



Numerical Analysis of Chemo-Mechanical Couplings in Geomaterials at the Microscale

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Abstract

To reduce the impact of human activities on climate change, engineering applications envision the injection of fluid into underground reservoirs, resulting in a modification of the chemical composition of the pore water. This destabilization can instigate an evolution of the microstructure of the host material through local dissolution/precipitation reactions, impacting the mechanical parameters at the sample scale. The development and application of numerical models, which explicitly describe the microstructure, have emerged as a promising method for enhancing our comprehension of the interactions between mechanics and chemistry along the different scales involved. Indeed, the local addition/removal of mass (chemistry) occurs at the scale of the microstructure. Subsequently, the mechanical properties at the sample scale evolve while the morphology of the grains and the microstructure are modified.

This study focuses on three phenomena involving chemo-mechanical couplings: the debonding of sedimentary rocks, the hydration of a cement-based material, and the pressure-solution phenomenon. In these investigations, the chemistry is captured with a Phase-Field description, while the mechanics are modeled with a Discrete Element or Finite Element Model. Furthermore, these formulations have been coupled to develop the Phase-Field Discrete Element Model, a formulation available to capture (i) granular reorganization, (ii) irregular grain shape, (iii) force transmitted at the contacts, (iv) heterogeneous dissolution/precipitation, (v) diffusion of the solute in the pore space and (vi) rate-limiting processes.

This thesis depicts the pivotal impact of chemistry on the mechanical characteristics of a geomaterial. Notably, the state of stress of a cemented granular material appears impacted by the dissolution of bonds. In a similar vein, the mechanical properties of a cement-based material can be deduced from the evolution of the microstructure modeled explicitly during the hydration process. Finally, the novel Phase-Field Discrete Element Method has been calibrated and validated with experimental data available in the literature for the pressure-solution phenomenon. Furthermore, the impact of the precipitation and granular reorganization, which have been frequently neglected in the literature, on creep behavior due to pressure-solution has been emphasized.

1

Introduction

The Paris Agreement, signed in 2016, delineated the objective of limiting the rise in global surface temperature to well below 2°C , with a preference for a 1.5°C limit [UNF15]. However, 2023 and 2024 were two record-breaking years in terms of global temperatures, with 2024 surpassing the 1.5°C above the preindustrial level [Cop24]. The consequences of climate change are numerous, with a multitude of recent notable events, including floods, heatwaves, and wildfires [Los24, CSvL⁺25, RBR⁺24, Smi24].

To diminish the impact of human activity on climate evolution, one approach involves the utilization of renewable energy sources, such as wind and solar power, to generate electricity. However, these energy sources are characterized by variability of energy production, necessitating the development of strategies for energy storage and utilization. A promising approach involves the transformation of excess energy into H_2 . The challenge, however, lies in identifying suitable methods to store the produced H_2 , which must be subsequently extracted and consumed during periods of energy deficiency. It has been posited that underground storage and salt caverns hold considerable promise for this purpose, offering a greater storage capacity than conventional aboveground infrastructure such as pipelines or tanks [HAM⁺23, RKHC⁺23]. Likewise, geothermal energy appears as an efficient method to produce energy, and it is defined as the injection of a fluid underground to extract the thermal energy of the Earth [MST16, Bar02]. Furthermore, deep aquifers have emerged as a promising medium for the sequestration of greenhouse gases, in-

cluding CO_2 [KGB⁺24]. This engineering application, added to the emergence of renewable energy production, participates in the reduction of the impact of human activities on climate change. If H_2 storage and geothermal energy production involve a fluid injection and extraction, CO_2 sequestration implies only injection, necessitating underground retention. To assess the viability of the H_2 storage and CO_2 sequestration techniques, various pilot projects have been initiated [GAO⁺18, Car07, HyP21, INH⁺19].

As depicted in Figure 1.1, the injection of the fluid into a geomaterial reservoir induces a modification of the fluid chemical composition, and thus its reactivity with the surrounding solid phases, activating or enhancing chemical processes [LSPDB12]. The consequences are numerous: settlement at the surface [LGRH⁺07, BSPH14], modifications of the mechanical [WLS16, RKHC⁺23] and hydraulic [Hue05, VPFW13, LPV20a] properties or threat to the stability of the caprock [RPR16, MR16]. It has even been correlated to earthquake nucleation [BCJ⁺18, RV20, RDSV21, LSD⁺23]. These phenomena and consequences observed in the context of the previously described engineering applications are similar to the numerous examples in nature where geomechanics and chemistry appear deeply intertwined, such as weathering [PR73, VK84], cementation [DMN91, PC04], and pressure-solution [TS89, BRS89]. Even if the kinetics of the natural processes is much slower than the kinetics of the engineering-induced consequences, *Terzaghi* pointed out that long-term phenomena are the main causes of the instabilities rather than single events [Ter50], requiring investigation.

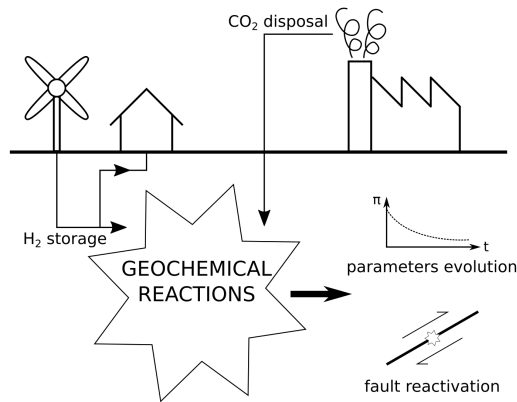


Fig. 1.1 Underground storages are envisioned by engineering applications to reduce the impact of human activities on global warming.

The correlation between chemistry and mechanics is not the sole coupling in geomechanics. Numerous other physical phenomena, such as the temperature effect [JCB⁺16, SCC23, WPW⁺24, VDT⁺21, VDT⁺20] or the impact of the fluid pressure [SRV20, CGBLC24, YKJ⁺25, APT⁺14, AFY⁺24], can be incorporated into the analysis. A comprehensible review of the role of the multiphysics phenomena in instabilities in geomaterials has been published by Hueckel in 2021 [Hue21]. However, the ensuing discussion will center on chemo-mechanical couplings and investigate how they can be considered in numerical models.

The chemo-mechanical couplings involve along several scales a multitude of processes, such as dissolution, precipitation, diffusion, or granular reorganization for example, [GCH15, BD16, LPV20a, LRV22, HH07]. For instance, chemical reactions occur at the grain scale, thereby affecting the mechanical properties of the sample, and potentially inducing mechanical failure at a larger scale. Consequently, the initial scale of this study is the grain scale, where mass removal/addition and microstructure reorganization occur. Subsequently, the properties are upscaled to the macroscopic scale, allowing the simulations and the predictions of engineering applications.

While experimental campaigns remain the optimal strategy for identifying novel phenomena in geomechanics, a comprehensive understanding is predicated on the model of diverse physics. In this regard, the numerical laboratory offers a safer, more economical, and more expeditious tool with which to explore phenomena. As depicted in the following with several examples, it appears difficult to reproduce the temperature, pressure, and time exposure conditions involved at the depth of the underground reservoir. Furthermore, classical mechanical tests often restrict access to the sample, and the acquisition of data appears limited.

For an example of this approach, see *Harmon et al.*, who have developed a digital twin of a 160-meter multiblock tower to predict its behavior during seismic events [HGR⁺23]. Even if the physics at stake is mechanics only, this investigation remains a relevant illustration of the power of numerical analog. While experiments could have been conducted to achieve similar outcomes, they would necessitate a substantial spatial commitment for setup and execution. Moreover, conducting simulations appears considerably more economical than producing the necessary 7144 concrete blocks (measuring $1.36 \times 2.82 \times 4.25$ m). This numerical approach also appears to be safer than an experimental configuration. In the context of chemo-mechanical problems, where hazardous chemical products can be employed, the development of numerical analogs is favored. For instance, a lot of experimental research is

conducted on concrete material to optimize notably its formulation, see Section 1.2 and Chapter 3. However, it is important to note that concrete is a product that can induce chemical burns, and the development of numerical models offers a safer alternative for exploration [BGB⁺06].

Likewise, Wang *et al.* developed a numerical model for the fragmentation of zeolite granules under compression based on XCT observations [WKA19]. While these experiments might be considered easier to conduct than constructing a 160-meter tower, the particle breakage inherent in the experiments does result in material loss. The development of a numerical analog facilitates the exploration of different configurations without material constraints. This numerical approach is particularly advantageous in the context of chemo-mechanical couplings, where material changes occur by dissolution/precipitation. This inherent nature of chemical reactions is often irreversible. In the case of debonding, see Section 1.1 and Chapter 2, the bond material is dissolved and can not be retrieved. Similarly, in the case of cement hydration, see Section 1.2 and Chapter 3, the microstructure evolves with the consumption of the source material and the generation of the bonds between the aggregates. In the same vein, the pressure-solution phenomenon depicted in Section 1.3 and Chapters 5-7 induces a shape evolution of the grains. The microstructure evolution appears unilateral, and not reversible.

In other configurations, the numerical approach proposes a time-saving option. Pinzón *et al.* investigated experimentally the mechanical behavior of an inherent anisotropic specimen composed of anisometric particles under tri-axial compression [PADV23]. To prepare the granular sample, lentils were deposited into a given orientation, and this operation was made by hand. Utilizing a numerical model [PPW⁺23, WPAV21] offers a substantial reduction in the time required. This advantage is particularly pronounced in the context of chemo-mechanical problems, where reactions can extend over several weeks/months/years, as evidenced by the weakening of the host rock due to CO₂ sequestration, see Section 1.1 and Chapter 2, the hydration of the concrete, see Section 1.2 and Chapter 3, or the pressure-solution phenomenon, see Section 1.3 and Chapters 5-7.

However, it is imperative to recognize that the utilization of a numerical model, by itself, is insufficient. Indeed, it is essential to ensure that the model's predictions are validated through an experimental campaign. The integration of experiments and models to create a synergistic approach is a promising avenue for advancement. For instance, Hurley *et al.* have developed a framework that quantifies interparticle forces from experimental granular materials by combining imaging techniques and governing equations

[HMRA14, HHAW16]. Conversely, once validated, numerical twins can be utilized independently. For instance, a one-to-one avatar of a Hostun sand has been employed to explore shear banding [KAVA18] or necking [CKTA25] problems during triaxial experiments. It should be noted that this numerical approach incorporates additional information, such as the internal stress state within the specimen, compared to experiments. This methodology has also been utilized in the investigation of an Ottawa sand specimen under oedometric conditions, with a focus on the chain force during grain crushing phenomena [HSBA24]. Moreover, the numerical laboratory has been found to facilitate more efficient grain tracking than scanning experiments. This approach is particularly advantageous in problems involving rapid compaction of granular materials, where conventional imaging techniques are unable to scan the interior of a sample at high frequencies [TGH24].

The present work focuses on three cases that induce chemo-mechanical couplings: the debonding of a cemented granular sample (Chapter 2), the hydration of a concrete material (Chapter 3), and the pressure-solution phenomenon (Chapters 4, 5, 6 and 7). These phenomena are investigated using existing and newly developed numerical models, considering the couplings between chemistry and mechanics at the microscale. These explorations offer new insight into the behavior of geomaterials under chemical solicitations.

It should be noted that these three cases are not an exhaustive list of chemo-mechanical couplings in geomechanics. For instance, soil improvement methods employ microbially induced carbonate precipitation (MICP) [GCH19, ZD23, TLF⁺24] to enhance the performance of soils by generating bonds between grains. Furthermore, volcanic flank collapses appear to be induced by volcanic and non-volcanic processes [Det16, NDH⁺23, DDR⁺23, DHOD15]. Indeed, hydrothermal alterations occur and modify mineralogical, physical and mechanical properties of the volcanic edifice, activating the failure of the sector and the production of debris avalanche. Similarly, chemical reactions occur in concrete between the reactive silica from the aggregate and the alkalis in the pore solution [FSC⁺19, FB13, MGN20]. This reaction produces a gel, which tends to fill the void space. However, the gel exerts a supplementary pressure on the material once this available space is filled, generating cracks in the material and reducing the mechanical properties of the sample. It appears that an extended range of materials and configurations is impacted by these chemo-mechanical couplings.

Summary and objectives concerning the chemo-mechanical couplings

In the context of the fight against global climate change, underground storage appears as a promising technique for temporarily or permanently storing fluids such as H_2 or CO_2 . However, these injections lead to locally perturbing the chemical equilibrium between the reservoir material and the underground fluid. These induced chemical reactions impact the mechanical parameters of the material along several scales (even if other physics are involved, hydraulic for instance, this thesis is restricted to the mechanics).

Even if experiments represent a relevant approach to investigate the chemo-mechanical couplings, the development of numerical models allows for controlling the conditions of the couplings. Moreover, the numerical laboratory offers a safer, more economical, and more expeditious environment with no restrictions on data acquisition.

This thesis explores strategies to investigate, at the microscale, chemo-mechanical couplings involved in the context of underground storage through three distinct cases: the debonding of a cemented granular material, the hydration of a concrete material, and the pressure-solution phenomenon.

1.1 The impact of debonding on a cemented granular material

As previously explained, the majority of rocks are susceptible to weathering, particularly in engineering applications such as underground storage or geothermal energy. The injected fluid reacts with the surrounding rock, inducing dissolution and/or precipitation that affects the permeability of the rock [LPV20b, FMCM⁺07], its mechanical behavior [RKHC⁺23, NCT03], and its stress state [SSC08].

The impact of weathering on the mechanical behavior of geomaterials has been previously investigated through both experiments [CCdP15, CCCH15b, BCB09, HV21] and numerical simulations [SS14, GCH15, LHG02, Bus12, HH19, HH13] for sands (unbonded material) or rocks (bonded material) in a range of configurations.

In the case of sand, the process of weathering is characterized by a gradual loss of mass, accompanied by the continuous dissolution of grains. This size reduction can be localized [BG19, CS16] or homogeneous [AVD22, VD19] within the sample. Even if there are related to a microstructure evolution (and so a mechanical behavior evolution), it is imperative to distinguish between

the dissolution problem, which involves the reduction in size of the particle, and the suffusion/internal erosion problem, which pertains to the sudden evacuation of the finest particles [NBA⁺19, Li19, LRW24, TNM⁺22].

In the context of rocks, weathering can be conceptualized as three distinct phenomena, see Figure 1.2. The first chemical alteration is the substitution of a mineral for one with a weaker stiffness or lower density. The second phenomenon is the dissolution of grains and the bonds located between them. This degradation is exemplified by calcarenite, wherein the grains and bonds are composed of calcium carbonate. Indeed, the dissolution kinetics for the bond and the grain appear comparable. The third case is the dissolution of the bonds only, while the grains remain intact. An illustrative example is provided by silicic sand, which contains carbonate bonds. The dissolution kinetics of the bond is assumed to be considerably faster than that of the grain. This phenomenon is referred to as debonding and is detailed in Chapter 2 [SMRV25b]. *Ciantia et al.* have even identified two distinct kinds of bonding within the rock, temporary and persistent bonding, affecting the weathering process [CCCH15a]. The temporary bonding origin is identified as the mineral suspension, which deposits if the material is dried. In the case of fluid saturation of the sample, these bonds dissolve, with a fast kinetics reaction, as the material is suspended in the pore fluid. Conversely, the persistent bonding origin is the diagenesis phenomenon, and the dissolution kinetics is much smaller. This differentiation between the bonds involves a short-term and long-term aspect of the mechanical evolution of the geomaterial during weathering.

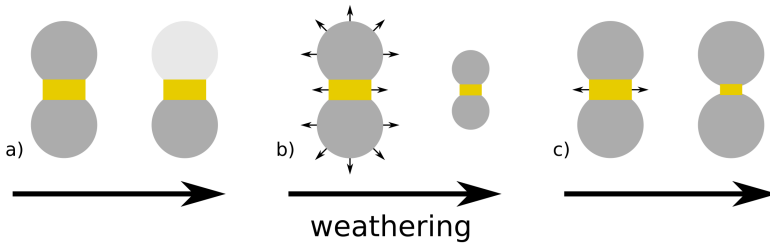


Fig. 1.2 Scheme of the weathering in the context of rock. Three phenomena are distinct: a) the mineral replacement by a weaker phase, b) the dissolution of grains and bonds (calcarenite for example), and c) the dissolution of the bonds, while the grains remain intact (silica sand+carbonate bonds for example).

Despite the potential of constitutive relations to address chemo-mechanical couplings [NCT03, GCH15, LHG02, Bus12], these approaches remain constrained to the macroscale. The phenomena occurring at the microscale, such as granular reorganization and material dissolution, are merely postulated rather than modeled. By doing so, the localized aspect of the chemo-mechanical couplings can be miscaptured. For instance, it has been shown that chemically induced compaction bands can form due to the coupling between the softening of the geomaterial and the grain damage [SS14]. Indeed, the mechanical breaking of the material leads to an increase in its specific surface, favoring the chemical dissolution of the grains, reducing the strength of the skeleton (positive feedback between the fundamental processes). In the same vein, the constitutive relations often consider a homogeneous dissolution within the sample, which is not in agreement with experiments where wormhole formations are observed while injecting acid into a triaxial cell [Xsx11, AAAM⁺24]. This heterogeneous pattern is induced by the dissolution of the material, favoring the infiltration of the reactive fluid, increasing the specific surface (positive feedback between the fundamental processes). Coming back to one of the engineering applications of this thesis, CO₂ sequestration, chemo-mechanical responses appear localized, and not homogeneous, in the host rock during [INH⁺19]. The question that remains is *how numerical models that explicitly consider the microstructure predict the mechanical behavior of geomaterials subjected to debonding*.

The Discrete Element Model (DEM) [O'S11], developed in 1979 by *Cundall and Strack*, has emerged as a pertinent method to predict the mechanical behavior of sands [CS79] and rocks [PC04] at the microscale. In the seminal approach, the granular material is modeled as spheres. The existing bonds in rock are conceptualized as additional stiffnesses between the grains. Then, the interactions between the spheres are captured to compute the granular organization.

This discrete description can be readily extended to capture the chemistry of the weathering. Indeed, the size of the particles and the bonds (in the calcarenite case) or the bonds only (in the silica + carbonate case) can be reduced. These modifications destabilize the granular microstructure and affect the properties at the sample scale.

This destabilization of the granular microstructure can be captured experimentally by the state of stress of the sample [SS09]. In particular, the state of stress is approximated by the coefficient $k_0 = \sigma_{II} / \sigma_I$, where σ_I is the vertical stress and σ_{II} is the lateral stress. To do so, a soft oedometer has been developed from the classical device [KB93, SS09, CN04]. This extended testing

apparatus is composed of a thin surrounding wall, allowing lateral deformation, and ensuring these deformations remain small. Subsequently, the lateral stress can be captured with strain gauges on this lateral soft wall. These experiments have already been modeled with a Discrete Element Model in the context of sands (unbonded granular material) [SS09, CS14, CS16, CS19], but it appears the Discrete Element Model has not been employed for rock (bonded granular material) in similar configurations.

The ensuing Chapter 2 formulates a Discrete Element Model of the debonding problem, with a particular emphasis on the impact of the debonding on the material's state of stress. Indeed, this aspect of the problem remains underexplored in the literature, even if it can induce fault reactivation and shear failure [KW18, SSC08].

Summary and objectives concerning the debonding

The debonding is a weathering phenomenon involved in the context of a cemented granular sample, where the cement dissolves, while the granular skeleton remains intact. This problem is explored numerically by reproducing oedometer tests during acid injection. A special focus is dedicated to the state of stress, which represents a potential cause for material failure.

To capture the involved microscale phenomena, such as granular reorganization, the problem is tackled at the grain scale with an explicit description of the sample through one of the most employed approaches to model cemented or uncemented granular material, the Discrete Element Model.

However, it appears that this description has not yet been considered to investigate the debonding phenomenon.

1.2 The hydration of concrete material

The opposite phenomenon to debonding is cementation, which is defined as the process of binding aggregates together [IJRM02, PAGS⁺20]. Compared to the sintering process [Wan06, Shi14, YRB⁺19], the material required to establish the bond originates from a source. As exposed in Section 1.1 and Chapter 2, the presence of cement bonds inside the geomaterial hugely impacts the mechanical performances [GCH19, BD16, IJRM02]. For instance, some aging effects have been pointed out for steel piles employed as foundations of offshore wind turbines [Sag24, BLZ24]. The mechanical performance of the host sand appears reinforced with time, while granular reorganization and cementation

occur. Furthermore, it appears the ongoing cementation process modifies the porosity and the permeability of the material [PSN⁺18, KKBP23, LPV20b]. These hydraulic parameter evolutions require consideration in the context of H_2 storage or CO_2 sequestration to monitor the available storing volume and to adapt the injection flux.

To elucidate the impact of cementation on mechanical performances at the microscale, concrete, a material with a long history in construction [Gag14] despite its inherent complexity [Ben99], is used as an example. Indeed, concrete is a multiphase [IKB⁺16] and multiscale [ZIU⁺19, ILM22] material. Specifically, cement-based materials are composites based on aggregates and bonds between them [BJL⁺11, SJM15]. The bond, referred to as cement paste, is responsible for the majority of the material's mechanical properties. As illustrated in Figure 1.3, this cement paste is produced by the hydration of source particles. Then, the paste hardens and forms the sample structure. A primary objective of research in this field is to understand and predict the mechanical behavior of this complex material [NE23]. Indeed, it appears that the concrete industry is responsible for 7 – 14% of the global carbon footprint [PWF⁺24]. Consequently, efforts are made to optimize the formulation or to find an alternative one [SMJM22], and methods are developed to sequestrate CO_2 into the cement paste itself [JDP24]. Furthermore, it appears in the context of CO_2 sequestration that the cement paste of the well reacts with supercritical, liquid, and gas CO_2 [DCPG22].

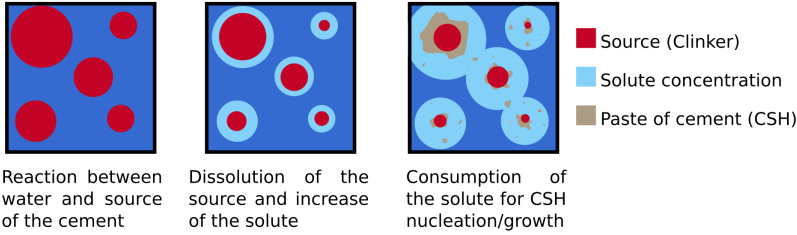


Fig. 1.3 Scheme of the hydration of a concrete material.

The traditional methodology to explore the mechanical performances entails subjecting the hardened samples to an axial compression load after a 28-day testing period [LP06]. Subsequently, the impact of a multitude of variables can be investigated. The initial parameter to be considered is the water-cement mass ratio w/c . It appears that an increase in this water-cement mass ratio w/c has the effect of reducing the compressive strength of the sample

[Kar74, MC16]. It must be acknowledged that the water-cement mass ratio w/c is not the sole factor required to predict the properties of a cement-based material. Indeed, numerous influences have been identified as potential sources of variability, including source properties, source size distribution, and the presence of additives [DL99, TJC09, LADB⁺20, NLC⁺21, KHCS13]. Consequently, a multitude of analytical and empirical models have been devised over the years. The initial model was developed by *Feret*, which correlates concrete strength with the volume fractions of cement, water and air [Fer92]. Following numerous reformulations and modifications, [NE23] for a comprehensive review, the most promising model currently appears to be that proposed by *Chidiac et al.* [CMM13]. However, this approach is time-consuming as the cement-based material must undergo a 28-day hardening period. To address this issue, constitutive models have been developed from idealized microstructures of the cement paste. As previously mentioned, concrete material is a multiphase and multiscale material. To determine the idealized microstructure, the information from the different scales and phases must be homogenized. This homogenization method involves three distinct steps: description, localization, and upscaling [Ago15, Sam17]. The description step consists of characterizing the distinct phases at the microscale by their shape and fraction. The subsequent localization step focuses on the impact of the deformation between the phases at the microscale on the deformation of the sample at the macroscale. To illustrate, two springs in parallel exhibit a distinct mechanical behavior compared to two springs in series. Finally, the upscaling step determines the mechanical properties of the macroscale from the intrinsic parameters of the phases at the microscale. A multitude of approaches exist [Bud65, McL77, Gha10, HAK76, PHE09]. However, the most frequently employed methods in the existing literature appear to be the dilute [Esh57], self-consistent [Hil65], or Mori-Tanaka [MT73] schemes. This homogenization method can even be repeated on several scales, ranging from the hydrate foam ($20\text{ }\mu\text{m}$) to the cement paste (0.7 mm), and from the cement paste to the mortar (1 cm) [PH11, PHE⁺13, PSH08]. Subsequently, the evolution of the mechanical properties of the cement-based material during the hydration process can be interpolated by combining this homogenization method with kinetics laws associated with the hydration phenomenon [WZL17].

However, the microstructure remains idealized, and recent advances in computing sciences have made it possible to consider explicitly the microstructure and its evolution [BGB⁺06]. This numerical laboratory offers a safer, more cost-effective, faster, and more reproducible alternative to the real laboratory. To do so, models based on Cellular Automata are currently employed

[vB95, HKT20, Bul07, BS09, PNS05]. However, this method includes coefficients obtained with a semi-empirical estimation. *Which indispensable elements are required to design a numerical analog based on physical considerations to explicitly describe the microstructure evolution during hydration?* To answer to this question, a physics-based Phase-Field formulation [AC79, CH58, Lan36], is presented in Chapter 3 to investigate the hydration process at the microscale of concrete material and its impacts on the mechanical behavior of the sample.

Summary and objectives concerning the hydration

Cementation is a microstructure evolution process involving the chemical formation of a binding material on a skeleton. This phenomenon is instigated through the example of the hydration of concrete material.

In the goal of predicting the mechanical performance, this multiphase material is numerically modeled at the microscale, skipping the 28-day waiting period induced by experimental campaigns. Even if homogenization methods are available in the literature, the idea is to explicitly describe the microstructure of the material and its evolution.

One of the most employed approaches to do so is based on Cellular Automata. However, this method includes coefficients obtained with a semi-empirical estimation. A more physics-based description, the Phase-Field theory, allow to address those issues.

1.3 The pressure-solution phenomenon

Debonding/cementation phenomena could be characterized as one-way chemo-mechanical coupled processes, wherein chemistry (bond dissolution or generation) affects the mechanics (stiffnesses and state of stress). There is no direct feedback from the mechanics to the chemistry. Indeed, it is noteworthy that the scales of these disparate physical phenomena are distinctly separated: the chemistry occurs at the grain scale, while the mechanics is manifest at the sample scale. As suggested by Table 1.1, more complex chemo-mechanical couplings exist, such as the case of pressure-solution. This phenomenon establishes a two-way coupling between the chemistry and mechanics at the grain scale.

As illustrated in Figure 1.4, pressure-solution involves three chemo-mechanical processes at the microscale [Rut76, Raj82, TS89]: dissolution due to stress concentration at grain contacts, diffusive transport of dissolved mass from the contact to the pore space, and precipitation of the solute on the less stressed surface of the grains.

	chemistry $\rightarrow$ mechanics	chemistry $\leftrightarrow$ mechanics
debonding	x	
cementation	x	
pressure-solution		x

Table 1.1 The chemo-mechanicals couplings are divided into two categories: the one-way and the two-way couplings.

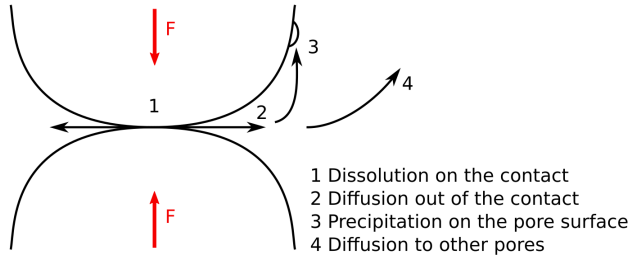


Fig. 1.4 Scheme of the pressure-solution phenomenon.

These processes result in a time-dependent compaction of the rock by changing its microstructure, pore structure and composition. Furthermore, it has been demonstrated to induce modifications in the strength of a wide range of geological materials. As such, it has been suggested as a mechanism for long-term evolution of fault strength during interseismic periods [SB92], but also to control faults' frictional behavior at low speed and thus influences earthquake nucleation [BPC00]. In the context of CO_2 sequestration, it has been pointed out by experiments that the kinetics of the pressure-solution phenomenon is accelerated ($\times 50$) by the presence of the reactive fluid [LSPDB12]. As previously explained, the success of the engineering application depends on controlling the consequences of pressure-solution as it is suspected to be the origin of earthquake nucleation in sheared faults, often defining the underground reservoir. In particular, a competition exists between the hardening behavior due to pressure-solution (dominant at low velocities) and the weakening behavior due to dilation of a shear layer (dominant at high velocities) [NS06]. The natural oscillations in fault motion rates are presented as the origin of seismic activities. It is reasonable to extend this observation to other engineering applications, such as H_2 storage and geothermal energy production. Furthermore, the concept of pressure-solution has been identified as a foundational aspect in comprehending the diagenetic transformations [BRS89, TS89].

During the diagenetic processes, sediments are transformed into sedimentary rocks. These processes influence reservoir quality in hydrocarbon exploration and the formation of economically valuable mineral deposits.

Pressure-solution has already been investigated with constitutive relations at the meso/microscale [Rut76, Raj82, SSB⁺90, GGR⁺09]. However, the validity of this kind of formulation is contingent on the selected models, which are not well constrained due to their reliance on specific microstructures and chemical reactions. To enhance our comprehension of the underlying mechanisms, it is imperative to consider simulations focused on the microstructure. To this end, micro-mechanical models with simplifying assumptions have been developed, considering an idealized microstructure [SS90, PS15, LCN⁺21], assuming a granular assembly with only dissolution [CS19, vdEMNS18] or ignoring the granular reorganization [GRV20]. However, a comprehensive understanding of this complex phenomenon for granular materials necessitates the capture at the microscale of at least two key aspects: the granular reorganization [PMWT05, TWL10, RWJM98] and the evolution of particles' shapes [BPA19, GRV22, LPD⁺25]. It is imperative to acknowledge that these two aspects exert a substantial influence on the force transmitted in the granular media. Given that stress concentration at the contacts is the driving force for pressure-solution, it stands to reason that it should strongly influence pressure-solution rate. *How can granular reorganization and grain morphology evolution be explicitly modeled, considering their impacts on the mechanics and chemistry in a tightly coupled problem such as pressure-solution?*

The Discrete Element Model (DEM) has been demonstrated to be capable of capturing mechanics (granular reorganization and stress transmission). However, the formulation remains inadequate in capturing chemistry. Conversely, the Phase-Field (PF) description has been shown to provide a satisfactory description of chemistry (evolution of particles' shapes). Nevertheless, it is not efficient enough to solve the mechanics. Even if contact problems have been solved with a Phase-Field formulation [LPK24], the computational cost is much larger than with the Discrete Element Model. Chapters 4, 5, 6 and 7 present the development and the application of a Phase-Field Discrete Element Model (PFDEM) framework [SMVR24a, SMRV25a] allowing to capture: (i) granular reorganization, (ii) irregular grain shape, (iii) force transmitted at the contacts, (iv) heterogeneous dissolution/precipitation, (v) diffusion of the solute in the pore space and (vi) rate-limiting processes. In particular, this new formulation is applied to the pressure-solution problem.

Summary and objectives concerning the pressure-solution

Compared to debonding and cementation, pressure-solution represents a chemo-mechanical coupling with feedback at the microscale. Indeed, this phenomenon involves a diffusive mass transfer driven by the gradient of the stress induced in the grain, and this shape evolution impacts the force transmission in the granular material.

Even if constitutive relations have already been developed, they remain based on experimental observations. To increase the knowledge, numerical models have started to be formulated. However, it appears that some relevant phenomena, such as the granular reorganization and the shape evolution, are mainly simplified.

A new method employing the Discrete Element Model and the Phase-Field formulation is envisioned to capture multiple pivotal mechanisms, such as the granular reorganization, the irregular grain shape, the force transmitted at the contacts, the heterogeneous dissolution/precipitation, and the diffusion of the solute in the pore space.

1.4 Scope and structure of the thesis

The present thesis tackles the numerical model of chemo-mechanical processes at the microscale, with three distinct phenomena investigated for their importance relative to the energy transition and carbon emissions.

The first example, developed in Chapter 2, concerns the weathering of a rock material. In this example, the sample is modeled as a cemented granular medium, while the size of the bonds is gradually reduced. A particular focus is placed on the evolution of the state of stress. This aspect remains under-explored in the literature, yet it is pivotal to the integrity of the material. To this end, a Discrete Element Model is employed, as it is well-suited to capture the mechanical aspect of the problem. The chemical solicitation (bond dissolution) is considered as an input of the problem. In this formulation, the relation between mechanics and chemistry is a one-way coupling for dissolution.

The second example, developed in Chapter 3, concerns the hydration of a cement-based material. Through a series of chemical reactions, a source material is consumed, resulting in the formation of bonds between aggregates. The strength and stiffness of the resulting hydrated sample are determined by the properties of these bonds and the microstructure obtained. The development of a reliable numerical model capable of predicting the microstructure, and consequently the mechanical performance, during the hydration process, rep-

resents a crucial next step in the field of cement research. The Discrete Element Model is inadequate in its ability to accurately consider the intricacies of the chemical processes involved. To address this limitation, a physics-based formulation known as Phase-Field is employed to model the chemical aspect of the problem. The distinct microstructures thus computed are then employed as input to a Finite Element Model to predict the mechanical performance of the hydrated sample. Similarly, the relationship between mechanics and chemistry in this description is a one-way coupling involving dissolution and precipitation.

The third example, developed in Chapters 4, 5, 6 and 7, concerns the pressure-solution phenomenon. Compared to the previous examples, chemistry and mechanics are deeply correlated in this context. Indeed, pressure-solution is characterized as a mass transfer by dissolution/diffusion/precipitation from the more stressed areas to the less stressed areas. A novel framework, designated as Phase-Field Discrete Element Model, is delineated in Chapter 4. This novel approach consists of integrating the Phase-Field description and the Discrete Element Model to simultaneously capture the chemical and mechanical aspects of the problem. The formulation is then calibrated and validated on experimental data and constitutive relations available in the literature, see Chapter 5. Subsequently, the capacity of the framework to capture irregular grain shape and heterogeneous dissolution/precipitation is emphasized in Chapter 6. These aspects, frequently overlooked in existing models, are shown to be pivotal in the creep behavior induced by pressure-solution. Finally, Chapter 7 extends the framework to consider the real geometry of the grains and microstructure. To do so, the geomaterial can be scanned with X-ray technology, and a 3D image of the sample can be reconstructed with computed tomography. Subsequently, this digital sample can be employed as an input of the PFDEM formulation. This approach enables the investigation of the impact of the granular organization on the pressure-solution phenomenon. This aspect is frequently not incorporated into models or is overly simplified in the current literature.

2

Stress state evolution of a cemented granular material subjected to bond dissolution by Discrete Element Modeling

How do numerical models that explicitly consider the microstructure predict the mechanical behavior of geomaterials subjected to debonding?

As delineated in Chapter 1, rock weathering is instigated in numerous engineering applications involving underground operations, such as underground storage or geothermal energy extraction. This weathering process is induced by the circulation of a reacting fluid within the pores of the rock, which can induce changes in materials properties and stress state. This Chapter presents Discrete Element Modelization [CS79, O'S11] of the dissolution of sedimentary rocks to study their stress state evolution [SMRV25b]. Despite extensive experimental [CCdP15, CCCH15b, BCB09, HV21] and numerical [SS14, NCT03, GCH15, LHG02, Bus12] research on the weathering problem,

2 | Stress state evolution of a cemented granular material subjected to bond dissolution by Discrete Element Modeling

only a limited number of studies have focused on examining the influence of weathering on the stress state of the material.

A seminal paper on the evolution of the stress state during weathering was published by *Vaughan and Kwan* in 1984 [VK84]. In this work, the authors developed a theoretical model to study the evolution of the stress state during the weathering of rocks to form residual soils. More recently, experimental investigations of dissolution have been conducted using soft oedometer tests, which allow the measurement of radial stresses. These tests have been performed with calcarenite and artificially cemented sand [CN04], glass beads mixed with salt grains [SS09] or carbonate sand [VD20]. The majority of these studies have focused on non-cohesive granular materials, except [CN04], in which the authors observed an increase in radial stress during dissolution by an acid solution in both the artificially cemented silica sand and the fully calcareous soft rock. However, the rate of increase differed in each case, reaching an asymptotic value in both cases.

The theoretical and experimental work has been completed through the implementation of numerical studies, predominantly using the Discrete Element Method [SS09, CS14, VD20], method presented in Section 2.1. It should be noted that, to the author's knowledge, all existing numerical studies focus on non-cohesive granular materials and model dissolution as a homogeneous decrease in diameter. For instance, *Shin et Santamarina* were able to reproduce experimental results in which an initial decrease of k_0 was observed [SS09]. This k_0 coefficient is the ratio of the lateral stress over the vertical effective stress, and it is employed as a proxy of the state of stress. With the dissolution process, k_0 evolves and reaches the Rankine active pressure coefficient k_a during dissolution. Additionally, the authors noted that k_0 may eventually increase to recover its initial value if dissolution continues. In their investigation of the effect of dissolution kinetics [VD20], the authors have observed a similar behavior for rapid dissolution, a decrease of k_0 followed by an increase. However, they observed a monotonic decrease for slower dissolution rates.

Sedimentary rocks can be described as a cohesive granular material following the model introduced in [BKCF13] as they are formed by cementing sediments' particles. Mechanical parameters for this discrete element model were calibrated by *Sarkis et al.* [SAN⁺22] on biocemented sands [DGE⁺17]. Indeed, these biocemented sands can be considered as a suitable proxy for natural sandstones [KBJS21, WHF23]. While the pressures examined herein might not fully reflect the conditions encountered in an underground reservoir, the observed behavior can be readily extrapolated through an equivalent contact stiffness number ($\propto$ Young modulus/pressure applied) [DCEP⁺05, RC02].

The present Chapter investigates the role of several parameters, including the degree of cementation, the confining pressure, and the history of load on the evolution of the stress state. In particular, the initial value of the k_0 coefficient, which serves as a proxy for the state of stress, is monitored and studied. Indeed, this parameter can be affected by tectonic solicitations in the context of underground reservoirs [Hoe07, TFAF16, Dem18], reaching a larger value than in experimental setups where the sample is loaded vertically by its own weight only.

Some examples of scripts used are available on Github: https://github.com/AlexSacMorane/YADE_oedo_acid.

First, the theory and formulation of the Discrete Element Model is presented. Then, the numerical model of the oedometric test is described. Additionally, the results are displayed and a discussion is raised from them. Finally, the preliminary conclusions of this Chapter are advanced.

2.1 Theory and formulation

The Discrete Element Model (DEM) is an approach developed by Cundall & Strack [CS79] for simulating granular materials at the particle level. This model was extended to rock materials by [PC04], adding a bond between the particles. The fundamental premise of this methodology is to explicitly consider the individual particles and their interactions within the material itself [O'S11]. Even if the method has been extended to consider the realistic shapes of the grains [KAVA16, GLXH09, BHU12, Hou09, NHZG04], the seminal approach is to model the grains as spheres, the approach employed in this Chapter to diminish the computational cost. Newton's laws (linear and angular momentum) are employed to compute the motion of the grains, which is formulated as follows for a single grain:

$$m \frac{\partial v_i}{\partial t} = m g_i + f_i \quad (2.1)$$

$$I \frac{\partial \omega_i}{\partial t} = M_i \quad (2.2)$$

where m is the particle mass, v_i is the particle velocity vector, g_i is the gravity acceleration vector, f_i is the sum of contact force vectors applied to the particle, I is the moment of inertia of the particle, ω_i is the angular velocity vector, M_i is the sum of contact moment vectors applied to the particle (torques due to bending, twisting, and tangential forces). Here, the notation u_i refers to

2 | Stress state evolution of a cemented granular material subjected to bond dissolution by Discrete Element Modeling

the coordinate i of the vector u . To solve these equations, various integration methods can be used [SPBF13]. For example, the software *YADE* (mainly used during this thesis) follows a Verlet scheme [Sa21]. The time integration depends on a time step dt that must verify the P-wave critical time step condition [BH17], see Equation 2.3.

$$dt < dt_{crit} = \frac{R_{min}}{\sqrt{E_m/\rho}} \quad (2.3)$$

where R_{min} is the radius of the smallest grains, E_m is the Young modulus of the contact and ρ is the density of the material. Herein, a safety factor is considered, $dt = 0.6 dt_{crit}$.

Considering two particles with radii R^1 and R^2 , the interaction between particles is computed only if the distance between grains satisfies the following inequality:

$$\overline{x_i^1 - x_i^2} < R^1 + R^2 \quad (2.4)$$

where x_i^1 (resp. x_i^2) is the center of the particle 1 (resp. 2) and $\overline{u_i}$ is the norm of the vector u_i . Once contact is detected between grains 1 and 2, the normal vector of the contact n_i^{12} is computed as $n_i^{12} = (x_i^1 - x_i^2) / \overline{x_i^1 - x_i^2}$. Then the normal overlap vector Δ_{ni} and the tangential overlap vector Δ_{si} are determined.

$$\Delta_{ni} = (R^1 + R^2 - (x_i^1 - x_i^2) \cdot n_i^{12}) n_i^{12} \quad (2.5)$$

The tangential component Δ_{si} is computed incrementally, integrating the relative tangential velocity between particles during the contact. Einstein's summation convention is employed here (the index j is repeated).

$$\Delta_{si} = \Delta_{si} + v_{si}^{12} \times dt \quad (2.6)$$

where v_{si}^{12} is the relative tangential velocity vector defined in Equation 2.7 and dt is the time step used in the simulation.

$$v_{si}^{12} = v_i^{12} - (v_j^{12} n_j^{12}) n_i^{12} \quad (2.7)$$

$$\begin{aligned} v_i^{12} = & v_i^1 - v_i^2 + (R^1 - \delta/2) \epsilon_{ijk} n_j^{12} \omega_k^1 \\ & + (R^2 - \delta/2) \epsilon_{ijk} n_j^{12} \omega_k^2 \end{aligned} \quad (2.8)$$

where v_i^{12} is the relative velocity vector between grains and $\delta = \overline{\Delta_{ni}}$ is the norm of the normal overlap vector. It should be noted that the terms $(R - \delta/2)$

represent the corrected radii at the contact. Here, the angular velocity vectors ω_i of the grains are taken into account for the calculation of the tangential overlap vector Δ_{si} . As the contact orientation can evolve, it is crucial to update the tangential overlap vector by projection and then scaling: $\Delta_{si}^{new} = \Delta_{si}^{old} - \Delta_{sj}^{old} n_j^{12} n_i^{12}$ and $\overline{\Delta_{si}^{new}} = \overline{\Delta_{si}^{old}}$.

A relative angular velocity vector $\Delta\omega_i$ is also needed to compute the twisting and bending behaviors.

$$\Delta\omega_i = \omega_i^1 - \omega_i^2 \quad (2.9)$$

This relative angular velocity vector $\Delta\omega_i$ is divided into a twisting component $\Delta\omega_{ti}$ and into a bending component $\Delta\omega_{bi}$.

$$\Delta\omega_{ti} = \Delta\omega_i n_j^{12} n_i^{12} \quad (2.10)$$

$$\Delta\omega_{bi} = \Delta\omega_i - \Delta\omega_{ti} \quad (2.11)$$

These relative angular velocity vectors $\Delta\omega_{ti}$ and $\Delta\omega_{bi}$ are used to compute a twisting and a bending relative angular rotation vectors $\Delta\theta_{ti}$ and $\Delta\theta_{bi}$ incrementally.

$$\Delta\theta_{ti} = \Delta\theta_{ti} + \Delta\omega_{ti} \times dt \quad (2.12)$$

$$\Delta\theta_{bi} = \Delta\theta_{bi} + \Delta\omega_{bi} \times dt \quad (2.13)$$

As the contact orientation can evolve, it is crucial to update the twisting and bending relative angular rotation vectors by projection and then scaling: $\Delta\theta_{ki}^{new} = \Delta\theta_{ki}^{old} - \Delta\theta_{kj}^{old} n_j^{12} n_i^{12}$ and then $\overline{\Delta\theta_{ki}^{new}} = \overline{\Delta\theta_{ki}^{old}}$, with $k = t$ or b .

The contact models between particles considered in this Chapter are governed by a cohesive law following [BKCF13]. Other formulations, such as the Hertz law [Her82, Joh85, DRDM04], could have been employed. However, it appears that a calibration campaign [SAN⁺22] has already been conducted employing this model developed by [BKCF13]. The impact of the contact model remains small on the behavior of the sample. The introduced cohesion permits the relative displacement between bonded particles. However, due to the presence of cementation, an additional stiffness is introduced. The normal, tangential, bending, and twisting models are illustrated in Figure 2.1 and described in the following.

2 | Stress state evolution of a cemented granular material subjected to bond dissolution by Discrete Element Modeling

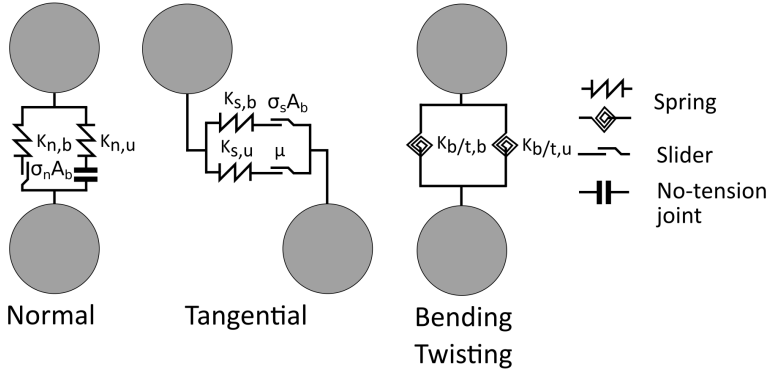


Fig. 2.1 The contact between two particles obeys normal, tangential, bending and twisting elastic-plastic laws. A bond can be present if the contact is cemented. It increases the shear and the tensile strengths.

As illustrated in Figure 2.2, a cemented contact can be classified into three distinct types: I) Frictional, II) Mixed/Cohesive (Frictional+Cemented), or III) Cemented [SAN⁺22]. In the case of type I, no cementation is present. In types II and III, the contact can be modeled as two springs in parallel (type II) or in series (type III). One spring represents the bond $K_{,b}$ and the other represents the unbonded grain-grain contact $K_{,u}$. In the following Sections, the assumption is made that the sample is composed of contacts type II, as depicted in Figure 2.1 where springs are represented in parallel.

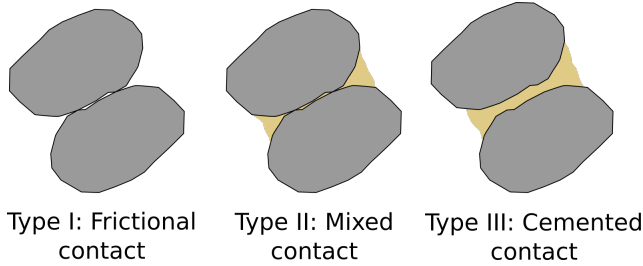


Fig. 2.2 Definition of the contact types: I) Frictional, II) Mixed or cohesive (Frictional+Cemented), and III) Cemented.

The contact force vector f_i applied to the particle, see Equation 2.1, is defined as the sum of the normal force vectors F_{ni} and the tangential force vectors F_{si} over the contacts including the particle. The normal force vector F_{ni} is

described in Equation 2.14. An elastic stiffness $K_n = K_{n,b} + K_{n,u}$ is required, formulated Equation 2.15.

$$F_{ni} = K_n \Delta_{ni} \quad (2.14)$$

$$K_n = 2E_m \frac{R^1 R^2}{R^1 + R^2} \quad (2.15)$$

where E_m is the contact Young's modulus, R^1 and R^2 are the radii of the particles in stake.

Similarly, the tangential force vector F_{si} is described in Equation 2.16. An elastic stiffness $K_s = K_{s,b} + K_{s,u}$ is required, formulated Equation 2.17.

$$F_{si} = K_s \Delta_{si} \quad (2.16)$$

$$K_s = \nu K_n = 2\nu E_m \frac{R^1 R^2}{R^1 + R^2} \quad (2.17)$$

where ν is the contact Poisson's ratio.

In the same vein, the contact moment vector M_i applied to the particle, see Equation 2.2, is defined as the sum of the bending moment vectors M_{bi} , the torque due to the tangential force vectors F_{si} , and the twisting moment vector M_{ti} over the contacts including the particle. The bending moment vector M_{bi} is described in Equation 2.18. An elastic stiffness $K_b = K_{b,b} + K_{b,u}$ is required, formulated Equation 2.19.

$$M_{bi} = K_b \Delta \theta_{bi} \quad (2.18)$$

$$K_b = \alpha_b K_s R^1 R^2 = 2\alpha_b \nu E_m \frac{(R^1 R^2)^2}{R^1 + R^2} \quad (2.19)$$

where α_b is a non-dimensional factor, relating the bending and the tangential stiffnesses.

Similarly, the twisting moment vector M_{ti} is described in Equation 2.20. An elastic stiffness $K_t = K_{t,b} + K_{t,u}$ is required, formulated Equation 2.21.

$$M_{ti} = K_t \Delta \theta_{ti} \quad (2.20)$$

$$K_t = \alpha_t K_s R^1 R^2 = 2\alpha_t \nu E_m \frac{(R^1 R^2)^2}{R^1 + R^2} \quad (2.21)$$

where α_t is a non-dimensional factor, relating the twisting and the tangential

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stiffnesses. The bending and the twisting resistances aim to reproduce the shape of the grain [ACRO11, MQAV20, SMVR24b] as spheres are used in this framework (numerically more efficient).

These contact laws are linear in the elastic domain. Furthermore, a Coulomb friction limit is introduced at the contact level, see Equation 2.22

$$\overline{F}_{si} \leq \mu \overline{F}_{ni} \quad (2.22)$$

where μ is the friction coefficient between two particles. This friction coefficient is constant before and after the bond breakage.

The bond exists until one of the two criteria presented in Equation 2.23 is not verified.

$$\begin{aligned} \overline{F}_{si} &\leq \mu \overline{F}_{ni} + \sigma_s A_b \text{ (Shear condition)} \\ \overline{F}_{ni} &\leq \sigma_n A_b \text{ (Tensile condition)} \end{aligned} \quad (2.23)$$

where σ_s is the shear strength of the bond, σ_n is the tensile strength of the bond and A_b is the surface of the bond. It is worth noting that no criterion is employed for the compression condition. This value of the bond surface A_b is determined initially and is reduced during the simulation, see Section 2.2. During the debonding phenomenon, the mechanical rupture of the bond can be induced by a stress reorganization, increasing the tensile/shear force transmitted in the contact $\overline{F}_{ni}/\overline{F}_{si}$. Furthermore, the rupture can occur even if the tensile/shear force transmitted stays constant $\overline{F}_{ni}/\overline{F}_{si}$ as the bond surface A_b decreases during the dissolution. The last rupture case is due to chemistry when the bond surface reaches $A_b = 0 \text{ m}^2$. Once the bond breaks (by mechanics or chemistry), the bond surface A_b is set to 0 m^2 and the tensile stiffness of the contact is deactivated.

2.2 Numerical model

The Discrete Element Model is solved using the *YADE* open source software [Sa21]. Some examples of scripts used are available on GitHub: https://github.com/AlexSacMorane/YADE_oedo_acid.

The initial condition algorithm is presented in Figure 2.3. A $2,8 \times 2,8 \times 2,8 \text{ mm}$ box is generated. Subsequently, 3000 particles are generated, despite 1600 would suffice to obtain a representative elementary volume [O'S11, SAN⁺22]. It is crucial to note that the grains are initially incorporated with a radius

smaller than the final one. Indeed, a radius expansion algorithm is applied to generate the initial condition [O'S11]. The objective of this algorithm is to verify a uniform grain size distribution similar to [SAN⁺22] ($R_{min} = 75 \mu\text{m}$ and $R_{max} = 125 \mu\text{m}$). Once the particles have reached their final dimension, the position of the top wall is controlled in order to apply a vertical pressure equal to $P_{cementation}$ (see Equation 2.24 for details). The positions of the remaining walls are maintained at a fixed position. Once the vertical pressure is equal to $P_{cementation}$, the friction between the grains, the twisting resistance, and the bending resistance are activated. The top wall is then controlled to attain once more a vertical pressure equal to $P_{cementation}$, while the other walls remain fixed. Subsequently, the cementation between the particles is applied. At each contact, a random draw is conducted with a probability equal to p_c to ascertain whether a bond is formed. The bonds are defined by a shear strength σ_s and a tensile strength σ_n . Additionally, the bonds have a surface area A_b obtained by a lognormal distribution presented in Appendix A and defined by the expected value m_{log} and the variance s_{log} [SAN⁺22]. The parameters p_c , m_{log} , and s_{log} characterize the initial degree of cementation, see Table 2.2. Subsequently, the position of the top wall is controlled in order to apply a vertical pressure equal to $P_{confinement}$ (see Equation 2.24 for details). The remaining walls are maintained in a fixed position. Subsequently, the position of one lateral wall (the remaining ones are fixed) is controlled to reach an initial coefficient of lateral earth pressure $k_0 = \sigma_{II}/\sigma_I$ (σ_I is the vertical pressure, σ_{II} is the lateral pressure). The sample is subjected to oedometric conditions (the control of the top plate is active and it aims at verifying the vertical confining pressure at any given instant) [SMVR24a, CN04]. Once the lateral pressure has been obtained, the position of the moving lateral plate is fixed to verify the oedometric conditions (fixed lateral walls), and the control of this element is deactivated. The initial configuration is reached, and the destabilization due to the debonding phenomenon starts. An illustrative example of an initial configuration is provided in Figure 2.4.

Bond breakage can be triggered during the initialization of the test, preceding the commencement of the bond dissolution through acid injection. The portion of the broken bond is given Table 9.1 in Appendix B. Bond breakage will inevitably occur as a consequence of the initialization algorithm, as illustrated in Figure 2.3. The cementation occurs at a specified pressure $P_{cementation}$, and the pressure is then elevated to the confining pressure $P_{confinement}$ before the start of the test. This increase is the source of some bond breakage (even prior to the commencement of dissolution). Moreover, the objective is to reproduce numerically the experiments. In an oedometric test with acid

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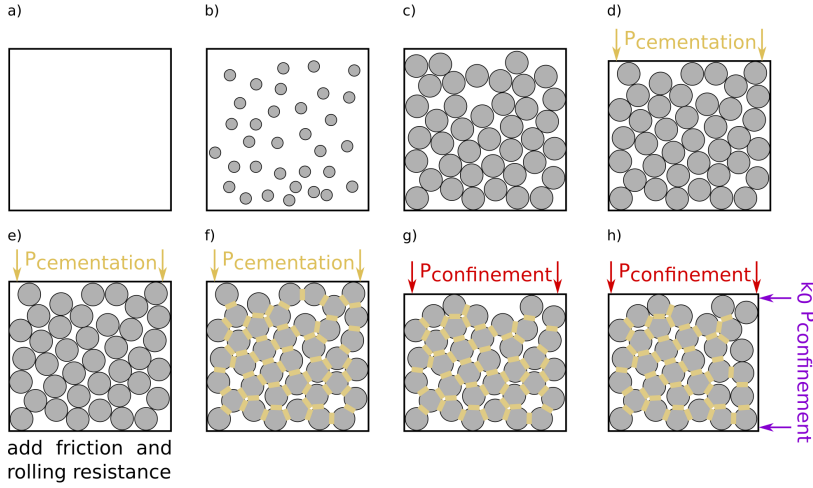


Fig. 2.3 Initial condition algorithm: a) A box is created. b) All the particles are generated with a reduced radius. c) The different radii increase steeply until reaching the final values. d) A vertical pressure $P_{cementation}$ is applied by moving the top plate. e) The friction, the twisting resistance, and the bending resistance are activated. f) The cementation is applied by generating bonds at the contacts. g) A vertical pressure $P_{confinement}$ is applied by moving the top plate. h) An initial stress state k_0 is applied by moving the lateral plate.

injection (bond dissolution), the sample is initially cemented, placed in the oedometer, loaded at confining pressure, and then subjected to acid injection (bond dissolution) [CN04]. In the experiments, the step of loading to the confining pressure also induces bond breakage. The occurrence of bond breakage is more prevalent in samples with $k_0^{init} \leq 0.3$. Indeed, the value of k_0 is approximately equal to 0.3 prior to the formation of the bonds. In order to achieve the objective of $k_0^{init} \leq 0.3$, it is necessary to extend the lateral dimension of the sample by moving the lateral wall. The combination of this extension with the application at the top of the confining pressure results in shear and tensile conditions at the contact level. Consequently, bonds breakage occurs if one of the conditions presented Equation 2.23 is reached. This phenomenon occurs less frequently in the case of $k_0^{init} \geq 0.3$. Indeed, the lateral dimension of the sample is compressed, and it does not result in shearing and tensile solicitations at the contact level, but in compression of the bonds. This phenomenon does not instigate bond breakage as no condition on compression is considered as

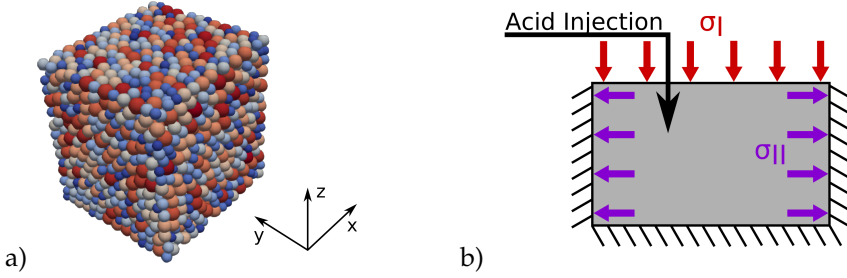


Fig. 2.4 a) An example of an initial configuration obtained by the algorithm presented in Figure 2.3. b) The sample is then in oedometric conditions: the lateral and bottom walls are fixed and a constant vertical pressure is applied at the top during the injection of the fluid that induces debonding.

breakage criterion.

The control of the wall (in the vertical or lateral direction) is achieved through the use of a proportional controller k_p described in Equation 2.24. A maximum speed of the plate v_{plate}^{max} ($= 0.00005 R_{mean} / dt$) is applied to verify quasi-static conditions [O'S11], where R_{mean} is the mean radius and dt is the time step defined Equation 2.3. These aforementioned parameters were determined through a trial-and-error method, minimizing the oscillation of the obtained confining pressure around the target value and maximizing the control kinetics.

$$\begin{aligned} v_{plate} &= k_p \times (P_{plate} - P_{target}) \\ v_{plate} &\leq v_{plate}^{max} \end{aligned} \quad (2.24)$$

where v_{plate} is the velocity of the plate (in the direction of the control), k_p is the value of the proportional controller, P_{plate} is the pressure applied on the plate (in the direction of the control), P_{target} is the targeted pressure applied on the plate (in the direction of the control) and v_{plate}^{max} is the maximum velocity of the plate.

The walls are considered to have no friction, cohesion, bending resistance and twisting resistance with the grains.

Once the initial configuration has been established, the dissolution process commences. As presented in Algorithm 1, these steps are subdivided into distinct phases. Initially, the bonds are dissolved, with the surface area of each intact bond reduced. Subsequently, the reorganization of the grains occurs

2 | Stress state evolution of a cemented granular material subjected to bond dissolution by Discrete Element Modeling

Algorithm 1 The weathering of the rock is modeled as a debonding phenomenon.

```
while bonds are remaining do
  Dissolve the bonds ▷ the bonds' surfaces are decreased
  Update the mechanical properties, considering the current cementation
  while DEM equilibrium not reached do ▷ granular reorganization occurs
    Compute solicitations
    Solve the momentum balances
    Check the equilibrium criteria for DEM
  end while
  Take a snapshot of the configuration ▷ several parameters are tracked
  Count the number of bonds still existing
end while
```

until an equilibrium state is reached. To ensure the representativeness of the method, and to respect the fact that the mechanical kinetics (instantaneously) is faster than the chemical kinetics (depending on the reaction, ≈ 10 hours in [CN04] for example), the magnitude of the reduction must be sufficiently small. Moreover, this limit depends on the size of the bonds determined by the bond size distribution function defined by the expected value m_{log} and the variance s_{log} , see the Appendix A. As depicted by the Table 2.2, m_{log} and s_{log} determine the cementation level. After a trial-and-error method, a factor 0.02 appears suitable to define the dissolution of the bond at each step. Similarly, this factor can be increased to 0.05 once most of the bonds are broken. This process can be sped up without diminishing the quality of the model. It is worth noting that the dissolution is applied homogeneously through the sample. The model depicted herein is unable to predict the behavior of the weathered sample if the acidity is governed by a transport mechanism, such as during wormhole formation [X SX11, AAAM⁺24]. To do so, another layer should be added to the model to compute the reactive transport. For instance, the Phase-Field description has been employed in [LWW⁺23] to consider the pore structure evolution due to the localized dissolution of the mineral. Furthermore, the dependency of the dissolution kinetics on the specific surface is neglected herein, even if it has been emphasized that the smaller elements offer a greater specific surface [RDSV21]. The bonds reduce at a constant speed, without consideration for the variation of the specific surface. Moreover, the model assumes no saturation for the dissolution, considering the continuous addition of reactive in the domain. The dissolution process is schematized in

Figure 1.2c, where the granular skeleton remains intact, while the bond size at the contact is steeply reduced.

Concerning the criterion to detect the mechanical equilibrium between two dissolution steps, it is based on two indices:

- the unbalanced force (defined as the ratio of the mean summary force on bodies and mean force magnitude on interactions) is smaller than a criterion value (here 0.01).
- the difference between the pressure applied on the top plate and the targeted pressure is smaller than a criteria value (here $0.01 P_{target}$).

It is crucial to provide a commentary on the concept of grain reorganization. In the configuration under investigation, the positions of the particles remain largely unchanged. Indeed, the sample is dense and in oedometric conditions. Furthermore, it is assumed that no grain breakage occurs. Nevertheless, some fluctuations in the organization do occur, resulting in an evolution in the chain force structure.

Once the equilibrium is reached, a snapshot of the sample is taken. This enables the tracking of the evolution of the various trackers presented in Section 2.3. These steps are repeated until all the bonds have disappeared. It should be noted that a bond can disappear because of the dissolution (the surface is null or negative) or the mechanical loading (criteria presented Equation 2.23 are reached).

The parameters used in this Chapter are presented in Tables 2.1 and 2.2. These parameters have been obtained by observation of the microstructure and by calibration from triaxial tests [DGE⁺17, SAN⁺22]. The influence of several parameters such as the vertical confinement pressure $P_{confinement}$ [Hoe07], the initial coefficient of lateral earth pressure k_0^{init} [Hoe07, TFAF16, Dem18] and the degree of cementation [SAN⁺22] are investigated in this Chapter.

$P_{confinement}$	0.1 - 1 - 10 MPa
$P_{cementation}$	$0.01 P_{confinement}$
Initial k_0	0.2 - 0.7 - 1.5
Cementation	2T - 2MB - 11 BB - 13BT - 13MB
Bond dissolution	$0.02 e^{m_{log}}$ ($0.05 e^{m_{log}}$ when 95 % of the initial number of bonds are broken)

Table 2.1 Presentation of the parameters used (see Table 2.2 for the details about the cementation).

2 | Stress state evolution of a cemented granular material subjected to bond dissolution by Discrete Element Modeling

The confining pressures $P_{confinement}$ have been selected from the vertical stress reached during the triaxial tests in [SAN⁺22], from where the mechanical parameters are extracted. Subsequently, the cementation pressure $P_{cementation}$ is determined from the confining pressures. It is pivotal that the cementation pressure remains lower than the confining pressure to reproduce the experiments described in [CN04]. Indeed, experimental sample preparation involved cementation at low/no confinement, followed by the application of the investigated confining pressure. In the context of the Discrete Element Model, some confinement should be applied to contain the particles in contact. The ratio $P_{cementation}/P_{confinement} = 0.01$ is a good approximation of the experimental setup, respecting the limitations of the model.

		Lightly ce- mented		Medium ce- mented	Highly ce- mented	
Sample	Untreated	2T	2MB	11BB	13BT	13MB
Density (kg/m ³)	2650					
E_m (MPa)	80	300	320	760	860	1000
ν (-)	0.25					
α_b (-)	0.5					
α_t (-)	0.5					
μ (-)	0.36					
p_c (%)	0	13	88	98	100	100
m_{log} (-)	0	6.79	7.69	8.01	8.44	8.77
s_{log} (-)	0	0.70	0.60	0.88	0.92	0.73
σ_s (MPa)	6.6					
σ_n (MPa)	2.75					

Table 2.2 Mechanical parameters depending on the cementation. The parameters have been obtained by calibration from a biocemented sand (Fontainebleau), see [SAN⁺22].

To explore the effect of the cementation, five distinct initial cementations, exhibiting disparate microscopic parameters, are considered. During the debonding process, the bond surfaces A_b are reduced, and the sample aims to reach the untreated granular state. The reduction of the bond surfaces results in a reduction in the strength of the cemented contacts, see Equation 2.23. Such weakening may ultimately result in the mechanical rupture of the bond. Moreover, in the event that the bond remains intact and its surface area reaches $A_b = 0m^2$, it may also undergo a chemical rupture. These ruptures weaken

the sample, and the current state during the debonding phenomenon is interpolated from the only known states: the initial cemented state and the final unbonded state, see Figure 2.5.

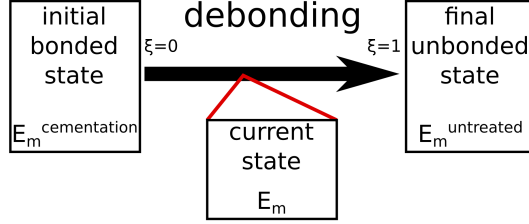


Fig. 2.5 During the debonding phenomenon, the current state is interpolated from the initial (cemented) and final (unbonded) states.

Table 2.2 highlights the fact that the Young modulus E_m exhibits variation between the unbonded and bonded states. To ensure the sample is representative, and because of the data available in [SAN⁺22], an interpolation between the two known states is performed to characterize the current state. This approach is commonly applied in the literature to model chemical damage at the macroscale [GCH15, TH23, VD19, HH19]. In particular, the Young modulus (and thus, the different contact springs K_n , K_s , K_r , K_t) is updated following Equation 2.25. This assumption results in the dependency of the contact scale on the sample scale through the debonding factor ξ . In this investigation, a linear approximation is employed as it represents the most straightforward relation available for a system comprising only two known states. Should supplementary data become available, this relation can be readily modified in accordance with the new information. The impact of this stiffness reduction will be examined in Section 2.3.2 and a discussion will be presented in Section 2.4.2.

$$E_m = (E_m^{cementation} - E_m^{untreated}) \times (1 - \xi) + E_m^{untreated} \quad (2.25)$$

where E_m is the current Young modulus used in the simulation, $E_m^{cementation}$ is the initial Young modulus depending on the initial degree of cementation, $E_m^{untreated}$ is the Young modulus without cementation (here 80 MPa), and ξ is the debonding factor defined as the ratio of the bonds dissolved (by dissolution or by loading) over the initial number of the bonds. As the time step employed for the temporal integration depends on the Young modulus E_m , see Equation 2.3, it becomes important to update the time increment dt with

2 | Stress state evolution of a cemented granular material subjected to bond dissolution by Discrete Element Modeling

the dissolution of the bonds.

The relationship between the contact scale (E_m) and the sample scale (ξ) could be a matter of contention. An alternative approach would have been to consider a local surface stiffness $E_m(A_b)$ at each contact, with the stiffness dependent on the bond surface [SEB16, SEB18]. This approach is explored in Section 2.4.3. However, this relationship is not available in the data set used [SAN⁺22], and can only be extrapolated.. Consequently, the model choice has been to interpolate the current state, see Figure 2.5. Nevertheless, contact strength depends on the local bond surface area A_b , see Equation 2.23.

2.3 Results

The results of all the simulations performed (plus some complementary investigations) are presented in the following Subsections. Two main variables are investigated:

- the coefficient of lateral earth pressure $k_0 = \sigma_{II}/\sigma_I$, where σ_I is the vertical stress and σ_{II} is the lateral stress. This parameter is a proxy of the state of stress inside the sample [SS09, CS14].
- the debonding variable $\xi = 1 - n_{bond}/n_{bond}^0$, where n_{bond} is the number of bonds and n_{bond}^0 is the number of bonds after the initial configuration. This variable is equal to 0 when the simulation starts (no bond broken) and equal to 1 when the simulation ends (all bonds broken).

Thanks to the DEM, much more data are available to understand the mechanisms operating at the microstructural level, such as the coordination number, the mode of rupture of the bonds, or the mean force transmitted in the contact, among others. These data will be used, if necessary, to understand our results.

2.3.1 The existence of an attractor value k_0^{attr}

The evolutions of k_0 are gathered in Figure 2.6 for the five initial degrees of cementation, the three values of k_0^{init} and the three distinct confining pressures $P_{confinement}$. Unfortunately, no experimental data exist in the literature, except [CN04], to validate the results depicted here. Comparing qualitatively, it appears that the pattern followed by the k_0 evolution (in the case $k_0^{init} = 0.2$) is similar to the results depicted in [CN04]. Indeed, the k_0 increase with time is divided into two steps: an initial fast evolution, followed by a slower fluctuation. Even if the Figure 2.6 does not present the temporal evolution of the

k_0 coefficient, it is available in Figure 2.16. No calibration has been tried to replicate the results of [CN04] due to the lack of available information.

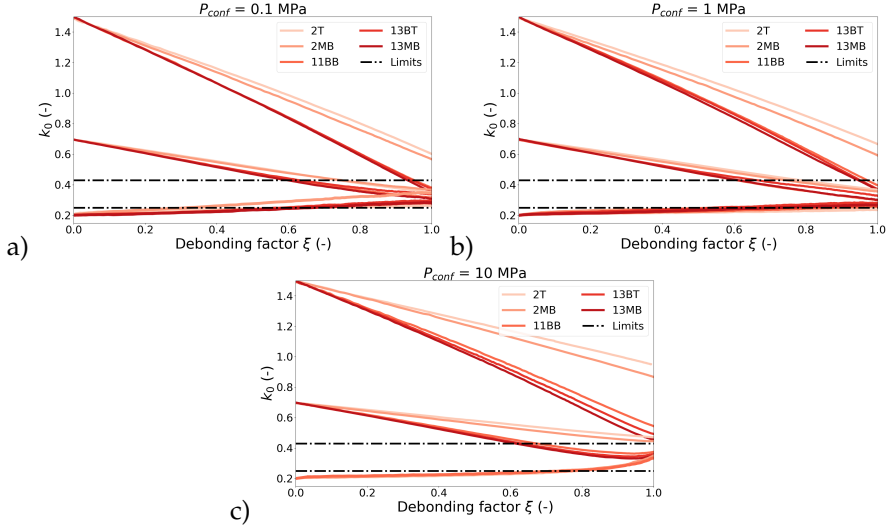


Fig. 2.6 Evolution of k_0 with the debonding factor ξ for $P_{confinement} =$ a) 0.1, b) 1 and c) 10 MPa. Limits considering $k_0^{attr} = \nu / (1 - \nu)$ are plotted with $\nu = 0.2 - 0.3$.

It appears the k_0 aims to reach an attractor value k_0^{attr} with the dissolution of the bonds. Applying the principle of superposition, it has been shown analytically by [VK84] that k_0 approaches a limit given by $k_0^{attr} = \nu / (1 - \nu)$ during weathering and stiffness reduction. Considering a window of $[0.2 - 0.3]$ for the value of ν , the attractor value window is $[0.25 - 0.43]$, in agreement with the results obtained. This evolution of the k_0 illustrates the granular reorganization allowed by the weathering [SS09, CS14]. The sample being dense and under oedometric conditions, the positions of the particles remain mostly unchanged. Nevertheless, these small fluctuations widely affect the distribution of forces between particles and thus the stress state of the sample.

To better understand the attractor configuration, the fabric description of the sample and its evolution are investigated. Three simulations are considered: a 13MB sample with a confining pressure $P_{confinement} = 1$ MPa and initial values of $k_0 = 0.2, 0.4$ or 0.7 . While contact-based fabric tensors are frequently referenced in the literature [RWJM98, SG18, LZM⁺20], this study

2 | Stress state evolution of a cemented granular material subjected to bond dissolution by Discrete Element Modeling

employs a normal forces-based fabric tensor F_{ij}^n [LZM⁺20, GZ13, GZZ⁺19]. Indeed, the normal forces-based fabric tensor underlines information on the fabric anisotropy, weighted by the norm of the normal force transmitted at the contacts. Being dense and under oedometric conditions, the normal forces are dominant in the stress transmission. The debonding process results in an evolution of chain forces, even if the position of the grains remains similar. The primary cause of this evolution can be attributed to the modification of normal forces. To quantify this variation, a normal forces-based tensor is defined as the average of the outer product of the normal forces at contacts, see Equation 2.26.

$$F_{ij}^n = \frac{1}{N_c} \sum_c \frac{f^n n_i n_j}{1 + D_{kl} n_k n_l} \quad (2.26)$$

where N_c is the total number of contacts, c is a contact in the sample, f^n is the norm of the normal force of the contact c , n_i is the unit vector of the contact direction and D_{kl} is the fabric tensor of the second order defined in Equation 2.27 [LZM⁺20].

$$D_{ij} = \frac{15}{2} \left(\Phi_{ij} - \frac{1}{3} \delta_{ij} \right) \quad (2.27)$$

where Φ_{ij} is the contact-based fabric tensor, defined in Equation 2.28 [RWJM98, LZM⁺20, GZZ⁺19] and δ_{ij} is the Kronecker tensor. This contact-based fabric tensor and its fluctuation could also be employed to investigate the evolution of the microstructure. However, the normal forces-based tensor F_{ij}^n is preferred for the reasons mentioned previously.

$$\Phi_{ij} = \frac{1}{N_c} \sum_c n_i n_j \quad (2.28)$$

where N_c is the total number of contacts, c is a contact in the sample, and n_i is the unit vector of the contact direction. A distribution function $f^n(n_i)$ can be defined in Equation 2.29 [LZM⁺20] and illustrated in Figure 2.7 at initial conditions for $k_0^{init} = 0.2$ (blue), 0.4 (red) and 0.7 (green) and at the attractor conditions (dotted). Even if the initial value of the k_0 influences the probability distribution function at the initial state, it appears that the fabric aims to reach an attractor configuration thanks to the granular reorganization. This attractor configuration is computed considering the average of the three final configurations (individually similar to the attractor).

$$f^n(n_i) = f_0 \left(1 + a_{ij}^n n_i n_j \right) \quad (2.29)$$

where $f_0 = \text{tr}(F_{ij}^n)$ and $a_{ij}^n = 15/2 \left(F_{ij}^n / f_0 - \delta_{ij} \right)$. This function represents the average normal force in a specific direction [GZ13].

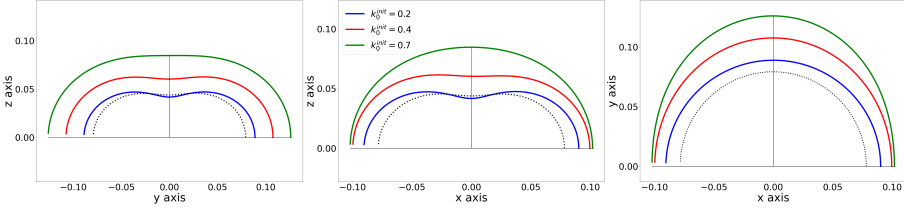


Fig. 2.7 Distribution function $f^n(n_i)$ at initial and attractor conditions (dotted). This function represents the average normal force in a specific direction.

It can be observed that the function $k_0^{\text{init}} = 0.2$ (depicted in blue) is situated within the function $k_0^{\text{init}} = 0.4$ (depicted in red), which in turn is situated within the function $k_0^{\text{init}} = 0.7$ (depicted in green). As illustrated in Figure 2.11, the mean force transmitted in contact is found to be larger for the case $k_0^{\text{init}} = 0.7$ than for either $k_0^{\text{init}} = 0.4$ or $k_0^{\text{init}} = 0.2$. This is consistent with the definition of the function f^n (representing the average normal force in a specific direction).

The eight-shape of the function $f^n(n_i)$ for $k_0^{\text{init}} = 0.2$ is common in granular media [SS09, CS14], emphasizing the principal directions of the stress in the domain. Furthermore, it is observed that as k_0^{init} increases, the distribution of f^n for the planes yz and xz approaches a circle. The sphericity of f^n indicates that the distribution of the forces is more isotropic, which is consistent with the values of k_0^{init} closer to 1. This tendency is even clearer in Figure 2.8, where the distribution function is normalized. This evolution of the shape from an eight to an ellipsoid/circle has also been observed for increasing k_0 due to the partial dissolution of uncemented granular material [CS14].

One can notice the fact that an anisotropy exists on the plane xy. Indeed, the initial configuration algorithm consists of moving only one wall to apply k_0^{init} , favoring one loading direction, see Figure 2.3. However, this anisotropy remains insignificant.

Then, this probability distribution function is normalized to compare the different organizations. A normalized function $\bar{f}^n$ is defined in Equation 2.30

2 | Stress state evolution of a cemented granular material subjected to bond dissolution by Discrete Element Modeling and shown in Figure 2.8.

$$\overline{f^n}(n_i) = f_0 \frac{1 + a_{ij}^n n_i n_j}{\int \overline{f^n}(n_i) d\theta} \quad (2.30)$$

where $\int \overline{f^n}(n_i) d\theta$ is the integral of f_n along the plane considered (xy, xz or yz). Thanks to this definition, the perimeter of $\overline{f^n}$ equals 1 in the plane. This function represents the probability of a contact to exist in the direction n_i weighted by the average normal force in this direction.

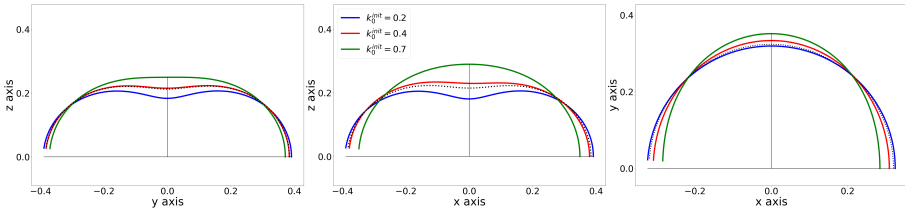


Fig. 2.8 Distribution function $\overline{f^n}(n_i)$ at initial and attractor conditions (dotted). This function represents the probability of a contact to exist in a direction weighted by the average normal force in this direction.

The normalization enables us to compare the cases between them. Looking at planes yz and xz, it is clear that the $k_0^{init} = 0.2$ (blue) case must create isotropy (k_0 will increase), whereas the $k_0^{init} = 0.4$ (red) or $= 0.7$ (green) cases must create anisotropy (k_0 will decrease). As a reminder, an isotropic state of stress is defined as $k_0 = 1$, and it is depicted as a perfect circle. The same observations can be done on the plane xy, one direction is favored because of the initial condition algorithm, see Figure 2.3. However, this anisotropy remains insignificant.

The evolution during the debonding of the shape of the normalized probability function $\overline{f^n}(n_i)$ can be captured by the evolution of the maximum and the minimum values, illustrated in Figure 2.9.

It appears that in planes yz and xz, the maximum values increase and the minimum values decrease for cases $k_0^{init} = 0.4$ and $= 0.7$. This distancing of the extrema reveals the creation of anisotropy. On the opposite, the maximum values decrease and the minimum values increase for the case $k_0^{init} = 0.2$, revealing the creation of isotropy (closing of the extrema). These observations are in agreement with the evolution of the k_0 , proxy of the isotropy/anisotropy of the sample [SS09, CS14]. In plane xy, the extrema are closing for the three

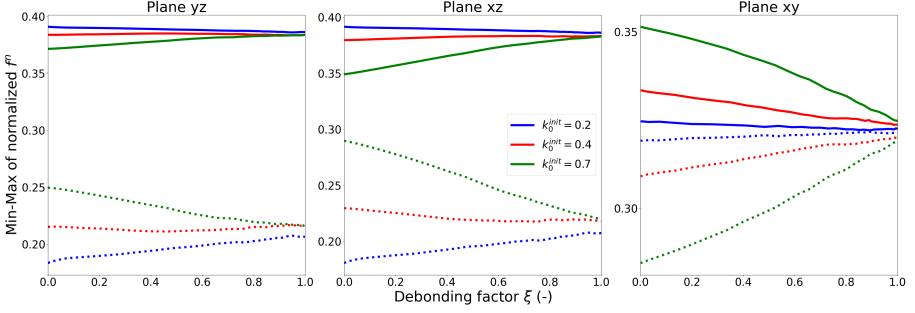


Fig. 2.9 Evolution of the maximum and the minimum values of the normalized probability function $\bar{f}^n(n_i)$ with the debonding factor ξ .

cases (creation of isotropy). The initial anisotropy is generated by the initial configuration algorithm, see Figure 2.3, and it is diminished with the debonding phenomenon.

It is crucial to acknowledge that k_0 is computed in this study from the stress applied on a single lateral wall. One might inquire as to how the stress states evolve in the minor and intermediate principal directions. Figures 2.7, 2.8 and 2.9 show that anisotropy exists initially on the plane xy (especially for $k_0^{init} = 0.4$ and 0.7). This is because of the initialization process, see Figure 2.3. Indeed, only a single wall (with the normal in the x-direction) is moving to control k_0 . Minor and intermediate stresses are different, even if they stay similar. Minor stress is in the direction used to compute k_0 . With the debonding the anisotropy on this plane disappears, see the attractor line (dotted), and minor and intermediate stresses aim to reach the same value.

2.3.2 The existence of two k_0 evolution mechanisms

This Section addresses the issue of the reduction in Young modulus during the dissolution process, see Equation 2.25. It also investigates the mechanisms of the k_0 evolution. The identical simulations conducted in the preceding Section are now executed without the assumption of a reduction in the Young modulus (the Young modulus is held constant throughout the debonding process). The results are presented in Figure 2.10.

In the case $k_0^{init} \leq k_0^{attr}$, the data illustrated in Figure 2.10a appears to demonstrate that a grain reorganization occurs (k_0 evolves) even when the Young modulus remains constant. On the other hand, Figure 2.10b illustrates

2 | Stress state evolution of a cemented granular material subjected to bond dissolution by Discrete Element Modeling

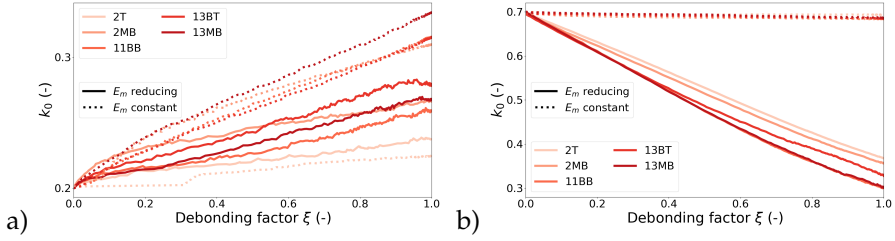


Fig. 2.10 Effect of the Young modulus reduction assumption for different cementations at a confinement pressure $P_{confinement} = 1$ MPa with an initial $k_0 =$ a) 0.2 or b) 0.7.

that grain reorganization does not occur (k_0 remains constant) when the Young modulus remains constant for $k_0^{init} \geq k_0^{attr}$. In this configuration, the reorganization of the grains is a consequence of the reduction in the material's Young modulus. Two distinct mechanisms appear to emerge, contingent on the state of stress.

This phenomenon is also highlighted by considering the evolution of the mean force and the coordination number (proxy of the grain organization). Three simulations are considered: a 13MB sample with a confining pressure $P_{confinement} = 1$ MPa and initial values of $k_0 = 0.2, 0.4$ or 0.7 . The results are shown in Figure 2.11.

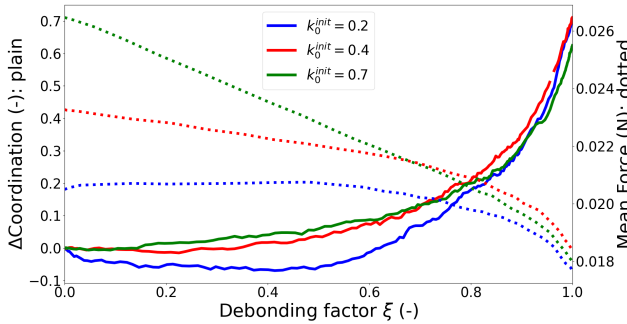


Fig. 2.11 Evolution of the coordination number (plain line), mean number of contacts per grain, with the debonding phenomena. The evolution of the mean force (normal + tangential) transmitted in contacts of the fabric (dotted lines) is plotted in parallel. Notice the coordination number evolutions have been set to start at 0 to be compared.

The distinction between the two mechanisms is underscored by the ob-

servation that the mean force evolution corresponding to $k_0^{init} = 0.2$ exhibits a distinct trajectory compared to the mean force evolutions associated with $k_0^{init} = 0.4$ or $= 0.7$. The first one remains constant (≈ 0.02 N), until a threshold value for the debonding is reached ($\xi \approx 0.6$). In contrast, the mean forces associated with $k_0^{init} = 0.4$ or $= 0.7$ decrease in a linear fashion from the outset of the simulation. A second evolution, exhibiting a more pronounced and less linear trend, can be observed following the attainment of a debonding threshold ($\xi \approx 0.8$). Similarly, it seems that the coordination number corresponding to $k_0^{init} = 0.2$ reduces at the outset of the simulation. Whereas, the coordination numbers corresponding to $k_0^{init} = 0.4$ and $= 0.7$ are intended to increase. This observation served to reinforce the hypothesis that two distinct mechanisms are at play, contingent on the state of stress.

2.3.3 Influence of the initial k_0 on the main grain reorganization mechanism

As emphasized in Section 2.3.2, the principal grain reorganization mechanism seems to depend on the state of the stress. This reorganization induces an evolution of k_0 , related to the evolution of the chain force [SS09, CS14]. It should be noted that the positions of the particles remain largely unaltered as the sample is dense in oedometric conditions. Nevertheless, the minor fluctuations impact the state of the stress within the sample.

The distribution of the mechanisms of bond rupture, illustrated in Figure 2.13, highlights the diverse stress reorganization mechanisms. This distribution considers only the bond rupture after the sample initialization described in Figure 2.3. Indeed, as explained in Section 2.2, this preparation step induces bond breakage before the commencement of the bond dissolution, in a manner analogous to that observed in experiments. The bonds may break in two modes: i) by dissolution (if the bond surface A_b reaches a null or a negative value) or ii) by mechanical loading (if criteria presented in Equation 2.23 are reached). It can be observed that, for a given cementation and confining pressure, the percentage of rupture by loading is greater for $k_0^{init} \leq k_0^{attr}$ than for $k_0^{init} \geq k_0^{attr}$. To gain insight into this discrepancy, the chain forces are classified into two categories: the unstable chain force and the stable chain force, see Figure 2.12.

An unstable chain force is maintained in position by the cementation at the contacts. Once the cement has undergone partial dissolution, the chain force collapses. It should be noted that while the particle positions remain largely unchanged, minor fluctuations induce the evolution of the chain force, resulting in the breaking of the reduced but existing cemented contacts. These

2 | Stress state evolution of a cemented granular material subjected to bond dissolution by Discrete Element Modeling

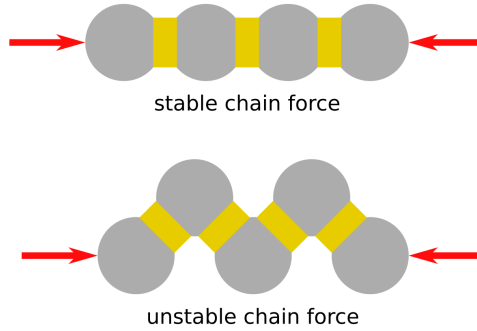


Fig. 2.12 The granular media comprises unstable and stable chain forces.

unstable chain forces induce the bond rupture by mechanical loading. In contrast, a stable chain force remains in place due to the particle-particle contact. In the event of the total dissolution of the cemented contacts, the chain force does not collapse. These stable chain forces induce the bond rupture by chemical loading. It has been demonstrated in the previous Section that grain reorganization will only occur in the case $k_0^{init} \leq k_0^{attr}$ if the cemented contacts are reduced enough. Indeed, the unstable chain forces are predominant in this case. For an illustration of this, one may refer to the k_0 evolution when the Young modulus E_m remains constant during the debonding process, Figure 2.10a. Even if the Young modulus remains constant during the debonding, k_0 evolves/granular reorganization occurs. Once the cemented contacts have been reduced, the cementation at the contacts breaks by mechanical loading, see criterion Equation 2.23. Similarly, it has been demonstrated in the previous Section that grain reorganization occurs directly in the case $k_0^{init} \geq k_0^{attr}$, without the need for a reduction in cemented contacts. Indeed, the stable chain forces are predominant in this case. This is evidenced by the constant k_0 when the Young modulus E_m remains constant during the debonding process, Figure 2.10b. As the Young modulus remains constant during the debonding, k_0 remains constant/granular reorganization does not occur. The cemented contacts break with a chemical rupture, as they are not solicited. The evolution of k_0 is a consequence of the softening of the grains. As the Young modulus decreases with the debonding process, the overlap between the grains increases, inducing grain reorganization (even if the particle positions remain largely unchanged) and a corresponding evolution of k_0 .

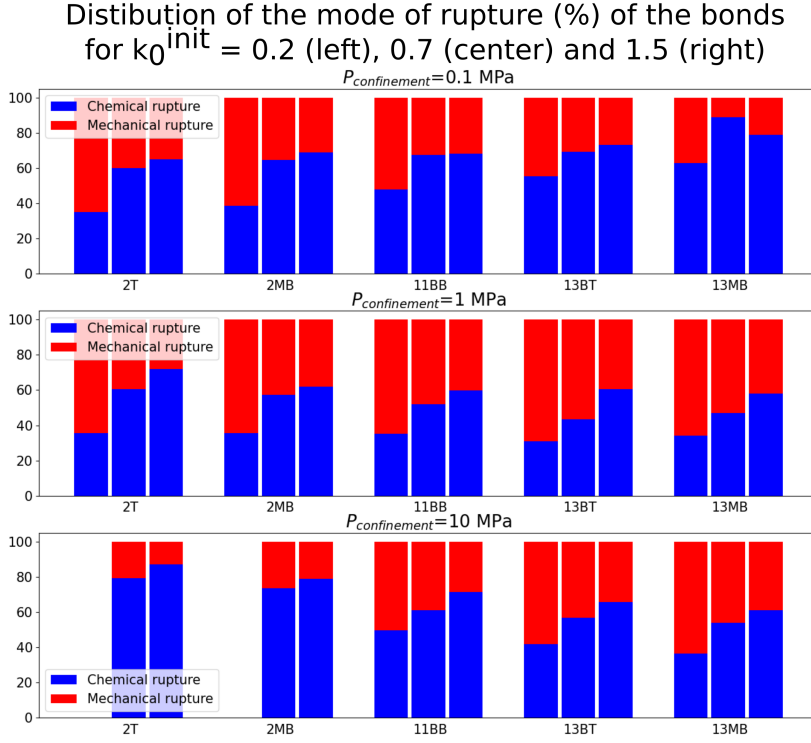


Fig. 2.13 Distribution of the mode of rupture of the bond at the end of the test. A bond can break by chemical dissolution (the bond surface reaches a negative or a null value) or by mechanical loading (criteria presented in Equation 2.23 are reached).

Once the two mechanisms have been described, it is crucial to note that in the cases of light cementations (2T or 2MB), the final values of the k_0 are larger than the others if $k_0^{init} \geq k_0^{attr}$, see Figure 2.6. In this case, the reduction of k_0 is attributable to the softening of the grains. Considering light cementations, the softening is less pronounced given that the Young modulus varies between 300 MPa (for 2T) or 320 MPa (for 2MB) and 80 MPa (for uncemented material). This is, for example, in contrast to 1000 MPa (for 13MB). In the case of light cementations, the Young modulus remains approximately constant, thereby precluding the grain reorganization. The impact of the initial Young modulus value is examined in the following Section, see Figure 2.15. It appears that the Young modulus exerts a notable influence, particularly in the case $k_0^{init} \geq k_0^{attr}$.

2 | Stress state evolution of a cemented granular material subjected to bond dissolution by Discrete Element Modeling

This influence is less pronounced in the case $k_0^{init} \leq k_0^{attr}$.

2.3.4 Influence of the cementation

Following the definition of the different degrees of cementation used by *Sarkis et al.* [SAN⁺22], it appears that the percentage of contacts cemented p_c , the Young modulus E_m , and the bond sizes distribution (defined by m_{log} and s_{log}) change with the cementation. To understand the impact of the cementation on the problem these three effects must be isolated.

The initial stage of the analysis focuses on the impact of the percentage of contacts that are cemented p_c . This parameter describes the ratio of contact cemented during the initial configuration (see step f in Figure 2.3) relative to the total number of contacts. Additional simulations were conducted for comparative purposes. An 11BB sample is generated under $P_{confinement} = 0.1$ MPa with an initial $k_0 = 0.2$ or 0.7 . Three distinct values are considered for the parameter $p_c = 50, 75$ or 100% . The results are presented in Figure 2.14.

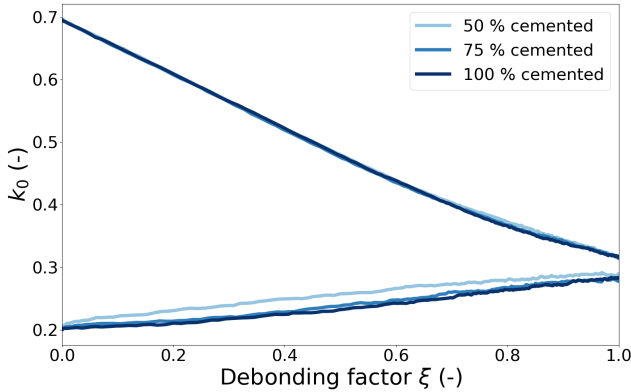


Fig. 2.14 Evolution of the k_0 with the debonding variable ξ for an 11BB sample under $P_{confinement} = 0.1$ MPa with 50, 75 or 100% initial contacts cemented.

It seems that p_c does not affect the evolution of k_0 . A slight discrepancy is observable for $k_0^{init} = 0.2$. However, it remains negligible in comparison to the discrepancies observed with the other cementations in Figure 2.6. This discrepancy can be attributed to the differing reorganization mechanisms at stake, depending on k_0^{init} . As previously outlined in Section 2.3.3, if $k_0^{init} \leq k_0^{attr}$ the main reorganization mechanism is the collapse of the unstable chain forces. In this case, the small amount of cemented contact (p_c smaller) can

weaken the global structure and exert a minor influence on the k_0 evolution. In the case $k_0^{init} \geq k_0^{attr}$ the main reorganization mechanism is grain softening. Here, the distribution of the cemented contact has no impact. In conclusion, it can be stated that the parameter p_c has no influence on the evolution of the k_0 during the debonding process.

The second parameter to be analyzed is the Young modulus E_m . To investigate the effect of this parameter, simulations similar to the results presented previously are conducted, but the initial value of the Young modulus is controlled (considered the same for all cementation: $E_m = 1$ GPa, Young modulus of the cementation 13MB). The results are presented in Figure 2.15.

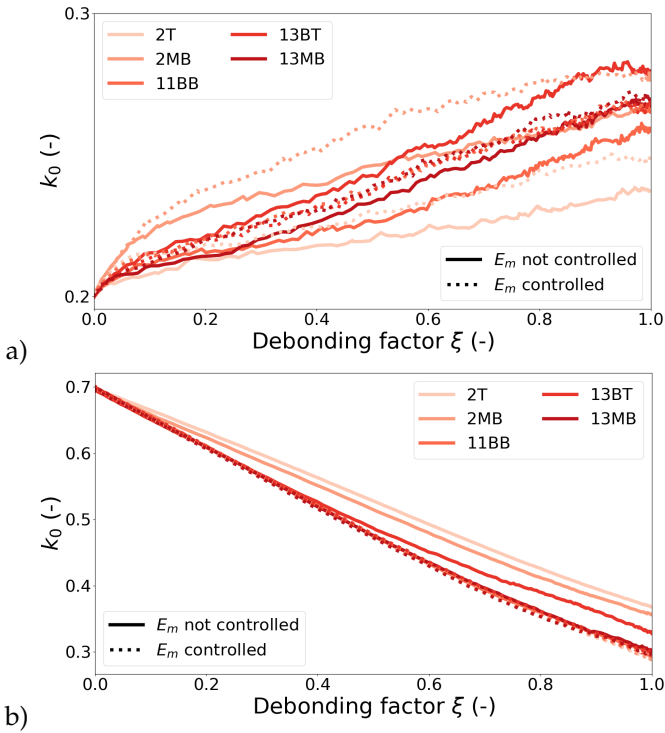


Fig. 2.15 Evolution of the k_0 with the debonding factor ξ for different cementations at a confinement pressure $P_{confinement} = 1e6$ Pa with an initial $k_0 =$ a) 0.2 or b) 0.7. The initial value of the Young modulus E_m is equal to 1000 MPa for the controlled simulations.

For $k_0^{init} \leq k_0^{attr}$, Figure 2.15a, the controlled k_0 evolutions appear to be

2 | Stress state evolution of a cemented granular material subjected to bond dissolution by Discrete Element Modeling

approximately equivalent to the k_0 evolution obtained with a not controlled 13MB cementation. This can be attributed to the fact that the initial Young modulus value is identical to the one employed for this cementation. It is crucial to note that the controlled 2T and 2MB simulations give disparate results. As explained in Section 2.3.3, the evolution of the k_0 is predominantly influenced by the collapse of unstable chain forces for $k_0^{init} \leq k_0^{attr}$, rather than the softening of the grains. The presence of fewer bonds between the grains in lightly cemented samples facilitates the collapse of chain forces. Therefore, it can be concluded that the initial Young modulus has an impact on the evolution of k_0 , although it is not the most significant factor.

For $k_0^{init} \geq k_0^{attr}$, Figure 2.15b, the controlled k_0 evolutions appear to be approximately equivalent to the k_0 evolution obtained with a not controlled 13MB cementation. This can be attributed to the fact that the initial Young modulus value is identical to the one employed for this cementation. Furthermore, the controlled 2T and 2MB simulations yield identical results. As explained in Section 2.3.3, the evolution of the k_0 is predominantly influenced by the softening of the grains for $k_0^{init} \geq k_0^{attr}$, rather than the unstable chain forces collapses. The grain reorganization depends significantly on the initial Young modulus value.

The third parameter to be analyzed is the bond size distribution, which is controlled by m_{log} and s_{log} , see Appendix A. As previously discussed in this Section, the bond size distribution affects the case $k_0^{init} \leq k_0^{attr}$, Figure 2.15a, but not in the case $k_0^{init} \geq k_0^{attr}$, Figure 2.15b. As previously presented in Section 2.3.3, the mechanism of the k_0 evolution can be attributed to the collapse of the unstable chain forces if $k_0^{init} \leq k_0^{attr}$. It is important to note that while the positions of the particles remain largely constant, minor fluctuations can induce changes in the chain forces. The bond size distribution exerts a notable influence on this phenomenon, particularly the variance of the distribution s_{log} . Furthermore, Figure 2.16 illustrates that the light cementations (2T and 2MB) undergo complete dissolution at a significantly faster rate than the high cementations (13BT and 13MB). This Figure represents the evolution of the k_0 with the cumulative bond surface dissolved (similar to the times). The mean of the distribution m_{log} appears to control the temporal aspect of the debonding phenomena.

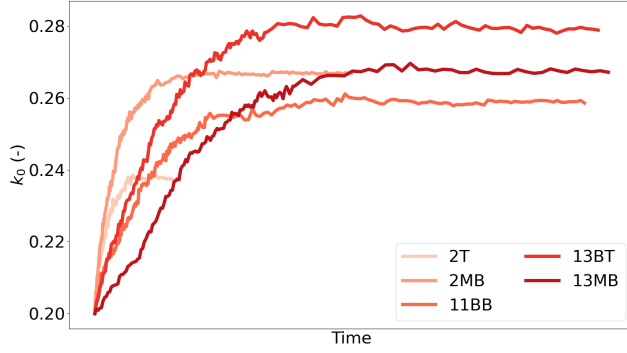


Fig. 2.16 Evolution of the k_0 with the time for the different cementations at $P_{confinement} = 1$ MPa.

2.3.5 Influence of $P_{confinement}$

The impact of the confinement pressure $P_{confinement}$ is studied in this Section. The results are shown in Figure 2.17.

It should first be noted that no results can be obtained for the light cementations (2T and 2MB) at $P_{confinement} = 10$ MPa when $k_0^{init} = 0.2$. The bonds break are found to break during the initial configuration set-up, due to the high confinement pressure. As previously explained in Section 2.2, k_0 is around k_0^{attr} at the step g of Figure 2.3. In order to obtain $k_0^{init} \leq k_0^{attr}$, it is necessary to extend the lateral dimension of the sample. The combination of this extension with the application at the top of the vertical pressure results in bond breakage. This phenomenon occurs less frequently in the case $k_0^{init} \geq k_0^{attr}$ (compression of the lateral dimension of the sample) because the bond breakage occurs only under shear or a tensile conditions, see Equation 2.23. Indeed, the sample is not under tensile loading and the shear condition occurs more frequently in extension ($k_0^{init} \leq k_0^{attr}$) than in compression ($k_0^{init} \geq k_0^{attr}$).

Figure 2.17 illustrates that the coordination number (the mean number of contacts per grain) increases with the confining pressure $P_{confinement}$. As the confining pressure increases, the grains are more squeezed and the number of contacts increases. In DEM, this phenomenon requires careful consideration, particularly in the case of rigid particles. Indeed, the models in question are built on the basis of the small overlap assumption. This limit is named the jammed state [LN98]. As illustrated in the figure, the grain reorganization can be divided into two distinct phases: first a linear part, then a nonlinear. It

2 | Stress state evolution of a cemented granular material subjected to bond dissolution by Discrete Element Modeling

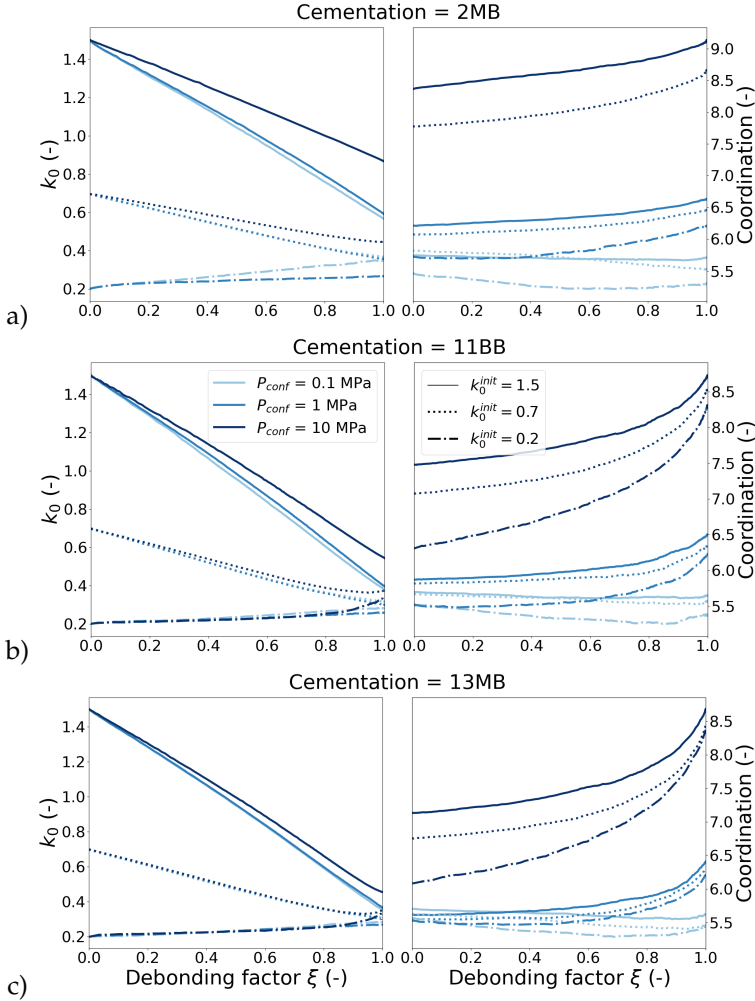


Fig. 2.17 Evolution of the k_0 and the coordination number with the debonding variable ξ at $P_{confinement} = 0.1, 1$ and 10 MPa, with $k_0^{init} = 0.2, 0.7$ and 1.5 for three different degrees of cementation: a) 2MB, b) 11BB and c) 13MB.

should be noted that the Young modulus of the grains E_m reduces as a result of debonding, which serves to indicate that the sample is progressing towards the jammed state. Given that the Young modulus is smaller for lighter cementations, this state is reached sooner. The examples $P_{confinement} = 10$ MPa (green lines) and $k_0^{init} = 1.5$ (plain lines) illustrate this aspect. The nonlinear

portion of the curve begins to emerge at approximately $\xi = 0.6$ for an 11BB sample and $\xi = 0.7$ for a 13MB sample. In a similar idea, the final value of the k_0 is globally larger when $P_{confinement}$ is larger for $k_0^{init} \geq k_0^{attr}$. As the sample approaches the jammed state, the available space for reorganization is reduced. This observation is less evident in the case $k_0^{init} \leq k_0^{attr}$. Indeed, the mechanism of the k_0 evolution is dominated by the collapse of the unstable chain forces, rather than the softening of the grain, see Section 2.3.3.

2.4 Discussion

2.4.1 The evolution of k_0 can generate failure

Figure 2.18 shows the evolution of k_0 ($\Delta k_0 = k_0^{final} - k_0^{initial}$) between the initial and final configurations for different initial $k_0^{initial}$ values at different confinement pressures $P_{confinement}$ and for all the degrees of cementation.

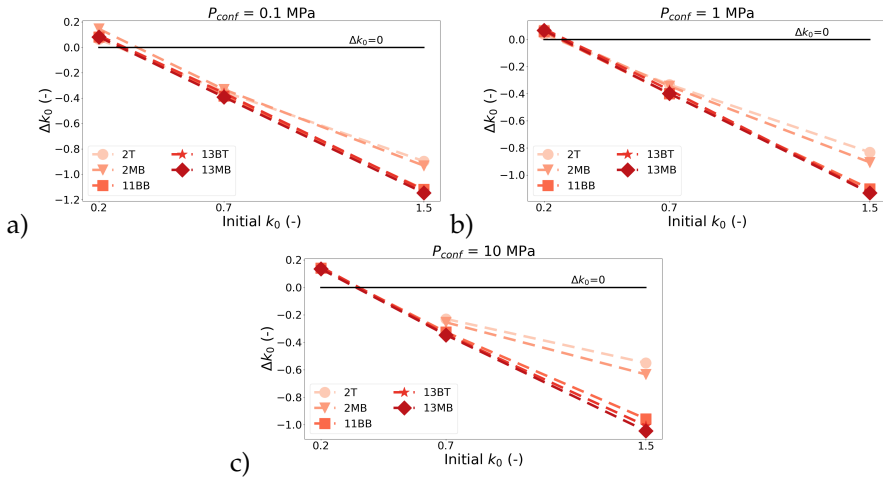


Fig. 2.18 Evolution of the k_0 between the initial and final configurations ($\Delta k_0 = k_0^{final} - k_0^{initial}$) for different initial $k_0^{initial}$ values and all the cements at different confinement pressures $P_{confinement}$ = a) 0.1 MPa b) 1 MPa or c) 10 MPa.

The evolution of the k_0 during dissolution can be of significant consequence, particularly in the context of an underground reservoir. The host rock or the triggering of slip along an existing fault can be modeled using a simple Mohr-Coulomb criterion, illustrated in Figure 2.19. It appears that

2 | Stress state evolution of a cemented granular material subjected to bond dissolution by Discrete Element Modeling

a reduction of $k_0 (= \sigma_{II}/\sigma_I)$ results in a failure. Indeed, the diameter of the Mohr circle increases ($D_{MC} = \sigma_I (1 - k_0)$), where D_{MC} is the diameter of the Mohr circle and σ_I is the vertical stress and remains constant [SSC08]. As previously demonstrated in this study, the k_0 reduction appears only in the case $k_0^{init} \geq k_0^{attr}$. Therefore, this evolution of the k_0 can potentially induce the nucleation of slip, which can lead to an earthquake if the fault is seismogenic [KW18]. This condition appears verified for the majority of tectonic regimes [Hoe07, TFAF16]. Specifically, it has been documented that the normal faults are characterized by $k_0^{init} \approx 0.5$, the strike-slip faults by $k_0^{init} \approx 1$, and the thrust faults by $k_0^{init} \approx 2$ [JC78, TFAF16]. The risk of earthquake nucleation is observed to be greater for strike-slip and thrust faults in comparison to normal faults. Indeed, the amplitude of the k_0 reduction is larger in these cases ($0.5 \rightarrow 0.35$) $\leq$ ($1 \rightarrow 0.35$). It is worth noting that in the context of a thrust fault, the risk of reactivation is initially reduced as the Mohr circle decreases during the step $k_0 = 2 \rightarrow 1$. However, similar to a strike-slip fault, this Mohr circle will increase during the step $k_0 = 1 \rightarrow 0.35$.

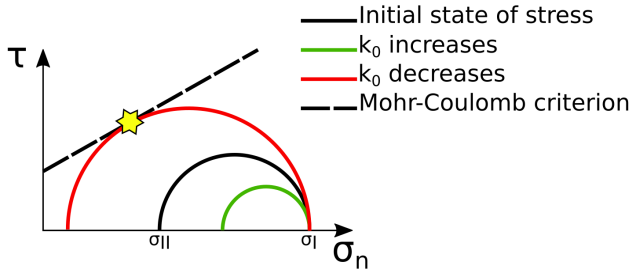


Fig. 2.19 The effect of an increase or a decrease of the k_0 in the Mohr plane, a reduction of this parameter can induce a failure.

2.4.2 On the Young modulus reduction assumption

As explained in Section 2.3.2 and illustrated in Figure 2.10, the assumption of a Young modulus reduction with the debonding (Equation 2.25) is pivotal for the evolution of the stress state of a sample subjected to dissolution of the bonds, particularly in the case of $k_0^{init} \geq k_0^{attr}$. It has been demonstrated that k_0 evolves only when the Young modulus is reduced with the debonding process. This assumption on the evolution of the Young modulus represents not only a numerical investigation of the phenomenon of dissolution but also the different types of contacts and loading history of the sample.

As illustrated in Figure 2.2 and detailed in Section 2.2, a cemented contact can be categorized into three distinct types: I) Frictional, II) Mixed/Cohesive (Frictional+Cemented), or III) Cemented [SAN⁺22]. For type I, there is no cement, so the Young modulus reduction assumption is not required. Otherwise, the contact can be modeled as two springs (one for the grains and one for the cement) in parallel (type II) or in series (type III). For these two types (parallel or series), the Young modulus reduction assumption should be employed, contingent on the loading history, as discussed in the following paragraph. The distinction between type II and III hinges on the ultimate value of the Young modulus E_m^{final} , post-complete dissolution of the bonds. For type II, the ultimate value will be the one which is assumed for frictional contact (type I) E_m^I . For type III, this value will be zero (unless a new contact of type I occurs).

As explained earlier in this Section, the Young modulus reduction assumption can be applied to Type II and III contacts, depending on the loading history. For the purposes of this discussion, it is assumed that cementation is initially generated at pressure P_i . The sample can be modeled as springs (one for the grains, one for the bonds) in parallel (Type II) or series (Type III). As illustrated in Figure 2.20, the cementation is considered loaded only when the applied pressure P_j verifies $P_j > P_i$. Subsequently, the stiffness of the bond spring reduces as the dissolution process occurs. The Young modulus reduction assumption is applied to ensure the sample is representative. An illustration of this configuration is provided in Figure 2.6. It seems that k_0 evolves to reach the value k_0^{attr} . If $P_j = P_i$, the cementation is unloaded, and the debonding has no impact on the mechanical behavior of the sample. It would be erroneous to apply the Young modulus reduction assumption. An illustration of this configuration is provided in Figure 2.10. It seems that k_0 reaches the value k_0^{attr} only in the case $k_0^{init} \leq k_0^{attr}$ and remains constant in the case $k_0^{init} \geq k_0^{attr}$. This preceding discussion is summarized in Table 2.3.

	Contact I	Contact II	Contact III
Bonds loaded	NO	YES ($E_m^{final} = E_m^I$)	YES ($E_m^{final} = 0$)
Bonds not loaded	NO	NO	NO

Table 2.3 Summarize the use of the Young modulus reduction assumption. If the hypothesis is applied, the final value of E_m is given.

2 | Stress state evolution of a cemented granular material subjected to bond dissolution by Discrete Element Modeling

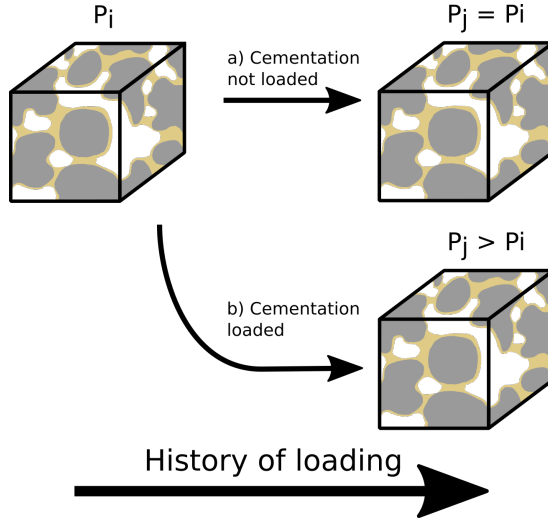


Fig. 2.20 Depending on the history of loading, the cementation can be loaded or not. This scheme illustrates the fact that a cementation that occurred at P_i can be considered a) not loaded if $P_j = P_i$ or b) loaded if $P_j > P_i$, where P_j is the current pressure applied.

2.4.3 A Young modulus dependency on the size of the bonds

As previously mentioned in Section 2.2, the relationship described in Equation 2.25 between the contact scale (E_m) and the sample scale (ξ) could be a matter of contention. This Section explores an alternative approach, in which the local stiffness at each contact is determined by the bond surface $E_m(A_b)$ [SEB16, SEB18], see Equation 2.31. This alternative approach eliminates the discussed relationship between the contact (E_m) and sample (ξ) scales.

$$E_m(A_b) = \frac{E_m^{cementation} - E_m^{untreated}}{A_{b,ref}^{cementation}} \times A_b + E_m^{untreated} \quad (2.31)$$

where E_m is the Young modulus of the contact, $E_m^{cementation}$ is the initial Young modulus depending on the initial degree of cementation, see Table 2.2, $E_m^{untreated}$ is the Young modulus without cementation (here 80 MPa), $A_{b,ref}^{cementation}$ is a bond surface of reference depending on the initial degree of cementation, and A_b is the bond surface of the contact. Each cementation presented in Table 2.1 is represented through the parameters $E_m^{cementation}$ and $A_{b,ref}^{cementation}$. This bond surface of reference $A_{b,ref}^{cementation}$ is computed to ensure that the mean Young

modulus within the sample after the cementation, see step f) in Figure 2.3, is equal to $E_m^{cementation}$ from Table 2.2. Compared to the previous model, a distribution of the Young modulus appears within the sample. From the bond size distribution depicted in Appendix A and the parameters p_c , m_{log} , and s_{log} from Table 2.2, the different values of $A_{b,ref}^{cementation}$ are available in Table 2.4.

Cementation	2T	2MB	11BB	13BT	13MB
$A_{b,ref}^{cementation} (\mu m^2)$	148	2303	4267	6577	8131

Table 2.4 Bond surface of reference with the different degrees of cementation.

Similar to Equation 2.23, the contact strength still depends on the local bond surface area A_b . If one of the rupture criteria is reached, the Young modulus of the contact is considered equal to the Young modulus without cementation (80 MPa). The results of the $E_m(\xi)$ and $E_m(A_b)$ simulations are depicted in Figure 2.21. Similar to Figure 2.6, it has been shown analytically by [VK84] that k_0 approaches a limit given by $k_0^{attr} = \nu / (1 - \nu)$ during weathering and stiffness reduction. Considering a window of $[0.25 - 0.3]$ for the value of ν [CYC⁺17, Zic24, MM24], the attractor value window is $[0.33 - 0.43]$, in agreement with the results obtained.

Moreover, it appears that the k_0 evolution mechanisms revealed for $E_m(\xi)$ in Section 2.3.3 remain the same in the case of $E_m(A_b)$. Indeed, Figure 2.22 emphasizes the mode of rupture of the bond at the end of the test for the distinct cementation and initial state of stress, and similarly to Figure 2.13, the bonds break more by mechanical loading in the case $k_0^{init} \leq k_0^{attr}$ than in case $k_0^{init} \geq k_0^{attr}$. As explained in Section 2.3.3, this behavior is due to the predominance of the unstable chain force in the case $k_0^{init} \leq k_0^{attr}$ and the stable chain force in the case $k_0^{init} \geq k_0^{attr}$.

Even if the attractor configuration exists and the evolution mechanisms are similar, the final states of the stress are different in the cases $E_m(\xi)$ and $E_m(A_b)$. In the case $k_0^{init} \leq k_0^{attr}$, the final value of k_0 appears smaller for $E_m(\xi)$ than for $E_m(A_b)$. To understand this behavior, it is worth remembering that the particles after the bond breakage are stiffer in the case $E_m(\xi)$ than in the case $E_m(A_b)$. While E_m is considered equal to 80 MPa after the breakage of the bond in the case $E_m(A_b)$, the value considered in the case $E_m(\xi)$ is larger, see Equation 2.25. The rupture of the unstable chain forces being the k_0 evolution mechanism in the case $k_0^{init} \leq k_0^{attr}$, stiffer $E_m(\xi)$ particles located on the sides limit the collapse of the unstable chain forces compared to softer $E_m(A_b)$

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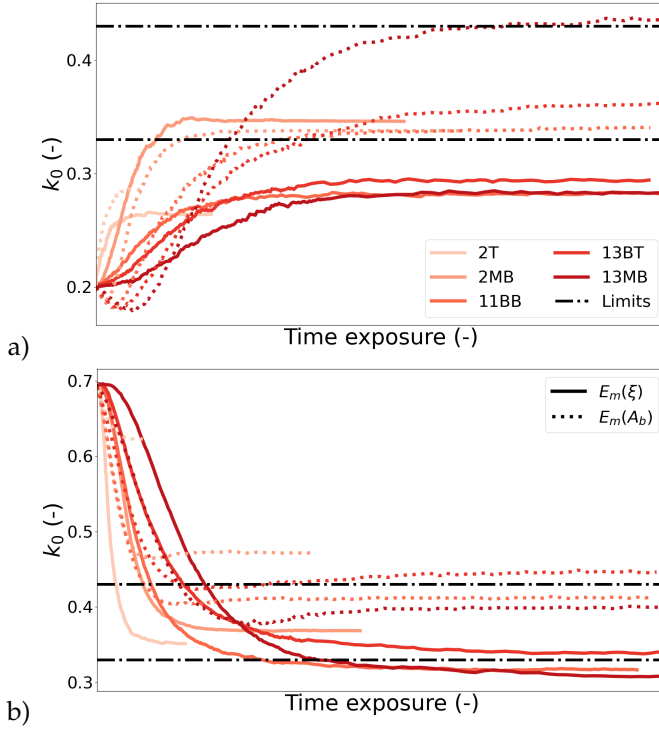


Fig. 2.21 Evolution of k_0 with the time exposure for $P_{confinement} = 0.1$ MPa for $E_m(\xi)$ and $E_m(A_b)$ in the case $k_0^{init} =$ a) 0.2 and b) 0.7. Limits considering $k_0^{attr} = \nu / (1 - \nu)$ are plotted with $\nu = 0.25 - 0.3$.

particles [RWJM98], reducing the amplitude of the k_0 evolution. In the same vein, the final value of k_0 appears larger for $E_m(A_b)$ than for $E_m(\xi)$ in the case $k_0^{init} \geq k_0^{attr}$. The softening of the particles being the k_0 evolution mechanism in the case $k_0^{init} \geq k_0^{attr}$, the k_0 evolution is limited in the $E_m(A_b)$ sample as E_m is considered equal to 80 MPa after the breakage of the bond, while the value considered in the $E_m(\xi)$ sample is larger, and remains decreasing, see Equation 2.25. The amplitude of the k_0 evolution is then smaller in the case $E_m(A_b)$ than in the case $E_m(\xi)$.

The remaining question is to determine the accurate model between the assumptions $E_m(\xi)$ and $E_m(A_b)$. The trivial answer is to consider the case $E_m(A_b)$ as the most accurate option. Indeed, the $E_m(\xi)$ model implies that the contact scale (E_m) depends on the sample scale (ξ), which is controversial. However, coming back to the assumption of the predominance of the type II

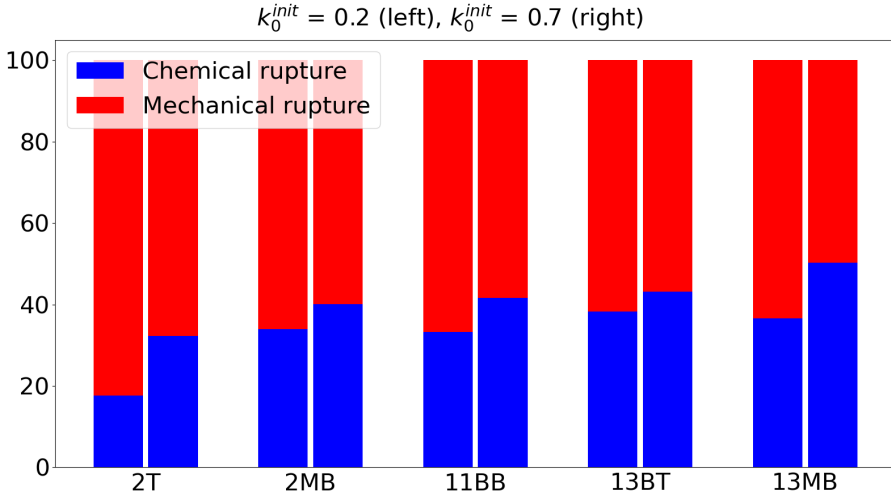


Fig. 2.22 Distribution of the mode of rupture of the bond at the end of the test. A bond can break by chemical dissolution (the bond surface reaches a negative or a null value) or by mechanical loading (criteria presented in Equation 2.23 are reached).

for the contacts, see Figure 2.2, it appears that the bond material participates in the stress transmission (not for traction), even if the contact is broken because of a mechanical loading. The Young modulus of this broken contact with residual bond material should be larger than the Young modulus considered for the uncemented grain-grain contact (type I) as the cement continues to act in parallel to the grain-grain contact and thus provide additional rigidity. The more progressive decrease of the contact modulus with $E_m(\xi)$ allows to take into account this effect to some extent, which is not verified by the model $E_m(A_b)$. It is worth noting that the model $E_m(A_b)$ can be extended to consider the additional rigidity provided by the cement for the broken bonds, increasing the accuracy of the formulation. However, the calibration of such a model seems complex. Indeed, the cement phase is not modeled explicitly. If enough computational power is available, the Phase-Field Discrete Element Model depicted in Chapter 4 appears as a suitable description.

As often with models, the experimental reality is located between boundary scenarios (in this work, $E_m(\xi)$ and $E_m(A_b)$). The existence of the attractor configuration, the mechanisms inducing k_0 evolution, and the main consequence (fault reactivation) are similar in the boundary scenarios; only the

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pattern of k_0 evolution is impacted by the model assumptions.

2.5 Preliminary conclusions

The work presented in this Chapter aims to fulfill the existing gap in the literature concerning the numerical investigation of the behavior of cemented granular material, while the debonding phenomenon occurs. The model consists of using the Discrete Element Method, considering steeply reducing cement, while the granular skeleton remains intact.

The debonding can result in the material failing as a consequence of the deterioration of its mechanical properties and the subsequent evolution of the state of stress. This effect has the potential to have significant implications for fault nucleation and reactivation in the context of underground storage projects. This Chapter explores the impact of several parameters, such as the degree of cementation, the confining pressure, the initial value of k_0 , and the loading history.

It has been demonstrated that an attractor configuration exists and that grain reorganization occurs during the debonding in order to reach this state. In particular, k_0 evolves to its attractor value, exhibiting either an increase or a decrease. It appears that a k_0 reduction, which is the most likely in a reservoir configuration, can be at the origin of fault reactivation and, consequently, induced seismicity.

Two main mechanisms have been identified as responsible for grain reorganization, contingent on the initial state of stress. It is necessary to distinguish between two categories of chain forces: the unstable chain force and the stable chain force. The unstable chain forces provide support for the force thanks to the cementation. However, these structures collapse when the debonding occurs. In contrast, the stable chain forces remain in place even in the absence of cementation. It appears that the unstable chain forces are dominant in the case $k_0^{init} \leq k_0^{attr}$ and the stable chain forces are dominant in the case $k_0^{init} \geq k_0^{attr}$. In the latter case, grain reorganization occurs with grain softening.

Compared to other methods available in the literature, the work depicted herein appears complementary. For instance, the numerical model enables investigations that are difficult to conduct experimentally. Indeed, the soft oedometer employed in [CN04] can not be used to control the initial state of the stress k_0^{init} , and configurations representative of the underground stor-

age ($k_0^{init} = 0.7 - 1.5$) are impossible to study. It would require modifying a triaxial experimental set-up, allowing the control of the initial state of stress during the initialization, and ensuring null lateral deformation during the test once the acid is injected. If the first condition is trivial with such a test (apply vertical and confinement loadings), the second condition is more difficult to realize. Moreover, the use of a numerical model that explicitly describes the microstructure opens an avenue to investigate the mechanisms (granular reorganization for instance) that dictate the behavior of the sample. It is worth noting that in-situ CT scans emerge in geomechanical testing, allowing the visualization of the microstructure evolution during chemical degradation [vS18]. However, this experimental approach remains difficult to conduct and to post-process.

Compared to a Finite Element approach employed to model similar configurations [GLL23, CN04], the Discrete Element Model captures the mechanisms at the microscale that induce the evolution of behavior at the scale of the material. A Finite Element description is unable to distinguish the main mechanism for the granular reorganization, discussed in Section 2.3.3. Moreover, numerous parameters that can be difficult to calibrate are introduced through the Finite Element model. Even if it is also the case for the Discrete Element Model, the Finite Element description requires some relation to model the microstructure of the material, which is explicitly described with the Discrete Element Model. For instance, it appears that the constitutive equation, depicted in [CN04], reproduces well the debonding phenomenon, but misses the prediction of the behavior if the granular skeleton is affected by the reactive fluid, case b) from Fig. 1.2, because of the large microstructure evolution [CN04]. On the contrary, the Discrete Element Model can readily be applied, even if the microstructure evolves, see the investigations conducted on uncemented granular samples during weathering [SS09, CS14, VD20].

The Discrete Element Model obviously implies drawbacks. For instance, the calibration of the parameters remains difficult, especially because of the scale separation (microscale for the parameters and macroscale for the behavior of the material). However, calibration frameworks exist in the literature, see [SAN⁺22]. Moreover, various micro experimental setups emerge [GLS⁺23], favoring the direct measurement of the parameters at the scale of the grain. Then, a second drawback could be the computational cost induced by the Discrete Element Method. However, the algorithms are now mature, optimizing the resolution of the problem. Similarly, the computational resources required are becoming more and more accessible. For instance, one

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simulation depicted herein is approximately 7 hours on a regular computer¹. It seems acceptable to employ a Discrete Element Model to investigate the chemo-mechanical couplings.

¹Intel(R) Core(TM) i5-10210U CPU @ 1.60GHz, 8 Go RAM

3

Hydration of a concrete material through a Phase-Field description

Which indispensable elements are required to design a numerical analog based on physical considerations to explicitly describe the microstructure evolution during hydration?

Chapter 2 presented chemo-mechanical couplings that occur in the case of the debonding of a cemented granular material. The Discrete Element Method (DEM) was utilized due to its ability to effectively capture the mechanical aspect of the problem (stress transmission and granular reorganization). However, the chemical aspect of the problem (dissolution of the bonds) was not sufficiently modeled. Indeed, the bond surfaces were reduced incrementally at a constant rate, which does not accurately reflect the actual behavior. Indeed, the dissolution rate of smaller bonds exceeds that of larger bonds due to their respective specific surface areas [RDSV21]. This Chapter proposes a novel numerical approach to address the limitation of the DEM on the chemical aspect. This new approach is then applied to investigate the hydration of a cement-based material, thereby offering a more comprehensive representation of the chemistry involved.

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Although concrete is one of the most widely used materials, the complex interplay between its microstructure, chemical composition, and mechanical properties is not yet fully understood and continues to be an area of active research, see the discussion in Chapter 1. The classical exploration method is through experimental campaigns. However, concrete requires some time to hydrate and harden conventionally 28 days to have reached a state sufficiently hard to sustain a significant load. As illustrated in Figure 1.3, the hydration process is divided into the dissolution of the source material, the diffusion of the solute, and the consumption of this solute to generate bonds between the aggregates. To circumvent the prolonged nature of experimental campaigns, a numerical laboratory approach has been designed to examine the hydration process at the microscale, employing high-performance computing resources [WRS85, JJ86, Ben97].

One of the earliest microstructure-based modelizations is *HYMOSTRUC* [vB95]. The sources and products of hydration are defined as continuum spheres. In the context of dissolution, the sphere sizes decrease, whereas in the context of precipitation, they increase. Subsequently, the framework has been extended to consider heterogeneous shapes. The microstructure is subdivided into voxels, which represent an individual phase. Following a random walk algorithm and using Cellular Automata, the voxels diffuse and react with each other if a collision occurs. This solver, designated *CEMHYD3D* [HKT20], induces the evolution of the microstructure and the formation of the hydrated phases. However, the size resolution is constrained by the size of the elementary voxel, which represents a single phase. To address this limitation, alternative solvers have been developed, including *HydratiCA* [Bul07], *µic* [BS09], and the *Integrated Particle Kinetics Model* [PNS05].

A remaining issue persists, the coefficients applied in the Cellular Automata reactions are obtained through a semi-empirical method. *Petersen et al.* have recently developed a framework to address this microstructure evolution with a Phase-Field method [PVPU18]. The Phase-Field description offers a physics-based description of the interface problem [Lan36, CH58, AC79]. To do so, the description is required to be continuous, and not discrete such as with Cellular Automata, see Figure 3.1.

This Phase-Field methodology has been successfully implemented in a variety of dissolution/diffusion/precipitation problems [MBW08, Tak14, GRV20, LWW⁺23, SMVR24a, SMRV25a] or fracture ones [UWA⁺21, XZ23]. In addition to the physics-based laws for dissolution/precipitation, the Phase-Field equations can be coupled with a diffusive conservative equation to model the dilute species [PVPU18, SMVR24a, SMRV25a]. The dissolution/precipitation

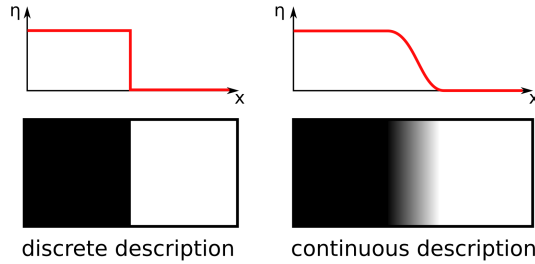


Fig. 3.1 Phase-Field formulation considers a continuous description to solve interface problems.

occurs if the concentrations of the solute species do not verify their equilibrium constants.

Nevertheless, the formulation described in [PVP18] appears to be suitable for further improvement. In particular, the free energy utilized, a fundamental component of the Phase-Field formulation, facilitates the spontaneous precipitation of the gel even if the system is at the equilibrium state. Moreover, the equilibrium concentration values employed for the reactions source-solute (dissolution) and solute-gel (precipitation) are not consistent with the current understanding of hydration. Indeed, they are considered equal in [PVP18], while they are distinct in reality [BJL⁺11, SJM15]. The present Chapter proposes an adapted Phase-Field formulation.

Once the hydrated microstructure has been computed, it becomes possible to determine the mechanical behavior of the hardened cement-based material using mechanical homogenization methods. This includes the calculation of the Young modulus, Shear modulus, Bulk modulus, Poisson's ratio, and strengths. These mechanical parameters depend on the microstructure, and so, on the hydration state. The phases (pore, aggregate, bond) can be distinguished and characterized based on their intrinsic properties. Herein, the approach followed is the computational homogenization: the composite microstructure can be subjected to a Finite Element Model to interpolate the parameters at the sample scale [IAM⁺23, NLYK24].

Some examples of scripts used are available on Github: https://github.com/AlexSacMorane/PF_CementHydration.

First, the Phase-Field formulation is presented. Then, the numerical model and the results of the microstructure evolution are displayed, considering two distinct limiting cases: $w/c = 0.3$ and $= 0.5$ (w/c is the mass ratio of the water and source of cement). These results are compared with previous numerical

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simulations obtained by Cellular Automata. Afterwards, the interpolation of the mechanical properties of the sample based on its microstructure is presented and applied.

3.1 Formulation of the microstructure evolution

This Section focuses on the modelization of the microstructure evolution during hydration. This chemical process is divided into two main reactions: dissolution and precipitation. The source phases (mainly C_3S , C_2S , C_3A and C_4AF) react with water and dissolve [Tay97, ZHY20]. The solute generated diffuses and is consumed during the precipitation of the phases of the cement paste (mainly calcium silicate hydrates CSH and Portlandite CH) [Tay97, ZHY20]. For simplicity reasons, only three phases are considered in this Chapter: the source (C_3S) which is the main clinker phase of Portland cement [ZHY20, BF10], the paste of the cement (CSH) which represents the main product of the hydration [ZHY20, NLYK24] and the solute (c). Moreover, the local packing fraction of the CSH is considered constant and homogeneous in the precipitated phase. This assumption is a limitation compared to the observations showing that this parameter is heterogeneous and evolves with the hydration process [IKB⁺16, IPDG14, HL14]. As shown in Figure 1.3, C_3S dissolves to generate c, and c is consumed to generate CSH after its diffusion. Of course, the framework presented here can be extended to the other phases and to an evolving local packing fraction for the CSH.

In the following Sections, the equations solved and the numerical model are presented. Then, a validation of the microstructure is performed by comparison with microstructures from the literature [TJC09, NLYK24].

3.1.1 Equations solved

Three coupled equations are solved with a finite element solver MOOSE [SAPT17, PGA⁺20]. In particular, this solver is able to consider multiphysics (chemistry, hydraulics, mechanics and/or temperature, for instance), while ensuring a reasonable computational cost. Equations 3.1 and 3.2 are Allen-Cahn formulations [AC79] applied to the phase variables C_3S (the source of the cement) and CSH (the cement paste). The variable C_3S equals 1 if it is located inside the source of cement and equals 0 elsewhere. In the same vein, CSH equals 1 in the CSH gel and equals 0 elsewhere. In the following of this Chapter, a variable η can be used, representing the variables C_3S or CSH . Modeling dissolution/precipitation phenomena, Allen-Cahn formulations are em-

ployed [SMVR24a, SMRV25a]. Equation 3.3 is a conservative diffusive equation applied to the variable c . This variable models the solute concentration in the water of the dilute species.

$$\frac{\partial C_{3S}}{\partial t} = -L_{C3S} \frac{\partial f_{C3S} + Ed}{\partial C_{3S}} + L_{C3S} \kappa_{C3S} \nabla^2 C_{3S} \quad (3.1)$$

$$\frac{\partial C_{SH}}{\partial t} = -L_{CSH} \frac{\partial f_{CSH} + Ep}{\partial C_{SH}} + L_{CSH} \kappa_{CSH} \nabla^2 C_{SH} \quad (3.2)$$

$$\frac{\partial c}{\partial t} = -\alpha_{CSH} \frac{\partial C_{SH}}{\partial t} - \alpha_{C3S} \frac{\partial C_{3S}}{\partial t} + \kappa_c \nabla^2 c \quad (3.3)$$

where L_η (η is $C3S$ or CSH in the following) is the effective mobility of the phase η (setting the kinetics of the relation, $= 1$ here), κ_η is the gradient coefficient of the phase η (influencing the width of the phase interface, see Figure 3.1), f_η is the free energy of the phase η , Ed/Ep are the tilting free energies. The formulation of the free energies $f_\eta/Ed/Ep$ are described in Section 3.1.2. Finally, κ_c is the diffusivity of the solute concentration c , defined Equation 3.4 [PVPU18].

$$\kappa_c = \kappa_{c0} (1 - C_{3S}) \exp(-\kappa_{cexp} C_{SH}) \quad (3.4)$$

where the term $1 - C_{3S}$ is a penalty term to avoid diffusion of the solute c in the source of cement. Similarly, the term $\exp(-\kappa_{cexp} C_{SH})$ models the decrease of the diffusivity of the solute in the gel [MTTA00, AN84], where κ_{cexp} is the penalty coefficient. A factor $\exp(-\kappa_{cexp}) = 1/400$ is used here [LQQ⁺19].

The Phase-Field parameters are correlated, see Equations 3.5 and 3.6 [Tak14].

$$\kappa_\eta = \frac{3}{2} \frac{\delta \cdot \gamma}{b} \quad (3.5)$$

$$W_\eta = 6 \frac{\gamma \cdot b}{\delta} \quad (3.6)$$

where κ_η is the gradient energy coefficient (from Equations 3.1 and 3.2), δ is the interface thickness (see Figure 3.1), γ is the interface energy, W_η is the barrier height (from Equation 3.10), and $b = 2.2$ a coefficient, see [Tak14]. Equations 3.5 and 3.6 can be combined to relate the gradient energy coefficient κ_η , the barrier energy W_η and the interface width δ , through Equation 3.7.

$$\kappa_\eta \propto W_\eta \cdot \delta^2 \quad (3.7)$$

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Usually, $\delta = 4\Delta - 10\Delta$ [MBW08, Tak14], where Δ is the mesh discretization. Even if a strong mesh dependency exists because of the Phase-Field definition, Appendix D presents a method to cancel this impact.

The terms $\frac{\partial c}{\partial t} = -\alpha_{CSH} \frac{\partial CSH}{\partial t} - \alpha_{C3S} \frac{\partial C3S}{\partial t}$ of the Equation 3.3 ensure the conservation of the total mass [SMVR24a, SMRV25a]. The coefficients α_{CSH} and α_{C3S} represent conversion terms (1 η gives α_{η} c). These coefficients can be determined with the mass conversation between the initial $\cdot_i$ and the final $\cdot_f$ configurations at the saturation limit, see Equation 3.8 and Table 3.1. The saturation limit is defined as the total consumption of the source particles, and the entire saturation of the domain by the CSH gel.

$$\alpha_{C3S} C3S_i + \alpha_{CSH} CSH_i + c_i = \alpha_{C3S} C3S_f + \alpha_{CSH} CSH_f + c_f \quad (3.8)$$

	initial state $\cdot_i$	final state $\cdot_f$
C3S	1/2.344 (see Equation 3.9)	0 (no source)
CSH	0 (no CSH gel)	1 (domain saturated in CSH gel)
c	$c_{eq,CSH}$ (equilibrium with the CSH gel)	$c_{eq,C3S}$ (equilibrium with the source)

Table 3.1 Values of the variables employed in Equation 3.8 at the saturation limit.

In this Chapter, the saturation limit is assumed to be $(w/c)_{sat} = 0.42$ [PVPU18], where w is the mass of water and c is the mass of the source. Considering $\rho_{H2O} = 1000 \text{ kg.m}^{-3}$ and $\rho_{C3S} = 3200 \text{ kg.m}^{-3}$, it is possible to determine $C3S_i$ by inversion of Equation 3.9.

$$(w/c)_{sat} = 0.42 \iff \frac{1 - C3S_i \rho_{H2O}}{C3S_i \rho_{C3S}} = 0.42 \quad (3.9)$$

By the nature of the problem, the equilibrium constants $c_{eq,C3S}$ and $c_{eq,CSH}$ must be different [BJL⁺11, SJM15]. Furthermore, it appears that $c_{eq,C3S}$ is several orders of magnitude larger than $c_{eq,CSH}$ [ZHY20]. Thus, it can be assumed that $c_{eq,C3S} = 1$ and $c_{eq,CSH} = 0$ in this Chapter. Injecting these assumptions into the Equation 3.8 and assuming $\alpha_{CSH} = 3$, it gives $\alpha_{C3S} = 9.376$. It is important to notice that the value of the coefficient α_{CSH} has been found with a trial-and-error method and must be large enough. Indeed, this coefficient affects the conversion term α_{C3S} between the source C3S and the solute c during the dissolution. If the value is too small, the solute c produced is not large

enough to saturate the pore fluid, and the supersaturation state observed in experiments is not verified [BJL⁺11, SJM15]. The consequence of a not large enough α_{CSH} coefficient is the fact that the source particles are significantly dissolved before the precipitation of the paste, not in agreement with the experimental observations.

3.1.2 Tilting the free energy f_η to obtain dissolution/precipitation

In this description, the source of cement is modeled by the phase variable $C3S$. In a similar vein, the CSH gel is modeled by the phase variable CSH . As a reminder, a variable η can be used in this Chapter to refer to $C3S$ or CSH . As emphasized by the Allen-Cahn formulation, Equations 3.1 and 3.2, a free energy f_η is employed to describe the problem. The equilibrium is reached in the system when the free energy is minimized. In the literature different expressions are available [PVPU18, Tak14, DSR00, Che02] but a double well shape is preferred, as the minimum locations are fixed and known. Furthermore, it appears as the most used one in the literature. The formulation of this function is given Equation 3.10 and is illustrated in Figure 3.2.

$$f_\eta(\eta) = W_\eta \times \eta^2(1 - \eta)^2 \quad (3.10)$$

where W_η is the barrier energy of the phase variable η ($= 1$ here), preventing phase transformation.

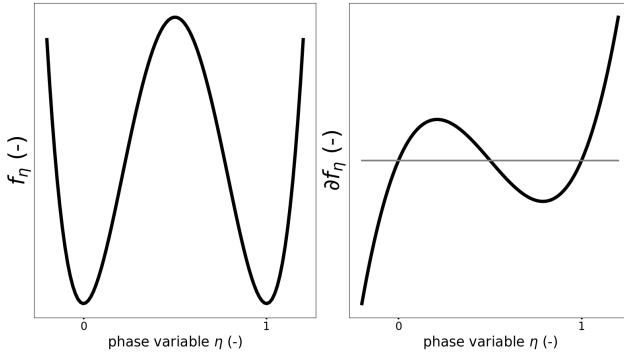


Fig. 3.2 Free energy f_η and its derivative ∂f_η .

It is important to notice that the minima of this potential energy are located at $\eta = 0$ and $\eta = 1$. These values are the ones used to describe the source and the gel. As the Phase-Field description minimizes the free energy

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in the domain, the phase variable stays at these values at the equilibrium and without external destabilization. There is no dissolution/precipitation. The idea is then to add an external source term Ed/Ep to tilt the initial free energy to favor localized dissolution or precipitation. Indeed, depending on the tilting, $\eta = 0/1$ is no longer the minimum of the free energy, some dissolution/precipitation needs to occur. These tilting free energy functions are defined in Equations 3.11 and 3.12.

$$Ed(c, C3S) = \chi_{c, C3S} \times (c_{eq, C3S} - c) \times h_{C3S}(C3S) \quad (3.11)$$

where $h_{C3S}(C3S) = 3C3S^2 - 2C3S^3$ is an interpolation function on the phase variable $C3S$ [Tak14], $\chi_{c, C3S}$ is the tilting coefficient related to the dissolution kinetics. This coefficient can be calibrated with experimental data. The choice of the interpolation function h_{C3S} has an insignificant impact. The required properties are $h_{C3S}(0) = 0$, $h_{C3S}(1) = 1$, and $\frac{\partial h_{C3S}}{\partial C3S}(0) = \frac{\partial h_{C3S}}{\partial C3S}(1) = 0$. For instance, other formulations have been employed in [PVPU18]. It is important to notice that the tilt occurs only if $c \neq c_{eq, C3S}$ and dissolution occurs in the case $c < c_{eq, C3S}$. The value $c_{eq, C3S} = 1$ is considered for the equilibrium for the source dissolution. Figure 3.3 illustrates an example of tilting. It is important to point out that the term $\chi_{c, C3S} \times (c_{eq, C3S} - c)$ determines the amplitude of the tilting, and so the kinetics of the dissolution. The larger the tilting is, the faster the dissolution is.

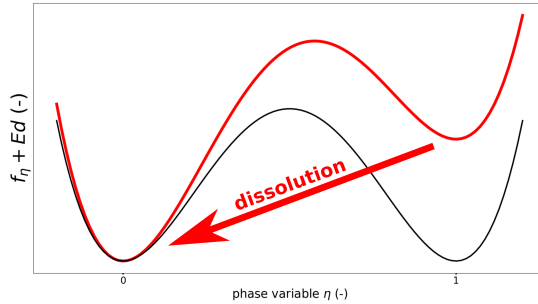


Fig. 3.3 Example of tilted free energy f_{C3S} (in red), the dissolution is favored ($c < c_{eq, C3S}$).

$$Ep(c, CSH) = \chi_{c, CSH} \times (c - c_{eq, CSH}) \times h_{CSH}(CSH) \quad (3.12)$$

where $h_{CSH}(CSH) = 1 - (3CSH^2 - 2CSH^3)$ is an interpolation function on the phase variable CSH [Tak14], $\chi_{c, CSH}$ is the tilting coefficient related to the

precipitation kinetics. This coefficient can be calibrated with experimental data. Similarly, the choice of the interpolation function h_{CSH} has an insignificant impact. The required properties are $h_{CSH}(0) = 1$, $h_{CSH}(1) = 0$, and $\frac{\partial h_{CSH}}{\partial CSH}(0) = \frac{\partial h_{CSH}}{\partial CSH}(1) = 0$. It is important to notice that the tilt occurs only if $c \neq c_{eq,CSH}$ and precipitation occurs in the case $c > c_{eq,CSH}$. The value $c_{eq,CSH} = 0$ is considered for the equilibrium for the CSH precipitation. Figure 3.4 illustrates an example of tilting. It is important to point out that the term $\chi_{c,CSH} \times (c - c_{eq,CSH})$ determines the amplitude of the tilting, and so the kinetics of the precipitation. The larger the tilting is, the faster the precipitation is.

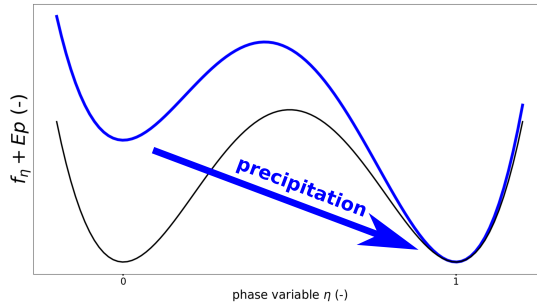


Fig. 3.4 Example of tilted free energy f_{CSH} (in blue), the precipitation is favored ($c > c_{eq,CSH}$).

Even if the model can predict the distribution of the volume fractions of the different phases, it is worth noting that the chemical shrinkage is not captured herein. This phenomenon is defined as a reduction of the source+paste+water volume and an increase of the air volume (in proportion to conserve the volume of the sample) [PB46]. For simplicity reasons, the air phase is neglected and the domain is assumed to be always saturated (addition of water during the hydration). Indeed, the effect of the shrinkage (and the required addition of water) remains small on the hydration phenomenon. Moreover, the advection of the fluid is not considered in these simulations, restricted to diffusion as a transport mechanism. Such a consideration would be possible, coupling the formulation depicted herein with a Computational Fluid Dynamics solver, adding a layer of complexity (and so some computational cost) to the framework.

The Phase-Field framework with dissolution/precipitation is ready to be employed to predict the microstructure evolution.

3 | Hydration of a concrete material through a Phase-Field description

3.2 Numerical microstructure evolution

Similarly to [NLYK24], two configurations are considered employing a $100 \mu m$ domain size: $w/c = 0.3$ and $w/c = 0.5$, where w is the mass of water and c is the mass of the source. Indeed, a water-to-cement ratio (w/c) of 0.42 has been assumed as the saturation limit to define the problem [PVP18], see Equation 3.9. Even if the framework is easily extended to 3D, only 2D slices have been considered in this Chapter. Indeed, the Phase-Field description can be computationally expensive. The different parameters are available in Table 3.2. Considering the lack of information on the value of the tilting coefficients $\chi_{c,CSH}/\chi_{c,C3S}$, they have been assumed equal. Moreover, the competition between precipitation/dissolution $\chi_{c,CSH}/\chi_{c,C3S}$ and diffusion κ_{c0} is primordial. Indeed, the slowest physics (which can evolve with the hydration) determines the rate of the global process. It appears that the diffusion in the CSH gel dictates the rate of the hydration reactions [BJL⁺11, SJM15]. This diffusivity value κ_{c0} is uncertain and has been determined by a trial-and-error method to correlate data from [NLYK24]. At the contrary, the values of the tilting coefficients $\chi_{c,CSH}/\chi_{c,C3S}$ have an insignificant impact on the results as the precipitation/dissolution physics is faster than the diffusion.

The mesh size ($0.2 \mu m$) has been determined to limit the computation cost induced by the Phase-Field description, while ensuring the quality of the result. Such as comparison, a mesh size of $1 \mu m$ is employed in the Cellular Automata formulation [NLYK24].

Domain size	$100 \mu m$
Mesh size Δ	$0.2 \mu m$
Tilting coefficients $\chi_{c,C3S}/\chi_{c,CSH}$	$0.1 W_{\eta}$
Diffusivity κ_{c0}	$1 \mu m^2.s^{-1}$

Table 3.2 Parameters used during the microstructure evolution simulations.

3.2.1 Initial conditions

Spheres are generated in a periodic domain, considering a given particle size distribution function [NLC⁺21, NIS05] and a random position avoiding overlap. This particle size distribution is modified, see Appendix C, as the nature of the Phase-Field theory limits the size of the particles ($R_{min} \geq 12\Delta$, where Δ is the mesh size). Even if it is unclear in [NLYK24], such modification seems also to be employed during the generation of the initial conditions for the Cellular Automata approach. Spheres are generated until the domain reaches a

targeted ratio w/c . Once the positions of the source of cement have been determined, they are considered fixed. Compared to the Discrete Element Model used in Chapter 2, no granular reorganization occurs. It is worth noting that sphere shapes have been used for simplification reasons, the Phase-Field formulation can capture any heterogeneous shape, see examples during the hydration in Figure 3.5.

Afterwards, it is possible to compute the map of the phase variable C3S. A signed distance to the interface water-cement is computed and a cosine profile is used [Tak14], defined Equation 3.13.

$$\begin{aligned}
 &= 1 \text{ if } d \leq -\delta/2 \text{ (inside the grain)} \\
 \text{C3S} &= 0.5 \left(1 + \cos \left(\pi \frac{d + \delta/2}{\delta} \right) \right) \text{ if } |d| < \delta/2 \text{ (in the interface of the grain)} \\
 &= 0 \text{ if } d \geq \delta/2 \text{ (outside the grain)}
 \end{aligned} \tag{3.13}$$

where d is the signed ($-$ if inside the grain, $+$ if outside the grain) distance of the node to the interface and δ is the interface thickness.

Concerning the map of the phase variable CSH , one would like to set $CSH = 0$ (no gel) everywhere. Then, the gel needs to nucleate and propagate with the consumption of the solute c . Nevertheless, Phase-Field formulation has some difficulties in capturing the nucleation phenomenon, in particular if it is localized. The physical mechanisms governing the initial formation of C-S-H are known to be complex, involving processes like frustrated nucleation and growth. To ensure the localization of the nucleation around the source particle [Tay97, ZHY20], a given number of nucleation seeds are generated. The same strategy was used in Molecular Dynamics precipitation simulations for the nucleation and growth of CSH [IPDG14, GIT⁺20]. Their positions are randomly selected in the source neighborhood. Then, a cosine profile, see Equation 3.13, is applied with a radius of several mesh sizes. An example of this initialization is depicted at the top of Figure 3.5. Furthermore, some noise is introduced in Equation 3.2 to obtain heterogeneous nucleation/growing due to imperfections or temperature fluctuations [PVPU18, Cas03].

Finally, the solute concentration c is set to $c_{eq, CSH} = 0$ in the domain, the value of the gel-water equilibrium. Without source grain, the domain is at the equilibrium. After the introduction of the source in the domain, dissolution occurs as the source-water equilibrium is not verified ($c = 0$ versus

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$c_{eq,C3S} = 1$). The consequence of this dissolution is the increase of the solute concentration c in the domain. With $c > c_{eq,CSH}$, the gel-water equilibrium becomes not verified, and precipitation occurs. As depicted in Figure 1.3, these processes verify the hydration phenomenon.

3.2.2 Results

Figure 3.5 shows examples of microstructure evolution. As expected, the source phase dissolves to produce the gel phase. Occasionally, a source grain may become entrapped within the cementitious matrix, subsequently acting as an inclusion within the hardened paste. Indeed, the solute generated from the source dissolution is trapped in the paste. Remember that the diffusivity of the solute is much smaller in the paste than in the pore [BJL⁺11, SJM15, SGXZ22], see Equation 3.4. As the solute is trapped, the solute concentration c reaches the equilibrium value of the dissolution reaction $c_{eq,C3S}$, and the dissolution stops locally. Furthermore, it appears the paste is not the only phase to precipitate (see at the bottom for $w/c = 0.3$). Indeed, the source phase precipitates also. The Phase-Field theory can induce curvature-driven shape evolution to reduce surface tension [AC79, MBW08]. The origin of this unphysical phase evolution is the gradient coefficient κ_η from Equations 3.1 and 3.2. The solution to this problem appears to be the use of new distinct phase variables for each grain, increasing the computational cost [SMVR24a]. The impact of this unphysical precipitation of the source material appears to be negligible in the following.

It is worth noting that microstructures from Figure 3.5 have not reached the final configuration. Indeed, some chemical reactions occur until the total consumption of the source particle (for the undersaturated configuration, $w/c = 0.5$) or until the saturation state is reached (for the oversaturated configuration, $w/c = 0.3$). However, the hydration kinetics are strongly slowed down by the trapping of the solute in the paste. The final configurations depicted herein are expected to be a sufficient approximation of the steady state.

Compared to microstructures obtained with a *CEMHYD3D* model [NLYK24] or observed after real hydration [TJC09], see Figure 3.6, the phase boundaries are smoother and the integrity of the phases is conserved in the Phase-Field framework. Indeed, the Phase-Field framework has been observed to facilitate the smoothing of interfaces [KGB⁺22], which may lead to the inaccurate capture of the fingering growth pattern [TJC09]. A finer mesh would help to capture heterogeneous shapes, increasing the computational cost.

This chemical process can be described by the degree of hydration h , de-

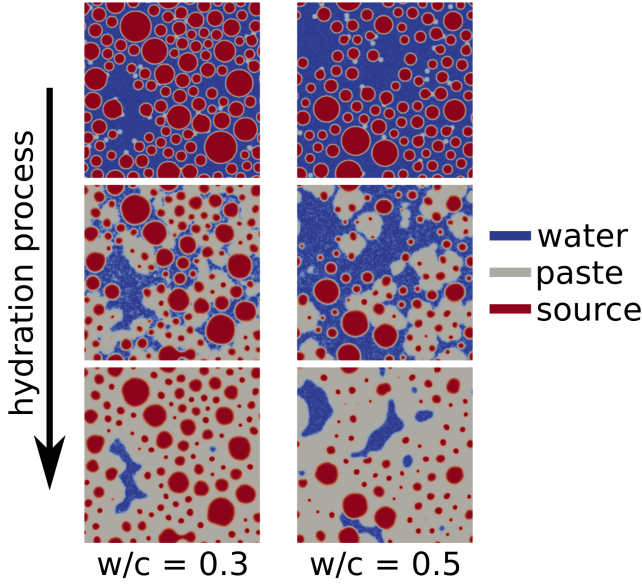


Fig. 3.5 Evolution of the microstructures during the hydration process (domain is $100 \times 100 \mu\text{m}^2$).

defined in Equation 3.14. This index evolves from 0 initially to 1 when all the source phase is dissolved. Figure 3.7 shows the evolution of the hydration in the two cases considered ($w/c = 0.3$ and 0.5). The results are compared to the hydration curves obtained with the Cellular Automata description in [NLYK24] and to experimental results obtained with $w/c = 0.4$ and $= 0.55$ [MI14]. To do so, the time has been normalized for each curve by the time at $h = 0.5$. Hydration appears to be divided into two parts: a fast dissolution period and a slow dissolution period [BJL⁺11, SJM15, SGXZ22]. In the first part of the curve, dissolution occurs. However, the diffusivity of the solute aims to decrease with the precipitation of the CSH, and the solute concentration reaches locally the water-source equilibrium value. This phenomenon slows-downs the dissolution of the source, explaining the second part of the curve. As expected, the hydration kinetics is faster for the configuration $w/c = 0.5$ than for $w/c = 0.3$. Indeed, $w/c = 0.5$ is an under-saturation configuration, and the dissolution of the source particles is favored. The results from the Phase-Field simulations appear to correlate well with the Cellular Automata prediction and with the experimental observations (even if the w/c are not similar).

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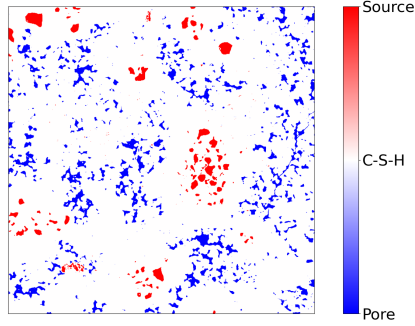


Fig. 3.6 Microstructure of a $w/c = 0.5$ sample after hydration, from [TJC09] (domain is $320 \times 320 \mu m^2$).

$$h = \frac{C3S_i - C3S_t}{C3S_i} \quad (3.14)$$

where $C3S_i$ and $C3S_t$ are the source variable's initial and current mean values.

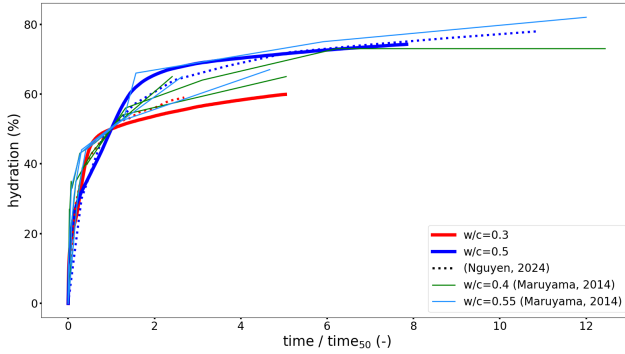


Fig. 3.7 Time evolution of the degree of hydration in the case $w/c = 0.3$ and 0.5.

Then, the microstructure evolution can be described through the evolution of the volume fractions of the different species, see Figure 3.8. The hydration phenomenon appears well divided into the dissolution of the source to generate some solute and then the consumption of the solute to precipitate the paste, with an intermediary supersaturation of the pore space with respect to the gel. If the mean value of the source quantity appears similar to the one obtained by [NLYK24] (C_3S , C_2S , C_3A , C_4AF species are considered), it

is not the case for the mean value of the paste quantity (CSH , CH species are considered), which is larger in the simulations presented herein. Even if supplementary phases were included such as the gypsum, the anhydrite, the ettringite, the AFm or FH_3 in [NLYK24], these phases represent only $\sim 19\%$ of the volume for $w/c = 0.3$ and $\sim 16\%$ of the volume for $w/c = 0.5$ [HGB⁺05]. It is not sufficient to fill the gap between the Phase-Field and the Cellular Automata descriptions. In order to determine the most accurate formulation, the final concentrations of the source and the paste obtained from the hydrated microstructure available in [TJC09] ($w/c = 0.5$) are depicted for comparison. The results obtained with the Phase-Field description appear more accurate. It seems that *CEMHYD3D* simulations overestimate the pore space, in particular for the case $w/c = 0.5$. Furthermore, it is not possible to know the mean value of the solute concentration in the data described in [NLYK24]. Indeed, the *CEMHYD3D* description does not consider this specific phase. In the Cellular Automata approach, the source phase is transformed directly into a paste phase if the chemical conditions are set (reaction between given phases). Compared to the data from [NLYK24], a delay can be appreciated in the Phase-Field formulation concerning the precipitation of the paste, due to the required diffusion of the solute.

The microstructure can be more deeply described by looking at the evolution of the perimeter of each phase (paste, source, paste+source), see Figure 3.9. To do so, the microstructure is segmented into three phases: paste, source, and paste+source. To do so, the node of the mesh is considered in the paste phase if $CSH > 0.5$. Similarly, the node is considered in the source phase if $C3S > 0.5$. The paste+source phase is a combination of the two previous phases. Then, the perimeter index is obtained by the function *measure.perimeter* from the Python module *skimage* [GRV22]. It appears the perimeter of the source phase decreases with the hydration (dissolution). On the contrary, the paste perimeter increases with the hydration (precipitation). Similarly to the phase distribution curves, the delay between the dissolution and the precipitation can be pointed out. Indeed, the perimeter of the paste does not evolve initially, while the perimeter of the source decreases, even at the initial times. Furthermore, some decreases of the paste perimeter during the hydration can be noticed at the end of the simulation. Indeed, as illustrated in Figure 3.5, the different paste seeds can interconnect, reducing the phase perimeter. This phenomenon also explains the slope variation of the paste+source perimeter curve. Once the seeds interconnect, the decrease of the perimeter for the combined phase accelerates. The nucleation and the coalescence of these aggregates are also depicted in Figure 3.11, where the number of the

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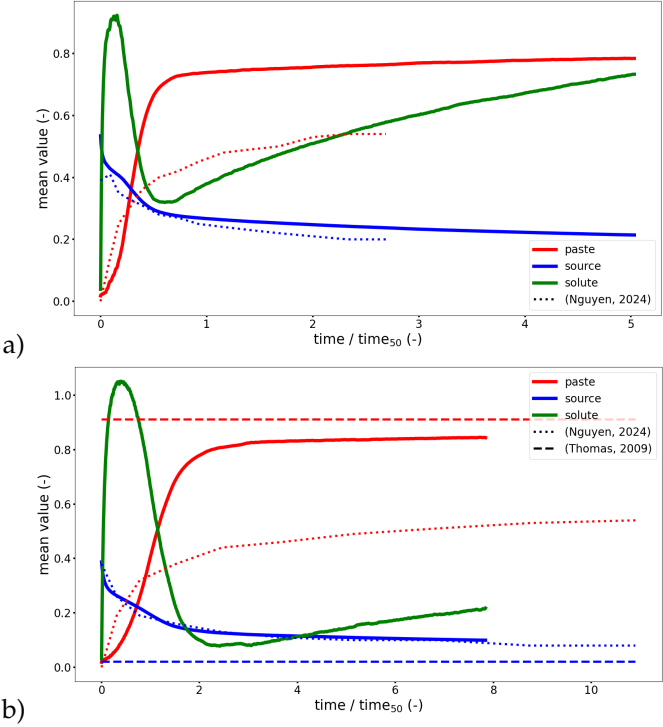


Fig. 3.8 Time evolution of the different volume fractions for the species (source, paste, solute) in the case $w/c =$ a) 0.3 and b) 0.5.

distinct islands (paste+source phase surrounded by pore) shows an increase followed by a decrease during the hydration process. Similarly, Figure 3.8 and [IPDG14] emphasize the fact that the CSH volume fraction evolves with a sigmoidal pattern. While a direct overlay of the plots would be inappropriate as they measure different quantities (morphology vs. bulk volume), the non-monotonic hump shape of the perimeter curve is the direct morphological signature of the sigmoidal growth, revealing the nucleation/growing of separate islands followed by the coalescence of these aggregates.

These segmented images can then be used to compute normalized two-point correlation function [Ben06], see Figure 3.10. This tool adds details on the structure of the microstructure by giving the characteristic size of the phase. In fact, this function takes a value between 1 (highly correlated) and 0 (not correlated) for different length dimensions. For example, it appears the paste correlation function drops at the initial condition ($h = 0.20$) for the dis-

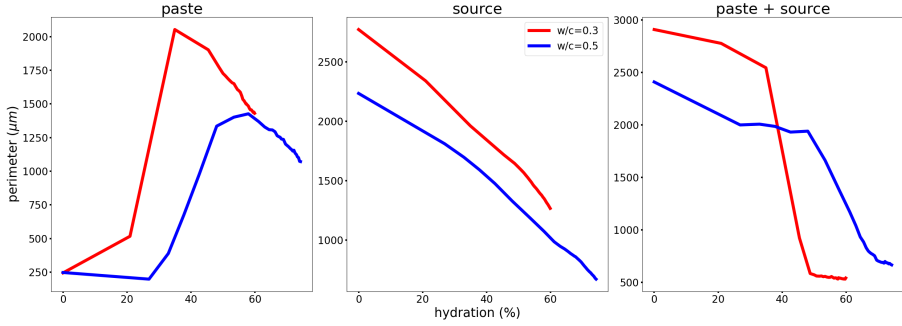


Fig. 3.9 Evolution of the perimeter of the different phases (paste, source, paste+source) during the hydration.

tance equal to $5 \mu\text{m}$ (initial size of the seeds). Then, the correlation function increases for the different sizes as the paste phase precipitates with the hydration phenomenon. Similarly, the source correlation function decreases for all sizes with the hydration as the source dissolves. For comparison with the case $w/c = 0.5$, the real microstructure, obtained by [TJC09] and depicted in Figure 3.6, is characterized. The phase paste+source appears well described by the Phase-Field formulation. It is worth noting that the paste correlation is lightly underestimated, whereas the source correlation is lightly overestimated. These differences may be filled by considering a wider source size distribution or capturing the fingering growth pattern of the cement paste.

Furthermore, the evolution of the two-point correlation function for the paste phase available in Figure 3.10 provides a quantitative signature of the developing microstructure. The progressive flattening of the curve at higher degrees of hydration indicates the establishment of long-range spatial correlations, which is the statistical marker of the percolation threshold. This signifies the physical transition of the paste from a collection of isolated aggregates into a continuous, sample-spanning network. This mechanism is also visible through the increase-decrease evolution of the paste perimeter, see Figure 3.9, and through the decrease of the number of isolated material islands, see Figure 3.11. This result is conceptually consistent with findings from more fundamental molecular dynamics studies of CSH formation, which also investigate the development of a cohesive, percolating gel network [IKB⁺16, IPDG14]. The model's ability to capture this critical topological transition therefore provides a validation of its physical realism.

As mentioned previously, the different phases of the segmented images

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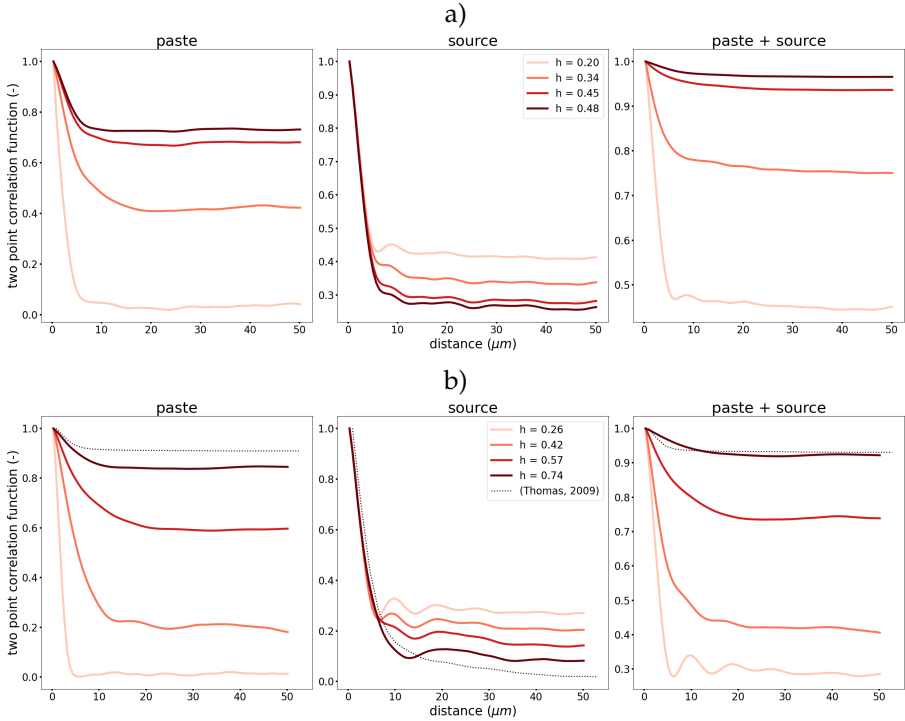


Fig. 3.10 Evolution of the correlation function for the different phases (paste, source, paste+source) in the case $w/c =$ a) 0.3 and b) 0.5.

can be labeled with the Python function `scipy.ndimage.label`. This operation distinguishes the individual features from a given phase. A feature is defined as a phase island surrounded by the pore/water. For instance, the number of features for the paste+source phase is depicted in Figure 3.11. It appears this number increases and then decreases as the source dissolves. The initial increase is due to the nucleation of the cement paste, while the reduction occurs as the source grains dissolve and the distinct paste seeds interconnect.

Please notice that other indices could have been applied to describe the microstructure [PVPU18, GRV22, Tor02, LPD⁺25], such as the chord-length density function, the pore-size function, the Euler number or the specific surface. These indices would characterize the microstructure with complementary information.

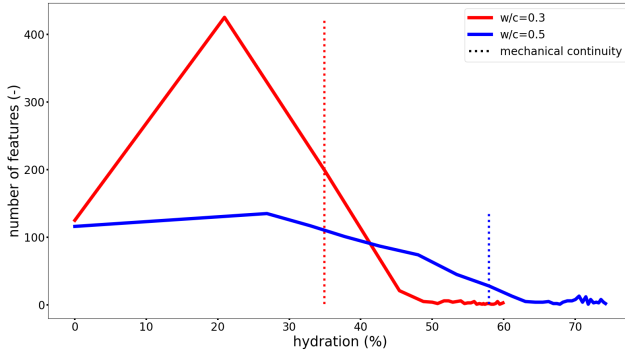


Fig. 3.11 Evolution of the number of features for the phase paste+source.

3.3 Mechanical characterization of the hydrated microstructure

3.3.1 Formulation of the mechanical homogenization

After estimating the microstructure evolution, mechanical loading (tensile and shear forces) is applied at the specimen's boundaries to determine the homogenized parameters, including Young's modulus, Poisson's ratio, Shear modulus, and Bulk modulus, see Figure 3.12. It is worth noting that the chemical aspect of the problem (microstructure evolution) is paused during this mechanical estimation of the composite material. The distinct microstructures obtained in Section 3.2 are employed as independent inputs in the following. Furthermore, the impact of the mechanics on the chemistry and microstructure evolution is neglected herein. However, this feedback influence is pivotal in some contexts, such as the underground storage (involving hydrating concrete wells under stress), and can be considered. For instance, a stress-dependent microstructure evolution has already been proposed in [GRV20]. In the same vein, Chapter 4 depicts the development of a new method to consider the impact of the stress and the microstructure reorganization on the chemistry.

A displacement (vertical in the case of pulling or lateral in the case of shearing) is applied on the top surface, whereas the bottom surface is assumed fixed. Periodic conditions are considered for the left and right surfaces to avoid any influence of the boundary conditions. It is worth noting that it is important to verify the mechanical continuity of the sample before the interpolation of the mechanical characteristics. To ensure force transmission be-

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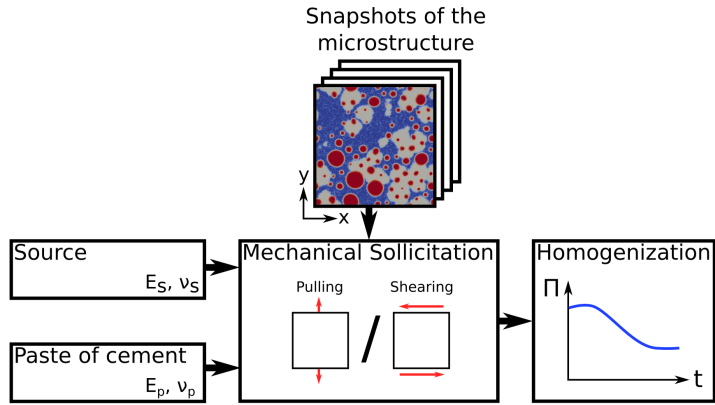


Fig. 3.12 The microstructure is loaded to compute homogenized mechanical parameters.

tween the top and bottom surfaces, the paste+source phase must be continuous, while the pore phase is not considered in the transmission of forces. Consequently, the initial microstructures formed during hydration are not used in the estimation of the sample’s mechanical parameters, see Figure 3.11.

Three phases are identified and assigned to the mesh: the paste, the source, and the water in the pore, all having an isotropic elastic mechanical behavior described in Table 3.3 [IKB⁺16, PVPU18, NLYK24, HGB⁺05]. It is worth noting that the mechanical behavior of the paste has been simplified herein as an initial approach. Indeed, this phase can be characterized through viscoelastic properties [ABR10, HHS⁺19, YPF⁺23]. Considering the viscosity of the paste, the model would be able to predict the creep behavior of the hydrated cement. To ensure the water is not transmitting stress in the medium, the Young modulus assigned is small compared to the other phases. Hence, the stress will concentrate on the harder phases: the paste and the source.

	Young Modulus (GPa)	Poisson’s ratio (-)
Paste	25	0.24
Source	120	0.3
Water	0.12	0.3

Table 3.3 Elastic properties considered for the different individual phases.

The loading is applied until reaching $\epsilon_y = \Delta_y / \text{height} = 0.2$ (pulling) or $\gamma = \Delta_x / \text{height} = 0.2$ (shearing), where Δ_y is the displacement following the

y-axis, Δ_x is the displacement following the x-axis, and *height* is the dimension of the sample in the y-axis. The mechanical problem is also solved with the finite element solver MOOSE [PGA⁺20]. An example of microstructure loading is depicted in Figure 3.13.

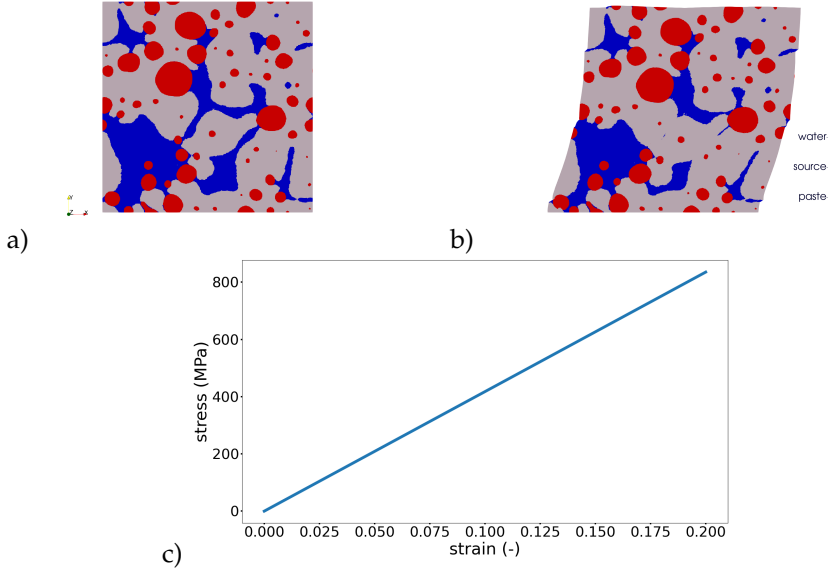


Fig. 3.13 Example of the prediction of the shear modulus for a $w/c = 0/5$ configuration: a) the composite material is b) loaded, and the parameter is estimated from c) the strain-stress curve.

Then, the mechanical parameters of the sample are computed by homogenization of the stresses in the domain. The Young Modulus E_h is determined with the traction test by interpolating the relation $\sigma_{yy} = E_h \cdot \epsilon_y$, where σ_{yy} is the mean stress in the source and paste phases and ϵ_y is the loading condition. The Poisson's ratio ν_h is determined with the traction test by interpolating the relation $\epsilon_x = \nu_h \cdot \epsilon_y$, where ϵ_x is the mean strain in the source and paste phases and ϵ_y is the loading condition. The Shear Modulus G_h is determined with the shearing test by interpolating the relation $\sigma_{xy} = G_h \cdot \gamma$, where σ_{xy} is the mean stress in the source and paste phases and γ is the loading condition. The Bulk Modulus K_h is computed with the relation $K_h = \frac{E_h}{3(1-2\nu_h)}$. It is worth noting that this parameter could also be interpolated with an isotropic loading test (not conducted herein).

It is worth noting that the framework presented herein could be extended

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to determine numerically the yield envelope of the sample. To achieve this, each distinct phase should be characterized by a plasticity criterion, and the sample should be subjected to various mechanical loading paths until the overall mechanical behavior deviates from linearity (after significant plastic deformation occurs locally) [LRV22, LPV21].

3.3.2 Results

The evolution of the homogenized Young modulus E_h , Poisson's ratio ν_h , Bulk modulus K_h and Shear modulus G_h are available in Figure 3.14. The cases $w/c = 0.3$ and $= 0.5$ are compared to the results from [NLYK24] and the intrinsic value of the parameter considered for the paste phase, dominant in the domain and representing the weaker phase (pore/water excluded). Moreover, a realistic microstructure obtained by Scanning Electron Microscope observation of a $w/c = 0.5$ sample described in Figure 3.6 [TJC09] is used as an input of the homogenization method depicted in Figure 3.12 for comparison purposes.

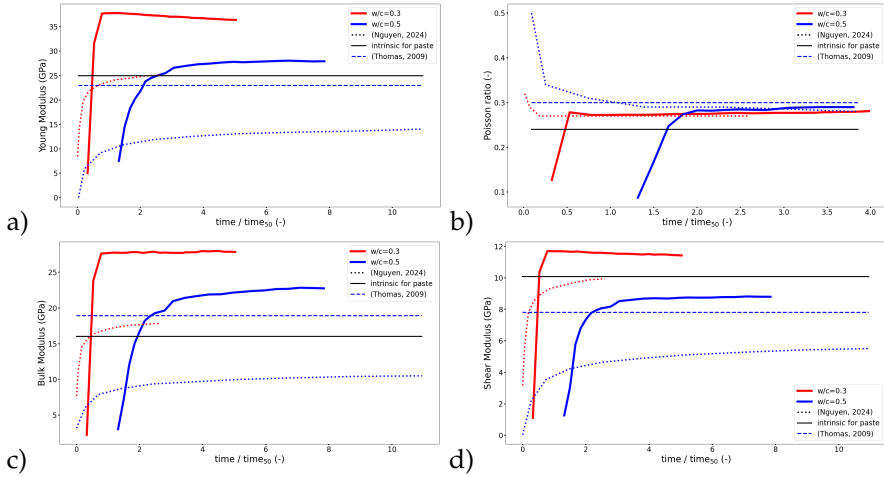


Fig. 3.14 Time evolution of the homogenized a) Young modulus E_h , b) Poisson's ratio ν_h , c) Bulk modulus K_h and d) Shear modulus G_h in the cases $w/c = 0.3$ and 0.5 .

As expected, the different moduli (Young, Bulk, Shear) increase with the hydration process. As the chemical process occurs, bonds are generated between the aggregates, and the mechanical properties of the sample harden. Similar to the tendencies observed in [NLYK24], the evolution consists of two

stages: an initial rapid phase followed by a slower final phase. This curve is correlated to the hydration evolution depicted in Figure 3.7. The microstructure remains weak at the initial mechanical continuity point (when it exists a continuous paste+source phase between the top and the bottom of the sample). As shown in Figure 3.5, the bonds between the aggregates remain small. However, the bond sizes increase with the hydration, and it reinforces the sample.

The results for $w/c = 0.5$ obtained by the Phase-Field formulation appear closer to the estimated moduli from the real microstructure obtained by [TJC09] than the results from [NLYK24]. Indeed, the microstructure computed with the *CEMHYD3D* description is more discrete, the different phases are less continuous than the ones obtained with a Phase-Field formulation. These localizations generate weak points in the *CEMHYD3D* microstructure and weaken the sample. Furthermore, it has been pointed out in Figure 3.8 that the *CEMHYD3D* formulation overestimates the volume fraction of the pore, weakening the microstructure. Because of these weakening origins, the moduli of the homogenized *CEMHYD3D* microstructure appear smaller than the intrinsic value of the cement paste (weakest phase after pore/water and dominant in the microstructure). The Phase-Field formulation appears more suitable than the *CEMHYD3D* description.

As a reminder, the saturation limit has been defined as $w/c = 0.42$. This limit is defined as the maximal source quantity with full hydration. If w/c is smaller, there are remaining source inclusions (rigid phase) after the hydration. If w/c is larger, there is not enough source to produce a saturation of the hydration. The $w/c = 0.3$ microstructure appears stiffer than the $w/c = 0.5$ microstructure for the different moduli (Young, Bulk, Shear). Indeed, Figure 3.5 emphasizes there are more source inclusions in the case $w/c = 0.3$. These inclusions are stiffer, see Table 3.3, and affect the mechanical behavior of the sample.

3.4 Preliminary conclusions

The numerical laboratory approach, describing explicitly the microstructure, provides a suitable framework for investigating the hydration process of concrete materials. Although discrete models such as *CEMHYD3D* are available, the coefficients used are largely derived from semi-empirical methods. Moreover, the intrinsic nature of Cellular Automata induces that the microstructure obtained is highly heterogeneous, and different concentrations of species at one location in the pore water can not be modeled. Consequently, a physics-

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based description, the Phase-Field formulation, is preferred in this Chapter. However, it appears that the state-of-the-art formulation requires revision, depicted in this Chapter, to compute the evolution of the microstructure accurately.

The results obtained with two distinct w/c ratios (under and over the saturation limit) have been characterized and compared with data from a *CEMHYD3D* model, experimental campaigns, and a real microstructure observation. The Phase-Field model proves effective in capturing the kinetics of the hydration phenomenon. Moreover, it appears that the Phase-Field approach reproduces more accurately the microstructure evolution driven by chemical processes than the Cellular Automata model.

Finally, various snapshots of the microstructure evolution can be utilized to numerically compute the mechanical properties of the sample at different stages. Specifically, the present microstructure, divided into distinct phases (paste, source, and pore), each with distinct mechanical characteristics, is homogenized at the sample scale to obtain effective macroscopic properties. As the hydration process progresses, the stiffness of the composite material increases, reflecting the hardening of the material, which is consistent with the expected evolution of the mechanical properties over time. Hence, the prediction of the mechanical performance of the cement material becomes available, skipping the waiting period induced by the hardening during experimental investigations.

In the same vein, it is worth comparing the framework depicted herein with the homogenization methods available in the literature. The difference is the fact that a Phase-Field describes the microstructure explicitly, while the homogenization approach requires making assumptions on the shape and the location of the distinct phases. It has been emphasized that the microstructure is pivotal for the estimation of the material behavior, emphasizing the importance of capturing it. Moreover, the Phase-Field approach enables the couplings with other physics, such as the temperature, the stress, or the presence of a fluid transport, while such considerations remain difficult through constitutive relations for the hydration of the material, a key ingredient of the prediction by homogenization.

Nevertheless, the computational cost of the Phase-Field simulations remains huge; the resolution of a simulation (microstructure evolution prediction and mechanical behavior interpolation) lasts approximately 10 hours on

a regular computer¹. However, numerous methods may be employed to diminish the resources required, allowing the use of the Phase-Field description for 3D problems [SSPT22, BCGT25].

¹Intel(R) Core(TM) i5-10210U CPU @ 1.60GHz, 8 Go RAM

4

Development of a PFDEM framework to study chemo-mechanical couplings in granular materials

How can granular reorganization and grain morphology evolution be explicitly modeled, considering their impacts on the mechanics and chemistry in a tightly coupled problem such as pressure-solution?

Chapters 2 and 3 described chemo-mechanical couplings in two distinct cases. The first one, described in Chapter 2, investigated the effect of debonding on the mechanical behavior of a cemented granular medium. The main aspect of this problem is to capture the mechanics. To do so, a Discrete Element Model (DEM) [CS79, O'S11] has been employed. Coming back to the seminal DEM formulations, it appears the grains are modeled as disks (2D) or spheres (3D). The dissolution/precipitation is then taken into account as a homogeneous decrease/increase of the grain diameter [CS19, AVD22] or with an addition/subtraction of a dissolved/precipitated layer thickness at the contacts [vdEMNS18]. The extrapolation of the results obtained from these approaches to geological applications is limited as they only consider disks or spheres as

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grains, but real particles often exhibit highly irregular shapes. These complex geometries of the grains significantly influence the macroscopic mechanical behavior of granular materials [GRV22, BPA19, LPD⁺25]. Therefore, accurate models should aim to capture this complexity. Several approaches have been developed within the framework of DEM and are presented in Section 4.1.1. However, none of these approaches considers a grain shape evolution due to chemo-mechanical couplings.

The Phase-Field (PF) description [Lan36, CH58, AC79, WLMF92] appears as a good candidate to model the local addition or reduction of material quantity using physics-based laws. This formulation is presented in Chapter 3, detailing a second chemo-mechanical coupling: the case of the hydration of cement. Nevertheless, it remains difficult to solve the mechanical aspect of the problem with a sole Phase-Field description. In granular material, grain reorganization is described as discrete displacements of the grains. Phase-Field formulation is solved with a Finite Element Method, so it is a continuous description, which is less suitable than DEM approaches to model at the grain scale large deformations and contact topology changes as involved in grain reorganization. It is important to report that a framework has recently been published to solve contact problems through a Phase-Field description [LPK24]. Nevertheless, this approach appears limited by the computational cost.

The aim of this Chapter is to present a novel coupling between a Phase-Field model and a Discrete Element Model (PFDEM) [SMVR24a, SMRV25a]. This new framework is designed to capture both the mechanical and chemical aspects of the problems. Previous studies have already explored the coupling between Finite Element Modeling and Discrete Element Methods to study deformable grains [Mun04] or grain growth/sintering [Shi14].

Even though the theory of the Discrete Element Model and the Phase-Field has been detailed in the previous Chapters, some details are initially presented herein. An attempt is made to discuss the different variations available in these formulations in the context of the global PFDEM framework. Then, the data exchanges and the main algorithm between the two distinct solvers are presented.

Even if this PFDEM method can be employed for numerous problems, it has been designed to investigate the pressure-solution phenomenon, a problem with deep chemo-mechanical couplings. A presentation of the pressure-solution phenomenon and its impacts is available in Chapter 1. The framework is then applied to pressure-solution in Chapters 5, 6 and 7.

4.1 Discrete Element Method

In the PFDEM framework, the Discrete Element Method (DEM) is used to compute the granular organization and the stresses transmitted in the microstructure. A formulation of the Discrete Element Method is available in Chapter 2.

4.1.1 Capture the real shape of the grains

Conventional DEM formulations [CS79, O'S11] presuppose that grains are disks (2D) or spheres (3D). However, the complex geometries of these grains considerably influence the macroscopic mechanical behavior of granular materials [GRV22, BPA19, LPD⁺25]. Therefore, it is imperative that accurate models aspire to encapsulate this complexity. Various approaches have been developed within the framework of DEM to account for irregular grain shapes, as depicted in Figure 4.1. These include incorporating rolling resistance calibrated with grain geometry [MQAV20, RAG⁺21], employing ellipsoids [RB91] or superquadric particles [PPK17], using grain clusters [GLXH09], assuming potential particles/blocks [Hou09, BHU12, BHU13], and even considering polyhedral shapes [Cun88, NHZG04, AMW09]. More recently, a Level-Set Discrete Element Model was developed to capture the complex shapes of grains and reproduce experimental results [KAVA16, KAVA18].

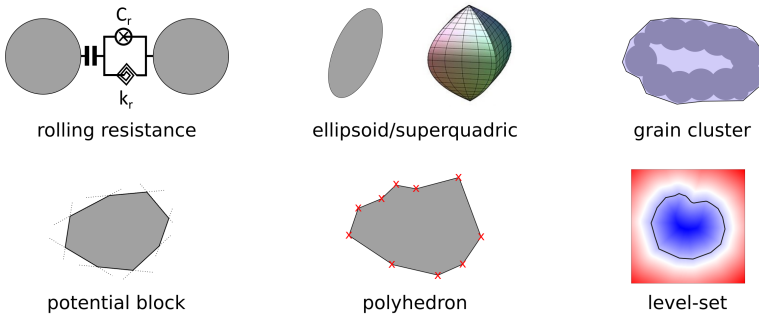


Fig. 4.1 Examples of DEM extensions to consider the grain shapes.

At the start of this PhD, the approaches based on the rolling resistances were set aside. Although it is the most efficient computationally, the calibration based on the shape remains a significant approximation. Furthermore, the focus remained exclusively on the rolling aspect, neglecting the impact

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of the shape on the stress organization. In the same way, the ellipsoids and superquadric particles were deemed too limited in their available shapes.

In order to model a heterogeneous shape, it is advantageous to employ a grains cluster approach, as it is straightforward to formulate from the classical approach. However, it should be noted that the computational cost increases exponentially as the definition of an individual grain is contingent on multiple spheres. The potential particles/blocks definition has been tried at some point in the PhD. In this approach, the shape is described through a system of equations for different planes. However, this method was unstable for high-resolution descriptions of the particles. Consequently, the polyhedral description and the Level-Set Discrete Element Model emerge as the most viable options for capturing a heterogeneous shape.

A notable similarity exists between the polyhedral description and the Level-Set Discrete Element Model. Indeed, polyhedral particles are described by the coordinates of their vertices. The contact between grains is then determined by comparing the positions of these vertices [NHZG04]. A similar approach is followed up by the Level-Set Discrete Element Model. Indeed, the vertex description is integrated within a level-set function to enhance the efficiency of contact detection. The level-set function is defined as the signed distance (< 0 inside the grain, > 0 outside the grain) applied on a background mesh [KAVA16, KAVA18]. Despite the availability of both approaches in YADE, DEM solver used during this PhD [Sa21], the Level-Set Discrete Element Model appears more employed in the literature.

4.1.2 Impact of the grain discretization

The discretization of the grain (= the number of vertices) is the main issue for the quality of the result for polyhedral particles or Level-Set Discrete Element Model. Hence, if the discretization is coarse, the shape is not well described and some errors can occur for contact computation. The goal of this Section is to discuss the impact of this parameter on the quality of the results.

Two simple cases in 2D illustrated in Figure 4.2 are considered: two grains in contact and one grain in contact with a wall. These cases represent the elementary phenomena in a granular sample.

Different grains with 10 to 60 (with a step of 5) vertices are generated to see the influence of grain discretization. Then, the grains are randomly rotated and the overlap is estimated with the common-plane algorithm [NHZG04]. This method is used to compute contacts with polyhedral particles. The results shown in the following are similar in the case of the level-set description.

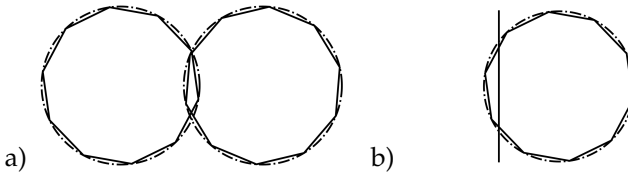


Fig. 4.2 Two cases are considered: a) a contact grain-grain and b) a contact grain-wall. The dashed lines represent perfectly circular grains.

The statistical result obtained with 100 repetitions is shown in Figure 4.3. It appears the variation of estimated overlap (see the size of the boxes) decreases with grain discretization.

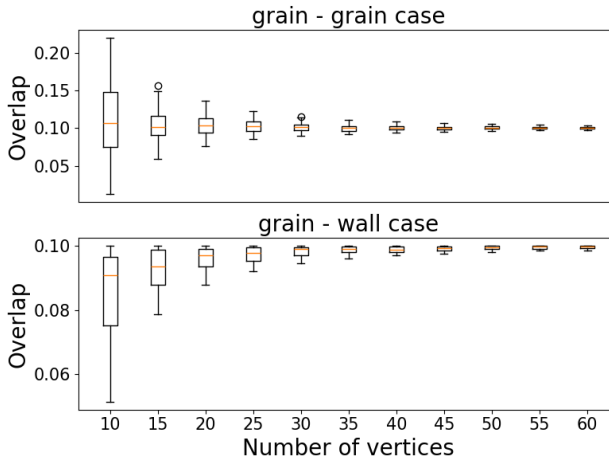


Fig. 4.3 Influence of the grain discretization on the overlap estimation (the targeted value is 0.10).

This study is repeated for different real overlaps. Indeed, for coarse discretization and low contact force, a theoretical contact cannot be detected because of the discretization. Figure 4.4 shows that grain discretization greatly influences the results' quality for small overlap, as is the case in the granular sample.

It appears that the discretization of the grains is a main parameter to capture accurately the interactions at the particle level.

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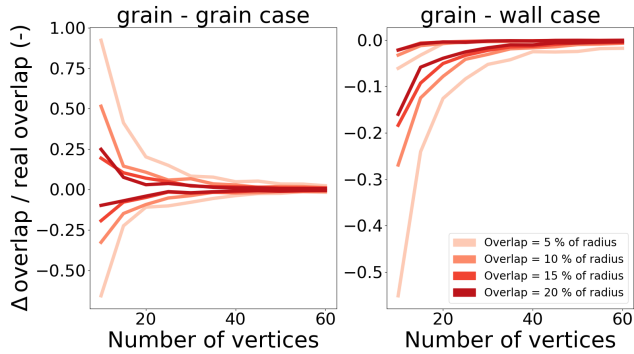


Fig. 4.4 Influence of the grain discretization on the overlap estimation for different solicitations. Only the first and the third quartiles of each data set are plotted.

4.1.3 Interaction between grains

In the Discrete Element Model, the detection of contact between two grains depends on the formulation [Cun88, NHZG04, AMW09, KAVA18]. Subsequent to the detection of contact, the algorithm performs computations on the normal force, tangential force, twisting moment and rotating moment. These reactions are estimated from two approaches: a distance-based one and a volume-based one.

The distance-based estimation of the overlap is the seminal approach of the Discrete Element Method. The contact is characterized by the maximum distance between the vertices of the grains. From these points, the orientation of the normal and the point of application are estimated. Subsequently, various laws have been proposed to compute the norms of the reactions from this distance [DRDM04]. One of the most widely employed is the classic Hertz contact solution [Joh85].

However, it is important to note that the distance-based approach has limitations, as it can potentially lead to undesirable effects. For instance, a contact force can be equivalent for two contacts with similar distance overlap but different overlapping volumes, see Figure 4.5. To address this challenge, laws based on the volume are preferred for estimating the reactions [vdHFE23, Fen23]. In such considerations, the norms of the reaction are frequently assumed to be linear with respect to the overlapping volume. Indeed, unlinear laws, such as the Hertz contact, have been developed to consider the volume from a distance-contact consideration. However, this volume is

explicitly described with a volume-based approach.

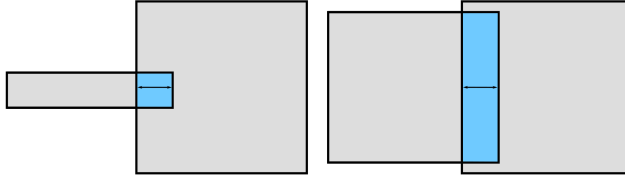


Fig. 4.5 Even if the distance overlaps are similar, the overlapping volumes differ.

4.2 Phase-Field Description

Even if the Discrete Element Method is used to capture the mechanical aspect (granular organization and stress transmission) of the chemo-mechanical couplings, this formulation remains incapable of capturing any chemical aspect. To address this limitation and to capture the shape evolution of the grains (local dissolution/precipitation), the Phase-Field description is incorporated into the global framework. A formulation of the Phase-Field description is available in Chapter 3.

The granular medium is composed of grains and pores. As illustrated in Figure 4.6, this porous matter is represented in the Phase-Field space by a combination of phase variables (one phase per grain). Specifically, the phase variable η_j equals 1 if it is inside the grain associated j and equals 0 elsewhere.

Then, a number of formulations have been developed to describe the dissolution/precipitation of the material and to ensure the mass conservation [LK16]. The seminal formulation is the Cahn-Hilliard equation [CH58], which was later extended to address multi-phase problems [SPN⁺96, NW98]. The use of conservative variables is paramount in the description of materials. However, it should be noted that this formulation appears to be computationally expensive. One potential solution to this issue is to utilize non-conservative variables. To do so, the Allen-Cahn equation [AC79] could be employed to reduce the computational cost. The coupling of this formulation with a conservative diffusive equation on a solute variable c ensures mass conservation [GRV20, SMVR24a, SMRV25a].

Similar to Equations 3.1 or 3.2 in Chapter 3, the conservative Allen-Cahn formulation, presented in Equation 4.1 is based on the free energy f_{loc} and the tilting term E_d .

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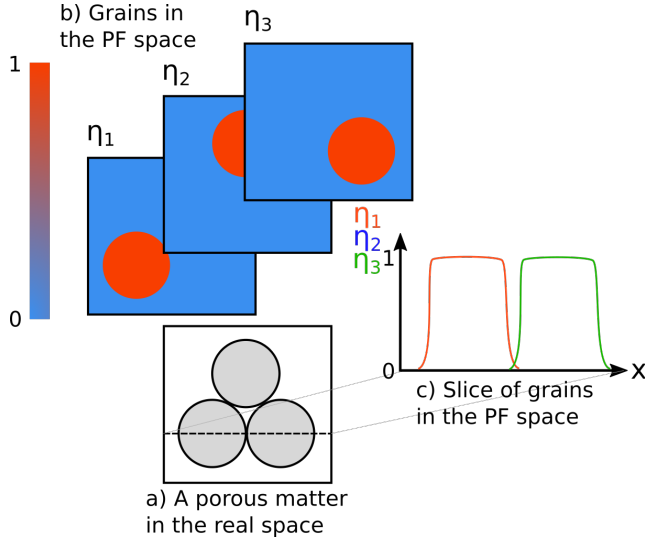


Fig. 4.6 The Phase-Field method is applied to granular matter: a) a granular matter is composed of grains and by pore, b) one phase variable η_i is generated by grain, c) the phase variable is equal to 1 if it is inside the grain associated and equal to 0 elsewhere.

$$\begin{aligned} \frac{\partial \eta_j}{\partial t} &= -L_j \frac{\partial (f_{loc,j} + E_{d,j})}{\partial \eta_j} + L_j \kappa_j \nabla^2 \eta_j \\ \frac{\partial c}{\partial t} &= -\sum_j \alpha_j \frac{\partial \eta_j}{\partial t} + \kappa_c \nabla^2 c \end{aligned} \quad (4.1)$$

where η_j is the phase variable describing the grain j , L_j is the mobility of the phase j (setting the global rate of the phase evolution), κ_j is the gradient coefficient of the phase j (source of the diffusive definition of the Phase-Field formulation, see Figure 3.1), c is the solute concentration variable, α_j is a conversion term employed during the dissolution/precipitation process ($1 \eta \leftrightarrow \alpha_j c$), and κ_c is the diffusion coefficient of the solute c . Even if distinct values could be considered for L_j , $f_{loc,j}$, $E_{d,j}$, κ_j , α_j depending on the phases j , in practice these parameters are similar ($L_j = L$, $f_{loc,j} = f_{loc}$, $E_{d,j} = E_d$, $\kappa_j = \kappa$, and $\alpha_j = \alpha$).

Despite the existence of numerous shapes for the local free energy density

f_{loc} , the double-well function is the most widely used in the literature. This function is defined with a barrier height W_η [Tak14, MBW08, Che02]. The local free energy density is specified in Equation 3.10 and is depicted in Figure 3.2. It is noteworthy that the minima of this potential energy are located at $\eta_j = 0$ and $\eta_j = 1$. At equilibrium and in the absence of external destabilization, the phase variables remain at $\eta_j = 0$ or $\eta_j = 1$ (no dissolution/precipitation).

Similarly, the term E_d encompasses additional sources of energy introduced into the system, such as mechanical, chemical, or thermal loading. As depicted in Figures 3.3 and 3.4, the free energy is tilted to favor dissolution/precipitation. When the dissolution phenomenon dominates, the double-well function is tilted towards $\eta_j = 0$, causing the material dissolution. Conversely, when the precipitation phenomenon dominates, the double-well function is tilted towards $\eta_j = 1$, indicating the material's tendency to precipitate. The amplitude of the tilting is correlated with the rate of the dissolution/precipitation. It can be calibrated with experimental data to reproduce the physical kinetics of the reaction. It is imperative to acknowledge the profound mesh-dependent nature of the formulation, see Equation 3.7. To address this challenge, a method outlined in Appendix D can be employed.

As depicted in Equation 4.2 [Pat73, LCN⁺21, Wey59], the tilting of the free energy in the case of pressure-solution is correlated to the rate of the dissolution/precipitation $k_{diss/prec}$, the solid activity a_s defined in Equation 4.3, the solute concentration c and the solute concentration at the equilibrium c_{eq} .

$$E_d = k_{diss/prec} \times a_s \times \left(1 - \frac{c}{c_{eq} a_s}\right) \times \sum_j \left(3\eta_j^2 - 2\eta_j^3\right) \quad (4.2)$$

$$a_s = \exp\left(\frac{P \times V_m}{RT}\right) \quad (4.3)$$

where P is the stress transmitted at the contact, V_m the molar species, R is the gas constant, and T is the temperature. If the stress applied P is unknown, it can be estimated with the Discrete Element Method, see the algorithm presented in Section 4.3.2. The coefficient $k_{diss/prec}$ is related to the rate of the dissolution/precipitation chemical reaction. The larger it is, the larger the tilting is, and the faster the dissolution/precipitation is. If $c < c_{eq} a_s$, dissolution occurs, $k_{diss/prec} = k_{diss}$. Conversely, if $c > c_{eq} a_s$, precipitation occurs, $k_{diss/prec} = k_{prec}$. It is important to notice that the chemical and mechanical aspects are deeply coupled in the formulation presented in Equation 4.2. Even if other formulations have been tried, see [SMVR24a], this formulation is closer

4 | Development of a PFDEM framework to study chemo-mechanical couplings in granular materials

to the mechanisms described for pressure-solution [Wey59, Pat73, LCN⁺21]. The solid activity a_s increases in proportion to the stress transmitted at the contact P . This modification affects the value of the solute concentration at the equilibrium $c_{eq} a_s$. The established chemical equilibrium in the fluid film (c versus $c_{eq} a_s$) becomes unverified. The material dissolves in the contact zone to reach the chemical equilibrium $c = c_{eq} a_s$. A gradient in the solute concentration values appears between the contact zone $c = c_{eq} a_s$ and the pore space $c = c_{eq}$ ($a_s = 1$ in the pore space as much less stress P is applied compared to the contact). This gradient gives rise to the diffusion of the solute concentration. Subsequently, the established chemical equilibrium in the pore space (c versus c_{eq}) becomes unverified. The material precipitates in the pore space to reach the chemical equilibrium $c = c_{eq}$. The scheme of pressure-solution, depicted in Figure 1.4, appears verified.

It is worth noting that the term E_d defined in Equation 4.2 considers only the elastic strain energy as a driving force through the term P (other problems may require a contribution of the shearing term). Moreover, the impact of the force transmission is homogenized around the contact point (same energy for the contact). A more complex framework, considering the explicit field of the elastic energy in the grain, remains available, see [GRV20], where it is done at the scale of the sample. However, such a consideration requires a Finite Element Model for each grain [BCBC⁺22], skyrocketing the computation cost of a simulation. Consequently, it has been decided to consider a homogenized energy per contact. Moreover, other tilting mechanisms exist, such as the plastic strain energy or the surface tension energy [TAK⁺18]. Indeed, the integration of the plastic strain energy requires an additional layer for a Finite Element Model, increasing the complexity. Concerning the contribution of the surface tension energy, the idea of this thesis was to build a global framework. Consequently, the effect of the surface tension has been neglected, verified for large grains with small local curvature [GRV20, LCN⁺21]. However, such a parameter could be calibrated from the observation of the microstructure obtained by CT scans or from models at the atomistic scale.

Furthermore, the dissolution kinetics are considered constant herein. However, some distribution for this parameter or some noise can be introduced to model the heterogeneity of the natural material. For instance, it has been emphasized that this heterogeneity is the origin of the initiation of the stylolite roughness [KRTP07]. The stylolites [TAK⁺18] are recurrent patterns observed in rocks, involving the same processes as the pressure-solution phenomenon: dissolution, diffusion, and precipitation. Contrary to pressure-solution, the stylolites are characterized by a rough surface at the contact.

Similar to Equation 3.3, the diffusive conservative equation on the solute concentration c described in Equation 4.1 ensures the mass conservation and the diffusion of the solute in the fluid. κ_c represents the diffusivity coefficient that controls the diffusion rate. Notably, κ_c is assumed to be 0 within the grains, and nonzero in the contact and the pore. Consequently, the diffusion of the solution into the grains is prevented. Even if a discussion exists on its nature [vNVS08], a water film is assumed at the contact between grains. However, the diffusion is larger in the pore (free fluid) than at the contact (trapped fluid) [vNVS08]. An arbitrary factor 100 could be applied to the diffusion coefficient κ_c . The algorithm's implementation for building the heterogeneous diffusivity coefficient κ_c is described in Appendix E. The terms $\frac{\partial c}{\partial t} = - \sum_j \alpha_j \frac{\partial \eta_j}{\partial t}$

in Equation 4.1 ensure the conservation of mass. Indeed, the variations of Phase-Field variables η_j act as a source term of the solute variable c . When a grain (η_j) dissolves, solute concentration (c) is generated, and vice versa, when η_j is generated through precipitation, some solute c disappears.

It is pivotal to note that the advection phenomenon induced by the grains coming closer or apart is neglected herein. Indeed, the pressure-solution remains a quasi-static phenomenon. However, this description can be readily coupled to a fluid solver to consider the advection. For instance, the phase-field model formulation has already been employed in the case of a reactive transport problem [LWW⁺23].

The different Equations are solved with the open-source finite element software MOOSE [PGA⁺20, SAPT17]. This software uses automatic differentiation to solve the system of equations with an implicit formulation.

4.3 PF-DEM Couplings

The data exchange and global scheme of the PF-DEM couplings are illustrated in Figure 4.7 and in Algorithm 2, respectively. In the Phase-Field simulation, the sample geometry is discretized into a mesh, and the grains are represented by phase variable maps. A grain detection algorithm is applied to determine the new grain shape and solute configuration based on the Phase-Field outputs. On the other hand, in the Discrete Element Modelization, grains are represented as Level-Set functions or polyhedra. This model aims to compute the new positions of the grains and the stress transmitted at each contact. The rigid body motions of the grains are applied to the phase variable maps to ensure the descriptions remain correlated. Similarly, the stresses observed at the contacts are transmitted to destabilize the phase description.

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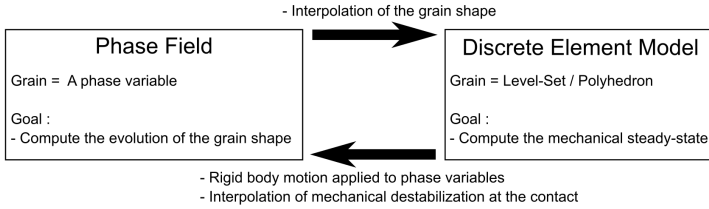


Fig. 4.7 Data exchange between the Phase-Field simulation and discrete element modelization.

It is important to note that although PF and DEM operate on different time scales, they are still connected. The mechanical equilibrium (DEM) is assumed to be instantaneous, while grain dissolution or precipitation (PF) occurs over longer time periods, typically several hours to days.

Algorithm 2 Global scheme of the simulation. Two time scales are used: one for DEM and one for PF.

```

while work not finished do
    Build grains from PF data
    while not DEM equilibrium do                                ▷ Start the DEM simulation
        Compute solicitations
        Solve the momentum balances
    end while
    Apply rigid body motions to the phase maps
    Update the map of the mechanical solicitations
    Solve PF equations                                          ▷ Start the PF simulation
end while

```

4.3.1 From Phase-Field to Discrete Element Model

After a Phase-Field step, the system does not immediately reach a mechanical equilibrium. Indeed, the shapes of the grains have evolved with ongoing dissolution/precipitation. Therefore, the new grain boundaries need to be detected. Depending on the description employed for the Discrete Element Method, distinct algorithms are used.

In the case of a polyhedral description, Figure 4.8 illustrates the division of the phase map into multiple layers (along the different axes). The grain boundary is assumed to occur at $\eta_j = 0.5$. The position of the vertex is interpolated with linear approximations from the phase map.

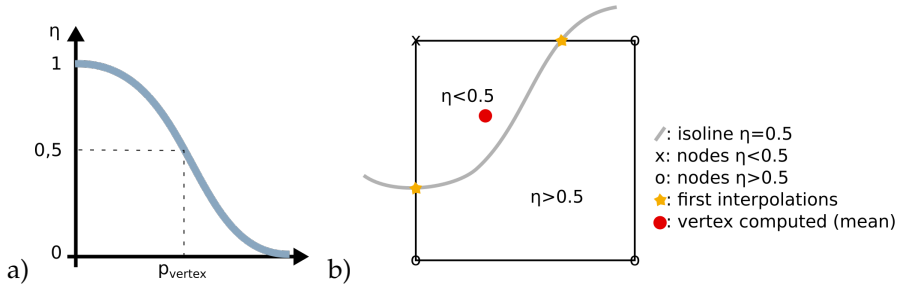


Fig. 4.8 Example of grain boundaries detections in a) 1D or b) 2D (similar in 3D). The grain boundary is assumed to occur at $\eta = 0.5$.

To reduce computational cost, only a certain number of vertices are used. Numerous algorithms exist [Sa21, SMVR24a, SMRV25a] to reduce the number of nodes describing the surface of the particles.

In the case of a Level-Set description, a binary image is extracted from the Phase-Field output, considering $\eta = 0.5$ as a threshold value. Then, a signed distance function (< 0 inside the grain, > 0 outside the grain) is computed with the Python function *skfmm.distance*. Thereafter, this signed distance field is employed to define the particle.

Once the grain boundaries are known, DEM iterations occur until the system reaches an equilibrium. Some damping is introduced to dissipate mechanical energy. Even if the convergence criteria to detect the equilibrium may vary depending on the problem, some examples are:

- the sum of the kinetic energy over the grains is smaller than a threshold value.
- the unbalanced force (defined as the ratio of the mean summary force on bodies and mean force magnitude on interactions) is smaller than a threshold value.
- the position of the walls controlled to apply the load is stable. The variance of the latest positions is below a threshold value.
- the confining pressure applied is equal to the confining pressure targeted (+ tolerance) during a given number of steps.

Moreover, a maximum number of iterations is set to avoid an infinite loop. Once the equilibrium is reached, new phase maps are interpolated to update the Phase-Field problem with the outputs of the DEM.

4 | Development of a PFDEM framework to study chemo-mechanical couplings in granular materials

4.3.2 From Discrete Element Model to Phase-Field

During the DEM simulations, the grains have moved. A rigid body motion, computed between the initial and final states of the DEM simulation, must be applied to ensure the phase variables η_j are representative of the new granular configuration. The feasibility of this operation is due to the use of an individual phase per grain. It becomes possible to apply distinct displacement fields to the different phase variables. The new phase map is obtained through interpolation from the previous one. As illustrated in Figure 4.9, at each iteration, the next mesh is computed based on the previous mesh by applying an inverse rigid body motion. Since the two meshes often do not perfectly match, bilinear (2D) or trilinear (3D) interpolation is performed to estimate the values of the next mesh.

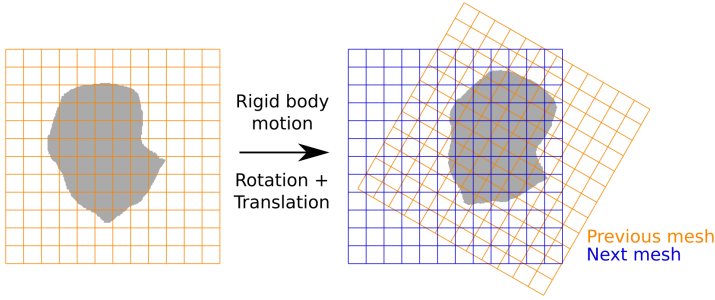


Fig. 4.9 Scheme of the interpolation algorithm. The next mesh is computed from the previous mesh by applying an inverse rigid body motion.

Then, the forces transmitted in the contacts are used to compute the mechanical destabilization of the free energy E_d through Equation 4.2. If a contact occurs between two grains, the solid activity a_s and the pressure P are unknown. Indeed, the pressure applied at the contact evolves with the shape evolution of the grains and the granular reorganization (in the case of multiple grains). The pressure is then interpolated from the DEM simulation, $P = F_n / S_c$. The applied pressure depends on the normal force F_n transmitted within the DEM contact and the contact surface S_c . It is noteworthy that the shear force F_s is not considered in the mechanical destabilization E_d . Indeed, the fluid film presented in the pressure-solution scheme does not transmit shear solicitations [vNVS08]. The contact surface S_c is computed based on the contact volume V_c . As illustrated in Figure 4.10, the contact volume is determined by iteration on the mesh nodes. The criteria for detecting contact is η_i and $\eta_j \geq \eta_{\text{criterion}}$, where $\eta_{i,j}$ are the phases linked to the grains in

contact and $\eta_{\text{criterion}}$ is a criterion value. The initial approach is to assume that $\eta_{\text{criterion}} = 0.5$ as it represents the grain boundaries. However, some approaches could consider $\eta_{\text{criterion}} < 0.5$ to account for the possibility that a supplementary part of the grain participates in the contact (in the following Chapters, we assume $\eta_{\text{criterion}} = 0.1$).

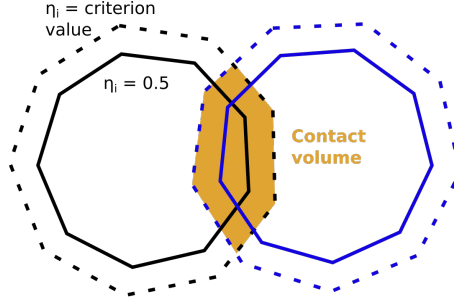


Fig. 4.10 Definition of the contact volume between two grains: a criterion value lower than $\eta_i = 0.5$ can be used to enlarge the part of the particle under the solid activity a_s increase.

Once the contact volume V_c has been determined, the contact surface S_c is interpolated. To this end, the maximum orthogonal line (2D) or plane (3D) to the normal contact vector $\vec{n}$ employed in the DEM part is sought. Once this parameter has been determined, the solid activity a_s is calculated, see Equation 4.3. It should be noted that out of the contact volume V_c the solid activity a_s is equal to 1. Finally, the tilting term E_d is computed, see Equation 4.2.

The deformation induced by the Phase-Field simulation and the grain displacements computed in the Discrete Element Modelization are closely interconnected. Moreover, the PFDEM algorithm considers explicit couplings between the PF and DEM methods involved. It is important to ensure that the deformation remains in the small-strain range, without hugely affecting the computational cost. Subsequently, adaptive coupling schemes have been developed to solve fluid-structure interaction problems [YNYZ20]. Indeed, the fluid induces a deformation of the structure, and this deformation of the structure has an impact on the fluid pattern. For instance, the Aitken method [Ait38] is commonly used to adapt the coupling between the fluid and the structure solvers. Herein, the deformation of the grain during a Phase-Field simulation can be controlled with an adaptive duration of the Phase-Field simulation (relative to shape evolutions). A classical threshold values system

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based on the tilting term E_d is employed to determine the duration of the simulation, and consequently the grain deformation during the Phase-Field simulation. The larger E_d is, the more shape evolution occurs in the Phase-Field simulation. The importance of this method is illustrated in Figure 4.11 where a lateral displacement for a two-grains configuration under pressure-solution, see [SMVR24a], is plotted without the inspired Aitken method. Oscillations appear, revealing large deformation in the Phase-Field simulations. At step i , a large amount of grain dissolves, a lot of solute is available, and the grains get closer. At step $i + 1$, the solute available generates a large amount of grain precipitation, and the grains get further. To address this issue, the duration of the Phase-field simulation must be smaller. The Aitken-based method allows the use of an efficient Phase-Field simulation duration, verifying a small deformation criterion.

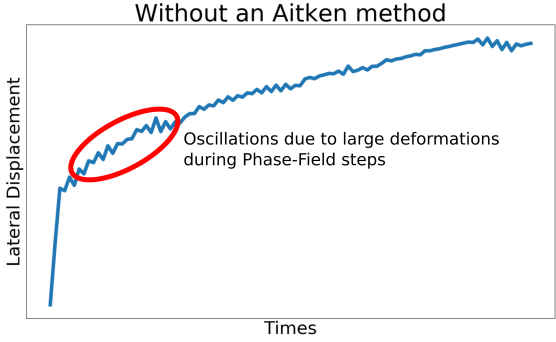


Fig. 4.11 Displacement for a 2 grains pressure-solution configuration without an inspired Aitken method. Oscillations appear because of the large deformation in the Phase-Field simulations.

5

Calibration and Validation of the Phase-Field Discrete Element Method

The purpose of this Chapter is to calibrate the Phase-Field parameters of the model described in Chapter 4 and then to validate the formulation in the context of pressure-solution [SMRV25a]. The formulation is applied to model indentation experiments described in [GGR⁺09, Gra93, DPR⁺02, GRV14] and the calibration is done by reproducing the data from [GGR⁺09]. The formulation is then verified by comparison with the two well-known macro-models for the compaction rate: the diffusion and the dissolution rate-limiting [Rut76, Raj82]. Finally, the preliminary conclusions of this Chapter are presented.

Some examples of scripts used are available on Github: https://github.com/AlexSacMorane/PF_PS_Indentation.

5.1 Numerical model

The framework employed for parameter calibration and formulation validation is presented herein. A schematic representation of an indentation experiment [Gra93, DPR⁺02, GGR⁺09, GRV14] is presented in Figure 5.1. A material

5 | Calibration and Validation of the Phase-Field Discrete Element Method

subjected to pressure-solution is situated beneath an indenter. This indenter exerts a constant pressure. It should be noted that this indenter is not subject to pressure-solution. The material dissolves at the contact. Subsequently, it diffuses in the fluid film, the tube, and the top reservoir, where it is finally evacuated. This top reservoir represents the pore space and acts as a well for the solute. From the initial scheme of the pressure-solution phenomenon depicted in Figure 1.4, precipitation does not occur.

Despite the existence of disparate discourses pertaining to the structural configuration of this film [vNVS08], it is postulated that a thin fluid film exists between the indenter and the material [GGR⁺09]. Indeed, it could be a film, an island-channel network, or a film with cracks. The real nature of the contact is still an ongoing research. Experimental evidence indicates that the film in question is approximately 2–10 nm in thickness, corresponding to a water molecule layer of 8–40 molecules [GGR⁺09]. From a numerical standpoint, it is not feasible to respect this size, particularly compared to the size of the indenter. Subsequently, the film width is artificially increased. Nevertheless, the coefficient of diffusion is decreased in proportion. The minimum size of this film is related to the Phase-Field interface width. Given that material dissolution occurs within this zone, the film must contain it.

Once the solute has reached the reservoir at the top, it is evacuated at a specified frequency. The frequency in question is of great consequence with regard to the quality of the results. Indeed, an increase in solute concentration within the well may result in a slowing of diffusion as the gradient diminishes, see Appendix G. The dimension of the well and the frequency of updates to the simulation can be modified in order to regulate the solute concentration within the well. In the following results, an effort has been made to compare simulations with the same solute concentration in the well.

As the stress is known (input of the problem) and there is no granular reorganization (the material is considered as continuous), the Discrete Element Modelization can be skipped. The results presented in this Chapter are obtained with a Phase-Field formulation only, see Section 4.2. It is important to notice that a constant pressure is applied along the indenter surface. However, the normal stress appears larger at the center of the contact than at the side [Wey59, Rut76, GGR⁺09]. A correction must be applied to the solid activity a_s described in Equation 4.3 and employed in Equation 4.2. A control factor $f_{control}$ is applied to force the material interface to stay as flat as possible, see Equation 5.1.

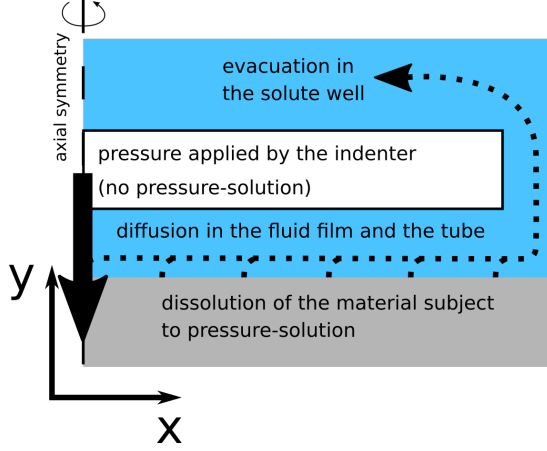


Fig. 5.1 Scheme of the indentation experiment composed of an indenter and a material subject to the pressure-solution phenomenon. The material is dissolved at the contact surface, diffuses into the fluid film and is evacuated in the well through a tube.

$$a_{s,i} = a_s \times \left(y_{front,i} - \overline{y_{front}} \right) \times f_{control} \quad (5.1)$$

where $a_{s,i}$ is the corrected solid activity applied in Equation 4.2 (the value is not constant along the material interface), a_s is the solid activity defined in Equation 4.3 (constant pressure applied as an input), $y_{front,i}$ is the coordinate of the front at a given point of the interface (the value is not constant along the material interface) and $\overline{y_{front}}$ is the mean coordinate of the front along the indenter. Thanks to this control factor $f_{control}$ the material surface remains approximately flat ($y_{front,i} = \overline{y_{front}}$).

5.2 Calibration of the model

An initial set of simulations is conducted to calibrate the model with the data from the experiments presented in [GGR⁺09]. The majority of the parameters are known, including the equilibrium concentration c_{eq} , the molar volume $V_s = 1/\alpha_j$ (with α_j defined in Section 4.2), the gas constant R , the temperature T or the indenter diameter d [GGR⁺09]. They are presented in Table 5.1. The sole unknown parameter is the coefficient $\kappa_c \times w$, where κ_c is the diffusion coefficient of the solute in the film and w is the film width. It should be noted

5 | Calibration and Validation of the Phase-Field Discrete Element Method

that the estimation provided in [GGR⁺09] appears to be dependent on the fitting method employed, with significant discrepancies observed between the reported values. For instance, the variation in the estimated coefficient, when fitted using either the proportionality ($\dot{y} \propto P$) or the power law ($\dot{y} \propto P^n$) models, is of a magnitude that spans several orders of magnitude. A trial-and-error method was employed to obtain simulated kinetics similar to experimental data. Moreover, as the sample is diffusion rate limited [GGR⁺09], it is not possible to determine the dissolution rate coefficient k_{diss} from the experiments. A numerical criterion is employed to estimate this parameter, $\overline{sat_{film}} \geq 80\%$, where $\overline{sat_{film}}$ is the mean saturation in the fluid film defined as $\overline{sat_{film}} = \frac{c - c_{eq}}{a_s c_{eq} - c_{eq}}$. Thus, a minimum is determined for the coefficient k_{diss} . The remaining parameters from Table 5.1 are numerical parameters, such as the barrier energy W , the mobility L , the mesh size Δ , the film width w and the well saturation sat_{well} . They are employed for the Phase-Field description and to define the update frequency, see Appendix G.

Equilibrium concentration c_{eq}	$0.73 \times 10^3 \text{ mol.m}^{-3}$
Molar volume $V_s = 1/\alpha_j$	$2.2 \times 10^{-5} \text{ m}^3.\text{mol}^{-1}$
Gas constant R	$8.32 \text{ J.mol}^{-1}.\text{K}^{-1}$
Temperature T	623 K
Indenter diameter d	$200 \times 10^{-6} \text{ m}$
Barrier energy W	1
Mobility L	1 s^{-1}
Mesh size Δ	$d/400$
Film width w	15Δ
Well saturation $sat_{well} = \frac{c_{well} - c_{eq}}{a_s c_{eq} - c_{eq}}$	30%
Diffusivity $\kappa_c \times \text{film width } w$	$4 \times 10^{-14} \text{ m}^3.\text{s}^{-1}$
Dissolution kinetics $k_{diss} = 10 k_{prec}$	$0.015/\Delta$

Table 5.1 Parameters used. The solute diffusion κ_c is obtained by calibration and the dissolution kinetics k_{diss} is adapted to verify the diffusion rate-limiting scenario.

The superposition of the results obtained with the data from [GGR⁺09] is presented in Figure 5.2. Two fits have been performed on the data from [GGR⁺09] for comparison with the results obtained: $\dot{y} = a \times P$ and $\dot{y} = a \times P^b$. Subsequently, the various parameters of the fits were subjected to deterioration in order to ascertain the boundary limits. For example, the upper envelope for the 75% limit is defined as 75% of the data points from [GGR⁺09]

being below it. Similarly, the lower envelope for the 75% limit is defined as 75% of the data points from [GGR⁺09] are larger. The results obtained with the Phase-Field description are in good agreement with the available data.

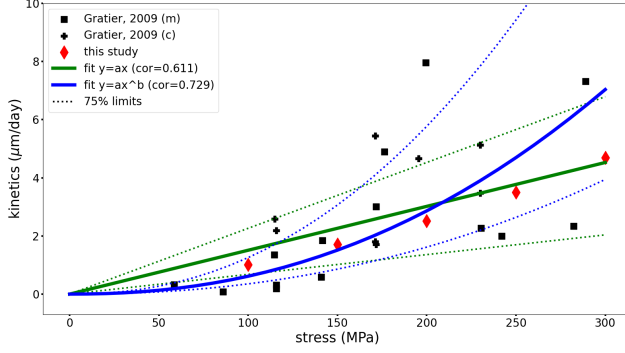


Fig. 5.2 Comparison of the experimental and simulated kinetics of the indenter test at different confining pressures.

5.3 Validation of the model with rate-limiting scenario

Despite the implementation of a calibration campaign, it is imperative to ascertain the accuracy of the model by replicating the different creep rate behaviors for pressure-solution associated with different parameters. As a reminder, pressure-solution is divided into three fundamental processes (dissolution, precipitation, diffusion), and its rate is limited by the slowest ones. Two well-known creep rate models exist, depending on the rate-limiting scenario [Rut76, Raj82].

5.3.1 The diffusion rate-limiting scenario

The diffusion rate-limiting one is defined as the diffusion kinetics is the slowest [Rut76, Raj82, SS90, GGR⁺09]. Numerically this scenario is verified by the criterion: $\overline{sat}_{film} \geq 80\%$, where $\overline{sat}_{film}$ is the mean saturation in the fluid film. It is defined as $\overline{sat}_{film} = \frac{c - c_{eq}}{a_s c_{eq} - c_{eq}}$, where c is the solution concentration, c_{eq} is the solution concentration at the equilibrium and a_s is the solid activity defined Equation 4.3. The displacement rate $\dot{y}$ during diffusion rate-limiting steady state is defined at Equation 5.2 [Rut76, Raj82, SS90, GGR⁺09].

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$$\dot{\gamma} = \alpha_{config}^{diff} \frac{\kappa_c w c_{eq} P^n}{d^2} \quad (5.2)$$

where κ_c is the diffusion coefficient, w is the film width, c_{eq} is the solution concentration at the equilibrium, P is the pressure applied, n is an exponent applied to the pressure ($\approx 1 - 2$ [BGB⁺19]), d is the diameter of the indenter ($\sim$ the distance to the free fluid), and α_{config}^{diff} is a coefficient depending on the configuration (material or temperature, examples among others).

A parametric investigation is done to verify the relation at Equation 5.2. As shown in Table 5.2, the effect of each parameter is isolated: bold values represent the default ones (from [GGR⁺09]), whereas the others represent the ones used only in the specific investigation (domain definition from [GGR⁺09]). Notice that the dissolution kinetics, related to k_{diss} from Equation 4.2, could have been modified to conserve the diffusion rate-limiting assumption ($\overline{sat}_{film} \geq 80\%$). Indeed, the value determined by calibration in Section 5.2 is only the lower limit of the coefficient k_{diss} . Results are given in Figure 5.3 and 5.4.

Diffusivity $\kappa_c \times$ film width w	1-4-10 $\times 10^{-14}$ m ³ /s
Concentration at the equilibrium c_{eq}	0.3-0.73-1.5 $\times 10^3$ mol/m ³
Pressure applied P	100-150- 200 -250-300 MPa
Distance to the well d	100-125-150-175-200 μ m

Table 5.2 Parameters used to verify Equation 5.2. Bold values represent the default ones, whereas the others represent the ones used only in the specific investigation.

The influence of the diffusivity κ_c on the strain rate $\dot{\gamma}$ is explored in Figure 5.3a. According to the Equation 5.2, a proportional relation is expected. In agreement with it, data from Figure 5.3a are well-fitted by a relation $\dot{\gamma} = a_{\kappa_c} \times \kappa_c$. Notice that the influence of the film width w could also be explored. Remember that the film width w is artificially increased compared to reality to allow numerical simulations. The results would be similar to Figure 5.3a if only the film fluid w varies.

The influence of the solubility (through the solute concentration at the equilibrium c_{eq}) on the strain rate $\dot{\gamma}$ is explored in Figure 5.3b. It is anticipated that a proportional relationship will be identified, see Equation 5.2. This factor has been observed experimentally [Rut76, ZRG⁺05]. In agreement with those observations, data from Figure 5.3b are well-fitted by a relation $\dot{\gamma} = a_{c_{eq}} \times c_{eq}$. As explained earlier, an effort has been made to compare simulations with the

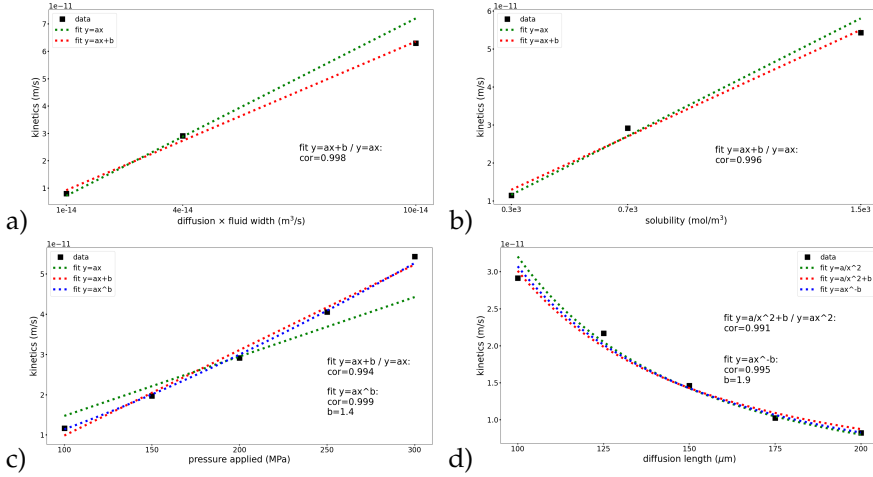


Fig. 5.3 Comparison with the analytical model of the simulated influence on the rate of the indenter test of a) the diffusivity, b) the solubility, c) the pressure applied and d) the distance to the free fluid.

same well saturation sat_{well} . The changing value c_{eq} affects this parameter, as $sat_{well} = \frac{c - c_{eq}}{a_s c_{eq} - c_{eq}}$.

The influence of the pressure applied P on the strain rate $\dot{\gamma}$ is explored in Figure 5.3c. Equation 5.2 predicts a power relation with an exponent between 1 and 2, observed experimentally [SSB⁺90, GGR⁺09, GRV14, BGB⁺19]. In agreement with those observations, data from Figure 5.3c are well-fitted by a relation $\dot{\gamma} = a_p^{diff} \times P + b_p^{diff}$. An even better fit has been found, considering $\dot{\gamma} = a_p^{diff} \times P^{b_p^{diff}}$ (the exponent b_p^{diff} equals 1.4). Indeed, the pressure applied P is inside an Arrhenius exponential function in Equation 4.3. The linear dependency is only an approximation in a small pressure domain, even if the exponent (1.4) is similar to a linear one (1). For instance, a proportional fit has been tried, $\dot{\gamma} = a_p^{diff} \times P$, but it seems worse than the others. It is worth noting that the influence of the pressure applied on a bigger domain can hardly be verified experimentally as the pressure-solution is dominant in the low-pressure domain, but phenomena like dislocation, plasticity, or microcracking appear in the high-pressure pressure domain [USSK08].

The influence of the indenter diameter d ($\sim$ distance to the free fluid) on the strain rate $\dot{\gamma}$ is explored in Figure 5.3d. According to Equation 5.2 and experimental observations [SSB⁺90], a relation $\dot{\gamma} \propto 1/d^2$ is expected. In agreement

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with those observations, data from Figure 5.3d are well-fitted by a relation $\dot{y} = a_d/d^2$.

The different data obtained in this Section are plotted together in Figure 5.4, representing $\dot{y}_{simulation}$ versus $\dot{y}_{theory}$. From Equation 5.2, one can define $\dot{y}_{theory} = \alpha_{config}^{diff} \frac{\kappa_c w c_{eq} P^{1.4}}{d^2}$, with α_{config}^{diff} a coefficient describing a combination of the other parameters (well saturation, barrier energy, mobility, temperature, molar volume, examples among others). This coefficient α_{config}^{diff} is estimated from the average of the different simulations through a postprocessing $\dot{y}_{simulation} \frac{d^2}{\kappa_c w c_{eq} P^{1.4}}$. Then, the mean relative error with the target line $\dot{y}_{simulation} = \dot{y}_{theory}$ is computed. It appears the relative error of the simulated kinetics to the theoretical one is less than 4% (with a maximum value of 12%), a reflection of the simulations' consistency with the theoretical framework.

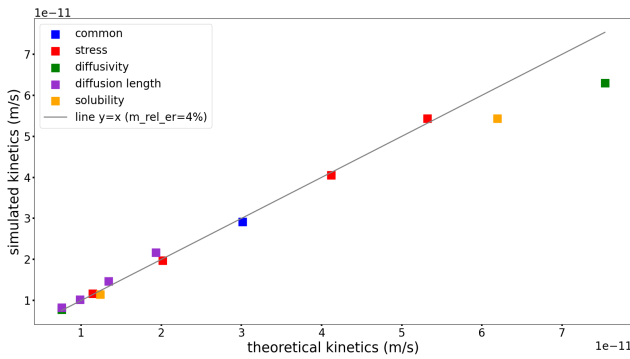


Fig. 5.4 Comparison of the simulated and theoretical kinetics of the indenter test in the case of the diffusion rate-limiting.

5.3.2 The dissolution rate-limiting scenario

The second rate-limiting scenario is the dissolution one, defined as the dissolution process is the slowest [Raj82, SS90, vNSP08, GGR⁺09]. Numerically this scenario is verified by the criterion: $\overline{sat}_{film} \leq 20\%$, where $\overline{sat}_{film}$ is the mean saturation in the fluid film. It is defined as $sat_{film} = \frac{c - c_{eq}}{a_s c_{eq} - c_{eq}}$, where c is the solution concentration, c_{eq} is the solution concentration at the equilibrium and a_s is the solid activity defined Equation 4.3. The displacement rate $\dot{y}$ during dissolution rate-limiting steady state is defined at Equation 5.3 [Raj82, SS90, GGR⁺09].

$$\dot{\gamma} = \alpha_{config}^{diss} k_{diss} P^n \quad (5.3)$$

where k_{diss} is the dissolution kinetics, P is the pressure applied, n is an exponent applied to the pressure ($\approx 1 - 2$ [BGB⁺19]), and α_{config}^{diss} is a coefficient depending on the configuration (material or temperature, examples among others).

Similar to the previous Section, a parametric investigation is conducted to verify the relation at Equation 5.3. The parameters are shown in Table 5.3. To isolate the effect of each parameter, default values are considered (in bold), whereas a domain is explored in the specific investigation (default and domain definition from [GGR⁺09]). Results are given in Figure 5.5 and 5.6.

Dissolution kinetics k_{diss}	0.01-0.02-0.05- 0.1 -0.2
Pressure applied P	50-100-150- 200 -250-300 MPa

Table 5.3 Parameters used to verify Equation 5.3. Bold values represent the default ones, whereas the others represent the ones used only in the specific investigation.

The influence of the dissolution kinetics (through the coefficient k_{diss}) on the strain rate $\dot{\gamma}$ is explored in Figure 5.5a. According to the Equation 5.3, a proportional relation is expected. This factor has been observed experimentally [DMSP97]. In agreement with those observations, data from Figure 5.5a are well-fitted by a relation $\dot{\gamma} = a_{k_{diss}} \times k_{diss}$.

The influence of the pressure applied P on the strain rate $\dot{\gamma}$ is explored in Figure 5.5b. It is reasonable to posit a power relationship between the variables in question, see Equation 5.3 and experiments [DMSP97, NSB02]. In agreement with those observations, data from Figure 5.5b are well-fitted by a relation $\dot{\gamma} = a_p^{diss} \times P + b_p^{diss}$. Similar to the case of the diffusion rate-limiting, an even better fit has been found, considering $\dot{\gamma} = a_p^{diss} \times P^{b_p^{diss}}$ (the exponent b_p^{diss} equals 1.3). As explained above, the pressure applied P is inside an Arrhenius exponential function in Equation 4.3. The linear dependency is only an approximation in a small pressure domain, even if the exponent (1.3) is similar to a linear one (1). For instance, a proportional fit has been tried, $\dot{\gamma} = a_p^{diss} \times P$, but it seems worse than the others. As explained above, the influence of the pressure for large values cannot be investigated during experiments as other mechanisms are triggered [USSK08].

Similar to the previous Section, the different data obtained in this Section are plotted together in Figure 5.6, representing $\dot{\gamma}_{simulation}$ versus $\dot{\gamma}_{theory}$. From

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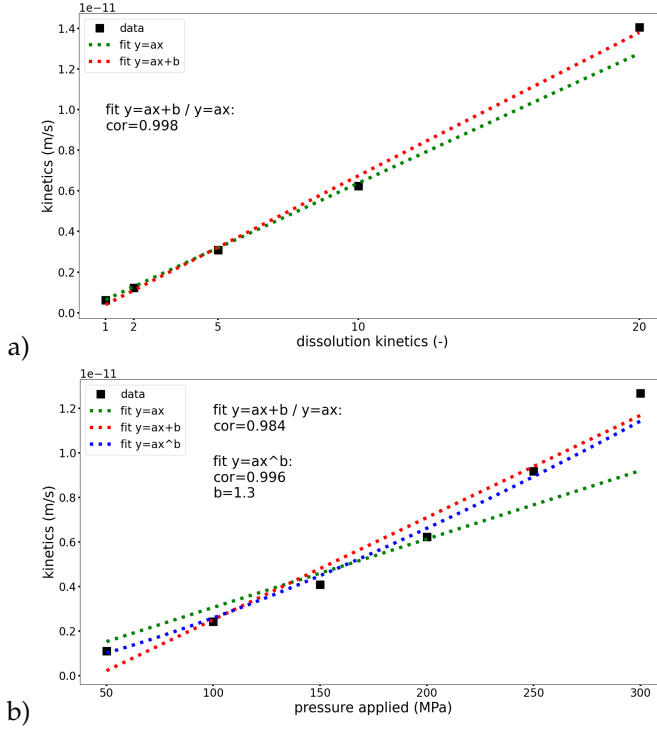


Fig. 5.5 Comparison with the analytical model of the simulated influence on the rate of the indenter test of a) the dissolution kinetics and b) the pressure applied.

Equation 5.3, one can define $\dot{y}_{theory} = \alpha_{config}^{diss} k_{diss} P^{1.3}$, with α_{config}^{diss} a coefficient describing a combination of the other parameters (well saturation, barrier energy, mobility, temperature, molar volume, examples among others). This coefficient α_{config}^{diss} is estimated from the average of the different simulations through a postprocessing $\dot{y}_{simulation} \frac{1}{k_{diss} P^{1.3}}$. Then, the mean relative error with the target line $\dot{y}_{simulation} = \dot{y}_{theory}$ is computed. It appears also that the relative error of the simulated kinetics to the theoretical one is less than 4% (with a maximum value of 11%).

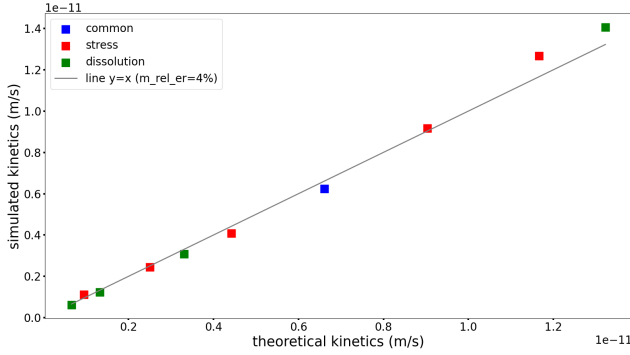


Fig. 5.6 Comparison of the simulated and theoretical kinetics of the indenter test in the case of the dissolution rate-limiting.

5.4 Preliminary conclusions

This Chapter presented a methodology for calibrating the Phase-Field parameters employed in the formulation outlined in Chapter 4. For this purpose, data from prior indentation experiments on quartz are employed. The numerical approach appears capable of reproducing the experiments.

The Phase-Field formulation is then tested by considering two limiting scenarios. Indeed, pressure-solution is a complex phenomenon divided into three fundamental processes: dissolution, diffusion, and precipitation. The rate of the pressure-solution is determined by the slowest process. Here, the diffusion and the dissolution rate-limiting scenarios, which are well defined in the literature through experiments, are reproduced, and the Phase-Field formulation appears verified.

In comparison to experiments, this numerical laboratory is significantly faster (a few hours versus months) and can capture additional information, such as the degree of saturation in the fluid or the state of the stress in the solid.

6

Importance of precipitation on the slowdown of creep behavior induced by pressure-solution

Once the formulation of the Phase-Field description presented in Chapter 4 has been calibrated and validated in Chapter 5, it can be coupled to a Discrete Element Model to capture the heterogeneous dissolution/precipitation and the granular reorganization. In fact, the Phase-Field formulation itself is not able to compute the mechanical steady-state and interpolate the stress at the contacts.

A new numerical configuration is considered in this Chapter: a constant force is applied to a grain subject to pressure-solution at the contact with a plate not subject to pressure-solution. Compared to the previous indenter test, see Figure 5.1, the material subject to pressure-solution moves and the pressure at the contact is initially unknown as the contact surface evolves. The Discrete Element Method is employed to estimate these mechanical aspects.

Particular attention is paid to the examination of the influence of precipitation on the phenomenon kinetics [SMRV25a]. In fact, precipitation has been observed to induce an augmentation of the contact surface. This increase in

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surface area leads to a reduction in the stress transmitted at the contact level. Furthermore, it has the effect of slowing down the creep settlement. However, it is noteworthy that current microscale models [SS90, LCN⁺21, PS15] do not incorporate this precipitation-induced effect.

Some examples of scripts used are available on Github: https://github.com/AlexSacMorane/MY_PFDEM_1G_2D.

6.1 Numerical model

Figure 6.1 depicts the configuration investigated in this Chapter. A constant force is applied to a grain that is subject to pressure-solution over a plate that is not subject to pressure-solution. The material undergoes dissolution at the contact, subsequent diffusion within the fluid film, and finally precipitation on the surface less stressed, following the pattern of pressure-solution, see Figure 1.4. Table 6.1 presents the relevant parameters utilized in this study. The majority of these parameters are consistent with the ones employed in the calibration and validation campaigns detailed in Chapter 5. Particular attention is directed towards the impact of precipitation kinetics coefficient k_{prec} on creep behaviour. Indeed, this impact on creep behavior is not considered in the current models, or only partially. It should be noted that, in contrast to previous simulations in Chapter 5, the solute concentration is not evacuated (the domain being closed). Indeed, it is consumed during the precipitation.

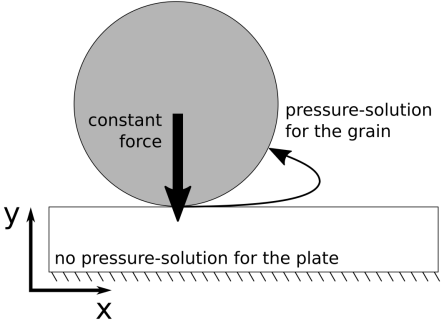


Fig. 6.1 A constant force is applied to a grain subject to pressure-solution over a plate not subject to pressure-solution.

Initial radius	100 μm
Thickness of the simulation	100 μm
Volume overlap / Initial grain volume	1.6 %
Mobility L	3 s^{-1}
Mesh size Δ	Initial radius / 40
Dissolution kinetics k_{diss}	$0.005/\Delta$
Precipitation kinetics k_{prec}	$0.5 - 1 - 2 - 5 - 8 - 10 - 13 - 16 k_{diss}$
Equilibrium constant c_{eq}	see Table 5.1
Molar volume V_s	
Gas constant R	
Temperature T	
Diffusivity $\kappa_c \times \text{film width } w$	

Table 6.1 Parameters used for the grain-plate configuration.

6.2 Results

Figure 6.2 presents the vertical strain’s time evolution for distinct precipitation kinetics. The definition of the vertical strain is $\epsilon = \Delta y/2R$, where Δy is the cumulative vertical displacement of the grain and R is the initial radius.

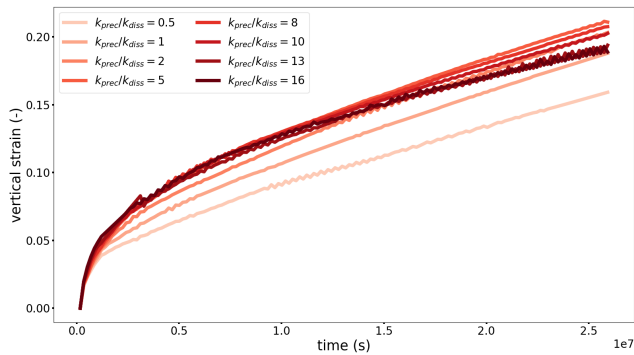


Fig. 6.2 Time evolution of the vertical strain for different precipitation kinetics.

As detailed in [SSB⁺90, SS90], the settlement kinetics can be estimated, see Equation 6.1, under the assumption of a close-packed (face-centered-cubic lattice) array of spherical grains with identical diameters. Equation 6.2 provides the solution to this partial differential equation, which is a $n + 1$ root law. The

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exponent n determines the extent of the slowdown in creep behavior; a larger value of n corresponds to a stronger slowdown.

$$\dot{\epsilon} = k \cdot 1/\epsilon^n \quad (6.1)$$

where k contains the different factors such as the pressure applied, the grain diameter, and the diffusivity of the solute, among others.

$$\epsilon(t) = (n k t + k t)^{1/(n+1)} \quad (6.2)$$

This relationship is employed to compute a fit of the results obtained. It appears the fit provides a correlation coefficient of approximately 0.997 for the various curves. The factor $n + 1$ appears to be approximately 1.95 and 2.25, which is consistent with the experimental observations in [SSB⁺90]. Subsequently, the impact of the precipitation kinetics on the exponent n can be discerned in Figure 6.3.

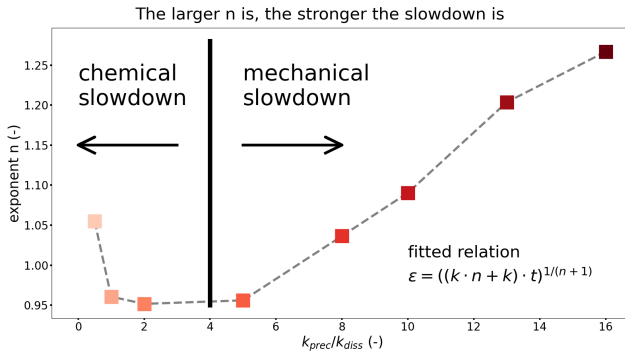


Fig. 6.3 Influence of the precipitation kinetics on the slowdown (through the exponent n) of the evolution of the vertical strain $\epsilon(t)$.

It seems that at low precipitation rates ($k_{prec}/k_{diss} \leq 4$), the slowdown declines in proportion to the precipitation kinetics. Conversely, the slowdown increases with the precipitation kinetics at fast precipitation ($k_{prec}/k_{diss} \geq 4$). As explained in [LCN⁺21], the slowdown of the pressure-solution creep is caused by (i) a chemical mechanism or (ii) a mechanical one. Indeed, if the solute concentration builds up in the pore space, the mass transfer by diffusion is slowed down, case (i). Similarly, an increase in the contact surface results in a reduction in pressure (driving force of pressure-solution), and the mass flux by dissolution is slowed down, case (ii) [LCN⁺21]. The rate of the settlement

appears to decrease for the two cases.

Figure 6.4 illustrates the evolution of the solid activity ($\sim$ pressure at the contact) in relation to the vertical strain for varying precipitation kinetics. The impact of the precipitation kinetics is readily discernible. As expected, the solid activity is observed to be smaller at a given strain for faster precipitation kinetics. It demonstrates the slowdown of the pressure-solution due to a mechanical mechanism.

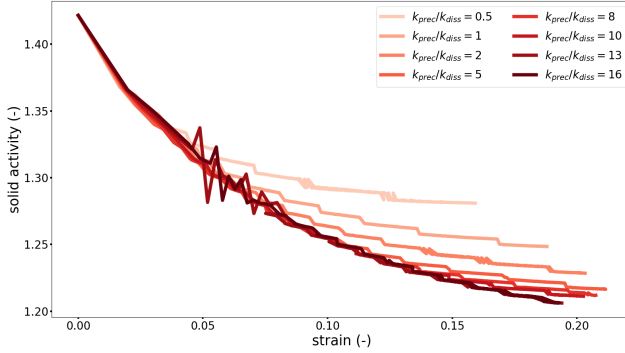


Fig. 6.4 Influence of the precipitation kinetics on the solid activity ($\sim$ pressure at the contact) during the creep behavior. At a given strain, the solid activity decreases with precipitation kinetics.

Nevertheless, Figure 6.3 underscores a slowdown in the creep behavior, even when the precipitation kinetics decreases. This is particularly evident in the case of slow precipitation ($k_{prec}/k_{diss} \leq 4$). This is contrary to the indications provided by Figure 6.4. Figure 6.5 illustrates the evolution of the mean value of the solute concentration (in comparison to the equilibrium value) within the pore space for varying precipitation kinetics coefficient. The solute concentration appears to build up in the pore space for slow precipitation. The slowdown of the pressure-solution is attributed to a chemical mechanism.

Upon returning to Figure 6.3, two distinct domains become evident. In the case of slow precipitation ($k_{prec}/k_{diss} \leq 4$), the creep slowdown (due to chemistry) decreases in line with the precipitation kinetics. In contrast, for fast precipitation ($k_{prec}/k_{diss} \geq 4$), the creep slowdown (due to mechanics) increases with the precipitation kinetics. As observed by [LCN⁺21] through a 1D model, these two limiting scenarios can be seen to occur when the solute outflux from the contact zone is either prevented or allowed [LCN⁺21]. Preventing the solute outflux results in the accumulation of the solute concen-

6 | Importance of precipitation on the slowdown of creep behavior induced by pressure-solution

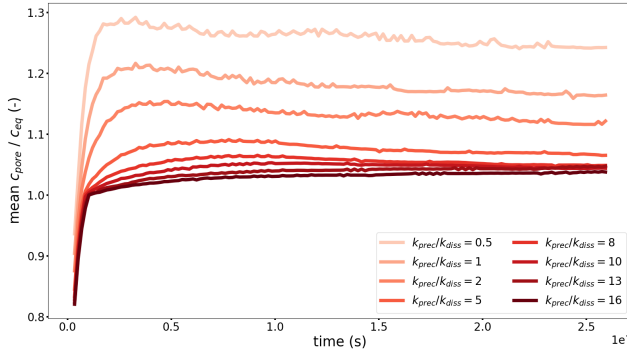


Fig. 6.5 Influence of the precipitation kinetics on the mean value of the solute concentration in the pore space during the creep behavior. As precipitation kinetics increases, the accumulation of the solute concentration in the pore space decreases.

tration in the pore space. It is a chemical slowdown. Conversely, allowing the solute outflux results in an increase in the surface contact, as the dissolution occurs. However, the model of [LCN⁺21] does not account for the impact of the precipitation on the increase of the contact surface or the consumption of the solute concentration in the pore space. Precipitation was included in the model proposed by Yasuhara *et al.* in 2003 [YEP03]. However, their simplifying assumptions on the geometry and processes employed hinder the effect of precipitation on the strain rate. Nevertheless, the model allows for the observation of the impact of the precipitation on the porosity evolution. Similarly, Xu and Arson considered the precipitation as a healing process [XA22]. The consequence of this phenomenon is an increase in the stiffness of the sample at the continuum scale. However, this model does not account for granular reorganization. Additionally, it has been suggested that the precipitation kinetics can control the global creep behavior if the process is the slowest [Mul91]. Nevertheless, this assessment is only based on the rate-limiting theory and does not consider the evolution of the grain shapes and configuration. The PFDEM framework presented here enables solving for the multi-physical processes in the whole microstructure geometry and is also capable of capturing the evolution of the grain shape, see Figure 6.6. The shape of the grain seems to depend on the precipitation kinetics. In particular, the contact surface increases in proportion to the precipitation kinetics. The complex geometries of the grains exert a significant influence on the macroscopic mechanical behav-

ior of granular materials [BPA19, GRV22] and need to be considered.

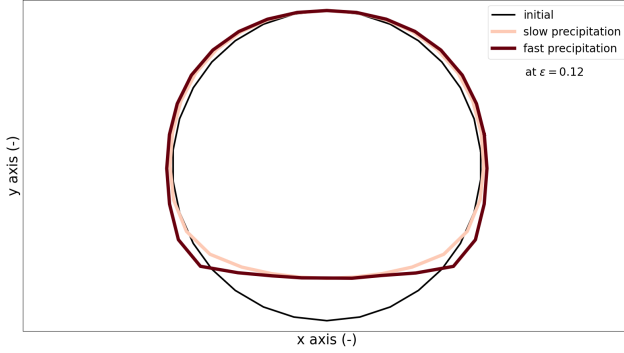


Fig. 6.6 Comparison of the initial grain shape with the current one at a given strain for slow and fast precipitation kinetics. The contact surface increases with the precipitation kinetics.

Emphasizing the impact of the precipitation kinetics on the grain shape, Figure 6.6 seems to indicate that the coefficient k_{diss} may be calibrated from experimental observations. However, to the knowledge of the authors, no experiments at the scale of a single grain, tracking its shape, have been conducted. Considering the data available at the scale of a granular sample, [SFBA22, ZRG⁺04] for instance, appears inefficient as the history of the granular organization hugely affects the shape of the individual grains. Such calibration based on micro data (shape of the grain) becomes impossible for a multiple-grain configuration. It would be relevant to conduct new experiments considering an individual grain to track its shape evolution and to calibrate this parameter.

In the same vein, the results presented in Figure 6.2 can be processed to investigate the transient aspect of the creep. Indeed, it has been shown in [DPR⁺02] that the creep law can be divided as $\epsilon(t) = \epsilon_0 + \beta t^{1/3} + \kappa t$, where ϵ_0 is the instantaneous plastic strain, $\beta t^{1/3}$ is the Andrade transient creep [And10, Cot96], and κt is the steady-state creep. In the following, the focus is on the Andrade transient creep $\beta t^{1/3}$, the instantaneous plastic strain ϵ_0 being null here, while the steady-state creep κt has already been explored in Chapter 5. Figure 6.7 depicts the evolution of the logarithm of the vertical strain versus the logarithm of the time for different precipitation kinetics.

It appears that the curves aim to reach $\epsilon \sim t^{1/3}$ while the time evolves.

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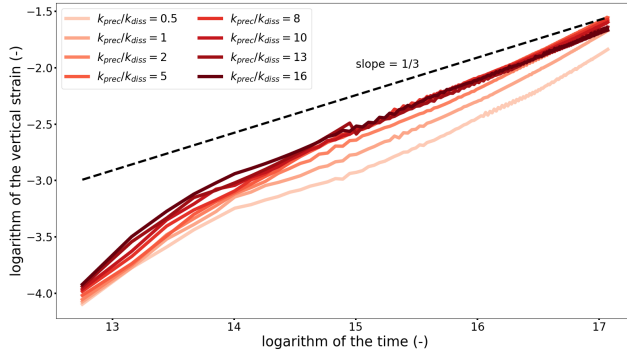


Fig. 6.7 Evolution of the logarithm of the vertical strain versus the logarithm of the time for different precipitation kinetics.

The coefficient of the slope (being $1/3$) is related to the evolution of the contact shape. Indeed, [DPR⁺02] has highlighted the presence at the contact of an island structure through white light interferometer micrographs. The contact between two ‘flat’ surfaces will occur only at a few contact points, depending on the waviness and roughness of the surfaces. This binary mixture (solid-water) at the contact will evolve following a spinodal decomposition [DPR⁺02] until the contact surface is filled by the solid. It is worth noting that this spinodal decomposition of mixtures is characterized by an evolution of the length scale $d \sim t^{1/3}$.

Even if the observations of [DPR⁺02] are at the contact scale and the island structure of the contact is not modeled herein, the transient aspect of the creep behavior is emphasized in Figure 6.7 with similar mechanisms at stake. Once the contact surface remains approximately constant, the creep behavior will be dictated by the steady-state regime, investigated in Chapter 5.

6.3 Preliminary conclusions

The Phase-Field Discrete Element Model framework has been employed to examine the influence of precipitation on the slowdown of creep behavior induced by pressure-solution. It is noteworthy that this particular aspect is not currently included in the models that are employed to describe the strain rate due to pressure-solution or their simplifying assumptions on the microstructure hinder its influence. To this end, the model is applied to a grain-plate configuration while pressure-solution is activated. The consideration of the

precipitation by the Phase-Field Discrete Element Model implies an acceptable computational cost (a few hours on a regular computer¹ for a simulation depicted herein). This required resource is expected to be reduced in the future, as the algorithm is at its genesis and can become more mature.

At low precipitation rates, the slowdown rate declines in proportion to the kinetics factor. The underlying mechanism is linked to the accumulation of solute concentration within the pore space. Conversely, the slowdown increases with the kinetics at fast precipitation. In this case, the mechanism is due to the larger surface area at the contact. It decreases the stress, which is the driving force behind the phenomenon. Precipitation appears to determine the slowdown mechanism (chemical or mechanical) and the amplitude of the slowdown.

This Chapter illustrates the necessity of integrating all relevant processes in the case of multi-physics phenomena, such as pressure-solution, but also solving them numerically at the microstructure scale. Indeed, this chemo-mechanical phenomenon is subdivided into three distinct processes: dissolution, diffusion, and precipitation and the global kinetics of this creep behavior is controlled by the slowest rate-limiting process. However, the rate-limiting process may undergo changes over time as the microstructure configuration is modified. For instance, the rate-limiting process for pressure-solution is frequently dissolution during the initial stage. Indeed, the diffusion length is relatively short, and the solute dissolved in the fluid film evacuates rapidly into the pore space. However, the diffusion length increases in proportion to the material dissolution and precipitation around the contact. At a certain point, the diffusion may become the rate-limiting process. This transition can only be captured if models integrate a sufficient number of phenomena. Finally, this lays the foundation for a deeper understanding of pressure-solution at the microscale, enabling to investigate in the future complex microstructures, but also their role in diagenesis and earthquake nucleation for various minerals and environmental conditions.

Moreover, an Andrade creep has been reproduced through the application of the Phase-Field Discrete Element Method to this configuration. This typical behavior is characteristic of the transient behavior of the material, when the kinetics of the phenomenon decrease with time. Combined with the validation of the rate-limiting scenarios, depicted in Sections 5.3.1 and 5.3.2, it

¹Intel(R) Core(TM) i5-10210U CPU @ 1.60GHz, 8 Go RAM

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emphasizes the ability of the framework to capture the physics involved.

7

Numerical twin of a granular media under chemo-mechanical couplings to consider the impact of the microstructure

As discussed in Section 1.3, the role of the microstructure in stress transmission within granular or rock media is crucial [BPA19, GRV22, LPD⁺25, PMWT05, TWL10, RWJM98]. The microstructure can be divided into two distinct categories: the morphology of the grains and the granular organization. These distinct aspects are examined in this Chapter utilizing the PFDEM framework developed in Chapter 4.

After highlighting the impact of the microstructure (morphology and organization), a framework is introduced to incorporate PFDEM within the field of Digital Rock Physics [LRV22, ACD⁺13, DDDF11]. This discipline is defined as the computation of numerous rock properties, such as strength, stiffness, or permeability, employing numerical simulations based on realistic microstructures. Indeed, these microstructures can be obtained through current imaging

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techniques, such as computed tomography scans [BSJ25, PADV23, SFBA22, KAP⁺19], and numerous databases are available online [Imp14, The22].

Some examples of scripts used are available on Github:

- https://github.com/AlexSacMorane/PFDEM_AC
- https://github.com/AlexSacMorane/MY_PFDEM_MG_3D
- https://github.com/AlexSacMorane/SandAtlas_extraction_2D
- https://github.com/AlexSacMorane/MY_PFDEM_MG_2D

7.1 Impact of the grain's morphology

7.1.1 Stress-state evolution of spherical versus non-spherical particles subjected to dissolution

In 2009, *Shin and Santamarina* conducted experiments similar to the configuration depicted in Figure 2.4b [SS09]. A granular sample was maintained under oedometric conditions, while a fluid induced the dissolution of grains. To do so, *Shin and Santamarina* mixed glass beads with table salt (halite), and the obtained mixture was immersed into deaired water. This operation results in a localized dissolution, where the glass beads remain inert while the table salt grains undergo a reduction in size. The activated chemistry triggers a change in the stress state, quantified using the coefficient $k_0 = \sigma_{II}/\sigma_I$ (where σ_I represents the vertical pressure and σ_{II} the lateral pressure). To improve the understanding of the experiments, a Discrete Element Model has been utilized [SS09, CS14]. However, the dissolving particles were modeled as spheres. This model choice does not align with the observation of halite particles through a scanning electron microscope, where particles appear more square-shaped [ZRG⁺04]. Herein, the impact of the shape of the dissolving particle is investigated with a 2D Phase-Field Discrete Element Model, see Chapter 4 for the formulation and [SMVR24a] for further details. As depicted in Figure 7.1, the undissolvable grains are always assumed to be disks, while the dissolvable grains can be either a) squares or b) disks (although other shapes are possible, the simulations are restricted to these two). Compared to the pressure-resolution phenomenon described in Chapters 4, 5 and 6, the dissolvable grains know solely a homogeneous dissolution and no precipitation occurs.

While dissolution occurs, the $k_0 = \sigma_{II}/\sigma_I$ coefficient, the compacity = $S_{grains}/S_{oedometer}$ (with S_{grains} being the sum of the grains surface, and $S_{oedometer}$

	undissolvable particle	dissolvable particle
a		
b		

Fig. 7.1 The undissolvable grains are disk-shaped, while the dissolvable grains are disk-shaped or square-shaped.

being the surface of the domain), and the vertical strain are tracked, considering dissolvable grains as disks or squares. Two different ratios of dissolvable surface to total surface are studied (5 and 15%). As highlighted in [SS09, CS14] and observed in Figure 7.2, the dissolution of grains leads to an evolution (increase or decrease) of the coefficient k_0 . In the investigation presented herein, a stronger reduction in k_0 is observed when the percentage of dissolvable grains is larger. This reduction occurs due to the reorganization of grains around the dissolved grains, as shown in Figure 7.3. The number of undissolvable–dissolvable contacts decreases with material dissolution, while the number of undissolvable–undissolvable contacts remains relatively constant.

Figure 7.2 emphasizes that the decrease of the coefficient k_0 is larger in the case of disk-shaped dissolvable grains than square-shaped ones, while the compacity and the vertical strain remain similar. This observation highlights the importance of considering explicitly the grain shape to obtain an accurate response of the system. This impact of the shape has also be explored in numerous configurations such as a sheared layer [BPA19, SMVR24b].

7.1.2 An elementary configuration during pressure-solution

The impact of grain morphology on the pressure-solution phenomenon is elucidated in the comparison of the results presented in Chapters 5 and 6. Indeed, Chapter 5 considered an indentation experiment based on a constant reactive surface, and the settlement curve appeared linear with time. However, Chapter 6 considered a configuration based on an evolving surface. Indeed, precipitation occurs and affects the morphology of the grains, resulting in a nonlinear settlement curve with time, as illustrated in Figure 6.2. The morphology appears to have a pivotal role in the creep behavior.

Furthermore, Figure 6.6 emphasizes the increase in the contact surface, at-

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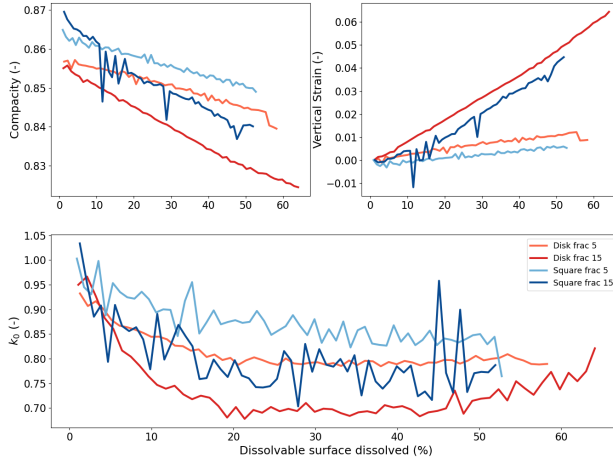


Fig. 7.2 Evolution of k_0 (bottom), of the compacity (left) and the vertical strain (right) with the dissolution of the dissolvable material, considering dissolvable grains as disks or as squares. Two ratios of the dissolvable surface over the total surface are studied.

tributed to two distinct phenomena. The first one is the dissolution of the matter at the contact. In nature, grains tend to be convex in shape, and the dissolution of matter leads to an increase in the contact surface. The second phenomenon is the precipitation on the less stressed side of the grains, which enhances the increase in the surface at the contact. In the context of pressure-solution, an increasing reactive surface corresponds to a decrease in the stress, see Figure 6.4. As pressure-solution is a stress-driven chemo-mechanical process, the rate of the settlement decreases over time.

Furthermore, the evolving shapes of the grains impact the mechanical properties of the sample, and so stress transmission in the granular medium [BPA19, GRV22, LPD⁺25]. Shape appears as a pivotal aspect to capture.

7.2 Impact of granular organization

After the morphology of the grains, the second aspect of the microstructure is the organization of the grains. This specific aspect is investigated considering the pressure-solution phenomenon. As depicted in Figure 7.4, two 3D granular organizations are compared: three grains tilted, representative of a face-centered cubic crystal, and four grains aligned, representative of a primi-

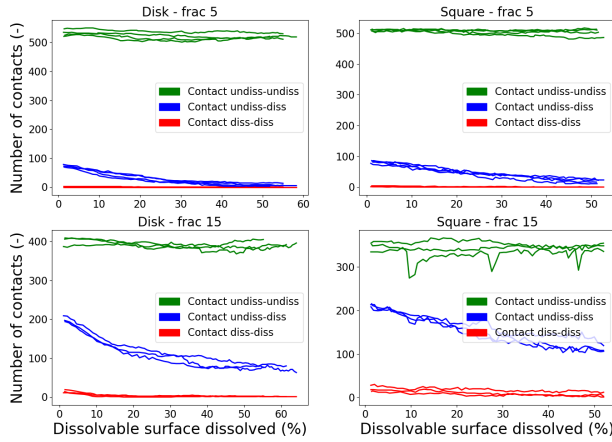


Fig. 7.3 Evolutions of contact distribution with the dissolution of the dissolvable material, considering dissolvable grains as disks or as squares. Two ratios of the dissolvable surface over the total surface are studied.

tive cubic crystal.

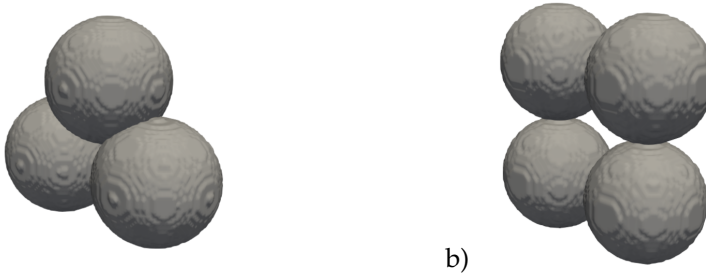


Fig. 7.4 Initial configurations of the a) three grains tilted and b) four grains aligned.

The microstructures are then loaded under oedometric conditions, lateral displacements are prevented and a constant force is applied on the top, see Figure 7.5. Compared to Chapter 2 and Section 7.1.1, no reactive fluid is injected. The settlement observed is only induced by chemo-mechanical processes, such as pressure-solution. The parameters calibrated in Section 5.2 are employed. From a macroscopic point of view, the evolution of the settlement,

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while pressure-solution occurs, is shown in Figure 7.6. This settlement has been computed considering the coordinates of the top wall that applies the load in the two configurations.

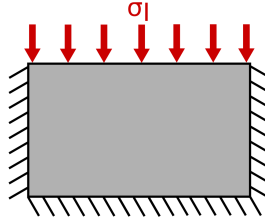


Fig. 7.5 Scheme of the oedometer: the bottom and lateral walls are fixed, while the top wall is controlled to apply a confining loading.

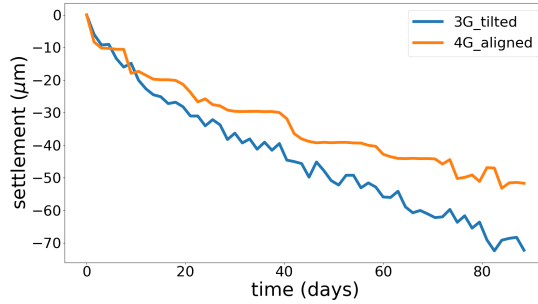


Fig. 7.6 Evolution of the settlement of the face-centered cubic (three grains) and primitive cubic crystals (four grains).

It appears that the settlement kinetics of the face-centered cubic configuration is faster than the primitive cubic configuration. Indeed, the force transmitted at the contact appears larger in the tilted microstructure than in the aligned microstructure because of the angle between the force applied and the orientation of the contact between the grains, see Figure 7.7. Even if the force applied at the macroscale is similar in the two cases, the granular organization impacts the forces transmitted at the microscale, enhancing or not the pressure-solution phenomenon.

Furthermore, the behavior of the distinct configurations is different at the microscale, as illustrated by the final configurations of the microstructure in Figure 7.8.

Pressure-solution patterns appear well depicted in the two configurations,

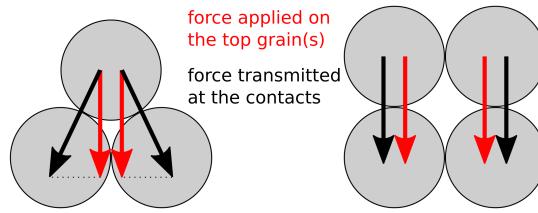


Fig. 7.7 The angle between the force applied and the contact orientation increases the force transmitted by projection in the tilted configuration compared to an aligned configuration.

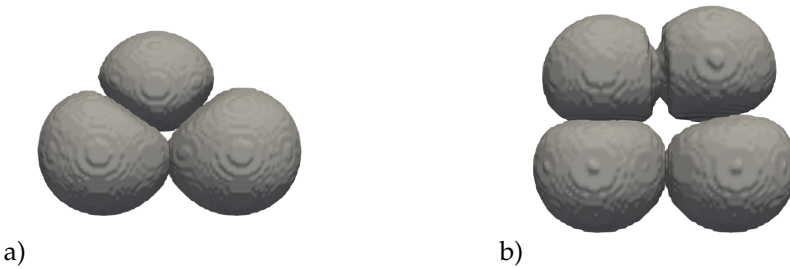


Fig. 7.8 Final configurations of the a) three grains tilted and b) four grains aligned.

with the material dissolving at the contact and a contact surface becoming flat. However, some distinctions are visible between the two distinct configurations. The top grain in the face-centered cubic configuration is more dissolved than the ones in the primary cubic configuration, as two main reactive contacts are active for this grain, compared to only one main reactive contact for the top grain in the primary cubic configuration. Even if a second reactive contact located between the two top grains can be pointed out in the four grains configuration, it remains minor in the vertical creep behavior, and its origin is the oscillations introduced by the discretization of the grains in the DEM steps. The impact of the granular organization on the morphology evolution requires to be correlated to the results presented in Section 7.1 where the shape of the grain appears to influence the mechanical behavior of the granular sample and the creep behavior due to pressure-solution. Similarly, the mechanical behavior at the sample scale is also affected by this impact of the granular organization on the size evolution [Bus12, RSSM⁺22].

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7.3 Development of a numerical twin

7.3.1 Extension of the PFDEM framework to the Digital Rock Physics discipline

As previously mentioned, it is imperative to capture the true morphology of the grains and the particle organization as these parameters have a significant impact on the behavior of the sample. In accordance with the principles of the Digital Rock Physics discipline [LRV22, ACD⁺13, DDDF11], a framework must be established to incorporate real microstructure geometries obtained mainly from X-ray micro-computed tomography as inputs into the PFDEM description. In particular, *Hamburg sand* entry [MHA⁺21] from *The Sand Atlas* database, accessible online [The22], is employed for this purpose.

Although the framework presented in Chapter 4 is available, it has been extended to minimize computational costs. Indeed, employing a phase variable η for a single grain increases the computational cost exponentially. Therefore, the approach involves considering multiple grains per phase variable. For instance *Guével et al.* employed a single phase variable to describe the entire sample [GRV20]. However, this method induces unphysical shape evolution, as illustrated in Figure 7.9. Indeed, the Phase-Field theory can induce curvature-driven shape evolution to reduce surface tension [AC79, MBW08]. The origin of this unphysical phase evolution is the gradient coefficient κ_j from Equation 4.1.

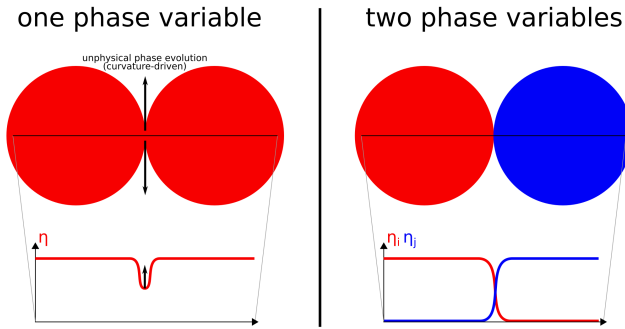


Fig. 7.9 Unphysical phase evolution can be induced to reduce the curvature of the shape. Two phase variables are required to describe grains in contact.

The solution to this problem appears to be the use of new distinct phase variables $\phi_i = \sum_{j(i)} \eta_j$, which are defined as a combination of the initial ones η_j , see Figure 7.10. For instance, $\phi_1 = \eta_1 + \eta_3$ and $\phi_2 = \eta_2$ in the configura-

tion depicted in Figure 7.10. To prevent curvature-driven shape evolution, see Figure 7.9, the variable η_2 can not be considered in the variable ϕ_1 .

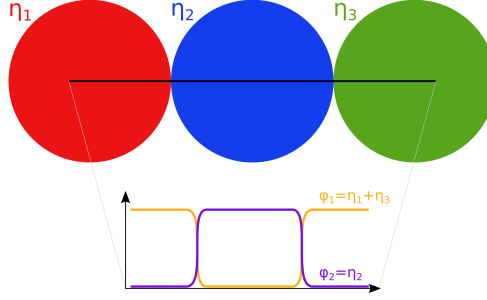


Fig. 7.10 New phase variables ϕ_i are defined as a combination of the variables η_j , preventing unphysical phase evolution, see Figure 7.9.

Once the framework is extended to consider multiple grains without an exponential increase of the computational cost, it is applied to the microstructure obtained by computed tomography scans [The22, MHA⁺21], see Figure 7.11. This visualization technique consists of scanning the sample with X-rays and reconstructing a 3D image of the sample. Notwithstanding the cost savings, the framework remains expensive. Consequently, a 2D simulation is utilized in the subsequent analysis.

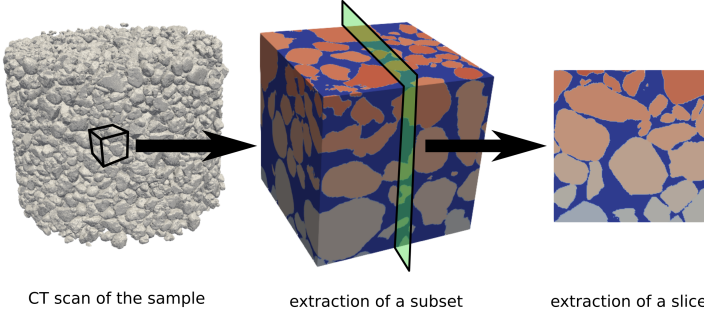


Fig. 7.11 The initial condition of the PFDEM framework is interpolated from computed tomography scans of a real granular sample (the blue area represents the pore).

Following the acquisition of the sample scans, the images must undergo processing, [Kar18, TWS24, TGXD25] for deeper details. This process involves

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the application of a filter to reduce noise, which is inherent to the CT scan nature. Subsequently, algorithms can be employed to enhance image resolution and interpolate sub-pixel information. Thereafter, through the implementation of image binarization, each pixel is assigned to a label, either a grain or void phase. Finally, a segmentation algorithm is applied to identify individual grains from the grain phase. These operations could also be employed to obtain synthetic microstructures that are not a scan of a real sample [GRV22].

Once the microstructure is identified, the DEM particles and the phase variables can be generated. As depicted in Figure 7.12, binary images are extracted from the postprocessed scans for each individual grain. Then, a signed distance function (< 0 inside the grain, > 0 outside the grain) is computed with the Python function `skfmm.distance()`. Thereafter, this signed distance field is employed to compute the phase variable, employing a cosine profile described in Equation 3.13. Similarly, it is used to define the DEM particle (level-set or polyhedral description in *YADE* [Sa21]). It is worth noting the *From Phase-Field to Discrete Element Model* step described in Section 4.3.1 follows the same algorithm. A binary image is built from the phase variable considering $\eta = 0.5$ as a threshold value, allowing the interpolation of a DEM particle.

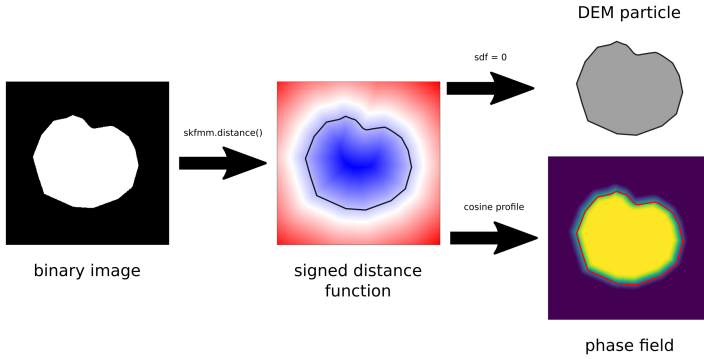


Fig. 7.12 The binary images of the sample scans are employed to define the initial phase fields and DEM particles, through a signed distance function.

7.3.2 Numerical model and results

In the following, a thin 2D layer ($2453 \times 2035 \mu m$) is extracted and employed as an input of the method. It is pivotal to specify that the sample considered is not a Representative Element Volume of the granular sample, the d_{50} being $680 \mu m$ [MHA⁺21]. It has been employed as a showcase to emphasize the

features of the Phase-Field Discrete Element Method in the case of the Rock Digital Physics framework. As mentioned previously, the database used is named *The Sand Atlas* [The22]. In particular, the scans of the *Hamburg sand* have been employed [MHA⁺21].

The numerical analog of the sample is loaded under oedometric conditions: the bottom and lateral walls are fixed, while the top wall is controlled to apply a confining loading, see Figure 7.5. Compared to Chapter 2 and Section 7.1.1, no reactive fluid is injected. The settlement observed is only induced by chemo-mechanical processes, such as pressure-solution. The parameters calibrated in Section 5.2 are employed. To model the interlocking in 3D granular media, the particle rotation is hindered [ACRO11, SMVR24b]. Several snapshots of the microstructure evolution are available in Figure 7.13 (simulation is 2D, the extrusion is used only for visualization).

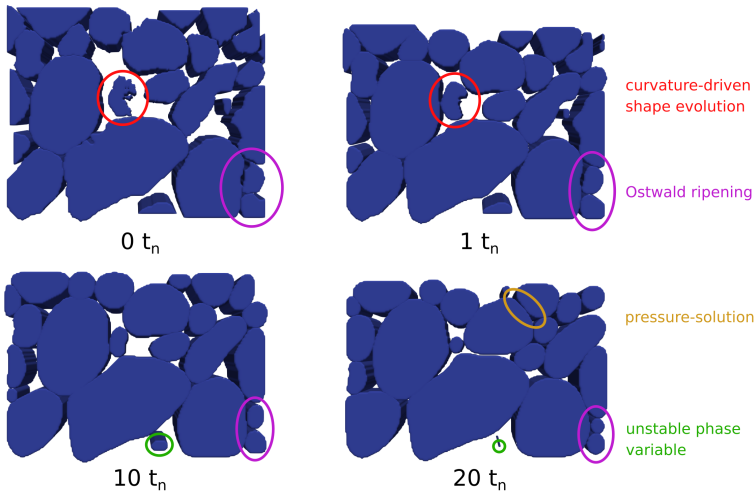


Fig. 7.13 Snapshots of the microstructure at distinct times. Numerous phenomena that induce shape evolution are identified.

As illustrated in Figure 7.13, a multitude of phenomena have been identified as inducing factors for shape evolution. These phenomena can be categorized into two distinct groups: unphysical phenomena, including curvature-driven or unstable phase dissolution, and physical phenomena, encompassing pressure-solution or Ostwald ripening.

As previously delineated and illustrated in Figure 7.9, the Phase-Field formulation instigates curvature-driven shape evolution. As depicted in Figures

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7.11 and 7.13, shapes derived from the scans can exhibit significant irregularities. This effect is particularly pronounced when utilizing a slice (rather than a volume). The origin of these shape evolution is the gradient coefficient κ_j employed in Equation 4.1. Nevertheless, this coefficient is primordial as it defines the diffuse aspect of the Phase-Field description, see Figure 3.1. A competition exists between the curvature-driven shape evolution (kinetics $\sim$ gradient coefficient κ_j employed Equation 4.1) and the physical shape evolution (kinetics $\sim$ tilting E_d defined Equation 4.2). The impact of curvature-driven phase evolution can be mitigated by reducing the coefficient κ_j (or the mesh, see Equation 3.7) or by increasing the tilting E_d . However, it should be noted that this method is not without its limitations. Specifically, reducing the gradient coefficient or increasing the tilting requires a smaller time step to ensure the stability of the simulation. A compromise must be made between the conservation of the real shape and the use of the Phase-Field description. Similarly, this curvature-driven shape evolution can be restricted by considering fewer nodes for the interface, decreasing the gradient coefficient κ_j , see Equation 3.7. However, a certain number of nodes must be considered (4 – 10 [MBW08, Tak14]) to verify the diffusive aspect of the interface, see Figure 3.1. It appears the larger angularities of the shape inducing the larger surface tension are smoothed at the initial iterations (between $0 t_n$ and $1 t_n$ in Figure 7.13). Subsequently, the shapes of the grains are preserved.

The second unphysical shape evolution phenomenon is the dissolution due to an unstable phase. As emphasized in Section 3.2.1 and Appendix C, a minimum size is required for the phase to remain stable. This minimum size is related to the interface width $\delta = 6 \Delta$, where Δ is the mesh size. If the particle size is smaller than the minimal size ($\sim 2 \times \delta$), the maximum value of the phase variable is smaller than 0.5. Because of the Phase-Field formulation, see Figure 3.2 and Equations 3.10 and 4.1, dissolution ($\eta \rightarrow 0$) occurs. This phenomenon is depicted at the frames $10 t_n$ and $20 t_n$ in Figure 7.13, where the bottom grain highlighted dissolves, while no chemo-mechanical solicitations are applied on this specific grain. The solution to this unphysical shape evolution is the use of finer meshes, impacting the computational cost.

Despite some unphysical shape evolutions due to the Phase-Field description, most of the dissolution/precipitation phenomena are physical. Figure 7.13 shows some pressure-solution patterns. As explained in Section 1.3 and Chapters 4 and 6, the surfaces at the contacts aim to become flat. Dissolution occurs at the contact, where stress concentrates, and precipitation occurs at the sides, where no stress is present.

The second physical phenomenon illustrated in Figure 7.13 is referred to as

Ostwald ripening. As depicted in Figure 7.14, the phenomenon is characterized by a mass transfer, from the smallest particles to the largest ones [Kar12]. Indeed, the surface energy of the smallest grains is higher, while the energy is lower for the largest grains. This difference serves as the driving force for dissolution/precipitation [GDR13]. The Phase-Field description appears to be a suitable formulation to investigate this specific interaction [OKS01, Pet19]. Also occurring during diagenesis, Ostwald ripening is dominant at low effective pressure and in poorly sorted granular medium [KMEN06]. Similar to pressure-solution, it affects the sample properties (mechanical and hydraulic) as the microstructure evolves. However, the driving forces of the mass transfer differ: stress for pressure-solution and size for Ostwald ripening.

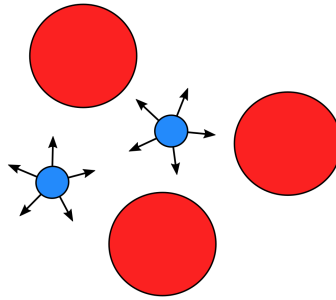


Fig. 7.14 Scheme of the Ostwald ripening. The smallest particles dissolve, while the largest ones precipitate.

The initial and final shapes of two distinct particles are extracted from the snapshots of the microstructure, and the comparison is available in Figure 7.15.

The grain a) from Figure 7.15 is situated at the bottom left within the sample, see Figure 7.13. The precipitation, emphasized in red, occurring at the top left of the particle, is attributed to the Ostwald ripening. Conversely, the dissolution, accentuated in blue, occurs at the top right due to the pressure-solution phenomenon, while the precipitation area is located at the top left and bottom right.

Similarly, the grain b) from Figure 7.15 is situated at the center left within the sample, see Figure 7.13. The precipitation, emphasized in red, occurring at the right of the particle, is attributed to the Ostwald ripening. Conversely, the dissolution, accentuated in blue, occurs in the left part due to the pressure-solution phenomenon.

From a macroscopic point of view, the evolution of the vertical strain is

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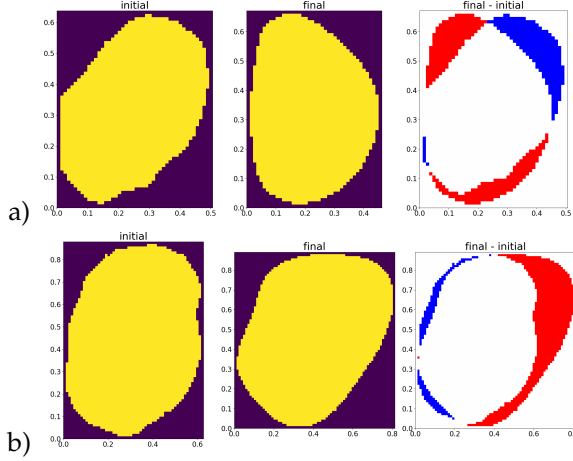


Fig. 7.15 Shapes comparison between the initial and final configurations for two distinct grains. A difference is computed to highlight the dissolution in blue and the precipitation in red.

depicted in Figure 7.16. The vertical strain is computed from the height h of the sample $\epsilon_i = (h_i - h_0)/h_0$. The height of the sample reduces while the chemo-mechanical processes occur as a constant confining pressure is applied at the top, see Figure 7.5.

The settlement process is comprised of two distinct steps, with a faster rate of settlement in the initial one. As depicted in frame $0t_n$ of Figure 7.13, the sample is initially in a loose state. The chemo-mechanical processes, such as Ostwald ripening and pressure-solution, impact the microstructure equilibrium, inducing granular reorganization and accelerating the settlement process. However, once the sample attains a dense state, see frame $20t_n$ of Figure 7.13, the impact of the granular reorganization diminishes, and the settlement rate reduces. Then, the chemo-mechanical processes continue and dictate the settlement kinetics. It is worth noting that the rate of the chemo-mechanical processes, in particular pressure-solution, is impacted by the evolving microstructure, see Chapter 6. Despite the granular organization remaining similar, the sample being in a dense state, the morphology of the grains evolves, affecting the stress transmitted, driving force of the pressure-solution phenomenon.

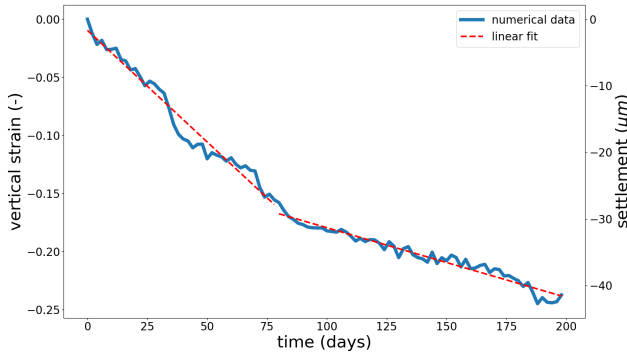


Fig. 7.16 Evolution of the vertical strain/settlement while the chemo-mechanical processes occur.

7.4 Preliminary Conclusions

The present Chapter underscores the pivotal role of the microstructure in dictating the mechanical behavior of the granular media. This microstructure can be categorized into two distinct components: the morphology of the grains and the granular organization. These individual aspects exert a discernible influence on the overall behavior of the system. For instance, angularly shaped grains exhibit a propensity for interlocking, thereby augmenting the sample's stiffness. In a similar manner, the geometric shapes of the particles influence the stress concentration at the contact points. In this regard, it has been observed that the presence of sharp edges tends to result in a larger mechanical solicitation, thereby enhancing mechanical-induced phenomena such as pressure-solution. In a similar vein, the granular organization exerts a profound influence on the stress transmission within the medium, affecting the occurrence of mechanically induced phenomena such as pressure-solution. The PFDEM framework appears to be a suitable approach for considering the shape and organization of a granular medium, while other methods available in the literature hinder the influence of such aspects. This formulation is extended with the principles of the Digital Rock Physics discipline, which is defined as computing sample properties from computed tomography scans. It is relevant to precise the cost of the application of this kind of approach on a regular computer¹: a couple of days for the 3D simulations and half a day for the 2D simulations with multiple grains.

¹Intel(R) Core(TM) i5-10210U CPU @ 1.60GHz, 8 Go RAM

7 | Numerical twin of a granular media under chemo-mechanical couplings to consider the impact of the microstructure

A numerical analog of a granular medium has been employed in oedometric conditions, and numerous phenomena have been identified as inducing factors for shape evolution. Because of the Phase-Field formulation, unphysical dissolutions/precipitations occur. These artifacts can be mitigated while maintaining a balance with the computational cost. However, Ostwald ripening and pressure-solution phenomena are identified as the predominant chemo-mechanical processes affecting the evolving microstructure. And, these impacts on the microstructure affect the behavior of the sample at the larger scale. For instance, the observed creep behavior is comprised of two distinct steps. The initial step is characterized by a granular reorganization (from a loose state to a dense one) induced by the chemo-mechanical processes, and the rate of the settlement appears large. In the subsequent step, the granular organization remains constant, reducing the settlement kinetics. However, the settlement pursues as the chemo-mechanical processes occur.

The framework depicted in this Chapter appears suitable to investigate in a controlled study domain and to predict the creep behavior of geomaterial due to the pressure-solution. A remaining restriction for the application to larger problems is the computational cost related to the method. Several compromises must be made between the accuracy, the domain size, and the solving duration.

8

Conclusions

8.1 Summary and key findings

The present study investigates the interplay between chemistry and mechanics in geomaterials. These disciplines are strongly interconnected to understand the evolution in time of mechanical behavior, but also in the context of various engineering applications that involve the injection of fluids into underground reservoirs. These injections induce changes in the chemistry at the microscale, activating or enhancing chemical reactions. These modifications have multifaceted consequences, affecting mechanical and hydraulic parameters, as well as introducing potential risks to the success of the operation.

This study employs a numerical laboratory approach, which has been demonstrated to offer numerous advantages over experimental investigations. While experiments are crucial for validation, models provide a safer, more economical, more controlled, and more expeditious tool to investigate chemo-mechanical couplings. In this thesis, three distinct chemo-mechanical problems have been examined: the stress-state evolution of a material subjected to dissolution, the hydration of a cement-based material, and the pressure-solution phenomenon.

The debonding phenomenon, characterized by the dissolution of bonds while maintaining the integrity of grains, occurs in a cemented granular medium

under weathering conditions. The underlying chemical process is straightforward: it entails a reduction in bond size. Chemistry appears to induce a destabilization of the mechanical equilibrium reached by the sample. This mechanical aspect of the problem is modeled with the Discrete Element Method.

To investigate this chemo-mechanical coupling, a cemented granular sample under oedometric conditions has been studied while the size of the bonds reduces. This chemical destabilization impacts the mechanical properties and the state of the stress of the sample. Numerous parameters have been investigated, such as the confining pressure, the initial state of the stress, the cementation, or the history of loading.

It has been observed that an attractor configuration exists concerning the state of the stress, approximated by the coefficient $k_0 = \sigma_{II}/\sigma_I$, where σ_I is the vertical pressure and σ_{II} is the lateral pressure. Irrespective of the initial configuration, the sample tends to reach this attractor state. This phenomenon is pivotal to understanding as it can cause the material to fail, reaching its yield limit, as a reduction of k_0 induces an increase of the shear stress. In the context of an underground reservoir, this failure at the material level could lead to stress redistributions at the reservoir scale, which could ultimately lead to stress change on a nearby fault, inducing an earthquake.

Two predominant phenomena have been identified as the driving forces behind of the evolution of the state of stress: the collapse of the unstable chain force and the softening of the granular material. The collapse of the unstable chain force is dominant in the case $k_0^{init} \leq k_0^{attr}$, and it is characterized by the rupture of the granular structure maintained by the dissolving cementation. Conversely, the softening of the grains prevails in the case $k_0^{init} \geq k_0^{attr}$, and it is defined by the reduction of the material stiffness concurrent with debonding. In both scenarios, these phenomena enable the particle to reorganize, thereby influencing the properties of the sample.

Nevertheless, the Discrete Element Method appears to be constrained in its capacity to adequately describe chemical processes. While it can capture homogeneous size dissolution (grains or bonds), more complex chemical phenomena are not covered. This limitation is particularly evident in the context of the second problem, namely the hydration of a cement-based material. During this intricate chemical process, source particles dissolve due to their reaction with the water, the solute generated diffuses, and a paste of cement precipitates. This paste, in turn, generates the bonds between aggregate and forms the skeleton that determines the mechanical performance of the material after the hardening period.

Despite the existence of hydration models based on Cellular Automata in the literature, it appears that this approach remains semi-empirical. Consequently, a physics-based model of the problem has been described employing the Phase-Field description. This formulation enables the investigation of the evolution of the microstructure during the hydration process for two limiting configurations. The model's outputs have been found to align closely with existing data in the literature.

Once the model for the evolution of the microstructure has been validated, the framework has been extended to consider the distinct snapshots of the results for the microstructure as an input of a Finite Element Model to compute the mechanical parameters of the sample. Indeed, the distinct phases (source, paste and pore) can be identified in the microstructure, and they are characterized by intrinsic elastic properties. The composite material is then employed to interpolate mechanical behaviors during pulling and shearing tests. The computed properties for the sample increase during the hydration process, and these evolutions match the experimental observations described in the literature.

The debonding and the hydration processes are characterized by an one-way coupling between chemistry and mechanics, lacking a noteworthy feedback mechanism. Indeed, the dissolution of the bond exerts an influence on the mechanical properties of the specimen; conversely, the mechanical aspect of the debonding problem, such as the state of stress, does not affect significantly the dissolution reaction. Analogously, the chemistry involved during the hydration problem is not significantly impacted by mechanical solicitations, as the cement-based material is required to undergo a period of hardening before carrying any load. While this is not a concern in the hydration formulation under consideration, the Phase-Field theory can be extended to consider the impact of the mechanics on the chemistry.

This approach serves as the foundation for models of more complex phenomena, such as pressure-solution, characterized by a two-way coupling between chemistry and mechanics. The phenomenon can be described as a mass transfer by dissolution/diffusion/precipitation from the more stressed regions to the less stressed regions. To model the entire phenomenon, it is necessary to capture heterogeneous dissolution/precipitation, granular reorganization, and transmission of the stress. The Discrete Element Model and the Phase-Field formulation are inadequate taken independently in meeting these requirements. However, a framework integrating these two methods appears capable of addressing the issue. This coupled method has been de-

veloped, and a calibration campaign has been detailed based on experimental data available in the literature. The formulation is then validated by reproducing constitutive relations employed in the literature for two limiting scenarios.

The novel framework's capacity to encompass both precipitation and granular reorganization, which have been overlooked in the relevant literature, has been underscored. Specifically, the precipitation has been observed to influence the slowdown of the creep behavior. In instances where the precipitation rate is slow, there is an accumulation of solute concentration within the pore domain, leading to a reduction in mass transfer by diffusion. Conversely, the mass transfer by dissolution decreases if the precipitation kinetics is fast, as the surface at the contact increases, decreasing the stress transmitted (driving force of the pressure-solution phenomenon). Additionally, the granular reorganization exerts an influence on the creep behavior. An extension to the Phase-Field Discrete Element Model is presented considering the philosophy of Rock Digital Physics, a theoretical framework that considers computed tomography scans of samples as inputs of numerical model to compute properties. This formulation underscores the role of grain reorganization and irregular grain shapes in influencing settlement behavior. In particular, the chemical destabilization instigates a reorganization of the microstructure, the creep rate tends to accelerate. Once a dense configuration is obtained, the creep kinetics is based solely on the kinetics of the chemo-mechanical processes, which reduces.

8.2 Future work and perspectives

The proposed formulation, coupling the Discrete Element Model with the Phase-Field theory, opens up avenues for further exploration into the influence of various parameters on the mechanical response of geomaterials undergoing dissolution/precipitation. Parameters such as solute diffusivity, grain morphology, microstructure organization, and chemo-mechanical destabilization can now be systematically studied to gain insights into their impact on the overall behavior. In particular, numerous perspectives may emerge from this PhD.

- *Roi et al.* have developed a solution to the reactive Lauwerier problem [RAS⁺24]. This problem is defined as injecting a non-isothermal fluid into an underground reservoir, inducing geochemical reactions. The temperature-dependent chemical reactions impact the hydraulic properties of the reservoir. However, the mechanical aspect of the problem

was not developed. Then, this work can be easily extended with the result obtained concerning the study of debonding in Chapter 2. The mechanical parameters (stiffnesses and state of stress) evolution with the chemical damage can be extrapolated from this part of the PhD. It would supplement the investigation of the problem described to understand the role of chemical reactions in induced seismicity at the reservoir scale.

- The Chapter 2 explores the impact of the debonding phenomenon on the stress state of the sample. The investigated sample is quite isotropic. However, it has been hugely emphasized in the literature that the anisotropy of the microstructure impacts the behavior of the sample [PADV23, SB24]. The framework depicted herein can be reemployed, considering more realistic grains, to capture the effect of the anisotropy in the failure mechanisms. Moreover, heterogeneous chemical reactions can also be introduced to investigate the impact of the location of the dissolving bonds. For instance, [BG19] has emphasized, for an uncemented granular sample, that the location of the dissolving particles induces the formation of a honeycomb fabric (stable structure) or the collapse of the chain forces.
- The framework developed in Chapter 3 to investigate the hydration problem of a cement-based problem is expected to be applied to determine constitutive relations between the particle size distribution of the source grains and the mechanical performance of the hydrated sample. Furthermore, this framework can be expanded to capture the influence of additives, such as fly ash.
- Chapters 4, 5, 6 and 7 developed the Phase-Field Discrete Element Model. In particular, this formulation has been applied to the pressure-solution phenomenon, and it is expected to be employed to predict the evolution of the mechanical properties of geomaterials during the phenomenon. For instance, pressure-solution is suspected in the literature to be the origin of earthquake nucleation in sheared faults. In particular, *Niemeijer et al.* have determined that competition exists between the hardening behavior due to pressure-solution (dominant at low velocities) and the weakening behavior due to dilation of a shear layer (dominant at high velocities) [NS06]. The natural oscillations in fault motion rates are presented as the origin of seismic activities. The PFDEM framework could be applied to investigate this competition.
- *Li et al.* has developed a Phase-Field model of the diffusion of a reactive

fluid into porous media [LWW⁺23]. The fluid impacts the pore structure and distinct scenarios have been identified, depending on the fluid injection rate. The granular reorganization was not considered in this work. The Phase-Field Discrete Element Model could be applied to introduce the mechanical considerations (granular reorganization, stiffnesses evolution) into the problem.

- The PFDEM framework appears suitable to investigate other problems which involve a mechanical aspect and phases evolution, such as frozen granular soils [WC21], hydrothermal alteration in volcanic rocks [Det16], grain boundary sliding mechanism in rock [GMR23, DCC⁺22] or metal [LMS⁺21] for examples.
- The emergence of X-ray micro-computed tomography techniques enables the visualization of the microstructure of geomaterials. Such experimental devices could be applied to calibrate and validate models that describe explicitly the microstructure and its evolution, such as the Phase-Field formulation. The data obtained at the microscale, and not the ones at the macroscale as the method used in the literature, could be employed to enhance the validation and calibration. For instance, *Paul et al.* have developed a framework to analyze and validate a finite element description of a mechanical problem with a digital image correlation of computed tomography [PAM⁺24]. This framework can be readily extended to chemo-mechanical problems.

9

Appendices

A The lognormal distribution

The probability of a bond to have a surface A_b follows a lognormal distribution formulated in Equation 9.1. This distribution is defined by the expected value m_{log} and the variance s_{log} .

$$p(A_b) = \frac{1}{A_b s_{log} \sqrt{2\pi}} e^{-\frac{(\ln(A_b) - m_{log})^2}{2s_{log}^2}} \quad (9.1)$$

It appears this distribution reproduces accurately experimental observations [SAN⁺22]. Indeed, smaller bond surfaces and larger ones can be considered, both are crucial to the mechanical behavior of the sample. Examples of lognormal distribution used in Chapter 2 are given in Figure 9.1.

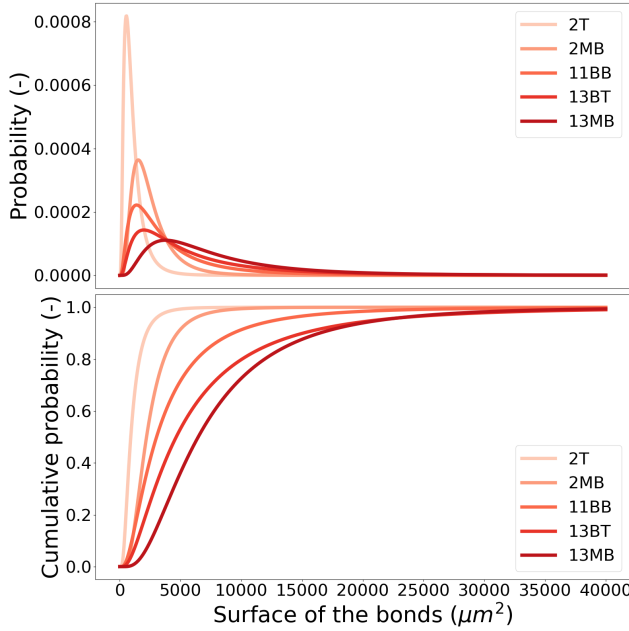


Fig. 9.1 Examples of lognormal distributions used in Chapter 2 with the different cementations considered (see Table 2.2).

B Bond breakage during the initialization

Table 9.1 shows the percentage of broken bonds (in comparison to the initial number of them) between the steps f (creation of the bonds) and h (loading at P_{conf} and at k_0^{init}) of Figure 2.3. It is inevitable that some bonds will be broken as a consequence of the initialization algorithm, see Figure 2.3. Indeed, the objective is to generate a cemented granular material at a specified pressure $P_{cementation}$. Subsequently, the pressure increases to the confining value $P_{confinement}$. This increase is the source of some bond breakage (even prior to the test commencement). However, the discrepancy between the two pressures is crucial. For the sake of argument, let us assume that $P_{cementation} = P_{confinement}$. The sample is generated, and the bonds are created. The sample is stable before the bond generation process, and thus, there are no unstable chain forces, see Section 2.3.3 for the definition. The softening of the grains exerts a dominant influence on the evolution of the sample. Moreover, the objective is to reproduce the experiments. In an oedometric test with acid injection (bond dissolution), the sample is initially cemented, set in the oedometer, loaded at confining pressure, and subsequently evolves with the injection of the acid (bond dissolution) [CN04]. In the experimental context, the step of applying the confining pressure also results in bond breakage.

It appears Table 9.1 there are more broken bonds for $k_0^{init} = 0.2 \leq k_0^{attr}$ than for $k_0^{init} = 0.7$ or $1.5 \geq k_0^{attr}$. k_0^{attr} is the attractor value reached during the evolution of k_0 during the debonding phenomenon, as emphasized in Subsection 2.3.1. During the initialization, the sample aims to reach the value $k_0 = k_0^{attr}$ at the step f) depicted in Figure 2.3. In the case, $k_0^{init} = 0.2 (< k_0^{attr})$, the lateral dimension of the sample needs to extend. It is crucial to remember that confining pressure is still applied at the top wall. The combination of the two loadings induces mechanical bond breakage, see Equation 2.23.

Test characteristics	N initial	N final	Broken (%)
$P_{conf} = 1 \text{ MPa}, k_0^{init} = 0.2, 2T$	892	588	34
$P_{conf} = 1 \text{ MPa}, k_0^{init} = 0.2, 2MB$	6192	5855	5
$P_{conf} = 1 \text{ MPa}, k_0^{init} = 0.2, 11BB$	6681	6379	5
$P_{conf} = 1 \text{ MPa}, k_0^{init} = 0.2, 13BT$	6614	6357	4
$P_{conf} = 1 \text{ MPa}, k_0^{init} = 0.7, 2T$	899	712	21
$P_{conf} = 1 \text{ MPa}, k_0^{init} = 0.7, 2MB$	6185	5928	4
$P_{conf} = 1 \text{ MPa}, k_0^{init} = 0.7, 11BB$	6802	6472	5
$P_{conf} = 1 \text{ MPa}, k_0^{init} = 0.7, 13BT$	6744	6476	4
$P_{conf} = 1 \text{ MPa}, k_0^{init} = 1.5, 2T$	944	784	17
$P_{conf} = 1 \text{ MPa}, k_0^{init} = 1.5, 2MB$	6104	5754	6
$P_{conf} = 1 \text{ MPa}, k_0^{init} = 1.5, 11BB$	6709	6258	7
$P_{conf} = 1 \text{ MPa}, k_0^{init} = 1.5, 13MB$	6664	6590	1
$P_{conf} = 1 \text{ MPa}, k_0^{init} = 1.5, 13BT$	6817	6635	3
$P_{conf} = 10 \text{ MPa}, k_0^{init} = 0.2, 11BB$	6973	3297	53
$P_{conf} = 10 \text{ MPa}, k_0^{init} = 0.2, 13MB$	6867	3855	44
$P_{conf} = 10 \text{ MPa}, k_0^{init} = 0.2, 13BT$	6988	4041	42
$P_{conf} = 10 \text{ MPa}, k_0^{init} = 0.7, 2T$	945	423	55
$P_{conf} = 10 \text{ MPa}, k_0^{init} = 0.7, 2MB$	6487	3659	44
$P_{conf} = 10 \text{ MPa}, k_0^{init} = 0.7, 11BB$	6847	3977	42
$P_{conf} = 10 \text{ MPa}, k_0^{init} = 0.7, 13MB$	6986	5218	25
$P_{conf} = 10 \text{ MPa}, k_0^{init} = 0.7, 13BT$	7079	4889	31
$P_{conf} = 10 \text{ MPa}, k_0^{init} = 1.5, 2T$	913	392	57
$P_{conf} = 10 \text{ MPa}, k_0^{init} = 1.5, 2MB$	6438	3205	50
$P_{conf} = 10 \text{ MPa}, k_0^{init} = 1.5, 11BB$	6886	3924	43
$P_{conf} = 10 \text{ MPa}, k_0^{init} = 1.5, 13MB$	6888	4565	34
$P_{conf} = 10 \text{ MPa}, k_0^{init} = 1.5, 13BT$	7084	4347	39

Table 9.1 Percentage of bonds broken during the initialization (steps f to h of Figure 2.3). Only the tests with a percentage $\geq 1\%$ are listed.

C Particle Size Distribution of the source

Chapter 3 presents the description of the formulation of a numerical laboratory to investigate the hydration of a concrete material. To ensure the model is representative of the experiments, it is important to reproduce most of the parameters available. Concerning the hydration problem, the particle size distribution of the source grains represents a parameter with a large impact on the hydration kinetics and the microstructure evolution obtained.

In the context of a numerical analog, the investigation pursued in Chapter 3 employed a particle size distribution from a database available [NLC⁺21, NIS05], see Table 9.2. This Table presents the mass and number ratios of different radius bins (from $0.5 \mu m$ to $36.5 \mu m$). Between the limits of the bins, a uniform distribution is assumed for the radius. However, the Phase-Field formulation described in Chapter 3 induces a minimal size for grains to remain stable. Indeed, if the particle size is smaller than the minimal size ($\sim 2 \times \delta$, where δ is the interface width), the maximum value of the phase variable is smaller than 0.5. Because of the Phase-Field formulation, see Figure 3.2 and Equation 3.10, dissolution ($\eta \rightarrow 0$) occurs.

As emphasized in Table 3.2, the mesh size Δ is $0.2 \mu m$. Then, the minimal radius appears equal to $2 \times \delta = 2 \times 6\Delta = 2.4 \mu m$. The particle size distribution is modified to consider this minimal size restriction. Several modified distributions are specified in Table 9.2. The results presented in Chapter 3 have been obtained with the modified particle size distribution starting at $2.5 \mu m$.

Radius (μm)	Mass (%) initial	Number (%) initial	Number (%) from 2.5 μm
0.5	13.5	95.8	not considered
1.5	13.0	3.4	
2.5	9.5	0.5	
3.5	7.3	0.2	
4.5	6.1	0.1	66.3
5.5	5.1	not enough (< 0.1)	18.6
6.5	4.2		7.3
7.5	3.8		3.3
8.5	3.4		1.7
9.5	2.8		1.0
10.5	2.6		0.6
11.5	2.3		0.4
12.5	2.1		0.2
13.5	1.9		0.2
14.5	1.9		0.1
15.5	2.3		0.1
17.5	3.5		0.1
20.5	2.7		0.1
23.5	4.5		not enough (< 0.1)
30.5	3.6		
36.5	4.0		

Table 9.2 Particle size distribution for the cement CCL 133.

D Mesh dependency

As with all the finite element resolutions, the mesh should be small enough. A special focus is required in the Phase-Field description presented in Chapters 3 and 4 on the kinetics of the interface dissolution/precipitation. Indeed, it appears the dissolution/precipitation kinetics is related to [Cha77, JL97] :

- the tilting amplitude e_d , see Figures 3.3 and 3.4 and Equations 3.11 and 3.12.
- the gradient coefficient κ used in the Allen-Cahn formulation, Equations 3.1 and 3.2. This coefficient is related to the mesh size, see Equation 3.7.

Two methods seem possible to conserve the rate constant with various meshes: adapt the number of nodes defining the interface width to have a constant gradient coefficient κ or adapt the tilting amplitude e_d . As the philosophy of the Phase-Field description is to keep a small number of nodes in the interface [Tak14], to approximate a sharp interface, the latter proposition is favored.

Considering the relation $e_d^j = e_d^i \times (m^i / m^j)$, the kinetics is conserved with different meshes, with e_d^k and m^k are the tilting term and the mesh size for the configuration k , The gradient coefficient κ is computed with a constant number of mesh nodes.

E Method to build the field of the solute diffusion coefficient

In the case of pressure-solution, the problem requires a heterogeneous solute diffusion coefficient field. The goal is to have diffusion at the contact area (to evacuate the solute generated) and in the pore area (as some fluid is assumed). However, it should not have diffusion in the grain material. The map of this coefficient follows the different steps :

1. for each node of the mesh, a Boolean value is attributed, depending on the different phase variable (if $\eta_i > \eta_{\text{criterion}}$ and $\eta_j > \eta_{\text{criterion}}$ returns True; if $\eta_i < \eta_{\text{criterion}}$ and $\eta_j < \eta_{\text{criterion}}$ returns True; else return False). A Boolean map is generated.
2. a Python dilation method *scipy.ndimage.binary_dilation* is applied to the Boolean map to generate a dilated map.
3. The diffusion coefficient map is generated. For each node, if the value of the dilated map is True, κ_c is attributed to the diffusion map; else, 0 is attributed to the diffusion map.

It is important to notice this method can be extended to distinguish the contact area and the pore space. Indeed, it appears the diffusivity is several order of magnitude smaller in the contact area because of the structure of the fluid film [vNVS08].

As Figure 9.2 highlights, the dilation step is required to ensure the contact zone is connected to the pore space. Depending on the configuration, the selection of the morphological operator is the main choice. The larger the size of the operator is, the more diffusion inside the grains occurs.

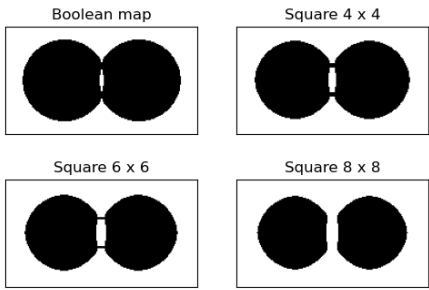


Fig. 9.2 Diffusion coefficient maps for different morphological operators.

F Method to move solute out of a grain

As illustrated in Figure 9.3, a conflict occurs between the solute concentration and the grains when the latter ones move. Indeed, the solute generated does not follow the grain motion and it produces nonphysical results. It can be noticed the troubles are located more at the top of the sample. Hence, the simulation is made as the upper wall moves to verify the confinement pressure, see configuration depicted in [SMVR24a]. Grains at the top move more than grains at the bottom. A new algorithm must be designed to push the solute with the grains.

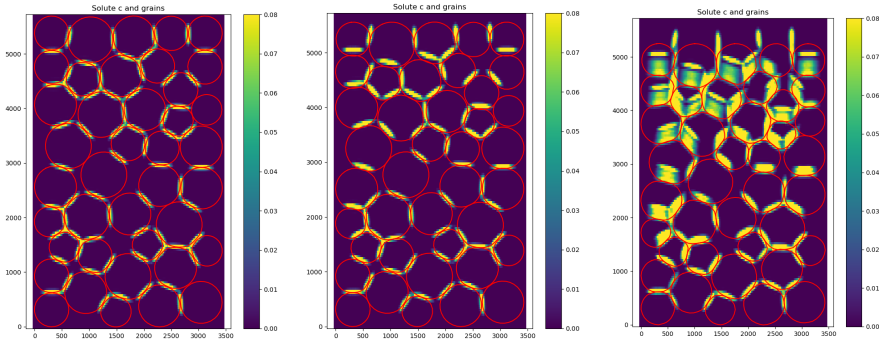


Fig. 9.3 Solute is generated initially (left). Then, the grains move after the DEM step to find a new equilibrium whereas the solute remains at the same place (center). Finally, it appears after multiple iterations that the solute requires to follow the grains (right).

The fundamental assumption is a small displacement of the grains. As illustrated by Figure 9.4, all nodes are considered available (in the pore space or in the contact area) or not (in only one grain) to host solute. Then, for nodes not available the solute is distributed to the nearest node available as illustrated in Figure 9.4. If there are multiple nodes available at the same distance, the concentration to move is divided into equivalent parts.

The algorithm can be resumed by the following steps :

1. a Boolean map is generated depending if the node can host or not solute.
2. a Python dilation method `scipy.ndimage.binary_dilation` is applied to the Boolean map to generate a dilated map.
3. For all nodes of the dilated map not available to host the solute, the nearest nodes are searched:

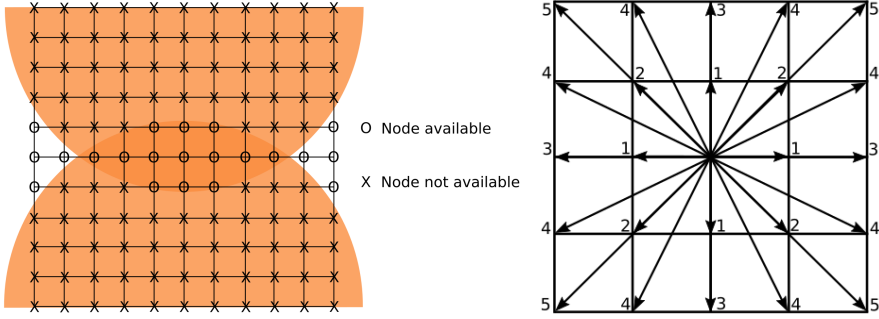


Fig. 9.4 A node is considered available to host solute if it is a pore space or a contact area (left) and an illustration of the priorities to move the solute to the nearest node (right).

- (a) It is verified if at least one node of the priority i can host solute.
- (b) If no node is available: the previous step is repeated with priority $i + 1$.
- (c) If at least one node is available: the solute is moved with the relation at every available node $c_{available} = c_{available} + c_{not\ available} / n_{available}$, where $c_{available}$ is the solute concentration at the available node, $c_{not\ available}$ is the solute concentration at the not available node and $n_{available}$ the number of available nodes at the priority i . The solute concentration at the unavailable node is set to the equilibrium value.

G Impact of the saturation on the indenter test

The update frequency is one of the most important parameters for the answer quality concerning the work presented in Chapter 5. Indeed, the solute in the well needs to be evacuated frequently (if not, the solute concentration aims to reach the saturation value and the diffusion kinetics slows down) and the diffusion map needs to be updated to follow the front evolution.

The effect of the saturation of the well sat_{well} is explored in Figure 9.5. A slowdown of the kinetics is well observed. Hence, it is important in Chapter 5 to compare simulations with the same saturation well. It can be controlled by changing the map update frequency or adapting the well's size.

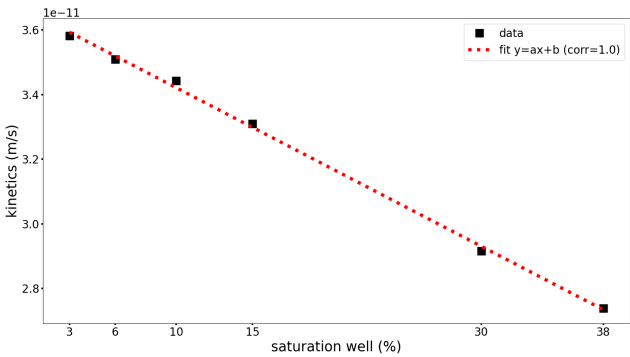


Fig. 9.5 Influence of the saturation well on the kinetics of the indenter test. An effort is required to compare simulations at the same sat_{well} .

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