

Comment on “Higher Surface Energy of Free Nanoparticles”

In a recent Letter by Nanda *et al.* [1], a surface energy of $\gamma(D) = 7.2 \text{ J/m}^2$ for Ag nanoparticles (D is diameter) has been determined by studying size-dependent evaporation of nanoparticles relating to the Kelvin effect, which is significantly higher than the corresponding bulk value γ_b [1]. The authors argue that this fact is usual since similar situations have been found in PbS, CdS, and Pd [1–3]. We comment on this prediction.

γ and surface stress f are defined as the reversible work per unit area involved in, respectively, forming a new surface of a substance and elastically stretching a surface [4]. $f = \gamma + \partial\gamma/\partial A$ where A is the surface area [4]. $\gamma = f$ for liquids while $\gamma < f$ for solids very often [4], although there are exceptions depending on the sign of $\partial\gamma/\partial A$ [5]. The obtained larger γ value [1] thus denotes the f value while $f > \gamma$ is understandable. Note that the cited f values of CdS [2] and Pd [3] are wrongly interpreted as γ values by the authors [1].

The f value at melting temperature T_m reads [4]

$$f = (h/2)\sqrt{3S_{\text{vib}}H_m/(R\kappa V)}, \quad (1)$$

where h is the atomic diameter, S_{vib} the vibrational part of melting entropy S_m , H_m the bulk melting enthalpy, R the ideal gas constant, k the compressibility, and V the gram atom volume of crystals. Equation (1) was originally derived for a solid-liquid interface where f decreases with T since the specific heat of an undercooled liquid has a negative slope [4]. Because the f here considered is for the surface, it decreases with T as γ does. The f determined by Eq. (1) should be thus its minimum f_{min} . The f_{min} values for the crystals mentioned in Ref. [1] are calculated and shown in Table I, where $f_{\text{min}} > \gamma$ as expected and $f_{\text{min}} < f$ except for Pt since the experiments considered are performed at room temperature.

In addition, $\gamma(D)$ can be related with the size-dependent cohesive energy $E(D)$ of nanocrystals where $\gamma(D) \propto E(D)$ since $\gamma(D)$ is a function of the broken bond number of surface atoms. Thus, $\gamma(D)/\gamma_b \approx E(D)/E_b$, which leads to [10]

$$\frac{\gamma(D)}{\gamma_b} = \frac{2D/h - 2}{2D/h - 1} \exp\left[-\frac{2S_b}{3R(2D/h - 1)}\right], \quad (2)$$

where S_b denotes the bulk coherent entropy. $\gamma(D)$ decreases with D , against the argument of the authors [1]. This is because an energetic difference between the surface and the interior atoms decreases as the energetic state of the interior atoms increases [10]. For Au nanoparticles with (111), (100), and (110) facets, Eq. (2) gives $\gamma(D = 3.8 \text{ nm})$ values of 0.87, 1.10, and 1.15 J/m^2 (the corresponding γ_b values are 1.28, 1.63, and 1.70 J/m^2 [9] with $S_b = 106.8 \text{ J/g-atom K}$ [4]) while the theoretical results

TABLE I. Comparisons among f_{min} , the experimental results f [1–3] and γ [1,9] in J/m^2 . All data of metals are from Ref. [4] while for CdS and PbS, V in $\text{cm}^3/\text{g-atom}$ and h in \AA , H_m in kJ/g-atom and S_{vib} in J/g-atom K , κ in $10^{-12}/\text{Pa}$ from Refs. [6], [7], and [2,8], respectively.

	Ag	Au	Pt	Pd	CdS	PbS
h	2.89	2.88	2.78	2.75	2.11	2.97
V	10.3	10.2	9.1	8.9	15.0	15.7
H_m	11.3	12.6	19.6	17.6	29.0	18.4
S_{vib}	9.16	9.38	9.58	9.64	6.02	4.96
κ	9.65	5.85	3.62	5.35	15.6	15.1
f_{min}	2.80	3.13	6.22	4.94	1.73	1.77
f	7.2	3.19	4.44	6.0	2.50	2.45
γ	1.25	1.5	2.5	2.0	0.75	1.4

are $\gamma(D = 3.8 \text{ nm}) = 0.93, 1.15, \text{ and } 1.18 \text{ J/m}^2$ [11]. A good agreement is found.

Moreover, $\exp(-x) = 1 - x$ when x is small, Eq. (2) is rewritten as $\gamma(D)/\gamma_b \approx 1 - 4h/D$ when $S_b/R \approx 12$ for metallic elements, which is the same as Tolman's equation for the size-dependent liquid-vapor interface energy $\gamma_{lv}(D)$ [1]. This consistency is because the structural and energetic differences between solid and liquid are much smaller than those between them and vapor.

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