LETTERS

Lattice Contraction and Surface Stress of fcc Nanocrystals

Q. Jiang,* L. H. Liang, and D. S. Zhao

Department of Materials Science and Engineering, Jilin University, Changchun 130025, China

Received: March 19, 2001

General equations for lattice contraction and surface stress of fcc nanocrystals are established based on the Laplace−Young equation and a consideration for the size-dependence of the solid−liquid interface energy. The predictions of our equations are in agreement with the experimental results on the measurement of lattice contraction and surface (interface) stress of nanoparticles and thin films and theoretical calculations.

It is well-known that nanocrystals with free surfaces have considerable lattice contraction induced by the large surface/volume ratio.[1−7] The lattice contraction increases as the size of the nanocrystals decreases. From a mechanical point of view, hydrostatic pressure on the surface induced by intrinsic surface stress f results in lattice contraction or lattice strain ϵ.[1−3,8−11] In fact, the measurement of lattice contraction has been considered as a general method to determine an isotropic f.[1,12−13] Note that f differs from the specific surface excess free energy γ. The latter describes the reversible work per unit area to form a new solid surface, whereas the former denotes the reversible work per unit area due to elastic deformation, which is equal to the derivative of γ with respect to the strain tangential to the surface.[12,13] Since surface stress is a fundamental thermodynamic quantity for which few reliable experimental and theoretical values are available, the derivation of a general expression for f without free parameters would be an important progress.

In this contribution, general equations without any free parameters for ϵ and f are developed by considering the relationship between γ and f and by determining two limit cases of the size-dependent γ function. The model predictions for ϵ and f are found to be consistent with experimental and theoretical results.

 * Corresponding author. Fax: +86/431-5687607; e-mail: Jiangq@jlu.edu.cn.

For a solid particle immersed in a fluid of the same composition, a scalar definition of f for the solid can be written as[13,14]

$$f = \partial G/\partial A = \partial(\gamma A)/\partial A = \gamma + A\partial\gamma/\partial A \approx \gamma + A\Delta\gamma/\Delta A \quad (1)$$

where G states the total excess Gibbs free energy and A shows the surface area with Δ being the difference, or

$$\Delta\gamma = (\Delta A/A)(f - \gamma) \quad (2)$$

For the particle with a volume of V and a diameter of D, according to the Laplace−Young equation,[12−13]

$$P = 2fA/(3V) = 4f/D \quad (3)$$

with P being the pressure difference between P_{int} inside the particle and P_{ext} in the fluid on the outside of the particle. Using the definition of compressibility $\kappa = -\Delta V/(VP)$, $\epsilon = \Delta D/D = \Delta A/(2A) = \Delta V/(3V)$ under small strain and $A/V = 6/D$, eq 3 can be rewritten as

$$\epsilon = -4\kappa f/(3D) \quad (4)$$

To find the mathematical solution of f and γ, we need two boundary conditions of γ. Since an understandable asymptotic

TABLE 1: Comparison of Surface Stresses among Different Model Estimations and Experimental Results[a]

	Au	Pt	Ag	Cu	Ni	Al	Pb	Ir
h(nm)[25]	0.2884	0.2775	0.2889	0.2556	0.2492	0.2863	0.3500	0.2174
V_m (cm^3 mol^{-1})[26]	10.2	9.1	10.3	7.1	6.59	10	18.17	8.54
H_m(KJ mol^{-1})[26]	12.55	19.6	11.3	13.05	17.47	10.79	4.799	26.1
T_m(K)[26]	1337.6	2045	1234	1357.6	1726	933.25	600.6	2716
S_m(J mol^{-1} K^{-1})	9.38	9.58	9.16	9.61	10.12	11.56	7.99	9.61
κ(10^{-12} Pa^{-1})	5.848	3.623	9.653	7.257	5.640	13.30	21.83	2.695
γ_0 (J/m^2)	0.119	0.136	0.111	0.160	0.189	0.168	0.045	0.110
f_1 (J/m^2)	2.097	2.795	1.578	2.051	2.502	1.648	0.737	2.577
f_2 (J/m^2)[12]	2.77	5.60				1.25	0.82	5.30
f_3(J/m^2)[28]	1.714		1.041	1.106	0.817			
f_4(J/m^2)[29]			1.94		1.67			
f_5(J/m^2)[1-3]	1.175 ± 0.2	2.574 ± 0.4	1.415 ± 0.3					

[a] $S_{vib} \approx S_m = H_m/T_m$, and $\kappa = 1/B$ where B is the bulk modulus cited from reference 27. γ_0 is calculated in terms of eq 10 at $T = 298$ K. The term f_1 is determined by eq 12 with $D_0 = 2h$ at $T = 298$ K, f_2 denotes the results of the first principles calculation and f_3 the computer simulation results, f_4 gives the results of the modified embedded atom method potentials, f_5 is the experimental results.

limit is that when $D \rightarrow \infty$, $\gamma \rightarrow \gamma_0$ where γ_0 as a reference state is the corresponding bulk value of γ, let

$$\Delta\gamma = \gamma - \gamma_0 \qquad (5)$$

Substituting eq 5 into eq 2 and taking it in mind that $V/A = D/6$ and $\Delta A/A = 2\epsilon = -8\kappa f/(3D)$ in terms of eq 4, we get

$$\gamma(D)/\gamma_0 = [1-8\kappa f^2/(3\gamma_0 D)]/[1-8\kappa f/(3D)] \qquad (6)$$

We assume that when almost all atoms of a particle are located on its surface with a diameter of D_0, the particle is almost indistinguishable from the surrounding fluid. Note that as the size of a solid particle decreases, the free energy density of the particle increases and would be equal to that of the corresponding fluid at $D = D_0$.[15] This assumption leads to another limit case: As $D \rightarrow D_0$, $\gamma \rightarrow 0$ where D_0 depends on the existence of curvature.[15] For a particle or a wire with curvature surface, D has a usual meaning of diameter (defined as the side length for the cubic or rhombohedral particle). For a thin film, D denotes its thickness. D_0 is determined by $hA/V \approx 1$ with h being atomic diameter and as the first-order approximation, D_0 is roughly given by

$$D_0 = 3h \qquad (7\text{-}1)$$

$$D_0 = 2h \qquad (7\text{-}2)$$

where equation (7-1) for particles and wires and equation (7-2) for thin films. Now eq 6 can be rewritten as

$$\gamma(D)/\gamma_0 = [1 - D_0/D]/[1 - \gamma_0 D_0/(fD)] \qquad (8)$$

with $8\kappa f^2/(3\gamma_0) = D_0$, or

$$f = \pm[(3\gamma_0 D_0)/(8\kappa)]^{1/2} \qquad (9)$$

Two roots of f have different signs with the same absolute value under the conditions of $\gamma(D_0) = 0$ and $0 \le \gamma(D)/\gamma_0 \le 1$. Since f is one order larger than γ_0 (see Table 1), the denominator in eq 8 is negligible. Thus, $\gamma(D)/\gamma_0 \approx 1 - D_0/D$ seems to be a good first-order approximation, which is consistent with general calculations of thermodynamics[16-19] and quantum chemistry[6] for particles as well as computer simulation results.[20]

TABLE 2: Comparison of f in J/m^2 for Incoherent Multilayers with Different Methods[a]

multilayer A/B	f_1	f_5[32]
Ag/Ni	−1.987	−2.27 ± 0.67, −2.24 ± 0.21, −2.02 ± 0.26
Ag/Cu	−1.803	−3.19 ± 0.43, −0.21 ± 0.10

[a] The subscripts of f have the same meaning as those in Table 1. As a first order approximation, γ_0 and κ on the layer interface are considered as an algebraic average value of two elements where γ_0 and κ values of each element are in Table 1 (for solid−solid interface, γ_0 here used is two times of that of a solid−liquid interface in Table 1,[30] which is also in agreement with a phenomenological model[31]).

In eq 9, γ_0 has been deduced according to Gibbs−Thomson equation:[21]

$$\gamma_0(T) = 2hS_{vib}H_m(T)/(3V_m R) \qquad (10)$$

where R is the ideal gas constant, $H_m(T)$ is the temperature-dependent melting enthalpy of bulk crystals, S_{vib} is the vibrational part of the overall melting entropy S_m, V_m is the molar volume. Although the melting entropy of crystals consists, at least, of three contributions (positional, vibrational, and electronic components[21,22]), the melting for metallic and organic crystals is mainly vibrational in nature, and $S_{vib} \approx S_m$ is used.[21,22] According to the Helmholtz function, $H_m(T) = g_m(T) - Tdg_m(T)/dT$ where $g_m(T)$ is the volume Gibbs free energy. For elements, $g_m(T) = H_m(T_m - T)7T/T_m(T_m + 6T)$,[23,24] and thus

$$H_m(T) = 49/(T_m/T + 6)^2 H_m \qquad (11)$$

where H_m is the melting enthalpy of bulk crystals at the melting temperature T_m. Finally, taking eq 11 into eq 10 and taking eq 10 into eq 9, eq 9 can be rewritten as

$$f = \pm \frac{7}{2(T_m/T + 6)} \sqrt{D_0 h S_{vib} H_m/(\kappa R V_m)} \qquad (12)$$

The term f, shown in eq 12, is the stress on solid−liquid interface, not the solid−gas interface. Under the assumption that the fluid has no effect on the surface strain of solids, f obtained by eq 12 is considered to be identical with solid−gas interface stress or surface stress.

In terms of eq 12, f values for particles and multilayer films have been calculated and are shown in Tables 1 and 2 and are compared with the summarized literature values for f. As seen in the tables, both positive and negative stresses are possible in a practical system, depending on different surface (interface)
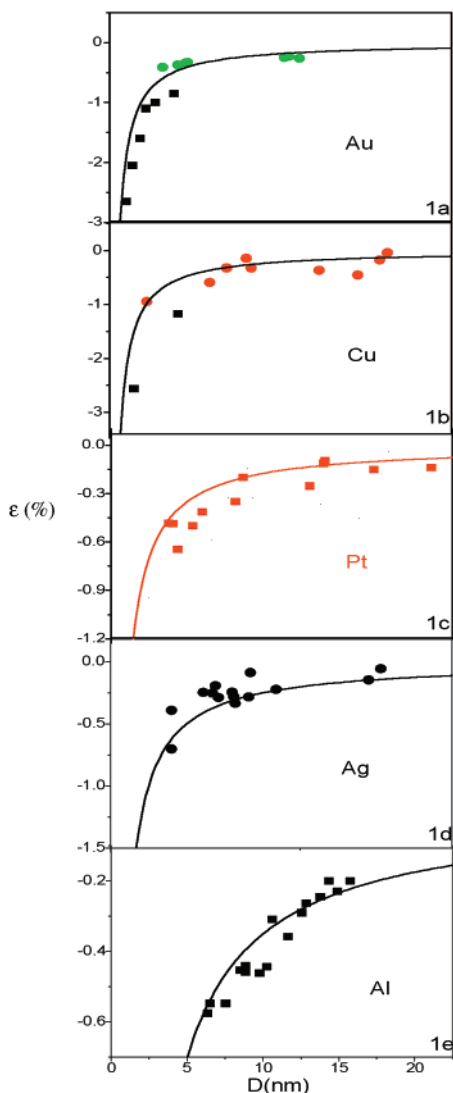
Figure 1. $\epsilon(D)$ functions of particles (solid lines) in terms eq 13 with parameters shown in Table 1 ($D_0 = 3h$). The symbols show the experimental data where ●[1] and ■[6] are the measured mean values of $\Delta a/a$ for Au in 1a; ●[3] and ■[4] are that of $\Delta a/a$ for Cu in 1b; ■[3] is the measured values of $\Delta a_{220}/a_{220}$ for Pt in 1c; ●[2] denotes that of $\Delta a_{220}/a_{220}$ for Ag in 1d and ■[5] shows that of $\Delta a/a$ for Al in 1e.

structures.[32] Our results of eq 12 correspond to the theoretical works[12,28−29] and the experimental results[1−3,32] very well.

In terms of equations 12 and 4,

$$\epsilon = \pm \frac{14}{3(T_m/T + 6)} \sqrt{\kappa D_0 h S_{vib} H_m/(RV_m)} \qquad (13)$$

Figure 1 gives $\epsilon(D)$ functions of particles in terms of eq 13 and experimental results of fcc Au,[1,6] Cu,[3,4] Pt,[3] Ag[2], and Al[5]

nanoparticles. The observed experimental data of $\epsilon(D)$, which are in the range of about 0.1−2.5%, correspond to the prediction of eq 13 perfectly.

In summary, general equations without any free parameters on surface stress and size-dependent strain of nanoparticles and thin films are established and confirmed by the experimental results for fcc metals. The results indicate that the values of surface stress and strain are related with the measurable materials constants. The equations show an expedient way to determine the surface stress and lattice strain.

References and Notes

(1) Mays, C. W.; Vermaak, J. S.; Kuhlmann-Wilsdorf, D. *Surf. Sci.* **1968**, *12*, 134.
(2) Wasserman, H. J.; Vermaak, J. S. *Surf. Sci.* **1970**, *22*, 164.
(3) Wasserman, H. J.; Vermaak, J. S. *Surf. Sci.* **1972**, *32*, 168.
(4) Apai, G.; Hamilton, J. F. *Phys. Rev. Lett.* **1979**, *43*, 165.
(5) Woltersdorf, J.; Nepijko, A. S.; Pippel, E. *Surf. Sci.* **1981**, *106*, 64.
(6) Müller, H.; Opitz, Ch.; Strickert, K.; Skala, L. *Z. Phys. Chemie Leipzig* **1987**, *268*, 634.
(7) Yu, X. F.; Liu, X.; Zhang, K.; Hu, Z. Q. *J. Phys. Condens. Matter* **1999**, *11*, 937.
(8) Shuttleworth, R. *Proc. Phys. Soc. A* **1950**, *63*, 444.
(9) Cahn, J. W. *Acta Metall.* **1980**, *28*, 1333.
(10) Hahn, H. *Nanostruct. Mater.* **1993**, *2*, 251.
(11) Skandan, G.; Hahn, H.; Roddy, M.; Cannon, W. *J. Am. Ceram. Soc.* **1994**, *77*, 1706.
(12) Cammarata, R. C.; Sieradzki, K. *Annu. Rev. Mater. Sci.* **1994**, *24*, 215 and references therein.
(13) Weissmüller, J.; Cahn, J. W. *Acta Mater.* **1997**, *45*, 1899.
(14) Vanfleet, R. R.; Mochel, J. M. *Surf. Sci.* **1995**, *341*, 40.
(15) Jiang, Q.; Shi, H. X.; Zhao, M. *J. Chem. Phys.* **1999**, *111*, 2176.
(16) Langmuir, I. *J. Am. Chem. Soc.* **1916**, *38*, 2221.
(17) Tolman, R. C. *J. Chem. Phys.* **1949**, *17*, 333.
(18) Kirkwood, J. G.; Buff, F. P. *J. Chem. Phys.* **1949**, *17*, 338.
(19) Buff, F. P. *J. Chem. Phys.* **1951**, *19*, 1591.
(20) Broughton, J. Q.; Glimer, G. H. *J. Chem. Phys.* **1986**, *84*, 5759.
(21) Jiang, Q.; Shi, H. X.; Zhao, M. *Acta Mater.* **1999**, *47*, 2109.
(22) Regel, A. R.; Glazov, V. M. *Semiconductors* **1995**, *29*, 405.
(23) Singh, H. B.; Holz, A. *Solid State Comm.* **1983**, *45*, 985.
(24) Perepezko, J. H.; Palk, J. S. *J. Noncryst. Solids*, **1984**, *61, 62*, 113.
(25) King, H. W. In *Physical Metallurgy*; Cahn, R. W., Ed.; North-Holland: Amsterdam, 1970; p 60.
(26) *Table of periodic properties of the elements*; Sargent-Welch Scientific Company: Skokie, Illinois, 1980; p 1.
(27) Brandes, E. A., Ed. *Smithells Metals Reference Book*, 6th ed.; Butterworth & Co (Publishers) Ltd: London, 1983; p 15−2.
(28) Streitz, F. H.; Cammarata, R. C.; Sieradzki, K. *Phys. Rev. B* **1994**, *49*, 10699.
(29) Streitz, F. H.; Cammarata, R. C.; Sieradzki, K. *Phys. Rev. B* **1994**, *49*, 10707.
(30) Kotze, I. A.; Kuhlmann-Wilsdorf, D. *Appl. Phys. Lett.* **1966**, *9*, 96.
(31) Weissmüller, J. *Nanostruct. Mater.* **1993**, *3*, 261.
(32) Spaepen, F. *Acta Mater.* **2000**, *48*, 31 and references therein.