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Atomistic modeling of the strengthening mechanisms in FCC and HCP metals

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“Service to others is the rent you pay for your room here on earth.”

Muhammad Ali

Resumen

El endurecimiento por precipitación es uno de los mecanismos más eficaces para mejorar el límite elástico de aleaciones metálicas. El movimiento de las dislocaciones es impedido por la presencia de una distribución homogénea de precipitados intermetálicos de tamaño nanométrico, lo que conlleva el aumento de la tensión de cizalla en el plano de deslizamiento para rebasar este obstáculo. Los precipitados de gran tamaño (> 50 nm) son rebasados formando un lazo de Orowan y diversas investigaciones han estudiado en detalle los mecanismos de interacción entre la dislocation y el precipitado usando modelos continuos. Estos modelos se apoyan en la interacción elástica entre la línea de la dislocación y el precipitado. Los precipitados más pequeños suelen ser cizallados por las dislocaciones y los mecanismos de endurecimiento asociados (químicos, fallos de apilamiento, diferencias en las constantes elásticas, deformaciones de coherencia y orden) son mas difíciles de cuantificar. Además, las hipótesis del continuo no se pueden aplicar en el caso de precipitados muy pequeños, como las zonas de Guinier-Preston.

El estudio de los mecanismos de interacción entre precipitados de pequeño tamaño (< 20 nm) y dislocaciones puede realizarse mediante estrategias de simulación atómica, basadas estática o dinámica molecular y técnicas para identificar caminos de

mínima energía. Sin embargo, su correcta aplicación es complicada y necesita superar varias dificultades: selección del potencial interatómico adecuado, desarrollar metodologías robustas para calcular la barrera de energía, extrapolación de los resultados atomísticos a las velocidades de deformación típicas de las aplicaciones en ingeniería, etc. Esta tesis doctoral está dirigida al desarrollo de nuevas metodologías de simulación atomística para estudiar la superación de estos obstáculos, de modo que puedan utilizarse en un futuro para desarrollar nuevas aleaciones metálicas endurecidas por precipitación.

En esta tesis doctoral se estudian tres problemas diferentes. El primero es la interacción de dislocaciones con zonas de Guinier-Preston en aleaciones de Al-Cu mediante simulaciones de mecánica molecular. Una nueva estrategia de estática molecular en combinación con relajación térmica se ha usado para simular la cizalla de las zonas de Guinier-Preston por las dislocaciones y las funciones termodinámicas que determinan la interacción entre ambas se obtuvieron mediante simulaciones atomísticas en combinación con la teoría de transiciones de estado. Esta información se usó para estimar la tensión crítica de cizalla en función de la temperatura y la velocidad de deformación, que se comparó con los resultados experimentales.

El segundo problema abordado es el deslizamiento cruzado de dislocaciones helicoidales. Este es otro mecanismo mediante el cual las dislocaciones pueden superar un precipitado y, además, juega un papel importante en la formación de redes de dislocaciones. El método de la banda elástica se ha usado para determinar la barrera de energía para el deslizamiento cruzado en ausencia de energía térmica, mientras que la probabilidad de deslizamiento cruzado se determinó mediante dinámica molecular en función de la tensión de Schmid en el plano de deslizamiento cruzado y de las tensiones de Escaig en los planos de deslizamiento y de deslizamiento cruzado en Al. Como resultado se postuló y validó una expresión de la barrera de energía libre para el deslizamiento cruzado en función de las tensiones de Schmid y Escaig.

Finalmente, las simulaciones atomísticas se usaron para estudiar la interacción de dislocaciones basales con precipitados β -Mg₁₇Al₁₂ en aleaciones Mg-Al. Se ha desarrollado una estrategia para insertar precipitados con intercaras semicoherentes en la matriz metálica asegurando que la estructura de la intercara es cercana a la de mínima energía. Se descubrió que las dislocaciones inicialmente sobrepasan al precipitado por la formación de un lazo de Orowan que es capaz de penetrar en el precipitado. Las sucesivas dislocaciones que alcanzan el precipitado dan lugar finalmente a la cizalla del mismo a lo largo del plano (110), paralelo al plano basal del Mg. Este mecanismo se ve favorecido debido a que el plano basal (0001) del Mg es paralelo al plano (110) del precipitado y este proceso es muy probable que ocurra en otras aleaciones de Mg

y puede ser responsable de la limitada capacidad de endurecimiento por precipitación de las aleaciones de Mg.

Abstract

Precipitate strengthening is one of the most efficient mechanisms to increase the yield strength of metallic alloys. Dislocation glide is hindered by the presence of a homogeneous dispersion of nm-sized intermetallic precipitates, and higher critical resolved shear stresses have to be applied on the slip plane to overcome the precipitate. Large precipitates (> 50 nm) are normally overcome by the formation of Orowan loops. In this case, the mechanisms of dislocation/precipitate interaction have been extensively analyzed in the past by means of continuum models based on the elastic interactions of the dislocation line with the precipitate. Smaller precipitates are often sheared by the dislocations and the associated strengthening mechanisms (chemical, stacking fault, elastic mismatch, coherency strains, and order) are more difficult to quantify. Moreover, the continuum hypothesis breakdown in the case of very small precipitates, such as Guinier-Preston zones.

Classical atomistic simulations, based on either molecular statics or dynamics and path sampling methods, are another type of strategies that can be used to analyze the interaction mechanisms between dislocations and precipitates in the case of small precipitates (< 20 nm). Nevertheless, their application is not straightforward and requires to overcome several challenges: selection of the appropriate interatomic potential, building atomistic models with realistic interfaces between the precipitate and the

metallic matrix, development of robust methodologies to calculate the energy barrier in the case of very rough energy landscapes, extension of the atomistic results to the typical strain rates of most engineering applications, etc. This doctoral thesis was aimed at developing methodologies to tackle these problems, so classical atomistic simulations can be eventually used to design novel precipitate-strengthened metallic alloys.

Three different problems were analyzed in this thesis. The first one was the interaction of dislocations with Guinier-Preston zones in an Al-Cu alloy by means of molecular mechanics simulations. A novel molecular statics - thermal annealing strategy was used to simulate the shearing of the Guinier-Preston zones the dislocations and the thermodynamic functions that control the dislocation/precipitate interaction were obtained from atomistic simulations in combination with transition state theory. This information was used to estimate the critical resolved shear stress as a function of temperature and strain rate, which was compared with experimental results in the literature.

Dislocation cross-slip is another mechanism to overcome the precipitates and it is also important to simulate the formation of dislocation networks during deformation. The nudged elastic band method was employed to determine the activation energy barrier for dislocation cross-slip in the absence of thermal energy, while the cross slip rate was determined by molecular dynamics as a function of the Schmid stress on the cross-slip plane, and of the Escaig stresses on the cross-slip and glide planes in Al. Based on these results, an analytical expression of the activation free energy barrier for cross-slip in Al as a function of the Schmid and Escaig stresses was developed and validated.

Finally, atomistic simulations were used to evaluate the interaction of basal dislocations with β -Mg₁₇Al₁₂ precipitates in Mg-Al alloys. A strategy was developed to insert a lozenge-shaped Mg₁₇Al₁₂ precipitate with Burgers orientation relationship within the Mg matrix in an atomistic model ensuring that the matrix/precipitate interfaces were close to minimum energy configurations. It was found that the dislocation bypassed the precipitate by the formation of an Orowan loop, that entered the precipitate. Within the precipitate, the dislocation was not able to progress further until more dislocations overcome the precipitate and push the initial loop to shear the precipitate along the (110) plane, parallel to the basal plane of Mg. This process was eventually repeated as more dislocations overcome the precipitate in agreement with experimental observations and indicate that precipitate shearing by basal dislocations in Mg-Al alloys is favored because the (0001) Mg basal plane is parallel to the (110) crystallographic plane of the precipitate. This process is likely to occur for other precipitates in Mg and is responsible for the limited precipitation hardening of Mg alloys.

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Gustavo Esteban Manzanares

*A todos esos luceros
que en algún momento
me han iluminado*

*To those bright starts,
who at some point
have enlighten me*

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1 INTRODUCTION AND STATE OF THE ART

Material science and engineering is a multidisciplinary research field with large implications for the development of the society. The importance of the materials is recognized by the fact that different ages of mankind were named after the main materials that moved the humanity forward e.g. *stone*, *bronze* and *iron ages*.

Materials can be classified according to different criteria. In the case of solids, the most general criterion is given by the nature of the chemical bond and of the atomic structure, leading to ceramics, polymers, composites and metallic materials (Callister, 2007; Shackelford et al., 2016). From the 12th century b.C., metallic materials have been regarded as the structural materials per excellence (Gordo and Piris, 2012) and they are widely used in many engineering applications. Our understanding of the processing-structure-mechanical properties relationships in metallic materials has increased during the last two hundred years parallel to the development of physical metallurgy and mechanics of materials. As a result, the properties of metallic materials (i.e. strength, toughness, chemical stability in different environments, etc.) have been improved dramatically but further improvements are needed because the more demanding operating conditions. In particular, increasing the specific stiffness and strength of metallic alloys is always important in transportation and this area of research is focused in light

Figure 1.1: Relative importance of use of materials along time. Image adapted from (Ashby and Cebon, 1993)

alloys (Al, Ti, Mg) whose application has increased exponentially in the last 50 years (Polmear, 2005; Polmear et al., 2017).

At the atomic scale, metallic materials have a crystalline structure with a long-range order. Deformation of the crystalline lattice is initially reversible, leading to elastic deformations that disappear when the external stress is removed. Nevertheless, permanent, plastic deformations are introduced in the material if the stress overcomes a certain threshold. Plastic deformation at the atomic scale is always linked to the nucleation and propagation of defects in the crystalline structure. Different types of defects can be distinguished (Hull and Bacon, 1968; Callister, 2007) and classified according to:

- Point defects: vacancies, interstitials.
- Linear defects: dislocations
- Surface defects: twin boundaries, grain boundaries, stacking faults.
- Volume defects: voids, bubbles.

All these defects play important roles to determine the threshold stress for plastic deformation as well as the subsequent hardening or softening of the material. However, dislocation glide is the main mechanism of plastic deformation in metallic materials.

Figure 1.2: Taylor's model depiction of the relative atomic displacement between two close-packed planes

Hardening of metallic materials is normally achieved through interaction of dislocations with other defects that hinder the dislocation movement, and this is the standard strategy to improve the strength of metallic materials.

1.1 Dislocations in metals

Dislocations are linear defects (also called one dimensional defects) of crystalline materials, which arise through the relative slip between two regions of the crystalline lattice. The theory of dislocations was developed in the first half of the 20th century, starting with the theoretical model for the strength of a perfect crystal under shear stress introduced by Frenkel (1926). The shear stress necessary to induce the relative displacement, δ , between two atomic planes in a close-packed direction was given by

$$\tau = \frac{\mu l}{2\pi h} \sin\left(\frac{2\pi\delta}{l}\right) \quad (1.1)$$

where μ is the shear modulus of the material, l the distance between atoms in plane and h the distance between close-packed planes, as illustrated in Fig 1.2. The critical shear stress (τ_{css}) necessary to promote a non-recoverable (plastic) displacement between both atomic planes was expressed as,

$$\tau_{css} = \frac{\mu l}{2\pi h} \quad (1.2)$$

The values of τ_{css} predicted by eq. (1.2) were orders of magnitude higher than the experimental results measured in metallic materials. Thus, several authors suggested that plastic deformation was triggered by the movement of dislocations within the crystal (Taylor, 1934b,c; Polanyi, 1934; Orowan, 1934a,b,c), bringing the theoretical predictions in agreement with the experimental observations. It is worth noting that these three authors reached the same conclusions independently and before dislocations were actually observed using electron microscopy. Since then, dislocation theory

Figure 1.3: Burgers circuit representation for an edge dislocation. (a) Perfect lattice with the clockwise Burgers circuit. (b) Lattice representation containing an edge dislocation. The same clockwise Burgers circuit is represented, however there is an extra jump after closing the circuit, which defines the Burgers vector ($\vec{b}$)

has become a fruitful field of research (Hill, 1950; Hull and Bacon, 1968; Hirth et al., 1983).

Dislocations can be classified according to the relative orientation between the dislocation line ($\bar{\xi}$) direction and the Burgers vector ($\vec{b}$), which stands for the extra vector required to close the atom-to-atom path circuit (Burgers circuit) around a dislocation, when compared to the perfect lattice without any defect (Hull and Bacon, 1968). The Burgers vector and Burgers circuit are depicted in Fig. 1.3.

Moreover, the dislocation lines can only finish in the surface of the crystal or form dislocation loops. Within a dislocation loop, the character of the dislocation changes depending on the angle between $\bar{\xi}$ and $\vec{b}$, Fig. 1.4, according to:

- *Edge dislocation:* $\bar{\xi}$ is perpendicular to $\vec{b}$.
- *Screw dislocation:* $\bar{\xi}$ is parallel to $\vec{b}$.
- *Mixed dislocation:* in any other case.

1.1.1 Dislocation motion in metals

Plasticity in solids is mediated by means of different phenomena in the crystal lattice (e.g. dislocation motion, grain boundary sliding or twinning). However, dislocation motion is known to be the main carrier of plastic deformation in metals. Two types of dislocation motion are found: conservative and non-conservative.

The conservative dislocation motion takes place without diffusion of atoms in the lattice. Therefore, the number of atoms involved in the process remains constant. There are two types of conservative dislocation motion, namely slip and cross-slip. Dislocation slip occurs along the slip systems, which are defined by the glide plane and the

Figure 1.4: Dislocation loop in a glide plane, showing the different character of the dislocation as a function of the relative orientation between the Burgers vector, $\vec{b}$ and the dislocation line tangent, $\vec{\xi}$.

slip direction. The glide planes are normally those with the highest atomic density and contain the dislocation line tangent ($\vec{\xi}$) and the Burgers vector ($\vec{b}$). The slip direction in the glide plane is normally parallel to the shortest distance between two atoms. Dislocation motion is hindered by a potential energy barrier along the slip direction, the so-called Peierls barrier. The driving force that has to be applied on the dislocation to overcome this barrier is defined by the Peach-Koehler force, $\mathbf{f}_{PK}$ (Hirth et al., 1983), which is expressed (by unit length of the dislocation line) as

$$\mathbf{f}_{PK} = (\boldsymbol{\sigma} \cdot \vec{b}) \times \vec{\xi} \quad (1.3)$$

where $\boldsymbol{\sigma}$ is the local stress tensor. The shear stress obtained as the projection of the local stress tensor on the slip plane is denominated the resolved shear stress that triggers dislocation slip. Furthermore, the resolved stress necessary to overcome the Peierls barrier, and to begin the slip process, is named the critical resolved shear stress (CRSS). Depending on the character of the dislocation, the CRSS will move the dislocation along different directions: edge dislocations move parallel to $\vec{b}$ while screw dislocations move perpendicular to it.

The other conservative movement, dislocation cross-slip, occurs when the dislocation changes from one glide plane to another slip plane which contains $\vec{b}$. This condition limits cross-slip to screw dislocation segments.

Dislocation slip and cross-slip are the main plastic deformation mechanisms at low temperature. Nevertheless, atomic diffusion is another important phenomena at high temperatures, and thus, dislocation climb from one atomic plane to another assisted by vacancy diffusion also represents an important deformation mechanism. However,

this mechanism is not analyzed in the thesis.

1.1.2 Dislocation motion in FCC metals

Dislocation motion in face centered cubic (FCC) metals takes place along the $\langle 110 \rangle$ directions of the compact $\{111\}$ planes, leading to 12 different slip systems characterized by their corresponding slip plane and a slip direction in the FCC lattice. The CRSS necessary to move dislocations in FCC metals is often very low, in the range 0.1 to 1 MPa (Hull and Bacon, 1968) and, thus, pure FCC metals are very soft. Perfect dislocations in FCC metals are characterized by a Burgers vector $\bar{b} = 1/2[\bar{1}01]$ and they are often dissociated into two Shockley partial dislocations, characterized by Burgers vectors $\bar{b}_1 = 1/6[\bar{1}\bar{1}2]$ and $\bar{b}_2 = 1/6[\bar{2}11]$, leaving a stacking fault ribbon between them, as shown in Fig. 1.5(a).

Two parallel (111) glide planes in the perfect FCC lattice are shown in Fig. 1.5(b). The atoms lying on these (111) may be located in three stable position along the $[111]$ direction. As a result, the stacking sequence of (111) planes follows the ABCABC... pattern. Taking this atom arrangement into account, Fig. 1.5(c) isolates the slip plane with the atoms in the position B, which is considered the slip plane. From an atomistic viewpoint, the movement of Shockley partials along the slip plane follows the pattern defined below: the leading partial dislocation moves the atoms along the $\bar{b}_1 = 1/6[\bar{1}\bar{1}2]$ direction and the atoms in the stable position B are displaced to a metastable location C. Consequently, a fault in the stacking sequence of the planes appears in the lattice. Then, the trailing partial dislocation moves the atoms along the $\bar{b}_2 = 1/6[\bar{2}11]$ direction and the atoms located in the position C come back to the stable position B. However, the slip plane has been sheared by $\bar{b}$, represented as a navy blue surface in Fig. 1.5(a).

The elastic energy per unit length associated with a dislocation is proportional the $|\bar{b}|^2$ and, thus, the energy associated with a perfect FCC dislocation is proportional to $|\bar{b}|^2 = a^2/2$, where a is the lattice constant of the FCC structure. Nevertheless, the energy of each Shockley partial is proportional to $|\bar{b}_1|^2 = |\bar{b}_2|^2 = a^2/6$ and the dissociation of the perfect dislocation into two Shockley partials is favored by the reduction in the total elastic energy. It should be noted that there is an elastic repulsion between Shockley partials and that the equilibrium distance between them is controlled by the magnitude of the stacking fault energy. If the stacking fault energy is large (as in the case of Al), the separation between Shockley partials is small and viceversa. Moreover, the dissociation of the full dislocation facilitates the dislocation motion in the slip plane, by the simultaneous movement of both partial dislocations which have smaller Burgers vector (Fig. 1.5(b) and (c)). However, cross-slip is hindered by this dissociation

Figure 1.5: (a) Leading and trailing partial dislocations on the (111) the glide plane and the stacking fault ribbon between them. (b) Illustration of the (111) slip planes in the FCC lattice. The green (111) atomic plane is located in the A stacking position while the green plane has the atoms in the B position. (c) Atomistic viewpoint the (111) slip system with atoms located in the B stable position. A and C denotes the the atomic position of the (111) planes above and below.

because both partial dislocations have to recombine into one full dislocation before the dislocation can change the slip plane.

Dislocation cross-slip has been extensively studied and different physical processes have been proposed (Püschl, 2002; Caillard and Martin, 2003). Among them, the Friedel-Escaig mechanisms (Escaig, 1968) seems to be in very good agreement with both experiments (Bonneville and Escaig, 1979; Bonneville et al., 1989) and atomistic simulations (Kang et al., 2014). In this process, cross-slip takes place by the creation of two Stroh constrictions along the dislocation line on the glide plane. These constrictions partially re-assemble the leading and trailing partial dislocations and form a perfect $\langle 110 \rangle \{111\}$ dislocation segment between them. The Burgers vector ($\bar{b}$) of the dislocation segment is contained in both the glide and cross-slip planes and as a consequence, the dislocation is allowed to dissociate along the cross-slip plane between the Stroh nodes.

This process is thermally-activated (Caillard and Martin, 2003) and, hence, the cross-slip rate can be determined using an Arrhenius-type equation which depends on the attempt frequency and on the magnitude of the energy barrier associated with the event. This energy barrier in FCC crystals depends on the Escaig and Schmid stresses (Duesbery et al., 1992a; Martinez et al., 2008; Kang et al., 2014; Malka-Markovitz and Mordehai, 2018). The Escaig stress acts on the edge component of the Shockley partial

dislocations, and controls the distance between them. The Schmid stresses acts on the screw component of the dislocation and favor dislocation slip on either the glide or the cross-slip plane.

The determination of the cross-slip rate is crucial to simulate the evolution of the dislocation network during plastic deformation and is a key ingredient of realistic discrete dislocation dynamics (DDD) models (Kubin et al., 1992; Weygand et al., 2002; Martinez et al., 2008; Hussein et al., 2015). Thus, different approaches have been proposed in the literature to determine the energy barrier for cross-slip. Line tension models are based on elastic interaction between Shockley partials. In these models the energy barrier for cross-slip is obtained from the balance between repulsive interaction between partial dislocations on the glide plane and the energy to re-dissociate the partials in the cross-slip plane. Both contributions depend on applied stresses on slip and cross-slip planes (Martinez et al., 2008; Kang et al., 2014; Malka-Markovitz and Mordehai, 2018). Linear-elastic continuum models determine the cross-slip barrier as the extra energy that has to be supplied in order to create a perfect screw dislocation between constriction along Shockley partials. However, they do not deal explicitly with the forces and displacements of partial dislocations. Moreover, these models do not account for the re-dissociation contribution to the energetic barrier (Püschl, 2002).

1.1.3 Dislocation motion in HCP metals

The hexagonal compact (HCP) atomic arrangement is an anisotropic structure, defined by the a and c axis. The a axis corresponds to the minimum atomic distance in the basal plane, while the c axis is perpendicular to the basal plane and is always longer than the a axis. As a result of this anisotropy, different slip systems can operate in HCP lattices depending of the ratio between c/a . Taking this into account, dislocation slip takes place along basal, prismatic and/or pyramidal planes (Fig. 1.6), but different slip direction are possible depending on the glide plane. Basal slip always takes place along the $\langle 11\bar{2}0 \rangle$ direction. However, prismatic slip can take place along the $\langle 11\bar{2}0 \rangle$ or $\langle 0001 \rangle$ directions and pyramidal slip may occur along the $\langle 11\bar{2}0 \rangle$ or the $\langle c + a \rangle$ direction $1/3 \langle 11\bar{2}3 \rangle$ (Hull and Bacon, 1968; Hirth et al., 1983; Martin, 2012)

The CRSS for each slip system depends on the c/a ratio and on the nature of the atomic bond, which are different for each HCP metal. When the c/a ratio is close to the ideal one ($c/a = \sqrt{8/3} \approx 1.633$), as in the case of Mg, the CRSS for basal slip ($\langle 1\bar{2}10 \rangle$ $\langle 0001 \rangle$) is very small ($\tau_{crss} < 1$ MPa), similar to the one found in the $\{111\} \langle 110 \rangle$ slip system of the FCC lattice (Hull and Bacon, 1968).

Moreover, deformation by twinning often takes place in HCP metals. Twinning is a process in which the perfect lattice is homogeneously sheared leading to a reorientation

Figure 1.6: Main slip systems for dislocation motion in HCP metallic materials. (a) Basal slip in the (0001) planes along the $\langle 11\bar{2}0 \rangle$ direction. (b) Prismatic slip in the $\{1010\}$ planes parallel to $\langle 11\bar{2}0 \rangle$ or $\langle 0001 \rangle$. (c) Pyramidal slip in the $\{1011\}$ plane parallel to $\langle 11\bar{2}0 \rangle$ or to $\frac{1}{3}\langle 11\bar{2}3 \rangle$ direction. (d) $\{1012\}$ twin plane along the $\langle 10\bar{1}1 \rangle$ direction.

of the atomic arrangement in the lattice. The twinned and parent regions of the crystal are related by a reflection in some plane (the twin plane). The twinning systems in each crystal are defined by the twin plane and the twin direction as well as by the shear deformation that is accommodated in the twin direction. It should be noted that twinning is a polar mechanism that only occurs when the shear deformation is applied in the appropriate direction, so the twinned region has a mirror symmetry with the parent region across the twin plane, as illustrated in Fig. 1.6(d).

Similarly to FCC metals, the dissociation of basal dislocations into Shockley partials is favored. In the Miller-Bravais notation, the dissociation $\bar{b} = \bar{b}_1 + \bar{b}_2$ is expressed as

$$\frac{1}{3}[11\bar{2}0] = \frac{1}{3}[01\bar{1}0] + \frac{1}{3}[10\bar{1}0] \quad (1.4)$$

The dissociation reaction reduces by a factor of three the elastic energy per unit length stored in the dislocation, and leads to the formation of an intrinsic stacking fault ribbon between both Shockley partials. The coordinated movement of the partial Shockley dislocations in the basal plane is depicted in Fig. 1.7. Additionally, this dissociation into partial dislocations makes the movement of the dislocation very similar to that of the Shockley partials in FCC lattices (see sec.1.1.2). The stacking sequence of the basal planes in HCP metals follows a ABABAB... pattern perpendicular to the c axis, as depicted in Fig. 1.7(a). In this case, the (0001) plane with the atoms on the A position is the glide plane, Fig. 1.7(b). The movement of the leading partial dislocation displaces the atoms from its position A to a metastable position C, forming a stacking fault along the (0001) pile-up sequence. Then, the trailing partial dislocation moves and the atoms located in the position C return to a stable position A but shifted a distance equal to a full $\bar{b}$ with respect to the original position A.

Figure 1.7: (a) Representation of the stacking sequence of (0001) basal planes in the HCP lattice. (b) Viewpoint of the (0001) plane along [0001] direction. Atoms are located in the stacking position A. Red arrows stand for the coordinated movement of the Shockley partial dislocations in the basal plane, while black arrows define the $\bar{b}_1$ and $\bar{b}_2$ directions of the Shockley partials.

1.2 Precipitate hardening

The CRSS necessary to move dislocations in metallic crystals is very low and the design of metallic alloys with higher resistance to dislocation glide has been one of the main goals of physical metallurgy. This is achieved by the introduction of obstacles that hinder the dislocation motion through the lattice. Besides the strain hardening due to dislocation-to-dislocation interactions and to the interaction of dislocations with grain boundaries, solute and precipitation hardening are the main strengthening mechanisms in metallic alloys. All these hardening strategies result in the creation of energetic barriers inside the crystal, that have to be overcome by the dislocations. Precipitation hardening is achieved by the dispersion in the metallic matrix of nm-sized intermetallic particles by means of a thermal treatment involving the decomposition of a supersaturated solid solution and the formation of a series of metastable precipitates as a function of the temperature and time (Martin, 2012). The strengthening provided by these nm-sized intermetallic precipitates is much higher than that obtained by solute hardening (Kelly and Nicholson, 1963) and it is always present in high strength metallic alloys.

From the viewpoint of the lattice correspondence between the precipitate and the matrix, these secondary phases are divided in three different categories, denominated coherent, semi-coherent and incoherent (Fig. 1.8). Coherent and semi-coherent precipitates share the same lattice structure with the matrix, leading to the continuity in the crystallographic planes at the interface, which facilitates the glide of the dislocations from the matrix into the precipitate. In the case of coherent precipitates, the lattice

Figure 1.8: Schematic representation of atomic structure of interfaces between the metallic matrix and coherent, semi-coherent and incoherent precipitates.

parameters are also similar (although not identical), leading to the development of coherency strains at the interface to accommodate the mismatch in lattice parameters. The mismatch in the lattice constants in semi-coherent precipitates is too large to be accommodated by elastic strains and misfit dislocations are periodically found along the interface. Finally, incoherent precipitates have different crystalline structure and there is no continuity between the crystallographic planes at the interface, making difficult the glide of matrix dislocations into the precipitate. The interface energy is also associated with the type of interface, being minimum for coherent interfaces ($< 200 \text{ mJ/m}^2$) and increasing with the degree of incoherency (Argon, 2008).

Precipitate hardening depends on the size, shape, volume fraction and spatial distribution of the precipitates in the matrix as well as on the mechanisms of dislocation-precipitate interaction. Large precipitates, normally incoherent with respect to the matrix, are usually considered impenetrable for dislocations that have to overcome the obstacle by the formation of an Orowan loop (Orowan, 1948). In the ideal case of two cylindrical precipitates of radius r perpendicular to the glide plane and separated a distance L (Fig. 1.9), the CRSS to overcome the precipitates, τ_O , is controlled by the line tension of the dislocation. Assuming a constant the line tension equal to $\mu|\bar{b}|^2/2$, the CRSS for Orowan loop can be expressed as

$$\tau_O = \frac{\mu|\bar{b}|}{L} \quad (1.5)$$

where μ stand for the shear modulus of the matrix (Ardell, 1985). A dislocation loop (named Orowan loop) remains around the precipitate once the dislocation has overcome the obstacle. When the next dislocation tries to overcome the precipitate, the strong repulsion with the Orowan loop around the precipitates, (which, in fact, reduces the effective distance L between the precipitates) leads to an increase in the CRSS and to a progressive strain hardening. The Orowan model captures very well the physics of dislocation/precipitate interactions in the case of impenetrable precipitates and has

Figure 1.9: Schematic of the formation of an Orowan loop by the interaction of a dislocation with two cylindrical precipitates of radius r separated by L .

been refined over the years (within the framework of continuum models) to take into account the attraction between opposite dislocation segments during the formation of the loop (Bacon et al., 1973) as well as of the shape, size and spatial distribution of the precipitates (Ardell, 1985; Nembach, 1997; Nie, 2003, 2012). More recently, dislocation dynamics simulations have been used to account for the influence of the elastic mismatch, precipitate shape and orientation, the presence of eigenstrains, etc. on the CRSS to overcome the precipitate (Xiang et al., 2004; Queyreau and Devincre, 2009; Monnet et al., 2011; Gao et al., 2015; Zálezák et al., 2017; Santos-Güemes et al., 2018).

On the contrary, small precipitates are usually coherent with the matrix and tend to be sheared by dislocations (Fig. 1.10). This is the case of Guinier-Preston (GP) zones in many metallic alloys (Byrne et al., 1961; Rodríguez-Veiga et al., 2018), θ'' and Ω precipitates in Al-Cu and Al-Cu-Mg alloys (Nie, 2014), β'_1 -MgZn₂ in Mg-Zn alloys (Wang and Stanford, 2015), β_1 in Mg-Nd alloys (Zhou et al., 2018; Huang et al., 2019), γ' -Ni₃(Al, Ti) and γ'' -Ni₃Nb in Ni-based superalloys (Xiao et al., 2008; Cruzado et al., 2015), etc. In general, the critical stress required to shear a precipitate of circular cross-section is a function of different factors that are opposed to the shearing of the precipitate, namely chemical, stacking fault, modulus mismatch and order strengthening (Ardell, 1985; Nembach, 1997). Chemical strengthening is characterized by the increase of the energy barrier due to the presence of the precipitate because of the creation two interface ledges when the dislocation passes through the precipitate. Stacking fault strengthening is due to the differences in the stacking fault energy between the matrix and

Figure 1.10: Schematic of the precipitate shearing process by an edge dislocation.

the precipitate, which leads to an elastic precipitate/dislocation interaction. Modulus mismatch increases the stress necessary to shear the precipitate due to the difference in the elastic modulus between the matrix and the precipitate. Coherency strengthening comes about as a result of the interaction of stress field created by the lattice mismatch between matrix and precipitate with the dislocation stress field. Finally, the order strengthening occurs when the precipitate stands for a super-lattice coherent with the matrix and the perfect dislocation in the matrix is only a partial dislocation in the precipitate, leading to the formation of antiphase boundaries with high energy.

All these strengthening mechanism can appear simultaneously in engineering alloys. Hence, the different contributions of each mechanism have been evaluated using continuum models based on the dislocation line tension (Ardell, 1985; Nembach, 1997) or, more recently, through dislocation dynamics simulations (Vattré et al., 2009; Gao et al., 2015; Huang et al., 2012; Hussein et al., 2017). These strategies were able to capture the experimental trends in the case of Ni-based superalloys, although direct comparisons were more difficult because some of the critical parameters for these models (stacking fault energy of the precipitate, coherency strains, antiphase boundary energy) are not always easy to estimate. Moreover, the validity of these approaches can be questioned when the continuum hypothesis is no longer applicable due to the small dimensions of the precipitate. The paradigmatic case are the GP zones formed by a single layer of atoms coherent with the matrix and with diameter from 2 to 10 nm (Rodríguez-Veiga et al., 2018). Shearing of the precipitate is controlled by the atomic interactions between matrix and solute atoms, leading to a very complex energy landscape that cannot be captured by simple continuum line tension models. Atomistic simulations seems to be more appropriate for this task.

Figure 1.11: Schematic of the periodic array of dislocations models to carry out simulations of dislocation slip. PBC denotes periodic boundary conditions. (a) Periodic array of single dislocations model. (b) Periodic array of dislocation dipoles model.

1.3 Atomistic analysis of dislocations

1.3.1 Dislocation motion and cross-slip

Atomistic models have been widely used to evaluate different physical characteristics that define the dislocations behavior at the nanoscale. To this end, different approximations were developed (Sinclair et al., 1978; Rao et al., 1998; Bacon et al., 2009), being the periodic array of dislocations (PAD) model (Baskes et al., 1989; Daw et al., 1993) the most suitable model so far (Fig. 1.11(a)). In this approach, an infinitely long crystal containing a straight dislocation is represented by means of the application of periodic boundary along the dislocation line. In addition, periodic boundary conditions are applied in the direction perpendicular to the dislocation line in the slip plane, leading to a periodic array of dislocations. Stresses (or strains) can be applied to the simulation domain by controlling the displacement of the atoms on the upper and lower free surfaces of the simulation box, allowing the simulation of the dislocation glide under different conditions (stress, strain, temperature, etc.). In addition, the dislocation behavior has also been analyzed using a modified PAD model depicted in Fig. 1.11(b) (Chang et al., 1999; Bulatov and Cai, 2006). In this model a second dislocation, with opposite Burgers vector to the original one, is introduced and periodic boundary conditions are imposed along the three spatial directions of the atomistic domain, leading to an infinite array of dislocation dipoles placed in parallel slip planes.

Pioneer atomistic studies of dislocations were focused on the evaluation of the dislocation core in different kinds of lattices (Cotterill and Doyama, 1966; Doyama and Cotterill, 1966; Basinski et al., 1970; Vitek et al., 1970; Duesbery et al., 1973; Yamaguchi et al., 1982; Vitek and Igarashi, 1991) at the ground state. These investigation were carried out by means of molecular statics simulations, which ascertained the main aspects of the dislocation core, from a crystallographic and energetic viewpoint.

Molecular statics simulations were also applied to the assessment of lattice friction at 0 K. The Peierls barrier of screw dislocations in Mo was investigated by Xu and Moriarty (1998) who suggested that the lowest energy mechanism to move screw dislocations in body centered cubic (BCC) lattices was by the nucleation of a double kink screw dislocations lying on $\{110\}$ planes. Similar work was carried out by Ito and Vitek (2001) in Mo and Ta, who established that the glide of screw dislocations is not only a function of shear stresses parallel to the Burgers vector, but also perpendicular to it (Ito and Vitek, 2001). More recently, Cereceda et al. (2013) carried out an exhaustive comparison of the interatomic potentials that best represent the main characteristics of dislocations in W (with a BCC lattice) and this information was used to establish the basis of a crystal plasticity model. Hence, this particular atomistic methodology has been widely used to analyze the behavior of dislocations in absence of kinetic energy, particularly in the case of non-planar core dislocations (i.e. screw dislocations in BCC) (Xu and Moriarty, 1998; Ito and Vitek, 2001; Vitek, 2004; Gröger et al., 2008; Cereceda et al., 2013), because of the larger Peierls barrier as compared to planar core dislocations.(Olmsted et al., 2005; Groh et al., 2009).

All these studies provided valuable insights on diverse aspects of dislocation motion but they were confined to the athermal limit. Dislocation motion at finite temperatures was studied via molecular dynamics simulations. Chang et al. (1999, 2001) carried out an investigation of the mobility of straight dislocations in Mo Chang et al. (1999, 2001). They observed the nucleation of pair kinks to begin the glide process, suggesting that molecular dynamics simulations were able to capture actual mechanisms of dislocation motion. Olmsted et al. (2005) ascertained the velocity of edge and screw dislocation as a function of stress and temperature in pure Al and Ni and Al-Mg alloy. They concluded that the linear dislocation mobility model (in which the dislocation velocity is proportional to the resolved shear stress) is not valid when stress/temperature ratio is high. In addition, they observed different behaviors depending on the character of the dislocation . A similar work was carried out by Kuksin et al. (2008); Kuksin and Yanilkin (2013) in Al (FCC) and Mo (BCC). In the case of HCP alloys, Groh et al. (2009) analyzed the mechanisms of basal, pyramidal and prismatic dislocation

mobility in Mg. They determine the Peierls barrier for both screw and edge dislocations and also studied the effect of stress and temperature on the dislocation velocity. This investigation showed the large differences in the CRSS among the different slip systems in Mg, which results in the strong plastic anisotropic of this metal.

Other atomistic investigations were focused in the analysis of dislocation cross-slip. Molecular dynamics simulations were used to assess the time necessary for a dislocation segment to cross-slip as function of the temperature and of the applied stress (Vegge et al., 2000; Hatano et al., 2008; Rao et al., 2015; Oren et al., 2017). Moreover, the annihilation process of screw dislocations via cross slip was also successfully ascertained as a function of the applied stress (Rao et al., 2015) and this methodology have been successfully used to determine the cross-slip activation free energy in Cu (Vegge et al., 2000). However, the characteristic timescale of the molecular dynamics simulations limits their application in certain conditions (particularly, low temperatures or stresses).

The path sampling methods (such as the nudged elastic band method and the string method) have been utilized to overcome this limitation. These methods have been widely employed to ascertain the energetic barrier and the minimum energy path associated with dislocation cross-slip (Rasmussen et al., 1997; Vegge et al., 2001). This strategy has permitted to determine the influence of different chemical species (hydrogen (Wen et al., 2007) or solid solution Al atoms in Ni (Du et al., 2014)) on the energy barrier for cross-slip. Moreover, the atomistic string method have been used to determine the barrier for cross slip as a function of the applied stress. These results were directly compared with the line tension model, showing very similar results (Kang et al., 2014). More recently, an atomistically based model has been proposed to compute the energy barrier for cross-slip as a function of the type and volume fraction of solute atoms (Nöhring and Curtin, 2017, 2018). Additionally, Chen et al. (2019) studied the effect of vacancy clusters on the cross slip activation energy in pure Ni, employing the free-end nudged elastic band methodology. They reported an overcoming mechanism map (cross-slip *vs.* shearing) as a function of the stress and obstacle spacing. Further investigation on the cross slip process have shown that approaches based on either line tension or atomistic string methods provide equivalent results (Kang et al., 2014). A recent investigation examined explicitly the effect of the applied stress tensor on the cross-slip energetic barrier (Kuykendall, 2015). Atomistic path sampling methods along with the replica trimming algorithm were employed to investigate the influence stress tensor on the cross-slip process. In addition, molecular dynamics simulations have been used to assess the time necessary for a dislocation segment to cross-slip as function of the temperature and of the applied stress and they were successfully used

to determine the cross-slip activation free energy in Cu (Vegge et al., 2000) and, in combination with path sampling, to determine the influence of stress on the cross-slip rate without previous assumptions (Oren et al., 2017). Finally, Xu *et al.* (Xu et al., 2017) compared molecular dynamics simulations with the multiscale concurrent atomistic-continuum (CAC) methodology, which provided comparable results with lower computational cost.

It should be finally noted that the information obtained from atomistic simulations about the dislocation mobility and cross-slip has been crucial to simulate the evolution of dislocation networks in discrete dislocation dynamics models (Kubin et al., 1992; Weygand et al., 2002; Martinez et al., 2008; Hussein et al., 2015; Yanilkin et al., 2014; Santos-Güemes et al., 2018; Martinez et al., 2008; Hussein et al., 2015).

1.3.2 Dislocation/obstacle interactions

Classical atomistic simulations have also been used to analyze the mechanisms of dislocation/obstacle interaction in the athermal limit and at finite temperatures. Hu et al. (2000) examined the interaction of a dislocation in Fe with spherical precipitates of Cu at 0 K. This investigation was focused on the evaluation of the dislocation core inside the precipitate and determined the critical resolved shear stress to overcome the precipitate at the athermal limit. Rodney and Martin (1999) investigated the effect of self interstitial atoms (SIA) clusters in Shockley partial dislocations in Ni by means of molecular dynamics simulations. Their simulation suggested SIA clusters are absorbed by partial dislocations. However, further investigations of the same authors suggested that the dislocation may be additionally a focal point for recombination and coalescence of interstitials with vacancies (Rodney and Martin, 2000).

A special mention should be given to the work carried out by Osetsky and Bacon (2003a), that established an accurate strategy to simulate the interactions between dislocations and obstacles under different conditions (constant or variable stress and strain rates and temperature). They analyzed the influence of a periodic array of nm-sized voids on the glide of an edge dislocation in BCC Fe at 0 K and finite temperatures (Osetsky et al., 2003; Osetsky and Bacon, 2003b). This strategy has been widely used by many other investigators to ascertain the dislocation/precipitate interactions in different materials and precipitates (Bitzek and Gumbsch, 2005; Hatano and Matsui, 2005; Lee et al., 2007; Monnet, 2007; Singh and Warner, 2010; Bonny et al., 2011; Monnet et al., 2011; Singh and Warner, 2013; Liao et al., 2014; Granberg et al., 2014; Yanilkin et al., 2014; Bahramyan et al., 2016; Lehtinen et al., 2016).

Obviously, these approaches only provided information about the dislocation/precipitate interaction mechanisms and the CRSS necessary to overcome the obstacles

Temperature effects on the dislocation/obstacle interactions and on the CRSS can be theoretically considered using molecular dynamics simulations. However, these simulations require a timestep of the order of fs, allowing to study only extremely high strain rates ($> 10^7 \text{ s}^{-1}$). Thus, the standard atomistic results obtained are valid at 0 K (MS) or at extremely high strain rates for finite temperatures (MD). This information is useful to understand the interactions mechanisms in these two extreme conditions but cannot be directly extrapolated to provide quantitative values of the influence of the precipitates on the resolved shear stress as a function of strain rate and temperature under standard loading conditions. Thus, new strategies are needed to upscale the information obtained from atomistic simulations to the mesoscale.

Dislocation/precipitate interaction is a thermally-activated process (Kocks, 1975) and the stress necessary to overcome the precipitate as a function of the strain rate and temperature is given by the free energy barrier. According to the transition state theory (Glasstone et al., 1941), the energy barrier is only a function of the applied stress and at certain stress level this barrier becomes zero. The specific stress to bypass the obstacle without thermal energy is called obstacle strength (τ_0). Thus, the goal of atomistic simulations is to determine τ_0 and the variation of energetic barrier with the applied shear stress τ . As explained above, the former can be achieved by means of MS simulations (Terentyev et al., 2008; Monnet, 2015; Singh and Warner, 2010) while different strategies have been proposed for the latter based on the combination of classical atomistic simulations with the transition state theory. This strategy has been applied to determine the energy barrier for dislocation cross-slip (Vegge et al., 2000; Warner and Curtin, 2009), dislocation nucleation (Hara and Li, 2010; Nguyen et al., 2011) and dislocation motion in the presence of solute atoms and precipitates (Saroukhani et al., 2016; Saroukhani and Warner, 2017).

Following this path, recent research efforts have been concentrated on the development of models that analyze the energy landscape of the dislocation/obstacle interaction. Saroukhani et al. (2016) studied the interaction of dislocations with Guinier-Preston zones in an Al-Cu alloy assuming the validity of the harmonic transition state theory. Under this assumption, the free energy barrier can be obtained from the activation potential energy (that can be computed using minimum energy path techniques, such as the nudged elastic band method) while the entropic activation only depends on the vibrational entropy and anharmonic effects are neglected. However, the predictions based on these assumptions were grossly inaccurate, as compared with direct MD simulations, and the differences were attributed to the presence of anharmonic effects. Better results were obtained through the application of interface sampling techniques, which are not based on the minimum energy path calculations. Monnet et al.

(2010) obtained the influence of the shear stress on the free energy barrier by means of direct MD simulations in the case of voids sheared by dislocations. This approach is computational costly because many simulations are necessary for each combination of applied stress and temperature to have statistically significant results of the rate at which the dislocations overcome the obstacle. Thus, there is not a well-established atomistic strategy that analyze the interaction of dislocations with precipitates which provide information to predict the strengthening in the flow stress at the strain rates and temperatures using found in engineering applications.

1.4 Objectives

Classical atomistic simulations have shown their potential to analyze the mechanisms of dislocation mobility and of dislocation/precipitate interactions. Nevertheless, they can be further exploited and the present PhD is aimed at the development of novel simulation strategies, within an atomistic framework, which are able to provide better understanding of the physical processes of dislocation motion at the nanoscale as well as information that can be used in mesoscale models (i.e. discrete dislocation dynamics simulations) or directly to predict the flow stress of materials. Within this framework, the work in the thesis has been focused in three main problems: dislocation cross-slip, interaction of dislocations with coherent precipitates and interaction of dislocations with non-coherent precipitates.

As stated above, cross slip is an important dislocation glide mechanism to overcome obstacles and/or generate more dislocation sources. Although several investigations have used atomistic models to analyze dislocation cross-slip, the influence of the different component of the stress tensor on the cross slip barrier has not been evaluated. Thus, the first goal of the thesis is to develop a physically-based model of the cross slip probability, based on atomistic simulations, that takes into account the influence of the different stress components projected on the glide and cross-slip planes which contain the Burgers vector.

Shearable nm-sized precipitates increase the strength of metallic alloys by hindering the dislocation motion. The atomistic models used to ascertain and model the interaction between both defects overestimated the strength and sometimes predicted interaction mechanisms which were not observed experimentally. These differences are a consequence of the roughness of energetic landscape and the second objective of this thesis was the development of a novel atomistic strategy that accurately evaluates the energetic pathway and the energy barrier that dislocations have to overcome to shear nm-sized coherent precipitates. Based on these analyses and on the transition

state theory, a strategy was developed to determine the strengthening induced by the presence of the precipitates on the critical resolved shear stress for dislocation slip as a function of the strain rate and temperature.

Precipitate hardening is a well-established strategy to strengthen metallic alloys. Nevertheless, this strategy is very efficient in Ni and Al alloys but not in the case of Mg. Thus, atomistic simulations were carried out to ascertain the mechanisms of dislocation/precipitate interactions in Mg-Al alloys to ascertain why precipitates do not strengthen efficiently these alloys

2 METHODOLOGY AND ATOMISTIC STRATEGIES

2.1 Transition state theory

Dislocation motion takes place along pathways through the energetic landscape in the crystal. Dislocations move from local energy minimum to another minimum in the energy landscape and have to overcome energetic barriers between these minima. Mechanical stresses and thermal vibrations are the driving forces to overcome the barriers, and thus, dislocation motion is a thermally-activated process. The energy barrier is linked to the transition pathway and both can be related through the rate theory which was first proposed by Arrhenius (Arrhenius, 1889).

Physical systems of particles at finite temperature and thermodynamic equilibrium are constantly moving. As a result, the system visits diverse metastable states along the energy landscape. Rate theory is the discipline that characterizes the flux of escape from these metastable states. Arrhenius suggested that the rate of escape, Γ , is an exponential function of the absolute temperature, T , according to

$$\Gamma = A \exp \left(-\frac{E_{act}}{k_b T} \right) \quad (2.1)$$

where A is a prefactor, k_b the Boltzmann's constant and E_{act} accounts for the energetic barrier that the system has to overcome in order to go from one metastable position to another (Arrhenius, 1889; Van't Hoff, 1884). Further investigations during the 20th century led to the development of the classical transition state theory (TST) (Krammers, 1940; Hänggi et al., 1990), that has become a fundamental tool to analyze dislocation motion.

TST is a statistical mechanics theory that establishes the rate at which a system in equilibrium crosses a dividing energy surface between two metastable basins. Thus, this theory provides a quantitative description of infrequent processes, also called "rare" or infrequent events. Classical TST is based in Newtonian physics and neglects quantum mechanical effects.

A simple example can be used to introduce the concept of infrequent events. Hence, a one-dimensional energy profile ($E(\omega)$) is considered with two minima along the reaction coordinate ω (Fig. 2.1). The reaction coordinate defines the trajectory that a particle should follow to cross from one local minimum to another and, of course, depends of the surrounding environment. The two energetic basins are separated by a maximum ($\omega^\ddagger$), which fulfills the condition $dE(\omega)/d\omega = 0$ and it is usually denominated as the first order saddle point barrier. Moreover, a dividing surface is established at this saddle point to define explicitly the separation between basins. A particle at a finite temperature is then inserted in one of the basins ($E(\omega_a)$), as depicted in Fig. 2.1. As a result of the thermal vibrations of the particle, the system visits randomly the ω domain in time (t), around the vicinity of ω_a , and hence ω becomes a non-deterministic, but stochastic variable. The amplitude of the thermal fluctuations ($f(t) = \omega(t) - \langle \omega(t) \rangle$) dictates the time necessary to escape from the basin. If the thermal fluctuations $f(t)$ are related to an appropriate energy scale ($\beta^{-1} = k_b T$), the transition between states ω_a and ω_b will become an infrequent event when

$$\beta E_{act} \gg 1. \quad (2.2)$$

The characteristic time for an infrequent event to happen, τ_e , is related to the thermal vibration characteristic time of the system, τ_f , according to

$$\tau_e \sim \tau_f \exp(\beta E_{act}) \quad (2.3)$$

and a large difference between characteristic times ($\tau_e \gg \tau_f$) defines an infrequent or rare event. In other words, an event is rare when there are large differences between the time that the system spends exploring the energy landscape and the interval of time at which the rare event happens.

Figure 2.1: Schematic of a double-well potential energy profile where the horizontal axis represents the reaction coordinate (ω). ω_a and ω_b stand for the positions of the local energy minima, while $\omega^\ddagger$ denotes the saddle point.

It should be noted that the reaction coordinate depends on the degrees of freedom (DoF) of the particle, which are easy to deal with when a single particle is considered but almost intractable for large systems. To overcome this problem, the DoF can be reduced assuming that the full phase space can be described by the generalized position and momenta of all the particles in the system ($\Omega \rightarrow [\mathbf{r}(t), \mathbf{p}(t)]$), which are located in a certain point of this phase space at $t = 0$ (Hänggi et al., 1990). Thus, the reaction coordinate of a N -particle system can be defined as the different micro-states that the system has to reach in order to cross the dividing surface at the saddle point.

The rate of an infrequent event is defined as the probability that the system is at the transition state multiplied by the flux out from this transition state. A simple expression of the rate can be derived for a finite N -particle system within the framework of TST. The total energy of the system is characterized by the Hamiltonian (H), which is given by,

$$H(\mathbf{r}, \mathbf{p}) = V(\mathbf{r}) + K(\mathbf{p}) \quad (2.4)$$

where $K(\mathbf{p})$ and $V(\mathbf{r})$ stand for the kinetic and potential energies of the system, respectively, which depend on the momentum, $\mathbf{p}$, and the position, $\mathbf{r}$, of the particles. Henceforth, $V(\mathbf{r})$ provides the energetic landscape, which depends on the $3N$ -configurational DoF of the system (Fig. 2.2). TST assumes that the system is in equilibrium, and consequently, it follows a Boltzmann distribution of states. Within this framework, the probability, P , of finding the system located at a certain point of the phase space $(\mathbf{r}, \mathbf{p})$ in the range of $\{\mathbf{r} + d\mathbf{r}, \mathbf{p} + d\mathbf{p}\}$ is equal to

$$P(\mathbf{r}, \mathbf{p}) d\mathbf{r} d\mathbf{p} = \hat{\rho} \exp\left(-\frac{H(\mathbf{r}, \mathbf{p})}{k_b T}\right) d\mathbf{r} d\mathbf{p} \quad (2.5)$$

where $\hat{\rho}$ accounts for a normalization factor. Since $K(\mathbf{p})$ and $V(\mathbf{r})$, (2.5) can be re-written as

$$P(\mathbf{r})d\mathbf{r} P(\mathbf{p})d\mathbf{p} = \hat{\rho}_V \exp\left(-\frac{V(\mathbf{r})}{k_b T}\right) d\mathbf{r} \hat{\rho}_K \exp\left(-\frac{K(\mathbf{p})}{k_b T}\right) d\mathbf{p}. \quad (2.6)$$

The potential energy landscape can be divided into two subspaces $\mathbf{V}_a$ and $\mathbf{V}_b$, where the subindex a denotes the reactant subspace and b the product subspace. Given that the system is initially located at a certain point in the subspace $\mathbf{V}_a$,

$$\int_{\mathbf{V}_a} P(\mathbf{r})d\mathbf{r} = \hat{\rho}_V \int_{\mathbf{V}_a} \exp\left(-\frac{V(\mathbf{r})}{k_b T}\right) d\mathbf{r} = 1. \quad (2.7)$$

The prefactor $\hat{\rho}_V$ is a normalization factor defined as the probability of being in certain position of the potential space, and is given by

$$\hat{\rho}_V = \frac{1}{\int_{\mathbf{V}_a} \exp\left(-\frac{V(\mathbf{r})}{k_b T}\right) d\mathbf{r}} = \frac{1}{Z_{\mathbf{V}_a}} \quad (2.8)$$

where $Z_{\mathbf{V}_a}$ denotes the sum of all the possible potential micro-states within the sub-domain $\mathbf{V}_a$. It is worth noting that Z (also known as the partition function) defines all the statistical information necessary to determine the thermodynamics conditions of the system.

If a potential subspace $S^\ddagger$, which belongs to $\mathbf{V}_a$ ($S^\ddagger \subset \mathbf{V}_a$) (Fig. 2.2(a)), is isolated, the probability of finding the system located in some point of the subspace $S^\ddagger$ is expressed as

$$P_{S^\ddagger}(\mathbf{r}) = \frac{\int_{S^\ddagger} \exp\left(-\frac{V(\mathbf{r})}{k_b T}\right) d\mathbf{r}}{\int_{\mathbf{V}_a} \exp\left(-\frac{V(\mathbf{r})}{k_b T}\right) d\mathbf{r}} = \frac{Z_{S^\ddagger}}{Z_{\mathbf{V}_a}} \quad (2.9)$$

where $Z_{S^\ddagger}$ and $Z_{\mathbf{V}_a}$ stand for the partition functions of both subspaces of $V(\mathbf{r})$, also known as the configuration integrals. $S^\ddagger$ can be defined as the transition state that separates the metastable states a and b . This transition state is assumed to be the dividing surface between the two potential basins considered with the minimum number of recrossings. As mentioned above, the rate $\Gamma_{\mathbf{V}_a \rightarrow \mathbf{V}_b}^{TST}$ is the probability of being in $S^\ddagger$ times the flux out of this dividing surface per particle ($\eta_{S^\ddagger}$). If the $S^\ddagger$ dividing surface has a constant depth ($d_\ddagger$) along the dividing line ($l_\ddagger$) (Fig. 2.2 (a)) and assuming that all the states are the same in the parallel hyper-planes, the configuration integral can be expressed as $d_\ddagger^\ddagger Z_{l_\ddagger}$. Considering the reference system located at an infinitesimal spot along $l_\ddagger$, denominated s , the flux out $\eta_{S^\ddagger}$ is equal to

Figure 2.2: (a) Representation of the potential energy as a topographical landscape. Dashed red and blue lines are the dividing hyper-surfaces at the local minima (r^a) and at the saddle point (r^s), respectively. (b) Section of the potential energy landscape parallel to the line connecting both local minima passing through r^s . Harmonic approximations of the potential energy in the vicinity of r^a and r^s are represented by dashed lines.

$$\eta_{S^\ddagger} = \frac{\langle \mathbf{p}_\perp \rangle}{d^\ddagger \mathbf{m}_\perp} = \frac{\langle \mathbf{v}_\perp \rangle}{d^\ddagger} \quad (2.10)$$

where $\langle \mathbf{v}_\perp \rangle$ denotes the average velocity of the particles crossing the transition state perpendicular to $l_\ddagger$ from $\mathbf{V}_a$ to $\mathbf{V}_b$ and $\mathbf{m}_\perp$ is the mass of the crossing particle, which is considered to be the same (m) for all particles in the system for simplicity.

The kinetic energy of the system is given by

$$K(\mathbf{p}) = \frac{1}{2} \frac{p^2}{m} \quad (2.11)$$

and the momentum $\mathbf{p}$ is a function of the the velocity of the particle according to $m\mathbf{v}$. The complete set of kinetic states is given by the kinetic partition function, which can be written as

$$Z_K = \frac{1}{\hat{\rho}_K} = \int_{-\infty}^{\infty} \exp\left(-\frac{mv^2}{2k_bT}\right) = \sqrt{\frac{2\pi k_bT}{m}}. \quad (2.12)$$

The probability of finding the system at some kinetic state is given by

$$P(\mathbf{p}) = P(\mathbf{v}) = \sqrt{\frac{m}{2\pi k_bT}} \exp\left(-\frac{m\mathbf{v}^2}{2k_bT}\right). \quad (2.13)$$

The expected value of a variable function $f(x)$ that follows some statistics is a function its probability $P(f(x))$ according to

$$\langle f(x) \rangle = \int f(x) P(f(x)) dx \quad (2.14)$$

and, thus, the average velocity of the particles, assuming positive flux ($\mathbf{V}_a \rightarrow \mathbf{V}_b$), can be written as

$$\langle \mathbf{v} \rangle = \int_0^{\infty} \mathbf{v} P(\mathbf{v}) d\mathbf{v} = \sqrt{\frac{k_bT}{2\pi m}} \quad (2.15)$$

where $P(\mathbf{v})$ is the probability given in (2.13). Finally, combining (2.9), (2.10) and (2.15), the rate of escape from $\mathbf{V}_a$ to $\mathbf{V}_b$ within classical TST is given by

$$\Gamma_{\mathbf{V}_a \rightarrow \mathbf{V}_b}^{TST} = \eta_{S^\ddagger} \frac{d^\ddagger Z_{l_\ddagger}}{Z_{\mathbf{V}_a}} = \langle \mathbf{v}_\perp \rangle \frac{Z_{l_\ddagger}}{Z_{\mathbf{V}_a}} = \sqrt{\frac{k_bT}{2\pi m}} \frac{Z_{l_\ddagger}}{Z_{\mathbf{V}_a}}. \quad (2.16)$$

It should be noted that this expression to obtain the rate of an infrequent event is an approximation, which is exact in few cases (e.g. rate of escape of noble gases from

a reservoir (Jónsson, 2012)) and further considerations have been taken into account for other systems.

It is known that the rate of infrequent events is given by the Arrhenius law (eq. (2.1)) and, thus, an Arrhenius-type equation should be derived from eq. (2.16). To this end, the system is macroscopically constrained, apart from the thermal reservoir constriction. Consequently, the total energy during the exploration of the landscape is not constant. In the case that the number of particles, N , the volume, V , and the temperature, T , are constrained, the system is within a canonical ensemble (NVT) and the Helmholtz free energy, F , is proportional to the partition function of the system (Z_{V_a}) according to

$$F = U - TS = k_b T \ln(Z_{V_a}). \quad (2.17)$$

Similarly, the Helmholtz free energy at $l_{\ddagger}$ can be written as a function of the partition function, in the same way as in eq. (2.17), and, hence, the ratio between the partition function in $l_{\ddagger}$ and V_a , can be expressed as

$$\frac{Z_{l_{\ddagger}}}{Z_{V_a}} = \exp\left(-\frac{(F_{l_{\ddagger}} - F_{V_a})}{k_b T}\right). \quad (2.18)$$

Thus, the rate of crossing a free energy surface can be obtained by combining eq. (2.16) and eq. (2.18) as

$$\Gamma_{V_a \rightarrow V_b}^{TST} = \sqrt{\frac{k_b T}{2\pi m}} \exp\left(-\frac{(F_{l_{\ddagger}} - F_{V_a})}{k_b T}\right) \quad (2.19)$$

where $(F_{l_{\ddagger}} - F_{V_a})$ is the activation Helmholtz free energy, and the pre-exponential factor is proportional to the attempt frequency, ν . This way eq. (2.19) is normally expressed according to

$$\Gamma^{TST} = \nu \exp\left(-\frac{\Delta F}{k_b T}\right) \quad (2.20)$$

where ΔF is the activation Helmholtz free energy, which is equal to

$$\Delta F = \Delta U - T\Delta S. \quad (2.21)$$

It should be noted that the energy obtained during the exploration of the energy landscape could change in the case that other macroscopic observables are constricted and, in consequence, the activation energy of the process could also change. For instance, if the pressure is fixed instead of the volume, the system is contained under the NPT ensemble. Consequently, the energy obtained during the exploration of the

landscape is the Gibbs free energy G and can be related to the partition function of the system according to

$$G = U - TS + PV = k_b T \ln(Z_{V_a}). \quad (2.22)$$

Following the same procedure used with the canonical ensemble, the rate of one infrequent event under the NPT ensemble can be expressed according to

$$\Gamma^{TST} = \nu \exp\left(-\frac{\Delta G}{k_b T}\right) \quad (2.23)$$

and ΔG is expressed in this particular case as

$$\Delta G = \Delta U - T\Delta S + P\Delta V = \Delta F + P\Delta V. \quad (2.24)$$

The classical TST is built upon some assumptions that limit its applicability. Firstly, classical TST neglects all quantum effects assuming only the conventional dynamics of the nuclei (see Sec. 2.2 for further information about nuclei dynamics). Furthermore, TST does not take into account the dynamical recrossing of the dividing surface. In other words, there is not return to the initial point once the system reaches the transition state. Consequently, a dividing surface with the lowest probability of recrossing between initial and final states should be defined. This is given by the saddle point, but sometimes it is difficult to define this point due to the complexity of the energy landscape. Finally, it should be remembered that TST only considers systems in equilibrium.

2.1.1 Harmonic transition state theory

An analytical expression for the rate of infrequent events within classical TST has been developed above. The rate is proportional to the partition functions of the potential surface, which can be transformed into an activation energy and an attempt frequency inherent to the system under study. Eq. (2.20) is valid for multiple types of systems in thermodynamic equilibrium (i.e. gases, topological changes in molecular systems, etc.). However, it has been demonstrated that the rate of infrequent event of systems lying in a smooth potential surface, which contains a first order dividing surface, can be simplified using a harmonic approximation (Vineyard, 1957). This is the case of defect motion in solids (Vineyard, 1957; Kocks, 1975) and it simplifies the calculation of the rate.

Harmonic Transition State Theory (HTST) is based on three assumptions: quantum effects are neglected (as in classical TST), the solid is macroscopically constrained, so

translational or rotational vibration modes are zero, and all vibrations can be represented by simple harmonic oscillators (theory of small oscillations) (Vineyard, 1957). In order to develop an analytical expression of the rate within HTST, the same potential energy landscape $V(\mathbf{r})$, and N -particle system are considered. The minimum energy path (MEP) profile between $\mathbf{V}_a$ and $\mathbf{V}_b$ domains passing through r_s is shown in Fig. 2.2(b). It should be noted that r_s is a first order saddle point, located between two quadratic basins, highlighted with dashed lines in Fig. 2.2(b). Taking into account the quadratic profile of the MEP, $V(\mathbf{r})$ can be considered as a harmonic potential under the theory of small vibrations. Under this assumption, the second order Taylor's expansion of $V(\mathbf{r})$ in the vicinity of r^a leads to

$$V(\mathbf{r}) = V(r^a) + \sum_{i=1}^{3N} \frac{1}{2} m_i (2\pi\nu_i^a)^2 r_i^a \quad (2.25)$$

where $V(r^a)$ accounts for the potential energy at the ground state, i denotes an individual particle, m the mass of the particle, ν the normal frequencies and r the position of the particle.

The harmonic approximation of $V(\mathbf{r})$ can also be applied in the saddle point. However, the configurational constraint along the dividing surface has to be taken into account. This condition leads to one imaginary frequency (out of $3N$ normal frequencies) at r^s . Thus, the potential energy in the vicinity of r^s is equal to

$$V(\mathbf{r}) = V(r^s) + \sum_{i=1}^{3N-1} \frac{1}{2} m_i (2\pi\nu_i^s)^2 r_i^s. \quad (2.26)$$

According to classical TST, eqs. (2.7), (2.8) and (2.16), the rate is a function of the configurational integrals ratio in the dividing surface and the local minimum sub-domain. Furthermore, applying the small oscillations theory, the rate can be written as

$$\Gamma_{\mathbf{V}_a \rightarrow S^\dagger} = \sqrt{\frac{k_b T}{2\pi m}} \frac{Z_{S^\dagger}}{Z_{\mathbf{V}_a}} \quad (2.27)$$

where the two partition functions are given by eqs. (2.28) and (2.29):

$$Z_{\mathbf{V}_a} = \prod_{i=1}^{3N} \left(\sqrt{\frac{k_b T}{2\pi m_i}} \frac{1}{\nu_i^a} \right) \exp \left(-\frac{V(r^a)}{k_b T} \right) \quad (2.28)$$

$$Z_{S^\dagger} = \prod_{i=1}^{3N-1} \left(\sqrt{\frac{k_b T}{2\pi m_i}} \frac{1}{\nu_i^s} \right) \exp \left(-\frac{V(r^s)}{k_b T} \right). \quad (2.29)$$

By combining the previous three equations, the rate of an infrequent event within HTST can be expressed as

$$\Gamma^{HTST} = \left(\frac{\prod_{i=1}^{3N} \nu_i^a}{\prod_{i=1}^{3N-1} \nu_i^s} \right) \exp \left(-\frac{\Delta V}{k_b T} \right) = \nu_{eff} \exp \left(-\frac{\Delta V}{k_b T} \right). \quad (2.30)$$

where ΔV is the activation energy within the configurational space, but without any macroscopic constriction. The prefactor, ν_{eff} , stands for the effective attempt frequency and is defined by the ratio between $3N$ and $3N - 1$ normal modes in the vicinity of the minimum and of the saddle point, respectively.

If the system is under the NVT ensemble and the phase space subdomain V_a and the hypersurface $S^\dagger$ are considered, the rate is given by eq. (2.19). Given that the rates in TST and HTST should be equal, the rate within HTST can be expressed as

$$\Gamma^{HTST} = \left(\frac{\prod_{i=1}^{3N} \nu_i^a}{\prod_{i=1}^{3N-1} \nu_i^s} \right) \exp \left(-\frac{\Delta U}{k_b T} \right) = \nu \exp \left(\frac{\Delta S}{k_b} \right) \exp \left(-\frac{\Delta U}{k_b T} \right) \quad (2.31)$$

where ΔU is the activation internal energy and ΔS the activation entropy. It is possible to define an effective attempt frequency, ν_{eff} , which is proportional to the normal attempt frequency and to the activation entropy according to

$$\nu_{eff} = \nu \exp \left(\frac{\Delta S}{k_b} \right). \quad (2.32)$$

This result suggests that the activation entropy is independent of the temperature and of the macroscopic constriction if HTST holds, and it is just a function of the normal vibrational modes at the local minimum and at the saddle point of the configuration phase space. Thus, TST provides a useful framework to determine the rate of infrequent events from a number of thermodynamic variables. These variables can be obtained for a given system using atomistic approaches that will be detailed below.

2.2 Atomistic simulations

Atomistic simulations describe the evolution of the discrete atomic systems and are based on the Born-Oppenheimer approximation which establishes a time-scale separation between the movement of atomic nuclei and electrons. The most remarkable effect of this assumption is that the energy of the nuclei does not depend on the energy of the

electrons, and the total energy of the atoms can be split into a sum of energetic terms with respect the nuclei and the electrons (Tadmor and Miller, 2011).

Atomistic simulations can be divided in two main groups:

- *First principles*, also called *AB Initio*, which are based on the quantum-mechanical treatment of electrons in the atoms, while the nuclei of the atoms are assumed to follow a classical behavior. The main goal of this kind of calculations is to find the ground state of the electrons and the most relevant strategy is the Density Functional Theory (DFT), which optimizes the electronic energy as a function of electron density.
- *Molecular mechanics*, which emulates the interaction between atoms, assuming nuclei and electrons as a unified particle. These unified particles, henceforth called just atoms, follow the principles of classical mechanics, and their interaction is dictated by empirical interatomic potentials.

DFT can provide a very accurate description of the energy landscape but it is computationally very expensive. As a result, DFT is limited to analyze the interactions of up a few hundreds atoms. Moreover, DFT calculations are usually carried out to obtain the ground state of a given configuration. By the contrary, molecular mechanics based on classical atomistic simulations are able to simulate the dynamics of up to millions of atoms. However, the accuracy of the results depends on the empirical interatomic potential.

2.2.1 Density Functional Theory

Density functional theory is a modeling method based on quantum mechanics. Essentially, DFT determines the electronic ground state of many-body systems such as atoms, molecules as well as condensed phases. To this end, functionals of the electron density are used in order to describe the properties of a many electron system.

DFT set its basis on the *Thomas-Fermi* model and it has been further reinforced by the *Hohenberg-Kohn* and *Kohn-Sham* theorems (Hohenberg and Kohn, 1964; Kohn and Sham, 1965). These theorems show that the energy at the ground state and charge density of interacting electrons in the potential from nuclei are the same as those of non-interacting electrons in a potential from nuclei plus some extra potential. Consequently, the Coulomb potential can be treated as a static external potential in which electrons are moving. Within this framework, the many-body problem of interacting electrons is reduced to non-interacting electrons moving in an effective potential, such as:

$$E_k + E_{e-e} = E_k^{n-i} + E_{e-e}^{n-i}(\rho) + E_{ex}(\rho) \quad (2.33)$$

where E_k and E_e are the kinetic energy and the electron energy, respectively and the $n - i$ upper-index denotes the non-interaction. Moreover, E_{ex} stands for a functional, which is called the *exchange correlation functional*. It should be noted that E_{e-e} and E_{ex} depend on the electronic density ρ , which can be calculated depending on the wavefunctions (ψ_i) as follows

$$\rho(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 \quad (2.34)$$

where $\mathbf{r}$ stands for the coordinates of the particle i . Following this approximation, the Schrödinger equation can be expressed as

$$H(\rho)\psi_i(\mathbf{r}) = \left[-\frac{\hbar^2}{2m_e} \nabla^2 + \hat{V}_{e-e}^{n-i}(\rho) + \hat{V}_{e-n}(\rho) + \hat{V}_{ex}(\rho) \right] \psi_i(\mathbf{r}) \quad (2.35)$$

where $\hat{V}_{e-e}^{n-i}(\rho)$ is the non-interacting electron potential, $\hat{V}_{e-n}(\rho)$ the electron-nucleus potential and $\hat{V}_{ex}(\rho)$ the exchange correlation potential. Although the electron and electron-nucleus potentials can be precisely calculated, the exchange correlation potential has to be estimated.

Several approaches to estimate the exchange correlation potential have been developed. The most used among them are the so-called *local density approximation* (LDA) and the *generalized gradient approximation* (GGA). Within the LDA approximation, the exchange correlation functional only depends on the electron density at the position where the functional is evaluated. The GGA approximation goes a step further and exchange correlation functional depends not only on the local electron density, but on its gradient as well.

2.2.2 Molecular Mechanics

Classical atomistic simulation strategies rely on the description of the atoms as classical particles using Newtonian mechanics. The Hamiltonian H of an adiabatic system containing N atoms with mass m is given by eq. (2.4). Moreover, the kinetic energy follows the standard definition for a Boltzmann distribution of particles, as stated in the eq. (2.11). Under the Born-Oppenheimer approximation, the potential energy only depends on the position of the nuclei $\mathbf{r}$. The velocity of each particle, $\mathbf{v}$, can be expressed as a function of H as

$$\mathbf{v} = \frac{d\mathbf{r}}{dt} = \frac{\partial H}{\partial \mathbf{p}} \quad (2.36)$$

and the force that every atom experiences due to the presence of other atoms is equal to

$$\mathbf{f} = \frac{d\mathbf{p}}{dt} = -\frac{\partial H}{\partial \mathbf{r}} = -\frac{\partial V(\mathbf{r})}{\partial \mathbf{r}}. \quad (2.37)$$

The interatomic potential are empirical functions that describe this interatomic interaction. They depend on the type of atoms and bonding between them considered.

Interatomic potentials

Properties of materials depend on the interactions between atoms. Classical atomistic simulations account for these interactions using many-body interatomic potentials. They define the potential energy of the system as function of the position of the atoms. The interatomic potentials are usually semi-empirical expressions fitted to reproduce certain properties. The fitting parameters are obtained from either first principles calculations or experimental data. It is worth noting that the most important characteristic of any potential is its transferability, i.e. its accuracy to reproduce other properties than those fitted (Bulatov and Cai, 2006; Tadmor and Miller, 2011).

There are different approaches to model atomic interactions depending on the nature of the atomic bond. In this thesis, three different interatomic potentials were used: the embedded-atom method (EAM), the modified embedded-atom method (MEAM) and the angular dependent potential (ADP).

The EAM interatomic potential describes the behavior of metals and intermetallic compounds. It was developed by (Daw and Baskes, 1983) as an alternative to pair potentials, which do not take into account the effect of the electron cloud in the metallic lattice. The EAM includes the effect of the electron cloud via the embedding energy function. The energy of each atom is computed from the energy needed to embed one atom in the local-electron density provided by the rest of the atoms in the system. The electron density is obtained by means of the linear superposition of all the atomic-electron densities (Tadmor and Miller, 2011). In addition, there is an electrostatic energy contribution due to core-core overlap (Foiles et al., 1986) and the total energy associated to the atom i is given by

$$V(\mathbf{r}_i) = \frac{1}{2} \sum_{i \neq j} U_{i,j}(r_{i,j}) + F_i(\rho_i^{EAM}) \quad (2.38)$$

where $F_i(\rho_i^{EAM})$ is a functional that stands for the embedding energy of atom i with a background density of ρ_i^{EAM} , and $U_{i,j}$ the pair energy between atoms i and j separated by a distance r_{ij} . The electron density is given by

$$\rho_i^{EAM} = \sum_{i \neq j} \phi(r_{i,j}) \quad (2.39)$$

where $\phi(r_{i,j})$ stands for the contribution to electronic density of the closest atoms of the atom i in a linear superposition.

A complete description of a system with x different types of atoms requires $x(x + 1)/2$ pair interaction functions as well as x electron density functionals and embedding energy functions. The EAM approximation is an extremely efficient approach, which is able to reproduce accurately many metallic materials and intermetallic compounds with a slight increase of computational cost compared to pair potentials. However, this model does not take into account bonding directionality due to the linear superposition of electron densities.

In order to overcome this problem, Baskes (1987) developed the MEAM interatomic potential. This approximation was first applied to simulate the covalent bonds of silicon and it was rapidly extended to cubic metallic materials (Baskes, 1992). A major extension of the model to deal with second nearest-neighbors (2NN) was carried out by Lee and Baskes (2000). The MEAM interatomic potential preserves the EAM formalism. However, unlike EAM, the MEAM potential establishes the basis of its embedding function on a cluster potential, rather than on a pair potential. Apart from pairs, cluster potentials take into account the interaction of triplets and quadruplets as well.

The potential energy of the atom within the MEAM approximation follows eq. (2.38), but the embedding function F_i is given in this case by

$$F_i(\mathbf{r}_i) = A E_0 \rho_i \ln(\rho_i) \quad (2.40)$$

where A and E_0 are fitting parameters and the electron density ρ_i is equal to

$$\rho_i = \frac{\rho_i^0}{\phi_i^0} \sqrt{1 + \Lambda_i(w, \phi, s)} \quad (2.41)$$

where ρ_i^0 and ϕ_i^0 are also fitting parameters dictated by the crystal structure of the material at ground state. $\Lambda_i(w, \phi, s)$ is an element-dependent functional, which is a function of a weighting function w , the screening function s , and the directional contribution to the electron density provided by surrounding atoms given by the function ϕ_i . More details on the MEAM formalism can be found in the Appendix A.

It should be noted that accounting for directionality of bonds in the MEAM interatomic potential increases the computational cost. To reach a compromise between computational cost and accuracy of the bond directionality, Mishin et al. (2005) developed the ADP interatomic potential. This potential includes the directionality of the

bonds by means of the addition of an angular-dependent term to the pair interactions of the system within the EAM approach, eqs. (2.38) and (2.39). The final expression of ADP interatomic potential is

$$V(\mathbf{r}_i, \mathbf{X}_i, \mathbf{X}_j) = \frac{1}{2} \sum_{i \neq j} U_{i,j}(r_{i,j}) + F_i(\rho_i^{EAM}) + E_{i,j}(\mathbf{X}_i, \mathbf{X}_j) \quad (2.42)$$

where the two first terms respond to regular EAM, eq. (2.38), and $E_{i,j}$ is the angular dependent term. The angular part of the equation depends on internal coordinates of the atom i and j within the local reference system $\mathbf{X}_i$ and $\mathbf{X}_j$. This extra term is given by

$$E_{i,j} = \frac{1}{2} \sum_i [\mu_i(\mathbf{X}_i)]^2 + \frac{1}{2} \sum_{i,j} [\lambda_{i,j}(\mathbf{X}_i, \mathbf{X}_j)]^2 + \frac{1}{6} \sum_i (\nu_i)^2 \quad (2.43)$$

and the angular-dependent forces are introduced through the dipole vector μ_i^α , the quadrupole tensor $\lambda_{i,j}$, and the trace of this tensor, ν_i .

The forces between atoms in classical atomistic simulations are derived from the interatomic potentials according to eq. (2.37). This way, in order to compute overall force of a given system taking into account all the interatomic contributions a large number of calculations must be done, increasing dramatically the computational cost of calculating ($\mathcal{O}(N^2)$). However, it can be observed in the Fig.2.3 (a) that V and f are almost zero for large r and the interactions between atoms can be neglected above certain interatomic distance, leading to the concept of the cut-off radius (r_c). The r_c is the maximum interatomic distance that provides non-negligible interactions.

The cut-off, r_c , is normally defined using two different approaches. The first one is a direct truncation according to (Fig 2.3(b))

$$f_{i,j} = \begin{cases} -\frac{dV_{i,j}}{dr_{i,j}} & , \quad r_{i,j} \leq r_c \\ 0 & , \quad r_{i,j} > r_c \end{cases} \quad (2.44)$$

where the $V_{i,j}$ and $f_{i,j}$ are considered zero when $r_{i,j} > r_c$.

An smooth transition from non-negligible to negligible interactions can also be considered. To this end, a second cut-off radius, named skin radius (r_s) is introduced, and the interaction of the atoms inside the spherical volume inside ($r_s - r_c$) is given by

$$f_{i,j} = \begin{cases} -\frac{dV_{i,j}}{dr_{i,j}} & , \quad r_{i,j} < r_c \\ -w \frac{dV_{i,j}}{dr_{i,j}} & , \quad r_c \leq r_{i,j} < r_s \\ 0 & , \quad r_{i,j} > r_s \end{cases} \quad (2.45)$$

Figure 2.3: (a) Potential energy versus distance for the interaction between two atoms. The minimum corresponds to the equilibrium distance of the pair. (b) Pair potential energy truncation as a function of the distance. The truncation can be sharp (red dashed line) or smooth (green dashed line). (c) Representation of the cutoff radius and skin radius for the atom i . Green and yellow atoms interact with atom i . Red atoms are not taken into account to calculate the potential energy.

where w denotes the weighting function that varies from 1 to 0 and depends on the position between r_c and r_s . In any case, the strategy followed by atomistic simulations is to compute force on the atom i only by using the sum of the contributions from the individual atom, j , inside a sphere of radius r_c . This nearest neighbor atoms are included in the Verlet list (Frenkel and Smit, 2001). The Verlet list is updated when a particle moves more than $(r_c - r_v)$ (Fig. 2.3(c)). This strategy is utilized to reduce the computational cost from $\mathcal{O}(N^2)$ to $\mathcal{O}(N)$.

Molecular Dynamics

Molecular dynamics (MD) is a widely utilized atomistic strategy to simulate the motion of atoms. The dynamic problem is solved accounting for the forces provided by the interatomic potentials.

But before elaborate further on molecular dynamics, it is important to introduce the concept of ergodicity. The ergodic hypothesis states that the system must visit all the possible thermodynamic microstates in order to estimate macroscopic attributes based on microscopic observables. Statistical ensembles, which provide all the atomic configurations compatible to a given set of macroscopic properties, are used to achieve this condition. Thus, a set of macroscopic attributes (e.g. total energy, temperature, volume, number of atoms, etc.) are constrained during the dynamical procedure and all the atomic arrangements within the phase space (i.e. $\mathbf{r}(t)$, $\mathbf{p}(t)$) are explored for a given

time. In this way, thermodynamic balances are carried out during MD simulations by means of the application of statistical ensembles, assuming an ergodic system.

The most common statistical ensembles used in molecular mechanics simulations are the microcanonical ensemble (NVE) and the canonical ensemble (NVT). The NVE ensemble constrains the total number of atoms N , the volume of the domain V and the total energy of the system E , while the NVT sets the number of atoms, volume and temperature T . Additionally, there are other types of ensembles, e.g. NPT (number of atoms, pressure and temperature are fixed) or μ VT (also called grandcanonical ensemble) in which the chemical potential μ of the system is constrained, together with volume and temperature, while the number of atoms can vary.

Once the statistical ensemble is applied to the domain under study and stabilized, other not-constrained macroscopic attributes (χ) are calculated as an average of all the values of this property along the time, such as

$$\langle \chi \rangle = \frac{\sum_{t=0}^{t_{tot}} \chi(t)}{t_{tot}} \quad (2.46)$$

where t_{tot} accounts for the total time calculated.

Although it has been demonstrated that phase averaging provides an accurate prediction of the macroscopic observables, it should be noted that it assumes ergodicity. Consequently, the accuracy of phase averaging depends on the total time calculated. However, the ergodic condition can be also achieved by computing parallel replicas of the same system starting from different points of the phase space (Tadmor and Miller, 2011).

The integration of the equations of motion and the computation of forces are the core of MD simulations. To this end, different schemes can be utilized, from classical Euler explicit methods to high order algorithms. It is worth noting that the choice of the integration algorithm in MD is crucial from the viewpoint of energy conservation and computational cost. Among the available options, the velocity Verlet (VV) algorithm is the one that presents the best balance. VV is an explicit second order algorithm, which is stable and ensures the conservation of the macroscopic properties (e.g. total energy) with a low computational cost (Frenkel and Smit, 2001). The VV algorithm provides the new position of each particle, following a second order truncation of the Taylor's expansion according to

$$\mathbf{r}_i^{n+1} \simeq \mathbf{r}_i^n + \mathbf{v}_i^n \Delta t + \frac{\mathbf{f}_i^n}{m_i} \Delta t^2 \quad (2.47)$$

where n indicates the current step, i the atom, $\mathbf{v}$ the velocity, $\mathbf{f}$ the force, m the atom

Figure 2.4: General flow chart of the molecular dynamics numerical procedure.

mass and Δt the time increment between steps. Stable time increments are in the order of femtoseconds ($10^{-15} s$), depending on the mass of the atom. It should be noted that the Euler scheme is not used to update the velocity, but the eq. (2.48):

$$\mathbf{v}_i^{n+1} = \mathbf{v}_i^n + \left[\frac{\mathbf{f}_i^{n+1} + \mathbf{f}_i^n}{2m_i} \right] \Delta t. \quad (2.48)$$

It is worth noting that the position in the next timestep must be calculated afterwards in order to account for momentum of the particles. Even though a second calculation to obtain the velocity is needed, the VV framework avoids the two step integration of conventional Verlet, thus decreasing the computational cost (Frenkel and Smit, 2001).

To summarize, the overall MD computational approach used in this thesis is depicted in Fig. 2.4.

Molecular Statics

The potential energy landscape of an N -particle system depends on the position of all the atoms and is very complex, containing valleys and ridges (Fig. 2.5(b)). The presence of many local minima is very important because they represent the possible potential basins that the system dynamically explores. Molecular Statics (MS) is used to determine the positions of the atoms that minimize the total energy of the system and to determine the potential energy landscape.

Several algorithms can be used to determine the minimum potential energy of the system within the framework of MS, e.g. the steepest descent, Newton-Raphson or conjugate gradient. As mentioned above, the selection of the algorithm is critical for

Figure 2.5: (a) Flow chart of the conjugate gradient algorithm. (b) Graphical representation of the conjugate gradient algorithm in a $3N$ particle energy landscape.

the accuracy and computational cost. Accordingly, the non-linear conjugate gradient algorithm (CG) (Hestenes and Stiefel, 1952) has been utilized in all the MS simulations presented in this thesis.

The CG is one of the most widely used energy minimization methods due to its efficiency and fast convergence. This iterative method tries to find directions that descent, $\mathbf{d}$, through the energy function. The direction for a new iteration $\mathbf{d}^n$ is not only based on the steepest descent direction but also constructed to fulfill a set of conditions with previous descent directions $\mathbf{d}^i$ ($i = 1, n-1$; conjugacy of the vectors). The CG is usually combined with a linesearch strategy, which is aimed at finding the optimum size of the step (α) towards the direction $\mathbf{d}$ that reduces enough the potential energy. Nevertheless, it should be finally noted that the CG aims at finding a local energy minimum from an initial position but does not ensure that the final configuration corresponds to a global minimum.

Path sampling methods

MD simulations provide information about the dynamics of the particle system while MS simulations determine the potential energy landscape. Thus, they are able to provide useful information about the transition between two local minima along the landscape, but none of them determines explicitly the transition pathway or the activation energy of an infrequent event. The so-called landscape path sampling (LPS) methods are numerical procedures developed to this end. The most relevant among them are the activation-relaxation technique (ART) (Barkema and Mousseau, 1996; Mousseau and Barkema, 1998) and the string-based techniques (Bergonzo and Simmerling, 2011). Although both techniques are very useful, the present thesis has used the string methods.

String methods use a finite number of copies the same system, also called replicas, which are located along the energetic landscape between two local minima. These replicas between both energetic minima have to be obtained *ad-hoc*. All these copies are interconnected along the pathway with the previous and the next replica by the so-called strings. This connection penalizes the motion towards the local minima, but promotes the motion towards the MEP along the energetic landscape from the initial minimum energy to the final. Thus, this technique tries to form a smooth curve along the MEP based on the optimization of intrinsic parameters that connect the two initial local minima on the configurational surface. There are different ways to define the interaction between replicas (e.g string method, modified string method or nudged elastic band). The nudged elastic band (NEB) method, first proposed by Mills et al. (1995), was used in this thesis and is detailed below.

The NEB method allows to track the evolution of the atomic arrangement by sampling the MEP between the initial and final states, both of which are located in local energy minima. The MEP describes the variation of the energy of the system along the path from one minimum to another. Normally, one maximum value of energy is found along the landscape, which establishes the energy barrier that has to be overcome to transit from the initial equilibrium position to the final one.

The NEB method uses two equilibrium states of the system as the initial and final points of the pathway and N replicas of the system are generated using linear interpolation of the particle coordinates between the initial and final point according to

$$\mathbf{R}_j = \mathbf{R}_1 + \frac{j-1}{N-1} (\mathbf{R}_N - \mathbf{R}_1) \quad (2.49)$$

where $\mathbf{R}_j$ are the atomic positions ($\mathbf{r}_i$) in the replica j and N the total number of replicas.

The atoms in each replica are subjected to two different types of forces: those originated by fictitious springs that link each replica with the previous ($\mathbf{F}^S$) and the next

replicas and those coming from the interactions with other atoms in the replica ($\mathbf{F}^P$). The fictitious springs forces, $\mathbf{F}^S$, come from the interconnection between replicas. Each atom (i) of each replica (j) is connected by harmonic springs to the corresponding atom i in the previous ($j - 1$) and the next ($j + 1$) replicas. These springs ensure the continuity of the energetic pathway and prevent the intermediate replicas from falling into the local energy minimum wherein the first and the last replica are. They also maintain the replicas equally spaced. The fictitious forces are defined as:

$$\mathbf{F}_j^S = k (|\mathbf{R}_{j+1} - \mathbf{R}_j| - |\mathbf{R}_j - \mathbf{R}_{j-1}|) \hat{\tau}_j \quad (2.50)$$

where k is the spring constant and $\hat{\tau}_j$ is a unit vector along the path. $\hat{\tau}_j$ is updated in each timestep of the analysis to obtain the equilibrium position of the replica j depending on the values of the interatomic potential energy (V) in the replicas $j + 1$, j and $j - 1$ according to:

- If $V(\mathbf{R}_{j+1}) > V(\mathbf{R}_j) > V(\mathbf{R}_{j-1}) \rightarrow \hat{\tau}_j = \frac{\mathbf{R}_{j+1} - \mathbf{R}_j}{|\mathbf{R}_{j+1} - \mathbf{R}_j|}$
- If $V(\mathbf{R}_{j+1}) < V(\mathbf{R}_j) < V(\mathbf{R}_{j-1}) \rightarrow \hat{\tau}_j = \frac{\mathbf{R}_j - \mathbf{R}_{j-1}}{|\mathbf{R}_j - \mathbf{R}_{j-1}|}$
- If $V(\mathbf{R}_{j+1}) > V(\mathbf{R}_j) < V(\mathbf{R}_{j-1}) \rightarrow \hat{\tau}_j = \frac{(\mathbf{R}_{j+1} - \mathbf{R}_j)\Delta V_j^{max} + (\mathbf{R}_j - \mathbf{R}_{j-1})\Delta V_j^{min}}{|(\mathbf{R}_{j+1} - \mathbf{R}_j)\Delta V_j^{max} + (\mathbf{R}_j - \mathbf{R}_{j-1})\Delta V_j^{min}|}$
- If $V(\mathbf{R}_{j+1}) < V(\mathbf{R}_j) > V(\mathbf{R}_{j-1}) \rightarrow \hat{\tau}_j = \frac{(\mathbf{R}_{j+1} - \mathbf{R}_j)\Delta V_j^{min} + (\mathbf{R}_j - \mathbf{R}_{j-1})\Delta V_j^{max}}{|(\mathbf{R}_{j+1} - \mathbf{R}_j)\Delta V_j^{min} + (\mathbf{R}_j - \mathbf{R}_{j-1})\Delta V_j^{max}|}$

where ΔV_j^{fn} (superscript fn indicates maximum or minimum) is given by eq. (2.51).

$$\Delta V_j^{fn} = fn (|V(\mathbf{R}_{j+1}) - V(\mathbf{R}_j)|; |V(\mathbf{R}_j) - V(\mathbf{R}_{j-1})|). \quad (2.51)$$

The fictitious spring forces are parallel to the ascending or descending energy path and, near the saddle point, the direction of $\hat{\tau}_j$ is interpolated between both directions. This strategy to determine $\hat{\tau}_j$ increases the stability of the method and avoids the nucleation of kinks in the nudged band (Henkelman and Jónsson, 2000).

In addition to the spring forces, forces derived from the atomic interactions in the replica j , obtained from the interatomic potential, are considered. In the initial ($j = 1$) and final situation ($j = N$), these are the only forces taken into account leading to minimum energy (equilibrium) situation. In the intermediate states, only the contribution of this force perpendicular to $\hat{\tau}_j$, $\mathbf{F}_j^P$, is included in the analysis to obtain the equilibrium position of the replica j . Thus, $\mathbf{F}_j^P$ is given by eq. (2.52).

$$\mathbf{F}_j^P = \left(-\frac{\partial V}{\partial \mathbf{R}_j} \right) (\mathbf{I} - \hat{\tau}_j \hat{\tau}_j^T) = \left(-\frac{\partial V}{\partial \mathbf{R}_j} \right) \hat{\eta}_j \quad (2.52)$$

Figure 2.6: Graphical representation of nudged elastic band method.

where $\mathbf{I}$ is the identity matrix, the superscript T denotes a transpose and $\hat{\eta}_j$ is a unit vector perpendicular to $\hat{\tau}_j$. This force tries to drive each inter-replica to a minimum potential energy position in the direction perpendicular to $\hat{\tau}_j$. So, the forces acting on replica j are given by

$$\begin{aligned} \mathbf{F}_j &= \mathbf{F}_j^P \quad (j = 1 \text{ or } N) \\ \mathbf{F}_j &= |F_j^P| \hat{\eta}_j + |F_j^S| \hat{\tau}_j \quad (j = [2, N - 1]) \end{aligned} \quad (2.53)$$

Although the NEB method provides accurate information about the shape of the MEP between initial and final local minima, sometimes the saddle point is not well converged. In consequence, the value of the activation energy is not accurate (Henkelman et al., 2000). In order to avoid this problem, regular NEB procedures are usually combined with the called climbing image NEB (CI-NEB). This strategy is a modification of the regular NEB procedure, which consists of the identification of replica with highest energy after regular NEB calculation. Then, the forces in this image are computed taking into account the full force due to the potential but inverting the fictitious forces, according to

$$\mathbf{F}_j^{V_{max}} = \left(-\frac{\partial V(\mathbf{R}_j^{max})}{\partial \mathbf{R}_j} \right) + 2 \frac{\partial V(\mathbf{R}_j^{max})}{\partial \mathbf{R}_j} \hat{\tau}_j \hat{\tau}_j. \quad (2.54)$$

Imposing eq. (2.54) to the saddle point replica, forces this replica to move upward along the elastic band and downhill in the perpendicular direction. It should be noted that the maximization process along the landscape has only 1 DoF defined by the other replica position.

Different energy minimization algorithms can be applied in order to determine the equilibrium condition ($\mathbf{F}_j = 0$) for each replica (Sheppard et al., 2008). Linesearch minimization strategies have synchronization problems between replicas in the case of multireplica minimization and, therefore, damped dynamic methodologies are used (Bitzek et al., 2006). For the calculations carried out in this thesis, the fast inertial relaxation engine (FIRE) has been used. Further information about FIRE is provided in Appendix B.

It must be finally indicated that all the molecular mechanics and DFT simulations of the present thesis were carried out using LAMMPS (Plimpton, 1995) and Quantum-Expresso (Giannozzi et al., 2009), respectively. OVITO (Stukowski, 2009) was used to visualize and represent the atomistic pictures of the results. Finally, the open source code ATOMSK was employed set up the atomistic models of dislocations (Hirel, 2015).

3 ATOMISTIC MODELING OF CROSS-SLIP IN Al

Cross-slip of dislocations is an important process during plastic deformation. This mechanism helps to overcome obstacles, promotes the creation of new dislocation sources or the annihilation of dislocations and influences the formation dislocation patterns. In the case of FCC metals, cross-slip occurs when a screw dislocation segment with Burgers vector moving in a $\{111\}$ slip plane, changes to another slip plane which also contains the same Burgers vector.

The cross-slip process has been widely investigated and different physical mechanisms have been proposed (Püschl, 2002; Caillard and Martin, 2003). The Fleischer mechanism takes place by folding the stacking fault ribbon over from the glide plane to the cross slip plane. Thus, the leading partial splits into a $1/3\{100\}$ Hirth dislocation (stair rod) and a Shockley partial dislocation in the cross-slip plane. The Fleischer mechanism is depicted in Fig. 3.1(a).

The Friedel-Escaig (FE) mechanism consists of the creation of two Stroh constrictions along the dislocation line on the glide plane. These constrictions partially re-assemble the leading and trailing partial dislocations and form a perfect $\langle 110 \rangle \{111\}$ dislocation segment between them. The Burgers vector of the dislocation segment is contained in both the glide and cross-slip planes and, as a consequence, the dislocation

Figure 3.1: Schematic of the mechanisms of cross slip in FCC lattices. (a) Fleischer mechanism. The red lines correspond to Shockley partial dislocations, while the yellow line stands for the stair rod. (b) Friedel-Escaig mechanism.

is allowed to dissociate along the cross-slip plane between the Stroh nodes, as shown in Fig. 3.1(b). Even though both mechanisms seem to be valid, the FE mechanism shows a better agreement with both experiments (Bonneville and Escaig, 1979; Bonneville et al., 1989) and atomistic simulations (Kang et al., 2014; Nöhring and Curtin, 2017, 2018).

It is well-established that cross-slip is thermally-activated (Caillard and Martin, 2003) and hence, it depends on the magnitude of the energy barrier associated with the event. This energy barrier in FCC crystals varies with the Escaig and Schmid stresses (Duesbery et al., 1992b; Martinez et al., 2008; Kang et al., 2014; Malka-Markovitz and Mordehai, 2019). The Escaig stress (E) acts on the edge component of the Shockley partial dislocations, and controls the distance between them. The Schmid stress (S) acts on the screw component of the dislocation and favors dislocation slip on either the glide or the cross-slip plane.

Different approaches have been proposed in the literature to determine the energy barrier for cross-slip. Linear-elastic continuum models determine the cross-slip barrier as the extra energy that has to be supplied in order to create a perfect screw dislocation between constriction along Shockley partials (Püschl, 2002; Duesbery et al., 1992a; Schoeck and Seeger, 1955; Duesbery et al., 1992b). However, they do not deal explicitly

with the forces and displacements of partial dislocations. Moreover, these models do not account for the re-dissociation contribution to the energetic barrier (Püschl, 2002). Line tension models are based on the elastic interaction between Shockley partials and the energy barrier for cross-slip is obtained from the balance between repulsive interaction between partial dislocations on the glide plane and the energy to re-dissociate the partials in the cross-slip plane. Both contributions depend on applied stresses on slip and cross-slip planes (Martinez et al., 2008; Kang et al., 2014; Malka-Markovitz and Mordehai, 2018, 2019; Liu et al., 2019b). Atomistic approaches use path sampling methods (such as the nudged elastic band (NEB) method and the string method) in order to evaluate the minimum energy path between two stable (or metastable) configurations to determine the energy barrier (Kang et al., 2014).

However, linear superposition of Schmid and Escaig stresses has been considered valid to date (Martinez et al., 2008; Kang et al., 2014) and a limited number of investigations have taken into account the influence of multiaxial stress states Malka-Markovitz and Mordehai (2019); Kuykendall (2015). Therefore, the present atomistic study of cross-slip was aimed at combining classical atomistic strategies with TST in order to provide simple analytical expressions to predict the cross-slip rate as a function of temperature and stress in Al. In particular the coupling effect between the Escaig stresses in the glide (g) and cross-slip (cs) planes was explicitly treated.

The theoretical background to interpret the results, the details of the atomistic simulations of cross-slip as well as the results obtained and the analytical model of the cross-slip rate are presented in this chapter (Esteban-Manzanares et al., 2019d).

3.1 Theoretical background

As explained in section 2.1.1, HTST assumes that the entropic contribution is independent of temperature, and equal to the ratio between the product of the normal frequencies in the local minima and in the saddle point (Vineyard, 1957). According to this assumption, the rate Γ_{HTST} is given by eq. (2.31) and the cross-slip rate, $\Gamma(T, \sigma)$, can be expressed as a function of the applied stress and temperature according to

$$\Gamma(T, \sigma) = \nu_{eff} \left(\frac{L}{L_n} \right) \exp \left(-\frac{\Delta H(\sigma)}{k_b T} \right) \quad (3.1)$$

where ν_{eff} stands for the effective attempt frequency, ΔH is activation enthalpy, L is the length of the screw dislocation segment considered and L_n the nucleation length, i.e. the length between constrictions to nucleate the cross-slip process. Thus, the ratio L/L_n stands for the total number of sites where cross-slip can nucleate along the dislocation line.

The activation enthalpy represents the energy barrier between the saddle point and the local minimum and, for a process at constant applied stress, it is given by

$$\Delta H = H^s(\sigma_{ij}) - H^m(\sigma_{ij}) \quad (3.2)$$

where σ_{ij} stand for the relevant components of the applied stress. It is well-known that the free energy landscape for a given configuration is locally changed in the vicinity of a defect (Schober, 1984), as compared with the one of the perfect crystal at the same configuration. In this case, the enthalpy H can be expressed as

$$H = H_{conf} + H_{el}^{st} + H_{el}^{int} \quad (3.3)$$

where H_{conf} is the configurational energy contribution and H_{el}^{st} stands for the stored elastic energy as a result of the applied stress (σ^e) and of the internal stress (σ^i) induced by the defect, which is given by

$$H_{el}^{st} = \sigma_{ij}^e S_{ijkl} \sigma_{kl}^e + \sigma_{ij}^i S_{ijkl} \sigma_{kl}^i \quad (3.4)$$

where S_{ijkl} is the fourth order compliance tensor, characteristic of the material. The last term, H_{el}^{int} , stands for the energetic contribution due to the interaction of the applied stress with the local stress field created by the defect. According to (Clouet et al., 2018), this latter term can be determined by means of the elastic dipole approximation, which is shown to be equivalent to the infinitesimal Eshelby inclusion, within the framework of continuum elasticity (Schober, 1984; Puls and Woo, 1986; Ackland, 1988). Following this work, the interaction energy contribution at constant stress can be expressed as a function of the relaxation volume tensor (V_{ij}) according to (Stoneham, 1983; Puls, 1985; Puchala et al., 2008)

$$H_{el}^{int} = -V_{ij} \sigma_{ij} = -V_{ij}^0 \sigma_{ij} - \frac{1}{2} \Omega_{ijkl} \sigma_{ij} \sigma_{kl} \quad (3.5)$$

where σ denotes the total stress tensor (applied and internal stresses). $V_{ij}^0 = -\partial H_{int} / \partial \sigma_{ij}$ and $\Omega_{ijkl} = -\partial^2 H_{int} / (\partial \sigma_{ij} \partial \sigma_{kl})$ are two tensors, of second and fourth rank, respectively, that determine the change of the energy landscape due to the applied stress and to the interaction between the applied stress and the internal stress associated with the defect, respectively. The polarization tensor Ω_{ijkl} can be defined as the difference of curvature in the free energy landscape basin because of the interaction of the stress fields, which stands for the difference of the compliance tensor in the vicinity of the defect (Dudarev and Ma, 2018; Dudarev et al., 2018).

If the difference in the stored elastic energy H_{el}^{st} between the saddle and the local minimum is neglected (i.e. $\Delta H_{el}^{st} \approx 0$), eq. (3.2) can be re-written as

$$\Delta H = \Delta U_0 - (V_{ij}^{s,0} - V_{ij}^{m,0}) \sigma_{ij} - \frac{1}{2} (\Omega_{ijkl}^s - \Omega_{ijkl}^m) \sigma_{ij} \sigma_{kl} \quad (3.6)$$

where ΔU_0 stands for the free energy difference between the saddle point and the local minimum in the athermal limit due to the differences in the atomic arrangement between both configurations. Moreover, $(V_{ij}^{s,0} - V_{ij}^{m,0})$ stand for the activation volume, which is equal to

$$V_{ij}^{act} = -\partial \Delta H_{int} / \partial \sigma_{ij} \quad (3.7)$$

multiplied by the applied stress provides the contribution of the applied stress to the energy landscape (Kocks, 1975). Thus, eq. (3.6) can be written as a function of the applied stress according to

$$\Delta H = \Delta U_0 - V_{ij}^{act} \sigma_{ij} - \frac{1}{2} \Omega_{ijkl}^{act} \sigma_{ij} \sigma_{kl} \quad (3.8)$$

where the fourth rank polarization tensor Ω_{ijkl}^{act} enables to compute the interaction energy between the saddle and the local minimum.

3.2 Atomistic simulation methodology

All atomistic simulations were carried out in a parallelepipedic box (Fig. 3.2). The x , y and z axes of the box were parallel to the $[11\bar{2}]$, $[111]$ and $[1\bar{1}0]$ crystallographic directions of the Al FCC lattice, respectively. These directions stand for the normal to the dislocation line, the normal to the glide plane and the dislocation line, in the same order. The dimensions of the domain were $25.4 \times 43 \times 10 \text{ nm}^3$ along the x , y and z axes, respectively. Periodic boundary conditions were applied along the three axes of the box. Two screw dislocations with opposite sign and equally spaced in the y axis, were inserted in two (111) planes perpendicular to the y axis with the dislocation line parallel to $[1\bar{1}0]$ (z axis). The perfect screw dislocations were introduced by applying the corresponding isotropic displacement field to each atom. The dislocations were located along the y axis, on parallel (111) planes, separated 21.5 nm each other, as illustrated in Fig 3.2(a). The energy of the screw dislocation dipole was minimized using the CG algorithm and the perfect dislocations were split into two Shockley partials. The internal atomic coordinates were considered optimized once the global interatomic force was below 10^{-9} eV/nm . The EAM interatomic potential developed by Mishin et al. (1999) for Al was used.

Two different types of simulations were carried out with the optimized structure. A multi-replica static optimization strategy using the NEB method was applied to obtain

Figure 3.2: (a) Schematic of the atomistic domain used in all simulations. The red planes stand for the primary glide planes (g) of the screw dislocations while the green one is the secondary cross-slip glide plane (cs). Red lines depict the dissociated Shockley partial dislocations. (b) Escaig (σ_E^g and σ_E^{cs}) and Schmid (σ_S^{cs}) stresses along the primary and secondary glide planes.

the minimum energy path (MEP) and the activation energy for cross-slip in Al. Afterwards, MD simulations were performed to obtain the enthalpy barrier and the attempt frequency as a function of the temperature and of the stress state. The following sections (3.2.1 and 3.2.2) explain in detail both simulation procedures.

3.2.1 Determination of the activation energy at 0 K

The standard NEB algorithm along with the climbing image nudged elastic band (CI-NEB) method were employed. The combination of both algorithms allows an accurate determination of the MEP and of the activation energy for cross-slip in Al. This static procedure is based on the energy minimization of a set of replicas of the same system located between two local minima along the potential energy landscape. Both the initial and final states were inputs for the analysis. In the initial state of the system, both screw dislocations lie along the glide plane (g). In the final state, one dislocation continues on the glide slip plane while the second dislocation is located on the cross-slip plane (cs). The atomic positions between both minima were obtained by linear interpolation and 32 replicas were used in the simulations. The stiffness constant of the band between replicas was set to 10^{-2} eV/nm. The FIRE algorithm was used to optimize the path along the potential landscape with the interconnected replicas. The timestep for the dynamic calculation was 1 fs. The set of replicas was considered to

be located along the minimum energy path when the overall force of each replica was below 10^{-4} eV/nm.

3.2.2 Determination of the rate at finite temperature and stress

MD simulations were used to analyze the cross-slip process in Al as a function of the stress state. The Schmid stress on the glide plane (σ_S^g) is parallel to the Burgers vector of the full dislocation and moves both partial dislocations in the same direction, while the Escaig shear stress on the glide plane (σ_E^g) is perpendicular to the full dislocation Burgers vector and expands or shrinks the stacking fault area between partials. Similar definitions can be given for the Schmid (σ_S^{cs}) and Escaig (σ_E^{cs}) shear stress on the cross-slip plane. Considering the orientation of the atomistic domain illustrated in Fig. 3.2, they are expressed by

$$\begin{aligned}\sigma_S^g &= \tau_{yz} & \sigma_S^{cs} &= \frac{2\sqrt{2}\tau_{yz}-\tau_{xz}}{3} \\ \sigma_E^g &= \tau_{xy} & \sigma_E^{cs} &= \frac{2\sqrt{2}(\sigma_{xx}-\sigma_{yy})-7\tau_{xy}}{9}\end{aligned}\quad (3.9)$$

The equilibrium condition ($\sigma_S^g = 0$) was assumed in all the MD simulations. Thus, the dislocation does not move on the primary glide plane, and the rate for dislocation cross-slip depends only σ_S^{cs} , σ_E^g and σ_E^{cs} . Different combinations of stresses along the glide and cross slip planes were used to analyze the process, uncoupled (σ_E^g , σ_S^{cs} and σ_E^{cs}), two stresses coupled ($\sigma_E^g + \sigma_E^{cs}$, $\sigma_E^g + \sigma_S^{cs}$ and $\sigma_E^{cs} + \sigma_S^{cs}$) and three stresses coupled ($\sigma_E^g + \sigma_E^{cs} + \sigma_S^{cs}$). They were obtained by controlling the applied stresses τ_{xz} , τ_{xy} , σ_{xx} and σ_{yy} on the simulation box.

The stress states applied to the atomistic system in order examine cross-slip under different stress states were the following:

Uncoupled stress states

(i) Escaig stress in the glide plane:

$$\sigma_{ij} = \begin{bmatrix} \frac{7}{4\sqrt{2}}\sigma_E^g & -\sigma_E^g & 0 \\ -\sigma_E^g & -\frac{7}{4\sqrt{2}}\sigma_E^g & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (3.10)$$

(ii) Escaig stress in the cross-slip plane:

$$\sigma_{ij} = \begin{bmatrix} \frac{9}{4\sqrt{2}}\sigma_E^{cs} & 0 & 0 \\ 0 & -\frac{9}{4\sqrt{2}}\sigma_E^{cs} & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (3.11)$$

(iii) Schmid stress in the cross-slip plane:

$$\sigma_{ij} = \begin{bmatrix} 0 & 0 & 3\sigma_S^{cs} \\ 0 & 0 & 0 \\ 3\sigma_S^{cs} & 0 & 0 \end{bmatrix} \quad (3.12)$$

Two stresses coupled

(i) Escaig stress in the glide and cross-slip planes

$$\sigma_{ij} = \begin{bmatrix} \frac{9}{4\sqrt{2}}\sigma_E^g + \frac{7}{4\sqrt{2}}\sigma_E^{cs} & -\sigma_E^g & 0 \\ -\sigma_E^g & -\frac{9}{4\sqrt{2}}\sigma_E^g - \frac{7}{4\sqrt{2}}\sigma_E^{cs} & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (3.13)$$

(ii) Escaig and Schmid stress in the cross-slip plane

$$\sigma_{ij} = \begin{bmatrix} \frac{9}{4\sqrt{2}}\sigma_E^{cs} & 0 & 3\sigma_S^{cs} \\ 0 & -\frac{9}{4\sqrt{2}}\sigma_E^{cs} & 0 \\ 3\sigma_S^{cs} & 0 & 0 \end{bmatrix} \quad (3.14)$$

(iii) Escaig stress in the glide plane and Schmid stress in the cross-slip plane:

$$\sigma_{ij} = \begin{bmatrix} \frac{7}{4\sqrt{2}}\sigma_E^g & -\sigma_E^g & 3\sigma_S^{cs} \\ -\sigma_E^g & -\frac{7}{4\sqrt{2}}\sigma_E^g & 0 \\ 3\sigma_S^{cs} & 0 & 0 \end{bmatrix} \quad (3.15)$$

Three stresses coupled

$$\sigma_{ij} = \begin{bmatrix} \frac{9}{4\sqrt{2}}\sigma_E^g + \frac{7}{4\sqrt{2}}\sigma_E^{cs} & -\sigma_E^g & 3\sigma_S^{cs} \\ -\sigma_E^g & -\frac{9}{4\sqrt{2}}\sigma_E^g - \frac{7}{4\sqrt{2}}\sigma_E^{cs} & 0 \\ 3\sigma_S^{cs} & 0 & 0 \end{bmatrix} \quad (3.16)$$

All the MD simulations were carried out using the NPT ensemble, in which different stress states were used to change the Escaig and Schmid stresses. The timestep employed in these simulations was 2 fs. An initial temperature/stress stabilization was carried out by increasing linearly the temperature and stress up to the chosen level during 40 ps. The time elapsed for cross-slip, t^{MD} , was computed from the instant at which temperature and stress attained the target levels. t^{MD} was measured until the cross-slip process was carried by one of the dislocations of the dipole. More specifically, the position of the dipole stacking faults between partial dislocations along $[11\bar{2}]$

direction was traced every 2 ps. It should be noted that the dislocation lying on the cross-slip plane, after the cross-slip process was completed, moved towards the other dislocation of the dipole and annihilated immediately. This effect was used as an indicator to finalize the MD simulations. Fifteen uncorrelated simulations were carried out for each temperature/stress pair to obtain statistically significant results. The average cross-slip rate as a function of temperature and stress was calculated as

$$\bar{\Gamma}(T, \sigma_{ij}) = \frac{2}{\langle t^{MD}(T, \sigma_{ij}) \rangle} \quad (3.17)$$

where $\langle t^{MD} \rangle$ stands for the average MD simulation times for all the simulations performed for cross-slip at given temperature/stress pair and the factor 2 is due to the existence of two dislocations in the simulation box.

For each stress state, the average rates were computed for at least two different stress values at five different temperatures in the range 400 K to 600 K in steps of 50 K.

3.3 Results and discussion

3.3.1 Nudged elastic band results

The NEB calculations provided the activation energy (ΔU_0) for cross-slip at 0 K as well as the particular cross-slip mechanism that follows the MEP in absence of thermal energy. The evolution of the internal energy along the MEP is plotted in Fig. 3.3(a). The curve shows a smooth transition between both the initial and final minima and the activated state. The energy barrier ΔU_0 given by the saddle point in the curve was 0.582 eV.

The cross-slip mechanism provided by NEB simulations is shown in Fig. 3.3(b). Different snapshots of the atomic positions along the dislocation line during the cross-slip process are illustrated in this figure, together with the schematic representation of the position of the partial dislocations. The process follows the Friedel-Escaig mechanism. Both Shockley partials (red lines) can be seen in their ground state on the (111) plane in (i). Two constrictions, represented as blue dots, are formed in (ii), near the saddle point. They are linked by a perfect [110](111) dislocation (green line). The distance between both constrictions was approximately 2.8 nm. This distance is the nucleation length, L_n , i.e. the length between constrictions to nucleate the cross-slip process. At the saddle point, depicted in (iii), the perfect dislocation dissociates along the $(11\bar{1})$ plane. Thus, the MEP for cross-slip involves the creation of two Stroh constrictions along the dislocation line tangent and the re-dissociation of the dislocation segment between the two constrictions on the cross-slip plane. It is worth noting that

this mechanism is slightly different from Friedel observations, who considered that the maximum energy was attained before re-dissociation of partial dislocations along the cross-slip plane. This effect was reported recently by Oren et al. (2017) Once the saddle point is reached, both constrictions expand in opposite directions, enforcing the re-dissociation of the partials on the cross-slip plane. This process is illustrated in (iv) and (v). Finally, both partial dislocations are completely dissociated in the $(11\bar{1})$ plane, as shown in (vi).

The cross-slip barrier obtained by NEB is in good agreement with the cross-slip line tension models (Escaig, 1968). These models claim that the activation barrier for cross-slip is defined by the contribution of three different energetic sources, i.e. the elastic repulsion energy between two partials, the change of line energy and the variation of the stacking fault due to the effect of Schmid and Escaig stresses along either glide and cross-slip planes (Kang et al., 2014). However, the effect of the stress state effect was not evaluated using NEB. The mechanism reported was already observed in other atomistic studies of cross-slip (Wen et al., 2007; Du et al., 2014; Oren et al., 2017).

3.3.2 Molecular dynamics results

Uncoupled stresses

The average cross-slip rates for the uncoupled stresses are plotted in Fig. 3.4. The rates are represented as a function of $1/k_bT$ for different values of the Escaig stress on the glide and cross-slip planes (σ_E^g in Fig. 3.4(a) and σ_E^{cs} in Fig. 3.4(b), respectively) and the Schmid stress on the cross-slip plane, σ_S^{cs} (Fig. 3.4(c)). It should be noted that only the Friedel-Escaig cross-slip mechanism was observed for all temperatures and stress states.

As expected, the energy barrier decreased as the stress increased and also the probability to overcome the barrier increased with the temperature. Moreover, the logarithm of the rates showed a linear dependence with $1/k_bT$ in all cases, indicating that the energetic barrier does not depend on the temperature. Moreover, it was observed that the pre-exponential factor decreased as the applied stress increased, indicating that the entropic barrier was also a function of the stress. This behavior can be rationalized through the so-called Meyer-Neldel (MN) rule (Meyer and Neldel, 1937), which establishes that the reduction of the activation energy is compensated by a reduction of pre-exponential factor and, consequently, of the entropic barrier because of anharmonic effects associated with the dependence of the some materials properties (elastic constants, thermal expansion coefficients, and stacking fault energy) with temperature (Kemeny and Rosenberg, 1973; Sobie et al., 2017a).

Figure 3.3: (a) Energy landscape along the minimum energy path for cross-slip at 0K in Al. The activation energy ($\Delta U_0 = 0.582$ eV) for the process corresponds to the saddle point of the curve. (b) Atomistic snapshots along with schematic representations of the partial dislocation lines during the cross-slip process obtained from the NEB calculations. The Friedel-Escaig mechanism is clearly observed.

Figure 3.4: Average rates of the cross-slip process (expressed in s^{-1}) as a function of $1/k_bT$ obtained from the MD simulations. (a) Influence of the Escaig stress on the glide plane, σ_E^g . (b) Influence of the Escaig stress on the cross-slip plane, σ_E^{cs} . (c) Influence of the Schmid stress on the cross-slip plane, σ_S^{cs} .

The MN rule assumes that the activation entropy is proportional to the activation enthalpy according to

$$\Delta S(\sigma) = \frac{\Delta H(\sigma)}{T_m} \quad (3.18)$$

where T_m is the melting temperature. Different studies have demonstrated the applicability of the MN compensation rule in solid mechanics (Sobie et al., 2017a; Nguyen et al., 2011; Ryu et al., 2011; Saroukhani et al., 2016; Saroukhani and Warner, 2017).

The activation enthalpy and entropy barriers for each applied stress was obtained according to eqs. (3.1) and (2.32), respectively. The length of the screw dislocation segment in all the MD simulations was $L = 10$ nm and L_n was considered equal to the nucleation length observed in the NEB simulations

The activation enthalpy (ΔH) obtained from MD simulations is plotted in Fig. 3.5 as a function of the applied stress (either the glide stress on the cross-slip plane or the Escaig stress in the glide or cross-slip planes). The solid lines stand for the best fit of the MD results according to eq. (3.8). It should be noted that a single value of the activation volume and of the interaction factor were assumed for each stress. So, the activation energy for cross-slip can be expressed as a function of the projection of the stress along the different planes according to

$$\Delta H(\sigma) = \Delta U_0 - V^{act}\sigma - \frac{1}{2}\Omega^{act}\sigma^2 \quad (3.19)$$

σ represents the three different uncoupled stresses ($\sigma_E^g, \sigma_E^{cs}$ and σ_S^{cs}).

The results of Fig. 3.5 reveal the different influence of the Escaig and Schmid stresses on the glide and cross-slip plane on the rate of the event. It can be observed that ΔH decreases linearly with the Escaig stress in both planes while the dependence of ΔH with the Schmid stress on the cross-slip plane is quadratic. Thus, the contribution of the quadratic interaction energy in the case of the Escaig stresses seems to be negligible and the enthalpy barrier can be expressed as.

$$\begin{aligned} \Delta H(\sigma_E^g) &= \Delta U_0 - V_E^g \sigma_E^g \\ \Delta H(\sigma_E^{cs}) &= \Delta U_0 - V_E^{cs} \sigma_E^{cs} \end{aligned} \quad (3.20)$$

according to the MD results in Fig. 3.5, where V_E^g and V_E^{cs} stand for the activation volumes for the Escaig stress on the glide and cross-slip planes, respectively.

In the case of the Schmid stress on the cross-slip plane, this first order approximation does not suffice to explain the effect of the external stress on the energy barrier and the second order polarization term has to be included to determine the activation enthalpy according to

Figure 3.5: (a) Activation enthalpy and (b) activation entropy as a function of the applied Schmid and Escaig stresses on the glide or cross-slip planes. The results of the MD simulations are given by the symbols. The lines represent the predictions of eq. (3.20) and eq. (3.18).

$$\Delta H(\sigma_S^{cs}) = \Delta U_0 - V_S^{cs,0} \sigma_S^{cs} - \frac{1}{2} \Omega_S^{cs} (\sigma_S^{cs})^2 \quad (3.21)$$

where V_S^{cs} stands for the activation volume at zero stress and Ω_S^{cs} expresses the effect of σ_S^{cs} on the activation volume due to the polarization.

The three activation volumes and Ω_S^{cs} were obtained by fitting the results of the MD simulations in Fig. 3.5 to eqs. (3.20) and (3.21) and they are depicted in the Table 3.1. It is worth noting that an important reduction of the barrier is evident in the case of the Schmid stress on the cross-slip plane with respect with the two Escaig stresses for large stresses (≥ 150 MPa). However, the three stresses have similar influence on the energy barrier when they are below 100 MPa.

Table 3.1: Activation volumes and C_S^{cs} for uncoupled Escaig and Schmid stresses

	σ_E^g	σ_E^{cs}	σ_S^{cs}
V (b^3)	13.6	11.6	9.4
Ω (b^3/MPa)	–	–	0.102

The effective attempt frequency ν_{eff} , obtained from MD simulations, was in the range from 5×10^{11} to $1 \times 10^{13} \text{ s}^{-1}$, which is in agreement with previous studies (Vegge

et al., 2000; Oren et al., 2017). The activation entropy, ΔS , was estimated from ν_{eff} , according to eq. (2.32) and assuming a fundamental attempt frequency $\nu = 1 \times 10^{11}$ (Saroukhani et al., 2016; Sobie et al., 2017b)

The activation entropies, ΔS , is plotted in Fig. 3.5(b) as a function of the applied stress. The symbols stand for the results obtained from the MD results while the lines define the predictions according to eq. (3.18) with $T_m=933$ K, which is the melting temperature of the Al (Meyrick and Powell, 1973). It was found that ΔS decreased as applied stress increased and that this dependency was in agreement with the enthalpy-entropy MN compensation rule.

Coupled stresses

The same strategy employed in the previous section was used to examine the effect of coupled stresses ($\sigma_E^g = \sigma_E^{cs}$, $\sigma_E^g = \sigma_S^{cs}$ and $\sigma_E^{cs} = \sigma_S^{cs}$) the enthalpy and entropy barriers. The average rates as a function of $1/k_b T$ are depicted in Fig. 3.6 for the case of coupled stresses. As in the uncoupled case, the application of stress and/or temperature increases the cross-slip rate and coupled stress led to a larger reduction of the activation energy when compared to the single stress cases in Fig. 3.4. The dependence of the logarithm of the rates was also linear with respect to $1/k_b T$, indicating that transition state theory holds for these stress states. In addition, the values of ν_{eff} , obtained from the rates were also inversely proportional to the applied coupled stresses, as observed in the case of uncoupled stresses, indicating that ΔS depends on the stress. The evolution of ΔH and ΔS with each pair of stresses is shown in Fig. 3.7(a) and (b), respectively.

The interaction between coupled stress states on the free energy barrier was assumed to follow eq. (3.19). Thus, free energy barrier was reduced by the linear superposition of the individual contributions of each stress (eqs. (3.20) and (3.21)) which were corrected by second-order cross-terms that took into account the effects of stress coupling. Thus,

$$\begin{aligned}\Delta H(\sigma_E^g + \sigma_E^{cs}) &= \Delta U_0 - (V_E^g \sigma_E^g + V_E^{cs} \sigma_E^{cs}) - \frac{1}{2} \Omega_1 \sigma_E^g \sigma_E^{cs} \\ \Delta H(\sigma_E^g + \sigma_S^{cs}) &= \Delta U_0 - (V_E^g \sigma_E^g + V_S^{cs,0} \sigma_S^{cs}) - \frac{1}{2} [\Omega_2 \sigma_E^g \sigma_S^{cs} + \Omega_S^{cs} (\sigma_S^{cs})^2] \\ \Delta H(\sigma_E^{cs} + \sigma_S^{cs}) &= \Delta U_0 - (V_E^{cs} \sigma_E^{cs} + V_S^{cs,0} \sigma_S^{cs}) - \frac{1}{2} [\Omega_3 \sigma_E^{cs} \sigma_S^{cs} + \Omega_S^{cs} (\sigma_S^{cs})^2]\end{aligned}\quad (3.22)$$

where V_E^g , V_E^{cs} , V_E^g and the polarization factor Ω_S^{cs} were obtained from the MD simulations for uncoupled stresses (Table 3.1) and Ω_1 , Ω_2 and Ω_3 (that stand for the stress interaction factors) were obtained by fitting eq. (3.22) to the MD results in Fig. 3.7. They are shown in Table 3.2.

Figure 3.6: Average rates of the cross-slip process (expressed in s^{-1}) for coupled stresses as a function of $1/k_bT$ obtained from MD simulations. (a) Influence of the Escaig stresses on the glide and cross slip planes ($\sigma = \sigma_E^g = \sigma_E^{cs}$). (b) Influence of the Escaig stress on the glide plane and of the Schmid stress on the cross-slip plane ($\sigma = \sigma_E^g = \sigma_S^{cs}$). (c) Influence of the Escaig and Schmid stresses on the cross-slip plane ($\sigma = \sigma_E^{cs} = \sigma_S^{cs}$). The lines represent the fit obtained with eq. (3.22).

Figure 3.7: (a) Activation enthalpy and (b) entropy barriers as a function of the applied coupled stresses (σ) for $\sigma_E^g = \sigma_E^{cs}$, $\sigma_E^g = \sigma_S^{cs}$ and $\sigma_E^{cs} = \sigma_S^{cs}$. The lines stand for the predictions of eq. (3.22) and eq. (3.18), respectively. The symbols represent the activation energies obtained from MD simulations for each pair of coupled stresses.

Table 3.2: Stress interaction parameters (expressed in b^3/MPa) obtained from the MD simulations for coupled stress states.

Ω_1	Ω_2	Ω_3
-0.0516	-0.0652	-0.0294

Eqs. (3.22) were able to reproduce accurately the reduction in the free energy barrier under single or coupled stress states (Fig. 3.7). It can be observed that they reproduce the coupled stress behavior in the case that pair stresses have the same magnitude. In addition, these models recover their original shapes when only a single stress state is considered. Furthermore, although the energy barrier decreases under the application of coupled stresses (as compared with the uncoupled barriers), the non-zero value of Ω_1 , Ω_2 and Ω_3 indicates first order approximation is not accurate enough and the negative sign shows that there is some screening between the Escaig and Schmid stresses. Finally, it should be noted that Ω_S^{cs} is positive and almost twice as high in absolute value as Ω_1 , Ω_2 and Ω_3 , indicating that the influence of the Schmid stress on the cross-slip plane is dominant with respect to any other stress combination at high stresses. Furthermore, it should be noticed that the estimation of the entropic barrier combining eqs. (3.18) and (3.22) with $T_m = 933$ K follow the trend of the MD results, indicating that the MN compensation rule also holds for the biaxial case.

3.3.3 Cross-slip energy barrier as a function of the stress state

Eqs. (3.22) were able to reproduce accurately the reduction in the free energy barrier under single or coupled stress states (Fig. 3.7). They can be extended from the same assumptions used to develop the equations for coupled stresses to a general stress state characterized by σ_E^g , σ_E^{cs} and σ_S^{cs} , leading to a general expression for the energetic barrier

$$\Delta H(\sigma_E^g, \sigma_E^{cs}, \sigma_S^{cs}) = \Delta U_0 - (V_E^g \sigma_E^g + V_E^{cs} \sigma_E^{cs} + V_S^{cs,0} \sigma_S^{cs}) - \frac{1}{2} [\Omega_1 \sigma_E^g \sigma_E^{cs} + \Omega_2 \sigma_E^g \sigma_S^{cs} + \Omega_3 \sigma_E^{cs} \sigma_S^{cs} + \Omega_S^{cs} (\sigma_S^{cs})^2] \quad (3.23)$$

In order to evaluate the accuracy of eq. (3.23), additional MD simulations were carried out to determine the rate of cross slip under a multiaxial stress states with $\sigma_E^g = \sigma_E^{cs} = \sigma_S^{cs}$. The natural logarithm of the average rates is plotted as a function of $1/k_b T$ in Fig. 3.8(a). The enthalpy and entropy barriers were obtained, for each stress state, from the slope of straight lines and the pre-exponential factor in this figure. They are plotted in Figs. 3.8(b) and (c) as a function of the applied stress, together with the predictions from eq. (3.23) for ΔH and from eq. (3.18) for ΔS (black lines). The agreement between the predictions of the analytical expressions and the MD simulations results is evident, showing that the model proposed is able to provide an accurate estimation of the influence of σ_E^g , σ_E^{cs} and σ_S^{cs} on the free energy barrier for cross-slip in Al.

Probabilistic models of cross-slip have been extensively used to account for the stochastic nature of this process at the mesoscale (Kubin et al., 1992; Zbib et al., 1998; Weygand et al., 2002). They assume that the activation energy is given by an energy barrier, which depends on the applied shear stress projected in the cross slip plane (Kubin et al., 1992; Zbib et al., 1998; Weygand et al., 2002). Hussein et al. (2015) assumed that cross-slip was only controlled by the Escaig stress along the glide and cross slip planes and neglected the influence of the Schmid stress on the cross-slip plane. This hypothesis is not in agreement with the conclusions of atomistic simulations (Fig. 3.5) and line tension models (Kang et al., 2014) that demonstrate the important role of the Schmid stress on the cross-slip plane on the cross-slip rate. Martinez et al. (2008) assumed that the contribution of the applied stresses to the cross-slip rate could be calculated by a linear superposition of the Schmid stress on the cross-slip plane and of the Escaig stresses on both glide and cross-slip planes but it did not take into account the second order interactions in the case of combined Escaig and Schmid stresses along different planes, that are very important to determine the energy barrier (Fig. 3.7). Our

Figure 3.8: (a) Natural logarithm of the average cross-slip rates (expressed in s^{-1}) as a function of β for $\sigma = \sigma_E^g = \sigma_E^{cs} = \sigma_S^{cs}$. The standard deviation from the average rate is represented by the vertical bars. (b) Enthalpy (c) and entropy barriers for cross-slip obtained from MD simulations (white squares) and predictions from eq. (3.23) for ΔH and from eq. (3.18) for ΔS .

results provide an accurate estimation of the effect of the Schmid and Escaig stresses on the activation free energy for cross-slip rate in Al due to the polarization of the energy landscape and the dependence of the entropic barrier with the applied stress. Thus, a general expression of the rate of cross-slip as a function of the applied stress and temperature is obtained from MD simulations using TST, and this methodology can be readily extended to other FCC metals.

3.4 Conclusions

The influence of the stress state on the cross-slip rate in Al was analyzed by means of molecular dynamics simulations and transition state theory. The energy barrier in the absence of thermal energy was determined through the nudged elastic band method while the cross-slip rates were determined by means of molecular dynamics simulations for different magnitudes of the Schmid stress on the cross-slip plane, σ_S^{cs} , and of the Escaig stresses on the cross-slip and glide planes, σ_E^{cs} and σ_E^g in the temperature range 400K-600K. Cross-slip followed the Friedel-Escaig mechanism in the whole range of stresses and temperatures explored.

It was found that the influence of the stresses on the activation energy barrier followed the postulates of harmonic transition state theory and the enthalpy barrier and the activation entropy were determined from the average rates of cross-slip obtained from the molecular dynamics simulations. The Schmid stress on the cross-slip plane led to the largest reduction in the energy barrier at high stresses while at low stresses all stress projections showed very similar behavior. In addition, the coupling effect of the Schmid stress in the cross-slip plane and of the Escaig stresses in cross-slip and glide planes was evaluated and the synergistic contribution of all the stresses to reduce the energy barrier was determined. Based on these results, an analytical expression of the activation enthalpy for cross-slip in Al as a function of the Schmid and Escaig stresses was developed and validated for stress states involving all different combinations of the Schmid stress in the cross-slip plane and of the Escaig stresses in cross-slip and glide planes. The different terms in the analytical expressions were identified with the different contributions to the enthalpy energy barrier (configurational and due to the interaction of the applied stress with the local stress field created by the defect). Finally, it was found that the Meyer-Neldel rule is able to estimate the entropic contribution to the activation energy as a function of the applied stress. These expressions can be easily used in dislocation dynamics simulations to evaluate the probability of cross-slip of screw dislocation segments.

4 DISLOCATION/GUINIER- PRESTON ZONES INTERACTION IN Al-Cu

Precipitation hardening is one of the most efficient strategies to increase the yield strength of metallic alloys (Ardell, 1985; Nembach, 1997), as detailed in section 1.2. Al-Cu alloys are well-known for showing a large increase of their strength by in the presence of precipitates (Nie, 2014). Size, volume fraction and morphology of second phase precipitates determine the amount of precipitation strengthening. They are controlled by the parameters of the aging treatment, namely temperature and time, which govern the precipitation kinetics of each alloy. The precipitation process is a very complex phenomenon involving the decomposition of a supersaturated solid solution and the formation of a series of metastable precipitates at different stages of aging, which has been extensively analyzed in Al-Cu alloys (Guinier, 1939; Preston, 1938; Laird and Aaronson, 1966; Rosen et al., 1982; Vaithyanathan et al., 2004; Liu et al., 2017; Rodríguez-Veiga et al., 2018). The precipitation sequence starts with a supersaturated solid solution of Cu in Al and continues along the following precipitation sequence

Solid Solution $\rightarrow$ Guinier-Preston zones $\rightarrow \theta'' \rightarrow \theta' \rightarrow \theta$

where the Guinier-Preston (GP) zones and θ'' , θ' and θ precipitates have different characteristics that are presented in the table 4.1. All of them have a disk shape parallel to the $\{100\}$ planes of the FCC Al lattice.

Table 4.1: Characteristics of the different precipitate phases that appear during aging of an Al-Cu alloy (Laird and Aaronson, 1966; Rodríguez-Veiga et al., 2018). ϕ denotes the diameter of the disc precipitate whereas t is the thickness.

Phase	Structure	Lattice parameters (nm)	ϕ (nm)	t (nm)
GP zones	FCC	-	2-4	0.26
$\theta''(\text{Al}_3\text{Cu})$	FCC	$a=0.405, c = 0.384$	15-40	1-3
$\theta'(\text{Al}_2\text{Cu})$	BCT	$a=0.405, c=0.580$	100-200	4-8
$\theta(\text{Al}_2\text{Cu})$	Tetragonal C16	$a=0.607, c=0.487$	500-1000	20-50

Different combinations of precipitates with different sizes can be obtained as a function of the alloy composition and heat treatment temperature and time. The peak-aged condition (which corresponds to the maximum strength) is normally achieved by a combination of θ' and θ'' precipitates (Rosen et al., 1982; Vaithyanathan et al., 2004; Liu et al., 2017, 2019a).

Nevertheless, if the Al-Cu is aged at ambient temperature for a long time (> 100 hours), the only precipitate phase present are GP zones (Rodríguez-Veiga et al., 2018). GP zones were first reported by Guinier (1939) and Preston (1938) in separate studies, and essentially stand for clusters of Cu atoms, arranged in the form of a single layer disk parallel to the $\{100\}$ planes of the FCC lattice with a diameter in the range 2 to 4 nm. The arrangement of the atoms in the disk is coherent with the FCC lattice of Al (see Fig. 4.1).

The coherent structure of the GP zones with respect to the α -Al makes them sheareable by dislocations. The CRSS to shear precipitates is dictated by many factors such as chemical energy, stacking-fault energies, elastic modulus and order strengthening. All of these parameters have been examined by continuum models based on the line tension model (Ardell, 1985; Nembach, 1997) and, additionally, by dislocation dynamics simulations (Vattrè et al., 2009; Gao et al., 2015; Huang et al., 2012; Hussein et al., 2017). However, the validity of these approaches can be questioned when the continuum hypothesis is no longer applicable due to the small dimensions of the precipitate. In this particular case, precipitate shearing is controlled by the atomic interactions between matrix and solute atoms, leading to a very complex energy landscape that cannot be captured by simple continuum line tension models. This is the case of the GP zones,

Figure 4.1: Guinier-Preston zone image obtained by TEM (Rodríguez-Veiga et al., 2018), alongside with a model of a GP zone embedded in the α -Al matrix. TEM image courtesy of Bárbara Bellón.

which stands for a paradigmatic instance to predict the flow stress. Atomistic simulations can be used to study the strengthening provided by these precipitates and to gain a deeper understanding of the dislocation/precipitate interaction mechanisms and this is the main objective of this chapter. Particularly, the interaction of edge dislocations with GP zones with different orientation relationships was analyzed through atomistic simulations. Based on these simulations, a predictive model of the flow stress of naturally aged Al-Cu alloys was developed (Esteban-Manzanares et al., 2019c,a).

4.1 Atomistic strategy for dislocation/GP zones interaction

The dislocation/precipitate atomistic analysis were carried out in a parallelepipedic domain of volume of $34 \times 42 \times 16 \text{ nm}^3$ (Fig. 4.2). These dimensions were chosen following the results reported by Szajewski and Curtin (2015) to minimize the image stresses in the simulation box. The x , y and z axes of the domain were parallel to the $[\bar{1}10]$, $[111]$ and $[11\bar{2}]$ orientations of the FCC lattice. The simulation domain contained an edge dislocation (dissociated in leading and trailing Shockley partials) in the (111) glide plane and a single GP zone. Periodic boundary conditions were applied along the x and z axes, while free surfaces remained along y direction, following the PAD model (sec.

Figure 4.2: (a) Schematic of the atomistic simulation domain for the orientation GP 0. (b) Schematic of the atomistic simulation domain for the orientation GP 60.

1.3.2). Two different GP zones orientations were considered. In the first one (henceforth denoted as GP 0), the Burgers vector of the edge dislocation is parallel to the intersection of the GP zone in the slip plane 0° , Fig. 4.2(a). This configuration stands for the GP zones parallel to the (001) plane. In the second orientation (denominated GP 60), the Burgers vector and the intersection of GP zone with the slip plane form an angle of 60° , as depicted in Fig. 4.2(b). This configuration includes the GP zones parallel to either (010) or (100) planes (Esteban-Manzanares et al., 2019c).

The edge dislocation was introduced in the domain by applying the perfect dislocation displacement field for an isotropic elastic medium. After the dislocation was introduced, the system was optimized using the CG algorithm at constant volume, followed by another relaxation at zero Virial stresses. This led to the dissociation of the edge dislocation into two Shockley partials. A GP zone of 4 nm in diameter was introduced by substituting the corresponding layer of Al atoms by Cu atoms and the energy of the system was minimized again, leading to a mechanical equilibrium configuration between the dislocation and the GP zone. Deformation was introduced by applying an atomic displacement along the x axis and parallel to the slip plane to five layers of atoms on the top surface of the domain, while the five layers of atoms at the bottom surface remained fixed during the simulations.

For each orientation, three different types of atomistic simulations were carried out. The following sections will elaborate further on the atomistic strategies used in this

particular investigation.

4.1.1 Determination of the obstacle strength

The energy landscape of the edge dislocation-GP zone interaction presents many local minima. Standard energy minimization procedures based on the application of the CG algorithm does not ensure that global minima are attained before and after the dislocation has overcome the precipitate. This limitation was partially mitigated by the application of an iterative strategy that combines MS simulations with thermal annealing using MD. The procedure is detailed in Fig. 4.3. Starting from the equilibrium configuration detailed above, a shear strain was applied to the simulation domain by applying displacement of 2.5×10^{-3} nm to the upper fixed region, followed by an energy minimization using the CG algorithm. Then, the potential energy surface at this strain was explored via thermal annealing using MD. To this end, a linear temperature ramp from 100 K to 500 K was applied in 0.4 ns using a Langevin thermostat within the NVT ensemble, and the temperature was held constant at 500 K during 2 ns. Configurations were stored each 0.02 ns and their energy was minimized. A negligible decrease in stress was observed between the directly minimized configuration and after thermal annealing. The configuration with the minimum energy was selected and it was used as the initial structure for the next strain increment. This thermal annealing procedure to obtain the minimum energy configuration is obviously dependent on the annealing temperature. The energy landscape will not be sufficiently explored if the annealing temperature is too low and the minimum energy configuration will not be reached. On the other hand, the dislocation will completely overcome the obstacle if the temperature is too high (Argon, 2008). Thus, the annealing temperature (and time) was selected by a trial-and-error approach for this particular configuration. Finally, a temperature of 500 K during 4 ns of annealing time was chosen to ensure that high annealing temperatures did not bias the sampling procedure (Esteban-Manzanares et al., 2019c).

4.1.2 Determination of the activation energy

The activation energy was computed as a function of the applied shear stress using NEB and CI-NEB algorithms. The initial configuration for each value of the applied strain was given by the minimum energy configuration obtained via the thermal annealing procedure detailed above. The final atomic configuration at each strain ($\mathbf{r}_N(\gamma)$), was obtained using MD simulations. To this end, the initial atomic configuration $\mathbf{r}_0(\gamma)$ was held at 600 K until the dislocation overcomes the obstacle using the NVT ensemble

Figure 4.3: Flowchart of the iterative procedure to explore the energy landscape and obtain the minimum energy configurations in the phase space considered. In order to explore different states of the energy landscape MD thermal annealing was used. This way, small transition barriers were overcome without changing the energy landscape.

and the atomic configuration after this event was taken as $\mathbf{r}_N(\gamma)$ after minimization. The temperature of 600 K was selected so the dislocation bypasses the GP zone in a time affordable for MD simulations. It should be noted that the bypass mechanism was identical to the one determined obtained with the thermal annealing strategy already detailed.

FIRE algorithm with a timestep of 0.01 ps was used along with a spring constant of 1 eV/nm. Each NEB simulation was carried out with sixteen replicas and the intermediate replicas were obtained by linear interpolation between the initial and the final atomic positions. Nevertheless, it has been shown that this strategy may lead to transition paths that are different from the minimum energy path in complex energetic landscapes because one or more intermediate replicas may get stuck in a local minimum along the elastic band (Wales and Doye, 1997). Thus, the basin hopping (BH) global optimization strategy (Smidstrup et al., 2014) was also applied within the NEB

framework to determine the minimum energy path. In this strategy, a perturbation in the form of small random displacements of the atoms is introduced in each replica along the energetic path, originally obtained through linear interpolation. Each replica is perturbed independently, i.e., atomic displacements were introduced using a different random number seed. The maximum random displacement of the perturbation was 8×10^{-3} nm in each direction. Then, the minimum energy path is calculated using FIRE, as in traditional NEB, but starting from a perturbed condition at each intermediate replica. Four independent perturbations for each strain were carried out using this BH-NEB methodology and the one showing the minimum energy barrier was accepted as the MEP.

4.1.3 Determination of the rate

The rate at which dislocations overcome the GP zone was determined through MD simulations as a function of the applied strain and temperature. The minimum energy configurations for a given strain obtained as indicated in section 4.1.2 were used as the starting point. MD simulations at constant shear strain were carried out using an NVT ensemble at 400, 450, 500, 550 and 600 K and the time needed for the dislocation to overcome the precipitate, t^s , was determined for each case. Hydrostatic stresses were present in the NVT ensembles at finite temperatures due to thermal expansion but their influence on the rate at which the edge dislocation overcomes the precipitate is negligible because the driving force is controlled by the shear stress. To validate this hypothesis, MD simulations were carried out using a slightly different strategy. The temperature was initially increased from 0 K using an NPT ensemble and the volume was changed to reach the simulation temperature with negligible pressure. Afterwards, simulations were run during 100 ps within the NPT ensemble. Then, an NVT ensemble was used to perform the MD simulation at a given value of the applied strain until the dislocation overcame the GP zone to determine the rate. The rates obtained with this procedure were equivalent to those found using just the NVT ensemble. Eight independent simulations were carried out for each strain and temperature to account for the stochastic nature of the process and the average rate, $\bar{\Gamma}$, was given by $8/\sum t_i^s$.

4.2 Results and discussion

4.2.1 CRSS and dislocation-GP interaction mechanisms

The dislocation/GP zone interactions were analyzed by means of MS simulations, with and without thermal annealing. The shear stress-strain curves and the energy

Figure 4.4: Dislocation interaction with the GP 60 precipitate. (a) Shear stress vs. shear strain curve. (b) Energy vs. shear strain curve.

stored-strain curves obtained from the simulations are plotted in Figs. 4.4 and 4.6 for GP 60 and GP 0 orientations, respectively. They are analyzed together below.

The shear stress *vs.* strain and the energy stored *vs.* strain curves of either GP 0 and GP 60 were initially superposed in the cases of MS and MS + TA simulations, that correspond to the begin of dislocation movement towards the GP zone. This first dislocation/GP zone interaction occurred when the applied shear strain $\gamma \approx 0.18\%$, which is marked as (i) in Figs. 4.4(a) and 4.6(a). At this point, MS + TA simulations show a clear attraction of the dislocation to the GP zone, which reduced the shear stress. However, MS simulations did not capture this phenomenon. The corresponding atomistic representation of this first interaction is as (i) in the Fig.4.5 for GP 60 and Fig. 4.7 for GP 0. The (a) and (b) subplots of these Figs. stand for the MS and MS + TA strategies, respectively. Hence, in the case of GP 60 (Fig. 4.5), it was observed that the dislocation is not in contact with the GP zone ((a)-(i)) in the MS simulation, while the leading Shockley partial already sheared the GP zone in the MS-TA simulation ((b)-(i)). A similar behavior was observed in the GP 0 simulations (Fig. 4.7), in which the dislocation was not in contact with the precipitate in the MS simulation ((a)-(i)), but a segment of the dislocation was attracted by the GP zone in MS + TA simulation. Nevertheless, the leading partial did not shear the GP zone but formed a Stroh node in the edge of the GP zone ((b)-(i)).

After the first interaction, the dislocation started to bow around the GP zone in the MS simulation of GP 60. Then, the dislocation overcame the energetic barrier that impeded the contact with the GP zone when the applied strain was 0.71% (Fig. 4.5(a)-(ii)) leading to a kink in the stress- and energy-strain curves (Fig. 4.4). Subsequent

Figure 4.5: Mechanisms of GP 60-dislocation interaction as a function of the applied shear strain, γ , according to (a) MS simulations and (b) MS + TA simulations. Figures (i), (ii), (iii) and (iv) correspond to the points marked with the same letters in blue in Fig. 4.4(a).

Figure 4.6: (a) Shear stress vs. shear strain and (b) Energy stored vs. shear strain curves corresponding to the GP 0.

application of strain led the trailing partial bow and form an Orowan loop around the GP 60 at 0.8% of shear strain. The CRSS to carry out this mechanism was 235 MPa. This last interaction is illustrated in 4.5(a) (iii) and (iv), that correspond to the same points of the MS curve in Fig. 4.4. On the contrary, the trailing partial dislocation sheared the precipitate in the MS + TA simulations (Fig. 4.5(b) (iii) and (iv)). The critical shear stress and strain to overcome the GP zone in this case were 186 MPa and 0.71%, respectively, which are significantly lower than those obtained with MS.

In MS simulation of GP 0 orientation, it was observed that the dislocation immediately made contact with the GP zone and began to bow around (Fig. 4.7(a) from (i) to (ii)). Finally, an Orowan loop was formed, as depicted in 4.7(iii). The CRSS and strain were 185 MPa and 0.81%, respectively, as it can be observed in Fig. 4.6. The GP 0 precipitate was sheared by the dislocation in the MS + TA simulation (Fig. 4.7(b) from (i) to (iii)). The obstacle strength in this case was only 150 MPa, also significantly lower than the one obtained in the MS simulation. The shearing of the GP zone in the MS + TA simulations took place at constant strain and both stress and energy dropped to 0 once the GP zone was sheared. Shearing at constant strain while the applied stress decreases indicates that the largest energy barrier was found when the trailing dislocation entered the GP zone. Once this barrier was overcome, the dislocation progressed and the shear stress decreased to zero while a displacement of one Burgers vector in the glide plane was evident in the GP 0 structure, Fig. 4.7(b) (iii). This final stage was different from the one obtained in the MS simulations, in which the stress did not drop to zero after the dislocation overcame the GP zone because of the presence of the Orowan loop. The details of both GP zones strength obtained by MS + TA strategy are

Figure 4.7: Atomistic representation of the dislocation-GP zone successive interactions in the 0° orientation for (a) MS simulations and (b) MS + TA simulations. The plots (i), (ii) and (iii) correspond to the points marked with the same letters in Fig 4.6(a).

shown in table 4.2.

Table 4.2: Obstacle strength, τ_0 , activation energy at zero strain, ΔU_0 , critical strain for GP zone shearing, γ_0 , and activation volume, V^{act} , for GP 0 and GP 60 orientations.

Orientation	τ_0 (MPa)	ΔU_0 (eV)	γ_0 (%)	V^{act}
GP 0	150	0.86	0.85	$40b^3$
GP 60	186	0.45	0.80	$12b^3$

GP 0 and GP 60 orientations show a linear relationship between the shear stress and strain from the beginning of the dislocation/obstacle interaction (see Figs. 4.4(a) and 4.6(a)). This relationship is very important because it will allow to relate the activation Helmholtz free energy at constant strain, $\Delta F(\gamma)$, with the activation Gibbs free energy at constant stress, $\Delta G(\tau)$, as explained below.

Shearing mechanisms of the GP zones

Molecular statics along with thermal annealing simulations provided valuable insights on the shearing mechanisms of the GP zones. More specifically, different shearing process were observed in these simulations depending on the orientation of the GP zone. Thus, the shearing process of the GP zones oriented at either 0° and 60° are detailed below.

The shearing of GP 60 is illustrated in Fig. 4.8. The process begins with the leading partial overcoming a small energetic barrier when the applied strain was 0.1%, Fig. 4.4(a). Afterwards, the leading Shockley partial shears the GP zone, reaching a metastable position denoted by the minimum in the shear stress-strain curve when the applied shear strain was 0.17%. The current configuration of the Shockley partials at this position is schematically depicted in Fig. 4.8(a). At this stage, the leading Shockley partial (green line) has already sheared the GP zone while the trailing partial (red line) is stopped at the interface. Both partial dislocations join together to form two Stroh nodes (blue dots) but they remain dissociated within the GP zone. The displacement of the Cu atoms in the (111) plane during the shearing of the GP zone by the leading partial is detailed in Fig. 4.8(b) from (i) to (ii). Cu atoms that do not move during shearing are marked as brown spheres while those that are displaced are blue spheres. Shearing by the leading partial led to the displacement of the Cu atoms in blue by b_1 from the B position to the C position in the FCC lattice, where $\bar{b}_1 = \frac{a}{2}[11\bar{2}]$ is the Burgers vector of the partial dislocation and a the lattice parameter. The atomic displacements during the shearing of the GP zone by the trailing partial are depicted in Fig. 4.8(b) from (ii) to (iii). The blue Cu atoms located in B positions move to C

positions, leading to the full shearing of the GP zone by a Burgers vector $\bar{b}$. It should be noted that the highest energetic barrier to shear the precipitate in this configuration is found to introduce the trailing partial in the precipitate. Moreover, the detailed analysis of the atomistic simulations showed that shearing of the GP by the leading partial took place by the simultaneous movement of all the Cu atoms from B to C while the displacement from C to B follows a staircase sequence in the case of the trailing partial. Thus, the analysis of the atomic sequence of the shearing of GP zone by dislocations in the GP 60 orientation shows that there is a major energetic barrier (corresponding to the penetration of the trailing partial in the GP zone) followed a finite number of very small energetic barriers as the trailing partial shears the precipitate. Nevertheless, the magnitude of these barriers is very small compared with the large barrier to introduce the trailing partial into the GP zone and the whole process could be modeled with only one energetic barrier within the framework of TST (Esteban-Manzanares et al., 2019c,a).

In the GP 0 orientation, as in the previous case, the first energetic barrier is found at an applied shear strain of 0.12%, leading afterwards to a local minimum in shear stress when the applied shear strain was 0.18%, Fig. 4.6(a)). The two Shockley partials are re-combined and form a perfect dislocation at the GP zone interface in this situation, as schematically depicted in Fig. 4.9(a). The perfect dislocation is limited by two Stroh nodes and the partials remain dissociated within the Al. This segment of perfect dislocation cannot penetrate the GP zone and the shear stress increases with the applied strain until the critical stress of 150 MPa is attained. Then, the dislocation segment at the edge of the GP 0 dissociates with the leading partial entering the GP zone and extending the stacking fault within the GP zone, followed by the propagation of the trailing partial until the GP zone is sheared. The displacement of the Cu atoms in the (111) plane during the shearing of the GP zone by both partials is depicted in Fig. 4.9(b). The initial atomic configuration, corresponding to Fig. 4.9(a), is shown in Fig. 4.9(b)-(i). Starting from this configuration, shearing of the GP by both partials is shown in the atomic arrangements (ii) to (iv). It should be noted that the distance between the partials varied from 0.7 to 1 nm during the shearing of the GP zone and that the Cu atoms in the slip plane did not move at the same time to the perfect stacking fault positions in the lattice. Moreover, slightly different sequences of atomic displacements to shear the GP zone were observed in different simulations, although the main mechanism did not change. Thus, the analysis of the atomic sequence shows that the major energetic barrier to shear the GP zone in the GP 0 orientation is found to split the full dislocation into partials and to introduce the leading partial into the GP zone. This is followed by other smaller barriers associated with the propagation of the leading and

Figure 4.8: (a) Schematic representation of the interaction between Shockley partial dislocations with the GP zone in the GP 60 orientation. (b) Atomistic representation of the shearing of the GP zone by the Shockley partial dislocations along the (111) plane. (i) stands for the initial configuration before the Shockley partials have reached the GP zone. Atoms with light colors are in the upper plane and with dark color in the lower plane. These atoms move by b_1 from (i) to (ii) and by b from (ii) to (iii), as shown by the red arrows.

Figure 4.9: (a) Schematic representation of the initial position of the Shockley partial dislocations with respect to the GP zone in the GP 60 orientation. (b) Atomistic representation of the shearing of the GP zone by the Shockley partial dislocations along the (111) plane. Starting from the initial configuration in (i), the progression of the leading and trailing partials through the GP zone is shown from (ii) to (iv). The leading partial is shown as a green line and the trailing partial as a red line. Blue dots stand for Stroh nodes and the full dislocation is shown as a yellow line. Al and Cu atoms that do not move are shown as grey and brown spheres, respectively, while Al and Cu atoms that move during shearing of the GP zone are shown as green and blue spheres, respectively. Atoms with light colors are in the upper plane and with dark color in the lower plane.

trailing partial dislocations along the GP zone. These results are in the agreement with the experimental observations of Muraishi et al. (2002), who reported that energetic barrier of the GP zones consists of a number of short range barriers proportional to the diameter of the precipitate along a first order barrier profile (Esteban-Manzanares et al., 2019a).

4.2.2 Thermodynamic parameters of the dislocation/GP zone interaction

As detailed in Chapter 2, TST establishes that the rate, Γ , at which an ergodic system crosses a first order dividing surface is given by

$$\Gamma = \nu \exp \left(\frac{-\Delta G(\tau)}{k_b T} \right) \quad (4.1)$$

where G is the Gibbs free energy barrier (which depends on the applied shear stress τ), ν the fundamental attempt frequency, k_b the Boltzmann constant, and T the absolute temperature. Within this scenario, MD simulations were used to obtain the rate at which edge dislocations overcome the GP zones as a function of the applied strain and temperature. It should be noted that if the MD simulations were carried out at constant shear strain γ , and eq. (4.1) can be expressed as

$$\Gamma = \nu \exp \left(\frac{-\Delta F(\gamma)}{k_b T} \right) \quad (4.2)$$

where $\Delta F(\gamma)$ is the Helmholtz activation free energy. $\Delta F(\gamma)$ is the energy barrier due to the presence of the obstacle in absence of external work and is given by

$$\Delta F(\gamma) = \Delta U(\gamma) - T \Delta S(\gamma, T) \quad (4.3)$$

where $\Delta U(\gamma)$ stands for the activation energy, which depends on the applied strain, and $\Delta S(\gamma, T)$ is the activation entropy at constant strain, which may depend on the applied strain and temperature. It was demonstrated in (Ryu et al., 2011) that $\Delta G(\tau) \approx \Delta F(\gamma)$ when the volume of the crystal is much larger than the activation volume of the thermally activated process and τ and γ are conjugate variables. Under these conditions, the rate at which the obstacle is overcome is independent of whether the crystal is subjected to a constant stress or to a constant strain that corresponds to the same stress.

In the case that HTST is applicable, the entropy of the system does not depend on the temperature, and the slopes of the $\bar{\Gamma}$ vs. $1/k_b T$ lines provide the activation energies $\Delta U(\gamma)$. Thus, eq. (4.2) can be re-written as

Figure 4.10: Average rate, $\bar{\Gamma}$, for the dislocation to overcome the GP zones as function of $1/k_bT$ for different applied strains. (a) GP 60 and (b) GP 0. The straight lines stand for the best fit of the MD results to eq. (4.4) and the slope is equal to $\Delta U(\gamma)$.

$$\Gamma^{HTST} = \nu_{eff} \exp\left(-\frac{\Delta U}{k_bT}\right) \quad (4.4)$$

where ν_{eff} , is the effective attempt frequency, which contains the activation entropy contribution, ΔS , according to

$$\nu_{eff} = \nu \exp\left(\frac{\Delta S(\gamma)}{k_b}\right) \quad (4.5)$$

where ν is again the fundamental attempt frequency.

Activation energy

The activation energy ($\Delta U(\gamma)$) was evaluated by means of MD simulations within HTST framework. To this end, the average rate to bypass the GP zones was determined from direct MD simulations at different temperatures and applied shear strains. In each case, the initial configuration of the dislocation/GP zone was given by the minimum energy configuration at the given applied shear strain obtained with the MS+TA strategy (see section 4.1.1). The results are plotted in Fig. 4.10(a) and (b) for GP 60 and GP 0, respectively. The average rates are in agreement with eq. (4.4) for each value of the applied strain and the slopes of the linear fit to the rates obtained by MD provided $\Delta U(\gamma)$.

The activation energies of the interaction of edge dislocations with GP zones in the GP 0 and GP 60 orientations are depicted in Fig. 4.11. It is interesting to notice that the energy barrier associated with the GP 0 orientation is much higher than that for GP 60,

Figure 4.11: Activation energy, ΔU , as a function of the applied strain γ for different dislocation/GP zone orientations. The straight lines stand for the linear extrapolation of the values obtained by MD.

although the obstacle strength was slightly lower (Table 4.2). These differences are obviously associated with the different shearing mechanisms detailed above. The higher energy barrier of the GP 0 orientation can be attributed to the contribution of the multiple barriers along the glide plane after the full dislocation has been dissociated and the leading partial penetrates the precipitate while the energetic barrier in the GP 60 orientation only depends on the introduction of the trailing partial into the precipitate. The energy barrier at zero stress, ΔU_0 , as well as the critical strain equivalent to the CRSS of the obstacle, γ_0 , could be obtained by linear extrapolation of the results in Fig. 4.11 and are reported in Table 4.2 for both precipitate orientations.

Additionally, the activation energy $\Delta U(\gamma)$ of GP zones was evaluated using the standard NEB and the basin hopping global optimization methodology (NEB-BH). It was observed that only the energetic barrier to shear GP 60 can be approximated to a single first order saddle point (Esteban-Manzanares et al., 2019c), while multiple barriers have to be overcome in order to shear the GP 0. As a result, this calculations were only successfully accomplished in the case of GP 60 and in consequence only the results of GP 60 are presented.

The results of the calculations obtained with the standard NEB method are shown in Fig. 4.12(a) for different applied strains. The saddle points of the NEB calculations

depicted in this figure provide the evolution of the energy barrier, $\Delta U(\gamma)$, with strain. It is worth mentioning that the final configuration is an intermediate minimum but the barrier to reach the final minimum is one to two orders of magnitude smaller than the barrier shown, which becomes the rate limiting step.

In the case of BH-NEB optimization, the four random perturbations applied led to different transition paths, which are plotted in Figs. 4.12(b) and (c) for applied shear strains of 0.591% and 0.685%. Similar results were obtained for other values of the applied strains and are not included for the sake of brevity. Large differences in the energy barrier were found for the different transition paths and the energy barriers corresponding to the minimum energy paths shown in Figs. 4.12(b) and (c) were much lower than those found following the standard NEB method (Fig. 4.12(a)). The transition paths that led to the minimum energy barrier for different values of the applied strain γ according to the basin hopping global optimization are plotted in Fig. 4.12(d). The differences with those obtained with the standard NEB minimization in Fig. 4.12(a) are very large and these results indicate – in agreement with previous investigations (Nguyen et al., 2011) – that the standard NEB method with linear interpolation is not able to provide an accurate estimation of the minimum energy path due to the roughness of the energy landscape.

For the sake of comparison, the activation energies obtained with the different atomistic techniques (MD, NEB and BH-NEB) are plotted in Fig. 4.13 as a function of applied the shear strain. The activation energies decrease linearly with the strain in all cases and the values of the activation energy obtained through the MD simulations and the basin hopping NEB are in very good agreement, taking into account the scatter associated with both types of simulations. This result indicates that entropic contribution to the rate is independent of the temperature and strain and that HTST can be applied to study the interaction of edge dislocations with GP 60. It should also be noted that the standard NEB method leads to transition paths which are far away from the MEP and that the differences increased rapidly as the strain decreased. Thus, this methodology is not appropriate to determine the activation energy due to the roughness of the energy landscape.

Figure 4.12: Evolution of the energy of the system along the reaction path as a function of the applied shear strain. (a) Results of standard NEB calculations with linear interpolation between basins. (b) and (c) Results of the basin hopping global optimization NEB calculations for applied strains of 0.591% and 0.685%, respectively. Four different transition paths were obtained in (b) and (c) for each strain as a function of the initial random perturbation. (d) Minimum energy paths according to the basin hopping NEB calculations.

Figure 4.13: Variation of the activation energy, ΔU , as a function of the applied shear strain γ obtained by different atomistic techniques for GP 60

Activation entropy and activation volume

The activation entropy ΔS could also be obtained from the rates in Fig. 4.10 and eqs. (4.4) and (4.5) assuming that $\nu \approx 10^{10} \text{ s}^{-1}$ (Ma and Roters, 2004; Sobie et al., 2017b). The activation entropies are plotted as a function of the applied strain γ in Fig. 4.14 for the GP 0 and GP 60 orientations (Esteban-Manzanares et al., 2019c,b). It can be observed that entropy is independent of the applied strain in both orientations but the magnitudes are different. ΔS in the GP 60 orientation is in the range $1.3\text{-}1.8k_b$, which is similar to the values reported for the dislocation nucleation (Hara and Li, 2010; Ryu et al., 2011) and compatible with the entropic contribution associated to the vibrational entropy of solids. The activation entropy in the GP 0 orientation was $\approx 5k_b$, suggesting the presence of anharmonic effects during shearing of the GP zone in this orientation.

The activation volume (V^{act}) in both orientations were also determined by means of the MD atomistic simulations. The activation volume can be defined as (Kocks, 1975)

$$V^{act} = - \left. \frac{\partial \Delta G(\tau)}{\partial \tau} \right|_T. \quad (4.6)$$

It should be noted that the MD simulations presented above were carried out at constant strain γ . Thus, the result provided by these simulations is value of $\Delta F(\gamma)$ instead of $\Delta G(\tau)$. Nevertheless, the relationship between the Gibbs activation free energy at constant stress, $\Delta G(\tau)$ and the Helmholtz activation free energy at constant

Figure 4.14: Activation entropy, ΔS , as a function of the applied strain γ for different dislocation/GP zone orientations.

strain, $\Delta F(\gamma)$ can be derived following the work carried out by Ryu et al. (2011). The Helmholtz activation free energy $\Delta F(\gamma)$ is the difference between the Helmholtz free energy between the local minima F^m and the saddle point F^s at given γ . Moreover, the Gibbs free energy analogous to these two states can be written as

$$F^m(\gamma) = G^m(\tau^m) + \tau^m \gamma V \quad \text{and} \quad F^s(\gamma) = G^s(\tau^s) + \tau^s \gamma V \quad (4.7)$$

where the sub-indexes m and s denote the local minimum and the saddle point, respectively. It is worth noting that G in the local minimum and the saddle point do not correspond to the same shear stress, which is τ_m in the minimum and τ_s in the saddle point.

The activation Helmholtz free energy can be expressed as a function of the Gibbs free energy as

$$\Delta F(\gamma) = F^s(\gamma) - F^m(\gamma) = G^s(\tau^s) - G^m(\tau^m) + \gamma V(\tau^s - \tau^m) \quad (4.8)$$

and it should be noted that that $G^s(\tau^s) - G^m(\tau^m)$ is not the activation Gibbs free energy since $\tau^m \neq \tau^s$. If $G^s(\tau^m)$ is added and subtracted to eq. (4.8),

$$\Delta F(\gamma) = \Delta G(\tau^m) + G^s(\tau^s) - G_s(\tau^m) + \gamma V(\tau^s - \tau^m) \quad (4.9)$$

where $\Delta G(\tau^m) = G^s(\tau^m) - G^m(\tau^m)$.

Expanding $G(\tau)$ around $(\tau^s - \tau^m)$, assuming τ^m constant and neglecting the third order terms, eq. (4.9) can be rearranged as

$$\Delta F(\gamma) \approx \Delta G(\tau^m) + \gamma V(\tau^s - \tau^m) + \left. \frac{\partial G}{\partial \tau} \right|_V (\tau^s - \tau^m) + \frac{1}{2} \left. \frac{\partial^2 G}{\partial \tau^2} \right|_V (\tau^s - \tau^m)^2. \quad (4.10)$$

τ and γ are related to each other according to

$$\gamma = - \left. \frac{1}{V} \frac{\partial G}{\partial \tau} \right|_T \quad (4.11)$$

and introducing eq. (4.11) in eq. (4.10), leads to

$$\Delta F(\gamma) = \Delta G(\tau^m) + \frac{1}{2} \left. \frac{\partial^2 G}{\partial \tau^2} \right|_V (\tau^s - \tau^m)^2. \quad (4.12)$$

Moreover, differentiating eq. (4.11) leads to

$$\left. \frac{\partial^2 G}{\partial \tau^2} \right|_T = -V \left. \frac{\partial \gamma}{\partial \tau} \right|_T = \frac{-V}{\mu'} \quad (4.13)$$

where μ' is the slope of the τ - γ curve that describes the elastic interaction of the dislocation with the GP zone before the obstacle is overcome. If eq. (4.13) is introduced into eq. (4.12)

$$\Delta F(\gamma) = \Delta G(\tau_m) - \frac{1}{2} V \frac{(\tau_s - \tau_m)^2}{\mu'} \quad (4.14)$$

with V being the total volume of the crystal and τ_m and τ_s stand for the applied stress at the local minimum and the saddle point, respectively. Both stresses correspond to the points (i) and (ii) in Figs. 4.4 for 60° and 4.6 for 0°. Furthermore, μ' denotes the shear modulus of the crystal on the local coordinates, which is defined by the slope of the τ - γ linear relationship between the point (i) and (ii) of the figures mentioned above. In the case of the interaction between the dislocation and the GP zone, the difference $\tau_s - \tau_m \approx 1$ MPa and the second term in eq. (4.14) is negligible. Thus, $\Delta F(\gamma) \approx \Delta G(\tau)$ and the activation volume can be estimated in this case, following eq. (4.14), as

$$V^{act} = - \left. \frac{\partial \Delta G(\tau)}{\partial \tau} \right|_T \simeq - \frac{1}{\mu'} \left. \frac{\partial \Delta F(\gamma)}{\partial \gamma} \right|_T = - \frac{1}{\mu'} \frac{\Delta U_0}{\gamma_0} \quad (4.15)$$

but the right side of in eq. (4.15) is valid only when $V_0 \ll V$. Following this, the corresponding activation volumes for the GP 0 and GP 60 orientations are shown in Table 4.2 and reflect the differences in the strength and in the energy barrier between

both orientations. They are in good agreement with experimental estimations reported by Byrne et al. (1961).

4.3 Prediction of flow stress

The yield strength of a crystalline material (τ_y) is basically ruled by the presence of obstacles. These hinder the dislocation motion, acting as barriers. In general, the obstacles may be athermal or thermally activated. Non-thermal barriers (τ_{ath}) depend weakly on the temperature and are associated to the elastic dislocation-dislocation interactions and also the formation of dislocation nets. By contrary, thermally activated barriers are controlled by the thermal fluctuations, leading to a strong dependence of the yield strength (τ_{th}) with the temperature and strain rate (Kocks, 1975). To accurately predict τ_y , both contributions must be taken into account according to

$$\tau_y = \tau_{th} + \tau_{ath}. \quad (4.16)$$

The experimental evidence indicates that the athermal contribution to the yield strength can be expressed by the Taylor model (Taylor, 1934a) according to

$$\tau_{ath} = \alpha\mu|\bar{b}|\sqrt{\rho}, \quad (4.17)$$

where $\mu = 25$ GPa stands for the shear modulus, $\bar{b} = 0.286$ nm the Burgers vector of a perfect dislocation in Al (Rubio et al., 2019), ρ the dislocation density and $\alpha = 0.7$ is a constant in the range 0.5 - 1 that accounts for the different dislocation interactions (Kocks and Mecking, 2003). Both μ and $\bar{b}$ depend weakly on the temperature and, thus, this contribution is practically athermal.

The contribution of the thermal barriers to the yield strength was analyzed by (Kocks, 1975) by means of TST. The relationship between the free energy barrier, the temperature and the plastic strain rate ($\dot{\gamma}_p$) is given according to

$$\dot{\gamma}_p = \dot{\gamma}_{p0} \exp\left(\frac{-\overline{\Delta G}(\tau)}{k_b T}\right) \quad (4.18)$$

where $\dot{\gamma}_{p0}$ the reference plastic strain rate, given by Orowan equation 4.19 (Orowan, 1934a,b,c),

$$\dot{\gamma}_{p0} = \rho|\bar{b}|L\nu \quad (4.19)$$

with L being the mean free path of the dislocations, ρ the dislocation density and ν the attempt frequency. The term $\overline{\Delta G}$ stands for an effective activation Gibbs free energy

that depends on the different types of barriers to the dislocation motion, to be defined below for the interaction of dislocations with GP zones in Al.

As detailed in the section above, in the special case that the volume of the system under investigation is much higher than the activation volume of the process, $\Delta G(\tau) \approx \Delta F(\gamma)$ (Ryu et al., 2011; Esteban-Manzanares et al., 2019c). Hence, eq. (4.18) can be written as

$$\dot{\gamma}_p = \dot{\gamma}_{p0} \exp\left(\frac{-\overline{\Delta F}(\gamma)}{k_b T}\right) \quad (4.20)$$

The effect of the applied stress (or strain) on the activation free energy in the case of dislocations that have to overcome obstacles was analyzed in detail in (Kocks, 1975). For short range obstacles (and neglecting the work carried out by the external force), he proposed the following general phenomenological model for the Helmholtz activation free energy

$$\Delta F(\gamma) = \Delta U_0 \left[1 - \left(\frac{\gamma}{\gamma_0}\right)^p\right]^q \quad (4.21)$$

where ΔU_0 and γ_0 were obtained from the atomistic simulations, while q ($1 < q < 2$) and p ($0.5 < p < 1$) are two parameters that control the potential energy profile along the minimum energy path (q), and the randomness of the obstacle distribution in the glide plane (p). In the case of a periodic array of GP zones, $p = 1$ (Caillard and Martin, 2003), while the Helmholtz activation free energy was assumed to be a linear function of τ in the case of the GP 60 orientation ($q = 1$).

Combining the eqs. (4.19), (4.21) and (4.20), and also taking into account that there is a linear relationship between the shear stress and strain for the dislocation/GP zone interaction, as explained in section 4.2.1, the thermal contribution to the yield strength is given by

$$\tau_{th} = \bar{\tau}_0 \left[1 - \frac{k_b T}{\overline{\Delta U}_0} \ln\left(\frac{\dot{\gamma}_{p0}}{\dot{\gamma}_p}\right)\right] \quad (4.22)$$

where τ_{crss} stands for the obstacle strength (the stress necessary to overcome the obstacle without thermal assistance) and ΔU_0 denotes the activation energy barrier.

As indicated above, GP zones grow on $\{100\}$ family of planes of the FCC α -Al, leading to two orientation relationships between the Burgers vector of the dislocation and the GP zones, GP 0 and GP 60. The GP 60 orientation is twice more probable than the GP 0 (Nie, 2014; Rodríguez-Veiga et al., 2018) and, thus, the effective values of the obstacle strength ($\bar{\tau}_{crss}$) and of the activation energy barrier ($\overline{\Delta U}_0$) in eq. (4.22) can be determined from those obtained by atomistic simulations for each orientation according to

$$\overline{\Delta U}_0 = \frac{1}{3} (2\Delta U_0^{\text{GP } 60} + \Delta U_0^{\text{GP } 0}) \quad (4.23)$$

$$\bar{\tau}_0 = \frac{1}{3} (2\tau_{crss}^{\text{GP } 60} + \tau_{crss}^{\text{GP } 0}). \quad (4.24)$$

Of course, another type of averaging (e.g. geometric mean) could also be used to determine the effective values of the obstacle strength and of the energy barrier but the differences were negligible in this case.

Thus, the yield strength of an Al-Cu alloy reinforced with GP zones considering the athermal, eq. (4.17), and thermal, eq. (4.22), contributions, is given by

$$\tau_y = \alpha\mu|\bar{b}|\sqrt{\rho} + \bar{\tau}_0 \left[1 - \frac{k_b T}{\Delta U_0} \ln \left(\frac{\dot{\gamma}_{p0}}{\dot{\gamma}_p} \right) \right]. \quad (4.25)$$

The experimental investigation carried out by Byrne et al. (1961) analyzed the influence of the temperature on τ_y , in the range from 4 K to 400 K and in single crystals oriented for single slip of a naturally-aged Al - 4 wt. % Cu alloy. This alloy only contained GP zones but no information about the size and spacing between GP zones and of the initial dislocation density was given.

Microstructural information was obtained from the TEM analysis and micropillar compression test to an Al - 4 wt. % Cu. These experimental procedure provided the necessary data to in eq. (4.25). The information obtained by means of these experiment was: the average diameter of the GP zones (3-4 nm), the distance between them ($L = 34$ nm) and the average dislocation density $\rho = 2.2 \times 10^{13} \text{m}^{-2}$. Taking into account this experimental results, the prediction of the flow stress as a function of temperature is plotted in Fig. 4.15, assuming a strain rate $\dot{\gamma} = 10^{-2} \text{s}^{-1}$.

As illustrated in Fig. 4.15, the linear dependence of τ_y with temperature disagrees with the experimental data. One possible reason may be that the thermal contribution in eq. (4.25) assumes a regular distribution of GP zones while they are actually randomly dispersed within the matrix, as evident in the TEM image shown in Fig. 4.1. The effect of a random precipitate distribution on the thermal contribution to the flow stress was evaluated by (Leyson et al., 2012; Leyson and Curtin, 2016), which modified eq. (4.22) to account for this effect, leading to

$$\tau_y = \alpha\mu|\bar{b}|\sqrt{\rho} + \begin{cases} \bar{\tau}_0 \left[1 - \left[\frac{k_b T}{\Delta U_0} \ln \left(\frac{\dot{\gamma}_{p0}}{\dot{\gamma}_p} \right) \right]^{\frac{2}{3}} \right], & \text{if } \tau_y/\bar{\tau}_0 \geq 0.55 \\ \bar{\tau}_{crss} \exp \left[-\frac{1}{0.51} \frac{k_b T}{\Delta U_0} \ln \left(\frac{\dot{\gamma}_{p0}}{\dot{\gamma}_p} \right) \right], & \text{if } \tau_y/\bar{\tau}_0 < 0.55 \end{cases} \quad (4.26)$$

Figure 4.15: Predictions of the flow stress of an Al alloy containing GP zones as a function of temperature and experimental data from Byrne *et al.* (1961). The dashed blue line stands for a model that accounts for a perfect array of precipitates, eq. (4.25), while the solid red line takes into account the random distribution of GP zones, eq. (4.26).

The predictions of the flow stress taking into account the random distribution of GP zones are also plotted in Fig. 4.15, leading to a better agreement with the experimental data. Nevertheless, the model predictions tend to overestimate the strength in the low temperature regime, pointing out to the current limitations of the scale bridging methodologies. The first one is that the obstacle strength and the energy barrier were only determined for edge dislocations and they may be different from those obtained for screw and mixed dislocations. In addition, there is also an important uncertainty in the linear extrapolation of the activation energies obtained at different values of the applied strain to zero strain. Regardless of these limitations, the overall methodology provides coherent results of the effect of GP zones on the flow stress of Al alloys.

4.4 Conclusions

Precipitate strengthening with coherent precipitates in Al-Cu alloys has been studied by means of atomistic simulations in combination with transition state theory. Particularly, the interaction of edge dislocations with Guinier-Preston zones, oriented either 60° and 0° with respect the Burgers vector were examined. To this end, a strategy based on molecular statics in combination with thermal annealing was developed

to determine the stress necessary to overcome the obstacle in the absence of thermal energy. The annealing after each strain increment was critical in enabling the simulations to overcome local minima, which would lead to an overestimation of the obstacle strength and to unrealistic interaction mechanisms between the dislocation and the GP zone in both orientations. Besides, molecular dynamics simulations were carried out to determine the average rate at which dislocations overcome the GP zone as a function of the applied strain and temperature. Furthermore, the initial and final configurations attained by molecular dynamics were minimized and used to determine the activation energy in the athermal limit through the nudged elastic band method in combination with BH-NEB. The information obtained throughout both strategies was used to compute the thermodynamic quantities that control the shearing process.

It was found that MD and BH-NEB results of GP zones oriented at 60° were in very good agreement with each other, suggesting that the rate at which dislocations overcome the precipitate is mainly controlled by the activation energy. This is in agreement with the postulates of harmonic transition state theory. On the other hand, multiple barriers were observed in the case of GP zones oriented at 0° , which impeded the successful application of the nudged elastic band method.

This information was used to develop of an atomistic-based model to predict shear flow stress of Al-Cu alloy containing GP zones as a function of temperature based on Kocks' model (Kocks, 1975). The flow stress was assumed to depend on two different contributions, namely the athermal and the thermal. The former is given by the Taylor model (Taylor, 1934a) and only depends on the elastic constants of the Al alloy, the dislocation density and the Burgers vector. The latter can be calculated following the transition state theory (Kocks, 1975) from the obstacle strength and the free energy barrier. The predictions of the model were compared with experimental data in the literature as well as new data obtained by means of micropillar compression tests carried out in an Al - 4 wt. % Cu alloy naturally aged at ambient temperature to obtain a homogeneous distribution of GP zones. The experiments were in good agreement at ambient temperature although overestimated the flow stress at low temperature and the possible sources of the discrepancy were indicated.

5 DISLOCATION/PRECIPITATE INTERACTION IN Mg-Al

Al-Cu or Ni-based superalloys are excellent examples of precipitation strengthening alloys. However, precipitate strengthening is not always successful in metallic alloys and this is the case of Mg alloys (Nie, 2012; Gao et al., 2005; Bettles et al., 2004; Mendis et al., 2009; Jayaraj et al., 2010). Mg has a hexagonal compact (HCP) lattice that leads to different plastic deformation mechanisms, as compared by FCC metals (Clark, 1968; Gharghouri et al., 1998; Stanford et al., 2012). In particular, plastic deformation of Mg and Mg alloys takes place by dislocation glide in three different slip systems as well as by twinning (see 1.1.3). The large differences in the CRSS to promote plastic slip among the different slip systems in Mg as well as the polarity of twinning, which only takes place when the c axis of the HCP lattice is extended, lead to the plastic anisotropy of Mg alloys that has very negative effects on the ductility (Hutchinson and Barnett, 2010; Herrera-Solaz et al., 2014b).

As detailed in sec. 1.1.3, basal slip is the softest slip system in Mg. Increasing the CRSS for dislocation slip in this system is necessary to reduce the plastic anisotropy (Herrera-Solaz et al., 2014b) and also improve the yield strength, but the contribution of precipitates to strengthen basal slip has been limited, particularly in Mg-Al

alloys (Hutchinson et al., 2005; Herrera-Solaz et al., 2014a; Rada et al., 2016; Hidalgo-Manrique et al., 2017). Continuum models, based on the Orowan mechanism, have been applied to ascertain the influence of the precipitate size, shape, orientation and spatial distribution on the CRSS of different slip systems in Mg (Nie, 2003; Stanford et al., 2012; Hidalgo-Manrique et al., 2017). Although these models were able to rationalize some of the experimental trends, it should be noticed that the Orowan model assumes a very simplistic approach for the dislocation/precipitate interaction: the precipitates are rigid obstacles overcome by dislocations by the formation of an Orowan loop. Nevertheless, recent micropillar compression tests in Mg - 5 wt.% Zn alloys (Wang and Stanford, 2015; Alizadeh and LLorca, 2019) have shown evidence of precipitate shearing basal dislocations and similar results were found in transmission electron microscopy observations of dislocation/precipitate interactions in Mg-Al alloys (Voisin et al., 2017; Cepeda-Jiménez et al., 2019). Thus, simulations at smaller length scales, such as classical atomistic strategies (Hu et al., 2000; Singh and Warner, 2010; Bonny et al., 2011; Liao et al., 2014; Lehtinen et al., 2016; Esteban-Manzanares et al., 2019c), are required to get a better understanding of the physics and to develop more accurate models.

Molecular statics and dynamics simulations were carried out using a new interatomic potential (Dickel et al., 2018) to assess the interaction between basal dislocations and β -Mg₁₇Al₁₂ intermetallic precipitates in Mg-Al alloys, which are well-known among Mg alloys for their excellent castability and corrosion resistance (Bamberger and Dehm, 2008; Nie, 2012). The main intermetallic precipitate in this alloy is β -Mg₁₇Al₁₂ that appears when the cooling rate of the casting is sufficiently slow or by means of aging treatments (Nie, 2012). β phase has a complex BCC structure within the space group $I - 43m$ with a lattice parameter of 1.056 nm. The unit cell includes 34 Mg atoms and 24 Al atoms (Fig. 5.1) (Bamberger and Dehm, 2008). The generalized stacking fault energies (γ surfaces) corresponding to the potential slip systems were recently determined using first principles methods and compared with the Griffith surface fracture energy (Xiao et al., 2013). It was concluded that high shear stresses were necessary to promote dislocation slip in this intermetallic and that its behavior was brittle in the presence of a crack because it was more likely to show crack propagation than to emit dislocations from the crack tip, according to Rice's criterion (Rice, 1992),

These precipitates grow in the matrix along preferred orientations. Different orientation relationships (OR) and precipitate shapes have been reported in the literature (Crawley and Milliken, 1974; Crawley and Lagowski, 1974; Duly et al., 1994a,b, 1995;

Figure 5.1: Unit cell of the β -Mg₁₇Al₁₂ intermetallic phase

Shepeleva et al., 2001; Zhang and Kelly, 2003) but the most typical one is the denominated as Burgers OR. Precipitates in Burgers OR have a lozenge shape (Celotto, 2000; Crawley and Milliken, 1974) and, according to the X-ray diffraction pattern, the growth habit plane is given by $(0001)_{\text{Mg}} \parallel (110)_{\beta}$ with a coincident direction $[1\bar{2}10]_{\text{Mg}} \parallel [1\bar{1}1]_{\beta}$. This direction defines a symmetry axis for the two variants that grow in $[1\bar{1}00]_{\text{Mg}} \parallel [1\bar{1}0]_{\beta}$ (v_1) and $[0\bar{1}10]_{\text{Mg}} \parallel [1\bar{1}4]_{\beta}$ (v_2) directions along the same habit basal plane (Fig. 5.2). Hence, the lateral interface planes of these variants (perpendicular to the $(0001)_{\text{Mg}}$) are $(\bar{1}\bar{1}20)_{\text{Mg}} \parallel (001)_{\beta}$ and $(\bar{2}\bar{1}10)_{\text{Mg}} \parallel (2\bar{2}\bar{1})_{\beta}$, as shown in Fig. 5.2. It should be indicated that the growth directions of v_1 and v_2 present a misorientation of 5° with respect to the $\langle 1100 \rangle$ direction of the Mg lattice. 12 different variants of the β precipitate with Burgers OR can be distinguished, combining the different possible interfaces. From the viewpoint of the interaction of an edge basal dislocation with the precipitate, there are 6 independent orientations in which the growth directions of v_1 and v_2 precipitates form angles of 0° , 60° and -60° with Burgers vector of the dislocation, as depicted in Fig. 5.2.

It has been argued that the limited precipitation hardening of Mg-Al alloys occurs because most of the precipitates grow parallel to the basal plane, and this orientation is the least efficient to block basal slip (Hutchinson et al., 2005). It was also suggested that the precipitate distribution is relative coarse because of the high diffusion rate of Al atoms in the Mg matrix (Wang et al., 2016). Based on the Orowan model, it was proposed that rod-shaped precipitates that grow perpendicular to the basal plane with Crawley OR ($\{0001\}_{\text{Mg}} \parallel \{111\}_{\beta}$; $\langle 1210 \rangle_{\text{Mg}} \parallel \langle 112 \rangle_{\beta}$) are more efficient because they intersect a larger number of basal planes for a given precipitate volume fraction (Celotto, 2000; Hutchinson et al., 2005; Nie, 2003; Robson et al., 2011). Nevertheless, previous atomistic simulations of the interaction of basal and prismatic edge dislocations with β precipitates did not show any evidence of the formation of Orowan loops (Liao et al.,

Figure 5.2: Schematic of the orientation and interface planes of the different variants (v_1 and v_2) of a lozenge-shape β precipitate in the Burgers OR. The edge basal dislocation is shown as a horizontal black line.

2013, 2014). Thus, the details of the dislocation/precipitate interaction in these alloys as well as the strengthening provided are not well known. Consequently, MS and MD were carried out to assess the interaction between basal dislocations and β -Mg₁₇Al₁₂ precipitates in Mg-Al alloys (Esteban-Manzanares et al., 2019b).

5.1 Atomistic simulation strategy

5.1.1 Selection of the interatomic potential

Five interatomic potentials were considered to model the Mg-Al alloy. The different potentials taken into account were Liu et al. (1999) EAM alloy potential, Mendelev et al. (2009) EAM Finnis-Sinclair type, Jelinek et al. (2012) MEAM potential, and Kim et al. (2009) and Dickel et al. (2018), which stand for 2NN-MEAM potentials. The interatomic potential developed by Jelinek et al. (2012) predicts a positive formation energy of 49 meV/atom for the Mg₁₇Al₁₂ phase, as compared to -30 meV/atom obtained from density functional theory (DFT) calculations, and consequently, this potential was discarded.

The elastic constants of Mg and β -Mg₁₇Al₁₂ phase were obtained by means of MS with the four remaining interatomic potentials. To this end, a given strain was given

to the unit cell in the ground state and the corresponding stresses were calculated after the atom coordinates in the unit cell were relaxed using the CG algorithm. The same strategy was used with DFT to determine the elastic constants and assess the accuracy of the MS results with the different potentials. The results are shown in Tables 5.1 and 5.2. It can be observed that Kim et al. (2009) and Dickel et al. (2018) potentials provide the best results, close to the DFT and to the experimental values for Mg (Herrera-Solaz et al., 2014b) and β -Mg₁₇Al₁₂.

The Peierls Stress (τ_p) of a basal dislocation and the stacking fault energy (SFE) along the basal plane of Mg were also examined (tab. 5.1). It can be seen that only Dickel's potential is in quantitative agreement with experimental results of τ_p reported in the literature (Yasi et al., 2009), while both Kim's and Dickel's potentials underestimate slightly the stacking fault energy.

Table 5.1: Peierls stress (τ_p) of an $\langle a \rangle$ edge basal dislocation (MPa), stacking fault energy (SFE) of $1/3 \langle 1010 \rangle$ (mJ/m²) and elastic constants of Mg (GPa).

Method	τ_p	SFE	C_{11}	C_{12}	C_{33}	C_{13}	C_{44}	C_{66}
EAM-FS (Mendelev et al., 2009)	0.33	44.2	61.9	26.2	68.2	22.1	18.2	18
EAM-Alloy (Liu et al., 1996)	24.5	54.2	68.2	26.1	71.3	16.1	12.8	21.3
MEAM (Dickel et al., 2018)	0.25	23	64.4	25.3	70.9	20.3	18	19.5
MEAM (Kim et al., 2009)	3.03	29.6	62.9	26.32	69.9	21.2	17.2	18.2
DFT (Esteban-Manzanares et al., 2019b)		36	59.8	22.6	62.5	25.6	16.8	16.7

Table 5.2: Elastic constants of β -Mg₁₇Al₁₂ (GPa).

Method	C_{11}	C_{12}	C_{44}
EAM-FS(Mendelev et al., 2009)	137.8	46.5	28
EAM-Alloy (Liu et al., 1996)	135.3	47.8	23.2
MEAM (Dickel et al., 2018)	89.4	33.5	19.6
MEAM (Kim et al., 2009)	84	32.5	13.7
DFT (Esteban-Manzanares et al., 2019b)	83.2	29.6	17.1

Preliminary MS simulations were carried out to analyze the dislocation/precipitate interaction in Mg-Al alloys with the remaining potentials. In the case of EAM-alloy potential, a spurious jog developed when the dislocation approached the precipitate. The dislocation inside the precipitate climbed to the precipitate/matrix interface and

Figure 5.3: Structures of the interfaces between Mg and $\beta\text{-Mg}_{17}\text{Al}_{12}$ precipitate in the Burgers OR. (a) $(0001)_{\text{Mg}} \parallel (110)_{\beta}$ interface. (b) $(\bar{1}\bar{1}20)_{\text{Mg}} \parallel (001)_{\beta}$ interface.

slipped along the interface without shearing the precipitate. This behaviour has been reported already in (Liao et al., 2014).

The interface energy between the precipitate and the matrix is another important parameter which influences the dislocation/precipitate interaction. Thus, the energies of the two main interfaces between Mg and the β precipitate in the Burgers OR are $(0001)_{\text{Mg}} \parallel (110)_{\beta}$ and $(\bar{1}\bar{1}20)_{\text{Mg}} \parallel (001)_{\beta}$ (Fig. 5.3) were evaluated with the two MEAM interatomic potential that better predicted the properties of the β precipitate using MS. The interface energies obtained with the interatomic potentials were benchmarked against DFT results. It should be noted that different methodologies were used for MS and DFT.

MS optimizations were carried using the CG algorithm in five supercells with different N -atoms for the two main OR. The interface surface of the five cells was the same, while the length of the simulation box increased with the number of atoms N . Approximately the same number of atoms of both phases, Mg and β were considered in all the supercells and periodic boundary conditions were imposed in all directions. Under these conditions, the total energy of the system can be expressed as

$$E_{\text{tot}} = E_{\text{Mg}} + E_{\beta} + E_{\text{int}}2S + E_{\text{el}}V \quad (5.1)$$

where $2S$ is the interface area (two interfaces appear because of the periodic boundary

Figure 5.4: (a) Excess of energy as a function of the length of the domain obtained by MS optimization methodology with Dickel's interatomic potential (Dickel et al., 2018). (b) ΔE vs L obtained MS with Kim's potential (Kim et al., 2009). In both cases the excess of energy per unit of surface when $L \rightarrow 0$ represents the interface energy.

conditions), V the total volume of the supercell, E_{Mg} and E_{β} stand for the energy of the individual phases, E_{int} denotes the interface energy per unit of area and E_{el} is the elastic energy per unit volume due to the elastic mismatch between Mg and β . Considering a constant interface area, S , eq. (5.1) can be expressed as a function of the length L of the supercell perpendicular to the interface as

$$\frac{\Delta E}{2S} = E_{\text{int}} + \frac{1}{2}E_{\text{el}}L \quad (5.2)$$

with $\Delta E = E_{\text{tot}} - (E_{\text{Mg}} + E_{\beta})$. Given that the left part of eq (5.1) is known, the interface energy can be obtained with the independent term of a linear fitting of $\Delta E/2S$ vs L , as depicted in Fig. 5.4

In the case of DFT calculations, three N -atom supercells containing equal amounts of Mg and β were considered for each OR. The exchange-correlation energy was evaluated employing the Perdew-Burke-Erzenh (PBE) approach (Perdew et al., 1996) within the Generalized Gradient Approximation (GGA). Ultrasoft pseudopotentials were used to reduce the basis set of plane wave functions used to describe the real electronic functions (Vanderbilt, 1990). After careful convergence tests, a cut off of 37 Ry (503 eV) was found to be sufficient to reduce the error in the total energy to less than 1 meV/atom. A k-point grid separation of 0.03 was employed for the integration over the Brillouin zone according to the Monkhorste Pack scheme (Monkhorst and Pack, 1976).

The formation energy (ΔE_f) of the supercells can be expressed as

Figure 5.5: Enthalpy of formation of the supercell divided by the interface area as a function of inverse number of atoms for two different interfaces obtained by DFT calculations. The slope of each curve denotes the chemical interface energy as per eq. (5.4)

$$\Delta E_f = E_{tot} - \left(\frac{N_{Mg} E_f^{Mg} + N_{\beta} E_f^{\beta}}{N} \right) \quad (5.3)$$

where E_{tot} is the total energy of the system, N is the total number of atoms in the box, N_{Mg} and N_{β} are the number of atoms of Mg and β phase, respectively, and E_f stand for the formation energies of each phase at the ground state. ΔE_f can be decomposed into two main contributions: E_{int} stands for the energy from atomic interactions at the interface (Laird and Aaronson, 1966) and E_{cs} is the elastic energy associated with coherency strain energy required to accommodate the lattice mismatch between both phases. It should be noted that E_{cs} scales with the volume of the supercell and E_{int} with the interface area, which is the same for the different supercells. Hence, the eq. (5.3) can be expressed as

$$\Delta E_f = \frac{E_{int} 2S}{N} + E_{cs} \quad (5.4)$$

where again the factor $2S$ is due to the periodic boundary conditions perpendicular to the interface. Thus, E_{int} was calculated from the slope of the $\Delta E_f/2S$ vs $1/N$ curves, which are plotted in Fig. 5.5.

The interface energies obtained with MS and DFT are shown in Table 5.3. Both

interatomic potentials provide equivalent results, which were in qualitative agreement with the DFT results.

Table 5.3: Interface energies (mJ/m^2) of the different orientations between Mg and β - $\text{Mg}_{17}\text{Al}_{12}$ in the Burgers OR.

Method	$(0001)_{\text{Mg}} \parallel (110)_{\beta}$	$(\bar{1}\bar{1}20)_{\text{Mg}} \parallel (001)_{\beta}$
MEAM (Dickel et al., 2018)	166	459
MEAM (Kim et al., 2009)	165	459
DFT (Esteban-Manzanares et al., 2019b)	246	348

Taking into account all the previous results, the MEAM interatomic potential for Mg-Al-Zn developed by Dickel et al. (2018) was used in the simulations. This potential was selected among different interatomic potentials based on the accuracy to predict the properties of dislocations in Mg, the elastic constants of the Mg and β precipitates as well as the interface energies between Mg and β precipitates for the Burgers OR.

5.1.2 Semicoherent interfaces atomistic model

The relative positions of the atoms at the precipitate/matrix interface are known in coherent interfaces, and this information can be used to build the atomistic model. However, this is not always the case for incoherent or semi-coherent interfaces, in which matrix and precipitate atoms at the interface may occupy different positions. Building a realistic interface that reproduces accurately the shape and orientation of the precipitate within the matrix and the corresponding interface planes is critical to assess the interaction between the dislocations and the precipitate because the propagation of the dislocation along the interface will depend on the interface features. To this end, a sequential strategy was developed to insert a lozenge-shaped β precipitate with Burgers OR within the Mg matrix in an atomistic model. In this particular case, the variant v_1 of the precipitate in Fig. 5.2 was chosen.

The first step was to build the lozenge-shaped precipitate of β - $\text{Mg}_{17}\text{Al}_{12}$. The angle between the long and short edges of the precipitate in the plane parallel to the Mg basal plane was 70.53° . This value satisfied the lozenge shape and the orientation of the interface planes between matrix and precipitate (Celotto, 2000; Hutchinson et al., 2005). The $[1\bar{1}0]$ direction of the precipitate (long edge) was aligned with the $[1\bar{1}00]$ direction of the matrix (Fig. 5.6 and 5.7). The dimensions of the precipitate were $12.4 \times 3.14 \times 2.8 \text{ nm}^3$. The aspect ratio of the precipitate parallel to the Mg basal plane was 4:1, in agreement with the experimental observations (Lai et al., 2009). The overall dimensions

Figure 5.6: Orientation of the β -Mg₁₇Al₁₂ lozenge-shaped precipitate with respect to Mg matrix in the atomistic model. The z axis is perpendicular to the basal plane of the Mg lattice.

of the precipitate were chosen to provide affordable models from the computational viewpoint and to obtain realistic interface boundaries.

Afterwards, the precipitate was inserted in a small periodic Mg domain with dimensions $19 \times 17 \times 8 \text{ nm}^3$ along the x , y and z axes, respectively. These axes correspond to the crystallographic orientations $[10\bar{1}0]$, $[\bar{1}210]$ and $[0001]$ of the Mg lattice. The matrix and precipitate atoms were overlapped in the domain but it was not possible to determine the exact interface. A lozenge-shaped area inside the precipitate was selected and Mg atoms inside this area were removed. However, matrix and precipitate atoms were still overlapped at the interface. Thus, a cut-off radius was defined and all the atoms belonging to the Mg matrix within the cut-off radius of an atom of the precipitate were deleted. The energy per atom of the atomistic models obtained with different values of the cut-off radius (in the range 0.1 nm to 0.55 nm) was minimized using the conjugate gradient algorithm with periodic boundary conditions in all directions. This strategy was developed to ensure that the incoherent matrix/precipitate was close to a stable, minimum energy configuration.

The energy minimization was initially carried out at constant volume and afterwards under the condition that the Virial stress tensor was zero. The excess of energy of the relaxed domains, compared to the perfect Mg and β lattices are plotted in Fig. 5.8 as a function of the cut-off radius. The minimum energy was obtained for a cut-off

Figure 5.7: 3D representation of the β precipitate embedded inside the HCP Mg matrix. The coincident crystallographic planes are denoted on both β precipitate (yellow) and Mg Matrix (white). The color coding of the edge of the precipitates is the same as illustrate in Fig. 5.2.

radius of 0.29 nm and this structure was subjected to a thermal annealing using molecular dynamics to relieve the residual stresses that may still exist locally at the interface. To this end, the temperature was increased to 350 K in 100 ps within an ensemble under periodic boundary conditions and imposing zero stress. The temperature was kept constant during 200 ps and the final structure was obtained by minimizing the energy with the conjugate gradient algorithm. This final structure was then inserted into a larger domain of the Mg matrix detailed in the next section. To this end, a hole with the dimensions of the relaxed small domain was created and both domains were combined. This process may lead to the development of a boundary between both domains in which the atoms are not located in a perfect HCP lattice. This boundary was eliminated by annealing the whole domain using an NPT ensemble at 350 K and zero pressure during 10 ps. Finally the whole domain was relaxed using the CG algorithm.

In order to analyze the effect of the precipitate size on the dislocation/precipitate interaction mechanisms, two smaller β -Mg₁₇Al₁₂ with the same orientation and aspect ratio were created following the same procedure and inserted into the Mg matrix. The dimensions of these precipitates were $4 \times 1 \times 2.8 \text{ nm}^3$ and $8 \times 2 \times 2.8 \text{ nm}^3$. They were inserted in the Mg matrix and the optimum cut-off radius, which led to the semi-coherent interfaces with minimum energy, was obtained as indicated above. Nevertheless, the original precipitate structure (that is shown in Figs. 5.9(a) and (c) for both precipitate sizes) was destroyed during the process to minimize the energy of the interfaces, as shown in Figs. 5.9(b) and (d). This dramatic change of the precipitate structure can be attributed to the large surface/volume ratio of these small precipitates where the interface energies determine the actual atomic arrangement within the precipitate.

Figure 5.8: Excess of energy vs. cut-off radius. The optimum cut-off radius to minimize the interface energy was 0.29 nm.

Figure 5.9: (a) Initial atomic structure of the $4 \times 1 \times 2.8 \text{ nm}^3$ $\beta\text{-Mg}_{17}\text{Al}_{12}$ precipitate embedded the Mg matrix. (b) Idem after energy minimization to create interfaces with minimum energy. (c) Initial atomic structure of the $8 \times 2 \times 2.8 \text{ nm}^3$ $\beta\text{-Mg}_{17}\text{Al}_{12}$ precipitate embedded the Mg matrix. (d) Idem after energy minimization to create interfaces with minimum energy.

5.1.3 Atomistic simulation

A parallelepipedic domain of $50 \times 25 \times 31 \text{ nm}^3$ along with the periodic array of dislocations and precipitates model (Osetsky and Bacon, 2003a) was utilized for the present investigation. Periodic boundary conditions were applied along the x and y directions, while the boundaries perpendicular to the z direction were free. The dimensions of the domain were chosen to minimize the image stresses which developed as a result of the bowing of the dislocation during the simulations (Szajewski and Curtin, 2015). An edge basal dislocation was introduced in the domain containing the precipitate by inserting a semi-plane of atoms into the model and applying the corresponding Volterra's displacement field for an isotropic elastic medium. The dislocation line was parallel to the x axis and the Burgers vector was parallel to the y axis (Fig. 5.6). The energy of the whole domain was minimized afterwards using the CG algorithm and the perfect dislocation was split into two Shockley partials.

The basal plane of the Mg matrix is parallel to the $(110)_\beta$ plane of the β precipitate. This is the preferential slip plane for the intermetallic compounds according to first-principles calculations, which found the lowest energy barriers in the γ energy curves for the 110_β slip system (Xiao et al., 2013). Nevertheless, due to the complex atomic structure of the precipitate, the γ energy curves for the 110_β slip system also depend on the interplanar distances between pairs of equivalent $(110)_\beta$ planes and decreased as the distance between planes increased. To account for this effect, the edge dislocation was placed in two different basal slip planes, A and B , of the Mg matrix that were separated by 0.8 nm (two atomic planes). The slip planes A (that coincide with the center of the box) and B are aligned with two 110 slip systems in the β precipitate (Fig. 5.10). A and B slip planes in the precipitate correspond to the largest interplanar distances in the $[110]_\beta$ direction and, thus, to the lowest energy barriers in the γ energy curves (Xiao et al., 2013).

Two different types of atomistic simulations were carried out. The dislocation-precipitate interaction at 0K was assessed by means of MS simulations. Discrete shear displacements of 5×10^{-3} were successively applied in four atomic layers on the top surface of the domain, parallel to the slip plane, while four layers of atoms at the bottom surface remained fixed. The displacements in the top layers were constrained to one direction parallel to the slip direction. The energy was minimized after each displacement at constant volume using the CG algorithm. This procedure was repeated until the dislocation overcame four times the precipitate. Further simulations were carried out in domains whose length along the y axis was 20, 30, and 35 nm (in addition to the standard domain of 25 nm) to analyze the effect of the distance between precipitates on the CRSS.

Figure 5.10: Plain views of the crystal structure perpendicular to the (001) (left) and (110) (right) planes. The two slip planes (A and B) corresponding to the 110 slip system (left) and $[001](110)$ slip system (right) in the β precipitate are indicated by broken red and blue lines. These planes correspond to largest interplanar distances in the $[110]$ direction. Mg atoms are red and Al atoms blue.

The interaction between the dislocation and the precipitate at finite temperature (10K and 300K) was evaluated by means of MD simulations. The dynamic stabilization of temperature and stress was carried out using the NPT ensemble. A temperature ramp was applied to the system from 0K to the desired temperature in 10 ps. Afterwards, the temperature was kept constant during 15 ps using the same ensemble and the volume of the domain was allowed to expand by relaxing the normal stresses. MD simulations were then carried using the NVT ensemble by imposing the shear displacement to the atoms on the top surface while those at the bottom were fixed. The applied shear strain rate, $\dot{\gamma}$, was $1.3 \times 10^8 \text{ s}^{-1}$. Stress, energy and atomic position data were computed and stored every 1 ps. The timestep in all MD simulations was 1 fs.

5.2 Results and discussion

5.2.1 Basal dislocation / β precipitate interactions at 0 K

The shear stress - shear strain (τ - γ) and the stored energy - shear strain curves (ΔE - γ) obtain by MS simulations are depicted in Figs. 5.11(a) and (b), for slip plane A and B respectively. Similar behaviors, either in stress or stored energy *vs* strain, were found when the basal dislocations slipped along the A and B planes and they will be discussed together. The stress and the energy stored increased initially with γ due to the elastic interaction of the dislocation with the precipitate and a local minimum in the stress is reached (from (i) to (ii)). This drop of stress corresponded to the attraction of the leading partial from the interface.

Afterwards, the shear stress necessary to bypass the precipitate increased as the dislocation propagated along the interface, in both cases. The critical stress at which

Figure 5.11: Molecular statics simulations of dislocation/precipitate interaction. (a) Shear stress vs. strain curves ($\tau - \gamma$) corresponding to slip planes A and B. (b) Stored energy vs. strain curves ($\Delta E - \gamma$) corresponding to slip planes A and B.

the dislocation overcame the precipitate was reached at (iii). At this point the dislocation has propagated along the one long and one short interfaces and it is about to close the loop around the precipitate. An atomistic depiction of the interaction is shown in Fig. 5.12(a), where partial dislocations are illustrated as red lines and only the atoms of the (110) crystallographic slip plane A are shown. The colour of the atoms stands for the shear strain in the slip plane, γ_{yz} . Firstly, the dislocation was attracted by the $(\bar{2}\bar{1}10)_{Mg}/(2\bar{2}\bar{1})_{\beta}$ short interface, and thus was able to penetrate slightly. However, advancing further was not possible and partial dislocations surrounded the precipitate (Fig. 5.12(a)-(ii) and (iii)). The dislocation overcame the precipitates by the formation of Orowan loops, but no clear loop in the Mg matrix around the precipitate was evident. The loop was formed into the precipitate, as the larger strain of the edges of the precipitate in Fig. 5.12(b)-(i) suggests. Nevertheless, due to the complexity of the precipitate lattice, this loop could not be specifically located. This first bypass process was associated with a large reduction in the shear stress and in the stored energy (5.11 from (iii) to (iv)).

Subsequently, the second dislocation appeared due to periodic boundary conditions. This new dislocation precipitate/interaction caused the increase of the stress and stored energy, which corresponds to Fig. 5.11 (a) and (b) from (iv) to (v), respectively. Similar values of the peak stress and of the energy stored were obtained in this second bypassing mechanism. It is worth mentioning that the arrival of this new

dislocation did not lead to an increase in the CRSS (as it would be expected for an Orowan-type mechanism) and thus, it suggested that the plastic strain was somehow transferred to the precipitate. Furthermore, it can be observed that when the second dislocation approached the precipitate, a repulsive interaction with the Orowan loop inside the precipitate was evident (Fig 5.12(b)-(i)). Then, further deformation led to the penetration of the leading partial into the precipitate through the same interface, which was followed by the trailing partial, as shown in Fig. 5.12(b)-(ii) and (iii). Moreover, a gradient in the plastic atomic shear strain along the slip plane of the precipitate was evident. This suggests that due to the second dislocation, the Orowan loop formed in the first interaction was able to advance further inside the precipitate. Finally, the dislocation overcame the precipitate leaving two Orowan loops, which have penetrated deeper into the precipitate, as depicted in Fig. 5.12(c)-(i).

In this figure, the movement of the third dislocation towards the precipitate is also illustrated. The new dislocation/precipitate interaction caused another increase of the shear stress and stored energy as the applied strain increased. This corresponds to the Fig. 5.11 (a) and (b) from (vi) to (vii)). Similar peak stress and energy values as with the second dislocation were evident. In Fig 5.12(c) this third interaction is represented. First, the leading partial approached the precipitate through the short interface, Fig. 5.12(c)-(i), as in the previous cases. As soon as the leading partial entered the precipitate, the first Orowan loop within the precipitate collapsed and sheared the precipitate, Fig. 5.12(c)-(ii). This instant corresponds to the blue dot in Figs. 5.11(a) and (b). The propagation of the leading and trailing partials along the interface finally led to the collapse of the Orowan loop induced by the second dislocation, Fig. 5.12(c)-(iii), and the precipitate was sheared again.

Successive dislocation passes led to close values of shear stress and stored energy, as Figs. 5.11(a) and (b) depicts, reaching a maximum value with the second dislocation and the dislocation overcoming mechanism did not change in the subsequent passes, although the disorder at the interface increased due to the absorption the previous dislocations. The slight differences in the $\tau - \gamma$ and $\Delta E - \gamma$ curves between slip planes *A* and *B* can be attributed to the differences in the interface structure and also to the mechanisms of deformation in the precipitate. It is interesting to notice that this mechanism of dislocations gliding along the matrix/precipitate interface has been recently reported during *in situ* nanoindentation experiments in the transmission electron microscope in Mg-Nd alloys (Huang et al., 2018).

To better ascertain the overcoming mechanism, the contour plot of the shear strain in the cross-section of the precipitate is shown in Figs 5.13 for slip planes *A* and *B*. The precipitate was strain-free at the initial state but shear strains were very localized

Figure 5.12: Details of the interaction of the partial dislocations (red lines) with the Mg₁₇Al₁₂ precipitate, which is sheared along the (110) crystallographic slip plane. (a) First dislocation. (b) Second dislocation. (c) Third dislocation. The contour plot of the precipitate section shows the shear strain, γ_{yz} . Only the atoms of the (110) crystallographic slip plane of the precipitate, which is the continuation of the slip plane A, are shown.

Figure 5.13: Contour plots of the shear strain parallel to the slip plane (γ_{yz}) in the cross-section of the precipitate as a function of the number of dislocations that bypass the precipitate. The results on the left correspond to the slip plane A and those on the right to the slip plane B.

around the slip plane (particularly for the precipitate sheared along the slip plane A) after the first dislocation has overcome the precipitate. The boundary region affected by the large shear strain, increased with the number of dislocations bypassing the precipitate (Fig. 5.12) but the thickness of this shear-deformed zone remained very thin (just a few atomic planes) and, finally, the precipitate was sheared. This process is compatible with the progressive shearing of the precipitate by the successive dislocation loops. The first dislocation penetrated the precipitate but could not propagate further and remained close to the surface. The following dislocation loop pushed the initial dislocation loop further into the precipitate and this process was repeated until the first dislocation loop completely sheared the precipitate and was annihilated. This point is associated with a reduction of the shear stress and energy storage, as shown by the blue and red solid circles in Figs. 5.11(a) and (b). Further deformation led to progressive shearing of the precipitate by the successive dislocations.

These static simulations depict a dislocation/precipitate interaction mechanism that it is a mixture of Orowan looping and precipitate shearing. The initial dislocations overcome the precipitate by the formation of an Orowan loop that penetrates the precipitate but it was not able to shear it because of the differences in the structure and

the high CRSS necessary to move dislocations in the precipitate. Another Orowan loop was introduced into the precipitate after the next dislocation bypassed the precipitate, and the first Orowan loop is pushed further into the precipitate. This process continued until the first dislocation loop completely sheared the precipitate and was annihilated. This mechanism was repeated as more dislocations overcome the precipitate, and the precipitate was eventually sheared.

Lattice transformation of β precipitate during dislocation/precipitate interaction

A detailed investigation of the shear process and how it affected the lattice of the precipitate was carried out. The cross-sections of the atomic arrangement in the precipitate have been plotted in Fig. 5.14 along the slip plane *A* at different stages. The cross-sections in Figs. 5.14(a) and (d) correspond to the initial atomic arrangement of the precipitate, while those in Figs. 5.14(b) and (e) show the strain indicated by the blue circles in Figs. 5.11(a) and (b). Finally, Figs. 5.14(c) and (f) show the atomic arrangement of the precipitate at the end the simulations in Fig. 5.11 after four dislocations sheared the precipitate. Shearing of the precipitate took place along the (110) plane and it was localized along one crystallographic plane indicated by the broken blue line in Fig. 5.10(b). The atoms moved in this plane along the $[\bar{1}10]$ and $[00\bar{1}]$ directions and the overall shear took place along the $[1\bar{1}1]$ direction, which is parallel to the Burgers vector of the edge dislocation in Mg (Fig. 5.6). This process was repeated as more dislocations overcame the precipitate, leading to the shearing of the precipitate. These results indicate that precipitate shearing by basal dislocations in Mg-Al alloys is favored because the (0001) Mg basal plane is parallel to the (110) crystallographic plane of the precipitate.

The cross-sections of the precipitate that was sheared along the slip plane *B* are depicted in Fig. 5.15 at different stages of the shearing process: initial configuration in (a) and (d), at the strain marked by the red circles in Fig. 5.11 (b) and (e) and at the end of the simulations in (c) and (f). Shear deformation also occurred parallel to (110) planes but it was not localized in one single plane and it was difficult to assess the dominant orientation of the shear deformation. Moreover, the long range order in the upper part of the precipitate was lost after several dislocations sheared the precipitate (Figs. 5.15(c) and (f)). Thus, the shearing mechanism of the precipitate depends on the location of the slip plane in the Mg matrix with respect to the precipitate lattice but the shear stress necessary to overcome the precipitate was similar for slip planes *A* and *B*. Moreover the maximum shear stress (which is the CRSS) was attained after the second dislocation bypassed the precipitate in both cases.

Figure 5.14: Shearing of the precipitate along the slip plane A. (a) and (d) Initial cross-sections. (b) and (e) cross-sections for the strain marked by a blue circle in Fig. 5.11(a) and (b). (c) and (f) Cross sections at the end the molecular statics simulations after four dislocations have bypassed the precipitate. The crystallographic directions in this figure correspond to the β precipitate.

Figure 5.15: Shearing of the precipitate along the slip plane B. (a) and (d) Initial cross-sections. (b) and (e) cross-sections for the strain marked by a red circle in Figs. 5.11(a) and (b). (c) and (f) Cross sections at the end the molecular statics simulations after four dislocations have bypassed the precipitate. The crystallographic directions in this figure correspond to the β precipitate.

Figure 5.16: Shear stress vs. strain curves ($\tau - \gamma$) corresponding to slip planes A and B obtained by molecular dynamics. (a) $T = 10$ K. (b) $T = 300$ K. The peaks denoted as (i), (ii), (iii), and (iv) indicate when the successive dislocations overcome the precipitate.

5.2.2 Dislocation/precipitate interaction mechanisms at finite temperatures

The effect of temperature on the dislocation/precipitate interactions was analyzed by means of MD calculations. Simulations were carried out for dislocations located in the planes A and B and the corresponding shear stress *vs.* shear strain curves are depicted in Fig. 5.16(a) and (b) at 10 K and 300 K, respectively. The mechanical response at both temperatures was very similar and these curves were also very close to those obtained at 0 K (Fig. 5.11), indicating that the energy barrier to bypass the precipitates was very large and it was not influenced by the temperature in the MD simulations. The curves present successive peaks in the shear stress (marked (i), (ii), (iii) and (iv)), which correspond to the bypass of the precipitate by the successive dislocations. The maximum value of the shear stress was attained after the second dislocation overcome the precipitate and its magnitude was similar to the one reported at 0 K in Fig. 5.11. Afterwards, the precipitate was sheared following a mechanism equivalent to the one reported above (Figs. 5.14 and 5.15) and the CRSS necessary to overcome the precipitate by the following dislocations decreased.

The mechanisms of dislocation/precipitate interaction reported above are different from those observed in other precipitate-strengthened alloys. Precipitate shearing by dislocations is normally reported in the case of coherent precipitates; the matrix dislocation enters the precipitate through the coherent interface and slips along the most suitable slip plane. This phenomenon is most clear when the matrix and the

precipitate share the same crystallographic lattice (for instance, γ' precipitates in a γ matrix in Ni-based superalloys (Vattrè et al., 2009) or Guinier-Preston zones in Al-Cu alloys (Esteban-Manzanares et al., 2019c) but it has also been reported in the case of basal dislocations with β' precipitates in Mg-RE alloys (Solomon and Marquis, 2018; Bhattacharyya et al., 2018). Under these circumstances, the CRSS necessary to shear the precipitate depends on the coherency strain, the modulus mismatch, the chemical strengthening and, in the case of ordered precipitates, on the energy penalty due to the formation of antiphase boundaries (Nembach, 1997). On the contrary, dislocations cannot enter the precipitate in the case of incoherent interfaces, and the obstacle to the dislocation motion is overcome by the formation of an Orowan loop around the precipitate. The shear stress necessary to overcome the precipitate can be calculated using dislocation line tension models (Orowan, 1948; Bacon et al., 1973) and the interaction of successive dislocations with the Orowan loops around the precipitates leads to a strong hardening.

Nevertheless, shearing of non-coherent precipitates by basal dislocations in Mg-Zn (Wang and Stanford, 2015), Mg-Al alloys (Varvenne et al., 2017; Cepeda-Jiménez et al., 2019) and Mg-Nd alloys (Zhou et al., 2018; Huang et al., 2019) has been recently reported in several experimental studies. The common feature of all these investigations is that the Mg basal plane is parallel to one crystallographic plane of the precipitate: $(0001)_{\text{Mg}} \parallel (11\bar{2}0)_{\beta}$ in Mg-Zn, $(0001)_{\text{Mg}} \parallel (110)_{\beta}$ in Mg-Al, and $(0001)_{\text{Mg}} \parallel (110)_{\beta_1}$ in Mg-Nd. This crystallographic correspondence between the basal plane of Mg and closely packed crystallographic planes of the precipitates occurs spontaneously during precipitate nucleation. Even though the favourable matrix/precipitate interfaces may be incoherent (due to the different crystallographic structure and the mismatch in the lattice parameters), basal dislocations in the Mg matrix can glide into the precipitate without changing the slip plane. Of course, the stress necessary to shear the precipitate is much higher than that for basal slip in Mg and several basal dislocations have to pile-up at the interface before the precipitate is sheared. The presence of dislocation pile-ups before precipitate shearing has also been experimentally reported in Mg-Al (Cepeda-Jiménez et al., 2019) and Mg-Nd (Huang et al., 2019), supporting our atomistic results. It should be also noted that precipitate shearing in Mg alloys by either prismatic or pyramidal dislocations was not observed because of the lack of crystallographic continuity between the corresponding slip planes in the matrix and in the precipitate (Bhattacharyya et al., 2018). Thus, the strength of Mg alloys is limited by the low CRSS for basal slip, which is always the main plastic deformation mechanism. Precipitate shearing by basal dislocations limits the strengthening provided by precipitates (hardening due to the interaction of dislocations with Orowan loops around the

precipitates is not active) and, thus, hinders precipitation hardening in Mg alloys.

Finally, it is worth noting the importance of creating a low energy matrix/precipitate interface with the proper interface orientations to analyze the dislocation/precipitate interactions. If these details are not included in the atomistic model, the interaction of the dislocations with the interface as well as the residual stresses created to introduce the precipitate into the matrix may lead to the appearance of spurious deformation mechanism in the atomistic simulations.

5.2.3 Comparison with theoretical models

The atomistic simulation results showed that the dislocations initially overcome the precipitates by the formation of an Orowan loop and it is interesting to compare the predictions of the τ_O after the first dislocation has overcome the precipitate with those of the Orowan model (Orowan, 1948). To this end, molecular statics simulations were carried out using simulations boxes with different widths along the x axis (from 20 nm to 35 nm) while the other dimensions and orientation were not modified. The CRSS in the simulations was equal to the stress necessary to overcome the precipitate by the first dislocation. These results are compared in Fig. 5.17 with the predictions of the Orowan model, $\tau_O = \mu|\bar{b}|/L$, where μ is the shear modulus of the Mg crystal parallel to the basal plane (18 GPa), $\bar{b}$ the Burgers vector of basal dislocations (0.32 nm) and L the distance between precipitates along the dislocation line, which is equal to the simulation box width.

It was found that the Orowan model overestimated obstacle strength along both slip planes A and B (Fig. 5.17) and the differences may be attributed to the significant bowing of the dislocations to overcome the precipitate (Figs. 5.11(c) and (d)). The energy associated with the interaction of opposite dislocation segments can provide an important contribution to the precipitate strength that can be rationalized by means of the Bacon-Kocks-Scattergood (BKS) model (Bacon et al., 1973). In this model, the resolved shear stress necessary to overcome the precipitate takes into account the interaction between dislocation segments and scales with the natural logarithm of the harmonic mean between the precipitate diameter ϕ and the distance between precipitates L according to

$$\tau_{\text{BKS}} = \frac{\mu|\bar{b}|}{2\pi AL} \left(\ln \left[\frac{|\bar{b}|}{\phi} + \frac{|\bar{b}|}{L} \right]^{-1} + B \right) \quad (5.5)$$

where $A = 1$ for edge dislocations and B an adjustable parameter. In this case, $\phi = 10.6$ nm was taken as the projection of the precipitate on the dislocation line. The predictions of the BKS (with $B = 0.075$) are plotted in Fig. 5.17 together with results of

Figure 5.17: Critical resolved shear stress (τ_O) to form an Orowan loop as a function of the distance between precipitates, L . Results obtained with molecular statics simulations, Orowan model ($\tau_O = \mu|\bar{b}|/L$) and BKS model (eq. (5.5)) are plotted for comparison.

the MS simulations. They are in good agreement and indicate that the BKS model can provide reasonable predictions of the stress necessary to form an Orowan loop around the β precipitates in Mg-Al alloys.

The CRSS necessary to overcome the precipitate was controlled by the stress necessary to shear the precipitate in the MS and MD simulations. This stress was attained by the pile-up of two dislocations around the precipitate. Further deformation did not lead, however, to the accumulation of dislocations at the precipitate and to strain hardening, because the precipitate was sheared. Thus, this dislocation/precipitate interaction mechanisms limits the strain hardening capability of Mg alloys as compared to metallic alloys containing precipitates that cannot be sheared by dislocations. Moreover, it should be noted that precipitate shearing has been experimentally reported in β -Mg₁₇Al₁₂ precipitates much larger than those analyzed in the atomistic simulations in this investigation (Voisin et al., 2017; Cepeda-Jiménez et al., 2019).

5.3 Conclusions

The interaction between edge basal dislocations and β -Mg₁₇Al₁₂ precipitates was studied using atomistic simulations. A strategy was developed to insert a lozenge-shaped Mg₁₇Al₁₂ precipitate with Burgers orientation relationship within the Mg matrix in an atomistic model. To this end, the precipitate with the right shape and orientation relationship (according to the experimental data) was introduced into the Mg matrix. Afterwards, all the atoms belonging to the Mg matrix within the cut-off radius of an atom of the precipitate were deleted and the optimum cut-off radius was obtained by energy minimization. Finally, the simulation box was annealed to relieve the remaining residual stress. In this way, the incoherent matrix/precipitate interfaces in the atomistic model were close to stable, minimum energy configurations.

Molecular statics and dynamics simulations of the dislocation precipitate interaction showed similar mechanisms. The dislocation bypassed the precipitate by the formation of an Orowan loop, that entered the precipitate but it was not able to progress further until more dislocations bypass the precipitate and push the initial loop to shear the precipitate along the (110) plane, parallel to the basal plane of Mg. This process was eventually repeated as more dislocations overcome the precipitate. These mechanisms were in agreement with the experimental evidences (Voisin et al., 2017; Cepeda-Jiménez et al., 2019) and indicate that precipitate shearing by basal dislocations in Mg-Al alloys is favored because the (0001) Mg basal plane is parallel to the (110) crystallographic plane of the precipitate.

The resolved shear stress to form an Orowan loop around the precipitate was in agreement with the predictions of the Bacon-Kocks-Scattergood model that takes into account the interaction between dislocation segments. The mechanisms of dislocation/precipitate interaction as well as the resolved shear stress to form an Orowan loop were independent of the temperature in the range of temperatures and strain rates explored by the molecular dynamics simulations. Finally, the details of the shearing mechanism of the precipitate depended on the particular (110) plane in which the shear strain was localized but they did not significantly influence the CRSS.

6 CONCLUSIONS AND FUTURE WORK

6.1 General conclusions

This doctoral thesis has been devoted to develop novel modeling strategies, based on atomistic simulations, to understand the mechanisms of dislocation/precipitate interactions and to quantify the precipitate strengthening in FCC and HCP metallic materials. The following results and conclusions were achieved:

- Atomistic simulations showed that dislocation cross-slip in FCC Al takes place through the Friedel-Escaig mechanism. The nudged elastic band method was employed to determine the activation energy barrier for dislocation cross-slip in the absence of thermal energy, while the enthalpy barrier and the effective attempt frequency were determined as a function of the Schmid stress on the cross-slip plane, and of the Escaig stresses on the cross-slip and glide planes from molecular dynamics simulations. Moreover, the three theoretical contributions to the enthalpy energy barrier (constitutional, elastic energy due to the applied stress and polarization due to the interaction of the applied stress with the local stress field created by the defect) were identified from the atomistic simulations. Additionally, it was found that Meyer-Neldel rule is

able to estimate the entropic contribution to the activation energy as a function of the applied stress. Based on these results, an analytical expression of the cross-slip rate in Al as a function of the different combination of Schmid and Escaig stress states was developed and validated.

- A scale-bridging modeling strategy based in molecular statics and molecular dynamics simulations in combination with transition state theory was developed to determine the flow stress of an Al-Cu alloy containing Guinier-Preston zones. The athermal contribution to the flow stress was determined from the Taylor's model, while the thermal contribution was obtained from the obstacle strength and the free energy barrier. These two magnitudes were obtained by means of molecular statics and molecular dynamics simulations of the interaction of edge dislocations with Guinier-Preston zones in two different orientations. The predictions of the model were compared with experimental data and were in reasonable agreement, showing the potential of atomistic simulations in combination with transition state theory to predict the flow stress of metallic alloys strengthened with precipitates.

- The interaction between basal dislocations and β -Mg₁₇Al₁₂ precipitates in Mg-Al alloys was studied using atomistic simulations. A strategy to insert semicoherent precipitates with the lowest interface energy was developed. Particularly, this methodology was used to insert a lozenge β precipitate shaped with Burgers OR. Molecular statics and dynamics simulations of the dislocation precipitate interaction showed similar mechanisms. The dislocation bypassed the precipitate by the formation of an Orowan loop, that entered the precipitate but it was not able to progress further until more dislocations bypass the precipitate and push the initial loop to shear the precipitate along the (110) plane, parallel to the basal plane of Mg. This process was eventually repeated as more dislocations overcome the precipitate. It is worth noting that these mechanisms observed in the molecular mechanics simulations are in agreement with the experimental results in other Mg alloys, suggesting that the crystallographic correspondence between the basal plane of Mg and closely packed crystallographic planes of the precipitates occurs spontaneously during precipitate nucleation. Even though the favorable matrix/precipitate interfaces may be incoherent (due to the different crystallographic structure and the mismatch in the lattice parameters), basal dislocations in the Mg matrix can glide into the precipitate without changing the slip plane, leading to precipitate shearing and limiting the potential of precipitates to strengthen Mg alloys.

6.2 Future work

This doctoral thesis has developed new strategies – based on atomistic simulations – to understand and quantify the mechanisms of dislocation cross-slip and of dislocation/precipitate interactions. Future work should be focused on the development of these strategies to assess their range of applicability and/or their application to other materials. Within this framework, the following avenues for future work are proposed:

- The thesis showed how atomistic simulations can be used to assess the effect of multiaxial stress states on the cross-slip rate in Al. The results were in agreement with theoretical analyses and identified the different contributions to the energy barrier. It would be very interesting to apply the same strategy to other metallic alloys with smaller stacking fault energy (Ni, Cu) to discover how multiaxial stresses influence the energy barrier and the cross slip rate.

- The strategy developed to analyze dislocation/precipitate interactions included several steps that are important to provide a realistic assessment: the combination of molecular statics with thermal annealing to explore the rough energy landscape, the process to obtain minimum energy interfaces between the matrix and the precipitate in the case of incoherent or semi-coherent interfaces, the use of molecular dynamics to determine the thermodynamic quantities (activation energy and entropy, activation volume) that control the interaction, the application of transition state theory to extrapolate the atomistic results to standard strain rates. These tools (individually or in combination) can be used to explore other precipitate-strengthened alloys and/or to design new alloys with improved properties. This is particularly relevant in the case of Mg alloys, where there is a huge potential for improvement.

- Although the computational power is exponentially increasing, large atomistic simulations (> 1 million atoms) can only reach a few nanoseconds. Nevertheless, novel atomistic simulations strategies have been developed (i.e. hyperdynamics, parallel replica and temperature accelerated dynamics) that allow, in combination with transition state theory to attain much longer time scales (of the order of seconds). Hence, it would be very interesting to explore the implementation of these techniques to the strategies presented in this doctoral thesis to evaluate dislocation/obstacle interactions.

A MODIFIED EMBEDDED ATOM METHOD FORMALISM

Modified embedded-atom method (MEAM) Baskes (1987, 1992); Lee and Baskes (2000); Tadmor and Miller (2011) is based on the embedded-atom method (EAM) formalism, which accounts for the potential energy between pairs and a functional describing the energy to embed an atom in a certain position on a given electronic background provided by its neighbors. Thus, the potential energy of an atom i located in a position $\mathbf{r}_i$ is given by

$$V(\mathbf{r}_i) = \frac{1}{2} \sum_{i \neq j} U_{i,j}(r_{i,j}) + F_i(\rho_i) \quad (\text{A.1})$$

where $U_{i,j}$ is the energy between pair of atoms and F_i is the embedding functional, which depends on the electronic density ρ_i . This functional can be expressed according to

$$F_i(\mathbf{r}_i) = A E_0 \rho_i \ln(\rho_i) \quad (\text{A.2})$$

where A and E_0 are fitting parameters and the electron density ρ_i is provided by eq. (A.3).

$$\rho_i = \frac{\rho_i^0}{\phi_i^0} G(\Lambda_i) \quad (\text{A.3})$$

being ϕ_i^0 fitting parameter, which depends on the crystal structure of the material. ρ_i^0 is the electronic density between pairs, and G and Λ_i are equal to the eqs. (A.4) and (A.5), respectively.

$$G = \sqrt{1 + \Lambda_i} \quad (\text{A.4})$$

$$\Lambda_i = \sum_{\kappa=1}^3 w_i^{(\kappa),(0)} \frac{\phi_i^{(\kappa)}}{\phi_i^{(0)}}. \quad (\text{A.5})$$

It should be noted that ϕ_i^l is a function of the interatomic distance (r_{ij}), as detailed below, and $w_i^{(\kappa)}$ is a weight function that follows the equation

$$w_i^{(\kappa)} = \frac{1}{\rho_i^{(0)}} \sum_{j \neq i} w_i^{(\kappa),(0)} \phi_i^{(0)} s_{ij} \quad (\text{A.6})$$

where $w_i^{(\kappa),(0)}$ is another material-dependent fitting parameter and s_{ij} is a function which depends on the relative distance between triplets and accounts for the screen effect between atoms.

Electron density in MEAM follows a cluster potential forms. Thus, four different functions, depending on the closest pairs and triplets of atoms, define ρ_i , and they are equal to

$$\rho_i^{(0)} = \sum_{j \neq i} \phi_j^{(0)} s_{ij} \quad (\text{A.7})$$

$$\rho_i^{(1)} = \sqrt{\sum_{\alpha=1}^3 \left(\sum_{j \neq i} \phi_j^{(1)} s_{i,j} \frac{r_{i,j}^\alpha}{r_{i,j}} \right)^2} \quad (\text{A.8})$$

$$\rho_i^{(2)} = \sqrt{\sum_{\alpha=1}^3 \left[\sum_{\beta=1}^3 \left(\sum_{j \neq i} \phi_j^{(2)} s_{i,j} \frac{r_{i,j}^\alpha r_{i,j}^\beta}{r_{i,j}} \right)^2 \right] - \frac{1}{3} \left(\sum_{j \neq i} \phi_j^{(2)} s_{i,j} \right)^2} \quad (\text{A.9})$$

$$\rho_i^{(3)} = \sqrt{\sum_{\alpha=1}^3 \left\{ \sum_{\beta=1}^3 \left[\sum_{\gamma=1}^3 \left(\sum_{j \neq i} \phi_j^{(3)} s_{i,j} \frac{r_{i,j}^\alpha r_{i,j}^\beta r_{i,j}^\gamma}{r_{i,j}} \right)^2 \right] - \frac{3}{5} \left[\sum_{j \neq i} \phi_j^{(3)} s_{i,j} \frac{r_{i,j}^\alpha}{r_{i,j}} \right]^2 \right\}} \quad (\text{A.10})$$

where α , β and γ denote the three spatial components of the position $\mathbf{r}_{i,j}$ and the functions $\phi_j^{(\kappa)}$ is provided by the expression observed in eq. (A.11).

$$\phi_j^{(\kappa)}(r_{i,j}) = \phi_j^{(0)} \exp \left\{ P_j^{(\kappa)} \left(\frac{r_{ij}}{r_j^0} - 1 \right) \right\} \quad (\text{A.11})$$

where P_j^κ is another fitting parameter, which depends on the material and on the distance of the atom i to the closest neighbor in the equilibrium structure (r_j^0). It is worth noting that $\rho_i^{(0)}$ is equal to the EAM pair potential electron density. However, MEAM is developed further to add directional bonds by means of cluster potential formulation.

Screening effects of the nearest atoms to the pair i, j can weaken the bonds between these atoms. As mentioned above, this phenomenon is taken into account in the MEAM potential by means of the screening function, according to

$$s_{i,j} = S_{i,j} \left(\frac{r_c - r_{i,j}}{r_s - r_c} \right) g_c \quad (\text{A.12})$$

where g_c is a smoothing function to take into account the screening effect gradually, r_c is the cut-off radius, r_s is the skin radius (see Sec. 2.2 in Chapter 2) and $S_{i,j}$ takes the form

$$S_{i,j} = \prod_{k \neq i,j} \left(\frac{C_{i,j,k} - C_{i,j,k}^{\min}}{C_{i,j,k}^{\max} - C_{i,j,k}^{\min}} \right) g_c(r_{i,j}, r_c) \quad (\text{A.13})$$

where $C_{i,j,k}^{\min}$ and $C_{i,j,k}^{\max}$ are fitting parameters and $C_{i,j,k}$ given by

$$C_{i,j,k} = \frac{2[(r_{i,j}r_{i,k})^2 + (r_{i,j}r_{j,k})^2 - (r_{i,j})^4]}{(r_{i,j})^4 - [(r_{i,j})^2 - (r_{j,k})^2]^2} + 1 \quad (\text{A.14})$$

It should be noted that there is a minimum of 14 fitting parameters for a single element and 41 for a binary alloy, including 13 for the interspecies interaction in addition to the 14 of each element. This large number of fitting parameters makes the transferability of MEAM potential more difficult than other interatomic potentials (Tadmor and Miller, 2011).

B FAST INERTIAL RELAXATION ENGINE

Fast inertial relaxation engine (FIRE) is a damped dynamics scheme for structural relaxation, which readjusts the particle trajectories by accelerating the system in the force direction. So particles can retard or steer following the equation of motion:

$$\mathbf{a}_i = \frac{\mathbf{f}_i}{m_i} - \gamma |\mathbf{v}_i| \left(\hat{\mathbf{v}}_i - \hat{\mathbf{f}}_i \right) \quad (\text{B.1})$$

where m_i is the mass of particle i , $\mathbf{v}_i$ the velocity of particle i and γ is a readjustment function which looks for the steepest direction.

FIRE relaxation method can be used with any MD integrator and it has been used in the work with the Velocity Verlet integrator (see section 2.2.2). The trajectory readjustment depends on the projection of the force vector in the velocity vector (P). This rearrangement of the particles is introduced by means of two different velocity modifications:

- If $P > 0$ set the new velocity as $\mathbf{v} = (1 - \gamma\Delta t)\mathbf{v}_i + \gamma\Delta t |\mathbf{v}_i| \hat{\mathbf{f}}_i$
- If $P \leq 0$ set $\mathbf{v} = 0$ to freeze the system.

Additionally, Δt and γ are dynamically updated every timestep. This condition impedes that the system moves in the uphill direction (Bitzek et al., 2006). A general flow chart of FIRE algorithm can be observed in Fig. B.1.

Figure B.1: Flow chart of fast inertial relaxation engine.

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