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Monte Carlo simulation of melting and lattice relaxation of the (111) surface of silver

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ABSTRACT

It is experimentally observed and theoretically proved that the distance between the topmost layers of a metal surface has a contraction. However, well-known potentials such as Lennard-Jones and Morse potentials lead to an expansion of the surface inter-layer distance. Such simple potentials therefore cannot be used to study metal surface relaxation. In this paper, extensive Monte Carlo simulations are used to study the silver (111) surface with both the Gupta potential (GP) and the Embedded Atom Method (EAM) potential. Our results of the lattice relaxation at the (111) surface of silver show indeed a contraction for both potentials at low temperatures in agreement with experiments and early theories. However at higher temperatures, the EAM potential yields a surface melting at ≃ 700 K very low with respect to the experimental bulk melting at ≃ 1235 K while the GP yields a surface melting at ≃ 1000 K closer to the bulk one. In addition, we observe with the EAM potential an anomalous thermal expansion, i. e. the surface contraction becomes a surface dilatation with respect to the bulk, at ≃ 900 K. The Gupta potential does not show this behavior. We compare our results with different experimental and numerical results.

1. Introduction

It is well known that surface atoms of a material have a behavior different from that of bulk atoms, mainly because of the lack of neighbors and the surface geometry. Different kinds of surface behavior can occur according to the nature of the material and the surface orientation. The case of metallic materials has been well studied theoretically [1–7] and by means of different experimental techniques [8–10].

The contraction of the lattice spacing is experimentally observed by Medium Energy Ion Backscattering (MEIS) [8], Low-Energy Electron Diffraction (LEED) [9] or X-ray scattering [11]. Other methods such as elastic He scattering and electron energy-loss spectroscopy have also been used. In a theoretical point of view, Gupta has shown analytically that for classical pairwise potentials (Lennard-Jones, Morse, …), inter-layer distance near the surface has an expansion. He has also shown that the Tight-Binding-Potential (TBP) and the so-called Gupta potential (GP) lead to a contraction of inter-layer distance at metallic surfaces.

Despite the important number of experimental and theoretical techniques used to observe this phenomenon, there exists an unsolved question on how the contraction evolves with increasing temperature. There are two contradictory answers in the literature: X-ray scattering [11] and LEED [9] as well as molecular dynamics (MD) simulations using the Embedded Atom Method (EAM) [7,12] show the surface inter-layer distance always smaller than the bulk one at the same temperature, namely surface is contracted, whereas MEIS experiments [8] and ab-initio density-functional theory (DFT) calculations [13] show an anomalous thermal expansion of the surface at some temperature below the bulk melt.

Facing this long-standing unsolved question, we wanted to carry out a Monte Carlo (MC) study in an attempt to answer that question. To our knowledge, there are no MC simulations in literature so far about this subject, although some MC simulations have been used to reproduce experimental patterns such as surface blocking pattern during scattering process [see Ref. [10] for the Pb (110) surface]. Given a tremendous number of numerical studies on surface problems, it is surprising that no MC simulation has been performed so far to see the variation of the surface inter-layer distance.

The purpose of this paper is thus to investigate by MC simulation the variation of the lattice spacing between the topmost layers of the (111) silver surface versus temperature.

In order to simulate such a behavior as accurately as possible, we have considered potentials which describe as well as possible the material. The EAM potential is often used in MD simulations and especially for the Ag (111) surface [7,12,14]. Working with this potential allows us to compare our results with other numerical studies using the same potential. Furthermore, the EAM potential reproduces accurately the bulk melting temperature of Ag with MC simulation [15]. On the other hand, the Gupta potential describes well the surface and cluster behaviors [16–20]. The melting temperature of bulk Ag is also well reproduced with this potential. That was the reason why the two potentials GP and EAM have been used since many years to simulate silver material and other metallic crystals. However, as will be seen below, the two potentials, although yielding the same

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result for low-temperature surface contraction, give different results at higher temperature concerning the surface contraction and the surface melting.

In Section 2 we recall essential properties of the two potentials with their sets of parameters and we briefly describe our algorithm. The results obtained by our computation are shown in Section 3. Concluding remarks are given in Section 4.

2. Model and Monte Carlo method

2.1. Potentials

2.1.1. Gupta potential

In computer simulation of metals, the Gupta potential is one of the most used semi-empirical potentials. There is a multiple reason for this success but the main ones are the accuracy of its results for metals and its easy and quick implementation. The Gupta potential is derived from the Gupta's expression of the cohesive energy of the bulk material and is based on the second-moment approximation of the electron density of states in the tight-binding theory. It includes implicitly some many-body interactions. The expression of the potential of an atom at the position $\vec{r}_i$ is the following:

$$V\left(\vec{r}_i\right) = E_0\left[A\sum_{j\neq i}^{n} e^{-p\left(\frac{r_{ij}}{r_0}-1\right)} - \sqrt{\sum_{j\neq i}^{N} e^{-2q\left(\frac{r_{ij}}{r_0}-1\right)}}\right] \quad (1)$$

where A is a constant given in eV, r_0 the equilibrium nearest-neighbor (NN) distance in the bulk metal, p the repulsive interaction range and q the attractive one. $r_{ij} = \left|\vec{r}_i - \vec{r}_j\right|$ is the distance between the atoms i and j and E_0 an energy constant given by the fit with the melting temperature of bulk Ag. The first sum runs over a cluster of n atoms surrounding atom i, and the sum in the square root runs over all atoms. In Eq. (1), the first part is a Born-Mayer pairwise repulsion energy term and the second part is the many-body attractive contribution.

The parameters used in this work are reported in Table 1.

2.1.2. EAM potential

Several authors [15,22–24] have proposed a method based on density-functional ideas called EAM. We used a version of the EAM potential given in Ref. [24]. The parameters of the EAM potential used in this work for silver are reported in Table 2. In the EAM potential, the total potential energy is given by:

$$E_p = \sum_i \left[F_i(\rho_i) + \frac{1}{2}\sum_{j\neq i}\phi\left(r_{ij}\right)\right] \quad (2)$$

where ϕ_{ij} represents the pair energy between the two atoms i and j at the distance r_{ij}. F_i is the embedding energy function which represents the energy to embed an atom into a local site with electron density ρ_i. The electron density ρ_i has the following expression:

$$\rho_i = \sum_{j\neq i} f\left(r_{ij}\right) \quad (3)$$

Table 1
Gupta parameters for silver.

Parameter	Value[a]
A (eV)	0.09944
p	10.12
q	3.37
r_0(Å)	2.892
E_0	2.52[b]

[a] Reference [17].
[b] Fitted with experimental bulk melting temperature [21].

Table 2
EAM parameters for silver.

Parameter	Value[a]	Parameter	Value
r_e	2.891814	F_{n_1}	−0.221025
f_e	1.106232	F_{n_2}	0.541558
ρ_e	15.539255	F_{n_3}	−0.967036
α	7.944536	F_0	−1.75
β	4.237086	F_1	0
A	0.266074	F_2	0.983967
B	0.386272	F_3	0.520904
κ	0.425351	η	1.149461
λ	0.850703	F_e	−1.751274
F_{n_0}	−1.729619		

[a] Reference [24]

with

$$f\left(r_{ij}\right) = \frac{f_e exp\left[-\beta\left(\frac{r_{ij}}{r_e}-1\right)\right]}{1+\left(\frac{r_{ij}}{r_e}-\lambda\right)^{20}} \quad (4)$$

where r_e, f_e, β and λ are the constant parameters which are given in Table 2. The embedding function has the following form:

$$F(\rho) = \begin{cases} \sum_{i=0}^{3} F_{n_i}\left(\frac{\rho}{\rho_n}-1\right)^i & \rho < 0.85\rho_e, \\ \sum_{i=0}^{3} F_i\left(\frac{\rho}{\rho_n}-1\right)^i & 0.85\rho_e \le \rho < 1.15\rho_e, \\ F_e\left[1-ln\left(\frac{\rho}{\rho_e}\right)^{\eta}\right]\left(\frac{\rho}{\rho_e}\right)^{\eta} & 1.15\rho_e \le \rho \end{cases}. \quad (5)$$

The pair energy expression between the atoms i and j is:

$$\phi\left(r_{ij}\right) = \frac{Aexp\left[-\alpha\left(\frac{r_{ij}}{r_e}-1\right)\right]}{1+\left(\frac{r_{ij}}{r_e}-\kappa\right)^{20}} - \frac{Bexp\left[-\beta\left(\frac{r_{ij}}{r_e}-1\right)\right]}{1+\left(\frac{r_{ij}}{r_e}-\lambda\right)^{20}}. \quad (6)$$

All constant parameters in the above expressions such as F_{n_i} etc. are listed in Table 2. Note that MC simulations using EAM potential yield the bulk melting temperature at 1170 K for Ag [15] which is to be compared to the experimental value of 1235 K [25].

2.2. The algorithm

We have first performed the bulk simulations using the *NPT* ensemble. A MC step consists of moving all atoms, each with an arbitrary displacement, and changing the system volume by a small amount. The transition probability to the new state is $exp\left(-\frac{W}{k_B T}\right)$ where

$$W = P(V_{new}-V_{old}) + (U_{new}-U_{old}) + Nk_B T\ln\left(\frac{V_{old}}{V_{new}}\right) \quad (7)$$

where P is the pressure which is set to zero here (constant pressure), V_{old} and V_{new} are the old and new system volumes, and U_{old} and U_{new} the old and new system energies.

One of the most difficult tasks in melting simulations is the application of the periodic boundary conditions. This is due to the random positions of atoms at the crystal boundaries. In order to save CPU time and without loosing accuracy, the following actions are taken:

i. each atom has a list of neighbors up to a distance r_d longer than the potential cutoff distance r_c. To establish the list for the first time, we have to calculate all distances and we select neighbors at $r \le r_d$. The fact to choose $r_d > r_c$ is to ensure that for