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Effects of size and shape on the specific heat, melting entropy and enthalpy of nanomaterials

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Abstract

A simple theory is proposed to study the size- and shape-dependent specific heat, melting entropy and enthalpy of nanomaterials. The particle size and shape are demonstrated to affect the specific heat, melting entropy and enthalpy of nanomaterials. The model is applied to Ag, Cu, In, Se, Au and Al nanomaterials in spherical, nanowire and nanofilms shapes. The specific heat is observed to increase with the decrease in particle size, whereas the melting entropy and enthalpy decrease as the particle size decreases. Our theoretical predictions agree well with available experimental and computer simulation results, thereby supporting the validity of formulation developed.

Keywords: Nanomaterials; Specific heat; Melting entropy; Surface properties; Thermodynamic properties

1. Introduction

It has been reported that nanomaterials exhibit interesting physical and chemical properties that are significantly different from the corresponding properties of bulk materials [1–5]. Because of the enormous surface-area-to-volume ratio of nanomaterials, the energy associated with the atoms of these nanomaterials will be different compared to that of conventional bulk materials, leading to the size-dependent thermodynamic properties of nanomaterials [6,7]. The cohesive energy, also known as the heat of sublimation, is an important physical quantity that accounts for the strength of metallic bonds, as it is the energy required to divide the metallic crystal into individual atoms. Experimental and theoretical studies of cohesive energy of W, Ag, Co, Al and Cu nanoparticles have been conducted by many researchers [8–10]. Modeling the size- and shape-dependent cohesive energy of nanoparticles and its applications in the heterogeneous systems has been calculated theoretically by Li [11], who reported that the cohesive energy of the free nanoparticles usually decreases as its size decreases. Considering the effects of particles size, lattice and surface packing factors and coordination numbers of the lattice, Shandiz et al. [12] calculated the melting entropy and enthalpy of metallic nanoparticles. A theoretical study involving modeling of the melting enthalpy of nanomaterials sought to define the conventional shape factor α [13].

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The melting temperature of nanosolids (such as nanoparticles, nanowires and nanofilms) has been predicted based on size-dependent cohesive energy [14]; it is shown that the melting temperature of nanomaterials decreases with decreasing particle size. Researchers have calculated the root mean square amplitude model, the size-dependent Debye temperature model and size-dependent thermal conductivity model [15,16] by considering Lindemann's criterion and Mott's equation. It is stated that the Debye temperature decreases for nanomaterials as the size decreases. The effects of particle size and thermodynamic energy, based on surface thermodynamics and the atomic bond energy, were used to calculate the mechanical properties, such as surface tension and Young's modulus of nanocrystals [17,18]. The cohesive energy is the basic thermodynamic property used to predict melting temperature, melting enthalpy, melting entropy and specific heat of nanomaterials. Scholars have proposed different models, namely the latent heat model, the liquid drop model and the surface area difference model [19–21], to predict cohesive energy of nanomaterials. Recently, using the concept of cohesive energy changes with the atomic coordination environment, Qi [22] presented a theory based on the bond energy model to highlights the thermodynamics for the nanoparticles, nanowires, and nanofilms. The size and coherence dependent cohesive energy, melting temperature, melting enthalpy, vacancy formation energy and vacancy concentration of nanowires and nanofilms have been reported [23]. The variation direction of the thermodynamic properties is observed to be determined by the coherent interface and the quantity of variation depends upon the crystal size. Shandiz et al. [12] developed a model for melting entropy and enthalpy of metallic nanoparticles, which is based on the effect of packing factors, coordination numbers of lattice and crystalline planes. Thus, it appears that there exist some attempts to study size-dependent thermodynamical properties. Moreover, because the thermodynamical properties also depend on the shape, it may be valuable to present a model that incorporates the effects of shape.

In this contribution, we present a surface free energy model that does not use adjustable parameters and depends upon the size and shape with respect to the cohesive energy of nanomaterials. Using the relationship between melting temperature and cohesive energy, the expressions for size- and shape-dependent specific heat, melting entropy and enthalpy are obtained. The theoretical predictions of these expressions are applied to Ag, Cu, In, Se, Au and Al nanomaterials in spherical, nanowire and nanofilms shapes.

2. Methodology

The total cohesive energy is defined as the energy due to the contributions of the interior atoms and the surface atoms of the nanomaterial and is expressed as [14]

$$E_{Total} = E_0(n - N) + \frac{1}{2}E_0N \tag{1}$$

where n is the total number of atoms in the nanosolid, and N is the number of surface atoms. Therefore, $(n - N)$ is the total number of interiors atoms in the nanomaterial. E_0 is the cohesive energy of the bulk material per atom. To determine the cohesive energy per mole, Eq. (1) may be written as

$$\frac{AE_{Total}}{n} = AE_0\left(1 - \frac{N}{n}\right) + \frac{1}{2n}AE_0N \tag{2}$$

where A is Avogadro's number. Here, AE_{Total}/n is the cohesive energy per mole of the nanomaterial E_n, and AE_0 is the cohesive energy per mole of the corresponding bulk material (E_b). On substituting the relevant parameters in Eq. (2), one can obtain

$$E_n = E_b\left(1 - \frac{N}{2n}\right)$$

It is reported [24,25] that the cohesive energy is linearly related to the melting temperature; we can therefore write the relation for melting temperature of nanomaterials as

$$T_n = T_b\left(1 - \frac{N}{2n}\right) \tag{3}$$

where T_b is the melting temperature of the bulk material.

The Lindemann's melting criterion, which states that a crystal melts when the root mean square displacement of atoms exceeds a certain fraction of the interatomic distance in the crystal, is valid for small particles. Using this theory, the relationship between the melting temperature and Debye temperature of the bulk material can be given as [25]

$$\theta_{Db} \propto \left(\frac{T_b}{MV^{2/3}}\right)^{1/2} \tag{4}$$

where M is the molecular mass, and V is the volume per atom.

Similarly, for the nanomaterials, the expression is

$$\theta_{Dn} \propto \left(\frac{T_n}{MV^{2/3}}\right)^{1/2} \tag{5}$$

Eqs. (3) and (5) give the following correlation:

$$\frac{\theta_{Dn}^2}{\theta_{Db}^2} = \frac{T_n}{T_b} \tag{6}$$

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