STUDY OF FORCES BETWEEN MICROCRYSTALS OF GYPSUM BY ATOMIC FORCE MICROSCOPY

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ABSTRACT
This paper introduces a new approach to the study of the interactions between gypsum faces. With an Atomic Force Microscope, the direct local measurement of forces permits to evaluate the free energy between gypsum faces. In air, measurements isolate the different forces between faces, which seem to be responsible of the crystal cohesion capillary force associated with Van der Waals interaction. In electrolytic solutions of calcium sulfate, the crucial feature of the crystal coagulation comes from the effective surface charge of each face. The discussion is oriented to evaluate the part of the coagulation forces compared to the rigidification in the process of setting.

1. INTRODUCTION
The study of the interactions at surfaces has a long history, in particular with regard to the adhesion of macroscopic bodies, because of their obvious technological relevance. The major experimental challenge comes from the control of the distance between the interacting bodies and the low force measurement. The molecular attraction due to Van der Waals forces was first investigated systematically in using a pair of orthogonal crossed mica cylinders as sample [1]. Among the first to perform quantitative measurements were Derjaguin and Israelachvili [2-4]. Nevertheless, a limiting aspect with the Surface Force Apparatus is the restriction of the solid to a molecularly smooth macroscopic surface, namely cleaved mica.
As concern gypsum samples, the pioneering work was done with the help of a magnetoelastic microdynanometer [5]. The statistical evaluation of the strength of individual contact between an edge of a crystal and a planar face has conducted to estimate a probability of bridging crystals under particular conditions. The time of contact, the mutual crystal orientation, the supersaturating degree of the solution and the forces compressing crystals seem to be the main parameters, which influence the agglutination of gypsum crystals. In the same spirit of Shchuckin, the purpose of this paper is to verify the factors defined above with a different technique at a geometrical scale of two-order magnitude lower. Indeed, the development of a new technology the Scanning Force Microscopy [6] has paved the way of new experiment [7]. This technique allows the deflection of a probe tip to be measured to an Angstrom scale. Atomic resolution being demonstrated, microcontact experiments have been extended to the nanometric regime. The feasibility of manipulating gypsum crystals as small as (20µm)³ instead of (2mm)³ as before becomes a valuable progress. In fact, in practice, we know that macroscopic bodies are never perfectly flat. A typical surface is always corrugated with myriad of atomic-scales protrusions. Reduce the contact area clearly tends to provide a better realization of what is at the root of the setting.

The second positive and innovating aspect is the orientation of the crystals according to all face indexes. The interfacial free energy can be therefore extracted without any statistical treatment.

At last, the Scanning Force Microscopy offers the possibility of imaging the state of the surface [8-9] from the atomic resolution in order to characterize the orientation of the faces to the micrometric scale to evaluate the contact area between crystals.

This paper is organized as follows:

Section 2 contains a short description of the experimental method with some of the technical aspect concerning the Atomic force Microscopy, the choice of the spring constant of the cantilever, the sample and the used solutions.

Section 3 presents the experimental results in a first part in air and then in solution.

Section 4 is devoted to discussing some particular aspects especially on the range and the nature of coagulation forces.

2. MATERIALS AND METHOD

In this study, we examine the deflection of the cantilever (perpendicular to the sample surface) due to the force produced by the sample when the latter is displaced towards and away from the former. The force acting on the cantilever was calculated from the sensitivity and the spring constant via the Hook's law.
Force measurements were performed in a cyclical manner (extending and retracting of the sample). The frequency of the sample movement was fixed at 0.1Hz (i.e. 50nm/s) in such a way that the effects of viscosity were avoided. A Nanoscope III scanning probe microscope (Digital Instruments Inc., Santa Barbara, CA) equipped with 15 and 150 µm type scanner was operated in contact mode. We have used various types of cantilevers depending on the sample environment. In air or controlled atmosphere, silicon cantilevers with nominal spring constant $k=30N/m$ were used; whereas in solution silicon nitride cantilevers with lower spring constant $k=0.3-1N/m$ have been chosen. All gypsum samples were epoxied onto stainless steel sample holders or at the free end of cantilevers. The standard surface area is respectively (20µm) for the crystal probe and (500µm)$^2$ for the gypsum substrate.

![Diagram](image)

Figure 1: **Schematic diagram of the AFM detection of force between crystals**

The natural faces of the gypsum crystal have four orientations; the most developed being the (010) and the (120) faces. The (-111) and (011) faces constituting the faces at the end of the crystal are difficult to position and glue at the free end of the cantilever. The studies of the natural faces have been carried out with the (010) and (120) faces. Nevertheless, with the aid of organic inhibitors, a well-developed (-101) face is formed having characteristics similar to those of the (-111) and (011) faces. The crystallographic orientation of the crystal is easily achieved by inspection of the surface under an optical microscope.

In air, all studies were conducted under controlled relative humidity (1 to 80% RH). Keeping a hygrometer and the head of the microscope under a glass bell-jar carried out measurement of RH. The temperature of the surrounding wall was fixed to 25°.

In solution, the AFM observations were conducted in a fluid cell with a volume of solution evaluated to 400µl. In order to avoid the problems of fluid leak and
maybe the hydrodynamic drift of the cantilever, the solution was simply put on
the sample with a micropipette. Concentrations of calcium sulfate solutions were
defined by the degree of supersaturating $\alpha$ of the solution given by the ratio
$\alpha = \frac{C}{C_0}$ where $C$ and $C_0$ (15mmol/l) represent respectively the calcium sulfate
concentration and the concentration at saturation with respect to gypsum. Sulfate
calcium solution with $\alpha = 0.5$, 1, 2, and electrolytic solutions such as $\text{CaCl}_2$
(30mmol/l), $\text{Na}_2\text{SO}_4$ (30mmol/l), and $\text{NaCl}$ (30mmol/l) were used.

3. EXPERIMENTAL RESULTS

3.1 In air
Adhesion forces between gypsum faces
We have investigated the adhesion forces between crystals oriented (010), (120),
and (-101) in all possible configurations. The time of contact between crystals is
roughly equal to 1.2s. During the approach-retract cycle, the greatest repulsive
force exerted between crystals is valued to 2.5µN. The relative humidity is fixed
for this series of measurement to 20%. To account for statistical uncertainties, for
each configuration, we recorded about 300 forces cycles at 10 various locations
on the surface. Varying the sample surfaces and especially the probes has carried
out the measurements. For the present experiment, we have used about 10
gypsum probes with a well-defined direction.
The values were found to only slightly vary with the size of the gypsum probe.
Measurements with the (-101) and (120) gypsum probes show a dispersion of
about 10%. The greatest deviation can be observed with the (010) probe. Indeed,
forces with gypsum needle elongated along the [001] direction glued
perpendicular to the cantilever can vary depending upon the length $L$ of the
crystal. For instance, a mean value of 0.4µN with a standard variation of 0.15µN
can be extracted for $L=35\mu m$. Forces can reach a value of 0.8µN when $L$
is greater than 80µm. Therefore, the contact area essentially depends on the length
of the crystal perpendicular to the cantilever. For all force measurements, this
length has a standard value estimated to 30µm whatever the oriented faces. In
this condition, the deviation on force values does not exceed 20%, causing a
good reproducibility of measurements from one face to an other one.
Figure 2 represents the results of these measurements.
The adhesion forces substantially depend on the type of faces, which are brought
together. The minimum adhesion force was measured between the (010) gypsum
faces. The forces between (120) faces are three times greater than the (010)
gypsum faces. The (-101) faces were found to have the greatest adhesion as
concerns the interaction of similar faces.
The shown results suggest that the greatest adhesion is not necessary between
faces of the same nature. In fact, a consistent adhesion 20 times greater than for
gypsum faces was measured between the (-101) face and the two other faces.
Effect of crystal orientations on the adhesion force.
In a fixed configuration, the sample was turned in order to check an effect of the crystallographic orientation. All measurements are conducted with brief contact at 20% RH.
As concern the (010) faces, an increase of adhesion (0.8µN) was measured when the probe and the sample crystals are in register (i.e. with the match of the elongation direction of crystal [001] direction). From this position, another maximum of adhesion (0.4µN) was found when the surface is turned with an angle of 60°. In these two positions, the maximum adhesion can be measured in a twist angle range of 10°.
As concern the (120) faces, the same effect described above has been put to the fore. The adhesion increases by a factor two when the [001]directions of the two crystals correspond. On the other hand, the AFM imaging reveals that the (120) face is constituted of microsteps oriented in the [001] direction. Consequently, the contact area and obviously adhesion should be reduced with cross steps.
As concern the (-101) faces, no effect of misorienting crystals have been observed.

Particular behavior of the (010) face
Among the gypsum faces, the (010) face provides a particular behavior. At 20%RH, the adhesion force increases with the duration of the contact of two (010) faces. Starting from a small force of 0.4µN for an instantaneous contact after 20min of contact, it seems that the adhesion reaches its optimum and stable value of about 2.4µN.
The greatest raise has been observed between two (010) faces. Some attempts have shown an evolution between the (010) and (120) faces but certainly not with the same amplitude. The adhesion was found to not depend on the duration of contact for the configuration (120)/(120) and (-101)/(-101).
Another experiment confirms the suggestion of the special feature of the (010) face. Two crystals have been brought together in contact during a quarter of hour with a great pressure. Then the gypsum probe was retracted from the surface and changed for an AFM tip. The use of piezoelectric element of 150µm range has permitted us to scan the previous contact area between the (010) faces. From the figure 3, we clearly see that a perturbation of the surface has occurred during the contact. A fine layer with a height of about 1nm partially covers an area by (10x10)µm². This area roughly matches with half of the area of the crystal probe. However, for a surface greatly perturbed by cleavage, the contaminant layer is observed on the top of surface steps. Therefore, at microscopic scale, the contact cannot be assumed to a well-delimited planar area but rather to nanoscopic roughness.
Figure 2: Adhesion forces between gypsum crystals in air at 20%RH and 80%RH

Same experiments in the configurations (120)/(120) or (-101)/(-101) have not shown any marks of contact as before. Attempts to find the contact area between (010) faces have failed when they are pressed very slightly (force below to about 2µN). Indeed, the contact area does not seem enough large to be able to be visualized. Only the end of the crystal probe has touched the surface. Nevertheless, with a greater pressure, the cantilever comes to bend in the sense of increasing the contact area between crystals.

**Effect of the capillary condensation**

The same experiment of the section 3.1 was reproduced in varying the relative humidity from 20 to 80-85%RH. Between 35-45%RH, an increase of the adhesion force for all surfaces in contact is measured [8]. That force remains to a constant value from the 50%RH. The adhesion forces are reported in the second row of the figure 2 when surfaces stay half an hour at 80%RH.

The general remark is the increase of the adhesion (about 2.3µN) whatever the orientation of faces. The effect of a high affinity of the (010) face for water observed with the silicon AFM tip was not found again. This raise is an evaluation of the capillary force due to the water condensation. The Laplace's force being above all a geometrical force, the constant capillary force suggests that the contact area between crystals is still the same whatever the orientation of faces.
Figure 3: *Mark of the contact between two (010) faces at 20% RH maintained with a great pressure during 20 minutes*

The total adhesion forces measured in such conditions between the (-101)/(120) and (-101)/(010) faces are so large that they cannot be evaluated due to the limited area of photodetectors.

**Adhesion force with other natures of crystals**
We have studied the eventual adhesion of the gypsum faces with other minerals as the cleavage plane of anhydrite CaSO₄ and calcite CaCO₃. The sample surface was either calcite or anhydrite whereas the tip was a gypsum probe as before. The results are shown in Table1.

Table 1. Adhesion force with other natures of crystals

<table>
<thead>
<tr>
<th>Force (µN)</th>
<th>Calcite (20%RH)</th>
<th>Calcite (80%RH)</th>
<th>Anhydrite (20%RH)</th>
<th>Anhydrite (80%RH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gypsum (010)</td>
<td>0.6</td>
<td>2.8</td>
<td>1.9</td>
<td>4.2</td>
</tr>
<tr>
<td>Gypsum (120)</td>
<td>2.9</td>
<td>5.1</td>
<td>2.9</td>
<td>5.3</td>
</tr>
<tr>
<td>Gypsum (-101)</td>
<td>4.6</td>
<td>6.8</td>
<td>4.9</td>
<td>7.4</td>
</tr>
</tbody>
</table>
In all cases, the adhesion forces are superior to the configuration of the (010) face. The calcite and the anhydrite seem to have the same cohesion with the (-101) and the (120) faces. Nevertheless, the calcite does not exhibit a real affinity for the (010) face. The interactions in high degree of humidity increase as described before, a raise of about 2.3µN.

3.2 In electrolytic solutions
In solution, an understanding of the mechanical motion of the cantilever is critical to yield insights into the force measurement. A repulsive force due to electrostatic contribution can create a hysteresis. During the approach of the tip, the cantilever is sensitive to the repulsive force until the force gradient does not exceed the value of the spring constant of the cantilever. At this point, the tip jumps into the contact with the surface. It must be emphasized that no attractive force can be detected in the approach motion of the cantilever in that case. However, during the retracting of the sample, the system is sensitive to the lowest energies and therefore to the attractive well. The real surface-tip separation cannot directly obtained by a linear relation. A continuous analysis of the cantilever motion has to be performed to evaluate the surface potential taking into account the mass of the gypsum probe, the non-linearity for the spring constant and the sensibility of the system for small applied forces. Some instances of interactions measured by AFM between gypsum crystals are shown on the following figures.

In calcium sulfate solution
Between (010) faces (figure 4) in saturated calcium sulfate solution, the bending of the cantilever is only sensitive to a repulsion (7nm, i.e. 8nN) onto a piezoelectric distance of 20nm that is to say to a tip-sample separation of about 5nm. A slight hysteresis is present between the approach and the retract motion of the sample. This hysteresis is due to a small attractive force which shifts the retract deflection. The point of contact of the tip with the surface occurs only in the rectilinear regime of deflection without any hysteresis pattern. The corresponding surface potential is presented on figure 9 for saturated and oversaturated solutions. Varying the calcium sulfate concentration has not a strong impact on the force curves.

Between (120) faces (figure 4), the cantilever deflection versus the piezoelectric tube elongation differs from that between the (010) faces. The force curves clearly depend on the concentration. In all cases, during the approach of the cantilever, a repulsive bending of the cantilever is measured onto a distance of about 75-150nm. This is due to a repulsive force component of 20nN onto a distance of 6nm (figure 5). The variation of the tip retracting with the degree of saturation of the solution is the main difference. In saturated solution, the bending of the cantilever reaches about 10nm from the contact point whereas the deflection reaches 200nm in an oversaturated one.
Figure 4: Cantilever deflection versus the elongation of the piezo-electric tube
   A: between (010) faces in saturated gypsum solution
   B: between (120) faces in saturated gypsum solution
   C: between (120) faces in supersaturated gypsum solution
Figure 5: Surface forces in calcium sulfate solution
A: between (010) faces
B: between (120) faces
C: between (-101) faces
The depth of the attractive well was found to have its greater value (150nN) between these two latest faces in supersaturated solution (figure 5). The interactions between (-101) faces do not seem to vary with the concentration. Indeed, no strong repulsion is observed in approaching the crystals. A constant adhesion (about 30-50nN) is greater than for the (010) faces but remains lower than between the (120) faces (figure 5).

Interactions between different faces have been studied. The results are summarized in the diagram of the figure 6. The aspect of curve remains the same as described before, a slight repulsive force following to an attractive well more and less important depending on the contact faces. All adhesions between faces of different natures keep lower than between the (120) faces. A notable adhesion is observed between the (-101) and the (120) faces. The presence of the (010) face in all shown configurations decreases the surface potential.

**In other electrolytic solutions**

The choice of other solutions is limited due to the gypsum solubility. Unfortunately, no electrolyte 1:1 such as NaCl or KCl can be checked without dissolution of the gypsum probe. Only measurements in NaCl (30mmol/1) solution between (010) faces have shown no repulsive pattern with a low adhesion of 10nN. The comparison with the calcium sulfate solution has mainly been performed with solutions of calcium chloride and sodium sulfate. (figure 7)
In CaCl₂ solution, measurements reveal repulsive forces during the approach of the tip. The range of the repulsive force has the same order of magnitude than that measured in CaSO₄ solution. Nevertheless, the great difference comes from the small adhesion forces, which never exceed 40nN in the most configurations. Only the facing (-101) faces exhibit a valuable attractive force of 50nN without repulsive pattern during the approach of the tip.

In Na₂SO₄ solution, the repulsive pattern is reduced compared to solutions of CaSO₄ and CaCl₂. Therefore, adhesion forces larger than measured in CaCl₂ solution are collected between faces during the retracting of the tip. It must be emphasized that under no circumstance a stronger interaction such as between the (120) faces in supersaturated CaSO₄ solution is reproduced. They are rather similar than those evaluated in saturated one.

4. DISCUSSION

Several results of the section 3 have to be discussed in order to answer the fundamental question: what is the origin of the cohesion of the hardened plaster? For this purpose, we need to evaluate the free energy of interaction to compare with the known surface energy.
4.1 Adhesion in air

The free energy of interaction $W$ is given by integrating the force during the approach of the two crystals. The range of the attractive force being about $d=2\text{nm}$, the free energy is then obtained by dividing by the contact area $A$ of the two crystals with a rough linearization of the attractive force. The estimation of the interfacial energies calculated from experimental results is reported on the Table 2.

The free energy has to be compared to the known dispersion Van der Waals interaction in calculating the Hamaker constant. It emerges from a local approximation of the dielectric function that is well justified for insulating material as gypsum for which the interaction can be through of as being a linear superposition of the interaction between individual atoms. The value of energy $W$ equal to $80\text{mJ/m}^2$ is directly comparable with the order of magnitude between the (120) faces or (-101) faces. The value of $80\text{mJ/m}^2$ corresponds to energy of about $3kT$ per molecule. This is worth noting that this energy is just greater than the average energy of translation per molecule $1.5kT$, the minimum energy where two molecules generally stay in contact.

The adhesion energy between the (010) faces is three times slower than between the (120) faces. One layer of water molecules composes the top of the (010) face. Consequently, the dispersion forces become lower against the dipole interaction. The adhesion energy between the (010) faces is certainly bettered described by the Keesom energy (interaction between permanent dipoles). We can notice that this interaction depending on the temperature perhaps plays a particular role in the behavior of the (010) face. The greater the temperature is, the lower is the adhesion. The Keesom energy has a known value inferior to $kT$ and does not permit the adhesion.

Table 2. Interfacial energy in air

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$W_{\text{air}}$ (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>gypsum (010) / gypsum (010)</td>
<td>27</td>
</tr>
<tr>
<td>gypsum (120) / gypsum (120)</td>
<td>87</td>
</tr>
<tr>
<td>gypsum (-101) / gypsum (-101)</td>
<td>127</td>
</tr>
<tr>
<td>gypsum (010) / gypsum (120)</td>
<td>146</td>
</tr>
<tr>
<td>gypsum (-101) / gypsum (010)</td>
<td>386</td>
</tr>
<tr>
<td>gypsum (-101) / gypsum (120)</td>
<td>427</td>
</tr>
<tr>
<td>anhydrite / gypsum (010)</td>
<td>120</td>
</tr>
<tr>
<td>anhydrite / gypsum (120)</td>
<td>192</td>
</tr>
<tr>
<td>anhydrite / gypsum (-101)</td>
<td>328</td>
</tr>
<tr>
<td>calcite / gypsum (010)</td>
<td>200</td>
</tr>
<tr>
<td>calcite / gypsum (120)</td>
<td>340</td>
</tr>
<tr>
<td>calcite / gypsum (-101)</td>
<td>453</td>
</tr>
</tbody>
</table>
If the dispersion forces are mainly responsible for the adhesion of the (120) and the (-101) faces, the adhesion energy of the (-101) face with the (120) face certainly has another cause. The polar interaction (fixed dipoles) and the polarization force (ion-polar molecule, fixed dipole-non polar molecule) has to be considered to a more accurate answer. Nevertheless, it is amazing that the greatest energy was measured between surfaces of different surface charges. In fact, the top of (120) face is composed by a majority of sulfate whereas the (-101) face is the sole surface of the crystal to have calcium host atoms on surface. Hence, it becomes conceivable that some bonds with ions are created to increase the adhesion energy of about 300mJ/m$^2$.

The influence of the orientation of crystal following the crystallographic orientations can easily be explained. The polarizabilities of molecules are anisotropic having different values along different molecular direction. As a consequence, the Van der Waals forces become dependent on their mutual orientation. The same effect has been observed between two cross mica cylinders [11].

4.2 Adhesion in liquid

**Double layer interaction** In order to quantify the characteristic parameters of the repulsive force and to compare with the known electrostatic result [11], we fit the repulsive part of the experimental force curves by an exponential decreasing. The free repulsive energy can therefore experimentally be obtained. In aqueous solutions, the repulsive component detected in approaching the sample is due to the electrostatic force. In our case, the charging of the surface comes from an adsorption of ions onto the surface. In fact, even in undersaturated solution, the dissolution liberates calcium and sulfate ions, which can adsorbate onto the surface. These surface charges cause an electric field, which decreases roughly exponentially with increasing distance from the surface. Surface charges attract counterions and the ion concentration increases near the surface. These ions cause an osmotic pressure, which repels the facing surfaces. Based upon the Poisson Boltzman equation, the free electrostatic energy for an electrolyte 2:2 can be obtained. Knowing the surface potential, the surface charge density $\sigma$ was calculated. Results between forces are summarized in the table 3.

<table>
<thead>
<tr>
<th>$(010)$</th>
<th>$U_{exp}$ (nN)</th>
<th>$\varphi$ (mV)</th>
<th>$\sigma$ (mC/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(010)</td>
<td>40</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>(120)</td>
<td>80</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>(-101)</td>
<td>10</td>
<td>2</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Table 3. Surface potential and surface charge density of gypsum faces
These results suggest a really poor effective surface charge for the gypsum sample especially for the (-101) face. 5mC/m\(^2\) corresponds to one effective charge per (6nm)\(^2\).

It is clear from our results than the repulsive part of the electrostatic contribution does not constitute a gate. In the most unfavorable case, the electrostatic energy does not exceed 0.3mJ/m\(^2\).

**Origin of the attractive well**

The experimental free energies are collected in the table 4.

<table>
<thead>
<tr>
<th>Free energy (mJ/m(^2))</th>
<th>CaSO(_4) ((\alpha=1))</th>
<th>CaSO(_4) ((\alpha=2))</th>
<th>CaCl(_2)</th>
<th>Na(_2)SO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(010)/(010)</td>
<td>1</td>
<td>0.6</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>(120)/(120)</td>
<td>3.5</td>
<td>10</td>
<td>0.6</td>
<td>2</td>
</tr>
<tr>
<td>(-101)/(-101)</td>
<td>2.6</td>
<td>4</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>(010)/(120)</td>
<td>2</td>
<td>2.5</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>(010)/(-101)</td>
<td>1.5</td>
<td>2</td>
<td>0.6</td>
<td>2</td>
</tr>
<tr>
<td>(120)/(-101)</td>
<td>2.6</td>
<td>6</td>
<td>0.6</td>
<td>1.3</td>
</tr>
</tbody>
</table>

These values have to be compared with the dispersion energy of Van der Waals commonly accepted in the DLVO theory to be responsible to the coagulation. In solution, the value of the Hamaker constant H is screened due to the polarizability of water (high value of \(\varepsilon=80\)). What is more, the presence of an electrolyte screens again the attractive interaction. As a result, the Hamaker constant H falls to a smaller value of 0.8\(\times\)10\(^{-20}\)J. Therefore, the free energy due to the Van der Waals interaction is about 4mJ/m\(^2\), that is to say about 0.2kT per molecule.

Theoretical value of 5mJ/m\(^2\) is consistent with the interaction between the (-101) faces and the (120) faces in saturated calcium sulfate solution. However, an interaction two times greater is measured between the (120) faces in oversaturated solution. If the Van der Waals dispersion forces are mainly responsible for the coagulation of crystals, an other phenomenon must to be superimposed between the (120) faces.

Indeed, with divalent counterions such as calcium, the diffuse double layer constitutes a highly polarizable layer. A net force below 2nm range is established which can exceed the Van der Waals interaction by a factor 2 even 3. This force known as the ionic correlation force has already been observed \([12-13]\). Their importance has believed to be the key of the strong adhesion of negatively charged \([14-16]\). As concerns gypsum, such ionic correlation seems to act between the (120) faces. Among all studied faces, the (120) face seems to have
the highest negatively surface charge due to the presence of sulfate group on the surface. The structural water layer of the (010) face provides an effective negative charge due to the water dipole with a scale lower than that of the (120) faces. The (-101) face is the sole face which has calcium entities in its upper plane.

The role of calcium ions is significant in comparison to the observed feature in Na$_2$SO$_4$. No real electrostatic repulsion is observed in Na$_2$SO$_4$ contrary to the calcium solutions. The calcium binding onto the surface probably charges the surface leading to charge reversal and creating repulsive potential far away from the surface. Nevertheless, the adhesion force remains to a constant value in CaCl$_2$ and Na$_2$SO$_4$ solutions. The origin of the adhesion in that case is certainly due the Van der Waals interaction not really dependent on the type of the solute.

The ionic correlation described above seems to impose some conditions: electrolyte 2:2 over its saturation between relative charged surfaces. The increase of the concentration of calcium sulfate solution favors the coagulation process.

### 4.3 Coagulation and strengthening

The free measured energy $W$ has to be compared with two values of energy to place the observed phenomenon in the context of the coagulation or the setting. The coagulation process will appear if the energy is not so far from the thermal bath of kT.

The strengthening process will appear if some chemical bonds are created between crystals. Typically, crystals are rigidified when the free energy equals the surface energy.

The series of the surface energy have been calculated in the literature [17-18]. Results are collected in the table 5.

**Table 5. Surface energy of gypsum faces [17]**

<table>
<thead>
<tr>
<th>Configuration</th>
<th>(010)</th>
<th>(120)</th>
<th>(011)</th>
<th>(-111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface energy E(mJ/m$^2$)</td>
<td>240</td>
<td>480</td>
<td>640</td>
<td>1440</td>
</tr>
</tbody>
</table>

In air, all free energies are superior to the value of kT except the (010) faces at low RH. All gypsum crystals attract themselves. The capillary forces enhance the adhesion but not in the same proportion. Indeed, the contribution due to the water condensation for (-101) and (120) faces represents only 25%. On the contrary, the capillary force is crucial for the cohesion of the (010) faces.

At low RH, we have noticed that upon great pressure a chemical bonding is created between the (010) faces. This process seems to be at the origin of the setting at low RH. A great pressure applied between crystals is able to remove the structural water in the upper plane of the (010) face and discover the sulfate plane. Therefore in this condition the interaction is more favorable to the adhesion (more consistent to a behavior similar to the (120) faces). On the other
hand, a matter reorganization [19] occurs around the contact between gypsum faces, which explains the precipitate visualized in figure 3.

In liquid, it seems that the coagulation process remains relatively limited. Only the (120) faces seem to collect the best condition. This result is confirmed by the observation in rheology with an optical microscope [20]. Without pressure between crystals and without duration of the contact, the free energy remains too low to permit a stable cohesion. Due to its too small surface energy, gypsum cannot evolve strong attraction by ionic correlation. London Van der Waals interactions are not sufficient to ensure the cohesion of crystal. In this condition, the setting will only occur by bringing crystals together as long as ionic bridging occurs with chemical bonding.

The first investigations of force measurements in the conditions of the setting of cement have been performed. The AFM probes made of silicon or silicon nitride are covered by a thin layer of oxide Si-OH. All observed interactions between the probe and samples such as silica, silicon, and alite have shown a very great adhesion in solution of Ca(OH)\(_2\). The observed adhesion is really greater than those presented in this paper. Coagulation forces involved in the process of setting seem to have different origin for plaster and cement.

5. REFERENCES


ACKNOWLEDGEMENT

The authors wish to acknowledge the contribution of C. Le Grimellec, A.Nonat, J. Baron, H. Van Damme, A. Delville and H. Pellenq, in offering stimulating discussions during the course of this work. We are deeply indebted to the Association Technique de l'Industrie des Liants Hydrauliques and the Lafarge LCR company for its financial support.