

Bulk cohesive energy and surface tension from the size-dependent evaporation study of nanoparticles

K. K. Nanda^{a)}

Materials Research Centre, Indian Institute of Science, Bangalore-560 012, India

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In this letter, it is shown that the bulk cohesive energy (E_B) and bulk surface tension (γ) can be deduced from the size-dependent evaporation (SDE) study of free nanoparticles. The surface tension of nanoparticles (γ_n) is obtained by analyzing SDE data on the basis of the Kelvin equation, while E_B is obtained by reanalyzing the SDE data. By comparing the size-dependent melting and the SDE of nanoparticles, γ is evaluated. © 2005 American Institute of Physics. [DOI: 10.1063/1.1994958]

Surface tension (γ) is one of the important physical quantities that controls the growth of a material on a substrate as well as different phenomena, such as melting, coalescence, evaporation, phase transition, growth, etc., of nanoparticles. Similarly, cohesive energy (E_B) is also one of the important physical quantities and is a measure of the thermal stability of the materials. Surface tension of solids is determined with contact angle method for which liquids with known surface tension are taken as a reference.¹ On the other hand, E_B is evaluated² from the heat of sublimation (ΔH_{sub}). In this letter, we evaluate E_B and γ of Au, Ag, and PbS from their size-dependent evaporation (SDE) data and conclude that the method can be employed to other systems as well. The SDE data³⁻⁵ are obtained by monitoring the onset temperature of evaporation (T_{onset}) as a function of particle size (d) where T_{onset} is the temperature at which the particle size (d) decreases as a consequence of the partial evaporation. Recently, we have shown that surface tension of nanoparticles (γ_n) and the onset temperature of evaporation ($T_{\text{onset},b}$) of large particles can be obtained from the SDE data by verifying the Kelvin effect.³⁻⁵ Here, we show that E_B can be evaluated by reanalyzing the same SDE data. Further, comparing our experimental results on SDE with the expression for the size-dependent melting (SDM),⁶ the variation of SDM and SDE is shown to be identical which establishes a correlation between γ_n and γ . As a consequence, γ can be evaluated directly if γ_n is known and vice versa. Similarly, SDM can be predicted if SDE is known and vice versa.

Apart from the SDE study, γ_n can also be deduced from the size-dependent lattice parameter (SDLP) of nanoparticles.⁷⁻¹⁷ Different theoretical models predict a variation of γ with d for very small particles ($d \sim 0.1$ nm),³ while γ_n is almost size independent in the intermediate size range ($d > 1.0$ nm). As the SDE and SDLP data are available in the intermediate size range, a discussion on γ_n for very small particles is beyond our scope. Values of γ_n reported for the Ag range⁷⁻¹² from 1.415 to 6.56 J/m² and that for the Au range¹³⁻¹⁶ from 1.175 to 7.7 J/m². Alivisatos and his co-workers¹⁷ have obtained $\gamma_n = 2.5$ J/m² for bare CdS nanoparticles and $\gamma_n = 1.74$ J/m² for capped CdS nanoparticles. Thus, the difference in γ_n for Au and Ag is believed to be due to the different surroundings and/or the different particle-substrate interaction. Further, any difference in the compressibility of nanoparticles and bulk, will affect the de-

termination of γ_n . On the other hand, γ_n is the only free parameter in the Kelvin equation and there is no ambiguity in evaluating γ_n from the SDE data of nanoparticles. We also use SDE data³⁻⁵ of free nanoparticles which implies that there is no influence of substrates and/or the surroundings.

According to the Kelvin equation, the vapor pressure (p_s) of nanoparticles is related to that of a flat surface (p_{s0}) as:¹⁸

$$\frac{p_s}{p_{s0}} = \exp\left(\frac{4\gamma_n M}{\rho_p R T d}\right), \quad (1)$$

where M is the molecular weight, ρ_p is the particle density, R is the gas constant, T is the temperature, and d is the particle diameter. For Wulff crystals, γ_n/d is constant for all crystal faces even though the surface energy is different for different crystal faces, which implies that Eq. (1) holds for all crystal faces of a nanoparticle. The vapor pressure (p_{s0}) can be related to ΔH_{sub} by the Clausius-Clapeyron equation as:

$$\ln p_{s0} = -\frac{\Delta H_{\text{sub}}}{RT} + C, \quad (2)$$

where R is the gas constant. Similar to bulk, the vapor pressure (p_s) of nanoparticles can be related to its heat of sublimation ($\Delta H_{\text{sub},n}$) as

$$\ln p_s = -\frac{\Delta H_{\text{sub},n}}{RT} + C. \quad (3)$$

Substituting Eqs. (2) and (3) in Eq. (1), we obtain

$$\Delta H_{\text{sub},n} = \Delta H_{\text{sub}} - \frac{4M\gamma_n}{\rho_p d} \Rightarrow \frac{\Delta H_{\text{sub},n}}{\Delta H_{\text{sub}}} = 1 - \frac{4v_0\gamma_n}{\Delta H_{\text{sub}}d}. \quad (4)$$

In this context, it may be noted that E_B , ΔH_{sub} , and the activation energy (E_A) for bulk are comparable and can be realized by comparing these quantities.² Here, we show that Eq. (4) can also be obtained from the total binding energy, $E(N)$ of nanoparticles, which can be expressed as

$$E(N) = E_B N - 4\pi R^2 \gamma_n = E_B N - 4\pi r_s^2 \gamma_n N^{2/3}, \quad (5)$$

where r_s is the radius of a sphere corresponding to the volume of one atom in bulk and N is the number of atoms in the nanoparticles related to the particle radius as $R = r_s N^{1/3}$. Based on Eq. (5), E_{An} can be expressed as

^{a)}Electronic mail: nanda@mr.c.iisc.ernet.in

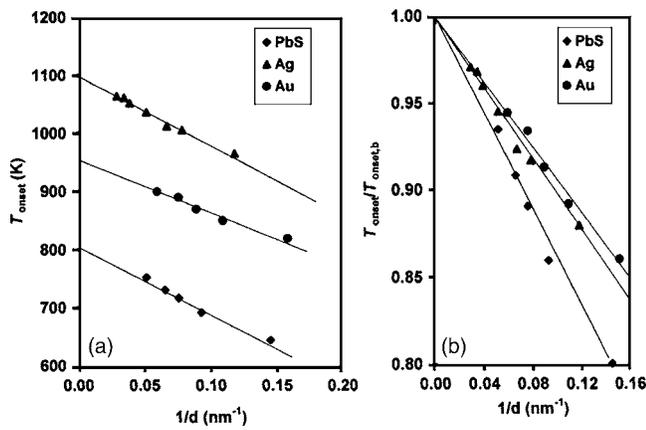


FIG. 1. (a) T_{onset} vs $1/d$ for PbS, Ag, and Au. The data are taken from Refs. 3–5. (b) The same data are plotted as $T_{\text{onset}}/T_{\text{onset},b}$ as a function of the inverse of particle size.

$$E_{An} = \frac{\partial E(N)}{\partial N} = E_B - \frac{8\pi}{3} r_s^2 \gamma_n N^{-1/3} \Rightarrow \frac{E_{An}}{E_B} = 1 - \frac{8\pi \gamma_n r_s^2}{3E_B N^{1/3}}. \quad (6)$$

It may be noted from Eq. (6) that $E_A = E_B$ for large N and Eq. (4) is same as Eq. (6). According to the Trouton's rule,¹⁹ the ratio of latent heat of vaporization (ΔH_{vap}) to the normal boiling point (T_b) is constant. It may be noted that E_{An} is the energy required to remove one atom from the nanoparticle, while T_{onset} is the temperature at which the atoms/molecules leave the particles and as a consequence the particle size decreases. This indicates that E_{An} can be scaled to T_{onset} and E_A can be scaled to $T_{\text{onset},b}$. Equation (6) can then be expressed as

$$\frac{T_{\text{onset}}}{T_{\text{onset},b}} = 1 - \frac{16\pi \gamma_n r_s^3}{3E_B d}. \quad (7)$$

Equation (7) predicts a linear relation between T_{onset} and the inverse of the particle size and the slope depends on γ_n and E_B . It may be noted that E_B can easily be evaluated from the slope obtained by plotting $T_{\text{onset}}/T_{\text{onset},b}$ as a function of $1/d$, if γ_n is known. It has been shown both experimentally and theoretically (based on the Kelvin equation) that T_{onset} is linear with respect to $1/d$ and the slope depends on γ_n .^{3–5} Analyzing the SDE data on the basis of Kelvin equation, γ_n for PbS, Ag, and Au has been found to be 2.45, 7.2, and 8.78 J/m², respectively.^{3–5} To deduce E_B from the SDE data, the data^{3–5} of PbS, Ag, and Au nanoparticles are plotted as T_{onset} versus $1/d$ and is shown in Fig. 1(a). The least-squares fit of the experimental data into a straight line, yields a slope of -1138 ± 75 , -1158 ± 55 , -895 ± 25 nm K, and an intercept of 805 ± 8 , 1097 ± 4 , 953 ± 4 K for PbS, Ag, and Au, respec-

tively. It may be noted that the intercept represents a temperature $T_{\text{onset},b}$ where large particles evaporate under the experimental conditions used to study the SDE. The lower value of $T_{\text{onset},b}$ for Au is believed to be due to surface melting.⁵ Now, we plot SDE data as $T_{\text{onset}}/T_{\text{onset},b}$ versus $1/d$ and shown in Fig. 1(b). The slopes are found to be -1.41 ± 0.11 , -1.05 ± 0.05 , and -0.94 ± 0.03 nm, respectively, for PbS, Ag, and Au. Taking $r_s = 0.158$ nm and $\gamma_n = 8.97$ J/m², E_B of 3.88 ± 0.09 eV is obtained for Au. Similarly, E_B of 2.88 ± 0.12 and 2.33 ± 0.18 eV are obtained for Ag and PbS from their SDE data.^{3,4} E_B of Au and Ag are in excellent agreement with the experimental values (Table I) of 3.81 and 2.95 eV, respectively.²⁰ By fitting the vapor pressure data²¹ of PbS in the temperature range of 1028–1381 K, ΔH_{sub} is determined as 234.4 kJ/mole (2.43 eV/atom). It may be noted that PbS evaporates²² in a molecular form and ΔH_{sub} can be considered to be equal to E_B which is in excellent agreement with that obtained from SDE data. Overall, it can be concluded that the cohesive energy per atom can be evaluated from the SDE data.

It is well established both experimentally and theoretically that the melting temperature (T_m) of nearly free nanoparticles drops linearly with the inverse of the particle size as is the case of SDE. Based on the experimental results (Fig. 1) on SDE, the slope of $T_{\text{onset}}/T_{\text{onset},b}$ is -1.41 , -1.05 , and -0.94 nm for PbS, Ag, and Au, respectively. On the other hand, the slope of T_m/T_{mb} versus $1/d$ curve is reported to be in the range from -2.0 to -0.8 nm for Au,^{23–26} while most of the theoretical models predict the slope as close to -1.0 nm.^{6,23,26–28} Similarly, the slope is found to be about -2.0 nm from the experimental data of Ag,²⁶ while the molecular dynamics simulations²⁹ and other theoretical models^{6,28} predict a slope of about -0.7 and -1.0 nm, respectively. As per the expression for SDM based on the liquid-drop model,⁶ the slope of T_m/T_{mb} versus $1/d$ curve is -0.97 and -1.13 nm for Ag and Au, respectively, and is nearly the same as that obtained from $T_{\text{onset}}/T_{\text{onset},b}$ versus $1/d$. This indicates that the variation of $T_{\text{onset}}/T_{\text{onset},b}$ and T_m/T_{mb} can be assumed to be identical. However, SDE data yield $\gamma_n = 7.20$ and 8.78 J/m² for Ag and Au, respectively,^{4,5} while γ of 1.065 and 1.363 J/m² is used⁶ to predict the SDM of Ag and Au nanoparticles, respectively. Further, cohesive energy per atom is obtained from the SDE data, whereas cohesive energy per coordination⁶ is used to evaluate SDM. The cohesive energy per coordination is six times lower than the cohesive energy per atom for Ag and Au. This is because the coordination number is 12 for Ag and Au (face-centered-cubic structure) and each bond is shared by two atoms. It may also be noted that γ_n obtained from the SDE data is approximately six times higher than γ for Ag and Au. This indicates that γ_n is related to γ in the same way as the co-

TABLE I. Different parameters obtained from the SDE data.

Materials	Slope (nm)	γ_n (J/m ²)		γ (J/m ²)		E_B (eV/atom)	
		$T_{\text{onset}}/T_{\text{onset},b}$	T_m/T_{mb} (Ref. 6)	(Our work)	(Ref. 27)	(Our work)	(Ref. 20)
PbS	-1.41	•••	2.45	0.82	$\sim 1.0^a$	2.33	2.43 ^a
Ag	-1.05	-0.97	7.20	1.20	1.1–1.2	2.88	2.95
Au	-0.94	-1.13	8.78	1.46	1.2–1.4	3.88	3.81

^aExpected γ and E_B for PbS (see text).

hesive energy per atom is related to the cohesive energy per coordination and γ can be evaluated directly if γ_n is known. A similar relation between γ_n and γ has also been obtained by analyzing the experimental data on the cohesive energy of Mo and W nanoparticles based on the liquid-drop model (to be published elsewhere).

As the coordination number of materials with body-centered-cubic, simple cubic, and diamondlike crystal structure is 8, 6, and 4, respectively, γ_n will be four, three, and two times higher than γ . The crystal structure of PbS is NaCl type and hence, the coordination number is 6 that yields $\gamma = 0.82 \text{ J/m}^2$. This value seems to be realistic as PbS is an ionic semiconductor and γ of an ionic semiconductor is $\sim 1.0 \text{ J/m}^2$.

In summary, it is shown that SDE data can be used to evaluate γ_n , γ , and E_B and the variation of T_m and T_{onset} is almost identical. As γ_n is evaluated and then used to determine E_B from the same data, E_B is believed to be independent of the influence of substrates or surroundings. However, as γ_n is influenced by the surroundings, the value obtained for free nanoparticles should be used to evaluate γ . Though the analysis of the SDE and SDM data elucidates a relation between γ and γ_n , investigation of elements with different crystal structure is required to confirm the validity of the relationship.

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