Technical Report

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AFM study of montmorillonite

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Abstract

Na-montmorillonite and Ca-montmorillonite particles have been attached to molecularly flat mica surfaces using simple evaporation of montmorillonite solutions. The particles stick to the surface by strong van der Waals forces. The homogeneity of the montmorillonite particle surfaces has been evaluated by AFM imaging and by AFM force raster measurements. As a control, molecularly smooth mica surfaces were used, and the data obtained for montmorillonite was compared with the data obtained for mica.

In images of the size 100×100 nm we can identify variations on the Na-montmorillonite particle surfaces. This variation is attributed to inhomogenities of the montmorillonite particles. The inhomogeneous nature of the montmorillonite surface is also clearly demonstrated by the force raster measurement, in particular the force raster adhesion maps show larger variations and a more patterned structure for montmorillonite than for mica. Thus, any attempt to model the interaction between montmorillonite particles using a model of ideally flat surfaces with a homogeneous charge distribution is an oversimplification. We suggest that this explains the differences between measured swelling pressures and modelling results.

Sammanfattning

Montmorillonitpartiklars ytor har studerats med AFM (atomkraftsmikroskåp) avbildning, samt med AFM kraftmätningar i rasterform som genererar kraftkartor av de studerade ytorna. Na-montmorillonit- och Ca-montmorillonit-partiklar har deponerats på molekylärt plan glimmer genom att droppa montmorillonitlösning på en glimmeryta som sedan får torka i luft. Montmorillonitpartiklarna fäster på ytan genom starka van der Waals krafter. En molekylärt plan glimmeryta har använts som referensmaterial, det vill säga mätningar på montmorillonit har jämförts med mätningar genomförda på glimmer.

I bilder med storleken 100×100 nm kan man identifiera variationer på Na-montmorillonitpartiklarnas yta. Denna variation beror på at montmorillonitpartiklarnas yta inte är homogen. Denna inhomogenitet demonstreras även tydligt med kraftmätningar. Speciellt vidhäftningskartan för montmorillonit visar stora variationer och ett mer strukturerat mönster i jämförelse med glimmerytan. Således är alla försök att modelera interaktioner mellan montmorillonitpartiklar med en modell där montmorillonit representeras av ideala plan som har en homogen laddningsfördelning en förenklad bild. Vi menar att den noterade inhomogeniteten kan vara en orsak till de skillnader man ser mellan experimentella mätningar och teoretiska beräkningar för svällningstryck av montmorillonit.

Contents

1 Background

The swelling behaviour of clays consisting of montmorillonite has so far not been possible to predict by theory and Monte Carlo simulations. It is conceivable that this discrepancy is due to charge inhomogeneities or other types of inhomogeneities on the individual clay particle surfaces.

2 Aim

The aim of this study was to investigate if there is any inhomogeneity, in terms of charge or other types, on the surface of individual clay particles of sodium and calcium montmorillonite by using the local probing capacity of the atomic force microscope (AFM). The AFM has been used to capture images on different length scales, and to measure force versus separation curves between a sharp AFM tip and clay particles. In order to perform such measurement we first needed to develop methods for anchoring montmorillonite particles to a surface in such away that it allowed accurate measurements to be conducted in both air and liquid media.

3 Materials

NaCl, H_2O (purified using a Milli-Q water unit), Na- and Ca-montmorillonite, 3-aminopropyl-triethoxysilane, toluene, AFM-cantilevers (tapping and contact mode). The AFM used was a Nanoscope Multimode III Pico Force from Veeco Instrument.

4 Experimental

4.1 Attachment of montmorillonite to a solid support

In a first experiment small amounts of Na-montmorillonite was dispersed in pure water. A drop of this dispersion was then placed on a cleaned silica surface and the water was allowed to evaporate. This sample was then imaged with AFM using tapping mode in air at different length scales (see Figure 4-1). Within these images it is observed that the montmorillonite particles are spread out on the silica surface and that at least some particles remains separate whereas others form aggregates on the surface. In the 100 x 100 nm image some irregularities are visible. However, the origin of these irregularities was at this stage unknown and different explanations were possible.

Next, positively charged surfaces, which are expected to attach montmorillonite more strongly than negatively charged silica, were prepared by covalently coupling of aminosilanes on the silica surface. The procedure by Howarter et al. /1/ was used, *i.e.* silanation in liquid phase (using toluene as solvent) at ambient temperature with a reaction time of 60 minutes. This procedure is expected to result in a smooth and homogeneous silanated surface. However, a close inspection of the modified surface by AFM imaging (Figure 4-2) revealed that it was not sufficiently smooth; instead it seems that the silanes have formed aggregates on the surface. If single montmorillonite particles are adsorbed on such a surface we would not be able to discriminate between variations in morphology of the particles and variations induced by the topography of the underlying substrate. An alternatively method of generating positive charges on the surface is to adsorb polyethylene imine (PEI) as suggested by Bickmore et al. /2/ However, after a closer look at the result presented by Dedinaite et al. /3/, it seems likely that also this method will result in a heterogeneous surface layer, and therefore makes it difficult to evaluate properties of small particle adsorbed to the surface.

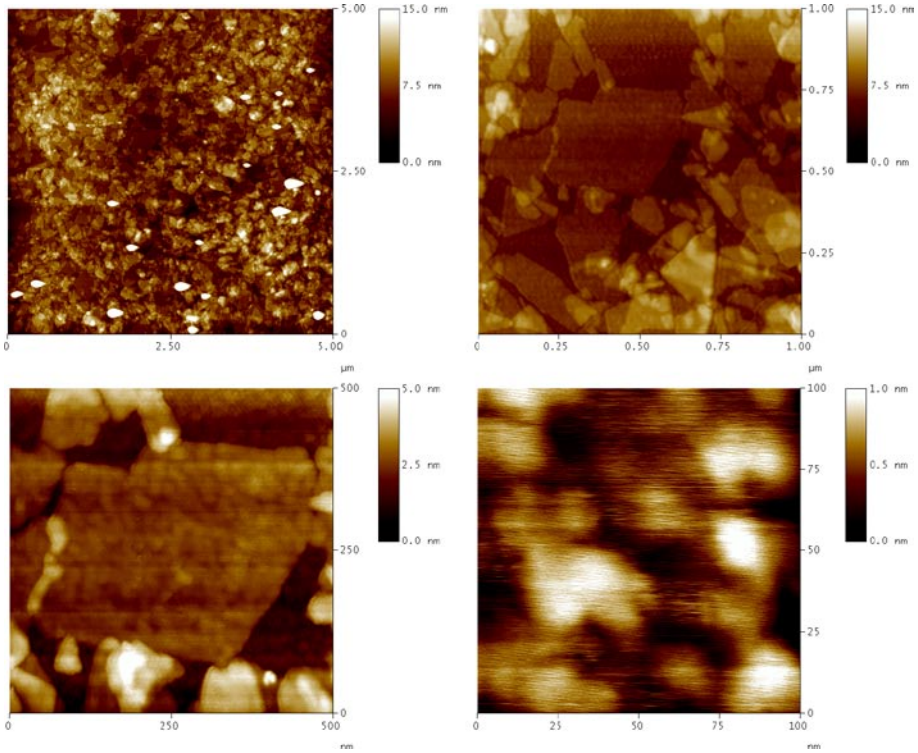

Figure 4-1. *Tapping mode height images of Na-montmorillonite measured in air at different length scales. Top left 5×5 µm, top right 1×1 µm, bottom left 500×500 nm and bottom right 100×100 nm.*

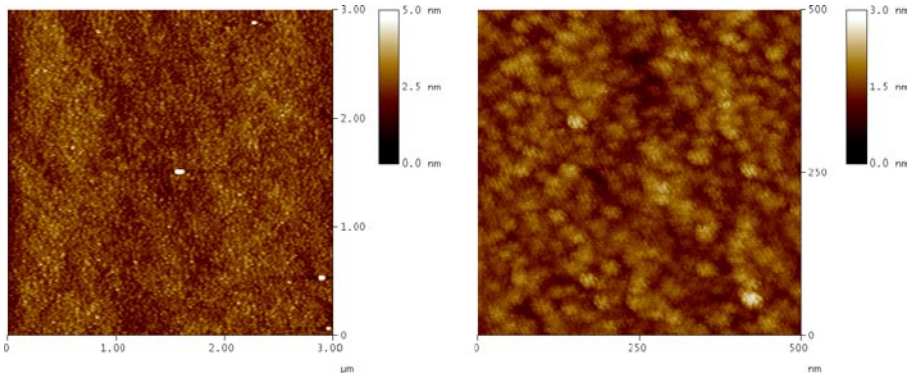

Figure 4-2. *Tapping mode height images of aminosilane modified silica measured in air at different length scales (left 3×3 µm and right 500×500 nm).*

Since our choice of using positively charged surfaces seemed to fail, we instead decided to test to use mica (which is atomically flat) as substrate. A disadvantage with mica as substrate is that it is negatively charged, and it might be that the negatively charged montmorillonite does not adhere to mica. To overcome this problem, the particles need to be able to reach the primary energy minimum that is present due to van der Waals interactions. To achieve this evaporation of the solvent during the preparation of the sample was tested. The test was done by dispersing 10 mg Na- and Ca-montmorillonite, respectively, in 100 ml water (100 mg/dm^3). One drop (~ 4 µl) of the solutions was placed on a freshly cleaved mica surface and allowed to evaporate, providing the means for the attractive van der Waals force to anchor the particle to the substrate. Next, the samples were imaged using contact mode AFM in air, see Figure 4-3. Clearly, montmorillonite particles are attached to the surface. The success of using mica as substrate and the ability to image in contact mode, opens the possibility of performing force versus distance curves with the same cantilever as used during imaging. Hence, we can image the surface at different length scales to navigate to individual particles on the sample and perform force measurements at the spot of interest. It also makes it possibly to do imaging and force measurements in liquid media.

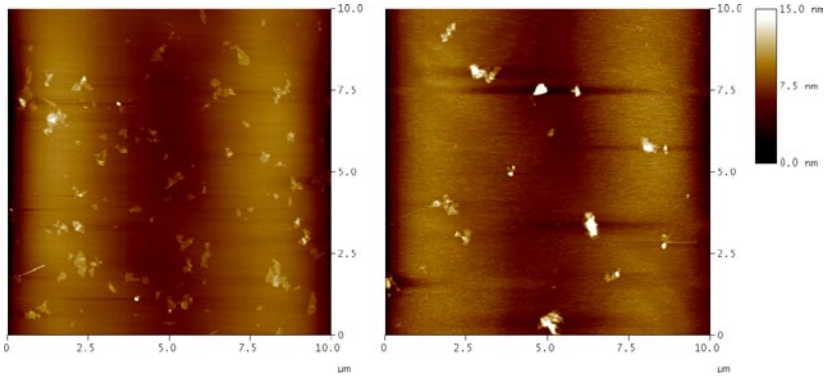

Figure 4-3. *Contact mode images of size 10×10µm determined in air using contact mode. Left; Na-montmorillonite on mica. Right; Ca-montmorillonite on mica.*

4.2 Force measurements

Force versus separation curves are measured by ramping the sample up and down against the tip instead of raster the sample under the tip as is done during imaging. Typical force curves are displayed in Figure 4-4, showing the force acting between the silica tip and mica measured in water, for four different mica surfaces. It is also possibly to measure force curves at different positions on the sample surface, by moving the contact position between each force curve in a controlled way. This type of measurements is called *force raster*. However, one needs to evaluate if the position of the sample relative to the tip is drifting during force raster measurements.

4.3 Evaluation of drift

When making images and/or force curve measurements employing small movements with the AFM scanner, the scanner made of piezo material will show some tendency to drift. This shows up as a motion of the object of interest with time. Figure 4-5 displays images captured on the same sample with approximately 7 minutes between the images. The drift is approximately 150 nm over 7 minutes, therefore it is important to measure the force raster in as short time interval as possibly.

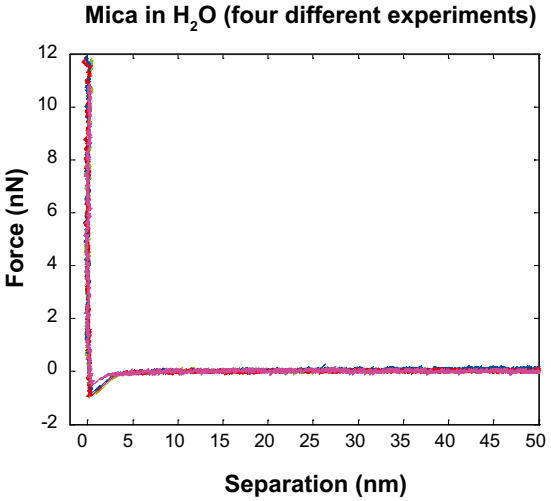

Figure 4-4. *Force profile when a silica tip is approaching a mica surface in water. Results obtained for 4 different mica surfaces are shown.*

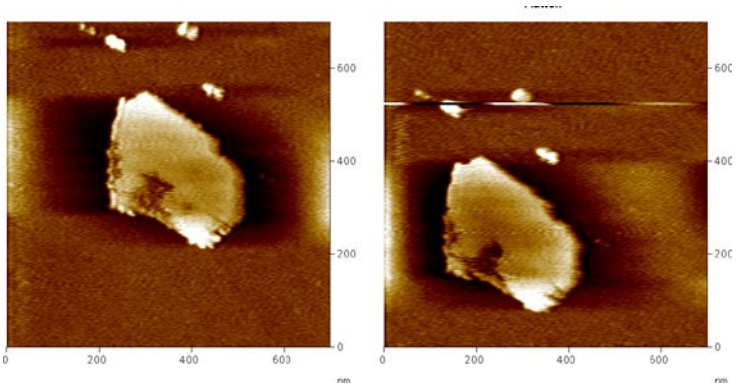

Figure 4-5. *Tapping mode images of Na-montmorillonite on mica in air. Measured during continuously scanning but captured with 7 minutes between the images.*

4.4 High-resolution AFM imaging

By using a fast scan rate (61 Hz) over a small area (12×12 nm) and no feedback in contact mode AFM, it is possibly to obtain images of the atomic lattice structure of flat sample. See, images in the Results section.

5 Results and discussion

5.1 Images 10×10 µm

Images covering a large area, 10×10 µm, was used to evaluate the density of the montmorillonite particles on the mica surfaces, see Figures 5-1 – 5-2. These images were captured on samples prepared using two concentrations of Na- or Ca-montmorillonite, 100 mg/dm^3 and 10 mg/dm^3. The difference between the Na- and Ca-montmorillonite samples is that the Na-montmorillonite particles are more spread as individual particles compare to the Ca-montmorillonite that shows more aggregates of particles on the mica surface. This is logical since Ca^{2+} are more efficient in screening repulsive electrostatic double-layer forces than Na^{+}. Comparing the 100 and 10 mg/dm^3 concentrations, we note a higher coverage of particles at the higher concentration. However, the particles do not seem to be to close to each other, and it is possible to find individual particles at least for the Na-montmorillonite. From these measurements it was decided to use the concentration of 100 mg/dm^3 in the following experiments. We have also focused mainly on Na-montmorillonite since it is more difficult to find individual particles of the Ca-montmorillonite on the mica surfaces.

5.2 Images 3×3 µm down to 200×200 nm

Figure 5-3 presents a series of images on different length scales, from 3×3 µm down to 200×200 nm, demonstrating how it is possible to navigate to individual particles for measuring force raster and high resolution atomic lattice images of the montmorillonite samples. In Figure 5-3 the top image shows an overview of many particles of which two particles were selected for additional measurements, *e.g.* 100x100 nm images, force raster and high resolution atomic lattice imaging. Images of the size 200×200 to 400×400 nm were also measured after these specific measurements to confirm that the force raster and high-resolution measurements indeed were conducted on a montmorillonite particle, *i.e.* to confirm that despite the drift discussed above we still were measuring on the montmorillonite particle.

5.3 Mica as reference

Images at different length scales of mica surfaces are presented in Figure 5-4. These images are to be regarded as references since mica easily can be cleaved to expose homogeneous and molecularly smooth surfaces. As expected we note that independent of the size of the images they seem flat with no irregularities. However, there are some horizontal stripes on the images that originate from electronic noise and thus carry no information. In the following we will compare images of montmorillonite to images of flat and homogeneous mica surfaces.

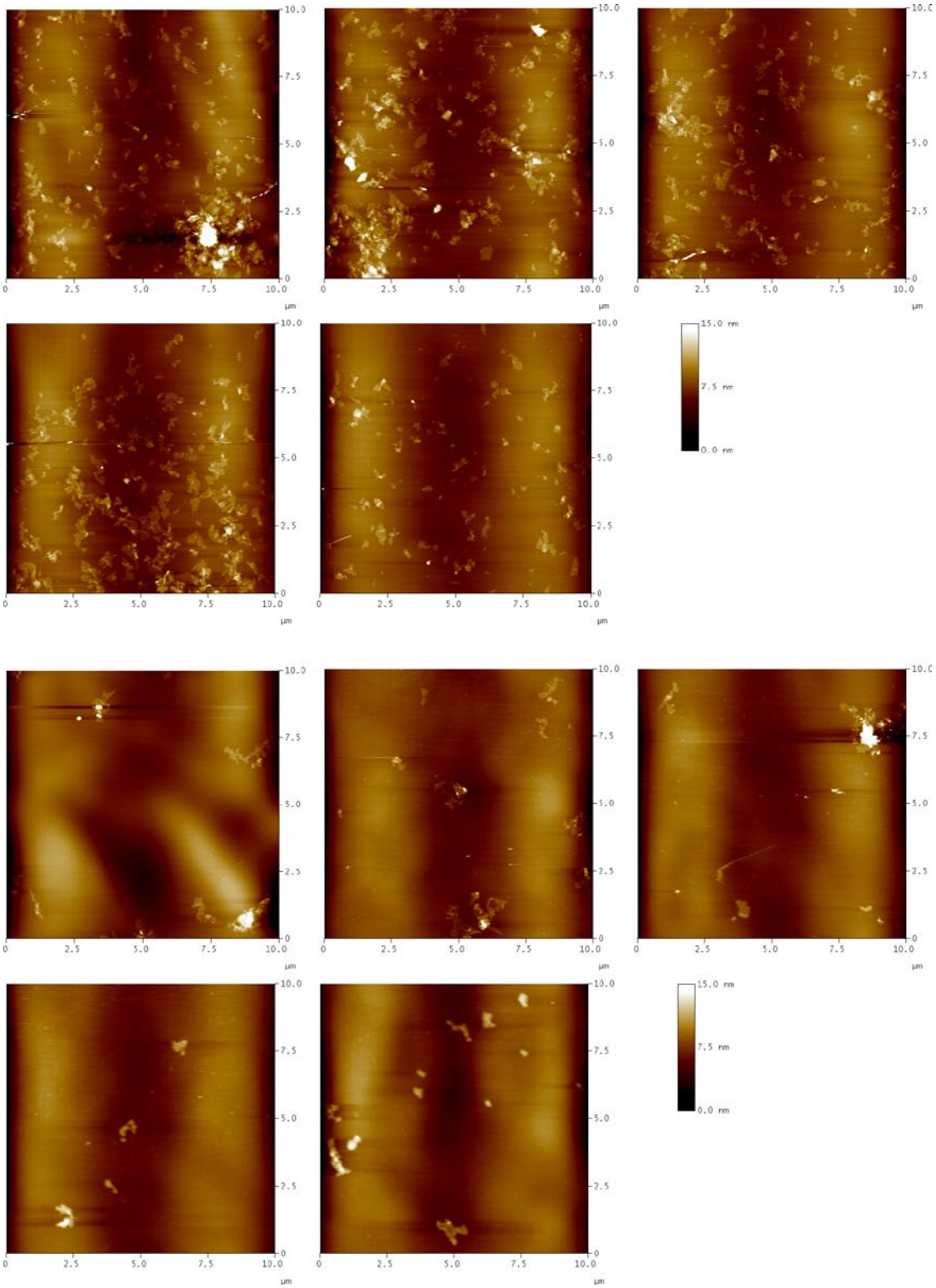

Figure 5-1. *Images of Na-montmorillonite on mica measured in air in contact mode. In the top 5 images the sample was prepared from a solution containing 100 mg/dm³ Na-montmorillonite. The sample shown in the bottom 5 images were prepared from a solution containing 10 mg/dm³ Na-montmorillonite.*

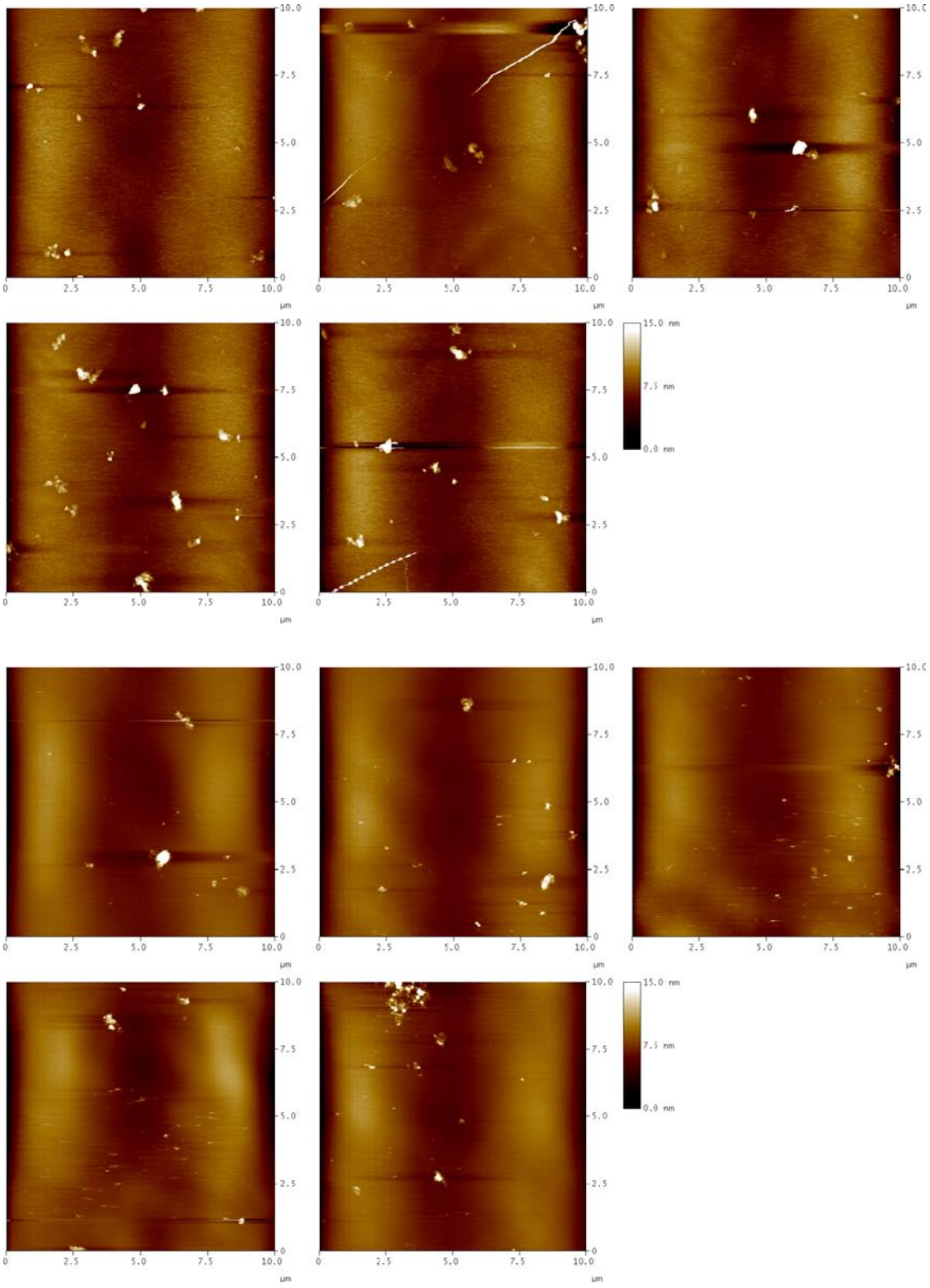

Figure 5-2. *Images of Ca-montmorillonite on mica measured in air in contact mode. In the top 5 images the sample was prepared from a solution containing 100 mg/dm³ Ca-montmorillonite. The bottom 5 images were prepared from a solution 10 mg/dm³ Ca-montmorillonite.*

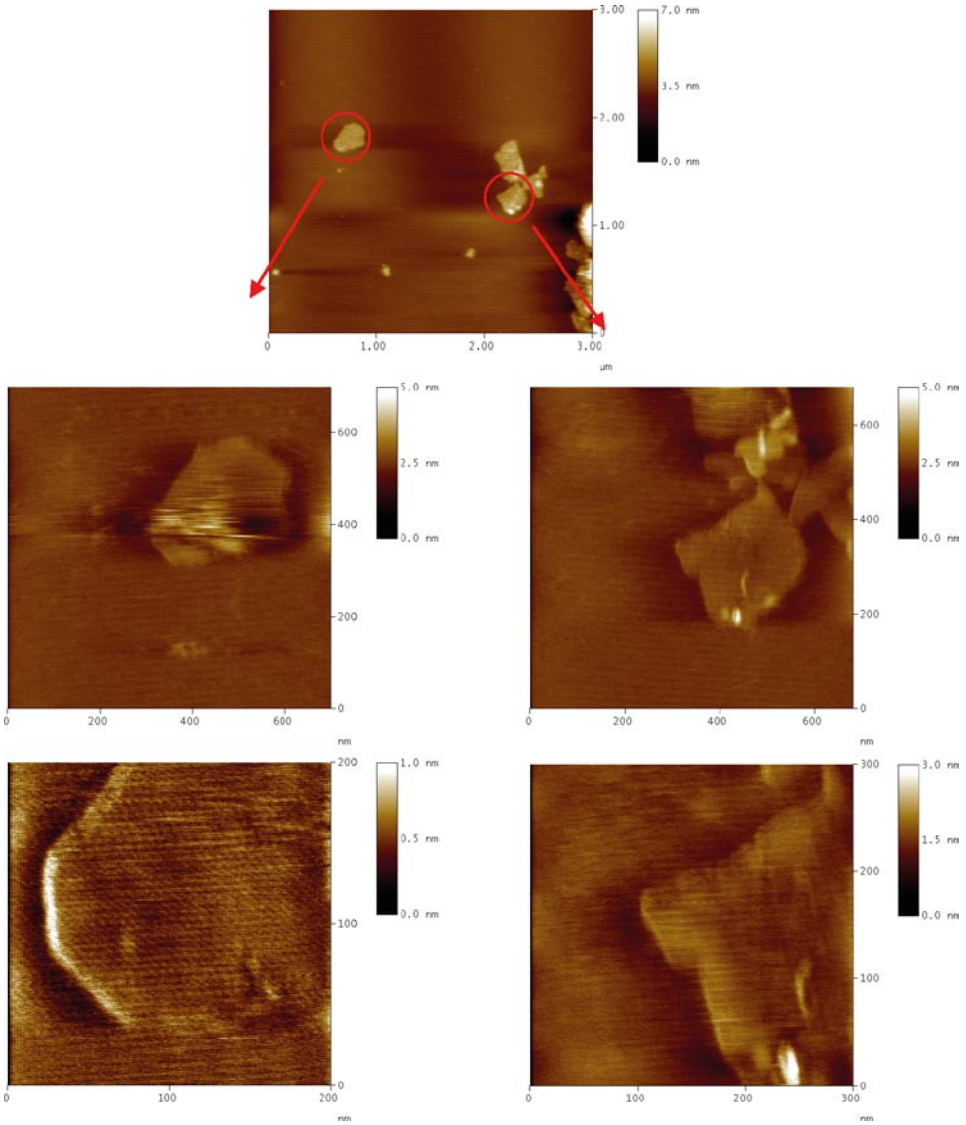

Figure 5-3. *Images of Na-montmorillonite on mica in air. The figure illustrates how images on different length scales were used to navigate to individual particles for imaging at smaller length scales and for positioning the force raster measurements.*

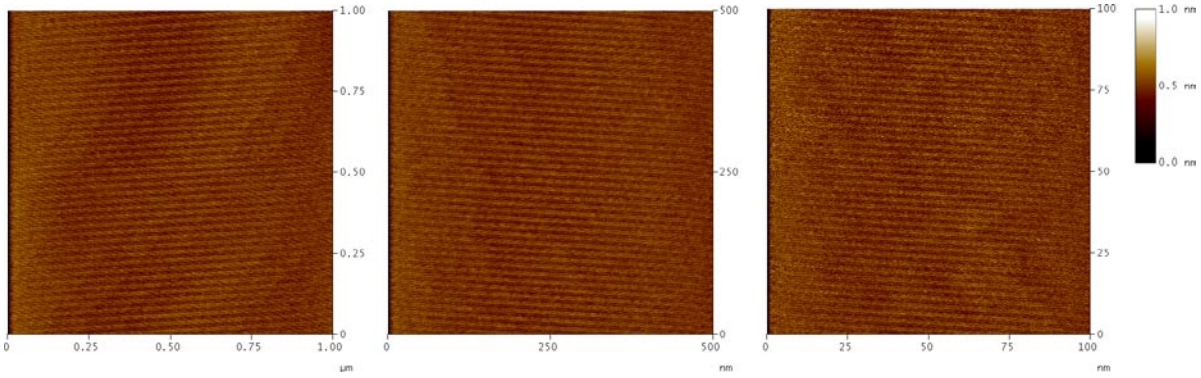

Figure 5-4. *Contact mode height images of mica at different length scales.*

5.4 Images 100×100 nm

Different Na-montmorillonite particles imaged over the size 100×100 nm are presented in Figure 5-5. By comparing the images in Figure 5-5 with images of mica at the same length scale (Figure 5-4), it is clear that the montmorillonite particle is not completely flat. There are height variations (~ 0.5 nm) that may originate from one of the following reasons:

- Some molecules being couched between the montmorillonite particle and mica; for instance cations or trapped water.
- The morphology of the montmorillonite particles is inhomogeneous.
- Different distribution of cations within the octahedral sheets between the two outer tetrahedral sheets building up the montmorillonite single particle.

Importantly, all of these possible explanations lead to the same conclusion; the Na-montmorillonite particle surface is inhomogeneous. Thus, to model the interactions between montmorillonite as occurring between ideally flat surfaces with homogeneous charge distribution will be a simplification and is not expected to capture all features of the real system.

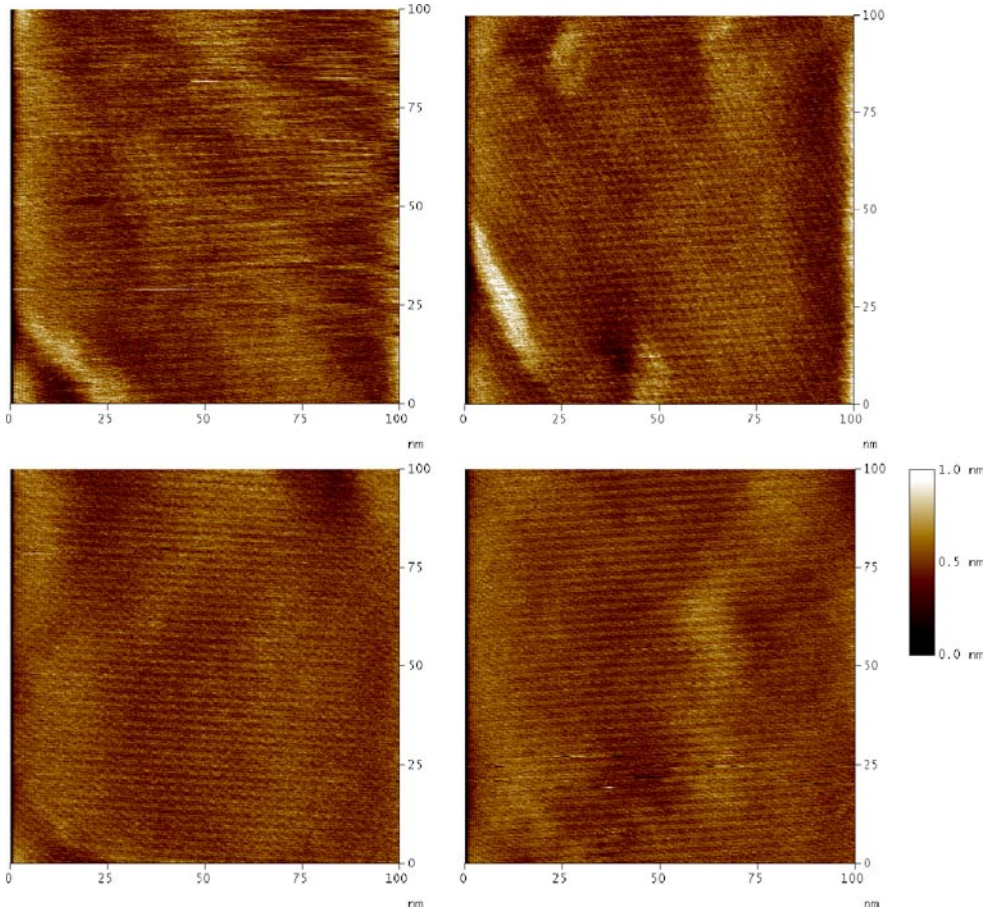

Figure 5-5. *Contact mode height images of Na-montmorillonite over the size of 100×100 nm, measured in air on different individual particles.*

5.5 Force curves and force raster

Typical force curves measured in air and water between the silica tip and mica, respectively between the tip and Na-montmorillonite are presented in Figure 5-6. No electrostatic double layer force is observed in water, but only a jump into contact from a distance between 3 and 15 nm. The jump in distance is longer in air compared to the jump in distance in water. One reason for this is the higher van der Waals interaction in air compared to in water. The reason that no electrostatic double-layer repulsion is observed is the small radius of the tip; in our case a tip with radius of curvature in the range 5–15 nm was used. We note that in our case a force of 10 nN corresponds to a force normalized by radius (F/R) in the order of 650 to 2,000 mN/m. In comparison, electrical double-layer forces between a micrometer sized silica probe and a mica surface is in the range 10 mN/m. Hence, it is clear that with a sharp tip it is not possible to detect the electrostatic repulsion. This can, however, be done if a colloidal probe is used instead of the tip.

In Figure 5-7 – 5-8 we present force raster measurements, displaying all approach and retraction force curves measured in each raster together with attraction and adhesion maps. The attraction map shows the minimum value of the approach force curve. This is essentially a measure of the range of the attractive force since the depth equals the spring constant multiplied by the jump-in distance. The adhesion force measured on retraction is, on the other hand, a direct measure of the attractive force when the tip is in contact with the substrate. Figure 5-8 also includes images around the area over which the force raster was measured, illustrating the degree of drift during the measurements. Figure 5-7 shows the force raster on mica in water. The data in this figure illustrates the degree of reproducibility that can be expected for a (close to) perfect homogeneous surface. In Figure 5-7 it is not useful to present images of the sample surface since it is really flat, recall Figure 5-4.

In Figure 5-8 force raster in water of Na-montmorillonite are displayed together with images of the raster area before and after the force raster experiment. In water the drift of the sample are pronounced compared to measurement in air (recall Figure 4-5). The reason is that the sample is clamped with an o-ring to allow the water to stay on the sample surface. While scanning the sample some tension in the o-ring causes the sample to drift more compared to the drift caused by the piezo material of the scanner. We note that the attraction maps measured on approach, given by the range of the attraction, are relatively homogeneous for both mica and Na-montmorillonite. This is expected since it reflects the strength of the long-range van der Waals force. However, the attraction map obtained for Na-montmorillonite is somewhat less homogeneous than that obtained for mica, giving an indication of a less homogeneous surface for Na-montmorillonite. The adhesion maps, that describe the more local interaction between the tip and the surface are less homogeneous. The spread in adhesion values obtained for mica shall be regarded as being due to the lattice structure of mica and the irregular distribution of cations on the surface. It reflects the reproducibility for an ideal clay mineral with which the data for montmorillonite should be compared. The variation in adhesion between the tip and Na-montmorillonite in water is significantly larger than between mica and the tip, and displays a more patterned feature (rather than random), which is consistent with the less homogeneous nature of the Na-montmorillonite surface displayed in the images reported in Figure 5-5. Thus, both imaging and force raster measurements show that the Na-montmorillonite surface is less homogeneous than the mica surface.

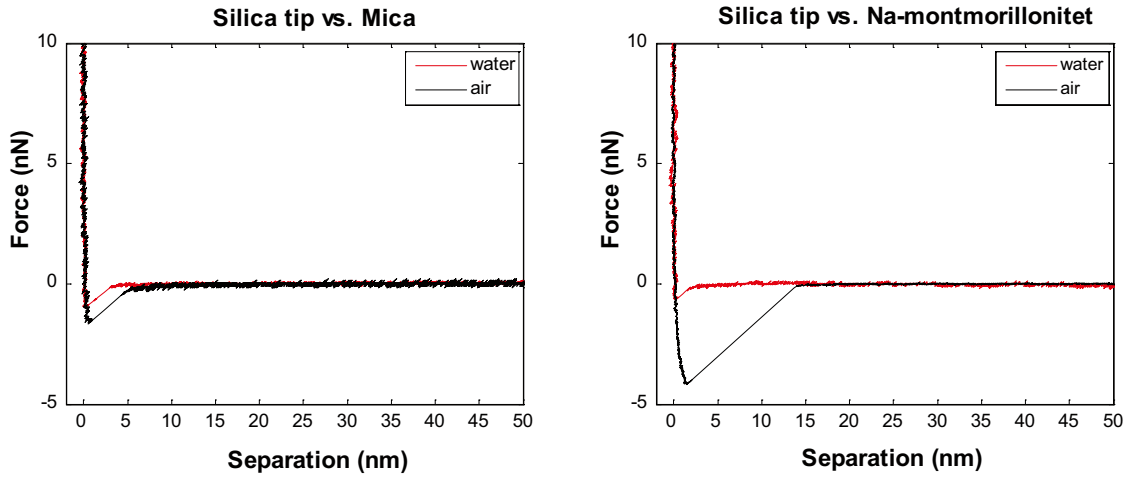

Figure 5-6. *Force profile when a silica tip is approaching a mica surface (left graph), respectively a Na-montmorillonite particle (right graph), measured in both air and water.*

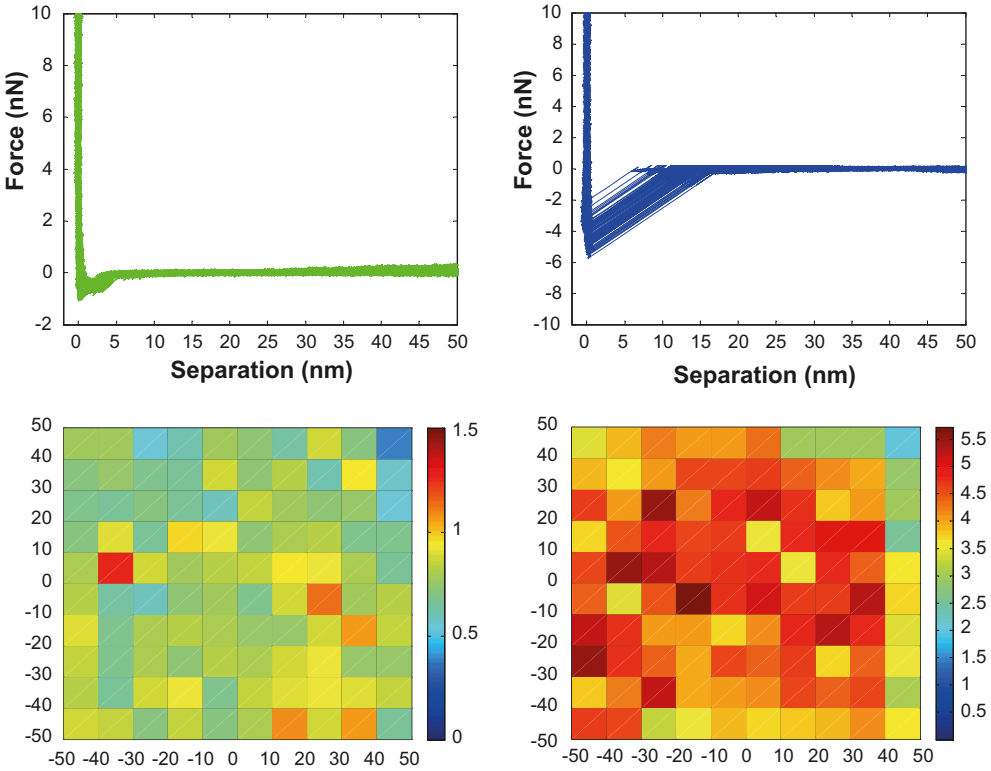

Figure 5-7. *Force profiles when a silica tip is approaching (top left) and retracting from (top right) a mica surface in water measured as a force raster, displaying 100 curves on different positions on the mica surface. The maps display the attraction on approach (corresponding to the range of the attraction) (left, and the adhesion value (right) measured on retraction at different positions on the surface.*

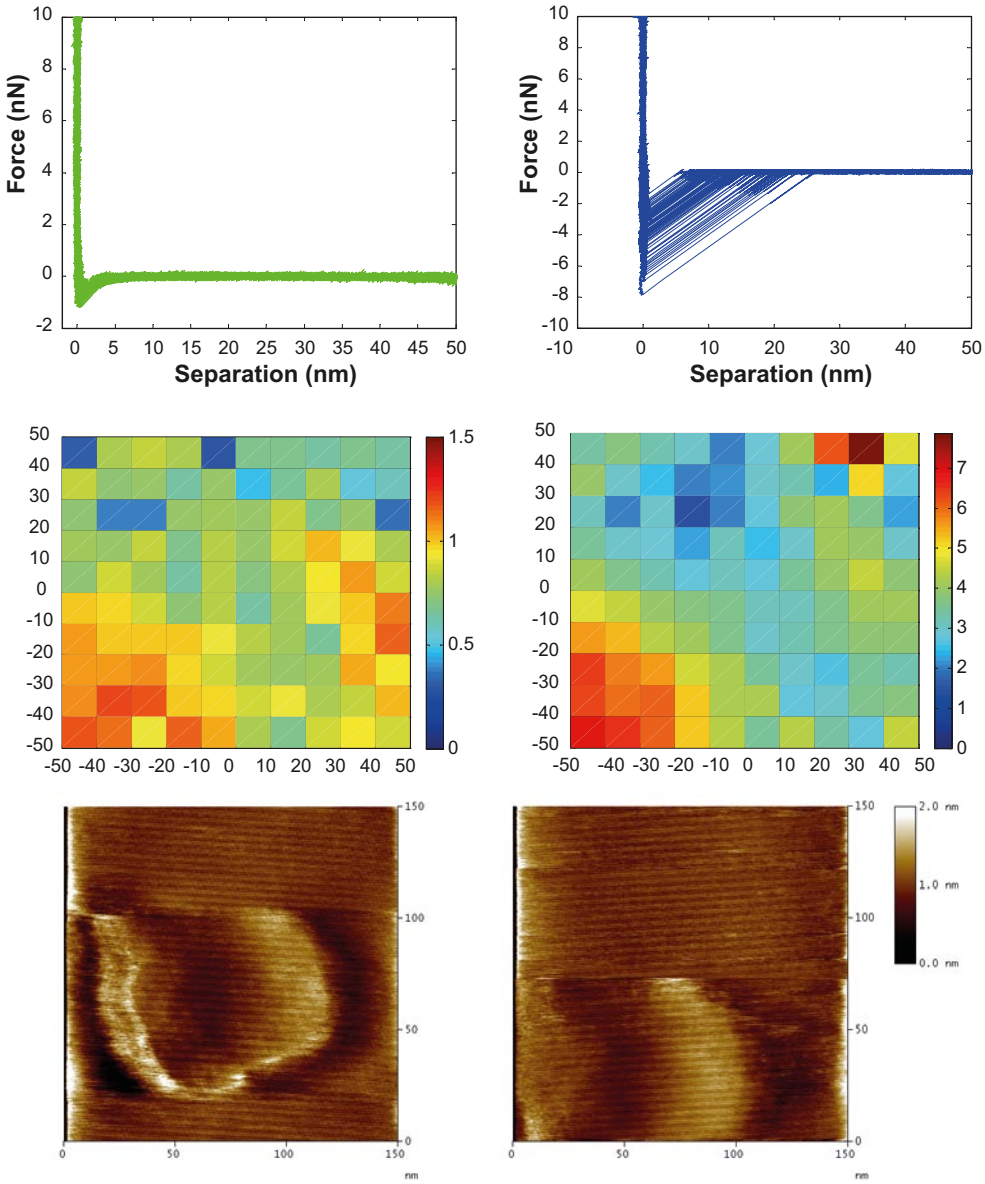

Figure 5-8. *Force profiles when a silica tip is approaching (top left) and retracting (top right) a Na-montmorillonite surface in water measured as a force raster, displaying 100 curves on different position on the montmorillonite surface. The maps (middle row) display the attraction (left) and adhesion value (right) value at the different positions on the surface. Bottom left image displays the position of the Na-montmorillonite particle just before the force raster measurements and the bottom right image after the force raster measurements.*

5.6 Atomic resolution images in air and water

The atomic lattice can be imaged on mica with contact mode AFM both in air and water, see Figure 5-9. The hexagonal close packed structure is clearly seen in these images. We have also successfully imaged the lattice structure of Na- and Ca-montmorillonite, Figures 5-10 and 5-11.

The distance between the lattice spots are on average the same on mica and on Na- and Ca-montmorillonite. This is not surprising since mica and montmorillonite have the same lattice structure in the tetrahedral plane.

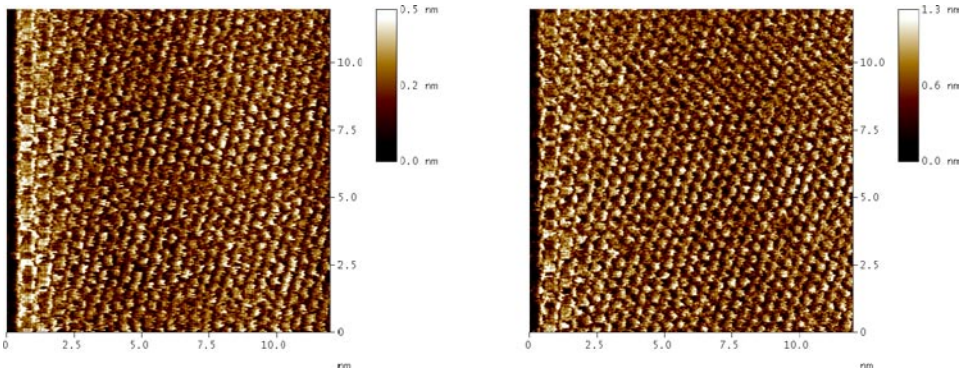

Figure 5-9. *Atomic lattice resolution of mica (deflection images), left in air and right in water.*

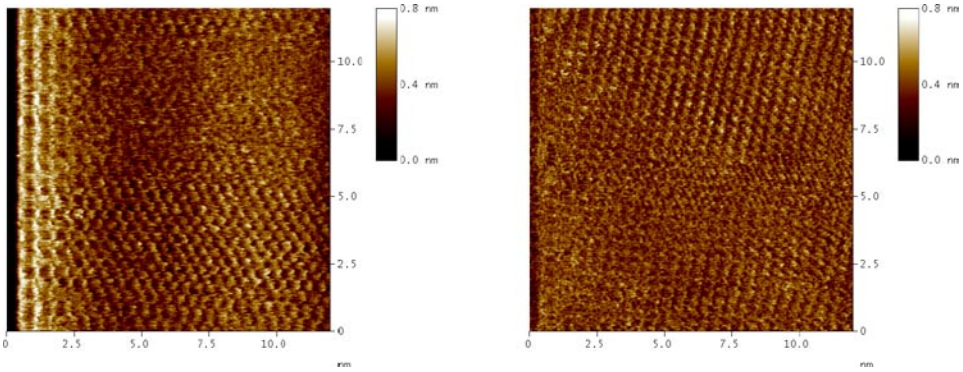

Figure 5-10. *Atomic lattice resolution of Na-montmorillonite (deflection images), left in air and right in water.*

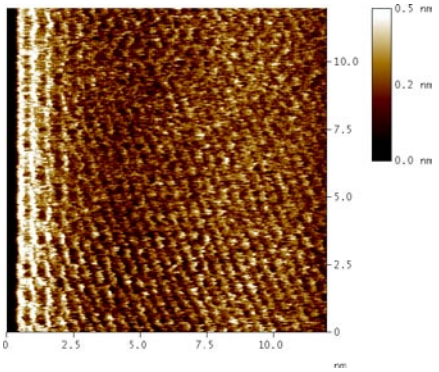

Figure 5-11. *Atomic lattice resolution of Ca-montmorillonite (deflection image) in air.*

6 Conclusions

To be able to measure and investigate separate montmorillonite particles they need to be adhered to an atomically flat substrate such as mica. A suitable concentration of the montmorillonite dispersion is 100mg/dm^3. Samples are easily prepared by placing a small drop of 4µl of the dispersion on a freshly cleaved mica surface and letting the water evaporate.

Samples prepared in the way described above are possible to image in AFM both with tapping and contact mode. The advantage of using contact mode imaging in this project is that one can do imaging and forces measurements with the same tip. This has enabled the navigation to individual montmorillonite particles and thus to perform force raster, 100×100 nm images, and also atomic lattice resolution images (12×12 nm). However, measurements in water at this small length scale are problematic due to the extra drift introduced due to the o-ring that is used to contain the liquid on the surface.

In images of the size 100×100 nm we can identify variations on the Na-montmorillonite particle surfaces. This variation is attributed to inhomogenities of the montmorillonite particles. The inhomogeneous nature of the montmorillonite surface is also clearly demonstrated by the force raster measurements. Thus, any attempt to model the interaction between montmorillonite particles using a model of ideally flat surfaces with a homogeneous charge distribution is an oversimplification. We suggest that this explains the differences between measured swelling pressures and modelling results.

7 Future recommendations

Study the interaction between colloidal silica particles and montmorillonite by imaging and/or colloidal probe AFM measurements. Additionally, QCM-D might be of interest to investigate if and to what extent silica particles bind to montmorillonite in liquid media.

Evaluate the effects of the charged edges of montmorillonite by adsorbing particles to mica and investigate if the particles are removed by increasing the pH in the surrounding medium. Alternatively, evaluate if montmorillonite adsorbs to mica at different pH-values.

8 References

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