Colloids and Interface Science Communications 1 (2014) 14–17

Contents lists available at ScienceDirect

Colloids and Interface Science Communications

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

Rapid Communication

3D X-ray Micro Computed Tomography on Multiphase Drop Interfaces: From Biomimetic to Functional Applications

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ARTICLE INFO

Article history:
Received 31 March 2014
Received in revised form 22 May 2014
Accepted 22 May 2014
Available online 24 June 2014

Keywords:
3D contact line
3D multiphase interface
X-ray micro-computed tomography (microCT)
Super-hydrophobicity
Wetting behavior on anisotropic surfaces
Drop

ABSTRACT

The investigation of multiphase interfaces and contact lines is a challenging research topic for comprehension of countless physical problems, both natural and imitated from nature, at the microscale (nearly 1 μm).
In presence of a three-phase interaction (liquid–gas–solid, or two immiscible liquids and a solid), different forces influence the evolution of the system and lead it towards its mechanical equilibrium. Even for the seemingly very simple case of drops on solid surfaces, there are many attempts to investigate the involved effects, with the main aim to profitably replicate them for functional applications (biomimetics).
Here we show that it is possible to visualize the real multiphase interface by X-ray micro-computed tomography (microCT), which is essentially a full volume 3D microscope, non-intrusive, with micrometric spatial resolution and suitable to operate even with matter opaque at visible wavelength.
Consequently, microCT can also be applied to investigate complex wetting scenarios, to validate the theoretical models already available for such cases.

1. Introduction

The efforts to visualize the resulting interface in multiphase systems have been, up to now, limited to non-intrusive methods (as they should not alter the system dynamics and the fluid equilibrium), usually derived from optical applications. In these cases the focal path-length, the resolution and magnification and the medium opaque to the used wavelengths emerge as major limitations, in addition to the fact that bi-dimensional images only are acquired, which may misrepresent the local information. Results reported in literature are often limited to contact angle estimation by two-dimensional optical images [1], while the surface topology at microscale plays a role that greatly impair the effectiveness of simplified models [2–5]. Recently different advanced optical techniques with significantly improved spatial resolution were investigated aimed at visualizing three-dimensionally the liquid meniscus, such as environmental scanning electron microscopy [6], confocal scanning microscopy [7] and reflection interface contrast microscopy [8]. A review of such techniques, particularly applied to very small drops, can be found in [9]. However, all these techniques still suffer from the described limitations due to optical observations.

On the contrary, X-ray micro-computed tomography (microCT) might act as a full volume 3D microscope, non-intrusive, with micrometric spatial resolution and suitable to operate even with matter opaque at visible wavelength. This offers exciting new possibilities of investigation. As significant examples, three cases will be presented here.

Two are micro-computed tomographies (microCT) of a sessile water drop on leaves that show super-hydrophobic properties. Despite the phenomenon is largely described in literature [10–14], it is still of major interest for the modeling and designing of biomimetic surfaces [15]. The third case is a sessile water drop on an artificial surface: a gas diffusion layer (GDL) developed for fuel cell application that needs to achieve a very high hydrophobicity. For the latter case, a method is also proposed to evaluate the volume and surface of the part of the drop which is enclosed within the apparent external contact line, to use them as indicators of the wetting behavior on anisotropic surfaces, where no simplified model can actually be applied due to the topological complexity.

2. Experimental Setup and Procedure

2.1. Sample Preparation

Leaves and GDL are portioned in dimensions of approximately 10 mm of side and the specimens are then fixed to the collimated rotation stage. Sessile drops of bi-distilled water are then deposed on them. When necessary, evaporation of fluids is limited by enclosing the specimen and the drop in a climate chamber in saturated environment. The GDL was prepared by the Mat4En[2] group of the Chemistry, Materials and Chemical Engineering Department of Politecnico di Milano: a commercial carbon cloth (S5, from SAATI, Italy) was soaked in an aqueous

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http://dx.doi.org/10.1016/j.colcom.2014.05.002
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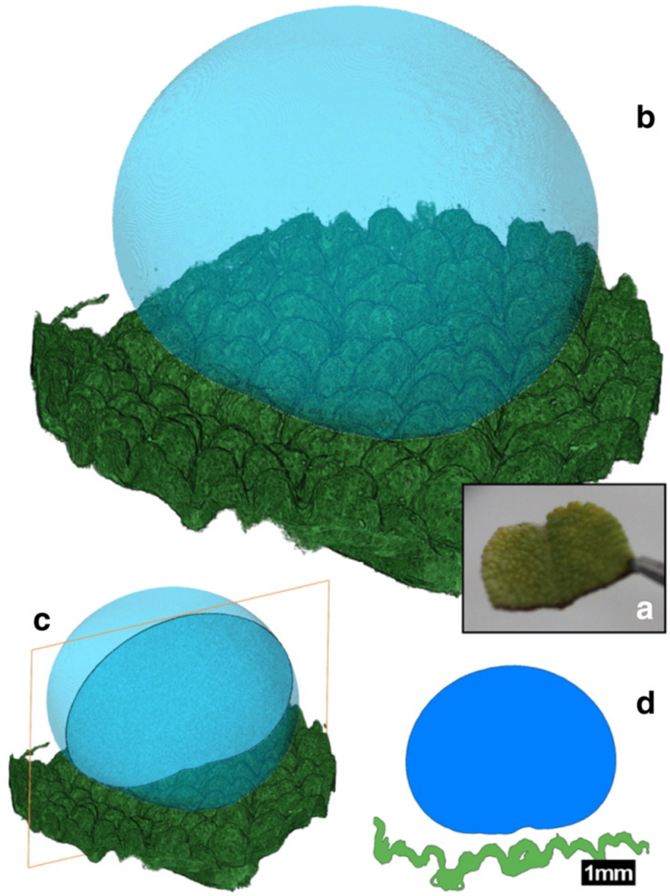

Fig. 1. X-ray microCT of portioned *Salvia officinalis* (a) leaf and sessile water drop. Segmented and rendered (with colors and transparencies) volume (b); an arbitrary cross-section where drop appears to hover over the leaf surface, in reality it is suspended on protruding nubs that have sub-micrometric or near micrometric dimensions (c); the drop shape and its surface can be realistically visualized and a quantitative description of the interface topology and curvature can be obtained (d). Isotropic voxel size: 6 μm.

solution of polytetrafluoroethylene-co-perfluoroalcoxy vinyl ether (DuPont™) for 20 min and then heated in air at 305 °C for 30 min.

2.2. Experiment

The reported microCTs were performed at the University of Bergamo (Italy) using equipment consisting of a microfocus X-ray cone-beam source, an air bearing rotation stage, and a CMOS flat panel detector. Magnification factor is in the range of 12.3 to 18.5 times, tube current and voltage are in the range of 30 μA and 50 kV respectively. Isotropic voxel size is specified in figure captions. Further details about the rig and a summary of the basic theory involved in the tomography procedure can be found in [16], which also describes the validation of the technique for drops on smooth surfaces.

2.3. Reconstructions

The X-ray images were processed and the tomographic volume reconstructions were performed using standard filtered back-projection based on Feldkamp algorithm.

3. Results

3.1. Biomimetics: Drops on Leaves

The microCT of sessile drops on leaves is a very good example of the complexity of the attempt to measure the real wetting interface. Nature selected many solutions to obtain very high leaves hydrophobicity, which is extremely useful for self-cleaning. In species as the *Salvia officinalis* the drop appears to hover over the leaves surface, but in reality it is suspended on protruding nubs that have sub-micrometric or near micrometric dimensions (see Fig. 3h in Ref. [5]). The latter are actually smaller than the resolution of the presented microCT, so that they cannot be directly visualized (Fig. 1). Nevertheless the drop shape and its surface can be realistically visualized and a quantitative description of the interface topology and curvature can be obtained. In Fig. 2 the genus *Lavandula* properties are more due to the chemical substrate and when a sessile water drop is placed on it, the localization of the drop anchor points and the areas where air is entrapped between the drop and the leaves surface are clearly visible in the microCT scans.

Similar natural behaviors inspired deeper investigations with the aim to replicate them for functional applications in many fields. Thus, the visualization capabilities of microCT for complex natural systems become interesting not only from a theoretical point of view, but even more to exploit the findings about the liquid–solid interaction to design

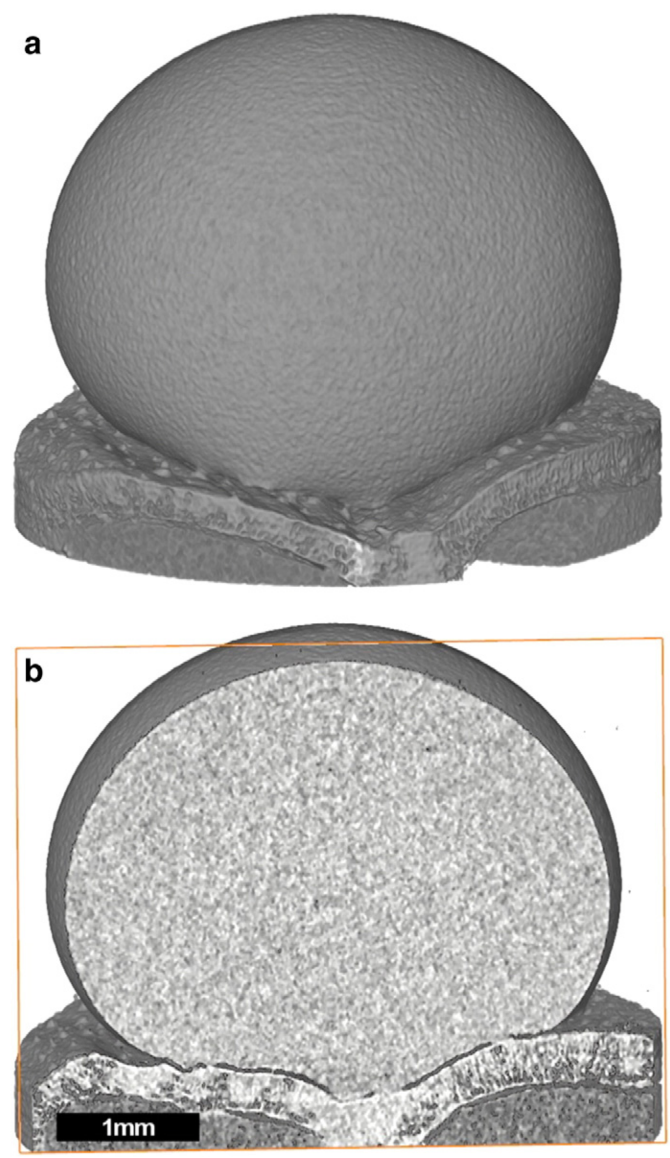

Fig. 2. X-ray microCT of *Lavandula* leaf and a sessile water drop, not-segmented grayscale volume resulting from back-projection reconstruction (a). In evidence (b) an arbitrary cross-section showing the leaf hydrophobicity with air entrapments between the drop and the surface. Isotropic voxel size: 4 μm.

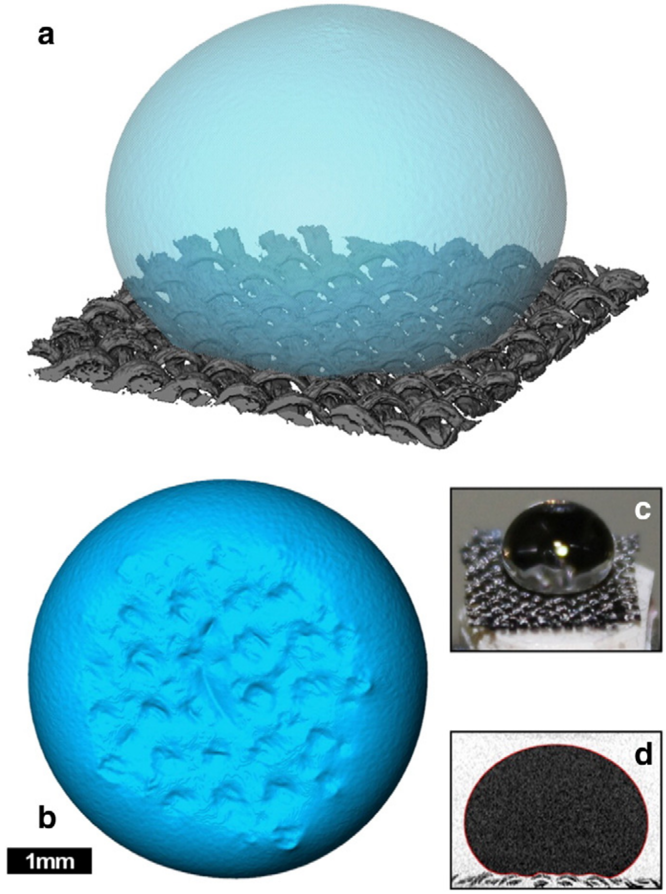

Fig. 3. X-ray microCT of GDL substrate and a sessile water drop. Segmented and rendered (with colors and transparencies) volume (a); the drop volume (measured by microCT equal to 40.945 μl) from the bottom (b) evidencing the topology of the real interface imprinted by the GDL in normal conditions (c); a slice extracted from the reconstructed volume, with the contour evidenced in red, to show how the drop is in a Cassie-Baxter wetting state (d). Isotropic voxel size: 5 μm.

artificially engineered surfaces [17]. Models already exist that predict several configurations — the most used are the Wenzel [18] and the Cassie–Baxter [19] — and many experiments are reported in literature for their validation. As already described, the latter were until now affected by several limitations: in particular the optical techniques are two-dimensional and with resolution of hundreds of microns, electron microscopy is still two-dimensional, even if with nanometer resolution, and it may suffer from the problem of vaporization in the vacuum chamber. On the contrary, microCT nowadays offers adequate resolution to investigate the complete system without constraints, and it is expected that technological improvements will soon offer even better performances, faster and more compact systems and cost reductions. This would move its application from a few highly qualified research centers (including those equipped with synchrotrons) or universities to a much larger number of laboratories.

3.2. Functional Applications

As an example of direct industrial interest, a third case is presented, referring to the microCT of a sessile water drop on a gas diffusion layer (GDL) used within polymer electrolyte membrane fuel cells [20] (Fig. 3). The investigated GDL is a carbon fiber cloth with polytetrafluoroethylene-co-perfluoroalcoxy vinyl ether (PFA) as a hydrophobic agent and binder. In this case, it is possible to investigate the liquid–wall interaction and the effects of the chemical deposition (aimed at enhancing the layer hydrophobicity) on the drop shape and the contact angle. From slices of the reconstructed drop surface, it is also possible to estimate the liquid surface tension using different types of axisymmetric drop shape analysis (ADSA) [21].

A direct measure of volumes can also be obtained from microCT if a proper calibration is implemented. In addition, segmentation of the microCT reconstruction allows the separation of the drop from the GDL, so that it is possible to identify the amount of water that partially wets the warp-and-weft of the cloth. Such region can be extracted as the part of the drop included between the lowest layer in which water

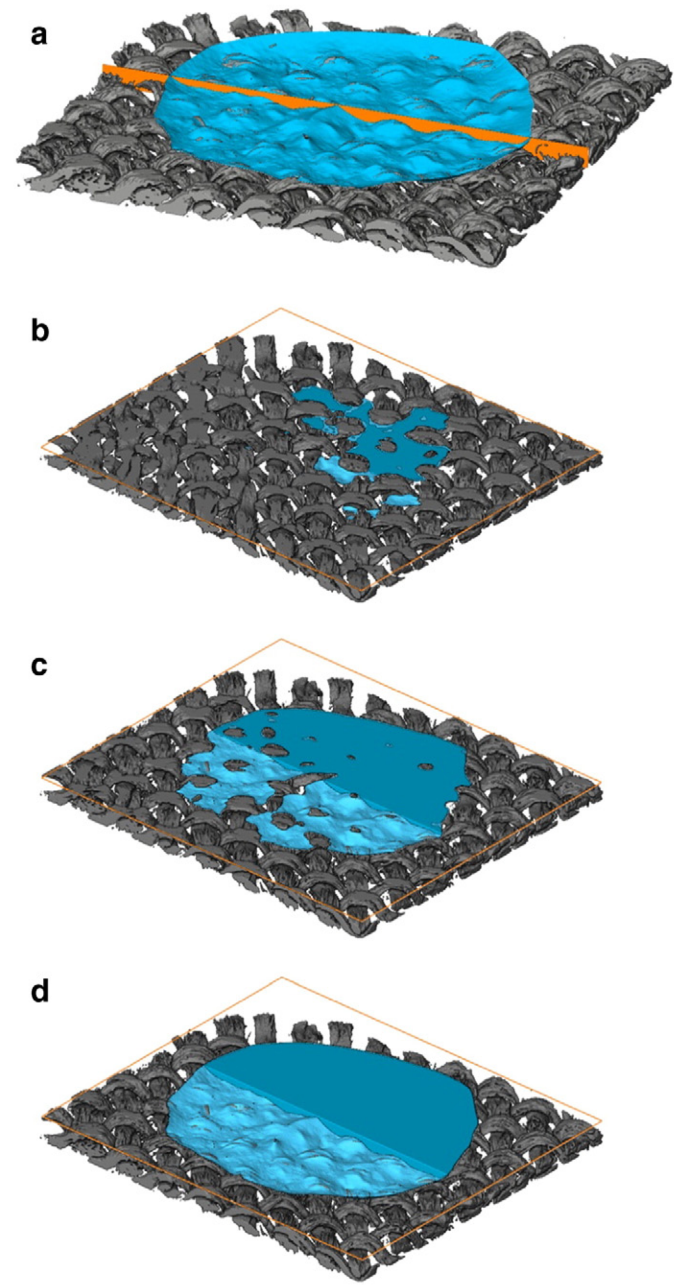

Fig. 4. X-ray microCT allowing to post-process the drop volume, selecting a partial region delimited by the first water presence from the bottom till the highest slice in which the GDL substrate is still detectable (in blue the wetted surface equal to 11.870 mm^2, in orange the cross-section of the liquid volume that interacts with the GDL). Images (b, c, d) represent 3 different height levels: in each one half of the picture shows the wetted surface, the other half the real water volume (panel b = 0.026 μl; panel c = 0.294 μl; panel d = 0.951 μl).

is present and the highest layer where GDL is still detected within the region delimited by the apparent external contact line (Fig. 4).

For the investigated case, the total drop volume measured by microCT is equal to 40.945 μl and the wetting volume, as above defined, is equal to 0.951 μl. The liquid surface in Fig. 4c is equal to 11.870 mm^2.

The wetting is only partial as the drop is in the heterogeneous Cassie–Baxter state, with air entrapped underneath the liquid, as it can be seen in Fig. 3d.

The shape and volume of the described region may be an indicator of the substrate coating wetting performances, thus microCTs of different substrates may be compared in this sense to provide information which is much more detailed and reliable of the commonly used apparent contact angle [22] or shedding angle [23].

It is worth underlining that similar investigations have been in general limited only to estimations extrapolated by 2D images, while the microCT is a truly full volume 3D technique. Moreover, the microCT approach can be used even in all those cases where a phase change is involved, which may alter the equilibrium and the interface topology in a complex way. Such modifications may have a significant effect on the heat transfer and evaporation ratios, but cannot usually be captured by conventional techniques.

4. Conclusions

Three examples of use of X-ray micro-computed tomography for investigating multiphase interfaces at the microscale were presented. Such analysis may be of interest for a very wide range of thermo-fluid dynamic investigations (both experimental and numerical) in presence of interfaces: for the first time in this field, a technique is applied that allows to simultaneously digitalize the three-dimensional volume of a liquid–solid–gas system and its separating surfaces, with all the quantitative post-processing opportunities this may offer.

The proposed studies may also be a starting point to visualize the evolution of 3D multiphase interface during phase transition (i.e., solidification and evaporation) on any surface configuration, even on porous media, with a resolution that recently reached sub-micrometer detachability. Previously available results only cite contact angle estimation by two-dimensional optical images, while the surface topology at microscale plays a role that greatly impairs the effectiveness of simplified models. The latter thus need further systematic investigation, which can be achieved with the microCT.

Acknowledgments

Authors wish to acknowledge the help provided by Mr. Massimo Lorenzi during X-ray acquisitions and tomographic reconstructions. The financial support from the Regione Lombardia (Italy) (Project ID-MAN11) within the call “Cooperazione Scientifica e Tecnologica Internazionale nelle aree tematiche agroalimentare, energia-ambiente, salute e manifatturiero avanzato” Project ID-MAN11 and the research fund grant to M.S. “Fondi di Ricerca di Ateneo” and even the prize “5 per 1000” of Bergamo University (Italy) are gratefully acknowledged.

Advice given by Prof. G.E. Cossali and Prof. G. Sotgia has been appreciated.

To Ferdinand.

Appendix A. Supplementary Data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.colcom.2014.05.002.

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