Solid State Communications 150 (2010) 254–257

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

Surface free energy of platinum nanoparticles at zero pressure: A molecular dynamic study

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ARTICLE INFO

Article history:
Received 9 November 2009
Accepted 11 November 2009 by S.D. Sarma
Available online 21 November 2009

Keywords:
A. Platinum
C. Nanoparticles
D. Surface energy
E. Molecular-dynamics

ABSTRACT

Metallic nanoparticles are interesting because of their use in catalysis and sensors. The surface energy of the FCC platinum nanoparticles are investigated via molecular dynamics simulation using Quantum Sutton–Chen (QSC) potential. We have calculated the Gibbs free energy for the FCC platinum bulk and also for its nanoparticle. All calculations have been carried out at zero pressure. We have used the thermodynamic integration method to obtain the Gibbs free energy. The total Gibbs free energy is taken as the sum of its central bulk and its surface free energy. We have calculated the free energy of a platinum nanoparticle as a function of temperature.

1. Introduction

Particles with diameter of 1–10 nanometer exhibit properties that are often an intermediate between those of the molecular and crystalline states. Nanoscience and nanomaterials have been identified worldwide as the key to unlocking a new generation of devices with revolutionary properties and functionalities. A good deal of experimental and theoretical work has been carried out in these fields. Nanomaterials are challenging since they involve components at scales that are not common and thus the conventional theories may fail. Understanding the behavior of materials at this scale is important both from basic science point of view and also for the future applications. Nanoparticles with unique properties have emerged as an interdisciplinary field involving solid state physics, chemistry, biology and materials science [1]. Comprehensive studies of the physical properties of nanoparticles, too small to be subjected to macroscopic thermodynamic analysis, have been carried out over the past decades [2–8].

Metal nanoparticles exhibit physical, chemical, and electronic properties different from those of the bulk and single molecules due to the large fraction of surface atoms.

Computer simulation offers an effective tool to study the properties of nanoparticles and complement ongoing experimental efforts [9–11]. The results reveal that the isolated nanoparticles and substrate-supported nanoparticles with relatively high free surface usually exhibit a significant deviation in physical properties, compared to the corresponding conventional bulk materials. The original reason for this phenomenon is that the ratio of the number of surface-to-volume atoms is enormous for a nanoparticle and as a result, the total surface free energy of a nanoparticle increases as particle size decreases.

We have used molecular dynamics (MD) simulation to study the surface free energy of a Pt nanoparticle. Therefore our aim is to extend the MD simulation, to investigate the thermodynamic properties of nanoparticles with a relatively simple strategy. Firstly, we calculate the Gibbs free energy of the platinum bulk material and its surface free energy using molecular dynamics (MD) with the QSC potential. Secondly, by taking the total Gibbs free energy as the sum of the central bulk and surface free energies [12–14], we have calculated the free energy of a platinum nanoparticle as a function of temperature.

There are some procedures reported in the literature for the numerical evaluation of the free energy, using some empirical descriptions for the total energy, either in MD or Monte Carlo (MC) frames [15,16].

2. Molecular dynamic simulation

2.1. Force field model

In the present study, molecular dynamic simulation on a solid platinum nanoparticle was done using the DL-POLY-2.20

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doi:10.1016/j.ssc.2009.11.013

Table 1
Potential parameters used in MD simulation for the Pt nanocluster.

	n	m	ε (eV)	c	a (Å)
QSC	11	7	0.0097894×10^{-3}	71.336	3.9163

program [17]. All thermodynamic properties are obtained as time averages over the particle position and velocity. The embedded atom potentials [18] and other long-range potentials like the Sutton–Chen [19] based on the Finnis–Sinclair type of potential have been used in the literature successfully to produce the properties of the FCC based metals such as Pt. On the basis of the Sutton–Chen potential, the potential energy of a finite system is given by

$$U_{tot} = \sum_i U_i = \sum_i \varepsilon \left[\sum_{j \neq i} \frac{1}{2} V(r_{ij}) - c \rho_i^{\frac{1}{2}} \right], \tag{1}$$

where $V(r_{ij})$ is the pair potential to account for the repulsion resulting from the Pauli's exclusion principle,

$$V(r_{ij}) = \left(\frac{a}{r_{ij}} \right)^n. \tag{2}$$

The local density accounting for the cohesion associated with atom i is given by

$$\rho_i = \sum_{j \neq i} \Phi(r_{ij}) = \sum_{j \neq i} \left(\frac{a}{r_{ij}} \right)^m. \tag{3}$$

Sutton and Chen restricted the value of m to be greater than 6 and fitted it to give a close agreement with the bulk modulus and elastic constants. The Sutton–Chen potential poorly predicts properties involving defects, surfaces, and interfaces. The quantum Sutton–Chen potential which includes the quantum corrections and the zero-point energy allowing a better prediction for the temperature dependent properties. The quantum Sutton–Chen (QSC) parameters for Pt are listed in Table 1 [3,20].

2.2. MD simulation details

The MD simulations are carried out in a *NPT* ensemble with a constant number of atoms N and pressure P and temperature T with the periodic boundary conditions. Platinum is a metal with a FCC structure. A FCC block was first constructed from a FCC unit cell by replication in the three dimensions with center located at (0, 0, 0). The fractional coordinates in FCC structure are (0, 0, 0), (0.5, 0.5, 0), (0.5, 0, 0.5), and (0, 0.5, 0.5). In order to obtain the free-energy as a function of temperature, MD simulations are implemented in a *NPT* ensemble. Temperature is controlled by a Nose–Hoover thermostat [21] and pressure kept at the 0 Pa. The equations of motion are integrated using the Verlet Leapfrog algorithm [9] with a time step of 0.001 ps for a system of 3430 atoms. The samples are heated in successive runs between 298.15 and 2000 K and cooled down to 298.15 K, with a temperature interval of 50 K. In each run, the first 5×10^4 time steps are used to equilibrate the sample, the statistical average of the thermodynamic variable (the internal energy in this case) is obtained on an additional set of 5×10^4 time steps.

All calculations of the surface free energy (part 3.2.) are performed in the *NVT* ensemble. We have employed finite slabs with the periodic boundary conditions in the lateral cells. The solid slabs contain 1836, 2152 and 2212 atoms for the Pt (111), Pt (100), and Pt (110) surfaces and consist of 13, 17, and 23 atomic layers with zero pressure lattice constants from the *NPT* simulation. For instance the former slab has 13 layers with a total of 1836 atoms. An odd number of atomic layers are taken for the sake of symmetry of the upper and lower surfaces. The three systems are chosen to have approximately equal spatial dimensions and the z axis is normal to the surface.

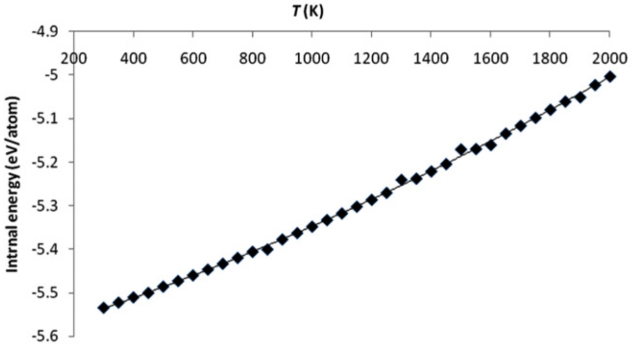

Fig. 1. Internal energy variation with temperature, fitted by a second order polynomial.

3. Theory

3.1. Calculation of bulk free energy

In this paper, the procedure used is similar to that introduced in references 15 and 16. All free-energy calculations are carried out at zero pressure. The Gibbs free energy per atom at temperature T and zero pressure, $G(T, P = 0)$, is related to the internal energy per atom, $U(T, P = 0)$, and the specific entropy, $S(T, P = 0)$, via the thermodynamic relation [22]:

$$G(T, P = 0) = U(T, P = 0) - TS(T, P = 0). \tag{4}$$

The entropy can be eliminated from Eq. (4) by expressing it in terms of temperature derivative of the Gibbs free energy, using the standard thermodynamic relation [22]:

$$S(T, P = 0) = -\left(\frac{\partial G(T, P = 0)}{\partial T} \right)_{P=0}. \tag{5}$$

Substituting Eq. (5) into Eq. (4) yields a differential equation for the Gibbs free energy in terms of the internal energy. Upon solving this differential equation, one obtains an expression, valid for any system, for the Gibbs free energy at any desired temperature:

$$G(T, P = 0) = T \left[\frac{G(T_0, P = 0)}{T_0} - \int_{T_0}^{T} \frac{U(T, P = 0)}{\tau^2} \mathrm{d}\tau \right] \tag{6}$$

where T_0 is a predetermined reference temperature. In order to calculate $G(T, P = 0)$, the temperature dependence of $U(T, P = 0)$ is needed. For such a task, we use the constant-pressure simulation to obtain the internal energy at different temperatures. As shown in Fig. 1, a second-order equation can be well fitted in the calculated data. The coefficients of fitting are found to be $a_0 = -5.6$, $a_1 = 2.06\text{E}{-4}$, and $a_2 = 4.64\text{E}{-8}$, were a_i is the coefficient of the ith power.

3.1.1. Calculation of free energy difference using the thermodynamic integration

Eq. (6) is a fundamental equation that will be used to determine the free energy as a function of temperature. In order to use Eq. (6), the Gibbs free energy at the reference temperature must be obtained separately by the thermodynamic integration (TI) method for a suitable ideal reference state. To do so, we consider a system with the switching Hamiltonian $H = (1 - \lambda)H_1 + \lambda H_2$, where H_2 describes the actual system and H_1 is the Hamiltonian of the reference system, with known free energy, and λ is the switching parameter. For the solid, the reference system H_1 is a set of Einstein oscillators centered on the average positions of the atoms in the ensemble corresponding to the Hamiltonian H_2.

$$H_1 = (1/2)m\omega^2(r_i - r_{i0})^2$$

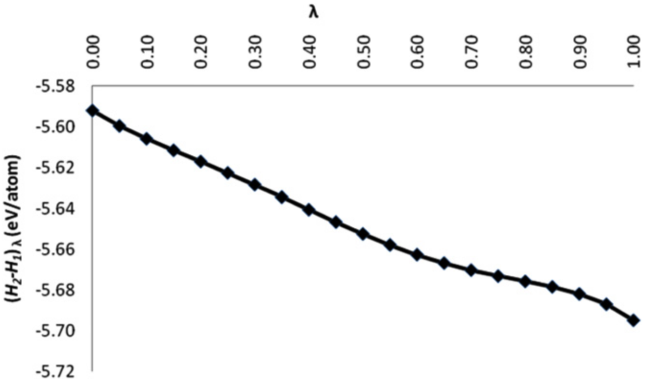

Fig. 2. Simulation results for the integrand $\langle H_2 - H_1 \rangle_\lambda$ appearing in the switching Hamiltonian method versus the switching parameter λ, corresponding to the solid phase, fitted by a fifth order polynomial.

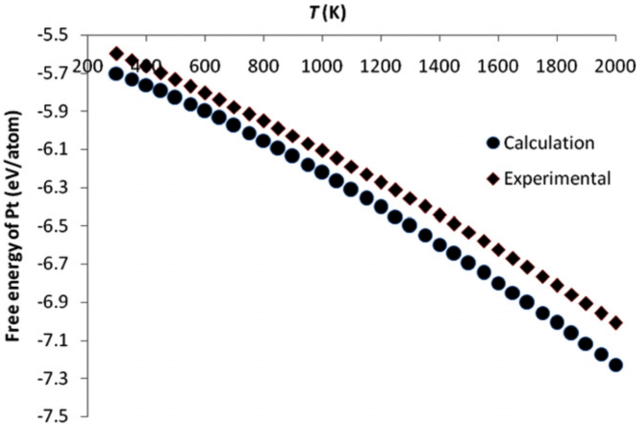

Fig. 3. Gibbs free energy versus temperature for the solid phase in units of eV/atom. (experimental values taken from Reference [29]).

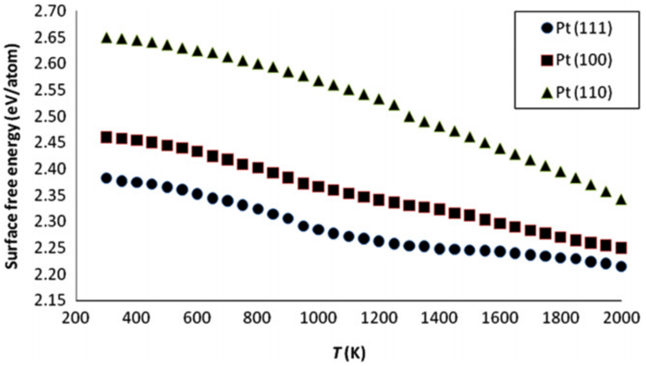

Fig. 4. Solid surface free energy versus temperature for the (111), (100) and (110) faces, obtained by using the thermodynamic integration method.

Table 2
Values of different contributions to the free-energy at the reference temperature T_0. (All entries are in units of eV/atom.)

Solid	$G(T_0, P = 0)$	ΔG_1	$G_w(T_0)$
$T_0 = 298.15$ K	−5.66822	−5.57582	−0.0924

where $\{r_{i0}\}$ are the ideal crystal lattice vector, m is the mass of an atom and ω is the frequency of oscillation. To obtain the most accurate results, the radial distribution function and mean-squared displacement of atoms of the actual system must be similar to those of the reference system at the temperature of interest.

The Gibbs free energy per atom relative to that of the reference system can then be obtained by the TI along the $\langle H_2\text{–}H_1 \rangle_\lambda$ path,

$$G(T_0, P = 0) = G_w(T_0) + \Delta G_1 \tag{7}$$

where,

$$\Delta G_1 = \frac{1}{N}\int_0^1 \left(\frac{\partial H}{\partial \lambda}\right)_{P=0} \mathrm{d}\lambda = \frac{1}{N}\int_0^1 \langle U - W \rangle_{\lambda, P=0} \mathrm{d}\lambda \tag{8}$$

where $G_w(T_0)$ is the free energy of the reference system at T_0. The integration is carried over the parameter λ, which varies between 0 and 1. In our case, the reference free energy of the solid Pt is calculated at $T_0 = 298.15$ K. Twenty one points within the interval $\lambda = 0$–1 has been used to carry the integration in Eq. (8). Again, the calculation for any given value of λ is carried out in two successive runs each with 5×10^4 steps and the average of $\langle H_2\text{–}H_1 \rangle$ is taken over the second time step. A fifth-order polynomial was fitted to the data, shown in Fig. 2.

3.1.2. Calculation of $G_w(T_0)$

The free energy of an Einstein crystal can be calculated analytically [23]:

$$G_w(T_0) = -3k_B T_0 \ln(T_0/T_E). \tag{9}$$

Here k_B is the Boltzmann constant, T_E is the Einstein temperature of the oscillators and $T_E = h\omega/2\pi k_B$, where h is the Planck constant and ω is the frequency of oscillation. Table 2 shows the values of different contributions to the free energy at the reference temperature T_0.

3.2. Calculation of surface free energy

The reversible work per unit area to form a new surface of a substance (for instance by cleavage) is defined as the specific surface free energy γ (or simply called the surface free energy), while the reversible work per unit area required to elastically stretch a surface is the surface tension σ [24]. The surface free energy constitutes a noticeable contribution to the total free energy of a nanoparticle. For solids, usually the surface tension is not equal to the surface free energy in value [24]. Thus γ for a solid is computed as

$$\sigma = \gamma + A_s \frac{\partial \gamma}{\partial A_s} \tag{10}$$

where σ is the surface tension, γ represents the surface free energy and A_s is the surface area.

To calculate the surface free energy, we use the approach given in Reference [25], in which the solid surface free energy can be obtained via the bulk and slab (with two surfaces) free energy, using Eqs. (6)–(9). We may define two surface free energies as,

$$\gamma^{area} = \frac{G_{slab} - NG_{bulk}}{2A_s} \tag{11}$$

$$\gamma^{atom} = \frac{G_{slab} - NG_{bulk}}{2N_{surface}} \tag{12}$$

where $\gamma^{area(atom)}$ represents the surface free energy per area (per atom), G_{slab} is the total free energy of the slab, N is the total number of atoms in the slab, N_{surf} is the number of atoms on each surface, G_{bulk} is the free energy per bulk atom and the 1/2 accounts for the two free surfaces of the simulation cell. The periodic boundary conditions are applied in the planar directions. In order to explore the size effect on the thermodynamic properties of a platinum nanoparticle, we first write the total Gibbs free energy G_{total} of a nanoparticle as the sum of the volume free energy G_{bulk} and the surface free energy $G_{surface}$,

$$G_{total} = G_{bulk} + G_{surface} = NG(T) + \gamma(T)A_s. \tag{13}$$

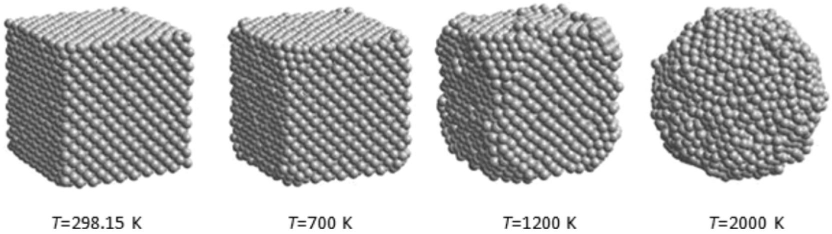

Fig. 5. Structural evolution of a platinum nanoparticle with temperature.

Assuming a spherical particle leads to the specific surface area of [26]

$$A_s = \frac{6NV_{atom}(T)}{R} \quad (14)$$

where N is the total number of atoms in the particle, R is the radius of the particle and $V_{atom}(T)$ is the volume per atom.

4. Results and discussion

Sturgeon and Laird [27] proposed that the optimal value for the Einstein temperature is what gives a similar mean-squared displacement for the reference and actual systems to reduce the numerical errors and obtain a good free-energy difference estimate. In our case, the reference free energy is calculated at $T_0 = 298.15$ K using Einstein temperature $T_E = 90$ K.

For calculation of the ΔG_1, it is necessary to use the thermodynamic integration. The integrand for the switching Hamiltonians, Eq. (8), is shown in Fig. 2 for Pt in the solid phase. A fifth-order polynomial is fitted to the data with the coefficients $b_0 = -5.592$, $b_1 = -0.1698$, $b_2 = 0.4279$, $b_3 = 1.3533$, $b_4 = 1.782$ and $b_5 = -0.7897$, where b_i is the coefficient of the ith power. The shape of the curve satisfies the Gibbs–Bogoliubov inequality $\left(\frac{\partial^2 H}{\partial \lambda^2}\right) < 0$ [23], which is used to test the accuracy of the integrand. The expression for $\langle H_2 - H_1 \rangle_\lambda$ is then integrated analytically, to obtain ΔG_1.

The free energy as a function of temperature is plotted in Fig. 3. The calculated results are in good agreement with experimental values, with the average percent difference of 2.89. Using the thermodynamic integration method, we have calculated the solid surface free energy of the (111), (100) and (110) faces by using Eq. (13). The results are depicted in Fig. 4.

It can be seen that the free energy of the faces at low temperatures are ordered precisely as expected from the packing of the atoms in the layers. The close-packed (111) face has the lowest and loosely-packed (110) face has the highest free energy. As the temperature increases, the anisotropy of the surface free energy becomes lower, because of the fact that the crystal slowly becomes disordered, see Fig. 5.

It should be emphasized that the measurement of the surface free energy of a crystalline metal is notoriously difficult and the wide spread of experimental values for a well-defined low-index orientation is substantial, as pointed out by Bonzel and Nowicki [28].

5. Conclusions

Using MD simulation with the QSC potential, we have studied the surface energy of a platinum nanoparticle. It was shown that the free energy of the faces at low temperatures is ordered precisely as expected from the packing of the atoms in the layers. The close-packed (111) face has the lowest free energy, while loosely-packed (110) face has the largest value. As the temperature increases, the anisotropy of the surface free energy becomes lower, because the crystal becomes slowly disordered. The free energy of a nanoparticle can be divided into two parts, namely the bulk and the surface. The impact of the size on the thermodynamic properties of a particle is determined by its surface atoms.

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