Experiment and Modelling in Structural NMR

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NMR diffusometry
Molecular dynamics
in complex systems
probed over many decades
of times

[05003]

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NMR diffusometry:
Molecular dynamics in complex systems
probed over many decades of time

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Outline:
- complex systems
- "normal" and "anomalous" diffusion
- dynamic structure factor
- field-gradient NMR diffusometry
- application to polymer melts
- incoherent neutron scattering
- dynamic light scattering
- intermolecular NMR relaxometry
- isotopic interdiffusion
- time scales of diffusion measurements
Complex systems:
- obstacles
- confinements
- pores
- surface adsorption and ordering
- domains
- anisotropy
- excluded volume
- chain connectivity
- topological constraints
- tortuosity

Random-walk trajectories can be extremely different:

Brown

Lévy

Characterization of trajectories by diffusion:

- Particles (atoms, molecules, colloids, droplets, ...) treated as random walkers
  → displacement $r$ in time $t$

- Propagator (probability distribution, probability density function, ...)
  → probability density $P(r, t)$
  for a displacement $r$ in time $t$

- $P(r, t) d^3r$ → probability that the particle is displaced from the origin to the volume element $d^3r$ in a distance $r$

- Mean square displacement (or variance or second moment of $P(r, t)$)
  → $\langle r^2 \rangle \equiv \int r^2 P(r, t) d^3r$

Formal classification

in the case of power-law limits

$\langle r^2 \rangle \equiv \int r^2 P(r, t) d^3r \propto t^\alpha$

- $\alpha = 0$: localized position
- $\alpha < 1$: subdiffusive displacements
- $\alpha = 1$: normal diffusion
- $\alpha > 1$: superdiffusive displacements
- $\alpha = 2$: ballistic displacements
- $\alpha = 3$: turbulent displacements

Fickian diffusion equation (in 1 dimension)
\[ \frac{\partial P}{\partial t} = D \frac{\partial^2}{\partial x^2} P \]

Fractional diffusion equation
\[ \frac{\partial P}{\partial t} = \alpha R^{1-\alpha}_D \frac{\partial^2}{\partial x^2} P(x,t) \]

\(R^{1-\alpha}_D\): Riemann-Liouville operator
\(\alpha\): diffusion exponent (R. Metzler, J. Klafter, 2000)

Gaussian:
\[ P(x,t) = \frac{1}{2\pi Dt} \exp\left(\frac{-x^2}{4Dt}\right) \]

Initial condition: \(P(x,0) \sim \delta(0)\)

Stretched exponential:
\[ P(x,t) \propto \frac{1}{\sqrt{4\pi D t^{\alpha/2}}} \exp\left(-\frac{2-\kappa}{2} \left(\frac{x}{\sqrt{D t^{\alpha/2}}}\right)^\kappa\right) \]

\(\kappa<1\):
\[ \langle x^2(t) \rangle \propto D t \]
\[ \langle x^2(t) \rangle \propto D t^{1/2} \]

2 classes of subdiffusive anomalies (\(\alpha<1\)):

a) Diffusion under geometrical restrictions
(waiting time distribution due to trapping
in geometric or energetic traps)

\(\rightarrow\) non-Gaussian propagator
examples: reptation, random walk on fractals

b) Time dependent diffusion coefficient
\(D=D(t)\) in a homogeneous medium
(due to mutual obstruction)

\(\rightarrow\) Gaussian propagator
examples: single-file diffusion, Rouse mode based diffusion
Probing of diffusive displacements:

a) tracer experiment
   → imaging of isotopic interdiffusion
b) inter-molecular dipolar relaxation
   → field-cycling NMR relaxometry
c) (incoherent) dynamic structure factor
   → (i) field-gradient NMR diffusometry
      (ii) incoherent neutron scattering
      (iii) dynamic light scattering

\[
G_{inc} = \exp\left\{ -\frac{1}{6}q^2 \left\langle r_{self}^2 \right\rangle \right\}
\]

\[ q \quad \text{“wave vector”} \rightarrow \text{specific for experimental technique} \]

normal diffusion: \[ \left\langle r_{self}^2 \right\rangle = \left\langle r_{self}^2(t) \right\rangle = 6Dt \]

\[ D \quad \text{self-diffusion coefficient} \]

Field Gradient NMR Diffusometry

time scale 1 ms … 1 s
**field-gradient NMR diffusometry:**

**experimental protocol: spin echo of any sort + field gradient**

- gradient echo
- Hahn
- stimulated
- coherence transfer
- rotary
- ...

**principle: dephasing + rephasing of spin coherences**

---

**gradient echo:**

Larmor frequency: \( \omega_L = \gamma B \)  
"helix"  
position: \( R(0) \)  
field: \( B(0) = gz(0) \)

"wave number" \( q = \gamma g \tau \)  
position: \( R(t) \)  
field: \( B(t) = gz(t) \)

180° RF pulse instead of inversion of the gradient
complex representation of transverse magnetization in the rotating frame:

\[
\begin{align*}
\phi &= \phi_i \\
x' &= m(0) = M_r(0) + iM_i(0) \\
&= |m(0)|\exp\{i\phi_0\}\ \\
y' &= m(t) = M_r(t) + iM_i(t) \\
&= |m(t)|\exp\{i\phi_t\}
\end{align*}
\]

Larmor frequency
\[
\omega_L = \gamma B
\]

\[
\exp\{i\omega t - \omega_0 t\} = \exp\{i(\gamma B(t) - \gamma B(0))\}
\]

\[
\exp\{i\gamma g_z(t) - \gamma g_z(0)\} = \exp\{e^{-iqR}\} e^{iqR(t)}
\]

→ incoherent dynamic structure factor

"wave number"
\[
q = \gamma g \tau
\]

**field-gradient NMR diffusometry**

measurand: The echo attenuation function

\[
a(t) \propto \mathcal{G}_{inc}(t) = \left\langle e^{-i\mathbf{q} \cdot \mathbf{R}(0)} e^{i\mathbf{q} \cdot \mathbf{R}(t)} \right\rangle
\]

\[
\text{Gauss}\ 
\exp\left\{- \frac{1}{6} q^2 \langle r_{self}^2 \rangle \right\}
\]

\[
\text{Einstein}\ 
\exp\left\{-q^2Dt \right\}
\]

"wave number"
\[
q = \gamma g \tau
\]

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Field-gradient NMR diffusometry

\[ a(q, \tau, t) = \exp \left\{-q^2 D \left( t - \tau / 3 \right) \right\} \]

NMR diffusometry in the fringe field of a superconducting magnet

Attenuation of the stimulated echo

\[ A \propto \exp \left( -\frac{1}{6} < r^2 > q^2 \right) \exp \left( -\tau_2 / T_1 \right) \exp \left( -2\tau_1 / T_2 \right) \]

wave number \( q = \gamma g \tau_1 \)

Application to polymer melts
under confinement in pores
Tube/reptation concept by Doi and Edwards

(definition of 4 characteristic time constants)

\[ \tau_s \] segment fluctuation time
\[ \tau_e \] entanglement time
\[ \tau_R \] (longest) Rouse chain relaxation time
\[ \tau_d \] disengagement time

NMR diffusometry and the tube/reptation concept

\[ a(\tilde{q}, t) = \left\langle e^{i\tilde{q} \cdot \tilde{r}(t)} \right\rangle = \left( \left\langle e^{i\tilde{q} \cdot \tilde{r}_s(t)} \right\rangle \right) \exp(-q^2D_0 t) \]

(wave vector \( \tilde{q} = \gamma \tilde{g} \tau \))

- anomalous segment diffusion

\[ a_s(\tilde{q}, t) = \left\langle \frac{1}{3} \left( \frac{2\pi}{3} d |s| \right)^{-1/2} e^{-3r_s^2/2d^2} e^{i\tilde{q} \cdot \tilde{r}_s(t)} dr_s \right\rangle = \exp \left( \frac{q^4d^2 \left\langle s^2(t) \right\rangle}{72} \right) \operatorname{erfc} \left( \frac{q^2d \sqrt{\left\langle s^2(t) \right\rangle}}{6\sqrt{2}} \right) \]

average over all \( r_s \) for a given \( s \)

- mean square curvilinear segment displacements (limits (II)DE and (III)DE)

\[ \left\langle s^2(t) \right\rangle = \frac{2D_0 t}{N + \frac{12d^2D_0 t}{N^2b^4}} + \frac{2b\sqrt{D_0 t}}{\sqrt{3\pi} + 18\frac{\sqrt{D_0 t}}{Nb}} \]

\( d \) tube diameter
\( (b, N, D_0 \text{ known}) \)


typical echo attenuation curves measured in linear PEO confined in pores of a solid methacrylate matrix (fringe field technique; 60 T/m; 200 MHz)

echo attenuation formalism:

a) reptation fits the data
b) 1 fitting parameter:

pore diameter \( d_{pore} = (8+/1) \text{ nm} \)
Quasielastic neutron scattering

time scale $10^{-11}$ s ... $10^{-7}$ s

quasi-elastic neutron scattering

experimental set-up:

scattering vector:

~ momentum transfer
The primary measurand:

Double differential cross-section

\[
\frac{d^2\sigma}{d\Omega dE_{k'}}
\]

= rate of counts of scattered neutrons relative to

(i) the incoming flux
(ii) the solid angle element of the detector \(d\Omega\)
(iii) the energy interval resolved by the detector \(dE_{k'}\)

Two cases:

a) incoherent scattering (\(\rightarrow\) protons):
   scattered waves of different scattering centers are uncorrelated
   (no constructive interference)

b) coherent scattering (\(\rightarrow\) deuterons):
   scattered waves of pairs of scattering centers are correlated
   (constructive interference)

incoherent scattering:

\[
\left( \frac{d^2\sigma}{d\Omega dE_{k'}} \right)_{\text{inc}} \approx \int_{-\infty}^{\infty} e^{-i\omega t} \left\langle e^{-i\mathbf{q} \cdot \mathbf{R}(0)} e^{i\mathbf{q} \cdot \mathbf{R}(t)} \right\rangle dt
\]

\[
\mathcal{G}_{\text{inc}}(t) = \left\langle e^{-i\mathbf{q} \cdot \mathbf{R}(0)} e^{i\mathbf{q} \cdot \mathbf{R}(t)} \right\rangle
\]

"incoherent dynamic structure factor"

or "incoherent scattering function"
incoherent quasi-elastic neutron scattering

incoherent scattering:

\[ G_{\text{inc}}(t) = \left\langle e^{-iq \cdot R(0)} e^{iq \cdot R(t)} \right\rangle \]

\[
\text{Gauss} = \exp \left\{ -\frac{1}{6} q^2 \left\langle r_{\text{self}}^2 \right\rangle \right\}
\]

\[
\text{Einstein} = \exp \left\{ -q^2 D t \right\}
\]

double differential cross-section for incoherent scattering:

\[
\frac{\partial^2 \sigma}{\partial \Omega \partial E_{k'}}_{\text{inc}} \propto \frac{\partial^2 \sigma}{\partial \Omega \partial \omega}_{\text{inc}} \propto \frac{Dq^2}{\omega^2 + (Dq^2)^2}
\]

incoherent quasi-elastic neutron scattering

exponential decays

Lorentzian shapes

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**dynamic light scattering**

**Experimental set-up:**

- **Light source (laser)**
- **Sample**
- **Detector (photomultiplier)**

**Measurand:** Intensity of scattered light

\[
I'(q,t) \propto \left| E'(q,t) \right|^2
\]

= square of electric-field amplitude

\[
q = \frac{4\pi n(r,t)}{\lambda} \sin \theta / 2
\]

= scattering vector

**Dynamic light scattering**

**Autocorrelator forms second-order correlation function**

\[
G_2(\tau) = \frac{\langle I'(q,t+\tau) I'(q,t) \rangle}{\langle I'(q,t) \rangle^2}
\]

**Scattering theory provides first-order correlation function**

\[
G_1(\tau) = \frac{\langle E'(q,t+\tau) E''(q,t) \rangle}{\langle |E'(q,t)|^2 \rangle}
\]

Siegert relation connects both correlation functions

\[
G_2(\tau) = 1 + \left[ G_1(\tau) \right]^2
\]
dynamic light scattering

\[ G_{\tau}(\tau) \equiv \frac{\langle E'(q,t+\tau)E''(q,t) \rangle}{\langle |E'(q,t)|^2 \rangle} = \frac{\langle \delta \tilde{c}(q,t+\tau)\delta \tilde{c}(q,t) \rangle}{\langle \delta \tilde{c}(q,t)^2 \rangle} = e^{-q^2D\tau} \]

**Equation**

same as before:

**incoherent dynamic structure factor**

Up to now:

Incoherent neutron scattering, field-gradient NMR diffusometry, and light scattering, i.e., 3 totally different experiments, are commonly sensitive to incoherent dynamic structure factors

"wave number"

\[ q_{\text{NMR}} = \gamma g \tau \]

scattering vector

\[ q_{\text{neutron}} = 4\pi \lambda^{-1} \sin \theta/2 \]

"\[ q_{\text{light}} = 4\pi n(r,t) \lambda^{-1} \sin \theta/2 \]

**Intermolecular field-cycling NMR relaxometry**

**Time scale** \(10^{-8} \text{ s} \ldots 10^{-4} \text{ s}\)
The temporal autocorrelation function of dipolar spin interactions,
\[ G_m(t) \propto \left\langle \frac{Y_{2,m}(\vartheta_0,\varphi_0)Y_{2,-m}(\vartheta_1,\varphi_1)}{r_0^3 r_1^3} \right\rangle_{\text{ens}} \]
decays by any fluctuation:
\[ r = r(t), \quad \varphi = \varphi(t), \quad \vartheta = \vartheta(t) \]

Intermolecular dipolar interactions:

correlation function of the dipole pair \( k,l \)
\[ G_{k,l}^{(m)}(t) = \left\langle \frac{y_{2,m}^*(r) y_{2,m}^*(0)}{r^3(t) r^3(0)} \right\rangle \]

probability that dipole \( l \) is displaced from \( r'(0) \) to \( r'(t) \)

mean squared displacement relative to dipole \( k \)
\[ \left\langle \Delta r'^2(t) \right\rangle = \frac{1}{2} \left\langle r^2(t) \right\rangle \]

Evaluation of the relative intermolecular mean square displacement from field-cycling NMR relaxometry data

- spin-lattice relaxation by dipolar coupling of protons
- distinction of intra- and inter-molecular contributions
- separable by mixtures of deuterated and undeuterated molecules

\[
\frac{1}{T_1^{\text{inter}}} = \frac{1}{T_1^{\text{total}}} - \frac{1}{T_1^{\text{intra}}} = \left( \frac{\mu_0}{4\pi} \right)^2 \frac{2\pi \sqrt{3} \left( 1 + 2\sqrt{2} \right) \gamma^4 h^2 \rho_{\text{spin}}}{5} \frac{\langle \Delta r^{12} \rangle}{\omega} \left( \frac{3}{3} \right)
\]

\[
\langle \Delta r^{12} \rangle = \left\{ \left( \frac{4\pi}{\mu_0} \right)^2 \frac{2\pi \sqrt{3} \left( 1 + 2\sqrt{2} \right) \gamma^4 h^2 \rho_{\text{spin}}}{5\omega} \frac{T_{1,\text{inter}}}{T_1} \right\}^{2/3}
\]

\[ t = \frac{1}{\omega} \rightarrow \text{variation of the angular frequency } \omega = \gamma B_0 \]


Field-cycling NMR relaxometry

- RF
- frequency: \( \omega = \gamma B_0 \)
- relax. rate: \( \frac{1}{T_1} = C \left[ I(\omega) + 4I(2\omega) \right] \)
- spectr. dens.: \( I(\omega) = F_r \{ G(t) \} \)

Dipolar correlation function:
\[
G(t) = \left\langle \frac{Y_2^m(0)Y_2^{-m}(t)}{r^3(0)r^3(t)} \right\rangle
\]

Quadrupolar corr. function:
\[
G(t) = \left\langle Y_2^m(0)Y_2^{-m}(t) \right\rangle
\]
Application of the combined techniques to polymer melts

time scale $10^{-11} \, \text{s} \ldots 10^{-1} \, \text{s}$

Neutron scattering (data from M. Krutyeva, D. Richter, FZ Jülich)
NMR microimaging of isotopic inter-diffusion

time scale 10 s ...

\[ C(x,t) = \frac{1}{2} C_0 \text{erfc} \left( \frac{x-x_0}{2\sqrt{Dt}} \right) \]

Interdiffusion

Probing **translational fluctuations** by diverse techniques

- quasi-elastic neutron scattering
- inter-molecular field-cycling NMR relaxometry
- variants of field-gradient NMR diffusometry
- NMR microimaging of isotopic (inter)diffusion

$10^{-12}$ $10^{-9}$ $10^{-6}$ $10^{-3}$ $10^0$ $10^3$ $10^6$

$t/s$

limit: molecular vibrations, collision times

limit: time frame of the study

*a take-home message:* combine and enjoy!