Confined water in complex networks: unifying our understanding of pore water and solutes at all scales

Lionel Mercury, Niel Tas, Michael Zilberbrand

Confined water in complex networks: unifying our understanding of pore water and solutes at all scales

Lionel Mercury[1], Niels Tas[2] and Michael Zilberbrand[3]

[1]Institut des Sciences de la Terre d'Orléans, UMR 7327 Université d'Orléans-CNRS-BRGM, 1A rue de la Férollerie, 45071 Orléans Cedex, France. lionel.mercury@univ-orleans.fr.

[2]Department of Transducers Science and Technology, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands. n.r.tas@utwente.nl.

[3]Israeli Water Authority, the Hydrological Service, Research Division, P.O.B. 36118. Jerusalem 91360, Israel. michaelz20@water.gov.il.

The arid regions experience geopolitical and sociological problems which are related to the lack of water. Yet, it is well-known that some residual water remains inside the thinner part of the porous space in the soil, possibly being supported by a non-rainfall recharge linked to dew formation. This residual non-evaporating liquid resides in an unsaturated zone which is occluded in pores and channels, can be stabilized in various ways, such as by capillary bridges concavely curved towards the atmosphere, by tiny filled porous spaces (solid-liquid-solid confinement) or by deposition on solid surfaces as adsorbed thin films (solid-liquid-air confinement). The properties of the liquid in each of these situations are of special interest for the management of the mobility and retention of this residual water. Indeed, the pathway to recharge water down to the aquifers through this unsaturated zone is notoriously complex, also because structural and textural heterogeneities occur that result in preferential flow coexisting with almost immobile water. Even deeper, in the saturated zone, it remains still a challenge to safely predict the reactive pathway of water-rock-pollutant interactions in natural settings, because of a similar complexity in the relationship between the structure of the hosting porous network, and the reactive and migrating properties of the guest fluids.

With such a wide background, the general aim of the workshop was:

- To define and discuss the different angles of view towards confinement and capillarity, with particular emphasis on the practical consequences in terms of mass balance and flux in real channels and pores, either of synthetic or of natural materials;
- To bring together a number of leading scientists in the field of the theoretical description, experimental investigation, and/or phenomenological modeling and to have an inter-disciplinary exchange around the good, the bad, and the ugly in each conceptual frame.

Altogether 30 participants from 11 countries attended the 5 day workshop. Some additional colleagues working at the University Ben Gurion of the Negev, quite close to the workshop venue, attended some of the sessions. The main feature of this group was its large interdisciplinarity: the scientific fields encompassed nano/micro-fluidics, fundamentals of surface forces, fluid physics, porous materials science, tree physiology, soil hydrodynamics and chemistry, reactive transport in aquifers. This scientific scope allowed the group to tackle the "confinement, phases, network, triangle" at different scales with very different approaches. The main goal of the present book of proceedings is to reflect the inter-disciplinary exchanges experienced by the participants: sharing common knowledge from such different points of view that, sometimes, it could be felt like different topics.

The book is organized thematically into four parts. The first is a general introduction to the surface forces which are clearly the nutshell of the special physics arising around interfaces and inside restricted spaces. The second part focuses on pore water flow at different scales, either to describe its special features in restricted spaces or to define the properties that cause the liquid to remain immobile ("Flow: from nano- to mega-scale"). The third part deals with the corresponding topic of the solute movement and behavior under the same surface forces fields, introducing the strong effect of coulombic forces in the discussion ("Ions, hydration and transport"). The fourth part starts the study of phase transitions with the liquid-vapor phase transition of superheated liquid. Superheating is a common event in natural thin channels and pores, especially under arid conditions, and the end of this metastable state is reached through an explosive boiling (known as cavitation), which is of fundamental and naturalistic value ("In-channels/pores cavitation"). The fifth and last part goes beyond to the solid-liquid phase transitions and their specific behavior when a growing crystal is confined in a thin channel or pore and brought in nanometric proximity to the host solid ("Crystallization under confinement"). Each part is briefly introduced by commenting the logics of the different contributions with respect to the workshop guidelines and the global questioning in the corresponding communities. In the rest of this foreword, we would like to describe how the workshop itself was organized and which lessons we learnt from this experience.

Scientific program

The introductory lecture was delivered by Jacob Israelachvili, worldwide renowned for his in-depth researches on surfaces and interfacial forces, on both experimental and theoretical points of view. He presented the static (interaction) and dynamic (viscous) properties of water adjacent to single mineral surfaces (solid-liquid interface) as well as of water confined between two such surfaces. This topic allowed him to open the discussion on the main force fields able to modify the classic behavior of liquids, which are the direct or indirect causes of many phenomena, further elaborated during the workshop.

The seven other keynote lectures structured the program according to one thematic session per half-day or day. The Tuesday was devoted to the nano-scale (properties and mechanisms), in direct continuation of Israelachvili's lecture. The first half-day (keynote speaker: Sumita Pennathur) focused on nanofluidics and especially on the role of electrokinetics. In this and subsequent sessions the dynamic and static behavior of water confined in synthetic pores were discussed, and many direct consequences or associated phenomena were developed: dissolution in nanochannels, electrocavitation (induced by electro-osmotic flow), proton release and pH of the in-filling liquid, ion or molecule transport, elastocapillary pressure and the deformation of the channel host, seismoelectric effect. The second half-day (keynote speaker: O. Vinogradova) dealt with the surface forces, not as a general topic but related to diverse practical situations: slip on superhydrophobic surfaces, the stability of confined electrolyte solutions, and the computer simulations of solid/liquid interfaces with clay, cement, and polymer membranes.

The Wednesday (keynote speaker: Dani Or) focused on the pore scale processes, especially on the conceptual modeling of the gas-liquid (evaporation, water flow and retention, fingering) and solid-liquid equilibria (pressure solution) in natural pores. Key observation was, that moving from the designed "pure" materials to the complexity and heterogeneity of natural samples, requires to develop a simplified sketch of the studied volume, only capturing the relevant features to account for the evolution through time.

The Thursday was entitled "Pore/channel to network", progressively shifting to a global grasp of 3d materials and the role and properties of the in-filling fluids. The first half-day (keynote speaker: Michael Steiger) was essentially focused on salt crystallization in pores with the important issue of the location and the dynamics of the precipitation, but also the way salts can colonize in-pore spaces. The special behavior of hydrates in pores was studied, with the pore size effect but also the role of the metastable solids. The second half-day (keynote speaker: John Sperry), was related to the cavitation events in nature (trees xylem, soil channels, mud volcanoes). This topic was approached by measurements in- and ex-situ, by analogous experiments in labs and by thermodynamic calculations (equation of state).

The last half-day was devoted to the reactive transport issue, especially connected to the correct way to involve local heterogeneities (pore spaces, chemical composition, water state) in the modeling of extended natural media.

Discussions

The format of the workshop did deviate from conventional scientific congresses that mainly present validated results to its natural audience ("the community"). Here, the speakers tried to present a state-of-the-art of questions and methods in their area, while presenting their own approaches and originality. That resulted in the presentation of many ongoing investigations, making the debate less affirmative but more reflective for many participants, even those belonging to the speaker fields. The workshop also offered to many of us a chance to see phenomena closely related to our own, but from different angles of view, described in different vocabularies and studied by different methodologies.

The focus of the event was to encourage fruitful discussions hence all participants were introduced at the beginning of the symposium, with their expertise and their special interests. The lectures were held in an informal atmosphere making it easy to intervene during the talk with commentaries or questions. The timing was consequently difficult to follow, with lively exchanges of ideas and opinions amongst the participants, during the talks and the question times. It was especially noticeable that the general interest for each other did not fade through the whole period of the workshop despite the broad range of topics. The discussions in the technical sessions after the presentations did highlight some main topics, which will be summarized in the following.

Outcomes

During the entire symposium it became obvious that the different communities are speaking different "languages". The gap between the micro/nanofluidics community and the natural pore sciences community for example was quite clear, despite the fact that they share work on channels filled with liquids. The real difference stems from their requisites and goals. The nanofluidics community works with well-designed systems and pure materials and targets a global understanding of these exact systems as well as the phenomena arising inside. The natural pores sciences try first to understand which features are essential (in which perspective?), to afterwards simplify the original (too complex) case studies in such a way that they can be quantitatively modeled. The game is then to test the initial assumptions by matching the results of simulations or modeling with practical observations or measurements. We could as well highlight the gap between the theoreticians and the naturalists, linked to the distinction between possible theoretical states (physical chemistry) and practical states (natural observations).

These two distinctions, and all the new concepts learnt when listening to colleagues from other scientific areas, made the workshop interesting for every participant, lively and interactive. Meanwhile, the multidisciplinarity caused a sort of limitation to define immediate practical outcome(s), though the cross-fertilization was felt very useful by all the participants. Upscaling the nano-processes and considering how they can act in natural settings at local (centimetric) and regional (megametric) scales were defined as one of the main challenges of further research. At the final round table, the participants expressed full satisfaction to have attended the workshop, predominantly because it broadened their scientific knowledge, and improved their networking. The informal setting, the opportunity to have discussions with colleagues from different, yet related, disciplines were often outlined in after-workshop messages, as well as the chance to gain new perspectives on research, especially by meeting potential collaborators. Despite this positive feeling, many participants were reluctant to build a proceedings book, because the workshop also highlighted the differences and the barriers from one community to the other.

Most of the participants agree that in the future the impact of confinement, superheating and capillarity on a better understanding of the natural phenomena should be developed. The studies that coupled different properties, like the cavitation processes (in nanochannels, membranes, glass capillaries, xylems, soil pores, …), the special nanoscale transport properties (related to the electrical double layer), the deformations due to the elastocapillary pressure (again, in different materials), the interplay between the chemical composition of the filling liquids and the surface forces, attracted much attention. Also critical is the use of well-defined nanochannels, not only to understand fundamental properties but also to serve as analogous materials to measure and quantify parameters specific to their scale. This knowledge could be embedded in renewed large-scale modelling. The nanochannels are known as key elements in "*Lab on a chip" systems*, but the workshop made clear to the participants that they could constitute "*Nature on a chip*" model systems as well.

The major outcome of the workshop was that the participants experienced the gap between fundamental science and research applied to natural sciences, and that the different communities talked to each other. By doing that, they started to learn each other's "languages" and were introduced to the problems and needs of the others. The event was an excellent start of a multi-disciplinary effort to develop cross-fertilization between physics, chemistry, biology, soil and earth sciences.

Conclusion

Eventually, we hope that the present proceedings book will reflect the valuable experience we lived through during this workshop, and will give a clear impression to readers of the richness gained by crossing disciplines to go in the *Terra incognita* area "where nobody feels comfortable", as one of the participants summed up.

This workshop was supported mainly by the NATO (grant ESP.MD.ARW 984162), but benefited as well of supports from the french ANR (Agence Nationale de la Recherche; grant CONGE BLAN-61001 & ANR-10-LABX-100-01), the French embassy in Israel, the MESA+ Institute for Nanotechnology (The Netherlands), and the University of Orléans (France).

Most of the participants at the top of the Masada fortress, close to the workshop venue: (from left to right) John Sperry, Sumita Pennathur, Itai Cohen, Dani Or (front), John Selker (rear), Brian Berkowitz, Olga Vinogradova (front), Leo Pel (rear), Michael Zilberbrand (kneeling), Michael Steiger, Attila Imre, Teemu Hölltä, Harvey Scher, Dag Kristian Dysthe, Rosa Espinosa (kneeling), Yuri Aristov, Chuanhua Duan (kneeling), Niels Tas, Rohit Karnik (kneeling), Jan Eijkel, Yukiko Oka (kneeling), Lionel Mercury, Andrey Kalinichev, Isabelle Bergonzi, Arnault Lassin, Vladimir Shilov, Shmuel Assouline, Marc Prat, Larissa Sologubovskaja.