

## Atomistic *Ab Initio* Studies of Precipitate/Host Lattice Interfaces

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Results of theoretical atomistic *ab initio* investigations of the interior of the [100]<sub>Al</sub> interface between Al and the C-type plate precipitate observed in the Al-Mg-Si-Cu alloy system are presented. Guidelines for a consistent model description of the strain field evolution along the interface are provided. This scheme can be used, in conjunction with an interface configuration study, for predicting theoretically, at the atomic level, the maximum dimensions, shapes, and full interfacial energies of isolated coherent precipitates with compositionally abrupt interfaces.

**Keywords:** Al-Mg-Si alloys, calculations, density functional theory, interfaces, C-type plate.

### 1. Introduction

Interfaces are gaining importance in the context of structural materials optimization, with recent improvements of transmission electron microscopy (TEM) techniques for direct structural imaging [1] raising the bar for manipulation of the material on the nanoscale: for the case of aluminium (Al) alloys, the structural details of the alloying element containing nanostructures (precipitates) responsible for material hardening [2] are now being clarified, with experiment providing information on the *macroscopic* influence of the precipitates, but with theory needed to address the influence on *mesoscopic* and *atomic* scales.

Atomistic *ab initio* modelling frameworks promise optimal reliability in the determination of the physical precipitate/host lattice interfaces, providing essential input for mesoscopic models [3], but are conventionally regarded as restricted to probing only the centre of the interface under consideration. Building upon previous work by the authors [4], it will be shown, through calculations for the C-type plate precipitate observed in the Al-Mg-Si-Cu alloy [4, 5], how a reliable modelling of an *arbitrary* segment at the interior of the interface can be carried out. This opens to describing atomistically issues connected to the complete precipitate.

### 2. Theory

Recently, Ehlers *et al.* [6] suggested a path to determining theoretically, at the atomic level, the energy and structure of a coherent and compositionally abrupt interface between two subsystems without resorting to the conventional limitations of a supercell modelling framework (see e.g. [7]). The new scheme builds on top of the usual one, focussing on a formally infinite interface through the implementation of periodic boundary conditions. However, evolution along the interface in response to the presence of a lattice mismatch between the subsystems can now be described, through (i) a truncation of the long range tails of the strain field away from the interface and (ii) a (hypothetical) coupling of symmetrically connected interface segments as the choice of interface pair in the supercell description (some of this is shown in Fig. 2). Moving away from the centre of the interface (defined as the point of minimal *local* interfacial energy) amounts, to a first approximation, to introducing shear stress on the supercell along the same direction, with the sign depending on which subsystem is stretched at the interface. The magnitude of this distortion is proportional to both the numerical subsystem lattice mismatch and the desired physical movement.

For the case where one subsystem grows surrounded by the other (such as a precipitate in an Al host lattice) and in the absence of defects at the interface under investigation, the first changes to the interface configuration when moving away from the centre should be encountered (excluding effects of interactions with other interfaces, which is not modelled within the scheme) at the point where the first shutdown of growth towards this configuration occurs, i.e., when the binding of atoms on a necessary growth path ceases to be energetically favourable when compared to thermal fluctuations. Likewise, the theoretical maximum extension of the structure can be defined as the point where the subsystem is unable to grow at all in the direction normal to the interface. Physically, binding of dislocations, and possibly interface compositional changes, are expected to further extend these theoretical growth ranges. All these issues are inaccessible within the conventional *ab initio* interface modelling scheme, but can be addressed using the scheme of [6], once (i) the relevant interface configurations have been determined and (ii) a physically sound modelling of the strain field evolution into the subsystems has been fully established.

The interaction between interfaces with different orientation, neglected in the modelling, poses a potential restriction to employing the scheme to the case of precipitates in a host lattice. Plate-like semicoherent precipitates, where the dimensions of the coherent interface can extend into the range of tens of nm along two directions, appear clearly favoured in the context of analysis compared to the needle-like coherent precipitates, where all interfaces are conventionally restricted to just a few nm along one direction. The C-type plate precipitate [4, 5] observed in the Al-Mg-Si-Cu alloy represents such a highly suitable candidate for theoretical interface investigations employing the scheme of [6], with plates of dimensions in the range 35 - 180 nm observed in experiment [5].

### 3. Computational details

Calculations have been performed within density functional theory [8], using Vanderbilt ultrasoft pseudopotentials [9] as implemented in the plane wave (PW) code VASP [10]. The Perdew-Wang 1991 generalized gradient approximation [11] to the exchange-correlation functional was employed throughout. A relatively modest precision, 234 eV PW cutoff and (5, 10, 2) *k*-mesh, was used for all systems, justified by the structural energy differences and parameters being fairly well converged at this stage. For the interface configuration determination in Sec. 4.2, a possibly hypothetical C-type plate precipitate of only one unit cell width was used for the modelling. The main conclusions however were supported by studies involving a precipitate of twice the thickness. All studies of interfacial energy evolution with position on the interface (Sec. 4.3, 4.4) involved the larger precipitate, with a Cu/Al ordering at the 'Cu sites' (see Sec. 4.1) as shown in Fig. 1 (b).

## 4. Results and discussion

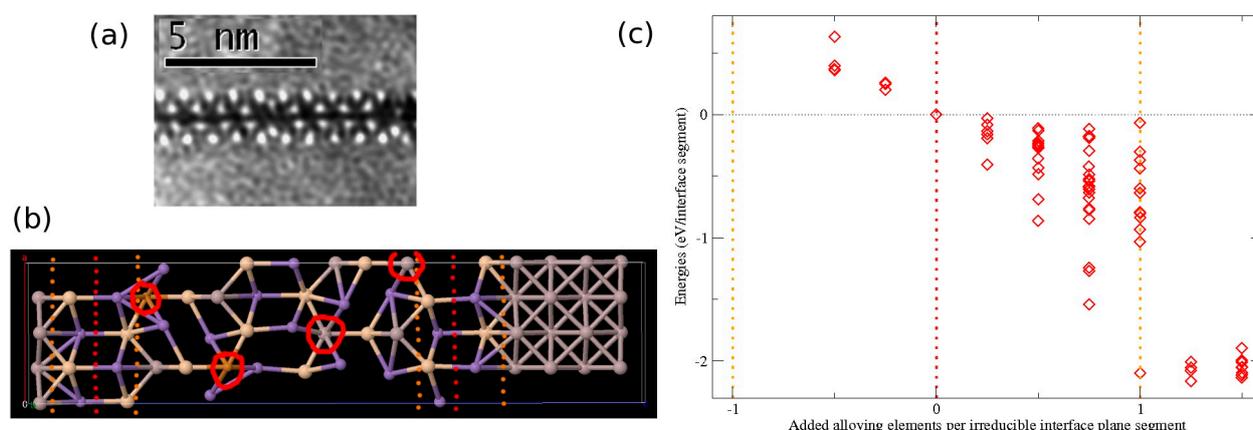
### 4.1 C-type plate precipitate bulk configuration

The atomic structure of the C-type plate precipitate was addressed experimentally by Torsæter *et al.* in [5]. The present work builds, in addition, upon more recent theoretical and experimental investigations of this structure, to be discussed in detail elsewhere. The bulk composition of the precipitate investigated is  $\text{Mg}_8\text{Al}_3\text{Si}_6\text{Cu}$ . This choice involves two presumed simplifications, made for computational simplicity, of the experimental C-type plate phase: for the atoms at the 'Cu sites' (see Fig. 1 (b)) of the precipitate, an occupancy of 50% Cu and 50% Al has been assumed, with only one atom type occupying sites connected along  $[001]_{\text{Al}}$ . Experimentally, a fluctuation in Cu/(Cu+Al) in the range 0.5 – 0.8 is likely for the Cu site atoms, possibly accompanied by incorporation of Mg at the remaining sites occupied by Al in Fig. 1 (b). The influence of these competing bulk configurations on the interface configuration analysis has not been addressed in this work.

#### 4.2 C-type plate/Al $[100]_{\text{Al}}$ interface configuration at the centre of the interface

As shown in Fig. 1 (a), the C-type plate precipitate grows primarily along the  $[001]_{\text{Al}}$  and  $[010]_{\text{Al}}$  directions, with the  $[100]_{\text{Al}}$  interface hence being the one of interest to the present studies. It is a prerequisite for an interface study employing the present methodology that the interface under investigation be coherent and compositionally abrupt. TEM studies of the precipitate suggest a structurally sharp  $[100]_{\text{Al}}$  interface with Al (see Fig. 1 (a)) but are unable to rule out the possibility of Si and Mg residing on the Al fcc sites, due to the low Z-contrast between these atoms and Al. Theoretically, fluctuations in the precipitate size around the structural interface have been investigated, within the structural restrictions suggested by TEM studies. Equivalent interfaces on both sides of the precipitate have been assumed throughout, with alloying elements added/removed only from the two rows along  $[010]_{\text{Al}}$  adjacent to the structural interface, unless otherwise noted. Finally, an interface configuration order consistent with the bulk C-type plate dimensions along  $[001]_{\text{Al}}$ ,  $[010]_{\text{Al}}$  has been introduced (see Table 1). This set of simplifications (and others, see Sec. 3, Sec. 4.1) will be critically addressed along with a more complete discussion in a future publication.

The results of the present investigations (Fig. 1 (c)) make it clear that the structural interface is unstable while also suggesting a strong stability (more than 0.5 eV/interface segment) of the interface configuration displayed in Fig. 1 (b). This configuration involves a relative displacement of precipitate and host lattice by 2.025 Å along  $[001]_{\text{Al}}$ , a distortion which however seems naturally connected with further precipitate growth and only leads to a weak expansion (0.15 Å along  $[100]_{\text{Al}}$  at each interface) of the precipitate and no additional disturbance of the host lattice, when compared to the structural interface configuration.



**Fig. 1** Calculated energies of various  $[100]_{\text{Al}}$  Al/C-type plate precipitate interface configurations. (a) Experimental Fourier filtered annular dark field (ADF) image of a C-type plate precipitate segment. The horizontal (vertical) lines denote the  $[010]_{\text{Al}}$ , ( $[100]_{\text{Al}}$ ) directions. Cu atoms are visible as the bright spots in the image. (b) Schematic presentation of the energetically most favourable interface configuration. Cu, Al, Si, and Mg atoms are labelled with orange, light brown, yellow, and purple spheres, respectively. Compared to (a), a rotation by  $90^\circ$  around  $[001]_{\text{Al}}$  has been performed, with periodic boundary conditions assumed along all directions in the modelling description. Cu sites are highlighted (red circles) and the structural interface and configuration fluctuations have been labelled with dotted red and orange lines, respectively. (c) Calculated energies, same dotted lines as in (b). Results of support for the stability of the configuration in (b) against further growth have also been displayed.

#### 4.3 Consistent modelling of an arbitrary segment at the interior of the interface

When moving away from the centre of a given interface, the strain field is expected to increase in both magnitude and extension into each subsystem. Hence, for the present modelling description,

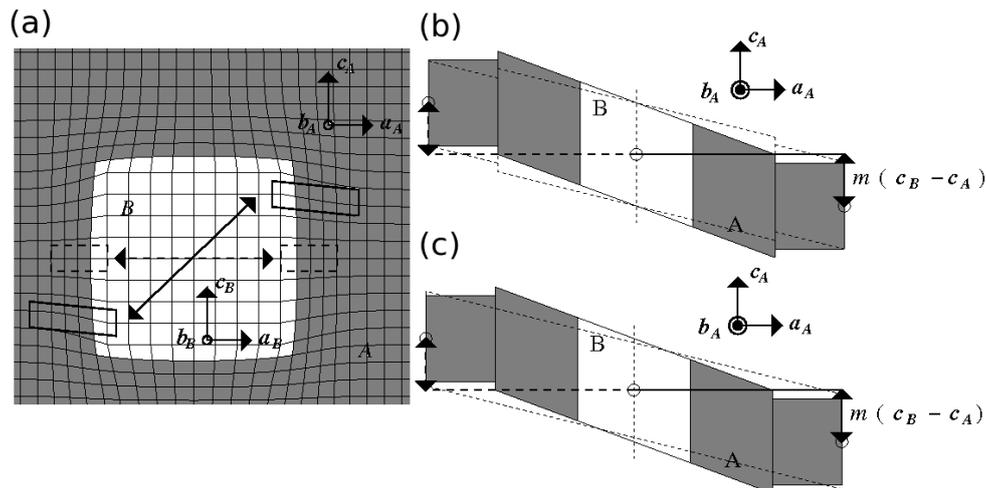
off-centre interface segments would likely require a larger cell along the interface normal, compared to the interface centre, for the strain field to be described at the same level of precision. The number of atoms in the cell (choice of subsystem ratio in particular) and the irreducible interface plane segment basis vectors are coupled as a consequence of the spatially constant strain field modelled. The question emerges what is physically most sound: to keep these vectors fixed when moving away from the centre or vary them in accordance with any required cell size changes?

Fig. 2 presents the modelling schemes that emerge from the above two scenarios (basic details in [6]) and how to test their validity. For each model description, and if part of the interior of subsystem B is always unaffected by the interface, a given segment ' $(n, m)$ ' on the interface, connected with the centre  $(0, 0)$  through the translation  $n\mathbf{b}_B + m\mathbf{c}_B$ , where  $\mathbf{b}_B$  and  $\mathbf{c}_B$  are the bulk subsystem B counterparts of the interface plane segment basis vectors  $\mathbf{b}, \mathbf{c}$  (see Fig. 2 (a)) and  $n, m$  are integers, is modelled by distorting the supercell for the interface centre as (for simplicity, Fig. 2 assumes  $n = 0$ )

$$\mathbf{a}(0, 0) \rightarrow \mathbf{a}(0, 0) + 2n(b_B - b_A)\mathbf{b}/|\mathbf{b}| + 2m(c_B - c_A)\mathbf{c}/|\mathbf{c}| + \gamma(n, m)\mathbf{n} = \mathbf{a}(n, m). \quad (1)$$

In Eq. 1,  $b_A$  ( $b_B$ ),  $c_A$  ( $c_B$ ) are the magnitudes of the bulk subsystem counterparts of  $\mathbf{b}, \mathbf{c}$ , while  $\gamma$  denotes a relaxation of  $\mathbf{a}$  that leaves the relative displacement of these systems unaffected ( $\mathbf{n} \perp \mathbf{b}, \mathbf{c}$ ).

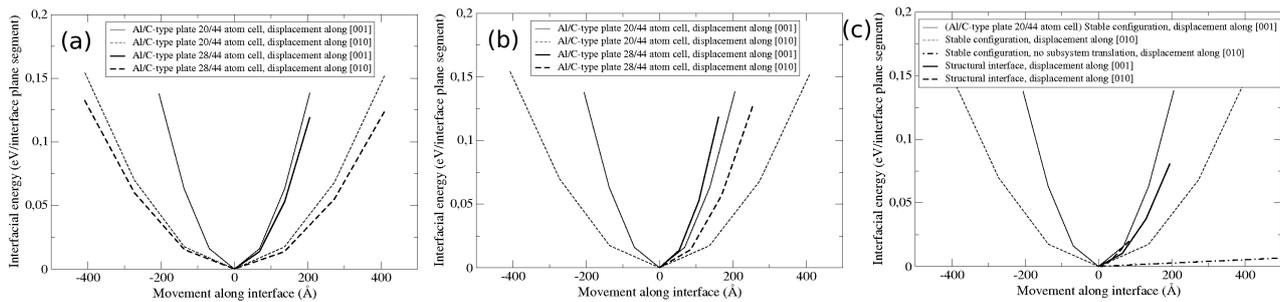
A need for a larger cell to incorporate the growing strain field is associated (see e.g. Fig. 2 (b)) with an energy lowering when more atoms are added to the cell along the interface normal, but with the 'boundary conditions' described by the first two distortion terms in Eq. 1 kept fixed (in physical terms, this would mean that the strain field benefits from being distributed over a wider range). If the interface plane segment basis vectors are regarded as fixed (Fig. 2 (b)), a consistent modelling scheme assumes that the new regions (compared to a consideration at the interface centre) affected by the strain field are not stretched in the interface plane. This follows from the conclusion [6] that the interface plane segment basis vectors are essentially independent of the distortion in Eq. 1 when the strain field range is assumed fixed for the entire interface. In Fig. 2 (c), by contrast, the interface basis vector magnitudes will depend on the given interface segment, as the entire region affected by the strain field at a given point on the interface is regarded as stretched along the interface plane.



**Fig. 2** Schematic presentation of two suggested schemes for modelling the strain field variation with position on a coherent and compositionally abrupt interface between two subsystems. (a) Full system, with the symmetrically connected interface segments combined in the model description highlighted. (b) Strain field evolution into subsystem A: fixed range of subsystem matching along interface assumed (outermost parts of larger, dotted cell not stretched along  $\mathbf{b}, \mathbf{c}$ ). (c) Same as (b), but stretching of entire region assumed. Cell size specific interface plane segment basis vectors  $\mathbf{b}, \mathbf{c}$ .

In contrast to the schematic presentation in Fig. 2 (a), it is plausible that *little or no bulk precipitate region* exists for the C-type plate precipitate under investigation, given that the width is only  $\sim 2$  nm (in other words, the whole precipitate is regarded as influenced, to some extent, by the choice of interface configuration). Eq. 1 should be modified accordingly, with  $b$ ,  $c$  (the meaning of which for the present studies have been clarified in Sec. 4.2) substituted for  $b_B$ ,  $c_B$ . This adds the fundamental change to the second modelling scheme addressed above that the connection between a given distortion of the cell and the position on the interface depends on the chosen cell size.

Fig. 3 displays the results of testing the schemes of Fig. 2 for the calculated energetically most favourable Al/C-type plate  $[100]_{Al}$  interface configuration of Fig. 1 (b). In all calculations, only Al/C-type plate 20/44 and 28/44 atom cell were compared. It was tested that  $\gamma$  in Eq. 1 could justifiably be set equal to zero. When the assumption of fixed interface plane segment basis vector magnitudes  $b$ ,  $c$  is used (Fig. 3 (a)), adding more host lattice atoms to the system yields a flatter curve, suggesting that the strain field range is increasing with the movement away from the interface centre as expected. For cell size specific values of  $b$ ,  $c$  (see Fig. 3 (b) and Table 1), the interfacial energy shows an unphysical increase with cell size. This suggests that while the strain field range increases upon movements away from the centre of the interface (Fig. 3 (a)), the matching of precipitate and host lattice along the interface is a comparatively short ranged effect. An energy change of 0.1 eV/interface segment in the figures corresponds to roughly  $50 \text{ mJ/m}^2$ .



**Fig. 3** Calculated interfacial energy variation for various Al/C-type plate  $[100]_{Al}$  configurations. (a) Energetically most favourable configuration (Fig. 1 (b)), scheme of Fig. 2 (a). (b) Same as (a), but using scheme of Fig. 2 (b). (c) Fixed cell size, configurations of Table 1. See text for details.

**Table 1:** Calculated irreducible interface plane segment basis vector magnitudes for various Al/C-type plate  $[100]_{Al}$  configurations. Parentheses: mismatch with bulk Al (lattice parameter  $4.044 \text{ \AA}$ ).

Interface configuration; Al/C-type plate cell	$[001]_{Al}$ ( $\text{\AA}$ )	$[010]_{Al}$ ( $\text{\AA}$ )
Structural; 24/40	4.063 (+0.46%)	8.002 (-1.06%)
Stable (centre); 20/44	4.062 (+0.45%)	8.070 (-0.22%)
Stable (centre); 28/44	4.067 (+0.56%)	8.059 (-0.36%)
Stable, no subsystem translation; 20/44	4.008 (-0.89%)	8.086 (-0.02%)

#### 4.4 Comparing the interface energy evolution for different interface configurations

Fig. 3 (c) shows the interfacial energy variation with movement along  $[010]_{Al}$ , as calculated for Al/C-type plate 20/44 atom cells only, for the three different interface configurations included in Table 1. As all configurations disturb the host lattice only little, the results of Fig. 3 (c) are regarded as justifiable in their emphasis on the influence of the configuration specific interface plane segment dimensions on the energy variation. Combined with a sufficiently detailed study of the set of competing interface configurations, such investigations can be used directly for predicting structural changes at the interface and even shutdown on precipitate growth, as discussed in Sec. 2.

#### 4.5 Additional comments

The chosen Al/C-type plate 20/44 atom cell used for description of the interface centre contains insufficient amounts of Al for the strain field to be fully incorporated. Presumably, this enhances all effects in Fig. 3 unphysically. Presumably more important is the seemingly unphysical increase in subsystem mismatch with increasing cell size displayed in Table 1 for the energetically most favourable interface configuration. Considering the extreme sensitivity of the modelling scheme on the calculated values of  $b$ ,  $c$ , it cannot be excluded at this stage that the conclusion arrived at in Sec. 4.3. should actually be the opposite, and the present discussion therefore should primarily be viewed as a presentation of a scheme for how to address the strain field evolution. Finally, the narrow thickness of the C-type plate precipitate means that segments on the interfaces on the two sides of the structure not actually physically coupled interact in the model description. The influence of this error, including the extent to which a bulk C-plate precipitate region is defined or not, should be addressed.

#### 5. Conclusions

Building upon the modelling framework of [6], a scheme for a physically acceptable atomistic *ab initio* modelling of the strain field evolution along a coherent and compositionally abrupt interface between two metallic subsystems has been suggested. Comparison with e.g. finite element method (FEM) modelling results for the same system would be highly interesting.

#### Acknowledgements

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