Molecular and granular translational dynamics measured by a novel NMR technique

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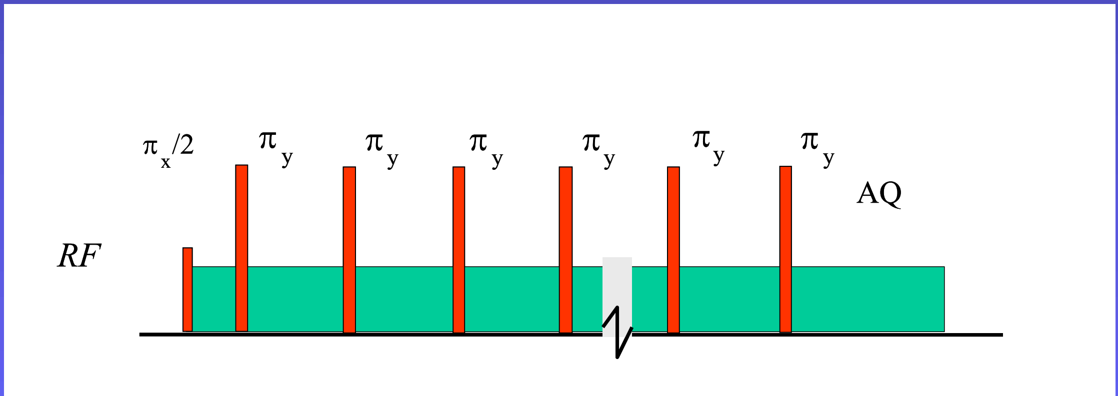
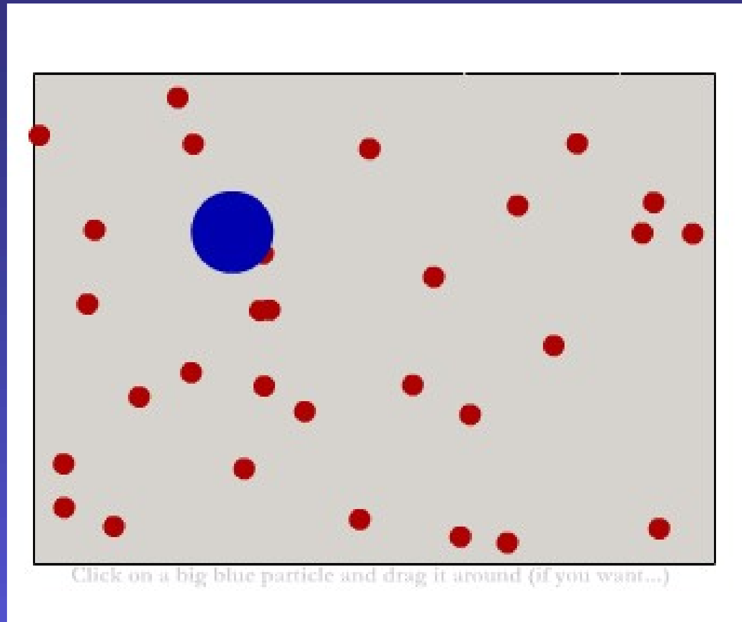
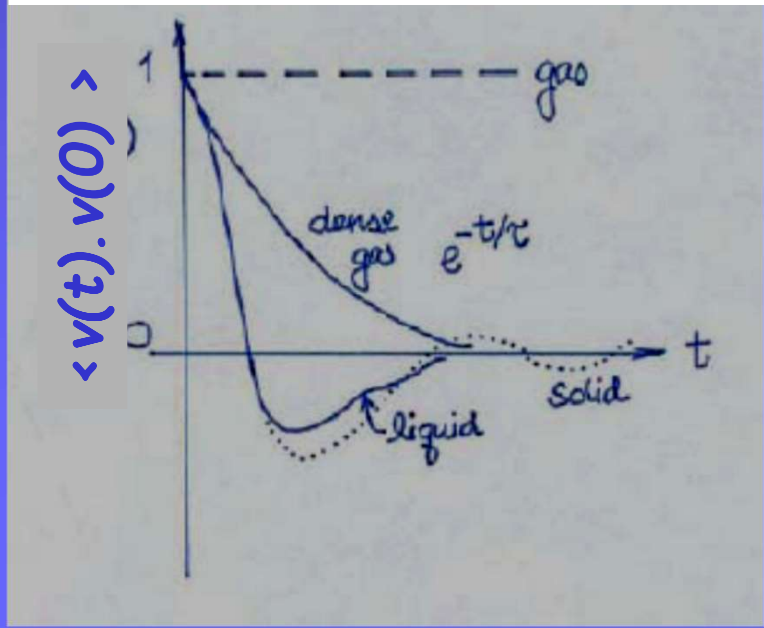
Measurement of the velocity autocorrelation by CPMG sequence and constant magnetic field gradient

CPMG sequence as a modulated gradient spin echo to measure spectrum of molecular velocity autocorrelation function





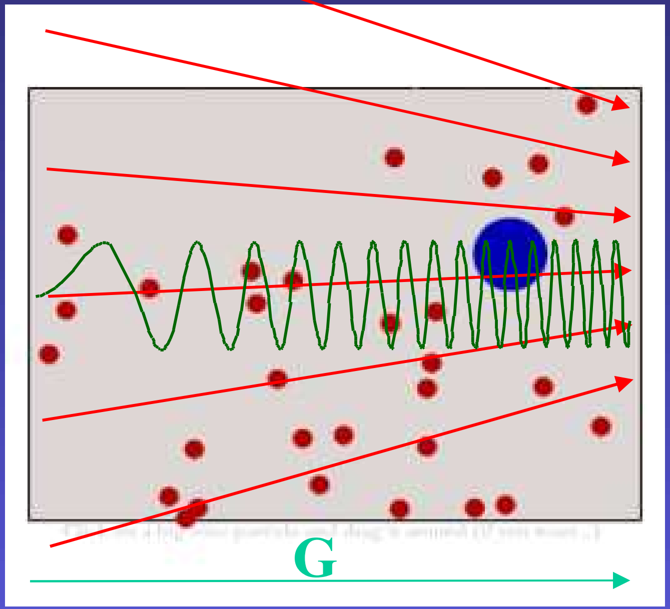
Velocity autocorrelation function

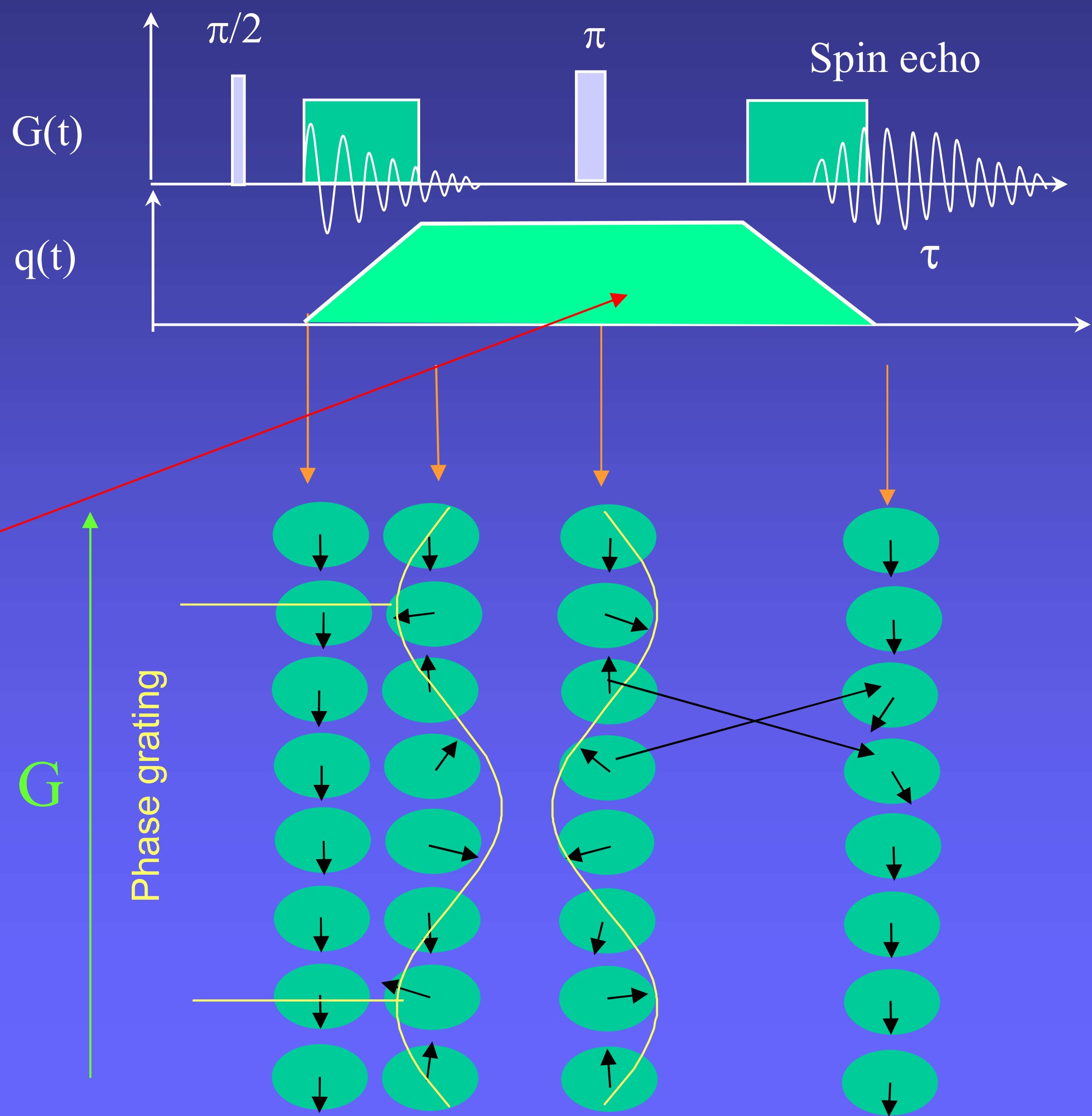


Applications to obtain the spectrum of

self-diffusion of fluid in porous media
self-diffusion in gels and water
and motion of fluidized granular systems

Spin motion by two-pulse gradient spin echo



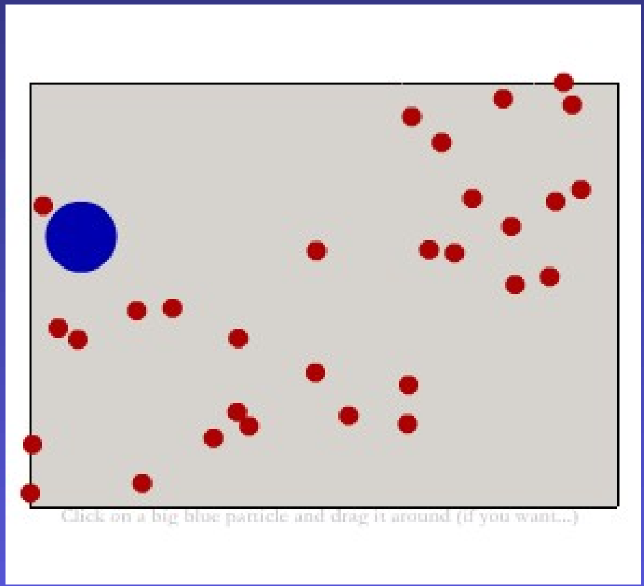


Encoding of the spin motion

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

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

Molecular random motion and spin echo: Torrey's approaches



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

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

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

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

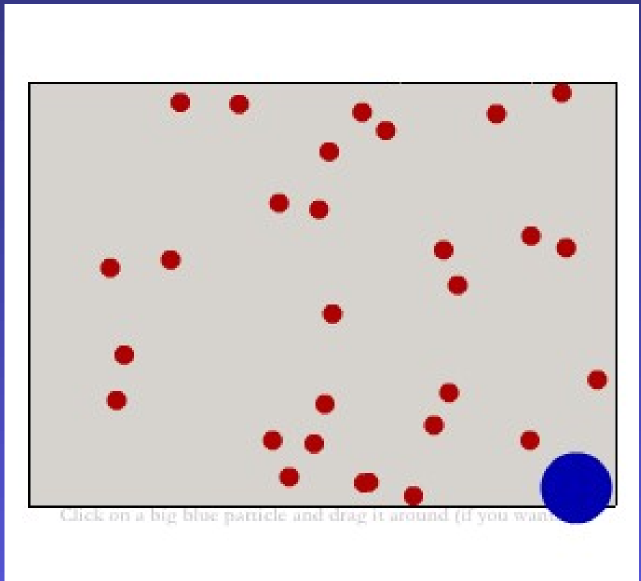
Mesurement in the short time-interval

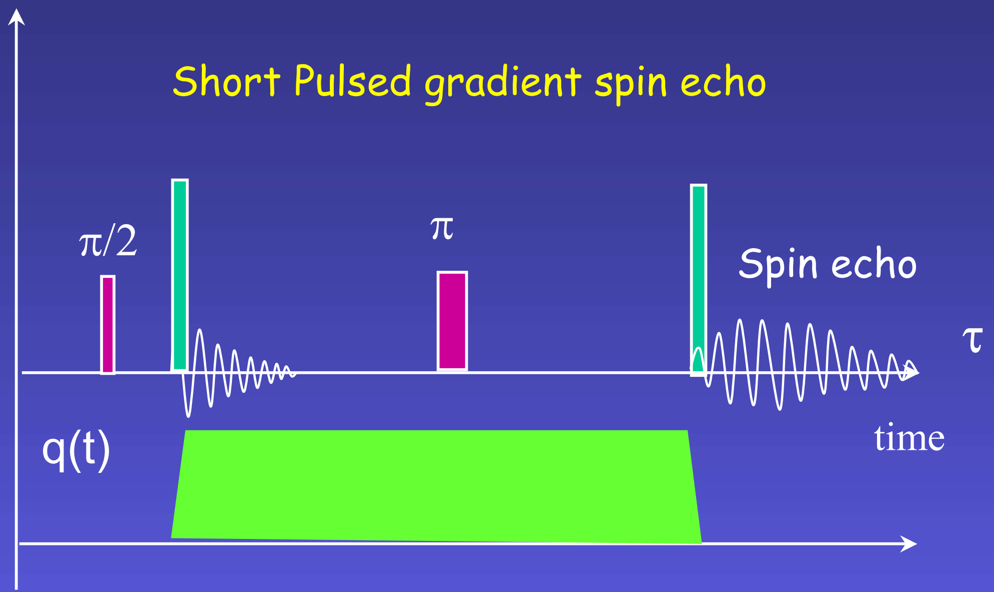
- diffusion can be time dependent
- different spin sub-ensembles can experience different diffusion propertie

$$E(\tau) \approx \sum_j m_j e^{-\int_0^\tau \mathbf{q}(t).\underline{\mathbf{D}}_j(t).\mathbf{q}(t)dt}$$

Summation over sub ensembles with different $D_j(t)$

Molecular motion and spin echo: average propagator approach





$$E(\tau) \approx \sum_i \left\langle e^{i\gamma \int_0^\tau \mathbf{q}(t).\mathbf{v}_i(t)dt} \right\rangle \approx \sum_i \left\langle e^{i\mathbf{qR}_i(\tau)} \right\rangle = \sum_i \int P(\mathbf{R}_i,\tau) e^{i\mathbf{qR}_i} dR_i \qquad \mathbf{r}_i(\tau) - \mathbf{r}_i(0) = \mathbf{R}_i(\tau)$$

Probability function

R_i is stochastic variables

$$= \int \overline{P(\mathbf{R},\tau)} e^{i\mathbf{qR}} dR$$

Average propagator in the limit of long τ

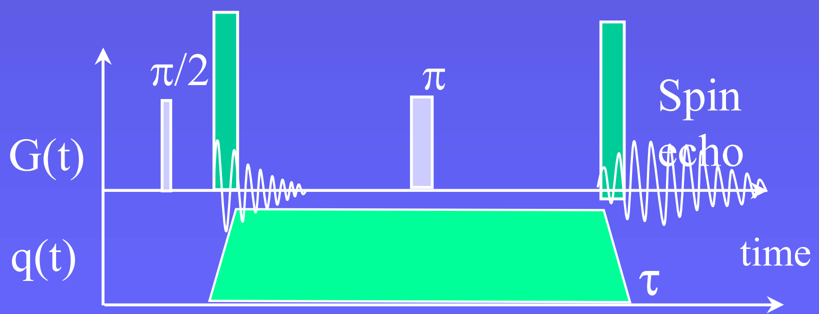
J. Karger and W. Heink. **The propagator representation of molecular transport in microporous crystallites** , J. Magn. Reson. 51, 1-7 (1983)

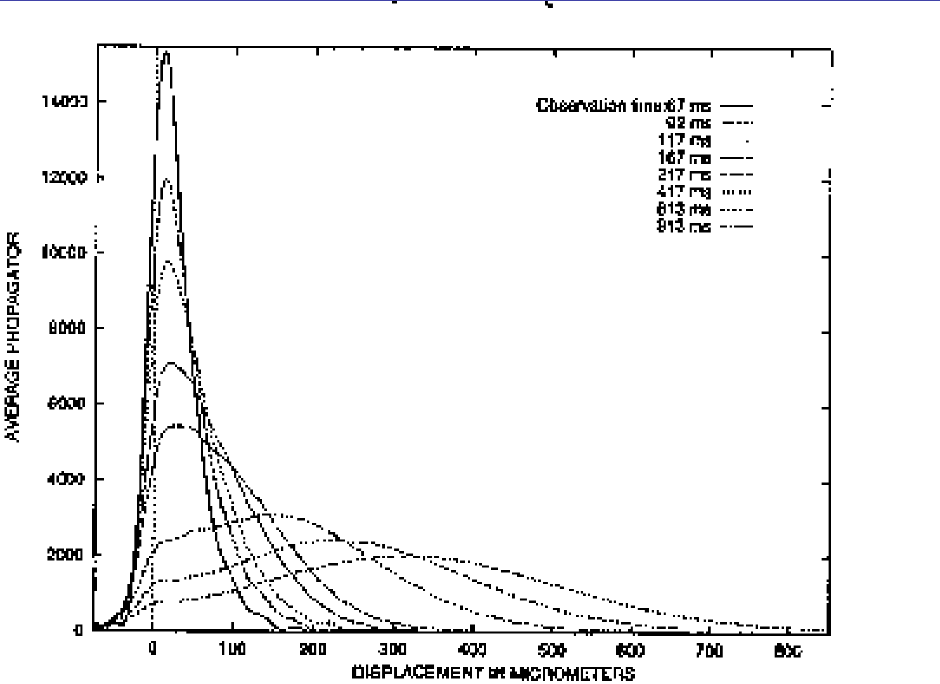
Probability distribution of flow in porous media

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

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

Short PGSE





e 2. The variation of $P_d(X)$ with d for displacements X measured along the axial direction of the cylindrical sample.

Stochastic processes and spin echo as a characteristic function

N. G. van Kampen, "**Stochastic Processes in Physics and Chemistry**," North-Holland, Amsterdam, 1981.

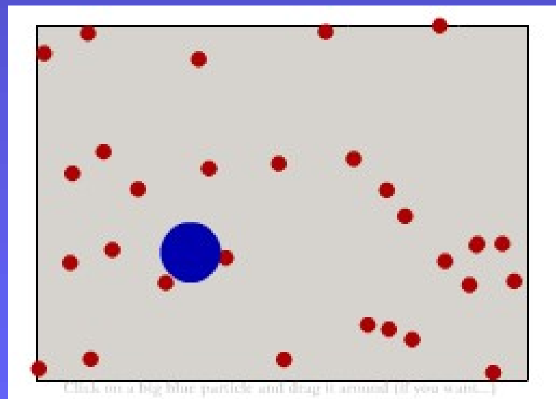
Random process of the stochastic variable *r* is characterized by the probabity distribution or by its Fourier transform, which is named the characteristic function of random process

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

$$r=\text{stochastic}\quad\text{variable}$$

$$f=\text{parameter}$$

$$\mathrm{P}(\mathrm{r})=\text{probabilit y functiom}$$



Signal of the short pulse gradient spin echo has the form of characteristic functional with the spin displacement $\boldsymbol{R}_i$ as a stochastic variable and the gradient dephasing $\boldsymbol{q}=\gamma\delta\boldsymbol{G}$ as the parameter

$$E(\tau,\mathbf{q})\approx\sum_i\left\langle e^{i\mathbf{q}\mathbf{R}_i(\tau)}\right\rangle\quad=\quad\sum_i\int P(\mathbf{R}_i,\tau)e^{i\mathbf{q}\mathbf{R}_i}dR_i$$

Characteristic function — Probability distribution

Stochastic processes and characteristic functional

Whenever the stochastic variable depends on another stochastic variable through relation:

$$r(t) = \int_0^t v(t')dt'$$

the process is described by the characteristic functional

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

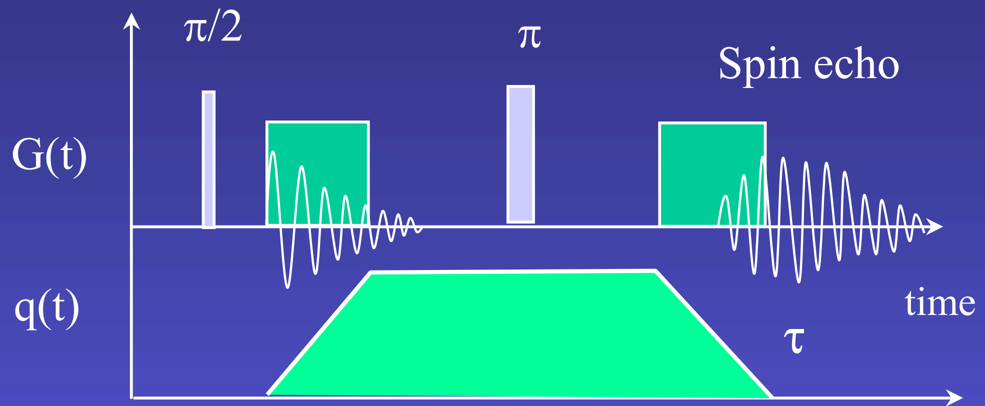
where $f(t) = \text{arbitrary function}$

The characteristic functional can be expanded into the cumulant series:

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

Spin echo as a characteristic functional and the Gaussian phase approximation

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



no limits with respect to the gradient pulse or gradient waveform

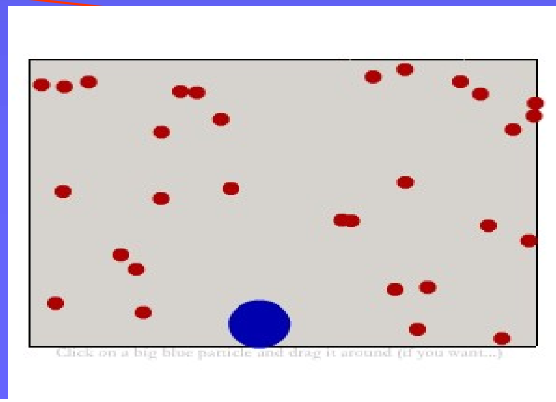
$$E(\tau)=\sum_i \left\langle e^{\,i\int_0^\tau \mathbf{q}(t).\mathbf{v}_{\rm i}(t)\,dt} \right\rangle = \sum_i e^{\,i\int_0^\tau \mathbf{q}(t).\langle \mathbf{v}_{\rm i}(t)\rangle\, dt - \frac{1}{2}\int_0^\tau\int_0^\tau \mathbf{q}(t).\langle \mathbf{v}_{\rm i}(t)\ \mathbf{v}_{\rm i}(t')\rangle_{\rm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

Gaussian phase approximation (GPA)

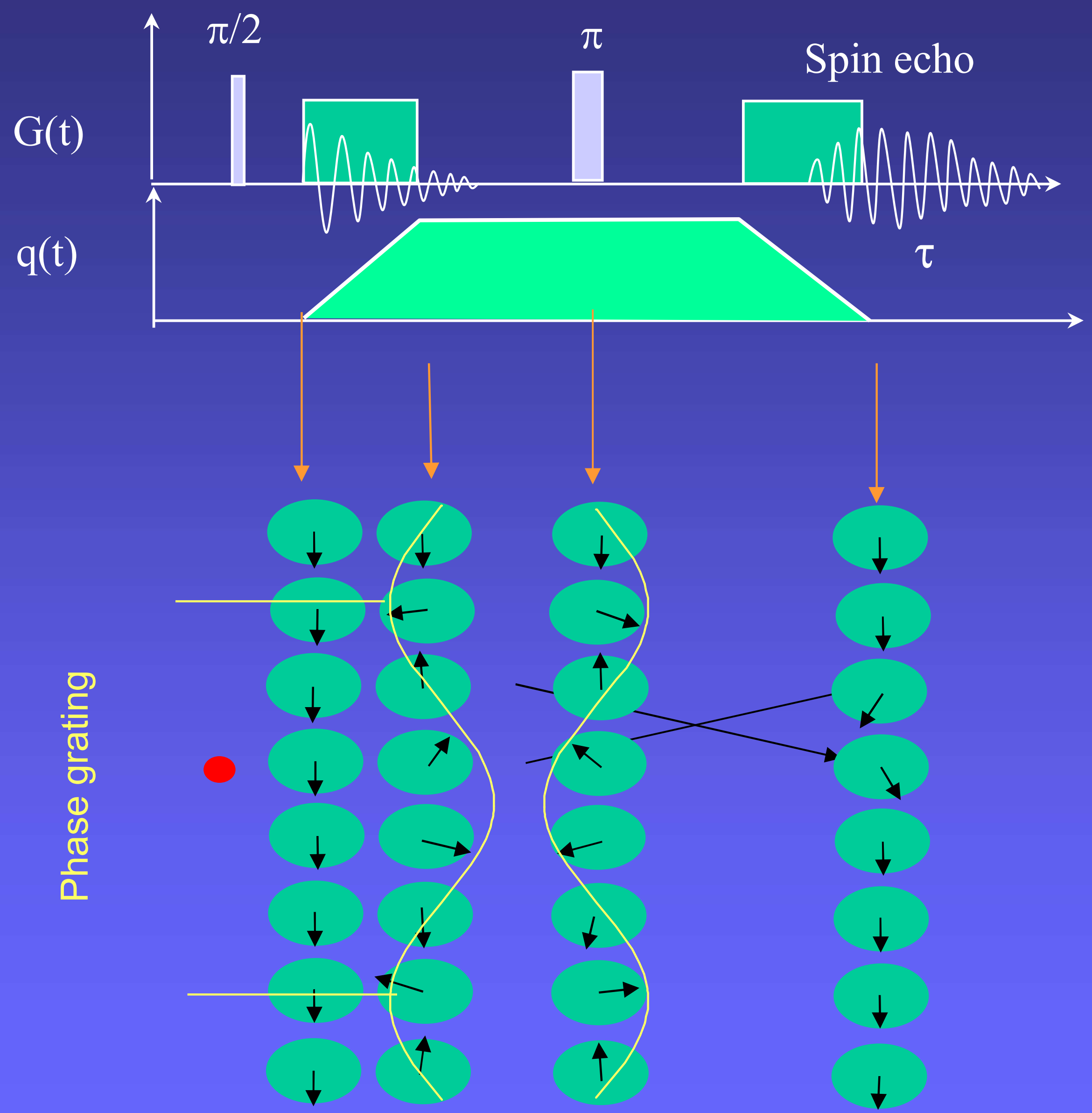
$$\times e^{\cancel{-\frac{i}{6}\int_0^\tau\int_0^\tau\int_0^\tau \mathbf{q}(t).\left\langle \mathbf{v}_i(t)\ \mathbf{q}(t').\mathbf{v}(t')\ \mathbf{v}_i(t'')\right\rangle_c .\mathbf{q}(t'')\,dt\,dt'\,dt''+\ldots}}$$

$$f(t)\equiv \mathbf{q}(t)$$ Spin dephasing

$$R_i(t)\equiv\int_0^t \mathbf{v}_i(t')\,dt'$$ Velocity as the stochastic variable



Two-pulse gradient spin echo and GPA



Condition for the Gausian phase approximation (GPA):

$$\sqrt{\overline{v^2}}\,\tau_c < \frac{1}{\sqrt{\overline{q^2}}}$$

$$\lambda < \frac{1}{\sqrt{\overline{q^2}}}$$

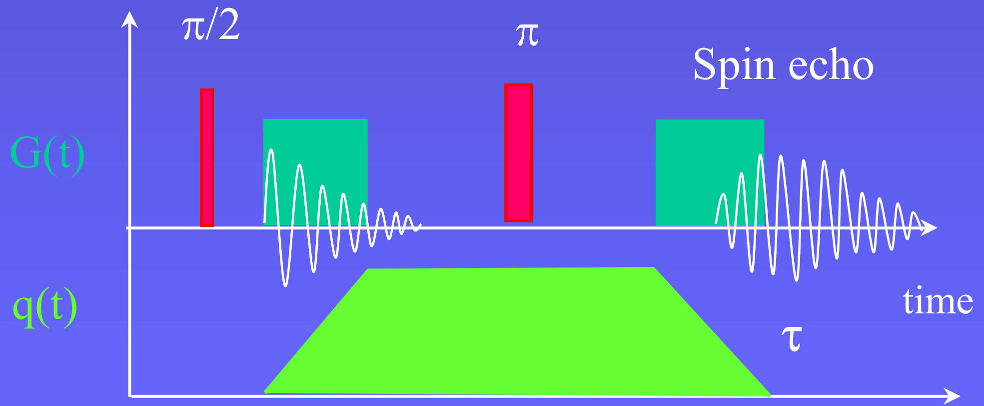
Characteristic lenght of motion is smaller than the phase grating created by applied gradient.

Gaussian phase approximation of spin echo

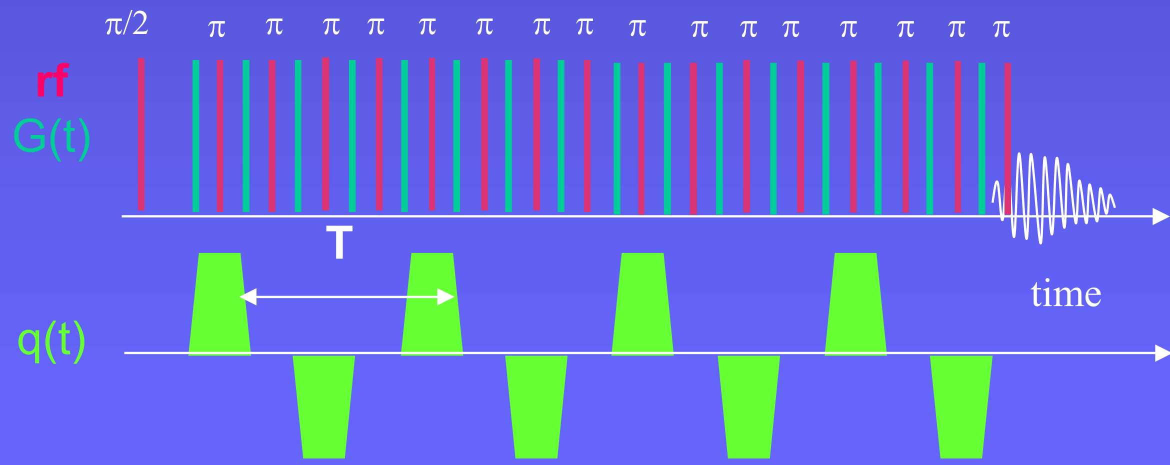
$$E(\tau)=\sum_i \left\langle e^{i\int_0^\tau \mathbf{q}(t).\mathbf{v}_i(t)\,dt} \right\rangle = \sum_i e^{i\int_0^\tau \mathbf{q}(t).\langle \mathbf{v}_i(t)\rangle\, dt - \int_0^\tau\int_0^t \mathbf{q}.\boxed{\langle \Delta\mathbf{v}_i(t)\,\Delta\mathbf{v}_i(t')\rangle}.\mathbf{q}\, dt'dt\, ..}$$

$$\Delta\mathbf{v}_i = \mathbf{v}_i - \langle \mathbf{v}_i(t)\rangle$$

Two gradient pulse spin echo



Modulated gradient spin echo (MGSE)



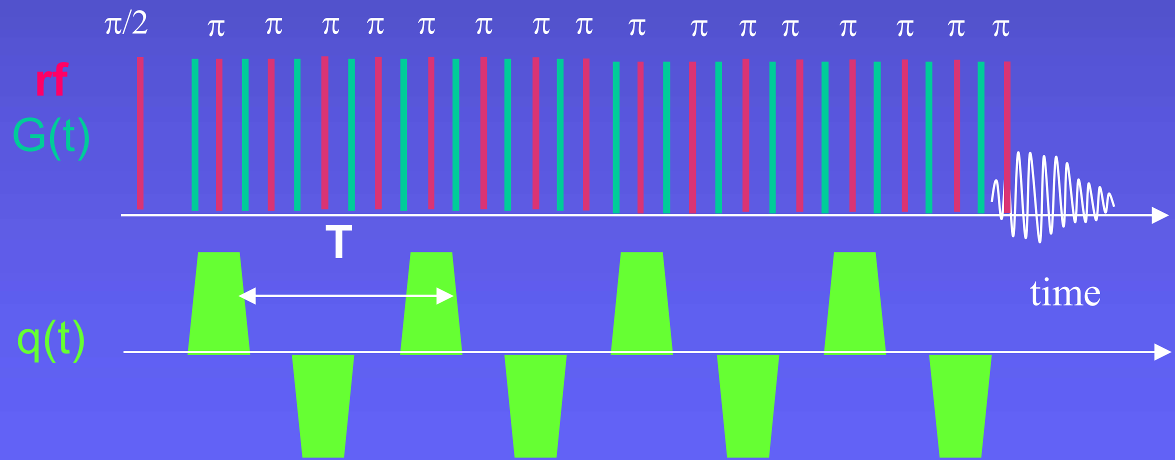
no limits with respect to the gradient pulse
or gradient waveform

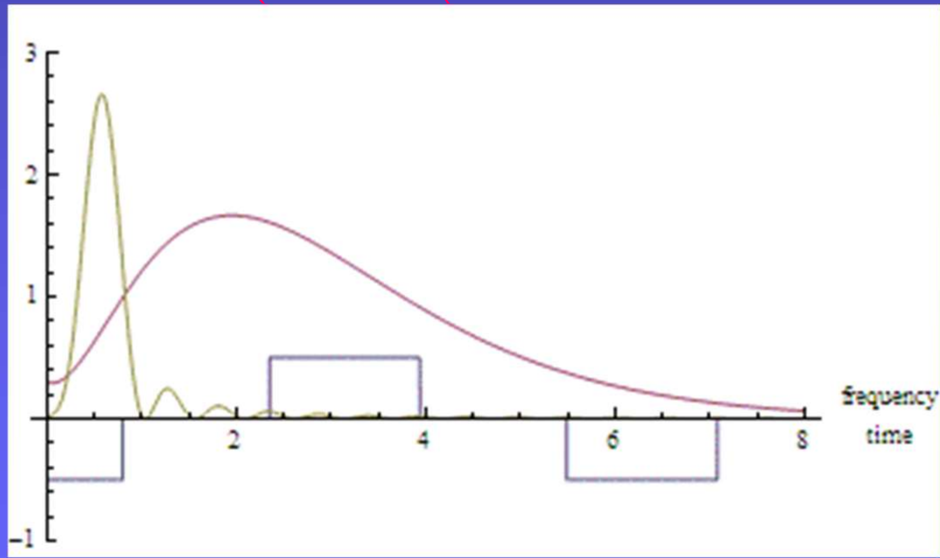
Modulated Gradient Spin Echo (MGSE): time-domain into frequency domain

Velocity autocorrelation spectrum

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

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

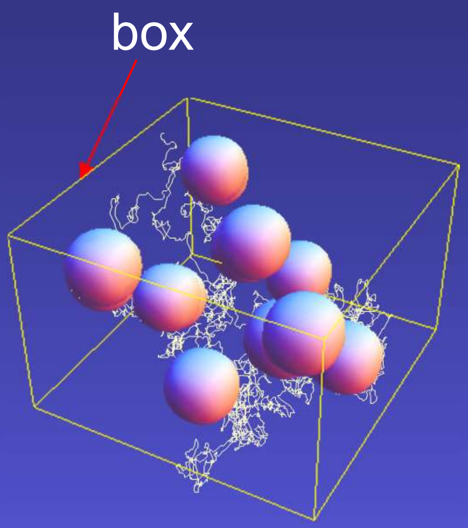




$$E(\tau)\approx e^{-\alpha\, D(\omega_{\mathrm{m}})\tau} \qquad \omega_{\mathrm{m}}=\frac{2\pi}{T}$$

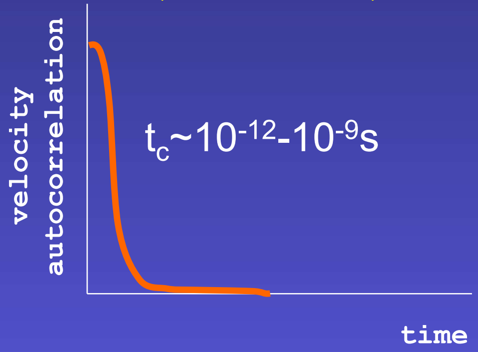
Long-time measurement: During the application of sequence each spin can roam over all characteristic voids of structure and D (ω) is identical for all spins.

Velocity autocorrelation of restricted motion

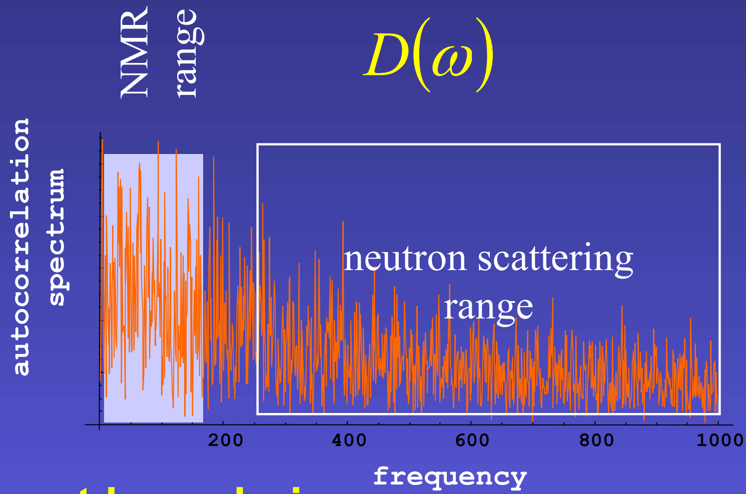


Free diffusion

$$\langle \mathbf{v}(t).\mathbf{v}(0)\rangle$$



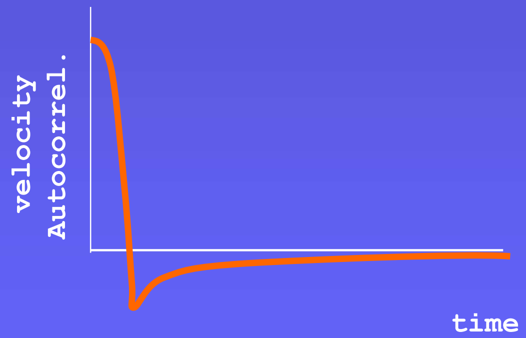
$$D(\omega)$$

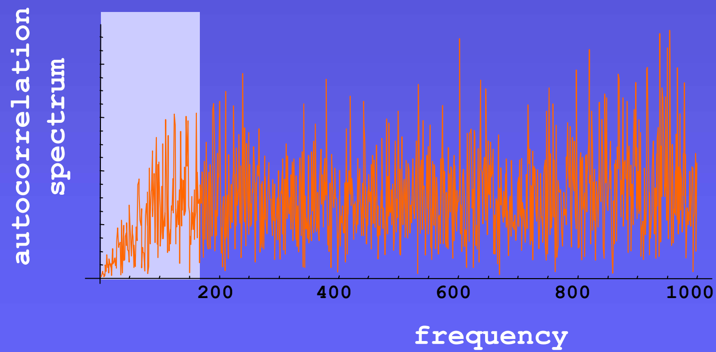


Restricted diffusion- reflection at boundaries

Langevine equation

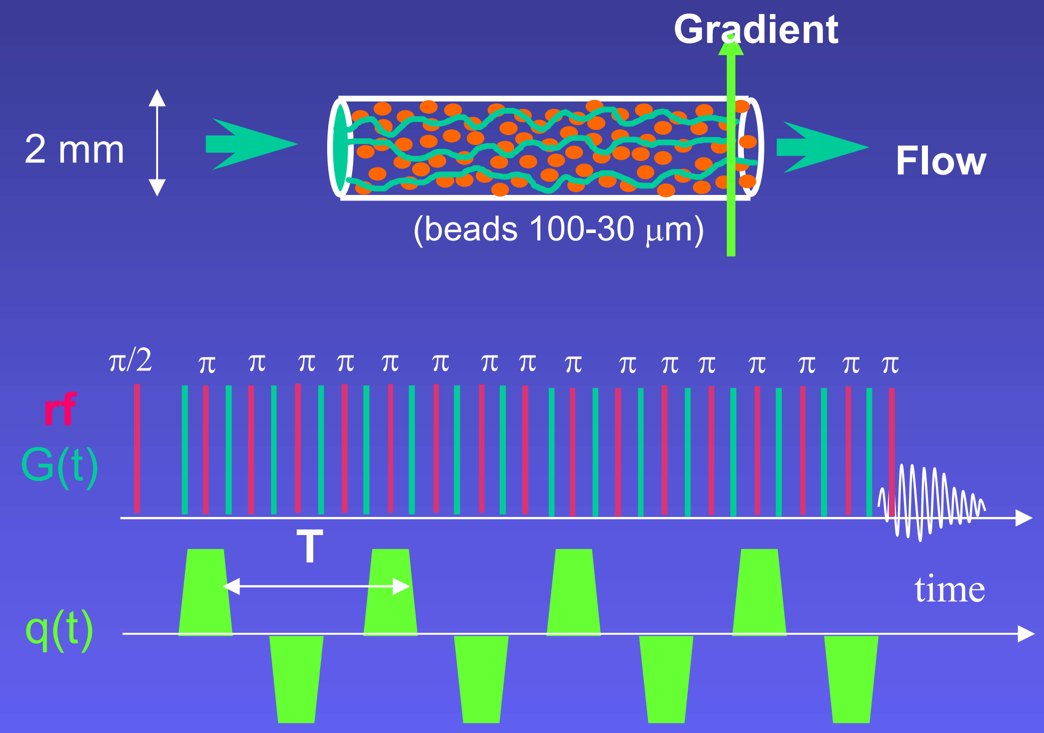
$$\frac{d\mathbf{v}}{dt}+\alpha\,\mathbf{v}=\mathbf{f}(t)$$

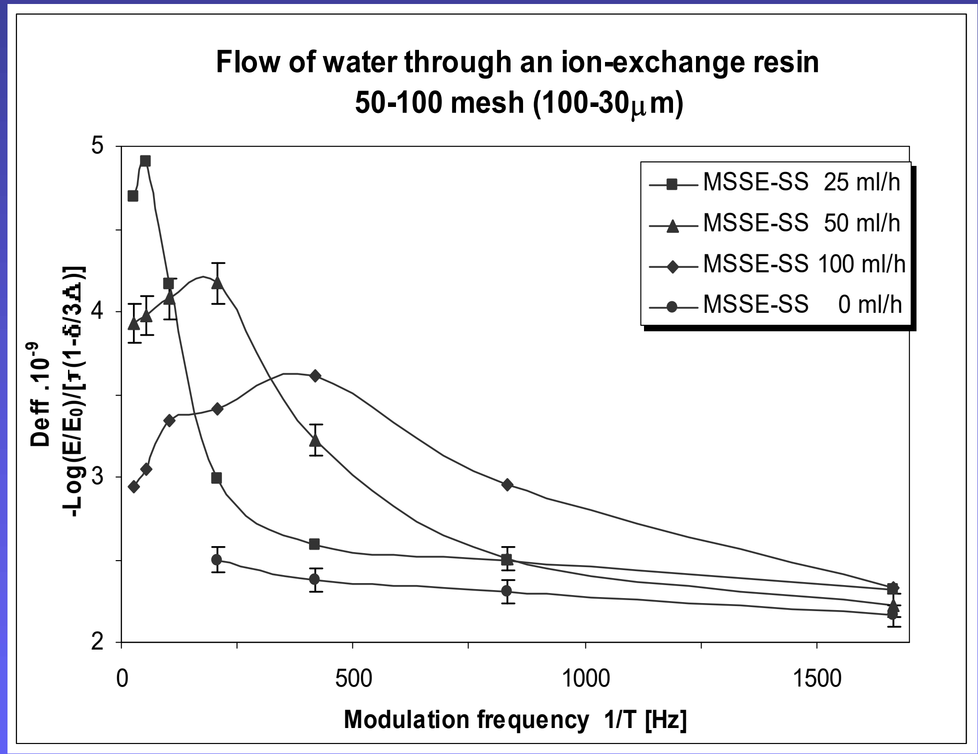




$$\mathrm{D}_{\mathrm{rest}}(\omega)=D_{\infty}+D\sum_k b_k\frac{\tau_k^2\omega^2}{1+\tau_k^2\omega^2}$$

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





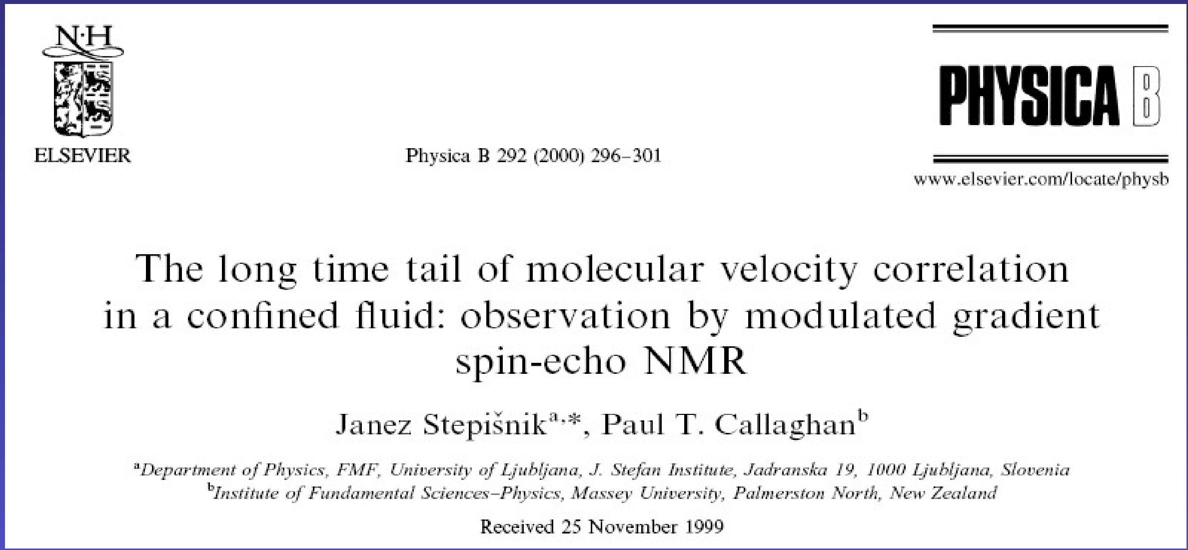
$$E(\tau) \approx \sum_j e^{-\alpha D_j (\omega_m)\tau} \qquad \omega_m = \frac{2\pi}{T}$$

Dispersion spectra for water flow through ion-exchange-resin bead pack at different velocities as measured by MGSE sequence (δ=70μs).

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

University of Ljubljana, FMF Slovenia

Diffusion spectra in porous medium



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Physica B 292 (2000) 296–301
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The long time tail of molecular velocity correlation in a confined fluid: observation by modulated gradient spin-echo NMR

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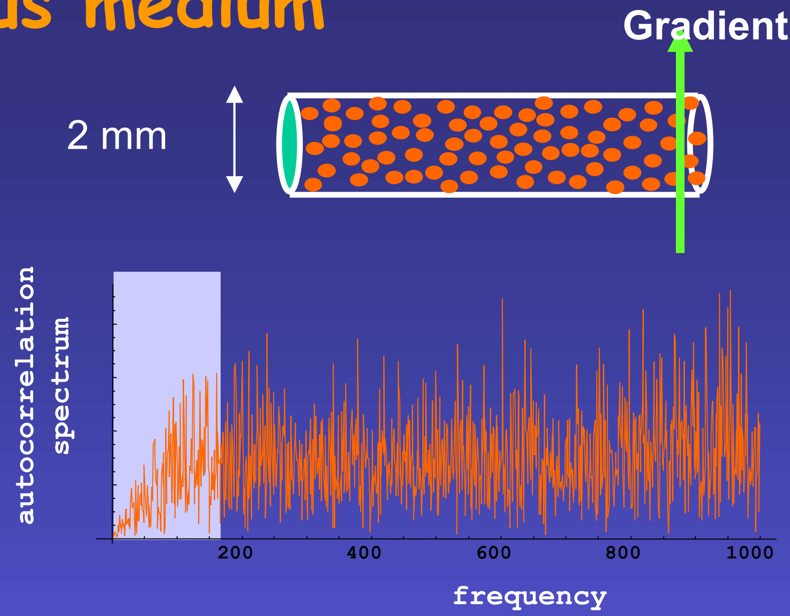
Received 25 November 1999



Frequency range to 1.5 kHz

Pore size ~10μm

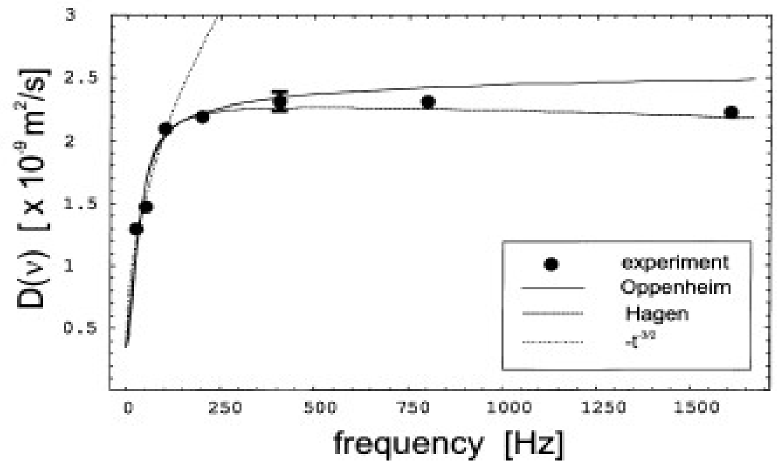


Fig. 3. The spectrum of velocity correlation function of particles confined in the porous structure of closely packed polystyrene beads of radius 15 μm as measured by modulated gradient spin echo and its fit with the theoretical results.

Restricted diffusion in emulsion droplets

Journal of Magnetic Resonance 156, 195–201 (2002)
doi:10.1006/jmre.2002.2556

Restricted Self-Diffusion of Water in a Highly Concentrated W/O Emulsion Studied Using Modulated Gradient Spin-Echo NMR

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Received September 21, 2001; revised April 4, 2002

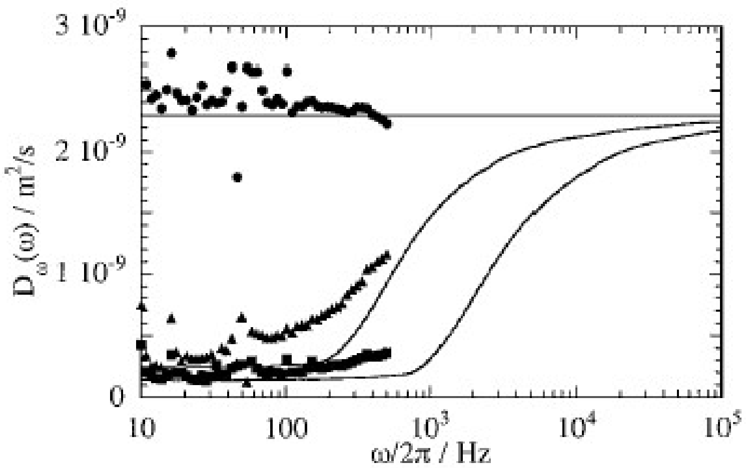
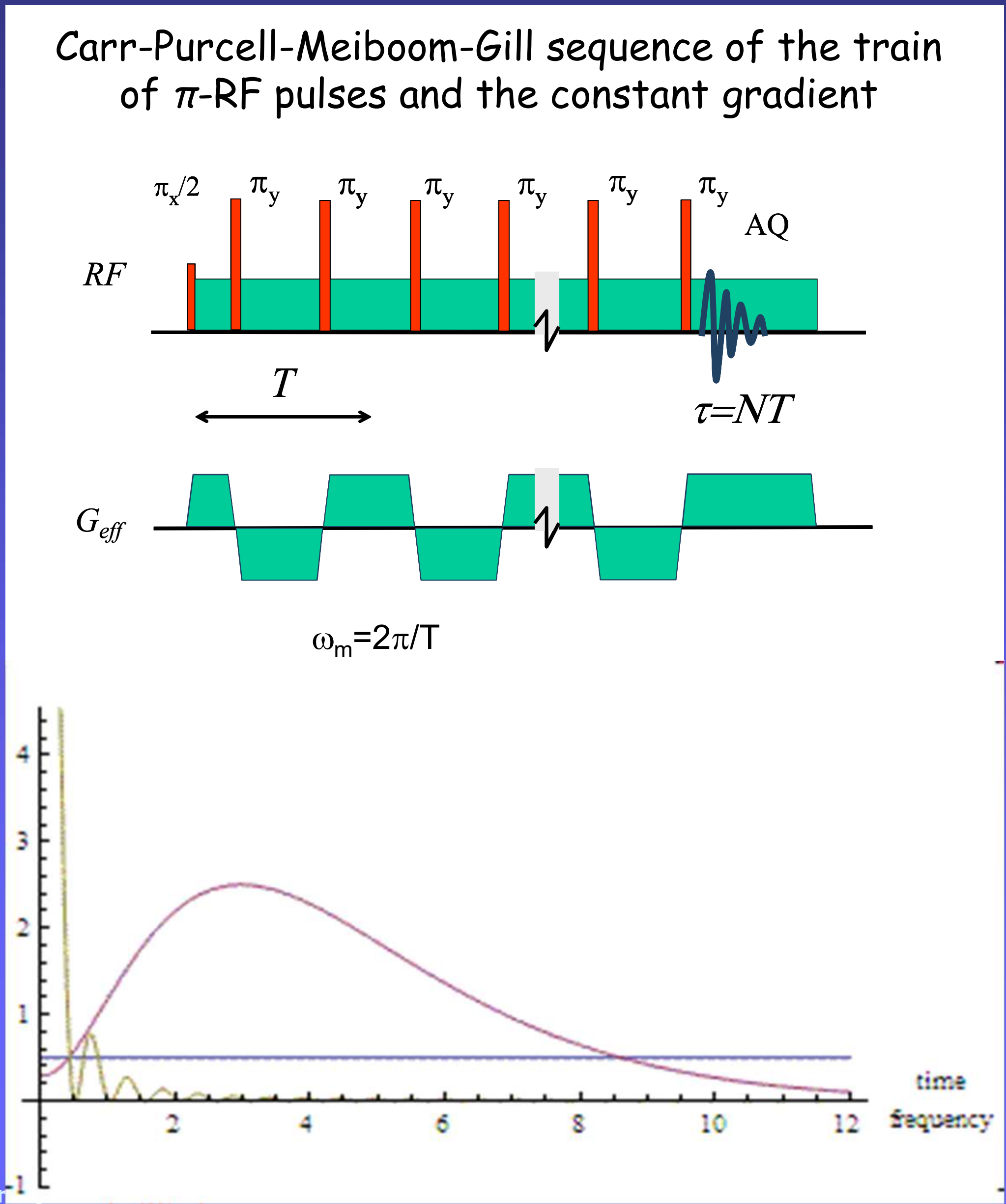


FIG. 5. The frequency-dependent diffusion coefficient $D_\omega(\omega)$ for free water (circles) and water confined within emulsion droplets in a highly concentrated fresh (squares) and aged (triangles) emulsion. The two lower lines are calculated according to the flow-scheme in Fig. 9. The upper line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

Frequency range to 0.5-1 kHz

[3] P.T. Callaghan, S.L. Codd, Flow coherence in a bead pack observed using frequency domain modulated gradient nuclear magnetic resonance, Phys. Fluids 13 (2001) 421–426.
[5] E.C. Parsons, M.D. Does, J.C. Gore, Modified oscillating gradient pulses for direct sampling of the diffusion spectrum suitable for imaging sequences, Magn. Reson. Imaging 21 (2003) 279–285.

CPMG sequence with the constant gradient as MGSE sequence



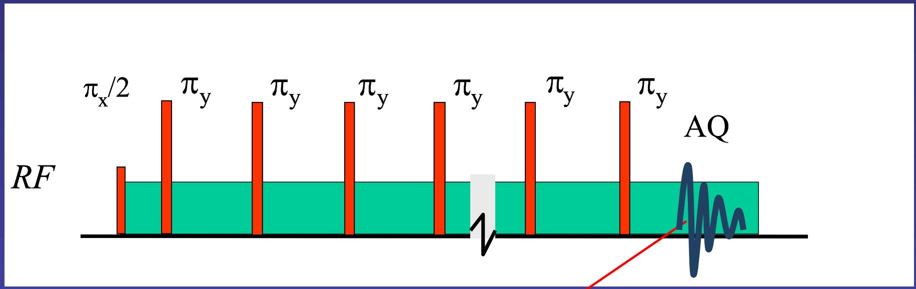
$$\beta(\tau) = \frac{\gamma^2}{2\pi} \int_{-\infty}^{\infty} D(\omega) \left| q(\omega,\tau) \right|^2 d\omega$$

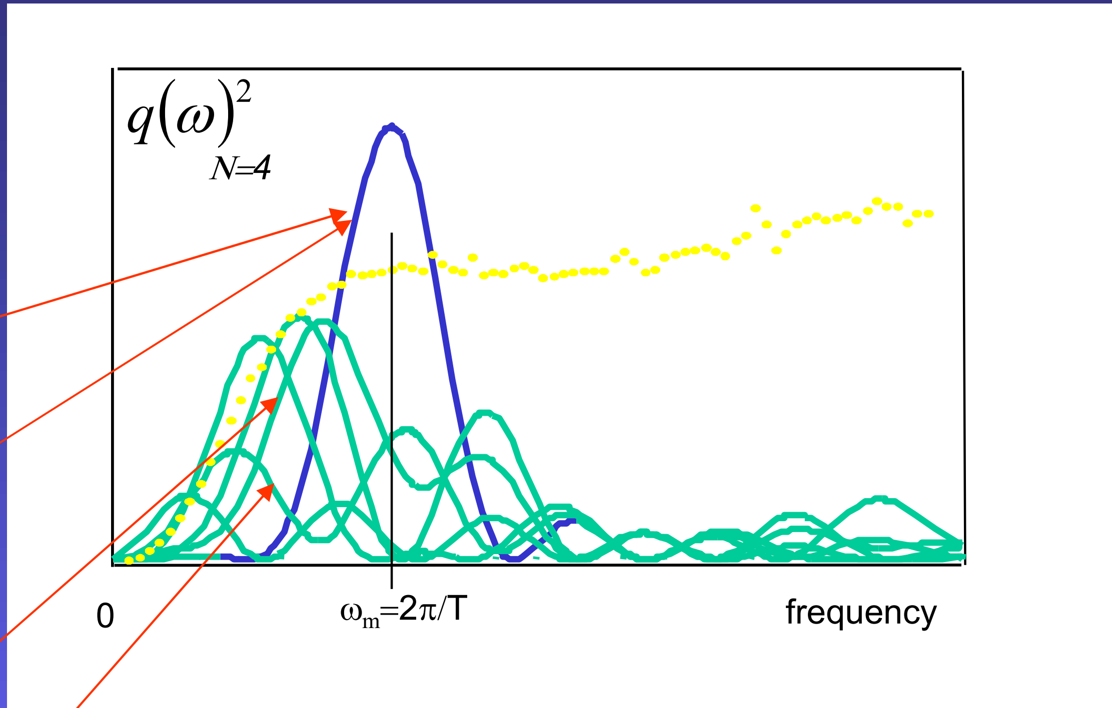
$$= \frac{8\gamma^2 G^2}{\pi^2 \omega_m^2} NT\, D(\omega_m)$$

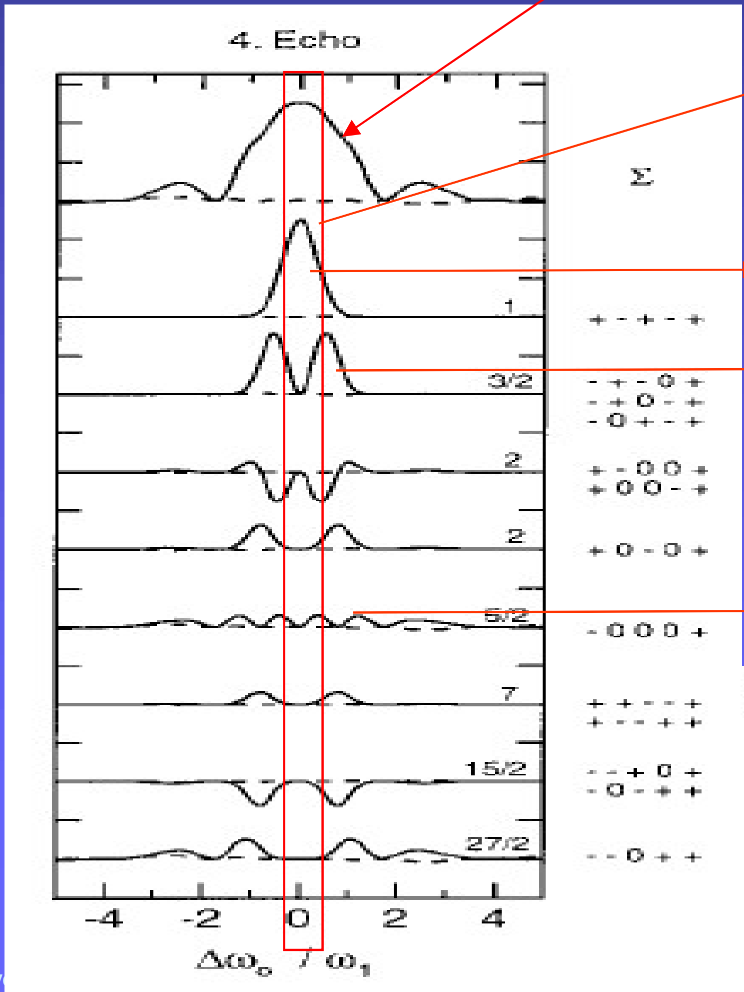
Frequency range to above 10 kHZ

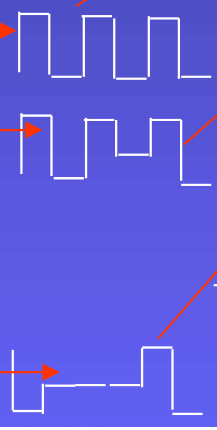
J. G. Seland, G.H. Sørland, K. Zick and B.Hafskjold: **Diffusion Measurements at Long Observation Times in the Presence of Spatially Variable Internal Magnetic Field Gradients,** J of Mag. Res. 146, (2000), 14-19

Resonance offset ⟹ coherence pathways









$$\frac{\Delta\omega_0}{\omega_1} = \frac{\gamma G \Delta z}{\pi/\delta} \ll 1$$

Journal of Magnetic Resonance 148, 367–378 (2001)
doi:10.1006/jmre.2000.2263, available online at http://www.idealibrary.com on IDEAL®

Diffusion and Relaxation Effects in General Stray Field NMR Experiments

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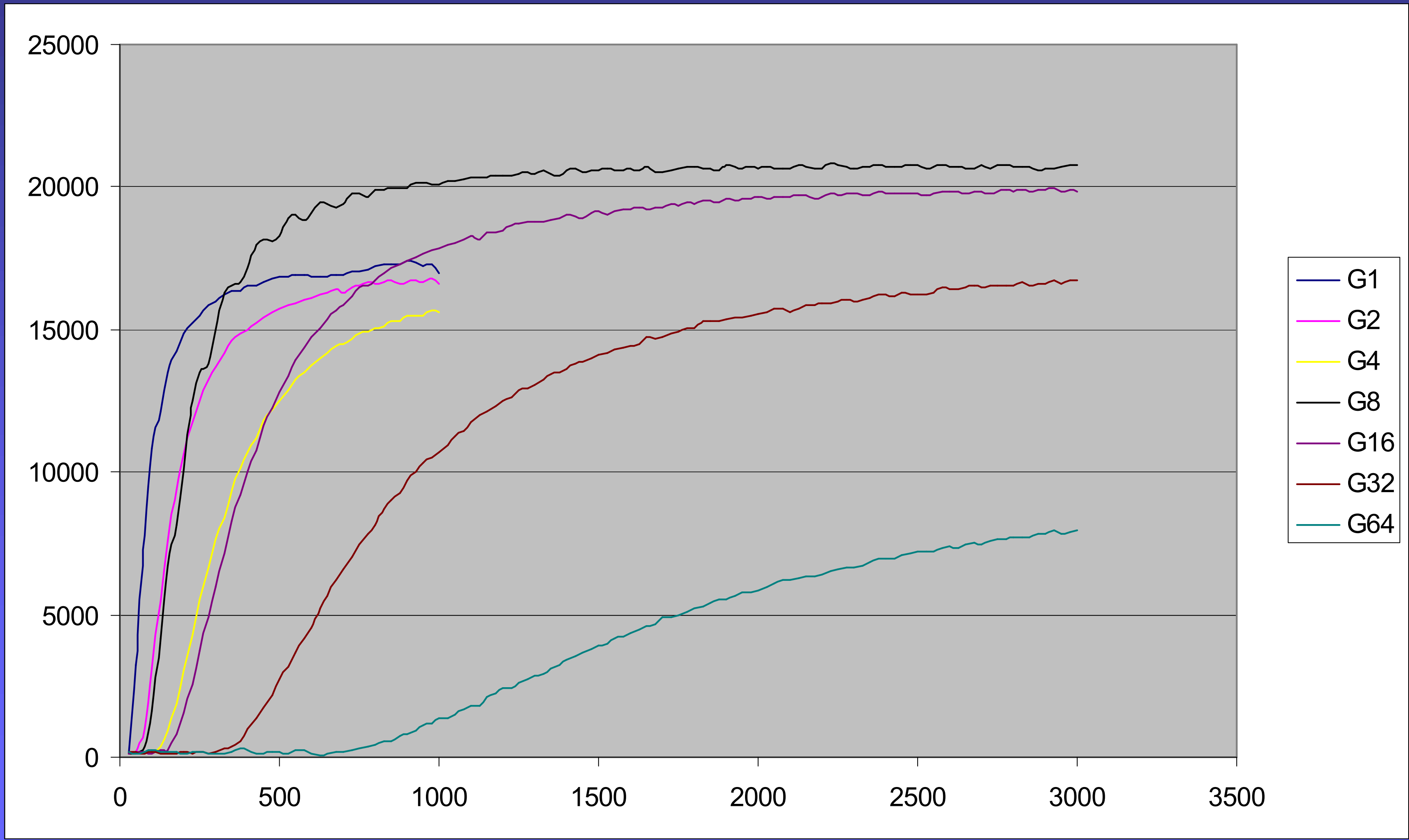
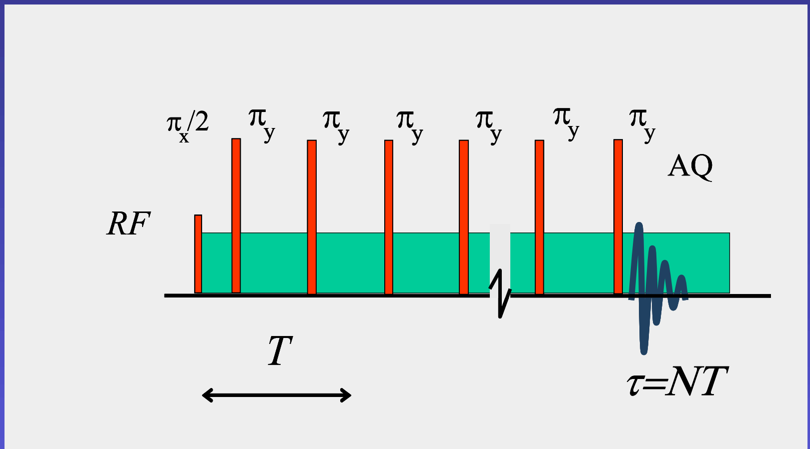
Received July 31, 2000; revised November 16, 2000

CPMG measurement of diffusion



Velocity autocorrelation spectrum of fluid in porous structure



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

$$\lim_{\omega\to 0} D_{rest}(\omega) = D(b_1 + \frac{\chi^4 a^4}{D^2}\omega^2 + \ldots),$$

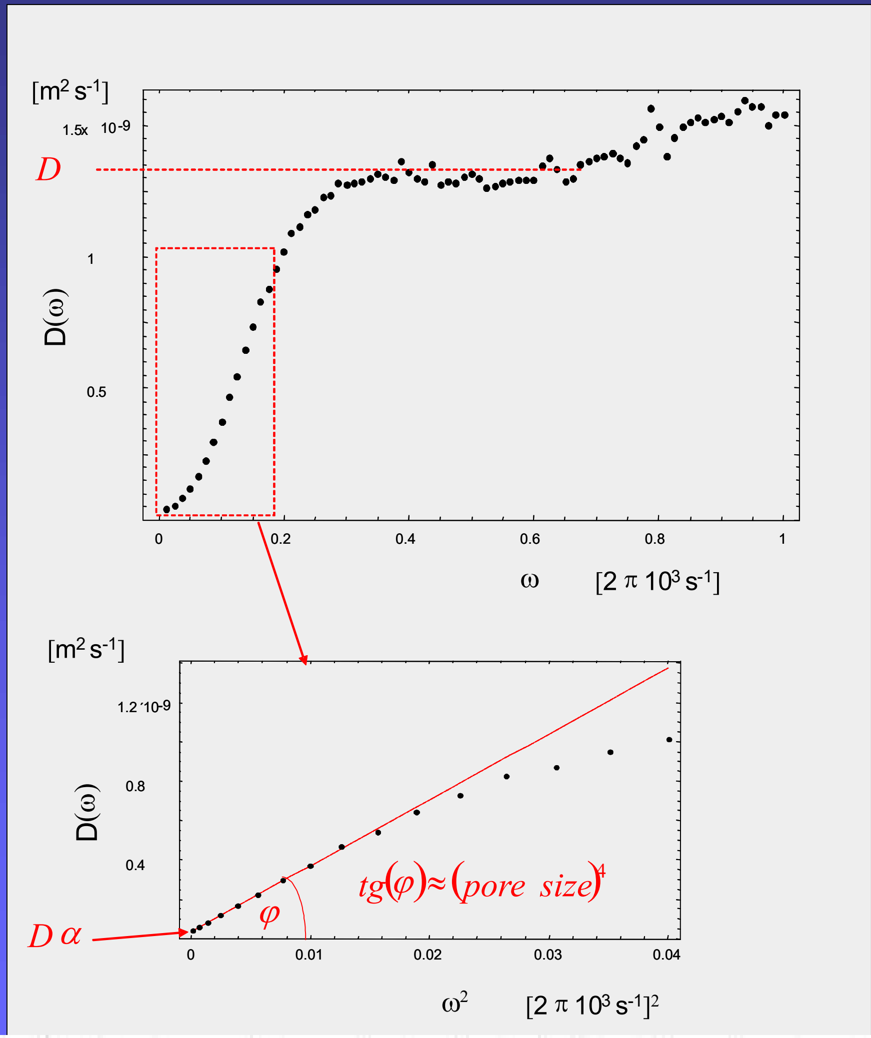
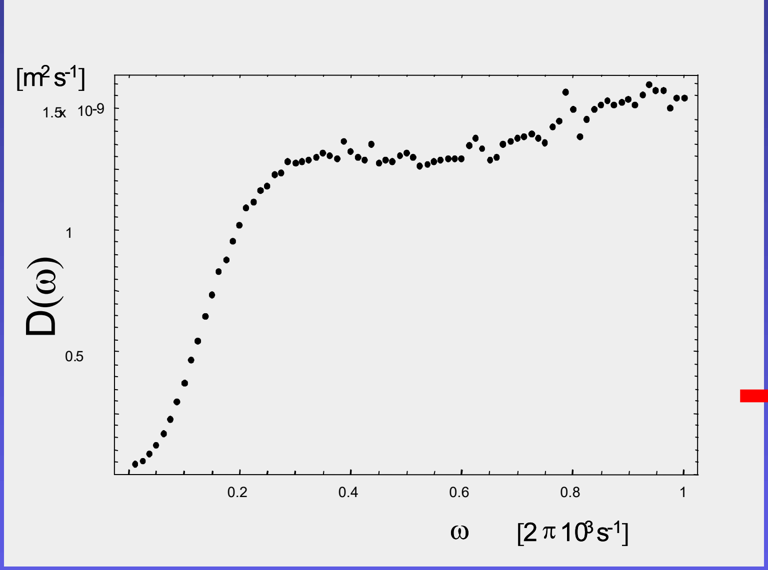


Fig. 2. Velocity auto-correlation spectra of molecular diffusion in the water-saturated silica powder derived from the power spectrum of displacement in Fig.1. Enlarged low-frequency part of the spectrum versus ω^2 exhibits a linear dependence with the slope proportional to the mean forth-power of pore size.

Mean squared displacement from VAS

$$\left\langle [z(t)-z(0)]^2 \right\rangle = \frac{4}{\pi}\int_0^\infty D(\omega)\frac{1-\cos(\omega t)}{\omega^2}d\omega$$



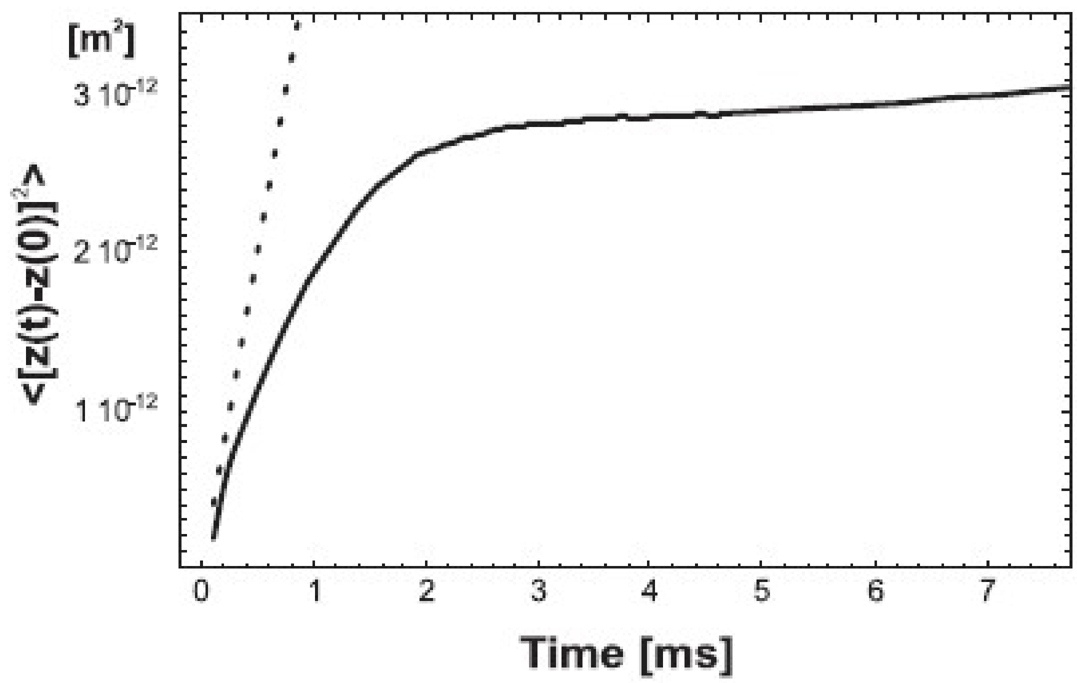
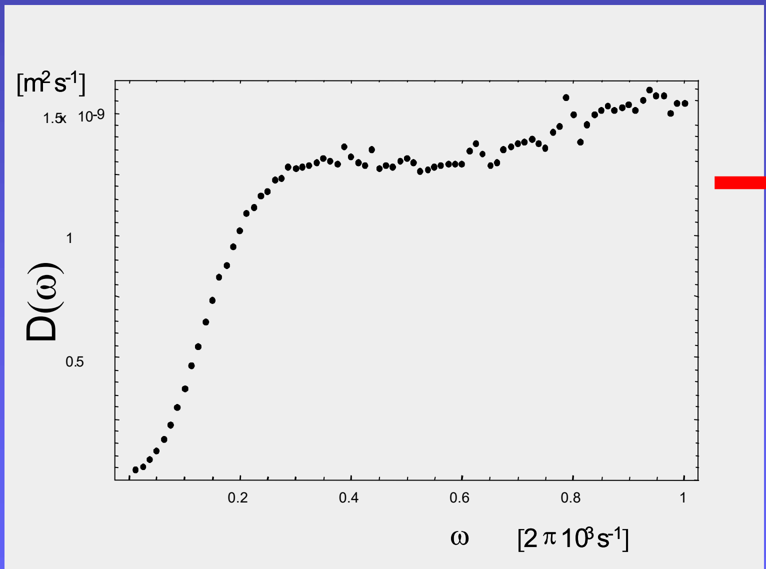
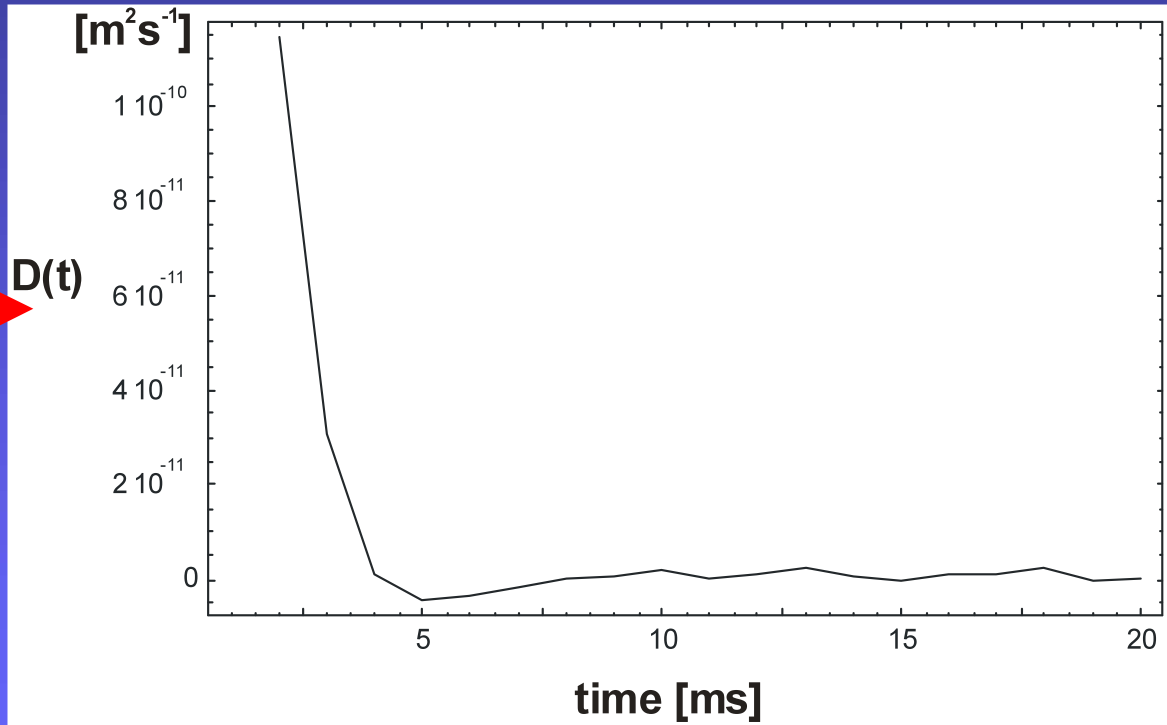


Fig. 4. Time dependence of the mean squared displacement obtained from the Fourier transform of the power spectrum of displacement in Fig.1 demonstrates the time resolution of the method.

Time dependent diffusion constant

$$D(t) = \frac{2}{\pi}\int_0^\infty D(\omega)\frac{\sin(\omega t)}{\omega}d\omega$$





Surface-to-volume ratio from VA spectrum

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

$$\lim_{1/\omega\to 0} D_{rest}(\omega) = D\left(1 - 1.11072\frac{4S}{\pi V}\sqrt{\frac{D}{\omega}} + ..\right)$$

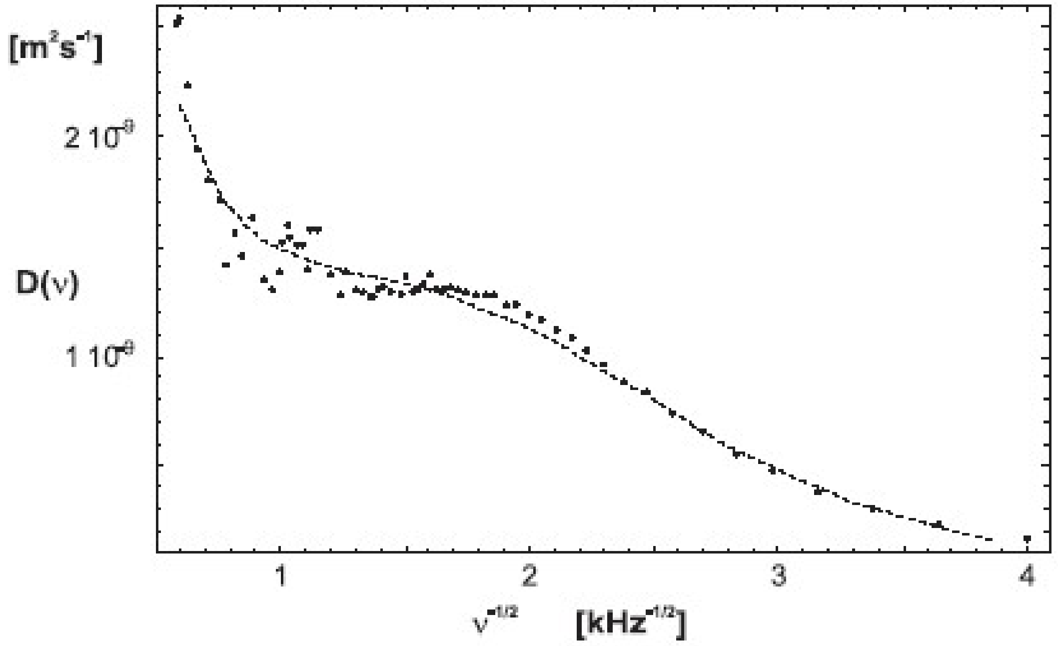
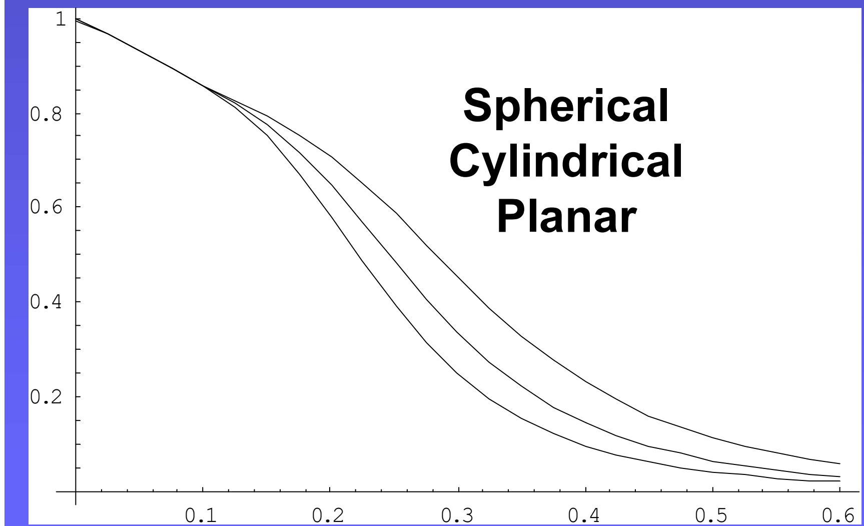
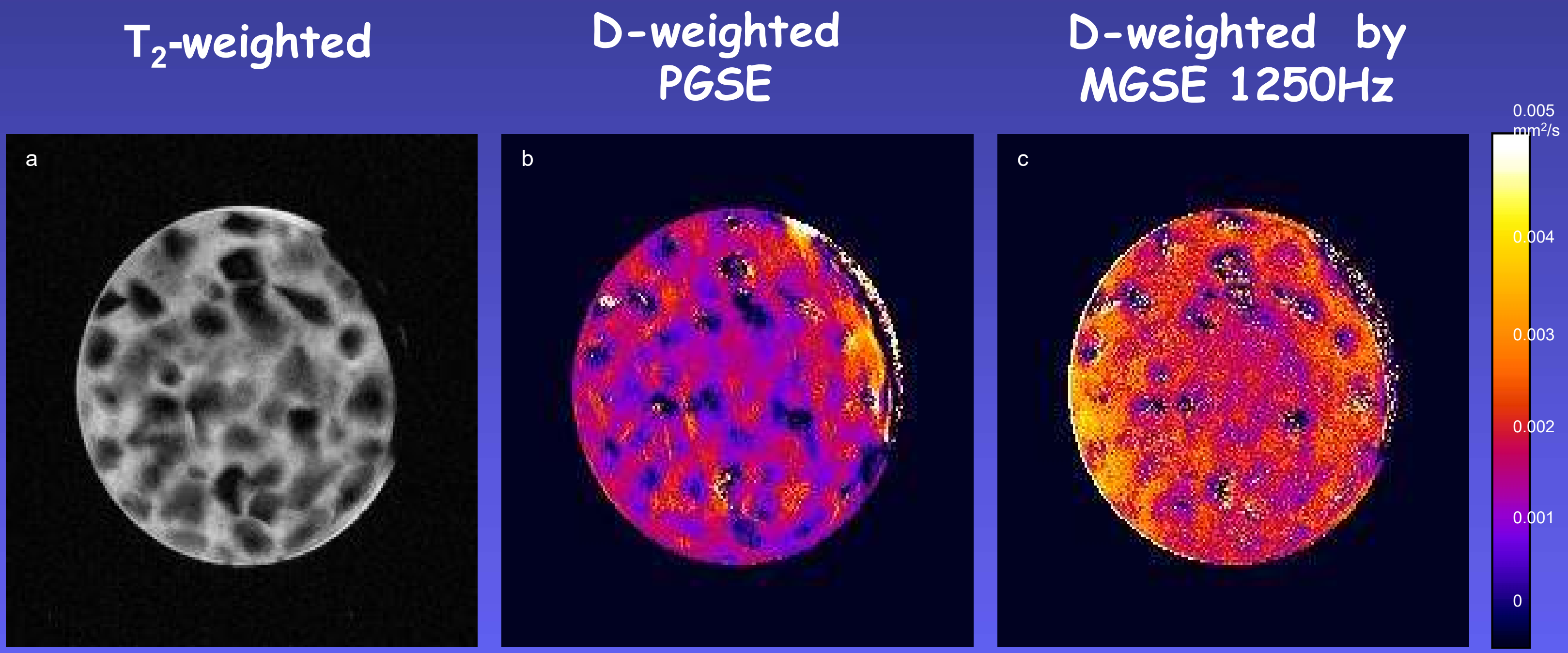


Fig. 3. Surface-to-volume of porous structure is proportional to initial slope in the plot of velocity auto-correlation versus inverse-squared-root of frequency. The dotted curve is the spectrum of distribution with 90% of spherical closed pores with the size of 3.4 μ and 10% with the size of 0.7 μ .

Calculations

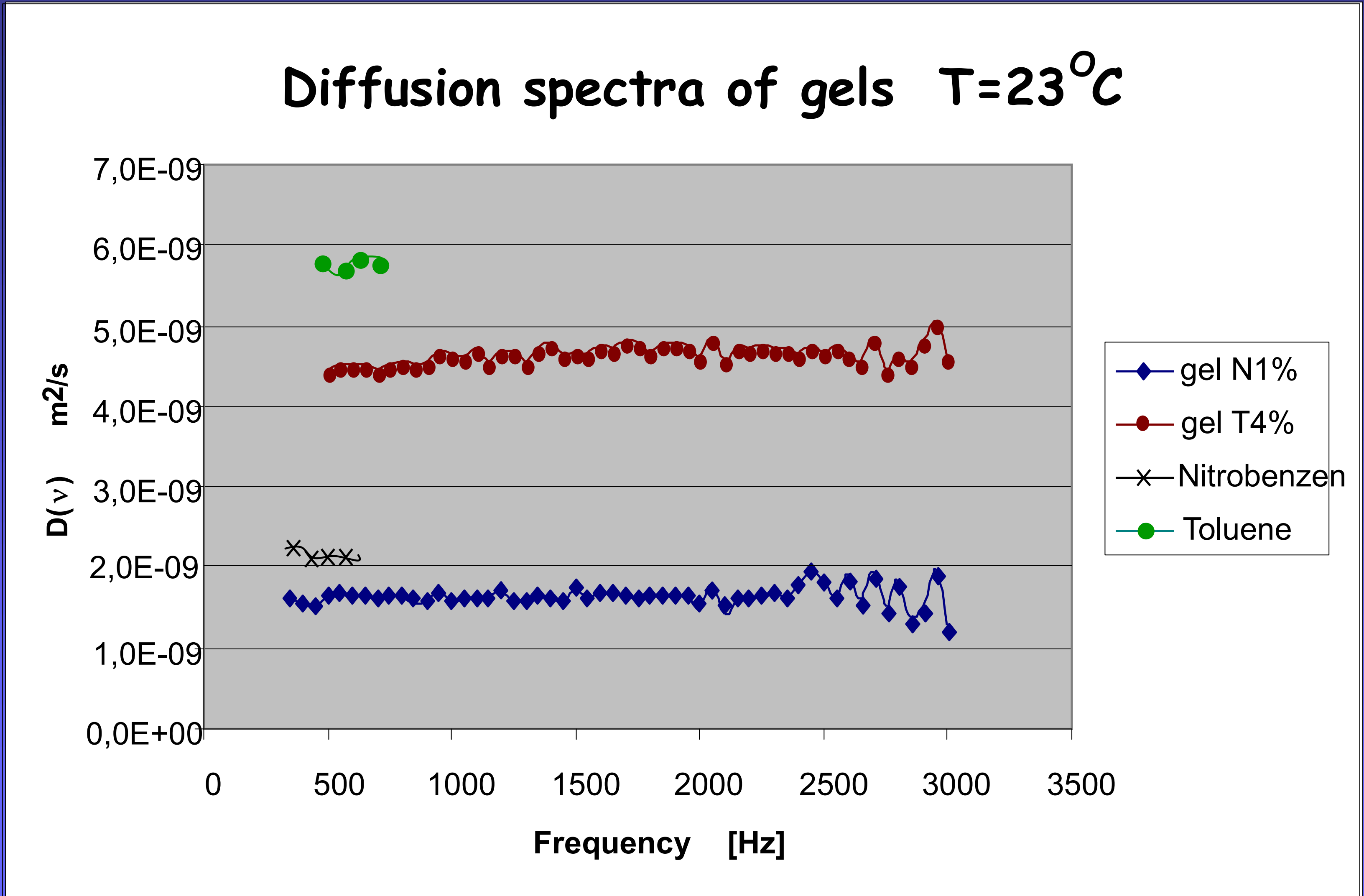


MRI of polenta after 2 minutes of cooking

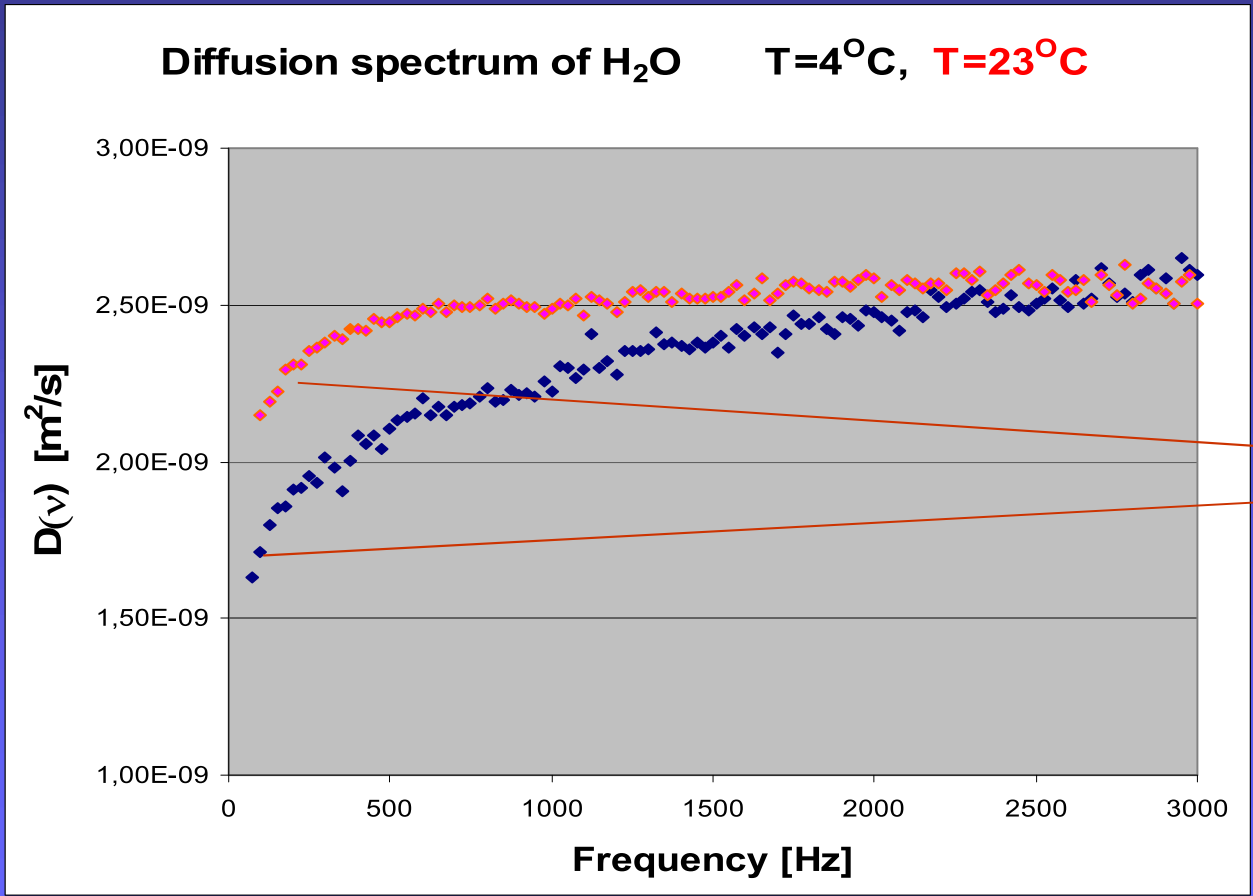


Igor Serša, Urša Mikac, J. Stefan Institute

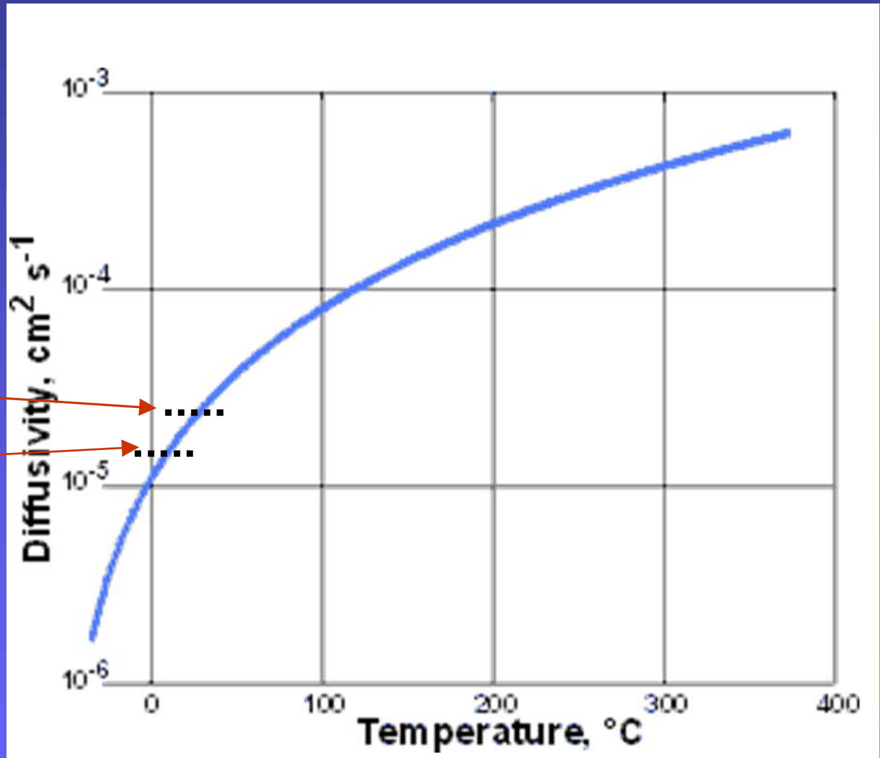
Self-diffusion spectra of gels



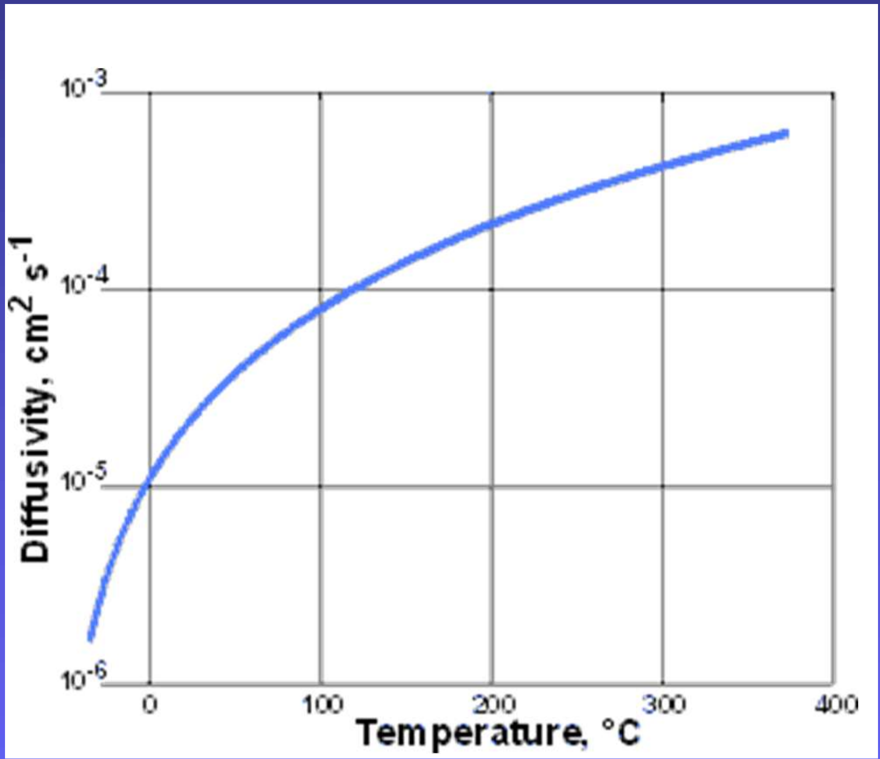
Self-diffusion of water



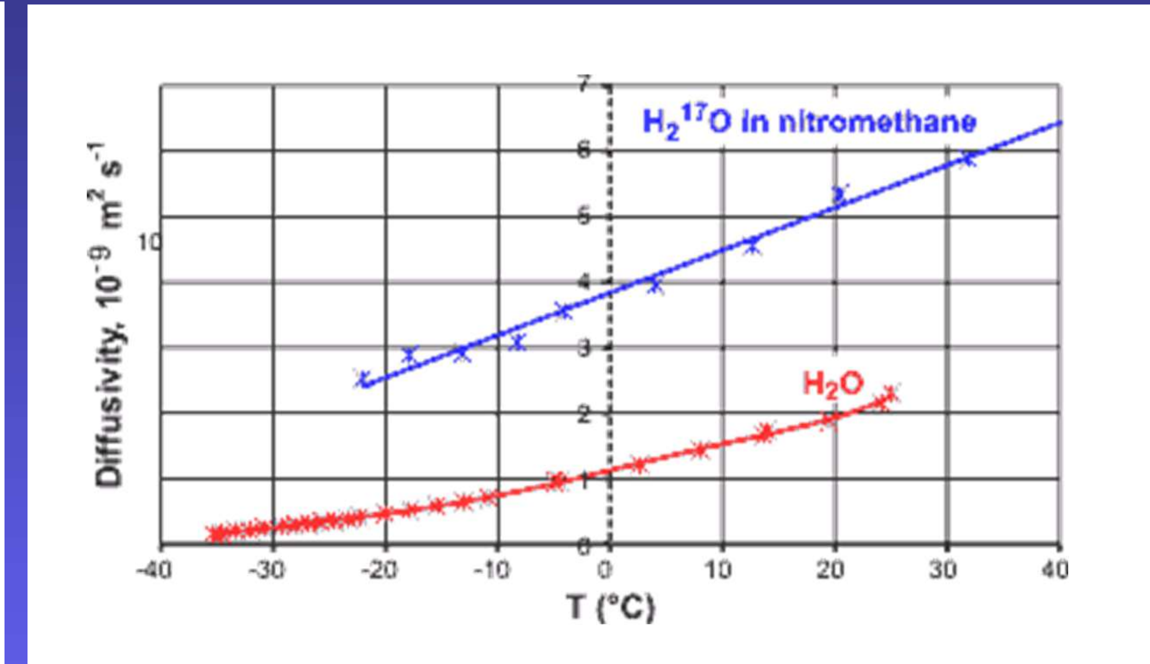
PGSE measurement



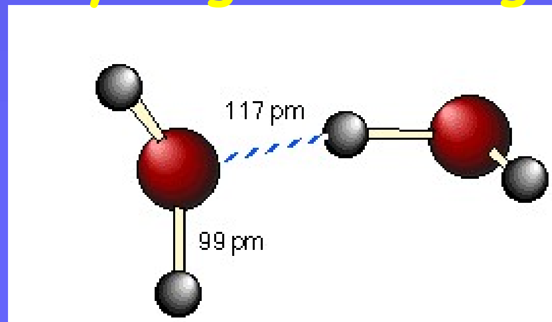
Anomalous self-diffusion of water



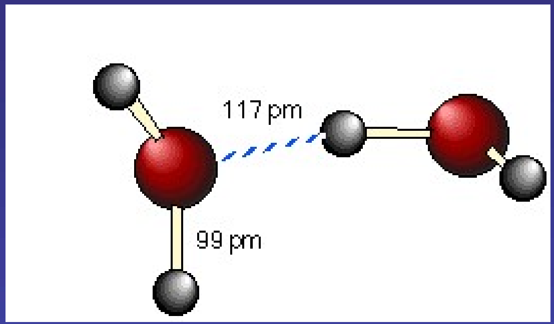
Water in nitromethane



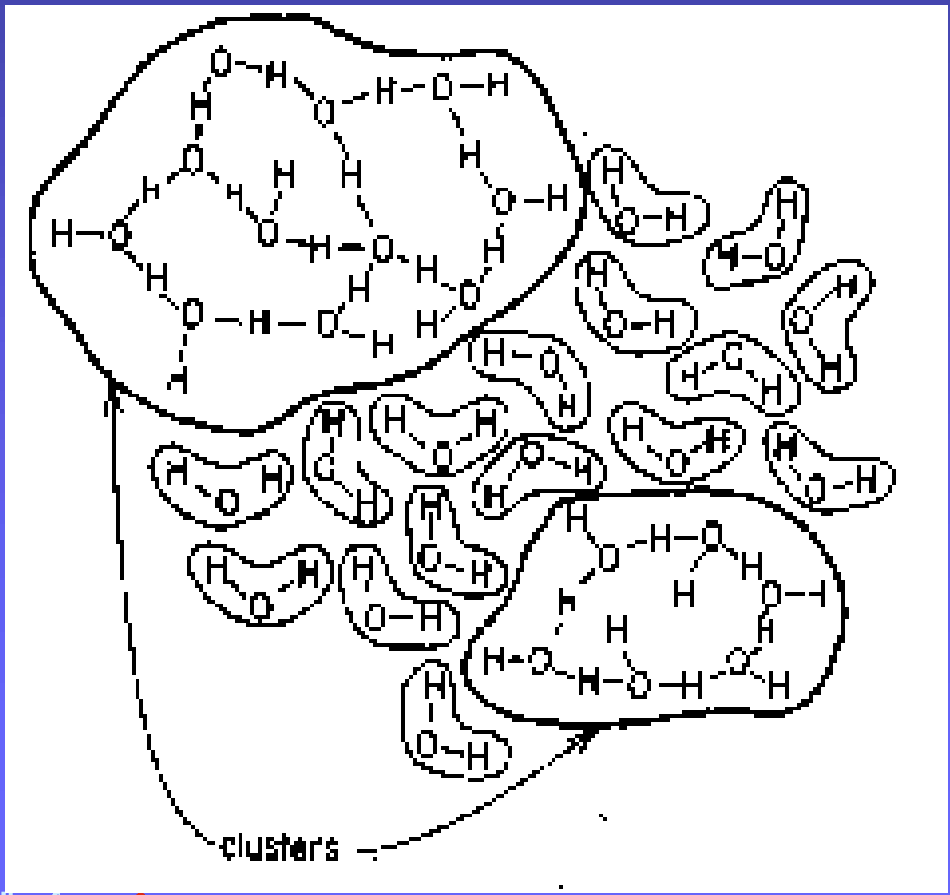
Hydrogen bonding



Models of water clusters



Hypothesis till 1950

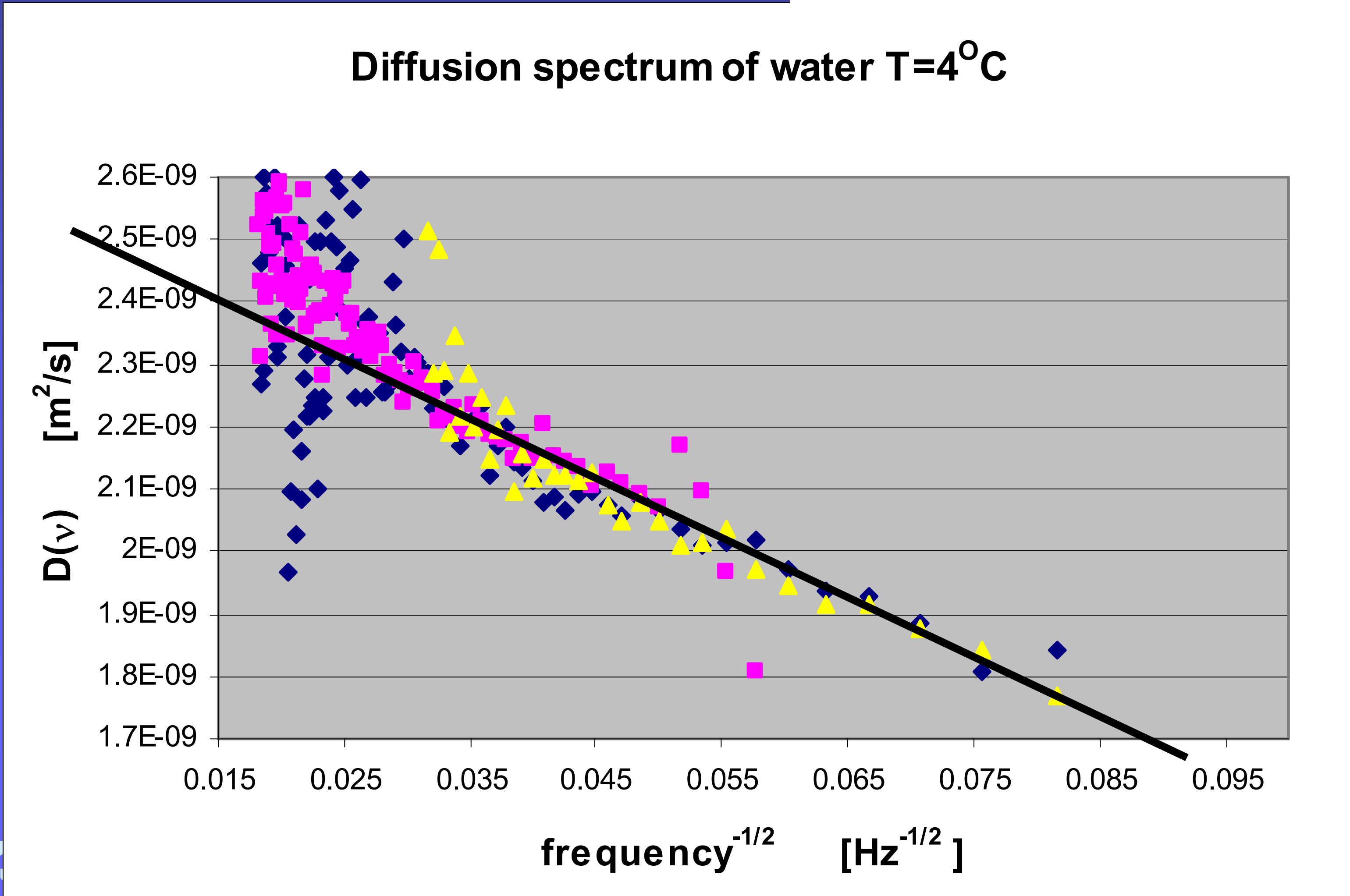


from 1980:

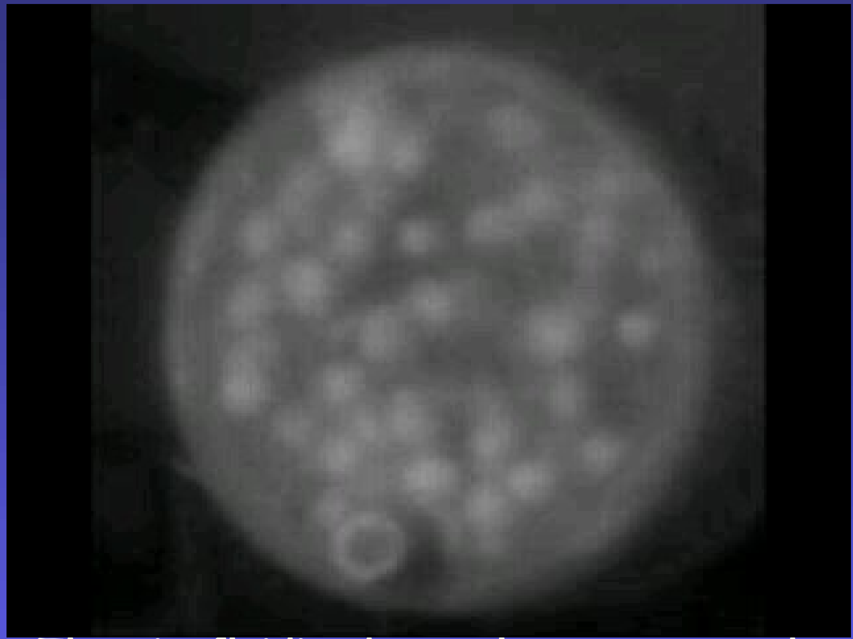
On a very short time scale (about a picosecond), water is more like a "gel" consisting of a single, huge hydrogen-bonded cluster.

Restricted self-diffusion of water ?

$$\lim_{1/\omega \to 0} D_{rest}(\omega) = D\left(1 - 1.11072 \frac{4\,S}{\pi\,V}\sqrt{\frac{D}{\omega}} + ..\right)$$



Air-fluidized granular system



The air-fluidized granular system made up of mustard seeds,
with the high speed camera 1frame/1 ms

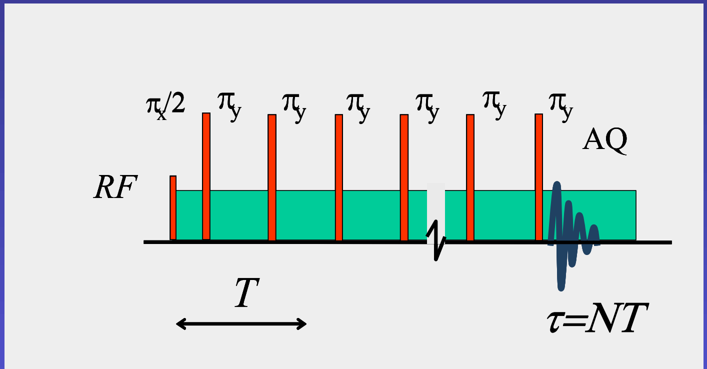
Sand dunes, grain silos,
building materials,
catalytic beds,
filtration towers,
riverbeds
snowfields, many foods….

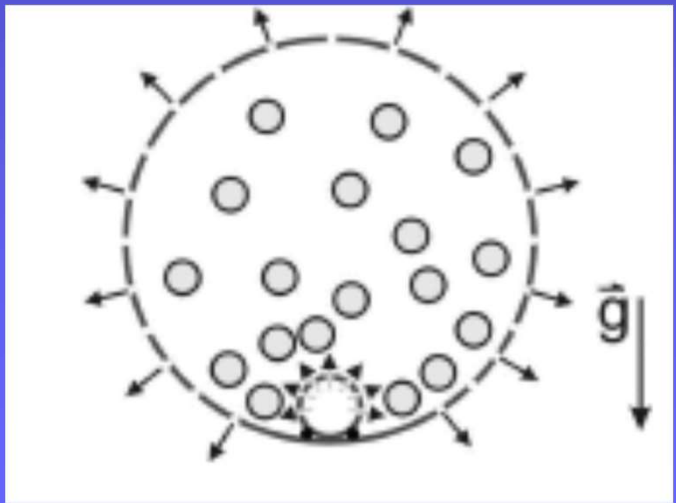
Fluidized granular systems:
catalysis of gas-phase reactions
transport of powders
combustion of ores

Measuring techniques:

high speed photography,
CCD camera,
diffusing-wave spectroscopy,
PGSE (MIT, Harvard, Aachen..)

Velocity autocorrelation spectrum of fluidized granular system by CPMG





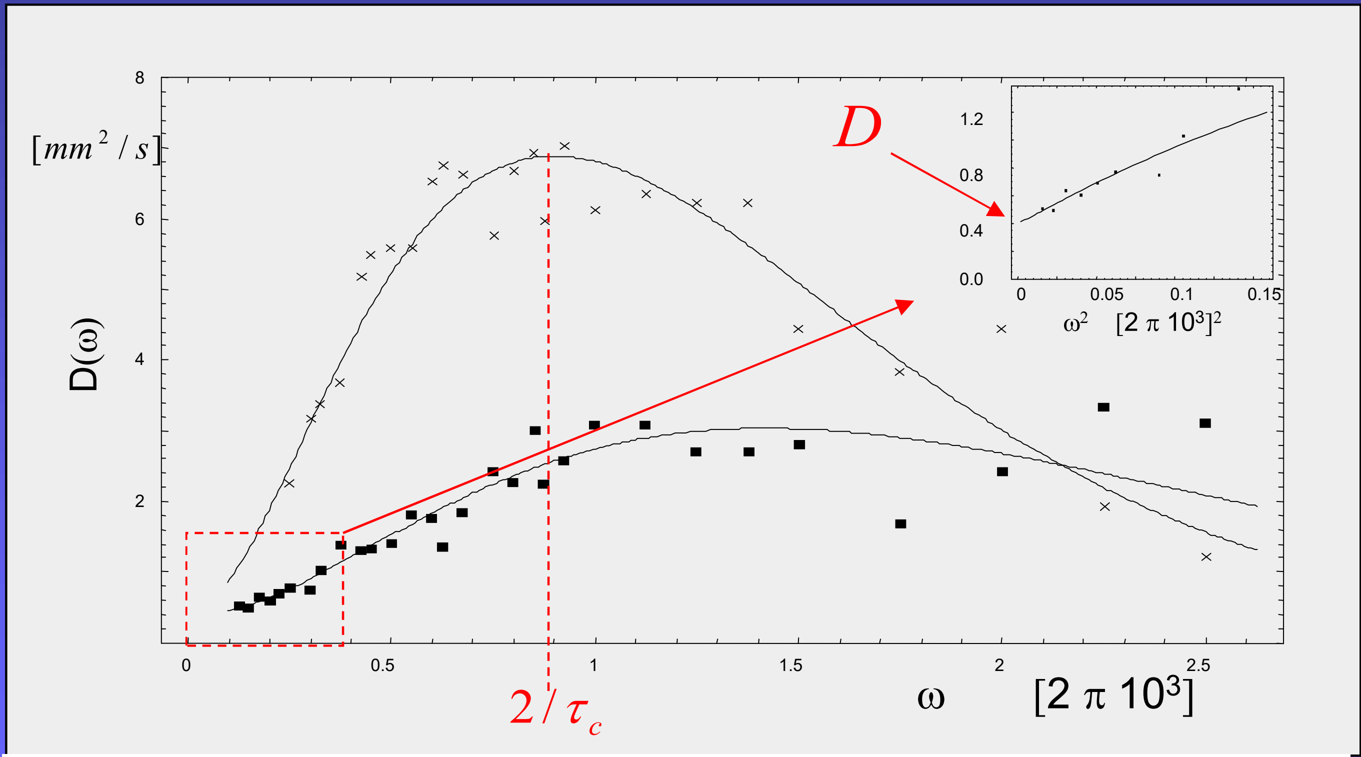


Fig. 3 – A) The velocity autocorrelation spectrum of grains in the system of oil-filled beads fluidized by the air flow at 0.25 bar (squares) and at 0.5 bar (crosses). B) The intersection $D(0)$ gives the cage-breaking rate, while the line slope is related to the mean path of beads between collisions.

Dependence of VA spectra on the grain density and the air-flow rate

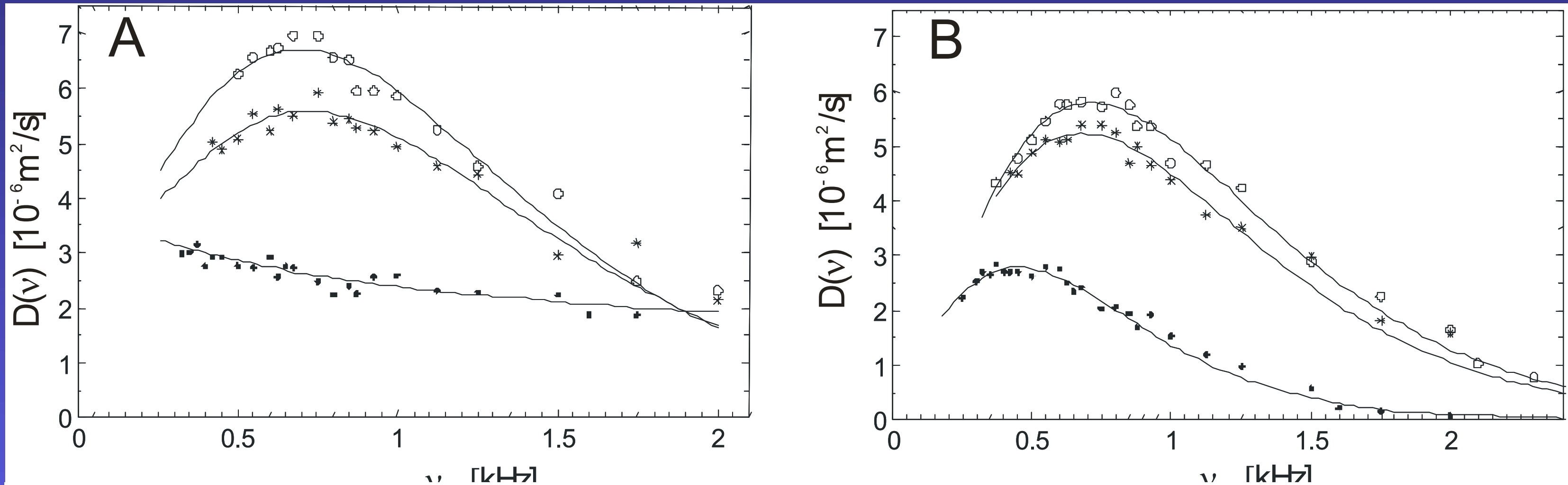


Fig. 4 – The power spectrum of grain velocity fluctuation in the system of mustard seeds fluidized by the air-flow at 0.25 bar (dots) and 0.5 bar (stars) and 1 bar (circles) at two different fillings: A) 150 seeds and B) 175 seeds. The fitting parameters of curves (from lower to upper) are: A) $\langle\xi^2\rangle = 0.22, 3.6, 4.8 \times 10^{-9}$ m^2, $\tau_c = 0.11, 0.39, 0.42$ ms, $D = 3.8, 3.8, 3.6 \times 10^{-6}$ m^2/s and B) $\langle\xi^2\rangle = 3.1, 4.2, 4.65 \times 10^{-9}$ m^2, $\tau_c = 0.65, 0.45, 0.44$ ms, $D = 1.4, 1.3, 0.6 \times 10^{-6}$ m^2/s

Empiric formula

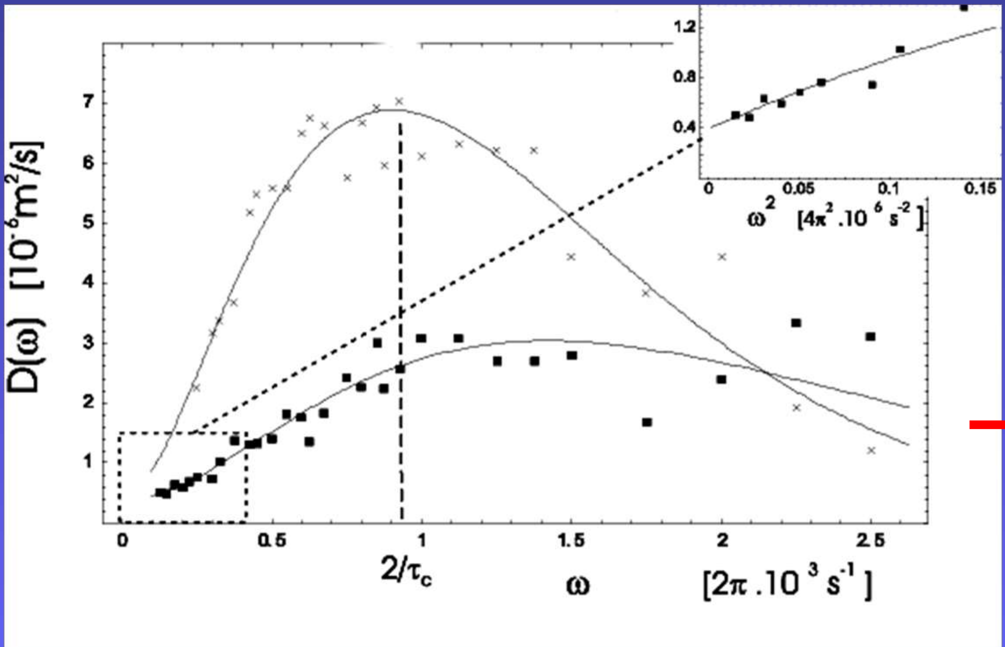
$$I_z(\omega) = \frac{D + \langle\xi^2\rangle\tau_c\omega^2}{\omega^2}\, e^{-\tau_c\omega}.$$

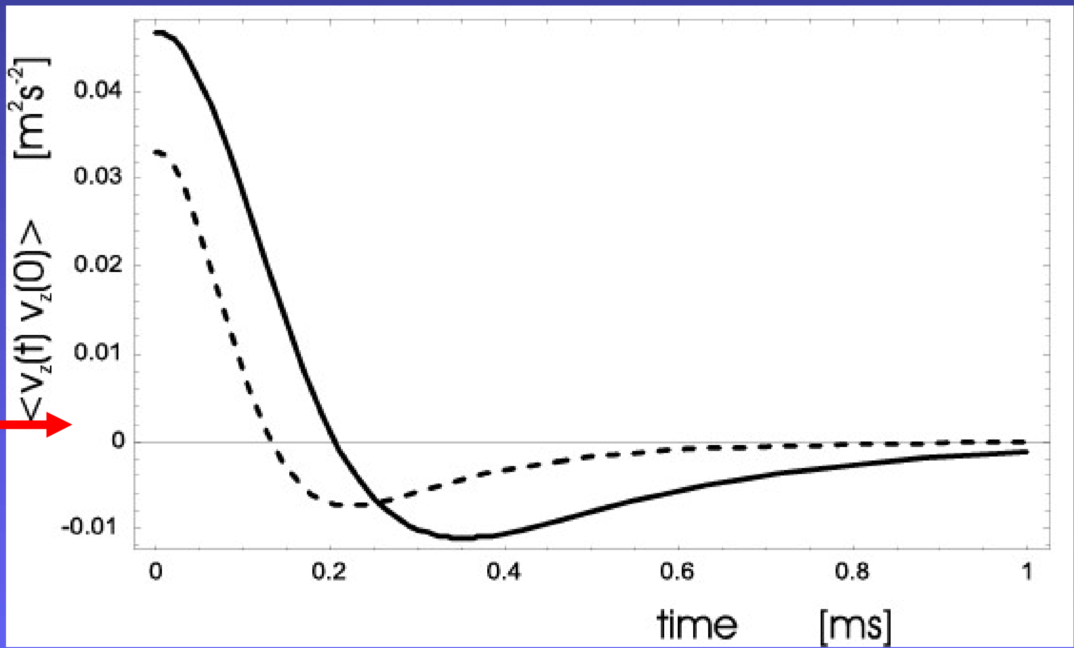
D – diffusion-like constant

τ_c – collision correlation time

ξ – free path

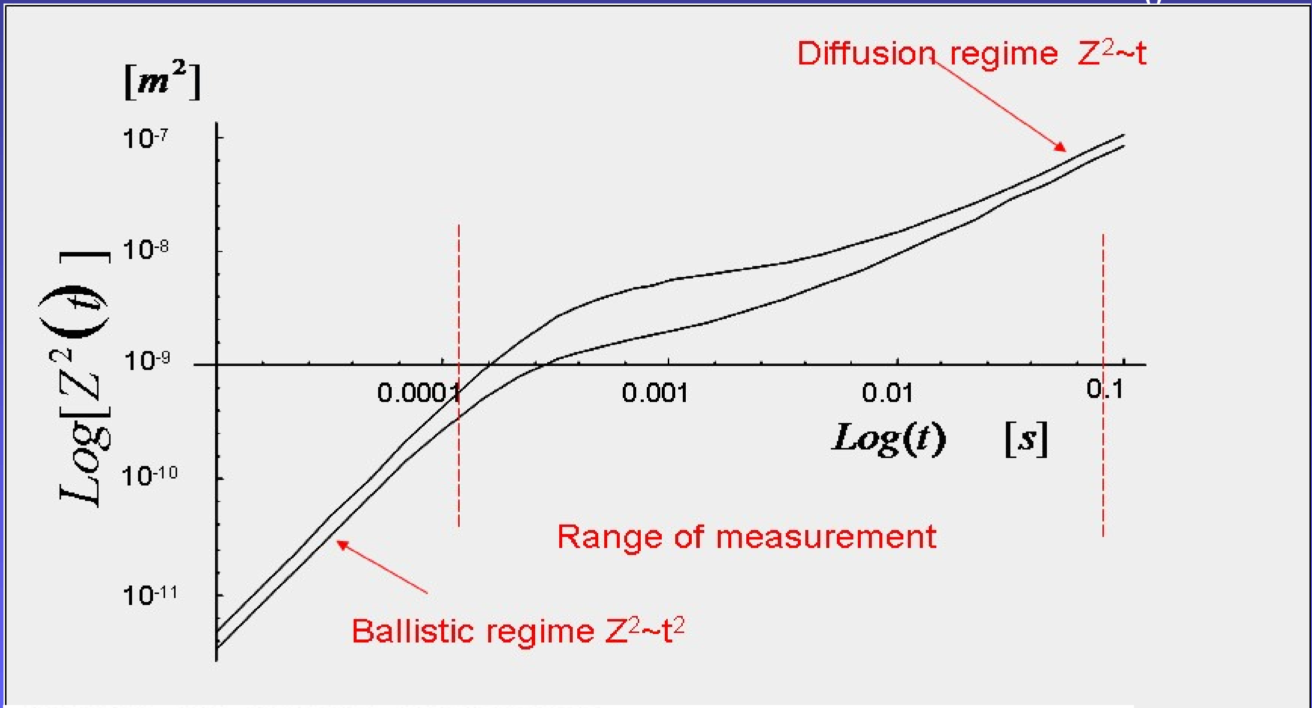
VAS to velocity autocorrelation function





Mean squared displacement of grain

$$Z^2(t) = \left\langle \left(z(t) - z(0)\right)^2 \right\rangle = \frac{4}{\pi}\int_0^\infty \left[1-\cos(\omega t)\right]\frac{D(\omega)}{\omega^2}\,d\omega$$



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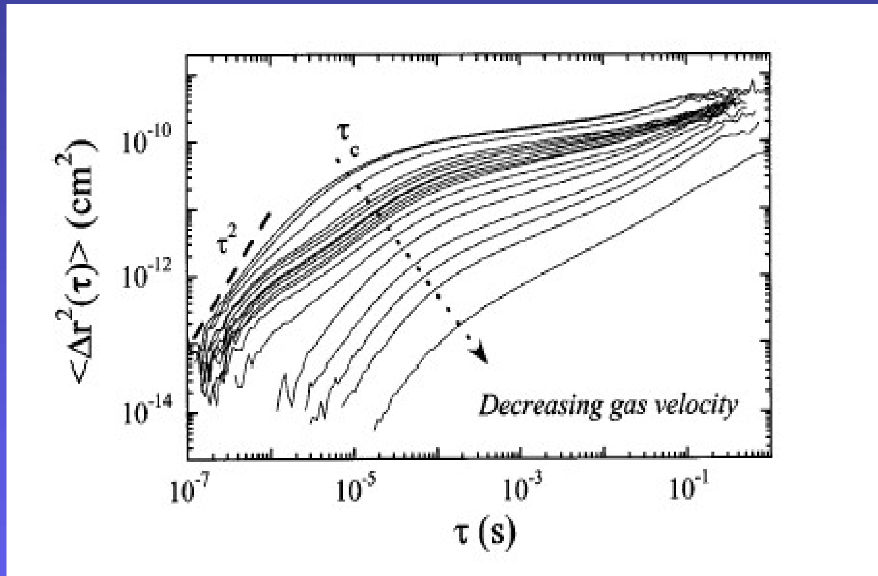
Autocorrelation spectra of an air-fluidized granular system measured by NMR

S. Lasič[1], J. Stepišnik[1,2], A. Mohorič[1], I. Serša[2] and G. Planinšič[1]



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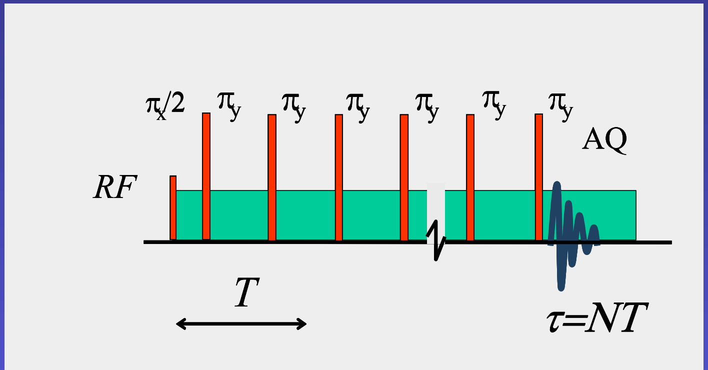
Particle Motions in a Gas-Fluidized Bed of Sand

Narayanan Menon and Douglas J. Durian

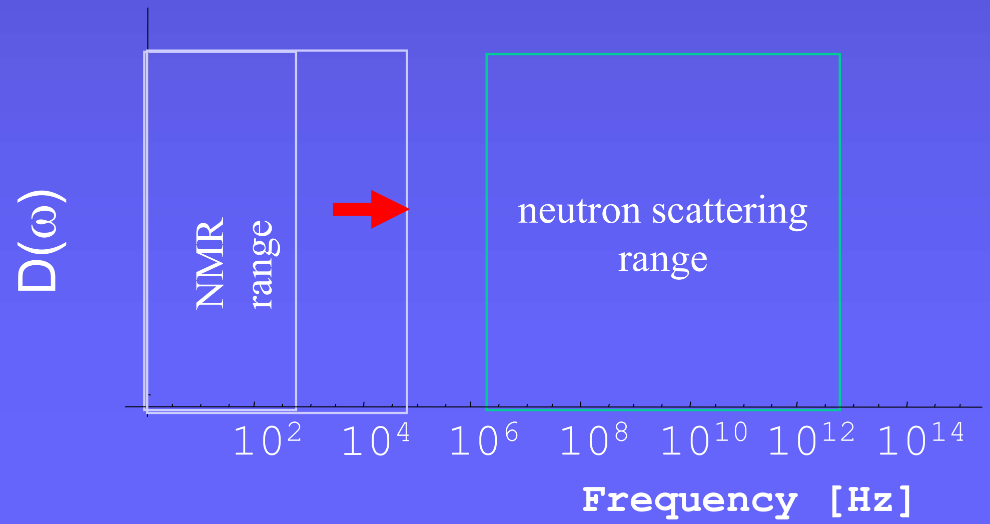
Conclusions



Spectral analysis of motion to about 10-100 kHz and, thus, the study of molecular diffusion close to nano lenght-scale.

-Application with non-uniform NMR magnets (one sided, NMR mouse etc.)

-Use of intrinsic susceptibility gradients to measure diffusion



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O. Söderman, Lund, Sweden
P.T. Callaghan, Wellington, New Zealand

Thank you for your attention !