Usage of internal magnetic fields for the characterization of porous materials by NMR CPMG sequence

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Usage of internal magnetic fields to study the early hydration process of cement paste by MGSE method

Janez Stepišnik, a, b, c, Ioan Ardelean

Hydration of cement paste

- Distribution of pore size
- Distribution of internal gradients
Spin echo peaks bear information about dynamics

Porous media

CPMG with externaly applied magnetic field gradient
- Modulated Gradient Spin Echo (MGSE method)

CPMG with Internaly created fields:
- magnetic susceptibility differences,
- magnetic impurities,
- chemical shifts of nonequivalent spins
Spin interaction with the magnetic fields in liquid

\[
\mathbf{B}(\mathbf{r}_i) = B_{zo} + \mathbf{B}[t, \mathbf{r}_i(t)]
\]

- Externaly magnetic field gradient, internally induced fields by the susceptibility difference in porous media, by the magnetic impurities, by chemical shifts or weak spin-spin interactions.

\[
\mathbf{B}_{rf}(t) \quad \pi/2_x
\]

\[
E(t)
\]
CPMG and dynamics of spins in liquid

\[ \hat{H}(t) = -\hbar \gamma B_0 \sum_i \hat{I}_{zi} - \hbar \gamma \sum_i B(t, r_i(t)) \hat{I}_i + \hat{H}_{RF}(t) \]

\[ \hat{H}(t) = \hat{H}_o + \hat{H}_G + \hat{H}_{cpmg}(t) + \hat{H}_{\pi/2}(t) \]

Transformation into rotating frame

\[ \hat{H}_G = -\hbar \gamma \sum_i B(t, r_i(t)) \hat{I}_i \Rightarrow -\hbar \gamma \sum_i B_z(t, r_i(t)) \hat{I}_{zi} \]
CPMG and dynamics of spins in liquid

\[ \hat{H}(t) = -\hbar \gamma B_o \sum_i \hat{I}_{zi} - \hbar \gamma \sum_i \mathbf{B}(t, \mathbf{r}_i(t)) \hat{I}_i + \hat{H}_{RF}(t) \]

\[ \hat{H}(t) = \hat{H}_o + \hat{H}_G + \hat{H}_{cpmg}(t). \]

\[ -\frac{i}{\hbar} \int_0^t \hat{H}_i(t') dt' \]

\[ \hat{U}_i(t) = Te^{-\frac{i}{\hbar} \int_0^t \hat{H}_i(t') dt'} = \hat{U}_{io} \hat{U}_{iR} \]

\[ \hat{U}_{io} = e^{-\frac{i}{\hbar} \hat{H}_{oi} t} = e^{i \omega_0 \hat{I}_{zi} t} \]

\[ -\frac{i}{\hbar} \int_0^t \hat{U}_{io} (\hat{H}_G + \hat{H}_{cpmg}(t))_i \hat{U}_{io} dt' \]

\[ \hat{U}_{iR} = Te^{-\frac{i}{\hbar} \int_0^t \hat{U}_{io} (\hat{H}_G + \hat{H}_{cpmg}(t))_i \hat{U}_{io} dt'} \]

Transformation into rotating frame

\[ \hat{H}^{\gamma}_{icpmg}(t) = -2\hbar \omega_\pi \cos(\omega_o t) \hat{I}_{iy} \Rightarrow -\hbar \omega_\pi \hat{I}_{iy} \]
Transformation into the tumbling frame

\[ \hat{H}_R(t) = -\hbar \gamma \sum_i B_z(t, r_i(t)) \hat{I}_{zi} - \hbar \omega (t) \sum_i \hat{I}_{yi} \]

\[ \hat{U}(t) = \hat{U}_o \hat{U}_R = \hat{U}_o \hat{U}_{GRT} \hat{U}_{cpmgR} \]

\[ \hat{U}_{GRT} = T e^{-i \int_0^t \hat{H}_{GRT}(t') dt'} \]

\[ \hat{H}_{GRT}(t') = \hat{U}_{cpmgR} \hat{H}_{GR}(t') \hat{U}_{cpmgR}^{+} = -\gamma \sum_i [\hat{I}_{zi} \cos(b(t)) - \hat{I}_{xi} \sin(b(t))] B_z(t, r_i(t)) \]

\[ b(t) = \int_0^t \omega (t') dt' \]
Spin dynamics

\[ \hat{U}_{GRT}(t) = Te^{-i \int_{0}^{t} \hat{H}_{GRT}(t') dt'} \]
\[ \hat{I}_{yi}(t) = \hat{U}_{GRT}(t) \hat{I}_{yi} \hat{U}^{+}_{GRT}(t) \]
Echoes contains information about spin location and spin dynamics

\[ \hat{H}_{GRT}(t) = -\gamma \sum_i \left[ \hat{I}_{zi} \cos(b(t)) - \hat{I}_{xi} \sin(b(t)) \right] B_z(t, \mathbf{r}_i(t)) \]

\[ f(t) = \int_0^t \cos(b(t'))dt' \]

\[ E(t) = \beta_o \sum_i \text{Tr}(\hat{U}_{GRT}(t) \hat{I}_{yi} \hat{U}_{GRT}^+(t) \hat{I}_{yi}) \approx \sum_i e^{-i\gamma \int_0^t B_z(t', \mathbf{r}_i(t')) \cos(b(t'))dt'} \]

\[ E(t) \approx \sum_i e \]

\[ \text{topology} \quad \text{dynamics} \]

\[ -i \gamma f(t) B_z(t, \mathbf{r}_i(t)) + i \gamma \int_0^t dB_z[t', \mathbf{r}_i(t')] f(t')dt' \]
Distinction between location and motion in the spin echo signal

With applied magnetic field gradient

\[ E(t) = \sum_i \left[ -i \gamma \int_0^t G_i \cdot r_i(t') f(t') dt' \right] \]

\[ = \sum_i \left[ i \gamma f(t) G_i \cdot r_i(t) + i \gamma \int_0^t G_i \cdot v_i(t') f(t') dt' \right] \]

\[ E(N\tau) \approx \sum_i \left[ i \gamma \int_0^N G_i \cdot v_i(t) f(t') dt' \right] \]

Spin echo peaks bear information just about dynamics
Gaussian phase approximation: Velocity autocorrelation spectrum

Spin velocity is the random variable

\[ E(N\tau) \approx \sum_i \left< e^{i\int_0^{N\tau} G_i \cdot v_i(t') f(t') dt'} \right> = \sum_i \left< v_i(t) \right> = 0 \]

Velocity autocorrelation spectrum

\[ D_i(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} \left< v_i(t) \otimes v_i(t_1) \right> e^{-i\omega t'} dt \]

Spectrum of spin dephasing

\[ f(\omega,t) = \int_0^t f(t) e^{-i\omega t} dt \]

\[ E(N\tau) = \sum_i \frac{-1}{\pi} \frac{1}{\gamma^2} \int_{-\infty}^{\infty} f(\omega, N\tau)^2 G_i D_i(\omega) G_i d\omega \]
CPMG sequence and spectrum of motion

\[ E(N\tau) \approx \sum_i \left\langle e^{i\gamma \int_0^{N\tau} \nabla B_z [\mathbf{r}_i(t')] \cdot \mathbf{v}_i(t') f(t') dt'} \right\rangle = \sum_i e^{-\frac{\gamma^2}{\pi} \int_0^{\infty} |f(\omega, N\tau)|^2 G_i D_i(\omega) G_i d\omega} = \sum_i e^{-\frac{8\gamma^2}{\pi^2 \omega_m^2} G_i D_i(\omega_m) G_i N\tau}

\[ |f(\omega, t)|^2 = \frac{8t}{\pi \omega_m^2} \sum_n \frac{\sin(n\pi/2)^2}{n^4} \delta(\omega - n\omega_m)
\]

\[ \approx \frac{8t}{\pi \omega_m^2} \delta(\omega - \omega_m) + \ldots
\]

f(t)

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Velocity autocorrelation spectrum of restricted diffusion

\[ E(t) = \sum_i e^{-\frac{t}{T_2}} -\frac{8\gamma^2 G_z^2}{\pi^2 \omega_m^2} D_i(\omega_m) t \quad t = N\tau \]

\[ D_{\text{rest}}(\omega) = D_\infty + D_o \sum_k b_k \frac{\tau_k^2 \omega^2}{1 + \tau_k^2 \omega^2} \]

- \( b_k \) = parameters of pore structure
- \( \tau_k \) = correlation times
MGSE measurement of restricted self-diffusion

Externaly applied MFG

\[ E(t) = \sum_i e^{-\frac{t}{T_2}} - \frac{t}{\pi^2 \omega^2} D_i(\omega_m) t \]

Spectral characterization of diffusion in porous media by the modulated gradient spin echo with CPMG sequence

Janez Stepišnik \(a, b, c\), Samo Lasic \(a\), Aleš Mohorič \(a\), Igor Serša \(b\), Ana Sepe \(b\)

Diffusion of water in ceramics with inclusion of magnetic impurities

\[ \omega_m = \frac{\pi}{\tau} \]

\[
\beta(t)/t = \frac{1}{T_2} + \frac{8\gamma^2 G_{zi}^2}{\pi^2 \omega_m^2} D_i(\omega_m) \approx \frac{1}{T_2} + \frac{4\gamma^2 G_{zi}^2}{\pi^2} b_1 \frac{\tau_1 \tau^2}{\tau^2 + \pi^2 \tau_1^2}
\]

Prof. dr. Ioan Ardelean,
Technical University of Cluj-Napoca, Romania
CPMG of water in ceramics

\[ \frac{\beta}{t} \approx \frac{1}{T_2} + \frac{4\gamma^2 G_z^2}{\pi^2} b_1 \frac{\tau_1 \tau_2}{\tau^2 + \pi^2 \tau_1^2} \]

Relaxation time

Pore size

Internal gradient

Gradient/susceptibility ratio

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe$_2$O$_3$ externally introduced (%)</th>
<th>Susceptibility difference (sample-water)</th>
</tr>
</thead>
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<tr>
<td>S0</td>
<td>0</td>
<td>2.9035E-5</td>
</tr>
<tr>
<td>S2</td>
<td>2</td>
<td>4.9035E-5</td>
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<tr>
<td>S4</td>
<td>4</td>
<td>7.1035E-5</td>
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<td>6</td>
<td>8.7035E-5</td>
</tr>
<tr>
<td>S8</td>
<td>8</td>
<td>1.12035E-4</td>
</tr>
</tbody>
</table>

The SEM image inter-granular spaces (aprox. 2-3 micrometers).
Field of magnetic susceptibility difference

$\Delta B$ resulting from a cylinder parallel to $B_0$.

$\Delta B$ resulting from a cylinder at a 30° angle to $B_0$.

$\Delta B$ resulting from a cylinder at a 60° angle to $B_0$. 
CPMG of cement paste

Internal gradient induced by the susceptibility difference

![Graphs showing relaxation time, pore size, and internal effective gradient over time and temperature.](image-url)
CPMG of cement paste: Echoes decay

Distribution of internal MF gradient
CPMG and resonance off-set artifacts

\[
\hat{H}_{GRt}(t) = -\gamma \sum_i \left[ \hat{I}_{z_i} \cos(b(t)) - \hat{I}_{x_i} \sin(b(t)) \right] B_z(t, r_i(t))
\]
Thank you for your attention!
Alpine NMR Workshop Bled

Bled, Slovenia, 21-24 September, 2017
Bled, Slovenia
Workshop venue will be Plemljeva villa. It has a conference room and can accommodate 18 attendees in 9 rooms.

Nearby hotel Astoria for additional accommodations.