



Surface free energy of alkali and transition metal nanoparticles



Fathi Aqra*, Ahmed Ayyad

Department of Chemistry, Faculty of Science and Technology, Hebron University, University Street, PO Box 40, Hebron, West Bank, Palestine

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ABSTRACT

This paper addresses an interesting issue on the surface free energy of metallic nanoparticles as compared to the bulk material. Starting from a previously reported equation, a theoretical model, that involves a specific term for calculating the cohesive energy of nanoparticle, is established in a view to describe the behavior of surface free energy of metallic nanoparticles (using different shapes of particle: sphere, cube and disc). The results indicate that the behavior of surface energy is very appropriate for spherical nanoparticle, and thus, it is the most realistic shape of a nanoparticle. The surface energy of copper, silver, gold, platinum, tungsten, molybdenum, tantalum, palladium and alkali metallic nanoparticles is only prominent in the nanoscale size, and it decreases with the decrease of nanoparticle size. Thus, the surface free energy plays a more important role in determining the properties of nanoparticles than in bulk materials. It differs from shape to another, and falls down as the number of atoms (nanoparticle size) decreases. In the case of spherical nanoparticles, the onset of the sharp decrease in surface energy is observed at about 110 atom. A decrease of 16% and 45% in surface energy is found by moving from bulk to 110 atom and from bulk to 5 atom, respectively. The predictions are consistent with the reported data.

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1. Introduction

Nanomaterials are of great interest, and they have applications in technologies because of their size- and shape-dependent, physical–chemical and magnetic properties. They are scientifically important due to their unusual optical, chemical, photoelectrochemical, and electronic properties [1,2]. In building advanced materials using nanoscale particles, there is a need for approaches to controlling the size and shape of nanocrystals [3,4]. Nanoscale metallic materials are important due to their potential in magnetic storage, magnetic fluid, medical diagnosis, catalysis and building single-electron devices [4,5]. Nanoparticles are used in catalysis because of their size-dependent electronic structure and large surface area [6] such as Ag and Au [7], in optics [8] and in surface enhanced Raman spectroscopy [9]. Silver nanoparticles are also used as an antimicrobial agent [10].

For nanoparticles, it was reported that [11,12] the surface energy should decrease with decreasing particle size, while others predicted [13] an increase of the surface energy with decreasing size. The effect of size on the surface energy is important when the size is comparable with that of an atom. Larger values of surface energy

as compared to the bulk material have also been indicated [14–22]. Nanometallic particle such as copper [23] and gold [24] exhibit surface energies that are smaller than that of the corresponding bulk materials, whereas silver nanoparticles showed surface energy that is either close [25] or greater [26] than the bulk. Since the data on the surface energy of bulk seem to be ambiguous, the higher surface energy of nanoparticles should be verified for many systems.

The surface tension of metallic nanoparticles depends on the particle size [27,28], and they are different from those of the corresponding bulk metals. Based on the fact that the cohesive energy can be regarded as the required energy to separate the metallic crystal into individual atoms by destroying the metallic bonds, an equation is developed to account for the size effect on the surface free energy of Cu, Ag, Au, Pt, W, Mo, Ta, Pd and alkali metallic nanoparticles with different particle shapes (spherical, cubic and disc). Therefore, the aim of this work is to establish a surface free energy model for nanoparticles with different particle shapes. The behavior of surface energy with the number of atoms for metals is investigated. The topic generally is interesting because theoretical model with reasonable predictive quality, for this subject, is not readily available. The novelty in present theoretical model is that the surface free energy of nanoparticles can be related to the heat of sublimation.

The model is based on some simplified assumptions, and so it is most likely that some error associated with the results, obtained

* Corresponding author. Tel.: +972599035566.

E-mail address: fathiaqra2009@hotmail.com (F. Aqra).

by this model, will occur, e.g., from having different bonds within the cluster and on the outside. Due to the simplicity of the model, errors in the calculated surface energy are expected by assuming that all bonds in the cluster (nanoparticle) are the same, i.e. the nanoparticle and its constituents are perfect spheres. The error in the surface energy values comes from errors in the reported sublimation energy and the molar volume (density). After extensive further analysis of the errors, the error in the former does not exceed 5% while the error in the latter is about 7%. Based on these values, an error of about 8.5% is predicted for the calculated surface energy values.

2. Theory and discussion

For thermodynamic properties of bulk metals, the surface effects results from the difference between the surface metallic atoms and interior atoms. This effect can be neglected, but it cannot be ignored for metallic nanoparticles because the surface atoms in nanomaterial are less stable due to their lower coordination number. There is a size dependence of the thermodynamic properties of metallic nanoparticles because the ratio of surface atoms to the total atoms is large [29]. Metal nanoparticles exhibit physical, chemical, and electronic properties different from those of the bulk due to the large fraction of surface atoms. The surface free energy of metallic nanoparticle consists of bulk and surface. The impact of the size on the thermodynamic properties of a nanoparticle is determined by its surface atoms. The free energy of surfaces and interfaces becomes a dominant factor for the formations of nanostructures. It determines the growth modes in thermal equilibrium. Nanoparticles have unique properties due to their large surface/volume ratio and special structures, which change properties as compared with that of the corresponding bulk materials.

The surface free energy of a solid is a half reversible work per unit area by cutting a solid into two parts along a crystalline plane at constant temperature and pressure [30]. It is an important energetic quantity for understanding crystal growth, surface faceting, growth and stability of thin films [31]. When the particle size reaches to nanoscale, the ratio of its surface to volume becomes very large, and so the total surface free energy becomes large, and thus, becomes prominent as compared to bulk material. Moreover, the cohesive energy of nanoparticle depends on its size, and increases with increasing the particle size. When the particle size is large enough, the cohesive energy will approach the value of the corresponding bulk material.

Recently, we established an equation to calculate the liquid–vapor (γ_{LV}) and the solid–vapor (γ_{SV}) surface tension of bulk metals and their temperature dependence [32,33], using Eqs. (1) and (2), respectively:

$$\gamma_{LV} = \varphi^{-1} \left(\frac{V_s}{V} \right)^2 kT \left[0.139 \frac{E_s}{RT} \right] \quad (1)$$

$$\gamma_{SV} = \varphi^{-1} \left(\frac{V_s}{V} \right)^2 kT \left[0.195 \frac{E_s}{RT} \right] \quad (2)$$

where

$$\varphi = \frac{\sqrt{3}}{2} \left(\frac{\sqrt{2}V_s}{N} \right)^{2/3} \quad (3)$$

where N is Avogadro number ($6.02 \cdot 10^{23}$ atom mol^{-1}), γ_{LV} is surface tension of the liquid metal (mJ m^{-2}), γ_{SV} is the surface energy of the solid metal (mJ m^{-2}), k is the Boltzmann constant ($1.38 \cdot 10^{-23}$ J K^{-1}), R is the universal gas constant (8.31 J K^{-1} mol^{-1}), T is the absolute temperature (K), V_s are the molar volume at the melting point ($\text{cm}^3 \text{mol}^{-1}$), φ is the area occupied ($\text{cm}^2 \text{atom}^{-1}$), E_s is the heat of sublimation and the values 0.139 and 0.195 are semi-empirical fitting parameters.

For a solid metal, $R = Nk$, then, Eq. (2) can be simply written as:

$$\gamma_{SV} = \varphi^{-1} \left[0.195 \frac{E_s}{N} \right] \quad (4)$$

The theory is based on a couple of assumptions. The first assumption is that the metallic nanoparticle is spherical in shape. Although a good number of metallic nanoparticles are spherical, there are a considerable number of nanoparticles that are not [34,35]. Thus, spherical, cubic and disc particle shape will be investigated. The sublimation energy of the bulk material has to be replaced by that of nano-particle because of size effects. According to the definition of cohesive energy, we suppose there exists a spherical metallic nanoparticle whose diameter is R , which is composed of spherical atoms each of radius r . The volume and the surface area of the nanoparticle are given by:

$$V_{\text{particle}} = \frac{4}{3} \pi R^3 \quad (5)$$

$$A_{\text{particle}} = 4\pi R^2 \quad (6)$$

The volume and surface area of each atom are given by:

$$V_{\text{atom}} = \frac{4}{3} \pi r^3 \quad (7)$$

$$A_{\text{atom}} = 4\pi r^2 \quad (8)$$

The second assumption is that all nanoparticles are made of identical spherical atoms. These atoms are closed packed within the nanoparticle and there is no empty space between them. Based on this assumption, the number of atoms in the nanoparticle is defined as the volume ratio of the nanoparticle and the atom. Usually, metallic nanoclusters retain fragments of packing typical of crystalline metals. Therefore, the number of atoms in the nanoparticle should depend on the interatomic distances and packing modes. Thus, the packing fraction parameter is taken into account. In geometry, close-packing of equal spheres is a dense arrangement of congruent spheres in an infinite, regular arrangement (or lattice). It is proved that the maximum packing fraction (ρ) and surface packing fraction (η) occupied by spheres are given by: $\rho = \pi/3\sqrt{2} = 0.74$ and $\eta = \pi/2\sqrt{3} = 0.9$, respectively.

Assuming that the particle can be separated into n identical spherical atoms without changing its volume, the total number of the atoms of the metallic nanoparticle n_t and the number of surface atoms of the metallic nanoparticle n^s are given by:

$$n_t = \frac{V_{\text{particle}}}{V_{\text{atom}}} \times \text{packing fraction} = \rho \times \frac{R^3}{r^3} \quad (9)$$

or,

$$(n_t)^{2/3} = \rho^{2/3} \times \frac{R^2}{r^2} \quad (10)$$

and,

$$n^s = \frac{A_{\text{particle}}}{A_{\text{atom}}} \times \text{surface packing fraction} = \eta \times \frac{R^2}{r^2} \quad (11)$$

or,

$$\frac{R^2}{r^2} = \frac{n^s}{\eta} \quad (12)$$

Substitute Eq. (12) in Eq. (10), we get Eq. (13). Therefore, the number of surface and interior atoms are given by:

$$n^s = \frac{\eta}{\rho^{2/3}} (n_t)^{2/3} \quad (13)$$

$$n^i = n_t - \frac{\eta}{\rho^{2/3}} (n_t)^{2/3} \quad (14)$$

A theoretical derivation of cohesive energy of the bulk materials is made which is based on the bond energy and the number of bonds

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