Physica B 481 (2016) 133–136

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

The influence of surface boundary conditions on the phonon contribution to the melting temperature of nanoparticles

Yuanyuan Xu [a,*], Kai Kang [b], Shaojing Qin [a]

[a] State Key Laboratory of Theoretical Physics, Institute of Theoretical Physics, Chinese Academy of Sciences, Beijing 100190, China
[b] Science and Technology on Surface Physics and Chemistry Laboratory, P.O. Box 718-35, Mianyang 621907, Sichuan, China

ARTICLE INFO

Available online 10 November 2015

Keywords:
Melting temperature
Nano-particle
Surface boundary condition
Upper bound

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.

1. Introduction

This work focuses on the quantum size effect with particular emphasis on environment-dependent melting temperature of nano-particles. The continuing progress in the design of nano-particles led to enhanced and novel functionality [1]. Concerning the thermal stability of heat resistant [2], 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 [3–5], 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 [6,7]. But only recently the finite spacing energy levels became a greater awareness in size-dependent melting [8]. 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 more than 100 years ago [9], and the pressing need for a deep understanding continues today [10–14]. In this study, we use the Lindemann melting criterion [15–17] 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:

$$L_c = \frac{u(T_m)}{a}. \tag{1}$$

2. Periodic boundary condition

The details of our model can be found in a previous work [8]. Thus we briefly show some necessary derivation for $u(T)$ in harmonic approximation in this section. In the model we have a lattice specified by a set of vectors $\mathbf{R_i}$, 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

$$H = \frac{M}{2}\sum_{i\alpha}\dot{u}_{i\alpha}^2 + \frac{1}{2}\sum_{ij\alpha\beta}\Phi_{\alpha\beta}(\mathbf{R_i}, \mathbf{R_j})u_{i\alpha}u_{j\beta}, \tag{2}$$

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

The equations of motion of the lattice is then

* Corresponding author.
E-mail address: xuyuanyuan13@itp.ac.cn (Y. Xu).

http://dx.doi.org/10.1016/j.physb.2015.11.003
0921-4526/

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

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

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

$\omega_\sigma(\mathbf{k})$ and $\mathbf{e}_{k\sigma}$ are phonon frequency and phonon polarization of wave-vector $\mathbf{k}$, respectively. The atomic mean-squared thermal displacement is [18]

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

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

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

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 α-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 [8]:

$$L_c^2 = \frac{u^2}{a^2} = \frac{3\hbar a}{16\pi^3 M}\int_{-\pi/a}^{\pi/a} d^3k \frac{1}{\omega(\mathbf{k})\tanh\left[\frac{\hbar\omega(\mathbf{k})}{2k_BT_{mn}}\right]} - \frac{3\hbar a}{16\pi^3 M}\int_{-\pi/La}^{\pi/La} d^3k \frac{1}{\omega(\mathbf{k})\tanh\left[\frac{\hbar\omega(\mathbf{k})}{2k_BT_{mn}}\right]}, \tag{7}$$

where $\omega(\mathbf{k}) = \omega_\sigma(\mathbf{k})$ is used when summing up the three polarized vibration directions in each $\mathbf{k}$ mode. $\mathbf{u}^{cm}$ 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. 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:

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

3. Boundary reflective phase shift

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. 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 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 the 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 α-direction, the general solution for Eq. (3) is in terms of waves moving in opposite directions, $f(k_\alpha, R_{i\alpha}) = ce^{ik_\alpha R_{i\alpha}} + de^{-ik_\alpha R_{i\alpha}}$, 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:

$$\frac{de^{-ik_\alpha R_\alpha}}{ce^{ik_\alpha R_\alpha}} = e^{i\delta_{k\alpha}}, \quad R_\alpha = La/2. \tag{9}$$

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 with the assumptions of an isotropic surface and environment, and the same phase shift in each α-direction. The phase shift for a small wave-vector is expanded up to the first order of $1/L$: $\delta_{k\alpha} = \delta + a_1k_\alpha$. δ is a constant phase shift and a_1 is the expansion coefficient for the first-order term. We will discuss on phase shift in the range of $[-\pi, 0]$, 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 equation (9). First, when the standing wave is of even parity, we have $c/d = 1$ in $f(k_\alpha, R_{i\alpha})$, and $e^{i(k_\alpha La+\delta_{k\alpha})} = 1$. The mode expansion for atom displacement on this kind of phonon mode is $f(k_\alpha^e, R_{i\alpha}) \sim \cos(k_\alpha^e R_{i\alpha})$, with $k_\alpha^e = \frac{2n_\alpha\pi + |\delta_k e_\alpha|}{La}$. The integer n_α 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 $e^{i(k_\alpha La+\pi+\delta_{k\alpha})} = 1$. The mode expansion for atom displacement on this kind of phonon mode is $f(k_\alpha^o, R_{i\alpha}) \sim \sin(k_\alpha^o R_{i\alpha})$, with $k_\alpha^o = \frac{(2n_\alpha-1)\pi + |\delta_k o_\alpha|}{La}$. The integer n_α runs from 1 to $L/2$. The low energy wave-vector has an increase $|\delta_{k\alpha}|/La$ when $\delta_{k\alpha} \neq 0$.

4. 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_α wave-vectors upward. The discrete summation of phonon modes in Eq. (5) can be written into $\int_{(2|\delta|-\pi)/2La} dk_\alpha$ for each α-component of wave-vector [8]. 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. [8]. When $|\delta_{k\alpha}| > \pi/2$, 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 $k_\alpha = (|\delta_{k\alpha}| + n_\alpha\pi)/La$ by a nonzero $\delta_{k\alpha}$. The range of the phase shift $\delta_{k\alpha}$ in k_α is $[-\pi, 0]$. If $|\delta_{k\alpha}| = \pi/2$, the density of the low energy