Diffusion and flow dynamics in porous media by nmr spin echo

Janez Stepišnik,
University of Ljubljana, FMF, Physics Department and J Stefan Institute, Ljubljana, Slovenia

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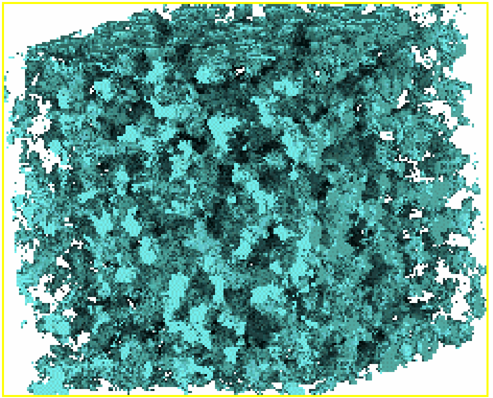
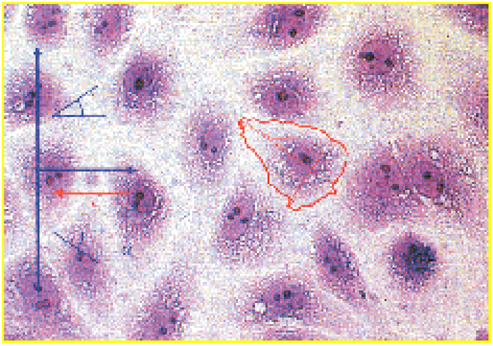
Molecular motion in heterogeneous structures by NMR

MEDIA:

- materials for distillation, filtration,catalysis….
- chromatographic sieves
- colloids and bio-colloids (viruses, bacteria)
- soil, concrete, rocks or clays
- biologic tissues etc





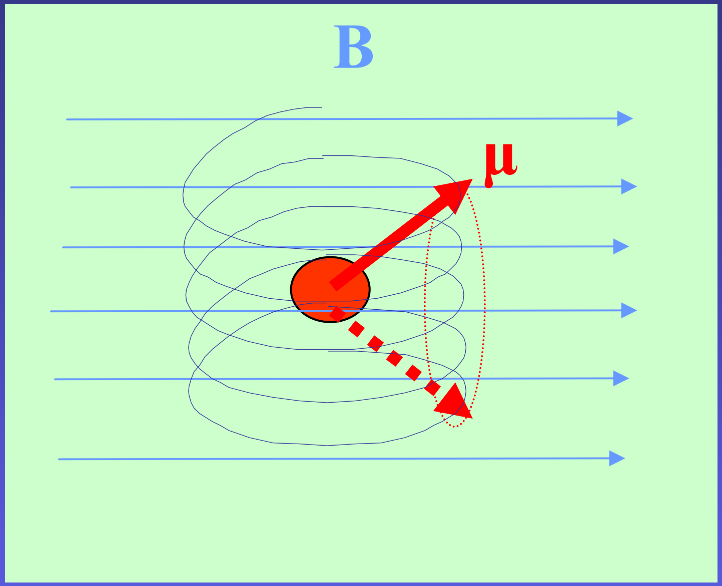
pore size:
$10^{-2} – 10^{-10}$ m

METHOD:

Analysis and interpretation of diffusion and flow measurement by the gradient spin echo:

- averaged propagator approach (Torrey method)
- Gaussian phase approximation (Hahn-Carr-Purcell method)

Spin in magnetic field- magnetic resonance



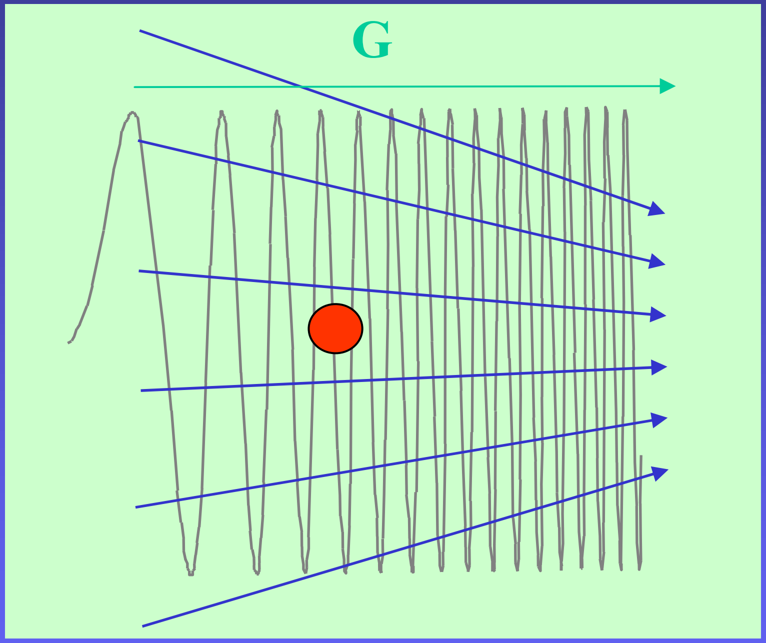
$$\frac{\partial \boldsymbol{\mu}}{\partial t} = \gamma\, \mathbf{B}(\mathbf{r},t) \times \boldsymbol{\mu}$$

μ=*magnetic moment*
B=*magnetic field*

$$E(\tau) \approx e^{i\omega_L t}$$

$$\omega_L = \gamma\, B$$

Spin in non-uniform magnetic field



$$\mathbf{B} = \mathbf{B}_o + \mathbf{B}_{inh}(\mathbf{r})$$

applied or internal magnetic fields

$$\mathbf{B}_{inh}(\mathbf{r}) = \underline{\mathbf{G}}.\mathbf{r}$$

magnetic field gradient

$$E(\tau) \approx e^{i\int_0^\tau \omega\left[t, \boxed{\mathbf{r}(t)}\right]dt}$$

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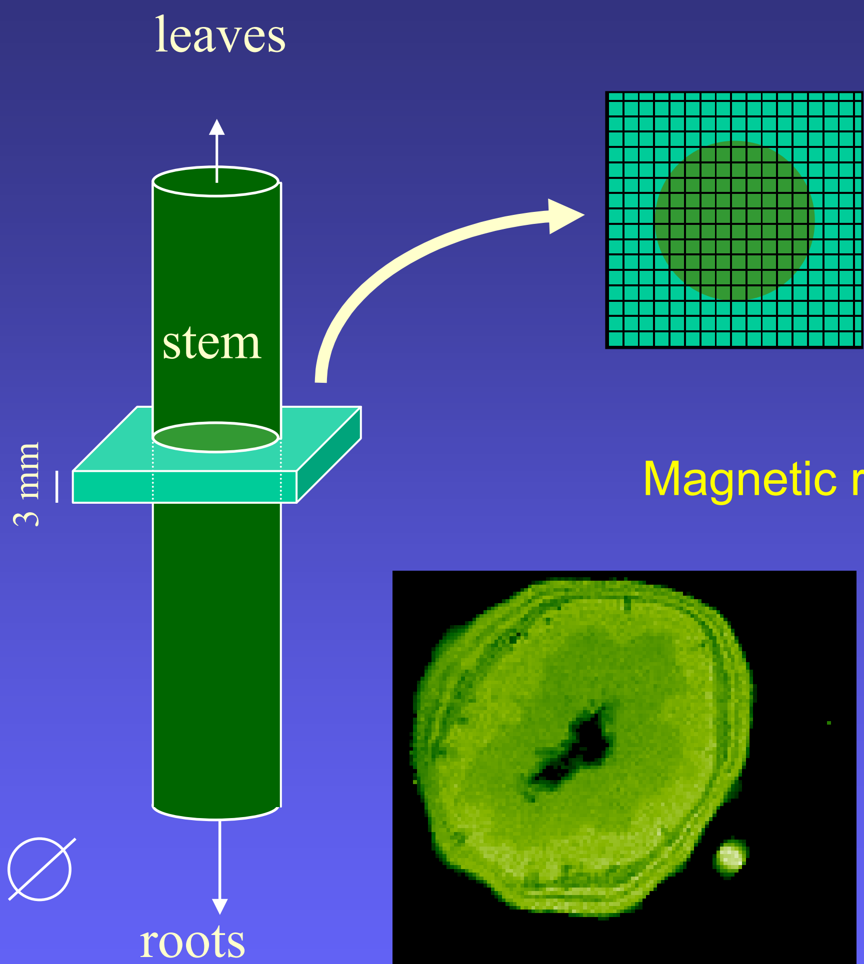
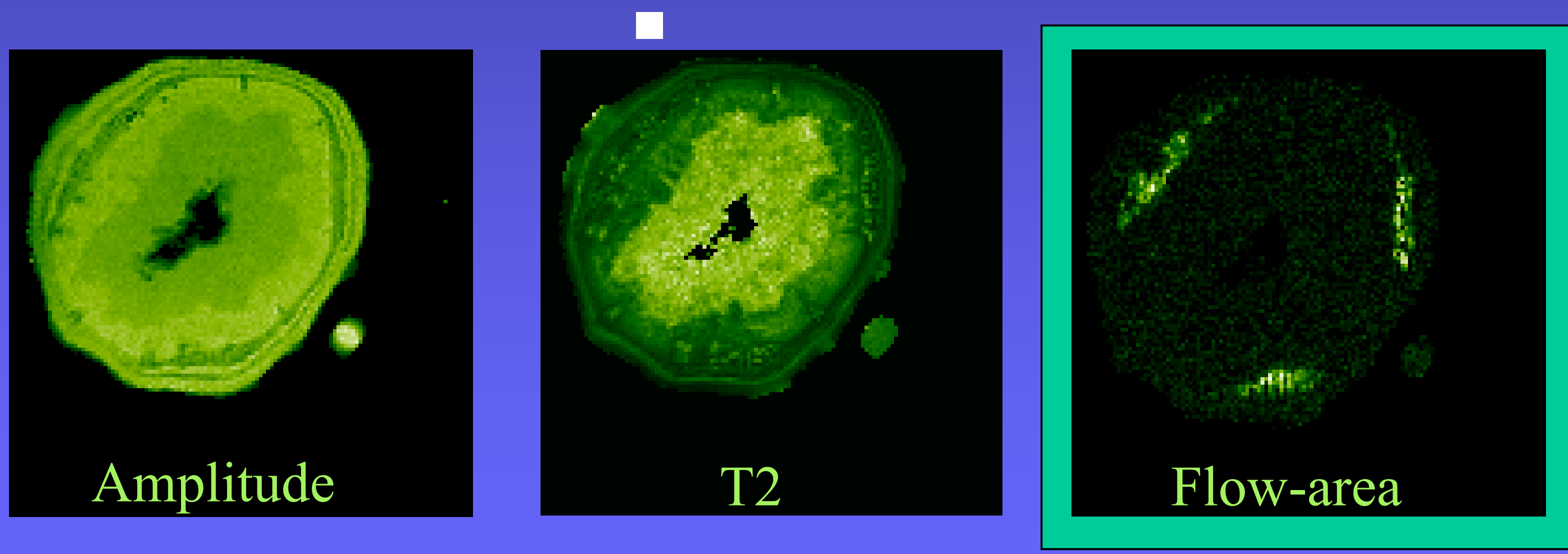
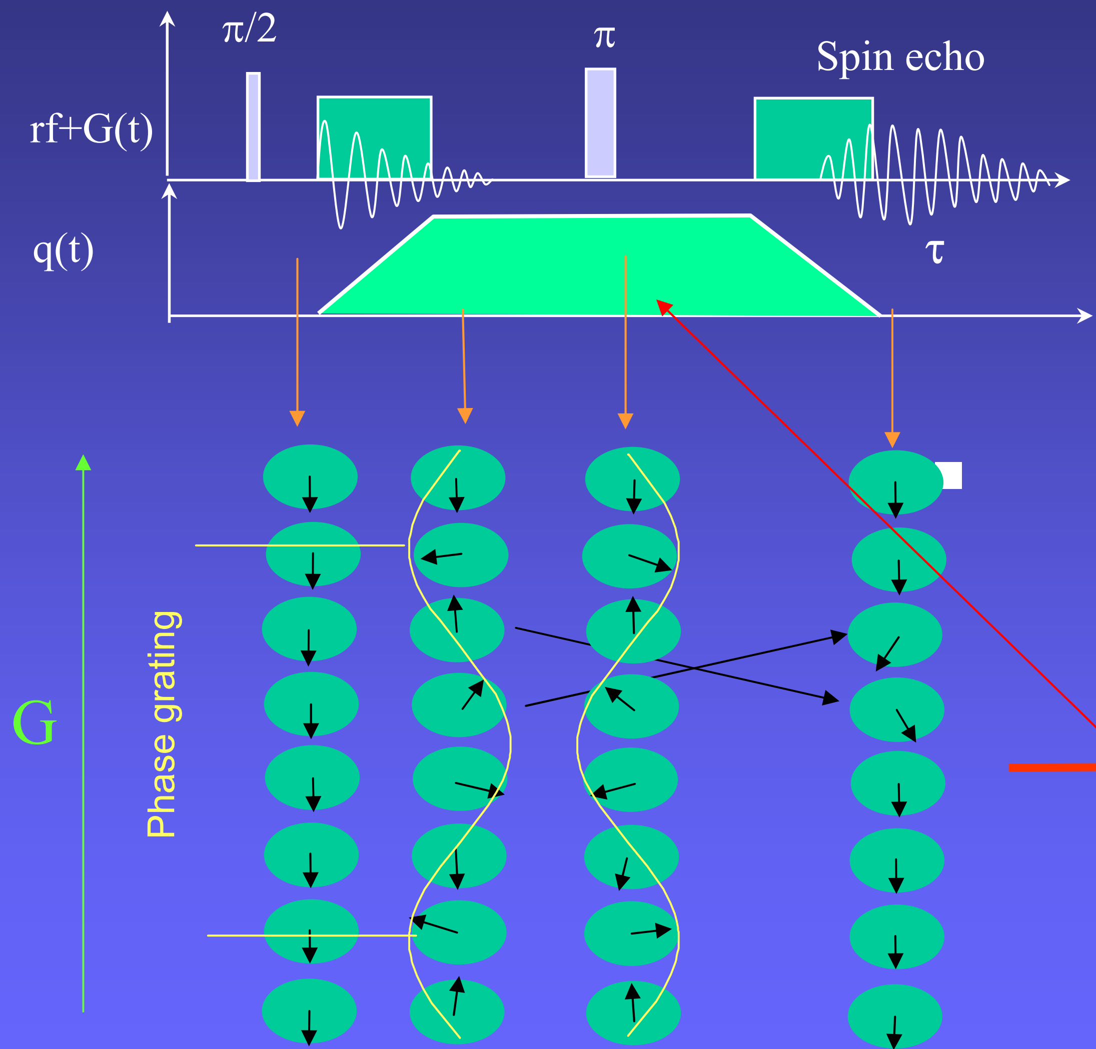
NMR imaging



Magnetic resonance imaging of tomato plant stem



Encoding of spin motion by spin echo



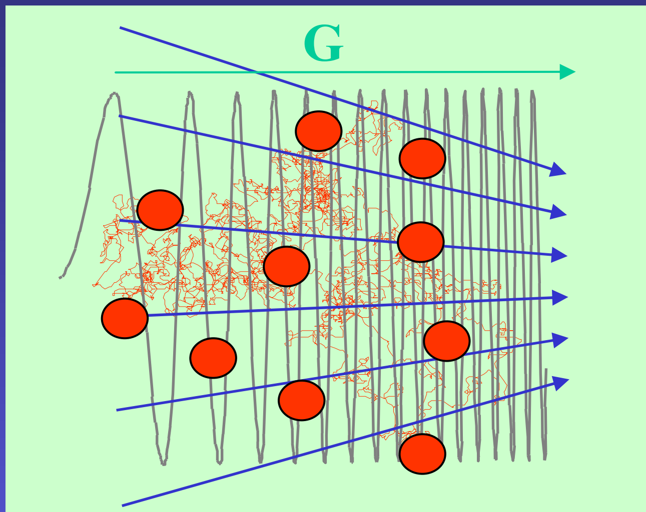
Hahn, E. L., **Spin-echoes**, Phys. Rev., 80, 580-94 (1950)

Applied MFG

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

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

Molecular motion and spin echo: approaches



H.C. Torrey. **Bloch equations with diffusion terms**, Phys. Rev., 104, 563-565, 1956

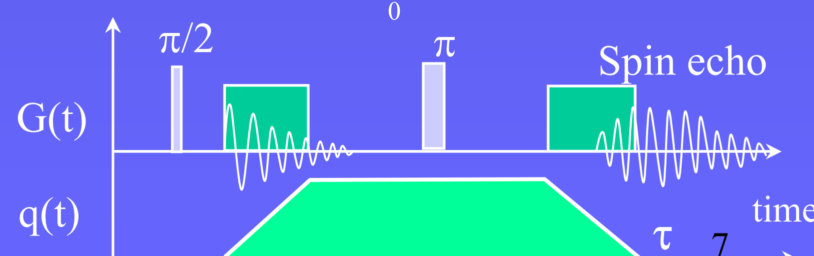
$$\frac{\partial \mathbf{m}}{\partial t} = \gamma\, \mathbf{B}(\mathbf{r},t)\times \mathbf{m} + \boxed{\nabla\left(\underline{\mathbf{D}}(\mathbf{r})\nabla\right)\mathbf{m}}$$

m=*magnetization density*
D=*self-diffusion tensor*

$$E(\tau) \approx \sum_i \left\langle e^{\,i\gamma\int_0^\tau \mathbf{q}(t).\mathbf{v}_i(t)dt} \right\rangle \approx \sum_i e^{-\int_0^\tau \mathbf{q}(t).\underline{\mathbf{D}}_i.\mathbf{q}(t)dt}$$

free diffusion

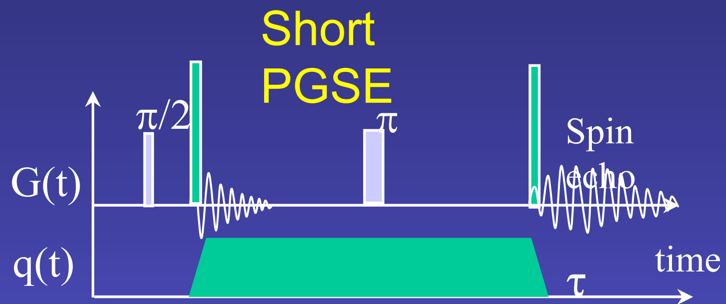
$$\mathbf{q}(t) = \gamma\int_0^t \mathbf{G}_{eff}(t')dt'$$



E.L.Hahn, **Spin-echoes**, Phys. Rev. 80, 580-94 (1950),

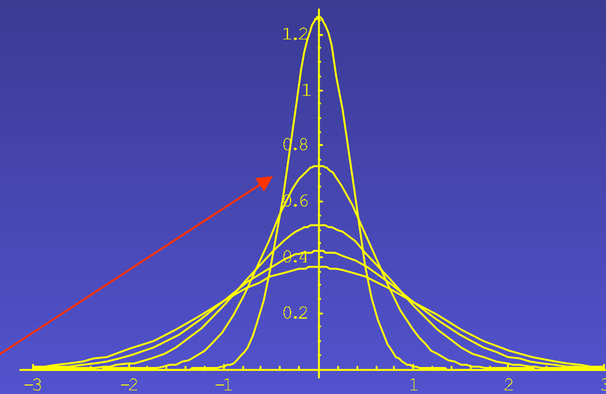
H. Y. Carr and E. M. Purcell, **Effects of diffusion on free precession in nuclear magnetic resonance**, Phys. Rev. 94 , 630-38 (1954)

Spin echo as Fourier transform of probability function



free isotropic diffusion

Probability function



$$\mathbf{q} = \gamma\,\delta\,\mathbf{G}$$

$$E(q,\tau) = \sum_i e^{-\int_0^\tau \mathbf{q}(t).\underline{\mathbf{D}}_i.\mathbf{q}(t)dt} = \sum_i e^{-q^2 D_i \tau}$$

q-space Fourier transform

$$= \sum_i \int \boxed{\frac{1}{\sqrt{4\pi D\tau}}\, e^{-\frac{\mathbf{R}^2}{4D\tau}}}\, e^{iqZ}\, d\mathbf{R}$$

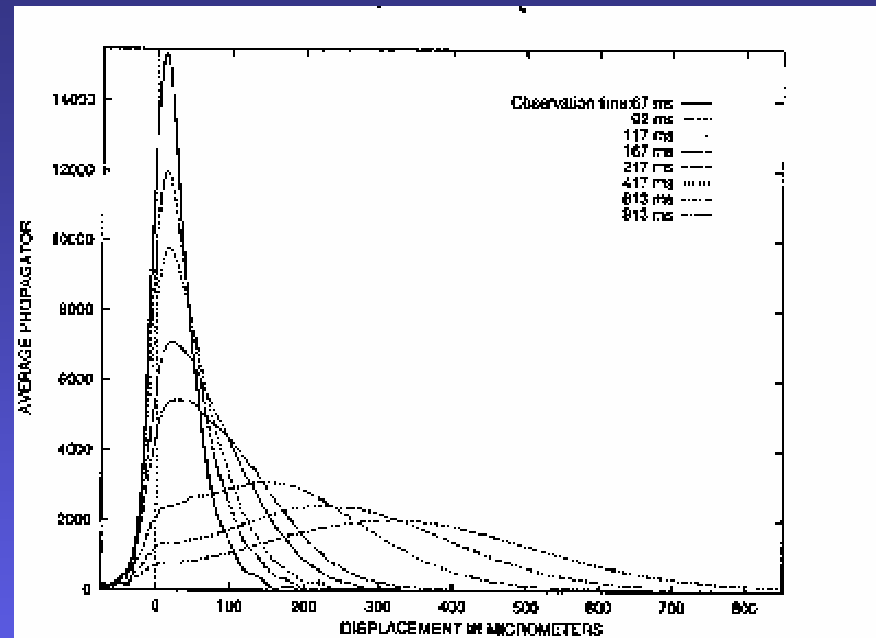
$$E(\mathbf{q},\tau) = N\int P(\mathbf{R},\tau)\, e^{i\mathbf{q}.\mathbf{R}}\, d\mathbf{R}$$ - propagator

J. Karger and W. Heink. **The propagator representation of molecular transport in microporous crystallites** , J. Magn. Reson. 51, 1-7 (1983)

Probability distribution of flow in porous media

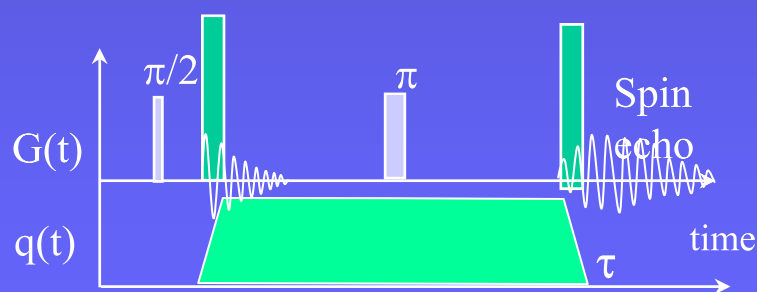
$$E(\mathbf{q},\tau)=\sum_i \int P(\mathbf{r},\tau\,|\,\mathbf{r}_i,0)\; e^{i\mathbf{q}(\mathbf{r}_i-\mathbf{r})}\,d\mathbf{r}$$

q-space Fourier transform of spin echo can provide probability distribution of flow dispersion



e 2. The variation of $P_\Delta(X)$ with Δ for displacements X measured along the axial direction of the cylindrical sample.

Short PGSE



K.J. Packer, J.J. Tessier, **The characterization of fluid transport in a porous solids by pulsed gradient stimulated echo NMR**, Mol. Physics 87, 267-72 (1996)

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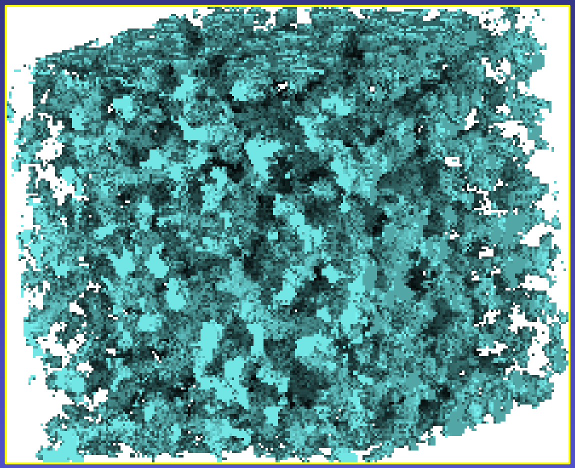
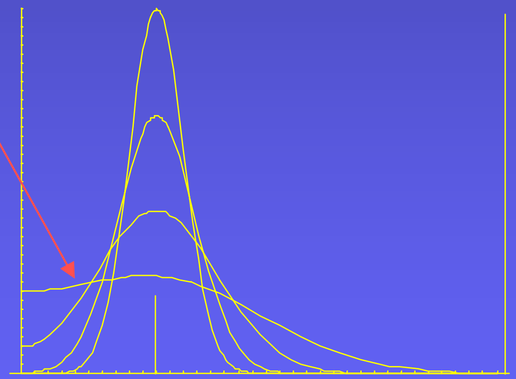
Restricted diffusion and propagator method



Propagator of restricted diffusion

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

$$P(\mathbf{r}',\tau \mid \mathbf{r},0) = \sum_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r})\, u_{\mathbf{k}}^{*}(\mathbf{r}')\, e^{-\mathbf{k}^2 D\tau}$$



$$E(\tau,\mathbf{q}) = \sum_i \int P(\mathbf{r}_i + \mathbf{R},\tau \mid \mathbf{r}_i,0)\, e^{i\mathbf{q}\mathbf{R}} d\mathbf{R} = N\int \overline{P(\mathbf{R},\tau)}\; e^{i\mathbf{q}\mathbf{R}} d\mathbf{R}$$

$$\overline{P(\mathbf{r},\tau)} = \frac{1}{N}\sum_i P(\mathbf{r}_i + \mathbf{R},\tau \mid \mathbf{r}_i,0)$$

Spin echo diffraction-like effect in porous media and propagator method

Spin echo of restricted diffusion

$$P(\mathbf{r}',\tau\,|\,\mathbf{r},0)=\sum_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r})\,u_{\mathbf{k}}^{*}(\mathbf{r}')\,e^{-\mathbf{k}^2 D\tau}$$

$$E(\tau,\mathbf{q})\approx\sum_{\mathbf{k}} S_{\mathbf{k}}(\mathbf{q})\,S_{\mathbf{k}}^{*}(\mathbf{q})\,e^{-\mathbf{k}^2 \mathrm{D}\tau}$$

In the long time limit:

$$E(\infty,\mathbf{q})\underset{\tau\to\text{long}}{\approx}\left|S_0(\mathbf{q})\right|^2=\left|\int_{Vol} e^{i\mathbf{q}\cdot\mathbf{r}}\,d\mathbf{r}\right|^2$$

like Fraunhofer diffraction in optics

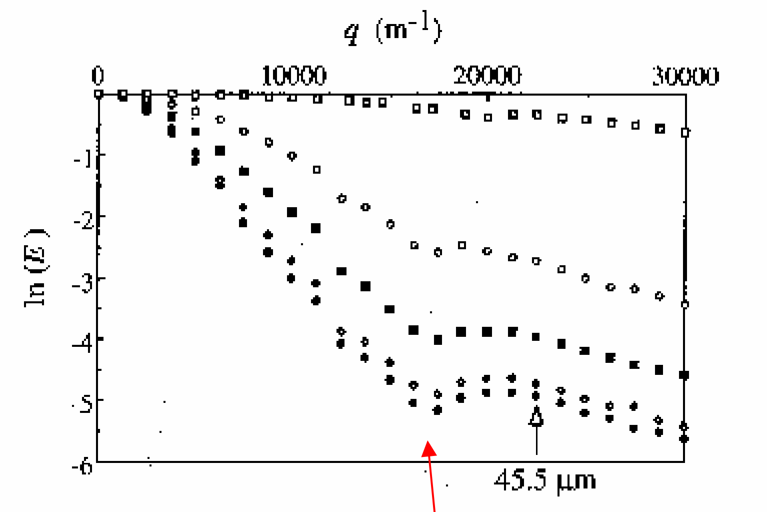
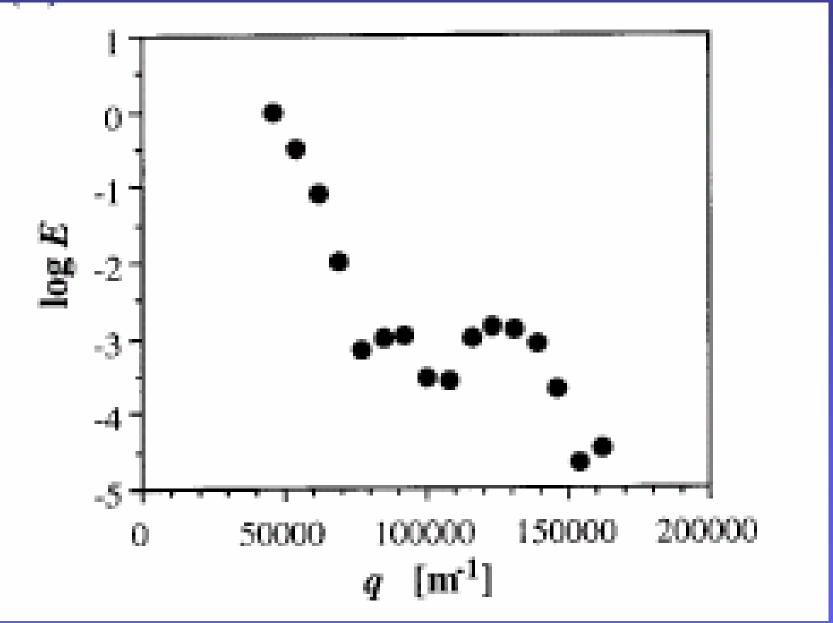


FIG. 2. Spin-echo-attenuation function for the direction transverse to the flow. The coherence peak is shifted to higher q, indicating a correlation length of the order of a sphere radius 45.5 μm. The velocities are (□) 0, (○) 3.3, (■) 8.7, (◇) 17.5, and (●) 21.8 mm/s.

$$q\,a=2\pi\,n$$

P. T. Callaghan, A. Coy, D. MacGowan, K. J. Packer and F. O. Zelaya, **Diffraction-like effects in NMR diffusion studies of fluids in porous solids,** Nature , 351, 467-9 (1991)

Flow and spin echo diffraction-like effect



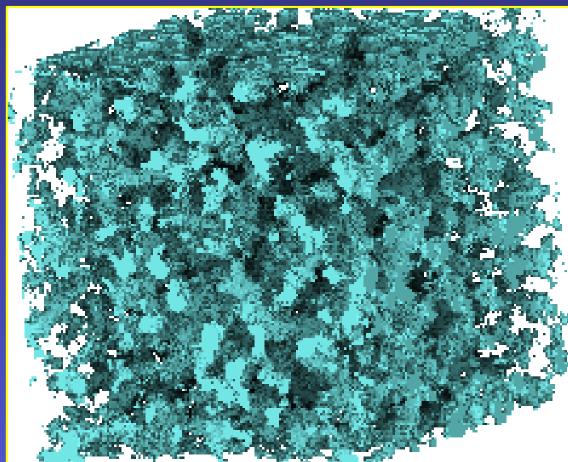
B. MANZ, J.D. SEYMOUR, AND P. T. CALLAGHAN, PGSE NMR Measurements of Convection in a Capillary, JOURNAL OF MAGNETIC RESONANCE **125,** 153–158 (1997)

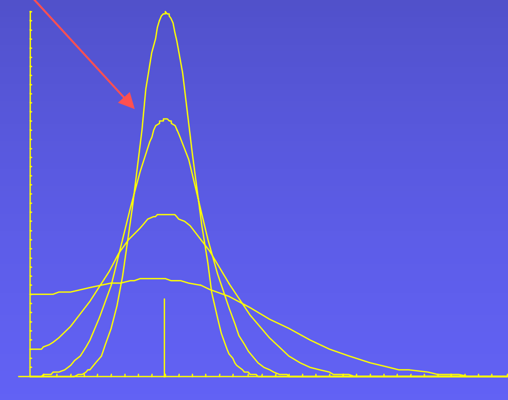
Spin echo of restricted diffusion with propagator method

Propagator of restricted diffusion

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

$$P(\mathbf{r}', \tau \mid \mathbf{r}, 0) = \sum_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r})\, u_{\mathbf{k}}^{*}(\mathbf{r}')\, e^{-\mathbf{k}^2 D\tau}$$





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

$$\overline{P(\mathbf{r}, \tau)} = \frac{1}{N} \sum_i P(\mathbf{r}_i + \mathbf{R}, \tau \mid \mathbf{r}_i, 0)$$

ensemble average $\longrightarrow$ **averaged propagator**

$\downarrow$

Spin echo by the cumulant expansion

$$E(\mathbf{q},\tau)=\sum_i \int P(\mathbf{r},\tau\,|\mathbf{r}_i)\,e^{iq.(z-z_i)}d\mathbf{r}=\sum_i\sum_{n=0}\frac{(iq)^n}{n!}M_{ni}(\tau)$$ Taylor series

$$\mathbf{q}.\mathbf{r}=q.z$$

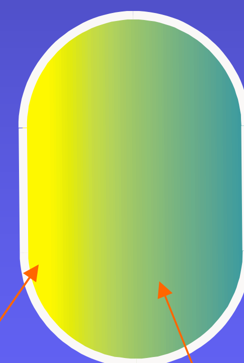
$$M_{ni}(\tau)=\int P(\mathbf{r},\tau\,|\mathbf{r}_i)(z-z_i)^n\,d\mathbf{r}\qquad =\sum_i e^{\sum_{n=1}\frac{(iq)^n}{n!}K_{ni}(\tau)}$$ Cumulant expansion

$$K_{1i}=M_{1i}=\langle z-z_i\rangle=\langle Z_i\rangle$$

$$K_{2i}=M_{2i}-M_{1i}^{\;2}=\left\langle\left(Z_i-\langle Z_i\rangle\right)^2\right\rangle=\langle\Delta Z_i^2\rangle$$

$$K_{3i}=M_{3i}-3M_{2i}M_{1i}+M_{1i}^{\;3}=\left\langle\left(Z_i-\langle Z_i\rangle\right)^3\right\rangle=\langle\Delta Z_i^3\rangle$$

$$K_{4i}=M_{4i}-6M_{1i}^{\;4}+12M_{1i}^{\;2}M_{2i}-3M_{2i}-4M_{1i}M_{3i}=\ldots.$$

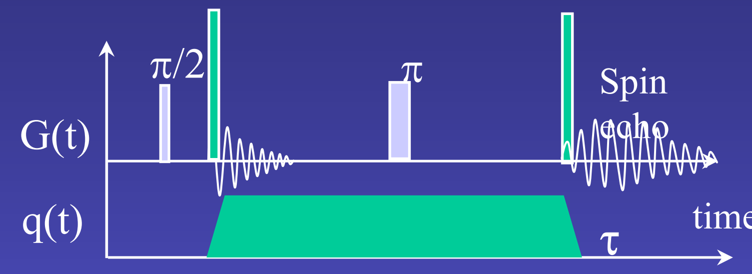


Gaussian phase approximation (GPA)

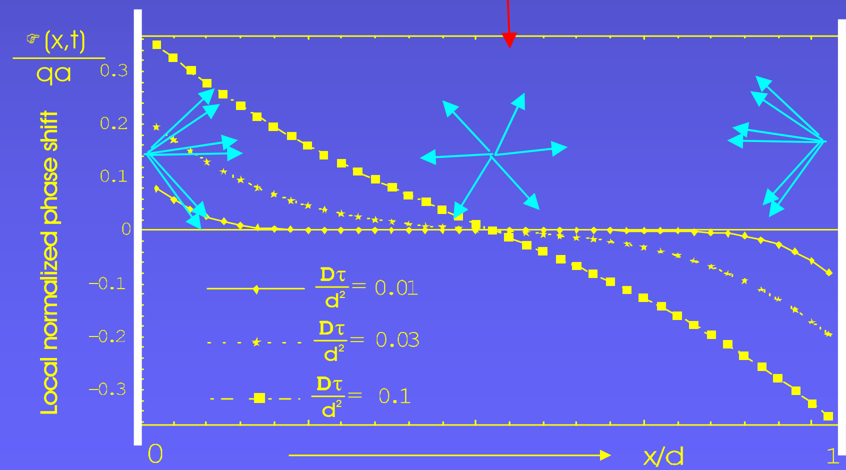
$$\boxed{E(q,\tau)=\sum_i e^{iq.\langle Z_i(\tau)\rangle-\frac{1}{2}q^2.\langle\Delta Z_i^2(\tau)\rangle\ldots}}$$

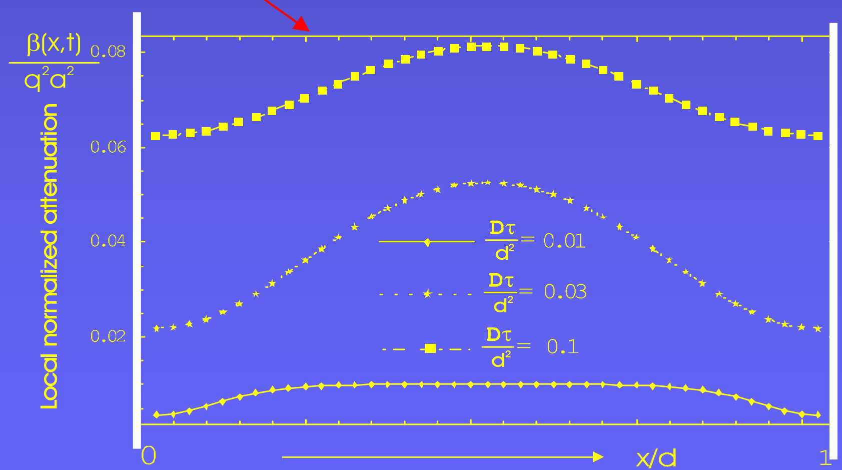
Distribution of phase and attenuation in the pore: short PGSE with the Gaussian phase approximation

Short PGSE



$$E(q,\tau)=\sum_i e^{iq.\langle Z_i(\tau)\rangle-\frac{1}{2}q^2.\langle \Delta Z_i^2(\tau)\rangle\ldots}$$



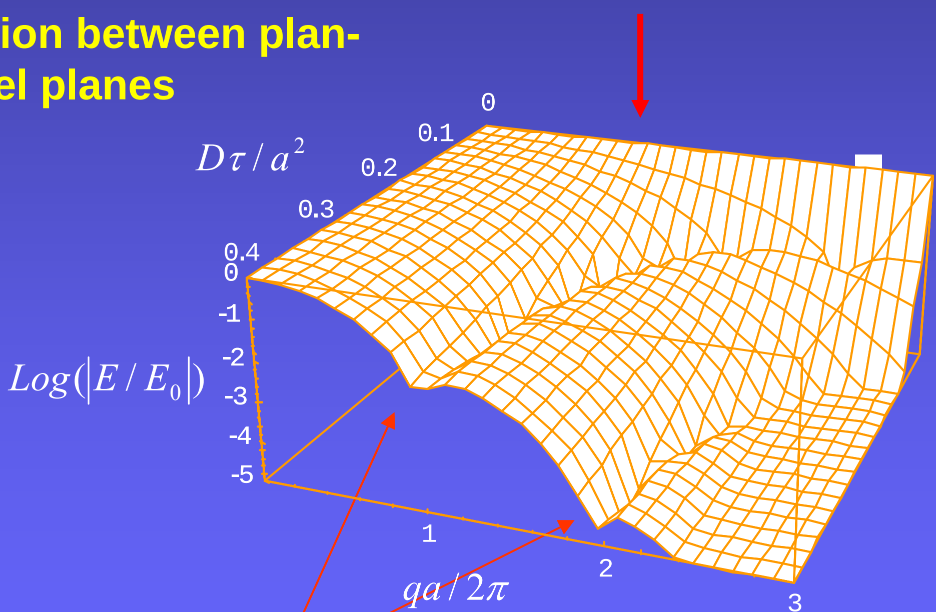


Diffusion between plan-parallel planes

Spin echo diffusive diffraction by the cumulant expansion in GPA

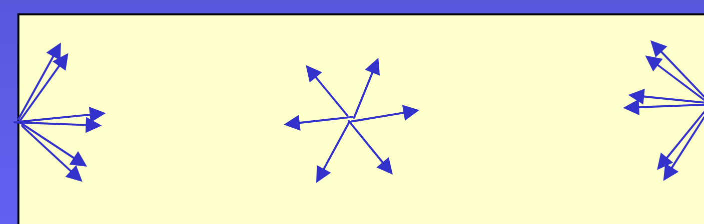
$$E(q,\tau) = \sum_i e^{iq.\langle Z_i(\tau)\rangle - \frac{1}{2}q^2.\langle \Delta Z_i^2(\tau)\rangle} \Rightarrow \int e^{iq.\langle Z(\mathbf{r},\tau)\rangle - \frac{1}{2}q^2.\langle \Delta Z^2(\mathbf{r},\tau)\rangle} d\mathbf{r}$$

Diffusion between plan-parallel planes



$qa = 2\pi n$ $\qquad$ $q = \gamma G \delta$

Diffraction-like effect results from phase interference of spins scattering at opposite boundaries.



$e^{iq.\langle Z(\tau)\rangle}$ $\qquad$ $e^{-iq.\langle Z(\tau)\rangle}$

$\cos(q.\langle Z(\tau)\rangle)$

J. Stepišnik, **A new view of the spin echo difusive diffraction in porous structures,** Europhysics Letters, 60, 353-9 (2002)

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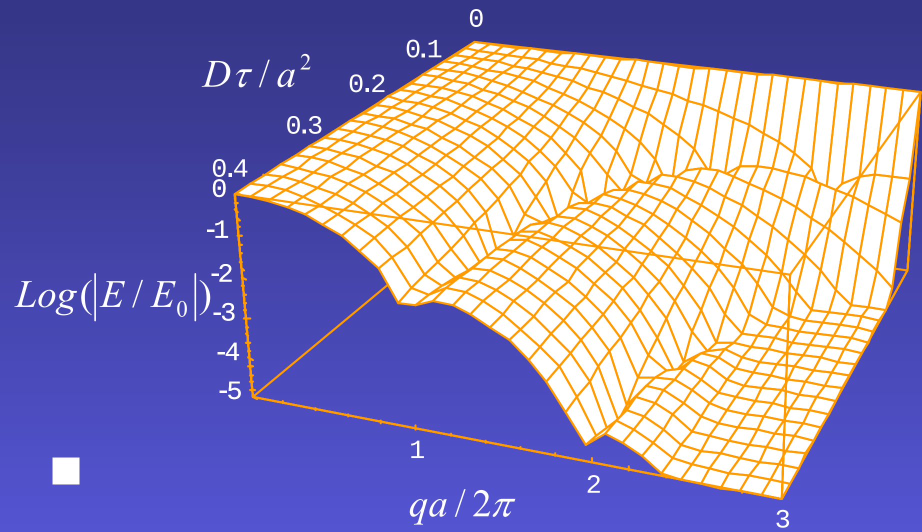
Diffusive diffraction

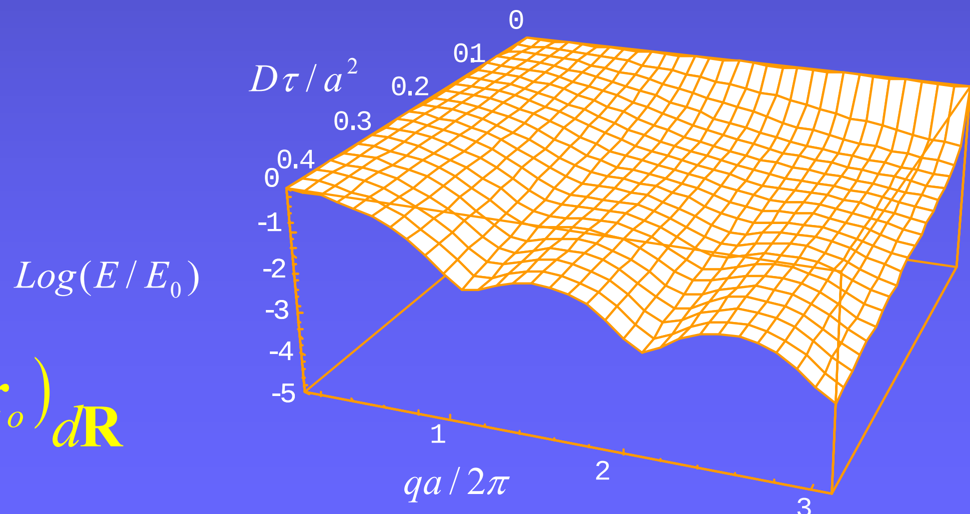
GPA method

$$E(q,\tau)=\sum_i e^{iq.\langle Z_{\mathrm{i}}(\tau)\rangle-\frac{1}{2}q^2.\langle \Delta Z_i^2(\tau)\rangle\ldots}$$

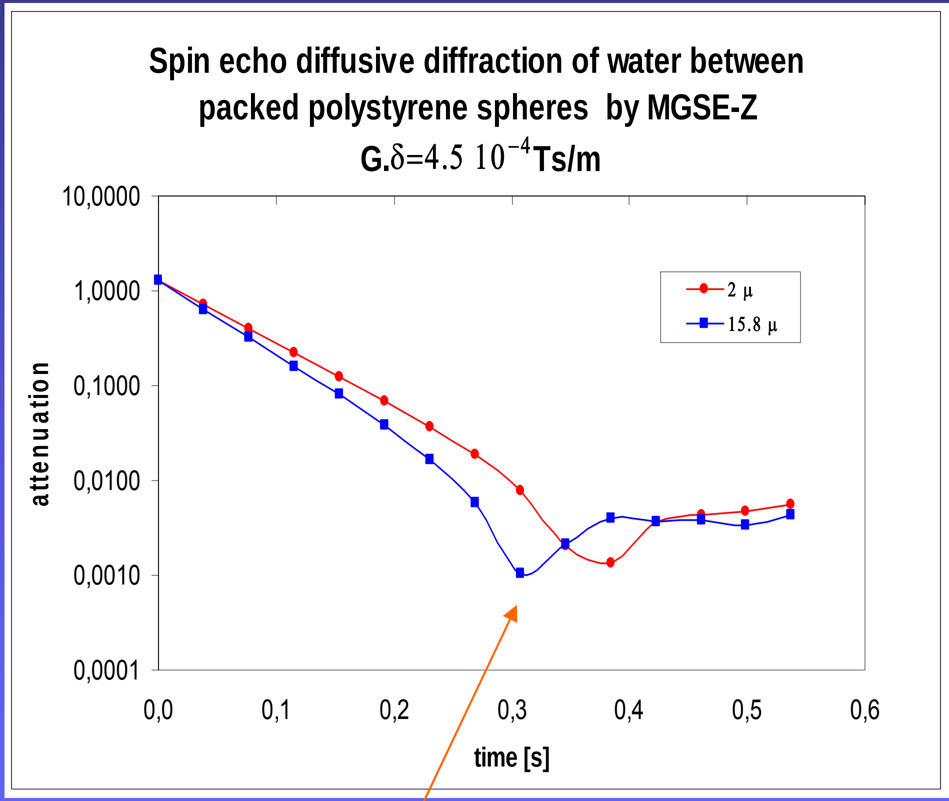


Propagator method

$$E(\tau,\mathbf{q})=\iint\rho(\mathbf{r}_o)P(\mathbf{r},\tau\,|\,\mathbf{r}_o,0)e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}_o)}d\mathbf{R}$$



Diffraction-like effect in spin echo time dependence



$$q\,\Delta z = 2\pi$$

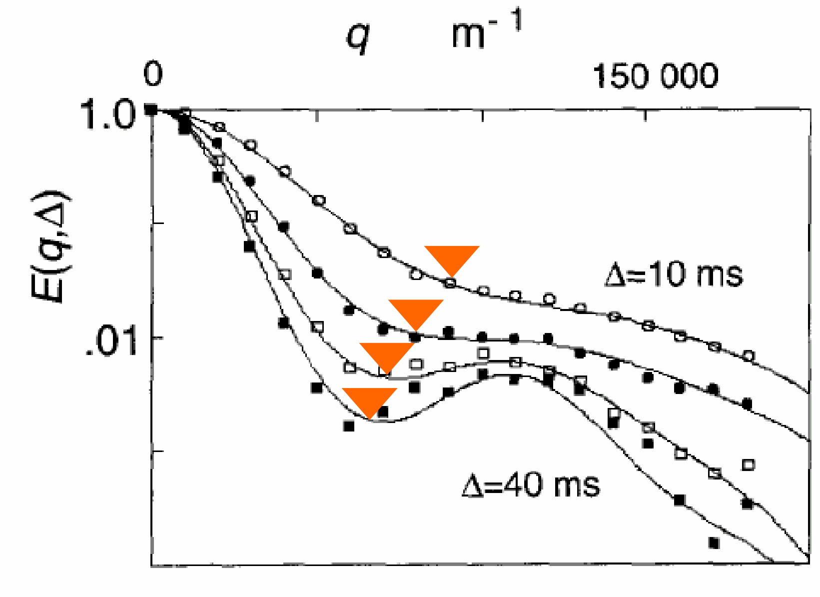


Fig. 6. Echo attenuation function $E(q,\Delta)$ as a function of q for water diffusing in the interstices between a close-packed 9.870 μm polystyrene sphere system (see A. Coy and P.T. Callaghan, Ref. 19). The times, Δ, are 10 ms (circles), 20 ms (filled circles), 30 ms (squares), 40 ms (filled squares).

P. T. Callaghan, **NMR imaging, NMR diffraction..** MRI, 14, 701 (1996)

Averaged propagator by GPA

$$E(\mathbf{q},\tau)=\sum_i e^{iq.\langle Z_i(\tau)\rangle-\frac{1}{2}q^2.\langle \Delta Z_i^2(\tau)\rangle}=\int \overline{P(\mathbf{R},\tau)}e^{i\mathbf{q}.\mathbf{R}}d\mathbf{R}$$

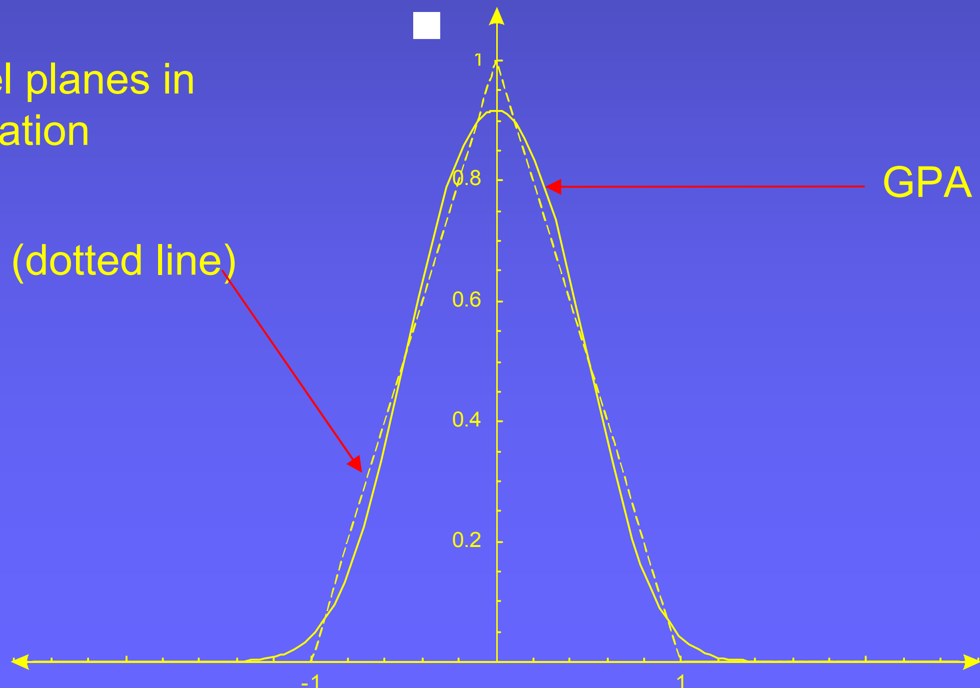
q-space Fourier transform

$$\overline{P(\mathbf{R},\tau)}=\sum_i\frac{1}{\sqrt{2\pi\langle \Delta Z_i^2(\tau)\rangle}}\exp\left[-\frac{\left(\mathbf{R}-\langle Z_i(\tau)\rangle\right)^2}{2\langle \Delta Z_i^2(\tau)\rangle}\right]\Rightarrow\int\frac{1}{\sqrt{2\pi\langle \Delta Z^2(\mathbf{r},\tau)\rangle}}\exp\left[-\frac{\left(\mathbf{R}-\langle Z(\mathbf{r},\tau)\rangle\right)^2}{2\langle \Delta Z^2(\mathbf{r},\tau)\rangle}\right]d\mathbf{r}$$

diffusion between parallel planes in long time approximation

propagator method (dotted line)

GPA method



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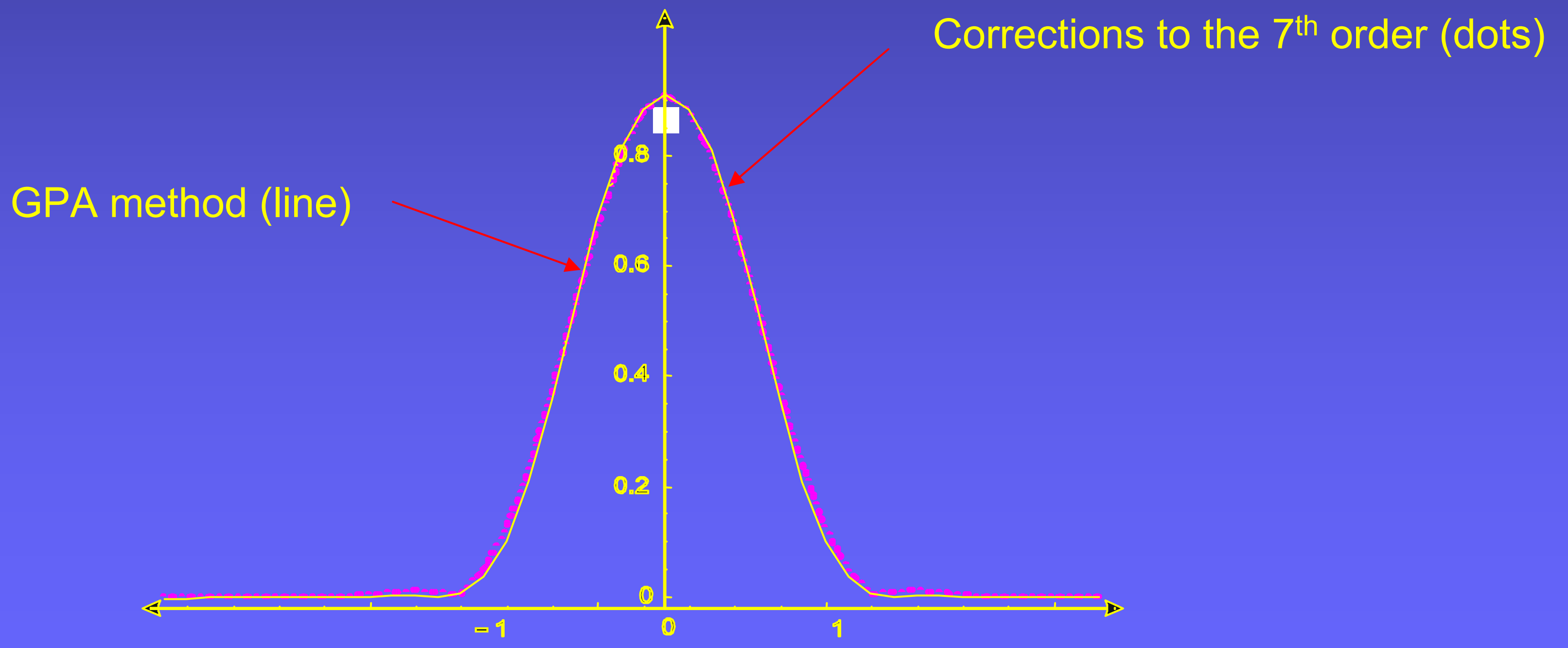
GPA propagator vs. averaged propagator

q-space Fourier transformation

$$E(\mathbf{q},\tau)=\int \overline{P(\mathbf{R},\tau)}e^{i\mathbf{q}.\mathbf{R}}d\mathbf{R}=\sum_i e^{iq.\langle Z_i(\tau)\rangle-\frac{1}{2}q^2.\langle \Delta Z_i^2(\tau)\rangle \quad -\frac{i}{6}q^3.\langle \Delta Z_i^3(\tau)\rangle+\frac{1}{24}q^4.\langle \Delta Z_i^4(\tau)\rangle+\frac{i}{120}q^5..}$$



Fast convergence of cumulant series

Cumulant expansion with ensemble average

$$E(\mathbf{q},\tau) = N\int \overline{P(\mathbf{R},\tau)}\; e^{i\mathbf{q}.\mathbf{R}}\, d\mathbf{R} = N\sum_{n=0} \frac{(iq)^n}{n!}\overline{M_n}(\tau)$$

Taylor series

$$= N e^{\sum_{n=1} \frac{(iq)^n}{n!}\overline{K_n}(\tau)}$$

Cumulant series   without odd terms

$$\overline{M_n}(\tau) = \int \overline{P(\mathbf{R},\tau)}\; Z^n\, d\mathbf{R} = \frac{1}{N}\sum_i \int P(\mathbf{r},\tau|\mathbf{r}_i)(z-z_i)^n\, d\mathbf{r}$$

$$\overline{K_1} = \overline{M_1} = \overline{\langle Z\rangle} = 0$$

$$\overline{K_2} = \overline{M_2} - \overline{M_1}^2 = \overline{\langle Z^2\rangle}$$

$$\overline{K_3} = \overline{M_3} - 3\overline{M_2}\,\overline{M_1} + \overline{M_1}^3 = \overline{\langle Z^3\rangle} = 0$$

$$\overline{K_4} = \overline{M_4} - 6\overline{M_1}^4 + 12\overline{M_1}^2\,\overline{M_2} - 3\overline{M_2}^2 - 4\overline{M_1}\,\overline{M_3} = \overline{\langle Z^4\rangle} - 3\overline{\langle Z^2\rangle}^2$$

Coarse graining in space

Ensemble average and low-q spin echo

$$E(\mathbf{q},\tau) \Rightarrow \sum_i e^{i\mathbf{q}.\boldsymbol{\varphi}'_i(\tau) - \mathbf{q}^2.\left[\beta_i(\tau) - \frac{1}{2}\boldsymbol{\varphi}'^2_i(\tau)\right]}$$

$$\boldsymbol{\varphi}'_i = \langle \mathbf{r}_i - \mathbf{r}_{io} \rangle$$

$$\beta'_i = \langle (\mathbf{r}_i - \mathbf{r}_{io})^2 \rangle$$

Cumulant expansion with respect to average over ensemble of spins

$$E(\mathbf{q},\tau) \Rightarrow N e^{i\mathbf{q}.\overline{\boldsymbol{\varphi}'(\tau)} - \mathbf{q}^2.\overline{\beta'(\tau)} + \cancel{i\mathbf{q}^3.\Delta\boldsymbol{\varphi}'(\tau)\Delta\beta'(\tau) + \mathbf{q}^4\Delta\beta'^2(\tau)} + \ldots}$$

$$\overline{\boldsymbol{\varphi}'} = \frac{1}{N}\sum_i \boldsymbol{\varphi}'_i \qquad \overline{\beta'} = \frac{1}{N}\sum_i \beta'_i - \frac{1}{2}\overline{\boldsymbol{\varphi}'}^2 \qquad \Delta\beta'^2 = \frac{1}{4N}\sum_i \left(\frac{1}{N}\sum_j (\beta'_i - \beta'_j)^2 - \frac{1}{3}\boldsymbol{\varphi}'^4_i \right)$$

GPA condition for the diffusion in closed pore

$$\mathbf{q}^2\Delta\beta' << \frac{\overline{\boldsymbol{\varphi}'}}{\Delta\boldsymbol{\varphi}'}, \frac{\overline{\beta'}}{\Delta\beta'}$$

$$q.\xi(t) < 1$$

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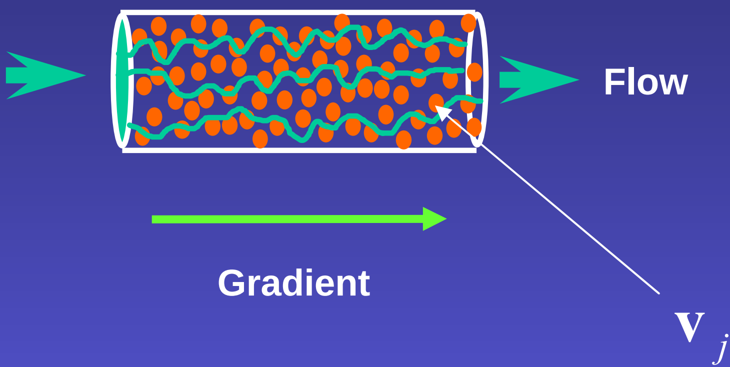
Gaussian phase approximation of spin echo

$$E(\mathbf{q},\tau)=\sum_i e^{iq.\langle Z_i(\tau)\rangle-\frac{1}{2}q^2.\langle\Delta Z_i^2(\tau)\rangle}$$

•Gaussian phase approximation is a sufficient condition for the spin echo of diffusion in enclosed pore as long as q|Z(τ)| <1.

Spin echo of flow dispersion in porous media with GPA



Taylor`s dispersion-diffusion equation:

$$\frac{\partial P}{\partial t} + \mathbf{v}(\nabla P) = D\nabla^2 P$$

$$P(\mathbf{r}',t\,|\,\mathbf{r},0) = \sum_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r}-\mathbf{v}\,t)\, u^*_{\mathbf{k}}(\mathbf{r}')\, e^{-\frac{t}{\tau_{\mathbf{k}}}}$$

$$E(\tau) = \sum_i e^{iq.\langle Z_i(\tau)\rangle - \frac{1}{2}q^2.\langle \Delta Z_i^2(\tau)\rangle} = \sum_j N_j e^{i\overline{\phi(\tau,\mathbf{v}_j)} - \overline{\beta(\tau,\mathbf{v}_j)}}$$

Summation over flow channels

$$\overline{\phi(t,\mathbf{v}_j)} = \mathbf{q}.\iint(\mathbf{r}-\mathbf{r}')P(\mathbf{r}',t\,|\,\mathbf{r},0)\,d\mathbf{r}\,d\mathbf{r}' = $$

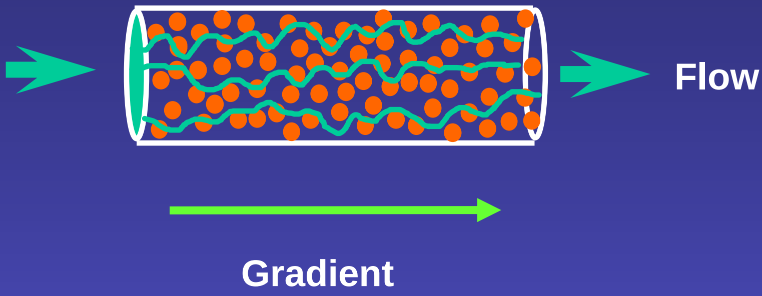
$$= \mathbf{q}.\left[\mathbf{v}_j t + \sum_k \mathbf{b}_{\mathbf{k}} \sin(\mathbf{k}\,\mathbf{v}_j\,t)\, e^{-\frac{t}{\tau_k}}\right]$$

$$\overline{\beta(t,\mathbf{v}_j)} \approx \left[q^2 D_j \tau + \frac{1}{2}(\mathbf{q.v})^2 + q^2 \sum_k c_k \left(1-\cos(\mathbf{k}\,\mathbf{v}_j\,\tau)\, e^{-\frac{t}{\tau_k}}\right)\right] - $$

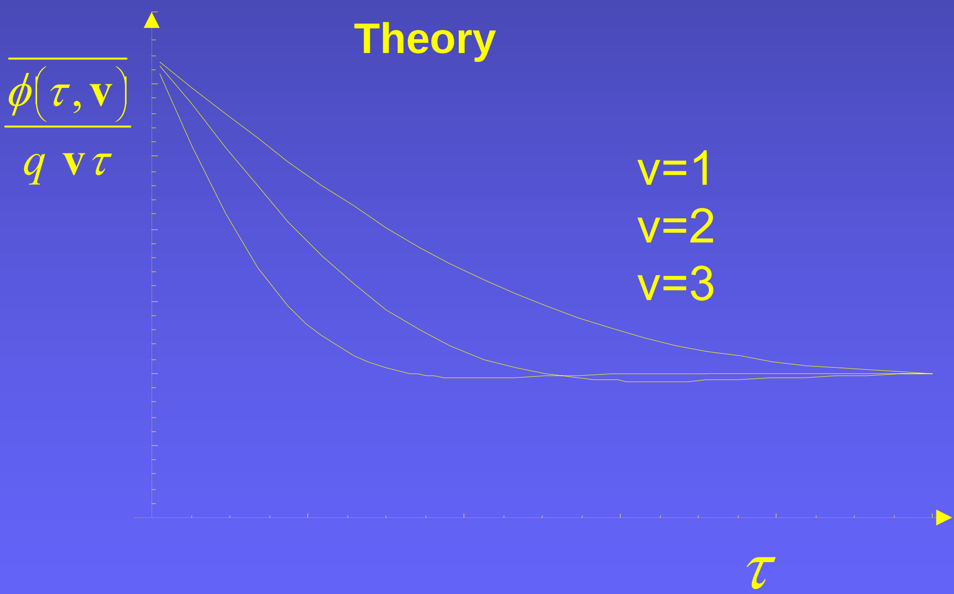
$$-\frac{1}{2}\overline{\phi(t,\mathbf{v}_j)}^2$$

$$\tau_k = \frac{1}{k^2 D}$$

Spin echo flow phase shift in porous media



$$\overline{\phi(\tau,\mathbf{v})} = \mathbf{q}.\left(\mathbf{v}\,t + \mathbf{b}_1 \sin(\mathbf{k}_1\,\mathbf{v}\,\tau) e^{-\frac{\tau}{\tau_1}} + .. \right)$$



Experiment

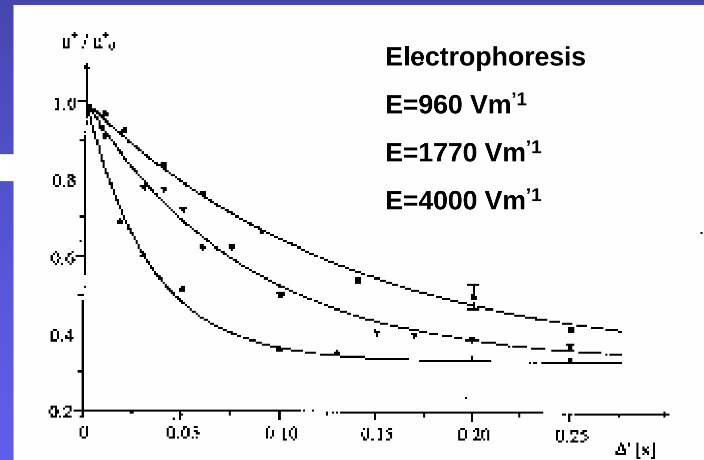
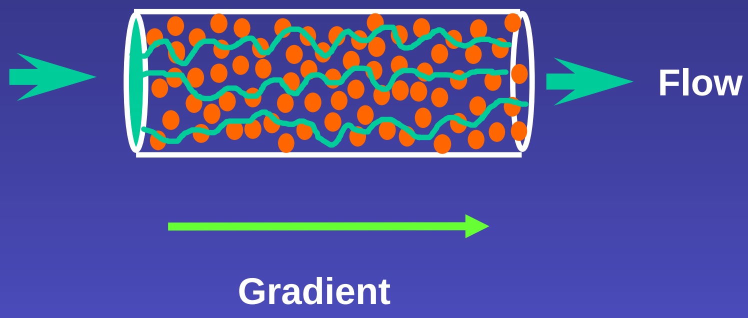


FIG. 3. Observation time Δ' dependence of the relative ionic mobility u^+/u_0^+ of $(C_4H_9)_4^+$ in aqueous solution confined in the porous medium Sephadex LH 20. T = 25°C. The measurements were performed at three different external electric fields E = 960 Vm^{-1} (■); 1770 Vm^{-1} (▼); 4000 Vm^{-1} (▲). The data are given relative to u_0^+ = 1.22 · 10^{-8} m^2 s^{-1} V^{-1}, the ionic mobility in the non confined bulk solution.

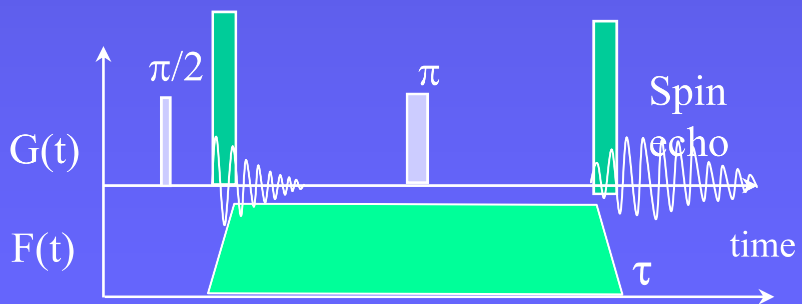
S.R. Heil, M. Holz, J. Mag. Res. 135 (1998) 17-22,
M. Holz, S. R. Heil. I. A. Schwab, Mag. Res, Imaging 19 (2001) 457–463

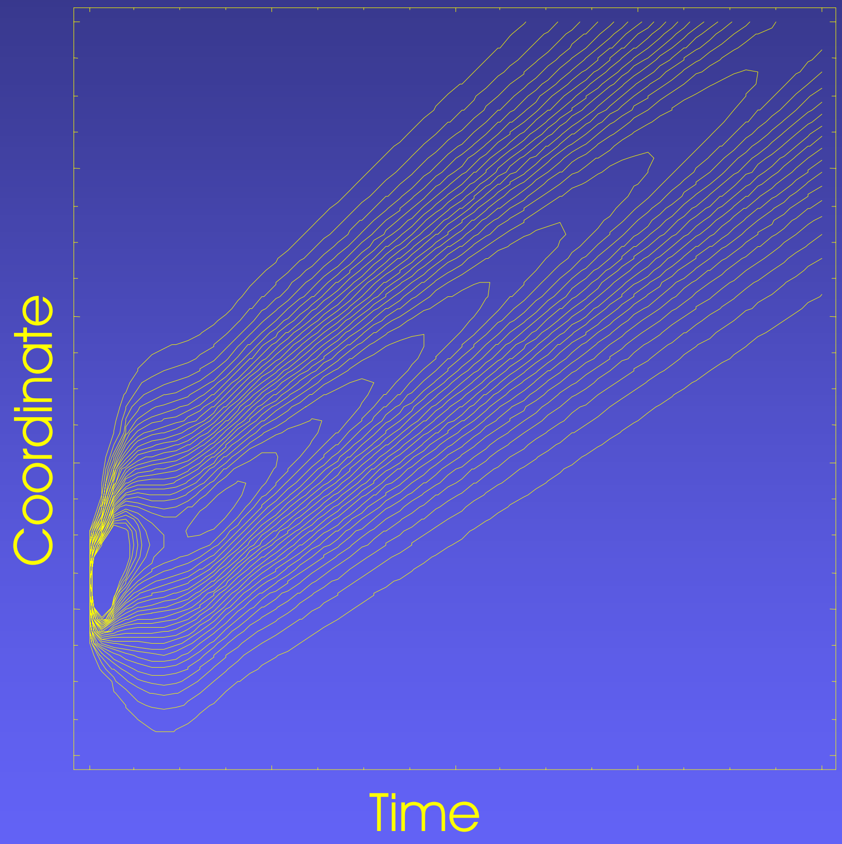
Evolution of flow dispersion propagator



$$E(\mathbf{q},\tau)=\sum_j N_j e^{i\overline{\phi(\mathbf{v}_j,\tau)}-\overline{\beta(\mathbf{v}_j,\tau)}}$$

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





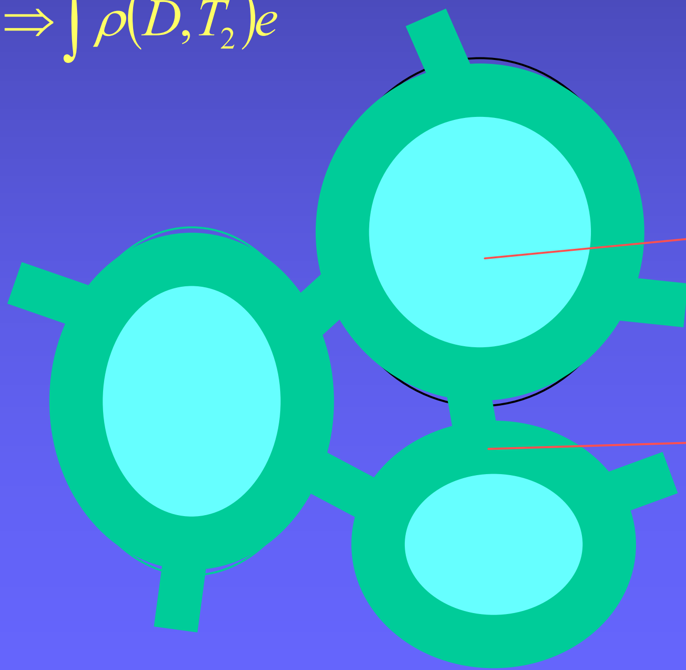
Evolution of flow dispersion propagator
through leaky plan-parallel planes

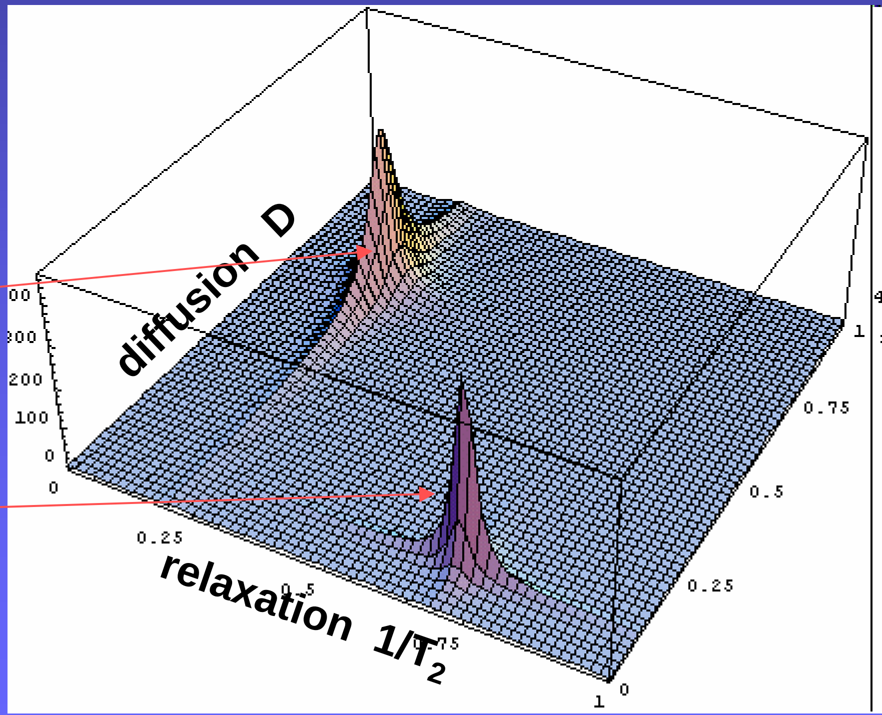
2-dimensional presentation of diffusion and relaxation

$$E(\mathbf{q},\tau)=\sum_i e^{iq\langle Z_i(\tau)\rangle-\frac{1}{2}q^2\langle\Delta Z_i^2(\tau)\rangle-\frac{\tau}{T_{2i}}}$$

$$\Rightarrow\int\rho(D,T_2)e^{iq\langle Z(D,\tau)\rangle-q^2D\tau-\frac{\tau}{T_2}}dDdT_2$$

2D-Laplace transformation





Distribution of diffusion and relaxation

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General theory: stochastic process with the cumulant expansion method

Spin echo is Fourier transform of the averaged propagator

$$E(\mathbf{q},\tau)=\sum_i\left\langle e^{i\mathbf{q}\left(\mathbf{r}(\tau)-\mathbf{r}_i(0)\right)}\right\rangle \Rightarrow \int \overline{P(\mathbf{R},\tau)}\, e^{i\mathbf{q}\mathbf{R}}\, d\mathbf{R}$$

Theory of stochastic processes

Fourier transform of probability function is its characteristic function

$$\Phi(f)=\int P(r)\, e^{i f r}\, dr=\left\langle e^{i f r}\right\rangle$$

It becomes its characteristic functional when $\Rightarrow r(t)=\int_0^t v(t')\,dt'$ $\quad r=\text{stochastic variable}$

$$\Phi(f,\tau)=\left\langle e^{i\int_0^\tau f(t')v(t')\,dt'}\right\rangle \Rightarrow$$

$f(t)=\text{arbitrary function}$

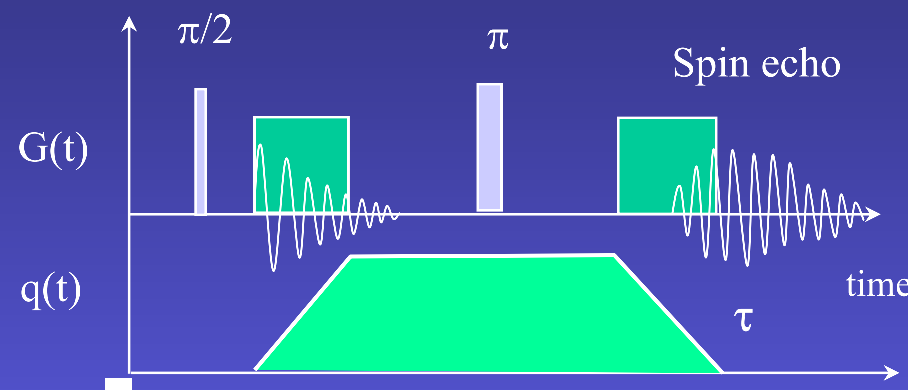
$$\Rightarrow e^{i\int_0^\tau f(t)\langle v(t)\rangle dt-\frac{1}{2}\int_0^\tau\int_0^\tau f(t)\langle v(t)\,v(t')\rangle_c f(t')\,dt\,dt'-\frac{i}{6}\int_0^\tau\int_0^\tau\int_0^\tau\langle f(t)v(t)\,f(t')v(t')\,f(t'')v(t'')\rangle_c\,dt\,dt'\,dt''+\dots}$$

Cumulant expansion

Spin echo with cumulant expansion in the Gaussian approximation

$$f(t) \equiv \mathbf{q}(t) \quad \text{spin dephasing}$$

$$v(t) \equiv \mathbf{v}_i(t) \quad \text{velocity of i-th spin}$$



$$\Phi(f,\tau) \Rightarrow E(\tau) = \sum_i \left\langle e^{i\int_0^\tau \mathbf{q}(t).\mathbf{v}_i(t)dt} \right\rangle =$$

no limits with regards to the gradient pulse or gradient waveform

$$= \sum_i e^{i\int_0^\tau \mathbf{q}(t).\langle \mathbf{v}_i(t)\rangle dt - \frac{1}{2}\int_0^\tau\int_0^\tau \mathbf{q}(t).\langle \mathbf{v}_i(t)\,\mathbf{v}_i(t')\rangle_c.\mathbf{q}(t')dt'dt - \frac{i}{6}\int_0^\tau\int_0^\tau\int_0^\tau \cancel{\mathbf{q}(t).\langle \mathbf{v}_i(t)\,\mathbf{q}(t').\mathbf{v}(t')\,\mathbf{v}_i(t'')\rangle_c.\mathbf{q}(t'').dt\,dt'\,dt''}\ldots}$$

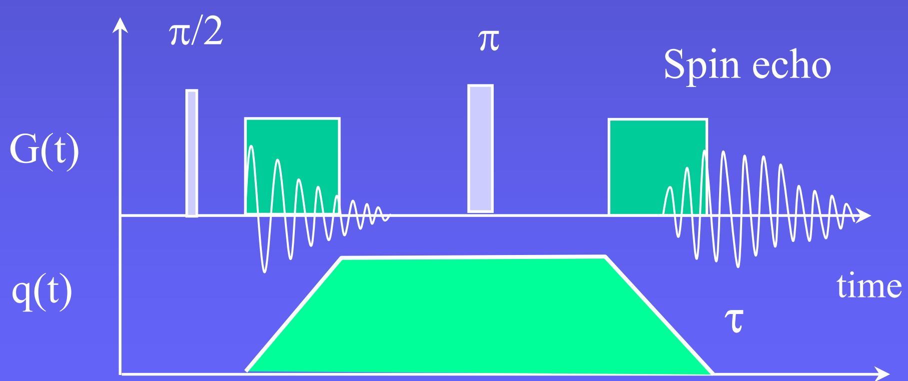
J. Stepišnik, **Validity Limits of Gaussian Approximation in Cumulant Expansion for Diffusion Attenuation of Spin Echo**, Physica B, 270, 110-117 (1999),

Gaussian phase approximation (GPA)

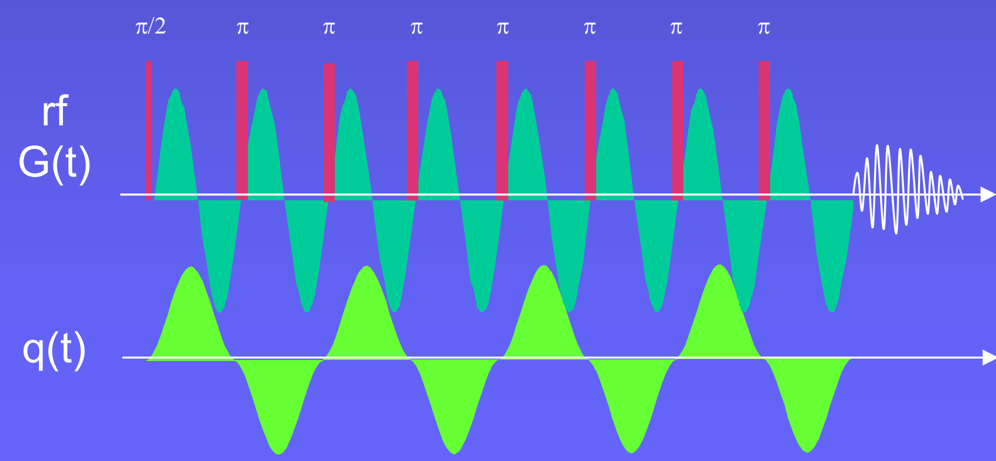
Spin echo with the cumulant expansion in Gaussian approximation - general method

Cumulant expansion of characteristic functional

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



Modulated gradient spin echo



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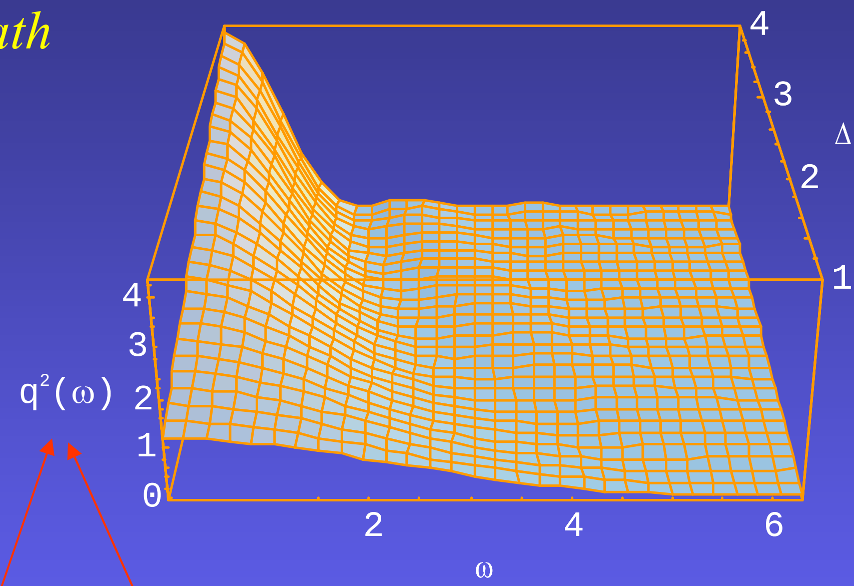
Relation of gradient spin echo to correlation function and spectrum of molecular motion

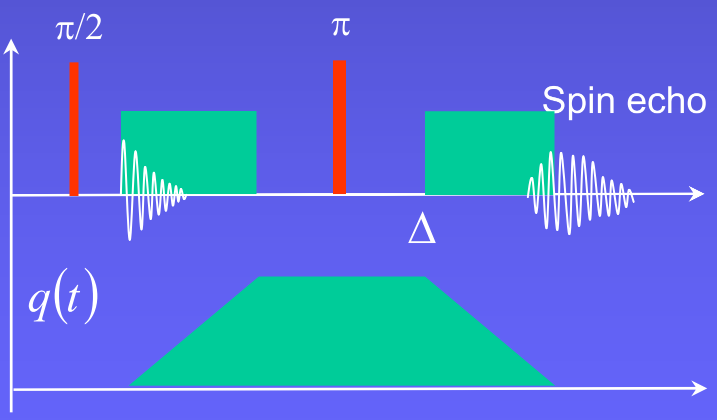
$$E(\tau)=\sum_i e^{i\phi_i(\tau)-\beta_i(\tau)} \qquad if \quad |q|.\xi \qquad \xi = free\ path$$



$$then: \qquad \phi_i(\tau)=\int_0^\tau \mathbf{q}(t).\langle \mathbf{v}_i(t)\rangle dt$$

$$\beta_i(\tau)=\int_0^\tau\int_0^t \mathbf{q}(t).\langle \mathbf{v}_i(t)\ \mathbf{v}_i(t')\rangle_c .\mathbf{q}(t')\,dt'dt$$

Time domain



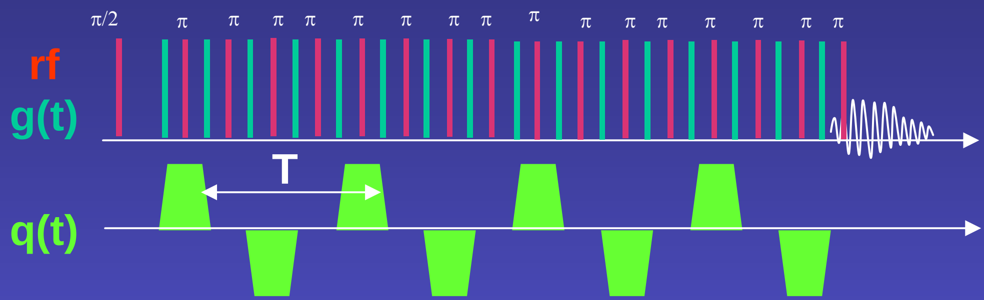
Frequency domain

$$\beta(\tau)=\frac{1}{\pi}\int_0^\infty \mathbf{q}(\omega,\tau).\mathbf{D}_i(\omega).\mathbf{q}^*(\omega,\tau)\,d\omega$$

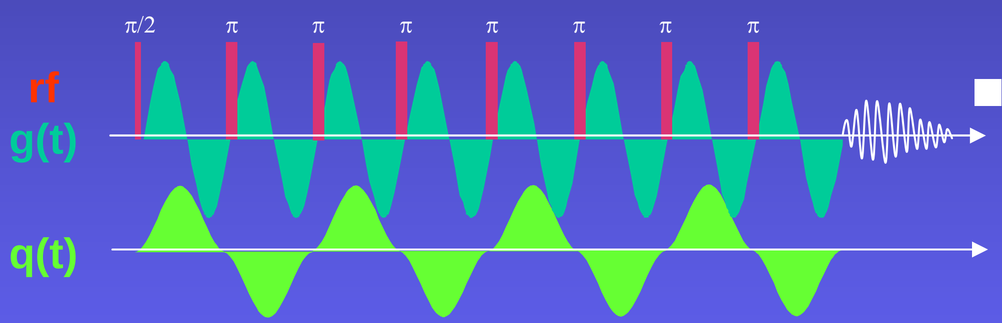
Spectrum of motion

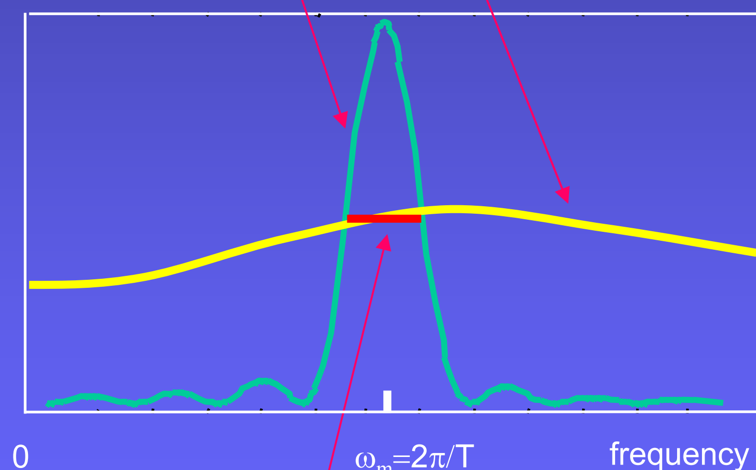
$$\mathbf{q}(\omega,\tau)=\int_0^\tau q(t)e^{i\omega t}dt \qquad \mathbf{D}_i(\omega)=\int_0^\tau \langle \mathbf{v}_i(t)\ \mathbf{v}_i(t')\rangle_c\, e^{i\omega t}dt$$

Modulated Gradient Spin Echo (MGSE)



$$\beta(\tau)=\frac{1}{\pi}\int_0^\infty \left|\mathbf{q}(\omega,\tau)\right|^2 D(\omega)\, d\omega \;\approx \alpha\, D(\omega_{\mathrm{m}})\tau$$





$$E(\tau)=\sum_i e^{i\cancel{\phi_i}(\tau)-\beta_i(\tau)}$$

$$E(\tau)\approx e^{-\alpha\, D(\omega_{\mathrm{m}})\tau}$$

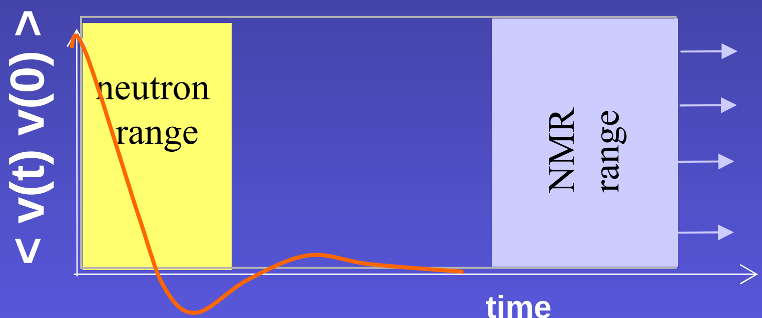
$$\omega_{\mathrm{m}}=\frac{2\pi}{T}$$

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

Velocity correlation function and self-diffusion

Velocity correlation function

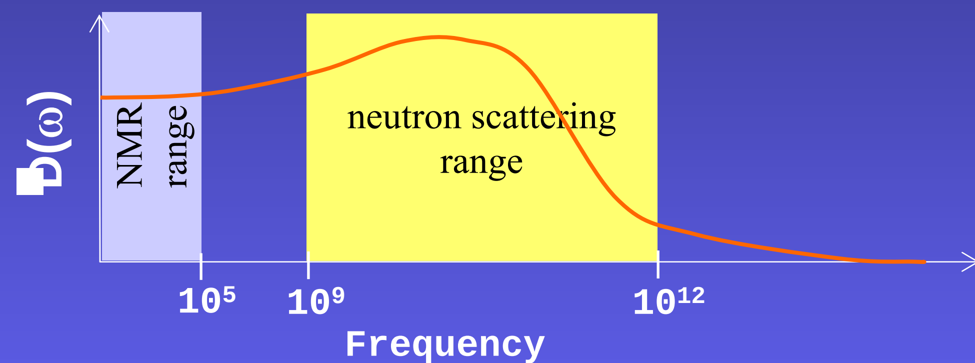
simple liquids – free diffusion



$$\tau_c \approx 10^{-12} s$$

$$\langle v_x(t).v_x(0)\rangle = 2D\delta(t)$$

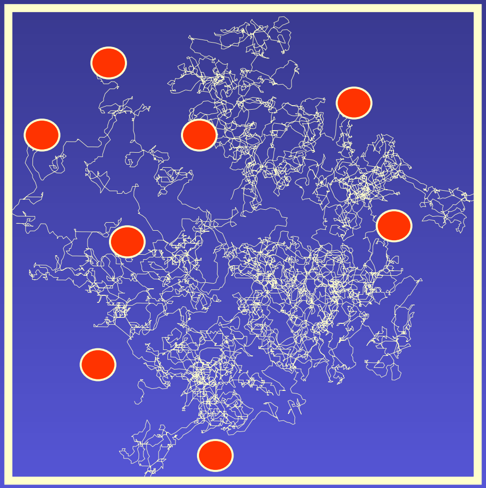
Spectrum of velocity correlation



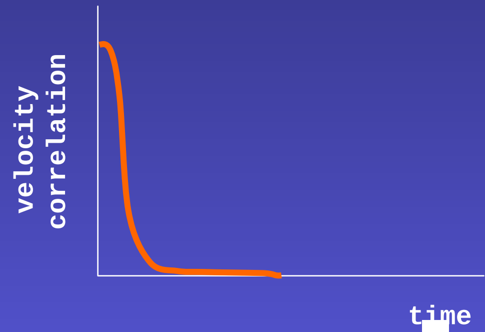
$$D(\omega) = \int_0^\infty \langle v_x(t).v_x(0)\rangle e^{i\omega t} dt$$

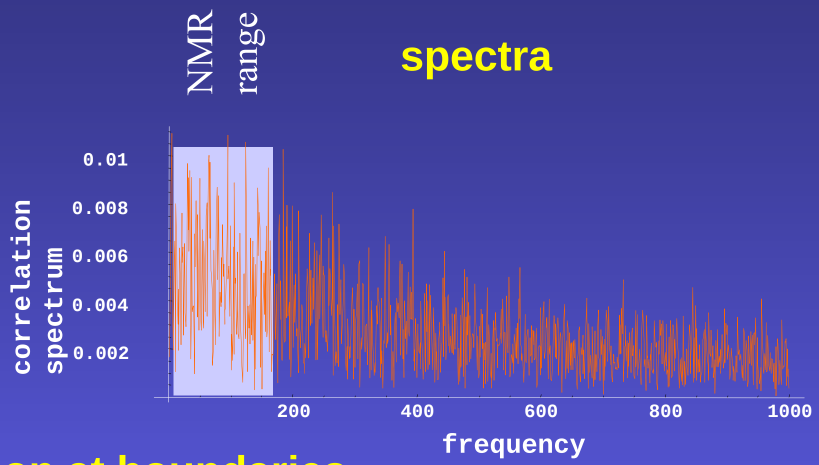
$$D(\tau) = \int_0^\tau \langle v_x(t).v_x(0)\rangle dt \underset{\tau\to\infty}{\Rightarrow} D(0) \equiv D$$

Velocity correlation function of restricted motion



Free diffusion

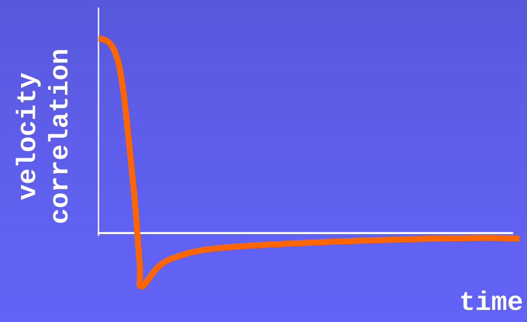


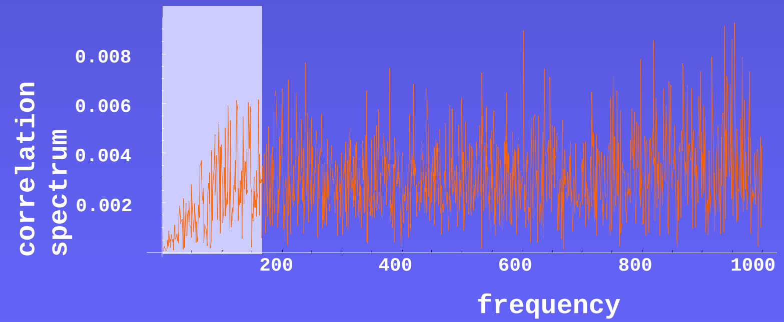


Restricted diffusion- reflection at boundaries

Langevine equation

$$\frac{d\mathbf{v}}{dt} + \alpha\,\mathbf{v} = \mathbf{f}(t)$$



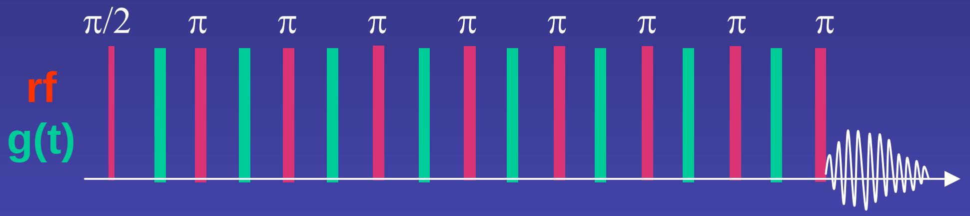


E. Oppenheim and P. Mazur, **Brownian motion in system of finite size,** Physica, 30, 1833--45, 1964.

J. Stepišnik, A. Mohorič and A. Duh, **Diffusion and flow in a porous structure by the gradient-spin-echo spectral analysis**, Physica B, 307, 158-168 (2001)

$$\mathrm{D}_{rest}(\omega) = D_{\infty} + \sum_k B_k \frac{\tau_k \omega^2}{1+\tau_k^2\omega^2}$$

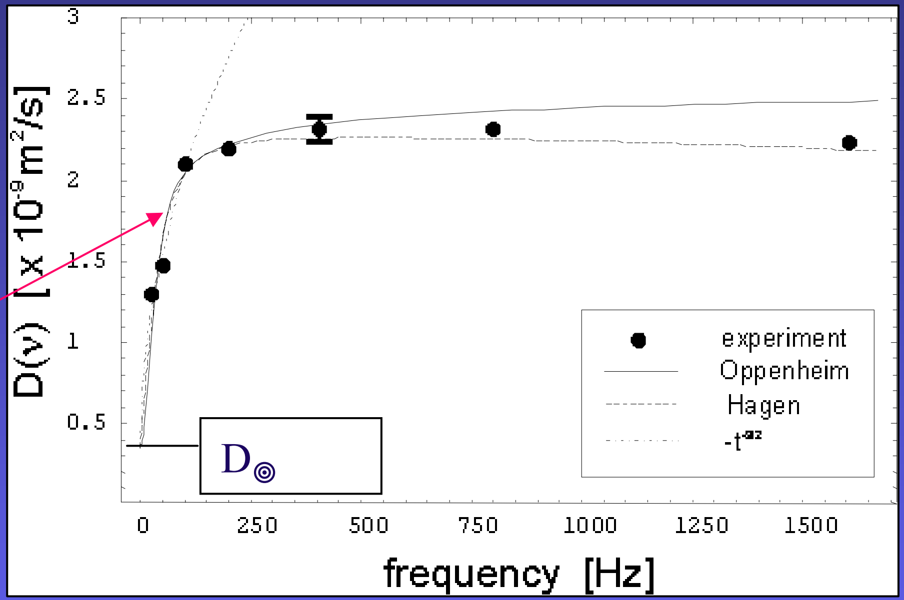
Velocity correlation spectrum of water in a porous media by MGSE



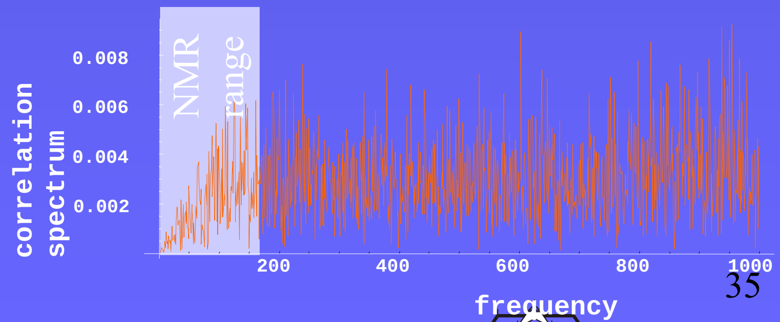
$$E(\tau) \approx e^{-\alpha D(\omega_m)\tau} \qquad \omega_m = \frac{2\pi}{T}$$

$$D_{rest}(\omega) = D_\infty + \sum_k \frac{B_k}{\tau_k} \frac{\tau_k^2 \omega^2}{1+\tau_k^2\omega^2}$$

diffusion correlation time $\quad \tau_k = \frac{1}{k^2 D}$



Velocity correlation spectrum of water between closely packed, mono-disperse, surfactant coated polystyrene spheres of 2r=15μm.



J. Stepišnik, P.T. Callaghan, **The long time-tail of molecular velocity correlation function in a confined fluid: observation by modulated gradient spin echo**, Physica B. **292**, 296-301 (2000)

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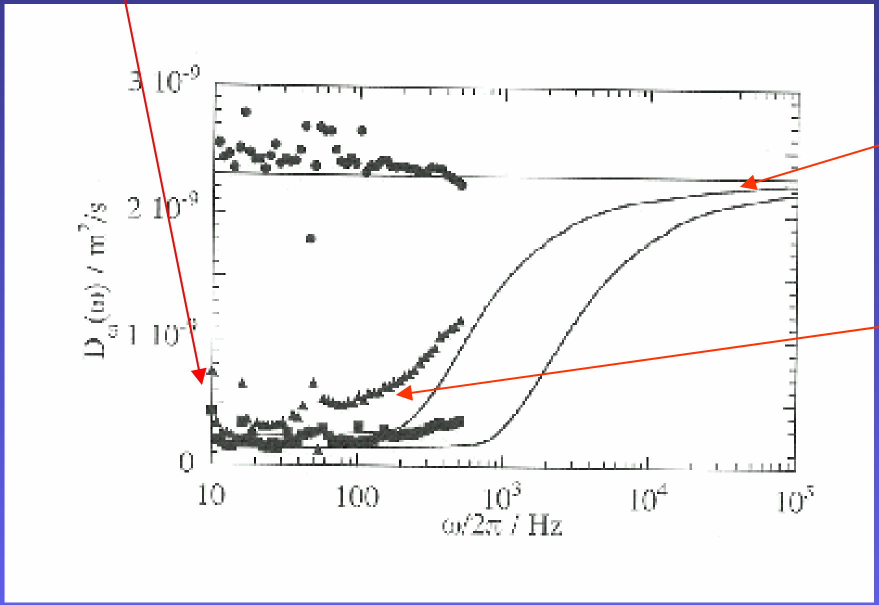
Velocity correlation spectrum of water in emulsion droplets by MGSE

D_∞



The frequency-dependent diffusion coefficient for free water and water confined within emulsion droplets in a highly concentrated fresh (squares),(r~0.71μm) and aged (triangles) ,(r~1.70μm) emulsion.

D.Topgaard, C. Malmborg, and O. Soderman, J. Mag. Res. **156,** 195–201 (2002)

High-frequencies

$$D_{rest}(\omega) \approx D$$

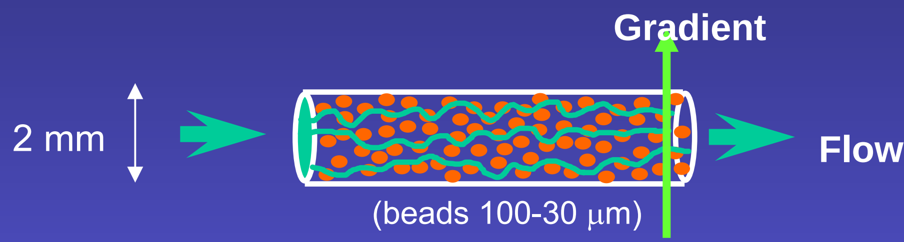
Low-frequencies

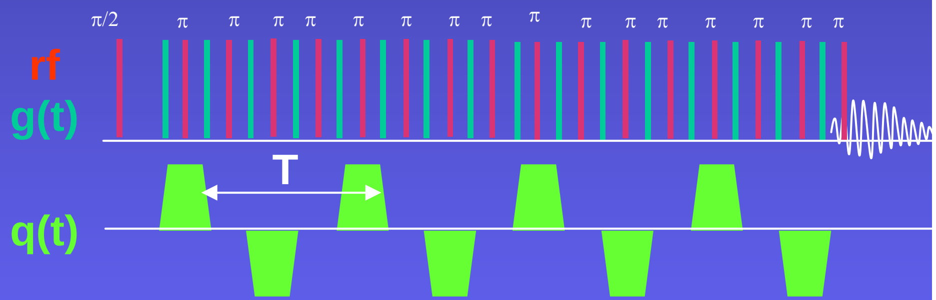
$$D_{rest}(\omega) \approx D_\infty + B_1 \frac{\tau_1 \omega^2}{1+\tau_1^2\omega^2} + \ldots \approx D_\infty + B_1 \tau_1 \omega^2 =$$

$$= D_\infty + \frac{\kappa^4 \; a^4}{D}\omega^2$$

	κ
Planar	0.30
Cylindrical	0.44
Spherical	0.36

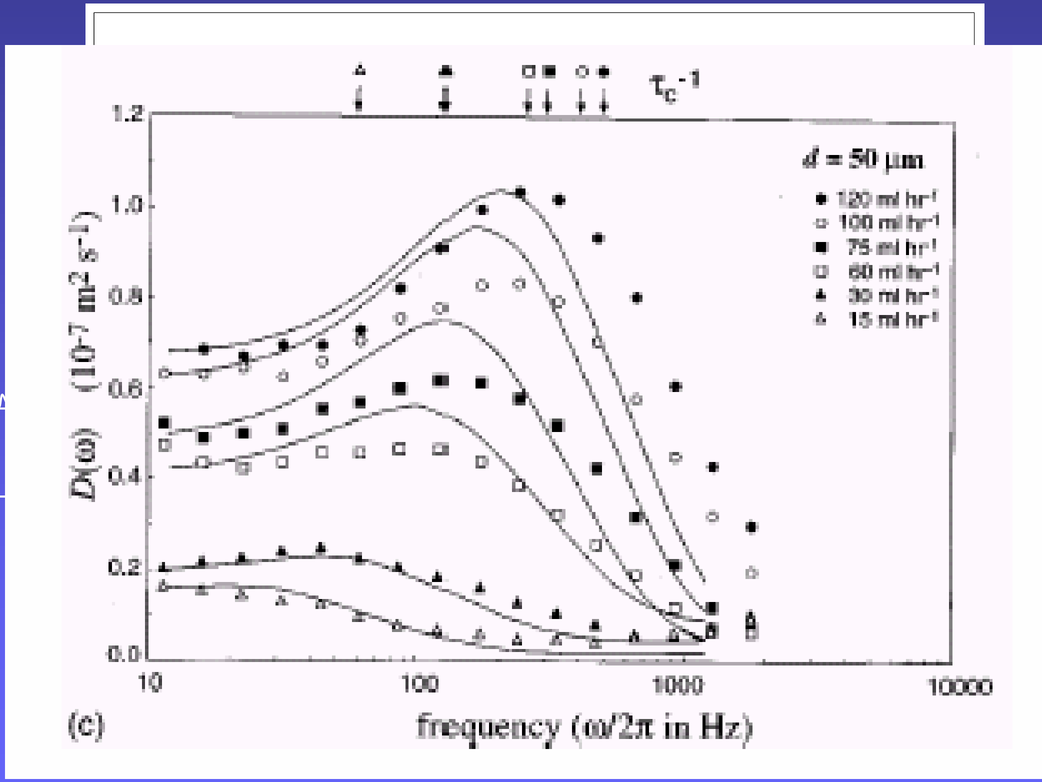
Velocity correlation spectrum of flows in a porous media measured by MGSE





$$E(\tau) \approx \sum_j e^{-\alpha D_j(\omega_m)\tau} \qquad \omega_m = \frac{2\pi}{T}$$

P.T. Callaghan, J. Stepišnik, J. of Mag. Res. A **117**, 118-122(1995)



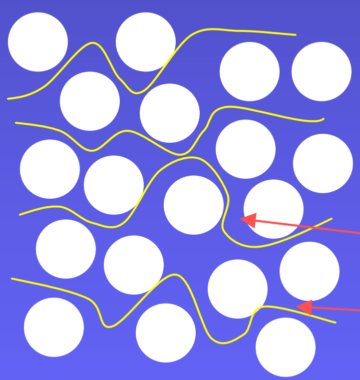
P. T. Callaghan and S. L. Codd, Phys. Fluids, Vol. 13, (2001)

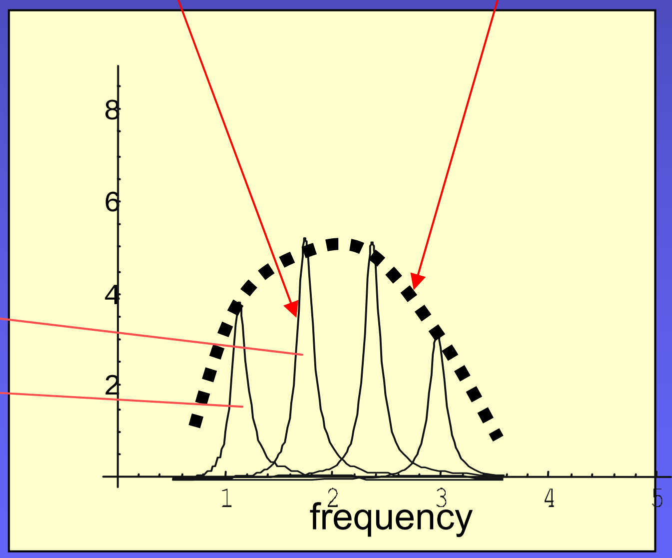
Attenuation time dependence of flows in porous media and dispersion spectrum

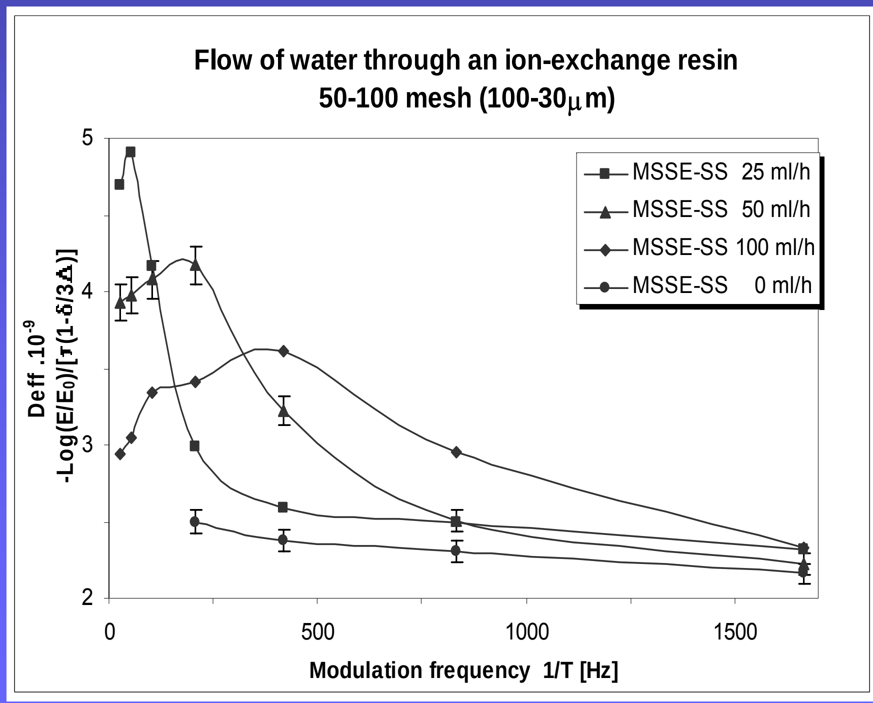
Taylor`s dispersion-diffusion equation:

$$D_j(\omega)=\frac{1}{2}\sum_{k\neq 0} c_k\tau_k\omega^2\left[\frac{1}{1+\tau_k^2\left(-kv_j+\omega\right)^2}+\frac{1}{1+\tau_k^2\left(kv_j+\omega\right)^2}\right]$$

$$\beta(\tau)=\alpha\tau\int_0^\infty \rho(v)\,\delta(kv-\omega_m)\,dv \approx \alpha\tau\rho\left(\frac{\omega_m}{k}\right)$$







Dispersion spectrum provides information about distribution of streams

Summary

$$E(\tau) \Rightarrow \sum_i e^{\, i\int_0^\tau \mathbf{q}(t).\langle \mathbf{v}_\mathrm{i}(t)\rangle dt - \int_0^\tau \int_0^t \mathbf{q}(t).\langle \mathbf{v}_\mathrm{i}(t)\ \mathbf{v}_\mathrm{i}(t')\rangle_\mathrm{c}.\mathbf{q}(t')dt'dt + \ldots} \Rightarrow \sum_i \int P(\mathbf{r}_i,\tau\,|\,\mathbf{r}) e^{i\mathbf{q}.r} d\mathbf{r}$$

Gaussian phase approximation:

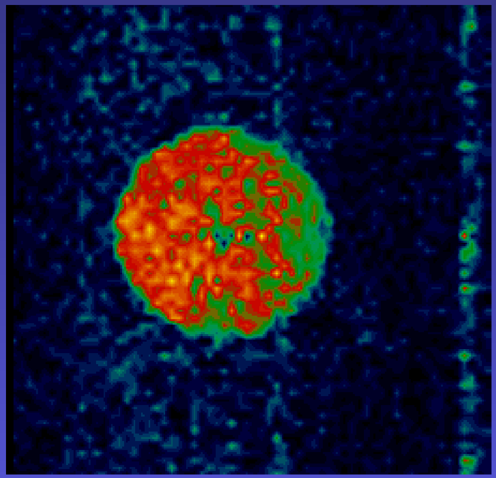
•links spin echo to the details of molecular motion

•can be used with any gradient sequence or gradient waveform

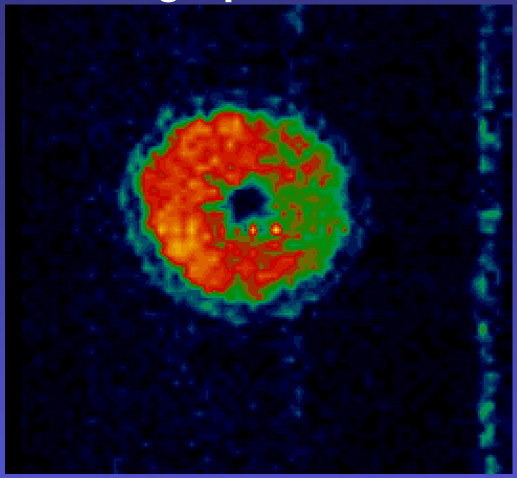
• can be used to describe measurement of diffusion and flow in restricted geometry when q $\xi<1$.

MRI in the geomagnetic field (50 μT)

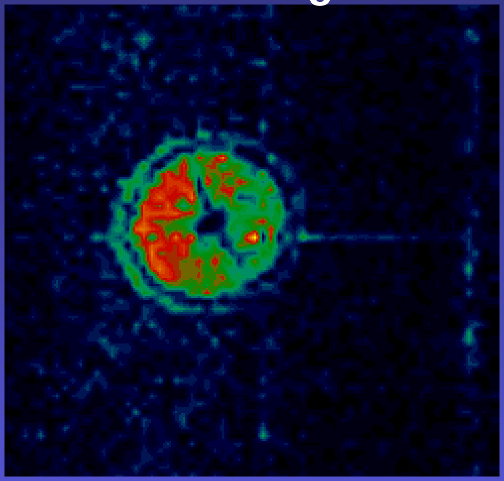
apple



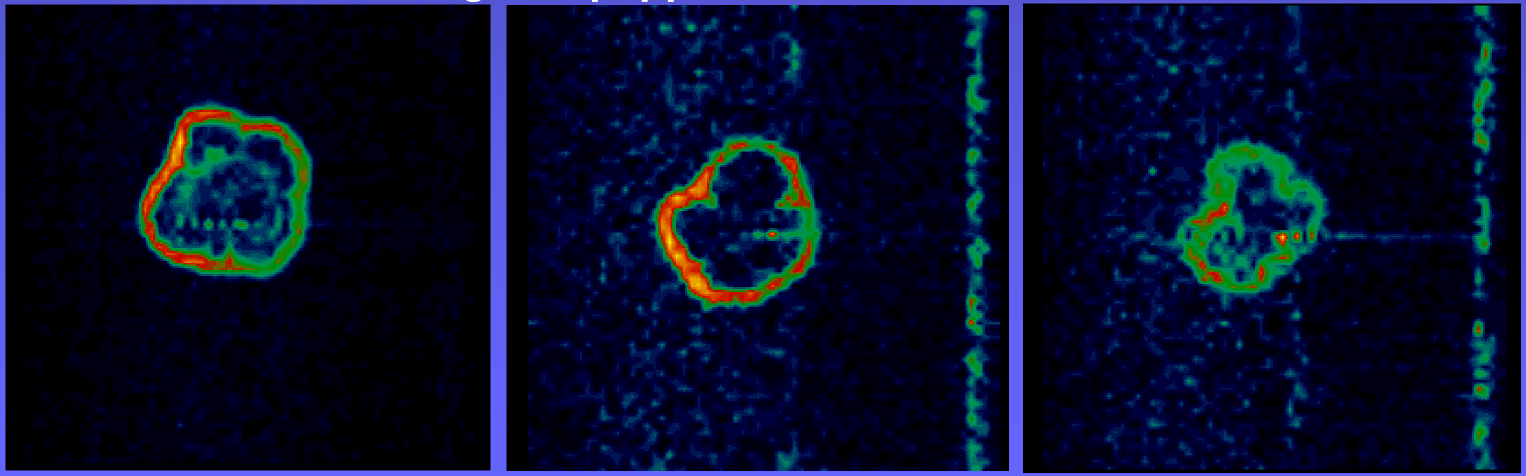
grapefruit



orange



green pepper : different slices

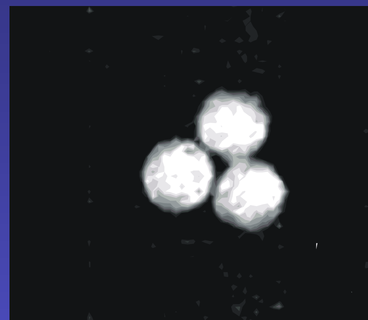


MRI of diffusion and convection in geomagnetic field (50 μT)

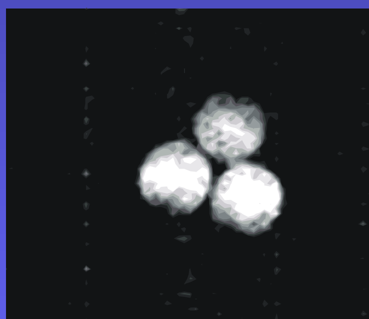
diffusion

G=1.8 10^{-3} T/m

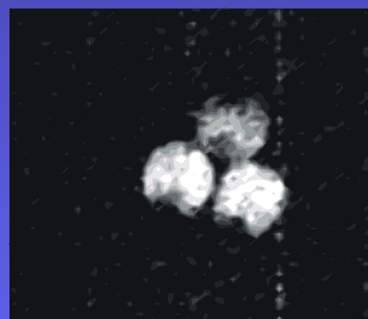
Δ=0



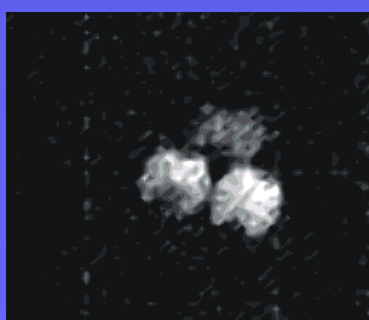
Δ= 150 ms



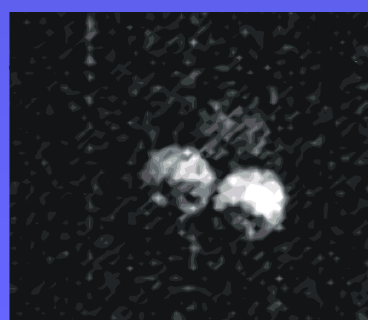
Δ= 175 ms



Δ= 200 ms



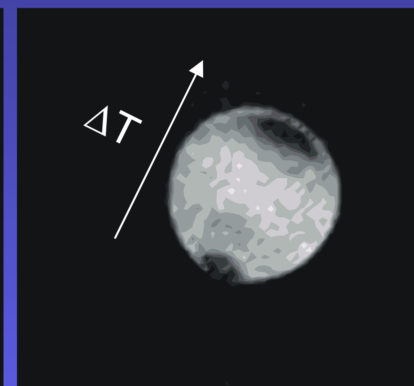
Δ= 250 ms



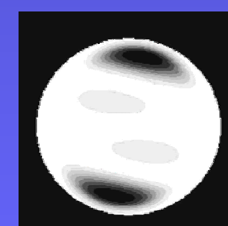
convection of water in the cylinder

G=0

G=1.8 10^{-3} T/m
Δ=200 ms



Expected



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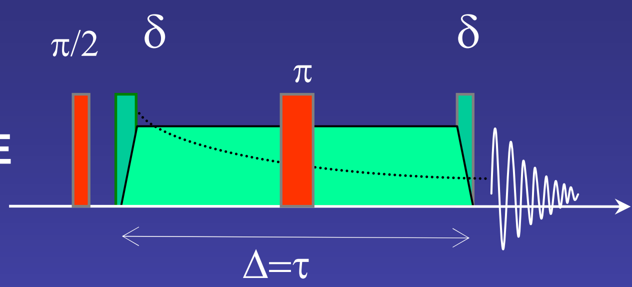
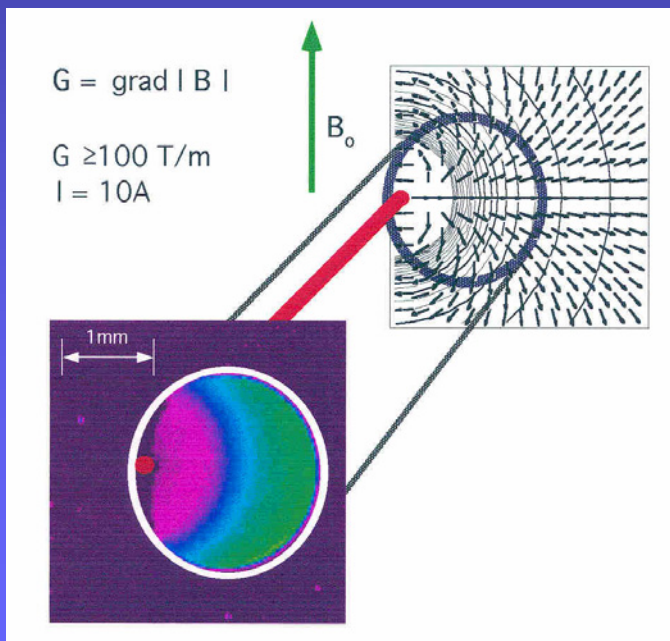
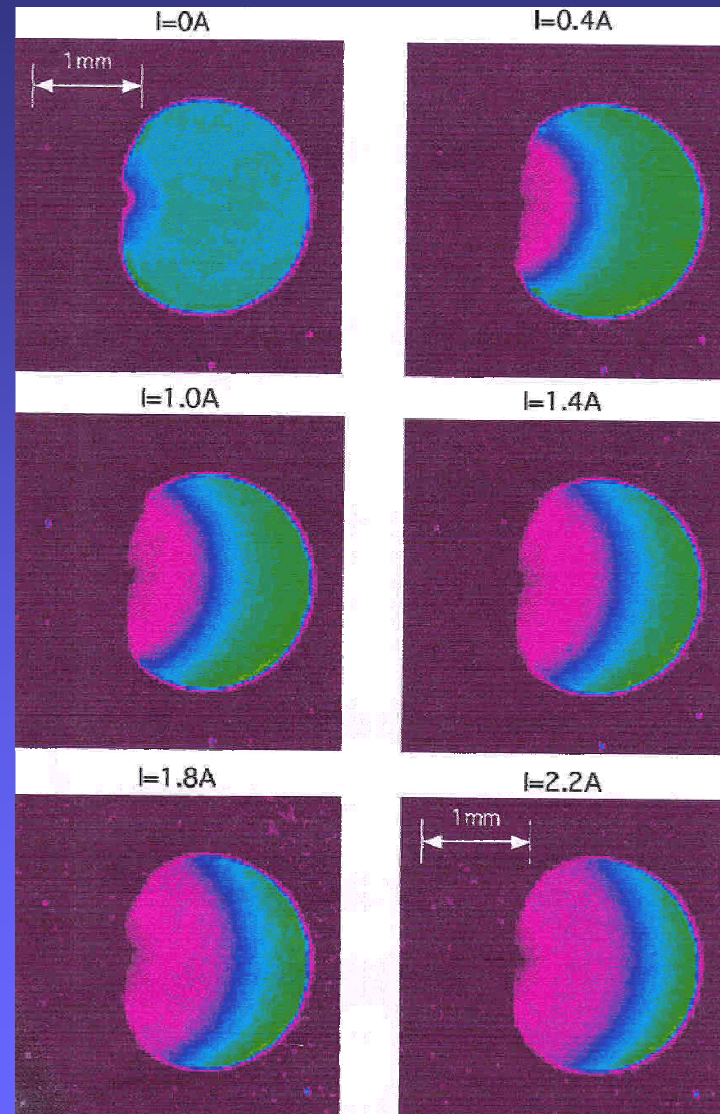
Spatially-distributed diffusion by spin echo and MRI

Short PGSE



$$e(\tau, \mathrm{r}) \approx e^{-\mathbf{F}(\mathbf{r}).\underline{\mathbf{D}}.\mathbf{F}(\mathbf{r})\ \tau}$$





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