The thermodynamics of decohesion

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Abstract

We present a thermodynamic description of decohesion that provides a link between first principles studies of decohesion and cohesive zone models used in continuum simulations of crack growth. The properties of a cohesive zone are described by thermodynamic excess variables extracted from first-principles calculations. Applied to decohesion of fcc aluminum, we find that the excess energy for decohesion along adjacent (1 1 1) planes is well described by the universal binding relation of Rose et al. [Phys. Rev. Lett. 47 (1981) 675; Phys. Rev. B 28 (1983) 1835]. We also present a first principles model to investigate the effect of impurity atoms on slow decohesion when the impurity chemical potential can remain constant by modifying the impurity concentration in the decohering zone. In studying the effect of hydrogen or oxygen impurities on decohesion of aluminum along a pair of (1 1 1) planes, the model predicts a Van der Waals transition above a critical impurity chemical potential. This transition involves the saturation with impurity atoms of the region between the decohering planes and leads to a dramatically reduced maximum stress for decohesion.

Keywords: Cohesive zone model; Aluminum; Hydrogen embrittlement; Fracture; First-principles electronic structure; Thermodynamics

1. Introduction

Crack growth is a complex materials phenomenon involving a combination of bond breaking and plastic deformation. The mechanisms of crack growth operate over several length scales and vary widely depending on the imposed loading conditions, the properties of the material and the environment. At the crack tip, crack growth can proceed with crack tip blunting caused by significant local plastic deformation and twinning or by brittle decohesion [2,3]. Impurities at the crack tip add an extra level of complexity, locally affecting cohesive properties [4–6] and potentially playing a role in nucleating crack tip dislocations [7]. All these phenomena occur embedded within a macroscopic solid undergoing elastic and plastic deformation.

Significant advances are being made with multi-scale modeling schemes that aim to model the crack tip atomistically and the surrounding solid with continuum mechanics [8–10]. Nevertheless, such schemes, due to computational requirements, are limited to the study of fracture phenomena occurring over short time scales. Continuum simulations that use a cohesive zone model to describe the solid ahead of the crack tip, however, continue to provide important insights about crack growth in solids under non-catastrophic conditions [11–13]. These simulations typically incorporate constitutive relations describing the dynamics of discrete dislocations embedded in bulk solid described with continuum elasticity along with a cohesive zone model for the region ahead of the crack. The use of a cohesive zone model ensures that crack formation and growth is a natural outcome of the simulation.

A cohesive zone model characterizes the energy associated with separating adjacent atomic planes of a crystal, be they the faces defining a grain boundary, or adjacent crystallographic planes within a particular grain. From it a traction curve can be obtained that describes the stress versus separation acting on the faces of the crack. In continuum descriptions of fracture that
explicitly incorporate a cohesive zone, the bulk regions adjacent to the crack faces are attributed continuum elastic and plastic properties while the separating atomic planes ahead of the crack are described with a cohesive zone model. An accurate cohesive zone model should capture the characteristics of atomic-level bond breaking between adjacent atomic planes of a crystal. Increasingly, first principles electronic structure methods are able to provide information on decohesion at the atomic level [14–16].

The purpose of this paper is to demonstrate how a cohesive zone model can be extracted from fully relaxed first principles calculations and how the effect of impurities can be incorporated in the description of a cohesive zone. To this end, we introduce a precise definition of thermodynamic variables that describe a cohesive zone using the concept of excess variables [5,6]. As an illustration of this formalism, we determine a cohesive zone model for fcc aluminum uniformly decohering along a pair of adjacent (111) planes. We also investigate the effect of hydrogen and oxygen impurities on uniform decohesion of aluminum at constant impurity chemical potential. The use of thermodynamic excess variables to describe a cohesive zone is not limited to decohesion along planes of a single crystal, but can also be applied to the separation of grain boundaries and interfaces.

While the characteristics of a cohesive zone model shed light on one aspect of crack growth, namely cleavage, crack growth in aluminum involves many additional phenomena operating simultaneously [18–20]. Evidence from atomistic simulations using embedded atom potentials have indicated that crack growth in aluminum is also accompanied by dislocation emission and twinning in the crack tip region [19]. A parameter relevant for dislocation nucleation is the unstable stacking fault energy [3] which has been calculated from first principles by Lu et al. [17,18]. Furthermore, hydrogen embrittlement is widely considered to play an important role in crack growth in aluminum and its alloys. The precise mechanism by which hydrogen enhances crack growth is still poorly understood, though several mechanisms have been put forward. One involves increased local plasticity due to the presence of hydrogen (hydrogen enhanced local plasticity, HELP) [7]. Both experimental and first principles evidence indicates that hydrogen facilitates dislocation glide [18,21,22], and it is believed that the enhanced local plasticity at the crack tip in hydrogen rich environments leads to embrittlement and void formation ahead of the crack tip. Another mechanism involves the role of hydrogen in affecting the cohesive properties of aluminum. While both mechanisms are qualitatively different in nature, they are not mutually exclusive. The inclusion of the effect of hydrogen on a cohesive zone model sheds light on the second mechanism of hydrogen embrittlement. We focus on this second mechanism in this paper.

The structure of this paper can be summarized as follows. In Section 2, excess thermodynamic variables are introduced to describe a cohesive zone model. As an illustration (Section 3), we determine excess variables for decohering fcc aluminum from fully relaxed first principles supercell calculations. In Section 4, we introduce a first principles thermodynamic model to calculate excess variables for decohering aluminum in the presence of hydrogen or oxygen impurities. The first principles model predicts a Van der Waals transition above a critical impurity chemical potential which leads to a dramatic drop in the maximum stress for decohesion. The significance and implications of these results for understanding and modeling crack growth are discussed in Section 5.

2. Excess variables and the cohesive zone

2.1. General

The cohesive zone defines the region along which decohesion is to occur. It could be a region along a grain boundary or phase interface, or the space between adjacent atomic planes of a single crystal. We focus on crystalline solids containing mobile interstitial impurities. We allow for the possibility of an impurity concentration in the cohesive zone that differs from the bulk and assume that the solid is immersed in an impurity reservoir at constant impurity chemical potential \( \mu \). Impurities could include hydrogen or oxygen atoms which are, for example, generated by dissociation reactions of gas molecules such as \( \text{H}_2 \), \( \text{O}_2 \) or \( \text{H}_2\text{O} \). Neglecting pressure–volume work, Gibbs’ fundamental equation for the change of internal energy \( E \) of the solid can be written as

\[
\text{d}E = T \text{d}S + F \text{d}L + \mu \text{d}N + \mu_m \text{d}N_m + \gamma \text{d}A, \tag{1}
\]

where \( T \) is the temperature, \( S \) the entropy, \( F \) the force acting on the solid (perpendicular to the plane defining the cohesive zone), \( L \) the length of the solid parallel to \( F \) and \( N \) the number of impurity atoms within the solid (including the cohesive zone). \( \mu_m \) and \( N_m \) are, respectively, the chemical potential and number of the metal atoms of the solid. \( \gamma \) is the “surface” energy of the decohering faces within the cohesive zone and \( A \) is the area along the cohesive zone. In the absence of decohesion, \( \gamma \) simply reduces to the grain boundary or interfacial free energy if the cohesive zone describes a grain boundary or phase interface. For a single crystal, \( \gamma \) is zero as long as the solid is uniformly elongated under the influence of \( F \). Once decohesion occurs along the cohesive zone, though, \( \gamma/2 \) equals the surface energy of
the decohering faces within the single crystal and its value depends on the extent of decohesion.

We restrict ourselves to a very specific mode of decohesion: the separation of the planar faces bounding the cohesive zone in the absence of surface reconstruction and contraction or expansion of the solid perpendicular to the applied force. These two assumptions specify that \( N_m \) and \( A \) remain constant during decohesion and therefore \( dN_m = 0 \) and \( dA = 0 \).

It is useful to introduce thermodynamic excess variables \([4,5]\) that characterize the cohesive zone. The dependence of these excess variables on externally imposed variables then constitutes the cohesive zone model. We define cohesive zone excess variables in such a way that the extensive variables of the complete solid (e.g., \( E, S, L, \) etc.) can be described as the sum of the extensive variables of ideal uniform elastic slabs I and II, and excess variables of the cohesive zone joining the slabs.

The ideal uniform slabs extend up to the decohering atomic planes that bound the cohesive zone. The excess variables describe the difference between the extensive variables of the actual solid and those of the ideal uniform slabs joined across the cohesive zone. Hence, the excess variables describe the region between the separating atomic planes defining the cohesive zone and its effect on the rest of the solid. As a result, they also include the contributions from the slabs resulting from non-uniformities in the bulk that arise from the broken symmetry introduced by the decohering region.

The excess length for example is defined as

\[
L^e = L - (L_I + L_H),
\]

where the lengths \( L_I \) and \( L_H \) of the ideal slabs are the equilibrium values for the same number of metal atoms in a uniform solid (without decohered region) at constant \( T, F, \mu \). While \( L^e \) is a measure of the separation between the decohering atomic planes bounding the cohesive zone, it is not necessarily exactly equal to the distance between decohering faces of the actual crystal since it may also include other non-uniform deformations within the bulk. Nevertheless, when the force \( F \) is zero, \( L^e \) reduces to the equilibrium distance \( d_0 \) between the two adjacent atomic planes bounding the cohesive zone.

In a similar way, we can define excess quantities for \( E^e, S^e \) and \( N^e \) as the difference between the corresponding variables of the solid with decohering region and the variables for the ideal slabs at constant \( T, F, \mu \).

The extensive thermodynamic quantities \( E, S, L \) and \( N \) satisfy Gibbs’ fundamental relation, Eq. (1), and their analogues of the idealized slabs (i.e., \( E_I, S_I, L_I, N_I \), etc.) also satisfy Gibbs’ fundamental relation for a uniform bulk. Therefore, a similar relation can be written for the excess quantities

\[
dE^e = T dS^e + F dL^e + \mu dN^e.
\]

This equation constitutes the fundamental thermodynamic relation describing a cohesive zone embedded between bulk material assigned with uniform properties. We point out that the excess variables defined above differ from those based on the Gibbs excess variables first introduced to describe surfaces and grain boundaries \([4,5]\) in that they not only account for the non-uniformities within the bulk of the solid, but also describe the corresponding property between the decohering faces.

2.2. Alternative boundary conditions

For most applications, the thermodynamic potential \( E^e \) is impractical since its natural variables \( S^e, L^e \) and \( N^e \) are difficult to control experimentally. More appropriate potentials can be derived from \( E^e \) by applying Legendre transforms. At fixed \( T, L^e \) and \( N^e \), we obtain the excess Gibbs free energy potential as \( G^e = E^e - TS^e \) which varies with its natural variables according to

\[
dG^e = -S^e dT + F dL^e + \mu dN^e.
\]

At fixed \( T, L^e \) and \( \mu \), we obtain the grand canonical potential \( \Omega^e = E^e - TS^e - \mu N^e \) which has as differential form

\[
d\Omega^e = -S^e dT + F dL^e - N^e d\mu.
\]

At fixed \( T, F \) and \( \mu \), we obtain what we refer to as the grand-force potential \( \Phi^e = E^e - TS^e - FL^e - \mu N^e \) with differential form

\[
d\Phi^e = -S^e dT - L^e dF - N^e d\mu.
\]

The potentials \( G^e, \Omega^e \) and \( \Phi^e \) play a central role in defining the equilibrium properties of a cohesive zone.

For example, at constant \( T \) and in the absence of impurities \( (N, N^e = 0) \), the mechanical work to separate the faces bounding the cohesive zone is equal to the change in excess Gibbs free energy since according to Eq. (4)

\[
\Delta G^e = \int_{d_0}^{\infty} F \, dL^e.
\]

(Note that this work does not include the elastic energy absorbed by the hypothetical uniform slabs.) The traction curve at constant \( T \) in the absence of impurities is simply the derivative of the excess Gibbs free energy

\[
\left( \frac{\partial G^e}{\partial L^e} \right)_{T,N^e} = F.
\]

At constant \( T \) and impurity chemical potential \( \mu \), the mechanical work of separation equals the change in the excess grand canonical potential since then

\[
\Delta \Omega^e = \int_{d_0}^{\infty} F \, dL^e.
\]

Likewise, the traction curve at constant \( T \) and \( \mu \) becomes

\[
\left( \frac{\partial \Omega^e}{\partial L^e} \right)_{T,\mu} = F.
\]
The cohesive zone characterized by its thermodynamic excess quantities can be viewed as a separate phase that equilibrates with adjacent ideal bulk phases having uniform properties. The boundary conditions of this equilibrium are constant $T$, $F$ and $\mu$. Equilibrium under these conditions is determined by a minimum in the grand-force potential $\Phi^g$.

2.3. Thermodynamic stability

Stability is another thermodynamic property that must be considered. Thermodynamic stability indicates whether a particular state is stable with respect to infinitesimal fluctuations of an extensive variable. The second derivatives of the characteristic potentials with respect to their extensive variables supplies information about stability. For example, the second derivative of the excess grand canonical potential with respect to excess length, according to Eq. (5) must be positive, i.e.

$$\left( \frac{\partial^2 \Omega^e}{\partial L^2} \right)_{T, \mu} > 0. \quad (9)$$

This stability condition requires that

$$\left( \frac{\partial^2 \Phi^e}{\partial F^2} \right)_{T, \mu} < 0, \quad (10)$$

i.e., a system is stable if its grand-force potential has a negative curvature.

2.4. Normalized excess quantities

It is often convenient to work with thermodynamic quantities that have been normalized by the area of the cohesive zone $A$. Neglecting changes in $A$ that may arise from the poisson effect, Gibbs’ fundamental equation relating the excess quantities becomes

$$d\varepsilon^e = T \, d\varepsilon^e + \sigma \, d\delta + \mu \, d\Gamma, \quad (11)$$

where $\varepsilon^e = E^e / A$, $\delta^e = S^e / A$ and $\Gamma = N^e / A$ are called normalized excess quantities and $\sigma = F / A$. We have also introduced $\delta = L^e - d_0$, where $d_0$ is the equilibrium spacing between the atomic planes defining the faces the cohesive zone. In a similar manner, we define $g^e = G^e / A$, $\omega^e = \Omega^e / A$ and $\phi^e = \Phi^e / A$.

3. Cohesive zone model for fcc aluminum

The introduction of thermodynamic excess variables to describe a cohesive zone offers a precise link between cohesive zone models used in continuum simulations of crack growth and first principles electronic structure calculations. In this section, we determine first principles excess variables for decohesion of fcc aluminum along adjacent (1 1 1) planes. In the absence of impurities, $N^e$ is zero and the thermodynamic properties of the cohesive zone (at constant temperature) are determined by the excess Gibbs free energy $G^e$. First principles calculations are performed at 0 K such that $G^e = E^e$. In this section, we illustrate the calculation of $E^e$ from first principles by calculating the energy of elongating a supercell consisting of several atomic planes.

3.1. Decohesion in a supercell

In this work we used density functional theory (DFT) within the local density approximation (LDA) as implemented in the Vienna ab initio simulation package (VASP), a plane wave pseudopotential code that solves for the electronic structure of periodic systems [23,24]. To calculate the energy of decohesion, we used a supercell containing 12 (1 1 1) planes. Within this supercell, the (1 1 1) planes are perpendicular to the c-axis. Elongation of the c-axis of the supercell is equivalent to stretching the 12 (1 1 1) planes. We calculated the energy for different values of $c$.

At least two locally stable states of internal deformation exist as the crystal is elongated perpendicular to the (1 1 1) planes. For small elongations ($c$ close to the equilibrium value $c_0$ corresponding to zero force) the crystal is homogeneously and elastically deformed. For large elongations (large $c$) the elongation is distributed non-uniformly and largely concentrated between one pair of ‘decohering’ (1 1 1) planes. At intermediate elongations, the two states of internal deformation are locally stable.

Fig. 1 illustrates the energy of the two states of internal deformation as a function of the elongation of the...
supercell \( A = \varepsilon - \varepsilon_0 \). The zero of the energy scale is set to that of the supercell when \( \varepsilon = \varepsilon_0 \). In the calculations, all atoms within the unit cell were relaxed to minimize the energy of the cell. The dashed curve is the energy for the state of uniform elongation where all \((111)\) planes are equally spaced. The solid curve is the energy for the "decohered" state. The energy for the "decohered" state levels off to a constant value as \( A \) increases. As \( A \) increases (by an increase in \( \varepsilon \)), the separation between the decohering planes also increases. Hence, the interaction between the decohering \((111)\) planes diminishes and the separating slabs relax to an inter-planar spacing that is close to that of bulk fcc aluminum. The plateau value of the solid line in Fig. 1 is therefore twice the surface energy of \((111)\) faces (after dividing by the surface area) since two new \((111)\) surfaces have been created per supercell.

The variable \( A_2 \) in Fig. 1 corresponds to the elongation of the cell for which the stored elastic energy in a uniformly elongated slab equals twice the surface energy. Above this elongation, the decohered state becomes thermodynamically stable. Nevertheless, an energy barrier separates the uniformly elongated state from the decohered state making both states locally stable. The variable \( A_2 \) depends on the size of the elongated solid \((12 \ (111)\) planes in case). In fact, Nguyen and Ortiz [25] showed that for an elastic system the elongation for which the energy of the uniformly elongated state equals the energy for the decohered state with two new surfaces scales as \( \sqrt{n} \), where \( n \) is a measure of the number of crystallographic planes perpendicular to the direction of elongation. The variable \( A_3 \) corresponds to the maximum elongation a uniformly elongated crystal can withstand before becoming unstable. Beyond this point, the energy for uniform elongation exhibits a negative curvature; any infinitesimal non-uniform fluctuation in the inter-planar spacing would lead to spontaneous decohesion of the solid. It is at \( A_3 \) that the maximal stress for decohesion is reached. The value of \( A_3 \) also depends on the size of the system, scaling linearly with \( n \). The variable \( A_1 \) is the elongation at which the decohered state becomes metastable. Below this value, the decohered state spontaneously relaxes to the state of uniform elongation.

### 3.2. First principles cohesive zone model

The energy and elongation plotted in Fig. 1 corresponds to that of the supercell containing 12 atomic planes. To derive a cohesive zone model from these values, we must obtain the excess energy \( E^x \) versus the excess elongation \( L^x \). For this particular supercell calculation, the excess energy becomes

\[
e^x(\varepsilon) = E(\varepsilon)/A - (n-1)e(\varepsilon),
\]

where \( E(\varepsilon) \) is the energy of the supercell at stress \( \varepsilon \), \( A \) is the area of the supercell face perpendicular to the \( c \)-axis and \( e(\varepsilon) \) is the elastic energy per unit area and per \((111)\) plane of a homogeneously elongated crystal at the same stress \( \varepsilon \). The variable \( n \) refers to the number of atomic planes in the supercell perpendicular to the direction of elongation (in this case 12). Analogously, the excess length becomes

\[
L^x(\varepsilon) = L(\varepsilon) - (n-1)l(\varepsilon),
\]

where \( L(\varepsilon) \) is the length of the supercell (i.e., the \( c \)-axis) at stress \( \varepsilon \) and \( l(\varepsilon) \) is the length between adjacent \((111)\) planes in a homogeneously elongated crystal at the same stress \( \varepsilon \). Fig. 2(a) illustrates \( e^x \) versus \( \delta = L^x - d_0 \) with \( d_0 \) the equilibrium spacing between adjacent \((111)\) planes.
at zero stress. Data from both curves in Fig. 1 were used to obtain Fig. 2(a).

The solid line in Fig. 2(a) is that of a universal binding curve, proposed by Rose et al. [1] and having the form

\[ e(\delta) = e_0 - 2\gamma(1 + \frac{\delta}{2}) \exp\left(-\frac{\delta}{\lambda}\right). \]  

(14)

The universal binding curve illustrated in Fig. 2(a) was fit to LDA calculations in which rigid slabs (again using the supercell) are separated without allowing internal relaxations within the slabs (i.e., the interplanar separation between adjacent planes within the slabs were kept at their zero stress equilibrium value). Remarkably, the unrelaxed energy versus separation of rigid slabs closely coincides with the excess energy determined from calculations that include internal relaxations within the slabs. This indicates that relaxations in the slabs are essentially equivalent to uniform elastic deformations as in a uniformly stressed solid. Furthermore, this result suggests that the energy of separating a pair of adjacent planes is negligibly affected by the state of separation between neighboring planes, justifying the use of local, non-interacting potentials to describe the energy of separating adjacent atomic planes. Fig. 2(b) illustrates the stress versus \( \delta \).

4. Cohesive zone model in the presence of impurities

4.1. Method

Of importance in determining the influence of corrosive environments on cohesive properties is the ability to model the effect of impurities such as hydrogen or oxygen atoms on the energy of the cohesive zone. The solid solubilities of hydrogen and oxygen within bulk solids such as fcc aluminum are often very low at typical chemical potentials of gas or fluid environments containing these species. For the same chemical potential values, the impurity concentration on solid surfaces can be quite large, sometimes attaining saturation levels. When decohesion occurs along a pair of atomic planes, the concentration of impurities at constant \( \mu \) between these planes could differ from the bulk. A difference in impurity concentration between the bulk and the decohering region locally modifies the mechanical response of the solid, altering the mechanisms and rates of crack growth from what it would be in the absence of impurities.

In this section, we introduce a first principles cohesive zone model that incorporates the effect of impurities. We make several assumptions. We investigate the effect of impurities on the excess thermodynamic properties associated with a pair of decohering adjacent (1 1 1) planes of fcc aluminum and assume that impurities are limited to the region between this pair of adjacent (1 1 1) planes. As a thermodynamic boundary condition, we assume constant impurity chemical potential. This condition holds for slow crack growth rates in which impurities have sufficient time to equilibrate with the instantaneous state of stress between the separating atomic planes.

Calculating the energy as a function of the extent of decohesion \( \delta \) for a fixed impurity arrangement between the decohering atomic planes is straightforward with standard electronic structure methods. At finite temperature, however, the impurity atoms sample many different arrangements, each characterized by a different energy. Calculating thermodynamic properties therefore requires the use of statistical mechanical techniques to appropriately average over the different arrangements of impurity atoms between the decohering atomic planes. We describe a formalism, based on the cluster expansion technique that allows us to perform these statistical mechanical averages in a computationally tractable way.

Within LDA, both hydrogen and oxygen energetically prefer the interstitial tetrahedral sites in fcc aluminum. The tetrahedral sites between one pair of adjacent (1 1 1) planes form an undulating honey-comb lattice. Once the separating planes are fully decohered, these sites become fcc surface sites which form a triangular lattice on both new surfaces (see Fig. 3). As the impurity concentration between the separating (1 1 1) planes is allowed to vary, configurational disorder will exist on the honey-comb lattice of the cohesive zone.
The thermodynamic properties are derived by obtaining suitable statistical mechanical averages over the different possible configurations.

A standard technique to describe the dependence of the energy on the atomic arrangement on a periodic lattice is a lattice model [26,27]. Such a model consists of assigning an occupation variable \( s_i \) to each site \( i \) of the honey-comb lattice between a pair of \((1 \, 1 \, 1)\) planes which is \(+1\) when it is occupied and \(-1\) when it is vacant. The collection of all occupation variables, denoted by \( \vec{s} = (s_1, s_2, \ldots, s_i, \ldots) \) uniquely specifies the impurity arrangement in the cohesive zone.

We model the configurational energy of the cohesive zone (per two-dimensional unit cell of the cohesive zone) at fixed \( \delta \) with the lattice model Hamiltonian

\[
E(\vec{s}, \delta) = \sum_i (V_\delta(\delta) + V_s(\delta)s_i) + \frac{1}{2} \sum_{ij} V_\delta(\delta)s_is_j + \frac{1}{2} \sum_{ij} V_s(\delta)s_is_j. \tag{15}
\]

The coefficients \( V_\delta, V_s, V'_\delta \) and \( V'_s \) called effective cluster interactions (ECIs), are independent of configuration. The first sum is over all sites on the honey-comb lattice in the cohesive zone. In the second sum \( i \) ranges over all lattice sites and \( j \) ranges over all nearest neighbor sites to \( i \). In the third sum, \( j \) ranges over all second-nearest neighbor sites to \( i \). Eq. (15) is a truncation of a cluster expansion [27] in which only those terms corresponding to the point and nearest neighbor pair clusters have been kept. Fig. 3 illustrates the pair clusters used in Eq. (15).

Eq. (15) is a parameterization of the configurational energy that enables us to approximate the energy of any arrangement of solute atoms between the decohering planes at fixed \( \delta \). Eq. (15) has only four parameters: \( V_\delta, V_s, V'_\delta \) and \( V'_s \). Hence, if the energies of at least four symmetrically distinct impurity arrangements are known, it is possible to obtain values for the four ECI of Eq. (15) by inversion. Note though, that the energy for each solute arrangement varies with the excess length. This means that the ECI, while constant at fixed \( \delta \), are functions of the extent of decohesion \( \delta \).

The configuration dependence of the stress \( \sigma \) can also be parameterized with a cluster expansion. This cluster expansion is simply the derivative of Eq. (15) with respect to the excess crack length \( \delta \).

Combining Eq. (15) with either Monte Carlo simulations or a mean field free energy model, we can obtain the desired thermodynamic potentials at any temperature. While Monte Carlo simulations are more accurate, the mean field approximation offers analytical expressions for the free energy.

Within the mean field approximation, the impurity atoms on the honey-comb lattice between the separating \((1 \, 1 \, 1)\) planes are assumed to be completely disordered. This means that short range order is neglected and the expression for the configurational entropy reduces to that of the well-known ideal solution model. With Eq. (15), the gibbs free energy per unit cell of the cohesive zone (a two-dimensional honey-comb lattice has two sites per unit cell) then becomes

\[
G = 2V_\delta + 2V_s\langle s \rangle + 6V'_\delta\langle s \rangle^2 + 3V'_s\langle s \rangle^2 + 2kT\theta \ln(\theta) + (1 - \theta) \ln(1 - \theta), \tag{16}
\]

where \( \langle S \rangle \) is the average of the site occupation variables and \( \theta \) is the concentration of impurities over the interstitial sites between the separating \((1 \, 1 \, 1)\) planes. \( \theta \) is linearly related to the occupation variables as \( 1/2(1 + \langle s \rangle) \). The factors 2, 3 and 6, respectively, follow from the multiplicity of the corresponding clusters. The Gibbs free energy \( G \) is normalized per unit cell of the cohesive zone which includes two interstitial sites. Hence, there are three equivalent \( \beta \) clusters and six equivalent \( \gamma \) clusters per unit cell of the cohesive zone. These multiplicities change depending on the crystallographic planes being separated. With the gibbs free energy (Eq. (16)), which depends on the excess length through the ECI, any thermodynamic potential for the cohesive zone can be calculated after applying suitable Legendre transforms.

4.2 Cohesive zone model with hydrogen or oxygen impurity

In this section, we consider the effect of hydrogen and oxygen on the decohesion of fcc aluminum. The interaction coefficients of the lattice model Hamiltonian, Eq. (15), of the cohesive zone were fit to first principles energy values of four different impurity arrangements between a pair of decohering \((1 \, 1 \, 1)\) planes. First principles energies were calculated with the pseudopotential method in the local density approximation. All supercells contained \((1 \, 1 \, 1)\) planes. In one arrangement, all honey-comb sites of the cohesive zone were occupied with hydrogen. Two arrangements consisted of hydrogen-vacancy ordering and the fourth arrangement had no hydrogen in the cohesive zone. Identical calculations were performed for oxygen impurities. Since as illustrated in Section 3, relaxations in the bulk contribute negligibly to the excess quantities of the cohesive zone, only the impurities were relaxed while the slabs were kept rigid in these calculations. The reference for the energy scale is pure aluminum at equilibrium interplanar separation and zero force. It was possible to fit a universal binding curve to the energy versus separation results for each of the four impurity arrangements.

We constructed separate lattice models for the H–Al and O–Al system by fitting the ECI of Eq. (15) to the energy versus separation relations of the four different arrangements. Fig. 4 illustrates the variation of \( V'_\delta \) and \( V'_s \) versus \( \delta \). Note that the distance between the endpoints of clusters of type \( \gamma \) (see Fig. 3) does not change.
with $\delta$. The distance between the points of the pair cluster $\beta$ do get larger with $\delta$. For hydrogen between decohering (1 1 1) planes, $V_\gamma$ exhibits very weak ordering tendencies as manifested by its small positive value. $V_\beta$ approaches zero as $\delta$ increases. The small values for $V_\beta$ and $V_\gamma$ indicate that the impurities will be randomly distributed over the available sites at elevated temperature. The negative value for $V_\gamma$ for the oxygen system indicates phase separating tendencies which will lead to island formation on the (1 1 1) surfaces at large $\delta$.

Inserting the separation-dependent interaction parameters of the lattice models in the Gibbs free energy expression Eq. (16) allows us to determine the thermodynamic properties of the cohesive zone for any set of thermodynamic boundary conditions. Below, all thermodynamic potentials were evaluated at 300 K.

### 4.2.1. Cohesive zone with hydrogen impurities

We assume the cohesive zone to be in mechanical equilibrium with adjacent slabs and in chemical equilibrium with an impurity chemical potential originating from either the slabs or an external environment (such as a gas or liquid). Hence, the thermodynamic boundary conditions of the cohesive zone are constant stress $\sigma$ and constant impurity chemical potential $\mu$. Equilibrium of the cohesive zone in the presence of impurities is then determined by a minimum in the grand-force potential $/e$ at fixed $\sigma$ and $\mu$. Fixed values for $\sigma$ and $\mu$ determine unique values for the separation $\delta$ and impurity concentration $\theta$ at equilibrium. The grand-force potential $/e$ can be obtained from the Gibbs free energy with a Legendre transform by $/e - \mu \Gamma - \sigma \delta$. At constant chemical potential, the mechanical work (per unit area) required to separate adjacent (1 1 1) planes of the cohesive zone is determined by the excess grand canonical potential $/e$ because of Eq. (8).

Insight about the effect of impurities on decohesion can be gained by considering the equilibrium of the cohesive zone for three different ranges of hydrogen chemical potential. Fig. 5 illustrates the fraction curves at intermediate and high impurity chemical potential. Also illustrated on each plot are stress versus separation curves for fixed hydrogen concentrations between the decohering (1 1 1) planes (shown for intervals of 0.2).
fraction curves. At very low hydrogen chemical potential, the driving force to saturate the cohesive zone is very low for all separations \( \delta \), resulting in a negligible hydrogen concentration on the sites between the decohering (111) planes for all \( \delta \). The \( \sigma \) versus \( \delta \) relation closely follows that for pure aluminum (see Fig. 2(b)). Likewise, the grand canonical potential \( \Omega^e \) as a function of \( \delta \) at low hydrogen chemical potential (curve (a) in Fig. 6) differs negligibly from the excess energy of separation for pure aluminum (Fig. 2(a)).

At higher hydrogen chemical potential, the equilibrium hydrogen concentration between the decohering (111) planes rises with \( \delta \), surging rapidly in a small interval of \( \delta \). This is illustrated in Fig. 7. The effect of the concentration surge is to cause the \( \sigma \) versus \( \delta \) curve to undulate, as it rapidly traces out the fixed concentration traction curves illustrated in Fig. 5(a). The grand canonical potential \( \Omega^e \) is also altered as illustrated in Fig. 6(b). Not only does the rise in \( \Omega^e \) with \( \delta \) decrease as a result of the saturation of the cohesive zone by hydrogen at large \( \delta \), but its shape also changes qualitatively. Hence, according to Eq. (8) and curve (b) in Fig. 6, increased impurity chemical potential reduces the work for decohesion.

The curves in Figs. 5–7 have been plotted versus \( \delta \), which is not a controlling variable. Some portions of the curves in these figures may be thermodynamically unstable or metastable. True equilibrium is given by a minimum in the grand-force potential \( \Phi^e \) at fixed \( \sigma \) and \( \mu \). Fig. 8 illustrates \( \Phi^e \) for the chemical potentials that produce the curves of Figs. 6 and 7. The concave down portions (bold lines in Fig. 8) correspond to states that are thermodynamically stable. The stable branches of \( \Phi^e \) in Fig. 8(a) along a–b and c–d correspond to similarly labeled regions of the \( \sigma \) versus \( \delta \) curve in Fig. 5(a). The branch of \( \Phi^e \) along a–b in Fig. 8(a) corresponds to the first hump of the \( \sigma \)–\( \delta \) curve with positive slope (Fig. 5(a)). Along this branch, the cohesive zone has a very low hydrogen concentration. The metastable
branch of $\phi^c$ in Fig. 8(a) along c–d corresponds to a saturated cohesive zone in which all the hydrogen sites are filled. At intermediate chemical potential, the grand-force potential $\phi^c$ for the saturated state (state along c–d in and 8(a)) is above the unsaturated state along a–b. This means that the thermodynamically most stable state during decohesion is along a–b, indicating that decohesion still occurs with negligible hydrogen present between the separating (111) planes.

At higher hydrogen chemical potentials, matters change qualitatively. Above a critical chemical potential $\mu_c$, the grand-force potential for the saturated state (c–d in Fig 8(a)) dips below $\phi^c$ of the unsaturated state as illustrated in Fig. 8(b). The cross-over of the two curves indicates a first-order transition whereby at constant stress, $\sigma_t$, the state with low hydrogen concentration, which we call the dilute cohesive-zone (DCZ) phase, transforms to the saturated state, which we call the saturated cohesive-zone (SCZ) phase. This first-order phase transformation can be understood as a Van der Waals transition. The crossing of $\phi^c$ for the two stable branches is equivalent to a Maxwell construction on the dashed curve of Fig. 5(b). The implication of this transformation on the traction curve is illustrated by the solid line in Fig. 5(b). The transformation drastically reduces the maximum stress along the traction curve from that of the initial hump to that of the second hump corresponding to the saturated state. The onset of the Van der Waals transition at a critical $\mu_c$, means that the maximum stress for decohesion should change discontinuously. The solid line in Fig. 9 gives the evolution of the maximal stress for decohesion as a function of the hydrogen chemical potential, showing an abrupt drop in maximal stress at $\mu_c$. In Fig. 9, $\mu_c$ has arbitrarily been set to zero.

4.2.2. Cohesive zone with oxygen impurities

Qualitatively similar results are obtained for the oxygen–aluminum system. While the trends with varying oxygen chemical potential are predicted to be similar to those in the hydrogen aluminum case, minor differences do arise due to the different oxygen–oxygen interaction between adjacent aluminum (111) planes. As shown in Fig. 4, oxygen atoms have an attractive effective interaction and therefore favor a degree of clustering behavior while hydrogen atoms exhibit weak ordering tendencies with vacancies. The difference manifests itself in the stress versus separation curve (Fig. 10) and the $\theta$ versus $\delta$ curve. At fixed oxygen chemical potential, the oxygen concentration between the decohering planes changes discontinuously as opposed to a smoother surge exhibited by hydrogen with $\delta$. The grand-force potential versus stress exhibits, as in the hydrogen case, the occurrence of a Van der Waals phase transformation from a DCZ phase to a SCZ phase. The variation of the maximum stress for decohesion is illustrated in Fig. 9 (dashed line) as a function of oxygen chemical potential. Here also $\mu_c$ has arbitrarily been set to zero.

5. Discussion

A cohesive zone model makes it possible to approximate the response of a solid ahead of the crack tip in continuum simulations of crack growth. To make a connection between first principles total energy calculations and continuum models for crack growth, we have defined excess variables that characterize the thermodynamic properties of a cohesive zone. These excess variables, strictly valid for uniaxial decohesion, can be applied to situations where the crack is characterized by an extended region of gradual decohesion.
Our definition of excess variables provides a well-defined partitioning of energy between the cohesive zone and the elastic energy in the surrounding continuum system. We have illustrated how excess variables such as energy can be determined from first principles total energy calculations using a supercell approach. Applying this to decohesion of fcc aluminum along a pair of adjacent (111) planes, we have recovered the universal binding curve proposed by Rose et al. [1].

With the help of a lattice model, we have also investigated a first principles cohesive zone model that includes interstitial impurities at constant impurity chemical potential. Applied to aluminum decohesion in the presence of hydrogen or oxygen impurities, the model predicts that above a critical impurity chemical potential, a first-order phase transformation occurs at a constant stress $\sigma_t$, whereby a DCZ phase transforms to a SCZ phase. The consequences of this first-order phase transition within the cohesive zone are twofold. First, it leads to a qualitative change in the traction curve that results in a drastic reduction of the maximal stress for decohesion. Second, it has important consequences regarding the precise mechanism by which impurities affect crack growth kinetically.

The predicted first-order phase transition at $\sigma_t$ involves a discontinuous change in impurity concentration and degree of decohesion $\delta$. As with other first-order phase transformations such as condensation, solidification, etc. the predicted phase transformation along the cohesive zone should occur with a nucleation and growth mechanism. This would presumably involve the creation and migration of an “interface” separating the SCZ phase from the DCZ phase. The “interface” contributes an energetic penalty arising from the abrupt change in impurity concentration and slab separation $\delta$.

This energy cost needs to be overcome by a free energy gain of the new phase which only occurs if there is a supersaturation with respect to the controlling thermodynamic variables $\sigma$ and $\mu$. Hence, for decohesion above $\mu_c$, the phase transformation along the cohesive zone will not occur exactly at $\sigma_t$ but rather at a stress higher than $\sigma_t$ such that the SCZ phase (with wider separation) can nucleate and grow. Once the SCZ phase has formed, the mechanical response of the solid (at least locally) is different than that of pure aluminum, decohering at a significantly lower maximum stress. Conversely, upon crack closure, a stress less than $\sigma_t$ must be reached before a DCZ phase can nucleate and grow within the pre-existing SCZ phase.

A constant impurity chemical potential boundary condition to the cohesive zone is valid as long as the impurity mobility is large enough to keep pace with the advancing crack tip. A likely source of impurities is the crack surfaces behind the crack tip, which when equilibrated with the environment, serve as an impurity reservoir at constant chemical potential. Other possible modes of mass transport involve decomposition of impurity-containing gas molecules at the crack tip [28], or fast impurity diffusion along dislocations that open at the crack tip. Typical bulk and surface diffusion lengths of hydrogen, as estimated from first principles calculations [16], are of the order of 1 $\mu$m which is in the range of several experimental measurements [29]. Crack growth rates consistent with such impurity diffusion lengths occur during stage I and II of stress corrosion cracking as well as during near threshold fatigue, which range between $10^{-8}$ and $10^{-6}$ m/s [28,30–36].

The Van der Waals transition can be interpreted as a stress induced phase transformation in the presence of mobile impurities. Above a critical stress and impurity chemical potential, it becomes favorable for aluminum to fill its interstitial sites with impurity atoms. While in the present model, we have restricted the formation of the new phase to the region between the pair of decohering atomic planes, in reality the stress-induced phase could extend over several atomic planes. Many regimes of fracture are intergranular as opposed to transgranular. An analogous study can be performed for decohesion along a grain boundary, though the computational costs are significantly higher due to the requirement of very large supercells to accommodate an explicit grain boundary. We have focussed on uniaxial decohesion. However, the state of stress at crack tips is triaxial. Large shear stresses along the cohesive zone may also be present. These have been neglected but could in principle be included within the thermodynamic formalism as another work term describing the energetics associated with sliding the two slabs with respect to each other. This, however, complicates the analysis by adding several degrees of freedom to the problem.

We emphasize that the analysis and results presented in this paper only shed light on one aspect of crack growth in most crystalline solids and in aluminum in particular. Crack growth involves the simultaneous occurrence of plasticity around the crack tip through nucleation and motion of dislocations along with bond breaking through cleavage. Even twin formation at the crack tip has been observed in embedded atom simulations of aluminum crack growth [19,20]. The results of this paper deal only with cleavage. To approximate plasticity and cleavage phenomena simultaneously, the first principles cohesive zone models should be used in continuum crack growth simulations that describe the solid around the crack with continuum elasticity together with constitutive relations describing the motion of discrete dislocations [11,12]. Even then, the use of a cohesive zone model derived from first principles calculations of uniform decohesion is an approximation as the bond breaking at the crack tip is likely to involve lattice trapping phenomena [37]. By themselves, the first principles results of this paper set bounds on the maximum cohesive strength of aluminum and show in which
manner and to what extent impurities such as hydrogen and oxygen can reduce the cohesive strength of a solid. The results offer insight as to how impurities can embrittle a solid susceptible to crack growth through cleavage. The qualitative predictions about the mechanisms of cohesive embrittlement are likely to persist even under conditions characterized by significant plastic activity around the crack tip.

Several approximations due to computational limitations have been made in our first principles investigation of the role of impurities during decohesion. One is the use of a short-ranged lattice model Hamiltonian containing only nearest-neighbor pair interactions. For the hydrogen–aluminum system, the calculated nearest neighbor pair interactions are small. This indicates weak interactions between hydrogen atoms between decohering aluminum planes and thereby justifies a short-ranged interaction between hydrogen atoms between decohering planes. For the oxygen–aluminum system, the nearest neighbor interaction $V_{\delta}$ is large and positive for small $\delta$, but decays rapidly with increasing $\delta$. For most chemical potentials in the vicinity of $\mu_c$, the oxygen concentration in the cohesive zone is predicted to be close to zero. $V_{\delta}$ is large and negative for all $\delta$ indicating phase separating behavior. For a phase separating system, it becomes less crucial to accurately predict the energies of ordered oxygen-vacancy arrangements in the cohesive zone since these states contribute negligibly in statistical mechanical averages made to obtain thermodynamic potentials. Therefore, for the oxygen system as well, a short ranged lattice model Hamiltonian is sufficient to capture the qualitative features of this system.

Another simplification in our analysis has been the use of the mean-field approximation. While often a crude approximation, it is reasonable for disordered solutions and for phase separating systems. In fact for the Hydrogen aluminum system, we found that the mean field approximation yields essentially the same results as more accurate Monte Carlo simulations.

6. Conclusion

We have linked the properties of a cohesive zone with results from first principles total energy calculations by introducing thermodynamic excess quantities. Applied to fcc aluminum decohering along a pair of adjacent (1 1 1) planes, we have shown that the cohesive zone model derived from fully relaxed first principles calculations closely follows the universal binding curve of Rose et al. [1]. We have also developed a first principles thermodynamic model to investigate the effect of impurities on decohesion at constant chemical potential. Applied to a study of the effect of hydrogen and oxygen on decohesion of fcc aluminum along (1 1 1) planes, the first principles model predicts a first-order Van der Waals phase transition whereby an unsaturated cohesive zone transforms to a saturated cohesive zone at constant stress above a critical impurity chemical potential. This phase transformation has important consequences regarding the role of impurities in affecting the cohesive properties of a metal. It qualitatively alters the pure metal traction curve, leads to a dramatic reduction of the maximum stress for decohesion and makes the relation between impurity chemical potential and critical stress discontinuous. Furthermore, the occurrence of such a phase transformation suggests that the effect of impurities is kinetically manifested by a nucleation and diffusional growth mechanism along the cohesive zone.

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