For Ga nanoparticles of 20 nm in radius, it is found that the initial surface disorder takes place at 185 K (\(\approx 65\) K below \(T_0\) of Ga), indicating the onset of surface melting. Then a linear \(T\) dependence of capacity in the \(T\) range of 185–220 K revealed an early stage of surface melting. Moreover, a more pronounced slope occurs from about 220 to 250 K, which is strictly related to the later stage of surface melting as evidenced by the comparison with TEM observations and ion scattering measurements.

The surface melting behaviour of small particles is also discussed in detail in Section 4.2.5.
4. Size-dependent melting of small particles

4.1. Experimental studies of size-dependent melting point depression

As the size of solids decreases, contribution of surfaces to their properties becomes more prominent. Melting behaviours of small solid particles are altered by an increased amount of surfaces relative to their bulk counterparts. Considering the condition that solid and liquid particles of the same mass are in equilibrium with the vapor, Pawlow [130] derived the melting temperature of small particles as a function of surface energy and particle size in 1909. He predicted a depressed melting point for small particles with respect to the bulk value.

Experimental verification of Pawlow’s prediction was given by Takagi in 1954 [131]. In his study, thin films of Pb, Sn and Bi were evaporated on a substrate, which can be treated as aggregates of small metal crystals. An electron diffraction camera was used to detect the structure change of the thin films subjected to heating and cooling. The melting temperature was determined as the temperature at which the diffraction patterns change from individual rings to halos. The experimental observations yielded the first evidence of the size-dependent melting point depression for Pb, Sn and Bi particles.

In early experimental studies of the melting point for small particles, several key aspects in experiments are crucial, including:

(a) preparation of small particles (with sizes in the nanometer range);
(b) detection of the melting transition;
(c) determination of particle sizes and their distribution;
(d) accurate measurement of temperature;
(e) methods to avoid oxidation of small particles.

The ED method has been frequently applied to study the size-dependent melting of small particles after Takagi. The studies include Sn by Blackman and Curson [132] and Wronski [133], In, Pb and Bi by Coomble [134], In by Boiko et al. [135], Au by Buffat and Borel [136], Pb, Sn, In and Bi by Koverda et al. and Skripov et al. [137,138]. Despite a general tendency of melting point depression with a decreasing particle size, discrepancies have been observed by different researchers. For example, Wronski [133] obtained a nonlinear size-dependence of the melting temperature in Sn, different from the linear relationship observed by Blackman and Curson [132]. Gladkich et al. [139] investigated the size-dependent melting of Ag, Cu, Al and Ge thin films, and obtained abnormally large depressions of melting point.

Pocza [140] used selected area diffraction in an electron microscope to investigate the melting behaviour of individual In particles for the first time. Using in situ electron microscopy, Blackman and Sambles [141] also studied the melting of individual Au small particles. Other similar studies include Pb on different substrates by Stowell et al. [142] and Al by Jones and Wood [143]. The melting point can also be determined by noting the loss of faceting of particles in the bright field mode. Using this method, Blackman et al. [144] studied Bi, Peppiatt and Sambles [145], Pb and Bi, and Rahman, Sn [146]. Another approach to determine the melting point of individual particles is using dark field microscopy—by noting the temperature when the dark field image greatly dims. Investigations using this method include Pb and Sn by Berman and Curzon [147], Sn by Bayels [148], and Sn, In, Pb and Bi by Allen et al. [149].
Up to the 1980s, experimental investigations of the size effect on melting has been performed in a large variety of simple elements of which the melting point is relatively low, such as Sn, In, Pb, Ge, Bi, Al, Ag, Cu and Na. Generally, despite the experimental errors in determining the melting temperature and particle size, evident melting point depression was observed for small particles, especially when the particle radius is below 10 nm, as shown in Fig. 13 [136]. In most cases, an approximately linear relationship between the melting point and the reciprocal particle size is obtained. As shown in Fig. 14, the experimental data falls between the lower and upper limits of the size-dependent melting temperature. It is also noted that defects in the particles, such as dislocations, stacking faults and grain boundaries and/or twin boundaries may have considerable effects on the size dependence of melting point, which is believed to be one of the reasons accounting for scattering of experimental data [145]. Also, the crystal shape and the supporting substrate influence the size-dependence of melting point, which will be discussed in detail later.

In recent years, developments of preparation and characterization techniques for nano-sized particles provide new opportunities for studying the size-dependence of melting. Dipple et al. [150] prepared self-assembled nanocrystals of In using a WSe_{2} substrate. By controlling the processing conditions such as evaporation rate and substrate temperature, In nanocrystal size varies from 5 to 100 nm. Melting points of the faceted In nanocrystals were determined by using STM combined with perturbed angular correlation (PAC). Nanocalorimetry measurements were first used by Lai et al. [151] to study the melting behaviour of Sn nanoparticles, revealing a size-dependent melting point depression. A calorimetric method which allows the measurement of heat capacity was used to study the melting behaviour of Na clusters [152]. In situ XRD technique was successfully employed to study the size-dependent melting of Pb small particles prepared by evaporation [128]. Melting point depression was revealed by DSC for nanocrystalline Al powders [153,154].

Details of the melting process were investigated using time-resolved electron microscopy for small particles (Sn, Pb, Ga, etc.) embedded in various matrices (SiO_{x}, SiO_{2} and Al_{2}O_{3}) [155,156]. Some important facts of size-dependent melting were revealed:

1. Surface melting was visible on particles, as shown in Fig. 15. The liquid layer thickness increases reversibly with an increasing temperature. Compared with the very

---

Fig. 13. Melting point of Au ultrafine particles as a function of particle size determined by means of scanning electron-diffraction method [136].
thin liquid layer for bulk surface melting, the surface liquid layer thickness can reach half of the particle radius at about 10 K below the melting point. As $T$ increases, a sharp and irreversible melting of the persistent core occurs within a time scale of microseconds.

(2) Besides the melting point depression, another remarkable feature is the broadening of range of temperature in which melting occurs. Such a behaviour is found to be size-dependent, i.e. the broadening is more evident for smaller particles than for larger ones.

(3) For very small particles (e.g. for Pb particles with a radius less than 3 nm), structural instabilities was observed instead of surface melting. It was proposed that for very small particles, the melting temperature becomes lower than the temperature where surface melting occurs. Therefore, surface melting vanishes, resulting in a sharp melting transition (see also Section 4.6.1).

Computer simulations have also been used to study the size dependent melting of small particles. Castro et al. [157] investigated the size-dependence of melting point of Au and Ag clusters with sizes of 1–20 nm, which can be fitted with reasonable accuracy by using the homogeneous melting model. Qi et al. [158] in a MD simulation study found that
melting of Ni clusters proceeds from the surface inwards and the melting process for the central core is abrupt.

Table 2 summarizes experimental results for size-dependent melting of small particles reported in the literatures.

4.2. Models for size-dependent melting point depression

4.2.1. Homogeneous melting model

The HM model was established based on an assumption that the solid and the liquid particles of the same mass are in equilibrium with their common vapour [130,136]. The free energy of a solid particle with a radius \( r \) is modified by an extra term: \( 2 \gamma_s V_s / r \), i.e. the total energy of the solid particle \( G_s(r_s) \) is

\[
G_s(r_s) = G_s(\infty) + 2 \gamma_s V_s / r_s \tag{21}
\]

and that of the liquid particle \( G_l(r_l) \) is

\[
G_l(r_l) = G_l(\infty) + 2 \gamma_l V_l / r_l, \tag{22}
\]

where \( V_s \) and \( V_l \) are the volumes of the solid and liquid particles, respectively, and \( G_s(\infty) \) and \( G_l(\infty) \) are the free energy of bulk solid and bulk liquid, respectively. The equilibrium state is achieved when

\[
G_s(r_s) = G_l(r_l). \tag{23}
\]

Combining Eqs. (21)–(23) yields the size-dependent melting point of small particles \( (T_m(r_s)) \) as

\[
T_m(r_s) = T_0 \left\{ 1 - \frac{2}{\rho_s r_s L_m} \left[ \gamma_{sv} - \gamma_{lv} (\rho_s / \rho_l)^{2/3} \right] \right\}. \tag{24}
\]

This is similar to the Thomson Equation [159] with contributions from the surface energies of both phases.

4.2.2. Liquid-skin melting model

In the LSM model [133,134,160,161], surface melting of the particle is considered as that the solid particle is coated with a thin liquid layer prior to melting. The melting point
Table 2
A summary of experimental results for the size-dependent melting of small particles

<table>
<thead>
<tr>
<th>Metal particle</th>
<th>Synthesis method</th>
<th>Determination of particle size</th>
<th>Measurement of melting</th>
<th>Description</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb, Sn, Bi</td>
<td>Evaporation</td>
<td>Particle size = the film thickness</td>
<td>ED</td>
<td>Melting point (m.p.) decreases with reducing particle radius (r)</td>
<td>[131]</td>
</tr>
<tr>
<td>Sn</td>
<td>Evaporation</td>
<td>Electron micrograph</td>
<td>ED</td>
<td>m.p. decreases linearly with 1/r</td>
<td>[132]</td>
</tr>
<tr>
<td>Ag, Cu, Al, Ge</td>
<td>Evaporation</td>
<td>–</td>
<td>ED</td>
<td>Abnormally large m.p. depression</td>
<td>[139]</td>
</tr>
<tr>
<td>Sn</td>
<td>Evaporation</td>
<td>Electron micrograph, modified</td>
<td>ED</td>
<td>m.p. decreases nonlinearly with 1/r</td>
<td>[133]</td>
</tr>
<tr>
<td>In, Pb</td>
<td>Evaporation</td>
<td>Electron micrograph</td>
<td>ED</td>
<td>m.p. decreases with reducing particle size</td>
<td>[134]</td>
</tr>
<tr>
<td>Au</td>
<td>Evaporation</td>
<td>Scanning ED</td>
<td>Scanning ED</td>
<td>m.p. vs r follows the homogeneous melting model</td>
<td>[136]</td>
</tr>
<tr>
<td>In</td>
<td>Evaporation</td>
<td>In situ TEM</td>
<td>SAED</td>
<td>m.p. of individual In particle</td>
<td>[140]</td>
</tr>
<tr>
<td>Pb, Bi</td>
<td>In situ evaporation</td>
<td>TEM micrograph</td>
<td>Change of particle shape</td>
<td>m.p. vs r follows the melt skin model, but with a second variable effect</td>
<td>[145]</td>
</tr>
<tr>
<td>Sn, In, Pb, Bi</td>
<td>In situ evaporation</td>
<td>TEM micrograph</td>
<td>Dark field image</td>
<td>Near linear relationship of m.p. vs 1/r, data falls between the upper and lower bounds</td>
<td>[149]</td>
</tr>
<tr>
<td>In</td>
<td>Self-assembled</td>
<td>STM</td>
<td>STM</td>
<td>Reduced slope for m.p. depression due to crystal shape</td>
<td>[150]</td>
</tr>
<tr>
<td>Sn</td>
<td>Evaporation</td>
<td>Scanning nanocalorimeter</td>
<td>Scanning nanocalorimeter</td>
<td>m.p. vs r follows the liquid skin model; reduced latent heat with decreasing r</td>
<td>[151]</td>
</tr>
<tr>
<td>Pb</td>
<td>Evaporation</td>
<td>In situ XRD</td>
<td>In situ XRD</td>
<td>The thickness of liquid skin is measured</td>
<td>[128]</td>
</tr>
<tr>
<td>Al</td>
<td>Mechanical attrition; evaporation</td>
<td>TEM; XRD</td>
<td>DSC</td>
<td>m.p. decreases linearly with 1/r</td>
<td>[154]</td>
</tr>
<tr>
<td>Sn/carbon</td>
<td>Evaporation</td>
<td>TEM micrograph</td>
<td>In situ TEM</td>
<td>Elevated m.p. relative to free particles due to pressure effect of the matrix</td>
<td>[174]</td>
</tr>
<tr>
<td>Sn/SiO₂</td>
<td>Sputtering</td>
<td>TEM</td>
<td>DSC</td>
<td>m.p. lowering with decreased r</td>
<td>[175]</td>
</tr>
<tr>
<td>In, Sn, Bi, Cd, Pb/Al</td>
<td>Ball-milling</td>
<td>TEM micrograph</td>
<td>DSC</td>
<td>Linear dependence of m.p. and latent heat with 1/r</td>
<td>[180]</td>
</tr>
<tr>
<td>Pb/Al₂O₃; SiO₂</td>
<td>Sol–gel</td>
<td>XRD</td>
<td>DSC</td>
<td>m.p. lowering by 3–5 K for r ~ 10 nm</td>
<td>[177]</td>
</tr>
<tr>
<td>Sn, Pb, Ga/matrix</td>
<td>Evaporation</td>
<td>In situ time-resolved TEM</td>
<td>In situ time-resolved TEM</td>
<td>Direct observations of liquid skin</td>
<td>[155]</td>
</tr>
</tbody>
</table>
of the particle is taken as the equilibrium temperature of the solid particle with the liquid shell. Using a similar thermodynamic treatment as stated above, the size-dependent melting point of the particle is described as a function of the liquid layer thickness ($\delta$):

$$T_m(r_s) = T_0\left\{1 - \frac{2}{\rho_s r_s L_m}\left[\frac{\gamma_{sl}}{1 - \delta/r_s} + \gamma_{lv}(1 - \rho_s/\rho_l)\right]\right\}. \quad (25)$$

The value of $\delta$ is a free parameter which is determined by fitting the theory to experimental data.

4.2.3. Liquid nucleation and growth model

Couchman and Jesser [162–164] treated the melting of small particles as a liquid nucleation and growth (LNG) process. The liquid nucleus is formed as an outlayer surrounding the solid phase, and moves into the solid with the help of an activation energy.

If a liquid layer is formed on the particle surface, the free energy change of the system can be written as (by neglecting the difference of atomic volume of the solid and liquid):

$$\Delta G = L_m(T_0 - T)\frac{4\pi}{3}\left[r^3 - (r - \delta)^3\right] + \gamma_{sl}4\pi(r - \delta)^2 + (\gamma_{lv} - \gamma_{sw})4\pi r^2. \quad (26)$$

This function has a stationary value with respect to $\delta$ at constant temperature when

$$\frac{L_m(T_0 - T)}{T_0} = \frac{2\gamma_{sl}}{r - \delta}. \quad (27)$$

Eq. (27) represents the condition that the solid core has the same chemical potential as the surrounding liquid layer, defining an unstable chemical equilibrium between them. It is also similar to Eq. (25) (LSM model) by neglecting the solid–liquid volume difference.

Normally, $\delta$ is very small compared to $r$, thereby, the upper limit of the melting temperature is derived if $\delta$ tends to zero

$$T_m(r) = T_0\left\{1 - \frac{2\gamma_{sl}}{\rho r L_m}\right\}. \quad (28)$$

From the above analysis, the solid–liquid transition is favored by the surface term in most cases where the wetting condition is fulfilled, and is retarded due to the volume term below $T_0$. While this is just the converse of the classic nucleation problem of freezing, it is a result of the surface-induced nature of melting. It should also be noted that formation of the surface liquid layer depends on the wetting of a solid by its own liquid. Only if the wetting condition is fulfilled the formation of an ideal surface liquid layer surrounding the solid particle is reasonable, which is the key factor to induce the size-dependent melting point depression. In this sense, one may also speculate the possible condition for superheating, i.e. if the non-wetting condition is obeyed (the surface energy term will be against melting), superheating is needed to provide the driving force for melt nucleation as in classic nucleation problems. The liquid nucleation and growth model is later extended by Skripov et al. [137], with considerations on the fluctuations on melting.

4.2.4. Thermodynamic model

Eq. (28) is believed to define the upper limit for the melting point of small particles. Meanwhile, based on thermodynamic considerations, a lower limit of the size-dependent
melting point can be obtained by using the condition that the total free energy of the initial solid particle and the final liquid particle vanishes [162]:

\[
T_m(r_s) = T_0 \left\{ 1 - \frac{3}{\rho_l r_s L_m} \left[ \gamma_{sv} - \gamma_{lv} \left( \rho_s / \rho_l \right)^{2/3} \right] \right\}.
\]  

(29)

As shown in Fig. 14, the experimental data has been found to be scaled well in this range.

4.2.5. Surface melting model

The surface-induced melting nature of small particles has been approved by many studies, and formation of liquid skin was observed, as mentioned above. Kofman et al. [156] derived the size-dependent melting point from a thermodynamic approach for surface melting of small particles.

The system is assumed to be a spherical particle of radius \( r \) containing \( N \) atoms. As shown in Fig. 16, three configurations of the particle are concerned. In configuration 1, the total free energy of the system is

\[
G_1 = N \mu_s + 4\pi r^2 \gamma_{sv}.
\]  

(30)

In configuration 2, a liquid layer exists at the surface of the particle. If the surface layer is assumed to be thin, and its interfacial energy per unit area is dependent on a short-range interaction term, then the free energy of the system is

\[
G_2 = (N - N') \mu_s + N' \mu_1 + 4\pi r^2 \times \left[ \gamma_{al} \left( \frac{r'}{r} \right)^2 + \gamma_{lv} + S' e^{-\delta / r} \right]
\]  

(31)

with

\[
S' = \gamma_{sv} - \left[ \gamma_{lv} + \gamma_{al} \left( \frac{r'}{r} \right) \right],
\]  

(32)

where \( N' \) is the number of atoms in the surface liquid layer.

In configuration 3, the solid particle transforms all into liquid. By neglecting the solid/liquid volume difference, the free energy of the systems can be written as

\[
G_3 = N \mu_1 + 4\pi r^2 \gamma_{lv}.
\]  

(33)

Supposing \( \Delta G \) represents the free energy difference between configuration 1 and configuration 2,

\[
\Delta G = G_1 - G_2 - G_3.
\]

Fig. 16. The three configurations demonstrating the melting process of small particles: solid particle (a), solid particle with a surface-melted layer (b) and liquid particle (c) [123].
\[ \Delta G = G_2 - G_1 = N'(\mu_1 - \mu_s) + 4\pi r^2 \times \left[ \gamma_s \left( \frac{r'}{r} \right)^2 + \gamma_{lv} - \gamma_{sv} + S' e^{-\delta/\xi} \right]. \] (34)

At a temperature close to \( T_0 \)

\[ N'(\mu_1 - \mu_s) = V L m \rho \frac{T - T_0}{T_0}. \] (35)

A minimization of \( \Delta G \) with respect to \( \delta \) yields

\[ \frac{T_0 - T}{T_0} = \frac{2\gamma_s}{\rho L m \rho} \left(1 - e^{-\delta/\xi}\right) + \frac{S' r^2}{L \xi^2} e^{-\delta/\xi}. \] (36)

Eq. (36) stands for the temperature dependence of the equilibrium surface liquid layer for small particles. In Eq. (34), \( \Delta G \) also has a maximum with respect to \( \delta \). The melting point is then taken as the temperature at which the minimum and the maximum of the energy curve joint, which can be obtained by numerical calculations.

From Eq. (36), it is expected that a negative crystal (replace \( r \) by \(-r\)) will also undergo surface melting. However, to achieve complete melting, superheating is needed, which increases with reduction of crystal sizes.

4.2.6. Vibration model

Bulk melting has been found to follow the Lindemann criterion. For small particles, the Lindemann parameter was also measured [165]. Measurement results showed that melting of small particles follows the rule of Lindemann criterion in bulk systems. Based on the Lindemann vibrational-lattice instability criterion, atomistic models considering the thermal vibrations of surface atoms were developed to account for the size-dependent melting point depression of small particles [166,167]. The basic idea is that the melting behaviour of a nanoparticle is related to the ratio of the rmsd of atoms at the surface to that of atoms inside a spherical solid (\( \lambda \)). If \( \lambda > 1 \), melting point depression is predicted, as the case of free-standing small particles. Detailed description of the model will be given in Section 5.5.3.

4.2.7. Correlations among various models

For many metals, \( \gamma_{sv} - \gamma_{lv} \approx \gamma_{sl} \). Eqs. (24), (25) and (28) yield essentially similar results if one neglecting the volume difference of the solid and liquid phases. Therefore, it is difficult to distinguish them by fitting the theory to experimental data as in previous studies. Nevertheless, one can still find some differences between them. In the HM model or the thermodynamic model, only the initial and the final states of the system are considered, and the melting point is dependent on the values of \( \gamma_{sv} \) and \( \gamma_{lv} \). Melting point depression is expected for \( \gamma_{sv} > \gamma_{lv} \). While if the melting process is considered as in the LSM and the LNG models, a melting point depression will be obtained only if the wetting condition is satisfied, i.e. \( \gamma_{sv} \geq \gamma_{lv} + \gamma_{sl} \). Theoretically it is expected that a study on a system with \( \gamma_{lv} + \gamma_{sl} > \gamma_{sv} \) \( \geq \gamma_{lv} \) should contribute a better understanding of the melting behaviour of small particles, although it may be difficult in experiments since the exact values of the interfacial energies are difficult to determine.

On the other hand, although Eq. (27) takes the form of Eq. (25) by neglecting the volume difference of solid and liquid, the LNG model is essentially different from the LSM model. In the LNG model, an unstable surface liquid layer is formed which stands for
an unstable equilibrium state of the system; melting occurs as the energy barrier is overcome by thermal fluctuations of the system, analogous to normal freezing. In the LSM model, surface melts before the solid core, i.e. the liquid skin existed in prior and is in stable equilibrium with the core below the melting point.

As one can see from the above analysis, thermodynamics of melting of small particles can be better understood if one combines Couchman and Jesser’s idea—critical liquid layer thickness with the surface melting idea—equilibrium liquid layer thickness. In the surface melting model, both a maximum and a minimum exist on the energy curve, which correspond to the critical liquid layer thickness and the stable equilibrium thickness, respectively. For a solid particle of given size, the equilibrium thickness \( \delta_e \) is smaller than \( \delta_c \) below the size-dependent melting temperature. With an increasing of temperature, \( \delta_e \) increases and \( \delta_c \) decreases. Melting happens at a critical temperature when \( \delta_c = \delta_e \), which is taken as the size-dependent melting point. Also, from Eq. (36) it is seen that \( \delta_c \) increases with a decreasing particle size, and from Eq. (27) \( \delta_e \) decreases with it. Therefore, there is a critical \( r_c \) that \( \delta_c \) can be larger than \( \delta_e \) for \( r < r_c \). Thus, melting of very small particles \( (r < r_c) \) will resemble bulk (internal) melting. This is supported by the observation that for very small particles (e.g. <3 nm), surface melting disappears (see Section 4.6.1 for details).

From this point of view, one can understand melting, freezing and superheating both in bulk and small systems based on the thermodynamic analysis. For example, in the case of surface-induced melting in bulk systems, below \( T_0 \), \( \delta_e \) is finite while \( \delta_c \) is infinite, thus surface melting instead of bulk melting occurs; at \( T_0 \), \( \delta_e \) is infinite while \( \delta_c \) is zero, thus bulk melting occurs without superheating. Also, if \( \delta_e \) is infinite while \( \delta_c \) is finite, melting will occur with superheating, as in the case of volume (internal) melting in bulk systems.

4.3. Effect of crystal shapes on size-dependent melting point depression

The crystal shape has been found to influence melting points of small particles. Metois and Heyraud [168] noticed that the melting temperatures of Pb small crystals with \{111\} and \{100\} facets are evidently different. The faceted Pb small crystals prepared via evaporation, have three kinds of morphologies: (i) large crystals with sizes of \( \approx 500 \) nm have shapes rather close to the equilibrium shape, displaying \{111\} and \{100\} facets connected by rounded regions in between; (ii) small crystals (with sizes \( \approx 200 \) nm) are polyhedra with sharp edges bounded either by \{111\} and \{100\} facets or (iii) by only \{111\} facets. TEM measurements showed that type (i) and (ii) all melt before \( T_0 \) is reached, but type (iii) can be superheated by \( 2 \approx 4 \) K above \( T_0 \). Spiller [169] showed that tabular Pb crystals with \{111\} facets only can be superheated by \( 2 \) K, which is attributed to the difficulty in liquid nucleation on the ordered (111) surface. Peppiatt [170] found that Bi small particles consisting largely of the basal (0001) plane have a larger time delay on melting than approximately spherical ones with (1120) facets, indicating that the liquid skin is less likely to form on the basal plane than on other planes. Also, as mentioned in Section 3, the \{111\} surface of Pb undergoes non-melting, while the \{100\} surface has pre-melting.

For self-assembled In nanocrystals on WSe_2 substrate [150], it is shown that the melting point decreases as their sizes get smaller. However, the melting point depression is evidently smaller than the theoretical values for spherical In nanoparticles, as shown in Fig. 17. It is believed that such a difference is related to the shape (faceting) of self-assembled In nanocrystals; however, theoretical descriptions are still not available.
Interestingly, Wautelet [171] showed that the size-dependence of melting point of non-spherical particles, such as the matter between spherical particles, might be larger than that of spherical ones. Recently, melting temperature of a needle-shaped single crystal Sn was measured as a function of the local radius by in situ heating experiment in a TEM [172,173]. The melting temperature decreases linearly with the inverse radius, and the size-dependence of the melting temperature of the needle is similar with that of spherical Sn particles.

Fig. 17. (a) STM images of indium nanostructures on WSe$_2$. The islands are faceted (upper right panel) and oriented. A size histogram is displayed (upper left panel) indicating an average island radius of 35 nm. (b) Relative melting-point depression as a function of indium island radius. The dashed curve represents the theory of melting for spheres including surface pre-melting [150].
Although a concise rationalization of the effect of crystal shape on melting is not available, it is believed that the surface energy plays a role in influencing the surface melting and the melting point of small particles. Dense-packed surfaces with a low surface energy might retard melting nucleation more effectively than those less dense-packed surfaces.

4.4. Effect of coating on size-dependent melting point depression

To eliminate surface contamination of small particles, properly coating the particles or embedding them in a solid matrix is desired. Usually, the coating or matrix should be chosen with the following conditions for studying the melting behaviour of small particles:

(a) the coating material or matrix has a higher melting point than particles;
(b) the coating or matrix and the particles form an immiscible system, with a neglectable inter-diffusion at least up to the melting point of particles.

A number of methods have been applied to obtain such kind of particle/matrix systems, including evaporating, sputtering, sol–gel, and ball milling. For example, Allen et al. [174] prepared Sn small particles embedded in a carbon matrix by evaporation. Unruh et al. [175] synthesized $\text{Sn}_x(\text{SiO}_2)_{100-x}$ granular films by using sputtering. Gladkikh [176] studied the melting points of thin metal films ($\text{Me} = \text{In}, \text{Sn}, \text{Bi}, \text{Pb}$) in Al/Me/Al film systems synthesized via sputtering. Bhattacharya and Chattopadhyay [177] produced Pb nanocrystals embedded in $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ matrix by sol–gel technique. Ehrhardt [178] prepared Pb small particle embedded in Al matrix by ball milling. The effect of matrix on the size-dependence of melting point has been investigated in different aspects, with emphasis on the modification of interfacial energies and the pressure effect.

4.4.1. Modification of interfacial energy

Sheng et al. [179,180] performed a systematic study of In, Pb, Sn, Bi and Cd small particles dispersed in Al matrix obtained via ball-milling. In most cases, the melting behaviour of small particles does not seem to be affected much by the matrix. As shown in Fig. 18,

![Fig. 18. Normalized melting temperature ($T_m/T_0$) as a function of $1/d$ for embedded particles. The dotted line is $T_0$ and the solid straight lines are the best fit to the data [180].](image)
the melting point depressions of In, Pb, Sn, Bi, Cd small particle dispersed in Al matrix all follow the linear relationship with the reverse particle size [180]. This behaviour was interpreted based on the thermodynamic model for free-standing small particles with considerations of the interfacial energies:

\[
T_m(r_s) = T_0 \left\{ 1 - \frac{3}{\rho_s r_{L_m}} \left[ \gamma_{sm} - \gamma_{lm} \left( \rho_s / \rho_l \right)^{2/3} \right] \right\}.
\] (37)

Since \( \gamma_{sm} = \gamma_{lm} + \gamma_{sl} \cos \theta \), as demonstrated in the insert of Fig. 19, by neglecting the solid–liquid density difference, Eq. (37) can be rewritten as

\[
T_m(r_s) = T_0 \left\{ 1 - \frac{3 \gamma_{sl} \cos \theta}{\rho_s r_s L_{lm}} \right\}.
\] (38)

It is seen from Eq. (38) that the melting behaviour of small particles depends on the wetting angle between the particle and the matrix. The contact angle for each system can be obtained by fitting the experimental results, which seems to be a function of the mixing heat of the system, as shown in Fig. 19.

The above results and analysis indicate that a reduced slope for size-dependence of melting point is noticed for the embedded nanoparticles compared with free-standing particles.

Also, the melting point of embedded particles can be described by modifying the corresponding interfacial energies in the LSM model for free-standing particles, as

\[
T_m(r_s) = T_0 \left\{ 1 - \frac{2}{\rho_s r_{L_m}} \left[ \frac{\gamma_{sl}}{1 - \delta / r_s} + \gamma_{lm} \left( 1 - \rho_s / \rho_l \right) \right] \right\}.
\] (39)

### 4.4.2. Pressure effect

For embedded particles, the pressure effect on size-dependent melting due to the constraint of the matrix was considered by Allen et al. [174]. They determined the melting temperature of Sn small particles embedded in an amorphous carbon matrix by using

![Image](attachment:image.png)

Fig. 19. The contact angle vs the heat of mixing of the particle/matrix binary system. Insert: a schematic diagram showing the definition of contact angle between the embedded particle and the matrix during melting [180].
TEM. Again the melting point of the embedded Sn small particles was found to decrease linearly as a function of inverse particle size. However, the melting temperature of the embedded Sn particles is evidently higher than the corresponding value of supported Sn particles with the same size. The effect of matrix is evidenced clearly as a higher extrapolated melting temperature is obtained for embedded particles. This behaviour was understood in terms of the strain energy changes on melting of small particles due to the constraint of matrix.

\[ T_m(r_s) = T_0 \left( 1 - \frac{3}{\rho_s r_s L_m} \left[ \gamma_{sn} + \gamma_{ln} \left( \rho_s/\rho_l \right)^{2/3} \right] + \Delta E/L_m \right), \]

where \( \Delta E \) can be estimated by the embedded model [181,182]. In Allen’s study, there is also a weak suggestion that a reduced slope is found for the embedded Sn particles, which was believed to be an indication of the lowering of interfacial energies by surface oxidation or other contaminations.

4.5. Size-dependence of melting enthalpy

While the melting point depression is a common phenomenon for small particles, other size-dependent melting properties are less evidenced. Only a few investigations concerned the size-dependence of melting enthalpy of small particles.

Jang and Koch [183] prepared dispersions of small Ge particles in a Sn matrix by ball milling. The melting behaviour of Sn was measured by using DSC. Considerable depression of melting temperature of Sn was observed. Moreover, the melting enthalpy was reduced to well below the bulk value or even vanished at a large fraction of Ge particles. Originally, Jang and Koch [183] explained this behaviour by supposing that at a certain fraction of Ge particles, Sn is in a disordered or amorphous state when in contact with Ge surfaces. Later, Turnbull et al. [184] proposed a two-state model to interpret this behaviour quantitatively.

Turnbull’s model goes with a suggestion that the total volume faction of Sn \( v_{Sn} = 1 - v_{Ge} \), is distributed after melting and freezing, between an interfacial and a bulk Sn state; the volume fraction of interfacial Sn, \( v_{iSn} \), is in a disordered state, forming a shell with a constant thickness of \( t \) coating the Ge surfaces; the remaining volume fraction of Sn \( v_{bSn} = v_{Sn} - v_{iSn} \), is in bulk crystalline state. If the total area/volume of the Ge/Sn surfaces is \( A \), then

\[ v_{iSn} = At. \]  

(41)

Meanwhile,

\[ A \propto nd^2 \quad \text{and} \quad n \propto v_{Ge}/d^3, \]

(42)

where \( n \) is the number/volume of Ge particles and \( d \) is the particle diameter. Therefore, it follows from Eqs. (41) and (42) that

\[ v_{iSn} \propto v_{Ge}t/d. \]  

(43)

According to the experiments, the melting enthalpy of Sn vanishes at a certain Ge fraction \( v^0_{Ge} \). If \( t/d \) is assumed to be constant, then,

\[ v_{Sn} = \frac{v_{Ge}v_{iSn}^0}{v_{Ge}^0}, \]

(44)
where $v_{\text{Sn}}^{\text{i}}$ is the fraction of interfacial Sn at $v_{\text{Ge}}^{\text{o}}$. With the assumption that only bulk crystalline Sn, $v_{\text{Sn}}^{\text{b}}$, contributes to the melting enthalpy ($\Delta H_m$), one gets

$$\Delta H_m = \left( \frac{v_{\text{Sn}}^{\text{b}}}{v_{\text{Sn}}^{\text{b}} + v_{\text{Sn}}^{\text{i}}} \right) \Delta H_m(\infty)$$

or alternatively

$$\Delta H_m = \frac{v_{\text{Ge}}^{\text{o}} - v_{\text{Ge}}^{\text{b}}}{v_{\text{Ge}}^{\text{o}}(1 - v_{\text{Ge}}^{\text{o}})} \Delta H_m(\infty).$$

A value of $t \sim 0.23$ nm is obtained for average Ge particle size 10 nm by fitting the model to the experimental data.

Unruh et al. [185] formed In small particles by filling molten In into to porous silica glasses. Samples with In particle sizes varying from 101 nm to 5.6 nm were obtained by using glasses with different pore sizes. The melting temperature of In is found to decrease linearly with the inverse pore size. Moreover, evident reduction of the melting enthalpy was observed, which however, is much larger than that estimated with thermodynamic considerations without considering the reduced latent heat of surface region of In.

Those studies indicated the validity of the two-state model, and it is introduced to interpret the experimental results in the followed studies. Lai et al. [151] studied the melting properties of Sn small particles by nanocalorimetric measurements. The melting enthalpy of Sn small particles with radii ranging from 5 to 50 nm was measured. An evident size-dependent melting enthalpy reduction was obtained. The two-state model was applied by considering the melting process of small particles. It is supposed that surface melting of small particles occurs continuously over a broad temperature range and the latent heat of which is difficult to be measured, while the homogeneous melting of the solid core occurs at the critical temperature, of which the latent heated is what measured. In order to quantitatively interpret their experimental results, the excluded volume of the liquid shell was defined in terms of the critical thickness $\delta_0$ of the liquid layer

$$\delta V = \frac{4}{3} \pi [r^3 - (r - \delta_0)^3].$$

An expression for the normalized melting enthalpy ($\Delta H_m(r)$) can be obtained in terms of the original particles size $r$

$$\Delta H_m(r) = \Delta H_m(\infty) \left[ 1 - \left( \frac{\delta_0}{r} \right)^2 \right].$$

By fitting the equation to the experimental data, a value of $\delta_0 = 1.6$ nm was obtained for In. It was thus predicted that In particles with $r \sim 1.6$ nm would melt completely in the mode of surface melting and the melting enthalpy would vanish at this critical size.

The melting enthalpies of small particles In, Sn, Bi, Cd and Pb dispersed in Al matrix prepared by ball milling were determined by using DSC [180,186], which were found to decrease with an increasing ball milling time and increase with the repeating DSC runs, as shown in Fig. 20. By excluding influence of the mass loss of In during ball milling, the measured enthalpy of In particles was plotted as a function of the inverse particle size determined by XRD and TEM. As shown in Fig. 20b, for the various elements, a linear relationship between the melting enthalpy and the inverse particle size was revealed.
Sheng et al. [186] then proposed a two-state model to interpret the result. The embedded particles are assumed to be uniformly spherical with a diameter $d$. An individual nanoparticle can thus be considered as an interfacial layer with a constant thickness $t_0$, plus a remaining core, or “bulk” crystal with a diameter $d - 2t_0$. The volume fraction of the interface layer, $x^{\text{in}}$, can be expressed as

$$x^{\text{in}} = \frac{1}{C_0} \left( \frac{d}{C_0}^2 t_0 \right)^{\frac{3}{d^3}}.$$  

(49)

For $t_0 \ll d$,

$$x^{\text{in}} \approx 6t_0/d.$$  

(50)

The melting of In particles is a sum of the melting of the interface layer and the crystallite core, i.e. the melting enthalpy of the nanoparticles may be approximated by

$$\Delta H_m(d) = (1 - 6\delta/d)\Delta H_m(\infty) + (6\infty/d)\Delta H_m^{\text{in}},$$  

(51)

where $\Delta H_m^{\text{in}}$ is the melting enthalpy of the interface layer, which is assumed to be independent of the grain size. Eq. (50) can be rewritten into the form:

$$\Delta H_m(d) = \Delta H_m(\infty) + 6\delta(\Delta H_m^{\text{in}} - \Delta H_m(\infty))/d.$$  

(52)
From Eq. (51), one can see that a difference between $\Delta H_m^{in}$ and $\Delta H_m(\infty)$ will lead to a variation of $\Delta H_m(d)$, which is inversely proportional to the particle size $d$. This equation seems to be in a good agreement with the experimental results shown in Fig. 20b. In Fig. 20b, the intercept of the straight line agrees well with the corresponding bulk melting enthalpy. From Eq. (51), a critical particle size for vanishing melting enthalpy is also predicted:

$$d_c = \frac{6 \delta}{\Delta H_m^{in}/\Delta H_m(\infty)}.$$  \hspace{1cm} (53)

The interfacial melting enthalpy can be obtained by fitting the experimental data to Eq. (51), by assuming an interface thickness $t_0 \approx 1$ nm. It is interesting to note that negative values of interfacial melting enthalpies were found for the various elements, which is believed to indicate the existence of the interfacial excess energy that is a function of interfacial excess volume. The excess interfacial enthalpy is also found to be related to the heat of mixing of the system, and there is an apparent trend that the two quantities scale with each other. A large positive heat of mixing between the solid particle and the matrix tends to lead to interfaces with a large excess enthalpy. The interface with a larger excess enthalpy will exhibit a smaller latent heat of fusion. As discussed in the previous context, this also tends to result in more pronounced melting point depression.

4.6. Melting of clusters

4.6.1. Critical size for surface melting

As described above, the size-dependent melting behaviour of small particles can generally be understood in terms of classic thermodynamics, indicating its validity in such a size range. For very small particles (clusters), application of the classic thermodynamics needs further investigations. Actually, the size-dependent melting point depression and enthalpy reduction, similar to that for small particles, have also been observed in clusters. For example, a melting point depression of 104 K and an enthalpy reduction by 46% were observed for free-standing Na clusters of 139 atoms (with a diameter $\approx 2.2$ nm) using a calorimetric method [152].

As mentioned previously, the surface melting model of small particles predicted that there is a critical particle size at which melting occurs in the form of surface melting without melting enthalpy, and below which the particle will melt sharply without surface melting. The critical size for vanishing melting enthalpy is also predicted by the two-state model. This indicates a transition of the melting process for clusters. Bachels et al. [187] investigated the melting behaviour of isolated Sn clusters with a mean size of about 500 atoms, by calorimetrically measuring the clusters’ formation energies as a function of their internal temperature. The melting point of the investigated Sn clusters was found to be lowered by 125 K and the melting enthalpy is reduced by 35% of bulk Sn. However, the melting enthalpy of Sn clusters is much higher than those measured by Lai et al. [151], as shown in Fig. 21. It is believed that for Sn particles with radius $r > r_c$, melting is proceeded with a precursor of surface melting. With a decrease of particle sizes, surface melting is enhanced, and to a critical size $r_c$, melting is proceeded completely by surface melting without melting enthalpy. However, for clusters smaller than $r_c$, the homogeneous melting temperature is lower than the surface melting temperature; thereby melting occurs in a sharp mode without surface melting, and the melting enthalpy will be greatly enhanced. While Bachels et al. interpreted their results based on such a surface melting model of
small particles, Kofman et al. [188] thought it is not proper to compare Bachel’s results of the isolated Sn clusters with Lai’s for the supported Sn, and that their result can simply be understood considering the surface energies of the solid and liquid phases.

An earlier computer simulation study on Au clusters also indicated the existence of a critical particle size for surface melting and the vanishing of melting enthalpy [189]. The study provided a microscopic description of the melting process of Au clusters of \( N = 100–900 \) atoms. For larger clusters with \( N > 350 \), formation of a surface liquid layer is found as a precursor of melting. The melting point and enthalpy decreases with the cluster size. It was predicted that the melting enthalpy would vanish at a critical cluster size \( d_c/\sqrt{2.1} \text{ nm} \) (300 atoms). The simulation also indicates that surface melting tends to disappear when the cluster is so small that the surface diffusion temperature is higher than the melting point. This condition is estimated to occur at \( N \sim 300 – 500 \) atoms. Their study did show that Au cluster of 219 atoms appears to melt as a whole without any precursor effect.

### 4.6.2. Abnormal size effect on melting

In most cases, a linear melting point depression as a function of the inverse particle size is observed for small particles. However, studies also reveal some abnormal size effect on melting of very small clusters. By using a technique in which cluster acts as its own nanometer-scale calorimeter, the melting point and enthalpy melting of ionized sodium clusters containing 70–200 atoms were determined [190]. Surprisingly, as shown in Fig. 22, rather strong variations of melting point were observed: a change of the cluster size by just one atom induces a melting point variation by several degrees. The local maxima of melting point occur at clusters with “magic number” atoms \( N = 13, 55, 147, 309 \). A strong variation of the latent heat of melting was also detected corresponding to the melting points. Such a size-dependence of melting point is supposed to be related to the interplay between geometric and electronic structure for very small clusters. In another study, Alexandre et al. [191] measured the melting points of Sn clusters with 10–30 atoms by mobility measurements of the Sn clusters. It was found that that Sn clusters with 19–31 atoms can be
superheated by at least 50 K above $T_0$. As shown in Fig. 23, compared with the results for mesoscopic tin particles of which the melting point decreases with a reduction of cluster sizes, the melting point elevation of very small Sn clusters is striking. Lu et al. [192] modelled the melting of Si, Ge and Sn clusters with up to 13 atoms by computer simulations. They noticed that these clusters have melting temperatures higher than bulk values. This abnormal size effect was believed to be due to the heavily reconstructed geometries and altered electronic structures relative to the corresponding bulk structure.

In summary, previous studies of clusters indicated that with a decreasing cluster size, transformation of the melting modes may occur at a critical size. Meanwhile, the geometry reconstruction and electronic structure of very small clusters may have important effects on the size-dependent melting behaviours.

Fig. 22. Variations of (a) the melting point and (b) latent heat of Na with the cluster size [190].

Fig. 23. Melting points of tin clusters as functions of the average cluster radius [191].
5. Superheating of embedded particles

Unlike supercooling, superheating of solids is usually difficult in experiments as solids will melt at or below \( T_0 \) due to the surface pre-melting. Nevertheless, if the surface melting process is somehow suppressed, the solid will not melt at \( T_0 \), i.e. superheating is observable.

Superheating of solid has been investigated by various methods in different systems in the past decades. Generally, there are four basic strategies to allow access to the superheated state in solids:

(a) to limit the solid/liquid interface kinetics;
(b) to make a crystal with a negative surface curvature and keep the edges stable;
(c) to heat the interior of a crystal while keeping its surfaces below the equilibrium melting point;
(d) to coat/embed a crystal particle epitaxially with/in a high-\( T_0 \) material while excluding the inter-diffusion at the particle/coating or matrix interfaces up to the melting point of the particle.

Strategy (a) has been achieved experimentally in some oxide crystals which melt to viscous liquids. Day and Allen [193] observed 300 K superheating in albite in 1905. Ainslie [194] observed 300 K superheating in quartz and Uhlmann [195] found 450 K in the same material. For most materials, such as metals, superheating due to limited interface kinetics is usually not observable. But by applying a very high heating rate, large transient superheating might be obtained by suppression of the melting kinetics. Recently, Luo et al. [196–199] applied shock-wave loading and intense laser irradiation to a number of metals and compounds. They found that the maximum superheating under ultrafast conditions (with a heating rate \( \sim 10^{12} \text{ K/s} \)) can be 0.5 \( T_0 \). The systematics of superheating (\( \phi = T/T_0 - 1 \)) was established as a function of heating rate (\( q \)), by

\[
\beta = A(q)(\phi + 1)\phi^2,
\]

where the normalized energy barrier for homogeneous nucleation is \( \beta = 16\pi^3\rho_s l/(3kT_0\Delta H_m^2) \), and \( A \) is a \( q \)-dependent parameter.

Rethfeld et al. [200] studied the melting kinetics in the rapid melting of solids achieved by ultrashort pulsed laser irradiation. The superheating was found to be related to the melting time, e.g. for a superheating of 0.5\( T_0 \), most materials can melt within a few picoseconds, lying between the longer time scale for heterogeneous, surface-induced melting and the shorter time scale for nonthermal melting. In all experiments, homogeneous melting was considered as the melting mechanism at high superheatings under ultrafast heating, which is also supported by computer simulations. The heating rate dependence of superheating can be understand based on the homogeneous nucleation theory taking into account the melting kinetics.

Strategy (b) is practically difficult. One may consider the melting of voids in a crystal, which has a negative curvature. However, melting of voids is undetectable as melting will occur readily from the outer surfaces and invade into the whole crystal. Strategy (c) was used by Khaikin and Benet [201], who obtained 2 K superheating of single crystal Sn by heating it resistively and keeping its surface cool.
Most of superheated solids studied previously are achieved via strategy (d) following the pioneering work of Daeges et al. in 1986 [5]. They coated Ag particles (120–160 μm in diameter) with Au, and a superheating of Ag up to 25 K was observed for about one min. The superheating was believed to relate to the suppression of melt nucleation at the surface coated by Au, and the inter-diffusion between Au and Ag and the hydrostatic pressure effect due to the constraint of Au can be excluded. Thereafter, various techniques have been utilized to prepare the coated or embedded particles that exhibit superheating behaviors in a number of systems. In this review, we will concentrate on this kind of superheated solids

5.1. Techniques for preparing superheated particles embedded in a matrix

To prepare nanoparticles embedded in a matrix (with a higher $T_0$ than that of the particle) which may be superheated, the following conditions should be satisfied [202]:

(a) the binary system is immiscible or has very limited solubility up to the melting point;
(b) the size of the embedded particles should be small enough, normally in the nanometer range;
(c) the particle/matrix interfaces have a low-energy configurations.

5.1.1. Rapid quenching

Rapid quenching allows production of nano-sized precipitates in a matrix due to the very short solidification time. Saka et al. [203] first prepared In nanoparticles (less than 40 nm in diameter) dispersed in Al matrix by splat quenching. They prepared an Al–4.5at.%In alloy from starting element materials of Al and In with a purity of 99.999%, then the alloy ingot was remelted and splat-quenched. Faceted nano-sized In precipitates dispersed homogeneously in Al matrix were formed during the rapid solidification process. TEM analysis revealed that an epitaxial orientation relationship between In particles and Al matrix. Melting of In particles was measured by using in situ TEM and DSC. It was found that a part of the In nanoparticles (with sizes less than 30 nm in diameter) can be superheated, and the degree of superheating increases with a decreasing particle size.

Zhang and Cantor [204] produced In and Pb nanoparticle embedded in Al matrix in a similar way but by using melt spinning technique. They prepared Al–7wt%In, Al–5wt%Pb and Al–2wt%Pb alloy ingots, respectively, by induction melting 99.999% pure Al, In and Pb elements. Then each alloy ingot was rapidly solidified by melting spinning. The resulting melt spun ribbons, typically 0.1 mm in thickness, 3–5 mm in width and 300–1000 mm in length, contained In or Pb nanoparticles dispersed evenly in Al. The In and Pb particles exhibit near cube–cube and cube–cube relationship with the Al matrix respectively, with truncated shapes bounded by {111} and {100} facets. In particles of 10–150 nm in diameter and the Pb particles of 5–150 nm in diameter, can be superheated by 0–40 K, as measured by DSC and in situ TEM experiments. The superheating of Pb and In particles is attributed to the kinetic barrier of due to lack of nucleation sites caused by the special structure of particle/matrix interfaces. By using melt spinning, Chattopadhyay and co-authors [10,205,206] have produced Pb particles embedded in various matrices such as Al, Zn, Cu and Ni. Epitaxial relationships are observed for all cases. Except for the Ni matrix, large superheatings up to 125 K of Pb were observed in DSC measurements.
Superheating was normally obtained in low-$T_0$ metals (below 600 K), such as In, Pb, Cd and Tl. Recently, Zhong et al. [202] succeeded in obtaining superheating in Ag nanoparticles embedded in a Ni matrix. The lattice mismatch between Ag and Ni is only 16%, which is smaller than other superheated systems (normally greater than 22%) reported. Ag nanoparticles embedded in Ni matrix were prepared by melt spinning. A superheating of about 70 K was obtained for Ag particles with a mean size of 30 nm, as revealed both by DSC and in situ XRD measurements. The measured results are supported by MD simulations that Ag clusters (4.65 nm in size) coated by Ni have a melting point 100 K higher than $T_0$, and 290 K higher than that of free-standing Ag particles [207].

While many studies have successfully obtained superheating in particle/matrix systems formed by rapid solidification, there are also some unsuccessful cases. For example, no superheating was observed for In particles embedded in Fe matrix [208]. Melting point depression, instead of superheating, was observed for Pb particles embedded in Cu matrix [209], and for Cd particles in Al matrix [210,211]. The melting behaviour of Bi embedded in Zn and in an amorphous Al–Fe–Si matrices was studied by using DSC, and most Bi particles melt close to $T_0$ [212,213]. The unsuccessful superheating experiments might be attributed to either the non-epitaxial particle/matrix interfaces or the undetectable volume fraction of nanoparticle that can be superheated.

5.1.2. Ion implanting

Ion implanting is another effective method to produce nano-sized particles embedded in a matrix. In this method, thin films or disc-shaped samples of the matrix were first prepared; then ions of the particle elements were implanted into the matrix. Under proper implantation conditions, nano-sized inclusions can be produced. Using this method, Ros-souw and Donnelly [214] produced small Ar bubbles (of mean diameter $\sim$2.7 nm) with Ar$^+$ ions into Al. The Ar bubbles are fcc solids in epitaxy with the Al matrix, which can be superheated by 480 K above $T_0$ (250 K). The suppression of thermal vibrations of Ar atoms near the Ar–Al interface is supposed to account for the superheating, which is also supported by measurements of the rmsd value and Debye temperature of Ar bubbles (about 140 K in contrast to a bulk value of 110 K). Graebæk et al. [215,216] obtained Pb nanoparticles dispersed in Al by ion implanting Pb into Al matrix. They first prepared Al(111) single crystal disk of 9 mm in diameter and 1 mm in thickness, then Pb$^+$ ions were implanted at an energy of 150 keV to a fluence of $2 \times 10^{16}$ cm$^{-2}$. The sample temperature during implantation was controlled to be less than 330 K to avoid coarsening of the Pb inclusions. The reproducible superheating behaviour of Pb nanoparticles was revealed by in situ XRD measurements. For Pb particles with a mean size of 14 nm and 27 nm, the corresponding superheatings are 67 K and 44 K, respectively. The superheating behaviour was attributed to the lack of free surfaces due to the matrix coating with a cube–cube relationship for the Pb/Al interface. The measured variation of the rmsd of the Pb atoms with an increasing temperature is in consistent with the Lindemann criterion—the rmsd values reached 12% of the nearest-neighbour distance at $T_0$.

Systematical studies have also been performed on the meltig behaviours of Bi, Cd, In and Tl nanoparticles embedded in Al matrix prepared by ion implanting [217,218]. The particles (mostly 1–15 nm in diameter), exhibit various epitaxial relationships with the matrix, depending on the lattice structures of the particle and matrix. Except for Bi, all the other particles can be superheated, as revealed by in situ XRD and in situ RBS-channeling measurements.
5.1.3. Ball milling

As mentioned in Section 4.4, ball milling can also be applied to produce nanoparticles dispersed evenly in a matrix. Normally, melting point depression rather than superheating was observed for the embedded nanoparticles prepared via ball milling [180]. Unlike those in rapid solidification and ion implantation, ball milling produces embedded particles that normally lack regular shape and have no orientation relationships with the matrix. However, if the as-milled samples are undergone heating/cooling cycles, some embedded particle that are melted on heating may solidify into simple truncated octahedral shapes via solidification on Al matrix in the cooling process. A cube–cube particle/matrix orientation relationship might be formed. Superheating is possible if there was no substantial growth of the particles after the thermal cycles. There have actually been unsuccessful [219] as well as successful attempts [220] trying to obtain the regular particle shapes and an orientation relationship and hence superheating by annealing the as-milled Pb/Al samples. In the unsuccessful case, only melting point depression was observed, because most Pb particles are still not formed in regular shapes and no epitaxial interface are constructed after annealing [219]. In another case, superheating of Pb particles was successfully obtained due to the faceting of Pb by annealing [220].

A summary of the experimental results for superheating in particle/matrix systems was given in Table 3. In all cases, superheating of embedded particles was found to be closely related to the particle/matrix interface structure.

5.2. Effect of interfacial structure on superheating

5.2.1. Experimental results

The crucial role of interface in superheating is demonstrated by a comparative study by Sheng et al. [221,222]. They prepared Pb and In nanoparticles embedded in Al matrix by means of ball milling and melting spinning, respectively. For the ball-milled samples, In or Pb particles are irregular and incoherent random interfaces were formed between particles and the matrix. While for the melt-spun samples, In and Pb particles were found to distributed partly in grain boundaries of Al, and partly within the Al grains. The particles within Al grains having much smaller sizes than those at grain boundaries, are of truncated octahedral shapes bounded by \(\{111\}\) and \(\{100\}\) facets. A cube–cube orientation relationship was identified between the particles and the Al matrix. Melting behaviours of the two kinds of samples were measured by using DSC, in situ TEM and in situ XRD. For the ball-milled sample, a single endothermic peak occurs below \(T_0\) in the DSC melting curve, as shown in Fig. 24a. The nanoparticles exhibit a size-dependent melting point depression, as described previously. For the melt-spun samples, typically two endothermic peaks appear in the DSC melting curves, as shown in Fig. 24b. The first melting peak corresponds to melting of intergranual particles, and the peak at high temperatures to melting of superheated particles with semi-coherent particle/matrix interfaces. The characteristic temperature of the superheating peak increases with a decreasing particle size. Fig. 25 summaries the measurement results of melting temperatures of the ball-milled and the melt-spun samples as a function of particle size. It is demonstrated clearly that samples prepared by the two methods undergo completely different melting behaviours. For ball-milled samples, a size-dependent melting point depression was observed.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthesis method</th>
<th>Epitaxial relationship</th>
<th>$d$ (nm)</th>
<th>$\Delta T$ (K)</th>
<th>Measurement of superheating</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb/Al</td>
<td>Melt spinning</td>
<td>(111)$_{\text{Al}}$</td>
<td></td>
<td>(111)$<em>{\text{Pb}}$ [110]$</em>{\text{Al}}$</td>
<td></td>
<td>(110)$_{\text{Pb}}$ (cube/cube)</td>
</tr>
<tr>
<td>Pb/Al</td>
<td>Melt spinning</td>
<td>Cube/cube</td>
<td>10–70</td>
<td>103</td>
<td>DSC</td>
<td>[206]</td>
</tr>
<tr>
<td>Pb/Al</td>
<td>Melt spinning</td>
<td>Cube/cube</td>
<td>5–30</td>
<td>20–60</td>
<td>DSC, in situ XRD</td>
<td>[165,221]</td>
</tr>
<tr>
<td>xPb/Al</td>
<td>Ion implanting</td>
<td>Cube/cube</td>
<td>1–15</td>
<td>$\sim$70</td>
<td>In situ XRD, TEM and RBS</td>
<td>[216,217]</td>
</tr>
<tr>
<td>Pb/Cu</td>
<td>Melt spinning</td>
<td>(111)$_{\text{Cu}}$</td>
<td></td>
<td>(111)$<em>{\text{Pb}}$ [110]$</em>{\text{Cu}}$</td>
<td></td>
<td>(110)$_{\text{Pb}}$</td>
</tr>
<tr>
<td>Pb/Zn</td>
<td>Melt spinning</td>
<td>(0001)$_{\text{Zn}}$</td>
<td></td>
<td>(111)$<em>{\text{Pb}}$ (1120)$</em>{\text{Zn}}$</td>
<td></td>
<td>(110)$_{\text{Pb}}$</td>
</tr>
<tr>
<td>In/Al</td>
<td>Melt spinning</td>
<td>Near cube/cube</td>
<td>10–150</td>
<td>0–40</td>
<td>In situ TEM, DSC</td>
<td>[204]</td>
</tr>
<tr>
<td>In/Al</td>
<td>Melt spinning</td>
<td>Near cube/cube</td>
<td>5–80</td>
<td>5–48</td>
<td>In situ TEM, DSC</td>
<td>[222]</td>
</tr>
<tr>
<td>In/Al</td>
<td>Ion implanting</td>
<td>Near cube/cube</td>
<td>1–15</td>
<td>20</td>
<td>In situ TEM, RBS</td>
<td>[217]</td>
</tr>
<tr>
<td>Cd/Al</td>
<td>Ion implanting</td>
<td>(111)$_{\text{Al}}$</td>
<td></td>
<td>(0001)$<em>{\text{Cd}}$ (110)$</em>{\text{Al}}$</td>
<td></td>
<td>(1120)$_{\text{ca}}$</td>
</tr>
<tr>
<td>Ti/Al</td>
<td>Ion implanting</td>
<td>Cube/cube</td>
<td>1–15</td>
<td>40</td>
<td>In situ TEM, RBS</td>
<td>[217]</td>
</tr>
<tr>
<td>Ag/Ni</td>
<td>Melt spinning</td>
<td>Cube/cube</td>
<td>10–45 (mean 30)</td>
<td>29–70</td>
<td>In situ XRD, DSC</td>
<td>[202]</td>
</tr>
<tr>
<td>Pb/Al</td>
<td>Ball milling and annealing</td>
<td>Cube/cube</td>
<td>3–15</td>
<td>0–10</td>
<td>DSC</td>
<td>[220]</td>
</tr>
</tbody>
</table>
For melt-spun samples, superheating was observed, and the degree of superheating increases with a decreasing particle size.

A recent study demonstrated the importance of the particle shape (faceting) on superheating in the Pb/Al system [223]. The results showed that if de-faceting of Pb nanocrystals was caused by several plastic deformation, melting point depression (rather than superheating) of Pb was observed even if the epitaxial relationship was maintained.

It is worth noting that many studies have concerned with the freezing behaviour of embedded particles, which is indeed found to be closely related to the interfacial structure, as one would expected from the corresponding melting behaviour. Multi-step freezing process [224–226] and large hysteresis [227,228] between melting and freezing are usually observed for embedded particles. A comparative study of melting and freezing behaviours of the same systems provided useful information on the effect of interfacial structure on the solid–liquid phase transformations, as demonstrated by Zhong et al. [229].
5.2.2. Computer simulations

The effect of the particle/matrix interfacial structure on the melting behaviour of embedded particles was investigated by means of computer simulations. Jin et al. [230] simulated melting processes of Pb clusters coated by Al with different Pb/Al interface structures. Two Pb clusters, Pb

\[ \text{N} = 5201 \] (A) and 249 (B) were selected and both of them were embedded in the core of an Al 4033 cubo-octahedron, but with different orientation relationships with Al coatings. As demonstrated in Fig. 26, for cluster A, a parallel cube–cube relationship exists with the Al lattice, while cluster B has no parallel orientation relationship with Al. The melting curves (the mean average potential energy as a function of the temperature) of the two clusters indicated that the Pb core in cluster A can survive at about 140 K above \( T_0 \), while that in cluster B melts at 100 K below \( T_0 \), and in both cases, the whole system (Pb core and Al coating) melt at round 750 K.

Configurations of the two systems at different temperatures were recorded to reveal the structure change and melting transition of the two types of clusters upon heating. For cluster A, it was found that first a structural reconstruction happens at the Al–Pb grain boundaries, which has resulted in not only a fully relaxed stable interface but also coherency between the confined Pb cluster and the Al coating. As illustrated in Fig. 27a, the Pb–Al interfaces have become more relaxed compared with the initial input structure as shown in Fig. 26. Semi-coherent interfaces was formed after the structural reconstruction, accompanied by the generation of a few dislocations at the grain boundaries to accommodate the lattice misfit (Fig. 27a). For cluster A, melting of the whole system was believed to be induced by melting of the superheated Pb core, destroying the Pb/Al interface from inside, rather than the destroy of the Pb/Al interface by the melting of the Al coating, since the Al coating has a melting point above 800 K.

For cluster B, the behaviour is quite different. No structural change at low temperatures is detectable, indicating that lack of a cube–cube parallel relationship between Pb and Al makes it rather difficult to form an effective semi-coherent interface. This was also reflected by the cross section plot of cluster B as show in Fig. 27b. After low temperature relaxation (which also generates some dislocations), some point defects (vacancies) at the Al–Pb
interfaces were redistributed. Hence, the Pb core appeared much less bounded by the Al coating, and the energy difference between the two clusters is large, indicating that B is less stable than A. Heterogeneous nucleation sites can thus be formed at the Al–Pb interface or even inside the Pb core of cluster B, facilitating the pre-melting of the Pb core at about 500 K, or 110 K below $T_0$ for bulk Pb. Interestingly, contrary to the case of cluster A,
melting of the Pb cluster does not induce a combined melting of Al coating. Instead, the Al coating was found to be relaxed to a more stable state after the melting of Pb core. The whole cluster will melt not too far below 750 K because an Al cluster with a melted core is much unstable than a perfect cluster of the same size.

Again, the simulation demonstrated that melting is closely related to the interfacial structure. As Cahn supposed [4], superheating depends on epitaxy between the constrained particle and the coating/matrix, and it is possible that an incoherent interface might not permit superheating.

5.3. Effect of particle size on superheating

The degree of superheating of embedded particles is found to be strongly dependent on particle sizes. As shown in Fig. 25, for the melt spun In/Al sample, the melting temperature increases with a decreasing particle size, just the opposite to that for the ball-milled sample. Besides, plotting the superheating as a function of the inverse particle size, a linear relationship is approximated, similar to that of the size-dependence of melting point depression.

The superheating-particle size relationship can also be investigated by in situ XRD measurements. As shown in Fig. 28a, from the in situ XRD profiles of Ag (111) in a Ag/Ni sample prepared via melt spinning it is seen that Ag crystals can be superheated by about 40 K. Meanwhile, as the broadening of XRD peaks is dependent on the crystal size following the Scherrer Equation, the relationship between superheating and the particle size of Ag can be deduced from the variation of FWHM of XRD peaks with the temperature. As shown in Fig. 28b, an evident trend of an increasing degree of superheating with decreasing Ag size is seen. This method has also been used to obtain the superheating-particle size relationship in Pb particles embedded in Al [179], in which a nearly linear relationship between superheating and particle size was also obtained.

5.4. Observation of melt nucleation for superheated particles

Normal melting is transient and difficult to be observed in detail. The superheated particles embedded in a matrix provide an opportunity to observe the melting process. Sakaki and Saka [231] observed systematically the melting process of In particles embedded in Al matrix using in situ HRTEM. The In particles embedded in Al prepared by melt spinning were cube-octahedra in shape, bounded by eight \{111\}_Al/In and six \{100\}_Al/In facets, as illustrated in Fig. 29a. Electron diffraction revealed that the In particles have a cube–cube orientation relationship with Al. For almost all cases, melting of In was found to start on a \{100\} facet. In their observations, the melting process was found to proceed in six stages in a way that at each of the stages, one of the \{100\} facets becomes covered successively by the liquid phase. Fig. 30b–f demonstrated schematically these stages [231].

Stage 1 (Fig. 29b)

At this stage, a liquid was nucleated on a \{100\} facet, say (100), and a hemispherical interface between Al and liquid In and a hemispherical interface between liquid In and solid In were formed. The Al(s)–In(l) interface was restricted to the vicinity of what had been the \{100\}_Al facet. Interestingly, the hemispherical In(s)–In(l) interface assumed two metastable positions, as can be seen clearly from Fig. 30a and b. The liquid phase in (b)
has a much larger volume than that in (a). The liquid droplet assumed these two configurations alternatively before it reached the next \(\{100\}\) facet. The time needed in this stage ranged from a few to several minutes and is the longest in the whole process of melting, which therefore is the rate-controlling one.

Stage 2 (Fig. 29c)

The hemispherical In\(\text{(s)}\)–In\(\text{(l)}\) interface started to propagate into the interior of the In particles and reached one of the four nearest \(\{100\}\) facets (i.e. \(\{001\}\), \(\{010\}\), \(\{001\}\) and \(\{010\}\)).
Fig. 29. A model showing schematically the melting process in an In particles embedded in Al [231].

Fig. 30. Electron micrographs showing the melting processes of an In particle viewed along the \( \frac{1}{2} \langle 001 \rangle \) direction. Material projected onto the densely dotted area is crystalline, and that onto the undotted area is liquid. A curved solid–liquid interface is projected onto the sparsely dotted area. (a) and (b) schematically showed the two metastable configurations of the solid–liquid interface on nucleation. In (c) the liquid phase grew and covered \( (100), (0\bar{1}0) \) and \( (001) \) facets, as also schematically illustrated in (d) [231].
Stage 3 (Fig. 29d)

At stage 2, four \{100\} facets were still not covered by the liquid phase. Two of them were completely free from the liquid phase and the other two contacted the liquid phase along the edges of the now wet \{111\} facets. At stage 3, the liquid phase crossed over these edges and covers either of those \{100\} facets contacted by the liquid, e.g. (001) as shown in Fig. 30c.

Stage 4 (Fig. 29e)

Now both of the two \{100\} facets that contacted the liquid phase in stage 2 are now covered by the liquid. The In(s)–In(l) interface was anchored at the two vertices where two \{111\} and one \{100\} facets intersect. Consequently, the In(s)–In(l) interface bowed out at this stage.

Stage 5 (Fig. 29f)

One of the last two \{100\} facets which had not been covered with the liquid phase now became covered with it, and the In(s)–In(l) interface became parallel to the \{100\} facet.

Stage 6

The In(s)–In(l) interface propagated, while keeping the interface parallel to the \{100\} facet, until the whole In particle was melted.

The in situ HRTEM observations provided detailed information of the time-dependent melting process of the embedded particle, from which it was indicated that

(a) The \{100\} facets provide nucleation sites for liquid nucleus.
(b) Most importantly, the time-consuming process is the growth of the liquid nucleus into the whole volume, which is proceeded by the successive covering of the remaining \{100\} facets by the liquid.
(c) The \{111\} facets, which separate the \{100\} facets alternatively, retard the progress of the liquid phase.

Generally, the superheating of embedded particles was attributed to the difficulty of melt nucleation at the semi-coherent particle/matrix interface. However, the above HRTEM observations also indicated that the suppression of the melt growth may also be a major factor in determining the superheating of embedded particles. In fact, it is found that the superheating observed in the confined thin films can be attributed to the suppression of the melt growth (see Section 6 for details).

Sakaki and Saka’s observation ambiguously demonstrated that melt nucleation in the superheated particles starts at the particle/matrix interface. A MD simulation study on Ag/Ni by Xu et al. [207] suggested that melting of Ag particles is nucleated at defective regions at the Ag/Ni interface and propagates inwards, as shown in Fig. 31. These observations showed that heterogeneous nucleation at the interface dominates the melting kinetics of the superheated nanoparticles even a low-energy semi-coherent interface is constructed. A MD simulation showed that if Pb thin film crystals are ideally confined in Al matrix with fully coherent interfaces, i.e. no defects such as cavities or dislocations at the film/matrix interface, the Pb film melts well above $T_0$, and it is interesting that melting is initiated homogeneously within the crystal interior, rather than heterogeneously at the interface [232]. This result indicates that when the crystal is confined perfectly by the matrix, which is practically difficult to obtain, it will have a very high instability.
temperature so that homogeneously melting within the lattice is observable. It is therefore clear that the nature of confinement is key in determining the melt nucleation behaviour, and hence the extent of superheating for confined crystals.

5.5. Interpretations to superheating of embedded particles

Although it is now generally accepted and experimentally evidenced that superheating of embedded particles is essentially related to the nature of the particle/matrix interfaces, models or explanations accounting for this effect diverse. The effect of interface on melting has been interpreted based on different considerations.

5.5.1. Effect of interfacial energies

As described in Section 4.2, in the HM or the thermodynamic models, the initial and final states of the small particle melting were considered. As can be seen from Eq. (37), the melting temperature of small particles can be either depressed or elevated, depending on the value of ($\gamma_{\text{ms}}-\gamma_{\text{ml}}$). This explanation is phenomenally simple, and is able to explain the linear relationship between the superheating and the reverse particle size as described above. It has been applied to semi-quantitatively account for superheatings observed in In in Al [203], Pb in Al [222] and Ag in Ni [202].
On the other hand, according to the LSM and LNG models with consideration of the melting process, superheating is expectable if the non-wetting condition is satisfied, i.e. $\gamma_{sm} < \gamma_{lm} + \gamma_{sl}$.

As discussed in Section 4.2, a system with $\gamma_{lm} + \gamma_{sl} > \gamma_{sm}$ should then be interesting, because superheating is expected according to the LSM and the LNG models, while is not according to the HM model and the thermodynamic model. Although it may be difficult in practice, Xu et al. [233] in a very recent study managed to find a system of Ge nanocrystals embedded in SiO$_2$. The interfacial energies of the Ge/SiO$_2$ system satisfied the condition $\gamma_{lm} + \gamma_{sl} > \gamma_{sm} / \gamma_{lm}$, and it is interesting that a large superheating of 200 K is obtained. The results seem to support the LSM and LNG models rather than the HM and thermodynamic models for the small particle melting.

It is noted that if a semi-coherent/coherent interface with a low energy configuration is formed between the particle and the matrix, $\gamma_{ms}$ is more likely to be smaller than $\gamma_{ml}$; hence, the particle can be superheated as observed in most cases. The study of Xu et al. [233] also demonstrated in some special systems, the interfacial energy condition can also be satisfied even without an epitaxial relationship as in the case of Ge between amorphous SiO$_2$.

5.5.2. Suppression of melt nucleation at interfaces

Another consideration is the change of melting kinetics induced by the epitaxial particle/matrix interfaces. As proposed by Daeges et al. [5] for Ag in Au, and Zhang et al. [204] for Pb in Al, superheating is associated to the kinetic difficulty for melting at the ordered particle/matrix interfaces, due to lack of preferable sites for melt nucleation compared with the disordered surfaces/interfaces.

5.5.3. Suppression of atomic vibration at interfaces

Bulk melting is related to the thermal vibration of atoms by the Lindemann criterion. This idea has also been introduced to melting of embedded particles. Shi [166] considered the amplitude of thermal vibrations for surface atoms than that for interior ones, and developed a model to account for the size-dependent suppression or elevation of melting temperature of nanocrystals due to suppression or intensification of thermal vibrations of atoms near the surface or interfaces. According to Shi’s model, the melting temperature of a nanocrystal of radius $r$ ($T_m(r)$) is given by

$$ T_m(r) / T_0(n) = \sigma_m^2(\infty) / \sigma_m^2(r) = \exp[-(\lambda - 1)/(r/3h - 1)], $$

where $h$ is approximately the height of a monolayer of atoms at the bulk surface, and $3h$ is a critical radius at which almost all atoms of the nanocrystals are located on the surface.

It is seen from the above model, the melting temperature depends on the value of $\lambda$. For free-standing nanocrystals, $\lambda > 1$, a size-dependent melting point depression is expected. However, if the thermal vibrations of surface atoms can be effectively suppressed by confinement of a matrix, to such an extend that $\lambda < 1$, the size-dependent superheating is predicted.

Jiang et al. [234,235] later extended the model and obtained a simple formula for calculation of $\lambda$ to interpret the superheating of embedded nanocrystals with coherent or semi-coherent interfaces:

$$ \lambda = \{[h_n^2/h_M^2]T_0(n)/T_0(M) + 1\}/2. $$
The equation indicates the necessary condition for superheating of embedded nanocrystals \((\lambda < 1)\), i.e., coherent or semi-coherent interface is formed between the nanocrystal and the matrix with a higher melting point. Also, a smaller atomic diameter of the matrix is important for superheating.

Jiang’s model indicates that the rmsd of surface atoms is smaller than that of the interior atoms (bulk values) for nanocrystal embedded coherently in a matrix (with higher melting point). Consequently, one may expect melting will nucleate preferably from the interior of the nanocrystal rather than at the interfaces. Although this might be true for a fully coherent interface, it does not explain the experimental results that melting of embedded nanocrystals with semi-coherent interfaces initiates at the interfaces. This discrepancy may result from the defective structure of the semi-coherent interfaces compared with the fully coherent ones.

As in the above studies of Shi and Jiang et al., many theoretical analyses assume that the Lindermann criterion is also valid for nanocrystals. Sheng et al. [165] provided supportive experimental evidence for this assumption. As shown in Fig. 32, the rmsd values of different nanocrystal samples were measured by in situ XRD. It was found that the rmsd values reach nearly 10% of the nearest-neighbour distance prior to melting, for both samples undergoing melting point depression and superheating. Thereby, it is concluded that the Lindermann criterion can be applied to nanomaterials, either with melting point depression or superheating.

![Fig. 32](image)

Fig. 32. The rmsd of Pb atoms as a function of temperature in three samples: the melt-spun sample (a), the ball-milled sample (b) and the ‘bulk’ as-cast sample (c). For all three samples, the rmsd values reach \(\sim 10\%) of the nearest neighbour distance prior to melting [219].
5.5.4. Melt-nucleation model

Meanwhile the thermodynamic model has been successfully applied in explaining many experimental results reported in the literature, the melting kinetics of the embedded particles has not been fully understood. In addition, several key problems related to this thermodynamic model are to be addressed. For example, in terms of Eq. (38), superheating is only possible when $\theta > 90^\circ$. But this is not the case for Ag particles embedded in Ni matrix with $\theta \approx 89^\circ$, in which a substantial superheating of 70 K has been observed experimentally [202,207]. Moreover, following Eq. (38), one may get an unrealistically high superheating when the particle size tends to atomic size, which may even exceed the superheating limits for surface-free perfect crystals proposed previously [41,63]. In other words, the thermodynamic model does not predict a superheating limit for embedded particles with semi-coherent interfaces.

To clarify these problems, one needs to investigate the melting kinetics with a special consideration of interfacial structures in which misfit dislocations play a crucial role. The recent study [236] shed light on the melting nucleation kinetics on misfit dislocations at semi-coherent interfaces.

Based on previous studies [237–239], the misfit dislocations at the semi-coherent interfaces were assumed to act as heterogeneous sites for melt nucleation. A simplified model, namely a semi-coherent interface in a semi-infinite system, is then proposed to analyse the effectiveness of misfit dislocations in catalyzing melting. As in Fig. 33a, a semi-coherent interface was formed between a low-melting-point solid in a high-melting-point matrix. Melting of the solid nucleates by forming a melt nucleus at the misfit dislocation, which lies along the core of the misfit dislocation, and its cross-section is perpendicular to the dislocation line is spherically curved (Fig. 33b). The total free energy change ($\Delta F_c$) is a function of the nucleus radius ($r_n$):

$$\Delta F_c = -J \ln (R \sin \theta) + (2\theta - \sin 2\theta)\gamma_{sl} r_n - \theta \Delta H_m (T_0 - T) / T_0 r_n^2 + \text{const}, \quad (57)$$

![Fig. 33. Schematic illustrations of (a) the semi-coherent interface between a low melting point solid and a high melting point matrix, showing the misfit dislocations at the interface, (b) melt nucleus of the solid along the misfit dislocation line, and (c) variation of free energy per unit length with $r_n$ for two different cases: $\eta < 1$ (curve A) and $\eta > 1$ (curve B) [236].](image)
where \( J = G_s G_m b^2 / (G_s + G_m) 2\pi (1 - \nu) \). The Burgers vector \( b \) and Poisson’s ratio \( \nu \) for the misfit dislocation can be calculated from \( b = (b_s + b_m)/2 \) and \( \nu = 2/(1/v_s + 1/v_m) \), respectively, where \( b_s, v_s \) and \( b_m, v_m \) are the Burgers vector and Poisson ratio for the solid and the matrix, respectively.

It was found that \( \Delta F_c \) depends on \( r_n \) in such a manner that a minimum of it will exist at small values of \( r_n \) (curve A in Fig. 33c). Its radius \( r_{n0} \), is given by the minimum in the free-energy per unit length

\[
\begin{align*}
  r_{n0} = & \frac{\gamma_{sl}^2 (2\theta - \sin 2\theta)^2}{8f\theta} \left[ 1 - \sqrt{1 - \frac{8Jf\theta}{\gamma_{sl}^2 (2\theta - \sin 2\theta)^2}} \right].
\end{align*}
\]  

(58)

In this case, there is a barrier to growth of the melt. A fluctuation that thickens the nucleus requires energy, while beyond a certain size continued growth will result again in a lowering of energy (curve A in Fig. 33c). The superheating needed to induce melting of the solid depends on the energy barrier that must be overcome.

If \( \eta = 8Jf\theta/\gamma_{sl}^2 (2\theta - \sin 2\theta)^2 > 1 \), it is evident that there will be no energy barrier for the continued growth of the melt nucleus along the dislocation line (curve B in Fig. 33c). Hence the condition \( \eta = 1 \) provides a critical superheating limit for heterogeneous melt nucleation on misfit dislocations at the interface (\( \Delta T_m^l \)), i.e.

\[
\Delta T_m^l = (2\theta - \sin 2\theta)^2 \gamma_{sl}^2 T_0 / 8\theta J \Delta H_m. \tag{59}
\]

When the temperature \( T > T_0 + \Delta T_m^l \), the misfit dislocations are so effective that no energy barrier for melt nucleation exists, analogous to that at a free surface; hence melting of the solid sets in.

Taking into account \( \Delta E \), the upper superheating limit for melt nucleation on misfit dislocations in embedded particle systems can also be obtained:

\[
\Delta T_m^l = (2\theta - \sin 2\theta)^2 \gamma_{sl}^2 T_0 / 8\theta J \Delta H_m + T_0 \Delta E / \Delta H_m. \tag{60}
\]

Similarly, the superheating limit for melt nucleation on lattice dislocations (\( \Delta T_m^l \)) within the solid can be obtained:

\[
\Delta T_m^l = \pi \gamma_{sl}^2 T_0 / 2J' \Delta H_m + T_0 \Delta E / \Delta H_m, \tag{61}
\]

where \( J' = G_s^2 b^2 / G_s 4\pi (1 - \nu) \). The superheating limits \( \Delta T_m^l \) and \( \Delta T_m^l \) for various systems are plotted as a function of the contact angle \( \theta \) in Fig. 34a and b. For the particle/matrix systems studied, it was found that \( \Delta T_m^l \) is larger than \( \Delta T_m^l \), indicating that misfit dislocations at the interface are more effective in catalyzing melt nucleation than lattice dislocations within the particle, i.e. melting prefers to nucleate at the semi-coherent interfaces with misfit dislocations, even if lattice dislocations exist.

As mentioned previously, the thermodynamic model cannot explain the superheating in the Ag/Ni system with \( \theta < 90^\circ \). Using the measured \( \theta \) (89°), the present model yields a superheating limit of 104 K for Ag, which agrees well with the simulated superheating (100 K) [207], and is reasonably consistent with the maximum superheating measured experimentally (70 K) [202]. Similar comparisons made for other available systems show a good consistency between the theory and experimental data, as listed in Table 4.

The model indicated that \( \theta \) and \( G_m \) are important for a substantial superheating of the embedded particles, for example in order to increase the superheating of the particle, the most effective way is to choose a matrix with a larger \( \theta \) and/or a larger \( G_m \).
It is noted that the above model is based on semi-coherent interfaces. For a full coherent interface, the melting point may approach the highest superheating limit of solids.

5.6. Pressure induced superheating

As mentioned above, formation of epitaxial interfaces is always considered to be necessary for achieving superheating in particle/matrix systems. In fact, a compression pressure will be generated onto the embedded particles upon heating due to the matrix confinement. The pressure can be caused by the difference in CTEs between particles and the matrix, or the volume change upon melting. The pressure change due to the

Table 4
Calculated Δ\(T_m^I\) and Δ\(T_m^L\), as well as Δ\(T_m^K\) and the maximum superheating obtained in experiments (Δ\(T_{\text{exp}}^m\)) for different particle/matrix system [236]

<table>
<thead>
<tr>
<th>System</th>
<th>(T_0)</th>
<th>(\theta)</th>
<th>Δ(T_m^I) (K)</th>
<th>Δ(T_m^L) (K)</th>
<th>Δ(T_m^K) (K)</th>
<th>Δ(T_{\text{exp}}^m) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb/Al</td>
<td>601</td>
<td>125</td>
<td>105</td>
<td>126</td>
<td>175</td>
<td>103 [10]</td>
</tr>
<tr>
<td>Pb/Cu</td>
<td>601</td>
<td>161</td>
<td>120</td>
<td>132</td>
<td>175</td>
<td>125 [10]</td>
</tr>
<tr>
<td>In/Al</td>
<td>430</td>
<td>154</td>
<td>52</td>
<td>66</td>
<td>90</td>
<td>44 [203]</td>
</tr>
<tr>
<td>Ag/Ni</td>
<td>1234</td>
<td>89</td>
<td>104</td>
<td>148</td>
<td>221</td>
<td>70 [202], 100*</td>
</tr>
</tbody>
</table>

* Computer simulation result [207].

It is noted that the above model is based on semi-coherent interfaces. For a full coherent interface, the melting point may approach the highest superheating limit of solids.

Fig. 34. Calculated superheating limits Δ\(T_m^I/T_0\) as a function of \(\theta\) for a variety of systems (a) without Δ\(E\) effect, and (b) with Δ\(E\) effect [236].
thermal expansion mismatch between the embedded particles and the matrix was considered by Spaepen and Turnbull [240], as give by

\[ P = \frac{12K_p G_m}{3K_p + 4G_m} \varphi, \]  

(62)

where \( K_p \) is the bulk modulus of the particle, \( \varphi \) is the misfit parameter.

The pressure effect on the melting point of the embedded nanoparticles can be understood following the classical thermodynamic consideration (the Clausius-Clapeyron Equation), which relates the change of pressure (\( \Delta P \)) to the change of melting point (\( \Delta T \)):

\[ \Delta T = \Delta P T_0 \Delta V / L_m. \]  

(63)

For embedded nanoparticles of which a superheating is observed, the pressure effect has been estimated [10,202,204]. It was concluded that the superheating observed in these systems cannot be accounted by the pressure effect. In other words, the pressure effect is usually considered to be minor relative to the epitaxial interface effect for embedded particles. Indeed, it is suggested that a relief of pressure at the interface will be induced by relaxation of the metallic matrix via vacancies and diffusive processes [241]. This effect was further demonstrated by Malhotra and Van Aken [242] to be important in the melting of embedded particles.

Actually, substantial superheating has been achieved in metal particles embedded in a rigid matrix without an epitaxial particle/matrix interface. For example, a superheating of up to 270 K was observed in encapsulated metal particles (Pb, Sn) in fullerene like shells [243], which was attributed to the high pressure build-up in terms of atomistic simulations. As mentioned previously, a pressure induced melting point elevation (but not superheating) was also observed in tin particles embedded in amorphous carbon films [174]. However, in these studies, no quantitative measurement was performed to verify the pressure effect. Compared with the interface effect on superheating of embedded nanoparticles, the pressure effect still needs more experimental investigations and further clarification by quantitative measurements.

Determination of the pressure effect on melting point elevation in nanoparticle systems is practically difficult. To isolate the pressure effect from other influencing factors of the melting point variation for nanoparticles, one has to find a suitable system with the following conditions: (1) a rigid matrix or shell to sustain the pressure build-up without relaxation; (2) a large CTE difference to ensure a large pressure build-up in the encapsulated nanoparticles that facilitates the pressure measurement; (3) formation of incoherent particle/matrix interfaces to exclude the possible interface effect on suppression of melt nucleation.

Our recent investigation set out to clarify the problem by choosing an Al/Al_2O_3 system [244,245]. As one may find out, there is a large CTE difference between Al_2O_3 (8.4 \times 10^{-6}/K) and Al (23.6 \times 10^{-6}/K). Actually, Al_2O_3 is the stiffest and strongest oxide ceramics with a shear modulus of about 150 GPa. Another necessary condition is that the solubility of oxygen in Al is extremely small (<3 \times 10^{-8}) even at the melting point of Al. The Al/Al_2O_3 samples, i.e. Al nanocrystals encapsulated in Al_2O_3 shell were prepared by active H_2 plasma evaporation and condensation and subsequent thermal oxidation of the Al nanoparticles.

HRTEM observations confirmed that after oxidation, Al_2O_3 shells were formed and the Al core is well encapsulated in Al_2O_3. No epitaxial relationship was noticed between the Al
core and the $\gamma$-$\text{Al}_2\text{O}_3$ shell. The Al/$\gamma$-$\text{Al}_2\text{O}_3$ interfaces are mostly curved and no sharp edged particles with strong facets were observed. The random Al/$\gamma$-$\text{Al}_2\text{O}_3$ interfaces indicate that the epitaxial interface effect on superheating can be excluded as expected.

In situ XRD experiments were conducted to measure the melting behaviour of the oxidized samples. For comparison, a bulk Al sample with coarse grains (grain size > 100 $\mu$m) and the original sample were also tested. Fig. 36 shows variations of integrated intensities of Al (1 1 1), (2 0 0), (2 2 0) and (3 1 1) diffraction peaks with temperature for the original sample and the oxidized samples A, B and C. For the original sample, the integrated intensities of these diffraction peaks reduce gradually with an increase of temperature, and tend to zero at $T_0$. However, the diffraction intensities do not drop to zero until about 7, 15 and 10 K beyond $T_0$ for samples A, B and C, respectively. With consideration of the X-ray diffraction resolution and the substantial holding time scale at elevated temperatures above $T_0$, it is believed that a considerable number of Al nanoparticles have been superheated in these samples. The superheating phenomenon was also reproducible in the second heating, as demonstrated in Fig. 35d.

To understand the origin of the observed superheating in the encapsulated Al nanoparticles, the pressure build-up on the Al nanoparticles was determined according to the thermal expansion behaviour around the melting point. Fig. 36 shows the lattice spacing of Al(1 1 1) plane ($d_{111}$) as a function of temperature for all samples. It is obvious that the lattice spacing values of the five different samples are approximately identical from room temperature to 800 K. As shown in Fig. 36b, an obvious suppression in thermal expansion

Fig. 35. The variation of the integrated intensity of Al (1 1 1), (2 0 0), (2 2 0) and (3 1 1) diffraction peaks with temperature for (a) the original sample, (b) sample A, (c) and (d) sample B, and (e) sample C. $I_{RT}$: integrated intensity at room temperature [244].
is observed in the superheated samples around $T_0$. The pressure build-up on the Al core can therefore be determined from the reduced CTE of Al lattice in the superheated samples.

The pressure onto the Al cores was also estimated according to the shell model \[240\]. The results agree reasonably with the measured pressure from the temperature dependence of lattice spacing. With the measured pressure on the Al core for the superheated samples, the melting temperature elevation can also be calculated in terms of the Clausius-Clapeyron Equation. It is interesting to note that the calculated results are coincident with the measured superheating from the in situ XRD experiments for the three samples, as listed in Table 5. The coincidence between the measured superheating and the melting point elevation derived from the classical thermodynamics (Clausius-Clapeyron Equation) in the present samples verifies that the observed superheating is a pressure-induced phenomenon in which the epitaxial interface effect on suppressed melting nucleation can be excluded.

### 5.7. Physical properties of superheated particles

Superheated particles provide a good example for investigating the effect of interfaces on properties of nanomaterials. However, compared with melting, less is known about other properties of superheated particles as a unique state of matter. Actually, the superheated particles were found to exhibit some different physical properties besides the melting point.
5.7.1. Debye temperature

As described previously, Debye temperature was found to be lower than the bulk value for nanocrystals undergoing size-dependent melting point depression. The Debye temperature of superheated particles was also measured by in situ XRD [165]. The Debye temperature of the melt spun sample (containing superheated Pb particles embedded epitaxially in Al) is $89 \pm 5$ K, compared with a bulk value $84 \pm 4$ K, and the value for the ball-milled samples, $69 \pm 3$ K.

Besides Pb particles embedded epitaxially within the Al grains, there are also large particles located at the Al grain boundaries in the melt spun sample. The Debye temperature of the sample can be viewed as the contribution of these two kinds of particles by

$$\Theta_D^{-2} = g\Theta_{D1}^{-2} + (1-g)\Theta_{D2}^{-2},$$

(64)

where $\Theta_D$ is the apparent Debye temperature of the melt-spun sample; $\Theta_{D1}$ and $\Theta_{D2}$ are that of Pb particles on GBs and within grains, respectively; $g$ is the volume fraction of the GB particles. Assuming that the GB Pb particles have the same Debye temperature with the ball-milled sample with the same particle size, $\Theta_{D2}$ is estimated as $98$ K for $\Theta_D = 89$ K, $\Theta_{D1} = 79$ K (mean grain size $30 \text{ nm}$) and $g = 0.4$.

From the above analysis, it is evident that Debye temperature of nanocrystals depends strongly on the interfacial structure. The Debye temperature is enhanced by coherent interfaces, while is reduced by incoherent interfaces in nanomaterials. Such an effect of interface on Debye temperature will possibly be related to other physical properties of nanomaterials, of which melting is just one example.

5.7.2. Thermal expansion

Zhong et al. [246] performed preliminary measurements on lattice expansion of superheated particles. Since a precise measurement of the lattice expansion is practically difficult, they investigated the temperature dependence of lattice parameters for the superheated particles. The melt-spun Pb/Al sample was used for study, in which Pb particles (averagely $29 \text{ nm}$) have a maximum superheating about $40 \text{ K}$. The structure is similar to that described in Ref. [221].

![Fig. 37. Lattice parameter of various Pb samples as a function of temperature [246].](image-url)
As shown in Fig. 37, the thermal expansion behaviour of Pb nanoparticles was measured by using in situ XRD. The thermal expansion for the coarse-grained polycrystalline Pb above \( T_0 \) can be obtained by exploration of the literature data below \( T_0 \), and the thermal expansion of surface-free bulk Pb obtained by MD simulation was also demonstrated.

It is seen that the three kinds of Pb crystals undergo evidently different thermal expansion behaviours. The average CTE can be calculated for different crystallographic orientations. The CTEs of the three samples are listed in Table 6. Above \( T_0 \), the CTE of embedded Pb nanocrystals is lower than that of conventional polycrystal, and the surface-free bulk Pb has the lowest CTE. This behaviour indicates that the thermal vibration of embedded Pb crystals is reduced relative to conventional polycrystals, which is also in consistent with the measurement results of melting points and Debye temperatures.

### 6. Superheating of thin films

Superheating has been obtained in a large body of embedded particle systems, nevertheless, much fewer observations have been reported for superheating of two-dimensional thin films. Melting points of Pb, Sn and Bi thin films were found to be depressed relative to the bulk values, which was explained by considering the thin film as small islands of metal clusters [131].

Computer simulations [247,248] suggested that Pb thin films fully confined in Al matrix can be superheated substantially, due to successful suppression of melt nucleation at the interfaces. Also, the orientation of the host matrix was found to have a pronounced influence on the superheating. Pb(1 1 1) films confined in an Al(1 1 1) matrix can be superheated by up to 115 K, depending on the film thickness [248]. Pb(1 1 0) cannot be superheated by embedding into the Al(1 1 0) matrix, while it can be superheated by 300 K when confined in Al(1 1 1) matrix with an orientation transition from (1 1 0) to (1 1 1) [247]. Similar to that of small particles, an expression for the melting point of thin films \( (T_m(D)) \) embedded in a matrix was obtained by thermodynamic considerations [247]:

\[
T_m(D) = T_0 \left( 1 + \frac{2(\gamma_{lm} - \gamma_{sm})}{DL_m} \right),
\]

where \( D \) is the film thickness.

There are a few experimental results indicating that thin films could be superheated by confinements. For example, thin Ga films confined in grain boundaries of nanostructured Al2O3 were produced by ball milling, and it was found that about six atomic layers of Ga are prevented from melting at 17 K above the bulk melting point owing to the interaction with Al2O3 [249]. The compressed Pb epitaxial layer on Cu(1 1 1) has a melting temperature up to 200 K above \( T_0 \) [250]. Nevertheless, the necessary conditions for superheating

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method</th>
<th>Temperature range (°C)</th>
<th>CTE ( (10^{-5}/°C) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Superheated Pb/Al</td>
<td>XRD, (1 1 1)</td>
<td>325–350</td>
<td>3.7 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>XRD, (2 2 0)</td>
<td>325–340</td>
<td>5.2 ± 0.7</td>
</tr>
<tr>
<td>Coarsed-grained Pb</td>
<td>Literature</td>
<td>325–357</td>
<td>6.06 ± 0.09</td>
</tr>
<tr>
<td>Surface-free bulk Pb</td>
<td>MD simulation</td>
<td>325–357</td>
<td>2.78 ± 004</td>
</tr>
</tbody>
</table>

Table 6
A comparison of the measured CTEs of various Pb samples[246]
of two-dimensional thin films are practically hard to achieve. Even if a thin film could be sandwiched in a high-$T_0$ matrix with coherent or semi-coherent interfaces, heterogeneous nucleation of melt at various defects within the film (such as grain boundaries) and/or at the lateral free surfaces could not be avoided. Hence, superheating of 2D thin films is supposed to be experimentally difficult.

Recently Zhang et al. [251,252] attempted to achieve superheating in confined thin films experimentally. They prepared samples of Pb thin films confined epitaxially in Al by means of two different techniques, cold rolling (sample A) and alternative DC sputtering depositions (sample B).

6.1. Preparation and microstructure of thin film samples

In their study [251,252], to prepare sample A, Al and Pb foils (with a purity of 99.99%) were piled up alternately to make an Al/Pb/Al sandwich. The sandwich was then rolled and folded repeatedly at ambient temperature until the nominal thickness of the Pb layers was progressively reduced into the nanometer scale. During the process, the as-rolled ribbon was annealed to avoid work hardening. Final annealing at 593 K for 30 min was conducted to release the strain and stabilize the Pb/Al interface for the as-rolled Pb/Al samples. During the rolling, additive Pb/Al interfaces were processed in a way of simultaneous elongation of the Al/Pb/Al sandwich, which can avoid interfacial oxidation. The thickness of one Al/Pb/Al sandwich layer, as a whole, was 1/256 that of the as-rolled ribbon after eight times of folding and rolling. The nominal layer thickness of Pb films in the sandwich can be easily estimated. By controlling the thickness of the as-rolled ribbon, samples A with different thicknesses of Pb layers were produced.

For preparation of sample B, Pb/Al multilayer films were DC sputtering deposited at room temperature on a native oxide Si(100) surface. The purity of both Al and Pb targets was 99.99%. The deposition rates of 0.5 nm/s for Al and 3 nm/s for Pb were determined by the relationship between the employed deposition power and the film thickness with a relative error within 5%. Because the sputtering was under the same condition, the deposition time control resulted in a definite layer thickness. Modulated multilayer [Al(20 nm)/Pb($y$ nm)]$_n$ were deposited, where $y$ denotes the film thickness of Pb layer in nanometer. The period value $n$ adopted for each sample was determined by $y \times n \approx 1000$.

In both samples, a small portion (less than 10%) of Pb thin films exhibit a parallel-cubic orientation relationship with Al films, [011]Pb || [011]Al and $(1\overline{1}1)$Pb || $(1\overline{1}1)$Al, as indicated in Fig. 38. Such an epitaxial Pb/Al interface is coincident with that observed in the Pb particles embedded in Al matrix synthesized by means of melt quenching [204,221] and ion implantation [215]. Also TEM observations found that Pb films with a semi-coherent Pb/Al interface have a higher stability in morphology compared with those with an incoherent Pb/Al interface [253].

6.2. Measurements of superheating

Melting behaviours of the two samples were measured by means of DSC and in situ XRD, respectively. Fig. 39 shows typical DSC traces of sample A. Two endothermic peaks are clearly seen: one (P1) around 600 K, $T_0$ of Pb, the other (P2) at 653 K, about 53 K above $T_0$. Peak P2 was found to be reproducible by subsequent heating and cooling runs (as indicated in Fig. 39 with (2), (3) and (4)). It is believed that while the majority of Pb
thin films melt at $T_0$ (peak P1), there is still a small portion of Pb thin films exhibiting a substantial superheating (peak P2). It is also noted in Fig. 39 that peak P2 in the second heating run [252].

Fig. 38. Representative planar-view (a) and cross-sectional (c) TEM images of the cold rolled sample A. (b) shows a corresponding SAED pattern (indexed below) taken from the planar-view TEM observation (a) to demonstrate the orientation relationship between Pb and Al. The note DD indicates one of the double diffraction spots [252].

Fig. 39. Typical DSC traces of the cold-rolled sample A obtained during sequential heating runs at a heating rate of 10 °C/min. The inset at the upright corner is an amplification of the endothermic peak in the second heating run [252].
heating appears at a lower temperature than that in the first heating run, which might be attributed to the thickening of the Pb thin films.

Fig. 40 displays the in situ XRD profiles at high temperatures for Pb (111), (200), (220) and (311) for sample A and for a bulk pure Pb sample. Evidently, all Bragg diffraction lines in the bulk sample disappeared below 602 K, while in sample A, obvious diffraction profiles can still be observed above $T_0$. The temperatures at which the XRD profiles disappear are 6, 2 and 1 K above $T_0$ for (111), (200), and (220) reflections, respectively, indicating that a portion of Pb films can be superheated by at least 6 K. Considering the timescale of the in situ XRD measurements (about one hour), such a superheating observed is metastable, rather than an unstable transient superheating during rapid heating.

![XRD profiles](image-url)

Fig. 40. XRD profiles of Pb (111), (200), (220), and (331) around Pb bulk melting point for sample A (a) and for the pure Pb film (b) [251].
6.3. Effects of film thickness and heating rate

The effects of film thickness and heating rate on the melting kinetics of the superheated Pb films were examined for samples with different nominal Pb film thicknesses (9–27 nm for sample A and 6–18 nm for sample B). The superheating is displayed as a function of the film thickness for different heating rates in Fig. 41, from which an evident decreasing trend of superheating with a reduction of film thickness is seen. The maximum superheating is about 60 K for sample A with 9 nm Pb layers, and 80 K for sample B with 6 nm Pb layers. It is also seen from Fig. 41 that the heating rate has a substantial influence on the superheating. As the heating rate increases from 10 to 20 K/min, the superheating is enhanced by about 5 ± 3 K for both samples. This phenomenon is quite different from normal melting (surface-induced) of bulk samples without superheating, of which the heating rate has neglectable effect on the melting point due to the fast melting kinetics at high temperatures.

6.4. Melting thermodynamics

The epitaxial interfaces between the embedded nanoparticles and the matrix were often emphasized to contribute to the observed superheating of nanoparticles due to suppression of the melt nucleation at the interface. However, in the case of confined Pb thin films, the liquid will nucleate either at the film grain boundaries and film edges or at the random interfaces between the films and matrix. Therefore, it is believed that the epitaxy interfaces should work in a different way in the superheating of the confined Pb thin films from that of the embedded nanoparticles. This can be analysed by considering the configuration of the solid/liquid interface in contact with different Pb/Al interface structures during the advance of the melt front. As shown in Fig. 42a, the wetting angle (θ) is less than 90° as γ_{Pb(s)/Al} < γ_{Pb(l)/Al} due to the confinement of the thin film by semi-coherent Pb/Al interfaces which possess a low Pb/Al interfacial energy.

Fig. 41. The degree of superheating in the first heating run versus the nominal thickness of the Pb thin films at heating rates of 10 °C/min and 20 °C/min from the cold rolled samples A (a) and the sputtering deposited samples B (b), respectively [252].
In contrast, when the interface is randomly oriented with a high energy configuration, $\theta$ is greater than $90^\circ$ as $\gamma_{\text{Pb}(s)/\text{Al}} < \gamma_{\text{Pb}(l)/\text{Al}}$, as depicted in Fig. 42b. Here the driving forces for growth of the melt front are different in the two cases. For epitaxial interfaces, a positive $\Delta \gamma = \gamma_{\text{Pb}(l)/\text{Al}} - \gamma_{\text{Pb}(s)/\text{Al}}$ will hinder the growth of the melt. Superheating is therefore necessary to supply an excess work to compensate the interfacial energy change. In this case, the growth of the melt front is blocked although the liquid is nucleated somewhere and the material is in a metastable state. Clearly, in the case of randomly oriented interface, $\Delta \gamma$ is negative, which favors melting.

The superheating needed to overcome the barrier for melt growth can be estimated in the frame work of thermodynamics, by including an interfacial energy term in the total free energy change of a melting transition for the confined thin film [252]:

$$
\Delta T = \frac{2\gamma_{sL}T_0 \cos^2 \theta}{\tau L_m (\pi/2 - \theta)},
$$

where $\tau$ is the actual thickness of the column that undergoes melting, which is equal or less than $D$.

![Fig. 42](image)

Fig. 42. The interfacial energy conditions of the triple phase, Al solid, Pb solid and Pb liquid, with an epitaxial interface (EP) (a) and only random interfaces (RA) (b) [252].

![Fig. 43](image)

Fig. 43. The experimental data of the superheating versus film thicknesses and the theoretical prediction plots of the 2D nucleation and thermodynamics [252].
6.5. Melting kinetics

The melting kinetics of confined Pb thin films was further modeled based on the two-dimensional nucleation theory. A relationship between the critical radius $r_{2D}^*$ and superheating $\Delta T$ is given by [252]

$$r_{2D}^* = \frac{\gamma_m T_0 V_m}{L_m \Delta T - T_0 V_M K \Delta E_s},$$

(67)

where $\Delta E_s$ is strain energy density change per unit volume induced by the volume change in melting and the mismatch between film and matrix. The strain energy density change of 2D nucleation at the solid/liquid interface is only a portion of that of the homogeneous

Fig. 44. MD simulation results of melting sequence of the superheated Pb thin film confined in Al [254].
nucleation, so a coefficient $K$ is introduced with a value less than 1. The variation of degree of superheating with the film thickness is plotted in Fig. 43, which also includes the experimental results. The experimental data distributed between the curves of $K = 1$ and $K = 0$, indicating the maximum and minimum effect of the strain energy change on the superheating, respectively.

To understand the heating rate effect on superheating, the advancement of the Pb melt front with elapsed time was calculated based on the assumption of the mononuclear growth. It is found that for a transition controlled by such a 2D nucleation and later growth process, the apparent melting temperatures will increase with an increasing heating rate. For instance, the apparent melting point is elevated by about 2 K when the heating rate increases from 10 to 20 K/min, which is comparable with the DSC measurement results ($5 \pm 3$ K).

Fig. 44 (continued)
The melting process of the confined Pb thin films (sample A) was recorded in a MD simulation [254]. The melting sequence at various temperatures was shown in Fig. 44. It is seen that at 600 K, pre-melting occurred on the free surfaces, and the solid/liquid interface was curved due to the equilibrium condition at the interface, similar to the configuration demonstrated in Fig. 42. With the increase of temperature, the melt front advanced bilaterally into the solid, and the curvature of the solid/liquid interface kept unchanged. It is clear that melting of the confined Pb thin film nucleates at the free surfaces without superheating and proceeds by growth of the melt into the solid with the help of superheating, consistent with previous observations and analysis.

The superheating behaviour of confined Pb thin films in Al shed light on understanding the effect of epitaxial interfaces on melting: superheating may be induced not only by suppression of melt nucleation, but also by suppression of melt growth at the ordered interface. This may lead to a reconsideration of the superheating in the case of embedded nanoparticles in which the suppression of melt growth may also be involved as sometimes melt nucleation will occur easily on the defects such as corners and voids.

A very recent study [255] showed that Sn layers confined in epitaxial Sn/Si multilayers can be superheated to 802 K, significantly higher than \( T_0 \) of \( \beta \)-Sn (505 K). The electronic interactions between Sn and surrounding Si layers were evidenced to be the main reason for the superheating in thin films.

7. Melting of alloy particles

So far, most studies on melting behaviours of nanomaterials were carried out in pure elements in which surfaces or interfaces play a key role. For alloy systems, more variables are introduced in influencing the melting process in comparison with that of pure elements. In this chapter, we will address melting behaviours of several types of alloy particles including free-standing alloy particles, embedded multi-phase and single-phase alloy particles, respectively.

7.1. Free-standing alloy particles

The melting behaviour of free-standing Bi–Sn nanoparticles with different compositions (including single phase and two-phase) formed by using co-deposition was studied using TEM [256]. Melting was found to initiate at particle surfaces accompanied with formation of a liquid layer. The liquid layer appeared suddenly with an increase of temperature and thickened gradually; the remaining solid core melts suddenly into a whole liquid particle. The solidus and liquidus points were found to be reduced relative to the equilibrium values for the corresponding bulk systems. For Bi–Sn particles of 40 nm in diameter, the eutectic temperature was lowered by more than 60 K. Similar observations were also found in Pb–Bi and Pb–In systems [256].

Jesser et al. [257] provided a thermodynamic analysis to model the size-dependent melting behaviour of Sn–Bi systems, considering the size-dependent capillary effect analogous to that in monometallic nanoparticles. Ibuka et al. [258] observed melting in a eutectic Pb–Sn under in situ TEM, and they found that the melting process takes place preferentially at the Pb/Sn interface, or at the emerging point of the Pb/Sn interface at the sample surface, or at the triple points where grain boundaries in Sn (segregated with Pb) and the Pb/Sn
interface meet. Obviously, small alloy particles provide more sites for melt nucleation at various interfaces relative to that for single-element systems.

7.2. Embedded multi-phase alloy particles

7.2.1. Pb–Cd–Al system

Hagege and Dahman [259] prepared Pb–Cd inclusions embedded in Al by means of rapid solidification. Both the binary Al–Pb and Al–Cd alloys are simple monotectic systems, and Pb–Cd forms a simple eutectic. Previous studies showed that pure Pb particles embedded in Al can be substantially superheated [204], but no superheating is observed for Cd particles embedded in Al [226]. The eutectic inclusions consist of fcc Pb and hcp Cd, separated by a planar Pb–Cd interface that was parallel to the common close-packed planes. The particle sizes vary from 5 to 60 nm. As shown in Fig. 45, the orientation relationships of the Pb and Cd parts with the Al matrix are similar to those in the binary Al–Pb and Al–Cd systems, respectively. In situ TEM observations revealed that melting occurred at the equilibrium bulk eutectic temperature. Melting was seen to be initiated at triple junctions between Cd, Pb and Al, and the melt front extends slowly from the initial point of nucleation in an irregular process until eventually enveloping the whole particle, as demonstrated in Fig. 46 [260]. This behaviour is sharply different from that observed in free-standing multi-phase nanoparticles as described above, of which surface melting (formation of surface liquid layer) predominates. Therefore, it is deduced that surface melting is suppressed for the Pb–Cd inclusions embedded in Al due to the epitaxial Pb–Al and Cd–Al interfaces, different from that in free-standing multi-phase nanoparticles. The eutectic melting point is not lowered obviously. The triple junctions where the Pb–Cd interfaces and Al matrix meet serve as heterogeneous nucleation sites for melting. This explains why no superheating is observed in the Pb–Cd bimetal inclusion in Al, unlike that in binary Pb–Al alloys.

Nano-sized Pb–Cd particles of sizes ranging from 1 to 20 nm in Al have also been obtained by means of iron implanting [261–264]. The orientation relationships of the multi-phase inclusion are similar as those in the rapid solidification samples. Again, melting was found to take place close to the bulk eutectic melting point or a few degrees below. No superheating was achieved and nucleation was found to take place preferably at the Pb–Cd–Al triple junctions as well.

![Fig. 45. A typical structure of the Pb–Cd inclusions in Al [259].](image)

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7.2.2. Pb–Sn–Al system

The melting behaviour of Pb–Sn–Al systems was also investigated [265,266]. Eutectic Pb–Sn alloy inclusions in Al matrix were formed by iron implanting, which are similar to that observed in the Pb–Cd–Al systems [259], i.e. a two-phase structure consisting of Pb and Sn segments separated by a planar interface. The Sn segment has a complex orientation relationship which is different from that in the Sn–Al binary system, while the Pb segment has a similar relationship to the Pb–Al system. Upon heating to the eutectic temperature, owing to enhanced solubility at high temperature, Sn from the Sn segment dissolved into Pb, forming a single-phase inclusion prior to melting. Melting then takes place close to or above the eutectic temperature. However, it is difficult to determine if a superheating is associated since the solid line temperature depends on the exact composition of the inclusion which is difficult to be determined.

Pb–Sn inclusions with different Sn concentrations in Al have been prepared by using rapid solidification [267,268]. Similarly, the two-phase structures were formed as like that in the iron-implanting samples, although the exact orientation relationships between the corresponding phases are different. Again, melting occurred close to the eutectic melting point, although the initial point of melting is depressed.

7.2.3. Sn–In–Al system

Nano-sized Sn–In alloy inclusions in Al matrix have been synthesized by using rapid solidification [269]. Unlike the Pb–Cd system, In and Sn can solute into each other, forming In-rich and Sn-rich solid solutions. The In-rich phase is formed surrounding the Sn-rich phase and it has an orientation relationship with Al. In this case, again, the eutectic melting was observed close to the equilibrium eutectic point without superheating.
7.3. Embedded single-phase alloy particles

The single-phase Pb–Bi alloy inclusions in Al formed by using iron implanting exhibited a size-dependent superheating [263]. The Pb-rich inclusions with a high concentration of Bi (within the solubility limit of Bi at high temperatures) have the same structure and morphology as the pure Pb nanoparticles in Al. The single-phase Pb–Bi alloy inclusions can remain solid well above the solidus line in the equilibrium phase diagram. Smaller particles showed larger superheatings. Such a superheating behaviour, similar to that in the binary Pb–Al systems, may be attributed to the melt nucleation difficulty due to lack of melt nucleation sites (phase-boundaries) in the one-phase particles.

So far, the matrix used to confine nanoparticles epitaxially is always pure elements with higher melting points. Pb nanoparticles embedded in Zn and Cu matrices are known to be superheated substantially. Pb nanoparticles (5–65 nm in diameter) embedded in a Cu–Zn alloy matrix (single fcc phase) can also be superheated obviously [270]. The particle morphology and the epitaxial relationship with the matrix are similar to those in Pb/Cu alloys. Superheatings of up to 100 K were obtained depending on the interface structure.

7.4. Summary

The effect of surfaces and interfaces on melting processes has once again been evidenced in multi-component nanoparticles. In addition, some characteristics of melting behaviours of alloy particles are revealed by experimental measurements:

(1) Free-standing alloy nanoparticles (single phase or multi-phase) exhibit a size-dependent melting point depression, in which surface melting predominates as that in free-standing pure element nanoparticles.

(2) Multi-phase nanoparticles embedded in a matrix with epitaxial relationships do not show a substantial melting point depression or superheating; melting was found to nucleate at the junctions between the phase boundaries.

(3) Superheating can be obtained in single-phase alloy nanoparticles embedded in a matrix where an expitaxial interface is formed.

Analogous to pure element systems, melting of alloy nanoparticles prefers to nucleate at free surfaces and interfaces. In case of multi-phase alloy particles, phase boundaries provide alternative venues for heterogeneous melt nucleation. Therefore, to achieve superheating in alloy nanoparticles, one has to eliminate pre-melting at free surfaces and at particle/matrix interfaces (by proper expitaxial coating), and at the same time, to prevent melting at phase boundaries, which is only possible in single-phase systems where phase boundaries disappear.

8. Concluding remarks

Meanwhile significant progress has been made in understanding the melting process of solids from bulk forms to nano-sized crystals over past decades, the field of melting and superheating of solids is still a fertile territory to explore. A number of key issues are remained to be clarified related to the mechanism of melting. For example, quantitative effects of various kinds of defects in crystalline solids (including grain boundaries, triple
junctions, dislocations, vacancies, and interstitials) on melting kinetics are yet to be characterized experimentally and theoretically. Melting of extremely small particles (clusters) is not fully understood yet in which electronic structure and the quantum size effect might be predominantly involved. Melting of solids with different atomic bonding natures is another complicated theme without a clear picture.

Although various stability limits of crystalline solids have been proposed, direct experimental verification of any of them has not been obtained yet. The kinetic limit based on the homogeneous melt nucleation catastrophe seems to be a realistic stability limit of crystalline solids, but homogeneous nucleation of melt inside crystals is not observed experimentally, although demonstrated in MD simulations. In the superheating of confined nanoparticles, epitaxial interfaces are believed to be effective in suppressing heterogeneous nucleation of melt, and at the same time, in suppressing melt growth as well, as manifested in the case of superheated thin films. The build-in pressure due to different CTEs between the nanoparticles and matrix contributes additionally to the superheating. Therefore, identifications of each of these effects are to be done in different superheating systems. Alternative chemical, physical, or mechanical approaches to suppress nucleation and growth of melt in crystalline solids, especially in low-dimensional ones, are to be explored extensively. In additional, various physical and chemical properties as well as mechanical properties of superheated crystals should be revealed systematically.

Techniques for studying melting and superheating of solids are also important for advancement of this field. Accurate measurements of thermodynamic quantities of individual nanoparticle upon melting, such as specific heat and enthalpy change, are still difficult in experiments. Experimental identification of local microstructure at solid/liquid interfaces, which is fundamentally vital for understanding the melting kinetics, is still challenging condensed matter physicists and materials scientists. Alternative techniques to achieve superheating in solids are to be developed. Methodologies for accurately measuring the melting behaviours of high melting-point solids (such as compounds and intermetals) are highly desired. Practically, accurate processing controls of the melting of high-$T_0$ compound particles in molten steels are crucial in determining the subsequent properties and performance of the solidified steel products.

Apparently, many new interesting topics are in front of us in the field of melting and superheating of solids. Melting behaviours of extremely thin films (of a few atomic layers thick) and extremely small clusters will be a fascinating theme for adventure. Compared with monometallic systems, melting of intermetals and compounds has received much less attention so far. Melting behaviours of some unique geometries such as nano-wires or nano-belts or nano-tubes of different materials (semiconductor or metals) are to be investigated. In addition, external magnetic or electrical field effects on the melting kinetics of various types of low-dimensional materials are to be clarified via experimental and theoretical attempts.

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