
Molecular diffusion in porous media: a multimodal approach coupling 3D imagery, X ray scattering, NMRD and numerical simulations

Pierre Levitz*¹ and Anne-Laure Rollet¹

¹Physicochimie des Electrolytes et Nanosystèmes Interfaciaux – Institut de Chimie du CNRS, Sorbonne Université, Centre National de la Recherche Scientifique – France

Résumé

1 Introduction Diffusive transport of confined fluid in disordered porous media raise some challenging questions related to fluid dynamics inside these materials, at different time and length scales. Some examples can be mentioned such as the life cycle of building materials associated to concrete durability (water and ion long term diffusion) (1,2), the degradation of porous media belonging to the cultural heritage (3), the long-term confinement of nuclear wastes in geological horizons (clays) and the optimal design of catalyst supports (4). Molecular diffusion dynamics inside nanoporous and meso porous materials follows an intermittent dynamic (5-7) involving adsorption, surface diffusion and relocation inside the pore space. This coupling between dynamics and interfacial confinement, contributes to constraint the molecular diffusion inside pore network. In order to quantify this coupling, some parameters need to be measured such as the molecular surface diffusion coefficient, the average residence time on the pore surface, the time delay between two consecutive adsorptions where molecule diffuses inside the bulky part of the pore network (6). In the case of hierarchical disordered porous material such as soil, and mesoporous catalysts, molecular exchange between two or more pore networks, organized at different length scale, generalizes and extend molecular intermittent dynamics toward larger time. In both cases, the pore network organization on a length-scale ranging from nanometers to some micrometers is a cornerstone to properly understand diffusion-permeation properties. A strong need to a bottom-up approach mixing X-ray scattering (SAXS, SANS, 2D-3D imagery technics and numerical simulations is highly suitable for these types of multiscale complex systems (1,2,3,6). This multimodal structural analysis offers the possibility to use 3D reconstructions and to build constrained models mimicking geometrical features observed experimentally (6,8). These models can then be used to compute transport properties, allowing comparison with experimental determinations. In this presentation, we attempt to illustrate these topics and focus on two specific examples. 2 Molecular diffusion in a mesoporous material This first example concerns the water interfacial dynamics inside a mesoporous precursor of a catalytic support, the boehmite. As Al₂O₃ catalyst support inherits most of morphological properties of this precursor, understanding and optimizing molecular transport inside a boehmite pore network is a key parameter to improve molecular accessibility to a specific pore surface location. 3D morphology and topology of a commercial sample from was first investigated by electron tomography (8) and small angle scattering, providing a reliable 3D representation of the pore network at the nanometer scale. At the mesoscopic time scale (from 1ns to 10 ms), water dynamics

*Intervenant

was probed by NMRD (8) of ^1H and ^2H at different levels of water saturation of the pore network. In all cases, dispersion curves $R_1(\omega)$ follow a very similar algebraic law, highlighting the determinant contribution of the water dynamics on surface. In order to decipher different contributions of interfacial molecular dynamics, numerical simulations are conducted using the 3D reconstruction of the pore network, as it was formerly done in the case of the Vycor glass (6). Respective role of surface interaction and surface geometry on water dynamics were analyzed. Comparison with NMRD experimental data has allowed determining two important surface descriptors: First, the escaping time and/or the adsorption time found to be rather long: 8×10^{-6} s; second, the surface self-diffusion of the proton inside the surface layer estimated on the order of 10^{-10} m²/s. More technically, it was also concluded that the interfacial geometry and its curvature properties plays an important role to understand water proton diffusing on the surface of this porous material and its NMRD signature.

3 Bridging scales in hierarchical pore networks

In the second part of this presentation, more numerical oriented, we propose some possible ways to upscale the analysis of fluid dynamics, allowing decoupling the scale of the so-called "elementary pore" (which involves adsorption and relocation dynamics) and the long-range exploration, sensitive to the porous network structure. More specifically, in the case of a multiscale pore network and using first passage statistics, we analyze the possibility to quantify the molecular exchange between two pore networks organized at different length scales, Kinetics of a first encounter with a reactive site, located inside one specific pore network of a multiscale porous material is also discussed.

References (1) Soft X-ray Ptychographic Imaging and Morphological Quantification of Calcium Silicate Hydrates (C-S-H). S. Bae, R. Taylor, D. Shapiro, P. Denes, J. Joseph, R. Celestre, S. Marchesini, H. Padmore, T. Tyliczszak, T. Warwick, D. Kilcoyne, P. Levitz and P.J.M Monteiro. *J. Am. Ceram. Soc.*, 98, 4090-4095 (2015) (2) S. Brisard, C. A. Davy, L. Michot, D. Troadec, P. Levitz, Mesoscale pore structure of a high-performance concrete by coupling focused ion beam/scanning electron microscopy and small angle X-ray scattering. *J Am Ceram Soc.* 102:2905–2923 (2019) (3) G.P. Odin, V. Rouchon, F. Ott, N. Malikova, P. Levitz, L.J. Michot, Neutron imaging investigation of fossil woods: non-destructive characterization of microstructure and detection of in situ changes as occurring in museum cabinets, *Fossil record*, 20, 95-103, (2017) (4) J-B Pigot, Dynamique multi-échelle et échange inter-porosité par relaxométrie RMN au sein de zéolithes mésoporisées, PhD Thesis of Sorbonne-universite, <https://www.theses.fr/2020SORUS424> (2020) (5) P. Levitz, Random flights in confining interfacial systems, *J. Phys. Cond. Mat.* 17, S4059 (2005) (6) P. Levitz, Probing interfacial dynamics of water in confined nanoporous systems by NMRD. *Molecular Physics*, 117 (7-8), 952-959 (2018) (7) Colin Bousige, Pierre Levitz and Benoit Coasne, Bridging scales in disordered porous media by mapping molecular dynamics onto intermittent Brownian motion, *Nature Comm*, 12, Article Number1043, (2021) (8) Z. Gu, R. Goulet, P. Levitz, D. Ihiwakrim, O. Ersen, and M. Z. Bazant, Mercury cyclic porosimetry: Measuring pore-size distributions corrected for both pore-space accessivity and contact-angle hysteresis, *J. Colloid Interface Sci.*, vol. 599, pp. 255–261, (2021) (9) Field-cycling NMR Relaxometry; *New Developments in NMR Serie*, editor R Kimmich, RSC, (2018)