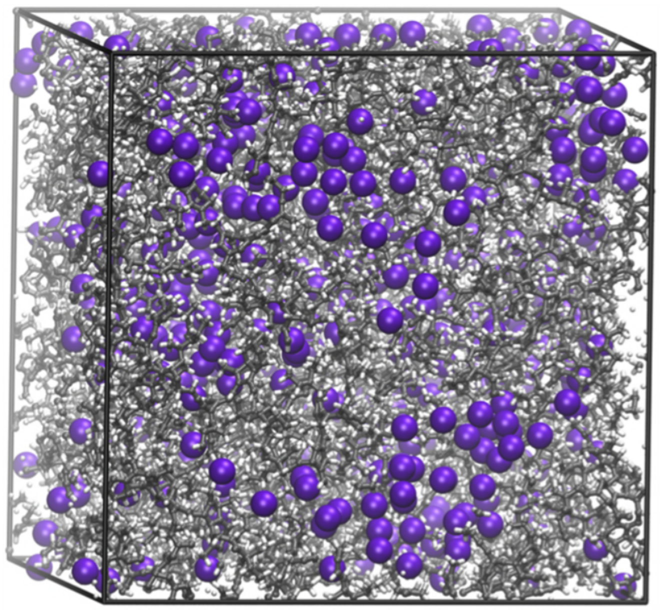
The simple biexponential relaxation to Fickian yet non-Gaussian diffusion in kerogen's microporosity

Amaël Obliger[1]

[1]Institut des Sciences Moléculaires de Bordeaux, Bordeaux, France



We show that adsorbed fluids in kerogen exhibit Fickian yet non-Gaussian diffusion (FnGD). Kerogen is the dispersed organic matter in sedimentary rocks from which natural gas and oil are generated over time by thermal maturation. There has been widespread interest in developing atomistic models of kerogen for numerical investigations of adsorption and diffusion behavior [1].

Molecular dynamics (MD) simulations have been used with an atomistic model of kerogen's microprosity that was initially developed to highlight the viscoelastic nature of such amorphous carbons (see the attached figure for a snapshot of the MD system of methane adsorbed in a swollen kerogen microstructure). Kerogen is prone to adsorption-induced swelling [2], hinting to a strong coupling between the fluctuating microstructure and the fluid dynamics that usually leads to FnGD in other systems such as colloids in biofilament networks where the phenomenon was first observed [3].

To quantify the transition to Fickian diffusion, we analyze the logarithmic derivative of the mean squared displacement (MSD). Our results reveal a successive biexponential relaxation "road" toward the long-time linear regime of the MSD, describing the entire diffusion dynamics down to the exit of the initial ballistic regime with remarkably few parameters. This is particularly impressive given the complex and heterogeneous pore space of kerogen.

In contrast to most other systems, FnGD in kerogen does not feature an exponential tail in the displacement distribution. Instead, the latter closely follows a stretched Gaussian form at all times, as in [4], allowing us to monitor non-Gaussian deviations from the resulting stretched exponent, in addition to the usual non-Gaussian parameter. We highlight that increasing the confinement or microstructure rigidity enhances non-Gaussian departures while slowing diffusion.

These findings clearly suggest that similar nanoporous systems could display FnGD as well as a potentitally universal "road" toward fickian diffusion. This could lead to the development of simple yet comprehensive models describing the entire dynamics of diffusion in similar media.

References:

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[4] Cherstvy et al. Non-Gaussianity, Population Heterogeneity, and Transient Superdiffusion in the Spreading Dynamics of Amoeboid Cells. Phys. Chem. Chem. Phys. 2018, 20 (35), 23034–23054.