Nuclear magnetic relaxation of liquids in porous media

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Abstract. Nuclear magnetic relaxation is useful for probing physical and chemical properties of liquids in porous media. Examples are given on high surface area porous materials including calibrated porous silica glasses, granular packings, plaster pastes, cement-based materials and natural porous materials, such as sandstone and carbonate rocks. Here, we outline our recent NMR relaxation work for these very different porous materials. For instance, low field NMR relaxation of water in calibrated granular packings leads to striking different pore-size dependencies of the relaxation times $T_1$ and $T_2$ when changing the amount of surface paramagnetic impurities. This allows separation of the diffusion and surface limited regimes of relaxation in these macroporous media. The magnetic field dependence of the nuclear spin–lattice relaxation rate $1/T_1(\omega_0)$ is also a rich source of dynamical information for characterizing the molecular dynamics of liquids in porous media. This allows a continuous characterization of the evolving microstructure of various cementitious materials. Our recent applications of two-dimensional (2D) $T_1$–$T_2$ and $T_2$-z-store-$T_2$ correlation experiments have evidenced the water exchange in connected micropores of cement pastes. The direct probing of water adsorption time on a solid surface gives access to an original characterization of the surface nano-wettability of porous plaster pastes. We show that such a parameter depends directly on the physical chemistry of the pore surfaces. Lastly, we outline our recent measurements of wettability in oil/brine/reservoir carbonate rocks.
1. Introduction

Nuclear magnetic relaxation methods offer a variety of opportunities for characterizing the molecular dynamics in confined environments [1]–[6]. Systems of interest are high surface area materials including biological tissues, chromatographic supports, heterogeneous catalytic materials, plaster, cements and natural microporous materials, such as clay minerals and rocks.

The magnetic field dependence of the nuclear spin relaxation rate is a rich source of dynamical information [7]–[11]. Varying the magnetic field changes the Larmor frequency, and thus the fluctuations to which the nuclear spin relaxation is sensitive. Moreover, this method permits a more complete characterization of the dynamics than the usual measurements as a function of temperature at fixed magnetic field strength because many common solvent liquids have phase transitions that may alter significantly the character of the dynamics over the temperature range usually studied. Further, the magnetic field dependence of the spin–lattice relaxation rate, $1/T_1$, provides a good test of the theories that relate the measurement to the microdynamical behavior of the liquid. This is especially true in spatially confined systems where the effects of reduced dimensionality may force more frequent re-encounters of spin-bearing molecules that may alter the correlation functions that enter the relaxation equations in a fundamental way. Now, concerning the measurement of the magnetic field dependence of the spin–lattice relaxation rate, a comprehensive study of field cycling NMR relaxometry of various systems in confinement can be found in [12]. Deuteron and proton field cycling NMR relaxometry are useful for revealing pronounced effects concerning the molecular dynamics of adsorbate molecules in calibrated porous glasses [10].

We may distinguish two classes of high surface area systems: solid phases that are proton rich, such as biological macromolecules, including proteins, carbohydrates and engineering polymers like polystyrene, and those that are proton poor, such as microporous glasses, zeolites,
plaster, cements or the clay minerals. In the first class, cross-relaxation between the protons of the liquid and those of the solid may make dominant contributions to the nature of the magnetic field dependence of the nuclear spin relaxation rate observed \([11]\). In a number of such proton-rich cases studied, the magnetic field dependence of the liquid spin relaxation reports the magnetic field dependence of the solid-phase relaxation. In the second case of the proton-poor solid, other effects dominate the liquid spin relaxation, including, in particular, those that are dependent on the translational diffusion of liquid in the neighborhood of solid surfaces \([4, 5]\).

In the present study, we are mainly interested in high surface areas, such as microporous chromatographic glass \([13, 14]\), granular packings \([15, 16]\), cements \([17]–[25]\) and rocks \([26]–[31]\) that contain concentrations of paramagnetic centers (iron or manganese) that may alter the nature of the relaxation significantly. In particular, the paramagnetic centers provide a large magnetic moment and local dipolar field in which the diffusing liquid spins move. The effects of the electron magnetic moments are large and dominate unambiguously the proton spin–lattice relaxation at low magnetic field strengths. These effects can seriously limit the use of pulsed gradient field (PFG) techniques for probing the self-diffusion coefficient of liquids in microporous media. However, some authors succeed in using these techniques even in hydrating cement pastes \([22]\). We also describe the particular case of plaster pastes that do not contain paramagnetic contaminants \([32]–[36]\). In all of these systems, we discuss more particularly the role of nuclear magnetic relaxation dispersion (NMRD) experiments for probing physical and chemical properties of various liquids in confinement.

2. Nuclear spin relaxation of liquids within pores

2.1. What is the limiting relaxation process in pores?

Basically, there are two limiting cases in the theoretical description of the relaxation of liquids filling pores with surface relaxation sinks \([37]\). These cases are either slow-diffusion or fast-diffusion (surface-limited) relaxation, provided that bulk diffusion or surface processes dominate, respectively. Theoretical expressions of the nuclear relaxation rates were proposed in each limited case \([37]\). We were interested to follow experimentally the transition between these two limiting cases. For that purpose, we measured the pore-size relaxation data of water in calibrated granular packings in the general situation when both processes occur \([15]\).

Let us first consider the theoretical description of the pore-size dependence of the relaxation rate \((1/T_1, 1/T_2)\) for a liquid fully saturating the macroporous system schematically represented in figure 1(a). Here, we consider only the pore-size dependence of these rates without consideration of the frequency dependence. We have considered explicitly the exchange rate \(W\) between the surface layer of thickness \(\lambda\) and the bulk, and their respective relaxation times \(T_{1,\text{surf}}\) and \(T_{1,\text{bulk}}\) \([15]\). One finds at long times \(t\) and under the condition of biphasic fast exchange \([15, 37]\), \(t \gg T_{1,\text{surf}} \gg 1/W\), an exponential time decay of the longitudinal magnetization with the following pore-size dependence of the spin–lattice relaxation rate,

\[
\frac{1}{T_1(d_{\text{pore}})} = \frac{1}{T_{1,\text{bulk}}} + \frac{2\alpha\rho_1}{d_{\text{pore}}} \frac{1}{1 + \rho_1 d_{\text{pore}}/4D}.
\]

In equation (1), \(d_{\text{pore}}\) is the characteristic pore dimension (diameter) of the model pore and \(\alpha = 1, 2, 3\) is the shape factor for planar, cylindrical and spherical pore geometry, respectively. The efficiency of the spin–lattice relaxivity is qualified by \(\rho_1 = \lambda / T_{1S}\) and \(D\) is the...
Figure 1. (a) Schematic diagram of a porous medium with indication of the relaxation variables used in the text. (b) The $^1$H measured water spin–lattice ($T_1$) and spin–spin ($T_2$) relaxation times as a function of the pore diameter $d_{pore}$, at 2.2 MHz and 34°C, before cleaning the surface (data from [15]). The quadratic continuous lines represent the best fits obtained with equation (2a). (c) The measured $^1$H water spin–lattice ($T_1$) and spin–spin ($T_2$) relaxation times as a function of $d_{pore}$, at 2.2 MHz, and 34°C after cleaning the surface (data from [15]). The lines represent the theoretical pore-size dependencies calculated with equation (2b), with the surface relaxivity parameters, $\rho_1 = 0.94 \mu$m s$^{-1}$ and $\rho_2 = 3.4 \mu$m s$^{-1}$.

translational self-diffusion coefficient of the embedded liquid within pores. This length-scale $\lambda$ represents a representative distance over which the effects of the surface relaxation disappear (figure 2(a)). The dipole–dipole correlation being proportional to the inverse of the sixth power of the distance, $\lambda$ is of the order of a few molecular sizes, as was shown by some calorimetric measurements [38]. The expression of the pore-size dependence of the spin–spin relaxation is similar, exchanging the indices 1 and 2. Here, we have omitted the frequency dependence of the dynamical spectral densities that are, of course, different for $1/T_1$ or $1/T_2$. Equation (1) shows clearly the independence of bulk and confined relaxation rates, whereas the confined rate depends on the two relaxation processes in series. A direct comparison of $4D/d_{pore}$ and $\rho_{1,2}$ shows that the slowest process limits the relaxation. For instance, when $4D/d_{pore} \ll \rho_{1,2}$ the relaxation is diffusion-limited, and equation (1) simplifies,

$$\frac{1}{T_{1,2}(d_{pore})} = \frac{1}{T_{1,2} \text{bulk}} + \frac{8\alpha D}{d_{pore}^2}. \tag{2a}$$

On the other hand, when $4D/d_{pore} \gg \rho_{1,2}$, the relaxation is surface limited, and one has

$$\frac{1}{T_{1,2}(d_{pore})} = \frac{1}{T_{1,2} \text{bulk}} + \frac{2\alpha \rho_{1,2}}{d_{pore}}. \tag{2b}$$

These expressions thus relate directly the relaxation times $T_1$ or $T_2$ to either $d_{pore}^2$ or $d_{pore}$ provided that the conditions of diffusion-limited or surface-limited relaxation are fulfilled, respectively. Equations (2a) and (2b) thus exhibit potentially two very different pore-size dependencies that allow identifying the limiting relaxation process that occurs in pores.

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Figure 2. (a) Schematic diagram of surface diffusion of the proton species of an aprotic liquid on a pore silica surface limited by exchange with bulk liquid with indication of the different correlation times used in equation (7). (b) Schematic diagram of the slit or channel pore model. The nuclear spins $I$ diffuse in an infinite layer of thickness $d$ between two flat solid surfaces in the dipolar field of a very small quantity of paramagnetic spins $S$ fixed on the surface.

2.2. Experimental transition between slow-diffusion and fast-diffusion relaxation processes in granular packings

We show by low field NMR relaxation that changing the amount of surface paramagnetic impurities leads to striking different pore-size dependencies of the relaxation times $T_1$ and $T_2$ of liquids in pores allowing to separate experimentally the surface-limited and diffusion relaxation processes.

We have prepared a series of packings of non-porous SiC grains individually sorted in the range between 8 and 150 $\mu$m that present 25% of the surface covered by SiO$_2$ [15]. The interest of these model samples is that they lead to pore sizes and surfaces comparable to oil-bearing sandstone rocks. Two series of packings were prepared before and after removing the surface paramagnetic impurities by hydrochloric acid cleaning. After cleaning, we evidence by electron spin resonance (ESR) the quantity of chemically bonded Fe$^{3+}$ paramagnetic ions. We measured at 2.2 MHz and 34 °C the pore-size dependence of $T_1$ and $T_2$ of water fully
saturating these samples. Experimental results show that for the uncleaned porous media presenting a high surface density of paramagnetic impurities (figure 1(b)), $T_1$ and $T_2$ relaxation times of water vary as the square of the pore diameter $d_{\text{pore}}$ (quasi-spherical pores). This dependence agrees well with the diffusion-limited relaxation (equation (2a) with $\alpha = 3$). On the other hand, the results show a linear pore-size dependence of $T_{1\text{corr}}$ and $T_{2\text{corr}}$ for the cleaned porous media, presenting a low surface density of paramagnetic impurities (figure 1(c)). Here, $1/T_{1,2\text{corr}} = 1/T_{1,2} - 1/T_{1,2\text{bulk}}$. This dependence agrees well with the surface-limited relaxation (equation (2b)). We therefore estimate the surface relaxivity parameters $\rho_1 = 0.94 \mu\text{m s}^{-1}$ and $\rho_2 = 3.4 \mu\text{m s}^{-1}$ from the slopes of the linear fits of figure 1(c). These values are typical of natural rock values, thus justifying that surface-limited relaxation process is relevant in these widely encountered porous systems.

3. Nuclear magnetic relaxation dispersion (NMRD) of surface spin–lattice relaxation rate

3.1. Theory

In the fast diffusion limit, one can apply the biphasic fast exchange model [37] where the exchange time between the surface and the bulk phases is shorter than their respective relaxation times. The overall proton relaxation rate $1/T_1$ is thus a linear combination of a bulk $1/T_{1\text{,bulk}}$ and a surface relaxation rate $1/T_{1\text{,surf}}$. We show here that the surface term is a superposition of the contribution $1/T_{1,2D}$ of the proton species ($I$) diffusing in the proximity of the fixed paramagnetic species ($S$) [13] and the contribution $1/T_{1,\text{param}}$ of the proton species linked to the first coordination sphere of paramagnetic centers,

$$\frac{1}{T_1(\omega_f)} = \frac{1}{T_{1\text{,bulk}}(\omega_f)} + \frac{N_{\text{Surface}}}{N} \frac{1}{T_{1,2D}(\omega_f)} + \frac{N_{\text{param}}}{N} \frac{1}{T_{1,\text{param}}(\omega_f)}.$$  

(3)

The bulk relaxation term, $1/T_{1\text{,bulk}}$, has no proton Larmor frequency $\omega/2\pi$ dependence in the range studied here [39]. The two surface relaxation terms are highly sensitive to the local physical-chemistry effects at the pore surface resulting in different frequency behaviors in disconnected ranges. The inclusion of the nuclear paramagnetic term is new and critical because it extends the theory to make the NMRD of protic liquid different to the aprotic one [40, 41].

The terms protic and aprotic are defined through the ability for the studied liquids to exchange or not their protons, respectively, this exchangeable character being independent of the polarity of such liquids. For instance, the protic liquid is revealed in the presence of a possible hydrogen bonding. The aprotic liquid exists in the presence of non-exchangeable protons as in $-\text{CH}_3$ or $-\text{CH}_2$ groups. We outline below the calculation of these two terms in the local layer geometry at proximity of the pore surface (figure 2(a)) or in the pore-slit model (figure 2(b)). In this model, $N_{\text{Surface}}/N = \lambda S_p \rho_{\text{liquid}}$ is the ratio between the number $N_{\text{Surface}}$ of liquid molecules diffusing within the thin transient layer $\lambda$ close to the pore surface and the bulk liquid population $N$. Here $\lambda$ is of the order of a few molecular sizes [38]. $S_p$ is the specific surface area of the sample and $\rho_{\text{liquid}}$ is the density of the proton liquid. $N_{\text{param}}/N = (N_{\text{param}}/N_s)(N_s/N) \ll N_s/N$ is the ratio between the number of liquid molecules bonded to the paramagnetic sites at the surface and in the bulk.

The paramagnetic sites located at the pore surface have a ligand field that either traps a moving proton species defined as a protic liquid wetting the surface (figures 2(a) and (b)), or does not trap a moving proton species defined as an aprotic liquid. These chemical behaviors
result in two distinct features of the NMRD that can be individualized by $1/T_{1,2D}(\omega_I)$ or $1/T_{\text{1,\,param}}(\omega_I)$ in equation (3).

3.1.1. Case of aprotic liquid. We first consider the case of $1/T_{1,2D}(\omega)$ corresponding to proton-bearing aprotic liquid diffusing in proximity to the solid–liquid interface in a porous medium, i.e. the proton species is not trapped in the ligand field of a paramagnetic site. This allows not considering the $1/T_{\text{1,\,param}}(\omega_I)$ contribution in equation (3). We consider also the presence of a very small quantity of fixed paramagnetic species of spins, $S$, uniformly distributed on these surfaces with a surface density, $\sigma_s$. Because the magnetic moment of the paramagnetic species is large ($\gamma_S = 659\gamma_I$), there is no ambiguity about the relaxation mechanism of the diffusing proton spins, $I$, which is the intermolecular dipolar relaxation process induced by fixed spins, $S$, and modulated by the translational diffusion of the mobile spins, $I$, in close proximity to these surfaces. Basically, the nuclear spin–lattice relaxation rate of the diffusing spins $I$, in proximity to the $S$ spins, is given formally by the general expression [39],

$$\frac{1}{T_{1,2D}(\omega_I)} = 2(\gamma_I\gamma_S\hbar)^2S(S+1) \left[ \frac{1}{3} J_L^{(0)}(\omega_I - \omega_S) + J_L^{(1)}(\omega_I) + 2J_L^{(2)}(\omega_I + \omega_S) \right], \quad (4)$$

where $J_L^{(m)}(\omega)(m \in \{-2, +2\})$ are the spectral densities in the Laboratory frame ($L$) associated with the constant magnetic field $B_0$ expressed at the Larmor frequencies of the electron and proton related by $\omega_S = 658.21\omega_I$ and defined as the exponential Fourier transforms,

$$J_L^{(m)}(\omega) = \int_{-\infty}^{+\infty} G_L^{(m)}(\tau)e^{-i\omega\tau} d\tau \quad (5a)$$

of the stationary pairwise dipolar correlation functions $G_L^{(m)}(\tau)(m \in \{-2, +2\})$ given by,

$$G_L^{(m)}(\tau) = \langle F_L^{(-m)}(t) F_L^{(-m)*}(t + \tau) \rangle. \quad (5b)$$

Equation (5b) describes the persistence of the autocorrelation of the dipole–dipole interaction $F_L^{(m)}(t) \sim 1/\lambda_S^3(t)$ between the magnetic moments associated with the spins $I$ and $S$ and modulated by the translational diffusion during a short time interval $\tau$ of spins $I$ at distance $r IS$ of a paramagnetic spins $S$ fixed on the pore surface. The notation $\langle \ldots \rangle$ stands for the ensemble average over all of the positions of the spins $I$ at time 0 and $\tau$ for a given density $\sigma_S$ of spins $S$. This ensemble average can be expressed as an integral average over the normalized diffusive propagator $P(\vec{r}_0, \vec{r}, \tau)$,

$$G_L^{(m)}(\tau) = \int d\vec{r}_0 p(\vec{r}_0) F_L^{(-m)}(0) \int d\vec{r} P(\vec{r}_0, \vec{r}, \tau) F_L^{(-m)*}(\tau). \quad (6)$$

Here, $P(\vec{r}_0, \vec{r}, \tau)$ is a solution of a diffusive equation with initial and boundary conditions and $p(\vec{r}_0) = \sigma_S/\lambda$ represents the equilibrium and uniform density of spin pairs $I–S$ at equilibrium.

We have detailed in [13] all of the calculations of the correlation functions $G_L^{(m)}(\tau)$ and spectral densities $J_L^{(m)}(\omega)$ within the following conditions. (i) We use the well-known properties of rotation of spherical harmonics in different bases to facilitate the calculations in the lamellar frame ($M$) of figure 2(b) before coming back to the laboratory frame ($L$) associated with the constant direction of the magnetic field $B_0$. (ii) We use the anisotropic dynamical model presented in figure 2(b) with an unbounded and isotropic diffusion $D_{1,\perp}$ perpendicular to the
normal axis $n$ and a bounded diffusion $D_{\perp}$ along such an axis. (iii) The pairwise dipolar correlation functions $G_{L}^{(m)}(\tau)$ have been estimated at times $\tau$ much longer than the transverse diffusion correlation time $\tau_{m} = \delta^{2}/(4D_{L\perp})$, where $\delta$ is the molecular size of the $I$ spin-bearing molecule with a translational diffusion coefficient $D_{L\perp}$ in the direction perpendicular to $n$. (iv) We introduce the effects of the finite time of residence $\tau_{S} \gg \tau_{m}$ at the pore surface by an exponential cut-off in the time dependence of the $I$–$S$ pair correlations. (v) Finally, a powder average of $J_{L}^{(m)}(\omega)$ over all the orientations of the $n$-direction relative to the constant direction of the magnetic field $B_{0}$ has been done (figure 2(b)). These calculations lead, at low frequency, to the following overall spin–lattice relaxation rate of the 2D diffusion of liquid diffusing in proximity to the pore surface,

$$\frac{1}{T_{1}(\omega_{I})} = \frac{1}{T_{1,\text{bulk}}} + C(\lambda_{I}S_{I}\rho_{\text{liquid}})\omega_{\text{dip}}^{2}\tau_{m}\left[3\ln\left(\frac{1 + \omega_{I}^{2}\tau_{m}^{2}}{\tau_{m}^{2} + \omega_{I}^{2}\tau_{S}^{2}}\right) + 7\ln\left(\frac{1 + \omega_{S}^{2}\tau_{m}^{2}}{\tau_{m}^{2} + \omega_{S}^{2}\tau_{S}^{2}}\right)\right].$$  \hspace{1cm} (7)

In equation (7), $C$ is a numerical constant that depends on the local pore geometry whether for a pore-slit model [13, 14] or at proximity of a pore surface [29],

$$\omega_{\text{dip}}^{2} = \frac{\sigma_{S}(\gamma_{I}\gamma_{S}\hbar)^{2}S(S + 1)}{\lambda^{2}\delta^{2}(1 + x^{2})}$$

is the $I$–$S$ dipolar frequency, $x = \delta/\delta'$ is a parameter introduced to take into account a variable distance $\delta'$ of minimal approach between $I$ and $S$ spins compared to the molecular size $\delta$ of the studied moving liquid. $\delta = S/2$ for the spins of Fe$^{3+}$ or Mn$^{2+}$ paramagnetic ions of surface concentration $\sigma_{S} = (\eta_{S}\rho_{\text{solid}}\xi)$, where $\eta_{S}$ is the volume concentration of paramagnetic ions measured by ESR, $\xi \sim 0.5$ nm is a thin layer of paramagnetic ions corresponding to the lattice constant of the solid structure at proximity of the pore surface and $\rho_{\text{solid}}$ is the density of the solid material. Equation (7) has a bilogarithmic frequency dependence (proton Larmor frequency $\omega_{I}$ and electronic frequency $\omega_{S} = 659\omega_{I}$) due to the numerous 2D molecular reencounters between spins $I$ and $S$ occurring within the thin transient layer $\lambda$. Equation (7) also contains two correlation times: the translational correlation time, $\tau_{m}$, associated with individual molecular jumps in proximity to the surface and the surface residence time, $\tau_{S}$, which is limited by the molecular desorption from the thin surface layer $\lambda$. $\tau_{S}$ controls how long the proton species $I$ and the Fe$^{3+}$ or Mn$^{2+}$ ion $S$ stay correlated. It depends on both the strength of the chemical bonds and the re-occurrence of first neighbor interactions induced by the fluid confinement in pores.

3.1.2. Case of protic liquid. We now consider the case of $1/T_{1,\text{param}}$ corresponding to proton bearing (water) staying in the ligand field of the paramagnetic ions for a time $\tau_{\text{ex}}$ longer than the surface or bulk correlation times. The nuclear paramagnetic relaxation rate is given by [40, 41]

$$\frac{1}{T_{1,\text{param}}(\omega_{I})} = \frac{2}{15}\omega_{\text{dip},I}^{2}T_{1,\text{elec}}(\omega_{S})\left[3\left[1 + \omega_{I}^{2}T_{1,\text{elec}}^{2}(\omega_{S})\right] + 7\left[1 + \omega_{S}^{2}T_{1,\text{elec}}^{2}(\omega_{S})\right]\right].$$  \hspace{1cm} (8)

The quadratic dipole–dipole frequency $\omega_{\text{dip},I}^{2} = (\gamma_{I}\gamma_{S}\hbar/\delta^{3})^{2}S(S + 1)$ represents now the interaction between a proton–water and a given Mn$^{2+}$ or Fe$^{3+}$ ion at a distance of minimal approach $\delta' = 0.27$ nm. The frequency dependence of equation (8) is a sum of two Lorentzian
spectral densities at frequencies $\omega_I$ and $\omega_s$. The electronic correlation time $T_{1,\text{elec}}(\omega_S)$ depends on the magnetic field through the electronic frequency $\omega_S$,

$$\frac{1}{T_{1,\text{elec}}(\omega_S)} = H_S^2 \tau_v \left[ \frac{1}{1 + \omega_S^2 \tau_v^2} + \frac{4}{1 + 4 \omega_S^2 \tau_v^2} \right], \quad (9)$$

where $\tau_v$ is the correlation time for the electron–lattice fluctuating interaction and $H_S^2$ is the intensity of the electron–spin fluctuations \([41]\) and typically $T_{1,\text{elec}}(\omega_S) \approx 10^{-10}$ s for Mn$^{2+}$ when $\tau_{\text{ex}} \gg T_{1,\text{elec}}$. Equations (8) and (9) are very well known from the magnetic resonance imaging in which Mn(II) ions or Gd(III) ions are used as contrast agents \([42]\).

Substitution of equations (8) and (9) into equation (1) reduced to the superposition of the bulk and paramagnetic contributions (without the $1/T_{1,2D}(\omega_I)$ contribution), i.e. gives the following expression for a protic spin–lattice relaxation rate in macropores,

$$\frac{1}{T_{1,\text{protic}}(\omega_I)} = \frac{1}{T_{1,\text{bulk}}} + \frac{N_{\text{param}}}{N} \frac{1}{T_{1,\text{param}}(\omega_I)}, \quad (10)$$

where $N_{\text{param}}/N = (\lambda_S \rho_{\text{liquid}}) \delta^2 \sigma_S f \ll N_S/N$ is the ratio between the number of liquid molecules bonded to the paramagnetic sites at the surface and in the bulk, $\delta = 0.3$ nm is the mean molecular size of water and $f$ is a geometrical factor that takes into account the increase in accessibility of water to the paramagnetic relaxation sink on the very convoluted surface of the porous media.

### 3.2. NMRD experiments on calibrated microporous silica glasses

The magnetic field dependence of the proton spin–lattice relaxation rates of aprotic and polar acetone solvent in 75 Å chromatographic and calibrated glass beads are reported for fields corresponding to $^1$H Larmor frequencies from 0.01 to 30 MHz over a range of temperature from 5 to 45 °C (figure 3) \([13]\). Similar NMRD profiles can be found for other aprotic liquids in \([13]\) in the same glass beads. A common feature of these data is that the relaxation rate has a bi-logarithmic dependence on the Larmor frequency, in agreement with equation (7). The iron content of these samples, checked by ESR and analytical chemistry measurements, is 45 ppm for the 75 Å pore glasses. This is sufficient to provide a dominant relaxation path for the proton spins at low magnetic-field strengths. From the specific area of the glass and if we assume a uniform volume density of paramagnetic species, the surface density $\sigma_S$ of paramagnetic centers is $3.463 \times 10^{11}$ Fe cm$^{-2}$. The average distance between the paramagnetic centers is then of the order of $1/\sqrt{\sigma_S}$, which is 170 Å for the 75 Å glass samples. This figure provides an estimate of the range for the persistence length of the two-dimensional (2D) character sensed by the magnetic relaxation of the proton spins induced by the paramagnetic center. The good fitting with the bilogarithmic frequency dependence of equation (7) obtained at different temperatures for the nuclear magnetic dispersion data of figure 3 proves the validity of the proposed model. From an individual fit, one deduces a value of the surface translational correlation time $\tau_m$ whose temperature dependence is typical of an activated diffusive process. It is important to note that equation (7) was derived without an explicit inclusion of the electron–spin relaxation rate, $1/T_{1,\text{param}}$, as a potential source of important fluctuations in the electron–nuclear coupling.
Figure 3. Magnetic field dependencies of $^1$H spin–lattice relaxation rates of aprotic and polar acetone embedded in a packed samples of calibrated porous glass beads at 5 (top), 15, 25, 35 and 45°C (bottom) (data from [13]). The continuous lines correspond to the best fits to equation (7), as discussed in the text.

4. Continuous multi-scales NMR relaxation investigation of microstructure evolution of cement-based materials

Concrete is a construction material composed of cement (commonly Portland cement) as well as aggregates, sand, water and chemical admixtures, such as silica fume and adjuvants. Concrete solidifies and hardens after mixing with water and placement due to a chemical process known as hydration. The water reacts with the anhydrous cement, which bonds the other components by hydrates and forms a hardened cement paste known as the main ingredient of concrete. The important mechanical and durable performances of concrete are mainly due to the high compactness of this material but also to the microstructure of hydrated cement paste. Here the microstructure includes different mesoscopic properties, such as porosity, specific surface area, distribution and connectivity of pore sizes, as well as tortuosity factor. Questions still exist about the microstructure of such a highly disordered and multiscale hydrated cement paste. Answering these questions is important because the microporous features influence the mechanical properties of materials as well as the transport efficiency of water and aggressive agents. A better control on the appearance and evolution of the microstructure during the hydration and setting is still needed to improve these properties. This is important because more than a cubic meter per human being on earth is produced each year that makes concrete the world’s most widely used manufactured material.

Here, we just outline some of our recent non-invasive NMR spectroscopy and low field nuclear spin–lattice relaxation approaches that do not require any drying or temperature modification [17, 19, 20] to investigate the evolution of the microstructure of various cement-based materials without perturbing the samples. Other recent studies focus on transverse relaxation in hydrated cements [21] or review the possibilities of field gradient NMR in diffusion studies on hydrating cements [22].
As a typical first example of a cement-based material, we consider a reactive powder mortar sample prepared by mixing cement, sand, silica fume, water and superplasticizer with a water to cement ratio \( w/c = 0.38 \). Before addition of water, the specific surface area of the various grains is very low, whereas after the dissolution–precipitation process, calcium silicate hydrate (CSH) structures appear at the surface of the grains leading to a very high surface area that increases continuously with time. We used the NMRD, the measurement of the longitudinal relaxation rate \( R_1 \) as a function of magnetic-field strength or nuclear Larmor frequency of water confined within the hydrated cement. The benefit of exploring here the range of low frequency is to isolate the typical NMRD dispersion features of \( 1/T_1 \) associated with the different processes of molecular surface dynamics. An original model based on solid/liquid cross-relaxation, proton surface diffusion and nuclear paramagnetic relaxation, in the presence of progressive hydration, is proposed to interpret the remarkable features of the proton NMRD profiles [17, 19]. We present in figure 4(a) the proton NMRD data obtained at 25 °C for an increasing duration of hydration for such a mortar. We evidence by ESR a quantity of \( \eta_S = 1.17 \times 10^{19} \) paramagnetic Fe\(^{3+}\) ions per gram of dry material. Assuming a uniform distribution, we deduce a proportion of surface Fe\(^{3+}\) impurities, \( \sigma_S = \eta_S \varrho_{\text{solid}} \xi \), to which relaxation of liquid protons of the saturated porous media is sensitive. Here, \( \varrho_{\text{solid}} = 2.5 \text{ g cm}^{-3} \) is the density of the solid material and \( \xi = 6 \text{ Å} \) is the average inter-layer distance between two Fe\(^{3+}\) ions. The surface density of Fe\(^{3+}\) impurities thus becomes \( \sigma_S = 1.8 \times 10^{12} \text{ Fe}^{3+} \text{ cm}^{-2} \) and is independent of \( S_p \). We note three remarkable features in the \(^1\text{H}\) NMRD of water in hydrated mortars (figure 4(a)). (i) There is a plateau below a cross-over frequency \( \omega_c/2\pi \sim 22 \text{ kHz} \). (ii) Above \( \omega_c \), one observes a bi-logarithmic dispersion behavior, characterized by a 10/3 slope ratio, for each duration of

Figure 4. (a) Measured water \(^1\text{H}\) spin–lattice relaxation rates of a hydrated reactive powder mortar at a water-cement ratio, \( w/c = 0.38 \), as a function of the proton Larmor frequency, for different durations of hydration: 0h34 (■), 7h27 (○), 8h45 (▲) and 9h40 (×), upwards (data from [17]). The inset represents the data obtained after a hydration time of 10h32 (+). The labels for the two axes are equivalent to those of the main figure. The continuous lines correspond to the best fits obtained with equations given in [17]. (b) Renormalization of the data obtained in (a) for all hydration times.
hydration. This frequency behavior is unambiguously consistent with 2D proton–water diffusion in the proximity of the paramagnetic relaxation centers (see equation (7)). (iii) Between 3 and 5 MHz, one notes an enhancement of the relaxation after 10 h of hydration. A renormalization of the $^1$H NMRD data collected for all durations of hydration has been achieved by subtracting the limiting constant bulk relaxation rate at high frequency and dividing the resulting data by the value of the respective low frequency plateau (figure 4(b)). This renormalization proves that the same NMR process occurs for the duration of hydration. Moreover, such a renormalization (figure 4(b)) has allowed us to measure, with equation (7), the surface diffusion translational correlation time $\tau_m = 0.7$ ns that gives a surface diffusion coefficient about two order of magnitude less than the surface diffusion coefficient of water in bulk. We measured a universal value about $\tau_m = 1$ ns on several different cement-based materials, including reactive powder concrete [43]. This clearly shows that nuclear spin relaxation is able to sense the translational dynamics of proton species at surface of CSH pores that are present in all of these materials.

We have shown in [17] how the net transition on the NMRD profiles from a bi-logarithmic frequency dependence to a plateau (figures 4(a) and (b)), at a cross-over frequency $\omega_c/2\pi \sim 22$ kHz is indicative of a fundamental modification in the relaxation processes occurring above and below such a frequency. For a proton frequency, $\omega > \omega_c$, the relaxation features are mainly due to the 2D translational diffusion of proton species at proximity to the paramagnetic ions fixed at the surface of CSH layers. For proton frequency inferior to a frequency $\omega_c/2\pi \sim 22$ kHz that is typical of the dipolar frequency in solid state, the observed transition to a plateau (figure 4(b)) is a clear signature of a cross-relaxation process between the liquid and solid proton species at the CSH interface [17]. An immediate consequence of such a transition at frequency $\omega_c/2\pi$ is that one can probe continuously the evolution of the specific surface area of a hydrated cement-based material by measuring the time evolution of $1/T_1$ at a very low and single frequency e.g. 10 kHz.

Another representative model cement-based material is the synthetized tricalcium silicate $\text{Ca}_3\text{SiO}_5$ (the so-called C$_3$S), which represents 60–70% of industrial Portland cement. Figure 5 shows the NMRD curves $1/T_1 = f(\omega)$ obtained on a one-year-aged C$_3$S sample [19, 20] with different spectrometers whose frequency ranges between 10 kHz and 500 MHz. The renormalization of all of these dispersion curves to a single one, shown in the inset of figure 5, proves that the same relaxation process occurs at each of the four classes of $1/T_1$ from 1 to 4000 s$^{-1}$. Such a renormalization factor is also indicative of the pore-size ratio [19]. The solid lines in figure 5 are the best fits obtained with equations (3)–(10), including the bumps seen between 30 and 80 MHz due to the nuclear paramagnetic relaxation contribution coming from equations (8)–(10). For these fits, we used the density of Fe$^{3+}$ impurities found by ESR for estimating $N_{\text{surface}}/N$. Moreover, the best fits obtained for the renormalized NMRD seen in the inset of figure 5 as well as for all the four NMRD curves prove that the same relaxation processes occurred for all the different pores. This allowed us to find the surface-to-volume ratio of the pores $(S/V)_i = 3/(R_i)$, giving the following average pore sizes $<R_i>$ = {1.8, 7.0, 50 and 600 nm}.

We have also used the nuclear spin relaxation method to probe directly the surface area of a hydrated cement-based material [17, 19, 20, 23]. We have discussed above why the surface contribution in equation (7) is dominant at low frequency in comparison with the frequency independence of the bulk contribution in this frequency range (figure 4). To obtain the specific surface area of the cement paste and prevent the kinetics effects occurring during the acquisition of the complete NMRD profile, we focus only on the measurement of the time evolution of
**Figure 5.** Logarithmic plot of the dispersion NMRD profiles showing the four longitudinal relaxation rates $1/T_1$ versus the Larmor frequencies of the proton for a C3S paste hydrated for 1 year with $w/c = 0.4$ at room temperature (data from [19]. The four curves have been successfully rescaled in the inset. The continuous lines correspond to the best fit obtained by the relaxation model given in [19].

the proton–water $1/T_1(t)$ at 10 kHz, which is on the plateau of the profile in figure 4. The method, which can be performed at room temperature, is sensitive both to open and closed porosity in a wide range of length-scales. This allows direct probing of the surface area and proton species surface dynamics of different cement-based materials from the NMRD data. The method is sufficiently rapid to be applied continuously during the progressive hydration and setting of cement. At this low frequency, we have shown [17] that the overall relaxation is mainly due to the liquid proton species in cross correlation with the solid protons at the still-growing CSH surfaces. We have displayed in figure 6 the time evolution of the specific surface area of a white cement paste up to the first 100 h of hydration [20]. Similar to the well-known calorimetric measurement, figure 6 shows the three periods of the cement hydration, namely the dormant period at the beginning, the setting due to the advancement of chemical reaction after 4 h and then the transition to the slower diffusive period at long times. It is well known that the calorimetric measurement gives a master curve for getting the degree of advancement of the chemical reaction at the origin of the hydration process. We show here that the time evolution of the remaining water protons $1/T_1(t)$ at 10 kHz displayed in figure 6 gives another master curve that reveals the decrease in the water dynamics at proximity of a time growing solid surface. This growing is due to the precipitation of the CSH hydrates during the so-called hydration period.
Figure 6. $^1$H spin–lattice relaxation rate of a white cement paste hydrated with $w/c = 0.4$ as a function of the hydration time measured at a Larmor frequency of 10 kHz in white cement (data from [20]). The weighting factors for each of the relaxation components are indicated. The inset represents the NMR-specific surface area deduced from the data in the main figure with the use of equations given in [20].

Lastly, the recent applications of 2D $T_1$–$T_2$ (figure 7(a)) and $T_2$-store-$T_2$ (figure 7(b)) correlation experiments [24, 25] are now briefly described. These experiments confirm the discrete pore-size distribution observed and have provided the first clear evidence (by the presence of cross peaks in figures 7(a) and (b)) of a chemical exchange of water protons between the connected gel micropores. The $T_2$-store-$T_2$ experiment has two significant advantages over the $T_1$–$T_2$ experiment [25]. Firstly, it clearly identifies and correlates measurements in two intervals, $t_1$ and $t_3$, that are separated in time by a third interval, $t_{store}$. It is therefore more straightforward to consider that there is an exchange period during which the proton species are moving between reservoirs. Secondly, the off-diagonal peaks can be assigned unambiguously to water exchange. If there is no exchange, then there are no off-diagonal peaks. Recent interpretation of $T_2$-store-$T_2$ experiment has confirmed that the 2D correlation spectral cannot be explained by exchange between regions of different Fe$^{3+}$ concentration but rather by exchange between regions of different pore sizes [44]. The ESR calibration of Fe$^{3+}$ concentration suggests that the two primary relaxation reservoirs seen both comprise rather small pores. The smallest pore radius is about 1.2 nm. This is consistent with estimates in the literature of the CSH inter-planar spacing, which range from 0.9 to 1.2 nm [43]. However, the second significant reservoir suggests a radius of 9–27 nm, dependent on the pore shape.
Figure 7. (a) The 2D spin-correlation spectrum $T_1-T_2$ of a white cement sample cured for 4 days (data from [24]). A series of discrete features lie along the line $T_1 = 4T_2$ parallel to the diagonal. Both this line and the principal diagonal $T_1 = T_2$ are shown as dotted lines. There is an off-diagonal feature at the position $T_1 = 10 \text{ ms}$ and $T_2 = 50 \mu\text{s}$. The intensity contours (arbitrary units) are equally spaced up from a zero base. (b) Experimental 2D spin-correlation spectrum $T_2-z$-store-$T_2$ for a white cement paste with water-to-cement ratio 0.4 and 3 days old. The storage time is 10 ms (data from [25]). There are two cross peaks that evidence an exchange process between the connected micropores.

This is much smaller than the expected size of capillary pores. We therefore suggest that the two observed reservoirs may be attributed to alternate gel structures. One possibility is that the smaller pore-size reservoir is associated with an inner product, the larger with an outer product, both created as the material hydrates. The exchange rate between these structures
has been estimated as 5 ms\(^{-1}\). From this, water diffusivity within the CSH structures has been calculated that broadly corresponds to the results of molecular dynamics simulations in related systems [43].

5. Direct probing of the nano-wettability of plaster pastes

How does the microstructure of a reactive porous medium appear and evolve during the hydration and setting and how is it possible to follow these processes by non-destructive techniques? Here, we propose to answer this question in the case of gypsum, a material of general interest in civil engineering. Basically, there are two main objectives in the research on gypsum: (i) improve the knowledge of the main steps of hydration of plaster to give key parameters for the mixing efficiency of this material; and (ii) improve the mechanical properties by a better knowledge of microstructure (specific surface area, pore-size distribution and connectivity) on this disordered solid system.

It is well known that proton NMR spectroscopy evidences the proton chemical species within the gypsum crystal [45]. With NMR techniques, no drying is necessary that could produce nanostructure modifications, by non-wetting fluid intrusion (nitrogen adsorption or mercury intrusion porosimetry). Here, we propose a direct non-perturbative characterization of the evolving microstructure of this building material during the setting of plaster, varying simultaneously the water-to-plaster ratio (\(w/p\)) between 0.4 and 1 [32]–[34], [46]. We evidenced by proton transverse relaxometry at low magnetic fields at least two transverse relaxation times that were associated with different water populations, and show that there are two evolution modes of organization of the microstructure in the range (0.4 \(\leq w/p \leq 0.6\)) and (0.7 \(\leq w/p \leq 1\)) in agreement with pulsed field gradient NMR experiments. We succeed in changing these populations by adding an increasing amount of crushed gypsum. We also validate the biphasic fast exchange model by saturation and desaturation experiments. Lastly, an original model of transverse spin relaxation in the presence of slow chemical exchange between the two evidenced populations gives an estimation of the rate \(W\) of this process [33, 34, 46]. The variation of this rate \(W\) with \(w/p\) exhibits a clear gap between two different regimes that confirmed the presence of two evolution modes of organization. This gap occurs between \(w/p = 0.6\) and 0.7 and could be representative of a percolation threshold. We believe that our experimental method is fast enough and robust enough to follow the progressive setting of the reactive interface of any porous medium without any dehydration.

Another question concerns the possibility of probing non-destructively the water nano-wettability of a reactive porous plaster paste and how this nano-wettability changes with the addition of additives? Answering these questions is very important in civil engineering to control the mechanical properties of such a material of great interest in the building industry. This is all the more important for wetting water because it controls the kinetics of hydration [47] and setting of the microstructure of such a widely used material. However, there is still no study for probing the water dynamics precisely at the solid interface. Here, we propose an in situ and non-invasive method based on the measurements of the low-frequency dependence of the proton spin–lattice relaxation rate \(1/T_1\) for measuring the average lifetime of the wetting water directly on the pore surface of gypsum. The benefit of exploring the range of low frequency is to isolate the typical NMRD features of the surface contribution of \(1/T_1\) associated with the different processes of molecular surface dynamics. As demonstrated above, varying the magnetic field changes the Larmor frequency and therefore the time and length-scales of the fluctuations.
responsible for $1/T_1$. This allows a clear discrimination of the anisotropic dynamical motions on or in proximity to the local proton acceptor on the basal plane of gypsum needles from the fast isotropic molecular motions of water in bulk.

The hydration of calcium sulfate hemihydrate ($\text{CaSO}_4, \frac{1}{2}\text{H}_2\text{O}$), usually called plaster, can be described as follows [47]. In the first step, the dissolution of hemihydrate leads to calcium and sulfate ions. Then, the crystallization of calcium sulfate dihydrate ($\text{CaSO}_4, 2\text{H}_2\text{O}$), usually called gypsum, starts as soon as over-saturation is reached [47]. Gypsum crystals are needle shaped, which lock in water molecules as evidenced by proton NMR spectroscopy. We used proton NMR transverse relaxometry at a fixed magnetic field of mixing water to probe continuously the evolution of a commercial $\beta$-plaster paste (Meriel quarry, Lafarge Plaster, France) without perturbing the system [32, 33, 46]. Recent $T_1$, $T_2$ and NMR profiling studies have been proposed for studying the other ‘wet’ $\alpha$-plaster commercial product [35]. The application of the 2D spin-correlation $T_1$–$T_2$ technique to plaster paste in the presence of accelerating or retarding agents has also been proposed for the $\beta$-plaster paste [36].

We prepared different samples of $\beta$-plaster paste by manual mixing of hemihydrate powder and distilled water, at a well-defined water-to-plaster weight ratio ($w/p$) from 0.4 to 0.8. In some experiments, some sodium trimetaphosphate (STMP) adjuvant was added to change the hydration kinetics and the microstructure configuration. The plaster paste was weighed and introduced into a sealed NMR tube, to avoid evaporation during the experiment. Measurements of the NMRD of the proton and deuterium nuclear longitudinal relaxation rates $1/T_1$ were performed at different stabilized temperatures. All measurements were carried out after the setting period (60 min), after which the hydration is complete and the microstructure does not evolve. Provided the use of real amagnetic tools for preparing the plaster paste, ESR spectroscopy does not evidence the presence of paramagnetic impurities.

We show in figure 8(a) the frequency dependence of $1/T_1$ for different values of the water-to-plaster weight ratio ($w/p$) between 0.4 and 0.8 at 25°C [34]. One notes that $1/T_1$ tends progressively to a constant below a cross-over frequency 22 kHz over which it seems to behave as a power law plus a constant, $1/T_1 \sim A\omega^{-0.85} + C$, over more than three orders of magnitude. It is possible to prove the power-law behavior of $1/T_1$ by plotting the frequency dependence of its first derivative, as shown in figure 8(b). The same experiments show the same behavior for either light or heavy water (figure 8(b)). This is in favor of an intramolecular diffusive process [39] on and at proximity of the entangled needle-shape gypsum flat surface. Another result for light water is that the exponent of such a power law is preserved when varying the water-to-plaster weight ratio between 0.4 and 0.8 (figure 8(a)) and the temperature between 25 and 45°C [34]. However, one observes an anomalous behavior of $1/T_1$ that increases with the temperature, thus revealing an interaction with the solid surface. Lastly, one observes in figure 9 a net decrease in the exponent of the apparent power law up to $1/T_1 \sim A\omega^{-0.5}$ in the presence of an increasing quantity of adsorbed STMP adjuvant. To interpret the data, we propose an analytical model of the NMR relaxometry based on the biphasic fast exchange model where the overall $1/T_1$ is a superposition of bulk and surface contributions,

$$\frac{1}{T_1(\omega_0)} = \frac{1}{T_{1,\text{Bulk}}} + \frac{\lambda S}{V T_{1,\text{Surface}}(\omega_0)}.$$

The bulk contribution $1/T_{1,\text{Bulk}}$ is a constant in the frequency range studied [39]. The surface contribution $1/T_{1,\text{Surface}}(\omega_0)$ is weighed by the surface to volume ratio $S/V$. It depends drastically on the proton Larmor pulsation $\omega_0$ due to the numerous molecular re-encounters.
between water protons and fixed surface hydrophilic proton species occurring within the thin surface relaxation layer $\lambda$. We have previously verified the validity of this model when observing, by saturation and desaturation experiments, a linear dependence of the transverse relaxation time $T_2$ with the filling factor $V/V_0$ [46]. Here, we confirm this model by the rescaling of all of the NMRD data of figure 8(b) to a single dispersion curve using a surface weighting factor, $\lambda\rho_{\text{Gyp}}S_p/\phi$, that depends on the specific surface area $S_p$, the porosity $\phi$, the density of gypsum $\rho_{\text{Gyp}}$ and a surface relaxation layer $\lambda$. Most of these parameters are independent of the plaster weight ratio ($w/p$), except for the porosity $\phi$, which is found to increase with $w/p$ (inset of figure 8(b)). We use the Levitz model involving elementary time steps near the interface (e.g. bulk bridges, adsorption trails and escaping tails [48, 49]) to obtain the frequency dependence of $1/T_1,_{\text{Surface}}(\omega_0)$ as the following linear combination of surface spectral density $J_{\text{Surface}}(\omega_0)$,

\[
\frac{1}{T_1,_{\text{Surface}}(\omega_0)} \propto \left[J_{\text{Surface}}(\omega_0) + 4J_{\text{Surface}}(2\omega_0)\right],
\]

\[
J_{\text{Surface}}(\omega_0) \propto \tau_A \left[\sqrt{\frac{\omega_0}{\omega_A}} + \frac{\omega_0}{\omega_A} + \frac{1}{2} \left(\frac{\omega_0}{\omega_A}\right)^{3/2}\right]^{-1},
\]

where

\[\omega_A = \delta^2/(2D\tau_A^2)\]

is a characteristic frequency (in rad s$^{-1}$) that is related to the water size $\delta = 0.3$ nm, the translational bulk diffusion coefficient $D$ of water and the average adsorption correlation

**Figure 8.** (a) Logarithmic plot of the frequency dependence of the proton-water longitudinal relaxation rate $R_1 = 1/T_1$ for different water-to-plaster ratios ($w/p$) (data from [34]). The continuous lines correspond to the best fits obtained with equations (12)–(13) and the corresponding bulk values. (b) Logarithmic plot of the renormalized frequency dependence of the derivative of data corresponding to (a). The continuous lines correspond to the best fits obtained with a single power law (see the text). In the inset, we have plotted the variation in the NMR and mercury invasion porosity with $w/p$. 

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time $\tau_A$. Equations (12a) and (b) are supported by our experimental data. The comparison with our data shows that this characteristic frequency does not vary much ($\omega_A \sim 0.1–0.2$ MHz) with $w/p$ (figure 8(a)). According to equation (10), this gives an adsorption timescale of about $\tau_A = 5.0$ ns. These relaxation features prove that the surface relaxation process does not change with $w/p$ and temperature as it should. On the contrary, we see in figure 9 that this is not the case in the presence of an increasing quantity of STMP adjuvant in the wetting water. Here, $1/T_1$ decreases as well as $\omega_A$ drastically increasing to 875 MHz in the presence of 6.5% of STMP adjuvant (figure 9) and a correlative adsorption timescale that decreases to $\tau_A = 64$ ps with 6.5% of adjuvant. These drastic changes might be explained by the presence of STMP adjuvant at the surface of the largest 010 planar structure of gypsum. It results in a net diminution of accessible bonding sites for water. The frequency dependencies of equations (12a) and (12b) simplify and tend to the following linear combination of single power laws,

$$\frac{1}{T_1(\omega_0)} \propto \frac{1}{T_{1,\text{Bulk}}} + B \omega_d^2 \tau_A \left( \frac{\omega_0}{\omega_A} \right)^{-1/2} + 4 \left( \frac{2\omega_0}{\omega_A} \right)^{-1/2},$$

when $\omega_0 \ll \omega_A$, (14)

where $B$ is a constant and $\omega_d$ is the intramolecular dipole–dipole frequency for proton–water. It results in an easy determination of the average adsorption time of water on the gypsum polycrystals from the NMRD data. The effect induced on $1/T_1(\omega_0)$ shows that the average timescale $\tau_A$ depends directly on the physical chemistry at the surface; it is thus indicative of the dynamical wettability of the material at the nanoscale. As the degree of hydration is directly related to the mechanical properties during the setting, such as compressive strength and modulus of elasticity [33], we deduce that the parameter $\tau_A$ (or the nano-wettability) controls most physico-chemical properties of the porous structure.
6. Dynamical surface affinity of diphasic liquids as a probe of wettability of multimodal macroporous rocks

Wettability is the ability of a fluid to spread onto a solid surface in the presence of other immiscible fluids. It is relevant in fundamental interfacial phenomena underlying coating, bonding, adhesion and other related effects in porous media. For instance, the wettability of a rock/oil/brine system affects fluid saturation, capillary pressures, electrical properties and relative permeabilities [50, 51]. The wettability of fluids in oil and gas reservoirs has a direct effect on the efficiency of hydrocarbon recovery. In most cases, massive water injection is performed to move oil towards the production zones, and if wettability variations occur, the water has the tendency to flow in the water wet locations leaving oil in the place of oil-wet locations. Due to its economical impact, control and monitoring of wettability in situ justify huge investments in core analysis for laboratory measurements.

Techniques capable of mapping wettability in the field are still not developed. Measurements on cores require long and tedious preparation, and never reflect the actual state of wettability. These cores are generally not tested in their native state. They are cleaned and saturated with known brine and oil. They are aged and tested in spontaneous drainage (oil in water saturated core) and imbibition (water in oil saturated core). An Amott index is then determined (from 1 for water wet rocks to −1 for oil wet cores) [52, 53]. A contingent method called USBM (U.S. Bureau of Mines) uses a pressure gradient to force the flow of oil in the core saturated with water and reciprocally to force the flow of water in the core saturated with oil [52]. The USBM index (varying for −∞ to +∞) is based on the logarithm of the ratio of energy required to move oil with water versus the energy required to move water with oil. Both Amott and USBM methods are accepted as standards by industry; however, they do not completely compare in all cases [54]. A more recently introduced NMR \( T_2 \) index [55]–[57] expresses the total surface of rock wetted by water minus the total surface of rock wetted by oil and divided by the total surface in contact with the fluid. This method uses the fact that a fluid surrounded by a wetting fluid shows a \( T_2 \) relaxation distribution of a bulk fluid, whereas a fluid in contact with the rock exhibits a shorter \( T_2 \) due to the confinement by the surface. This method has some limitations since it requires a measurement at complete water saturation and also requires the knowledge of the \( T_2 \) shape of the oil in bulk conditions. None of these techniques allow the local probing of interaction between the fluid and the rock-pore surface in a single non-invasive measurement.

Here, we have proposed again to use NMRD to probe the wettability of carbonate rocks in different conditions of saturation [29]. The rock samples used here are carbonate rocks from a Middle Eastern oil reservoir. They are intraclast skeletal ooid grainstone carbonates with 30% porosity and 700 mD permeability. The dual porosity of this rock is evidenced by the bimodal NMR \( T_1 \) distribution obtained after saturating this rock with brine [29]. Originally, the rock plugs are filled with native fluids, this is called ‘native state’. They were cleaned using a standard cleaning procedure in a petrophysical laboratory, using toluene and methanol in a Soxhlet extractor to remove all of the native fluids inside the rock (original crude oil and brine). Three rock plugs were then dried in an oven at 60°C during 48 h and each of them was prepared at a different saturation. (i) 100% water saturation (\( S_w = 100\% \)): this plug was vacuumed and saturated with a 50 kppm NaCl brine. The use of salty water prevents dissolution of the carbonate rock by fresh water. (ii) 100% dodecane saturation (\( S_w = 0\% \)): this plug was vacuumed and saturated with dodecane and said to be at 0% water saturation (\( S_w = 0\% \)).

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(iii) Irreducible water saturation \( S_{\text{wirr}} \): this plug was first saturated 100% with water, and then dodecane was forced into the plug by high-speed centrifugation.

This technique measures proton \( 1/T_1 \) over a large range of applied magnetic fields and yields unique information about the extent to which a fluid is dynamically correlated with a solid rock surface. Unlike conventional transverse relaxation studies, this approach is a direct probe of the dynamical surface affinity of fluids. We show that the low-frequency dispersion of the proton spin–lattice relaxation rates \( 1/T_1 \) of aprotic (oil) and protic (water) diphasic liquids can provide their relative wettabilities in porous media with complex pore-size distribution (multimodal). The use of aprotic and protic liquids allows a study of the physical chemistry effects that matter at a pore surface, such as binding effects with paramagnetic metallic ions or proton exchange with surface groups.

The NMRD data obtained in the case of a monophasic saturation of carbonate rocks with dodecane are shown in figure 10(a). At each frequency, the peaks of the \( T_1 \) distribution are extracted. These peaks are named \( T_{1\mu} \) for the microporosity and \( T_{1M} \) for the macroporosity. We observe bi-logarithmic frequency dependencies of the two relaxation rates \( R_{1\mu} = 1/T_{1\mu} \) and \( R_{1M} = 1/T_{1M} \). Owing to the constant value of the affinity ratio, \( R_{1\mu}(\omega) = 4R_{1M}(\omega) \), within all of the frequency range studied, we successfully rescaled the NMRD data onto a single bi-logarithmic master curve (inset of figure 10(a)). This rescaling unambiguously proves the existence of a unique intermolecular dipolar relaxation mechanism modulated by translational 2D diffusion of dodecane molecules, diffusing at the vicinity of paramagnetic impurities at the

**Figure 10.** (a) Measured NMRD of carbonate rock saturated with dodecane (\( S_w = 0\% \)) (data from [29]). \( R_{1\mu} \) and \( R_{1M} \) represent the relaxation rates corresponding to micro- and macroporosities, respectively. The solid lines were obtained from equation (15). The inset shows rescaled data on a single master curve. (b) Measured NMRD of carbonate rock saturated with 50 kppm NaCl brine (\( S_w = 100\% \)) (data from [29]). The solid lines were obtained from equation (16). Here again, the inset shows rescaled data on a single master curve.
signature of dodecane in large pores leading to microscopic wettability. The fit of figure at the pore surfaces. As such, protons have highly correlated 2D dynamics at proximity of the fixed paramagnetic sources. The proposed methodology would allow one to identify the wetting fluid for each pore type. At case of native states samples where there is no a priori that water preferably fills the small pores and dodecane the large ones. However, in a general only weakly, wetting. Because we saturated the cores with water first, it is indeed expected that water fills and wets the small pores, dodecane is located in the macroporosity but is not, or clear identification of the nature of the liquids saturating the dual porosity of carbonate rock: the typical NMRD signature of brine in small pores (figure (22 with monophasic saturations of dodecane (SM) are compared with the rates \( R_{1\mu} \) and \( R_{1M} \) (small empty dots) obtained with monophasic saturations of dodecane (\( S_w = 0\% \), data taken from figure 10(a)) and water (\( S_w = 100\% \), data taken from figure 10(b)), respectively. Here, \( R_{1M} \) has the typical NMRD signature of dodecane in large pores leading to \( A = 130 \) (figure 10(a)), whereas \( R_{1\mu} \) exhibits the typical NMRD signature of brine in small pores (figure 10(b)). These results thus reveal a clear identification of the nature of the liquids saturating the dual porosity of carbonate rock: water fills and wets the small pores, dodecane is located in the macroporosity but is not, or only weakly, wetting. Because we saturated the cores with water first, it is indeed expected that water preferably fills the small pores and dodecane the large ones. However, in a general case of native states samples where there is no a priori knowledge of preferred wettability, the proposed methodology would allow one to identify the wetting fluid for each pore type. At

\[
\frac{1}{T_1(\omega_I)} = \frac{1}{T_{1,\text{bulk}}} + \frac{N_{\text{param}}}{N} \frac{2}{15} \omega_{\text{I, liquid}}^2 T_{1,\text{elec}}(\omega_S) \times \left[ 3 \left( 1 + \omega_I^2 T_{1,\text{elec}}(\omega_S) \right) + 7 \left( 1 + \omega_I^2 T_{1,\text{elec}}(\omega_S) \right) \right],
\]

where we have introduced a microscopic dynamic surface correlation parameter \( A = \tau_S/\tau_m \) (affinity index) in lieu of the more traditional and loosely defined macroscopic wettability indices. This index \( A \) represents roughly the average number of diffusing steps of spins \( I \) in the vicinity of fixed paramagnetic sites \( S \) during the timescale of an NMRD measurement. The larger this index, the more numerous the 2D re-encounters and therefore the more correlated the \( I-S \) spins. Its value ranges between 1 for the bulk case and \( \infty \) for the case where the moving protons have highly correlated 2D dynamics at proximity of the fixed paramagnetic sources at the pore surfaces. As such, \( A \) reveals the affinity of the fluid to the pore surface, i.e. the microscopic wettability. The fit of figure 10(a) with equation (15) gives \( \tau_m = 1 \) ns, \( \tau_s = 130 \) ns, leading to a low surface dynamical affinity \( A = 130 \) for this well-known water-wet rock. This value is very close to the one, \( A = 200 \), found recently by Mitchell et al on limestone [31] from the frequency dependence of the ratio \( T_2/T_1(\omega_S) \).

The NMRD data obtained in fully brine-saturated carbonate rocks is shown in figure 10(b). Here also, we observe two relaxation rates \( R_{1\mu} \) and \( R_{1M} \). Owing to the constant value of the affinity ratio, \( R_{1\mu}(\omega_I) \approx 8R_{1M}(\omega_I) \), within all of the frequency range studied, we successfully rescaled the NMRD data in the inset of figure 10(b). The particular form of this NMRD profile proves that the relaxation process is the nuclear paramagnetic relaxation of water molecules bonded on the ligand field of the metallic paramagnetic ion at the pore surfaces. In that case, the frequency dependence of \( 1/T_1 \) is the sum of two Lorentzian spectral densities at nuclear \( \omega_I \) and electronic \( \omega_S \) Larmor frequencies, as shown in equations (8)–(10), that become

\[
\frac{1}{T_1} = \frac{1}{T_{1,\text{bulk}}} + \frac{N_{\text{param}}}{N} \frac{2}{15} \omega_{\text{I, liquid}}^2 T_{1,\text{elec}}(\omega_S) \times \left[ 3 \left( 1 + \omega_I^2 T_{1,\text{elec}}(\omega_S) \right) + 7 \left( 1 + \omega_I^2 T_{1,\text{elec}}(\omega_S) \right) \right],
\]

where the different parameters have been introduced in section 3.1.2. In this case, there is no need to define a wettability index provided that the ratio of the time of trapping the water molecule in the ligand field of a paramagnetic ion at the rock surface stays much larger than \( T_{1,\text{elec}}(\omega_S) \).

Lastly, the NMRD data obtained in the case of a diphasic mixture saturating the carbonate rocks with both dodecane and brine are shown in figure 11(a). The relaxation rates of the mixture (large full dots) are compared with the rates \( R_{1\mu} \) and \( R_{1M} \) (small empty dots) obtained with monophasic saturations of dodecane (\( S_w = 0\% \), data taken from figure 10(a)) and water (\( S_w = 100\% \), data taken from figure 10(b)), respectively. Here, \( R_{1M} \) has the typical NMRD signature of dodecane in large pores leading to \( A = 130 \) (figure 10(a)), whereas \( R_{1\mu} \) exhibits the typical NMRD signature of brine in small pores (figure 10(b)). These results thus reveal a clear identification of the nature of the liquids saturating the dual porosity of carbonate rock: water fills and wets the small pores, dodecane is located in the macroporosity but is not, or only weakly, wetting. Because we saturated the cores with water first, it is indeed expected that water preferably fills the small pores and dodecane the large ones. However, in a general case of native states samples where there is no a priori knowledge of preferred wettability, the proposed methodology would allow one to identify the wetting fluid for each pore type. At

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Figure 11. (a) Measured NMRD of carbonate rock saturated with both dodecane and 50 kppm NaCl brine ($S_{\text{wirr}}$ in large full dots). The solid lines were obtained from equation (15) for $R_{1\text{M}}$ and from equation (16) for $R_{1\mu}$. (b) Dual porosity observed through the $T_1$ distribution obtained by the 1D Laplace inversion of the longitudinal magnetization decay at 15 MHz. The vertical ticks represent the two $T_1$ values deduced from our own iterative approach. The comparison with the NMRD data allows the identification of the nature of the liquid-saturating individual pore. (c) Frequency dependence of the saturation (%) of brine and dodecane that is conserved in the whole frequency range studied. This saturation has been obtained by integration of the bimodal distribution obtained at each frequency. All of the data are from [29].

Each frequency, a bimodal $T_1$ distribution is obtained (figure 11(b)). Integrating this distribution gives an irreducible water saturation $S_{\text{wirr}} = 20\%$ for all of the frequency ranges studied (figure 11(c)).

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7. Conclusion

Various 1D and 2D low-field NMR relaxation techniques have been described to characterize the structure and molecular dynamics of liquids in porous media. We focused mainly on high surface area materials, including calibrated porous silica glasses, granular packings, cement-based and plaster materials, as well as natural porous rocks. In each case, we have briefly outlined the necessary modeling to interpret the multi-scaled NMR data.

We have particularly insisted on the NMRD on cement pastes and other cement-based materials. From these experiments, a quantitative method is proposed to characterize the time evolution of the microstructure of cement paste on different length-scales between 2 and 500 nm. This method allows one to follow the progressive setting of the pore-size distribution that evolves, after completion of hydration, to an equilibrium state characterized by a power-law representative of a hierarchical order that stabilizes after 4 months the same texture on different length-scales. This distribution is characteristic of a surface distribution where $D_f \approx 2.6$ is the surface fractal dimension that takes into account the hierarchical order in the texture of the material. Similarly, the NMRD technique gives a continuous and direct measurement of surface dynamics of proton species $\tau_m$ and specific surface area $S_{p,NMR}$ of various cement-based materials. This technique allows a clear separation of the NMRD of mobile water at the surface of the pores from that of the bulk. Although $S_{p,NMR}$ ranges within the results of most other techniques, there are several advantages in favor of our measurements. (i) Proton NMRD is neither invasive nor destructive because one measures the response of the mixing water itself in the normal saturated state of cement. No liquid or gas intrusion, no drying or other temperature and pressure modifications are required that risk damaging the microstructure. (ii) The measurement is sufficiently fast to be applied continuously during the progressive hydration and setting of the material. (iii) The remarkable features of the proton NMRD at low frequency allow one to probe directly the proton surface dynamics that contribute to $S_{p,NMR}$. The technique has also been applied to characterize the average pore sizes and distribution. 2D nuclear-spin-correlation $T_1-T_2$ and $T_2$-store-$T_2$ measurements in cements have been outlined. These experiments confirm the discrete pore-size distribution observed and have provided the first clear evidence of chemical exchange of water protons between connected gel micropores. These experiments have also provided further evidence in support of the 2D surface diffusion model of spin relaxation in cements. The $T_2$-store-$T_2$ 2D spin-correlation experiment confirms the existence of water exchange between connected micropores with an estimated rate of 5 ms$^{-1}$. From this, water diffusivity within the C–S–H structures has been calculated that broadly corresponds to the results of molecular dynamics simulations in related systems.

Finally, we have presented a new and non-invasive method for probing the wettability of plaster pastes and rock/oil/brine systems using NMRD. Unlike conventional transverse relaxation studies, this approach gives a direct probe of the dynamical surface affinity of fluids, thus allowing the separation of wetting from non-wetting fluids through their typical NMRD features. To quantify these features, we introduce a microscopic dynamical surface affinity index that measures the dynamical correlation (i.e. microscopic wettability) between a diffusive fluid and fixed Mn$^{2+}$ paramagnetic relaxation sources at the pore surfaces. We have applied this technique to carbonate reservoir rocks of bimodal porosity saturated with a mixture of dodecane and 50 kppm NaCl. The experimental NMRD results obtained on carbonate core plugs of bimodal porosity saturated with this oil/brine mixture clearly discriminate the wetting behavior of the fluids in the pore system. The data have been processed using a proposed model.
that clearly reveals the pore-size dependence of wettability. Here, the typical shapes of the two separated NMRD profiles allows us to conclude that water stays in the small pores while oil is in the large ones. This proves the existence of a flow path between the large pores that does not involve the small ones.

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