

Viewpoint Paper

# Approaches to atomistic triple-line properties from first-principles

Adham Hashibon\* and Christian Elsässer

*Fraunhofer-Institut für Werkstoffmechanik IWM, Wöhlerstraße 11, D-79108 Freiburg, Germany*

*Institut für Zuverlässigkeit von Bauteilen und Systemen, Karlsruhe Institute of Technology, Kaiserstraße 12, 76131 Karlsruhe, Germany*

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**Abstract**—Different approaches to study wetting and adhesion by applying density-functional theory (DFT) methods are highlighted. The ab initio thermodynamics method is used to demonstrate the link between the calculated work of separation and the work of adhesion and wetting angles from sessile-drop measurements. An approach to extend DFT calculations to the case of large-scale interfaces relevant for wetting systems is also discussed.

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**Keywords:** Ab initio electron theory; Wetting; Interface structure

## 1. Introduction

Wetting and adhesion at metal–metal and metal–ceramic interfaces play a significant role in many technological processes, such as brazing, lubrication, mold-casting and thin-film coatings. The ability to control wetting and adhesion requires a fundamental understanding of the atomistic and electronic structures of the interfaces as a function of morphology, chemical or physisorption of segregates, and of various environmental variables, such as temperature and oxidizing atmosphere. In a wetting system, particularly near the triple-line, intricate heterophase interfaces are formed between liquid, solid and vapor phases of dissimilar materials, which may additionally include new reaction products [1,2]. The bonding at the interfaces is therefore complex and requires an atomistic modeling approach capable of accurately describing the ionic or metallic interactions in each of the phases separately, in addition to the mixtures of covalent, metallic and ionic bonding in the interface region, as, for example, in the case of metal–ceramic interfaces.

First-principles density-functional theory (DFT) [3,4] can accurately describe the complex bonding at the interface. In particular, it accounts for chemical interactions with segregated impurities, which are important for the study of reactive wetting systems. It also enables

accurate estimation of the adhesion at the interfaces, which is strongly related to wetting and triple-line properties.

In this viewpoint paper, we shall discuss the connection between experimental measurements of contact angle and work of adhesion and the theoretical calculation of work separation, and we highlight the various approaches to study wetting behavior based on DFT methods.

## 2. Wetting and adhesion

The experimental study of high-temperature adhesion relies on the measurement of the wetting angle in a sessile-drop set-up [5], as shown schematically in Figure 1(a), where measurements of the contact angle,  $\theta$ , and of the liquid film surface energy,  $\gamma_{lv}$ , are combined to give the thermodynamic work of adhesion,  $W_{ad}$ , from the Young–Dupré equation:

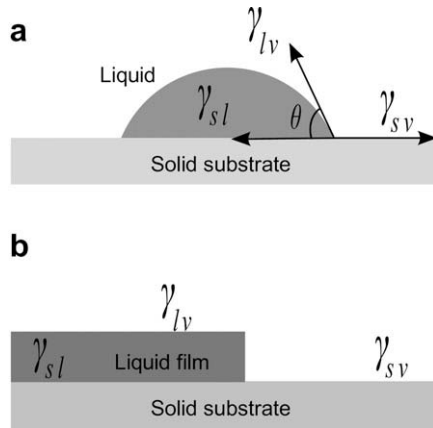
$$W_{ad} = \gamma_{lv}(1 + \cos \theta) \quad (1)$$

Furthermore, the work of adhesion, which is defined as the free energy change per unit area after separating the interface reversibly to create two surfaces, may be expressed by the Dupré equation:

$$W_{ad} = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} \quad (2)$$

where  $\gamma_{sv}$ ,  $\gamma_{lv}$  and  $\gamma_{sl}$  are the solid–vapor, liquid–vapor and solid–liquid interface energies, respectively. It is assumed in Eq. (2) that all interfaces are in thermodynamic

\* Corresponding author. Address: Fraunhofer-Institut für Werkstoffmechanik IWM, Wöhlerstraße 11, D-79108 Freiburg, Germany; e-mail: [adham.hashibon@iwm.fraunhofer.de](mailto:adham.hashibon@iwm.fraunhofer.de)



**Figure 1.** A schematic illustration of partial wetting of a liquid-drop on a solid substrate (a), and complete wetting (b).

equilibrium. From Eqs. (1 and 2) it is obvious that better wettability of the solid by the liquid is achieved by better adhesion at the interface, which requires in turn large free surface energies and small interface energies.

In the last two decades numerous studies have utilized DFT methods to investigate the nature of bonding and adhesion as a function of crystallographic orientation and interface and surface chemistry (for recent reviews, see, e.g., Refs. [6,7]). One should note, however, that in a DFT calculation a different but related quantity to  $W_{ad}$  is normally calculated, namely the ideal work of separation,  $W_{sep}$  [8]. The ideal work of separation is defined similarly to Eq. (2), but without allowing the free surfaces to exchange material with the environment, i.e. no adsorption or desorption of oxygen or other atoms are taken into account.

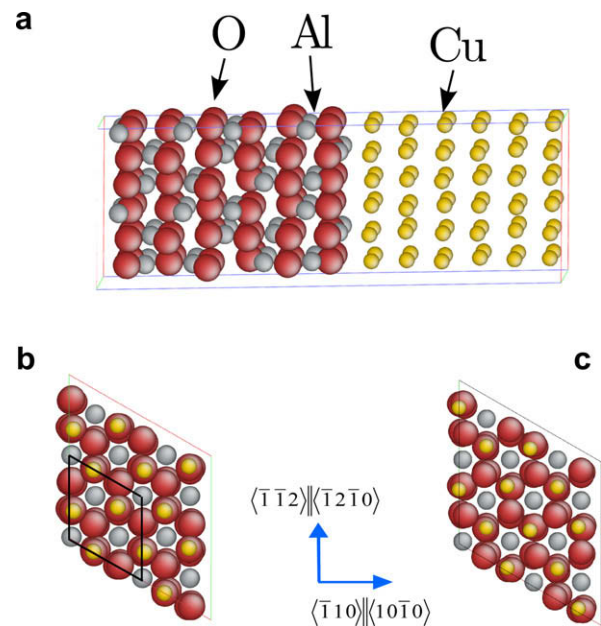
The work of separation as defined above gives a measure of the mechanical strength of the interface. It may be argued that  $W_{sep}$  is appropriate for studying fracture [7], where the cleaved surfaces during fast crack propagation are assumed not to be substantially equilibrated. Nevertheless, as noted by Finnis [8], the work of separation will always exceed the work of adhesion due to dissipative processes. Hence it may still be used to estimate the relative adhesion of interfaces, thus it is a useful quantity to know also for investigating wetting behavior.

## 2.1. Adhesion and wetting in metal/ceramic interfaces

As an example of the correlation between wetting behavior and adhesion, we consider the case of the Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> system, which, as a model case for metal–ceramic composites, has been subject to extensive experimental studies of electronic, mechanical and thermal properties [9–12] and of wetting behavior [13–20]. It has also been subject to theoretical DFT studies of adhesion and bonding [16,21–25]. The experimental results indicated that abrupt interfaces with two preferred orientation relationships [10–12], in both of which the Cu(111) planes are parallel to the close-packed  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) planes, are formed. Despite the large lattice mismatches, of +9% and –6% in the two observed orientations, incoherent interfaces with no misfit dislocations were observed.

DFT calculations are computationally intensive and therefore limited to small systems. Incoherent interfaces pose a challenge to DFT modeling, since large supercells are required to fit a commensurate interface model, which does not include residual misfit strains due to the periodic boundary conditions. A different approach is therefore taken, in which the metal slab is strained to fit the ceramic substrate. Since the ceramic elastic modulus is much larger, it is assumed that it will not deform under strain. In this manner, small supercell models are generated which are amenable to DFT calculations, and allow investigation of the adhesion and local bonding characteristic of a particular region in the system. The different atomic environments at the incoherent interface are accounted for by considering different translation states of the metal slab relative to the ceramic slab in the supercell, as shown in Figure 2. By calculating the ideal work of separation for each of these high-symmetry translation states and for different possible terminations of the interface, which for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) are O-terminated (O-rich), double Al-terminated (Al-rich) or single Al-terminated (stoichiometric) interfaces, an estimate of the bonding and adhesion for each of the environments can be obtained.

The first-principles DFT calculations conducted by the authors [23,25] using the mixed-basis pseudopotential method [26–29] showed that the O-terminated interfaces have much larger works of separations than the stoichiometric Al-terminated interfaces in both orientations, and that strongly bonded interfaces are Al-poor. Furthermore, it has been demonstrated [23] that a Cu–Al reaction layer does not preferentially form at the interface. Similar results have been obtained by various other groups [22,30–33].



**Figure 2.** The coherent supercell model used for the calculation of the work of separation of the Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> interface. The case of Al-terminated alumina at the interface is shown in (a) after complete relaxation of all atomic positions. Two different translation states, in (b) for Cu on top of O-sites and in (c) for Cu on top of a second layer of O-sites, are shown. For ease of visualization,  $2 \times 2$  unit cells are presented (the size of the single unit cell is marked in (b)).

These results correlate well with wetting experiments. In particular, they suggest that oxygen plays an important role in controlling the behavior of the wetting of alumina by Cu. The work by Alber et al. [14] demonstrated, by wetting experiments using a sessile-drop technique, that at low partial pressures of oxygen ( $P_{O_2} < 10^{-11}$  bar) the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> interfaces after solidification are weakly bonded. In fact, they fractured during preparation of specimens for transmission electron microscopy. On the other hand, at high partial pressures of oxygen ( $P_{O_2} > 1.5 \times 10^{-10}$  bar) interfaces were mechanically stable. Diemer et al. [15] showed that the wetting angle between liquid Cu and Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> varies from 125° to as low as 22° as the oxygen partial pressure increases in a sessile-drop set-up. Other experimental studies have also shown that the oxygen partial pressure affects the adhesion substantially [10–12,16].

## 2.2. Ab initio thermodynamics

The effect of the environment – in this case the oxygen partial pressure – and the effects of non-stoichiometry, as in the case of the O-rich interfaces, requires a thermodynamic grand canonical treatment. During the last decade, an approach to couple thermodynamic data with ab initio calculations has been introduced [22,34–37]. The basic idea is to relate the total energies at 0 K obtained from the DFT calculations to finite temperature values, which can then be used to estimate the Gibbs free energies as a function of temperature and pressure. The interface energies in Eq. (2) may then be calculated taking into account the relaxation and exchange of matter with the environment:

$$\gamma = \frac{1}{2A} \left( G - \sum_i N_i \mu_i \right) \quad (3)$$

where the sum is over all components of the system,  $\mu_i$  and  $N_i$  are the chemical potential and number of atoms for each component, respectively,  $G$  is the Gibbs free energy of the supercell model of the system and  $A$  is the area of the interface. The factor of two arises from periodic boundary conditions, which lead to two interfaces present in the supercell. In estimating the excess energies from Eq. (3), the Gibbs free energy of solid phases – in our case the Cu and the Al<sub>2</sub>O<sub>3</sub> – are obtained from DFT total energy calculations. DFT results give the internal energy of the system. For most applications the Gibbs free energy can be approximated by the internal energy [36] for solid phases, although corrections to high temperatures may also be included [35]. The chemical potential of the oxygen should be the energy of an O<sub>2</sub> molecule in the given partial pressure,  $P_{O_2}$ . Usually the ideal gas approximation is used:

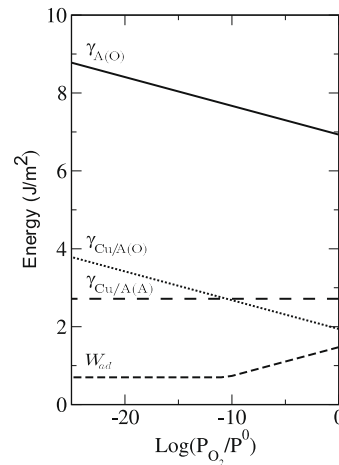
$$\mu_{O_2} = \mu_{O_2}^0 + \frac{1}{2} \log(P_{O_2}/P^0) + \Delta\mu_{O_2}^0 \quad (4)$$

where superscript 0 indicates quantities at standard pressure and temperature, and the last term in Eq. (4) gives the difference in the chemical potential of oxygen between the standard conditions ( $T = 298.15$  K) and high temperatures [36,37]. There are two main approaches to estimating the chemical potential in Eq. (4), depending on how to set the value of  $\mu_{O_2}^0$ . In the first,  $\mu_{O_2}^0$  is calculated from

first-principles [22,37], while in the second approach, a thermodynamic cycle linked to the chemical potential of solid phases is used to eliminate it from Eq. (4) [35,36]. In each case the appropriate correction terms must be used.

Using Eq. (3) in Eq. (2), the work of adhesion of the system is obtained, which in principle can be compared to experimental values. However, since most data on the work of adhesion are obtained from sessile-drop experiments at high temperatures, where the metal is in a liquid state, it is not certain that this comparison is valid. Nevertheless, for the cases of Cu, Ag and Nb on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> interfaces, studies conducted by various groups show agreement with experiments [22,35,38]. In particular, it is found that oxygen partial pressure directly affects the work of adhesion in these systems.

To demonstrate the ease with which these ab initio thermodynamics calculations may be applied to calculations of surface and interface energies, we apply the method of Batyrev et al. [35], with the correction term to high temperatures given in Ref. [36] to our previous results for the Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [23]. The mechanically most stable (i.e. strongest) interfaces in Ref. [23], which are the ones with the largest  $W_{sep}$  values in each termination, are considered. The surface energy of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) calculated within the same computational set-up as in [23] is 1.97 J m<sup>-2</sup>, and the surface energy of Cu is  $\gamma_{Cu} = 1.54$  J m<sup>-2</sup> [39]. The results for the free surface energy of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) and of the interface energies of the O- and Al-terminated interfaces as a function of oxygen partial pressure at a temperature of 1400 K are shown in Figure 3. The surface energy of O-terminated alumina decreases with partial pressure of O<sub>2</sub>, as expected. The interface energy of the O-terminated system also decreases. The work of adhesion calculated according to Eq. (2) is plotted for the most stable interface. At low  $P_{O_2}$  values, the Al-terminated interface is the most stable, but has a low work of adhesion of 0.7 J m<sup>-2</sup>, which is in good agreement with experimental values from sessile-drop studies. Above  $P_{O_2} = 10^{-10}$  atm, the O-terminated interface becomes more stable and the work of adhesion increases. These results are in agreement both with those



**Figure 3.** Surface energy of O-terminated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) and of Al- and O-terminated Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) interfaces as a function of the oxygen partial pressure at a temperature of 1400 K. The work of adhesion  $W_{ad}$  of the most stable system is also shown.

of Zhang et al. [22] and with experimental values (cf. Fig. 9 of Ref. [7]).

Furthermore, we may even estimate the wetting angle from Eq. (1). In this case, provided the surface energy of the metal does not vary too much between the solid and liquid states [40,20], at low partial pressures of oxygen the wetting angle is  $123^\circ$ , which drops at high oxygen partial pressures to almost  $90^\circ$  in our case. This shows the same trend as found in experiments [2,20,41].

This apparent agreement between experiment and DFT calculations raises some issues, as we have already mentioned above. A number of possibilities make this comparison more plausible. First, experimental measurements of adhesion energies may be done for solid–solid interfaces [19,40,42], which would make the comparison with the theoretical solid–solid models more justified. On the other hand, one important issue that is seldomly discussed in this context is the relation between the ordering in the liquid at the solid–liquid interface and the interface energy. For the case of Al/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> interfaces, it has been shown by modeling [43,44] as well as by experiments [45] (for a recent review see [46]) that the liquid near the interface possesses both a layered structure and in-plane ordering. This issue should be particularly important for non-reactive systems, where ordering is larger. If, indeed, liquid Cu at the interface exhibits ordering, which should span at least 2–3 atomic layers, this would imply that the structures employed in the DFT calculations, which assume an ordered solid at the interface, are not a bad approximation of the interface structure even at high temperatures, since in any case the number of metal layers at the interface is not much larger than those which show substantial ordering in a solid–liquid system. Further investigations of this point should reveal whether this is indeed a valid assumption.

Another point that relates to the discussion at the end of the previous section is that DFT calculations are done with the assumption of ideal coherent interfaces, although in most cases there is a substantial lattice mismatch between the lattice parameters of the metal and the ceramic, which results in large strains in the coherent supercell models used. A system where almost no misfit strains are present was investigated earlier by our group [47–49]. In this system, weak bonding was found between Ag and Al on MgAl<sub>2</sub>O<sub>4</sub>. Adding Ti to the interface resulted in a large increase in the work of adhesion and in a strong chemical bonding at the interface. The same “Ti effect” was also observed experimentally in the reactive wetting system of Cu–Ag on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [1,2].

Several studies have addressed the effect of misfit in DFT calculations [51,39,50]. The principle is to use the calculations on coherent models as a basis for the evaluation of the energy of a semicoherent or incoherent interface, taking into account various environments at the interface, and relaxation processes.

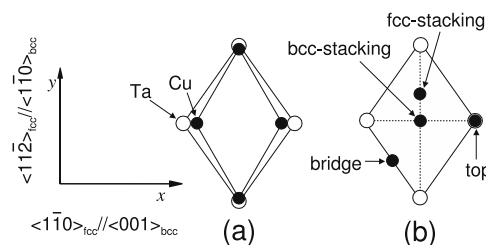
As an example of the applicability of this method to the study of wetting, we consider the stability and wetting behavior of thin Cu films (soft metal) deposited on Ta substrate (hard metal, similar to hard oxide) which has been the subject of several recent experimental and atomistic simulation studies [39,52–61]. This is a particularly interesting problem, for which a certain degree of controversy exists in the literature pertaining to

whether Cu completely dewets from the Ta substrate or whether it dewets but leaves stable monolayer (ML) coverage. The presence of completely wetting monolayer of Cu on the Ta would affect the interface and surface energies [40] and therefore the wetting behavior.

Because of the lack of experimental data on the actual orientation relationship of Cu on Ta, it was assumed in Ref. [39] that interfaces are formed with Cu(111) planes parallel to the Ta(110) planes (i.e. close-packed planes of face-centered cubic (fcc) and body-centered cubic (bcc) crystals being parallel). In this case, the surface unit cells of ideal fcc Cu and bcc Ta are shown schematically in Figure 4a. The lattice mismatch in this system is rather large ( $\epsilon_x = -22.4\%$  and  $\epsilon_y = -5.1\%$ ), which means that the Cu, being the “softer” metal, would have to be strained, as shown schematically in Figure 4b, to obtain a small coherent supercell model, which is suitable for DFT calculations. The excess energy of the pseudomorphic ML was found to be larger than that of the free surface of the substrate:  $\gamma_{ML} = \gamma_{sl} + \gamma_{lv} > \gamma_{sv}$  (cf. Fig. 1b), where  $\gamma_{sv} = 2.6 \text{ J m}^{-2}$  and  $\gamma_{ML} = 6.79 \text{ J m}^{-2}$  [39]. Hence these calculations have shown that the coherent or pseudomorphic Cu ML on the Ta substrate is not stable.

However, a more general interface structure may be considered since in lattice-mismatched systems one expects the formation of semicoherent interfaces rather than completely pseudomorphic ones [62]. A semicoherent interface is characterized by nearly perfectly matched coherent regions separated by disordered regions, which arise in order to relieve the lattice mismatch across the interface. The direct calculation of the excess energy of such a realistic interface model by first-principles DFT is still difficult since it would require prohibitively large supercells [50].

An estimate of the excess energy of an incoherent ideal Cu/Ta interface was obtained from rather basic assumptions. First, small coherent models, as described above, are used to calculate excess interface and surface energies relative to strained bulk [39], thus excluding the strain contributions, since an ideal incoherent interface is not strained. Each site at the interface is assigned to one such translation state. These energies are then used as local measures of the adhesion specific to the local environment, or translation state (see Fig. 4b). The total excess energy of the interface between one Cu monolayer and the Ta substrate is then obtained by taking



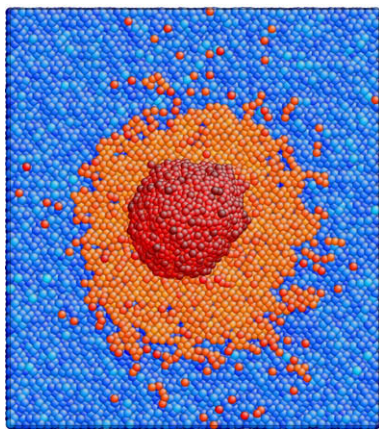
**Figure 4.** A schematic view of the Ta bcc(110) (black) and Cu fcc(111) (white) surface unit cells. In (a), the incommensurate cells are shown on top of each other. In (b), the commensurate cells (strained Cu on unstrained Ta) are shown together with the different translation states of Cu with respect to Ta. (From Ref. [39].)



an average of contributions from all local environments in the incoherent interface. The excess energy of the incoherent Cu monolayer was just lower than that of the free Ta substrate:  $\gamma_{\text{ML}} = 2.3 \text{ J m}^{-2}$ . This means that the monolayer is thermodynamically stable. This also holds for a relaxed, more realistic semicoherent interface [39,51]. The DFT calculations therefore indicate that Cu should dewet from Ta but leave a stable monolayer on it. Indeed, this dewetting behavior has recently been demonstrated both by molecular dynamics simulations, as shown in Figure 5, using an empirical interatomic potential fitted to DFT data [52], and by experimental observations [59,60]. Interface energies obtained on the basis of DFT calculations for realistic large-scale interface structures, as demonstrated for the Cu–Ta system, may therefore lead to new insight into the nature of wetting and triple-line properties.

### 3. Summary and conclusions

We have discussed the basic aspects of wetting and adhesion, namely the relation between the wetting angle and work of adhesion on the experimental side and the work of separation and thermodynamics on the theoretical side. We have demonstrated how coupling DFT calculations with thermodynamic data is simple and effective in describing experimental results related to triple-line properties [2]. The approach to studying large-scale interface structures, such as solid–liquid interfaces and semicoherent structures has been demonstrated for the case of a metal–metal interface system. A first-principles approach to triple-line properties may require a combination of these two approaches, i.e. extending DFT calculations with thermodynamic data and extending the calculations from small coherent cells to large-scale semicoherent structures. First-principles DFT calculations will probably remain computationally too heavy over the longer term to directly allow supercell



**Figure 5.** A top view of a Cu drop spreading on a Ta(110) surface. A stable monolayer of Cu on Ta is formed first, which spreads to eventually cover the Ta substrate [52]. The remaining Cu atoms form a drop with a wetting angle less than  $90^\circ$ . (Color code: dark red for Cu drop, light red for Cu ML and blue for Ta.) (For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)

simulations of atomistic triple-line (or tri-crystal) models with reasonably large dimensions, unlike already successful atomistic simulations with empirical potentials (cf. e.g. [63–69]). However, such simulations always depend crucially on the reliability of the potentials to describe the chemical bonds in varying environments properly. Therefore DFT approaches remains very useful and urgently required. Interatomic potentials for atomistic simulations, which are constructed and validated on the basis of predictive DFT data for properties of small systems (perfect crystal phases, point defects and coherent interfaces [52,62,70–72]) can be used with more confidence than empirically constructed and parametrized potentials for large systems like dislocations [73] and incoherent interfaces [39,62], and they are certainly applicable and promising for atomistic triple-line simulations in near future.

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