Basic field cycling relaxation features of liquids in porous media

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Collaborations: P. Levitz, D. Petit, R.G. Bryant
Academical Interest of studying the physics of liquids in porous media

- Dynamics of liquids at solid interfaces
- Transport in porous media (filtration, imbibition, conduction)
- Role of surface physical chemistry (interaction and wettability)
- Phase transitions in confinement
- Hydration of proteins, DNA et biological tissues
- MRI (origin of contrast)

Vycor (P. Levitz)
Industrial applications

- Microstructure of cements (Durability)
- Nuclear waste materials
- Oil recovery
- Environnement: filtration of water
- Transport of fluids in soils
- Gaz separation
- Chemical reactivity (catalyst)
- Food stuffs
Position of FFC relaxation in multiscale NMR

\[ \omega_0 = \gamma B_0 \]  
(Spin clock)

\[ \tau_c = 1 \]

- MRI Imaging
- Pulsed field gradient
- 3D Transport
- Physical chemistry
  - Surface dynamics
  - Exchange, interaction, wettability
- Spectroscopy
- Conventional relaxometry
- Field cycling relaxometry

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Outline

Dipolar relaxation processes in porous media

• 1. Intramolecular dipolar relaxation by translational diffusion at solid interfaces
• 2. Intermolecular dipolar relaxation by translational diffusion at solid interfaces
How is it possible to measure the surface relaxation from the overall $1/T_1(\omega_0)$? Model of biphasic fast exchange

Averaging between slowly relaxing “bulk” molecules and rapidly relaxing “surface” molecules (one $T_1$ and 2 phases): $\tau_{\text{ex}} << T_1$

$$\frac{1}{T_1(\omega_0)} = \frac{1}{T_{1,\text{bulk}}} + \frac{\varepsilon S}{V} \frac{1}{T_{1,\text{surface}}(\omega_0)}$$
**Bulk liquids**

Fast and local molecular motions, no frequency dependence

\[
\frac{1}{T_{1,Oil}} / \frac{1}{T_{1,Water}} \approx \frac{D_{Water}}{D_{Oil}} \approx 2.2
\]

\[T_1 \propto D \propto \frac{1}{\eta}\]

\[\frac{1}{T_{1,\text{bulk}}} = \text{Cte}\]
Nuclear magnetic dispersion of liquids in pores


Fast and local molecular motions, no frequency dependence

\[
\frac{1}{T_{1,\text{Oil}}} / \frac{1}{T_{1,\text{Water}}} \approx \frac{D_{\text{Water}}}{D_{\text{Oil}}} \approx 2.2
\]

Physical-chemistry on surface: aprotic vs protic liquids
Bonding to paramagnetic impurities
Surface translational diffusion enhances the probability of \(^1\text{H} - \text{Fe}^{3+}\) reencounters

\[
\frac{1}{T_1} = \frac{1}{T_{1,\text{bulk}}} + (\varepsilon S/V) \frac{1}{T_{1,\text{surf}}} (\omega_0)
\]
Aprotic liquids in calibrated microporous glasses beads with paramagnetic impurities
Reorientation mediated by translational dynamics (RTMD)

R. Kimmich and E. Anoardo,

Bioran and vycor d=4nm
No paramagnetic impurities

Evidence of a liquid dynamics at surface, in presence of a frozen bulk

FIG. 2. Frequency dependence of the proton spin-lattice relaxation time of water in Bioran B30 and Vycor at temperatures above (27°C) and below (-23 and -33 °C) the freezing region. The lines represent the power law $T_1 \propto \nu^{0.27}$.

Non polar liquid
Weak adsorption

Polar liquid
Strong adsorption

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I. Intramolecular dipolar relaxation by translational diffusion of liquids at surfaces of porous media

In science, in fact in most things, it is usually best to begin at the beginning

Lewis Carroll
Modeling the intramolecular relaxation at surface

Reorientation mediated by translational diffusion (RTMD) \textbf{R. Kimmich}

Intermittent Brownian Dynamics near a flat surface \textbf{P. Levitz, J.-P. Korb}

Periods of relocation in bulk \( L \) alternate with adsorption \( A \) on the surface

\[ p.d.f. \text{ at long times for a flat surface } \Psi_L(\tau) \]

\[ \Psi_A(\tau) = \frac{\exp(-\tau / \tau_A)}{\tau_A} \text{ Eyring, activated} \]

\( \tau_A = \text{average adsorption time} \)

Relaxation due to magnetic noise
Induced by molecular dynamics
at proximity (or on) the flat surface
P.d.f. $\Psi_L(t)$ at long times for a flat surface given by the bridge statistics over a plane: a Brownian 1D dynamics

$$B_{3D} = B_{2D} \otimes B_{1D}$$

First return at time $t$

$$\Delta C = \partial^2 C(r) / \partial r^2 = 0, \ C(r) = r / R$$

$$J(\delta, R) = - \frac{dC(r = \delta)}{dR} = \delta / R^2$$

Summing over all the different 1D Brownian paths, one finds at long times

$$\Psi_L(t) \approx \int J(\delta, R') \delta(t' - t) dR',$$

For diffusion, $t' = \frac{R'^2}{2D}, \ t = \frac{R^2}{2D} \Rightarrow R = (2Dt)^{1/2}$

$$\Psi_L(t) \approx \frac{2\delta / R^2}{R / D} = \frac{\delta}{\sqrt{2Dt^3}}, \ \text{Constraint} \Rightarrow \int \Psi_L(t) dt = 1 \ \Rightarrow \Psi_L(t) = \frac{\sqrt{\tau_L}}{2} \frac{1}{t^{3/2}} \ (\text{Pareto pdf})$$

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$\tau_L =$ Minimum loop duration
Random modulation of Intramolecular interaction

\[ G(\tau) = \langle I(t)I(t + \tau) \rangle, \quad J(\omega_0) = FT\{G(\tau)\}, \]
\[ R_1(\omega_0) \propto [J(\omega_0) + 4J(2\omega_0)] \]

\[ G(\tau) = \langle I(t)\ast I(-t) \rangle = \left\langle \int_{-\infty}^{+\infty} I(t)I(t - (\tau))dt \right\rangle = \langle I(t)I(t + \tau) \rangle \]

\[ I(t) = L(t) = \sum_i (-i)^j H(t - t_i) \quad \text{Sum of Heaviside functions} \]

\[ \langle I(t)\ast I(-t) \rangle \equiv L_2(t) \]
\[ L''_2(t) = -\langle I'(t)\ast I'(-t) \rangle = \omega_d^2 \sum_{i,j} (-1)^{i+j} \delta(t - (t_i - t_j)) \]
Summing all the events $i \rightarrow j$ assuming no correlation between successive temporal events

$$L''_2(t) = -\langle I'(t) * I'(-t) \rangle = \omega_d^2 \sum_{i,j} (-1)^{i+j} \delta(t - (t_i - t_j))$$

\[ -2\delta(t) \quad \Psi_A(t) \quad \Psi_L(t) \]

\[-\Psi_A(t) * \Psi_L(t) - \Psi_L(t) * \Psi_A(t) \]

\[+\Psi'_L(t) * \Psi'_A(t) * \Psi'_L(t) + \Psi_A(t) * \Psi'_L(t) * \Psi_A(t) + \ldots \]

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\[
L''_2(t \geq 0)/\omega_d^2 = -2\delta(t) + \Psi_A(t) + \Psi_L(t) - 2\Psi_A(t)\Psi_L(t) + \Psi_L(t)\Psi_A(t) + \Psi_A(t) + \Psi_L(t)\Psi_A(t)
\]

adding also the events for which \(L''_2(t \leq 0)/\omega_d^2\)

Property of the Fourier transform

\[
FT\{L''_2(t)\} = \tilde{L''}_2(\omega)
\]

\[
FT\{\Psi_A(t)\Psi_L(t)\} = TF\{\Psi_A(t)\}TF\{\Psi_L(t)\} = \tilde{\Psi}_A(\omega)\tilde{\Psi}_L(\omega)
\]

```
Summing the geometrical series

\[
L''_2(\omega) \propto -2\omega_d^2 \Re \left\{ \frac{\left(1 - \tilde{\Psi}_L(\omega)\right)\left(1 - \tilde{\Psi}_A(\omega)\right)}{\left(1 - \tilde{\Psi}_A(\omega)\tilde{\Psi}_L(\omega)\right)} \right\}
\]
```
\[ L_2(\omega) = -\frac{1}{\omega^2} L''_2(\omega) \propto \frac{2\omega^2}{\omega^2} \Re \left\{ \frac{\left(1 - \Psi_L(\omega)\right)\left(1 - \tilde{\Psi}_A(\omega)\right)}{\left(1 - \tilde{\Psi}_A(\omega)\tilde{\Psi}_L(\omega)\right)} \right\} \]

\[ \Psi_L(\tau) = \frac{\sqrt{\tau_L}}{2} \frac{1}{\tau^{3/2}} \quad \text{(Pareto)}, \quad \tilde{\Psi}_L(\omega) = 1 - \frac{\sqrt{2\pi}}{2} (1+i)\tau_L^{1/2} \omega^{1/2} + ... \]

\[ \Psi_A(\tau) = \frac{\exp(-\tau/\tau_A)}{\tau_A}, \quad \tilde{\Psi}_A(\omega) = \left(1 - \omega^2 \tau_A^2\right) - i\omega \tau_A \]

\[ J_{\text{Surface}}(\omega, \omega_A) \propto L_2(\omega) \propto \frac{\left(\omega A^2 / \omega A\right)^{3/2}}{\sqrt{\omega / \omega A + \omega A / \omega A + 1/2}} \]

\[ \omega A = \frac{\pi \tau L}{2 \tau_A^2} \quad \text{for a flat surface} \]

\[ R_{1,\text{Surface}}(\omega_0, \omega_A) \propto \left[ J_{\text{Surface}}(\omega, \omega_A) + 4J_{\text{Surface}}(\omega, \omega_A) \right] \quad \text{Not a single power law} \]
Theoretical dispersion $R_1(\omega_0)$ varying the average adsorption time

$$\omega_A = \frac{\delta_{\text{water}}^2}{2D_{\text{water}} \tau_A^2}$$

Drastic changes of $R_1(\omega_0)$ with $\omega_A$

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Reorientation translational mediated diffusion of water on the multiconnected interfaces of vycor (d=7nm)
(no paramagnetic impurities)


3D off-lattice reconstruction of the pore network from SAXS, MET

Model of orientation memory of the director \( n(t) \)

\[
\frac{-dR_1}{df} \propto \frac{1}{f^{1/2}}
\]

\( \omega_A = 0.1 \text{ MHz} \)

\( R_1 \propto 1/f^{1/2} \)

\( D_{\text{surface}} = D_{\text{bulk}}^{20/4} \)

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Application of proton field cycling relaxometry to plaster pastes

Objectives

1. Probe the average adsorption time of water at the surface of plaster paste by proton-water field cycling relaxometry

2. Vary the physical-chemistry at surface of plaster and relate this measurement to nanowettability

=> Improve the mechanical properties of this building material
Plaster paste

No paramagnetic impurities

CaSO$_4$·½H$_2$O$_{\text{solid}}$ (Hemihydrate)

CaSO$_4$·2H$_2$O$_{\text{solid}}$ (Gypsum)

Hydration

Disorderd polycrystalline (needle shape) porous material

Fragile microstructure → Possibility of alteration, dehydration of gypsum crystal, Shrinkage of porous network, ...

→ Necessity of a non destructive technique of characterization

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NMR degree of hydration and setting

Dissolution / precipitation

\[
\text{CaSO}_4, \frac{1}{2}\text{H}_2\text{O}_{(\text{solid})} + \frac{3}{2} \text{H}_2\text{O}_{(\text{aq})} \rightarrow \text{CaSO}_4, 2\text{H}_2\text{O}_{(\text{solid})}
\]

Transverse magnetization

NMR Degree of hydration

\[
\alpha(t_{hydr}) = \left(1 - \frac{M(0, t_{hydr})}{M(0, 0)}\right) \left(\frac{(w/p)_{stoi}}{(w/p)_{exp}}\right) \cdot \phi
\]


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Proton field cycling relaxometry allows separation of bulk and surface relaxation processes

$^1$H $R_1(\omega_0)$ data at various W/P after setting


$R_1(\omega_0) = R_{1,\text{bulk}} + \frac{\varepsilon S}{V} R_{1,\text{Surface}}(\omega_0)$

Biphasic fast exchange model verified by the rescaling data

\[ \frac{dR_1(\omega_0)}{d\omega_0} = \left( \frac{\varepsilon \rho_{\text{Gyp}} S_p}{\phi} \right) \frac{dR_{1,\text{Surface}}(\omega_0)}{d\omega_0} \]

$S_p \approx 1 m^2 / g, \varepsilon \rho \approx Cte$

Same surface relaxation process when varying W/P
Proton and deuterium $R_1(\omega_0)$

Same power laws for $R_1(\omega_0)$ of $^1$H and $^2$H

Intramolecular relaxation process by reorientational water dynamics at surface
Modifying the surface chemistry of plaster by adjuvant

When increasing the amount of STMP

$R_1$ decreases
due to reduction of $\tau_A$ and decrease of number of accessible sites on 010 surface

**Evolution to**

$$R_1(\omega_0) = R_{1,\text{bulk}} + A \left( \frac{N_S}{N_V} \right) (\omega/\omega_A)^{-1/2}$$

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Conclusion on plaster pastes

• The frequency dependence of the longitudinal relaxation rate of proton-water in plaster pastes depends drastically on the physical chemistry on the gypsum surface

• This allows us to probe directly the average adsorption time of water

• We succeed to change the physical chemistry of the surface of gypsum needles by adding adjuvant in the wetting water. It results a net decrease of the average adsorption time of water at the surface of gypsum polycrystals.

• These measurements are relevant to probe directly the wettability of plaster pastes at the nanoscale. This is useful to control the mechanical properties of this important building material
II. Intermolecular dipolar relaxation by translational diffusion of liquids at surfaces of porous media

Translational diffusion of liquids in micropores

- **Systems:** calibrated porous silica glasses (R=38Å and 80Å) with paramagnetic impurities Fe$^{3+}$ (40 ppm) fully saturated by aprotic liquids and water

- **Objective:** Probe the surface diffusion coefficient $D_{\text{surf}}$

- **Experiment:** Proton magnetic relaxation dispersion data $1/T(\omega_0)$

Model of biphasic fast exchange

\[ \tau_{\text{ex}} \ll T_1 \]

\[ \frac{1}{T_1(\omega_0)} \approx \frac{1}{T_{1,\text{bulk}}} + \frac{\epsilon S}{V} \frac{1}{T_{1,\text{surf}}(\omega_0, \omega_S)} \]

$D_{\text{surf}}$
$1/T_1(\omega_0)$ of aprotic liquids in confinement


2D diffusion of proton bearing molecules at proximity of Fe$^{3+}$

$D_{\text{surf}} << D_{\text{Vol}}$

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\[
\frac{1}{T} = \frac{2}{3} (\gamma_f \gamma_s \hbar)^2 S(S+1) \left[ \frac{1}{3} J_L^{(0)}(\omega_f - \omega_s) + J_L^{(1)}(\omega_f) + 2 J_L^{(2)}(\omega_f + \omega_s) \right]
\]

\[
J_L^m(\omega) = \int_{-\infty}^{\infty} G_L^m(\tau) e^{i\omega \tau} d\tau,
\]

\[
G_L^m(\tau) = \langle F_L^{-m}(t) F_L^{m}(t+\tau) \rangle
\]

It is much simpler to make the calculations in the lamellar frame \(M\) and use the well-known properties of the Wigner matrices to go to the lab frame \(L\)

\[
F_{\text{PAS}}^{(0)}(t) = \sqrt{(3/2)/r^3}, \quad F_{\text{PAS}}^{(\pm 1)}(t) = F_{\text{PAS}}^{(\pm 2)}(t) = 0.
\]

It is much simpler to make the calculations in the lamellar frame \(M\) and use the well-known properties of the Wigner matrices to go to the lab frame \(L\)

\[
F_L^{-m}(t) = \sum_{m' = -2}^{2} F_M^{-m}(t) D_{-m,m'}^{(2)}(\alpha = 0, \beta, \gamma = 0),
\]

\[
= \sum_{m' = -2}^{2} \left( \sum_{m = -2}^{2} F_{\text{PAS}}(t) \delta_{m,\alpha} D_{m,m'}^{(2)}(\phi, \theta, 0) \right) D_{-m,m'}^{(2)}(\alpha = 0, \beta, \gamma = 0),
\]

\[
= \sqrt{\frac{6\pi}{5} r(t)} \sum_{m' = -2}^{2} \gamma_2^{(m')}(\theta(t), \phi(t)) \gamma_2^{(2)}(\beta).
\]
Here $\alpha, \beta, \gamma$ are the Eulerian angles that rotate the L basis into the M basis. Because of cylindrical symmetry around $\mathbf{n}$, we have chosen these angles as $\alpha = \gamma = 0$; thus $D_{mm}^{(2)} (\alpha=0, \beta, \gamma=0) = d_{mm}^{(2)} (\beta)$ (Wigner rotation coefficients)

$$F_L^{(m)}(t) = \sum_{m'=-2}^{+2} f_2^{(m')} (t) e^{im'\varphi} d_{-m,m'}^{(2)} (\beta),$$

$$f_2^{(0)}(t) = \frac{1}{2} \sqrt{\frac{3}{2}} \frac{2z^2 - \rho^2}{(z^2 + \rho^2)^{5/2}}, \quad f_2^{(\pm 1)}(t) = \frac{3}{2} \frac{\rho z}{(z^2 + \rho^2)^{3/2}}, \quad f_2^{(\pm 2)}(t) = \frac{3}{4} \frac{\rho^2}{(z^2 + \rho^2)^{5/2}}.$$ (in cylindrical coordinates)

$$G_L^{(m)}(\tau) = \sum_{m'=-2}^{+2} \sum_{m''=-2}^{+2} d_{m,m'}^{(2)} (\beta) d_{-m',m''}^{(2)} (\beta) \left\{ f_2^{(m')} (\rho_0, z_0) f_2^{(m'')} (\rho, z) e^{im'\varphi_0 - mm''\varphi} \right\}$$

Ensemble average over a diffusing propagator

$$G_L^{(m)}(\tau) = \sum_{m'=-2}^{+2} \sum_{m''=-2}^{+2} d_{m,m'}^{(2)} (\beta) d_{-m',m''}^{(2)} (\beta) \left\{ \int_0^{2\pi} d\varphi_0 \int_{(C_{\rho_0})} d^2 \rho_0 \int dz_0 \ p(0) f_2^{(m')} (\rho_0, z_0) e^{im'\varphi_0} \right\}$$

$$\left\{ \int_0^{2\pi} d\varphi \int_{(C_{\rho,z})} d^2 \rho \int dz \ P(\rho, \varphi, z, \tau=0) f_2^{(m'')} (\rho, z) e^{-mm''\varphi} \right\}.$$
\[ B_{3D} = B_{2D} \otimes B_{1D} \]

\[ P(\rho, z, \tau; \rho_0, z_0, \tau = 0) = P_{\perp}(\rho, \tau; \rho_0, \tau = 0) P_{\parallel}(z, \tau; z_0, \tau = 0) \]

\[ P_{\perp}(\rho, \tau; \rho_0, \tau = 0) = \delta(\rho - \rho_0), \quad P_{\parallel}(z, \tau; z_0, \tau = 0) = \delta(z - z_0), \]

\[ \frac{\partial}{\partial z} P_{\parallel}(z = 0, \tau) = \frac{\partial}{\partial z} P_{\parallel}(z = d, \tau) = 0. \]

\[ P_{\perp}(\rho, \tau; \rho_0, \tau = 0) = \frac{1}{2\pi} \sum_{m=-\infty}^{\infty} \int_{0}^{\infty} dk \ k \ \exp(-k^2 D_{\perp} \tau) \ J_m(k\rho)J_m(k\rho_0) \exp[im(\phi_0 - \phi)]. \]

\[ P_{\parallel}(z, \tau; z_0, \tau = 0) = \frac{1}{d} \left[ 1 + 2 \sum_{l=1}^{\infty} \exp\left( -\frac{l^2 D_{\parallel}}{d^2} \tau \right) \cos\left( \frac{l\pi z}{d} \right) \cos\left( \frac{l\pi z_0}{d} \right) \right]. \]

Anisotropy of diffusion

At long times (low frequency) \( P_{\parallel} \) tends rapidly to \( 1/d \) and \( G_{L,(m)}(t) \rightarrow \text{Cte} \)

\[ P(\rho, \varphi, z, \tau; \rho_0, \varphi_0, z_0, \tau = 0) \approx \frac{1}{2\pi d} \sum_{m=-\infty}^{\infty} \int_{0}^{\infty} dk \ k \ \exp(-k^2 D_{\perp} \tau)J_m(k\rho)J_m(k\rho_0) \exp[im(\phi_0 - \phi)]. \]

\[ G_{L}^{(m)}(\tau) = \sum_{m'=-2}^{+2} |d_{m,m'}^{(2)}(\beta)|^2 G_{M}^{(m')} (\tau), \]
At long times (low frequency)

\[ G_M^{(0)}(\tau) \approx \frac{3}{8} \frac{\pi \sigma_s}{d^2 \delta^2} \left( \frac{\tau}{\tau} \right), \quad G_M^{(1)}(\tau) \approx \frac{1}{4} \frac{\pi \sigma_s}{\delta^4} \left( \frac{\tau}{\tau} \right)^2, \quad G_M^{(2)}(\tau) \approx \frac{1}{16} \frac{\pi \sigma_s}{\delta^4} \left( \frac{\tau}{\tau} \right)^2. \]

Powder averages

\[ \langle J_L^{(0)}(\omega) \rangle = \left\{ \sum_{m'=-2}^{+2} d_{0,m'}(\beta) \left| J_M^{(m')} \right|^2 \right\} = \frac{1}{5} \left[ 5 J_M^{(0)}(\omega) + 2 J_M^{(1)}(\omega) + 2 J_M^{(2)}(\omega) \right] \approx \frac{1}{5} J_M^{(0)}(\omega), \]

\[ \langle J_L^{(1)}(\omega) \rangle = \left\{ \sum_{m'=-2}^{+2} d_{1,m'}(\beta) \left| J_M^{(m')} \right|^2 \right\} \approx \frac{1}{5} J_M^{(0)}(\omega), \]

\[ \langle J_L^{(2)}(\omega) \rangle = \left\{ \sum_{m'=-2}^{+2} d_{2,m'}(\beta) \left| J_M^{(m')} \right|^2 \right\} \approx \frac{1}{5} J_M^{(0)}(\omega). \]

\[ J_M^{(0)}(\omega) = \frac{3\pi \sigma_s \tau}{2d^2 \delta^2} \left[ \ln \left( \frac{d}{\delta} + 1 \right) - 3.078 + \frac{1}{4} \ln \left( 1 + \frac{1}{\omega^2 \tau^2} \right) + O(\sqrt{\omega \tau}) \right], \]
NMRD for different pore sizes and diffusion coefficients

\[
\frac{1}{T_1} = \frac{\pi}{15} \sigma_3 (\gamma_1 \gamma_2 h)^2 S(S+1) \frac{\tau_\perp}{d^2 \delta^2} \left[ 10 \ln \left( \frac{d}{\delta} + 1 \right) - 30.8 + \frac{7 \ln \left( 1 + \omega S^2 \tau_\perp^2 \right)}{4} \right]
\]

**FIG. 2.** Calculated variations of the magnetic field dependences of proton spin-lattice relaxation times given by Eq. (19) (a) for pore size \(d=5\) Å, molecular size \(d'=3\) Å, \(d'=\delta=1\) Å and different values of the diffusion coefficient \(D_\perp\), from top to bottom 0.25 \(\times 10^{-6}\) cm²/s, 0.50 \(\times 10^{-6}\) cm²/s, 0.75 \(\times 10^{-6}\) cm²/s and 1.0 \(\times 10^{-6}\) cm²/s and (b) for \(D_\perp=0.50 \times 10^{-6}\) cm²/s, \(d'=7\) Å, \(d'=4.1\) Å and varying the pore size \(d'(\text{Å})\) as shown.
Experimental NMRD for aprotic solvents

FIG. 3. Magnetic-field dependences of $^1$H spin-lattice relaxation rates of acetone and acetonitrile embedded in a packed samples of calibrated porous glasses beads at (from top to bottom) 5°C, 15°C, 25°C, 35°C, and 45°C. The large and small experimental black points correspond to glasses of pore sizes 75 and 159 Å, respectively. The continuous lines correspond to the best fits to Eq. (19) as discussed in the text. The field strength is shown as the $^1$H Larmor frequency.

$D_{surf} << D_{Vol}$
Experimental NMRD for aprotic solvents

FIG. 4. Magnetic-field dependences of $^1\text{H}$ spin-lattice relaxation rates of DMF and DMSO embedded in packed samples of calibrated porous glasses beads at (from top to bottom) 5 °C, 15 °C, 25 °C, 35 °C, and 45 °C. The large and small experimental black points correspond to glasses of pore sizes 75 and 159 Å, respectively. The continuous lines correspond to the best fits of Eq. (19) as discussed in the text. The field strength is shown as the $^1\text{H}$ Larmor frequency.
Anomalous Temperature effects
(surface vs volume)

\[ \Delta E = E_m - E_s = -2.6 \text{ kcal/mol} \]

Anomalous temperature effect

\[ \frac{\partial P(r_{IS}, \tau)}{\partial \tau} = D_{\text{eff}}(T) \Delta S P(r_{IS}, \tau) \]

\[ D_{\text{eff}}(T) = n_0 \exp\left(\frac{E_s}{RT}\right) D_0 \exp\left(\frac{-E_m}{RT}\right) = D_{\text{eff0}} \exp\left(\frac{E_s - E_m}{RT}\right) \text{ with } E_s > E_m \]

\[ \Delta E < 0 \]

Water

\[ V \text{ (MHz)} = 4.8 \text{ kcal/mol} \]

\[ 75 \text{Å} \]

\[ E_m = 4.8 \text{ kcal/mol} \]

\[ \nu \text{ (MHz)} \]

\[ 1000/T \]

\[ 1/T_1 \text{ (s}^{-1}\text{)} \]

\[ 0.01 \]

\[ 0.04 \]

\[ 0.1 \]

\[ 0.25 \]

\[ 0.4 \]

\[ 1.0 \]

\[ 4.0 \]

\[ 10.0 \]

\[ 30.0 \]

\[ 3 \]

\[ 3.2 \]

\[ 3.4 \]

\[ 3.6 \]
Granular packings


\[ \text{SiC} \] 25\% Silice \( d_{\text{grain}} = \{8, \ldots, 150 \ \mu m \} \]

\[ K \propto \left( d_{\text{grains}} \right)^2 \]

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Universal results for water in granular packings of SiC and microporous silica glasses

Granular packing 8µm

Water

Microporous silica glasses

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Application of FFC to reservoir carbonate rock

$\phi = 24\%$, $K = 1.7\, \text{mD}$, intermediate wettability

Water: bilogarithmic NMRD
Diffusion 2D with surface interaction

Oil: quasi-bilogarithmic NMRD
Diffusion 2D with surface interaction

\[ \tau_m = 1.2 \, \text{ns} \]
\[ D \approx 10^{-7} \, \text{cm}^2/\text{s} \]

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Fig. 4. Measured water and oil (dodecane) spin-lattice relaxation rates as a function of the proton Larmor frequency in a reservoir carbonate rock for a monophasic saturation, for different temperatures between 10 and 65°C. The continuous lines correspond to the fits obtained with Eqs. (3 and 4).
Conclusion

Calibrated and natural porous media

FFC experiments
In various conditions of temperature, liquids, surfaces

Theories and simulations
Molecular dynamics at surfaces

Applications
Hydration of proteins
Oil recovery
Hydration and setting of cements and concretes