

Equilibrium and adhesion of Nb/sapphire: The effect of oxygen partial pressure

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We derive a formula, useful for first-principles calculations, which relates the free energy of an oxide/metal interface to the free energies of surfaces and the work of separation of the interface. We distinguish the latter *mechanical* quantity from the *thermodynamic* work of adhesion, and we describe explicitly how both may be calculated. Our formulas for interfacial and surface energies are cast in terms of quantities which can be calculated or looked up in tables, and include as additional parameters the ambient temperature and partial pressure of oxygen P_{O_2} . From total-energy calculations for the Nb(111)/ α -Al₂O₃ (0001) interface, free Nb and Al₂O₃ surfaces, we obtain firstly numerical estimates of the works of separation, which are independent of P_{O_2} . We then obtain surface energies, interfacial energies, and the equilibrium work of adhesion as a function of P_{O_2} .

I. INTRODUCTION

Oxide-metal interfaces continue to be studied intensively because of the many ways in which they are of commercial and scientific importance. Applications range from the nanoscale in microelectronics packaging to the macroscale engineering of thermal barrier coatings or the formation of protective scales. The science of these interfaces has been addressed in volumes of conference papers and reviews.¹⁻⁴ There are also reviews in the literature^{5,6} that specifically address the theoretical questions about the nature of the bonding at these interfaces, such as what determines the site preference of metal atoms on the oxide surface; whether the bonding can be thought of as predominantly covalent or metallic and how to quantify these concepts; whether a simple classical image model can be used to interpret the bonding; what is the strength of adhesion of metal to oxide. The basis for answering these questions is to have reliable calculations of the electronic structure and total energy of particular surfaces and interfaces. Such calculations came of age over the past ten years or so with the use of first-principles methods. These mainly apply density-functional theory (DFT) and the local-density approximation (LDA),^{7,8} which are the basis of the calculations we shall report here. Hartree-Fock calculations are also feasible and have been applied effectively to the Ag/MgO interface,⁹ although they tend to be more expensive than DFT for larger systems. Since the reviews cited, there have been numerous applications of DFT to study bonding in the initial stages of deposition of metal on oxide, with cluster or multilayer geometries, notably on MgO,¹⁰⁻²¹ but to a lesser extent on more complex oxides such as TiO₂,²² MgAl₂O₄,²³ and α -Al₂O₃.²⁴⁻²⁷

The bonding of Nb to α -Al₂O₃ has long been a subject for experimental work, because besides its relevance to electronic components it offers practical advantages for sample preparation: the two materials bond strongly²⁸ (anomalously strongly according to a recent study²⁹), do not react chemically and have similar coefficients of thermal expansion. In the orientation Nb(111)/Al₂O₃ (0001) there is a lattice mis-

match of less than 2%, allowing the preparation of a nearly coherent interface (using molecular beam epitaxy), the atomic structure of which has been studied by high resolution transmission electron microscopy (HRTEM) and analyzed in detail.³⁰⁻³⁴ This interface was the subject of first-principles calculations which used periodic boundary conditions, making the reasonable assumption that the effect of misfit dislocation can be neglected.²⁵⁻²⁷ Our recent work²⁶ analyzed the nature of the bonding in detail by calculating Mulliken populations and bond orders, concluding that the bonding across the interface is strongly ionic. The work of separation W_{sep} of the interface was calculated, and found to be very high: of order 10 J m⁻² when niobium was bonded to the oxygen-terminated Al₂O₃ surface. Lower energy pathways for the cleavage of this interface would be within the Nb metal or the oxide itself. Two other interfaces were studied corresponding to the two other possible terminations of bulk Al₂O₃ (0001); namely the stoichiometric, aluminum termination (one layer of aluminum) and the aluminum-rich termination (two layers of aluminum). HRTEM could not distinguish between the stoichiometric termination and the oxygen termination; however, evidence from electron-energy-loss spectroscopy³⁵ (EELS) favored the oxygen termination.

We point out here that as far as we know the question of which termination is more stable has not yet been addressed in all the theoretical work which has been published so far on any oxide-metal interfaces. The structural predictions have been confined to the question of the relative displacement of the crystals, parallel and perpendicular to the interface, and the local relaxations of atoms at the interface, as well as the energy needed to separate the crystals W_{sep} . This has been done for interfaces with different terminations or local stoichiometry; all calculations were carried out with atoms at rest ($T=0$ K) and minima in the total energy were located as a function of atomic positions. However, the question as to whether the oxygen-terminated or the aluminum-terminated interface is more stable was not discussed. There are special difficulties associated with calculating the absolute interface

energy for non-stoichiometric interfaces, a problem that was first addressed in a first-principles manner by Chetty and Martin.³⁶ These authors dealt with a part of the general problem, which is to formulate the total energy as a *local* quantity; it can therefore be used in the definition of thermodynamic excesses. A second important part of the problem, which they did not treat, is to bring the chemical potentials of the components into the formalism. These aspects of the problem were married in Ref. 26. It is now well known that the question of which termination is stable can only be answered with respect to the chemical potentials of the species in the environment with which the interfaces are in equilibrium, which is normally characterized by temperature and partial pressure of oxygen,³⁷ and the difficulty of relating the quantities accessible to a first principles calculation to these parameters may have been a reason for leaving this question to one side.

The main purpose of our present paper is to show how in fact we are already able to make predictions of the stability of different interfaces when they differ not only in structure but also in composition. With certain simplifying assumptions we show how this can now be done with little more effort than the calculations which need to be done to calculate the work of separation, and we present first results for the Nb/Al₂O₃ interface. The ingredients of the theory are the works of adhesion and surface energies. For these we draw upon the results reported briefly in Ref. 52 supplemented by some further calculations to discuss the case of oxygen on the Nb surface. The basic theory is outlined in Sec. II. We derive the equations for a general A_mO_n oxide in contact with a metal B ; it would be a short step to generalize them still further to an interface between arbitrary compounds. Essentially the same thermodynamics was applied by Wang *et al.*³⁸ in calculations of the surface energy of oxides with different terminations, over a range of chemical potentials of oxygen; our theory makes the further connection to the temperature and in particular the *pressure* of oxygen, which are the parameters directly under the control of the experimentalist. A detailed study of the Al₂O₃ surface is reported elsewhere.³⁹

The plan of the rest of the paper is as follows. Sections III–V cover aspects of our total energy calculations which were not dealt with, or dealt with only briefly, in our paper.⁵² In Sec. III our method of total-energy calculation is summarized. In Sec. IV we describe the atomic relaxations *parallel* to the interfaces which are generally not commented upon. Although this structural aspect is not central to the thrust of our paper, it turned out that lateral relaxations also have a strong part to play in determining the interplanar relaxations and energies reported previously, and we therefore describe them for completeness. In Sec. V we describe and comment on the results for the work of separation on different planes and with different terminations of the interface. Our calculated interfacial free energies are presented in Sec. VI and we conclude in Sec. VII.

II. PRINCIPLES OF CALCULATING INTERFACIAL AND SURFACE ENERGIES

Let us consider the interface between metal B and an oxide of metal A in equilibrium at temperature and pressure

(T, P) . The stoichiometric composition of the A oxide is A_mO_n . We obtain the definitions of interfacial quantities by referring to the contents of a periodically repeated supercell of area S parallel to the interfaces which it may contain. All extensive thermodynamic quantities in the following will refer to the contents of such a supercell. The interfacial energy per unit area, counting the two interfaces within each supercell, is given by:⁴⁰

$$\gamma_{int} = [G_{int}(T, P) - N_A \mu_A(T, P) - N_O \mu_O(T, P) - N_B \mu_B(T, P)] / 2S, \quad (1)$$

where G_{int} is the Gibbs energy of the contents of a supercell containing two interfaces, μ_A , μ_B , and μ_O are the chemical potentials of the three components, and N_A , N_B , and N_O are the numbers of atoms of the three components within the supercell. The denominator $2S$ occurs because there are two interfaces in the supercell, as required by periodic boundary conditions. Chemical potentials here are per atom rather than per mole, which would be the usual convention for macroscopic thermodynamics. Special cases of Eq. (1) are when either the metal B or the oxide is absent from the supercell, in which cases we recover expressions for the surface energies of the oxide γ_{AO} and the metal γ_B , respectively,

$$\gamma_{AO} = [G_{SAO}(T, P) - N_A \mu_A(T, P) - N_O \mu_O(T, P)] / 2S, \quad (2)$$

$$\gamma_B = [G_{SB}(T, P) - N_B \mu_B(T, P)] / 2S. \quad (3)$$

The quantities G_{SAO} and G_{SB} are the Gibbs energies of slabs of oxide and of metal, with free surfaces separated in their respective supercells by an adequate thickness of vacuum. We have assumed in Eq. (3) that the metal surface is clean; this will suffice for a calculation of the energy of the *interface* discussed below. However, we can easily consider for example adding a monolayer of oxygen to the metal surface in the calculation of $G_{SB}(T, P)$. Since there is no separate oxide phase, the number of oxygen atoms in the system, N_O , now resides on the metal surface. The contribution $-N_O \mu_O(T, P)$ must be subtracted in the calculation of the corresponding surface energy just as in the calculation of the interface energy. We shall in fact make this calculation of an “oxidized” Nb surface in the course of obtaining the work of separation of an interface by a pathway which leaves oxygen on the exposed metal surface.

The motivation for calculating γ_{int} is as follows. An interface between two crystals requires five parameters for its macroscopic specification, for example three to specify the relative crystallographic orientation of the materials and two more to specify the orientation of the interface. We note in passing that a free surface in contact with vapor or liquid only requires two parameters to specify its crystallographic orientation. There is always a large set of hypothetical interfaces that have the same five macroscopic parameters but which differ in their atomic structure and local stoichiometry. The member of this set which minimizes γ_{int} for given chemical potentials is the equilibrium interface. So provided we know the chemical potentials of the components, we could in principle predict the atomistic structure of the equilibrium interface, including its local stoichiometry, by evalu-

ating γ_{int} for each member of the set. In practice, of course, we can only calculate γ_{int} for a small subset of the entire set, and rely on our experience and intuition, together with experimental information, to ensure that we have not omitted an important structure. Prior to the present work we and others have calculated total energies for a number of structures at 0 K, in which the atomic positions are relaxed by energy minimization. The equations to be derived below show how to go the two important steps further, namely to correct the 0 K information to finite temperature and to take account of local stoichiometry.

The relationship between local stoichiometry and γ_{int} is well known in thermodynamics as the Gibbs adsorption equation, in which local stoichiometry is measured in terms of *excesses* Γ_i of one or more components labeled i . Our final version of Eq. (1) will be in terms of the excess of oxygen at the interface with respect to the metal A , per unit surface area, which is defined as

$$\Gamma_O = \left(N_O - \frac{n}{m} N_A \right) / 2S. \quad (4)$$

This choice of component i is arbitrary; we could equally well work in terms of Γ_{Al} , because they are related through

$$m\Gamma_O + n\Gamma_{Al} = 0. \quad (5)$$

We note three further points in connection with excesses. Firstly, each further component in the system would introduce another excess, each excess being referred to the same designated component. Secondly, a stoichiometric interface is by definition one for which all the excesses vanish. Finally, since one of the phases is the pure metal B , there can be no excess of the metal B . In particular, if B were in fact also Al, thereby reducing the number of components to two, the interface could not be described as having an excess of O or Al. For more discussion of the thermodynamics of excess quantities the reader is referred to Ref. 40.

A difficulty up to now has been to calculate the chemical potentials involved in these equations and, more specifically, to relate them to given experimental conditions. In the following we show how Eq. (1) can be reformulated to relate γ_{int} to the partial pressure of oxygen P_{O_2} .

First we define the *work of separation* W_{sep} of the interface. It does not refer to chemical equilibrium states and therefore does not involve chemical potentials of the separate components:

$$W_{sep} = (G_{SAO} + G_{SB} - G_{int}) / 2S = \gamma_{AO} + \gamma_B - \gamma_{int}. \quad (6)$$

For brevity we do not explicitly indicate the temperature and pressure dependence of all the terms unless it needs to be emphasized. An important point to note about this quantity, which makes it relatively straightforward to calculate, is that the separate slabs of metal and oxide have exactly the same composition as the two slabs which are joined to form an interface. This would not in general be the case if these slabs and the interface were in equilibrium with a given environment (constant μ_i), because one would expect for example some loss or gain of surface oxygen or metal from the oxide to the vapor phase when the surfaces are created. If the interface as well as the exposed surfaces are the ones which are

in chemical equilibrium (which we denote by superfix *eq*), an equation similar to Eq. (6) defines the *work of adhesion*:

$$W_{ad} = \gamma_{AO}^{eq} + \gamma_B^{eq} - \gamma_{int}^{eq}. \quad (7)$$

This is the quantity of relevance to contact angles and wetting for example, and unlike W_{sep} it is not obtainable by a simple comparison of three total energies.

Calculations of W_{sep} for Nb/Al₂O₃ were reported in our paper⁵² and these have been extended here, as described in the following sections. W_{sep} is probably more relevant than W_{ad} in formulating a fracture criterion, when internal surfaces are formed which are not in equilibrium, but in order to predict the equilibrium structure of interfaces we also need to be able to evaluate Eqs. (1)–(3).

We now introduce the quantity g_{AO} , the Gibbs energy per formula unit of bulk A_mO_n in equilibrium with metal A and oxygen in vapor form,

$$g_{AO}(T, P) = m\mu_A(T, P) + n\mu_O(T, P), \quad (8)$$

so that

$$G_{AO} = (N_A/m)g_{AO} \quad (9)$$

is the Gibbs energy of a stoichiometric cell containing N_A atoms of A . Inserting Eqs. (8) and (4) into Eq. (2) gives the surface energy of the oxide in a form which makes the effect of the excess oxygen explicit,

$$\gamma_{AO} = (G_{SAO} - G_{AO}) / 2S - \Gamma_O \mu_O. \quad (10)$$

Consider now how to go about calculating the two surface energies from Eqs. (3) and (10), which we will eventually combine with W_{sep} in Eq. (6) to give us γ_{int} . The Gibbs energy of all slabs can be calculated at $T=0$ K and $P=0$ from first principles; it is just the total energy. If the slabs are bulk pure material, their Gibbs energy can be corrected to temperature T by using experimental specific heat data. On the other hand, when the slabs are separated in the supercell by a layer of vacuum to represent free surfaces, there is no such experimental data and the correction to finite T could be done by calculating the phonon spectrum and using the quasiharmonic approximation for the free energy. This has been done previously for classical ionic models by Taylor and co-workers,⁴¹ in order to obtain the temperature dependence of their surface energy, but we have not yet made the equivalent calculation with our *ab initio* code. For a metal slab (Ag), the quasiharmonic free energy based on *ab initio* phonon frequencies was recently calculated by Xie and co-workers.⁴² In the case of the pure metal slab, the chemical potential μ_B is the Gibbs energy per atom of a bulk slab. The surface energy of B is therefore obtained from the results of two supercell total energy calculations in the standard way. The main present issue, which is less familiar in the context of total energy calculations, is how to calculate the significant term due to the chemical potential of oxygen, which must be included when the surface of the oxide is nonstoichiometric ($\Gamma_O \neq 0$).

The chemical potential of oxygen is well described in terms of its partial pressure P_{O_2} by the standard ideal gas expression

$$\mu_{\text{O}} = \mu_{\text{O}}^0 + \frac{1}{2}kT \log(P_{\text{O}_2}/P^0). \quad (11)$$

In Eq. (11), μ_{O}^0 is the oxygen chemical potential in its standard state (STP) at $T^0 = 298.15$ K, $P^0 = 1$ at. Chemists would set μ_{O}^0 to zero by definition, but we cannot do that since our zero of energy is already defined as the energy of separated ions and electrons at $T = 0$ K. On the other hand, the energy of oxygen molecules is not something we want to calculate, since there are well-known problems in using density-functional theory for this system. Fortunately, we can circumvent the problem by using a thermodynamic cycle. From the defining equation for the standard Gibbs energy of formation ΔG_{AO}^0 ,

$$g_{\text{AO}}^0 = m\mu_{\text{A}}^0 + n\mu_{\text{O}}^0 + \Delta G_{\text{AO}}^0, \quad (12)$$

we obtain the troublesome oxygen chemical potential at STP in terms of g_{AO}^0 and ΔG_{AO}^0 . The quantities g_{AO}^0 and μ_{A}^0 are things we *can* calculate accurately, and we can look up ΔG_{AO}^0 in tables of thermodynamic data. Once we have this value, it could be used in principle for calculations in any material containing oxygen. Since, however, the numerical value of g_{AO}^0 is strongly dependent on which pseudopotential is used, μ_{O}^0 obtained by this procedure should only be used if the same pseudopotentials are used throughout, otherwise it must be recalculated.

Inserting μ_{O}^0 from Eq. (12) into Eq. (11) and Eq. (11) into Eq. (10) gives us our final expression for the surface energy of the oxide:

$$\begin{aligned} \gamma_{\text{AO}} = & \left(G_{\text{SAO}}(T, P) - \frac{N_{\text{A}}}{m} g_{\text{AO}}(T, P) \right) / 2S \\ & - \Gamma_{\text{O}}(g_{\text{AO}}^0 - m\mu_{\text{A}}^0 - \Delta G_{\text{AO}}^0)/n - \Gamma_{\text{O}_2} \frac{1}{2} kT \log(P_{\text{O}_2}/P^0) \end{aligned} \quad (13)$$

from which we obtain the final expression for the interfacial energy by substituting Eq. (13) into Eq. (6),

$$\begin{aligned} \gamma_{\text{int}} = & \gamma_{\text{B}}(T, P) - W_{\text{sep}}(T, P) \\ & + \left[G_{\text{SAO}}(T, P) - \frac{N_{\text{A}}}{m} g_{\text{AO}}(T, P) \right] / 2S \\ & - \Gamma_{\text{O}}(g_{\text{AO}}^0 - m\mu_{\text{A}}^0 - \Delta G_{\text{AO}}^0)/n \\ & - \Gamma_{\text{O}_2} \frac{1}{2} kT \log(P_{\text{O}_2}/P^0). \end{aligned} \quad (14)$$

The quantities g_{AO}^0 and μ_{A}^0 entering the third line of Eq. (14) are well described by $T = 0$ K quantities which we calculate. It can be verified that correcting them to standard state has a negligible effect on the surface energy.

The minimum physically meaningful value of P_{O_2} , which we denote $P_{\text{O}_2}^{\text{min}}$, is set by the condition that if $P_{\text{O}_2} \leq P_{\text{O}_2}^{\text{min}}$ the oxide would spontaneously decompose into metal and oxygen. Neglecting the small variation in solid energies with temperature by comparison with ΔG_{AO}^0 this condition is

$$\log(P_{\text{O}_2}^{\text{min}}/P^0) = \frac{2}{nkT} \Delta G_{\text{AO}}^0. \quad (15)$$

TABLE I. Thermodynamic data used for calculating the dependence of surface and interfacial energies on oxygen partial pressure. The pressure represents the dissociation pressure of the oxide at 1500 K. P^0 is one standard atmosphere.

	α -Al ₂ O ₃	NbO
ΔG^0 (kJ/mol) ^a	-1582.3	-391.9
$\log_{10}(P_{\text{O}_2}/P^0)$	-36.8	-27.3

^aReference 51.

Similarly, the maximum physically meaningful value of P_{O_2} is defined by the lowest standard Gibbs energy of formation of a metal B oxide ΔG_{BO}^0 ,

$$\log(P_{\text{O}_2}^{\text{max}}/P^0) = \frac{2}{n'kT} \Delta G_{\text{BO}}^0, \quad (16)$$

where the first oxide to form would have the stoichiometry $B_{m'}\text{O}_{n'}$. The thermodynamic data used here are summarized in Table I.

III. METHOD OF TOTAL-ENERGY CALCULATION

For the interface calculations we use the total-energy plane-wave pseudopotential method based on Lanczos diagonalization of the Kohn-Sham density matrix.⁴³ The supercell has the form of a rhombohedral prism and in the stoichiometric slab it contains 45 atoms: 14 Al, 21 O, and 10 Nb atoms (see Fig. 1). By stripping off the outer plane of Al from each interface we obtain an interface which is O terminated with an O excess $\Gamma_{\text{O}}S = +1.5$ atoms per surface unit cell. By adding the surface plane of Al atoms to the neutral interface we make an oxygen poor interface, with the negative O excess $\Gamma_{\text{O}}S = -1.5$. The total energy of the contents of a supercell is minimized with respect to the atomic coordinates by the quasi-Newton method with Hessian updated using the Broyden-Fletcher-Goldfarb-Shanno (BFGS)

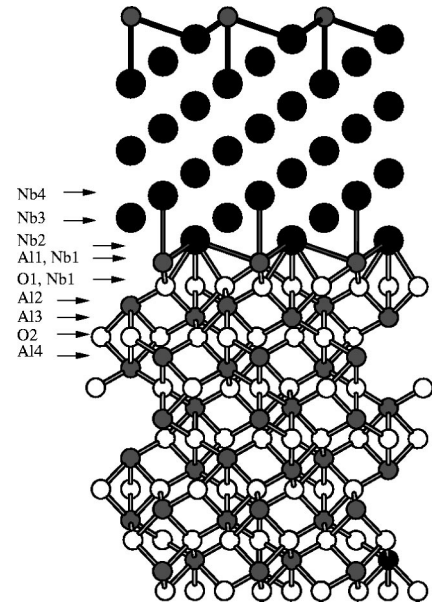


FIG. 1. Side view of the Nb(111)/Al₂O₃(0001) interface, showing labeling of the layers.

method. The pseudopotential for Nb was of Troullier-Martins form,⁴⁴ with s and d nonlocality. The pseudopotential for O was of optimized form,⁴⁵ with an s nonlocality. The pseudopotential for Al was of Gonze type⁴⁶ with s nonlocality.

All calculations were made with two k points in the irreducible wedge of the Brillouin zone, and with a plane-wave cutoff of 40 Ry. The effect of increasing the plane-wave cutoff from 40 to 60 Ry was to reduce W_{sep} by 3.3% for the Nb/Al interface, which we take as a satisfactory indication of the basis-set convergence. For the neutral 45-atom interface we have made test calculations with six k points which results in a decrease of total energy by about 4 mRy and very small ($<10^{-3}$ nm) changes of relaxed positions of atoms compared with two k -point calculations. The effect of increasing the k -point sampling from two points to nine is to change W_{sep} by less than 1%.

By doubling the original unit cell in the x - y plane we obtained a 180 atom cell, with which we recalculated the wave functions at the gamma point with the previously relaxed atomic coordinates. The gamma point wave functions in this cell were used for Mulliken population analysis which was made by projecting the optimized wave functions onto the pseudoatomic orbitals $|\phi_{i\alpha}\rangle$ (i labels site, α labels orbitals) according to the procedure suggested in Ref. 47. The ‘‘spillage’’ of each occupied orbital ψ was less than 1.5%.

IV. RELAXATION OF THE INTERFACE

The slab with which the Nb(111)/Al₂O₃ (0001) interface was modeled is shown in Fig. 1. The interlayer relaxation of the interface has been reported previously,⁵² and we refer to that paper for results. Here we mention a feature that has not previously been discussed, namely the relaxations parallel to the interface, which we refer to as in-plane relaxations. It has been found that to make a calculation of the interlayer relaxation of the alumina surface one needs to take into account the in-plane relaxations of the oxygen atoms,²⁶ which were neglected in some earlier work.²⁵ The present results show that in-plane relaxation of the oxygen ions is a general feature of the structure near the interface. The geometry of these relaxations is described by two parameters; the rotation α and the bond length extension δr of the equilateral triangle of oxygen atoms in a plane, illustrated in Fig. 2. The rotation and dilation of this equilateral triangle does not break any symmetry, preserving for example the threefold axis about the center of the triangle concerned.

The calculated values of α and δr are shown in Table II for the terminating and second layer oxygen planes (denoted by subscripts 1 and 2) in five cases. The first two cases, labeled $N(b)/A(O)$ and $N(b)/A(Al)$ are the O- and Al-terminated bulk Nb/Al₂O₃ interfaces. Cases three and four are pure alumina surfaces, labeled $A(O)$ and $A(Al)$ to indicate that they are oxygen and aluminum terminated, respectively. Case five, labeled $N(m)/A(O)$ is a Nb monolayer on an oxygen-terminated alumina surface. One can see that the in-plane relaxation is a feature of all the systems studied. From the evidence of the first two layers, the rotation of O triangles and the increase of the O-O bond lengths appears to be localized near the surface of the alumina. The Nb monolayer on the O-terminated surface of alumina shows this ef-

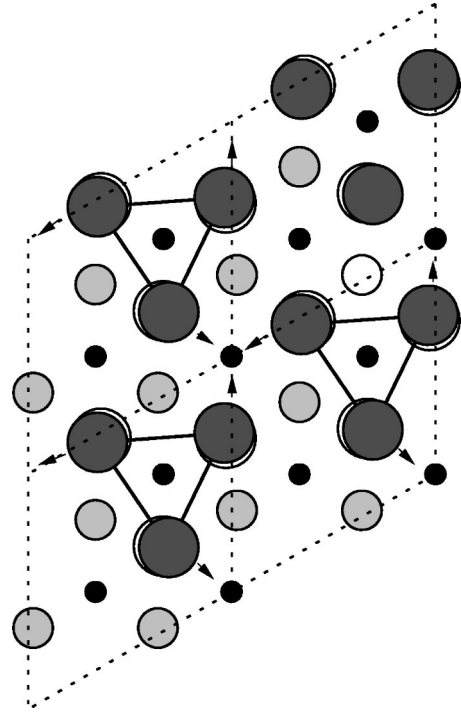


FIG. 2. Plane view of the (0001) surface of neutral alumina showing the lateral relaxation within the topmost O plane. The rotation and expansion of the O triangle below the surface Al atom is indicated by arrows.

fect most strongly, which is quite surprising, since the interplanar relaxation in this case is much less than that of the Al layer for which the Nb substitutes. There is experimental confirmation of the effect, obtained by small-angle x-ray diffraction,⁴⁸ in the case of the $A(Al)$ surface. In this case the experimental results are $\delta r_1 = 4.5\%$ and $\alpha_1 = 6.7^\circ$, compared with our calculated results of $\delta r_1 = 3.2\%$ and $\alpha_1 = 3.1^\circ$. The agreement is only qualitative.

V. WORK OF SEPARATION

All our results for the calculated work of separation W_{sep} of different interfaces and cleavage planes are shown in Table III. The column of ‘‘unrelaxed’’ results refers to values obtained by assuming bulk unrelaxed atomic positions both at the interface and for the free surfaces. The interplanar spacing between O and Nb across the interface in this case was simply taken as the bulk spacing between O and Al planes. The results in the ‘‘relaxed’’ column are calculated with atomic positions relaxed both before and after cleavage.

TABLE II. In-plane relaxation of O- and Al-terminated interfaces and surfaces of alumina. α and δr correspond to the angle of rotation and bond-length increase of O triangles; surface and sub-surface layers are indicated by the subscripts.

	$N(b)/A(O)$	$N(b)/A(Al)$	$A(O)$	$A(Al)$	$N(m)/A(O)$
α_1	4.1	4.2	4.1	3.1	8.4
α_2	0.1	0.2	0.5	0.2	0.4
δr_1	4.2	4.3	4.3	3.2	8.4
δr_2	0.2	0.2	0.2	0.5	0.6

TABLE III. W_{sep} (in J/m^2) for both unrelaxed and relaxed structures.

Interface	Cleavage plane	Unrel.	Rel.
$N(b)/N(b)$... Nb-Nb-Nb / Nb-Nb-Nb...	4.9	4.2
$A(\text{Al})/A(\text{Al})$... Al-O-Al / Al-O-Al...	7.0	3.9
$A(\text{Al})/A(\text{O})$... Al-Al-O / Al-Al-O...	13.3	12.7
$N(m)/A(\text{O})$	Nb / O-Al-Al...	10.9	10.8
$N(b)/A(\text{O})$... Nb-Nb-Nb / O-Al-Al-O...	9.3	9.8
$N(b)/A(\text{Al})$... Nb-Nb-Nb / Al-O-Al-Al...	4.2	2.7
$N(b)/Nb\text{-}A(\text{Al})$... Nb-Nb-Nb / Nb-O-Al-Al ...	4.0	3.8
$N(b)/Al\text{-}A(\text{Al})$... Nb-Nb-Nb / Al-Al-O...	4.4	2.8
$N(b)\text{-}O/Al\text{-}A(\text{Al})$... Nb-Nb-O / Al-Al-O...	7.3	4.9

The effect of relaxations on W_{sep} naturally depends on the interface. It is most pronounced when an Al-terminated Al_2O_3 surface is exposed, because of the large relaxation of this surface, which lowers its surface energy by about 1.5 J m^{-2} . On the other hand, if the relaxation of the *interface* dominates the energy balance in Eq. (6) then the relaxed value of W_{sep} can even be larger than the unrelaxed value, as in the case of cleavage between Nb and O at the $N(b)/A(\text{O})$ interface.

The lowest value of W_{sep} , 2.7 J m^{-2} , is found for the cleavage of bulk Nb from the stoichiometric Al-terminated alumina. The highest values are found for the cleavage of bulk Nb from the O-terminated alumina surface. Indeed we can deduce from Table III that this interface would be unlikely to separate between Nb and O planes, but would prefer to separate inside the Nb, leaving a monolayer of Nb on the surface, or even between O and Al, leaving a monolayer of O on the Nb surface.

The highest value (relaxed) of all in Table I is for the cleavage of pure Al_2O_3 between O and Al planes. Experimentally, $\alpha\text{-Al}_2\text{O}_3$ does not cleave on the basal plane at all, but its lowest-energy cleavage on this plane would clearly be between Al planes. This is what one expects on the basis of charge neutrality arguments, because by cleaving between Al planes two identical, neutral surfaces are created. On the other hand, by cleaving between O and Al, different surfaces are created which, in order to be neutral, require the oxygen or aluminum at the surface to be in an unfavorable valence state, hence this is a final state of especially high energy.

The above interpretations are supported by the Mulliken populations shown in Table IV for the three interfaces between bulk Nb and Al_2O_3 . We make the usual caveat here

TABLE IV. Mulliken charges for atoms near the interface as a function of the excess of O. The notation for atomic planes is as in Fig. 1.

$\Gamma_{\text{O}}S$	1.5	0	-1.5
Nb2	0.27	0.37	-0.13
Nb1/Al1	0.77	0.73	0.36
O1	-0.86	-0.93	missing
Al2	1.49	1.50	0.15
Al3	1.52	1.51	0.95
O2	-1.00	-1.00	-0.99

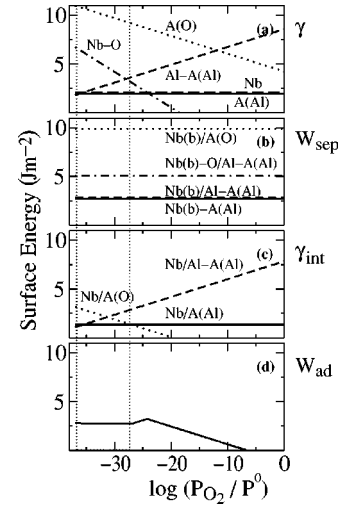


FIG. 3. (a) Surface energies as a function of oxygen partial pressure at 1500 K. (b) Works of separation W_{sep} (see Table III). (c) Interfacial energies. (d) Work of adhesion W_{ad} , obtained by subtracting equilibrium interfacial energy from equilibrium surface energies. The region to the left between the vertical lines corresponds to the possible equilibrium states of the interface.

that Mulliken charges do not have absolute significance, since they depend on the choice of basis set, but they are nevertheless a useful indicator of trends in ionicity or covalency. The interfaces in Table III are labeled by their oxygen excesses, to highlight certain trends with the stoichiometry of the interface. Bulk oxygen carries a Mulliken charge of -1 , and for the oxygen plane nearest the interface this value is reduced to -0.99 , -0.93 , and -0.86 in turn as the excess of oxygen at the interface is increased from negative to positive. The change is rather modest, indicating that oxygen does not readily alter its valence state. The charge on the interfacial oxygen is provided by the terminating layer of Al in the case of Al termination, or in the case of the oxygen terminated interface the electrons are provided mainly by the first two layers of Nb.

VI. INTERFACIAL FREE ENERGY AND OXYGEN PRESSURE

Five surface energies are shown in Fig. 3(a) as a function of P_{O_2} . The x axis is appropriate to a temperature of 1500 K; to obtain the results at temperature T the numbers on the x axis should be multiplied by $1500/T$. The O-rich ($\Gamma_{\text{O}}S = 1.5$) and O-poor ($\Gamma_{\text{O}}S = -1.5$) alumina surfaces have negative and positive slopes, respectively, while the stoichiometric Al_2O_3 and pure Nb(111) surface energies are constant, and by chance nearly equal. The most negatively sloping surface energy we have plotted here refers to the Nb(111) surface with an attached monolayer of oxygen. It becomes negative at an oxygen pressure inside the regime of stability of NbO.

The interfacial free energy from Eq. (1) is shown as a function of P_{O_2} in Fig. 3(c) for three interfaces, O rich, stoichiometric, and O-poor ($\Gamma_{\text{O}}S = 1.5, 0, -1.5$). To generate the interfacial free energies one has to subtract the work of separation shown for convenience in Fig. 3(b), from the sum of the equilibrium surface energies of the two corresponding

free surfaces. With increasing P_{O_2} the O-rich interface becomes increasingly stable, the Al-rich interface less stable, and the free energy of the stoichiometric interface remains constant, exactly parallel to the behavior of the free surfaces. The interfaces can only be in thermodynamic equilibrium in the range of oxygen pressure which is indicated on the figure. At 1500 K this range is as given in Table I; at values of P_{O_2} above this range, the Nb would oxidize to NbO, and below it the alumina would decompose.

The *work of adhesion* at a given P_{O_2} can also be estimated from the results on this graph using Eq. (7). The free surface and interface energies should be those with lowest free energy at the given oxygen pressure, and these can be read off from Figs. 3(a) and 3(c). The result is plotted in Fig. 3(d).

VII. DISCUSSION AND CONCLUSIONS

We have made a careful distinction between a work of separation, a mechanically defined quantity, and a work of adhesion, a thermodynamic quantity, focusing on how to go about calculating these quantities within an atomistic model. We particularly consider the interface between a metal and an oxide, since it is of practical importance and since oxygen is a troublesome component for which to calculate the chemical potential, a key quantity in interfacial energies. A useful practical equation for the free energy of an interface involving oxygen has been derived, namely Eq. (7), which gets around the previous difficulty by using a thermodynamic cycle to express the result in terms of quantities which can be readily calculated, namely the total energies of slabs, and quantities which can be obtained from tables, namely the standard Gibbs energy of formation of the oxide and the Gibbs energies of the bulk materials relative to their $T=0$ K values.

To illustrate and apply the method we have made a number of first-principles calculations for Nb(111)/Al₂O₃ (0001) interfaces, oxygen rich, oxygen poor, and stoichiometric, and for several surfaces. We fully relax the atomic positions in supercells using a plane wave, pseudopotential methodology. The relaxations are significant, and in all cases they involve in-plane as well as interlayer relaxations of the oxygen ions. Results on the work of separation of these interfaces were given in a paper⁵² recently, and we have extended them to include the possibility of a cleavage of the O-terminated interface which leaves the Nb coated with oxygen. This turns out indeed to be a lower-energy mode of separation (4.9 J m^{-2}) than the alternative which leaves an oxygen-rich Al₂O₃ surface behind (9.8 J m^{-2}), because the favorable degree of ionicity of oxygen is thereby preserved as it is in both bulk alumina and its stoichiometric surface. Considering further the strongly bound O-terminated Nb/Al₂O₃ interface, it turns out that the hypothetical processes of (i) cleavage within bulk Nb (4.2 J m^{-2}), or (ii) leaving a monolayer of Nb on the oxide surface (3.8 J m^{-2}), or even (iii) cleavage within bulk Al₂O₃ (3.9 J m^{-2}) are all marginally of lower energy than the cleavage which takes oxygen with the niobium.

By combining the results of our calculations with thermodynamic data we obtain surface energies and interfacial en-

ergies as a function of oxygen partial pressure and temperature. An approximation we make here is in omitting the temperature dependence of the solid-state free energy, but we include the $kT \log(P_{O_2}/P^0)$ term which describes the temperature dependence of the oxygen chemical potential; this is also the term which describes the dependence of all the interfacial and surface free energies on oxygen pressure. It is clear how a more accurate calculation could be made by implementing the quasiharmonic approximation to correct solid surface free energies, and it will probably become a routine matter to include such a correction in future work. Another approximation is made by considering only a small set of possible interface and surface compositions which we think are representative. Nevertheless, despite the present simplifications, some clear results have emerged.

Of the free surfaces of Al₂O₃, the stoichiometric one, terminated by a single layer of Al, is the most stable over the whole range of oxygen partial pressure up to over one atmosphere. It may be that a treatment of the temperature dependence of the energy of the slabs could modify the upper and lower bounds on pressure somewhat. Correction of the LDA error is also likely to lower surface energies by 10–20% [I. G. Batyrev, (Ref. 49)]. For example, work of Sims⁵⁰ with classical potentials indicates that the surface energies of Al-terminated Al₂O₃ can be reduced by up to $0.2\text{--}0.3 \text{ J m}^{-2}$ at 1500–2000 K. We expect an oxygen-terminated surface to be stable at a pressure not too far from atmospheric, but we cannot unfortunately be more quantitative in the prediction at this stage. At very low oxygen pressures it is also reasonable that the experimentally observed Al-rich ($\sqrt{31} \times \sqrt{31}$) structure is stable; we cannot model a supercell of the size needed to calculate this. Instead we modeled a much simpler Al-rich interface, which is predicted to become the most stable one just above $P_{O_2}^{min}$ where Al₂O₃ decomposes. Since the experimental $\sqrt{31} \times \sqrt{31}$ is a very Al-rich surface ($\Gamma_{OS} = -7.5$ in the present notation), the slope of its surface energy versus $\log_{10}(P_{O_2}/P^0)$ is correspondingly very steep and positive, and it must intersect all the other surface energies just above $P_{O_2}^{min}$.

The Nb free surface should obviously become unstable with respect to some adsorption of oxygen when $P_{O_2} > P_{O_2}^{max}$, the pressure at which NbO begins to form. The particular configuration and concentration of an oxygen monolayer which we have calculated is not likely to be the optimum configuration of the first oxygen-covered Nb(111) surface, but it does become more stable than the free surface at pressures somewhat above $P_{O_2}^{max}$ [Fig. 3(a)].

A significant new result is the theoretical analysis of the *thermodynamic* stability of the O-terminated interface, the strong bonding of which we discussed above. No interface is thermodynamically stable above the (very low) oxygen pressure at which NbO forms, but over most of the range below this the O-terminated interface is less stable than the Al-terminated one [Fig. 3(c)], despite its strong bonding. In fact at the very lowest pressure of oxygen, as would pertain in the presence of pure aluminum, our prediction is of an Al-enriched interface. The experimental indications from EELS (Ref. 35) show no evidence for Al-Nb bonding, and suggest rather the existence of the O-terminated interface. According

to our analysis this could only be marginally in thermodynamic equilibrium if the oxygen pressure is being “buffered” by Nb/NbO and lies close to $P_{\text{O}_2}^{max}$, which does not seem unreasonable.

We have not included in our comparison interfaces with a different macroscopic orientation such as the Nb(110)/Al₂O₃ (0001) interface.³⁰ Although this interface is believed to be thermodynamically more stable than the Nb(111)/Al₂O₃ (0001) interface, the kinetic barrier to changing the macroscopic orientation is presumably much greater than the barriers to changing the local interface structure.

The present work shows how vibrational entropy may be included with nonstoichiometry in the calculation of interfacial free energy. The formalism included the contribution of point defects if these are regularly arranged at the interface, such as the oxygen vacancies treated here. Another aspect arises if the nonstoichiometry is in the form of a high concentration of randomly distributed point defects. In this case an ensemble of interfaces would have to be calculated. If the concentration of defects is low, on the other hand, it would be adequate to include their individual formation energy and configurational entropy as additional terms in the above free energy.

Although the formalism has been developed for describing metal-oxide bonding, there are obvious applications to systems in which water or other substances may contaminate surfaces or interfaces. The comparison of the energetics of interfaces with differing amounts of segregation follows the same lines. The application of the present formalism using a thermodynamic cycle to avoid the most difficult calculations may be fruitful in other situations in the field of interface chemistry.

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