Can nano-particle stand above the melting temperature of its fixed surface partner?

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Abstract

The phonon thermal contribution to the melting temperature of nano-particles is inspected. Unlike in periodic boundary condition, under a general boundary condition the integration volume of low energy phonon for a nano-particle is more complex. We estimate the size-dependent melting temperature through the phase shift of the low energy phonon mode acquired by its scattering on boundary surface. A nano-particle can have either a rising or a decreasing melting temperature due to the boundary condition effect, and we found that an upper melting temperature bound exists for a nano-particle in various environments. Moreover, the melting temperature under a fixed boundary condition sets this upper bound.

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I. INTRODUCTION

This work focuses on the quantum size effect with particular emphasis on environment-depending melting temperature of nano-particles. The continuing progress in the design of nano-particles led to enhanced and novel functionality. Concerning the thermal stability of heat resistant, we ask a question: can nano-particles stand a temperature higher than the one its fixed surface partners melt at? There are many different thermodynamic theories of small systems, each considering different important aspects of size-dependent melting of nano-particles. The discrete quantum energy level has not been carefully considered in these theories. The critical role of phonon in thermal related phenomena is well-known. But only recently the finite spacing energy levels became a greater awareness in size-dependent melting. There is a chance to understand the rising of size-dependent melting temperature of nano-particles with more attention on the important aspect of quantum finite size effect. We estimate in this work the change of melting temperature by coating a fixed size particle or changing its environment. We give the upper limit of the change on melting temperature.

The melting temperature for small particles was modeled and studied in more than 100 years ago, and the pressing need for a deep understanding continues today. In this study, we use the Lindemann melting criterion for its simplicity in estimating the melting temperature of a nano-particle with different boundary conditions. By Lindemann criterion, a nano-particle melts at the temperature \( T_m \) at which the ratio of \( u \), the square root of the mean square of atom thermal displacement, to \( a \) the lattice constant reaches the Lindemann critical value \( L_c \):

\[
L_c = \frac{u(T_m)}{a},
\]

II. PERIODIC BOUNDARY CONDITION

We repeat some necessary derivation for \( u(T) \) in harmonic approximation. A lattice specified by a set of the vectors \( \mathbf{R}_i \) will be studied, with one atom at each lattice point. The displacement \( \mathbf{u}_i \) of an atom from its equilibrium position \( \mathbf{R}_i \) can be calculated by

\[
H = \frac{M}{2} \sum_{i\alpha} \dot{u}_{i\alpha}^2 + \frac{1}{2} \sum_{i\alpha j\beta} \Phi_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) u_{i\alpha} u_{j\beta},
\]
where $\alpha = x, y, z$ and $u_{i\alpha}$ is the $\alpha$th component of the displacement. $R_i = (i_x - \frac{L+1}{2}, i_y - \frac{L+1}{2}, i_z - \frac{L+1}{2})$, $i_{\alpha} = 1, \ldots, L$. The center of the nano-particle is at the origin of the coordinates, and the boundary of the nano-particle is set on $R_{\alpha} = \pm \frac{L}{2}$ surfaces in coordinate space. $N = L^3$ is the number of atoms of the nano-particle. $M$ is the mass of the atom. The potential energy $\Phi$ is expanded to the second order and $\Phi_{\alpha\beta}(R_i, R_j) = (\partial^2 \Phi / \partial u_{i\alpha} \partial u_{j\beta})_0$.

The equations of motion of the lattice is then

$$M \ddot{u}_{i\alpha} = - \sum_{j\beta} \Phi_{\alpha\beta}(R_i, R_j) u_{j\beta}.$$ (3)

The general solution can be written in vibration modes $Q_{k\sigma}$:

$$u_{i\alpha}(t) = \sqrt{\frac{1}{N}} \sum_{k\sigma} Q_{k\sigma} \epsilon_{k\sigma\alpha} e^{-i\omega_{\alpha}(k)t} \prod_{\alpha'} f(k_{\alpha'}, R_{i\alpha'}).$$ (4)

$\omega_{\sigma}(k)$ and $\epsilon_{k\sigma}$ are phonon frequency and phonon polarization of wave-vector $k$, respectively.

The atomic mean-squared thermal displacement is

$$\langle u_{i\alpha}^2 \rangle = \sum_{k\sigma} \frac{\hbar \epsilon_{k\sigma\alpha}^2}{NM\omega_{\sigma}(k)} \left[ \frac{1}{e^{\hbar \omega_{\sigma}(k)/k_B T} - 1} + \frac{1}{2} \right],$$ (5)

where $\langle \rangle$ means grand canonical ensemble average. The center-of-mass motion is $u^{cm} = \frac{1}{N} \sum_i u_i$. The square root of the mean square of atom thermal displacement, $u(T)$, is given by:

$$u(T) = \sqrt{\frac{\sum_{i\alpha} \langle u_{i\alpha}^2 \rangle - \langle (u^{cm}_{\alpha})^2 \rangle}{N}}.$$ (6)

Melting temperature $T_m$ is obtained by solving Eq. (1). We will use boundary conditions to account for various environments.

For periodic boundary condition the mode expansion function for atom displacement in each $\alpha$-direction is $f(k_{\alpha}, R_{i\alpha}) = \sqrt{\frac{1}{L}} e^{ik_{\alpha} R_{i\alpha}}$, $k_{\alpha} = 2n_{\alpha} \pi / La$, and $n_{\alpha} = -L/2 + 1, \ldots, L/2$. The melting temperature $T_{mn}$ for size $L$ nano-particle under a periodic boundary condition is then calculated:

$$L_c^2 = \frac{u_{\alpha}^2}{a^2} = \frac{3 \hbar a}{16 \pi^3 M} \int_{-\pi/a}^{\pi/a} d^3 k \frac{1}{\omega(k) \tanh \frac{\hbar \omega(k)}{2k_B T_{mn}}},$$ (7)

$$- \frac{3 \hbar a}{16 \pi^3 M} \int_{-\pi/a}^{\pi/a} d^3 k \frac{1}{\omega(k) \tanh \frac{\hbar \omega(k)}{2k_B T_{mn}}},$$
where \( \omega(k) = \omega_\sigma(k) \) is used when summing up the three polarized vibration directions in each \( k \) mode. \( u^{cm} \) is given only by the zero wave-vector phonon at \( k = 0 \). The second term removes contribution of the global moving \((u^{cm})^2\). This is the missing of phonon contribution from the zero-mode volume. We have repeated briefly the derivation of this zero-mode volume in the work of Sui et al.\(^8\). For the bulk system, melting temperature \( T_{mb} \) is the solution of the same equation in the limit of \( 1/L \to 0 \), which turns the second term into zero:

\[
L_c^2 = \frac{3\hbar a}{2\pi^3 M} \int_0^{\pi/a} d^3k \frac{1}{\omega(k) \tanh[\frac{\hbar \omega(k)}{2k_B T_{mb}}]}. \tag{8}
\]

III. BOUNDARY REFLECTIVE PHASE SHIFT

We analyze the phase shift of the low energy phonon mode for different boundary conditions. A theoretical estimated expression for the melting temperature of nano-particle will contain physical quantities with some uncertainty. Beside the main variable, the size \( L \), other physical factors may play a role in finite size melting, such as shape, surface reconstruction, and environmental effect etc. An expression has to have physical quantities not so certain to absorb all the different factors from material to material, environment to environment, and particle to particle. We will use the phase shift of low energy acoustic phonon for this function. A model with boundary is good for nano-particles under different boundary conditions. The phase shift of phonon mode depends on its scattering on the surface of a nano-particle. A phase shift can be drawn from the experimental data, or it has to be chosen with some uncertainty for a particular situation before we can make estimation for a design of the melting temperature.

The scattering and phase shift have been studied most thoroughly in the context of quantum theory. The notion of reflection of waves in one-dimensional scattering plays a central role in the following detailed discussion. We model the boundary of the nano-particle as an additional potential which is bigger than zero outside the nano-particle and zero inside the particle. In any \( \alpha \)-direction, the general solution for Eq. (3) is in terms of waves moving in opposite directions, \( f(k_\alpha, R_{i\alpha}) = c e^{ik_\alpha R_{i\alpha}} + d e^{-ik_\alpha R_{i\alpha}} \), for each vibration mode \( Q_k\sigma \). We study the standing waves under a general real boundary potential. The most general form for the reflection coefficient would then be \( r = e^{i\delta_{k\alpha}} \); the termination at the boundary could
at most introduce a phase change in the reflected wave:

\[
\frac{d \, e^{-ik_a R_\alpha}}{c \, e^{ik_a R_\alpha}} = e^{i\delta_{k_\alpha}}, \quad R_\alpha = La/2.
\] (9)

Different boundary conditions resulting in the same magnitude of phase shift are physically equivalent. A very careful but long and technical analysis on phase shift and boundary condition can provide considerable understanding of nano-particle’s surface and environment. We will put this study under control. We assume an isotropic surface and environment. The same phase shift will be assumed in each \( \alpha \)-direction. The phase shift for a small wave-vector is expanded up to the first order of \( 1/L \):

\[
\delta_{k_\alpha} = \delta + a_1 k_\alpha, \quad \delta \text{ is a constant phase shift and } a_1 \text{ is the expansion coefficient for the first order term. We will discuss on phase shift in the range of } [-\pi, 0], \text{ with corresponding boundary barrier effectively repulsive. This phase shift is the parameter we used to model the boundary effect.}
\]

The wave-vector is fixed by the boundary condition Eq. (9). First, when the standing wave is of even parity, we have \( c/d = 1 \) in \( f(k_\alpha, R_{i\alpha}) \), and \( e^{i(k_\alpha L a + \delta_{k_\alpha})} = 1 \). The mode expansion for atom displacement on this kind of phonon mode is \( f(k_{e\alpha}, R_{i\alpha}) \sim \cos(k_{e\alpha} R_{i\alpha}) \), with \( k_{e\alpha} = \frac{2n_\alpha \pi + |\delta_{k_\alpha}|}{La} \). The integer \( n_\alpha \) runs from 0 to \( L/2 - 1 \). The second group is the odd parity group for \( c/d = -1 \) in \( f(k_\alpha, R_{i\alpha}) \), and \( e^{i(k_\alpha L a + \pi + \delta_{k_\alpha})} = 1 \). The mode expansion for atom displacement on this kind of phonon mode is \( f(k_{o\alpha}, R_{i\alpha}) \sim \sin(k_{o\alpha} R_{i\alpha}) \), with \( k_{o\alpha} = \frac{(2n_\alpha - 1) \pi + |\delta_{k_\alpha}|}{La} \). The integer \( n_\alpha \) runs from 1 to \( L/2 \). The low energy wave-vector has an increase \( |\delta_{k_\alpha}|/La \) when \( \delta_{k_\alpha} \neq 0 \).

**IV. FIXED BOUNDARY CONDITION**

With the above inspection, we will be able to estimate the melting temperature of a nano-particle under a general boundary condition. The low energy wave-vector has an increase \( |\delta_{k_\alpha}|/La \). The melting temperature is increased by a boundary condition shifting \( k_\alpha \) wave-vectors upward. The discrete summation of phonon modes in Eq. (5) can be written into

\[
\int_{(2|\delta| - \pi)/2La} dk_\alpha \text{ for each } \alpha\text{-component of wave-vector.}
\]

When \( |\delta_{k_\alpha}| = \pi/2 \) the integration volume for low energy phonon starts at \( k_\alpha = 0: \int_0 dk_\alpha \), which results in the same amount of low energy phonon contribution to atom displacement as the case for bulk material in Eq. (8). The cases for \( |\delta_{k_\alpha}| < \pi/2 \) will depress the melting temperature of a nano-particle. The lower bound of this depression when \( |\delta_{k_\alpha}| \to 0 \) was carefully studied in the work of Sui.
et. al. When $|\delta_{ka}| > \pi/2$, the melting temperature of a nano-particle will be higher than its bulk parent.

We study the rising of the melting temperature due to the phase shift. The boundary scattering shifts wave-vectors up to $k_\alpha = (|\delta_{ka}| + n_\alpha \pi)/La$ by a nonzero $\delta_{ka}$. The range of the phase shift $\delta_{ka}$ in $k_\alpha$ is $[-\pi, 0]$. If $|\delta_{ka}| = \pi/2$, the density of the low energy phonon states in a nano-particle is the same as the density in the bulk material. We prefer a smaller thermal displacement of the atom when we study a heat resistant. We want less phonon contribution to atom displacement. The least contribution from phonon modes occurs when $\delta_{ka} = -\pi$. This situation is given by the ideal fixed boundary condition (fixed-BC), for which the boundary sets up a node surface for standing acoustic waves.

The upper melting temperature bound is set by the ideal fixed-BC for nano-particles. The phonon wave-vectors move up for this boundary condition and some more low energy phonon contribution is taken away by the deduction of the second $(u^{cm})^2$ term. In the picture of microscopic physics, less low energy phonon will contribute to atom displacements in finite size fixed-BC particle than in bulk material. Therefore, the melting temperature increases for the boundary effect and the finite size effect. Moreover, for all possible boundary conditions modeled in phase shifts, the low energy phonon modes shift up the most for fixed-BC, and their contribution missed the most for fixed-BC. Thus the melting temperature increases the most for fixed-BC.

The upper limit for effective phase shift is $|\delta_{ka}| = \pi$, and the melting temperature increases at most when a particle subject to a fixed boundary condition. However, this ideal boundary condition is not easy to achieve when preparing nano-powder heat resistant, since there is no infinitely heavy walls we can coat microscopically on a nano-particle. Fixed-BC is an unrealistic boundary condition but it is instructive. Nano-particles can be grown inside sieves, can be coated with other elements. The melting temperature of a nano-particle can approach but not reach the one for fixed-BC. From the above discussion on both finite size and boundary condition, we can conclude that the upper melting temperature bound is set by the ideal fixed-BC for nano-particles.

We derive this upper melting temperature bound in the following. For fixed-BC, the mode expansion for atom displacement is $f(k^e_{\alpha}, R_{i\alpha}) = \sqrt{2/L} \cos(k^e_{\alpha}R_{i\alpha})$ for even parity, and $f(k^o_{\alpha}, R_{i\alpha}) = \sqrt{2/L} \sin(k^o_{\alpha}R_{i\alpha})$ for odd parity. Quite different from periodic condition’s mode space, there is no $k = 0$ phonon mode for fixed-BC. Even parity $k^e_{\alpha}$ will contribute to
$u^{cm}$, since $|\sum_{i=1}^{L} \cos[k_i a(i - \frac{L}{2})]| = 1 / \sin \frac{k_i a}{2}$. The melting temperature $T_{mn}$ for size $L$ nano-particle under a fixed-BC is then calculated from Eq. (1):

$$L_c^2 = \frac{3h}{2a^2NM} \left[ \sum_{k_x,k_y,k_z} \frac{1}{\omega(k) \tanh\left(\frac{\hbar \omega(k)}{2k_B T_{mn}}\right)} \right]$$

$$- \sum_{k_x',k_y',k_z'} \frac{8}{\omega(k) \tanh\left(\frac{\hbar \omega(k)}{2k_B T_{mn}}\right) \prod_{\alpha} \left[ L \sin \frac{k_{\alpha} a}{2} \right]^2}$$

The first term is the summation of $u_{ia}^2$ defined by Eq. (5), in which $k_{\alpha} = n_{\alpha} \pi / La$ with $n_{\alpha} = 1, \cdots, L$. The second term removes the contribution of the global moving $(u^{cm})^2$, which sums only the even parity $k_{\alpha} = (2n_{\alpha} + 1) \pi / La$ with $n_{\alpha} = 0, \cdots, L/2 - 1$.

V. DISCUSSION AND APPLICATION

State-of-art functional designs of nano-particles developed in recent years$^{19,20}$. The first general factor came into our understanding on size-dependent melting was the surface volume ratio of number of atoms$^{21}$. Nano-materials are studied case by case in experiments and Ab initio calculations$^{22–26}$. With the help of computer simulation, in principle all the parameters can be fixed to certain extent for a particular design of a particular particle, of its surface and its properties$^{27,28}$. A designed melting temperature could be accurate up to 1 K$^{29}$. Mechanical stable region for nano-materials is also under current studying along with the estimation of $T_{mn}$, and giving the safe working temperature$^{30}$. Many on going theoretical researches are working for more general understanding on size-dependent melting.

Statistical mechanics is valid for an ensemble of big systems and small systems. Thermodynamics of small systems is well understood. New and powerful expressions were derived through thermodynamics$^{31}$ for size- and boundary-dependent melting, but they have not converged to physically equivalent ones yet. Size-effect on intensive variables can be included through thermodynamic equations or ensemble average of quantum states. In this study on general boundary conditions for nano-particles, it is clear that the boundary condition and size together determine the wave-vectors of phonon modes, and so determine the low energy density of states of phonon. Such a size- and boundary-dependent density of states was not included in previous approximations in a phonon Debye temperature. In real applications, a particle interacts with other surrounding atoms, molecules, and particles.
FIG. 1: The size dependent melting temperature for nano-particles under fixed-BC. The lines and points are $T_{mn}/T_{mb}$ with and without the second term in Eq. (10). Guiding lines simply connecting the points are presented.

simultaneously. Our analysis is right when the bulk phonon dispersion is almost kept in a nano-particle\(^{32}\). The individuality of the particle is retained under the statistical average. Vibration modes inside the particle see only an averaged reflective phase shift.

In this study, a simple procedure to estimate the melting temperature for nano-particles under a general boundary condition can be suggested. In this simple estimation procedure we use sound speed $v$ to approximate the phonon dispersion for all phonon modes in Eq. (8) for an integration, and in Eq. (10) for a discrete summation. For example, in Fig. 1 we plot the size-dependent melting for a simple cubic lattice under fixed-BC. Phonon dispersion is approximated by $\omega(\mathbf{k}) = \frac{2v}{a} \sqrt{\sin^2 \frac{k_xa}{2} + \sin^2 \frac{k_ya}{2} + \sin^2 \frac{k_za}{2}}$. We substitute $\hbar v/ak_BT_{mb}$ by 0.25 when solving Eq. (8) and Eq. (10) for $T_{mn}/T_{mb}$ at each size $L$.

Fig. 1 shows that the global movement contributes more in the variation of melting temperature as the size decreases down to $L = 20$ and smaller. The global movement deduction accounts for five percent of the change when $L = 10$. For a nano-particle at the size of $L = 20$, with $\hbar v/ak_BT_{mb} \sim 0.25$ for its parent bulk material, we can read on Fig. 1 that an increase of melting temperature less than 18 percent can be expected when we design a heat resistant coating for the nano-particle. This example shows that the reflective phase shift at the particle boundary plays an important role in size-dependent melting, and size and phase shift are both general factors in this phenomenon.
We investigated in this paper the melting temperatures for nano-particles under a general boundary condition. We find that the missed contribution from the low energy phonon will raise the melting temperature. This phenomenon comes from finite size effect, and boundary condition plays an important role in it. The melting temperature for the fixed boundary condition gives the upper bound for the melting temperature of a nano-particle in all kinds of environment. This upper bound is not reachable in any real nano-particle design.

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