MODELING THE ANOMALOUS FILLING DYNAMICS IN MESOPOROUS FILMS

Claudio L. A. Berli, Magalí Mercuri, Martin G. Bellino

cberli@santafe-conicet.gov.ar; magalímercuri@cnea.gov.ar; mbellino@cnea.gov.ar

Abstract: *The fluid front dynamics resulting from the coexisting infiltration and evaporation phenomena in nanofluidic systems has been recently studied by using well-characterized mesoporous thin films. A series of striking effects have been observed, namely (i) the infiltration rate is abnormally slow and decreases with increasing pore diameter, (ii) the fluid front manifest an optically invisible roughening, and (iii) under certain conditions, the infiltration-evaporation front presents backwards-forwards oscillations. The present work describes a simple model accounting for the mechanisms behind some of these effects, and presents perspectives on the study of the more complex behaviors, with particular emphasis on the searchig for novel applications.*

Key-Words: *nanofluidics, capillary infiltration, evaporation, front-broadening, complex dynamics*

Introduction: The versatility of mesoporous films is opening up many new uses in microfluidic devices, for instance in biocatalysis [1]. Nevertheless, despite the intense research activity in the field [2], understanding flow and mass transport at the nanoscale requires further efforts. One issue of rising interest is the spontaneous imbibition of fluids in structures with nanoscale morphology. A recent experimental work [3] posed challenging questions about the relationship between nanoscale structure and macroscopic fluid dynamics. Further works lately revealed the oscillating nature of the fluid front imbibitions [4] and put in evidence the front-broadening effect in both titania and silica films [5]. In this context, the present work discusses a theoretical interpretation of the apparent contradiction between experimental values of infiltration rates and pore size data and, at the same time, describes the infiltration-evaporation kinematics observed in practice. In addition, open questions on the complex behaviors mentioned above are prompted for future research directions.

Experimental: Material characterization, experimental setups, and measurements are reported in refs. [3-5].

Results and discussion: A phenomenological model for the dynamics of the liquid infiltration-evaporation in mesoporous films was derived, in order to describe the annular region of wetted material formed around sessile drops (Fig. 1a). The classical Lucas-Washburn model is employed for the capillary-driven infiltration velocity $u_c(x) = c/x$, where c is the dynamic coefficient and x is the position of the fluid front at time t (Fig. 1b). On the other hand, the mass loss due to the liquid evaporation induces a fluid front velocity $u_e(x) = -x/\tau$, where τ is the characteristic evaporation time (see ref. [4] for further details). The balance of these processes yields the following kinematics: $x^2(t) = c\tau[1-\exp(-2t/\tau)]$, which satisfactorily represents experimental data, as it is shown in Fig 2a.
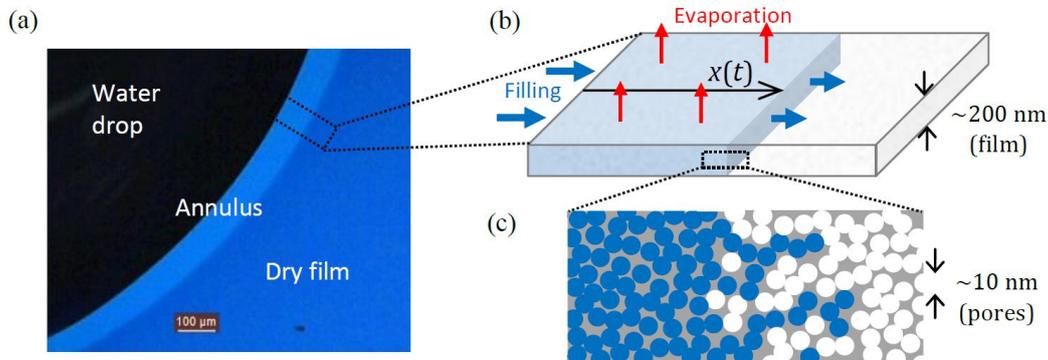
Fig. 1 (a) Typical microscope image of the mesoporous film during infiltration, (b) schematic representation of the transport processes considered in modeling, and (c) drawing of the transition from saturated to unsaturated zones at the macroscopic fluid front position.

The simplest fluid dynamics representation of the porous space is the capillary bundle model, in which the dynamic coefficient is $c = (\gamma\cos\theta r)/4\mu$, where γ is the surface tension, θ is the meniscus contact angle, r is the capillary radius, and μ is the fluid viscosity. The analysis of the experimental values of c by using this equation leads to anomalous values of r, which result orders of magnitude lower than pore sizes measured by porosimetry, or observed by electronic microscopy. A second controversial issue is that c systematically decreases when pore diameter increases [3], in contradiction with the linear relation $c \sim r$ written above. Adsorption-desorption experiments in mesoporous films [3,4] exhibits the existence of relatively wide pores of radius r_{max}, interconnected by small bottle-necks of radius r_{min} (Fig. 1c). A simple model that captures these features was derived [6]; it accounts for the existence of periodic changes in the cross-sectional area of the flow path, as shown schematically in the inset of Fig. 2b. The overall prediction is that the effective radius of the tube that produces the same infiltration rate is $r_{eff} = r_{min}(r_{min}/r_{max})^3$, which is always lower than r_{min}. This rather counterintuitive result is however physically consistent: the global hydrodynamic resistance is controlled by constrictions (r_{min}), while the time to infiltrate the porous matrix is controlled by the volume of the widest pores (r_{max}^3), and the infiltration rate decreases proportionally to the filling time. The agreement between the model and experiments is remarkable (Fig. 2b) and holds over several log decades of both c and r_{eff} (no adjustable parameters were used in calculations, see also [6]).
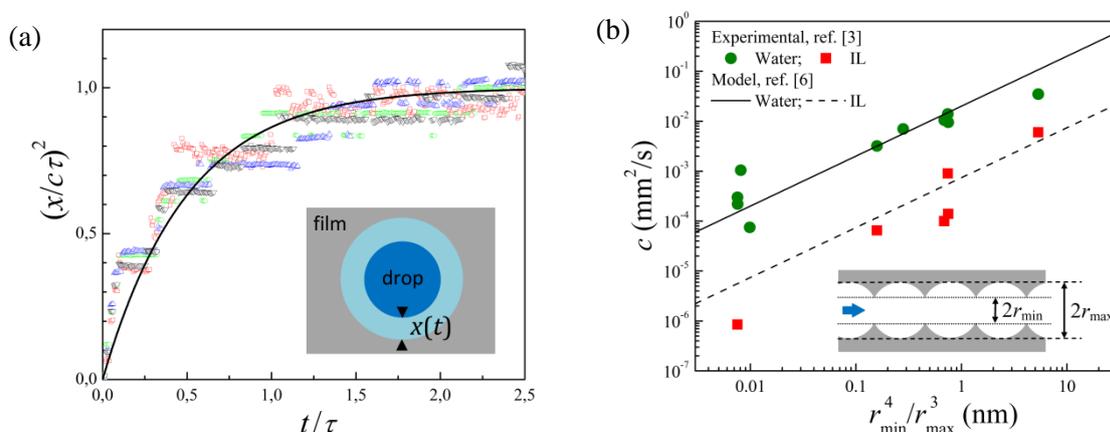
Fig. 2 (a) Squared position of the fluid front as a function of time: symbols are experimental data and the line is the model prediction; the inset shows the distance measured. (b) Dynamic coefficient as a function the effective radius for periodically constricted pores.

Conclusion: Firstly, it is observed that the filling dynamics in mesoporous films is defined by capillary driven infiltration at very short times, and by evaporation at intermediate and longer times. The parameter τ plays a key role controlling the process, which opens new possibilities to handle nanofluid transport in the pore space. Secondly, the connection of parameter c to pore sizes and architecture is a handy tool to characterize film nanostructures from simple microfluidic experiments, and constitutes a preliminary step to understand more complex phenomena. Finally, it is worth noting that studying unusual nanofluidic effects in mesoporous materials would lead to the design of novel operations in microfluidic platforms, such as localized reactions with microscopic patterns [5].

References and acknowledgements:

[1] N. Frančič, M. G. Bellino, G. J. A. A. Soler-Illia, A. Lobnik, Analyst **139**, 3127 (2014)
[2] P. Huber, J. Phys.: Condens. Matter **27**, 103102 (2015)
[3] D. R. Ceratti, M. Faustini, C. Sinturel, M. Vayer, V. Dahirel, M. Jardat, D. Grosso, Nanoscale **7**, 5371 (2015)
[4] M. Mercuri, K. Pierpauli, M. G. Bellino, C. L. A. Berli, Langmuir **33**, 152 (2017)
[5] M. Mercuri, K. Pierpauli, C. L. A. Berli, M. G. Bellino, ACS Appl. Mater. Interfaces **9**, 16679 (2017)
[6] C. L. A. Berli, M. Mercuri, M. G. Bellino, Phys. Chem. Chem. Phys. **19**, 1731 (2017)