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energie atomique • energies alternatives

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UNIVERSITÉ PARIS SUD
Comprendre le monde, construire l'avenir

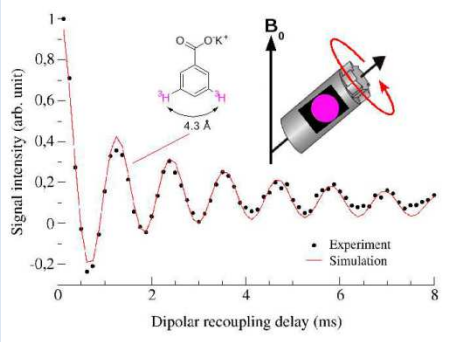
Experiment and Modelling in Structural NMR

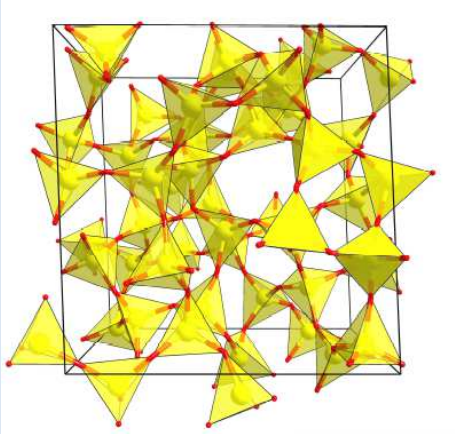
November 28th – December 2nd 2011
INSTN – CEA Saclay, France

Rainer Kimmich
University of Ulm, Germany

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

[05003]





SiO_2 structure from NMR studies

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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

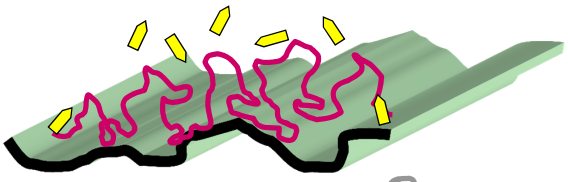
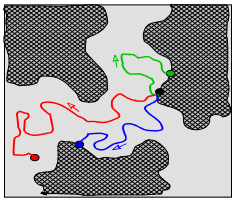
- field-gradient NMR diffusometry
- application to polymer melts

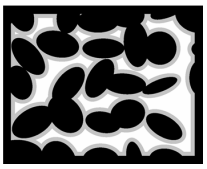
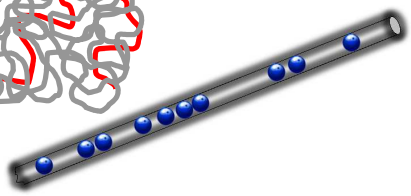
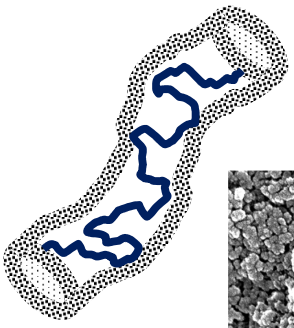
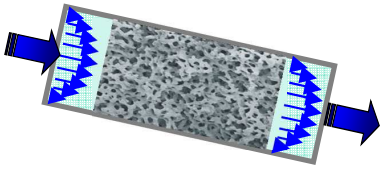
- incoherent neutron scattering
- dynamic light scattering

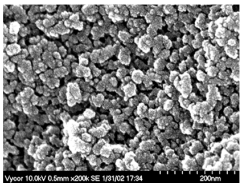
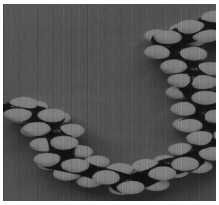
- intermolecular NMR relaxometry
- isotopic interdiffusion
- time scales of diffusion measurements

Complex systems:

- obstacles
- confinements
- pores
- surface adsorption and ordering
- domains
- anisotropy
- excluded volume
- chain connectivity
- topological constraints
- tortuosity

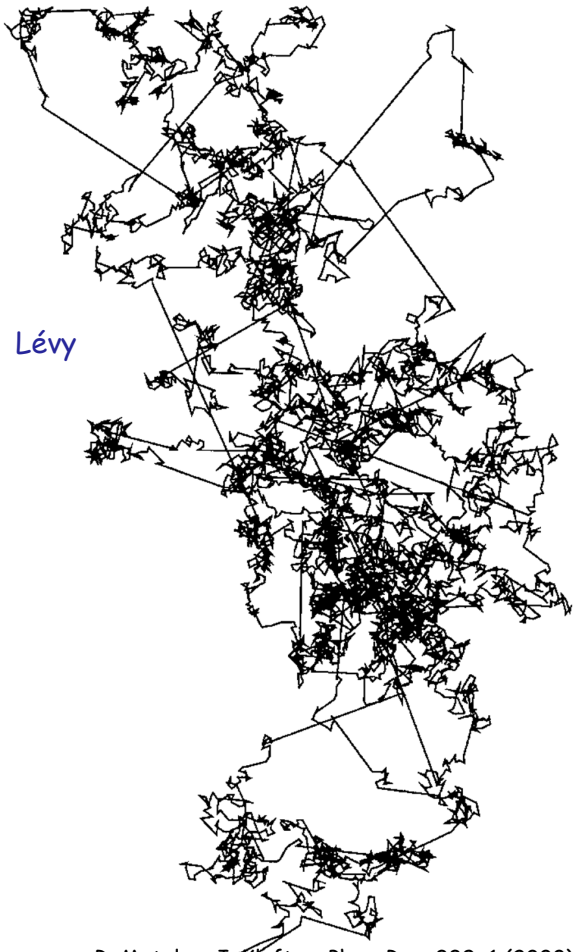




Random-walk trajectories

can be extremely different:



Lévy

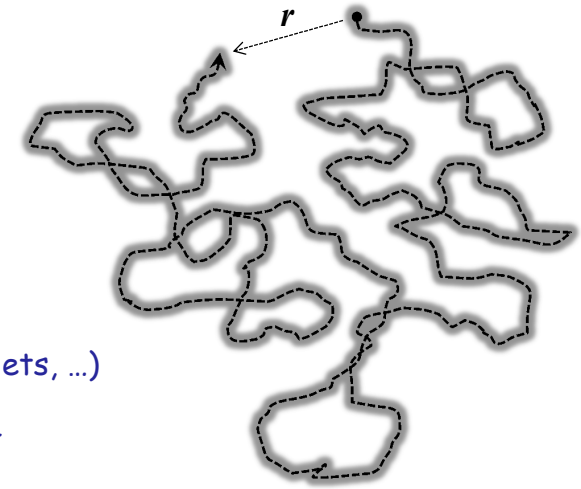
Brown

7000 steps

R. Metzler, J. Klafter, Phys. Rep. 339, 1 (2000)

Characterization

of trajectories by diffusion:



- Particles (atoms, molecules, colloids, droplets, …) treated as random walkers
  → displacement $\boldsymbol{r}$ in time t
- propagator (probability distribution, probability density function, …)
  → probability density $P(\boldsymbol{r}, t)$ for a displacement $\boldsymbol{r}$ in time t
- $P(\boldsymbol{r}, t)\, d^3r$ → probability that the particle is displaced from the origin to the volume element d^3r in a distance $\boldsymbol{r}$
- mean square displacement (or variance or second moment of $P(\boldsymbol{r}, t)$)

→ $$\langle r^2 \rangle \equiv \int r^2 P(\vec{r}, t)\, d^3 r$$

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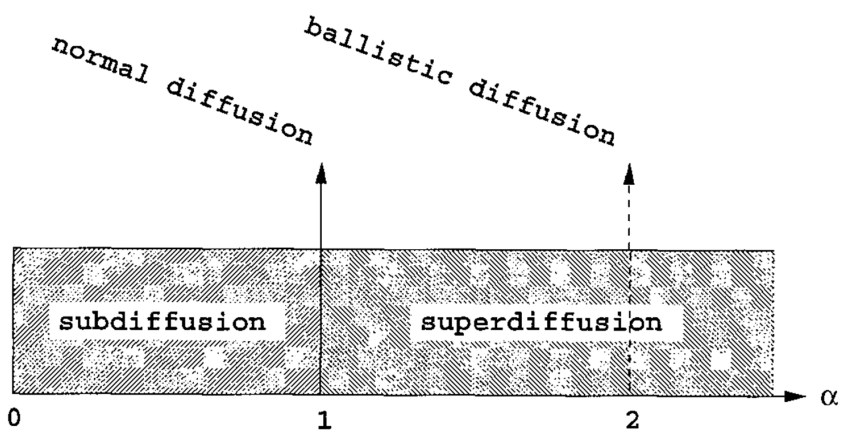
Formal classification

in the case of power-law limits

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

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



R. Metzler, J. Klafter, Phys. Rep. 339, 1 (2000)

Fickian diffusion equation (in 1 dimension)

$$\frac{\partial P}{\partial t} = D \frac{\partial}{\partial x^2} P$$

Fractional diffusion equation

$$\frac{\partial P}{\partial t} = {}_0R_t^{1-a} D_a \frac{\partial^2}{\partial x^2} P(x,t)$$

${}_0R_t^{1-\alpha}$: Riemann - Liouville operator

α : diffusion exponent (R. Metzler, J. Klafter, 2000)

initial condition:
$P(x,0) \sim \delta(0)$

Gaussian :

$$P(x,t) = \frac{1}{2(\pi D t)^{1/2}} \exp\left(\frac{-x^2}{4Dt}\right)$$

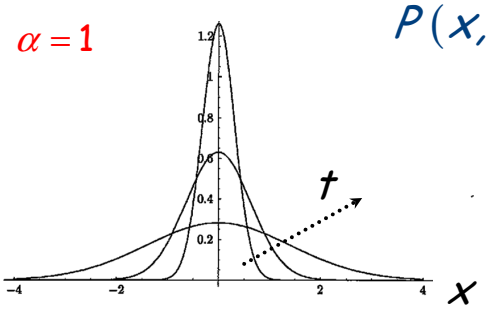
stretched exponential :

$$P(x,t) \propto \frac{1}{\sqrt{4\pi D_\kappa t^\kappa}} \sqrt{\frac{1}{2-\kappa}} \left(\frac{2}{\kappa}\right)^{\left(\frac{1-\kappa}{2-\kappa}\right)} \left(\frac{|x|}{\sqrt{D_\kappa t^\kappa}}\right)^{-\left(\frac{1-\kappa}{2-\kappa}\right)}$$

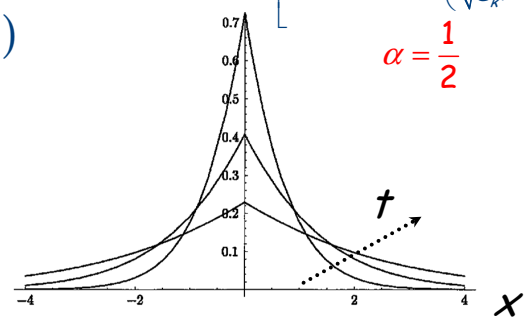
$$\exp\left[-\frac{2-\kappa}{2}\left(\frac{\kappa}{2}\right)^{\frac{\kappa}{2-\kappa}} \left(\frac{|x|}{\sqrt{D_\kappa t^\kappa}}\right)^{\frac{1}{1-\kappa/2}}\right]$$

$\alpha = 1$

$P(x,t)$



$\alpha = \frac{1}{2}$



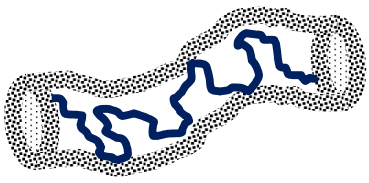
$$\langle x^2(t) \rangle \propto Dt$$

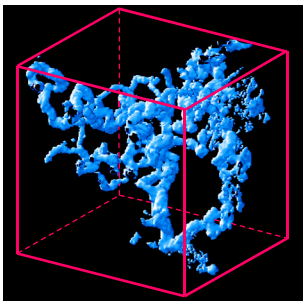
$$\langle x^2(t) \rangle \propto D_{1/2} t^{1/2}$$

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

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

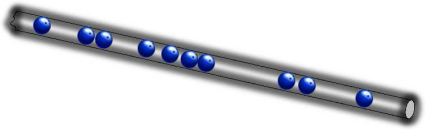
→ non-Gaussian propagator
examples: reptation, random walk on fractals

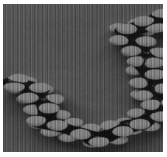




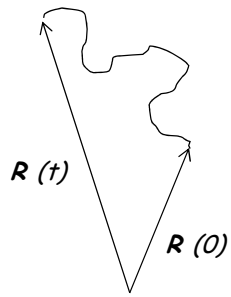
b) Time dependent diffusion coefficient
$D=D(t)$ in a homogeneous medium
(due to mutual obstruction)

→ 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

$$G_{inc} = \left\langle e^{-i\boldsymbol{q}\cdot\boldsymbol{R}(0)} e^{i\boldsymbol{q}\cdot\boldsymbol{R}(t)} \right\rangle \underset{propagator}{\overset{Gaussian}{\approx}} \exp\left\{ -\frac{1}{6} q^2 \left\langle r_{self}^2 \right\rangle \right\}$$

$\boldsymbol{q}$ "wave vector" → specific for experimental technique

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

D self-diffusion coefficient

Field Gradient NMR Diffusometry

time scale 1 ms … 1 s

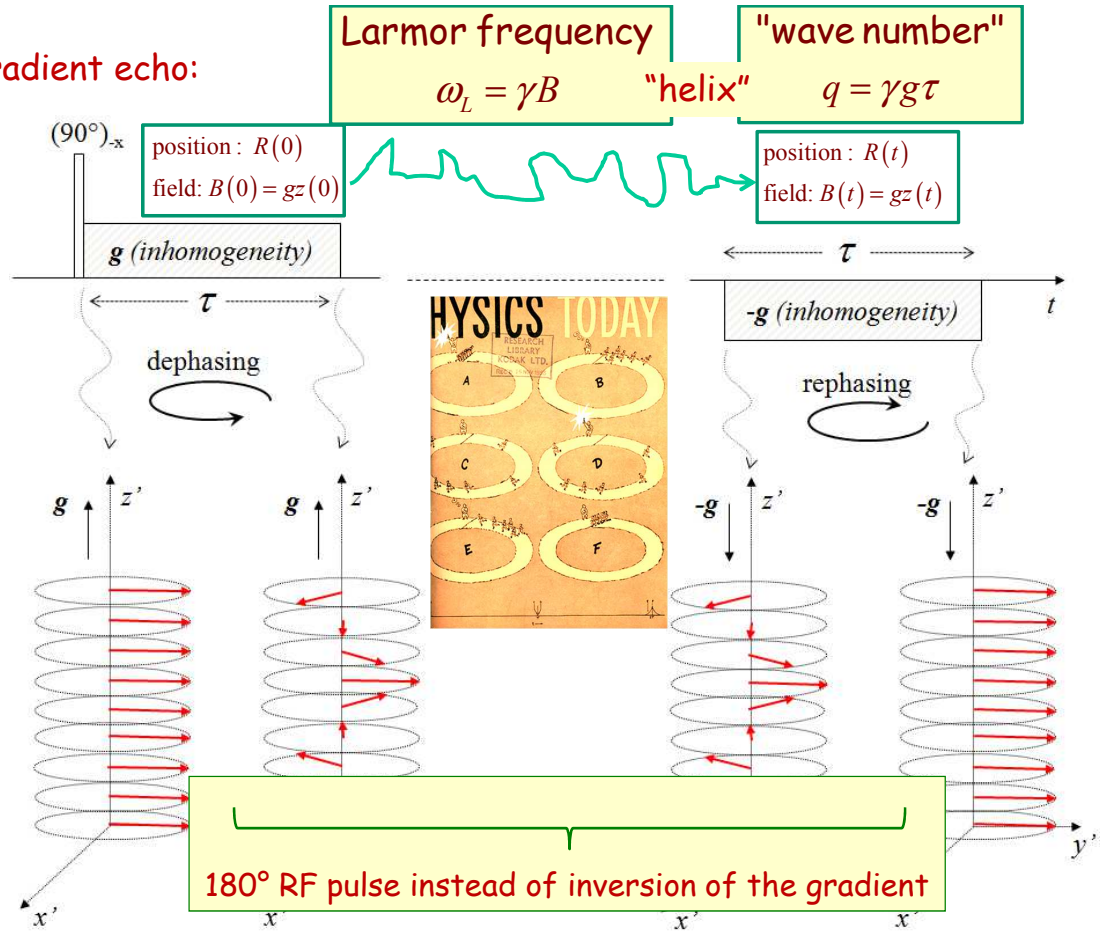
field-gradient NMR diffusometry:

experimental protocol: spin echo of any sort + field gradient

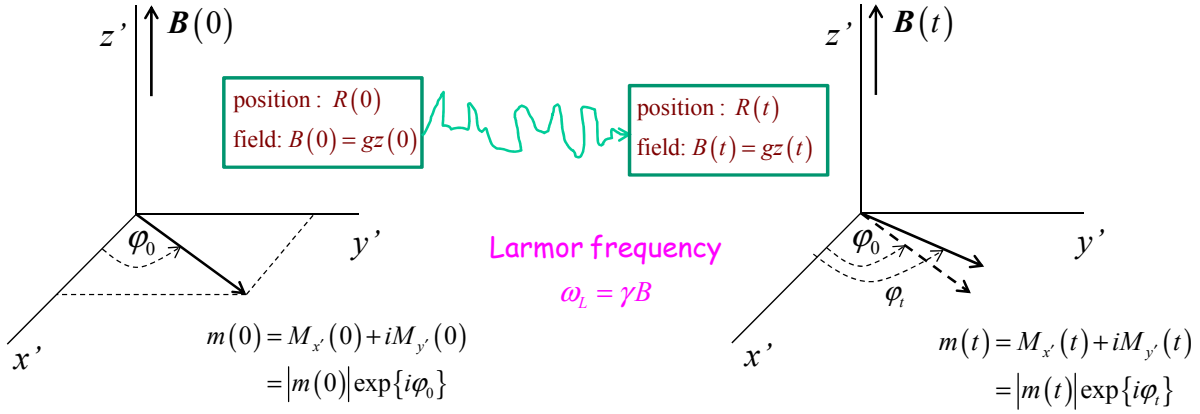
- gradient echo
- Hahn
- stimulated
- coherence transfer
- rotary
- ...

principle: dephasing + rephasing of spin coherences

gradient echo:



complex representation of transverse magnetization in the rotating frame:



echo attenuation function due to diffusion:
(apart from transverse relaxation)

$$a(t) = \left\langle \frac{m(t)}{m(0)} \right\rangle = \left\langle \frac{\exp\{i\varphi_t\}}{\exp\{i\varphi_0\}} \right\rangle = \left\langle \exp\{i(\varphi_t - \varphi_0)\} \right\rangle$$

$$= \left\langle \exp\{i(\omega_t \tau - \omega_0 \tau)\} \right\rangle = \left\langle \exp\{i(\gamma B(t)\tau - \gamma B(0)\tau)\} \right\rangle$$

$$= \left\langle \exp\{i(\gamma g z_t \tau - \gamma g z_0 \tau)\} \right\rangle = \left\langle e^{-i\boldsymbol{q}\cdot\boldsymbol{R}(0)} e^{i\boldsymbol{q}\cdot\boldsymbol{R}(t)} \right\rangle$$

→ incoherent dynamic structure factor

"wave number"
$q = \gamma g \tau$

field-gradient NMR diffusometry

measurand: The echo attenuation function

$$a(t) \propto \mathcal{G}_{inc}(t) \underset{\text{phase factors}}{\overset{\text{precession}}{=}} \left\langle e^{-i\boldsymbol{q}\cdot\boldsymbol{R}(0)} e^{i\boldsymbol{q}\cdot\boldsymbol{R}(t)} \right\rangle$$

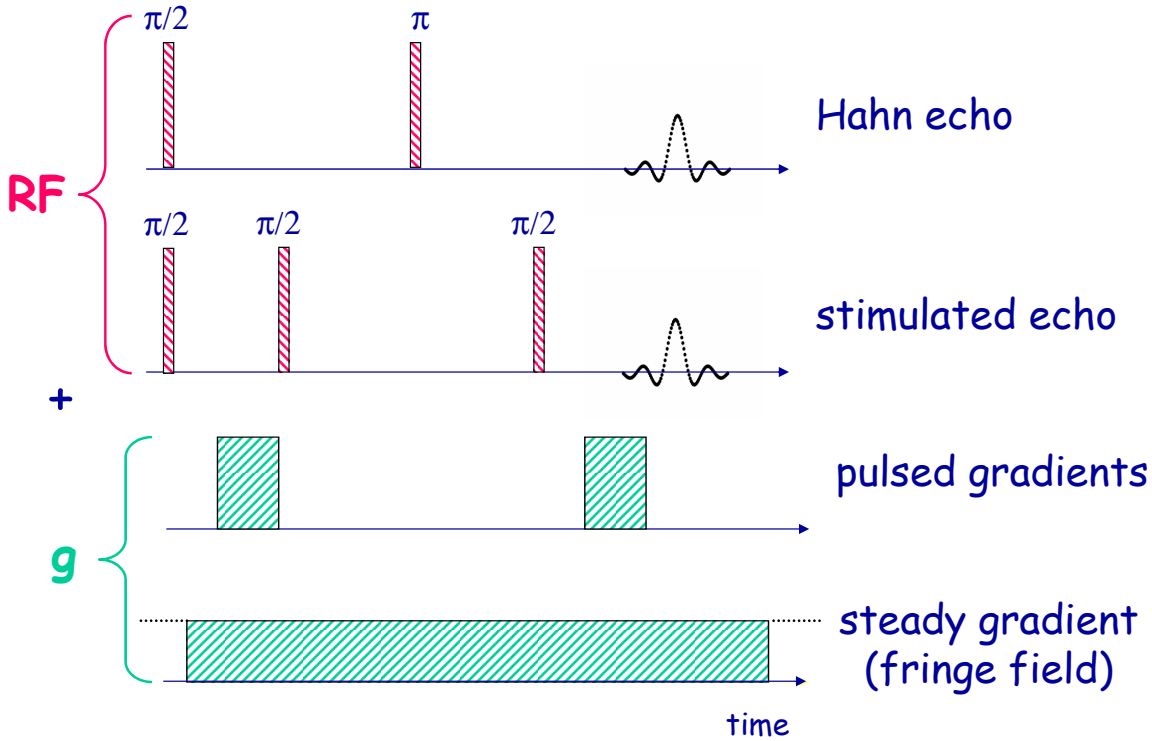
(incoherent) dynamic structure factor

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

$$\overset{\text{Einstein}}{=} \exp\left\{ -q^2 D t \right\}$$

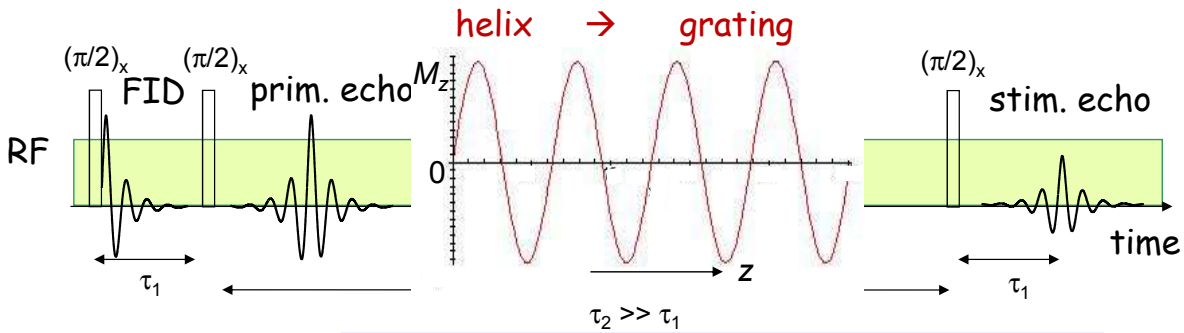
"wave number"
$q = \gamma g \tau$

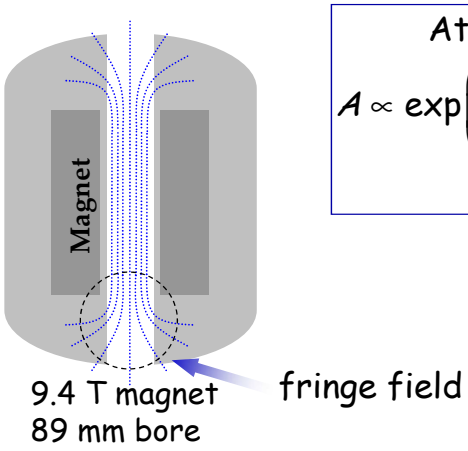
Field-gradient NMR diffusometry



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

NMR diffusometry in the fringe field of a superconducting magnet

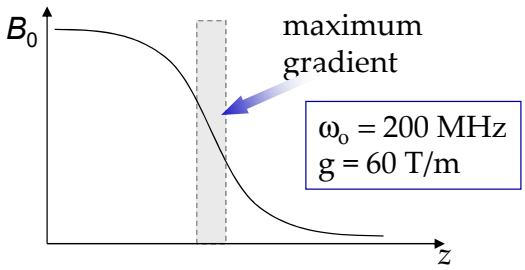




Attenuation of the stimulated echo

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

wave number $q = \gamma g \tau_1$



R. Ki., W. Unrath, G. Schnur, E. Rommel,
J. Magn. Reson. 91 (1991) 136

Application to polymer melts

under confinement in pores

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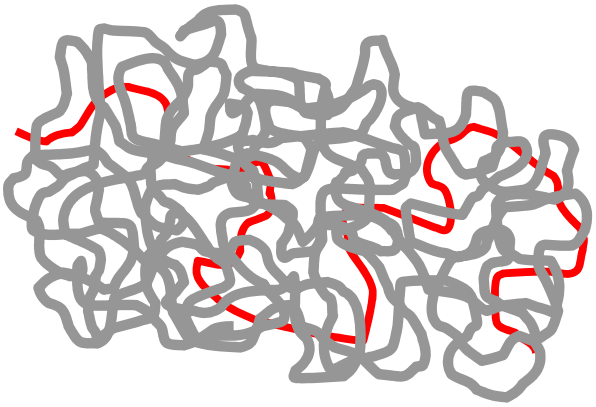

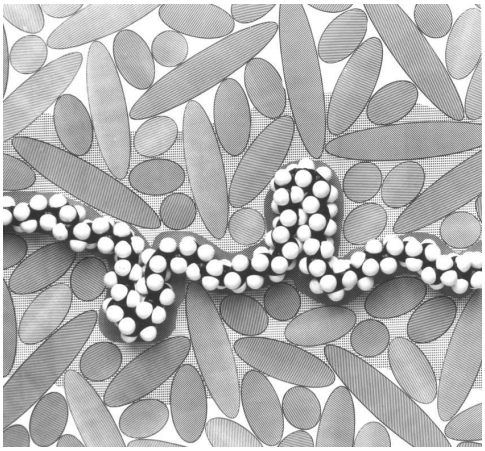

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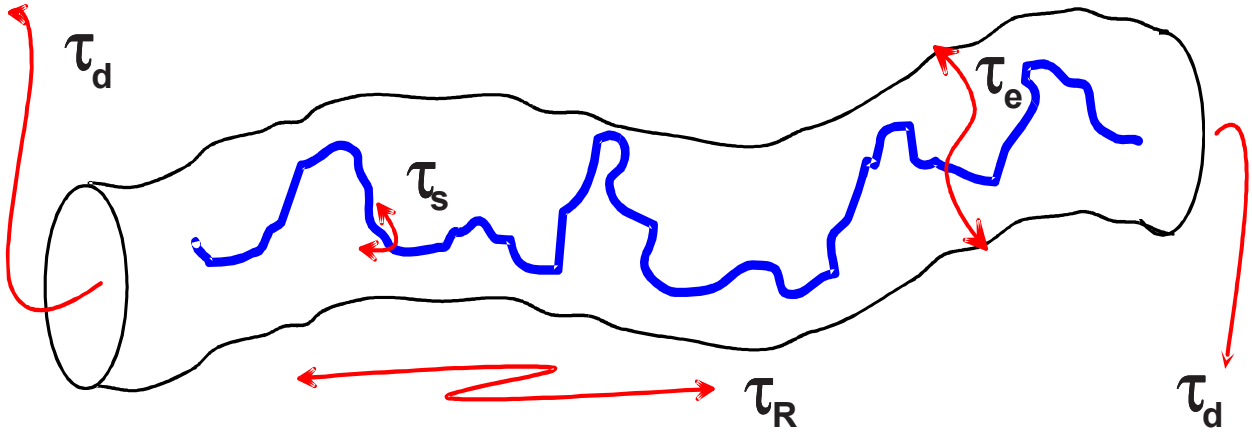
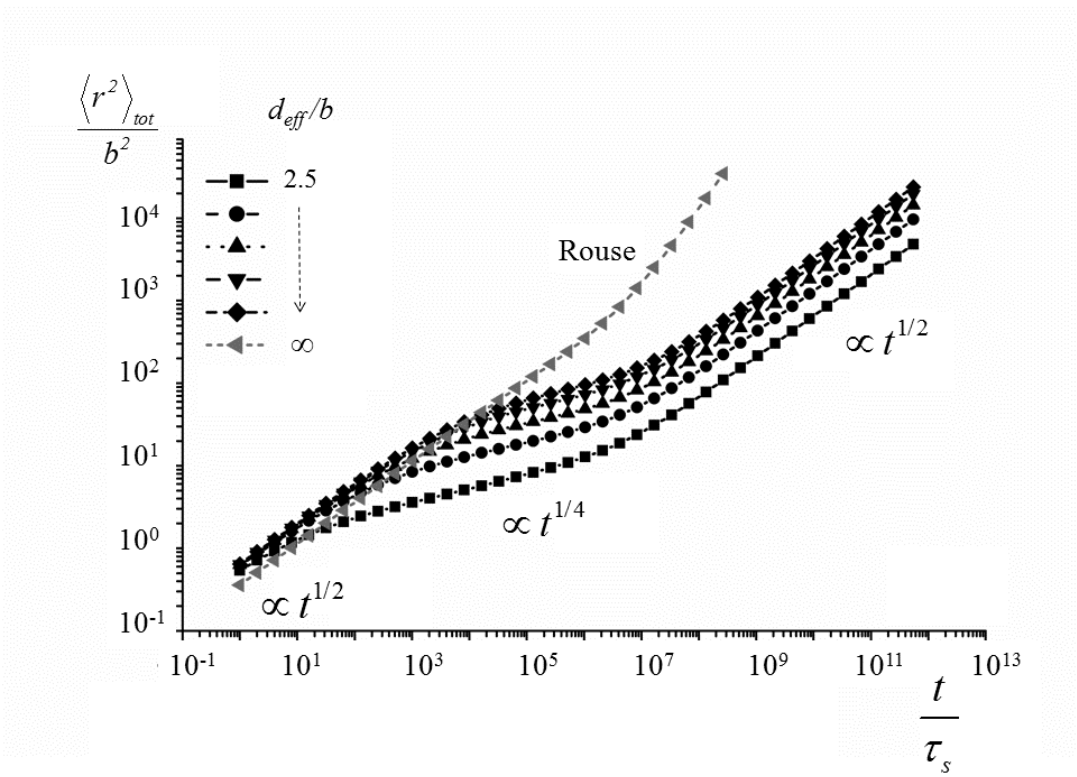
Tube/reptation concept by Doi and Edwards

(definition of 4 characteristic time constants)



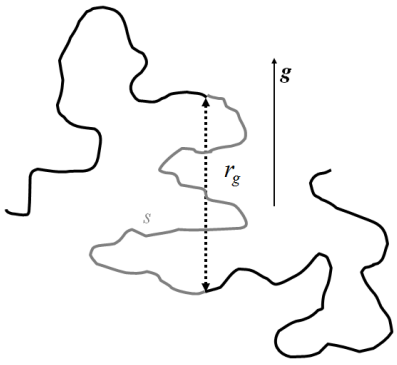
τ_s segment fluctuation time
τ_e entanglement time
τ_R (longest) Rouse chain relaxation time
τ_d disengagement time



A. Denissov, M. Kroutieva,
N. Fatkullin, R. Kimmich,
J. Chem. Phys. 116 (2002) 5217

NMR diffusometry and the tube/reptation concept

$$a(\vec{q},t) = \left\langle e^{i\vec{q}\cdot\vec{r}(t)} \right\rangle = \underbrace{\left\langle e^{i\vec{q}\cdot\vec{r}_s(t)} \right\rangle}_{\substack{a_s(\vec{q},t) \\ \text{segments}}} \underbrace{\left\langle e^{i\vec{q}\cdot\vec{r}_c(t)} \right\rangle}_{\substack{\exp(-q^2 D_c t) \\ \text{center-of-mass}}}$$



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

- anomalous segment diffusion

$$a_s(\vec{q},t) = \underbrace{\left\langle \underbrace{\int_{-\infty}^{\infty} \left(\frac{2\pi}{3} d|s| \right)^{-1/2} e^{-3r_s^2/2d|s|} e^{i\vec{q}\cdot\vec{r}_s(t)} dr_q}_{\text{average over all } r_s \text{ for a given } s} \right\rangle}_{\text{average over all } s} = \exp\left\{ \frac{q^4 d^2 \langle s^2(t) \rangle}{72} \right\} \operatorname{erfc}\left\{ \frac{q^2 d \sqrt{\langle s^2(t) \rangle}}{6\sqrt{2}} \right\}$$

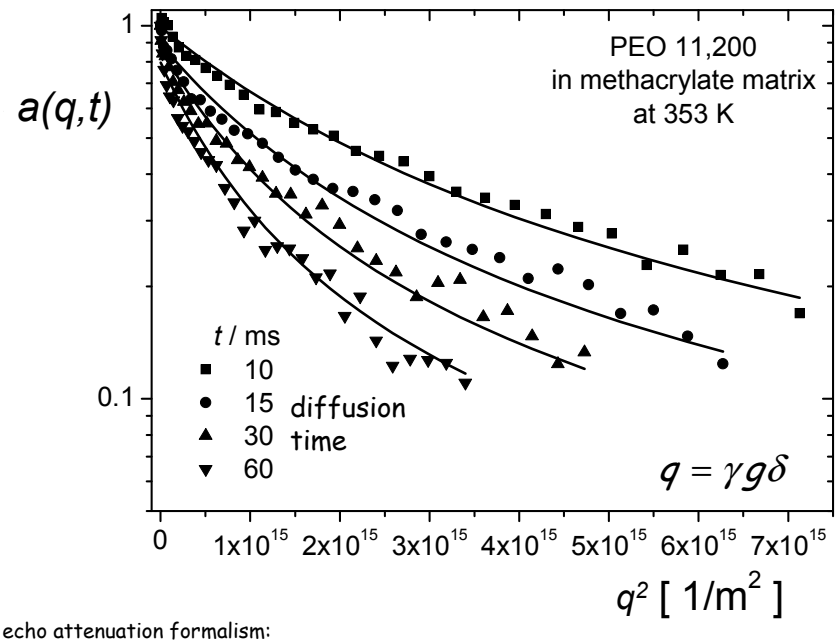
- mean square curvilinear segment displacements (limits $(II)_{DE}$ and $(III)_{DE}$)

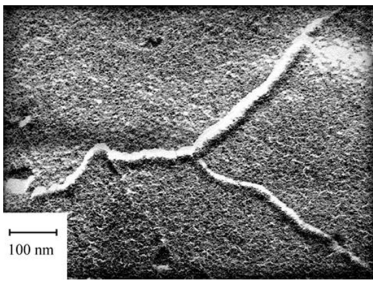
$$\langle s^2(t) \rangle = \frac{2D_0 t}{N + \frac{12 d^2 D_0 t}{N^2 b^4}} + \frac{2b\sqrt{D_0 t}}{\sqrt{3\pi} + 18 \frac{\sqrt{D_0 t}}{Nb}}$$

d tube diameter
(b, N, D_0 known)

N. Fatkullin, R. Kimmich, Phys. Rev. E 52 (1995) 3273
E. Fischer, U. Beginn, N. Fatkullin,
R. Kimmich, Macromolecules 37 (2004) 3277)

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:
(N. Fatkullin, R. Kimmich,
Phys. Rev. E 52 (1995) 3273
and
E. Fischer, U. Beginn, N. Fatkullin,
R. Kimmich, Macromolecules 37 (2004) 3277)

a) reptation fits the data
b) 1 fitting parameter:
pore diameter d_{pore} = (8+/-1) nm

Quasielastic neutron scattering

time scale 10^{-11} s … 10^{-7} s

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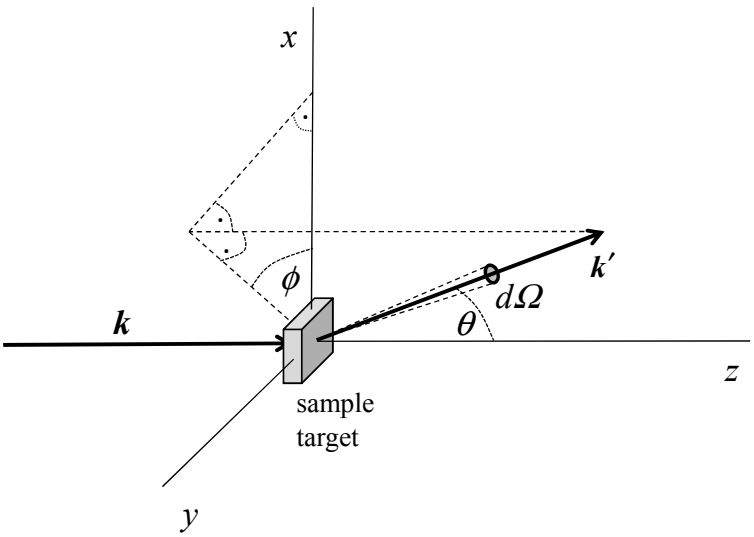
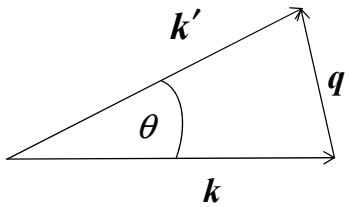
quasi-elastic neutron scattering

experimental set-up:



scattering vector:



~ momentum transfer

The primary measurand:

Double differential cross-section $\dfrac{d^2\sigma}{d\Omega dE_{k'}}$

= 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 (→ protons):
scattered waves of different scattering centers are uncorrelated
(no constructive interference)

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

incoherent scattering:

$$\left(\frac{\partial^2\sigma}{\partial\Omega\partial E_{k'}}\right)_{inc} \underset{approximation}{\overset{Born}{\propto}} \int_{-\infty}^{\infty} e^{-i\omega t}\left\langle e^{-i\boldsymbol{q}\cdot\boldsymbol{R}(0)} e^{i\boldsymbol{q}\cdot\boldsymbol{R}(t)}\right\rangle dt$$

$$\mathcal{G}_{inc}(t) = \left\langle e^{-i\boldsymbol{q}\cdot\boldsymbol{R}(0)} e^{i\boldsymbol{q}\cdot\boldsymbol{R}(t)}\right\rangle$$

"incoherent dynamic structure factor "
or "*incoherent scattering function*"

incoherent scattering:

$$\mathcal{G}_{inc}(t) = \left\langle e^{-i\boldsymbol{q}\cdot\boldsymbol{R}(0)} e^{i\boldsymbol{q}\cdot\boldsymbol{R}(t)} \right\rangle$$

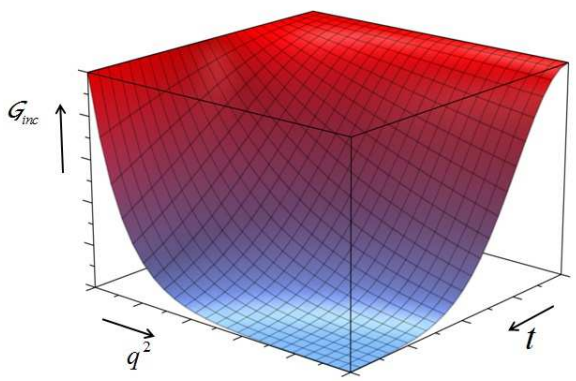
$$\overset{Gauss}{=} \exp\left\{-\frac{1}{6}q^2\left\langle r_{self}^2\right\rangle\right\}$$

$$\overset{Einstein}{=} \exp\left\{-q^2 Dt\right\}$$

double differential cross-section for incoherent scattering:

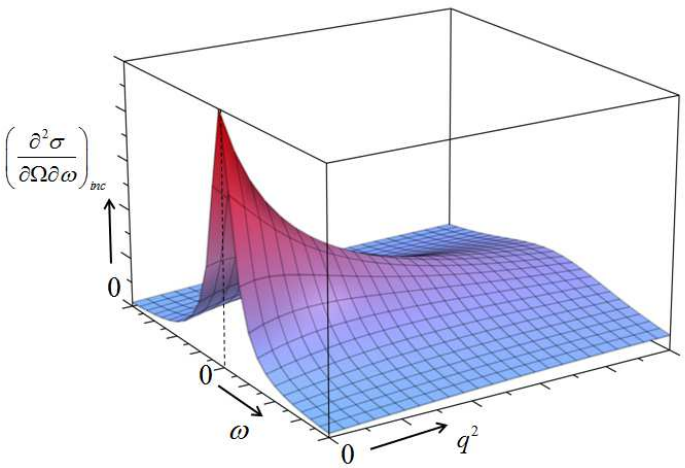
$$\left(\frac{\partial^2\sigma}{\partial\Omega\partial E_{k'}}\right)_{inc} \propto \left(\frac{\partial^2\sigma}{\partial\Omega\partial\omega}\right)_{inc} \propto \frac{Dq^2}{\omega^2 + \left(Dq^2\right)^2}$$

incoherent quasi-elastic neutron scattering



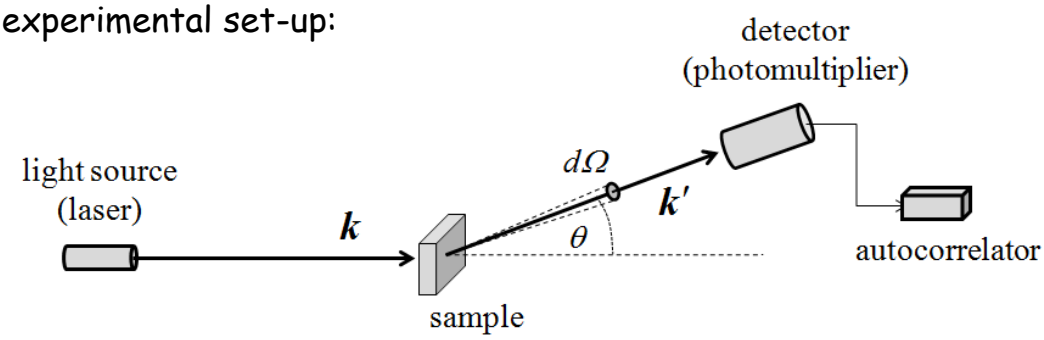
exponential decays

Lorentzian shapes



dynamic light scattering

experimental set-up:



measurand: intensity of scattered light

$$I'(\boldsymbol{q},t) \propto \left|E'(\boldsymbol{q},t)\right|^2$$

= square of electric-field amplitude

$$q = \frac{4\pi n(\boldsymbol{r},t)}{\lambda}\sin\theta/2$$ scattering vector

dynamic light scattering

autocorrelator forms second-order correlation function

$$G_2(\tau) \equiv \frac{\langle I'(\boldsymbol{q},t+\tau)I'(\boldsymbol{q},t)\rangle}{\langle I'(\boldsymbol{q},t)\rangle^2}$$

scattering theory provides first-order correlation function

$$\mathcal{G}_1(\tau) \underset{\text{refractive index}}{\overset{\text{fluctuations of}}{=}} \frac{\langle E'(\boldsymbol{q},t+\tau)E'^*(\boldsymbol{q},t)\rangle}{\langle |E'(\boldsymbol{q},t)|^2\rangle}$$

Siegert relation connects both correlation functions

$$G_2(\tau) = 1 + \left[\mathcal{G}_1(\tau)\right]^2$$

dynamic light scattering

$$\mathcal{G}_1(\tau) \equiv \frac{\left\langle E'(\boldsymbol{q},t+\tau)\,E'^{*}(\boldsymbol{q},t)\right\rangle}{\left\langle \left|E'(\boldsymbol{q},t)\right|^2\right\rangle} = \frac{\left\langle \delta\tilde{c}(\boldsymbol{q},t+\tau)\,\delta\tilde{c}(\boldsymbol{q},t)\right\rangle}{\left\langle \delta\tilde{c}(\boldsymbol{q},t)^2\right\rangle} \underset{equation}{\overset{diffusion}{=}} e^{-q^2 D\tau}$$

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" $q_{NMR} = \gamma g \tau$

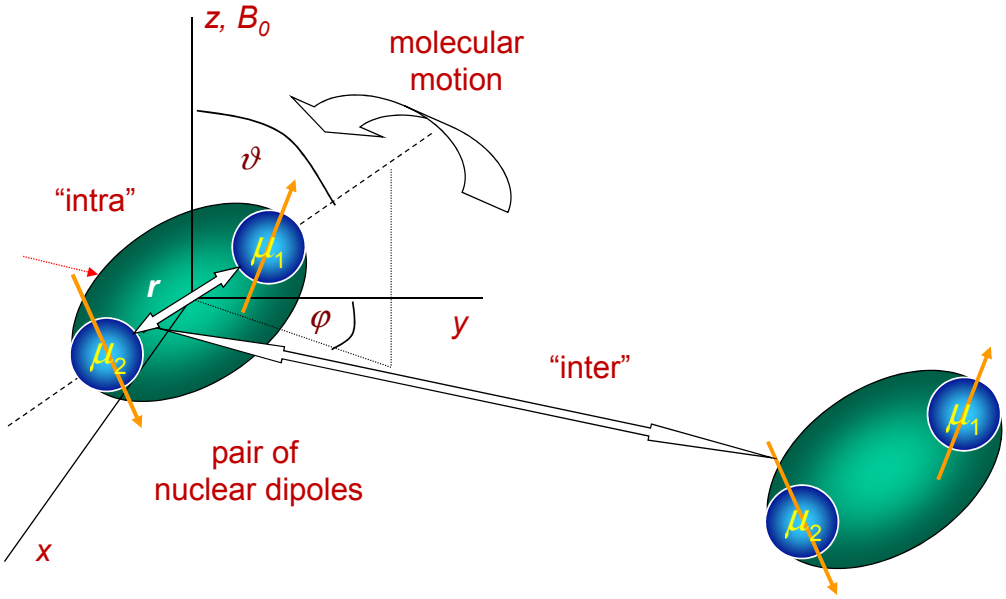
scattering vector $q_{neutron} = 4\pi\lambda^{-1}\sin\theta/2$

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

Intermolecular field-cycling NMR relaxometry

time scale 10^{-8} s … 10^{-4} s

NMR relaxometry



The <u>temporal</u> autocorrelation function of dipolar spin interactions,

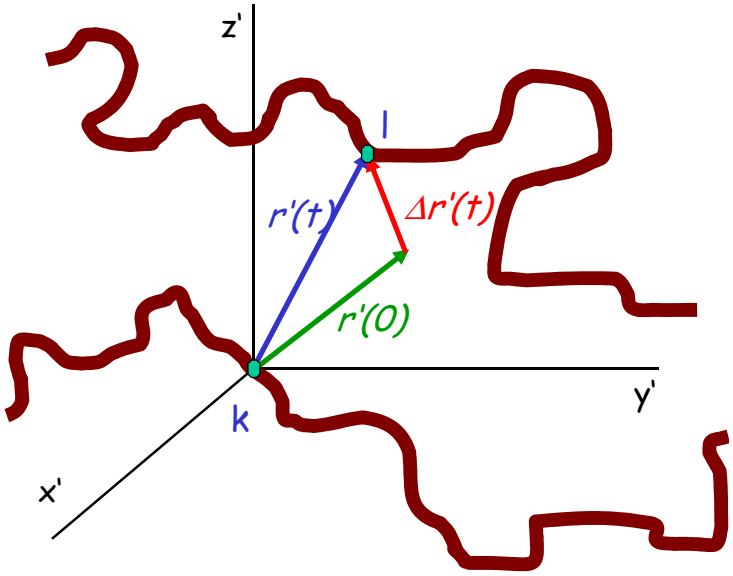
$$G_m(t) \propto \left\langle \frac{Y_{2,m}(\vartheta_0,\varphi_0)Y_{2,-m}(\vartheta_t,\varphi_t)}{r_0^3 r_t^3} \right\rangle_{ens}$$

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

$$G_{kl}^{(m)}(t) = \left\langle \frac{Y_{2,m}^*(t)}{r'^3(t)} \frac{Y_{2,m}(0)}{r'^3(0)} \right\rangle$$



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

mean squared displacement relative to dipole k

$$\langle \Delta r'^2(t) \rangle = \frac{1}{2} \langle r^2(t) \rangle$$

M. Kehr, N. Fatkullin, R. Ki., J. Chem. Phys. 126 (2007) 094903

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

undeuterated species

dilute solution of undeuterated molecules in deuterated matrix

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

$$\left\langle \Delta r'^2 \right\rangle = \left\{ \left(\frac{4\pi}{\mu_0}\right)^2 \frac{2\pi\sqrt{3}\left(1+2\sqrt{2}\right)\gamma^4\hbar^2\rho_{\text{spin}} T_1^{\text{inter}}}{5\omega} \right\}^{2/3}$$

$t = 1/\omega$ → variation of the angular frequency $\omega = \gamma B_0$

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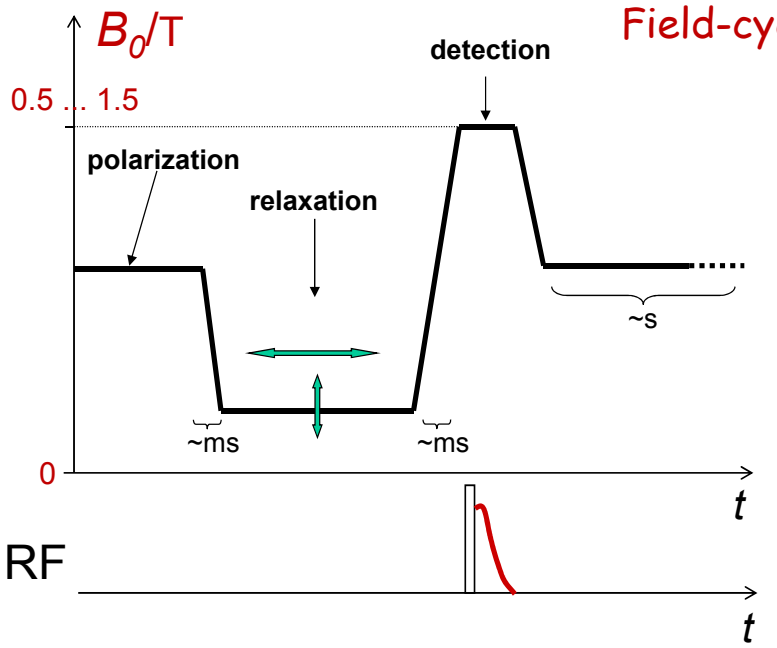
Field-cycling NMR relaxometry



^{1}H

10^3 Hz < $\frac{\omega}{2\pi}$ < 4×10^8 Hz

^{2}H

10^2 Hz < $\frac{\omega}{2\pi}$ < 6×10^7 Hz

frequency: $\omega = \gamma B_0$

relax. rate: $\frac{1}{T_1} = C\left[I(\omega) + 4I(2\omega)\right]$

spectr. dens.: $I(\omega) = \mathrm{F}_t\{G(t)\}$

dipolar correlation function:

$$G(t) = \left\langle \frac{Y_2^m(0)Y_2^{-m}(t)}{r^3(0)r^3(t)} \right\rangle$$

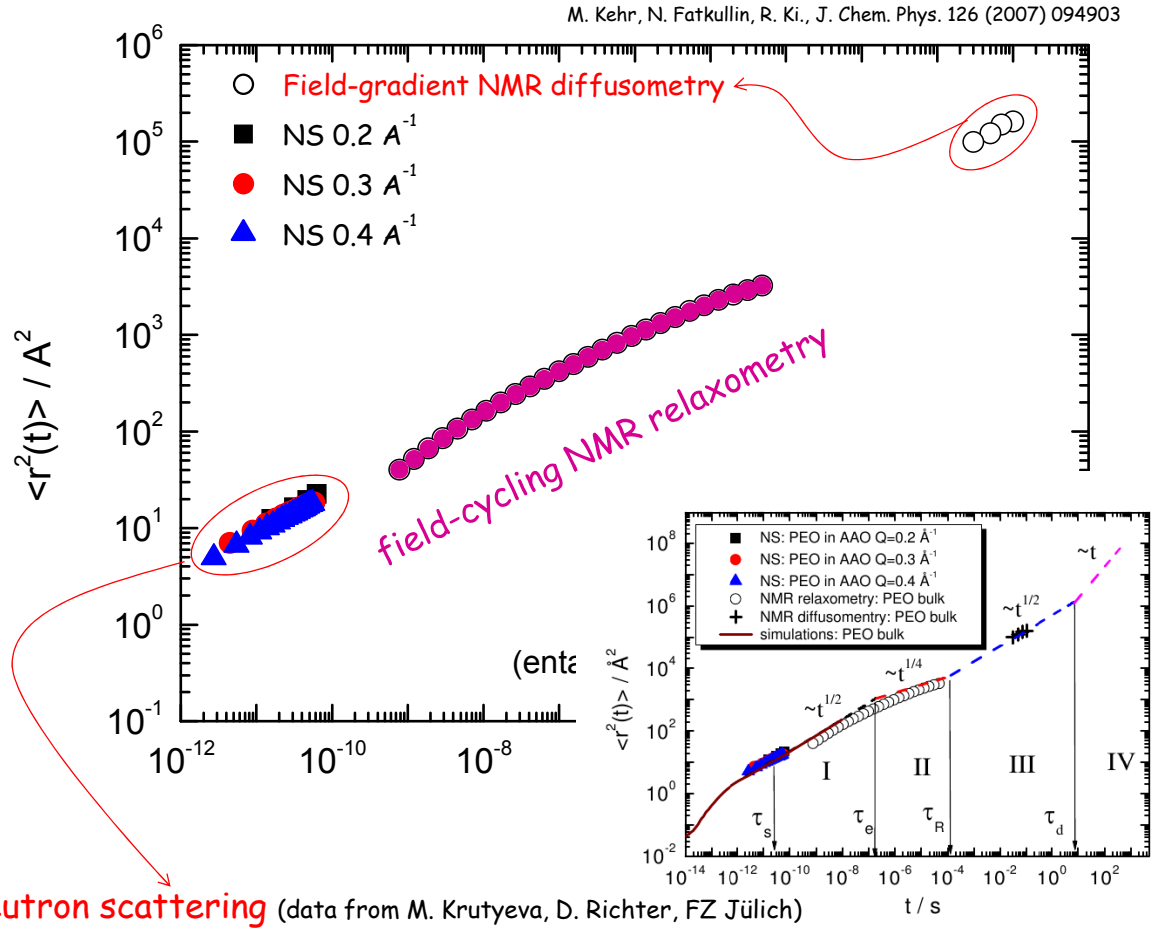
quadrupolar corr. function:

$$G(t) = \left\langle Y_2^m(0)Y_2^{-m}(t) \right\rangle$$

Application of the combined techniques to polymer melts

time scale 10^{-11} s … 10^{-1} s

M. Kehr, N. Fatkullin, R. Ki., J. Chem. Phys. 126 (2007) 094903

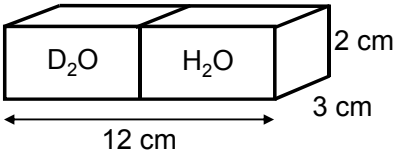


Neutron scattering (data from M. Krutyeva, D. Richter, FZ Jülich)

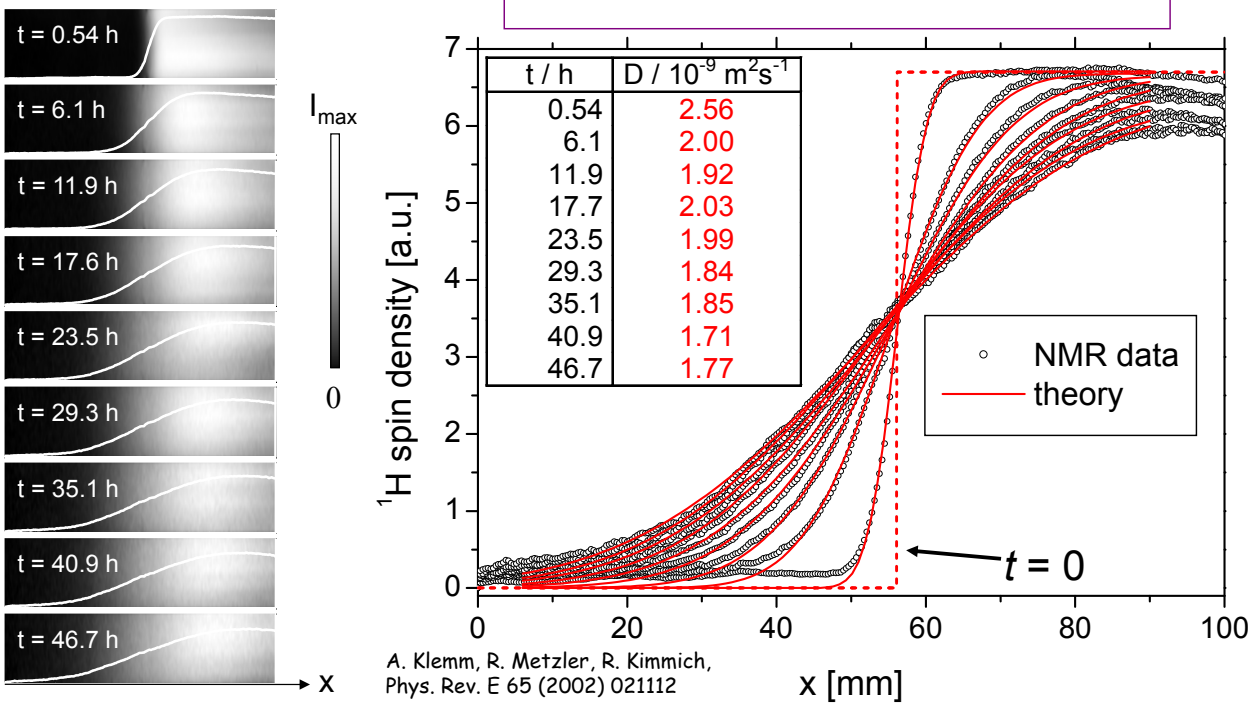
NMR microimaging of isotopic inter-diffusion

time scale 10 s …

Interdiffusion



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



A. Klemm, R. Metzler, R. Kimmich, Phys. Rev. E 65 (2002) 021112

Probing translational fluctuations by diverse techniques