## Subcontinuum mass transport of hydrocarbons in nanoporous media and the long-time kinetics of recovery from unconventional reservoirs

Lydéric Bocqueta

<sup>a</sup>Laboratoire de Physique Statistique, Ecole Normale Supérieure, 75005 Paris

Keywords : Darcy law, recovery, activated process

In this talk I will discuss the transport of hydrocarbons across nanoporous media and analyze how this transport impacts at larger scales the long-time kinetics of hydrocarbon recovery from unconventional reservoirs (the so-called shale gas).

First I will establish, using molecular simulation and statistical mechanics, that the continuum description – the so-called Darcy law – fails to predict transport within a nanoscale organic matrix. The non-Darcy behavior arises from the strong adsorption of the alkanes in the nanoporous material and the breakdown of hydrodynamics at the nanoscale, which contradicts the assumption of viscous flow. Despite this complexity, all permeances collapse on a master curve with an unexpected dependence on alkane length, which can be described theoretically by a scaling law for the permeance.

Then I will show that alkane recovery from such nanoporous reservoirs is dynamically retarded due to interfacial effects occuring at the material's interface. This occurs especially in the hydraulic fracking situation in which water is used to open fractures to reach the hydrocarbon reservoirs. Despite the pressure gradient used to trigger desorption, the alkanes remain trapped for long times until water desorbs from the external surface. The free energy barrier can be predicted in terms of an effective contact angle on the composite nanoporous surface.

Using a statistical description of the alkane recovery, I will then demonstrate that this retarded dynamics leads to an overall slow – algebraic – decay of the hydrocarbon flux. Such a behavior is consistent with algebraic decays of shale gas flux from various wells reported in the litterature.

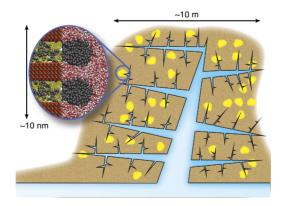


Figure 1: Hydrocarbon recovery from unconventional reservoirs. Schematic illustration of a fracture network (blue), created by hydrofracking, penetrating previously isolated hydrocarbon-rich kerogen pockets (yellow) within a mineral

matrix (brown). Here we consider the post-fracking situation in which water within the hydrofracking network is in contact with the kerogen surface. Extraction of the hydrocarbon requires formation of a nucleus with a high interfacial energy. The zoomed image illustrates such a scenario, in which a methane nucleus (dark grey) forms at a kerogen surface (yellow) adjacent to hydrophilic mineral surfaces present in shales (here quartz, with Si and O atoms as red and golden spheres). Considering other inorganic phases such as clays will lead to the same consistent picture of interfacial activated transport as they have similar wetting properties towards methane and water. However, local variations in surface chemistry and geometry will determine the magnitudes of the energy barriers preventing extraction, which will have a broad range of values due to the heterogeneous, multiscale texture of the shale.

## References

K. Falk, B. Coasne, R. Pellenq, F. Ulm, L. Bocquet, Nature Com 6 6949 (2015).
T. Lee, L. Bocquet, B. Coasne, Nature Com 7, 11890 (2016).

## Ackowledgements

This work was performed in collaboration with B. Coasne, K. Falk, T. Lee, R. Pellenq and F. Ulm, at the UMI CNRS-MIT, Massachusetts Institute of Technology, Cambridge, USA.