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### **Effects of Nano-pore Confinement on Fluids in Organic Shale using NMR Measurements and MD simulations**

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Nuclear magnetic resonance (NMR) relaxation is used to distinguish movable versus bound-fluids, hydrocarbon versus water, and wettability and surface-affinity in characterizing unconventional reservoirs wherein organic matter is trapped in pores that are tens of nanometers or less. Such nano-scale confinement not only affects the phase behavior and transport of the fluids but it also limits the use of NMR measurements, since the interpretation of NMR measurements still relies on models developed for bulk fluids. As part of PRF58859-ND6, we have been addressing this challenge using experiments, molecular simulations, and density functional theory of fluids. Here we summarize the progress to-date.

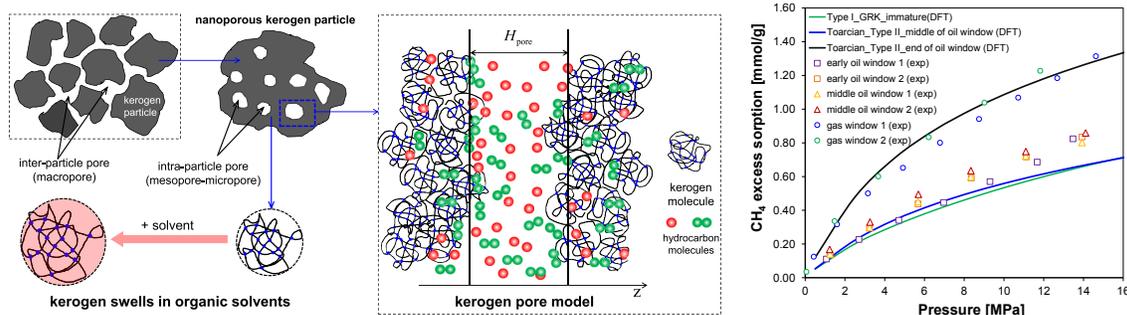
**Bulk fluids:** Our simulation work prior to the award of the PRF grant showed that for bulk fluids, the  $^1\text{H}$ - $^1\text{H}$  NMR autocorrelation function in hydrocarbons and water does not conform to the expectation based on the classical Bloembergen-Purcell-Pound and Torrey models for intra-molecular and inter-molecular relaxation, respectively. (However, the simulations well-describe the experimentally measured NMR  $T_1$  and  $T_2$  relaxation times and the bulk diffusion of the molecules.) In work following the award of the PRF grant, we investigated the causes for the deviation between the classical theories and prediction of relaxation from simulations [1]. We evaluated two assumptions inherent in the classical theories: (i) the molecules are nearly spherical, and (ii) the molecules are rigid, i.e. lack internal motion.

Comparison of neopentane and n-pentane shows that as the molecule becomes more spherical, the NMR  $^1\text{H}$ - $^1\text{H}$  autocorrelation tends towards the classical models (although in absolute terms the deviation between the classical model and simulation is significant). The same trend is seen when we increase molecular symmetry, as found by comparing benzene (a rigid, planar molecule) and n-hexane. Comparison of rigid versus flexible molecules shows that internal motions cause the intra-molecular and inter-molecular correlation times to get significantly shorter, and the corresponding NMR relaxation rates to get significantly smaller, especially for longer-chain n-alkanes. Simulations allow us to probe the  $^1\text{H}$ - $^1\text{H}$  relaxation along each  $\text{CH}_2$  unit of the n-alkane. This site-by-site simulations of  $^1\text{H}$ 's across the chains indicate significant variations in correlation times and relaxation rates across the molecule. We also find that cross-relaxation effects tends to partially average out the variation in relaxation rate across the chain. It is the averaged signal that one detects in NMR. The significance of our study is in highlighting the contributions to the NMR relaxation that need to be considered in creating models of relaxation.

Methane ( $\text{CH}_4$ ) is an important component of shale gas. In probing  $^1\text{H}$ - $^1\text{H}$  NMR relaxation in  $\text{CH}_4$ , the physics of spin-rotation relaxation also assumes importance. To this end, using simulations, we studied the translational diffusion-coefficient and the spin-rotation contribution to the  $^1\text{H}$  NMR relaxation rate over a wide range of densities and temperatures, spanning the liquid, supercritical, and gas phases [2]. (This article was chosen as "Editor's Pick.") We find that the simulated diffusion-coefficients agree well with measurements, without any adjustable parameters in the interpretation of the simulations. We developed a minimization procedure to compute the angular velocity of  $\text{CH}_4$  from atom-velocities available from simulations. We then used this to understand the spin-rotation relaxation. With increasing diffusivity, the autocorrelation function shows increasing deviations from the single-exponential decay predicted by the Langevin theory for rigid spheres, and the deviations are quantified using inverse Laplace transforms. The  $^1\text{H}$  spin-rotation relaxation rate derived from the autocorrelation function using the "kinetic model" agrees well with measurements in the supercritical/gas phase, while the relaxation rate derived using the "diffusion model" agrees well with measurements in the liquid phase. From the

perspective of shale gas, the significance of our study is in revealing that the  $^1\text{H}$  spin-rotation relaxation dominates the  $^1\text{H}$ - $^1\text{H}$  dipole-dipole relaxation at high diffusivity, while the opposite is found at low diffusivity.

**Partitioning of hydrocarbons/ $\text{CO}_2$  in nano-porous kerogen:** The estimation of fluid storage and the multicomponent compositional distribution in shale is a challenging problem. Information of composition in confined matrices is also a vital prelude to molecular simulation studies. To this end, we developed a new thermodynamic model that predicts both the adsorption of hydrocarbons in nanoscale pores and the dissolution of fluids in organic matter in equilibrium with the bulk fluid phase. By acknowledging the chemical and structural similarities of kerogen with asphaltene, we leverage the perturbed chain-statistical associating fluid theory model of asphaltene to create a cross-linked kerogen matrix model. The swelling ratios of five kerogens of varying maturities and types in different solvents are well quantified by phase equilibrium calculation using the new model. We incorporated the new kerogen matrix model (fig. 1) within the interfacial statistical associating fluid theory to form a nano-porous kerogen composite model [3]. With only limited experimental data on the swelling-ratio of kerogen samples as inputs, our model is able to capture the distribution of fluids in the nanoporous kerogen phase.



**Fig 1:** Illustration of the inter-particle and intra-particle space in kerogen (left), the new kerogen pore model that incorporates both fluid adsorption in the pore and absorption in the matrix (middle), and predicted  $\text{CH}_4$  sorption for different kerogen (solid line) and its comparison with experiments.

A key finding of our studies is that there is a significant amount of hydrocarbon storage both in pore space and kerogen matrix. We have extended these ideas to model the competitive adsorption of  $\text{CO}_2$  and  $\text{CH}_4$  in kerogen matrices [4], an aspect of interest in both hydrocarbon extraction and  $\text{CO}_2$  sequestration.

**NMR in Confined fluids:** One of the much debated mysteries in  $^1\text{H}$  NMR relaxation measurements of light fluids confined in the organic nano-pores of kerogen is the underlying mechanism for the NMR surface relaxation and large  $T_1/T_2$  ratio of the nano-confined fluid. Presently, we are studying the NMR relaxation of n-heptane in a polymer matrix, where the high-viscosity polymer is a model for kerogen. Our emerging results show that the surface relaxation component is dispersive, i.e. it depends on the frequency and confinement itself can lead to a high  $T_1/T_2$  ratio for n-heptane. Our results suggest that nano-confinement and not the physics of paramagnetism explains the NMR relaxation measurements of fluids under nano-confinement.

**References:** [1] Singer et al. J. Chem. Phys. 148, 164507 (2018); [2] Singer et al. J. Chem. Phys. 148, 204504 (2018); [3] Liu and Chapman, Energy Fuels 33, 891 (2019); [4] Liu et al. Langmuir 35, 8144 (2019)