Supporting information for: Critical Role of Confinement in the NMR Surface Relaxation and Diffusion of *n*-Heptane in a Polymer Matrix Revealed by MD simulations

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Simulation Details

Both *n*-heptane and the polymer are modeled using using the CHARMM General Force Field,¹ which is known to accurately describe the thermophyscial properties as well as the NMR relaxation and diffusion properties² of hydrocarbons. To construct the simulation system, we first created the structure of *n*-heptane using Avogadro³ and poly(isobutene) using the PRO-DRG server.⁴ We then created N copies of heptane and M copies of poly(isobutene), and pack them separately at a low density (0.1 g/cm^3) using PACKMOL.⁵ The initial numbers are chosen considering ideal mixing and using the experimental density of polymer (0.89) $g/cm^3)^6$ and heptane $(0.68 g/cm^3)^7$ NIST at 298.15 K. The numbers are chosen in such a way that 100% polymer corresponds to 40 molecules. The two boxes are then combined to form the initial simulation box. We use the NAMD⁸ code to perform the simulations. The equations of motion are integrated using the Verlet algorithm with a time step of 1 fs. To remove possible steric clashes, we minimize the system energy using 1000 steps of conjugate gradient minimization. This starting system is necessarily at a much lower pressure due to the low density. We then compress the system to atmospheric pressure using Langevin dynamics, where the temperature of 298.15 K is controlled using a Langevin thermostat and the pressure of 1 atm. is controlled using a Langevin barostat. Compressing from a low density state also ensures we have a well mixed system. This is critical because relying on diffusive motion to ensure mixing is not recommended for systems with low diffusivity, such as the polymer-alkane melt.

We find that after about 1 ns, all the systems studied here achieve a constant density and temperature. We equilibrate this system at constant temperature (*NVT* ensemble) for 1 ns. The temperature during this phase was controlled by reassigning velocities (obtained from a Maxwell-Boltzmann distribution) every 250 steps. The subsequent production run was carried out for 10 ns at constant NVE. Frames were archived every 100 steps for analysis. The Lennard-Jones interactions were smoothly switched to zero between from 13Å and 14 Å. We use the particle mesh Ewald procedure to describe electrostatic interactions, with a grid spacing of 0.5 Å.

Second Moment versus ϕ_{C7}

Figure S1 shows that the square root of the second moment $\Delta \omega_{R,T}^2$ is approximately independent of ϕ_{C7} and that $\Delta \omega_R^2 \approx 4\Delta \omega_T^2$.



Figure S1: Square-root of second moment (i.e. strength) of intra-molecular $(\Delta \omega_R^2)$ and inter-molecular $(\Delta \omega_T^2)$ interactions as a function of ϕ_{C7} in units of KHz.

Surface Relaxivity of Heptane

The surface-relaxivity parameter $\rho_{1,2}$ is given by the following expression:⁹

$$\frac{1}{T_{1S,2S}} = \rho_{1,2} \frac{S}{V_p}$$
(S.1)

where V_p is the pore volume, S is the surface area of the pore, and $\rho_{1,2}$ are the surfacerelaxivity parameters. S and V_p incorporate the geometric factors related pore geometry, while $\rho_{1,2}$ incorporate the surface interactions between heptane and the polymer surfaces. The surface to pore-volume ratio of the polymer matrix is related to the surface to grainvolume ratio of the polymer as such:

$$\frac{S}{V_p} = \frac{1 - \phi_{C7}}{\phi_{C7}} \frac{S}{V_g} = \frac{4}{d}.$$
(S.2)

 V_g is the grain volume of the polymer, which MD simulations have previously shown is $S/V_g \approx 0.859 \text{ Å}^{-1}$ for branched alkanes,¹⁰ independent of the chain length. d is the equivalent diameter of a cylindrical pore, where we imagine heptane to be extended in a cylindrical pore at high confinement. The diameter of the extended heptane is around d = 4.2 Å, which corresponds to $\phi_{C7} = 50$ vol% according to Eq. S.2. It is fair to assume that below $\phi_{C7} < 50$ vol%, heptane molecules interact mainly with the polymer surfaces, and can be thought of as being *ab*sorbed (i.e. dissolved) in the polymer matrix. Note that Eq. S.1 is valid in the small-pore regime, otherwise known as the "fast-diffusion" regime, where $\rho_{1,2} d/D_0 \ll 1$ holds. The fast-diffusion regime holds in the present case, as it also does for nano-pore systems such as those found in shale.

Using Eq. S.1 and S.2 with constant S/V_g results in the following expressions:

$$\frac{1}{\rho_{1,2}} = T_{1S,2S} \frac{1 - \phi_{C7}}{\phi_{C7}} \frac{S}{V_q}, \tag{S.3}$$

$$\frac{\rho_{1,2}}{T_{1S}} = \frac{\rho_2}{\rho_1}.$$
(S.4)

The resulting ρ_1 and ρ_2 are plotted in Figs. S2(a) and (b), respectively, while the ratio is plotted in Fig. S2(c). Also shown in Fig. S2 is the separation between dissolved and pore-fluid states at $\phi_{C7} = 50$ vol%. The simulations show that the surface-relaxivities ρ_1 and ρ_2 are independent of ϕ_{C7} and f_0 for $\phi_{C7} \gtrsim 50$ vol%, as expected in conventional pores. However below $\phi_{C7} \lesssim 50$ -60 vol%, both ρ_1 and ρ_2 increase with decreasing ϕ_{C7} , which we interpret as the "dissolved" region where heptane is no longer in contact with other heptane molecules due to increased confinement in the polymer matrix. We also find that ρ_1 decreases with increasing f_0 , i.e. is dispersive, in the dissolved region. The simulations also show that $T_{1S}/T_{2S} \simeq 1$ in the conventional pore-fluid region, while $T_{1S}/T_{2S} \gtrsim 4$ in the dissolved region which is consistent with previously reported measurements of light hydrocarbons dissolved in kerogen and bitumen.



Figure S2: Surface relaxivities (a) ρ_1 , (b) ρ_2 , and (c) $T_{1S}/T_{2S} (= \rho_2/\rho_1)$ ratio as a function of heptane volume fractions ϕ_{C7} for both simulations (closed symbols) and measurements (open symbols), at frequencies $f_0 = 2.3$ MHz, 22 MHz, and 400 MHz. Dashed vertical line shows dissolved heptane region $\phi_{C7} < 50$ vol%, and pore fluid region $\phi_{C7} > 50$ vol%.

Effect of dissolved oxygen on measurements

Solubility is determined by the excess chemical potential. Here we predict the excess chemical potential of O_2 in the alkane/polymer mixture using

$$\beta \mu_{\mathcal{O}_2}^{\mathrm{ex}} = \ln x_0 - \ln p_0 - \ln \langle e^{-\beta \Delta U} \rangle_0 \tag{S.5}$$

which is the quasichemical organization of the potential distribution theorem.^{11–13} In the above equation, $\ln x_0$ is the work required to move the solvent out of the inner shell defined around the oxygen molecule, $-\ln p_0$ is the work required to created the empty inner shell in the solvent (in the absence of the solute), and $-\ln \langle e^{-\beta\Delta U} \rangle_0$ is the contribution from the interaction of the oxygen with the rest of the solvent when the inner shell is empty. Exploratory calculations show that the interaction between O₂ and alkane/polymer matrix is

dominated by inner-shell exclusion (steric effects) and long-range van der Waals interactions. To this end, we choose an inner shell cavity that is large enough to accommodate the solute but small enough such that $\ln x_0 = 0$. We make a conservative choice of 2.9 Å for the inner shell radius. Here O₂ was modeled using the three site model that has both partial charge and dispersion contribution.¹⁴

For computing p_0 , we first define a cubic grid of size $13 \times 13 \times 13$ Å³. The grid sites are separated by 3 Å. (The simulation boxes are all about 40 Å and hence the grid sits entirely within the simulation cell.) Using the grid sites as reference, we find the number of occurrences for which no carbon atom of the solvent is within 2.9 Å of the grid site. All such sites are archived for further analysis. This calculation also directly provides the probability p_0 of finding a cavity of size 2.9 Å in the hydrocarbon matrix. For the cavities archived from the study above, we compute $-\ln \langle e^{-\beta \Delta U} \rangle_0$ by particle insertion.^{11–13,15} For these calculations, based on the convergence of the free energy, we used only a smaller subset (up to 1000 frames) of the overall 5000 frames. Note that for each site, we also consider three random orientations of the oxygen molecule, further enhancing the statistical reliability.

We obtain the solubility of oxygen in heptane to be 676 ppm. The experiments suggest that the solubility of oxygen in *n*-heptane is around 132 ppm (by weight).^{16,17} To obtain this value (assuming oxygen partial pressure of 0.21 atm.), we need $\beta \mu_{O_2}^{ex} \approx 5.0$. In energy units, the difference between our computed value and 5.0 is about 0.9 kcal/mol. This small difference may result from deficiencies of the force field itself. However, we suspect the relative solubility trends to be well-captured by our simulations. Since the solubility relative to the bulk is of most interest, in Fig. S3 we show the relative solubility of O₂ in the alkane/polymer mixture. Considering the relative solubility also serves to minimize the errors in the absolute solvation values, that are off by a factor of 5.

The relation between the measured $T_{1,2}^{\text{meas}}$ and the intrinsic $T_{1,2}$ of interest is given by the

following expression:^{18,19}

$$\frac{1}{T_{1,2}^{\text{meas}}} = \frac{1}{T_{1,2}} + \frac{C_{O_2}}{T_{1O_2,2O_2}}.$$
(S.6)

The measured $T_{1O_2} (= T_{2O_2})$ for pure heptane at ambient conditions are $T_{1O_2} = 2490$ ms, 2620 ms, and 5580 ms at $f_0 = 2.3$ MHz, 22 MHz, and 400 MHz, respectively.⁶ It was previously shown that T_{1O_2} is roughly constant for solvents with the molecular weight of heptane or higher.¹⁸ In other words, $T_{1O_2} (= T_{2O_2})$ in Eq. S.6 is assumed to be independent of ϕ_{C7} . As shown in Fig. S4, we find good agreement between simulated $T_{1,2}$ and measured $T_{1,2}$ assuming $C_{O_2} = 1$ for all ϕ_{C7} in Eq. S.6.



Figure S3: MD simulations of concentration C_{O_2} of dissolved oxygen in the polymer-heptane mix, as a function of heptane volume fraction ϕ_{C7} . C_{O_2} is defined relative to pure heptane $(\phi_{C7} = 100 \text{ vol}\%)$, under ambient conditions.

However, as shown in Fig. S3, C_{O_2} decreases at around $\phi_{C7} \simeq 50$ vol%, and therefore the assumption that $C_{O_2} = 1$ for all ϕ_{C7} may not be accurate. In order to quantify this effect, Fig. S4 shows the measured $T_{1,2}$ using the simulated C_{O_2} values as a function of ϕ_{C7} from Fig. S3, the results of which are shown as the leftmost point of the vertical lines in Fig. S4. Using the C_{O_2} values from Fig. S3 improves the comparison between measurements and



Figure S4: Correlation cross-plot of measurements vs. simulations of T_1 and T_2 at $f_0 = 2.3$ MHz, 22 MHz, 400 MHz, for various heptane volume fractions ϕ_{C7} . Symbols use $C_{O_2} = 1$ in Eq. S.6 to determine $T_{1,2}$ from measured $T_{1,2}^{\text{meas}}$, while leftmost point of the individual vertical lines uses C_{O_2} values from Fig. S3.

simulations in the region $\phi_{C7} \simeq 50$ vol%, however a discrepancy is then found in the region $\phi_{C7} > 70$ vol%. We note however that the simulated C_{O_2} in Fig. S3 are qualitative and designed to capture the overall trends in C_{O_2} , namely that C_{O_2} decreases around $\phi_{C7} \simeq 50$ vol%, which coincides with the discrepancy between measurements and simulations of $T_{1,2}$ in that region. This gives credibility, though not certainty, to the proposition that variations in C_{O_2} with ϕ_{C7} are the cause of the discrepancy between measurements and simulations at $\phi_{C7} \simeq 50$ vol%.

Diffusivity of Water in Kerogen



Figure S5: Diffusion- T_2 (D- T_2) measurement at ambient of water-saturated isolated kerogen pellets from a Kimmeridge outcrop (same kerogen as used in^{20,21}). Right panel shows Dprojection (red). Upper panel shows the T_2 projection from D- T_2 (red), along with full T_2 distribution (blue). The projection from D- T_2 (9.5 pu) shows less signal intensity than the full T_2 (35.8 pu) due to limitations in the D- T_2 measurement. The diffusion coefficient (taken at the peak of the D distribution) of the inter-granular water is detectable, while the diffusion coefficient for dissolved water is not detectable. Dashed horizontal line is the bulk D_0 for water, while the dashed diagonal line is the bulk alkane line.²²

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