On the self-diffusion measurement by the modulated gradient spin echo, a legacy of Sir Paul T. Callaghan

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Paul T. Callaghan and the modulated gradient spin echo

“An exceptional NMR tool is the method, in which the spectral density of the translational velocity autocorrelation is "probed" by a sampling function given by the frequency spectrum of the effective magnetic field gradient waveform“.

Paul termed it as MODULATED GRADIENT SPIN ECHO.

\[
\frac{1}{\pi} \int_{0}^{\infty} D(\omega) q^2(\omega, \tau) \ d\omega
\]

\[
D(\omega) = \int_{0}^{\infty} \langle \Delta v_x(t) \Delta v_x(0) \rangle e^{i\omega t} \ dt
\]

\[
q(\omega, \tau) = \int_{0}^{\tau} \int_{0}^{t} G_{\text{eff}}(t') \ dt' e^{i\omega t} \ dt
\]
Velocity autocorrelation function and gradient spin echo

\[ \beta(\tau) = \frac{1}{\pi} \int_0^\infty q(\omega, \tau) D(\omega) q^*(\omega, \tau) \, d\omega \]

**Velocity autocorrelation function**

\[ \langle v_x(t) v_x(0) \rangle \approx 2D \delta(t) \]

**Spectrum of velocity correlation**

\[ D(\omega) = \int_0^\infty \langle v_x(t) v_x(0) \rangle e^{i\omega t} \, dt \]


**Velocity autocorrelation function**

- Neutron range
- NMR range

**Spectrum of velocity correlation**

- NMR range
- Neutron scattering range

- Time: \(10^{-12} s \rightarrow 10^{-3} s\)
- Frequency: \(10^3 \rightarrow 10^{12} Hz\)
Notion of MGSE method in Paul’s NMR textbook

In Paul’s NMR lab 1994-95
Modulated Gradient Spin Echo (MGSE)

- Velocity autocorrelation spectrum

\[ \beta = \frac{1}{\pi} \int_{0}^{\infty} D(\omega) |q(\omega, \tau)|^2 d\omega \]

- Modulated gradient sequence:
  
  \[ \frac{\pi}{2}, \pi, \pi, \pi, \pi, \pi, \pi, \pi, \pi, \pi, \pi, \pi \]

- Time sequence:
  
  \[ T \]

- Frequency sequence:
  
  \[ \omega_m = \frac{2\pi}{T} \]

- Ln(\[E/E_o\]) \approx D(\omega_m)\tau
VAS of flow in the porouse medium

Dispersion spectra for water flow through ion-exchange resin bead pack at different velocities as measured by MGSE sequence ($\delta=70\mu s$).

VAS of diffusion in the porous medium

\[ Ln\left(\frac{E}{E_o}\right) \approx D \left(\omega_m\right)\tau \]

\[ \omega_m = \frac{2\pi}{T} \]

Velocity correlation spectrum of water between closely packed, mono-disperse, surfactant coated polystyrene spheres of 2r=15\(\mu\)m.

Frequency limit of pulsed MGSE


Frequency range is limited below 1 kHz due to the gradient coil inductance.

**FIG. 5.** The frequency-dependent diffusion coefficient $D_\omega(\omega)$ for free water (circles) and water confined within emulsion droplets in a highly concentrated fresh (squares) and aged (triangles) emulsion. The two lower lines are calculated according to the flow-scheme in Fig. 9. The upper line is the value of $D$ for free water.
Generalized Analysis of Motion Using Magnetic Field Gradients

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Fig. 4. Frequency-domain modulated gradient NMR rf and gradient pulse sequences, showing the (actual) gradient modulation waveforms \( G(t) \), the time integral of the effective gradient wave form \( \int G(t) \, dt \), and the spectrum of \( \mathcal{F}(G(t)) \). \( \mathcal{F}(\omega) \) directly samples the diffusion spectrum. The wave forms and spectra are for (a) double lobe/6c rectangular modulation, (b) single lobe/6c rectangular modulation, and (c) single lobe/4e sawtooth-shaped phase modulation. Note that pulse sequences (b) and (c) sample the diffusion spectrum at a single frequency.
By a proper phase cycling of rf-pulses one can remove the resonance off-set artifacts (or filter off unwanted coherences).

Frequency limit > 10 kHz
VAS of water in silica powder

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

VAS of air-fluidized granular system

Fig. 4 – The power spectra of the displacement of standard seeds fluidized by the air-flow at 0.5 m/s. The two upper traces correspond to the different fillings: A) 150 seeds and B) 175 seeds. The curves (right to upper) are: A) 10 m/s and B) 10 m/s.

Empiric formula:

\[ D(\omega) = \left( D + \langle \xi^2 \rangle \tau_c \omega^2 \right) e^{-\tau_c \omega} \]

Autocorrelation spectra of an air-fluidized granular system measured by NMR

S. Lasić, J. Stepišnik, A. Mohorič, I. Serša and G. Planinič
Velocity autocorrelation spectra of gels

VAS of organogels $T=23^\circ C$

- blue dots: gel N1%
- red dots: gel T4%

Frequency [Hz]

$D(v)$ $m^2/s$
VAS of liquids

G = 0.25-2.50 T/m, ν_L = 84 MHz

Self-diffusion coefficients
VAS of liquids with the NMR mouse

\[ G = 11.7 \, \text{T/m} \quad \nu_L = 11.7 \, \text{MHz} \]

\[ T = 28^\circ \text{C} \]

Self-diffusion coefficient
VAS of glycerol

Self-diffusion coefficient

$D = 4 \times 10^{-12} \text{ m}^2/\text{s}$
MGSE of Poly(isopren-1,4): polymer standard

\[ M_n = 704 \]

\[ M_n = 1610 \]

\[ M_n = 3920 \]

\[ M_w/M_n = 1.05 \]

\[ D(\omega) = D_{coil} + D_{seg} \sum_{p=1}^{m} \frac{\omega^2 \tau^2}{\omega^2 \tau^2 + p^4} \]

\[ \approx D_{coil} + D_{seg} \frac{\omega^2 \tau^2}{\omega^2 \tau^2 + 1} \]

<table>
<thead>
<tr>
<th>( M_n )</th>
<th>( D_{coil} )</th>
<th>( D_{seg} )</th>
<th>( \tau )</th>
<th>( T_2 )</th>
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<td>704</td>
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<td>---</td>
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<tr>
<td>Rouse</td>
<td>1/N</td>
<td>1/N</td>
<td>N^2</td>
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An exceptional NMR tool is the method, in which the spectral density of the translational velocity autocorrelation is "probed" by a sampling function given by the frequency spectrum of the effective magnetic field gradient waveform.

The method gives a new insight into the world of molecular displacement dynamics by providing information that give better understanding or help to develop a proper understanding of certain phenomena.
Acknowledgments

Aleš Mohorič
Samo Lasič
Igor Serša
Siegfried Stapf
Carlos Mateo

Institute Jozef Stefan Ljubljana, Slovenia
Thanks for your attention