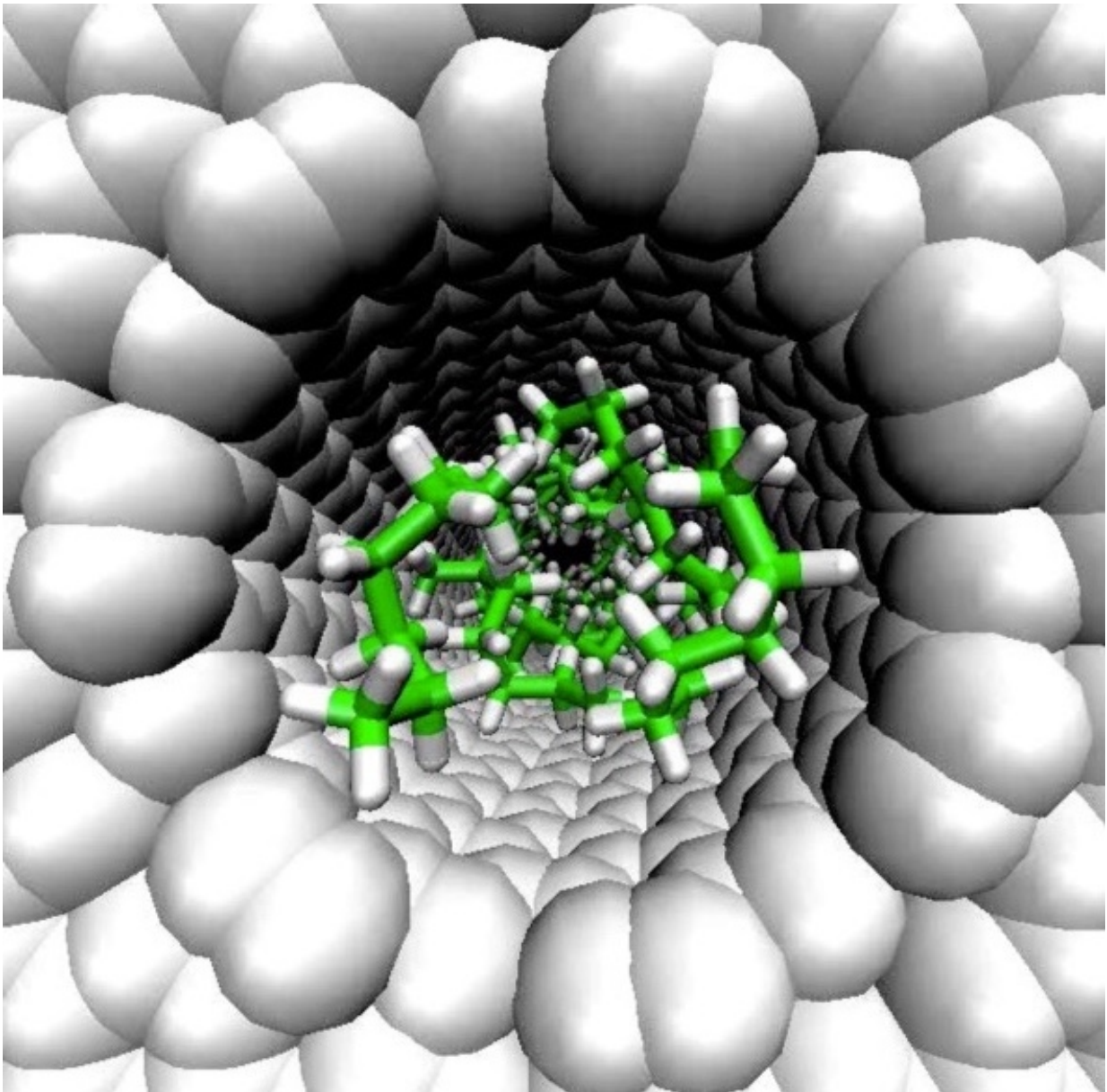


Team takes deeper look at unconventional oil and gas

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Simulations created by Rice University engineers will help them understand the effect of confinement on dipolar relaxation, a critical factor in interpreting nuclear magnetic resonance data. The image here is of heptane molecules in a nanotube. The study is a preliminary step toward understanding dipolar relaxation of fluids confined in the chemically and structurally heterogeneous kerogen matrix in oil shale. Credit: Dilip Asthagiri/Rice University

Understanding how oil and gas molecules, water and rocks interact at the nanoscale will help make extraction of hydrocarbons through hydraulic fracturing more efficient, according to Rice University researchers.

Rice engineers George Hirasaki and Walter Chapman are leading an effort to better characterize the contents of organic shale by combining standard nuclear magnetic resonance (NMR)—the same technology used by hospitals to see inside human bodies - with molecular dynamics simulations.

The work presented this month in the *Journal of Magnetic Resonance* details their method to analyze shale samples and validate simulations that may help producers determine how much oil and/or gas exist in a formation and how difficult they may be to extract.

Oil and gas drillers use NMR to characterize rock they believe contains hydrocarbons. NMR manipulates the hydrogen atoms' nuclear magnetic moments, which can be forced to align by an applied external magnetic field. After the moments are perturbed by radio-frequency electromagnetic pulses, they "relax" back to their original orientation, and NMR can detect that. Because relaxation times differ depending on the molecule and its environment, the information gathered by NMR can help identify whether a molecule is gas, oil or water and the critical size of the [pores](#) that contain them.

"This is their eyes and ears for knowing what's down there," said Hirasaki, who said NMR instruments are among several tools in the string sent downhole to "log," or gather information, about a well.

In conventional reservoirs, he said, the NMR log can distinguish gas, oil and water and quantify the amounts of each contained in the pores of the rock from their relaxation times—known as T1 and T2—as well as how diffuse fluids are.

"If the rock is water-wet, then oil will relax at rates close to that of bulk oil, while water will have a surface-relaxation time that is a function of the pore size," Hirasaki said. "This is because water is relaxed by sites at the water/mineral interface and the ratio of the mineral surface area to water volume is larger in smaller pores. The diffusivity is inversely proportional to the viscosity of the fluid. Thus gas is easily distinguished from oil and water by measuring diffusivity simultaneously with the T2 relaxation time.

"In unconventional reservoirs, both T1 and T2 relaxation times of water and oil are short and have considerable overlap," he said. "Also the T1/T2 ratio can become very large in the smallest pores. The diffusivity is restricted by the nanometer-to-micron size of the pores. Thus it is a challenge to determine if the signal is from gas, oil or water."

Hirasaki said there is debate on whether the short relaxation times in shale are due to paramagnetic sites on mineral surfaces and asphaltene aggregates and/or due to the restricted motion of the molecules confined in small pores. "We don't have an answer yet, but this study is the first step," he said.

"The development of technology to drill horizontal wells and apply multiple hydraulic fractures (up to about 50) is what made oil and gas production commercially viable from unconventional resources,"

Hirasaki said. "These resources were previously known as the 'source rock,' from which oil and gas found in conventional reservoirs had originated and migrated. The source rock was too tight for commercial production using conventional technology."

Fluids pumped downhole to fracture a horizontal well contain water, chemicals and sand that keeps the fracture "propped" open after the injection stops. The fluids are then pumped out to make room for the hydrocarbons to flow.

But not all the water sent downhole comes back. Often the chemical composition of the organic component of shale known as kerogen has an affinity that allows water molecules to bind and block the nanoscale pores that would otherwise let oil and [gas molecules](#) through.

"Kerogen is the organic material that resisted biodegradation during deep burial," Hirasaki said. "When it gets to a certain temperature, the molecules start cracking and make hydrocarbon liquids. Higher temperature makes methane (natural gas). But the fluids are in pores that are so tight the technology developed for conventional reservoirs doesn't apply anymore."

The Rice project managed by lead author Philip Singer, a research scientist in Hirasaki's lab, and co-author Dilip Asthagiri, a research scientist in Chapman's lab, a lecturer and director of Rice's Professional Master's in Chemical Engineering program, applies NMR to kerogen samples and compares it to computer models that simulate how the substances interact, particularly in terms of material's wettability, its affinity for binding to [water](#), gas or oil molecules.

"NMR is very sensitive to fluid-surface interactions," Singer said. "With shale, the complication we're dealing with is the nanoscale pores. The NMR signal changes dramatically compared with measuring

conventional rocks, in which pores are larger than a micron. So to understand what the NMR is telling us in shale, we need to simulate the interactions down to the nanoscale."

The simulations mimic the molecules' known relaxation properties and reveal how they move in such a restrictive environment. When matched with NMR signals, they help interpret conditions downhole. That knowledge could also lead to fracking fluids that are less likely to bind to the rock, improving the flow of hydrocarbons, Hirasaki said.

"If we can verify with measurements in the laboratory how fluids in highly confined or viscous systems behave, then we'll be able to use the same types of models to describe what's happening in the reservoir itself," he said.

One goal is to incorporate the simulations into iSAFT—inhomogeneous Statistical Associating Fluid Theory—a pioneering method developed by Chapman and his group to simulate the free energy landscapes of complex materials and analyze their microstructures, surface forces, wettability and morphological transitions.

"Our results challenge approximations in models that have been used for over 50 years to interpret NMR and MRI (magnetic resonance imaging) data," Chapman said. "Now that we have established the approach, we hope to explain results that have baffled scientists for years."

More information: Philip M. Singer et al, Molecular Dynamics Simulations of NMR Relaxation and Diffusion of Bulk Hydrocarbons and Water, *Journal of Magnetic Resonance* (2017). [DOI: 10.1016/j.jmr.2017.02.001](https://doi.org/10.1016/j.jmr.2017.02.001)

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