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Abstract

The froth flotation method, which is used for the processing of most non-ferrous ores, involves the adsorption of both organic and inorganic reagents at the mineral/water interface. Understanding the adsorption mechanisms of flotation reagents is a key step to enhance the flotation. New depressants and collectors formulations, more efficient, selective, and environmental friendly can be suggested. At the moment, few experimental methods can show surface molecular mechanisms with accuracy and confidence. Therefore, atomistic simulations allow to gain understanding in the mechanisms involved in the reagents adsorption. Nowadays, atomistic simulations can be applied to describe the solid/liquid interface and the adsorption mechanisms. Depending on the method, the interactions between atoms are described on the basis of density functional theory (DFT) or force-fields. They give access to various levels of accuracy, parameters consideration, sampling times, system sizes, and reactivity description, depending on the method used. In particular, *ab initio* molecular dynamics allows to investigate adsorption processes at liquid-solid interfaces at finite temperature with accuracy.

Keywords

Adsorption; water; mineral; Density Functional Theory; ab initio; molecular dynamics; collectors; depressants.

1. Introduction

A. The froth flotation process

The world demand in mineral commodities, including metals and industrial minerals, has been exponentially increasing over the past decades. Although physical separations are widely used to concentrate the target metal-bearing mineral(s), most of non-ferrous ores are, today, processed by the froth flotation method (Leja, 1981; Bulatovic, 2007; Fuerstenau et al., 2007; Nguyen, 2013). This method is based on the differences of surface properties between the target mineral(s), *i.e.* the metal-bearing mineral(s), and the gangue minerals, which have to be rejected. Performed on size fractions ranging from 10 µm to 300 µm (Leja, 1981; Fuerstenau et al., 2007; Ralston et al., 2007; Fornasiero and Filippov, 2017), the froth flotation uses the specific adsorption of amphiphilic molecules called collectors onto the target mineral(s) surfaces to make them hydrophobic. The injection of air bubbles in the flotation cell under strong stirring conditions allows to recover the hydrophobic mineral(s) in the froth, at the upper part of the cell. The flotation collectors are commonly composed of a polar function, which adsorbs onto the solid, and a non-polar aliphatic chain that make the particle hydrophobic. The polar function can be either a cationic group such as amine function, which is assumed to physisorb onto the mineral surfaces (Fuerstenau and Healy, 1972; Leja, 1981; Bulatovic, 2007), or an anionic group, which establishes covalent bond(s) with surface cations (Fuerstenau and Healy, 1972; Fuerstenau and Palmer, 1976; Leja, 1981; Bulatovic, 2007; Fuerstenau et al., 2007; Foucaud et al., 2018b). Depending on the target mineral(s), the anionic polar function can be carboxylic acids/alkali carboxylates, sulphate, sulfonate, xanthate, dithiophosphate... The collector adsorption depends strongly on the pH of the solution since the physisorption of cationic collectors is related to the zeta-potential while the surface hydroxylation can prevent the chemisorption of anionic collectors. Moreover, the collector adsorption can be modulated by adding a large range of molecules (organic or minerals) called depressants that keep the surface hydrophilic by preventing the collector adsorption and establishing hydrogen bonds with bulk water molecules. Finally, the flotation performances have been significantly increased over the past few years by mixing collectors with different aliphatic chains and/or with different polar groups as well as different depressants (Filippov et al., 2012; Filippova et al., 2014; Filippov et al., 2016, 2018; Y. Foucaud et al., 2019).

B. Importance of molecular modelling for flotation

Liberations sizes in most ores are nowadays low enough to make unable the use of classical physical separation methods, making the froth flotation mandatory to concentrate the target mineral(s). Also, the average ore grades are decreasing over time (Mudd, 2007; Calvo et al., 2016), which can be mostly attributed to the depletion of the high grade deposits, although some authors interpret this decline as innovation and improvements in extractive technologies (Drielsma et al., 2016). Along with the ore grades decline, ores displaying high separation contrast between the constitutive minerals will also decline. Since the froth flotation is mandatory for most ores, the gangue complexness as well as the low grades will be overcome by increasing the flotation performances, *i.e.* the selectivity between minerals and the flotation recovery. Hence, understanding the molecular mechanisms involved in the adsorption of flotation reagents (depressants, activators, and collectors) is of paramount interest. The determination of adsorption energies and structural configurations allows to adapt the reagents used during the flotation process to the ore mineralogical association. Moreover, it brings clarity in the comprehension of the synergistic effects that are commonly exhibited when reagents are used in combination. New reagents formulations can be developed based on the adsorption energies calculated from molecular simulations, which allow to improve the flotation selectivity or recovery. Because of the presence of a liquid phase, the molecular mechanisms are difficult to investigate with experimental methods, mainly when similar reagents are used in mixtures, which makes the molecular modelling a powerful tool.

Over the past few years, molecular modelling has gathered interest to understand the key mechanisms that are the basis of the froth flotation process. This increase can be assessed by expressing the number of original research articles that have included the words “flotation” and “molecular simulations” over the fifteen last years (Fig. 1a).

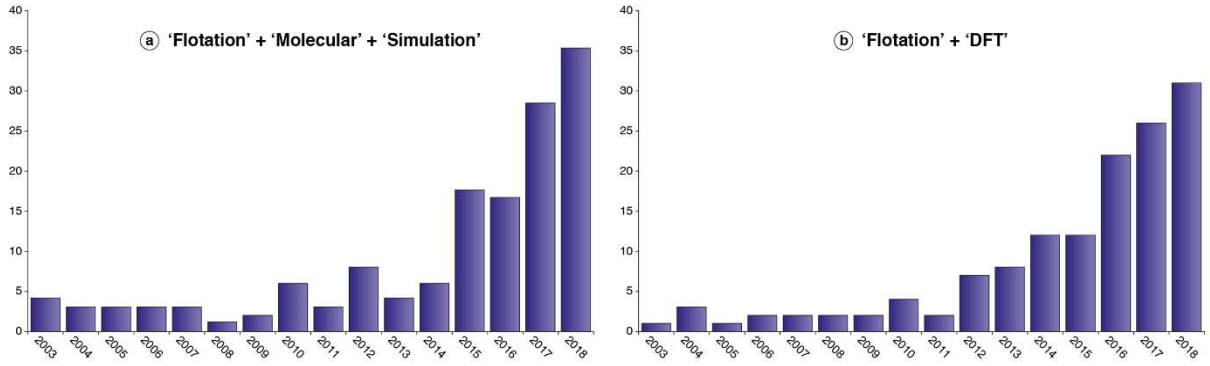

Fig. 1. Number of research articles per year over the past fifteen years including the words "flotation", "molecular", and "simulation" (a) and including the words "flotation" and "DFT" (b) from Web of Science.

The energy of systems describing the adsorption processes can be calculated using highly accurate methods based on quantum mechanical descriptions such as Hartree-Fock, post-Hartree-Fock, and density functional theory (DFT) (Sholl and Steckel, 2009; Evans et al., 2017). Besides, energies and structures can be determined using classical potentials-based simulations that require accurate force fields and are not able to fully describe quantum mechanisms such as chemical bond cleavage or formation (Evans et al., 2017). Most of the above-mentioned articles used DFT (Fig. 1b), which exhibits the best compromise between accuracy and computational demand among the current molecular modelling methods (Sholl and Steckel, 2009). In the present review, we report the different molecular simulation methods existing nowadays in theoretical physics and chemistry and that have been successfully used in the flotation field. Each method is described with its advantages and limitations and some model systems are given as examples. Finally, a global method for modelling the interactions between flotation reagents and mineral surfaces is suggested.

2. Quantum mechanical simulations

In quantum simulations, it is assumed that all the bonds and interactions between atoms are related to the electrons, which can be described using the Schrödinger equation, considered as time-independent to simplify the problem:

$$\hat{H}_T\psi(R_1, \dots R_n, r_1, \dots, r_n, \sigma_1, \dots, \sigma_n) = E\psi(R_1, \dots R_n, r_1, \dots, r_n, \sigma_1, \dots, \sigma_n) \quad (1)$$

Where $\hat{H}$ represents the total Hamiltonian operator of the system, ψ the wave function that is a function of the spatial coordinates of nuclei (R) and electrons (r) and the spin of electrons (σ) that will be ignored for the rest of the discussion, and E the total energy of the system. In equation (1), the Hamiltonian operator can be expressed as the sum of total kinetic energy operator and the Colombian interactions. The kinetic energy operator takes into account the electrons kinetic energy operator, $\hat{T}_e$, and the nuclear kinetic energy operator, $\hat{T}_n$, while the Colombian interactions include the electron-electron repulsion ($\hat{V}_{e-e}$), the electron-nucleus attraction ($\hat{V}_{n-e}$), and the nucleus-nucleus repulsion ($\hat{V}_{n-n}$) operators:

$$\hat{H}_T = \hat{T}_e + \hat{T}_n + \hat{V}_{n-e} + \hat{V}_{e-e} + \hat{V}_{n-n} \quad (2)$$

Hence, the time-independent Schrödinger equation depends on 4N+3M variables, where N is the number of electrons and M the number of nuclei, which makes nearly impossible a numerical resolution. To reduce the number of variables involved in the Schrödinger equation, the Born-Oppenheimer approximation is commonly used, in which the nuclei are considered immobile since their mass is significantly higher than the electrons (around 1800 times). Therefore, the nuclear kinetic energy operator can be neglected while the nucleus-nucleus Colombian interaction is constant. It induces that the total energy of the system corresponds to the sum of the total electronic energy of the system and a constant term representing the nucleus-nucleus interaction term.

In the Born-Oppenheimer approximation, the electron-electron repulsion term, $\hat{V}_{e-e}$ still does not have a simple analytical solution for systems with more than 2 electrons. The Hartree-Fock method (Slater, 1930; Hartree and Hartree, 1935) was developed to solve this problem, in which the wave function is expressed as a Slater determinant and the Schrödinger equation is solved self-consistently to minimize the total energy of the system (Nesbet, 2002; Epstein, 2014). Although the exchange is correctly described by this method, the correlation is not taken into account, which induces an energy overestimation. Hence, post-Hartree-Fock methods (Cramer, 2004; Jensen, 2007) were developed to take into account correlation terms, resulting in accurate energy determinations but high computational costs that make this method viable only for small systems.

Besides, Hohenberg and Kohn demonstrated that the total energy E_0 of a system in its fundamental state can be expressed as a functional that depends only on the electronic density (Hohenberg and Kohn, 1964). In this formalism, the total energy of the system (E) is the sum of the kinetic energies of the electrons T[ρ], the repulsive Colombian electron-electron interactions J[ρ], the electron-nucleus interaction potential $V_{ne}(\vec{r})$, and a term corresponding to the electron-electron exchange-correlation effects E_{ncl}[ρ]:

$$E[\rho] = T[\rho] + J[\rho] + E_{ncl}[\rho] + \int V_{ne}(\vec{r})\rho(\vec{r})d\vec{r} \quad (3)$$

To propose a practical mean to solve this equation, Kohn and Sham suggested a method (Kohn and Sham, 1965) based on an imaginary system in which the electrons do not interact between themselves and move in a potential V_s that is chosen so that the calculated electronic density of the imaginary system is equal to the real electronic density.

The unknown terms are gathered in a quantity called the exchange-correlation energy, E_{xc}[ρ], which cannot be determined analytically in the Kohn-Sham equations. A number of exchange-correlation functionals have been developed to calculate the exchange-correlation energy, for instance in the local density approximation (LDA) or in the generalized gradient approximation (GGA). LDA approximates the system by a uniform homogenous electrons gas (Perdew and Zunger, 1981; Hafner, 2008) while GGA takes into account the gradient density and, thus, is more accurate for systems exhibiting significant density variations (Perdew and Wang, 1992; Johnson et al., 1993; Perdew et al., 1996). Besides, GGA is known to not describe precisely dispersion interactions, which represent a part of van der Waals forces (Evans et al., 2017). Consequently, methods have been intensively developed to correct the dispersion interactions by adding a term in the exchange-correlation functional with various degrees of accuracy [see for instance (Grimme, 2006; Grimme et al., 2010; Bučko et al., 2010, 2013a, 2013b, 2014, 2016)]. Dispersion interactions should be included in the DFT calculations since the adsorption of flotation reagents, mostly collectors, is partly led by hydrophobic interactions between the aliphatic chains (Cases and Villieras, 1992).

Overall, DFT simplifies a 3N-dimensional problem (where N is the number of electrons) to a 3-dimensional problem with a high accuracy and a relatively low computational cost. Hence, it enables the electronic structure calculations of crystals and molecules in liquid or gas phases for relatively large systems. More than 15 000 papers including DFT are published each year in various fields including condensed matter physics (Csonka et al., 2009; Lebègue and Eriksson, 2009; Bučko et al., 2010; Srour et al., 2018), interface phenomena (Bučko et al., 2017; Chebbi et al., 2017; Chibani et al., 2018; Jabraoui et al., 2019), catalysis (Badawi et al., 2009; M. Badawi et al., 2011a; Michael Badawi et al., 2011; Badawi et al., 2013)… This method displays now a very good reproducibility that has been assessed recently on 71 elemental crystals (Lejaeghere et al., 2016) as well as very good agreement with high-precision experiments (Evans et al., 2017; Losch et al., 2018). The global development of high-performance computing (HPC) allows to perform DFT calculations on systems with up to 1500-2000 atoms in around 50 $Å^3$ cells (Evans et al., 2017).

3. Molecular dynamics simulations techniques

DFT calculations are used to determine the structure and energy of a system in its ground-state and, hence, do not describe atoms movements and the thermal motion. For that, molecular dynamics (MD) simulations can be used: they produce dynamical trajectories for a system composed of N particles by integrating Newton's equations of motion:

$$m_i \frac{d^2 r_i}{dt^2} = f_i = -\frac{\partial}{\partial r_i} U(r_1, r_2, \dots, r_n) \quad (4)$$

Where f_i represents the external forces acting on the particle i of mass m_i and position r_i, which corresponds to the negative of the gradient of the potential energy of the system. The external forces are calculated at each time step, which should be small enough to describe correctly the fastest intramolecular vibrational motions, so usually around 1 fs. The forces can be calculated either by means of DFT, which is called the *ab initio* molecular dynamics (AIMD) simulations, or by means of force fields (FF), which is called classical molecular dynamics (CMD) simulations. Both of these simulations are performed at constant number of particles (N), volume of the simulation cell (V), and temperature (NVT), pressure (NVP), or energy (NVE). For that, various thermostats or barostats,

respectively, are available (Hünenberger, 2005; González, 2011) and enable the comparison between the simulation results and experiments. Notably, the Nosé-Hoover thermostat is among the most widely used thermostats since it considers the heat bath as a part of the system, with an additional artificial variable and an associated mass (Shūichi Nosé, 1984; Shuichi Nosé, 1984; Hoover, 1985). Both CMD and AIMD will be discussed with upsides and downsides given for each method along with successful examples of use.

A. Classical molecular dynamics (CMD) simulations

CMD are based on force fields, which enable the calculation of the external forces acting on each particle for the integration of Newton's equations of motion. Force fields represent an expression of the energy of a system as a function of the coordinates of its particles (González, 2011). They include several terms that can be divided into three main groups: intramolecular, intermolecular, and special terms. The first ones mainly describe the bonds, angles, torsions, etc., the second ones refer to Coulombic and van der Waals interactions between atoms, while the special terms may include cross-terms or reactivity terms. Many different force fields have been developed over the past decades, among which some were designed to simulate the liquid/solid interfaces such as OPLS (Jorgensen et al., 1996) or COMPASS (Sun, 1998). Most force fields were developed based on *ab initio* calculations, which were used to determine the parameters acting on each term. The force field choice should be adapted to the modelled system since each force field exhibits particular strengths and weaknesses, depending on the parametrization. However, most force fields do not include any term for the reactivity, *i.e.* bond creation or destruction, which cannot be described accurately by simple force models since they result from electronic processes (Evans et al., 2017). However, CMD simulations supply a relatively accurate description of the physisorption phenomena, which represent a significant part of the molecular mechanisms involved in the flotation process. Moreover, reactive force fields such as the ReaxFF (van Duin et al., 2001) have been developed over the past decades to include chemical reactivity. They are based on high accurate *ab initio* calculations and allow continuous bond formation/breakage on, nonetheless, a restricted number of atom types at the moment (van Duin et al., 2001). Overall, CMD can be performed on systems containing millions of atoms (Freddolino et al.,

2006; Kadau et al., 2006; Klepeis et al., 2009; Schulz et al., 2009; González, 2011; Evans et al., 2015, 2017) with total simulations times reaching the order of microseconds, which enables the investigation of macroscopic properties such as the diffusion of molecules in liquid phase.

B. Ab initio molecular dynamics (AIMD) simulations

In Eq. 4, the external forces acting the particles can be determined by a DFT calculation since the total energy of the system can be easily related to the total forces. This allows to perform a MD simulation at finite-temperature with a DFT calculation for each time step. However, the quantum chemical calculation realized at every time step limits significantly the system size (Kühne, 2014). Nowadays, AIMD simulations are one of the most powerful methods for energy and structure determination as they associate the high accuracy of DFT and the temperature/pressure control of molecular dynamics simulations. Since the electrons are included, the chemical bonds can break and form, which enables the study of chemical-based molecular processes and reactivity. Today, with the development of HPC, AIMD simulations can reach total simulations times of 100 ps and up to 500 atoms with acceptable accuracy and computational costs. This allows to work with explicit solvents if the considered cells and the adsorbed molecule(s) are small enough. As all the molecular modelling methods, AIMD simulations determine the total energy of the system and, hence, one can calculate adsorption energies at finite temperature. This is usually performed by averaging the internal energy of each system (surface alone, molecule alone, and surface with the adsorbed molecule) on total simulation times of 100 ps with however eliminating the first 10 ps of simulations, which are considered as a thermalization period.

4. General methods for liquid/solid adsorption modelling

A. Surfaces exposed

Prior to the froth flotation process, a size reduction stage is performed to enable the transport of mineral particles by air bubbles. This crushing and milling stages cleave bonds existing between cations and anions in the mineral and generate new mineral surfaces. Minerals are cleaved following their usual cleavage planes, well described in the literature, which correspond to the surfaces with the lowest surface energy, *i.e.* the lowest surface density of broken bonds (Whittaker, 1982; Gao et al.,

2014) . Hence, a complete study has to be performed to investigate the most exposed surfaces for each mineral since all the adsorption processes will involve those surfaces (Gao et al., 2012; Hu et al., 2012; Gao et al., 2017, 2019). This investigation requires the calculation of surface energy for each different surface with accuracy and is usually performed by DFT or by HF methods.

In practice, different surfaces have to be generated from a bulk previously relaxed by first principles methods (DFT or HF), including the common cleavage planes that are usually well described in the crystallography area. Then, the different generated surfaces should be relaxed and the surface energy (in $J.m^{-2}$) is calculated using:

$$E_{surf} = \frac{E_{slab} + \frac{N_{slab}}{N_{bulk}} * E_{bulk}}{2A} \quad (5)$$

Where E_{slab} and E_{bulk} are the energies of the surface slab and the bulk cell, respectively, N_{slab} and N_{bulk} are the number of atoms contained in the slab and bulk unit cells, respectively, and A the slab area.

After the milling/crushing stages, the surface exposure follows a probability law that can be related to the surface energy differences between all the surfaces. However, at the moment, molecular modelling of the adsorption of flotation reagents cannot be performed on too many different surfaces since it would represent high computational costs. Hence, an assessment has to be done on the main exposed surface(s), which is/are selected for the following adsorption studies. The surface behaviour determination should constitute the first work to perform: for example, *ab initio* studies confirmed successfully that the (104) surface is the most exposed for calcite ($CaCO_3$), a calcium carbonate (Gao et al., 2012, 2017), the (001) and (112) for scheelite ($CaWO_4$), a calcium tungstate (Cooper and de Leeuw, 2003; Gao et al., 2013), and the (001) and (210) for barite ($BaSO_4$), a barium sulfate (Bittarello et al., 2018).

B. Hydration

The froth flotation process and, most of the time, the prior milling stage are performed in aqueous conditions. It induces that the surfaces generated during the milling stage are exposed to water molecules before being in contact with flotation reagents. Hence, these later, when added to the pulp, interact with hydrated surfaces, *i.e.* surfaces on which water molecules are already adsorbed.

Therefore, the molecular modelling of the adsorption of flotation reagents has to be preceded by a deep study of the surface hydration mechanisms. Overall, several molecular mechanisms are at play at the mineral/water interface:

1. Adsorption of molecular water
2. Adsorption of dissociated water, leading to a hydroxylation of surface cations
3. Substitution of a surface anion by a hydroxyl group (HO^-)
4. Influence of the surface on several water layers at the interface

To consider mechanisms 1 and 2, the adsorption energy of a lone water molecule should be calculated and compared with the adsorption energy of a dissociated water molecule, where the H atom is set on a surface anion while the HO group is placed on a surface cation. The point 3 should be investigated by considering the following reaction, with A being the surface anion:

$$\text{Surface-A} + H_2O = \text{Surface-OH} + HA \quad (6)$$

The 4 systems should be relaxed with their energy calculated, summed for each member of the equation (left and right), and compared with each other to assess the preference of the anion substitution. Finally, the point 4 should be investigated by increasing the surface coverage: from a lone water molecule, one should add sequentially water molecules to reach a 100% coverage prior to add a second and a third water molecules layer. The final step is to conduct a simulation with the cell full of water molecules with a calculated density of 1 $kg.dm^{-3}$. The 4 above-mentioned possible hydration mechanisms can be investigated either at 0 K or at a finite temperature using DFT (static or AIMD, respectively). Besides, the points 1 and 4 can be addressed by CMD simulations since they involve no reactivity (bond creation/breakage).

The hydration mechanisms of widely known mineral surfaces have been intensively investigated over the past fifteen years by atomistic simulations. Various sulphides were studied by DFT simulations (M. Badawi et al., 2011b; J. Chen et al., 2014; Haider et al., 2014; Long et al., 2016b; Li et al., 2019) to bring clarity in the hydration mechanisms, mostly accompanied by oxidation phenomena. In addition, oxide minerals were deeply investigated since they represent an important source for non-

base metals and mineral commodities. The hydration mechanisms of calcium/magnesium carbonates were described by CMD simulations (Perry et al., 2007; Wolthers et al., 2012; Fenter et al., 2013), by the HF method (Villegas-Jiménez et al., 2009), and, mainly, by DFT calculations (de Leeuw and Parker, 1997, 1998; Escamilla-Roa et al., 2013; Lopez-Berganza et al., 2015; Goverapet Srinivasan et al., 2017) including AIMD simulations (Ghatee and Koleini, 2017). Other sparingly soluble salts were also deeply investigated with atomistic simulations to consider hydrated surfaces for the flotation reagents adsorption, such as scheelite (Cooper and de Leeuw, 2003; de Leeuw and Cooper, 2003a), fluorite (CaF_2) (De Leeuw et al., 2000; Khatib et al., 2016; Foucaud et al., 2018a), apatite [$Ca_5(PO_4)_3(OH,F,Cl)$] (Zahn and Hochrein, 2003; Pareek et al., 2008, 2009; Ulian et al., 2018), and rare-earth-elements-bearing minerals (Srinivasan et al., 2016; Goverapet Srinivasan et al., 2017, 2017; Stack et al., 2018). Metallic oxides/hydroxides such as rutile (TiO_2) (Heydari et al., 2019), manganite [MnO(OH)] (Xia et al., 2007), corundum (Al_2O_3) (Janeček et al., 2014), pyrochlore (Bjørheim et al., 2012), goethite [FeO(OH)] (Aquino et al., 2007; de Leeuw and Cooper, 2007; Y. Chen et al., 2017), and hematite (Fe_2O_3) (de Leeuw and Cooper, 2007; Souvi et al., 2013) were also studied since they are known to form hydroxylated species at their surfaces in the presence of water molecules. In particular, some surfaces can be hydroxylated and hydrated at the same time, with specific terminations (Souvi et al., 2017). The same phenomenon occurs for silicates with various crystallographic structures, which constitute the most common gangue minerals in ores. Hence, their consideration in atomistic studies enables their better rejection by optimising the flotation reagents. The hydration mechanisms of many silicates, *e.g.* olivine (Kerisit et al., 2013; Prigiobbe et al., 2013; Liu et al., 2019) or various phyllosilicates (Wang et al., 2005; Wungu et al., 2012; Peng et al., 2016), have been investigated with however a high number of studies focussing on quartz (SiO_2) (Rignanese et al., 2004; Du and de Leeuw, 2006; Skelton et al., 2011; Wang et al., 2018). Interestingly, Skelton and co-workers compared different force fields for CMD simulations, used AIMD calculations to determine the best force field, and compared the water structure at the vicinity of the surface with experimental data. Along with hydration, interactions between electrolytes in the aqueous phase and mineral surfaces can be described by molecular modelling methods, mainly to investigate the depressing or activating effect of some ions such as phosphate anions (Ahmed et al., 2019), metallic cations (Liu et al., 2014;

Sarvaramini et al., 2016b; Liu et al., 2019), and alkali/alkali-earth cations (Sakuma et al., 2011; Pfeiffer-Laplaud and Gaigeot, 2016; Guichen et al., 2018). Overall, an accurate determination of the hydration state of a mineral is a crucial prerequisite for the investigation of reagents adsorption on a realistic surface.

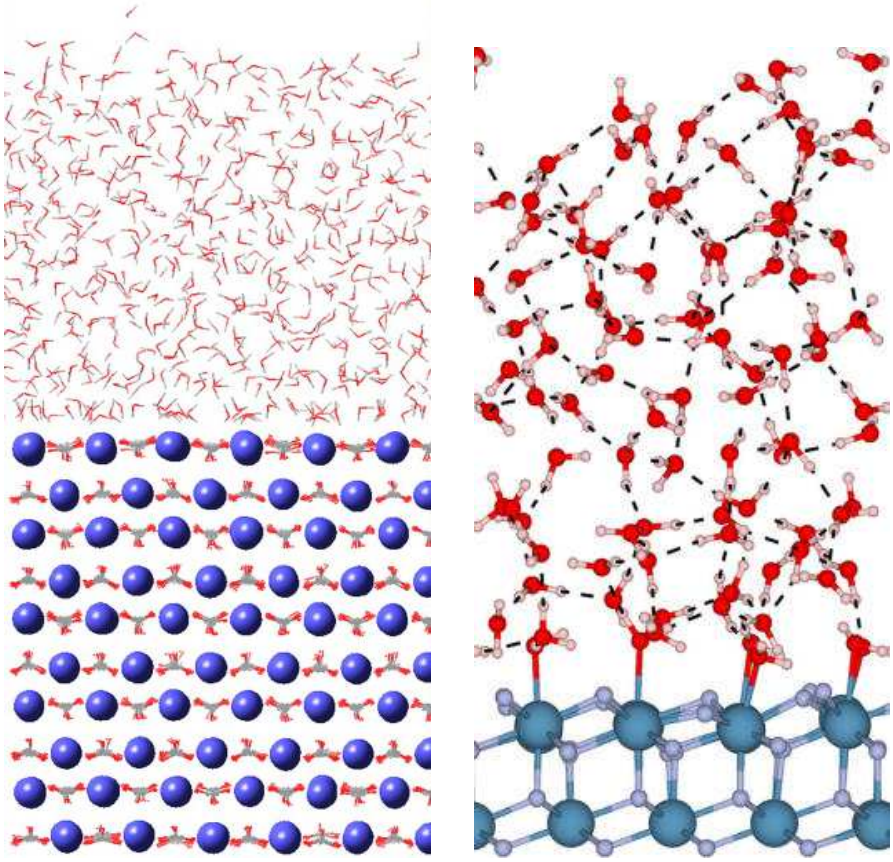

Fig. 2. Snapshots of MD simulations using force fields (left) or DFT (right) to investigate the hydration mechanisms of calcite (left) and fluorite (right) surfaces. Adapted from (Perry et al., 2007) (left) and from (Foucaud et al., 2018a) (right).

C. Adsorption of flotation reagents

1. On sulphide minerals

Considering their high importance for base metals (copper, zinc, lead…), sulphide minerals [pyrite (FeS_2), chalcopyrite ($CuFeS_2$), sphalerite (ZnS), galena (PbS),…] have been intensively and firstly studied by atomistic simulations to gain understanding in the molecular mechanism that are at the

basis of flotation. Several researchers have used DFT calculations to study the surface oxidation mechanisms of sulphides minerals (Fig. 3) such as galena (J. Chen et al., 2017), sphalerite (Chen and Chen, 2010), pyrite (Sun et al., 2004), and chalcopyrite (Xiong et al., 2018), since oxidation reactions are known to affect the collector adsorption. Most of them combined DFT with spectroscopic and other experimental techniques to bring insights from *ab initio* molecular modelling or to validate the developed models. Besides, the adsorption of the most widely used collectors for sulphides (xanthates, thiophosphate, carbamate…) have been investigated by DFT for pyrite (Hung et al., 2003, 2004), for galena (J.-H. Chen et al., 2014; Long et al., 2016b), chalcopyrite (Jiao et al., 2015; Zhao et al., 2016; Ma et al., 2017; Sarvaramini and Larachi, 2017), and sphalerite (Liu et al., 2013, 2014; Jiao et al., 2015; Long et al., 2016a; Sarvaramini et al., 2016b; Liu et al., 2018) with some concerns on the activation of sulphides by metallic ions such as Pb^{2+} (Sarvaramini et al., 2016b) or Cu^{2+} for sphalerite (Liu et al., 2014). Since all the sulphides collectors are anionic, the use of DFT is compulsory to describe accurately the chemical bonding between the surface cations and the collectors anions (O or S). Moreover, the low electronegativity difference existing between sulphur and cations comprised in sulphides (Cu, Fe, Pb, Zn, Ni…) induce a strong-covalent component for their bond, which makes the use of DFT mandatory for such systems.

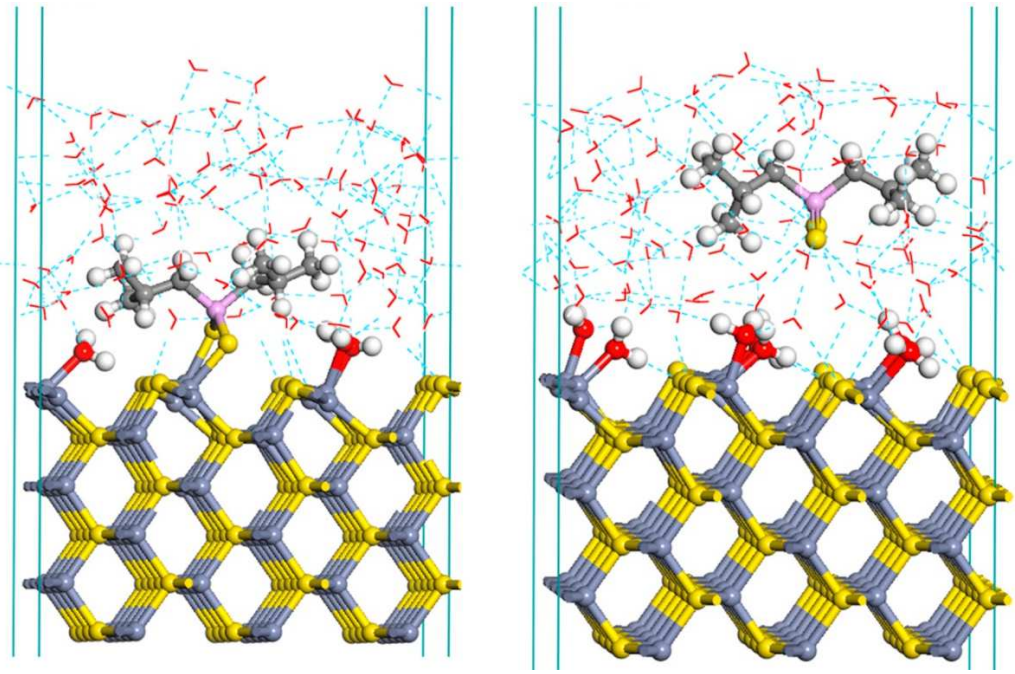

Fig. 3. Adsorption of solvated diisobutyl dithiophosphinate on sphalerite surface: most stable adsorbed configuration (left), non-adsorbed solvated collector (right), adapted from (Sarvaramini et al., 2016b).

2. On silicate minerals

Few studies exist which focus on the adsorption of flotation reagents onto silicates since these latter are usually gangue minerals that have to be rejected and, thus, not collected in flotation. However, reverse flotation processes, in which silicates are collected, have been increasingly used over the past decades to purify the final metallic concentrate after the main separation, *e.g.* for iron ores (Araujo et al., 2005; Veloso et al., 2018). Hence, cationic collectors, mostly amines, adsorption have been studied by CMD and DFT simulations on quartz (Huang et al., 2014; Rath et al., 2014a; Liu et al., 2015) which was in accordance with the generated experimental data (flotation tests and microcalorimetry results). The efficiency of new formulations such as ether and ester derivatives of primary aliphatic amines could be investigated, predicted and discussed based on DFT calculations (Rath et al., 2014a). Besides, some silicates are collected in flotation since they represent either a metal-bearing mineral or an industrial mineral. Hence, the adsorption of amines onto such minerals was investigated by DFT calculations, *e.g.* on muscovite (Xu et al., 2013; Wang et al., 2014) or on kaolinite (Xia et al., 2009). Moreover, the adsorption of anionic collectors, mostly fatty acids, was investigated by molecular modelling for quartz (Li et al., 2017) that can be activated by alkali-earth cations (Guichen et al.,

2018), but mostly for various valuable silicates that have a significant affinity for fatty acids such as feldspars (Xu et al., 2017a, 2017b) or spodumene (Fushun et al., 2014; He et al., 2014; Yu et al., 2015; Xu et al., 2017a; Zhu et al., 2018). Since silicates are usually gangue minerals, the molecular modelling of depressants adsorption onto their surfaces has been investigated by DFT (Han et al., 2016) although very few studies are currently reported.

3. On oxide and fluoride minerals

Oxide minerals were also strongly investigated by atomistic simulations to gain understanding in the flotation reagents adsorption mechanisms. As for sulphides, anionic collectors are widely used for oxides and require the use of DFT to describe correctly chemisorption (Yann Foucaud et al., 2019), although the covalent component is lower for oxides: except silicates, most of them include alkali, alkali-earth, or rare-earth elements as cations, which display higher electronegativity difference with oxygen compared to transition metals and sulphur. Otherwise, anionic collectors can be studied under their neutral, *i.e.* protonated, form to avoid the problem of reactivity. In this case, researchers have demonstrated that a physisorption occurs, based on electrostatic interactions between the collector polar group and the surface cation. Actually, one of the main limitation using DFT periodic codes is that the system has to be electrically neutral, inducing that either an extra-electron or a counter-ion that will give an electron to the anionic reagent must be added to the system.

The adsorption of anionic collectors has been mainly investigated on semi-soluble salt minerals since they constitute sources for some critical raw materials. For instance, researchers have studied the adsorption mechanisms of anionic collectors, mostly carboxylate and hydroxamate, by DFT onto rare-earth minerals (Sarvaramini et al., 2016a; Espiritu et al., 2018, 2019), onto scheelite (Cooper and de Leeuw, 2004; Zhao et al., 2013; Yin et al., 2015), cassiterite (SnO_2) (Gong et al., 2017; Liu et al., 2017; Tian et al., 2018), apatite (Mkhonto et al., 2006; Xie et al., 2018), hematite (Chernyshova et al., 2011; Rath et al., 2014b), and fluorite (de Leeuw and Cooper, 2003b; Foucaud et al., 2018b). In addition, AIMD simulations can be performed to assess the influence of the temperature on the adsorption mechanisms (bond lengths and angles, molecule steric configuration, adsorption energy, adsorption geometry…). We demonstrated that the adsorption of fatty acids under their anionic form

was impacted by the temperature. Finally, water molecules should be added under the form of an explicit solvent to consider the effect of the liquid phase on all the studied parameters. Remarkably, we reported that the fatty acids do not adsorb under the same geometrical configuration in 'static' DFT and AIMD (300 K) simulations (Foucaud et al., 2018b).

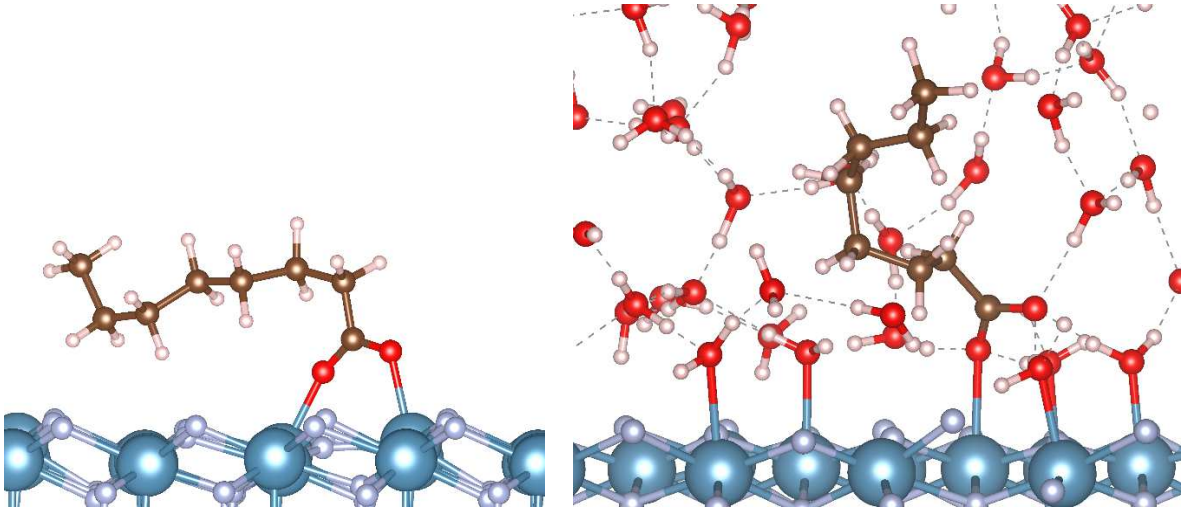

Fig. 4. Snapshots of AIMD simulations (300 K) presenting the configuration differences of the polar head and the non-polar chain of an octanoate molecule between the adsorption in vacuum (left) and in explicit water molecules (b), adapted from (Foucaud et al., 2018b).

5. Conclusion

The froth flotation process is led by the adsorption of various reagents, organic or mineral, at the liquid/solid interface, with the objective of selectively rendering the target mineral(s) hydrophobic to recover it in the froth phase. Collectors, which contain a polar group and a non-polar aliphatic chain, can be adapted in terms of chain length, unsaturation, and ramification, as well as functionalized polar group. Moreover, all reagents can be combined to improve the flotation performances (selectivity or target mineral(s) recovery). All these optimisations are difficult to investigate by experimental methods and molecular modelling is a powerful tool to gain understanding in the adsorption mechanisms of flotation reagents at the mineral surfaces. Two main methods are widely used, force-fields-based (CMD) and *ab initio* simulations (DFT), with significant differences in accuracy, considered phenomena, computational costs, system sizes and simulation times. One should adapt the atomistic method to the flotation system, mostly to the collector. These theoretical techniques can be

used as predictive methods to improve the flotation performances which, however, requires to characterize as well as possible the hydration state, the depressants adsorption, and the collector adsorption. The use of molecular modelling in flotation is tremendously increasing and will be, in the future, a crucial tool to attain the flotation performances required for the processing of low-grades fine-grained complex ores by predictive calculations.

Acknowledgements

The research leading to these results has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement N o. 641650 for the FAME project. We also want to acknowledge the support of Labex Ressoures 21, supported by the French National Research Agency through the national programme "Investissements d'Avenir" with reference ANR-10-LABX-21-LABEX RESSOURCES 21.

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