

Atomistic Simulations of Wetting and Spreading in Metal Systems

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ABSTRACT

Using molecular dynamics (MD) simulations, we examine wetting and spreading in metallic systems as described by the embedded atom method (EAM). We first discuss a common shortcoming of EAM potentials for describing metal surfaces and a theoretical correction to this problem. This correction has the ability to bring model predictions for surface properties into agreement with experiment with little or no effect on most material property predictions used in the original potential fitting procedure.

We wish to examine wetting and spreading in a case where alloying is expected and one where the metals are considered relatively bulk immiscible. We choose Ag(l) on Cu for the former case and Pb(l) on Cu for the latter. We briefly describe our efforts to parameterize the Pb/Cu EAM interaction using relevant experimental data and *ab initio* calculations. We then present preliminary results for the case of Ag(l) on Cu, focusing on the shape of the reaction zone and its dependence on temperature.

Keywords: metals, reactive wetting, simulation, EAM.

1 INTRODUCTION

A better understanding of bonding between liquid and solid metals can directly impact a range of technology including microelectronics, solder and braze materials, and cold-spray bonding. Studying metal surfaces is also motivated by the array of interesting diffusion mechanisms, growth behavior, surface phase formation, and reconstructions that are observed experimentally. Device miniaturization, typified by shrinking microcircuits and micro electromechanical systems, is challenging traditional notions about metallization and joining. Therefore, a more detailed, atomistic understanding of metal interfaces must be established. Advanced experimental techniques are being applied to this problem^[1] and are able to observe behavior at increasingly smaller length scales, with nearly atomistic resolution possible in many systems. However, experimental data are subject to interpretation which, in certain instances, can benefit greatly from guidance provided via modeling.

A collection of *ab initio* modeling methods exist which are ideally suited to studying metal surface properties including adatom formation energy, step and kink energy, adsorbate interaction energy, diffusion mechanisms, and

other properties^[2] where the system of interest need not be represented by too large a unit cell. While the specific size limitation is dependent upon the method and implementation, certain problems clearly are outside the realm of *ab initio* calculations and are better suited to empirical atomistic simulations.

An example calculation quite relevant to joining and metallization is simulating a liquid microdroplet on a solid substrate where one is interested in following the dynamics of interface formation over some hundreds of picoseconds or longer. For good contacts to be formed between liquid and solid metals the liquid must wet and spread on the solid, perhaps facilitated by interfacial reactions. The size and time scales accessible to empirical atomistic simulations allow such a system to be modeled with a high level of chemical detail. We wish to examine the differences in this process for metal systems where significant interfacial mixing is expected and those where it is not. The systems we are studying are Ag(l) on Cu to represent the former and Pb(l) on Cu for the latter. We base these selections on the relative bulk miscibilities^[3] for the two systems. Herein, we present results from modeling metal interfaces with the EAM along with a brief discussion of our work parameterizing the Pb/Cu EAM interaction. We then present results from microdroplet simulations of Ag(l) on Cu.

2 MD SIMULATIONS

The EAM is a semi-empirical model for metals incorporating a many-body contribution into the binding energy expression for an atomic system^[4],

$$E_s = \sum_{i=1,N} [F_i(\rho_i) + \frac{1}{2} \sum_{j \neq i} \phi_{ij}(R_{ij})]. \quad (1)$$

E_s is the energy of a system of N atoms, $F_i(\rho_i)$ is the energy associated with embedding an atom i into a background electron density ρ_i , and $\phi_{ij}(R_{ij})$ is a pair interaction between atoms i and j which is a function of their separation distance R_{ij} . The local electron density for an atom i is

$$\rho_i = \sum_{j \neq i} \rho_{j,a}(R_{ij}) \quad (2)$$

where $\rho_{j,a}(R_{ij})$ is the atomic electron density function for atom j . In the standard EAM, $\rho_{i,a}(R_{ij})$ is a function of separation distance only. The modified EAM incorporates angular dependence into $\rho_{i,a}$ but we restrict our present

consideration to standard EAM. Formulating an EAM potential for a given metal consists, then, of generating $F_i(\rho_i)$, $\phi_{ij}(R_{ij})$, and $\rho_{i,a}(R_{ij})$. Reasonable mathematical forms are typically adopted and the resultant parameters are fit to existing experimental data for the metal. In more recent years, including additional properties calculated via ab initio methods has considerably expanded fitting databases. This is especially useful for formulating interaction potentials in alloy systems where experimental data are often quite limited^[5].

In addition to utilizing a more physically intuitive representation of bonding, the EAM is a very attractive model for simulating metals since there exists a large collection of interatomic potentials. It is only marginally more difficult to implement than a pair potential and, as such, has been used in a vast number of studies of metallic properties^[4]. While many instances exist demonstrating the accuracy of EAM models when compared to experiment, a common shortcoming encountered in their use is in predicting surface energetics. In a number of examples, EAM potentials underpredict solid free surface energy quite significantly^[4]. Figure 1 shows data for liquid vapor surface tension γ versus temperature T for a collection of metals – Al, Ni, Cu, Ag, and Au.

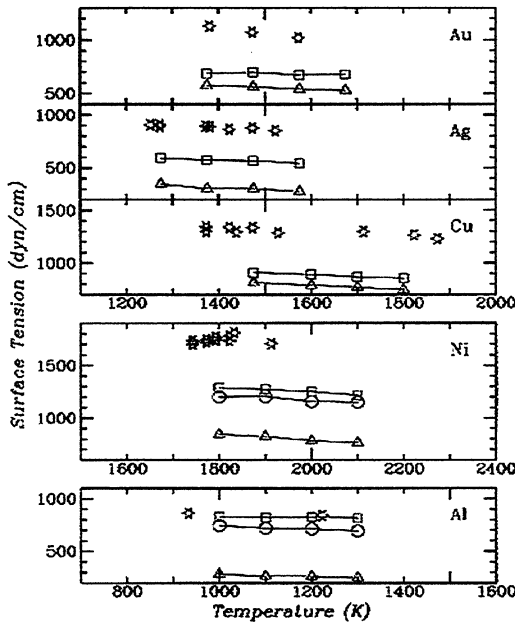


Figure 1: Surface tension versus temperature for a collection of metals as predicted by three EAM models – FBD (triangles), MFMP (circles), and VC (squares). Experimental data for each metal are shown with stars^[3].

Experimental data are shown along with γ predictions from different EAM models for each metal (γ was calculated employing the mechanical definition^[6]). The models are due to Foiles, Baskes, and Daw (FBD), Voter and Chen (VC), and Mishin *et al* (MFMP)^[7]. In nearly all instances

model predictions are under experiment by a considerable amount (Al in the VC model is a notable exception). All models do correctly predict the ordering of the metals by γ when compared to experiment. In addition, γ shows little dependence on T within the models, in agreement with experiment. Qualitatively, then, the EAM can perform quite well for surface properties but there exists a fairly consistent quantitative limitation. Because the problem we wish to study is very surface intensive, such quantitative inaccuracy is of concern. However, the ability to readily perform large-scale MD simulations within the EAM and the chemical level of detail one can derive from such simulations motivates us to seek a solution to this.

2.1 Charge Gradient Corrections

One solution is to create new potentials where surface properties are more heavily weighted in the fitting but this risks achieving less accuracy for bulk properties and does not allow one to make use of the large set of existing potentials. An alternate solution has been suggested^[8] which recognizes that, in the original development of the EAM, any dependence of system energy upon gradients in the background electron density was ignored. The expression for the embedding energy can be rewritten

$$F_i(\rho_i) \rightarrow F_i(\rho_i + \alpha \nabla^2 \rho_i + \beta |\nabla \rho_i|^2) \quad (3)$$

where $\alpha \nabla^2 \rho_i$ and $\beta |\nabla \rho_i|^2$ are the lowest order terms in charge inhomogeneity upon which the embedding energy can be shown to depend. Since charge gradients are, on average, negligible in bulk environments the values of α and β can be fit to surface properties without disturbing most properties used in fitting EAM potentials. This correction can be augmented by exploiting the invariance of EAM potentials to various linear transformations in ρ . While the details of applying this method to correcting surface energetic predictions are presented elsewhere^[9], we show in Figure 2 results for γ with varying β for both Ni and Au (we have chosen $\alpha = 0$ for the present study). The details of how one transforms the functions to achieve better results from applying charge gradient corrections relate to the specific shape of the embedding function. Similarly, the overall success one can achieve with or without transformation depends on specific features of the original parameterization^[9]. Here we wish to simply highlight that, while many EAM potentials demonstrate poor quantitative accuracy for surface energy predictions, this can be corrected for some models. It is also important to point out that similar behavior is experienced with predictions of solid free surface energy using this correction. Furthermore, the improvement in surface properties comes at relatively little expense in the accuracy of the potential for other properties where charge gradients will arise (vacancies, diatomic molecule configurations, etc.).

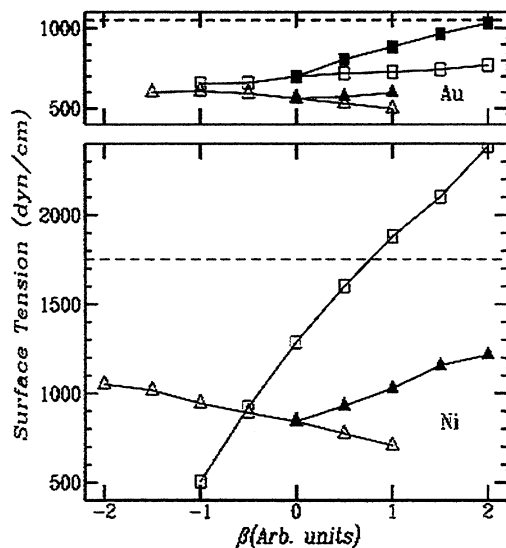


Figure 2: Surface tension versus β for FBD (triangles) and VC (squares) models of Ni ($T = 1800\text{K}$) and Au ($T = 1475$) using the original (open symbols) EAM functions as well as transformed functions (closed). Horizontal dashed lines show the experimental value of surface tension at the relevant T .

2.2 Wetting Simulations

We wish to study the process of wetting and spreading for a case where the two metals involved are miscible and one where they are not. For the former, which we represent with Ag(l) on Cu, significant interfacial exchange or alloying is expected while for the latter, represented by Pb(l) on Cu, it is not. We wish to compare the process of wetting in the two systems at relevant temperatures with regard to the melting points of the liquids. We also wish to examine the structure of the interfacial region and its dependence, in each system, upon temperature. Wetting has been simulated for systems described via the Lennard-Jones potential as well as the EAM previously^[10]. However, for the former, it is well known that pair potentials do not describe real metals very accurately. For the latter (and in general for much of the wetting simulations literature), the substrate is held static which prevents any attempt to describe systems where significant intermixing will occur during the wetting process. Even in the absence of intermixing, surface alloy phases may form and models using static substrates capture none of this behavior.

Briefly, our simulation methodology involves equilibrating a Cu bulk (periodic boundary conditions in 3 directions) in the NPT ensemble at the T of interest. A Nose-Hoover thermostat and a 1 fs timestep are used. After equilibrating the bulk, periodic boundary conditions are removed in one direction to generate a surface which is equilibrated in the NVT ensemble. This sets the lateral

dimensions of the system to maintain the equilibrium lattice spacing in the bulk. A surface thermostating method is then used where the Cu surface slab is divided into three regions separated by planes parallel to the surface. The first region (furthest from the surface to study) is slightly thicker than two times the interaction cutoff length (R_c) and atoms therein are fixed to their position for all subsequent calculations. The second region, between the fixed atoms and the surface region, is 4-5 R_c in thickness. Atoms therein are mobile and thermostated in the same way as in the bulk simulation. The third, or surface, region varies in thickness depending upon the degree of interfacial mixing for the system simulated. The surface region must be thick enough that the intermixing process is not affected by the termination of the simulation cell far from the Cu surface. Despite having knowledge of bulk miscibility, we cannot know how thick this region must be and it is probable that it will change with T . Results presented herein employ a surface region with an approximate thickness of 35 angstroms ($\sim 7 R_c$). Even for short simulation duration, it will be seen that this is not sufficiently thick above some T for Ag(l)/Cu, motivating our current simulations on much larger systems. For the liquid drops, a spherical section of atoms was removed from a bulk liquid that had been equilibrated in the NPT ensemble. The drop was then equilibrated in free space (NVT ensemble) before being joined in a simulation cell with the Cu surface. Subsequent calculations for atoms in the drop (as well as the surface region of Cu) are performed without an explicit thermostat (though they are coupled to a thermostat via interactions with atoms in the second region of the Cu bulk). In the present simulations, the initial drop radius was 30 angstroms and the substrate was 120 angstroms square.

It is obvious these studies require EAM potentials to describe the pure metals as well as the interaction between different metals. What is not known *a priori* is to what degree the results from simulations depend upon the specific model chosen for the interactions. It is also of interest to establish some idea of how strongly results from microdroplet wetting simulations depend upon the accuracy of the underlying potentials for predicting surface energetics. For Ag(l) on Cu, multiple models exist describing the binary system and our future work will compare wetting results from two of them. We will also compare wetting results obtained using charge gradient corrections to results from models without any correction for surface energetic predictions. In section 3, we present preliminary microdroplet simulation results for the FBD model of Ag/Cu.

For Pb/Cu, we are using the potential of Ercolessi *et al* to describe pure Pb^[11] (we will call this FE Pb). We are not aware of an EAM potential describing the interaction between Cu and FE Pb. Since surface energetic predictions are more accurate from VC Cu, we wish to develop an interaction, $\phi_{ij}(R_{ij})$, for VC Cu and FE Pb. Briefly the methodology we are using to do this is similar to what is described in [5] for formulating an interaction between Al

and Pb. One set of data we wish our Cu/Pb interaction potential to reproduce fairly accurately are the transition, or roughening, temperatures of the various submonolayer coverage surface phases of Pb on Cu that are observed experimentally. Our future work will apply our EAM potential by performing the same simulations as we are doing for Ag(l) on Cu.

3 WETTING RESULTS

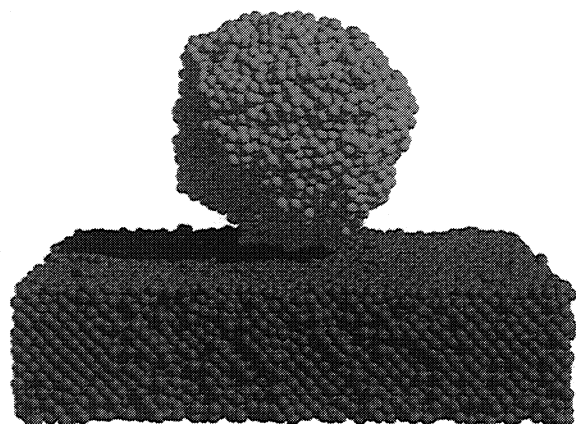


Figure 3: Snapshot showing initial configuration from a microdroplet wetting simulation of Ag(l) on Cu. Only the surface region (see text) of the Cu substrate is shown.

Figure 3 shows the starting configuration for the Ag drop above the Cu substrate. Short simulations (100 ps) were performed for two state points: 1) the substrate temperature ($T = 1000\text{K}$) was lower than the melting point of the drop ($T_m \cong 1225\text{K}$) and 2) the substrate T was equal to the molten drop ($T = 1275\text{K}$). Figure 4 shows cross sections through the middle of the simulation cell at the end of the simulations. The difference in the amount of intermixing for the two temperatures is obvious where for $T = 1275\text{K}$ there is a reaction zone “lens” which has formed while for $T = 1000\text{K}$ this is not so. While the Ag drop begins to wet the Cu surface, the T of the substrate is low enough that the drop begins to solidify, greatly slowing wetting and interfacial mixing. It can be seen at $T = 1275\text{K}$ that Ag is penetrating into the substrate deeply enough to be concerned that the surface region may not be sufficiently thick. Considering the phase diagram for Cu/Ag, it would be expected at this T that they would completely mix, given sufficient time. What is perhaps more interesting is how the shape of the reaction zone depends upon the degree of undercooling when the substrate T is lowered below T_m of the drop. Even for those simulations, we feel thicker substrates are necessary.

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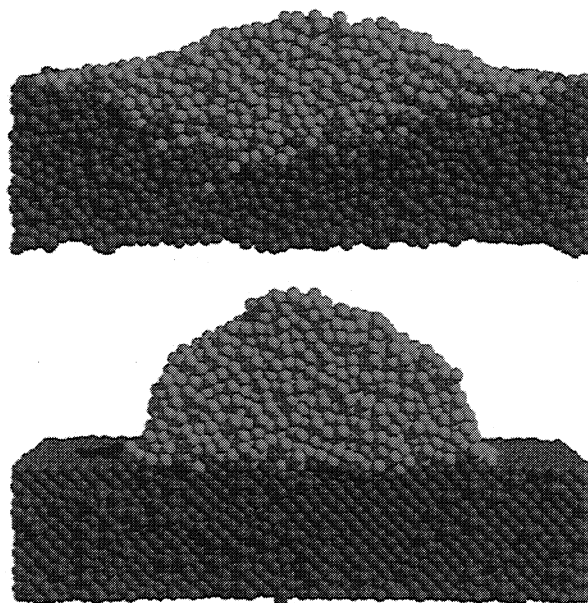


Figure 4: Snapshots showing final configuration after 100 ps of MD for substrate $T = 1000\text{K}$ (bottom) and 1275K (top).

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