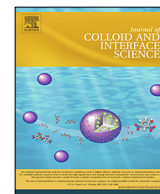




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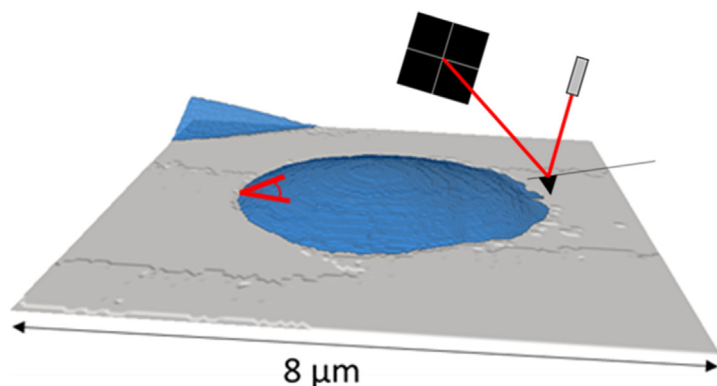
Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

Atomic force microscopy for the characterisation of pinning effects of seawater micro-droplets in *n*-decane on a calcite surfaceG.C. Savulescu^a, M. Rücker^{b,c,*}, A. Scanziani^d, R. Pini^b, A. Georgiadis^{b,e}, P.F. Luckham^b^a Norwegian University of Science and Technology, 7491 Trondheim, Norway^b Chemical Engineering, Imperial College London, SW7 2AZ, UK^c Mechanical Engineering, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands^d Earth Science and Engineering, Imperial College London, SW7 2AZ, UK^e Shell Global Solutions International B.V., 2288 GS Rijswijk, The Netherlands

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 28 November 2020

Revised 28 January 2021

Accepted 15 February 2021

Available online 22 February 2021

Keywords:

Atomic force microscopy

Wetting

Contact angle

ABSTRACT

Hypothesis: Roughness is an important parameter in applications where wetting needs to be characterized. Micro-computed tomography is commonly used to characterize wetting in porous media but the main limitation of this approach is the incapacity to identify nanoscale roughness. Atomic force microscopy, AFM, however, has been used to characterize the topography of surfaces down to the molecular scale. Here we investigate the potential of using AFM to characterize wetting behavior at the nanoscale.

Experiments: Droplets of water on cleaved calcite under decane were imaged using quantitative imaging QI atomic force microscopy where a force-distance curve is obtained at every pixel.

Findings: When the AFM tip passed through the water droplet surface, an attraction was observed due to capillary effects, such that the thickness of the water film was estimated and hence the profile of the droplet obtained. This enables parameters such as the contact angle and contact angle distribution to be obtained at a nanometer scale. The contact angles around the 3-phase contact line are found to be quasi-symmetrically distributed between 10–30°. A correlation between the height profile of the surface and contact angle distribution demonstrates a quasi-proportional relationship between roughness on the calcite surface and contact angle.

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Abbreviations: AFM, atomic force microscopy; QI, quantitative imaging.

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<https://doi.org/10.1016/j.jcis.2021.02.070>

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1. Introduction

The topic of wetting has received considerable interest in recent years of both fundamental and applied science. The effectiveness of many processes can be enhanced by ensuring that the liquid wets a surface in the desired way, whether that be ensuring that a pesticide fully wets the surface of a leaf in crop spraying, a lubricant wets the moving parts of an engine, or that a liquid, generally water, simply rolls off the surface of a window or paint in self-cleaning applications. The preferential wetting of one liquid over another in a two-liquid phase system is crucial in oil recovery, where it is desirable for water to wet the surface in preference to the oil phase, such that the oil phase is displaced by the water in the reservoir and hence is recovered. Wetting is commonly assessed through a contact angle measurement, where the contact angle is the angle made by one fluid in contact with a solid in the presence of a second fluid, measured through the denser fluid. Contact angles can be measured in a variety of ways, but generally, the macroscopic contact angle is measured through taking an image of a droplet and fitting an angle to the interfaces, where the solid can be a flat plate or a fibre. Under these circumstances what is happening on a microscopic or molecular scale is masked by the resolution available. What may appear smooth at the micro-scale may be rough at the nanometre scale for example.

Since its conception in the early 1980's atomic force microscopy, AFM has been used to obtain molecular-scale resolution of materials in liquids and hence in many instances in their natural environment. The techniques have also been used as a local surfaces force detector and for measuring the interaction between particles, various functional groups, droplets and surfaces, using a methodology which has become known as force spectroscopy [1–3]. AFM can also be used to image soft surfaces and particles, including droplets which has enabled the technique to measure contact angles of microscopic droplets [4,5]. This is important because in small droplets pinning and line tension effects at the three-phase contact line becomes significant compared to surface or interfacial tension as the droplet surface area becomes smaller compared to the circumference of the droplet [6,7]. Recently Deng et al [5] have used tapping mode AFM to image micron-sized water droplets on quartz in water vapour saturated air. Despite the fact that water is generally reckoned to totally wet quartz, it was observed that the contact angles of the drop varied between 28 and 50°, which was ascribed to the nanoscopic roughness of the polished surface estimated to be of order 10 nm. One issue with this approach, however, is that it gives no measure of the roughness of the surface directly under the drop and even small scale roughness has the potential to give pinning points for the drop which would alter the apparent contact angle that the liquid makes with the surface.

In the approach used in this paper, we utilise a JPK nano-wizard instrument in quantitative imaging (QI) mode to overcome this drawback. In QI mode a force-distance profile is obtained at every pixel of the image. When the AFM tip touches the droplet surface capillarity effects attracts the tip towards the surface, giving rise to an attractive force, which is detected in the force-distance profiles [8–11]. The distance from the onset of the attraction to the contact on the solid surface where a very steep repulsion is observed, corresponds to the thickness of the liquid film, hence by scanning over the entire droplet the shape and dimensions of the droplet can be obtained, together with the local topography of the surface underneath the liquid film [8,11,12]. In this paper, we apply this methodology to investigate seawater droplets on a calcite surface immersed in oil (decane). The calcite has some small cleavage steps in the surface, which the technique can determine together with the geometry of the droplet and hence the contact angle of the seawater droplet on the cleaved calcite surface.

1.1. Effect of pinning on droplet shape

On an ideal flat surface and chemically homogenous surface a droplet of sufficient size, where line tension effects could be neglected, the droplet would form the shape of a spherical cap (Fig. 1A). In this model, the contact angle along the 3 phase contact-line formed by the solid, the drop and the fluid surrounding it, would only show one fixed value specific to the chemical characteristics of the system, which is often referred to as an intrinsic contact angle Θ_i .

However, real surfaces always show a certain degree of roughness of varying intensity. At the smallest scale, roughness may be related to molecular or crystallographic characteristics of the solid. At larger scales, mechanical and chemical alteration may affect the surface structure [13]. The effect of roughness at the various length scales is particularly known from goniometer measurements, where the contact angle measured referred to as apparent contact angle Θ^* tends to vary even on surfaces considered flat such as mica or calcite [14–16]. The reason is, that on a rough surface pinning effects allow for multiple fluid arrangements, honouring the specifics of the intrinsic contact angle as illustrated in Fig. 1B. The droplet shape is therefore strongly depended on the deposition history. Correspondingly, wetting assessments often include measurements, from which advancing and receding contact angles are extracted [17–19]. Yet, this method does not reveal where and how the contact lines pin along the surface.

In this study, we used novel image processing techniques for AFM to obtain 3D visualization of micro-droplets on surfaces and to assess how and to which extend the nano-scale surface structure facilitates pinning effects.

2. Materials and methods

2.1. Sample preparation

The substrate used was the mineral calcite CaCO_3 (Iceland spar). It has perfect cleavage on the morphological coordinates [1 0 1 1] in all 3 directions at an angle of 74°. For sample preparation the substrate was cleaved in brine, of the composition displayed in Table 1, to prevent exposure to air. The corresponding electrolytes were obtained from Sigma Aldrich and were analytical grade material. The brine composition, taken from [20], represents a seawater composition. Afterwards, the brine was displaced with *n*-decane using a syringe and placed into an *n*-decane filled petri-dish made of glass. The measurements were conducted at room temperature (appr. 22 °C) right after sample preparation (within 8 h time frame). It needs to be noted, that the sample preparation procedure outlined showed no repeatability as the droplets obtained varied from the size of several mm to non-existing.

The reason may lie in both, the sensitivity of wetting properties of a fluid–fluid-system to impurities and heterogeneities, potential dissolution and variation in roughness obtained by cleavage and to the physical mechanism applied for the creation of the micro-droplets. Further, a reference scan of the substrate in decane was obtained.

2.2. Atomic force microscopy (AFM)

AFM is based on mechanical imaging by raster-scanning a surface with a sharp tip attached to the end of a cantilever. The tip interacts with the underlying surface through various intermolecular forces. These forces lead to a bending of the cantilever, which is monitored by a laser and a detector. This technique allows very precise visualization of the topography of a surface down to the atomic scale [21–23] and also the detection of various physical

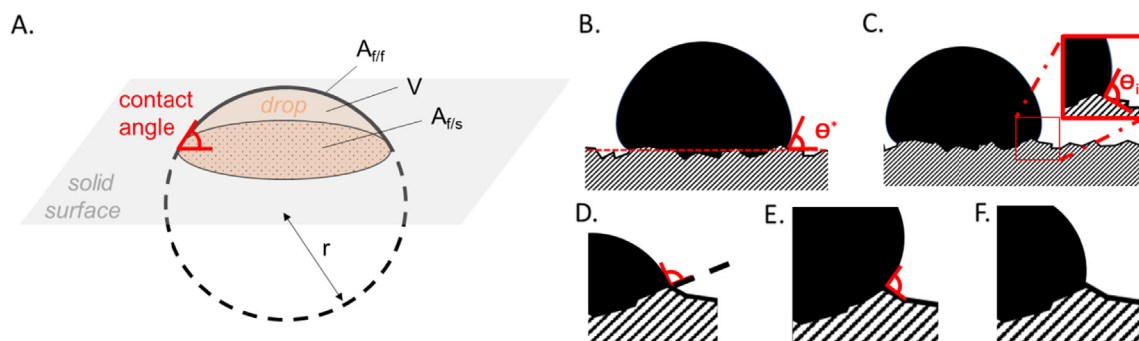


Fig. 1. Contact angle from a spherical cap model for an ideal droplet (A) and deviations in contact angles due to surface roughness (B–F).

Table 1

Brine composition.

Ion	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl [−]	SO ₄ ^{2−}	HCO ₃ [−]	Ionic strength [mol/L]	pH
[mg/L]	13,404	483	1618	508	24,141	3384	176	0.869	8.0

properties related to the molecular interactions when the tip is close to the surface. In this study, we used a NanoWizard 4 Nanoscience AFM from JPK instruments (now Bruker) and Quantitative Imaging Mode (QITM-mode) is provided, with which a force-distance curve is recorded for every pixel in parallel to the height-map. In contrast to previous studies imaging microscale droplets with AFM [4,5,24], we penetrated the fluid–fluid interface of the droplet and moved the tip through the drop until the signal indicated contact with the calcite surface similar to the workflows described by [12] and [10]. The approach force-distance curves are recorded at each pixel, detect the oil–brine interface due to capillary action on the tip and hence allow the creation of a 3D visualization of the microdroplet. The scans were obtained using a silicon PPP-NCHAuD tip from NANOSensorsTM, with a nominal force constant of 42 N/m, so that any molecular interactions of the tip with the fluid/fluid interface do not affect the deflection. The image processing, visualisation and analysis were conducted with the JPK-SPM data processing software (JPK instruments, now Bruker), ImageJ (Fiji) [25], MATLAB (R2018b) and AVIZO 9.0(a) and is described in detail in Supplement A.

3. Results and discussion

3.1. 3D visualization of micro-droplets with AFM

Fig. 2 displays the height (A) and adhesion images (B) obtained from a micro-droplet experiment. A freshly cleaved calcite substrate measured in decane for comparison can be found in Supplement B. As the tip pushes through the microdroplets, the height image detected represents the surface of the cleaved calcite underneath and shows a height variation of up to 36 nm along 40 μm × 40 μm (Fig. 2C), which is well in line with the values obtained for cleaved calcite in absence of microdroplets (Supplement C). The high noise level in the height image of the microdroplet experiments, is a result of the increased z-range of 5 μm, compared to 0.3 μm usually used, necessary to overcome the adhesion forces of the micro-droplet on the tip. The corresponding adhesion image is displayed in Fig. 2B. The inhomogeneity in adhesion from the rim to the centre of the droplet is a result of capillary forces due to the hydrophilic nature of the tip [12,26]. Due to the pyramidal shape of the tip, the surface area, along which the capillary force acts, increases, the thicker the brine-layer the tip passes through (Fig. 2D–F).

The droplets observed within the adhesion image are also reflected in the height image through a drop in height by approx. 5 nm (Fig. 2A,C). We believe that this artefact occurs as during the approach, where the capillary forces pull the tip into contact with the substrate (Fig. 2D), creating a more robust height signal as the slight repulsion observed in the areas away from the microdroplets (Fig. 2F). Also, possible dissolution of the calcite in seawater could provide an explanation for the drop in height observed [27,28].

However, the most important effect of the capillary forces which the brine droplets have on the tip is the jump-in observed, once the tip gets in contact with the fluid–fluid interface (Fig. 2D). This jump-in behaviour can be easily identified through the drop of the force below $F = 0$ as indicated in Figure XYZ, prior to the contact with the surface and therefore allows the reconstruction of the microdroplet. Fig. 2G displays the cross-section of the droplet which was manually obtained from the force-distance curves at each pixel. Fig. 2H displays the automated 3D reconstruction obtained through batch processing the force-distance curve to obtain the jump in-contact at each pixel and masking the result with threshold segmentation tool provided by ImageJ, to remove the noise created outside the droplet. The image height information of the droplet and the calcite substrate were then combined into a 3D voxelized image with a voxel size of 0.0383 × 0.0383 × 0.0383 μm³, filtered using a median filter and the closing function to remove image artefacts and visualized with AVIZO. The full workflow for this procedure is described in Supplement A and image artefacts are explained in Supplement C. The results show 6 full droplets of different size, which were analysed further to assess the impact of drop size and the underlying surface roughness on the morphology and contact angles of micro-droplets at the nanometer scale.

3.2. Droplet shape variation due to pinning

Assuming a homogenous wetting without any pinning artefacts and ignoring contact line effects, all droplets should have the shape of a spherical cap which relate to an intrinsic contact angle through

$$r - h = r \cos(\theta_i) \quad (1)$$

with r being the radius of the hypothetical sphere and h the maximum height of the drop. Correspondingly, the relation of volume to curvature $k = 1/r$, fluid–fluid interfacial area and fluid–solid inter-

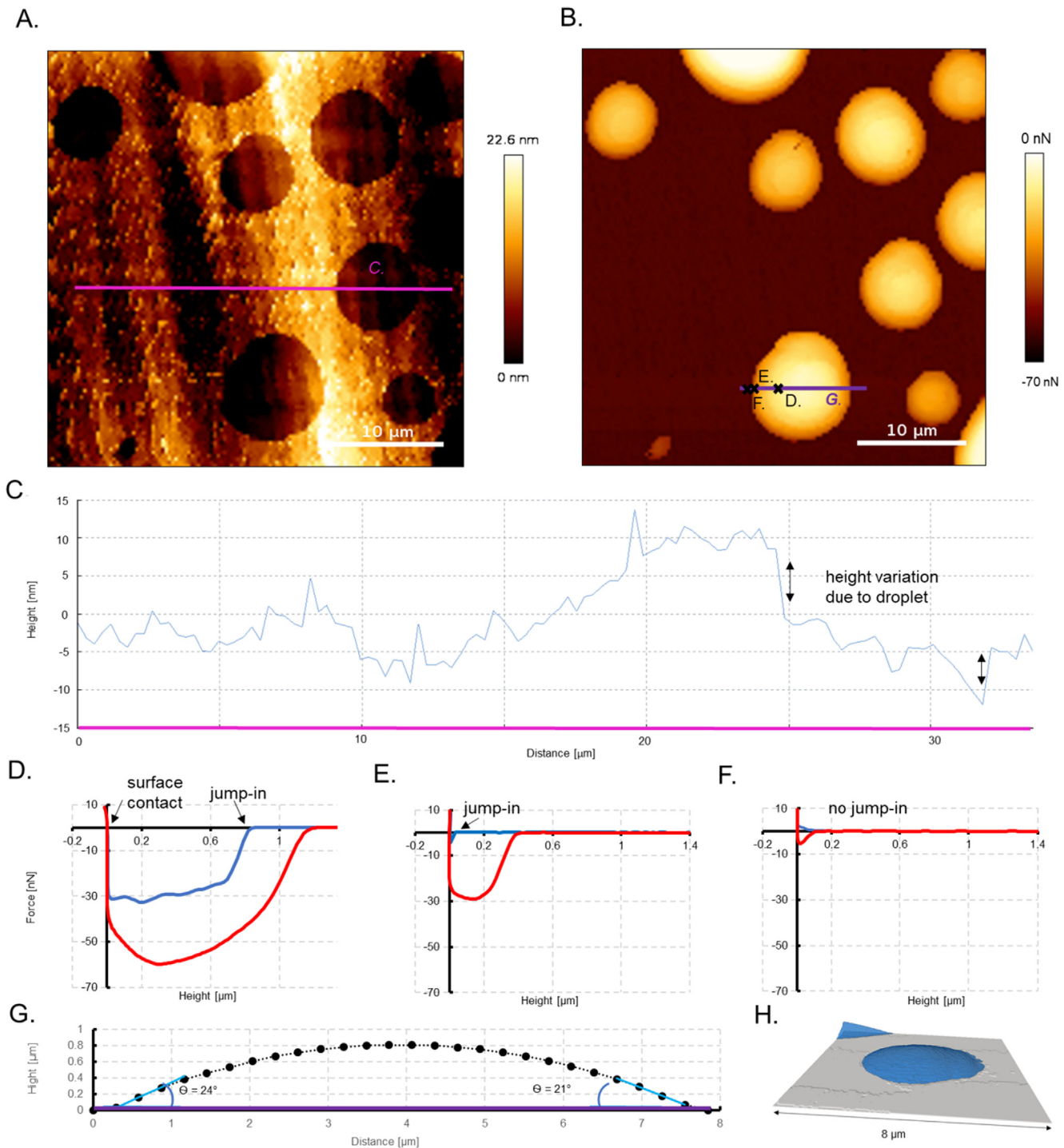


Fig. 2. The height image (A) and the adhesion image (B) show a response to the microdroplets present. In the height image, the presence of the droplet creates a shift of 5 nm, as illustrated in the cross-section (C). The steps of the calcite surface itself are of similar size, but can easily be distinguished due to the round structure of the droplet. The adhesion variation where the droplets are present is due to variation in droplet thickness. The more the pyramidal-shaped tip is submerged in the droplet, the stronger capillary forces of the droplets on the tip during retract as shown in the force-distance curves from different locations (D,E,F). In this force-distance curves, the blue curve refers to the approach and the red curve to the retract of the tip. More important than the adhesion force, is however the jump-in location, which occurs when the tip is getting in contact with the microdroplet during the approach. The height at which this happens represents the fluid–fluid interface. Retrieving this value for each force-distance curve allows for the reconstruction of the droplet as shown by the cross-section obtained through manual interpretation (I) and the 3D reconstruction using automated interpretation (J). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

facial area of the drop should be reflected for all sizes following the equations:

$$V = \frac{1}{3} \pi r^3 (2 - 3 \sin(\theta_i) + \sin^3(\theta_i)) \quad (2)$$

$$A_{F/F} = 2\pi r^2 (1 - \cos(\theta_i)) \quad (3)$$

$$A_{F/S} = \pi r^2 \sin^2(\theta_i) \quad (4)$$

with V being the volume and $A_{F/F}$ the fluid/fluid interfacial area and $A_{F/S}$ the fluid/solid interfacial area. The reconstructed voxelized image was used to determine the respective values.

In Fig. 3 the relation between those different parameters is plotted for the six complete droplets within the image in comparison to different spherical cap models for intrinsic contact angles varying from $\theta_i = 10^\circ$ to $\theta_i = 30^\circ$. The different droplets, though representing the same fluid–fluid–solid system, show a spread of contact angles, varying from $\Theta^* = 15^\circ$ to $\Theta^* = 20^\circ$, but also the same drops do show variation of apparent contact angle depending on the parameters used to for calculation.

For the volume-curvature relationship (Fig. 4B) all drops fall approximately on the line for a contact angle of $\Theta^* = 20^\circ$, however, for four of the droplets (green, yellow, dark blue and purple), the apparent contact angle falls to nearly $\Theta^* = 15^\circ$ when considering the volume – calcite surface area (Fig. 3C). For the red drop, the sphere fitting varies by 3° depending on whether the fluid/fluid interface (Fig. 3D) or fluid/solid interface (Fig. 3C) is used as the input. The deviation may be physical in nature, e.g. related to pinning due to sub-resolution roughness as explained at 1.1. Image artefacts and processing may also affect the accuracy of the measurement. An example is the yellow droplet, which shows a gap due to corrupted force-distance curves within this region. (further illustrations available in Supplement C). Optimization of the image processing workflow accounting for respective issues requires further investigation.

Yet, when comparing the droplets with directly with a spherical cap model reflecting the same volume as shown for the largest (red) drop in Fig. 4A, it becomes apparent that the deviation is related to a true distortion of the drop as no image artefact is apparent. The real drop shows a slight tilt (Fig. 4B) when compared to a perfect spherical cap of the same volume (Fig. 4C). While the majority of the voxels of the two droplets converge in the dis-

played overlap (Fig. 4A), significant deviations along the fluid–fluid surface can be observed. The distortion of the true drop therefore must be related to a variation of contact angles due to pinning associated with the roughness of the underlying surface.

3.3. Relation of contact angle distributions and underlying roughness

To investigate the distortion, we applied the automated contact angle measurement algorithm described in Scanziani et al. [29]. This code uses a 3D voxel-based image to extract the three-phase contact line, determine the cross-section perpendicular to it using a searching window of 10 voxels and fit a contact angle to the fluid/fluid and fluid/solid interface within the chosen distance to the three-phase contact line. Where either the three-phase contact line, fluid/fluid or fluid/solid interface cannot be extracted (e.g. due to noise or discontinuity) the script gives an error. Fig. 5A displays the contact angle distribution obtained for the red drop, the results for two additional drops are displayed in Supplement D. In total 911 contact angles were detected, with most of the values ranging between 5° and 35° . The average value for all the points on the contact line is 20.66° and the median is 21.01° . Under 3% of the values are outside the main interval, which can be attributed to image processing artefacts. The distribution takes a quasi-symmetric pattern: the highest count for the contact angles is in the proximity of the average value. The frequencies decrease quasi-linearly from 20° to both ends of the main range, 5° and 35° .

It is important to highlight here, that the contact angles detected are dismissing the nano-scale roughness of the calcite surface and therefore, truly represent small-scale apparent contact angles rather than intrinsic contact angles. The voxelization protocol comes with a decrease in z- resolution with one voxel having the size of $0.0383 \times 0.0383 \times 0.0383 \mu\text{m}^3$. Correspondingly, surface features which are larger than the voxel size are still visible

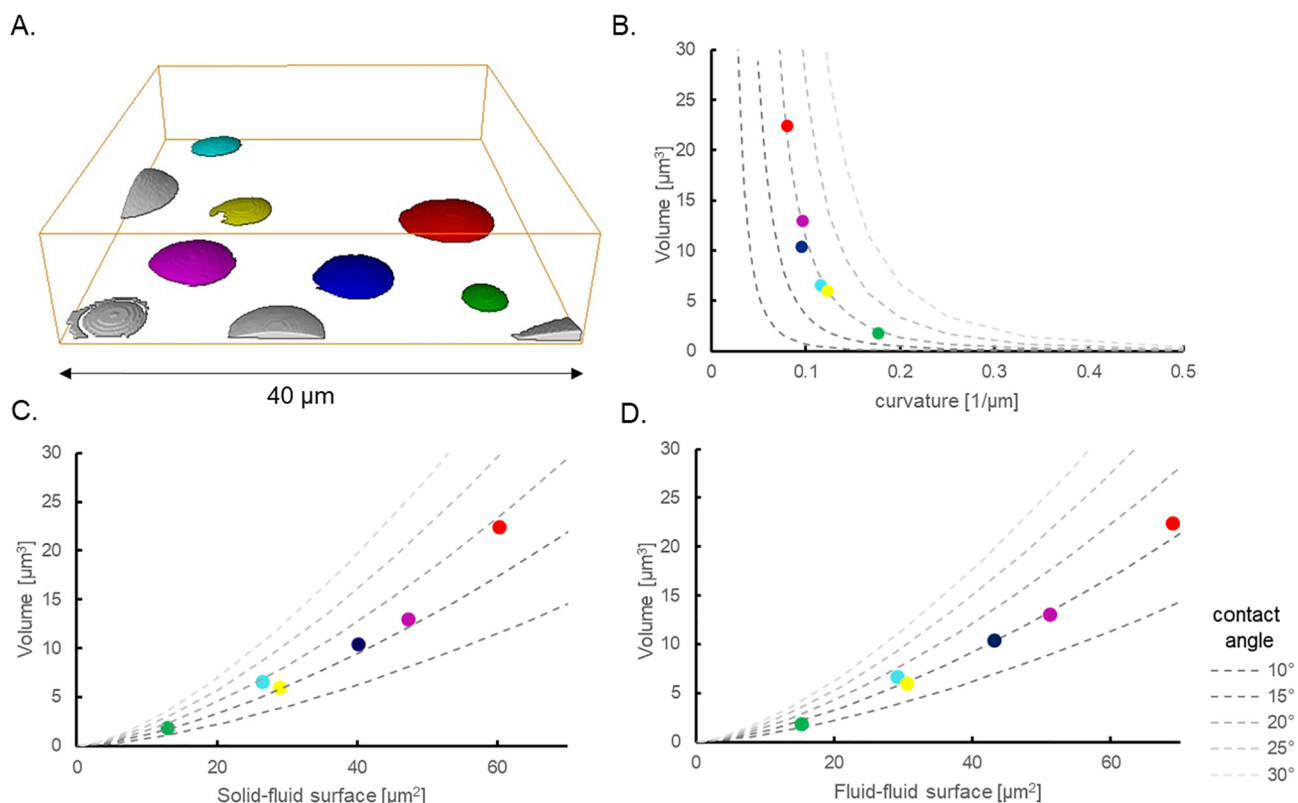


Fig. 3. 3D visualization of the measured drops (A) and the respective volume-curvature (B), volume- solid/fluid interface (C) and fluid/fluid interface (D) in comparison with a spherical cap model (dotted lines).

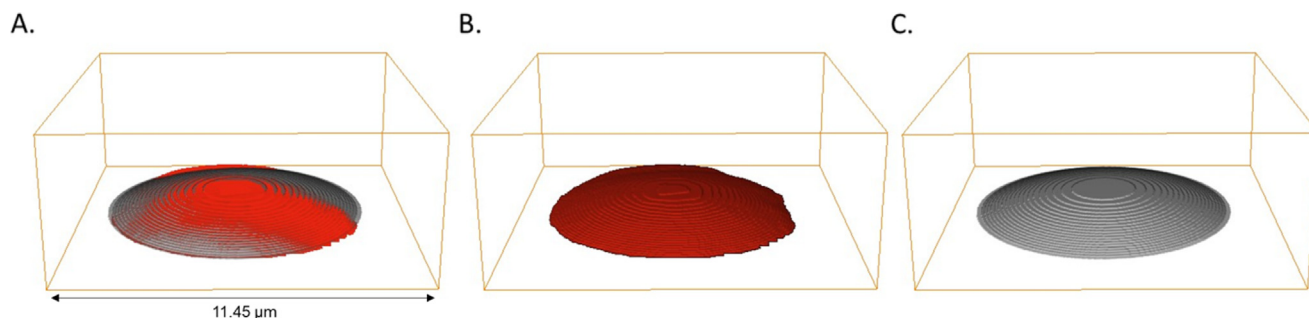


Fig. 4. Visualization of the measured drop (red) overlapped with a spherical cap model reflecting equal volume (grey) (A) and the individual respective shapes (B,C). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

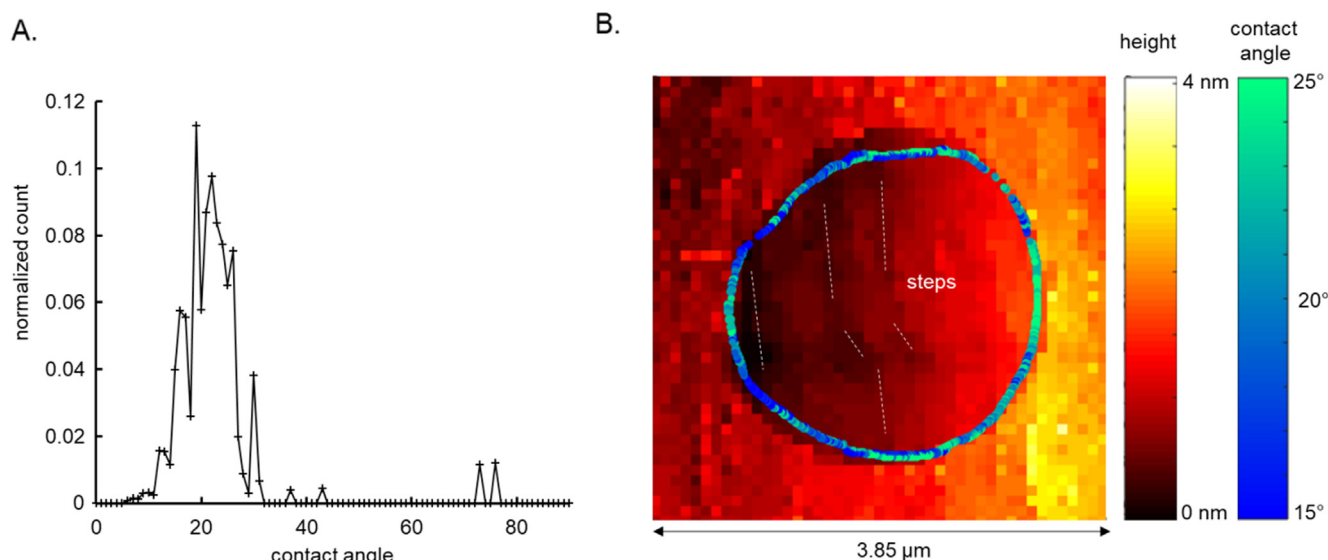


Fig. 5. Contact angle distribution obtained for the red drop (A) and spatial distribution of contact angles along the three-phase contact line, back-projected on the topographical image of the calcite surface. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in the reconstructed image, while sub-resolution roughness of the calcite surface, as displayed in Fig. 2A,C, with peak-to-valley roughness of $R_t = 36$ nm, average roughness of $R_a = 4.6$ nm and root mean square roughness of $R_q = 5.9$ nm are not accounted for.

To determine how the nano-scale surface features relate to the variation of apparent contact angles of the drop along the three-phase contact line, we back-projected the contact angle measurements on the original topographical AFM imaging of the calcite surface underneath the drop. The results are visualized in Fig. 5B.

As pointed out in section 3.1, the quality of the topographical image of the calcite surface is affected by the high z-length needed to capture the drops on top of it. Yet, the quality underneath the individual drops seems improved. For this reason, we focused on this region for further analysis. Underneath the drop, previously labelled red in Figs. 3 & 4, we identified 3 major steps indicated through a white dotted line in Fig. 5B, which becomes apparent through the steep shift from high (bright- yellow) to low (darker-brown) values.

The back-projected contact line points showed a slight misalignment with the droplet shape indicated by the improved image quality along the topographical image. This is likely due to image processing, incl. the voxelization and filtration steps. Yet, the distribution of high contact angles (green) and low contact angles (blue) observed, follow the surface pattern underneath.

In general, the contact angles appear higher (greener) on the right-hand side of the drop compared to the left-hand side which,

we assume is related to a slight tilt of the surface leading to the establishment of a more advancing angle on the right-hand side compared to a receding angle on the left-hand side. Further, we observe that the contact angles appear higher (greener) when the contact line is oriented parallel to the observed steps, whilst lower (blue) when the contact line is oriented orthogonally. Where the contact line is crossing the calcite steps, the contact line shows a change from high to low contact angles which corresponds approximately to the individual step width of the calcite. We assume this is due to capillary action with the crevasse of the step pushing the water into it and therewith making the contact angle appearing more water-wet at the larger length scale.

This visualization illustrates how very small surface features (nm-scale) affect the wetting behavior of droplets within the range of $22.47 \mu\text{m}^3$. The contact angle distribution along the three-phase contact line is thereby also controlled by the orientation of the surface features.

4. Conclusion

In this study we have assessed the effect of nano-scale surface features on the drop shape and wetting behaviour by introducing an experimental and image analysis workflow to image droplets using AFM at the same as the surface underneath, to create a 3D voxelized representation and a parameter analysis for various contact angle estimates building upon previous work by [8,10–12,29].

The data demonstrate deviations in contact angles within a narrow range of 15°–20° depending on the parameters used to evaluate the wetting, including the relationships between the volume of droplets, the surface area of the fluid–fluid and fluid–solid interfacial area, mean curvature and contact angle, which build on the assumption of a scaling related to the spherical shape of the droplet. Furthermore, direct contact angle measurements along the three-phase contact line, revealed that pinning at nm-sized calcite steps may be responsible for the macroscopic deviation observed.

The work has implications for future studies on wetting to the extent that it provides new insights into the behaviour of the three-phase contact line down to the nanometer scale, which cannot be assessed with techniques such as goniometer measurements due to lack in resolution [15]. The optimisation of the imaging and image processing methodology to improve accuracy, whilst minimizing artefacts, remains a topic to investigate. In the future, the nanoscale AFM investigation of wetting behaviour could be applied also for more complex surfaces or fluid/fluid/solid systems as they appear for instance in sub-surface reservoirs, where wetting is known to be a major controlling parameter, to predict the efficiency of applications such as CO₂- and H₂-storage, brine management, environmental remediation or oil-recovery and where currently, the link between the intrinsic wetting attributes and macro-scale response is missing [13,20,30–36].

CRediT authorship contribution statement

G.C. Savulescu: Methodology, Formal analysis, Investigation, Writing - original draft, Visualization. **M. Rücker:** Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Visualization, Supervision. **A. Scanziani:** Software. **R. Pini:** Resources, Funding acquisition. **A. Georgiadis:** Conceptualization, Supervision, Writing - review & editing. **P.F. Luckham:** Conceptualization, Supervision, Writing - original draft, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

Acknowledgements

We acknowledge Shell Global Solutions International B.V. for funding this work. Furthermore, we would like to thank Alex Winkel for the support in analysing the data and Huzaifa Patel & Yash G Nirmal for running repeat experiments.

Data statement

The authors confirm that the data supporting the findings of this study are available within the article and its [supplementary materials](#). The 3D reconstruction of the drops and the corresponding height map are available at <http://dx.doi.org/10.17632/4rvsy65stz.1>.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2021.02.070>.

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