Self-diffusion in nanopores studied by the NMR pulsed gradient spin echo

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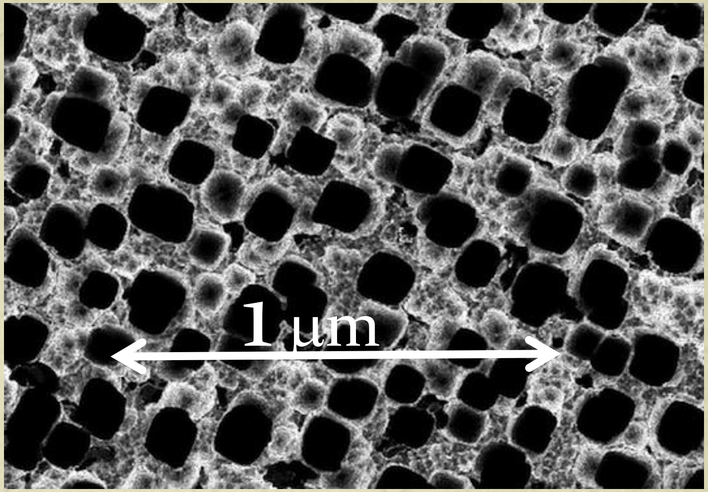
Application of PGSE method to study

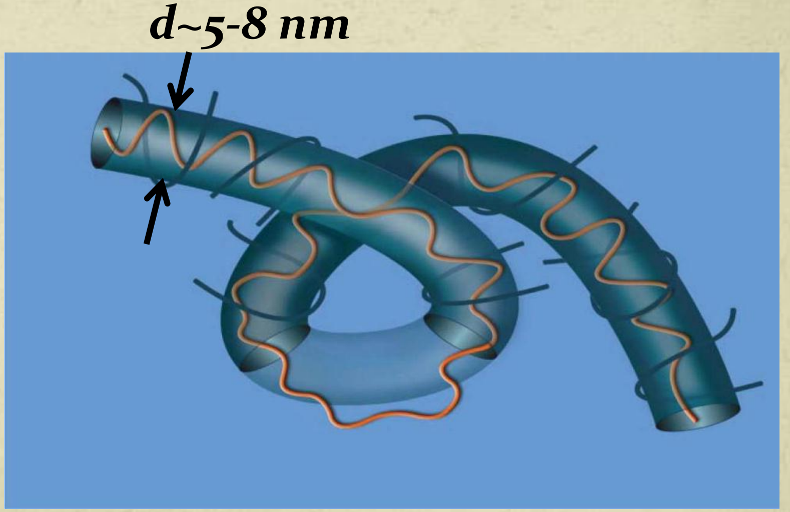
Structure of nanosieves:

Aleš Mohorič
Ulrich Scheler, Leibniz Institute of Polymer Research, Dresden
Igor Serša



Dynamics of polymer chain in molten polymer:

Aleš Mohorič
Gojmir Lahajnar



Measurement of sel-diffusion by the gradient spin echo

PHYSICAL REVIEW VOLUME 80, NUMBER 4 NOVEMBER 15, 1950

Spin Echoes*†

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Physics Department, University of Illinois, Urbana, Illinois
(Received May 22, 1950)

PHYSICAL REVIEW VOLUME 94, NUMBER 3 MAY 1, 1954

Effects of Diffusion on Free Precession in Nuclear Magnetic Resonance Experiments*†

H. Y. CARR, *Department of Physics, Rutgers University, New Brunswick, New Jersey*

AND

E. M. PURCELL, *Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts*
(Received January 19, 1954)

PHYSICAL REVIEW VOLUME 104, NUMBER 3 NOVEMBER 1, 1956

Bloch Equations with Diffusion Terms*

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Physics Department, Rutgers University, New Brunswick, New Jersey
(Received June 14, 1956; revised manuscript received August 2, 1956)

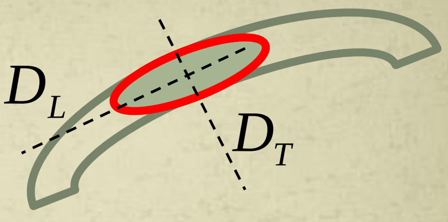
THE JOURNAL OF CHEMICAL PHYSICS VOLUME 43, NUMBER 10 15 NOVEMBER 1965

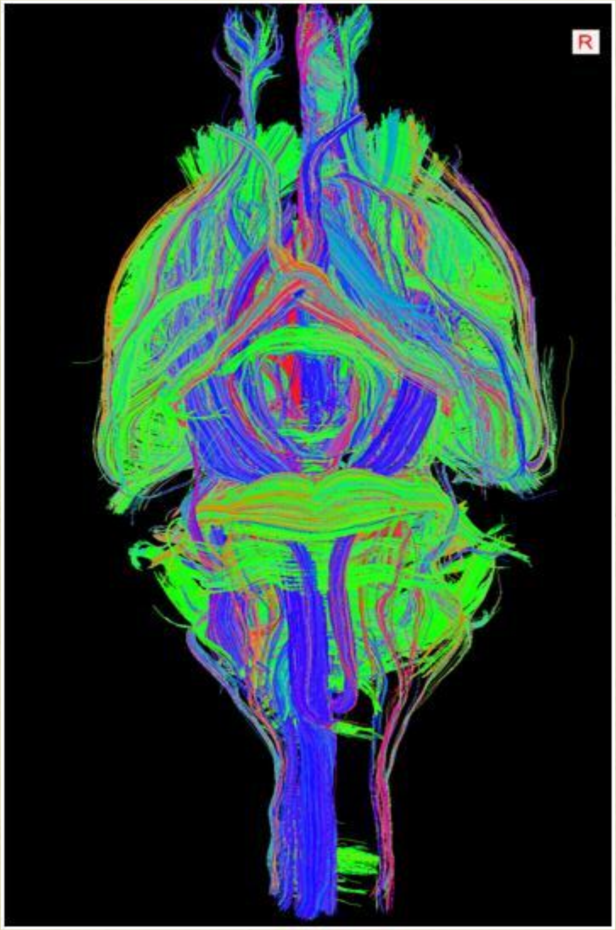
Use of Spin Echoes in a Pulsed Magnetic-Field Gradient to Study Anisotropic, Restricted Diffusion and Flow*

E. O. STEJSKAL
Department of Chemistry, University of Wisconsin, Madison, Wisconsin and
Central Research Department, Monsanto Company, St. Louis, Missouri†
(Received 19 April 1965)

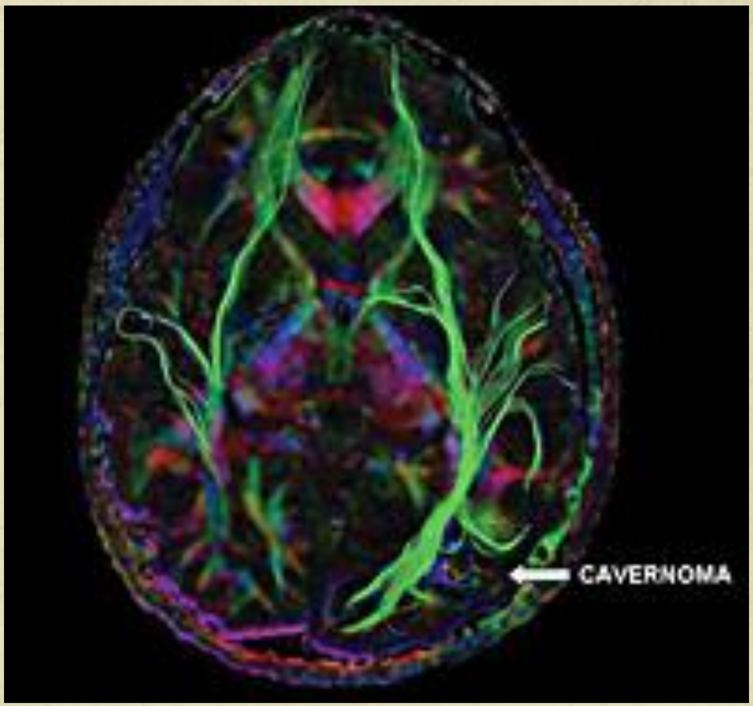
State of art: Neural connections via NMR Diffusion Tensor Imaging

$$\underline{\mathbf{D}} = \begin{vmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{vmatrix}$$





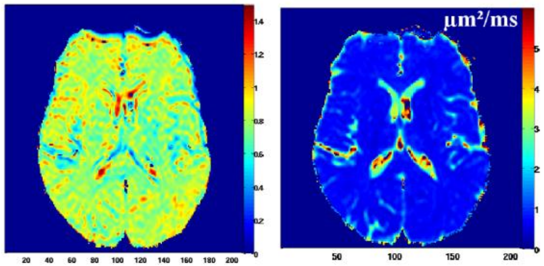
Tractography in the mouse brain by DTI: neural tracts diameter= 1 – 30 μm



White-matter neural tracts by DTI

Enigmas of diffusion weighted NMR images

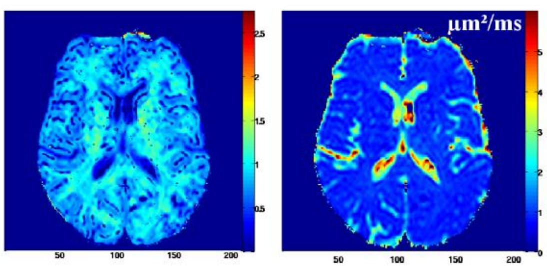
Anomalous diffusion imaging



α **DDC**

$$E \approx E_0 e^{\left(-b.DDC\right)^{\alpha}}$$

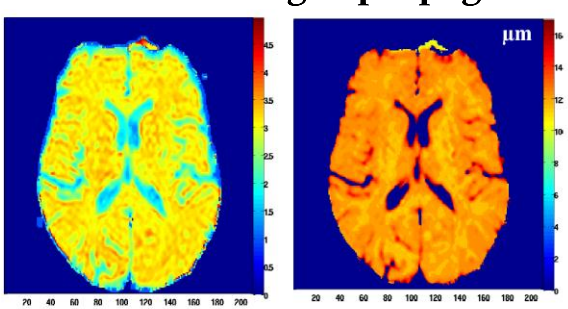
Diffusion kurtosis



ADK **ADCk**

$$E \approx E_0 e^{-b.ADCk + b^2.ADCk^2.ADK}$$

Diffusion averaged propagator



RMSD **P(RMSD=0)**

$$P\left(\mathbf{r}-\mathbf{r}_0,\tau\right) = \sum_i \int E\left(\mathbf{q},\tau\right)\, e^{-i\mathbf{q}\left(\mathbf{r}-\mathbf{r}_o\right)} d\mathbf{q}$$

Water Diffusion in q-space Imaging as a Probe of Cell Local Viscosity and Anomalous Diffusion in Grey and White Matter

R.Nicolas[1,2], F. Aubry[1,2], J. Pariente[1,2], X. Franceries[1,2], N. Chauveau[1,2], L. Saint-Aubert[1,2], F. Chollet[1,2], S. Breil[3] and P. Celsis[1,2]

[1] Inserm, Imagerie cérébrale et handicaps neurologiques, UMR 825, F-31059 Toulouse, France
[2] Université de Toulouse, UPS, Imagerie cérébrale et handicaps neurologiques, UMR 825, F-31059 Toulouse, France
[3] Philips Medical Systems, France

Use, Misuse, and Abuse of Apparent Diffusion Coefficients

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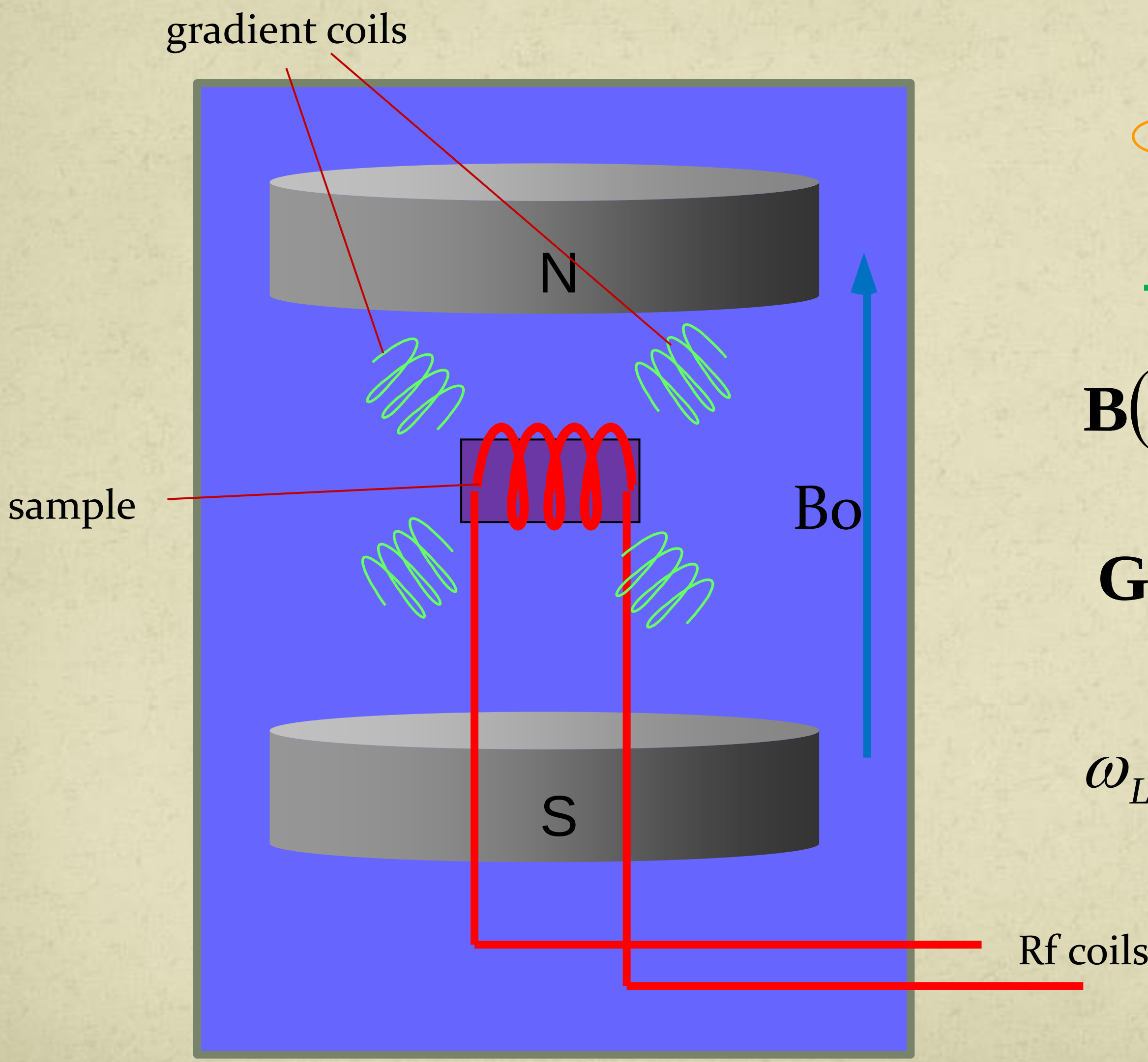
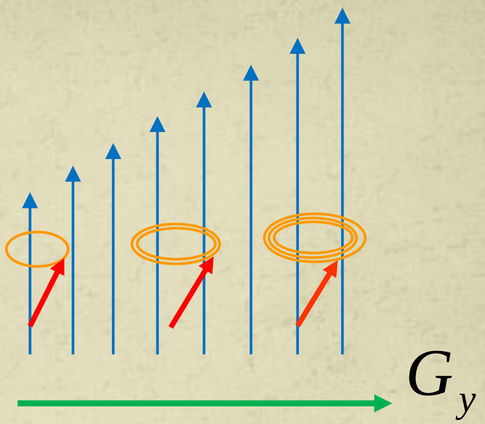
Concept Magn. Reson. A36 (2010) 24-35

Multiexponential decay

$$E \approx \sum_i E_{i0}\, e^{-b.D_i}$$

Spins in the magnetic field gradient



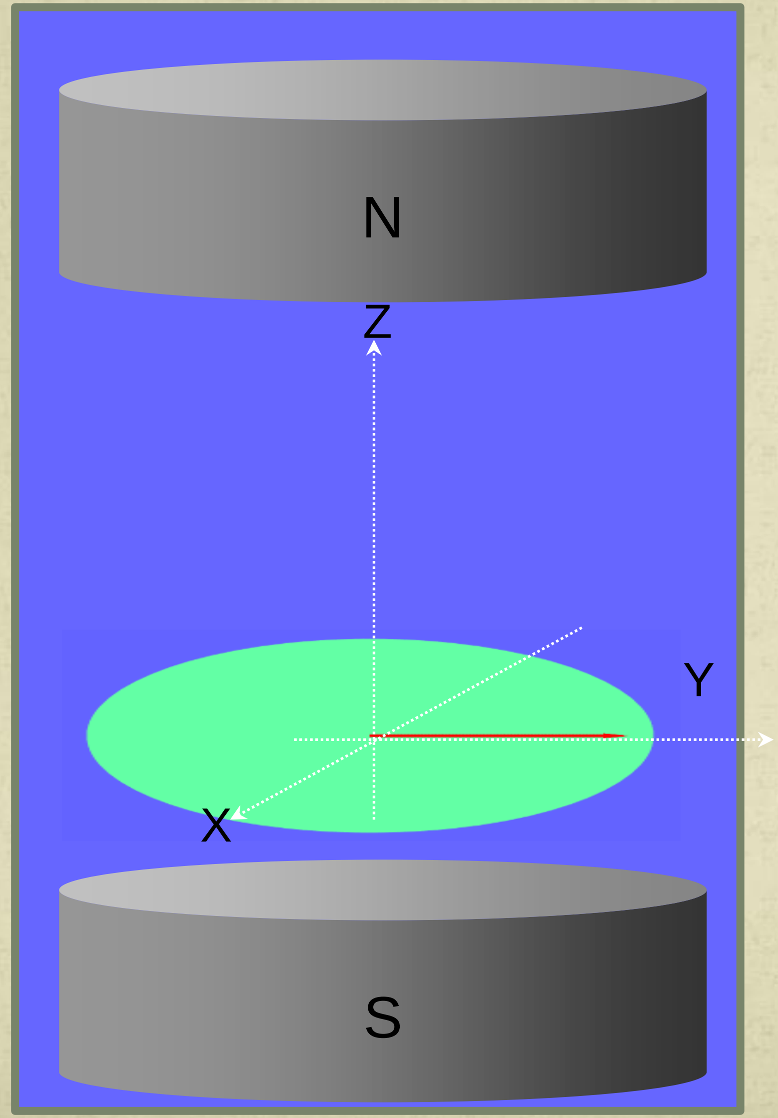


$$\mathbf{B}(\mathbf{r},t) = \mathbf{B}_o + \mathbf{G}.\mathbf{r}$$

$$\mathbf{G} = grad\ |\mathbf{B}(\mathbf{r})|$$

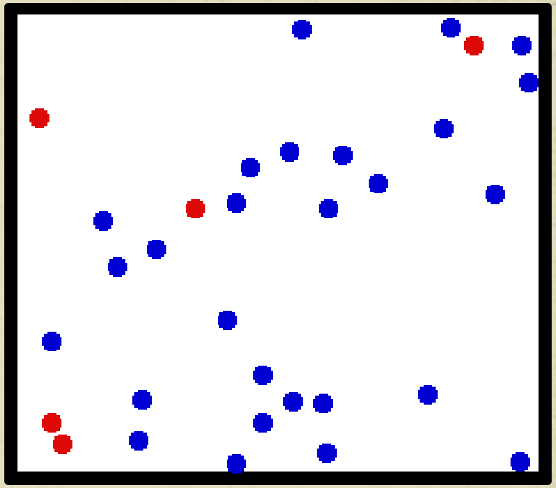
$$\omega_L = \gamma \mathbf{B}_o + \gamma \mathbf{G}.\mathbf{r}$$
$$= \omega_o + \gamma \mathbf{G}.\mathbf{r}_i$$

Spins in the magnetic field gradient



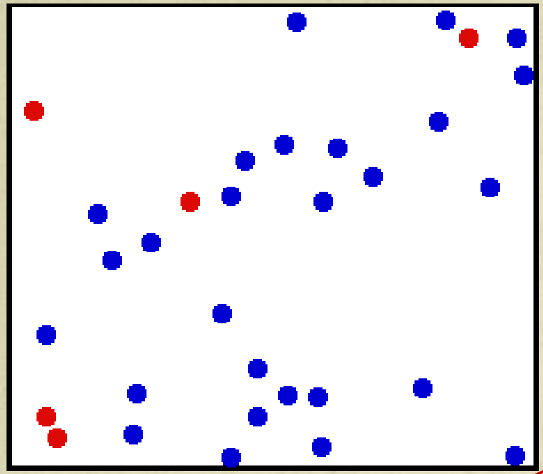
$$E(\tau) \approx e^{i(\omega_o + \gamma \mathbf{G.r})\tau}$$

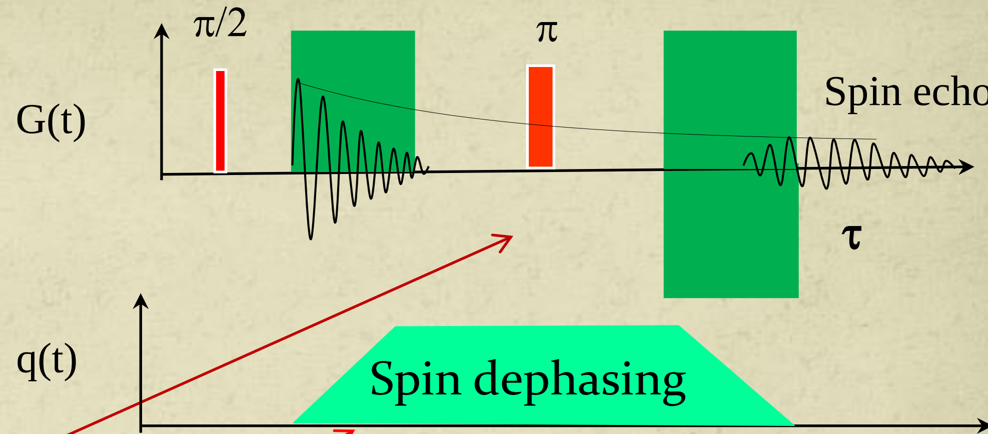
$$\omega_o = \gamma B_o$$



$$E(\tau) \approx e^{i\left(\omega_o \tau + \gamma \int_0^\tau \mathbf{G.r}(t)dt\right)}$$

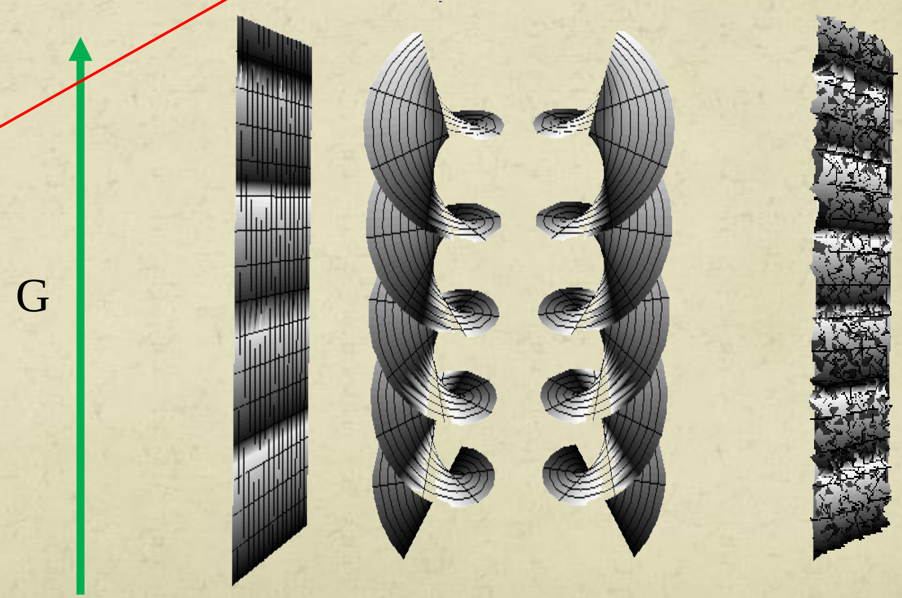
Motion encoding by PGSE





$$E_i(\tau) \approx e^{i\gamma\int_0^{\tau} \mathbf{G}_{eff}(t).\mathbf{r}_i(t)dt}$$

$$\approx e^{-i\int_0^{\tau} \mathbf{q}(t).\mathbf{v}_i(t)dt}$$



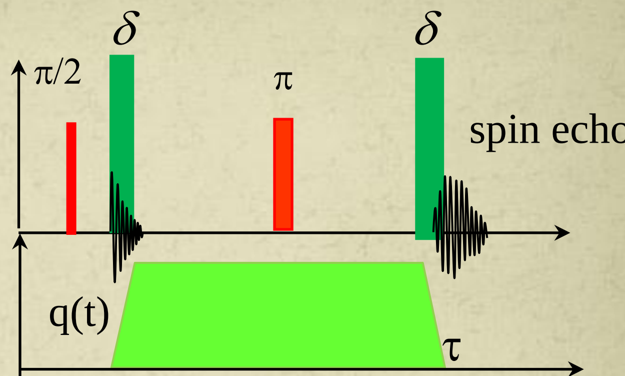
$$\mathbf{q}(t) = \gamma\int_0^{t} \mathbf{G}_{eff}(t').dt'$$

Probability distribution of spin displacement

$$E(\tau)=\sum_i\left\langle e^{-i\int_0^\tau \mathbf{q}(t)\mathbf{v}_i(t)dt}\right\rangle \qquad \mathbf{q}(t)=\gamma\mathbf{G}\delta \qquad \Delta\mathbf{r}_i=\mathbf{r}_i-\mathbf{r}_{oi}$$

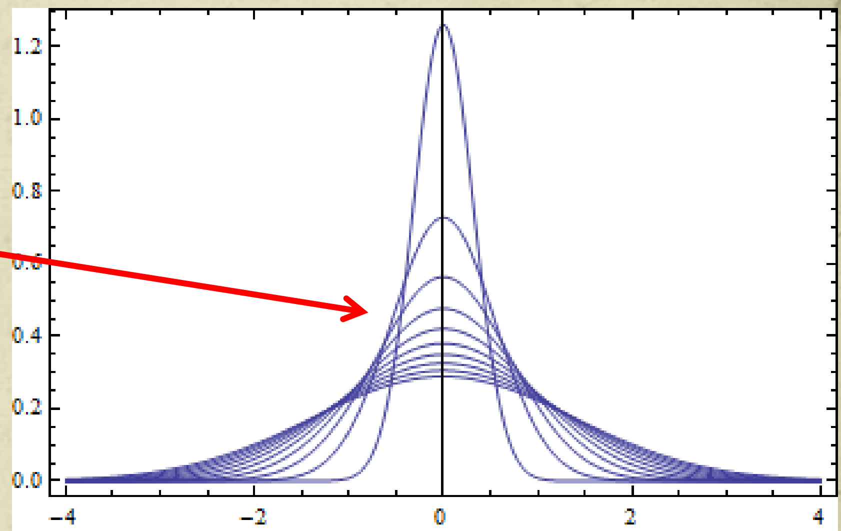
Random variable

$$=\sum_i\left\langle e^{i\mathbf{q}.\Delta\mathbf{r}_i(\tau)}\right\rangle=\sum_i\int P(\Delta\mathbf{r}_i,\tau)\; e^{i\mathbf{q}.\Delta\mathbf{r}_i}\,d\Delta\mathbf{r}_i$$



$$E(\tau,q)=\int P(\mathbf{r}_o)\sum_i P(\mathbf{r}_o|\mathbf{r}_i,\tau)\; e^{i\mathbf{q}(\mathbf{r}_i-\mathbf{r}_o)}d\mathbf{r}_o$$

Q-space Fourier transform of spin echo is the probability distribution.

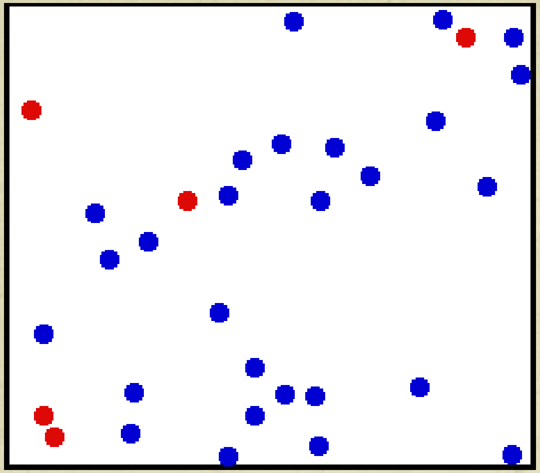


THE JOURNAL OF CHEMICAL PHYSICS VOLUME 42, NUMBER 1 1 JANUARY 1965

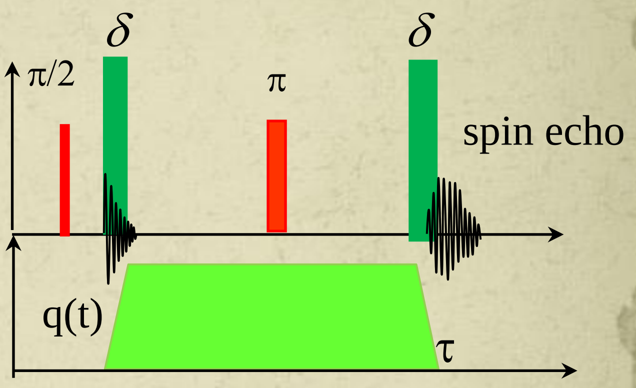
Spin Diffusion Measurements: Spin Echoes in the Presence of a Time-Dependent Field Gradient*

E. O. STEJSKAL† AND J. E. TANNER

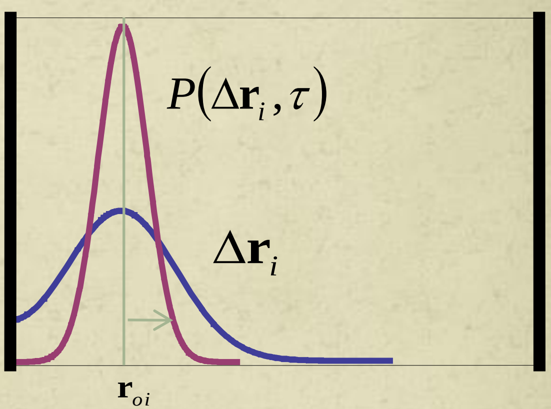
Probability distribution of restricted diffusion



Spin-echo with two short gradient pulses



Solution for the diffusion between reflecting boundaries



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

with the boundary conditions

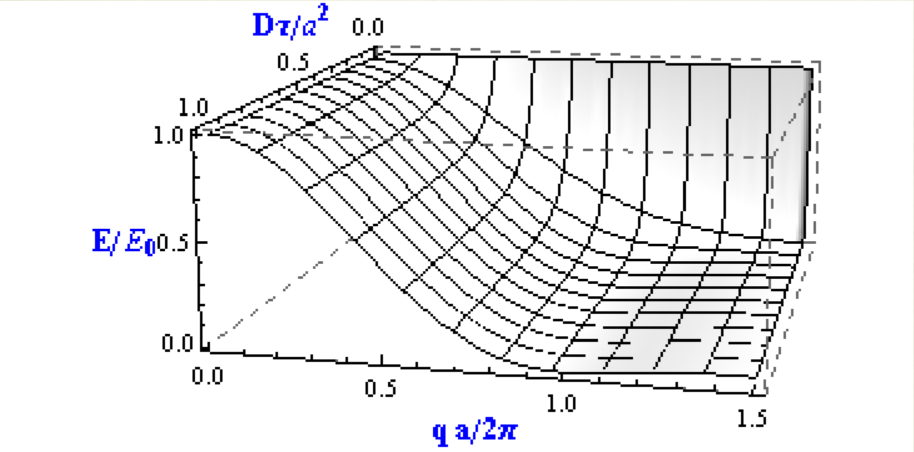
$$P(\mathbf{r}_o|\mathbf{r}_i, \tau) = \sum_k \varphi_k(\mathbf{r}_i)\varphi_{-k}(\mathbf{r}_o)e^{-\frac{\tau}{\tau_k}} \qquad \tau_k = \frac{1}{k^2 D}$$

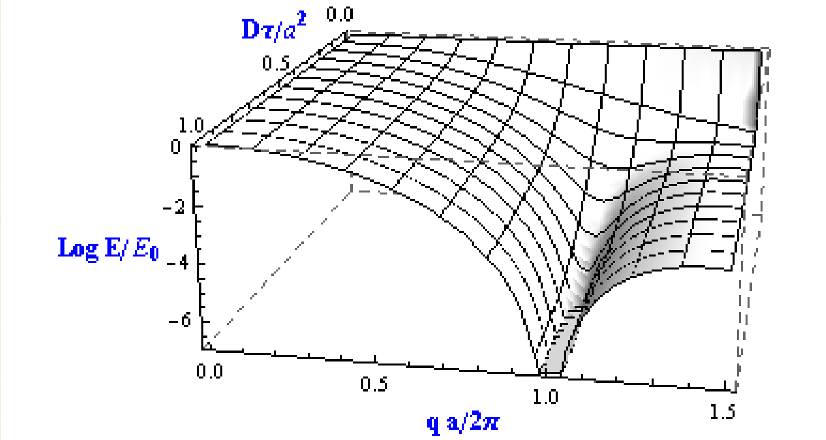
Restricted diffusion and diffusive diffraction

$$E_i(\tau,\mathbf{q}) = \sum_i \int P(\mathbf{r}_o)P(\mathbf{r}_o|\mathbf{r}_i,\tau)\; e^{i\mathbf{q}(\mathbf{r}_i-\mathbf{r}_o)}\, d\mathbf{r}_o = \iint P(\mathbf{r}_o)P(\mathbf{r}_o|\mathbf{r}_i,\tau)\; e^{i\mathbf{q}(\mathbf{r}_i-\mathbf{r}_o)}\, d\mathbf{r}_o\, d\mathbf{r}_i$$

$$= \sum_k |c_k(\mathbf{q})|^2\, e^{-\frac{\tau}{\tau_k}} \qquad\qquad c_k(\mathbf{q}) = \int \varphi_k(\mathbf{r})\; e^{i\mathbf{q}.\mathbf{r}}\, d\mathbf{r}$$

Gradient spin echo of diffusion between parallel planes





letters to nature

Nature **351**, 467 - 469 (06 June 1991); doi:10.1038/351467a0

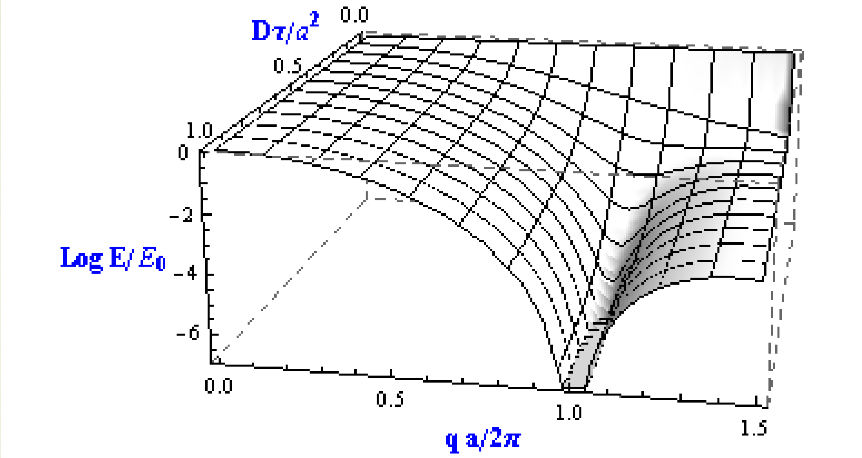
Diffraction-like effects in NMR diffusion studies of fluids in porous solids

P. T. CALLAGHAN*, A. COY*, D. MACGOWAN†, K. J. PACKER† & F. O. ZELAYA†‡

Averaged propagator of restricted diffusion

$$E(\mathbf{q},\tau)=\sum_i \int P(\mathbf{r}_{oi})P(\mathbf{r}_{oi}|\mathbf{r}_i,\tau)\; e^{i\mathbf{q}(\mathbf{r}_i-\mathbf{r}_{oi})}d\mathbf{r}_i$$

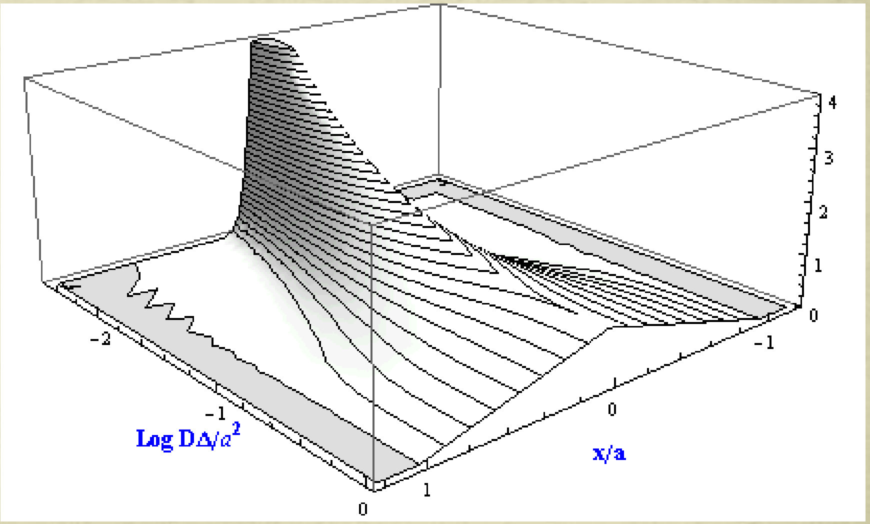
$$=\int \overline{P}(\mathbf{R},\tau)\; e^{i\mathbf{q}.\mathbf{R}}d\mathbf{R}$$



Time development of averaged diffusion
Propagator between parallel planes

Averaged propagator is
q-space Fourier transform of *E(**q**,t)*

$$\overline{P}(\mathbf{R},\tau)=\int E(\mathbf{q},\tau)\; e^{-i\mathbf{q}.\mathbf{R}}d\mathbf{q}$$

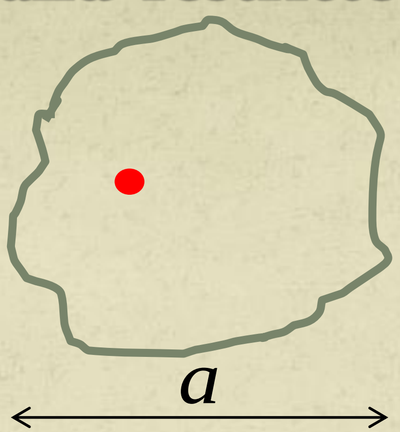


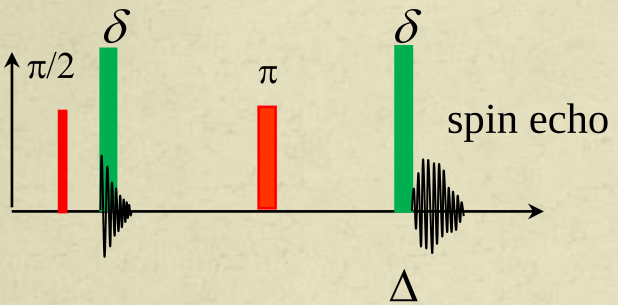
Pulse gradient spin echo and restricted self-diffusion

Range of pores:
a= $10^{-2} - 10^{-10}$ m

Short Gradient Pulse Approxiation

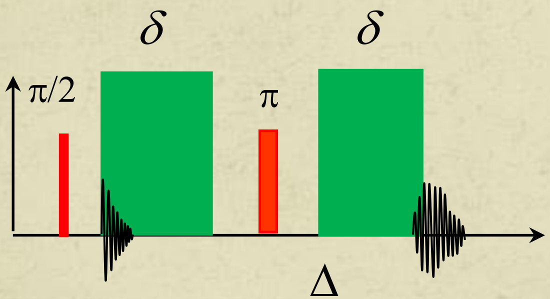
a > 1 μm





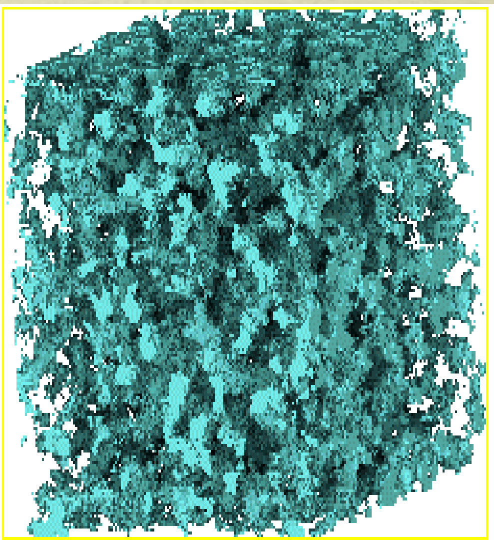
$$\delta << \tau_c << \Delta$$

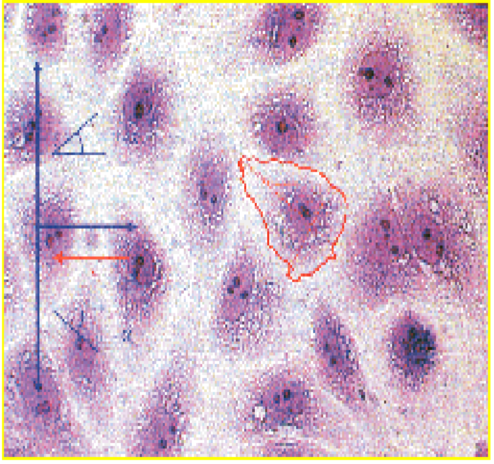
$$\tau_c = \frac{a^2}{2D}$$



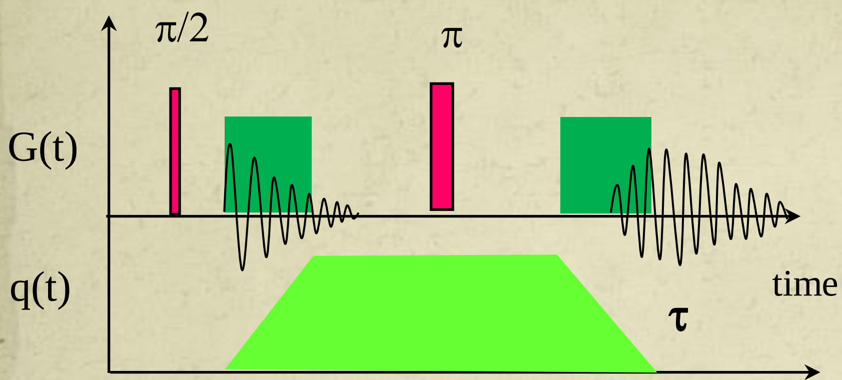
$$\tau_c < \delta \leq \Delta$$

$$size\ \ of\ \ pore < 1\mu m$$

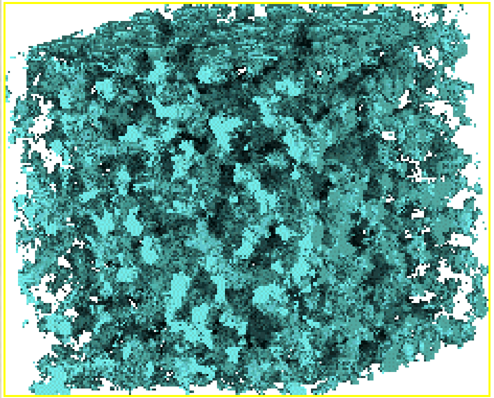


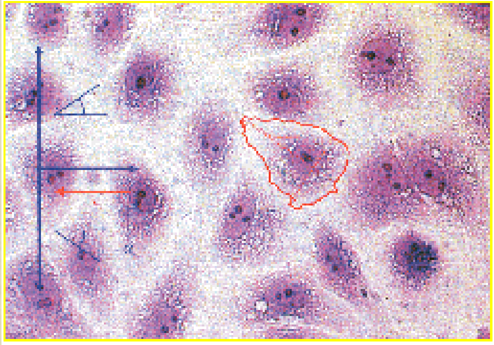


Gradient spin echo with finite width pulses



pore size:
a= $10^{-2} – 10^{-10}$ m





Multiple averaged propagator approach

A. Caprihan, L. Z. Wang, and E. Fukushima, J. Magn. Reson.,Ser. A **118, 94 (1996).**

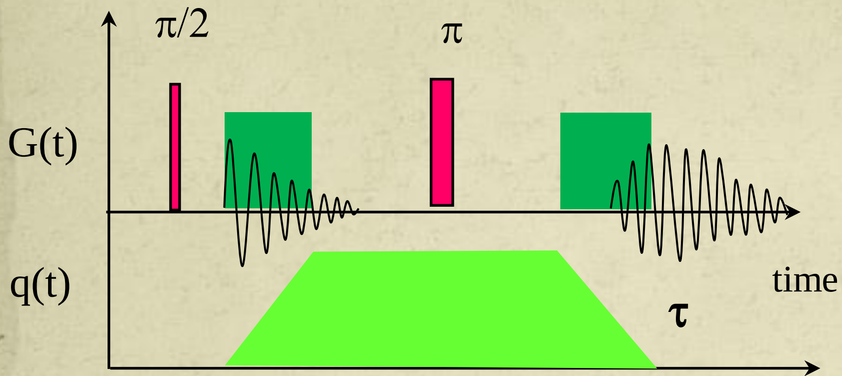
P. T. Callaghan, J. Magn. Reson. **129, 74 (1997).**

REVIEWS OF MODERN PHYSICS, VOLUME 79, JULY–SEPTEMBER 2007

NMR survey of reflected Brownian motion

Denis S. Grebenkov*

Gradient spin echo in the Gaussian phase approximation



no limits with respect to the gradient pulse width or gradient waveform

$$E(\tau)=\sum_i\left\langle e^{-i\int_0^\tau \mathbf{q}(t).\mathbf{v}_\mathrm{i}(t)dt}\right\rangle=\sum_i e^{-i\int_0^\tau \mathbf{q}(t).\langle\mathbf{v}_\mathrm{i}(t)\rangle dt-\frac{1}{2}\int_0^\tau\int_0^\tau \mathbf{q}(t).\langle\mathbf{v}_\mathrm{i}(t)\,\mathbf{v}_\mathrm{i}(t')\rangle_\mathrm{c}.\mathbf{q}(t')dt'dt}\times$$

Gaussian phase approximation (GPA)

$$\times e^{+\frac{i}{6}\int_0^\tau\int_0^\tau\int_0^\tau \mathbf{q}(t).\left\langle \mathbf{v}_i(t)\,\mathbf{q}(t').\mathbf{v}(t')\,\mathbf{v}_i(t'')\right\rangle_C.\mathbf{q}(t'')\,dt\,dt'\,dt''+\ldots}$$

Averaged velocity

Characteristic time

$$q\langle v\rangle\tau_c<1$$

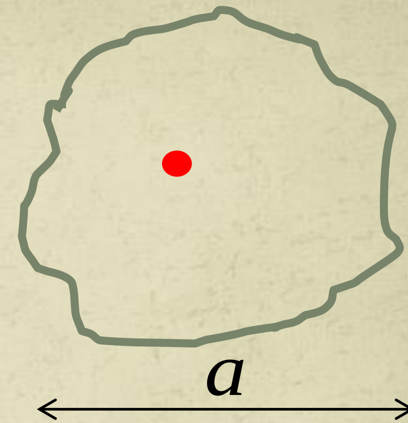
Gaussian Phase Approximation for the gradient spin echo

$$E(\tau,q)=\sum_i e^{i\varphi_i(\tau)-\beta_i(\tau)}$$

Requirement

$$q\langle v\rangle\tau_c<1$$

$$q\,a<1$$



$$\varphi_i(\tau)=-\int_0^\tau \mathbf{q}(t).\langle \mathbf{v}_\mathrm{i}(t)\rangle\,dt \qquad \beta_i(\tau)=\int_0^\tau\int_0^t \mathbf{q}(t).\langle \mathbf{v}_i(t)\mathbf{v}_i(t')\rangle_c.\mathbf{q}(t)\,dt'\,dt$$

$$\langle \mathbf{v}_\mathrm{i}(t)\rangle=\frac{d}{dt}\langle \Delta\mathbf{r}_i(t)\rangle \qquad \langle \mathbf{v}_i(t)\mathbf{v}_i(0)\rangle_c=\frac{1}{2}\frac{d^2}{dt^2}\langle \Delta\mathbf{r}_i^2(t)\rangle-\left(\frac{d}{dt}\langle \Delta\mathbf{r}_i(t)\rangle\right)^2$$

$$\langle \Delta\mathbf{r}_i(t)\rangle=\int(\mathbf{r}_i-\mathbf{r})P(\mathbf{r})P(\mathbf{r}|\mathbf{r}_i,t)\,d\mathbf{r} \qquad \langle \Delta\mathbf{r}_i^2(t)\rangle=\int(\mathbf{r}_i-\mathbf{r})^2P(\mathbf{r})P(\mathbf{r}|\mathbf{r}_i,t)\,d\mathbf{r}$$

$$P(\mathbf{r})=1,\quad P(\mathbf{r}|\mathbf{r}_i,t)=\sum_k\varphi_k(\mathbf{r}_i)\varphi_{-k}(\mathbf{r})e^{-\frac{t}{\tau_k}}$$

From GPA to normal distribution

$$E(\tau,\mathbf{q})=\sum_i e^{-i\int_0^\tau \mathbf{q}(t).\langle \mathbf{v}_{\mathrm{i}}(t)\rangle\, dt-\frac{1}{2}\int_0^\tau\int_0^\tau \mathbf{q}(t).\langle \mathbf{v}_{\mathrm{i}}(t)\ \mathbf{v}_{\mathrm{i}}(t')\rangle_{\mathrm{c}}.\mathbf{q}(t')\,dt'dt}$$

Ensemble average of cumulants

$$=Ne^{-\frac{1}{N}\sum_i\left(i\int_0^\tau \mathbf{q}(t).\langle \mathbf{v}_{\mathrm{i}}(t)\rangle\, dt+\frac{1}{2}\int_0^\tau\int_0^\tau \mathbf{q}(t).\langle \mathbf{v}_{\mathrm{i}}(t)\ \mathbf{v}_{\mathrm{i}}(t')\rangle_{\mathrm{c}}.\mathbf{q}(t')\,dt'dt\right)}$$

$$\text{II} \qquad\qquad \text{II}$$

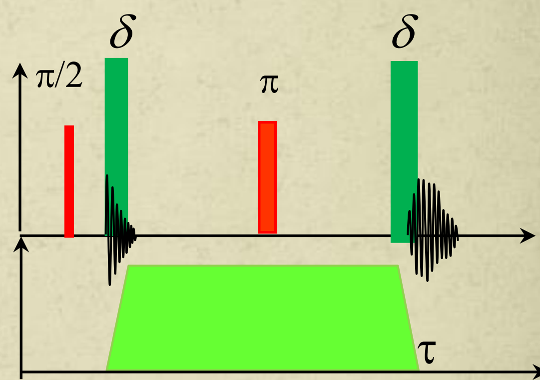
$$0 \qquad\qquad \int_0^\tau\int_0^\tau \mathbf{q}(t).\overline{\langle \mathbf{v}(t)\ \mathbf{v}(t')\rangle}.\mathbf{q}(t')\,dt'dt$$

$$E(\tau,\mathbf{q})=Ne^{-\frac{1}{2}\int_0^\tau\int_0^\tau \mathbf{q}(t).\overline{\langle \mathbf{v}(t)\ \mathbf{v}(t')\rangle}.\mathbf{q}(t')\,dt'dt}$$

SPGSE: Normal distribution

$$E(\tau,q)=Ne^{-\frac{1}{2}\mathbf{q}.\int_0^\tau\int_0^\tau \overline{\langle \mathbf{v}(t)\ \mathbf{v}(t')\rangle}.\,dt'dt\ .\mathbf{q}}=Ne^{-\frac{q^2}{2}\overline{\left\langle \Delta z(\tau)^2\ \right\rangle}}$$

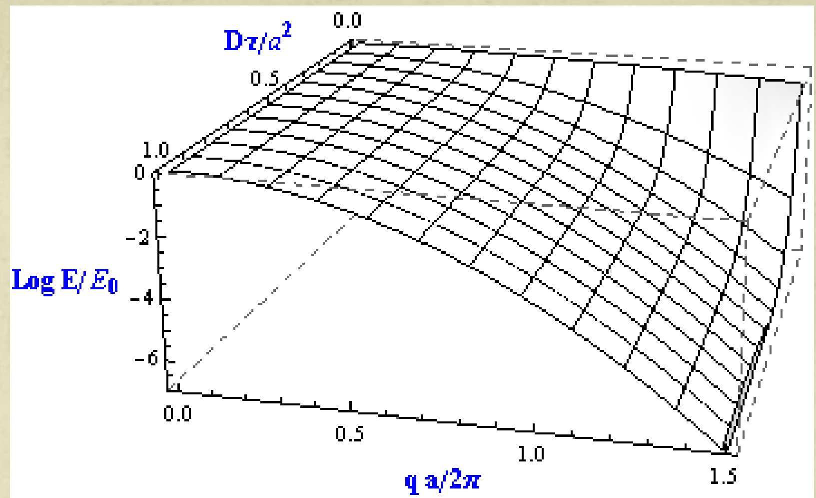
$$q=\gamma G\,\delta$$



$$\overline{\left\langle \Delta z(\tau)^2\ \right\rangle}=\sum_k b_k(1-e^{-\frac{\tau}{\tau_k}}) \qquad b_k=\int (z_i-z)^2\varphi_{-k}(z)\varphi_{-k}(z_i)dz\,dz_i$$

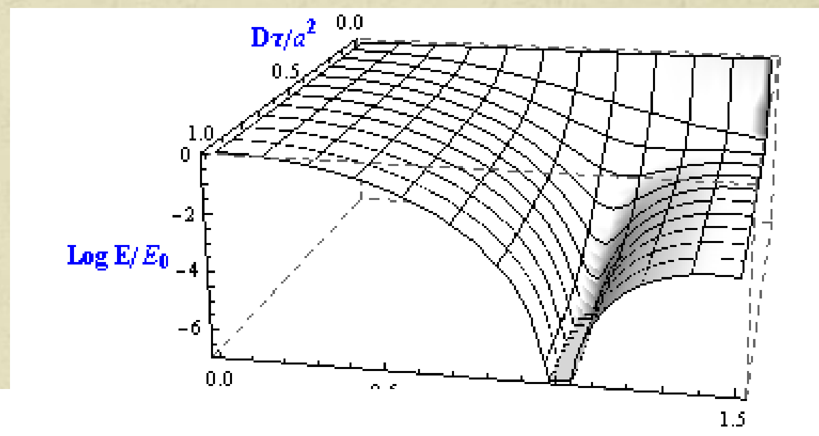
Normal distribution versus exact solution

$$E(q,\tau) = Ne^{-\frac{q^2}{2}\overline{\left\langle \Delta z(\tau)^2 \right\rangle}}$$



$$E(\mathbf{q},\tau) = \sum_i \int P(\mathbf{r}_{oi}) P(\mathbf{r}_{oi}|\mathbf{r}_i,\tau)\; e^{i\mathbf{q}(\mathbf{r}_i - \mathbf{r}_{oi})} d\mathbf{r}_i$$

$$= \int \overline{P}(\mathbf{R},\tau)\; e^{i\mathbf{q}.\mathbf{R}} d\mathbf{R}$$



REVIEWS OF MODERN PHYSICS, VOLUME 79, JULY–SEPTEMBER 2007

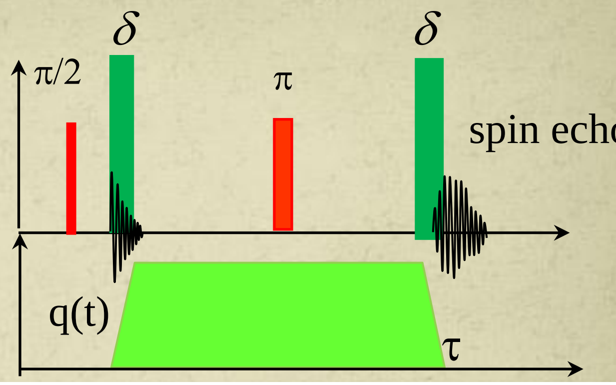
NMR survey of reflected Brownian motion

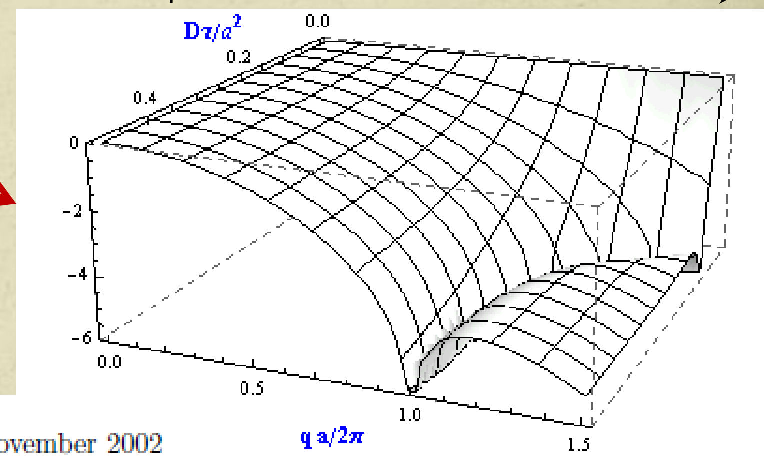
Denis S. Grebenkov*

Short PGSE and GPA of restricted self-diffusion

$$E(\tau,\mathbf{q}) == \sum_i e^{-i\int_0^\tau \mathbf{q}(t).\langle \mathbf{v}_i(t)\rangle dt - \frac{1}{2}\int_0^\tau\int_0^\tau \mathbf{q}(t).\langle \mathbf{v}_i(t)\ \mathbf{v}_i(t')\rangle_c .\mathbf{q}(t')dt'dt}$$

$$= \sum_i e^{-iq\left\langle \Delta z_i(t)\right\rangle - \frac{q^2}{2}\left\langle\left(\Delta z_i(\tau) - \left\langle \Delta z_i(t)\right\rangle\right)^2\right\rangle}$$





EUROPHYSICS LETTERS 1 November 2002

Europhys. Lett., **60** (3), pp. 453–459 (2002)

A new view of the spin echo diffusive diffraction in porous structures

J. Stepišnik(*)

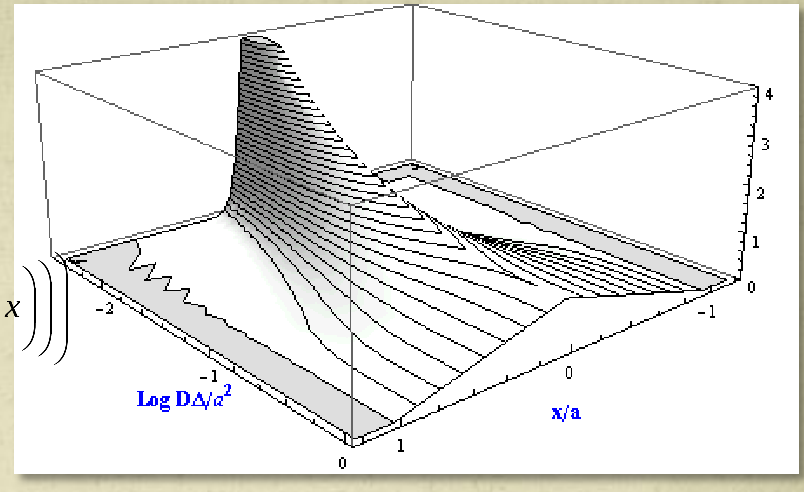
Time development of propagators

Averaged propagator

$$E(q,\tau)=\frac{4\sin\left(\frac{aq}{2}\right)^2}{a^2q^2}+4\sum_{n=1}^{\infty}\frac{a^2q^2\left((-1)^n\cos(aq)-1\right)}{\left(n^2\pi^2-a^2q^2\right)^2}e^{-\frac{n^2\pi^2}{a^2}Dt}$$

$$\overline{P(x)}=\frac{1}{a}\left(1-\left|\frac{x}{a}\right|+\sum_{n=1}^{\infty}e^{-\frac{n^2\pi^2}{a^2}Dt}\left(\left(1-\left|\frac{x}{a}\right|\right)Cos\left(\frac{n\pi}{a}x\right)-\frac{a}{n\pi\,Sgn(x)}Sin\left(\frac{n\pi}{a}x\right)\right)\right)$$

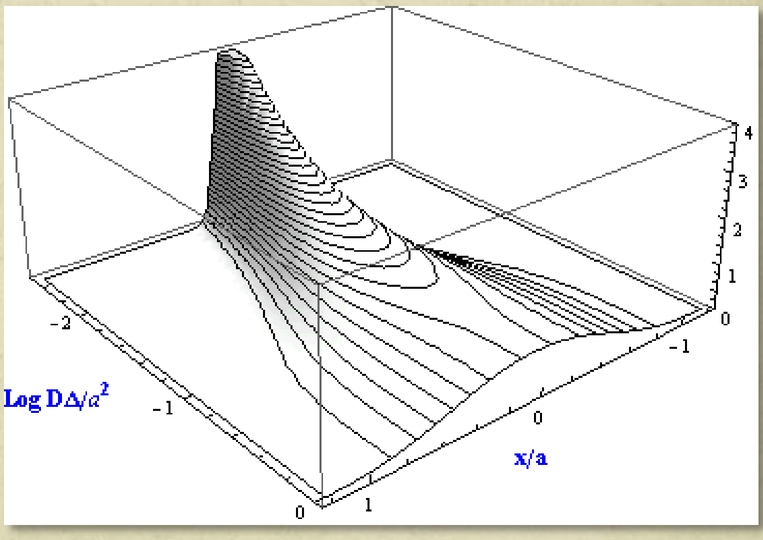
$$-a\le x\le a$$



Propagator of Gaussian Phase Approximation

$$E(q,\tau)\approx\sum_i e^{iq\langle\Delta x_i(\tau)\rangle-\frac{q^2}{2}\langle\Delta x_i(\tau)^2\rangle_c}$$

$$FT\left[E(q,\tau)\right]=\overline{P(x)}=\sum_i\frac{1}{\sqrt{2\pi\langle\Delta x_i(\tau)^2\rangle_c}}e^{-\frac{\left(x+\langle\Delta x_i(\tau)\rangle\right)^2}{2\langle\Delta x_i(\tau)^2\rangle_c}}$$



Asimptotic propagators: AP & GPA & GD (at long times)

Averaged propagator

$$E(q,\infty)=\left(\frac{2\sin(aq/2)}{aq}\right)^2$$

$$FT[E(q,\infty)]=P(x)=\frac{1}{2a}\left(\left|1+\frac{x}{a}\right|-2\left|\frac{x}{a}\right|+\left(1-\frac{x}{a}\right)Sign\left[1-\frac{x}{a}\right]\right)$$

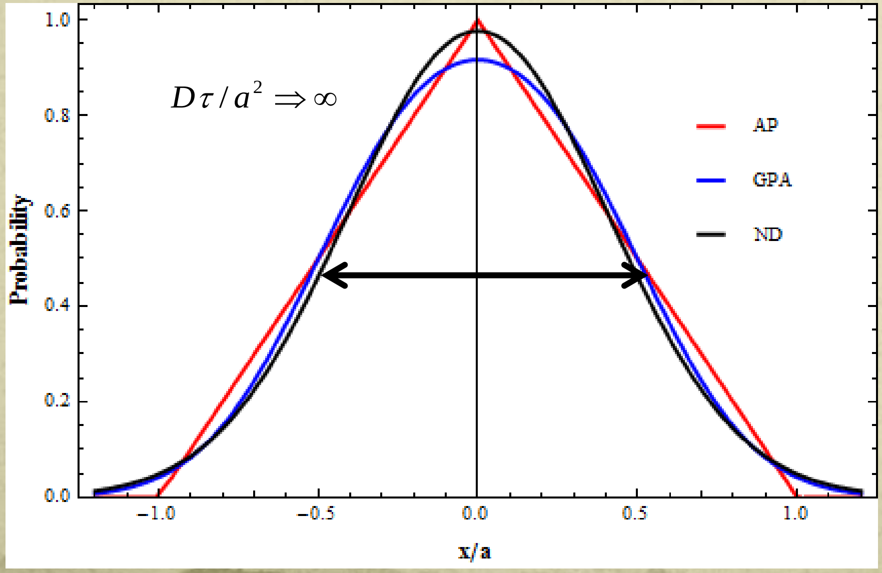
Propagator of normal distribution approx.

$$E(q,\infty)=e^{-\frac{q^2a^2}{12}} \qquad FT[E(q,\infty)]=P(x)=\sqrt{\frac{3}{\pi}}\frac{e^{-3\frac{x^2}{a^2}}}{a}$$

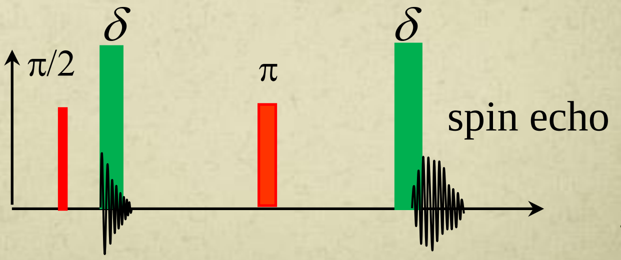
Propagator from GPA

$$E(q,\infty)=e^{-\frac{q^2a^2}{24}}\frac{2\sin(aq/2)}{aq} \qquad FT[E(q,\infty)]=P(x)=\frac{1}{2a}\left(Erf\left(\sqrt{\frac{3}{2}}\left(1-2\frac{x}{a}\right)\right)+Erf\left(\sqrt{\frac{3}{2}}\left(1+2\frac{x}{a}\right)\right)\right)$$

Diffusion between parallel planes

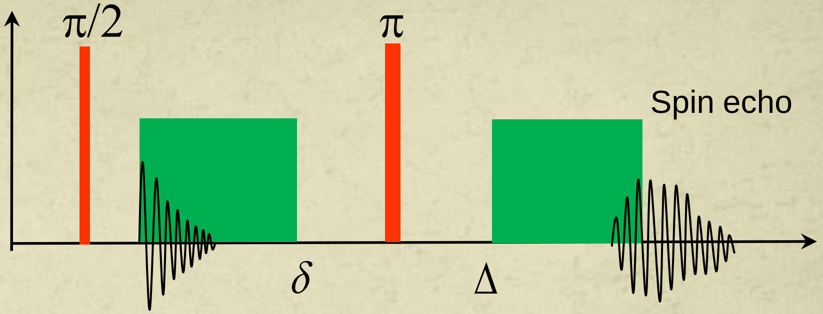


Second moment:
AP=GPA=ND=$a^2/6$
Kurtosis:
AP/GPA/ND=2.5/2.7/3



PGSE of restricted diffusion by normal distribution approximation

$$E(\tau,q)=\sum_i e^{i\varphi_i(\tau)-\beta_i(\tau)} = Ne^{i\overline{\varphi(\tau)}-\overline{\beta(\tau)}}$$



$$\overline{\varphi(\tau)}=\sum_k a_k\int_0^\tau q(t)\,e^{-\frac{t}{\tau_k}}\,dt=0 \qquad a_k=\int (x_i-x)\varphi_{-k}(x)\varphi_k(x')\,dx'\,dx=0$$

$$\overline{\beta(\tau)}=\sum_k b_k\int_0^\tau\int_0^t q(t)q(t').e^{-\frac{|t-t'|}{\tau_k}}\,dt'\,dt-\varphi(\tau)^2 \qquad b_k=\int (x_i-x)^2\varphi_{-k}(x)\varphi_k(x')\,dx'\,dx$$

$$\overline{\beta(\Delta,\delta)}=q^2\sum_k b_k f(\Delta,\delta,\tau_k)$$

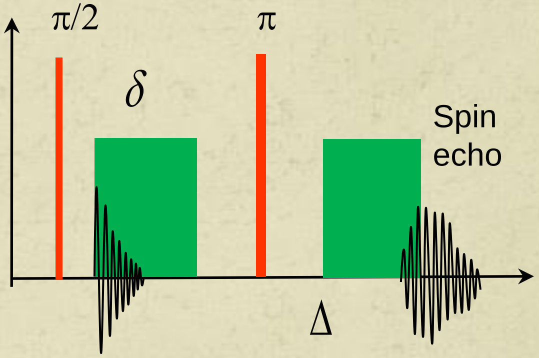
$$= Ne^{-q^2\sum_k b_k h(\Delta,\delta,\tau_k)}$$

$$h(\Delta,\delta,\tau_k)=\frac{\tau_k^2}{\delta^2}\left(2\left(\frac{\delta}{\tau_k}-1+e^{-\frac{\delta}{\tau_k}}\right)-e^{-\frac{\Delta+\delta}{\tau_k}}\left(1-e^{\frac{\delta}{\tau_k}}\right)^2\right)$$

PGSE measurement of nanoporosity: limit $\Delta,\delta>\tau_k$

$$h(\Delta,\delta,\tau_k)=\left(\frac{\tau_k}{\delta}\right)^2\left(2\left(\frac{\delta}{\tau_k}-1+e^{-\frac{\delta}{\tau_k}}\right)-e^{-\frac{\Delta+\delta}{\tau_k}}\left(1-e^{\frac{\delta}{\tau_k}}\right)^2\right)\xrightarrow{Lim\ \delta<\tau_k}(1-e^{-\frac{\Delta}{\tau_k}}-\frac{\delta}{3\tau_k})$$

$$h(\Delta,\delta,\tau_k)=\left(\frac{\tau_k}{\delta}\right)^2\left(2\left(\frac{\delta}{\tau_k}-1+e^{-\frac{\delta}{\tau_k}}\right)-e^{-\frac{\Delta+\delta}{\tau_k}}\left(1-e^{\frac{\delta}{\tau_k}}\right)^2\right)\xrightarrow{Lim\ \Delta,\delta>>\tau_k}2\frac{\tau_k}{\delta}$$



$$E(\Delta,\delta,q)=\sum_i N_i e^{-\overline{\beta_i(\Delta,\delta)}-\frac{\Delta+\delta}{T_{2i}}}$$

$$=\sum_l N_l e^{-q^2\sum_k b_{kl}(1-e^{-\frac{\Delta}{\tau_{kl}}}-\frac{\delta}{3\tau_{kl}})-\frac{\Delta+\delta}{T_{2l}}}+\sum_s N_s e^{-q^2\frac{2}{\delta}\sum_k b_{ks}\tau_{ks}-\frac{\Delta+\delta}{T_{2s}}}$$

$\delta<\tau_{kl}$ — Large pores

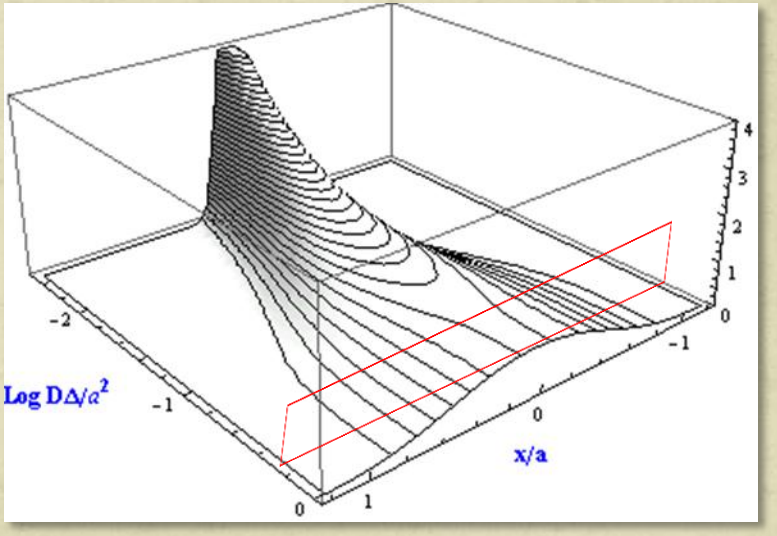
$\delta>\tau_{ks}$ — Small pores

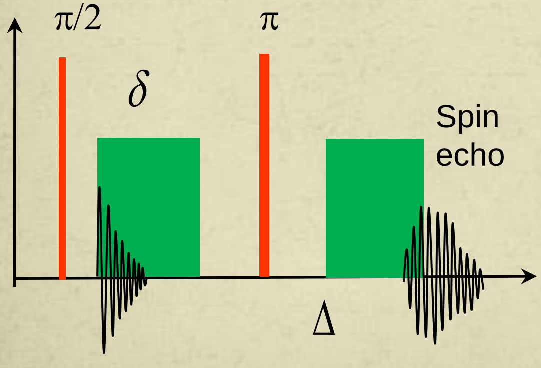
PGSE measurement of nanoporosity: limit $\Delta,\delta>\tau_\kappa$

$$E(\Delta,\delta,q)=e^{-q^2D(\Delta-\frac{\delta}{3})}\sum_l N_l e^{-\frac{\Delta+\delta}{T_{2l}}}+\sum_s N_s e^{-q^2\frac{2}{\delta}\sum_k b_{ks}\tau_{ks}-\frac{\Delta+\delta}{T_{2s}}}$$

$Spherical\ \ pore\ \ \ radius="r"$ $$E(\delta,q)=e^{-q^2k_1\frac{r^4}{D\delta}}$$ $k_1=0.712$

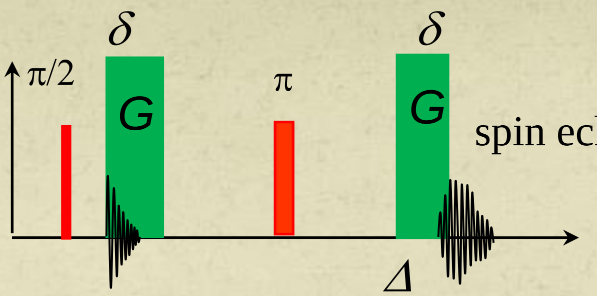
$FT[E(\Delta,\delta,q)]=$



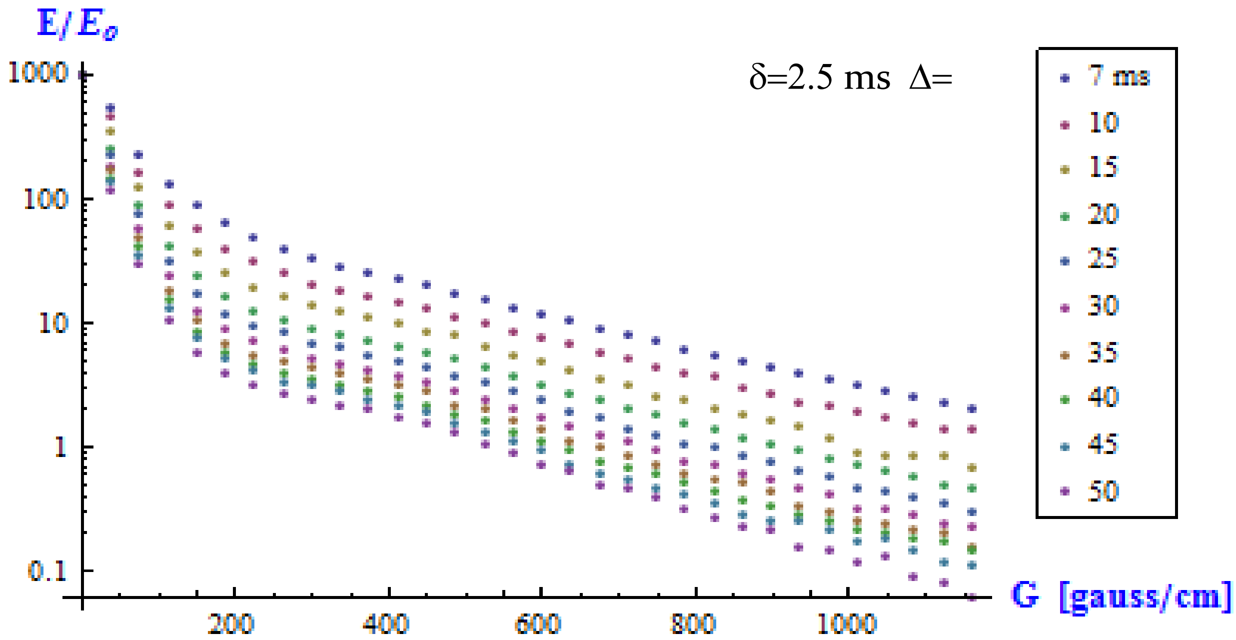


PGSE measurements of restricted diffusion

Sieve of polyamid membrane soaked in water

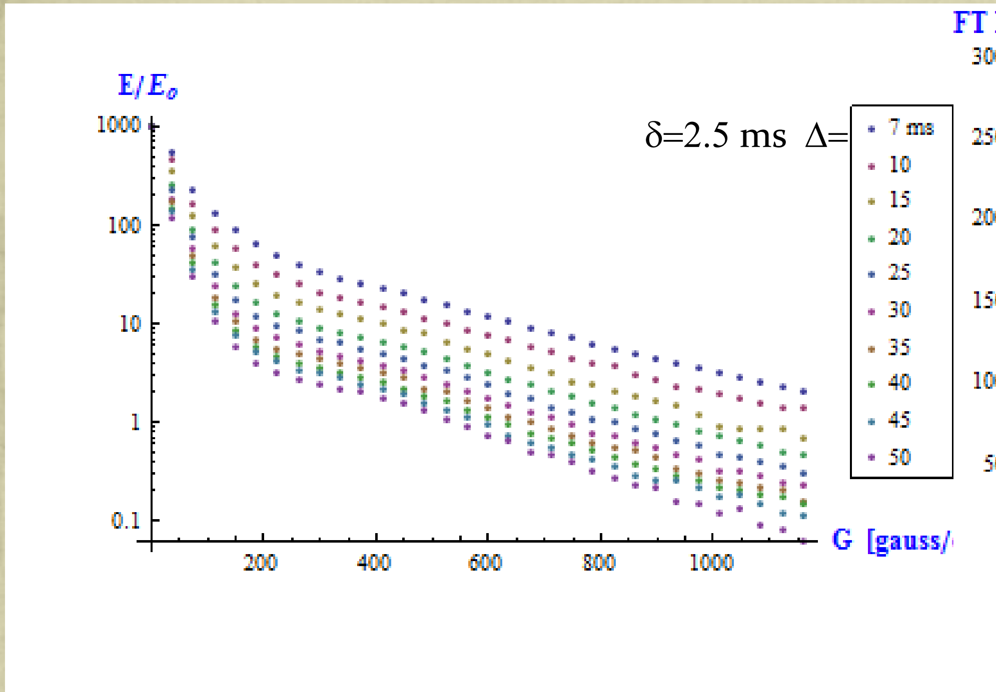


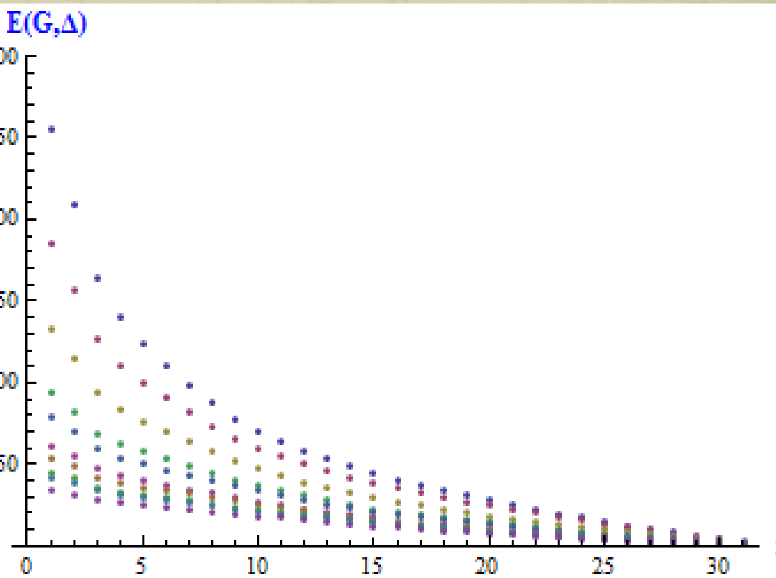
Bruker 500, 12T/m gradient coil

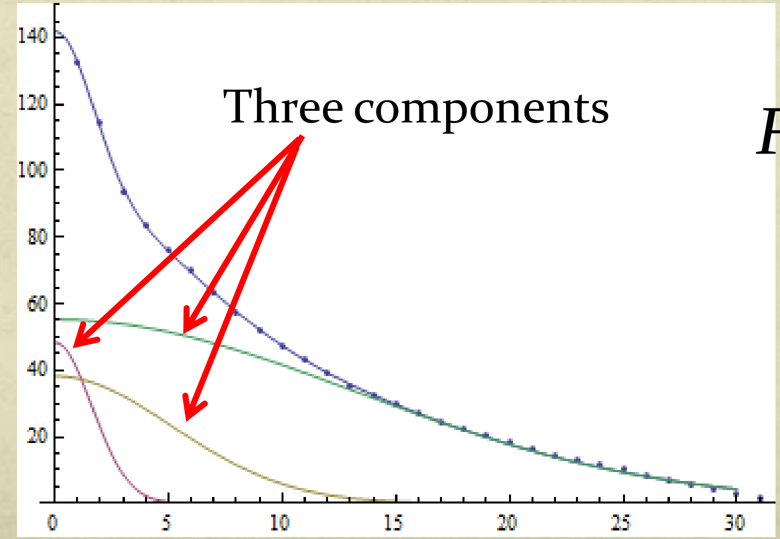


Ulrich Scheler,
Leibniz Institute of Polymer Research Dresden, Germany

Analysis of diffusion in a heterogeneous porous system

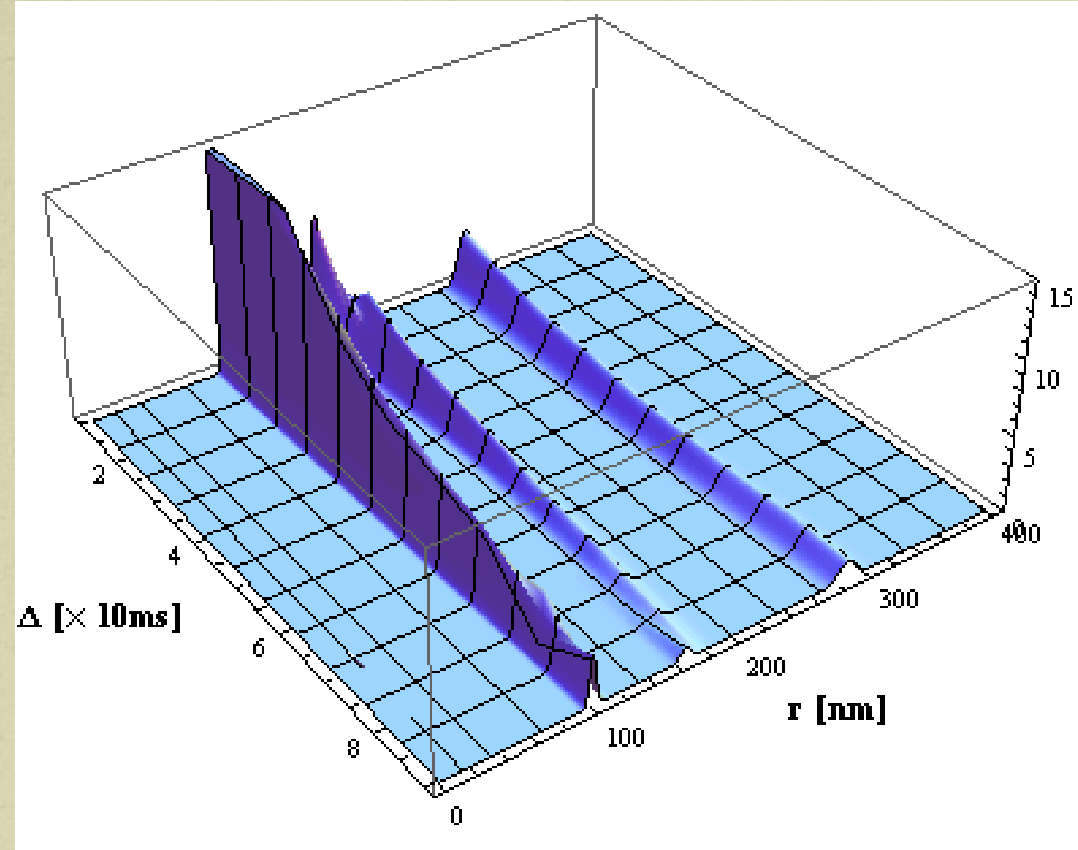


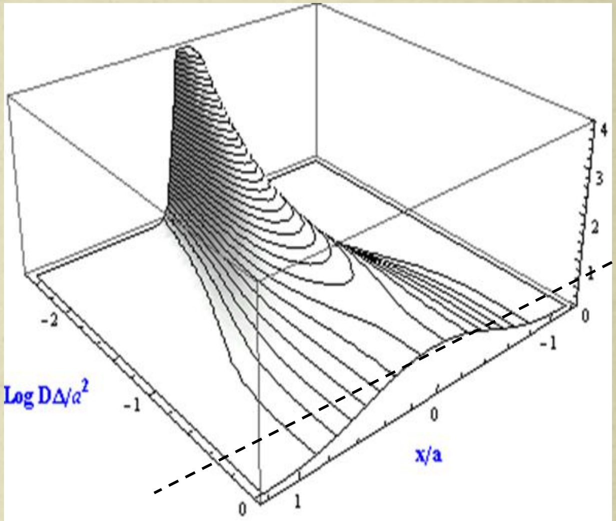




$$FT(E) = \sum_k A_k e^{-\alpha_k z^2}$$

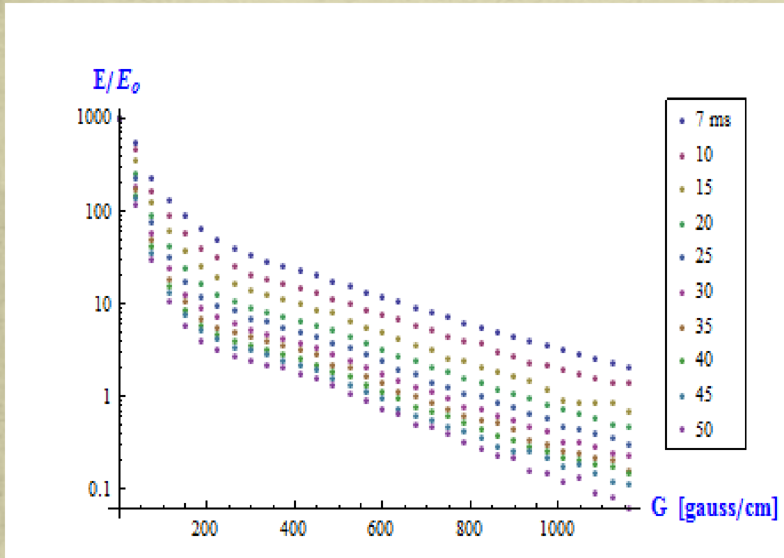
Distribution of pores in polyamid membrane





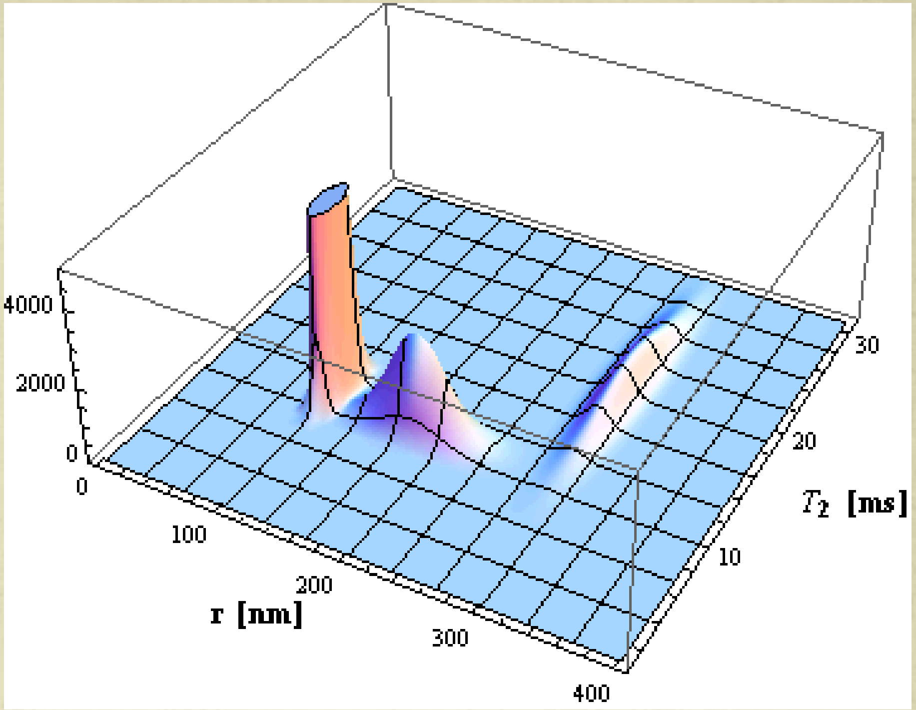
$$FT[E(\delta,q)] \approx \sum_s N_s FT\left[e^{-q^2 k_1 \frac{r_s^4}{D\delta}}\right] = \sum_s N_s \sqrt{\frac{D\delta}{2r_s^4}}\, e^{-x^2 \frac{D\delta}{4k_1 r_s^4}}$$

Size & relaxation distribution of pores in polyamid membrane



PGSE measurements

Result



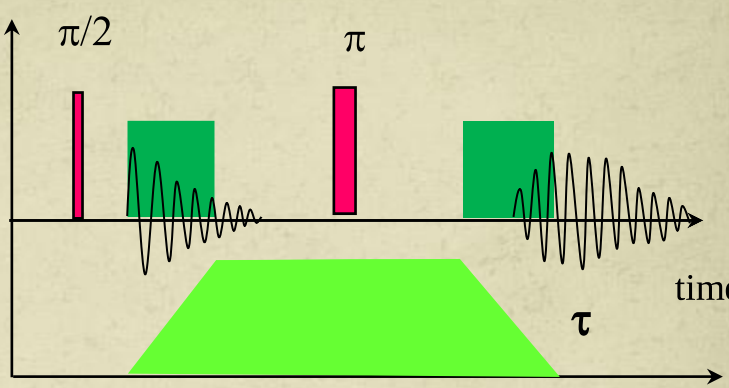
$$FT[E] \approx \sum_m N_m \sqrt{\frac{D\delta}{2r_m^4}}\, e^{-x^2 \frac{D\delta}{4k_1 r_m^4}}\, e^{-\frac{\Delta}{T_{2m}}}$$

Information about
- the porous structure
- the interactions with boundaries

Spin echo and velocity autocorrelation spectrum

$$E(\tau)=\sum_i e^{\,i\int_0^\tau \mathbf{q}(t).\langle \mathbf{v}_i(t)\rangle dt-\int_0^\tau\int_0^t \mathbf{q}(t).\langle \mathbf{v}_i(t)\ \mathbf{v}_i(t')\rangle_c .\mathbf{q}(t')dt'dt}$$

$$=\sum_i e^{i\varphi_i(\tau)-\beta_i(\tau)}$$



Time domain

↓

Frequency domain

J. Stepišnik, Analysis of NMR self-diffusion measurements by density matrix calculation, Physica B, 104, 350-64, (1981)

$$\beta_i(\tau)=\frac{1}{\pi}\int_0^\infty q^2(\omega,\tau).D_i(\omega)d\omega$$

Velocity autocorrelation spectrum

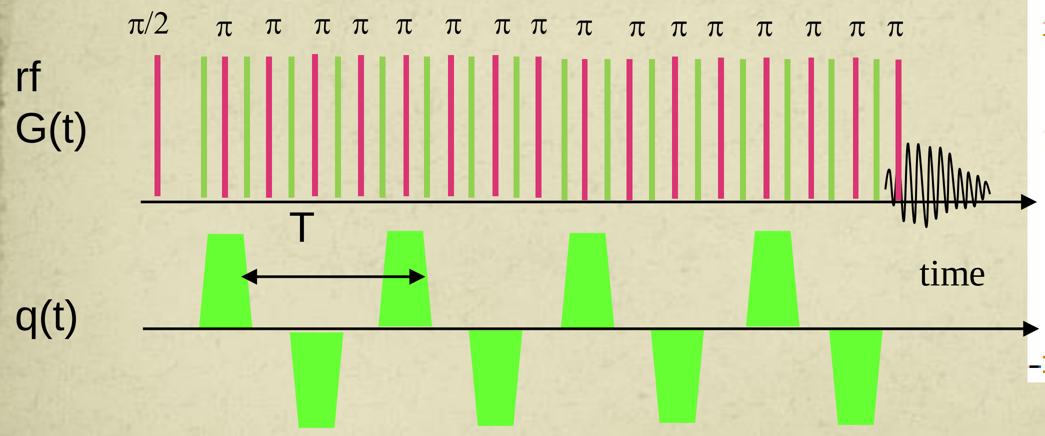
$$\mathbf{q}(\omega,\tau)=\int_0^\tau q(t)e^{i\omega t}dt \qquad D_i(\omega)=\int_0^\tau \langle v_i(t)\ v_i(t')\rangle_c\, e^{i\omega t}dt$$

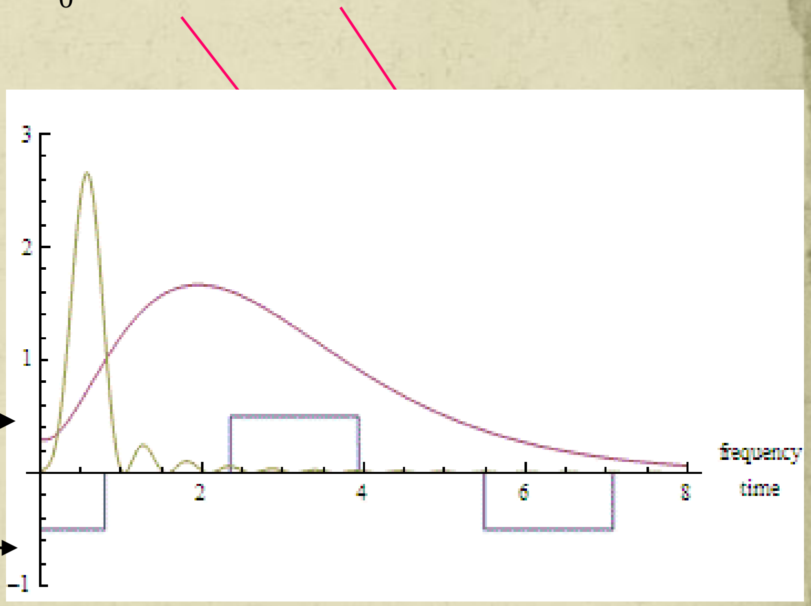
Modulated Gradient Spin Echo (MGSE)

Velocity autocorrelation spectrum

$$E(\tau)=\sum_i e^{\cancel{i\varphi(\tau)}-\beta_i(\tau)} \qquad \mathbf{q}(\omega,\tau)=\int_0^{\tau} q(t)e^{i\omega t}dt \qquad \mathbf{D}_i(\omega)=\int_0^{\tau}\langle\Delta\mathbf{v}_i(t)\Delta\mathbf{v}_i(t')\rangle e^{i\omega t}dt$$

$$\beta_i(\tau)=\frac{1}{2}\int_0^{\tau}\int_0^{\tau}\mathbf{q}(t).\langle\Delta\mathbf{v}_i(t)\,\Delta\mathbf{v}_i(t')\rangle.\mathbf{q}(t')dt'dt \;\Rightarrow\; \frac{1}{\pi}\int_0^{\infty}|\,\mathbf{q}(\omega,\tau)|^2\,D(\omega)\,d\omega$$





$$E(\tau)\approx e^{-\alpha\,D\,(\omega_{\mathrm{m}})\tau} \qquad \omega_{\mathrm{m}}=\frac{2\pi}{T}$$

PGSE study of polymer melt-system of entangled polymer

In last decades of his life prof. Peterlin was interested in the study of polymer dynamics by NMR gradient spin echo at Institute J. Stefan.

NMR self-diffusion study of polyethylene and paraffin melts
Zupančič, I. Lahajnar, G.; Blinc, R.; Reneker, D.H.; Vanderhart, D.L. *Journal of Polymer Science, Polymer Physics Edition*, 23, 387-404 (1985)

NMR study of diffusion of butane in linear polyethylene
Zupančič, I.,; Lahajnar, G.; Blinc, R.; Reneker, D.H.; Peterlin, A. *Journal of Polymer Science, Polymer Physics Edition*, 16, 1399-407 (1978)

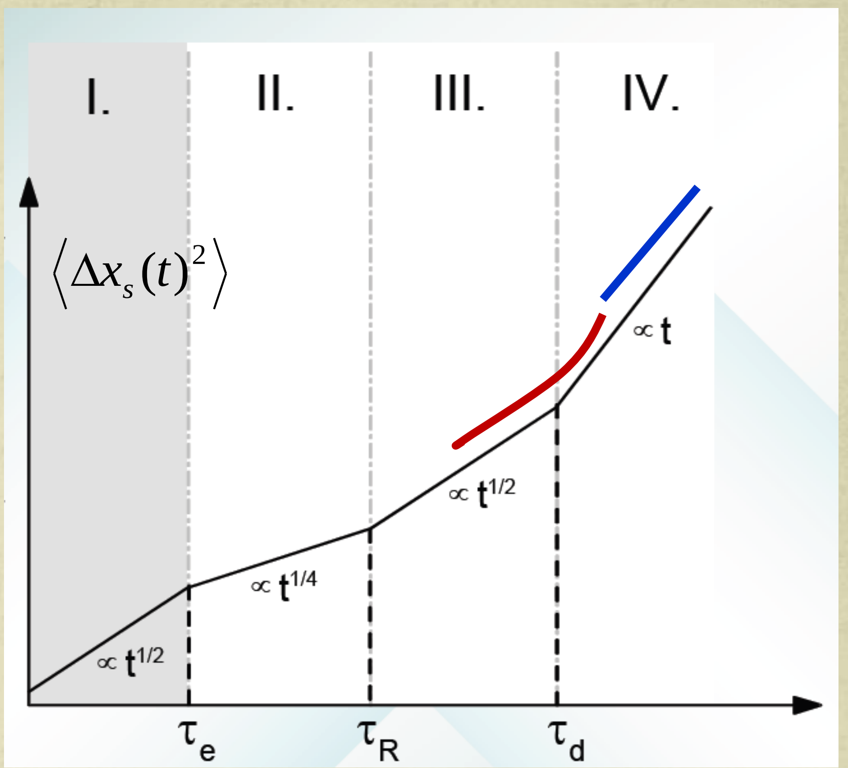
Aim to confirm de Gennes theory of reptation motion in polymer melt: Experimental data were left unexplained

$$\beta_i(\tau) = \frac{1}{\pi}\int_0^\infty q^2(\omega,\tau).D_i(\omega)\,d\omega$$

We need a model for $D(\omega)$!

Model of segmental motions in dense polymer

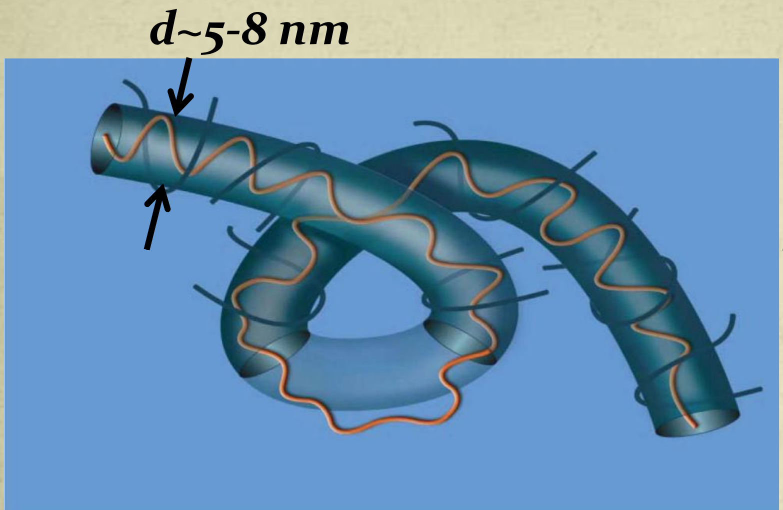
- P.R. Rouse, J.Chem Phys. 21, 1272 (1953)
- P.G. de Gennes, J. Chem.Phys. 55, 572-579 (1971),
- M. Doi and S. F. Edwards, J. Chem. Soc., Faraday Trans. 74, 1789 (1978)

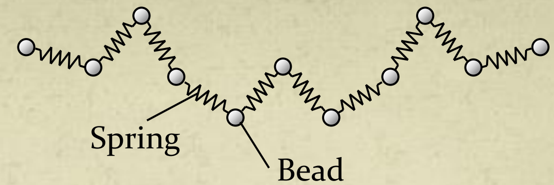


Times are in the range of few nanosecond to seconds.
Distance scale is between nanometers to micrometers.

Reptation-like motion in entangled system

d~5-8 nm





$$\left\langle \left(\Delta x_m(t)\right)^2 \right\rangle_R = 2D_{coil}\left(t + m\tau_m\left(e^{-\frac{t}{\tau_m}} - 1 + \sqrt{\frac{\pi t}{\tau_m}}\,Erf\left(\sqrt{\frac{t}{\tau_m}}\right)\right)\right)$$

Rouse motion

$$t < k^2\tau_m = \tau_e$$

$$\left\langle \left(\Delta x_k(t)\right)^2 \right\rangle_R < d^2$$

Reptation along tube

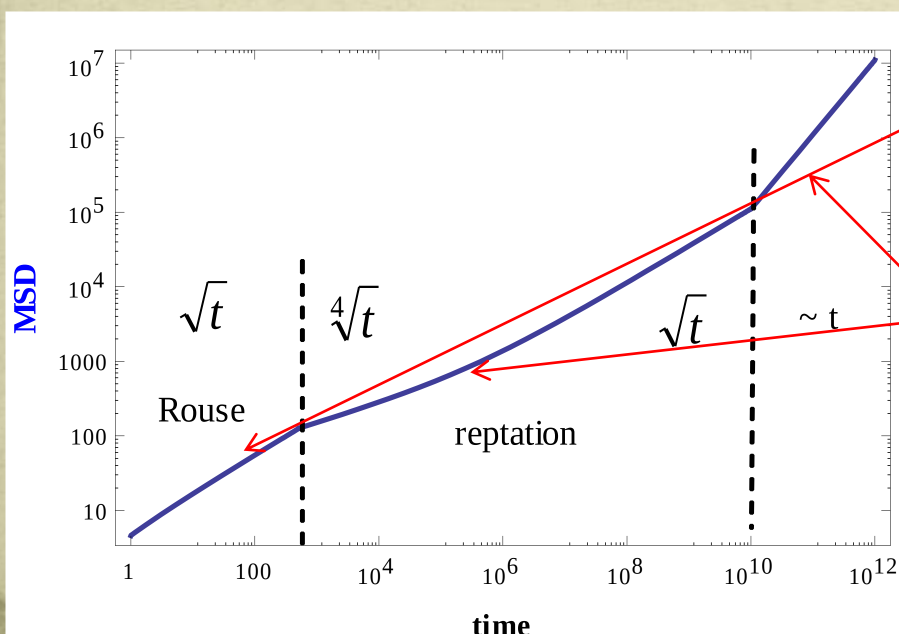
$$k^2\tau_m < t < m^2\tau_m = \tau_R$$

$$d^2 < d\sqrt{\left\langle \left(\Delta x_m(t)\right)^2 \right\rangle_R} < R^2$$

Creeping out of tube

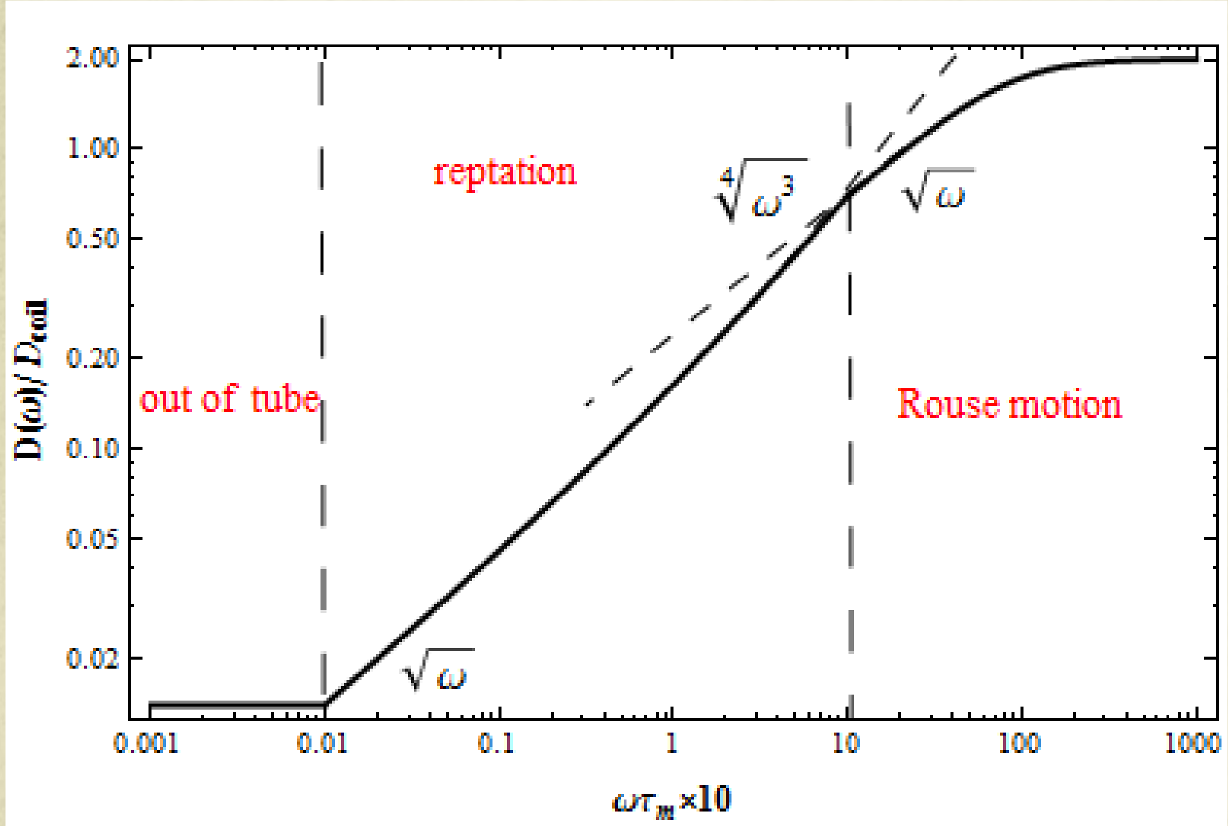
$$m^2\tau_m \approx \tau^* < t$$

$$R^2 < 2D_{self}\,t$$

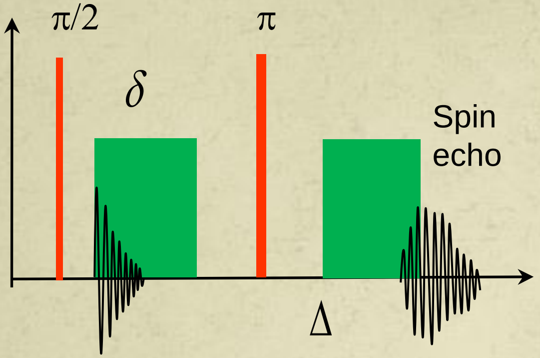


Velocity autocorrelation spectrum of polymer in melt

$$FT\left[\frac{1}{2}\frac{d^2\langle\Delta x^2(t)\rangle}{dt^2}\right] = D(\omega)$$



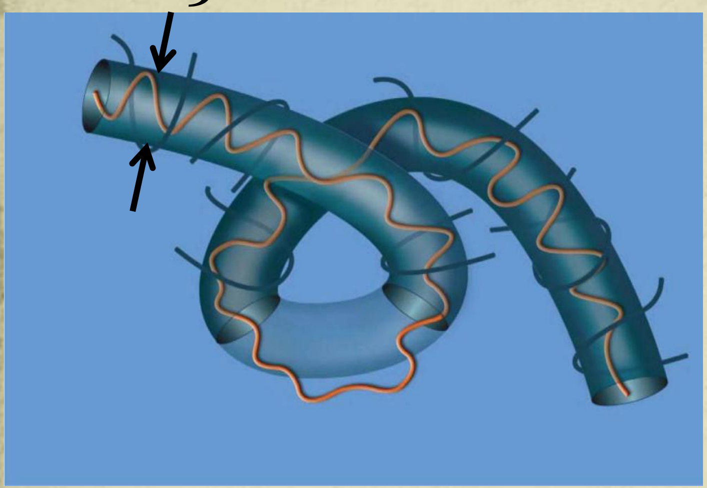
Polymer reptation-like motion by PGSE δ-dependence

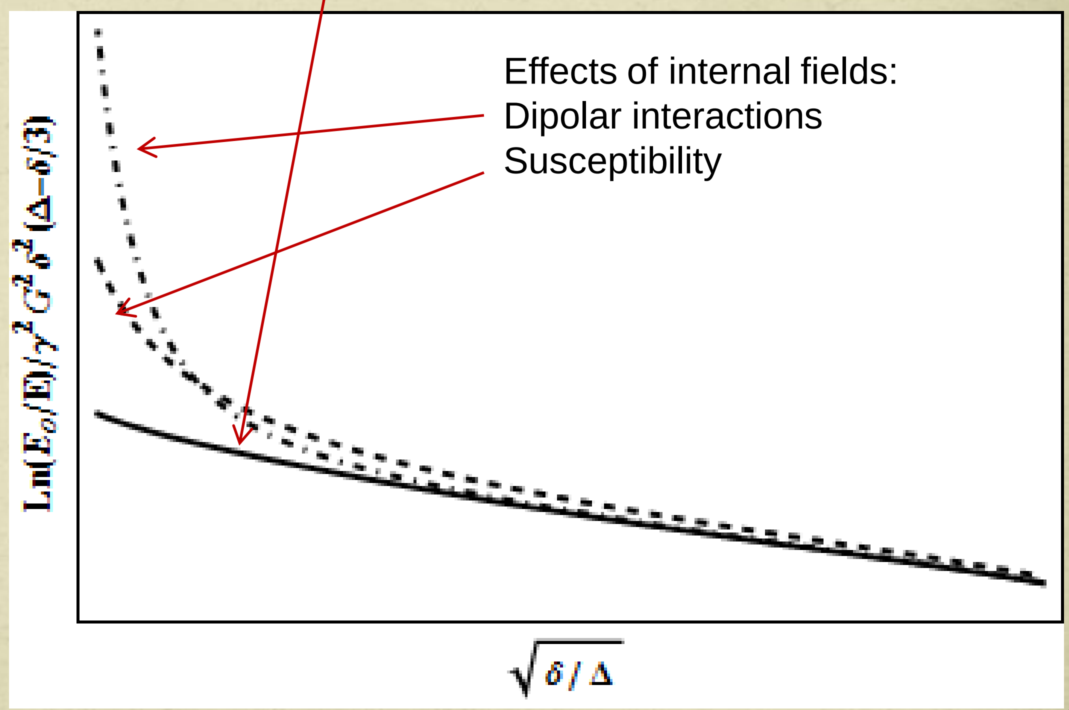


$$\beta_i(\tau) = \frac{1}{\pi}\int_0^\infty q^2(\omega,\tau).D_i(\omega)\,d\omega$$

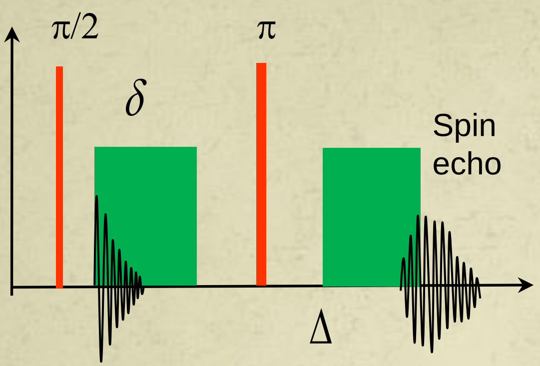
$$D(\delta) \approx D_c + \frac{d\sqrt{D_{rept}}}{\sqrt{\Delta}}\left(1 - \frac{8}{15}\sqrt{\frac{\delta}{\Delta}} + ...\right)$$

d~5-8 nm





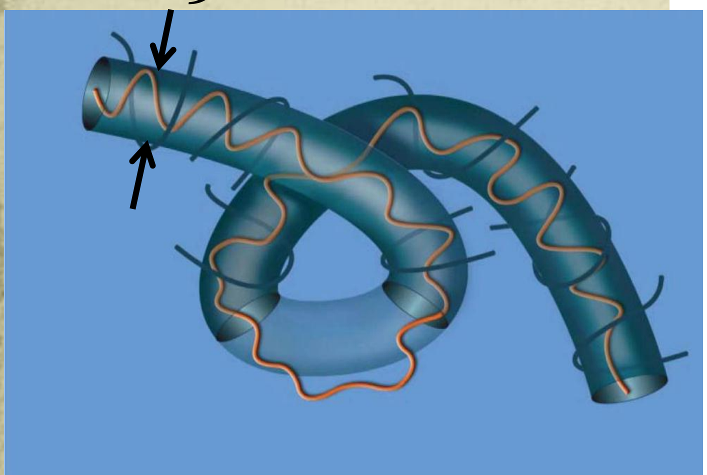
Verification of polymer reptation-like motion by PGSE

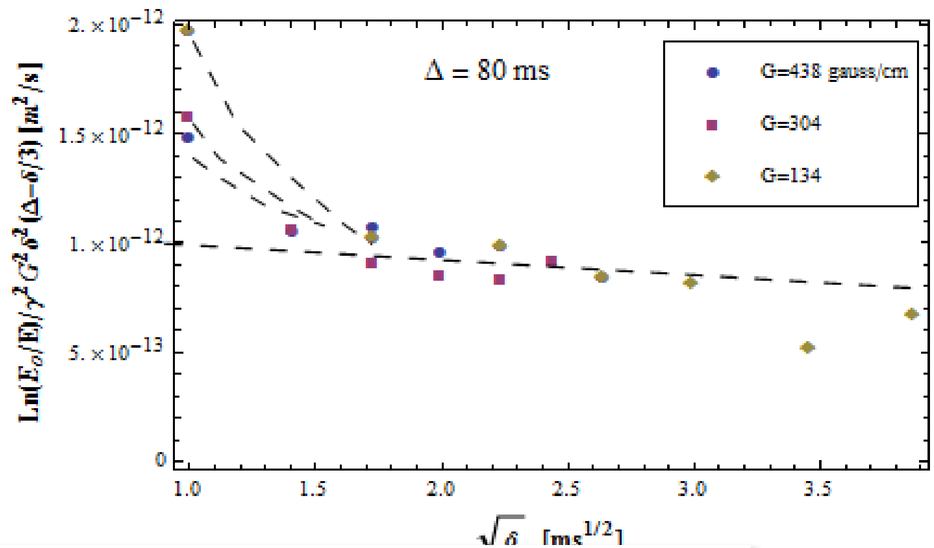


$$\beta_i(\tau) = \frac{1}{\pi}\int_0^\infty q^2(\omega,\tau).D_i(\omega)d\omega$$

$$D(\delta) \approx D_c + \frac{d\sqrt{D_{rept}}}{\sqrt{\Delta}}(1 - \frac{8}{15}\sqrt{\frac{\delta}{\Delta}} + ...)$$

d~5-8 nm





NMR self-diffusion study of polyethylene and paraffin melts
Zupančič, I. Lahajnar, G.; Blinc, R.; Reneker, D.H.; Vanderhart, D.L.
Journal of Polymer Science, Polymer Physics Edition, 23, 387-404 (1985)

Thanks for your attention!