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Structural and transport properties of hydrocarbons in clay nanopores

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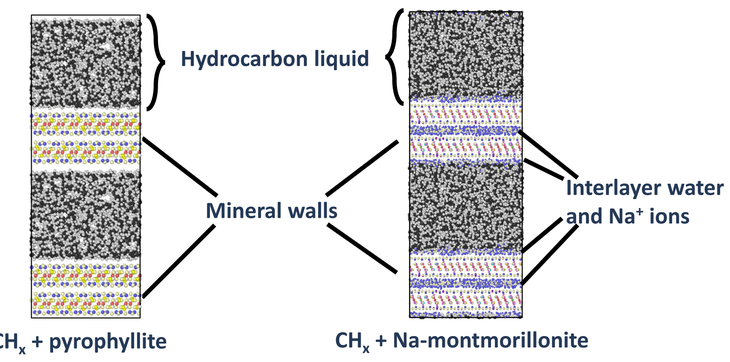
Motivation

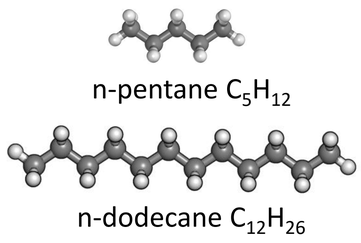
- Clays are a significant constituent of inorganic material in hydrocarbon reservoirs
- Tight oil reservoirs have nanopores with typical sizes as small as 2 nm
- The properties of reservoir hydrocarbon fluids may be affected by fluid-wall interaction

Test Systems

n-pentane and n-dodecane in slit pores of hydrated montmorillonite (hydrophilic walls) and water-free pyrophyllite (hydrophobic walls)



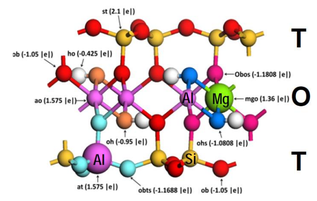
Hydrocarbons: OPLS-AA/CM1A force field[1]



Walls: ClayFF force field[2]

Pyrophyllite: $Al_4Si_8O_{20}(OH)_4$

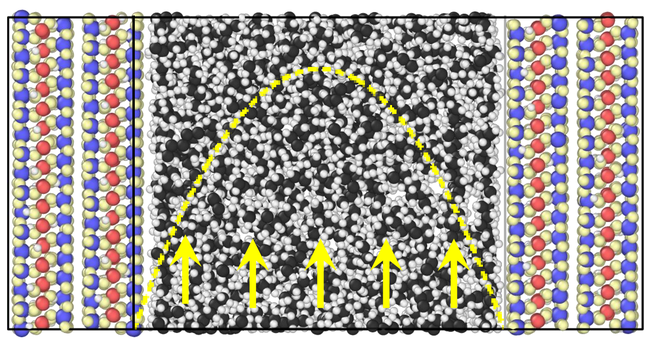
Montmorillonite: $Na^+_3(Al_{14}Mg_2)(Si_{31}Al)O_{20}(OH)_4 \cdot 16H_2O$

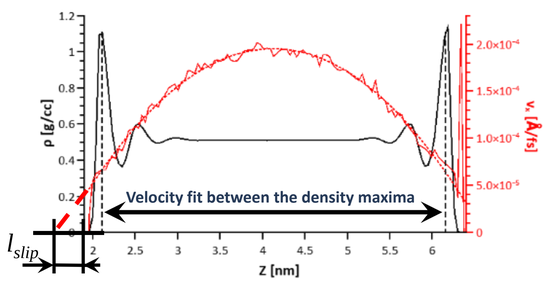


$$U_{mol} = \sum_{i,j} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \sum_b K_b(r_b - r_{0,b})^2 + \sum_a K_a(\theta_a - \theta_{0,a})^2 + \sum_{k=1}^{3} a_k\,(1 + (-1)^{k+1}\cos k\phi)$$

Poiseuille and Couette flows

Poiseuille flow



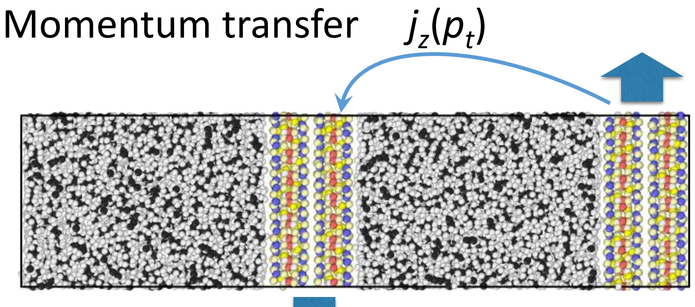


$$\eta = \frac{\partial P/\partial x}{d^2 v_t/dz^2}$$

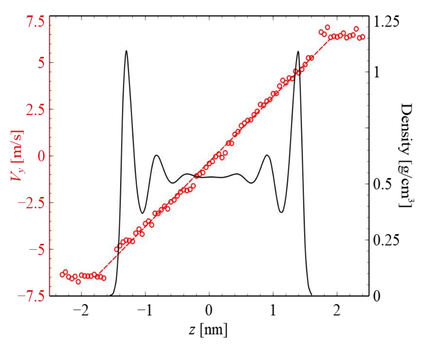
$$\partial P/\partial x = F_{total}/V_{fluid}$$

Couette flow

Momentum transfer $j_z(p_t)$



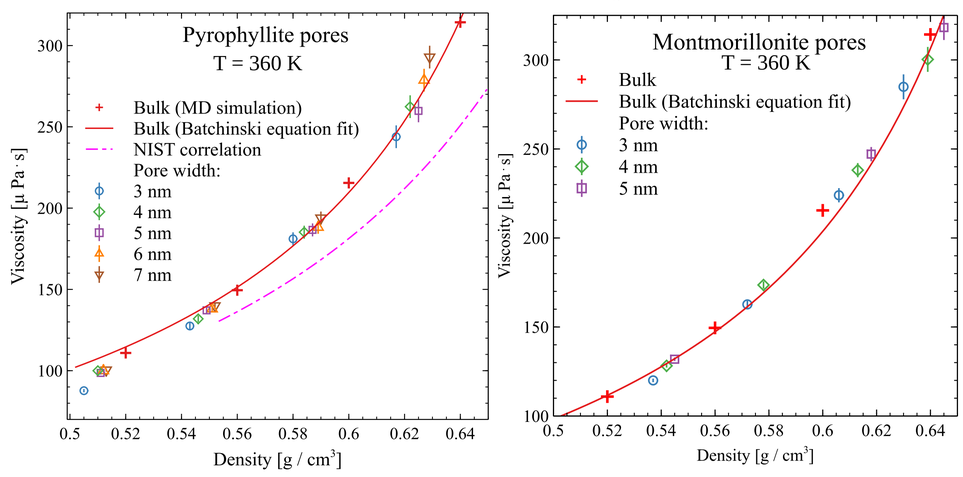
$$\eta = \left|\frac{j_z(p_t)}{\partial v_t/\partial z}\right|$$



$$l_{slip} = \frac{v_t(wall)}{(dv_t/dz)(wall)}$$

n-pentane in clay pores

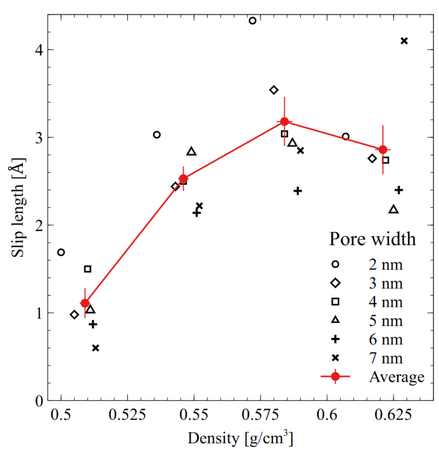
Shear viscosity



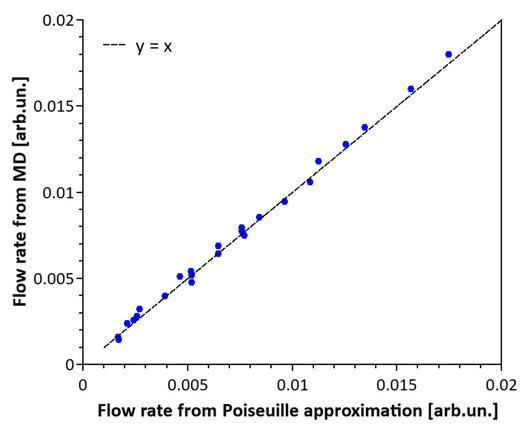
The viscosity-density relation is only weakly affected by the nanopores walls.

Mass flow rate in Poiseuille flow simulations

Slip length (pyrophyllite)



Flow rate



Poiseuille equation flow rate estimate (slip flow, l_{slip} = 3 Å):

$$Q_{Pois} = \rho\frac{\partial P/\partial x}{2\eta}L^2\left(\frac{L}{6} + l_{slip}\right)$$

Direct MD calculation of the flow rate:

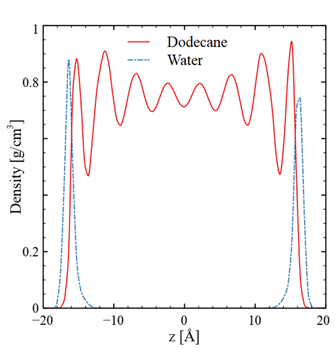
$$Q_{MD} = \int_0^L \rho(z)v_x(z)dz$$

Classical hydrodynamics adequately predicts the flow rate of short hydrocarbons, if appropriate slip conditions are used.

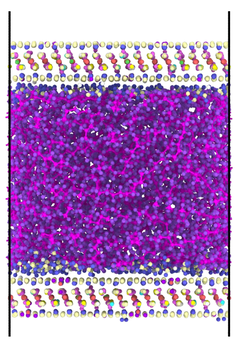
n-dodecane in clay pores

Montmorillonite pores

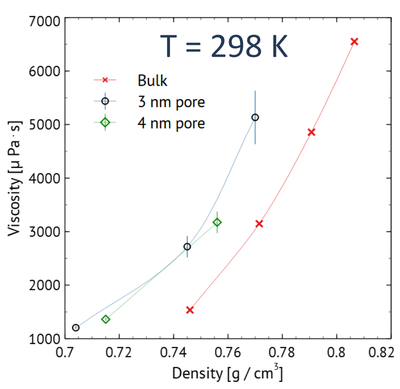
Density profile



Side view

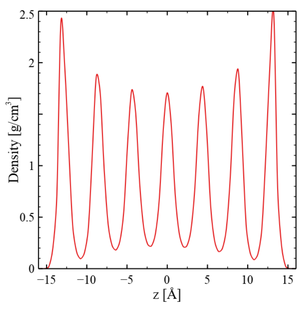


Shear viscosity

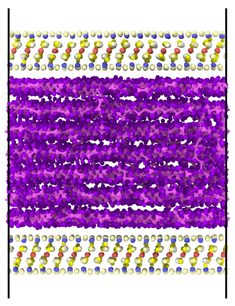


Pyrophyllite pores

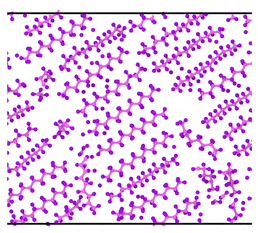
Density profile



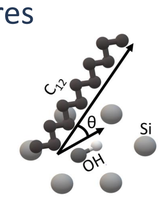
Side view



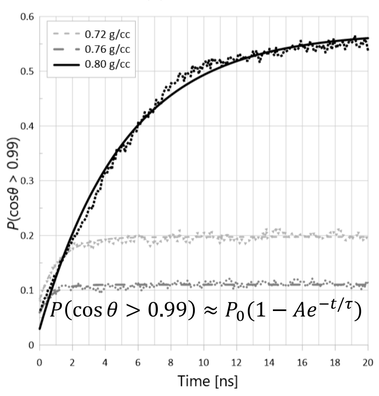
Top view on a layer



Transition to liquid-crystal-like structure at densities above 0.75 g/cc in 3 nm pores

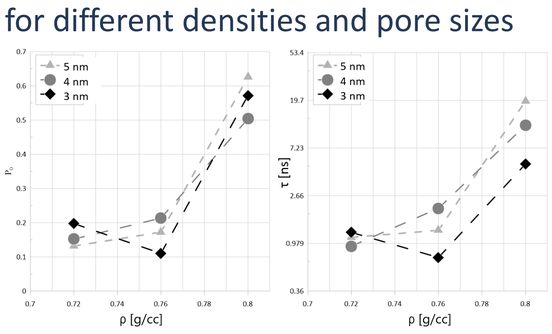


Ordering of molecules along the directions of hydroxyl groups



$$P(\cos\theta > 0.99) \approx P_0(1 - Ae^{-t/\tau})$$

Relaxation parameters for different densities and pore sizes



Conclusions

Properties of a short- and medium-chain hydrocarbons in slit pores are investigated

- The viscosity-density dependence of n-pentane is only weakly affected by the pores wider than 3 nm
- Pentane has a slip length of ~3 Å against pyrophyllite walls, and a negligible slip against hydrated montmorillonite walls
- Flows of n-dodecane are much more strongly affected by the liquid-wall interactions
- n-dodecane molecules show ordering along the hydroxyl direction in pyrophyllite pores

References

1. L.S. Dodda et al. J. Phys. Chem. B **121** (2017): 3864.
2. R.T. Cygan, J.A. Greathouse, A.G. Kalinichev. J. Phys. Chem. C **125** (2021): 17573.
3. V.V. Pisarev, A.G. Kalinichev. J. Mol. Liq. **366** (2022): 120290.
4. M.A. Logunov, A.G. Kalinichev, V.V. Pisarev. Polymer Sci. Ser. A **64** (2022): 908.

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