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On the computational calculation of adatom, vacancy and early stage surface nucleation island free energies on the (1 1 1) copper surface

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Abstract

Previously, in an earlier publication we developed a general method for calculating the free energy of surfaces with an arbitrary number of excess surface atoms. In subsequent work we showed how these surfaces can be combined to produce an ad hoc grand canonical ensemble of surfaces, and constructed such an ensemble for the disordered semi-hexagonal reconstructed Glue Model Au(1 0 0) system. In this work we use the previously developed methods to calculate and construct an ensemble of surfaces for a model Embedded Atom Method Cu(1 1 1) surface and show how from this ensemble, one can calculate 'exact' formation free energies, and hence equilibrium surface concentrations of adatom and vacancy monomers, and clustered adatom and vacancy dimers, trimers and quadrimers, which form early stage 2D island formations. Results for the model Cu(1 1 1) system at 1000 K show that singular vacancies are more than twice as likely as adatoms to populate the surface. The final formation free energies at 1000 K were found to be 0.60 eV and 0.73 eV for the vacancy and adatom respectively.

Keywords: Surface defects; Free energies; Surface thermodynamics; Molecular dynamics

1. Introduction

Equilibrium surface adatom and vacancy formation free energies and hence concentrations play a critical role in influencing properties such as, surface diffusion coefficients, island nucleation rates and surface atomic vibrational behaviour-all of which in turn influences crystal growth phenomena. In the last decade we have seen advances, both theoretical and experimental in the study of growth phenomena and associated surface thermodynamics, yet fundamental system quantities such as formation free energies cannot be obtained

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directly from experiment, instead they must be determined indirectly using approximate theories in conjunction with experimental spatial and temporal statistics; and hence partly using the very properties one is hoping to predict.

Molecular dynamic (MD) can aid researchers studying growth phenomena by providing detailed structural and dynamic system statistics from which valuable insights into the physics of the problem can be obtained. More importantly it provides a realistic model system on which theories can be tested. Alternatively, if the intermolecular potentials are accurate enough, MD can be used as a definitive tool to predict certain phenomena. For the study of crystal growth processes, all such uses of MD require the basic ability to obtain fundamental thermodynamic quantities such as the formation free energies mentioned above.

Attempts at finding such free energies, can at present be categorised into three different approaches. The first approach termed 'direct simulation' is where the frequency of observation of certain *well defined* structures (normally defined by order parameters) can be related to the free energy of formation for those structures. Into this category we can place related methods such as the Monte Carlo (MC) umbrella sampling methods including recent developments [1,2], and the method of Grand canonical ensemble MC simulation (and recently Grand canonical MD). The second approach involves the harmonic approximation where vibrational frequencies can be used to estimate entropic contributions [3–5].

The third approach (firstly developed by others [6–9]), is to construct thermodynamically reversible paths between two states in question, and then to integrate over them using λ-integration [10] (or alternatively using other methods such as for example Bennett's method [11]) finding the work needed to take the system from the bulk state to the surface state. The approach has been extensively tested and further developed recently for unreconstructed surfaces, i.e. those exhibiting roughly zero excess surface number [12–14]. Furthermore recent limited progress in finding methods capable of calculating the free energies of various surface defects including, low temperature FCC(110) (1×2) missing row reconstructed (MRR) surfaces, stepped surfaces, and adatom–vacancy pairs has been made [15], but the method was limited to surfaces and surface structures which can be formed via the exchange of atoms between the opposite sides of a slab cell with the limitation that the total simulation slab has a constant number of atoms.

In a further development of this approach we created a general path for calculating the surface free energies of surfaces with arbitrary excess surface atom numbers based on a technique termed constrained fluid λ-integration [16–18]. In subsequent work we showed how surfaces with differing excess surface atom numbers can be combined to produce an ad hoc grand canonical ensemble of surfaces, and then constructed such an ensemble for the disordered semi-hexagonal reconstructed Glue model Au(100) surface [19]. In the present work we use the previously developed methods to construct an ensemble of surfaces for a model embedded atom method (EAM) Cu(111) surface and show how, from this ensemble, one can calculate the 'exact' formation free energies, and equilibrium surface concentrations of adatoms, vacancies and early stage nucleation island formations.

The constructed ensemble can be used to calculate such properties as those mentioned above, i.e., surface diffusion coefficients, island nucleation rates and surface atomic vibrational behaviour. Such calculations would provide the most accurate representation of a model EAM Cu(111) surface to date. Our aim here is to demonstrate the methodology and exemplify conceptual problems that arise when attempting to calculate the free energy of surface *defects* using the previously developed method for calculating surface free energies. The methodology developed here can be applied to any surface defects and as such completes the set of methods required for the computational study of equilibrium surface phenomena.

2. Methods

We have detailed elsewhere the λ-integration methods used to obtain the free energy of surfaces with differing excess atomic numbers [18]. Briefly, the method involves finding the work done in