



The calculation of surface free energy based on embedded atom method for solid nickel

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ABSTRACT

Accurate prediction of surface free energy of crystalline metals is a challenging task. The theory calculations based on embedded atom method potentials often underestimate surface free energy of metals. With an analytical charge density correction to the argument of the embedding energy of embedded atom method, an approach to improve the prediction for surface free energy is presented. This approach is applied to calculate the temperature dependent anisotropic surface energy of bulk nickel and surface energies of nickel nanoparticles, and the obtained results are in good agreement with available experimental data.

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1. Introduction

The knowledge of surface free energies of crystalline metals is of utmost importance for the understanding of a large number of basic and applied phenomena, such as equilibrium surface morphologies, surface reconstructions, faceting and nucleation [1,2]. Experimentally these quantities are notoriously difficult to measure due to such problems as surface defects and/or impurities [3–5], and results from different researchers often being in very poor agreement [5,6]. Furthermore experimental determination of surface free energy anisotropy is well known to be almost impossible [7], and most resulting measurements of surface free energies represent averages over many stable crystal face orientations. Finally, very little is known about the temperature dependence of the surface free energies of solids since most experimental data were obtained at temperature near the melting point [5].

Computational techniques such as molecular dynamics (MD) or Monte Carlo methods can complement experiment with the ability to simulate different surface morphologies of various systems obtaining important structural, dynamics, and thermodynamic properties. Unfortunately for some systems direct comparison with experiment was often hampered by the overly simplistic representation of bonding inherent in using empirical pair potentials [8]. Developments such as the embedded atom method (EAM) type potentials [9,10] provided a more realistic representation of

metallic bonding. However, most EAM potential sets have been developed using only experimental data from bulk materials or, if experimental data for surface were considered, they were not highly weighted in fitting. This is one reason why most EAM parametrizations do not perform well when used to quantitatively predict material surface properties where charge densities are significantly different from the central bulk region, and some EAM potentials underestimate surface energies of low index metallic faces by up to 50% [10–12].

The nonuniformity of charge density in lattice defects may be a dominant factor to determine the prediction accuracy of EAM. Webb and Grest [12] modified the electron density with the square of the charge density gradient ($\nabla\rho_i$). In terms of their approach, the predictions of bulk material properties are almost unchanged since the charge distribution in an isotropic environment is uniform, and inhomogeneity corrections are negligible, while in the case of surface, $|\nabla\rho_i| \neq 0$, the prediction results for liquid/vapor surface tension γ can be improved by adding this correction to the argument of the embedding energy related to the nonuniformity in the charge density. This approach is valid, however, it is difficult to calculate the gradient of charge density, and the determination of the parameters with a trial and error approach is computationally expensive.

In the present paper, by using the available data of surface energies and vacancy formation energy, a new solution for correcting the electron density and an analytical method for determining the related parameters are proposed. This approach is applied to calculate the temperature dependent anisotropic surface free energies of bulk nickel material and surface free energies of nickel

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nanoparticles at 0K, and the results show that correspondence between theoretical prediction and experimental results is found.

2. Theory and method

The surface free energy per area is calculated as [13,14]:

$$\gamma^{\text{area}} = \frac{G_{\text{slab}} - Ng_{\text{bulk}}}{A_1} \quad (1)$$

where G_{slab} is the total Gibbs free energy of a slab, N is the total number of atoms in the slab, g_{bulk} is the Gibbs free energy per bulk atom, and A_1 is the surface area of the slab. The Gibbs free energy at an arbitrary temperature can be obtained according to the Gibbs-Duhem equation [14–17]:

$$g(T) = T \left[\frac{g(T_0)}{T_0} - \int_{T_0}^T \frac{h(\tau)}{\tau^2} d\tau \right] \quad (2)$$

where T_0 is a predetermined reference temperature, $g(T_0)$ is the Gibbs free energy at T_0 , which is calculated by means of the coupling parameter formalism [14,17], $h(\tau)$ is the enthalpy which is first computed as a function of temperature T using constant-pressure MD simulations and it is fitted with a second-order polynomial in T , which allows an analytic integration in Eq. (2).

The interatomic potential of nickel is modeled by using the modified analytic embedded atom method (MAEAM) [18,19] in which the energy of an N -atom system is

$$E = \sum_{i=1}^N \left[F(\rho_i) + \frac{1}{2} \sum_{j \neq i} \phi(r_{ij}) + M(P_i) \right] \quad (3)$$

where $F(\rho_i)$ is the embedding energy to embed atom i in an electron density ρ_i [20], $\phi(r_{ij})$ is the pair potential as a function of the atomic distance r_{ij} [18,19], and $M(P_i)$ is the modified term [18,21,22], which describes the energy change caused by the nonspherical distribution of atoms and deviation from the linear superposition of atomic density. The functions of $F(\rho_i)$, $\phi(r_{ij})$, and $M(P_i)$ for fcc crystal configuration take the following forms:

$$F(\rho_i) = -F_0 \left[1 - n \ln \left(\frac{\rho_i}{\rho_e} \right) \right] \cdot \left(\frac{\rho_i}{\rho_e} \right)^n \quad (4)$$

$$\phi(r_{ij}) = k_{-1} e^{(r_1/r_{ij}-1)} + \sum_{i=0}^4 k_i e^{i(1-r_{ij}/r_1)} \quad (5)$$

$$M(P_i) = \alpha \left\{ 1 - \exp \left[-10^4 \left(\ln \left(\frac{P}{P_e} \right) \right)^2 \right] \right\} \quad (6)$$

$$\rho_i = \sum_{j \neq i} f(r_{ij}) \quad (7)$$

$$P_i = \sum f^2(r_{ij}) \quad (8)$$

$$f(r_{ij}) = \left(\frac{r_1}{r_{ij}} \right)^{4.7} \left(\frac{r_{ce} - r_{ij}}{r_{ce} - r_1} \right)^2 \quad (9)$$

where $f(r_{ij})$ is the electron density distribution function of an atom, ρ_i is the electron density induced at site i by all others in the system, and P_i is the second order item of electron density. ρ_e and P_e correspond to their equilibrium values at $T=0$ K, respectively. The pair potential function is truncated at a specific cutoff distance $r_c = r_3 + 0.75(r_4 - r_3)$, and $f(r)$ is truncated at $r_{ce} = r_4 + 0.75(r_5 - r_4)$. r_i is i th nearest neighbor distance. The model parameters are determined analytically by fitting the physical properties of nickel [18].

In order to improve the prediction effect of the MAEAM on the surface free energy, according to Eq. (1), the total energy of a slab

should increase by means of new MAEAM. Since surface charge densities are different from the bulk, the embedding energy and modification term which are both related to charge densities is considered to enlarge by adding corrections to the argument of them. Due to the contribution from the modification term being trivial, it is reasonable to neglect its effect. Instead of the square of gradient of charge density [12], $(\rho_b - \rho_i)^2$ is used to correct the argument of the embedding energy:

$$F(\rho_i) \rightarrow F[\rho_i + \beta(\rho_b - \rho_i)^2] \quad (10)$$

where ρ_b is the bulk value of electron density, β is an adjustable parameter. The surface free energy can be further improved by taking into account the fact that EAM is invariant under the following transformations:

$$F_c(\rho_i) = F[\rho_i + \beta(\rho_b - \rho_i)^2] + c[\rho_i + \beta(\rho_b - \rho_i)^2]/\rho_e, \quad (11)$$

$$\phi_c(r_{ij}) = \phi(r_{ij}) - 2cf(r_{ij})/\rho_e,$$

where c is an arbitrary constant.

3. Results and discussion

The parameters β and c can be adjusted based on the difference between calculated surface energy and the first-principles value. For example, the calculation result for Ni (100) surface energy based on the original MAEAM is 2.00 (J/m²), and the first-principles value for same system is 2.42 (J/m²) [23]. The deviation between the calculated and the first-principles value is taken as the objective quantity for the surface energy adjustment, which is used to build the equation to determine parameters β and c according to the embedding energy difference between after and before the correction for a surface atom,

$$F[\rho_i + \beta(\rho_e - \rho_i)^2] + c[\rho_i + \beta(\rho_e - \rho_i)^2]/\rho_e - [F(\rho_i) + c\rho_i/\rho_e] \approx 0.42 \text{ (J/m}^2\text{)}. \quad (12)$$

It should be pointed out that as the calculation of parameters β and c is carried out at $T=0$ K, ρ_b equals ρ_e (12.7642). In order to avoid the vacancy formation energy becoming significant due to introduction of parameters β and c , we restrict the unrelaxed vacancy formation energy E_{1v}^f to be less than or equal 1.84 eV (the experimental value is 1.6 eV [24]) while adjusting parameters β and c , that is

$$E_{1v}^f(\beta, c) = E'_t(\beta, c) - E_t + E_{\text{coh}} \approx 1.84 \text{ eV} \quad (13)$$

where $E'_t(\beta, c)$ is the total energy of the lattice in which there is a vacancy, E_t is the total energy of perfect crystal configurations and E_{coh} is the cohesive energy of a nickel atom. By solving Eqs. (12) and (13) numerically, the adjustable parameters β and c can be obtained. Considering the form of the embedding energy function, positive charge density corrections ($\beta > 0$) are expected to be preferred to avoid producing the negative argument of the embedding energy $F(\rho)$ in extreme cases. Finally, we obtain $c=8$ eV, and $\beta=0.017$, which merely leads to a small relative change of 3.5% in the charge densities of surface site atoms, where the unrelaxed electron density ρ_i of the first layer surface site atoms is 8.5486. Fig. 1 shows the behavior of the embedding energy $F_c(\rho_i)$ as a function of relative change densities ρ_i/ρ_e . Due to large rate of change of embedding energy with relative change densities in the case of $c=8$ eV, slight change in the electron density will cause apparent increase in embedding energy.

Using MD simulation with the MAEAM potentials based on Eq. (11) and the results for β and c , the relaxed surface energy for Ni (100) surface and the vacancy formation energy are calculated to be 2.33 (J/m²) and 1.68 eV respectively, which are somewhat smaller than the corresponding objective value of 2.42 (J/m²) and

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