Explicit calculation of nuclear magnetic resonance relaxation rates in small pores to elucidate molecular scale fluid dynamics

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A model linking the molecular-scale dynamics of fluids confined to nano-pores to nuclear magnetic resonance (NMR) relaxation rates is proposed. The model is fit to experimental NMR dispersions for water and oil in an oil shale assuming that each fluid is characterised by three time constants and Lévy statistics. Results yield meaningful and consistent intra-pore dynamical time constants, insight into diffusion mechanisms and pore morphology. The model is applicable to a wide range of porous systems and advances NMR dispersion as a powerful tool for measuring nano-porous fluid properties.

Understanding molecular-scale fluid dynamics in micro- and meso-porous materials is central to understanding a wide range of industrially-important materials and processes: rocks for petroleum engineering; zeolites for catalysis; calcium-silicate-hydrates for concrete construction; bio-polymers for food production to name but a few. A molecular-scale model of fluid in a pore is depicted in Fig. 1. In this general picture, one considers fluid within the body of the pore and a surface layer of fluid at the pore wall. The pore body fluid behaves much as a bulk fluid, free to diffuse in three dimensions with motion characterised by a correlation time $\tau_c$. The surface layer diffuses in just two dimensions (2D) with motion characterised by a slower correlation time $\tau_s$. Molecular exchange is envisaged between the surface layer and the bulk fluid characterised by a desorption time $\tau_d$ and a corresponding adsorption time linked to $\tau_d$ by the requirements of mass balance. This model therefore simplifies the complex intra-pore dynamics of real fluids to three characteristic time constants, $\tau_c$, $\tau_s$, and $\tau_d$. Aspects of this general model, henceforth referred to as the 3$\tau$ model, are widely used throughout literature [1–8].

Nuclear magnetic resonance (NMR) relaxation analysis is a uniquely powerful tool to access molecular correlation times of fluids in porous media [1–9]. It is rivalled only by small-angle scattering techniques, especially with neutrons, but has the advantage of being widely available using laboratory-scale equipment. Two NMR relaxation methods are especially valuable. NMR relaxation dispersion (NMRD) measurement of the frequency dependence of the nuclear (usually $^1$H) spin-lattice relaxation time ($T_1$) of fluid molecules in the low-frequency range (kHz to MHz) is sensitive to fluid correlation times. Second, the $T_1$–$T_2$ correlation experiment measures the ratio of $T_1$ to the nuclear spin-spin relaxation time $T_2$. This is especially sensitive to different relaxation mechanisms.

However, for the NMR methods to be useful, a model is required to link fluid molecular dynamics in pores to NMR relaxation rates. Several models have been proposed (for example, [1–2, 6, 7, 10]) but that which builds most successfully on the general dynamics of the model illustrated in Fig. 1 in terms of fitting experimental data is due to Korb and co-workers [3, 6, 10]. Korb’s model reproduces the fundamental form of the $T_1$ dispersion curve at low frequency in most systems and predicts the $T_1/T_2$ ratio. The model supposes that the dominant relaxation mechanism involves repeated encounters of the diffusing surface layer molecules with static surface relaxation sites, most typically paramagnetic impurities. Korb’s model identifies 3 key parameters: two are the correlation times $\tau_c$ and $\tau_s$ of the general model (Fig. 1), the third is a frequency-independent bulk-fluid spin-lattice relaxation time $T_{1,b}$. It is roughly linked to $\tau_c$. From these parameters Korb produces, first, an approximate surface-diffusion-driven temporal nuclear magnetic correlation function $G(t)$ and, second, the relaxation rates. With time and varied application, two limitations of the Korb model have become apparent. The first is that the physical parameters $\tau_c$ and $\tau_s$ required to fit experimental data are remarkably uniform, typically about 1 ns and 1–10 $\mu$s, respectively. A lack of sensitivity to the diversity of experimental systems studied seems to imply an underlying problem. The second is that it is very hard to justify the correlation times in terms of physics and chemistry. Surface molecules must undergo $10^3$–$10^5$ surface hops across the pore surface without desorbing. That the molecules must be both “sticky” and “non-sticky” at the same time is seemingly contradictory.

In this letter, we propose a model of NMR relaxation of fluids in pores that: (i) preserves the presumed fluid dynamics captured in the 3$\tau$ model (Fig. 1); (ii) achieves improved fits to experimental data and (iii) predicts physically-realistic parameters. The model has exactly the same number of adjustable parameters as the Korb model. The model also retains the essential relaxation mechanism of Korb (surface interactions). However, three advances conspire to have critical and profound effect on the outcomes. The three key advances included in our model are as follows. First, we assume that the paramagnetic relaxation centres are embedded in the pore wall whereas the Korb model assumes them to reside on the pore wall. From this the correlation function...
may be written using cylindrical coordinates as

\[ P(r, t \cap r_0) = N \int P(\rho, t | \rho_0) P(z, t | z_0) \]

where \( N \) is the number of paramagnetic spins per unit volume, \( P(\rho, t | \rho_0) \) describes the probability that a spin pair has an in-plane displacement \( \rho \) at time \( t \) given the displacement was \( \rho_0 \) at \( t = 0 \) and is described by Lévy walk statistics via the transform

\[ P(\rho, t | \rho_0) = \frac{1}{4\pi^2} \int e^{-D\kappa^2} e^{i\kappa \rho} e^{-i\kappa \rho_0} d^2k \]

where \( k \) is an in-plane Fourier variable and \( 0 < \alpha \leq 2 \) is the Lévy parameter. If \( \alpha = 2 \), Eq. (2) represents the transform of a Gaussian function and normal Fickian diffusion is recovered. If \( \alpha < 2 \), the probability distribution possesses power-law tails providing enhanced probability density in the wings of the distribution.

The dipolar correlation function \( G(t) \) is \[ 7, 12 \]

\[ G(t) = \frac{4\pi}{5} \int \sum_{M=2}^{\infty} \frac{Y_m(\rho_0, \phi_0, z_0) Y_m^*(\rho, \phi, z)}{(\rho_0^2 + z_0^2)^{3/2} (\rho^2 + z^2)^{3/2}} \times P(r, t \cap r_0) d^4r_0 d^4r \]

where the \( Y \) are the spherical harmonic functions of degree 2 where the asterisk represents the complex conjugate. The powder average has been taken reflecting the (assumed) uniform random orientation of pores in experimental samples \[ 7, 12 \]. Substitution of Eqs. \[ 1 \] into Eq. \[ 4 \], application of the Jacobi-Anger expression followed by volume integrations finally yields

\[ G(t) = \frac{2N}{5\delta^3\Delta} \int_0^\infty e^{-t\kappa^2/4\tau} \kappa \left[ H(\kappa) + 2 \sum_{p=1}^\infty c_p(t, \kappa) \right] d\kappa \]

where \( \kappa = k\delta \) is a dimensionless Fourier variable and

\[ H(\kappa) = \frac{5\pi}{3} \left( e^{\kappa \Delta} - 1 \right)^2 e^{-2\kappa(\Delta+\eta)} \]

\[ c_p(t, \kappa) = \frac{5\pi k^4 \Delta^4}{3 \left[ k^2 \Delta^2 + p^2 \pi^2 \right]} \left[ e^{2\kappa \Delta} \right]^{p^2 \pi^2 t/6 \Delta^2 \tau} \]

The dimensionless distances \( \eta \) and \( \Delta \) are \( d/\delta \) and \( h/\delta \) respectively where \( \delta \) is a convenient molecular-scale distance taken as 0.27 nm, the approximate inter-molecular spin-spin distance in water. \( \delta \) also links \( \tau_i \) and \( \tau_n \) to their diffusion coefficient via \( D = \delta^2/6\tau \).
Finally, the spectral density function $J(\omega)$ is obtained from the Fourier transformation of $G(t)$ allowing $T_1^{-1}$ and $T_2^{-1}$ to be found as follows \[ J(\omega) = 2 \int_0^{\infty} G(t) \cos \omega t \, dt \] \[ T_1^{-1} = \frac{1}{3} \beta \left[ 7J(\omega_\sigma) + 3J(\omega_p) \right] \] \[ T_2^{-1} = \frac{1}{6} \beta \left[ 4J(0) + 13J(\omega_\sigma) + 3J(\omega_p) \right]. \] Here $\beta = (\mu_0/4\pi)^2 \gamma_p^2 \gamma_\sigma^2 \hbar^2 S(\bar{S} + 1)$, $\gamma_\sigma$ ($\gamma_p$) is the gyromagnetic ratio for the paramagnetic impurity (proton) and $S = \frac{1}{2}$ for Mn$^{2+}$ or Fe$^{3+}$. $\omega_p$ is the Larmor frequency of a proton in the applied static field and $\omega_\sigma = 658.21 \omega_p$.

The model is now fit to the $T_1^{-1}$ dispersions from the first (and only to date) experimental study of an oil shale due to Korb and co-workers \[3\]. The separate oil and water dispersions are presented in Figs. 2 and 3. Notice how the two data sets have different functional dependence on frequency indicating different distributions within the pore. Spin relaxation in this oil shale is due to the interaction of $^1$H in the water and oil with Mn$^{2+}$ ions identified as the dominant paramagnetic species by electron spin resonance \[3\]. Fits are undertaken by varying $\tau_s$, $\tau_b$ and $\tau_a$ with fit quality assessed using a simple least-squares measure.

The pore surface is found to be oil wetting. Contributions to $T_1^{-1}$, are due to the interaction of Mn$^{2+}$ impurities in the pore walls with surface oil ($T_{1,oil}^{-1}$) and bulk oil ($T_{1,b-oil}^{-1}$). $G_{b-oil}(t)$ is calculated from Eq. 5 using the parameters for bulk oil in Table 1 and $G_{o-oil}(t)$ may be written

$$G_{o-oil}(t) = f G(t) + (1-f) G(t) e^{-t/\tau_d} \tag{11}$$

where $G(t)$ is calculated using Eq. 5 using tabulated parameters for surface oil. Eq. 11 could arise if a fraction $f$ of the surface comprises a mono-layer of oil where no desorption occurs over the time scale of $T_1$ or $T_2$. This would arise with droplets of oil occupying (1 – $f$) of the surface area or in pits (Fig. 4). $T_{1,oil}^{-1}$ is then found via

$$T_{1,oil}^{-1}(\tau_s, \tau_b, \tau_a) = x T_{1,oil}^{-1}(\tau_s, \tau_b) + (1-x) T_{1,b-oil}^{-1}(\tau_a) \tag{12}$$

where the explicit dependence on the $\tau$ parameters is indicated. The quantity $x$ represents the fraction of oil in the surface layer and Eq. 12 is justified if $\min(T_1, T_2) \gg \max(\tau_s, \tau_b, \tau_a)$, the so-called fast-diffusion limit.

Parameters and fit outcomes are listed in Table 1. Satisfactory fits cannot be obtained using the experimental Mn$^{2+}$ spin density of $N \approx 0.5/mu^3$ \[3\]. It is found that the effective Mn$^{2+}$ density is about $N/20$. This is not unexpected, a non-linear relationship between relaxation rate and impurity density is well known. The impact of the Mn$^{2+}$ impurities is reduced due to clustering in the rock and, as would appear here, desorption of Mn$^{2+}$ at pore walls into the pore fluid.

Results show that $\tau_b \approx \tau_a$, suggesting that surface diffusion and desorption of oil molecules are linked processes, very different from the Korb model. A mechanism consistent with this result allows a surface molecule to deposit the surface, the vacancy filled by a second surface molecule (rather than by a bulk molecule whose passage is blocked) leaving a second vacancy which is either filled by the desorbed molecule (exchange), a bulk molecule or a another surface molecule. The mechanism is illustrated in Fig. 1. It is noted that since surface molecules only execute a few hops before desorbing, the surface only needs to be locally flat for the pore model of Fig. 1 to be valid.

$T_{1,oil}^{-1}$ was explored for different values of the Lévy parameter $\alpha$. For $\alpha = 0.5$, $T_{1,oil}^{-1}$ differs by at most 10% over the frequency range of fits but overall fit quality is unchanged compared to Fickian statistics with $\alpha = 2$. This is because the dominant contribution to $T_{1,oil}^{-1}$ arises for surface spins which make just a few hops on the surface prior to desorption. This contribution is adequately described by Fickian dynamics. Whilst surface spin diffusion is almost certainly a Lévy process, the difference between Fickian and Lévy dynamics does not in practice reveal itself in fits to this set of dispersion data.

| Parameter | Oil | Water |
|-----------|-----|-------|
| $\bar{f}$ | 0.1–0.2 | – |
| $d_b/d_h$ | 28/3δ | –/3δ |
| $h_b/h_h$ | δ/18δ | –/18δ |
| $\alpha$ | 2 | – |
| $\tau_b$ | 20–40 ps | 10–40 ps |
| $\tau_s$ | 0.1–0.5 μs | – |
| $\tau_d$ | 0.2–0.3 μs | – |

The bulk oil correlation time $\tau_b$ lies in the range 20–40 ps, consistent with, but slightly longer than, typical
pure alkanes (15 ps) [13]. The $T_{1,\text{oil}}/T_{2,\text{oil}}$ ratio, which ranges from 5 to 10 experimentally [8], is found to be a strong function of $\tau_1$ with $\tau_1 = 0.1 \mu s$ corresponding to $T_{1,\text{oil}}/T_{2,\text{oil}} \approx 5$ and $\tau_1 = 0.5 \mu s$ to $T_{1,\text{oil}}/T_{2,\text{oil}} \approx 10$. This result suggests that the $T_{1,\text{oil}}/T_{2,\text{oil}}$ ratio might provide a direct measure of surface affinity. Combined with peak-spread information, it may be possible to infer oil chain length and surface affinity from $T_1$–$T_2$ maps. With downbore $T_1$–$T_2$ mapping a possibility in the future, the significance of this result is obvious.

Analysis of the $T_{1,\text{wat}}^{-1}$ dispersion for water, that is a different shape to oil, reveals that $T_{1,\text{c-wat}}^{-1}$ does not contribute to the measured dispersion and therefore water is not located on the pore surface – an independent observation compatible with an oil-wetting shale. Yet the magnitude of the experimental $T_{1,\text{wat}}^{-1}$ dispersion provides unequivocal evidence of interaction with Mn$^{2+}$ ions. It is therefore proposed that Mn$^{2+}$ ions are present in the bulk water. This conclusion is supported by the earlier observation that Mn$^{2+}$ impurities are depleted at the pore surfaces, presumably having desorbed over millennia into the bulk water. It is noted that Mn$^{2+}$ was not found in the oil where it is insoluble. It is noted that $T_{1,\text{wat}}^{-1}/T_{2,\text{wat}}$ for water in oil shale is typically $\approx 2$ [9], close to that for MnCl$_2$ solution [14].

The contribution $T_{1,\text{wat}}^{-1}$ due to aqueous Mn$^{2+}$ is estimated from the expression obtained for bulk water [12] [15] adapted to describe the relative motion of water spins with respect to a Mn$^{2+}$ ion assumed to be static. Therefore

$$T_{1,\text{wat}}^{-1}(\tau_b) = T_{1,\text{s-wat}}^{-1}(\tau_b) + T_{1,\text{w-at}}^{-1}(\tau_b)$$  \hspace{1cm} (13)$$

which has a single fit parameter, $\tau_b$. Optimum fits (Fig. 3) are obtained for $\tau_b \approx 10$–40 ps, longer than for pure water at room temperature (5.3 ps) but consistent with a reduction of the diffusion coefficient due to dissolved ions and molecules. The aqueous Mn$^{2+}$ density is found from the fits to be 5–7.5 mM, a factor 100-150 more dilute than the measured equivalent density in the solid. Assuming pores are mostly water-filled and that all surface Mn$^{2+}$ has desorbed, the mean pore thickness is estimated at 50–80 nm.

![FIG. 3. $T_{1,\text{wat}}^{-1}$ is presented as a function of frequency for water in an oil shale. The experimental data (•) is from [9]. The theoretical curve (——) is composed of a contribution due to the interaction of bulk water with Mn$^{2+}$ in the pore walls (○○○) and aqueous Mn$^{2+}$ (− − −).](image-url)

In summary, a general model is proposed which captures the molecular dynamics of fluids in porous solids. The theory is presented which translates the model to $T_1^{-1}$ dispersions and is tested by fitting to NMRD measurements on an oil shale. The analysis yields a wealth of physically-reasonable time constants which are consistent between the two co-existing fluids, provides insights into diffusion mechanisms and pore morphology. The $3\tau$ model and theoretical results are applicable to any porous systems containing $^1$H spins in motion relative to fixed paramagnetic impurities and establishes NMRD as a powerful experimental tool for measuring the dynamical properties of fluids in porous solids.

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