Morse function for nanoscaled cubic metals

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HIGHLIGHTS

- Establishing the Morse function for metallic nanoparticles and nanostructured materials.
- The interatomic spacing is contracted for NPs but expanded for NS.
- The depth of the potential well becomes shallow with smaller size especially for NPs.
- The asymmetry of the binding energy curve becomes stronger in particular for NPs.

ARTICLE INFO

ABSTRACT

Relying on our size-dependent cohesive energy and lattice constant functions, we established the Morse function in a unified form for nanoscaled cubic metals, involving metallic nanoparticles (NPs) and nanostructured materials (NSs). At the equilibrium position at 0 K, the depth of the potential well becomes shallow with smaller D especially for NPs, where D denotes the diameter of NPs or the grain size of NSs. This gives rise to the contraction or expansion of the interatomic spacing for NPs or NSs, respectively. The asymmetry of the binding energy curve in NPs is stronger than in NSs. The difference between NPs and NSs is largely associated with the distinction in the coordination imperfection between the surface and the grain boundary. The established function was supported by available experimental and computer simulation results for NPs and NSs.

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1. Introduction

With the considerable progress in materials science, metallic nanoparticles (NPs) and nanostructured materials (NSs) have now received much attention [1,2]. Due to the increased surface (interface)/volume ratio or $1/D$ of NPs or NSs, the physical and chemical properties of NPs and NSs differ dramatically from their bulk counterparts, where D denotes the diameter of NPs or grain size of NSs [3–5]. For example, the thermal vibration amplitude $\sigma(T,D)$ and the thermal enthalpy $H(T,D)$ of NPs and NSs increase as D decreases, where T denotes the absolute temperature [2]. However, the varying amplitude of these parameters is found to be somewhat weaker in NSs than that in NPs. The fascinating properties of NPs and NSs are relevant to the coordination imperfection at the surface or interface, because it leads to high atomic internal energy there relative to the interior case [6,7]. As the thermophysics of cubic metals is concerned, these thermal properties are associated to the anharmonic vibration of atoms in solids, which is essentially decided by the basic amount of cohesive energy. Considering that an anharmonic potential can be used to predict the dissociation energy of diatomic molecules, it is thus of importance in the establishment of a suitable potential function for illustrating the distinct properties of NPs and NSs theoretically. However, it has remained unavailable yet.

As a central pairwise potential function, for bulk cubic metals, a binding energy curve elucidated by the Morse function $u(r,\infty)$ is a better approximation for vibrational structures of molecules than the quantum harmonic oscillator does, where r and ∞, respectively, denote the interatomic spacing and the bulk size, respectively. This is because the Morse function explicitly includes the effects of bond breaking, such as the existence of unbound states. It also accounts for the anharmonicity of real bonds and the non-zero transition probability for overtone and combination bands. Various crystal properties regarding the anharmonicity of atom vibrations, such as the cohesive energy, the lattice constant, the specific heat, the compressibility, the equation of state, and the elastic constants, can be described by the Morse function [8–11].

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The Morse function for a bulk is expressed as [12],

$$u(r, \infty) = -2E_c(\infty)/(ZN_A)\left\{e^{-2b[r-h(0,\infty)]} - 2e^{-b[r-h(0,\infty)]}\right\}, \tag{1}$$

where $E_c(\infty)$ is the bulk molar cohesive energy, Z the coordination number and the Avogadro constant $N_A = 6.02 \times 10^{23}$ mol^{-1}. b is a constant denoting the inverse line width of the potential [13],

$$b = R\theta(\infty)\sqrt{-MZ/[4N_A E_c(\infty)]}/\hbar, \tag{2}$$

with M denoting the reduced mass, $\theta(\infty)$ the bulk Debye temperature, $R = 8.314$ J mol^{-1} K^{-1} the gas constant and $\hbar = 1.054 \times 10^{-23}$ J s the Planck constant divided by 2π. In Eq. (1), $du(r,\infty)/dr = 0$ occurs at $r = h(0,\infty)$ and $u = 2E_c(\infty)/(ZN_A)$, where $E_c(\infty)$ is available from literature. However, $h(0,\infty)$ cannot be taken from literature directly. Instead, it is usually given by $h(0,\infty) = h(T,\infty) - \Delta h(T,\infty)$ with $\Delta h(T,\infty)$ being the effective displacement of the equilibrium position of atoms relative to 0 K level, where the action force of attraction and that of repulsion is equal. Considering that the coefficient of linear thermal expansion $\alpha(T,\infty)$ is one of the consequences of the anharmonicity of atom vibrations in solids, it plays an important role in determining $\Delta h(T,\infty)$ according to the equation $\Delta h(T,\infty) = h(0,\infty)\int_0^T \alpha(T,\infty)dT$ [13]. When the frequency distribution of the Morse oscillator is assessed from the Debye approximation, $\alpha(T,\infty)$ can be deduced as $\alpha(T,\infty) = \{-3ZRT/[4bh(T,\infty)E_c(\infty)]\}[T/\theta(\infty)]^3 \int_0^{\theta(\infty)/T} x^4 e^x/(e^x-1)^2 dx$. On the basis of assumption that $h(0,\infty)/h(T,\infty) \approx 1$, one has,

$$\Delta h(T,\infty) \approx \{-3ZRT/[4bE_c(\infty)]\}$$
$$\times [T/\theta(\infty)]^3 \int\limits_0^{\theta(\infty)/T} x^3/(e^x-1)dx. \tag{3}$$

In the binding energy curves, the potential $u_{eq}(r,\infty)$ at the equilibrium position of atoms with $r = r_{eq} = (r_1 + r_2)/2 = h(T,\infty)$ at a given T with r_1 and r_2 being the roots is derived as,

$$u_{eq}(r,\infty) = 2E_c(\infty)/(ZN_A)e^{-2b[r_{eq}-h(0,\infty)]}. \tag{4}$$

Along the equilibrium position $r = r_{eq}$, the slope $k(T,\infty) = \partial u_{eq}(r,\infty)/\partial r$ denotes the asymmetry in the potential well, reflecting the interaction of the nearest two atoms, i.e., lower $k(T,\infty)$ value means weaker interaction [14]. In terms of Eq. (4), one has,

$$k(T,\infty) = -4bE_c(\infty)/(ZN_A)/e^{-2b\Delta h(T,\infty)}. \tag{5}$$

By solving Eq. (1), $\sigma(T,\infty) = (r_1 - r_2)/2$ in the binding energy curves can be given with the help of Eq. (4). One can thus see that,

$$\sigma(T,\infty) = \ln\left\{\left[1 + \sqrt{1 - e^{-2b\Delta h(T,\infty)}}\right]\Big/\left[1 - \sqrt{1 - e^{-2b\Delta h(T,\infty)}}\right]\right.$$
$$\left.\times\right\}\Big/(2b). \tag{6}$$

Stimulated by the success in the bulk case, thanks to its advantage in elucidating the anharmonicity of vibrational structures of molecules, one may expect that the Morse potential function of $u(r,D)$ in the nanometer size range can be established for NPs and NSs. However, it was previously thought that the Morse potential could not reproduce the thermal properties of nanoscaled metals [15]. This is because, since the Morse potential considers only two-body interaction, it provides a poor description of the metallic bonding dependent on the local environment [15]. In

detail, the bond strength decreases as the local environment becomes too crowded due to Pauli's "exclusion principle", and increases at near surfaces or in small systems due to the localization of the electron density. In fact, such an issue can be addressed if the key parameters of $E_c(\infty)$ and $h(0,\infty)$ in Eq. (1) can be extended into the nanometer regime. Fortunately, as will be shown later, this extension has been realized in our previous works [16–18].

In the present work, the nanoscaled Morse function $u(r,D)$ will be established for NPs and NSs without any adjustable parameters, under the help of the proposed $E_c(D)$ and $h(0,D)$ functions. Here, $h(0,D) = h(T,D) - \Delta h(T,D)$, where the definition of $h(0,D)$ and $\Delta h(T,D)$ for NPs and NSs can be referenced to the bulk case. The established Morse function will be applied to predict the D- and T-dependent thermal properties of cubic metals, beneficial for our understanding to the difference between NPs and NSs.

2. Theoretical consideration

If the crystalline structure remains unchanged as D decreases from ∞, $u(r,D)$ could be a continuous function of D down to a certain value of $D_0 = 6h(T,\infty)$, at which almost all atoms or molecules are located on the surface and the crystalline structure is no more stable [19]. The Morse function for NPs and NSs can be conveniently established by extending Eq. (1) as,

$$u(r,D) = -2E_c(D)/(ZN_A)\left\{e^{-2b[r-h(0,D)]} - 2e^{-b[r-h(0,D)]}\right\}, \tag{7}$$

where $h(0,D) = h(T,D) - \Delta h(T,D)$. With a similar consideration, the related functions $\Delta h(T,D)$, $u_{eq}(r,D)$ and $k(T,D)$ can be given as,

$$\Delta h(T,D) = -3ZRT/[4bE_c(D)][T/\theta(D)]^3 \int\limits_0^{\theta(D)/T} x^3/(e^x-1)dx, \tag{8}$$

$$u_{eq}(r,D) = 2E_c(D)/(ZN_A)e^{-2b\Delta h(T,D)}, \tag{9}$$

$$k(T,D) = -4bE_c(D)/(ZN_A)e^{-2b\Delta h(T,D)}. \tag{10}$$

The relationship between $\theta(D)$ and $E_c(D)$ can be given by [20,21],

$$[\theta(D)/\theta(\infty)]^2 = E_c(D)/E_c(\infty). \tag{11}$$

To work out the above size-dependent functions, $E_c(D)$ and $h(T,D)$ functions should be explored. Note that the aforementioned constant b, which is determined by Eq. (2), is D-independent due to the same size dependence of $\theta(D)$ and $[E_c(D)]^{1/2}$ in light of Eq. (11).

For NPs, $E_c^{NP}(D)$ has been modeled as [16],

$$\frac{E_c^{NP}(D)}{E_c(\infty)} = \left(1 - \frac{1}{12D/D_0 - 1}\right)\exp\left(-\frac{2S_b}{3R}\frac{1}{12D/D_0 - 1}\right), \tag{12.1}$$

where $S_b = H_b/T_b$ is the bulk solid−vapor transition entropy, H_b the heat of vaporization and T_b the boiling point for a bulk. Since the coordination imperfection at grain boundaries of NSs is weaker than that at the surface of NPs, in accordance, the D-dependence of $E_c(D)$ is weak for NSs. Thus, one has [18],

$$E_c^{NS}(D)/E_c(\infty) = 1 - D_0/(4D). \tag{12.2}$$

From a mechanical point of view, the hydrostatic pressure on the surface induced by intrinsic surface stress results in lattice contraction or lattice strain. Based on the Laplace−Young equation