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## Modeling Tools: From the Atom to the Macroscopic Scale

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### 7.1. Introduction

The aim of this chapter is to briefly describe different techniques used for modeling structures from the atomic scale to the macroscopic scale and, where appropriate, their surrounding environment. For each method we will provide the general principle, references to books for more information, strengths and limitations, as well as some examples of recent applications drawn from the literature.

### 7.2. The atomic scale

Atomic scale simulations describe the material as a set of atoms and so the main element for simulations at this scale is the description of interactions between the atoms, or more commonly, knowing the dependence of the system's total energy on their positions. The accuracy of the atom interaction model greatly affects the quality of the results while its complexity determines the computation time necessary to obtain the result. The model is therefore always chosen by reaching a compromise.

The interaction potentials can be established using quantum mechanics and electronic structure calculations. However, this type of calculation, known as *ab initio*, is very expensive due to the computing time, and its use in an atomic-scale simulation code is only possible for small systems (at this time, a few hundred atoms to a thousand). In order to simulate systems with more particles, approximated solutions of these potentials are used (empirical or semi-empirical potentials), and adjusted to physical properties of the studied material.

### 7.2.1. Cohesive models

#### 7.2.1.1. “*Ab initio*” methods for materials: density functional theory

The so-called “*ab initio*” methods, which allow us to determine the electronic structure of an assembly of atoms, *a priori* arbitrary, have seen their field of application grow in material sciences thanks to the constant improvement of computational power and the theoretical developments which have occurred over the last three decades. In contrast to the so-called empirical and semi-empirical methods, these methods don’t require any adjustments to describe the interaction energy between atoms. They are not rigorously precise since they are based on a number of approximations, more or less well controlled depending on the case. The common goal of all *ab initio* techniques is to solve the Hamiltonian (i.e. calculate the energy) in a system of  $N_a$  atoms and  $N_e$  electrons. This is an  $N$ -body problem which can only be solved using a number of approximations. At zero order the Born-Oppenheimer approximation, or adiabatic approximation, is used, which consists of decoupling the movement of the nuclei from that of the electrons. This approximation is justified by the fact that the nuclei’s mass is three orders of magnitude larger than that of the electrons and so the electrons are at all times in the ground state, which corresponds to the nuclei’s current position. In practice, this enables us to define the interaction energy between the atoms, which is none other than the electronic energy of the ground state associated with the nuclei’s spatial configuration.

In works focusing on solids, the approach used is generally based on the density functional theory (DFT). In this approach, the energy of the ground state  $E$  is solely expressed as a function of the electron density. It was only after the work of Hohenberg and Kohn [HOH 64] and Kohn and Sham [KOH 65] in the mid-1960s that the DFT made it possible to deal realistically with the  $N$ -body problem. Kohn and Sham’s method (KS) makes it possible to express the electron density as the sum of squares of pseudo-mono-electronic wave functions that must verify the KS equations (a simplified set of Schrödinger equations) that can be numerically solved. A Hartree term appears in these equations, which is easily expressed according to the density, and an exchange-correlation term which we cannot evaluate in the general case. Nevertheless, this quantity can be determined if we approximate the electron gas by a homogeneous gas of density  $n_0$  (LDA, Local Density Approximation). However, the atomic or molecular systems are far from being a homogeneous electron gas and so we must consider functionals that involve the density gradient (GGA, Generalized Gradient Approximation). Other refinements have been developed such as hybrid exchange-correlation functionals or Hubbard corrections (LDA + U) to describe highly correlated systems. For more details on the DFT, please refer to [PAR 89].

These methods make it possible to calculate a very large number of physical properties (accessible or not to the experiments) with precision and confidence. They are increasingly used to generate data for the development of empirical potentials or cluster expansion models that provide a formalism for the construction of Hamiltonians based on the interaction decomposition in pairs, triplets, quadruplets, quintuplets, and so on [SAN 84].

The DFT limitations are, on the one hand, the size of the system: at present we are able to deal with workstations of a few tens of atoms, with this value sometimes reaching a few hundred or even a thousand atoms using calculation codes on massively parallel machines; and on the other hand, the fact that the calculations do not account for the temperature. It is possible to carry out a few hundred (thousand) molecular dynamic (MD) iterations (see next section) using the so-called Car-Parrinello technique [CAR 85], which in principle enables taking into account the effects of the temperature.

#### 7.2.1.2. *Empirical potentials or force fields*

The interatomic interaction potential is a function  $V(r_1, r_2, \dots)$  of the nuclei positions which represents the potential energy of the system. This function is invariant with respect to translations and rotations and is generally constructed from the relative positions of the atoms rather than from their absolute positions. The forces on the atoms are then obtained by calculating the potential gradient with respect to the atomic displacements.

The development of these potentials is done in two steps: 1) the analytical form of the function, which contains adjustable parameters, is chosen (which often depends on the type of bonds involved); 2) these parameters are adjusted to a number of wisely chosen physical properties – cohesive energy, elastic constants, vacancy formation energy, surface energies, interface energy, phonon spectrum, pressure-volume relation, etc. – according to the area of application.

The force field chosen depends on the type of bonds involved in the material we wish to simulate. Thus, Lennard-Jones potentials are typically used for van der Waals-type interactions; the Embedded Atom Method (EAM) potentials are used for metallic interactions and Buckingham's potentials [BUC 38, LEW 85] and variable charge potentials [DEM 99] are used for ionic bonds. For covalent materials, a distinction is usually made between reactive and non-reactive potentials. The reactive potentials are capable of describing chemical reactions involving bond breaks or the formation of new bonds. These include ReaXFF potentials [VAN 01] which are likely to describe a large number of reactive systems. Alternative potential building methods based on “machine learning” are being developed. They adjust the potential on a very large number of atomic configurations obtained using “*ab initio*” calculations [BEH 16].

One of the recurring problems of these potentials is their transferability irrespective of the construction method chosen, in other words, their ability to correctly model the material chosen under conditions far from the conditions used when adjusting the parameters. Thus, it is not at all guaranteed (it is moreover rarely the case) that a potential adjusted, for example, for the equilibrium properties of CC Fe can be used to model FCC Fe. In the same way, will a potential only adjusted for the elastic properties of a material give satisfactory results in studies involving diffusion or dislocation slips?

To describe atomic bonds we can use, from the most complex to the simplest, a quantum mechanical approach, or empirical models which are validated on a certain number of relevant properties. It should be noted, however, that there are intermediate techniques between these two extremes such as the strong bond technique, which is a calculation of the electronic band structure using a semi-empirical set of wave functions based on the superposition of wave functions for isolated atoms located at each atomic site.

In the case of hydrogen embrittlement, the stability and structure of complexes containing a few vacancies and some hydrogen atoms in iron [HAY 13] and their mobility can be determined by DFT, for example. However, to study the role of hydrogen on the plasticity, it will be necessary to use empirical potentials and classic MD such as in [LI 15]. Similarly, the structure and geometry of possible corrosion inhibitors can be studied by DFT; however, to model the interaction of the inhibitor with a surface, it is often necessary to use classical MD and force fields. This is the approach followed, for example, by Saha *et al.* [SAH 16] in the case of the protection of steels by N-heterocyclic organic compounds. The two approaches are also complementary; the “*ab initio*” calculations enable us, for example, to determine the property values for which the empirical potentials need to be adjusted. Thus, in the case of the Mo-Tc alloy, the E/pH diagram of the Tc-O-H system was developed using “*ab-initio*” calculations coupled with the resolution of the Nernst equations for the possible reactions between Tc and its corrosion products. The data obtained this way then made it possible to develop an empirical potential finally used in conjunction with an atomic Kinetic Monte Carlo (KMC) method to study the surface dissolution mechanisms according to its orientation and composition [KIM 13].

### **7.2.2. Molecular dynamics**

In MD we have access to thermodynamic averages of a particle system by taking the average of individual trajectories. The method consists in solving the Newton equations for each atom  $i$  of the crystal. In the most common case and for particles interacting through central forces, the degrees of freedom are reduced to the centers of mass' coordinates and the equations of motion of  $N$  coupled Newton equations:

$$m_i \ddot{\vec{r}}_i(t) = \vec{f}_i(t) = -\vec{\nabla}_i V(\{\vec{r}_j(t)\}) = \sum_{j(\neq i)} \vec{f}_{ij}(|\vec{r}_i - \vec{r}_j|) \quad [7.1]$$

where  $\vec{f}_{ij}$  indicates the force exerted by particle  $j$  on particle  $i$ . The total force exerted on atom  $i$  by the other atoms is given by the gradient of the interatomic potential with respect to the position of the atom.  $\ddot{\vec{r}}_i$  is the second derivative with respect to the time of the position vector of atom  $i$  with mass  $m$ .

The integration of the equations of motion must be done numerically by choosing a finite time step  $dt$  and by approximating the differential equations with finite difference equations. Thus, at time  $t$ , simultaneously, for a system of  $N$  particles,  $N$  classical equations of motion  $\vec{f}_i = m_i \ddot{\vec{r}}_i$  are solved. From these calculations the computer predicts the new positions for all the particles at time  $t + dt$ , their new speeds and the new forces. It is thus possible to trace the behavior of a material or rather a submicroscopic part of a material.

Molecular dynamics is therefore a fully deterministic method: the trajectory of the atoms is completely determined by the initial conditions. The classical MD calculation reproduces the properties of the microcanonical ensemble (or NVE ensemble). To be very precise, while Newton's classical equations of motion conserve the energy and the total momentum of the system (when there are no external forces applied), MD actually explores a subsystem of the microcanonical ensemble. For ensembles other than the microcanonical ensemble, the Newton equations are modified to sample the desired ensemble. Time averages similar to those made for the NVE ensemble are therefore obtained.

The size and time scales are of the order of a few hundred nanometers, and from a few picoseconds to a few nanoseconds depending on the case study and the cohesion model (DFT or empirical potential) [PAY 92]. The information obtained can be used as such (e.g. dislocation propagation rate and stress associated with the application of a deformation, number and arrangement of defects created by irradiation) or as starting data for larger scale calculations (finished elements, for example).

The details of the method's principles and examples of programs can be found, for example, in [ALL 89]. A list of public software is given in [BEC 10].

From the corrosion study's point of view, MD using a very recently developed empirical potential has enabled, for example, the highlighting of the formation of a double layer at the iron-water interface [FER 16]. Another recent example is the demonstration of the increased resistance of Zr's basal surface (0001) to oxygen

diffusion compared to the prismatic surface (10-10) [NOO 14]. Molecular dynamics can also be used to determine the input parameters of higher scale models. Thus, a recent study combining MD and cluster dynamics on the role of hydrogen has shown that during plastic deformation, a very large number of hydrogen-vacancy complexes could form and that would act as embryos for the formation of nano-cavities which are experimentally observed in hydrogen-embrittled steels [LI 15].

### 7.2.3. The Monte Carlo methods

The so-called Monte Carlo (MC) techniques, derived from statistical physics, have found many applications in materials science. The MC name comes from the fact that this method uses random numbers similar to those involved in games of chance. The use of sampling techniques is not recent, but the contribution made by Von Neumann and Ulam was to realize that deterministic mathematical problems (such as integral evaluation) could be solved by finding a probabilistic analogy which could then be solved using a random sampling technique [ALL 89]. In principle, only equilibrium situations can be studied using the classical Monte Carlo Metropolis algorithm [MET 53]. The underlying idea is to randomly generate microscopic configurations according to an equilibrium distribution known in advance (usually the canonical distribution, but sometimes also the grand canonical, etc.). In certain specific cases, when the microscopic mechanism that allows switching from one configuration to another is known, it is possible to introduce time into a Monte Carlo simulation. We are therefore dealing with the so-called kinetic Monte Carlo (KMC) algorithms. These algorithms are particularly well suited to study diffusion in solids.

#### 7.2.3.1. MC Metropolis

The Metropolis algorithm can generate microscopic configurations from a given initial configuration. The new configurations are generated in accordance with a probability law that often corresponds to a thermodynamic equilibrium distribution although this is not necessary in principle. In the case of the original Metropolis algorithm [MET 53], the probability law that generates the configurations is the canonical distribution.

From the practical point of view, it is assumed that the microscopic configurations  $S_0, S_1, \dots, S_{i-1}, S_i$  have been generated and so the next  $S_{i+1}$  configuration is what interests us:

- all the accessible configurations following the  $S_i$  configuration are determined;
- one of these configurations  $S'_{i+1}$  is randomly chosen;
- the energy of this new configuration is then compared to that of the previous one, that is,  $\Delta E = E(S'_{i+1}) - E(S_i)$ ,

– if  $\Delta E \leq 0$ , the new configuration is retained and  $S_i + 1 = S'_i + 1$  is obtained;

– if  $\Delta E > 0$ , the new configuration is accepted with the probability  $\exp\left(-\frac{\Delta E}{kT}\right)$

where  $T$  is the temperature and  $k$  the Boltzmann constant.

Thus, at each MC stage a single energy difference must be calculated, which, if the configurations are “topologically” close, can be evaluated quickly from a numerical point of view. But this algorithm is not very effective when the temperature decreases or when transition temperatures are getting closer. It should be noted that the Metropolis MC methods are often easier to implement than MD, but they do not generally provide access to the dynamic properties of the systems being studied. In order to obtain the reaction kinetics, a combination of the two methods is required as done by [KHA 09] to study the action of certain amino acids on the inhibition of mild steel corrosion in a sulfuric acid medium, or resort to the methods known as kinetic Monte Carlo.

A more accurate and detailed description of the method can be found in [ALL 89].

### 7.2.3.2. Kinetic MC at the atomic scale

In the Metropolis algorithm, at first glance, no “proximity” relation exists between the two successive configurations,  $S_i$  and  $S_i + 1$ . If, on the other hand, we are interested in the spatial configurations generated over time during a diffusion process, we notice that the chronological order of appearance of each new configuration is not arbitrary. Indeed, two successive micro-states differ only in the position of the diffusing defect (vacancy or interstitial for example) and which has moved by a jump length between the two configurations.

The random walk theory enables us to easily show that the probability for the residence time  $t_{\text{res}}$  of a defect in a site  $i$  to be  $t$  (knowing that the defect has arrived at the site being considered at  $t = 0$ ) follows a Poisson Law  $P(t = t_{\text{res}}) = \bar{\nu} \exp(-t\bar{\nu})$  where  $\bar{\nu}$  is the jump frequency. This relation is obtained by assuming that at any time  $t$ , the probability that the defect leaves its site between  $t$  and  $t + dt$  is  $\bar{\nu} dt$ . The Vineyard transition state theory [VIN 57] gives an expression for  $\bar{\nu}$  as a function of microscopic parameters (activation/migration barriers and vibration frequencies).

The residence time algorithm [YOU 66, BOR 75] is based on the above considerations. From a given configuration,  $S_i$ , all the possible successive configurations  $S_{i+1}^j$  obtained are determined by moving the defect, which diffuses from a jump length in each of the possible jump directions, each jump being performed with a jump frequency  $\Gamma_{ij}$ .

Then, a jump among the possible jumps remains to be chosen and this is done by juxtaposing the jump frequencies along a segment and a random number  $\zeta$  is chosen between 0 and  $\sum_j \Gamma_{ij}$ . The selected jump,  $k$ , is the one that verifies the relation

$\sum_{j=1}^{k-1} \Gamma_{ij} \leq \zeta < \sum_{j=1}^k \Gamma_{ij}$ . Thus,  $S_{i+1} = S_{i+1}^k$  and the average time step  $\Delta t$  associated with residence in site  $i$  can be approximated by  $\Delta t = \frac{1}{\sum_j \Gamma_{ij}}$ . The macroscopic time

accessible by the KMC is large.

Thus, for example to model the evolution of a group of vacancies, it can be assumed, such as in Young and Elcock’s model [YOU 66], that the diffusion is carried out through vacancy jumps onto neighboring first sites according to a thermally activated process with a frequency:

$$\Gamma_{i,j} = \nu \exp \left\{ -\frac{E_{a_i}}{kT} \right\} \quad [7.2]$$

$\nu$  is the attempt frequency which is supposed to be independent of the alloy configuration,  $E_{a_i}$  is the activation energy, that is, for an atom, the energy necessary to arrive to the saddle point.

Atomic kinetic Monte Carlo has been used extensively to study precipitation phenomena [BEC 18], and phase transformations.

For example, from the corrosion point of view, atomic kinetic Monte Carlo has been recently used to model the formation of crevices on a (100) surface of pyrite ( $\text{FeS}_2$ ) [HER 14] as a function of the temperature and in a reducing environment, the dissolution of the Fe-Tc [TAY 13] or Mo-Tc [KIM 13] systems or the formation of an oxide film on metal surfaces [DIA 10]. On the other hand, a review article on atomic scale modeling (*ab initio*, DM and KMC) of corrosion mechanisms is found in [TAY 12].

## 7.3. Mesoscopic scale

### 7.3.1. Object Kinetic Monte Carlo (OKMC)

As a generalization, the method described above can be applied not only to vacancies, but also to “objects” (vacancies, vacancy clusters, dislocation loops, interstitial clusters, etc.). The objects can be subjected to different types of events:



jumps, dissociation, agglomeration, etc. The jumps or dissociations are considered thermally activated processes characterized by an activation energy  $E_{a,n,i}$  and an attempt frequency  $V_{n,i}$ . The occurrence frequency (incorrectly referred to as “probability”)  $\Gamma_{n,i}$  (of the object  $n$  and the reaction  $i$ ) is then given by:

$$\Gamma_{n,i} = V_{n,i} \exp\left\{-\frac{E_{a,n,i}}{kT}\right\} \quad [7.3]$$

The objects can move on a rigid network or not according to the residence time algorithm. During the simulation a number of events can arise with a certain probability which is given by the often incorrectly named occurrence frequency. The types of events that objects can experience are:

- **migration**: a mobility governed by an Arrhenius law is associated with defect clusters. This mobility depends on their size and nature;
- the **recombination** between two objects. In the case where the objects are of the same type (vacancies or interstitials), the result of the recombination is an object of the same type but larger. When objects are of different types, recombination leads to the formation of a smaller final object of the same type as the largest initial object. Objects of different types and identical size are annihilated;
- the **dissociation** (when the object is sufficiently large and the dissociation is authorized) by emission of an entity;
- the **interaction/trapping** by impurities (C, N, etc.) or elements belonging to the microstructure such as dislocations, grain boundaries, etc.;
- **annihilation** on free surfaces.

Tohgo *et al.* [TOH 09] used this type of approach to develop a method for modeling the initiation and coalescence of microcracks; this method has also been recently used by Fujii *et al.* to study the stress corrosion of high temperature 304 steel in an aqueous environment [FUJ 15].

### 7.3.2. Cluster dynamics or chemical kinetics

Cluster dynamics, sometimes referred to as chemical kinetics, is a mean-field approach, very similar to object kinetic Monte Carlo, where only the evolution of cluster concentrations is considered. The evolution of these concentrations is governed by a system of coupled differential equations which describe both the growth and the dissolution of clusters due to reactions with mobile or solute defects, emission of these same species, and cluster coalescence if the clusters are mobile.

Cluster dynamics is a widely used method for modeling materials under irradiation and a typical example is the study of the formation of helium or hydrogen bubbles in structural materials such as tungsten or iron and the impact of stress on their growth as in [SHA 09].

### 7.3.3. The phase field method

The phase field method is a powerful numerical approach to modeling the evolution of material microstructures at the mesoscopic scale. It was initially used to solve all kinds of problems in materials science such as solidification and solid-state phase transformations. For example, in the latter case, it not only provides access to the size of the precipitates, their morphology but also their layout. In fact, the phase field method can be applied to the study of any chemical or structural heterogeneity that may appear in materials: dislocation loops, grain boundaries, cavities, bubbles, etc. This is the reason that has enabled it to be generalized for the study of the evolution of dislocations, crack propagation, microstructures under irradiation, etc. Moreover, given its mesoscopic nature, it fits naturally into multi-scale coupling, requiring input data computable by atomic approaches: elastic constants, interface energies, mobilities, lattice misfit, etc. When calculating a microstructure, it can provide input data to determine macroscopic properties such as porosity, thermal conductivity, etc.

The development of a phase field model is generally divided into three steps:

1) defining one or more variable fields that depend on time and which are referred to as order parameters (OP). Whatever their number, they must be chosen in such a way that knowledge of their value at any point in space  $\mathbf{r}$  at a given time  $t$  allows the complete description of the microstructure. There are two types of order parameters:

- the **conserved** order parameters, denoted  $c_i(\mathbf{r},t)$ , and which are referred to as such because they obey a conservation law. This is for example the case of an atomic fraction of solute in an alloy where the evolution is governed by a diffusion equation.

- the **non-conserved** order parameters, denoted  $\eta_j(\mathbf{r},t)$ , which do not obey any conservation equation, such as the long-range order parameters characterizing the crystallinity of a phase or the orientation of a grain.

A key point is that these fields take definite volume values, and that they continuously vary between these values through **diffuse interfaces**. In this approach, interface tracking is naturally taken into account with the resolution of the OP's evolution equations, which avoids the heavy numerical treatment often required by

approaches based on steep interfaces. The phase field method is thus able to simulate complicated microstructures such as dendrites;

2) the second step consists of expressing a **thermodynamic potential**,  $F$ , as a function of the OPs defined above; this potential by definition reaches a minimum at equilibrium. It generally includes two contributions: an  $F_{SR}$  contribution that integrates short-range chemical interactions and an  $F_{LR}$  contribution that integrates long-range interactions (elastic, magnetic, etc.):

$$F = F_{SR} + F_{LR} \quad [7.4]$$

$$F_{SR} = \iiint_V [f_{hom}(c_1, \dots, c_n, \eta_1, \dots, \eta_p) + \sum_{i=1}^n \frac{\alpha_i}{2} (\nabla c_i)^2 + \sum_{j=1}^p \frac{\beta_j}{2} (\nabla \eta_j)^2] dV \quad [7.5]$$

$f_{hom}$  is an energy density that incorporates short-range interactions while the gradient terms, non-zero only at the interfaces, may be related to the interface energy.  $\alpha_i$  and  $\beta_j$  are the stiffness coefficients.  $F_{LR}$  is usually more difficult to calculate. In the case of elastic interactions, each element of the microstructure (dislocations, precipitates, cracks, etc.) is assigned its own eigenstrain tensor (misfit between the lattice parameters of two different phases in the simplest case) which will generate an elastic field. This field interacts with the elastic deformations induced by the other microstructure elements. The elastic interactions can be determined analytically in the Fourier space according to the methodology developed by Khachaturyan [KHA 83]. The great diversity of phase field models seen in the literature arises from the different contributions used to describe the potential  $F$ ;

3) the final step is to calculate the system's kinetic evolution using the Cahn-Hilliard equation [CAH 58] for the conserved parameters and the Allen-Cahn equation [ALL 72] for non-conserved parameters:

$$\frac{\partial c_i}{\partial t} = M_i \nabla^2 \frac{\delta F}{\delta c_i}; \quad \frac{\partial \eta_j}{\partial t} = -L_j \frac{\delta F}{\delta \eta_j} \quad [7.6]$$

Where  $M_i$  and  $L_j$  are mobility tensors obtainable through calculations at the atomic scale.

The phase field method is used to solve all kinds of problems in materials science such as solidification, solid-state phase transformations, growth and coalescence, dislocation microstructure evolution, crack propagation and the evolution of microstructures under irradiation. For the more curious reader we recommend, for example, the article by Singer-Logovina and Singer [SIN 08], Chen's article [CHE 02] or Bellon's chapter [BEL 12].

The limits are related to the mesoscopic nature of the phase field models, which cannot be substituted for atomic methods to obtain certain data already mentioned above (interface energies, dislocation core, etc.). In addition, time and space scales are usually too large to handle nucleation in the right way, but too small compared to macroscopic scales. It is therefore necessary to combine phase field models with higher scale models.

From the corrosion point of view, this method, which allows the environment, the stresses and the microstructure to be easily taken into account, has been used to study different types of corrosion: stress corrosion [NGU 17, STA 15], pitting corrosion [MAY 16],  $V_2O_5$  corrosion [ABU 15], etc.

#### **7.3.4. Dislocation dynamics (DD)**

The purpose of dislocation dynamics models is to simulate the collective behavior of dislocation lines in interaction. In this sense, these models are close to MC codes that do not simulate all the atoms in the crystal lattice, but rather each of the linear defects, that is the dislocations.

##### **7.3.4.1. The models**

The first models were constructed in 2D [FOR 67, VAN 95] and the first 3D models appeared in the 1990s [KUB 90]. At present about 10 codes have been developed around the world including the French codes mM [LAB 11], the 3D Discrete Dislocation Dynamics code [NUM 18b] and the Numerical Model for Dislocations [NUM 18a]; the US codes ParaDis [MIC 18], the Multiscale Dislocation Dynamics Plasticity code [CMM 18], Paranoid [SCH 99], PDD [GHO 00]; and the German code from [WEY 02]. Although there are some differences between these codes, the general principle is similar and is based on three stages: 1) discretization of the dislocation lines into elementary entities; 2) calculation of the line mobility from the interaction forces; 3) management of the events arising during the line movement.

Let us look at them in detail:

1) For the line discretization, two large families of discretization models are seen:

i) the screw-edge model [NUM 18b] and its extended version: screw-mixed-edge [LAB 11, MAD 01] for which the lines are cut into elementary segments where the orientation defined by the angle between the line and the Burgers vector is arbitrarily fixed;

ii) the nodal codes for which the dislocation lines are built on support nodes [MIC 18, CMM 18, NUM 18a]. In these nodal codes, the dislocation lines are made up of segments in any orientation linking two nodes; however, some more

elaborate models propose descriptions in terms of cubic spline functions [GHO 00] which have the advantage of preserving the continuity of the derivative in each node.

2) The dislocation theory is applied for the calculation of the interaction forces and the mobility law [FRI 64, HIR 82], which is established within the linear elasticity setting, although dislocations are the plasticity propagation vectors. The dislocation lines are comparable to elastic inclusions immersed in a matrix which is also elastic. They interact with each other through the stress fields they create in the simulated environment.

In the linear elasticity theory setting, the effective stress tensor  $\boldsymbol{\sigma}_{eff}$  can be evaluated at any point of the crystal resulting from the superposition of the applied stress tensor  $\boldsymbol{\sigma}_{app}$  with the tensor of the internal stresses  $\boldsymbol{\sigma}_{int}$  generated by the dislocations. The force per unit length generated by this stress field on a segment of the unit line vector  $\mathbf{dl}$  and the Burgers vector  $\mathbf{b}$  is calculated using the Peach-Koehler formula [PEA 50]:

$$\mathbf{F}^{PK} = \boldsymbol{\sigma}_{eff} \cdot \mathbf{b} \wedge \mathbf{dl} = (\boldsymbol{\sigma}_{app} + \boldsymbol{\sigma}_{int}) \cdot \mathbf{b} \wedge \mathbf{dl} \quad [7.7]$$

We deduce the effective shear stress,  $\tau$  resolved on the slip-plane of the segment by projecting this force along the normalized flight direction  $\mathbf{g}$  and the climb component  $\sigma_n$  pushing the dislocation outside its slip-plane by projecting along the slip-plane normal  $\mathbf{n}$ :

$$\tau = \frac{1}{b} \mathbf{F}^{PK} \cdot \mathbf{G} \quad ; \quad \sigma_n = \frac{1}{b} \mathbf{F}^{PK} \cdot \mathbf{n} \quad [7.8]$$

The segment mobility is then calculated from these components. The simplest case adheres to the following linear relationship:

$$v = \frac{\tau b}{B} \quad [7.9]$$

for which the viscous friction coefficient  $B$  models the dissipations due to the interactions with the phonons. This law is generally used to simulate face-centered cubic materials. For other crystallographic structures, such as centered cubic (CC), the mobility law strongly depends on the dislocation's temperature and nature. Thus, the double-kink mechanisms that make it possible to move the screw dislocation of a Peierls valley to the next, are modeled by analogy with the elastic cord theory [DUE 69, LOU 79] using the following thermally activated expression:

$$v = v_D L \left( \frac{b}{l^*} \right)^2 \exp \left[ \frac{-\Delta G(\tau)}{kT} \right] \quad [7.10]$$

where  $v_D$  is the Debye frequency,  $L$  the length of the dislocation considered,  $l^*$  the length of a stable double kink,  $k$  the Boltzmann constant,  $T$  the temperature and  $\Delta G(\tau)$  the activation energy. This energy is usually determined from temperature jump tests. A phenomenological expression often used is Kocks' law [KOC 75]:

$$\Delta G(\tau) = \Delta H_v \left[ 1 - \left( \frac{\tau}{\tau_0} \right)^p \right]^q \quad [7.11]$$

Expressions [7.9] and [7.10] are conservative mobility laws that consider dislocations to move in their slip-plane defined by the plane containing the line and its Burgers vector. When diffusion phenomena are introduced, such as, for example, a high temperature or irradiation flux, the velocity vector may have a non-conservative component outside the slip-plane which depends on the vacancy concentrations diffusing on the dislocation lines [MOR 08, KER 15]. Ideally, the vacancy concentration at any point in the simulated volume would then be estimated by solving the diffusion equations, for example by a finite element method [LIU 17] or using FFT techniques [GAO 17].

3) For managing the events, a DD code must be able to take care of all possible collision events during the dislocation segment displacement. When a dislocation segment of length  $L$  moves on a given slip system, it sweeps a flight area  $dA = L.v.dt$  which increases the cumulative plastic deformation on this system according to Orowan's equation:  $d\gamma^{(s)} = b.dA/V$  from which the whole plastic deformation tensor is reconstructed.

If the segment encounters another dislocation, the different possibilities of creating a junction resulting from the recombination of the dislocation lines must be considered. The segment may also encounter a grain boundary, a precipitate or any other limit condition that must be managed through local rules.

Dislocation Dynamics codes manage time scales and intermediate spaces between atomic (MD) and continuous (FE) models. In fact, DD is a particularly interesting tool for multiscale modeling, widely used in a bottom-up approach, for example to determine constitutive laws which are reliable at the macroscopic scale, and can be used by finite element techniques or when studying the mechanical behavior of confined environments. Nevertheless, the model has limits that are difficult to get around. The first limitation concerns the computation time which can quickly become prohibitive as soon as the number of dislocation segments becomes

too large. In fact, unlike atomic simulations (see section 7.1.2), the number of degrees-of-freedom to be managed during a DD simulation increases with plastic deformation due to the lengthening of the dislocation lines that bend and multiply under the effect of the applied stress. The direct consequence is that the computation time required to perform a simulation step increases more and more. This is partially remedied by deploying the code on parallel architectures and the challenge is therefore to build a parallel code with very high scalability [MIC 18]. Another important limitation of DD models is the taking into account of large deformations. In fact, all the DD codes assume that the network on which the dislocation lines are moving is rigid while in reality, the dislocation displacement disrupts the position of the entire solid domain located each side of its flight area. Therefore, the collective movement of thousands of dislocations causes a distortion of the crystal lattice that cannot yet be taken into account because it would require updating the orientation of the crystal lattice and managing the jogs printed on the intersecting dislocation lines.

A reference work for this method is the book by Bulatov and Cai [BUL 06].

Many corrosion studies have been conducted using 2-D DD. A first application of the 3-D DD was able to quantify the effect of hydrogen on the dislocation movement [GU 18].

## 7.4. Macroscopic scale: crystal plasticity

At the macroscopic scale, the material is seen as a continuous medium. The finite element method based on this hypothesis makes it possible, by discretizing the geometry, to obtain the approximate solutions of the partial differential mechanical and physical equations. The polycrystalline heterogeneities of the metals are taken into account through the specific constitutive laws of crystalline plasticity based on the fact that plastic strain results from dislocations slipping under the effect of an applied stress. Crystal plasticity is the name given to the modeling at the continuous scale for which the constitutive laws are written by slip systems, as opposed to the “von Mises” plasticity models which do not make this distinction.

### 7.4.1. The models

#### 7.4.1.1. Slip systems

We have seen in Chapter 1 that dislocations are linear defects that move in the crystal's dense planes and propagate a displacement called the Burgers vector,  $\mathbf{b}$ . This vector shears the crystal by translating the upper part relative to the lower part of the plane containing the dislocation. The Burgers vector is therefore contained in the slip plane and the plastic deformation generated by the movement of the

dislocation line is a pure shear that occurs at constant volume. A slip system is therefore defined by the  $(\mathbf{b}, \mathbf{n})$  couple where  $\mathbf{n}$  is the dislocation's slip-plane normal. Thus, for the face-centered cubic (FCC) structures, there are four dense planes of the  $\{111\}$  family and six Burgers vectors of the  $a/2 \langle 101 \rangle$  family, where  $a$  is the crystal's lattice parameter. There are therefore 12 slip systems (often identified using the Schmid and Boas notation). For each dense plane of the FCC network, there are three coplanar systems, that is, three possible shear directions within the same plane. Similarly, each Burgers vector is shared by two slip planes. Thus a dislocation may potentially change its slip plane. The only requirement is that the line direction is contained in the two slip planes, forcing it to be oriented in the Burgers vector direction  $[110]$  and thus implies that it is a screw dislocation. The direct consequence is that a screw dislocation of the FCC network can change its slip plane, which is the cross-slip mechanism.

#### 7.4.1.2. *Crystal plasticity formulation*

The classical crystal plasticity models often rely on a multiplicative decomposition of the transformation gradient into an isoclinic plastic part and an elastic part according to the approach proposed by J. Mandel [MAN 71]. The details of the crystal plasticity tensor formalism are beyond the scope of this book, but the reader is invited to read S. Forest's continuum mechanics course available on the Ecole des Mines de Paris website.

The key point of the tensor formulation relates to the constitutive law connecting the stress tensor to the deformation tensor.

In the next two sections, we present two main families of constitutive laws available for FCC structures: physically based laws for which each equation is based on local dislocation movement considerations and a much simpler set of phenomenological laws which have proved to be very efficient for modeling complex behaviors. More details on the differentiation of the various equations are available in the journal article [FIV 04].

#### 7.4.1.3. *Physically-based crystal plasticity laws*

Considering the landscape of shear stresses applied on a dislocation moving on a slip system  $s$ , we can split the stress actually perceived by the dislocation while in motion into a long-range athermal component  $\tau_{\mu}^s$ , and a thermally-activated component  $\tau^{*s}$ , reflecting the local obstacles that must be overcome by the dislocation in order to progress:  $\tau^s = \tau_{\mu}^s + \tau^{*s}$  with  $\tau^{*s} \ll \tau_{\mu}^s$ . By neglecting the flight time of the dislocation before its waiting time on the obstacles, its speed is written as:



$$v = \frac{bv_D}{\exp\left(\frac{\Delta G_0}{kT}\right) \left[ 2\text{sh}\left(\frac{\tau^{*(s)} \Delta V^*}{kT}\right) \right]^{-1}} \quad [7.12]$$

where  $T$  is the temperature,  $v_D$  the Debye frequency,  $\Delta G_0$  the activation energy at 0K and  $\Delta V^*$  the activation volume. Assuming that the average velocity of all mobile dislocations on the system  $s$  (with density  $\rho_m^{(s)}$ ) is written in the same form, Orowan's law gives the shear rate:

$$\dot{\gamma}^{(s)} = \rho_m^{(s)} b \bar{v}^{(s)} = \frac{\rho_m^{(s)} b^2 v_D}{\exp\left(\frac{\Delta G_0}{kT}\right) \left[ 2\text{sh}\left(\frac{\tau^{*(s)} \Delta V^*}{kT}\right) \right]^{-1}} \quad [7.13]$$

If we assume that the stress applied is moderate, the probability of inverse jump can be neglected to only keep the positive term of sh. Finally, a limited development gives an expression in the classical power law:

$$\dot{\gamma}^{(s)} = \rho_m^{(s)} b^2 v_D \exp\left(\frac{-\Delta G_0}{kT}\right) \left(\frac{\tau^{(s)}}{\tau_\mu^{(s)}}\right)^{\frac{\tau_\mu^{(s)} \Delta V^*}{kT}} = \dot{\gamma}_0^{(s)} \left(\frac{\tau^{(s)}}{\tau_\mu^{(s)}}\right)^{1/m} \quad [7.14]$$

It is a purely viscous flow law (with no threshold) that links the shear strain rate to the shear stress on a system  $s$ .

In this equation,  $\tau_\mu^{(s)}$  is an isotropic hardening stress that evolves with the dislocation density stored on all slip systems according to the formula:

$$\tau_\mu^{(s)} = \mu b \sqrt{\sum_{u=1}^{12} a_{su} \rho^{(u)}} \quad \text{where} \quad \dot{\rho}^{(s)} = \frac{1}{b} \left( \frac{\sqrt{\sum_{u=1}^{12} d_{su} \rho^{(u)}}}{K} - 2\beta R \rho^{(s)} \right) \dot{\gamma}^{(s)} \quad [7.15]$$

which involves an interaction matrix  $\mathbf{a}$  between the systems. The system of equations is completed with the dislocation density evolution law which can be proved by assessing the different dislocation densities [FIV 04]. In this equation,  $K$  is the mean free path of the dislocations,  $\mathbf{d}$  an interaction matrix similar to  $\mathbf{a}$  and  $\beta R$  a capture radius between dislocations of opposite signs. Note that this equation

includes a production term and an annihilation term of the dislocation densities. As a result, when these two terms are equal, the dislocation density will saturate in the same way as the isotropic hardening stress  $\tau_\mu^s$ .

Finally, the physically based constitutive law is completely described by this set of three equations. This law is classically programmed in user routines (UMAT) for finite element codes, which simply requires writing the derivative of the hardening law as a function of the strain rate:

$$\dot{\tau}_\mu^{(s)} = \sum_{u=1}^{12} \left\{ \frac{\mu a_{su}}{2 \sqrt{\sum_{p=1}^{12} a_{sp} \rho^{(p)}}} \left( \frac{\sqrt{\sum_{q=1}^{12} d_{uq} \rho^{(q)}}}{K} - 2\beta R \rho^{(u)} \right) \dot{\gamma}^{(u)} \right\} = \sum_{u=1}^{12} h_{su} \dot{\gamma}^{(u)} \quad [7.16]$$

to find a classical formalism of phenomenological models.

Finally, it should be noted that this constitutive law was created by only taking into account monotonous loading paths, that it only comprises isotropic hardening and that no kinematic hardening component has been introduced. To date, there is no physically-based law that models kinematic hardening in a general way. Some developments have been made in particular cases such as piling at grain boundaries or oligocyclic fatigue.

#### 7.4.1.4. Phenomenological crystal plasticity laws

Simultaneous to the development of these physical laws, solid state experts have also developed constitutive laws for single crystals taking into account the plasticity's discrete nature for the different slip systems. The reader interested in a general view of these developments may read Asaro's review [ASA 83]. For small strains, the viscoplasticity flow law is written as:

$$\dot{\gamma} = \left( \frac{|\tau^{(s)} - X^{(s)}| - \tau_c^{(s)}}{k} \right)^n \cdot \text{sign}(\tau^{(s)} - X^{(s)}) \quad \text{where } \langle x \rangle = \begin{cases} x & \text{if } x > 0 \\ 0 & \text{otherwise} \end{cases} \quad [7.17]$$

In this equation,  $\tau_c^{(s)}$  is the isotropic hardening variable and  $X^{(s)}$  the kinematic hardening component. Just as for the previous model, the system of equations will be complete if we specify the evolution of these two components. The kinematic hardening evolution law will have to be identified using fatigue or Bauschinger tests.

The continuous plasticity models presented above have a relatively large number of applications. The physically-based models are, at present, limited to isotropic hardening cases and still have difficulty simulating kinematic hardening. On the other hand, the simplified model has demonstrated its ability to simulate fatigue tests through the precise identification of kinematic hardening laws. These two groups of models can be used for corrosion studies if we add diffusion equations modeling the distribution of the concentrations of the different envisaged elements to the viscoplasticity constitutive laws. For example, the macroscopic multi-physics approach is used to determine the background hydrogen concentration in finite element calculations [KRO 99] which will be discussed in more detail in Chapter 18.

## 7.5. Conclusion

The different techniques presented here are complementary and which one is selected strongly depends on the problem to be dealt with, the mechanisms to be modeled and the amount of detail required for the elementary mechanisms. Most of the time, the upper-scale methods benefit from the results of the lower scales providing physical quantities and/or information on the fundamental physical mechanisms.

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