# Geometry For Transport

## Decay Diffusion and Dispersion

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# Inverse Problems

- Ubiquitous Porous Media

Human body: Transport of fluids, Drugs, nutrients

Geophysics :Hydrocarbob, hydrology

Chemical Engineering:Catalysis

Food Matter: Cheese

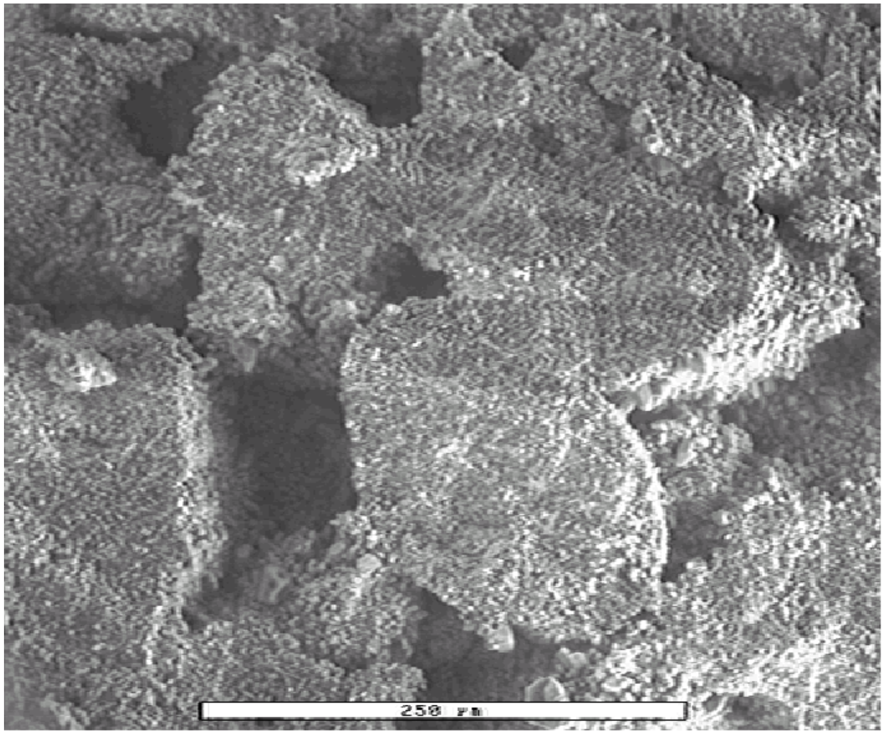
Plants

**Inverse problems: Kac vs. Laplacian Eigenvalue—Model dependent vs universal**

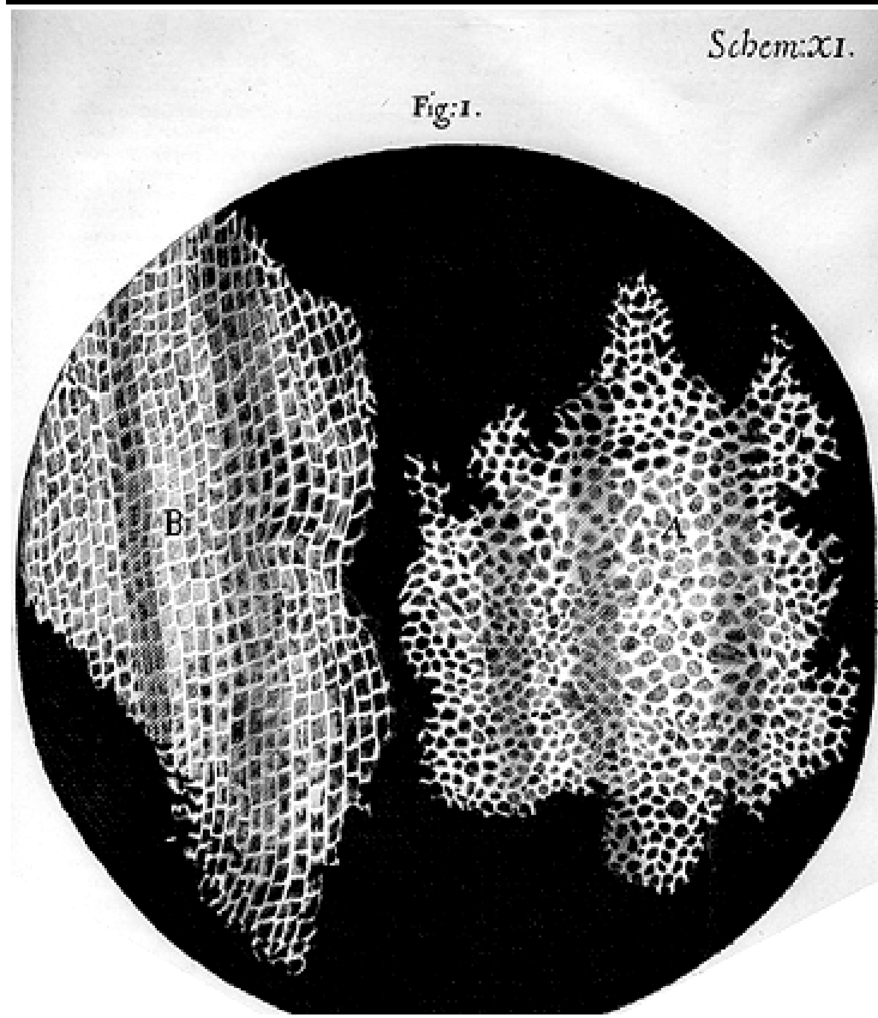
- Laplacian Limited use—simple geometry, (Mostly) Bounded Problems
- Select cases Dispersion via Laplacian
- SHORT TIME ROBUST, KAC Universal
- OPEN system-- in LONG-TIME perturbative, periodic

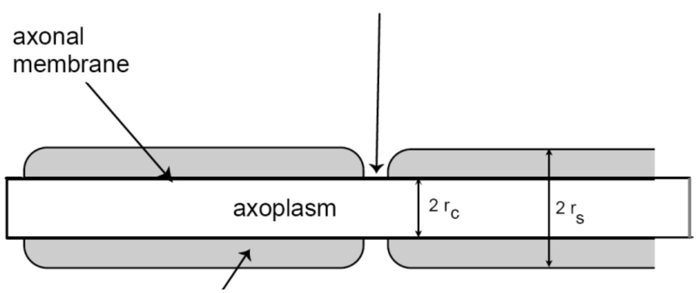
**Magnetic Resonance in Porous Media**
AIP Conference Proceedings
Hürlimann, M.; Song, Y.-Q.; Fantazzini, P.; Bortolotti, V. (Eds.)
2009, 148 ,
ISBN: 978-0-7354-0612-4

# Porous Media  Every where
# with permeable & impermeable grains/cells

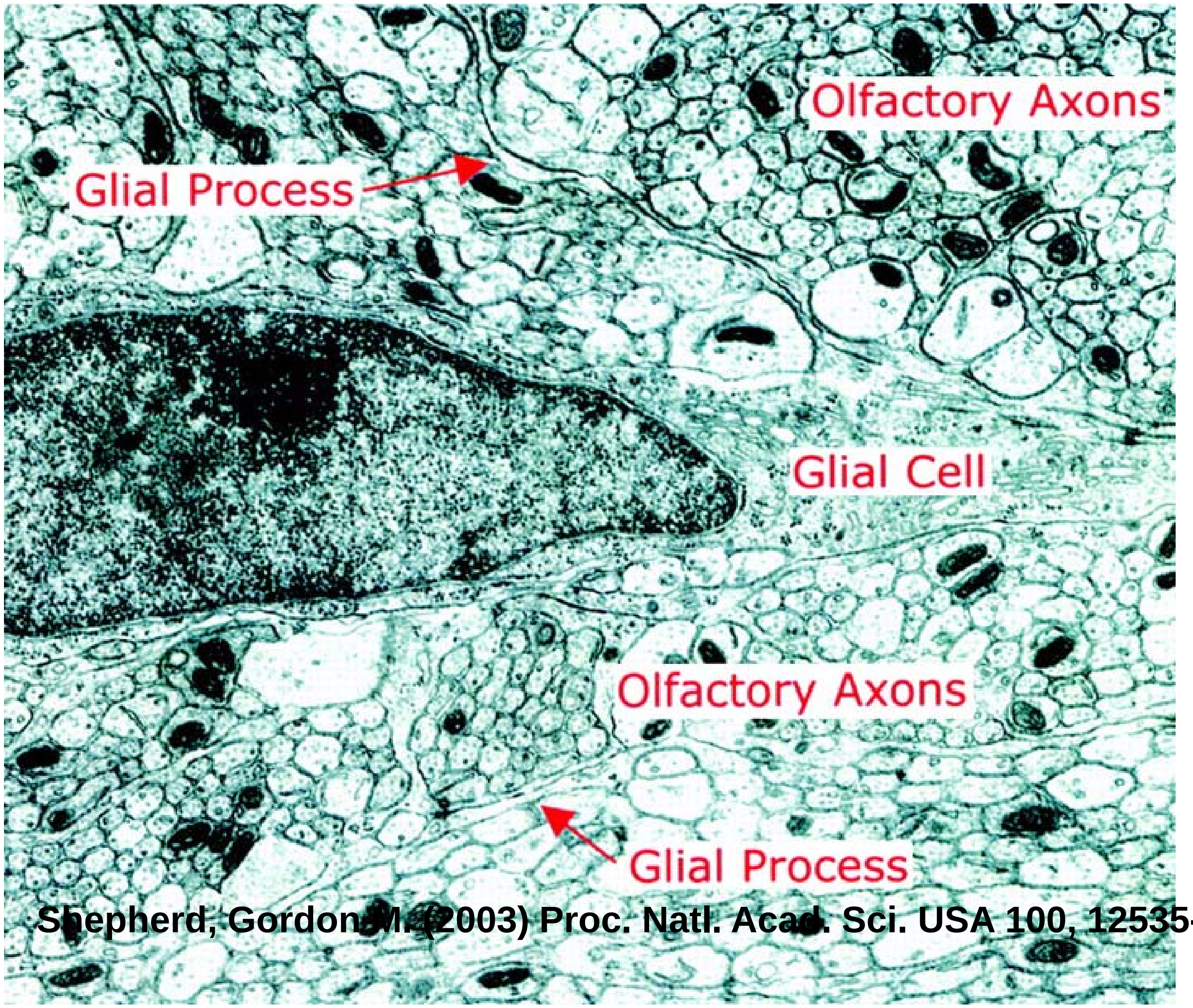


Robert Hooke
*Micrographia, or Some Physiological Descriptions of Minute Bodies* (1665)



# Electron micrograph of the olfactory nerve layer of the rat olfactory bulb, showing unmyelinated olfactory axons arranged in bundles, demarcated by glial processes (arrows)




Shepherd, Gordon M. (2003) Proc. Natl. Acad. Sci. USA 100, 12535-12536

# Diffusion Reveals Ischemic Regions Fast (Life Saving)

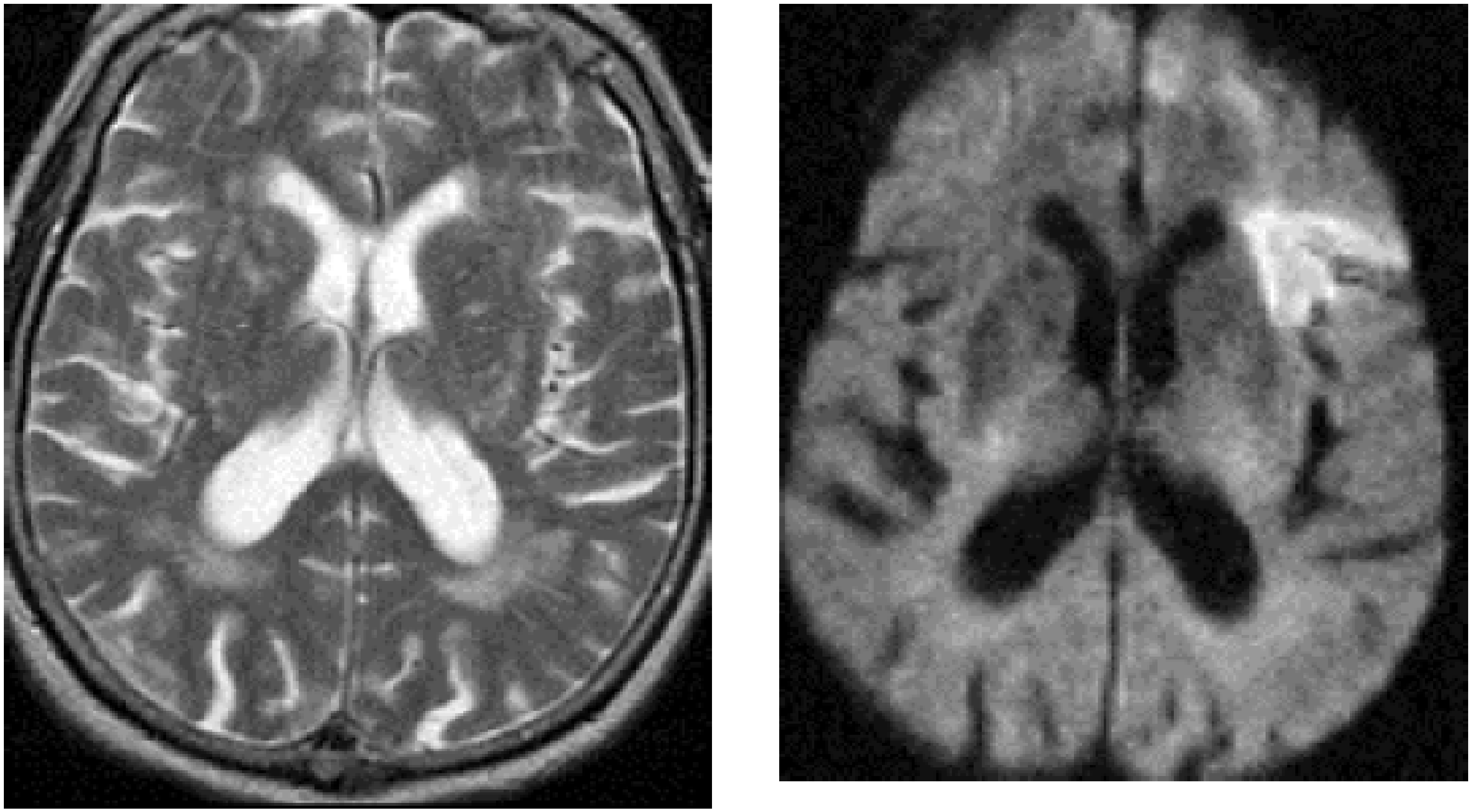
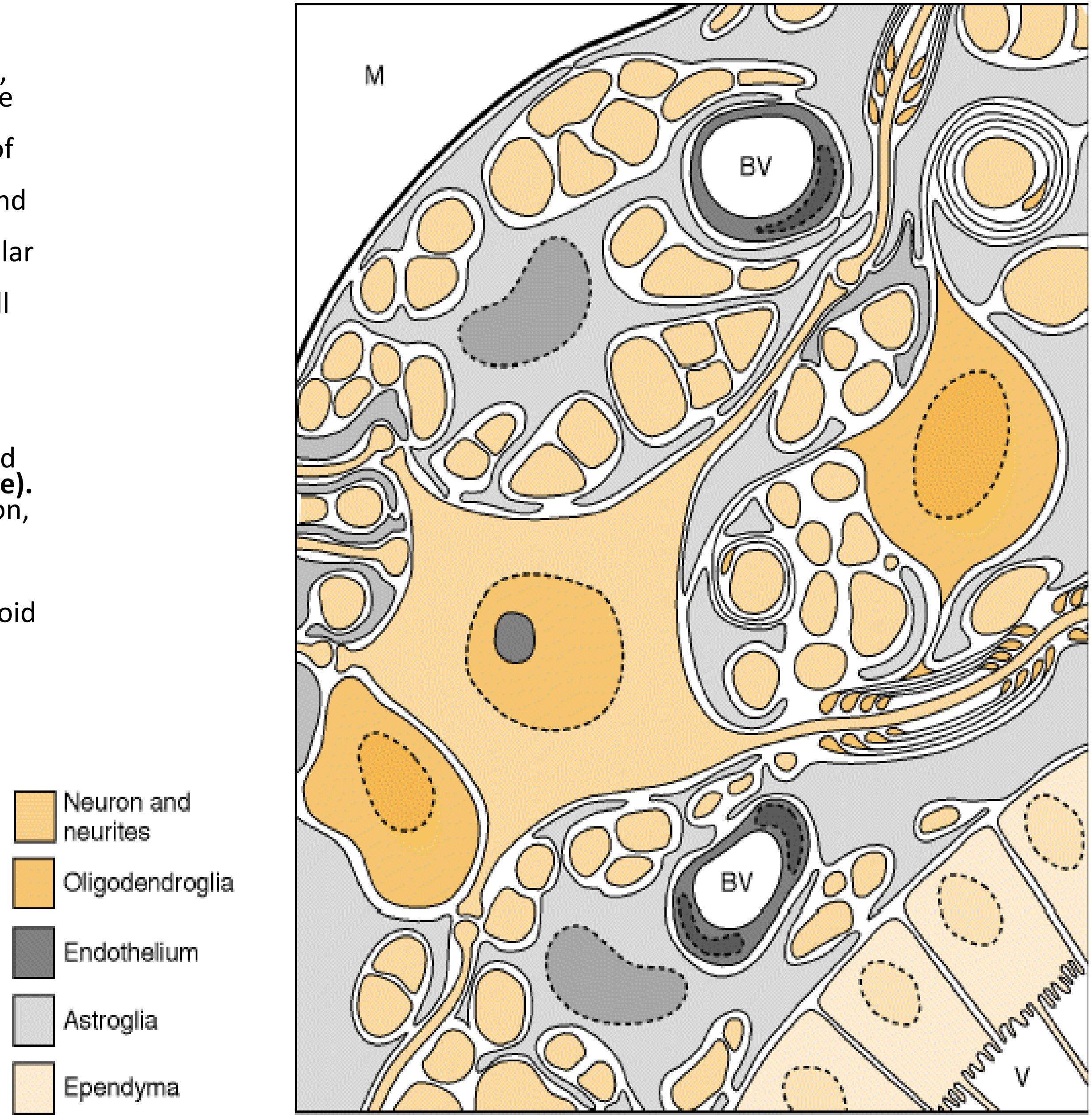
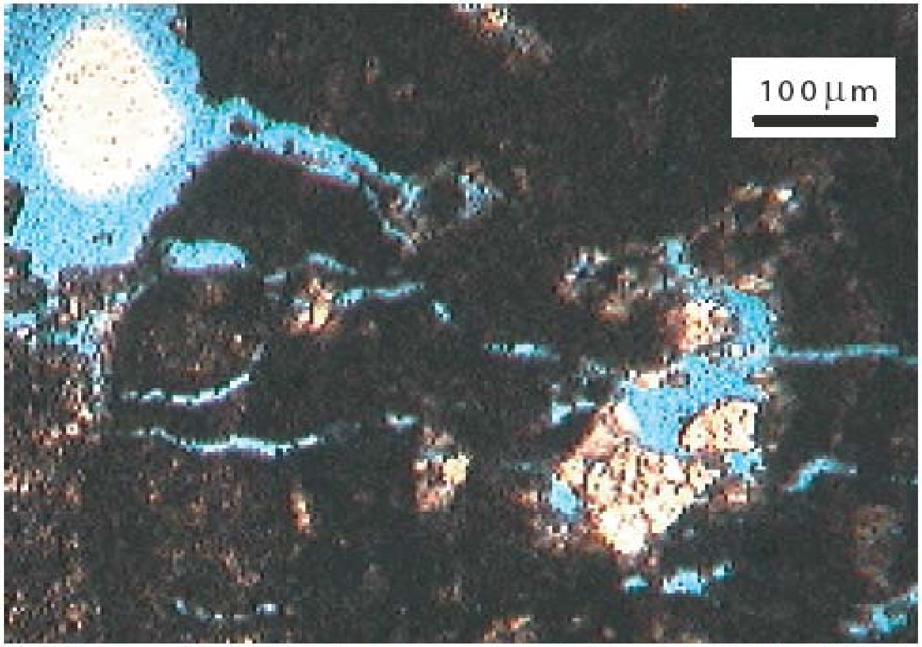


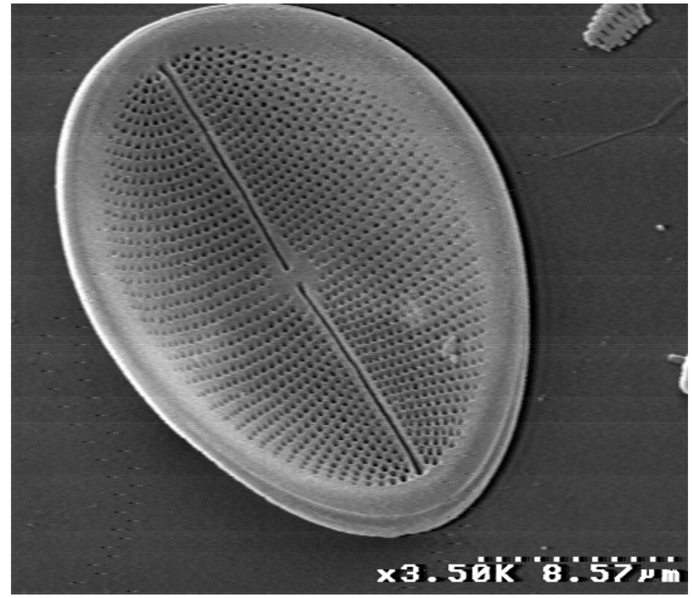
**Figure 2: Acute brain ischaemia.** A major clinical application of diffusion MRI has been acute brain ischemia. Images (*left*: conventional T2w-MRI) and (*right*: diffusion-weighted image) were obtained a few hours after the onset of aphasia in patient. The diffusion image clearly shows the infarcted tissue with an intense signal corresponding to reduced water diffusion in the ischemic territory.

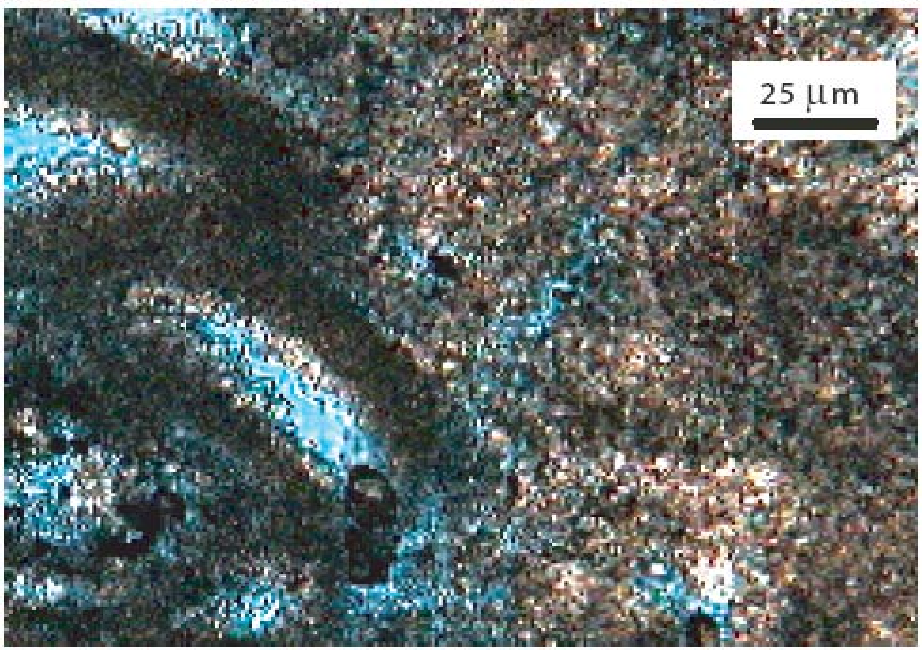
- **Figure 1-3.** The major components of the CNS and their interrelationships. Microglia are not depicted. In this simplified schema, the CNS extends from its meningeal surface *(M)* through the basal lamina *(solid black line)* overlying the subpial astrocyte layer of the CNS parenchyma and across the CNS parenchyma proper (containing neurons and glia) and subependymal astrocytes, to ciliated ependymal cells lining the ventricular space *(V).* Note how the astrocyte also invests blood vessels *(BV),* neurons and cell processes. The pia-astroglia (glia limitans) provides the barrier between the exterior (dura and blood vessels) and the CNS parenchyma. One neuron is seen **(center),** with synaptic contacts on its soma and dendrites. Its axon emerges to the right and is myelinated by an oligodendrocyte **(above).** Other axons are shown in transverse section, some of which are myelinated. The oligodendrocyte to the lower left of the neuron is of the nonmyelinating satellite type. The ventricles *(V)* and the subarachnoid space of the meninges *(M)* contain cerebrospinal

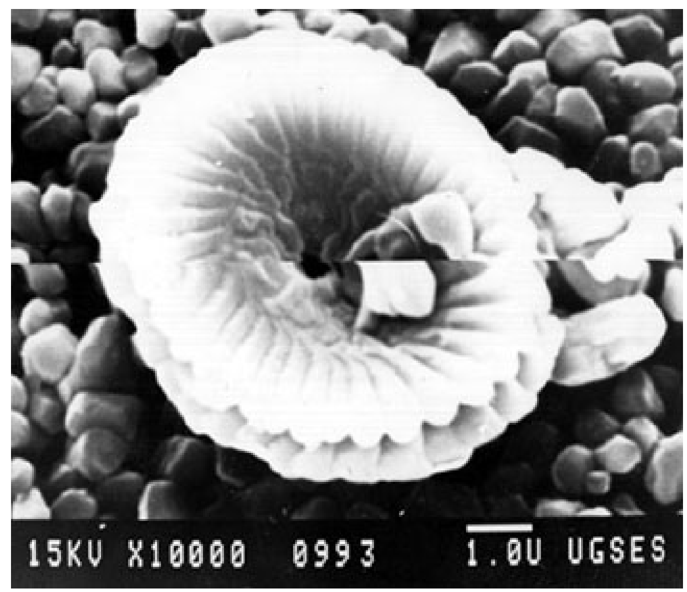


# Rock Micrographs



# Transport in porous media--biological to geological

- Typical length of the order of micron
- Many length and Time scales—NMR is a nice probe of fluid transport
- Relaxation time sets length limitation
- Robust Inversion of S/V, $\kappa$ (cell wall permeability) from Short time
- LONG-TIME: Tortuosity, Dispersion

P. N. Sen Concepts in Magnetic Resonance, **23 A (1)**, 1 (2004)

**Magnetic Resonance in Porous Media,** AIP Conference Proceedings , Vol. 1081
Hürlimann, M.; Song, Y.-Q.; Fantazzini, P.; Bortolotti, V. (Eds.), 2009, 148 p., ISBN: 978-0-7354-0612-4

# Equations of Motion

## Diffusion with Partially Absorbing Boundary

$$D_0\nabla^2 M(\vec{x}) = \frac{\partial M(\vec{x})}{\partial t},$$

$$L_D = \sqrt{D_0\tau}, \quad L_G = \left(\frac{D_0}{g}\right)^{1/3}, \quad L_\rho = \frac{D_0}{\rho}.$$

$$D_0\hat{n}\cdot\nabla M(\vec{x}) + \rho M(\vec{x})|_\Sigma = 0,$$

$$\frac{\partial G(\mathbf{r},t,\mathbf{r}')}{\partial t} = D_o\nabla^2 G(\mathbf{r},t;\mathbf{r}'),\ t>0 \qquad D_o\hat{\mathbf{n}}\cdot\nabla G(\mathbf{r},t;\mathbf{r}') + \rho G(\mathbf{r},t;\mathbf{r}')|_{\mathbf{r}\in\boldsymbol{\Sigma}} = 0$$

subject to the initial condition $G(\mathbf{r}, t = 0^+; \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$.

$$M(\mathbf{q},t) = \langle e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}')}\rangle$$
$$= \int\int d\mathbf{r}d\mathbf{r}' G(\mathbf{r},t;\mathbf{r}')e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}')}M(\mathbf{r}',0).$$

$$-\lim_{q\to 0}\frac{\partial \log[M(q,t)]}{\partial q^2} = \frac{\langle[\mathbf{r}'(t)-\mathbf{r}(0)]^2\rangle}{6} \equiv D(t)t.$$

# Laplacian Eigenvalue
## Diffusion with Partially Absorbing Boundary

$$D_0\nabla^2 M(\vec{x}) = \frac{\partial M(\vec{x})}{\partial t},$$

$$L_D = \sqrt{D_0\tau}, \quad L_G = \left(\frac{D_0}{g}\right)^{1/3}, \quad L_\rho = \frac{D_0}{\rho}.$$

$$D_0\hat{n}\cdot\nabla M(\vec{x}) + \rho M(\vec{x})\big|_\Sigma = 0,$$

$$G(\vec{x}, t; \vec{y}) = \sum_{n=0}^{\infty} \psi_n(\vec{x})\psi_n(\vec{y})e^{-\lambda_n t}.$$

$$D_0\nabla^2\psi_n(\vec{x}) = -\lambda_n\psi_n(\vec{x}),$$

$$D_0\hat{n}\cdot\nabla\psi_n(\vec{x}) + \rho\psi_n(\vec{x})\big|_\Sigma = 0,$$

$$M(\vec{x}, t) = \int_V d\vec{y} \sum_{n=0}^{\infty} \psi_n(\vec{x})\psi_n(\vec{y})e^{-\lambda_n t}M(\vec{y}, 0).$$

$$M_n(t=0) = \left(\int_V d\vec{x}\ \psi_n(\vec{x})\right)^2.$$

INITIAL STATE---1/V, BUT SONG et al
PFG
Final state Uniform Pick-up

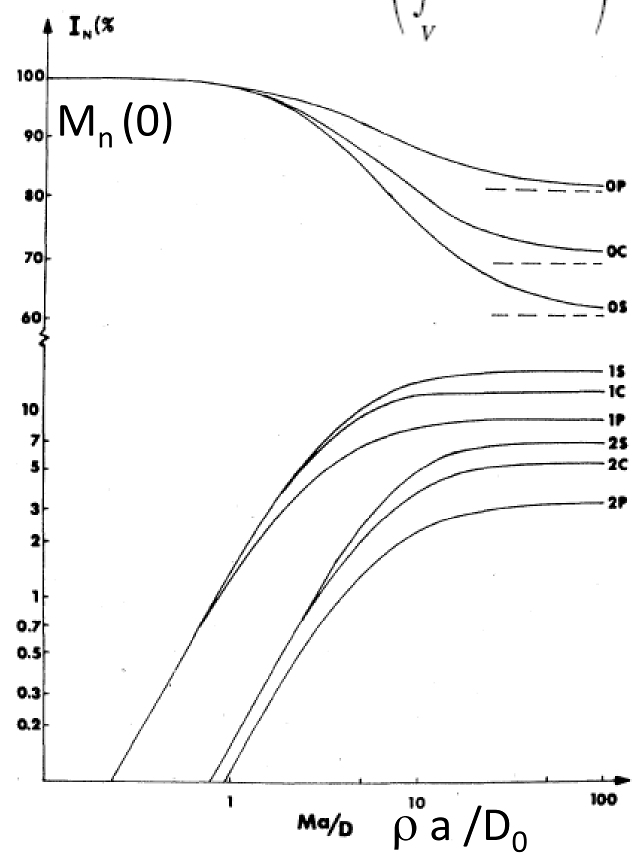
$$M(t) = \int_V d\vec{x}\ M(\vec{x}, t) = \sum_{n=0}^{\infty} M_n(t=0)e^{-\lambda_n t}.$$

P. M. Morse and H. Feshbach, *Methods of Theoretical Physics I* (McGraw-Hill, New York, 1953), Chap. 7.

## Decay: Simple Isolated Pores

$$M(t) = \int_V d\vec{x}\, M(\vec{x}, t) = \sum_{n=0}^{\infty} M_n(t=0) e^{-\lambda_n t}.$$

$$M_n(t=0) = \left( \int_V d\vec{x}\; \psi_n(\vec{x}) \right)^2 .$$




$$M(t)/M(0) = 1 - \rho t S/V_P + O(t^{3/2})$$

$$\lambda_0 = \rho\, S/V_p \approx \rho /a$$

$$\lambda_n \approx n^2 D_0/a^2$$

$$L_D = \sqrt{D_0 \tau}, \quad L_G = \left(\frac{D_0}{g}\right)^{1/3}, \quad L_\rho = \frac{D_0}{\rho}.$$

## PORE-SIZE DISTRIBUTION: LOWEST MODES

$$M(t) = \Sigma_{\text{pore } i}\, e^{[-\rho\, t/a_i]}$$

K. R. Brownstein and C. E. Tarr, Phys. Rev. A 19, 2446 (1979).

# Relaxation

## PORE-SIZE DISTRIBUTION

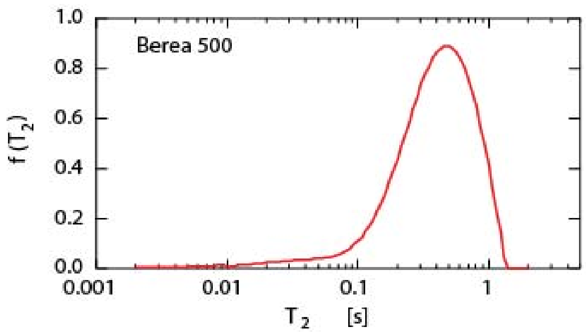
$$M(t)=\Sigma_{\text{pore } i}\, e^{[-\rho\, t/a_i]}$$

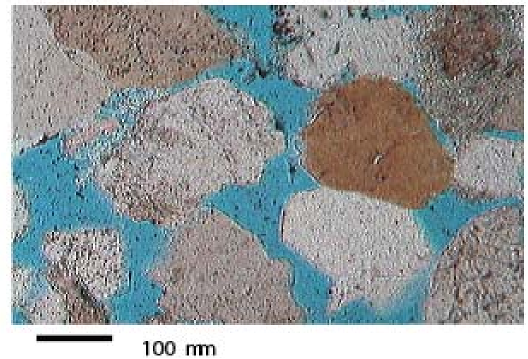
Laplace Transform

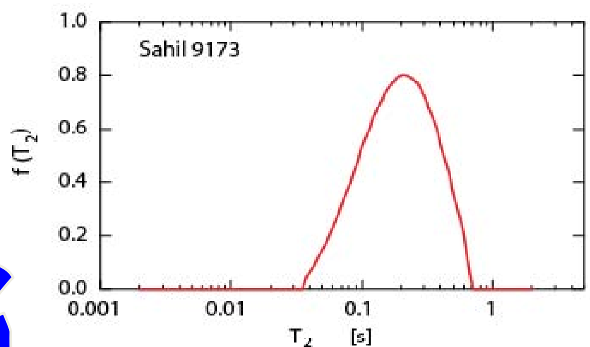
D. M. Grant and R. K. Harris, in *Encyclopedia of Nuclear Magnetic Resonance*, edited by D. M. Grant and R. K. Harris (Wiley, New York, 1996).

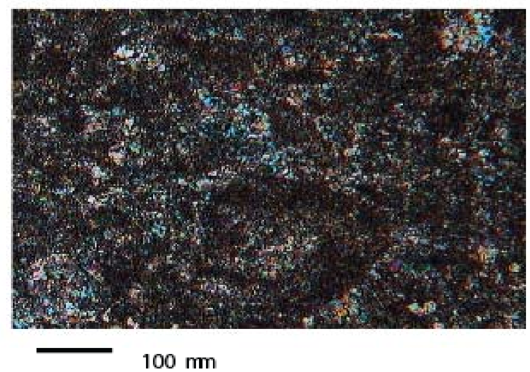
R. L. Kleinberg, *Encyclopedia of Nuclear Magnetic Resonance* (Ref. 8), p. 4960.

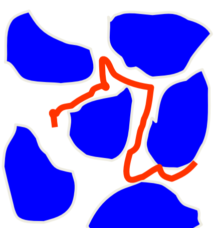
# Relaxation, Diffusion ~100 μm Vs Flow ~1mm:



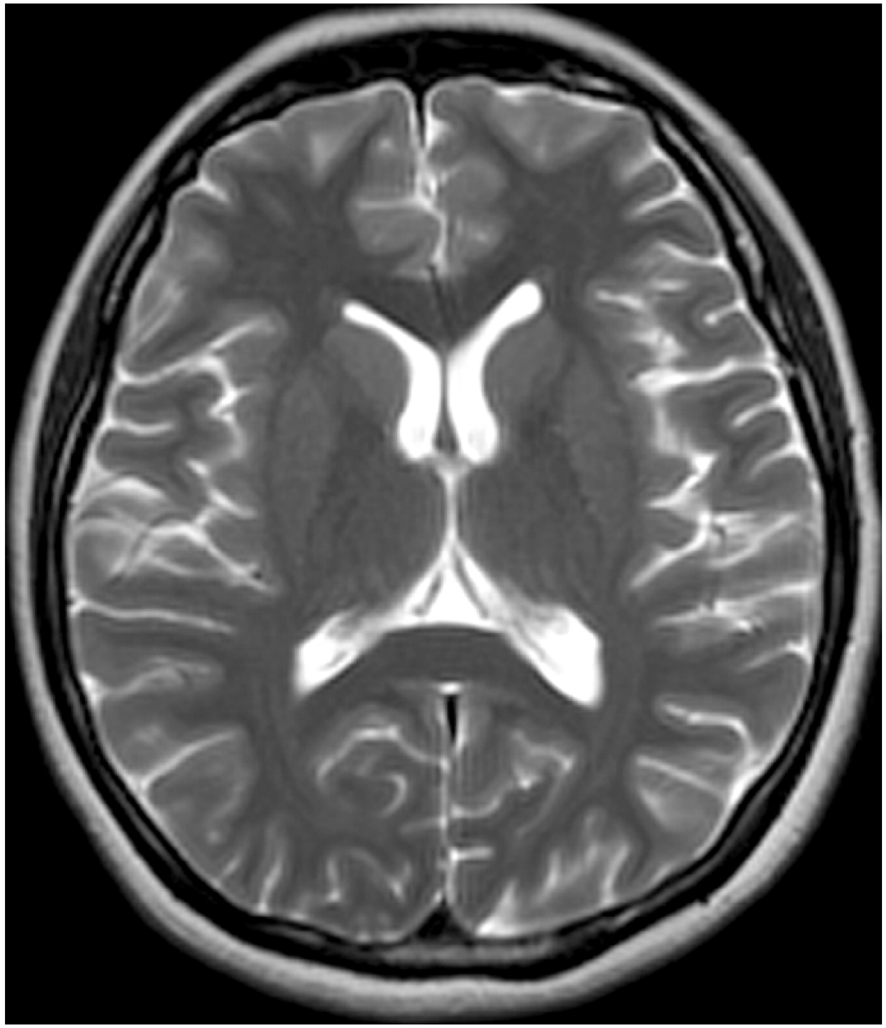



Carbonate: Similar $T_2$ Distribution, Different Pore Geometry

- Fluid parcels traverse *many* pores during the NMR measurement. (~ 1 mm)
- Diffusion Relaxation (~ 100 μm) measurements.

**Figure 1b. Epidermoid tumor depicted on sagittal T1-weighted (a), axial T2-weighted (b, c), axial (d) and coronal (e) gadolinium-enhanced T1-weighted, and axial fluid-attenuated inversion recovery (FLAIR) (f) images**



Forghani, R. et al. Radiographics 2007;27:1489-1494

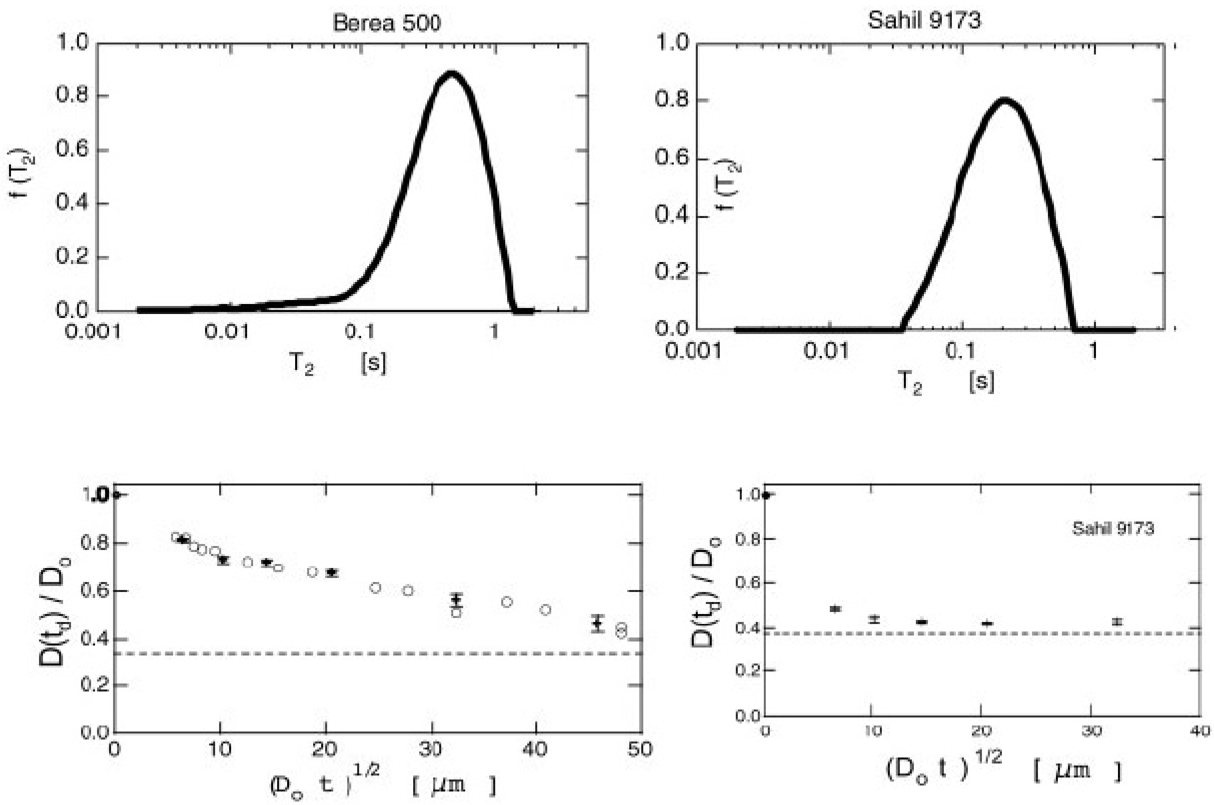
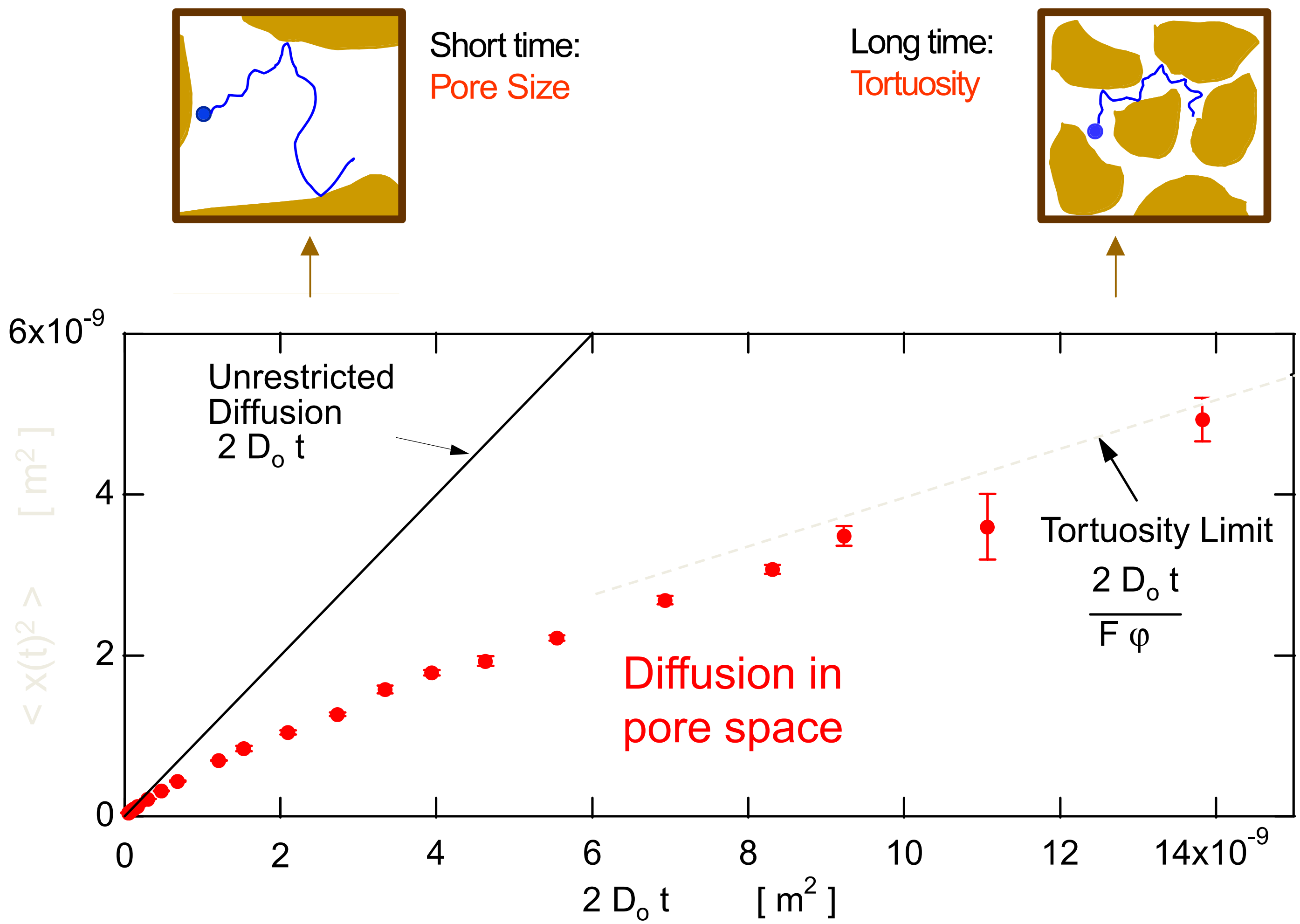
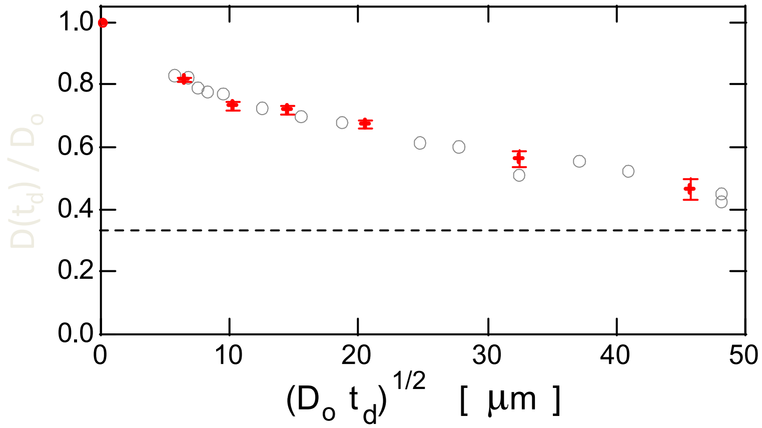



**Figure 13** Relaxation time distribution in two very dissimilar rocks—Berea permeability about 0.17 Darcy (1 Darcy = 1 $\mu m^2$) with relatively uniform pores and a carbonate with coexistent macro- and micro-porosity, with a permeability about 16 times smaller. The distributions are rather similar and the pore-size distribution from relaxation data alone cannot be made. Time-dependent diffusion coefficient reveals clearly the differences between these two dissimilar rocks.

# Restricted Diffusion with impermeable walls

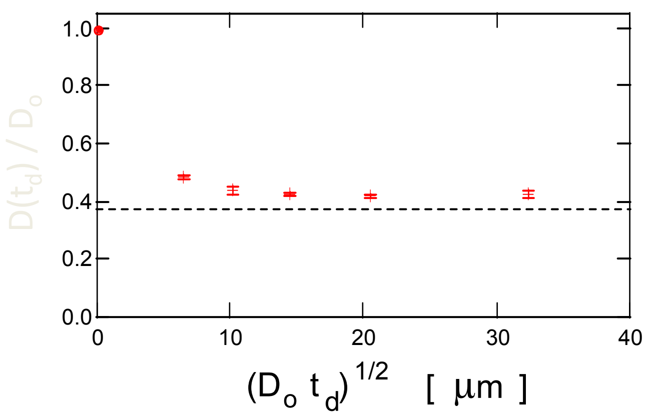


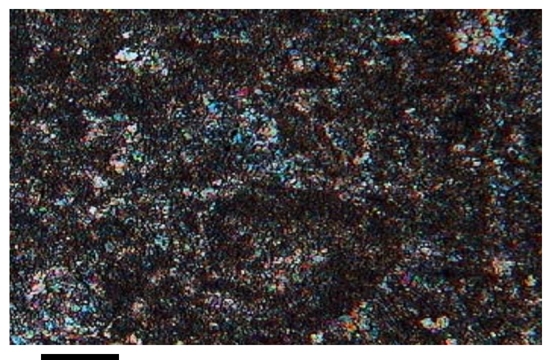
## Berea Sandstone

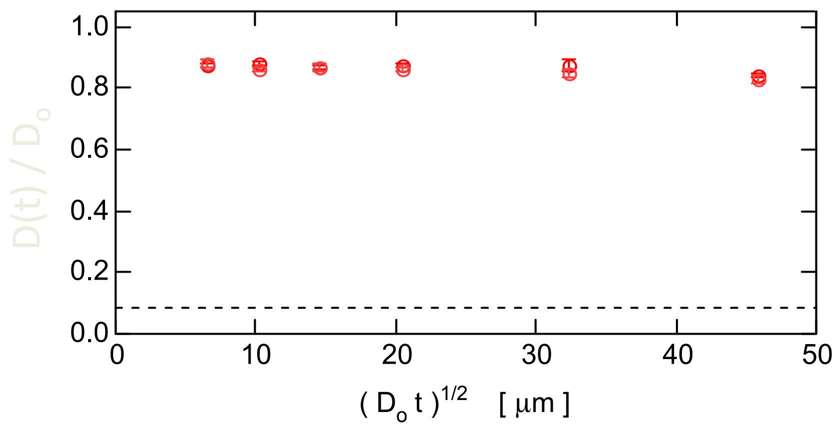




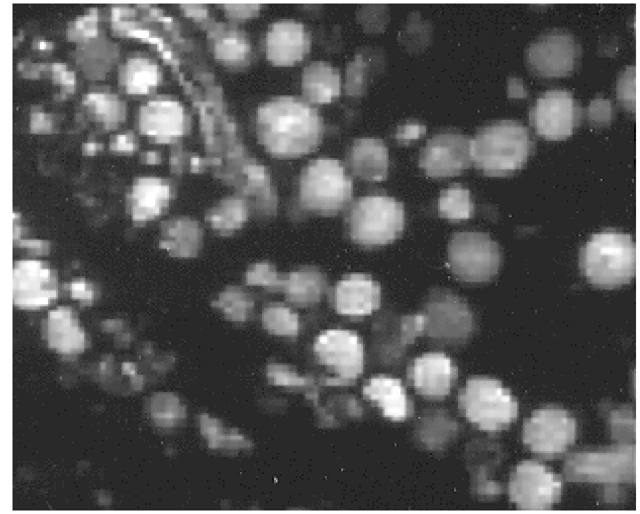
## Thamama Carbonate

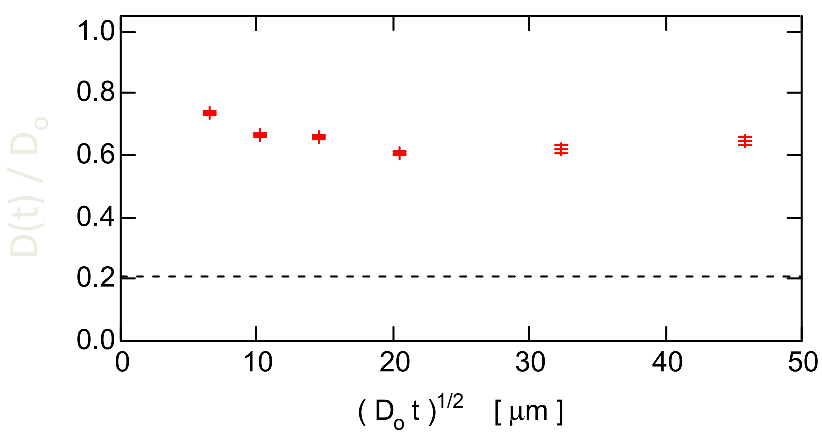




D(t) / Do
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
( Do t )1/2 [ µm ]



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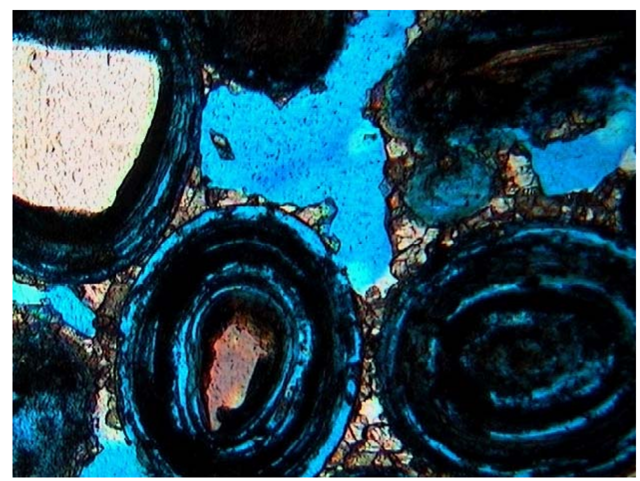
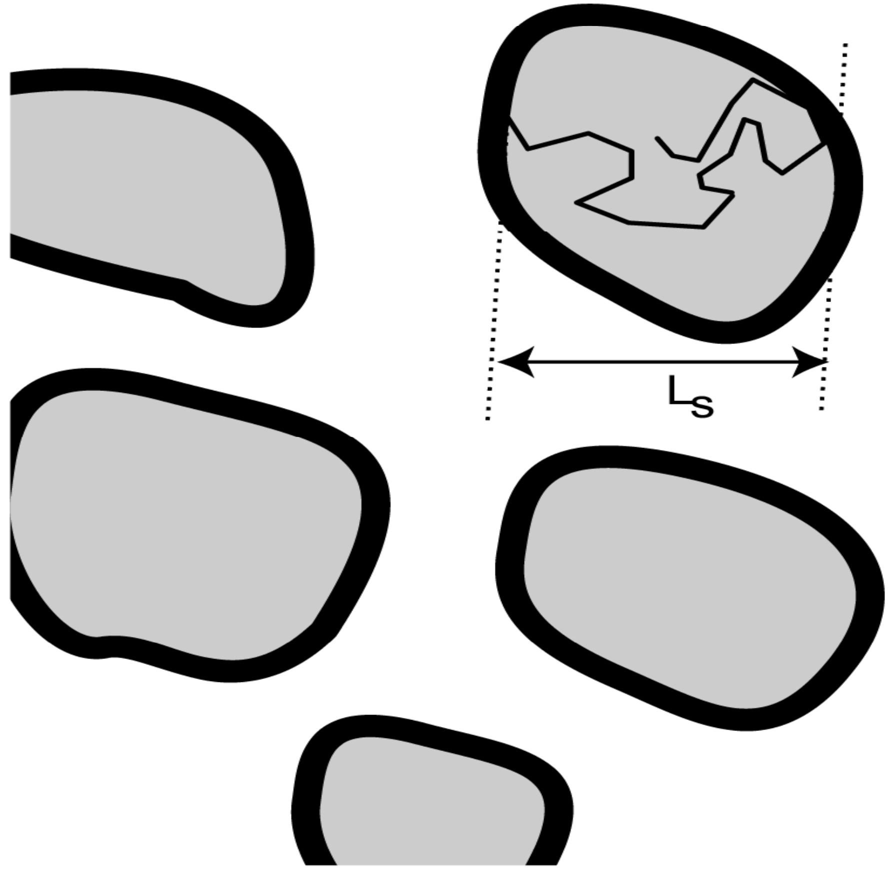


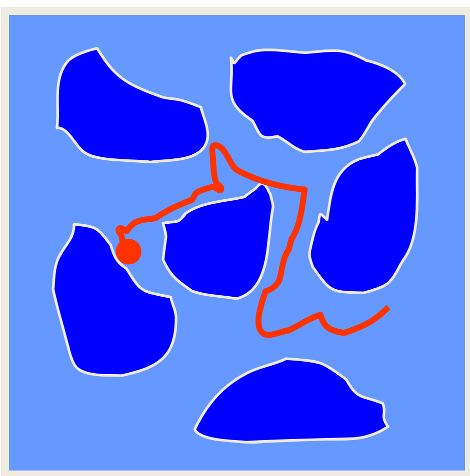
Restricted Diffusion in Isolated Cells or Pores

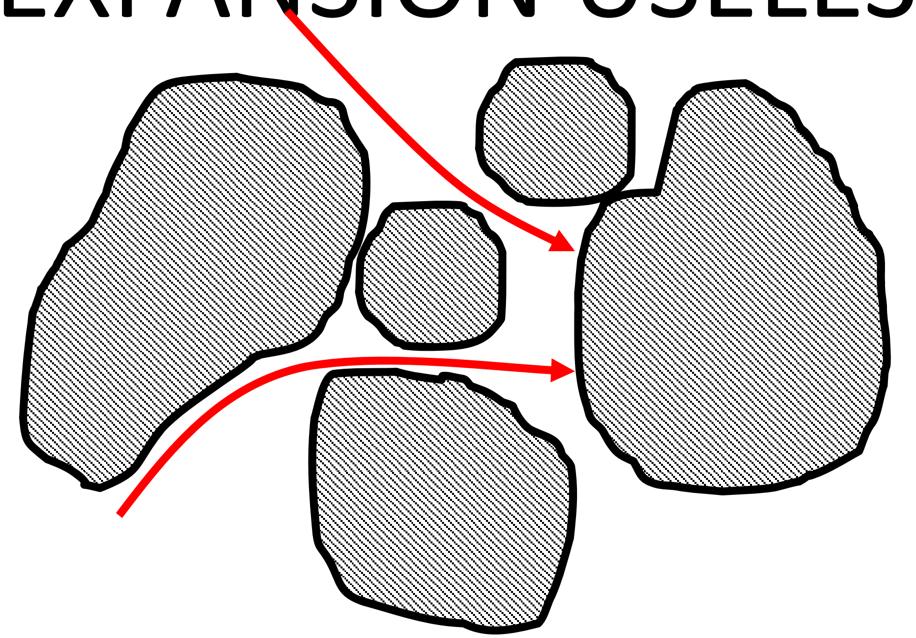
$$D(t) = \frac{{L_s}^2}{2\,t} \Rightarrow 0$$



# Unbounded Regions and Complex Geometry

## EIGEN FUNCTION EXPANSION USELESS





DISPLACEMENT MEASUREMENTS

# Limitations and Gaps

| **Geometry** / **Time** | **Isolated** Simple | **Isolated** Complex | **Connected** Simple | **Connected Complex** ***MOTHER NATURE*** |
|---|---|---|---|---|
| Short $L_D << L_s$ | Laplace<br>Kac | Kac | Kac | Kac |
| Long $L_D >> L_s$ | Laplace | Numerical | Periodic<br>Bloch Floquet<br>Numerical | Perutrbative<br>Statistical<br>Numerical |

"Can one hear the shape of a drum?" M. Kac (*1*)

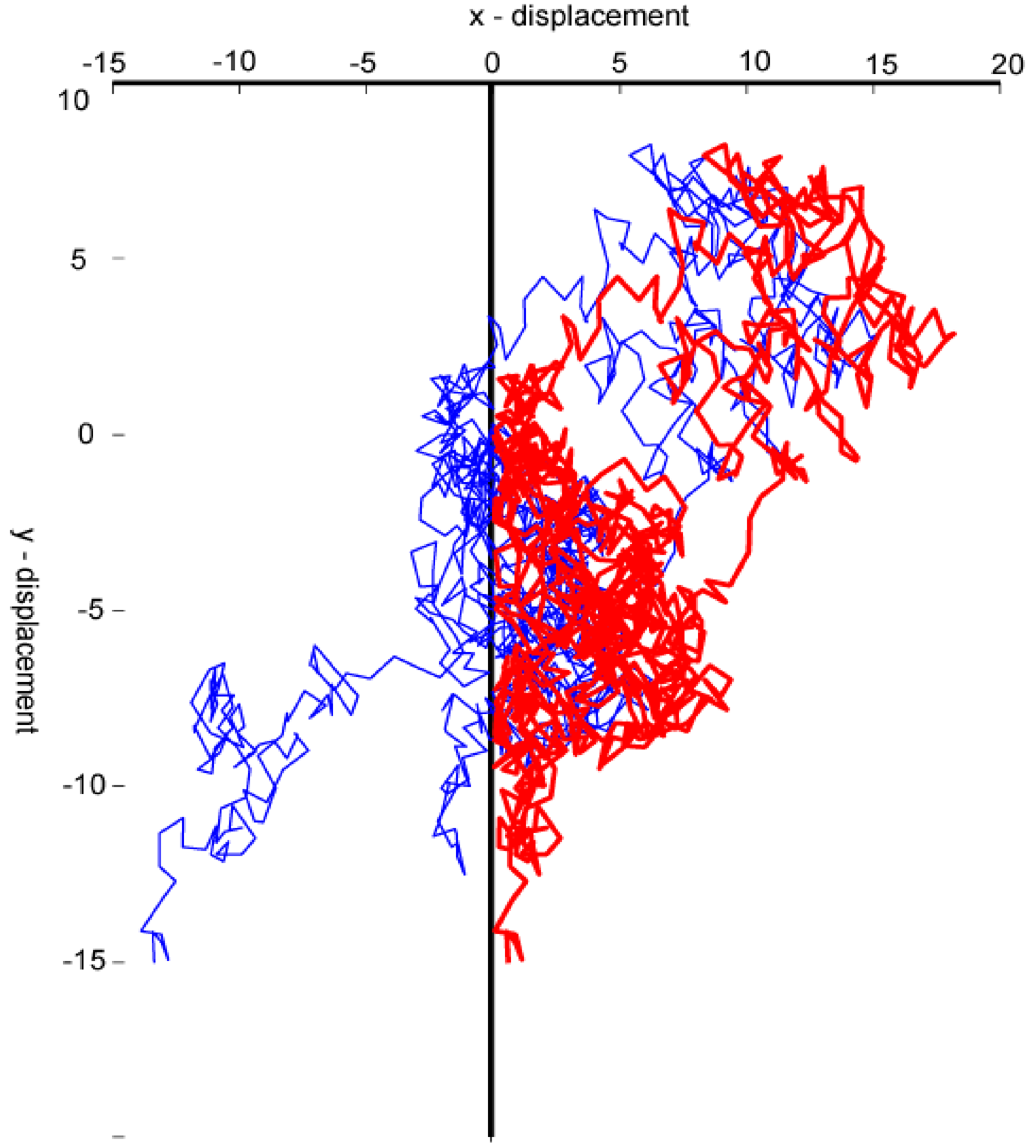
- Vibrations of a drum with immovable boundary ( $\rho = \infty$)---**ISOLATED PORES**

$$\theta(t) = \sum_{n=1}^{\infty} \exp(-\lambda_n t) , \qquad (1)$$

where $\{\lambda_n\}$ are the eigenvalues of the diffusion equation in a region surrounded by perfectly absorbing walls.


1. (a) Kac M. 1966. Can one hear the shape of a drum? Am Math Mon 73:1–23; (b) Chapman SJ. 1995. Drums that sound the same. Am Math Mon (February) 102:124–138.

# 2-d restricted walk near a wall



# Propagators near a wall

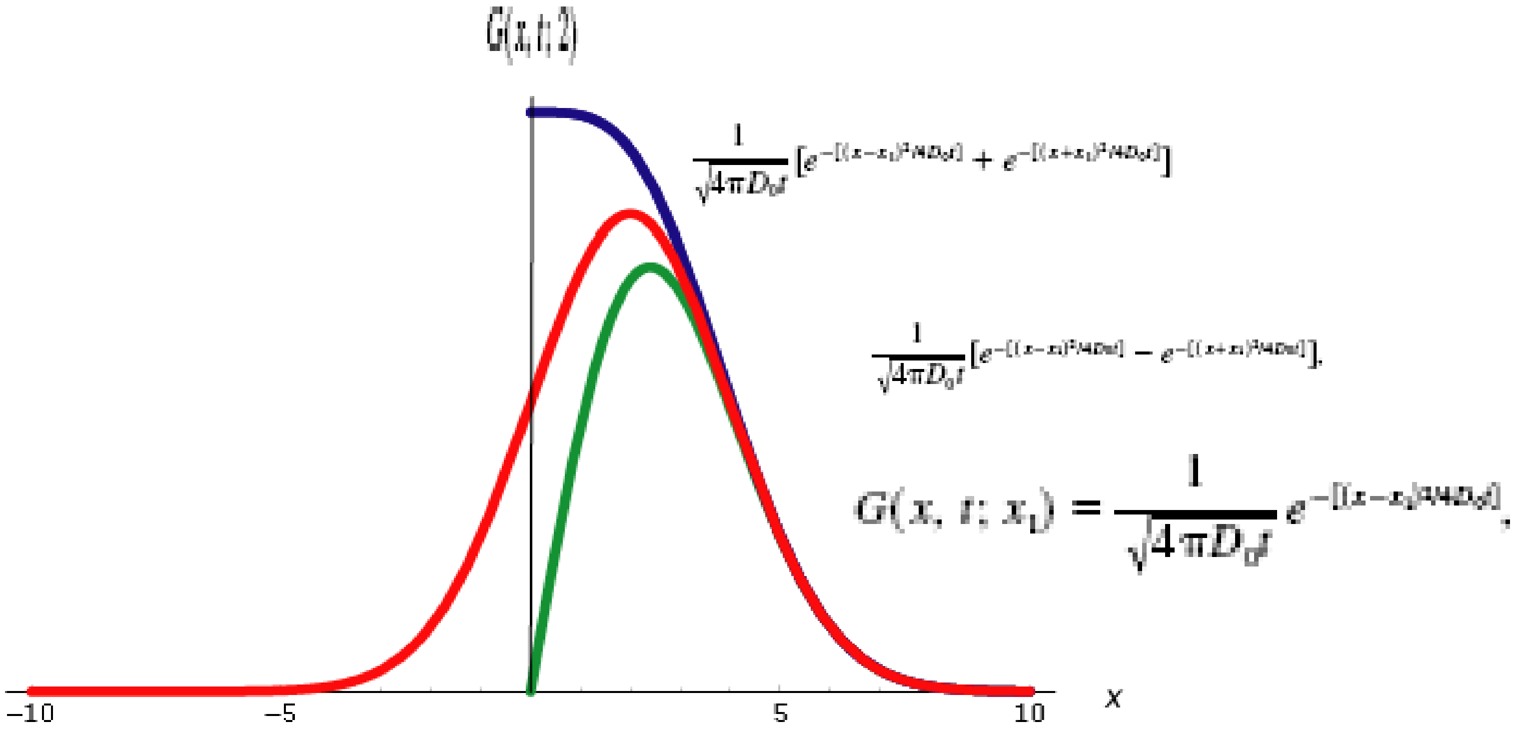
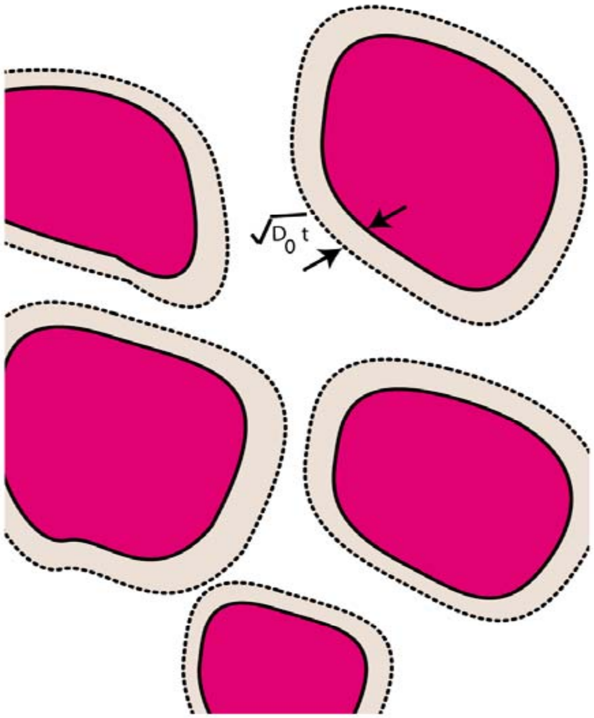
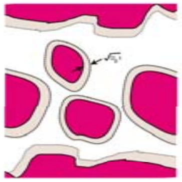



**Figure 17** The probability density $G(x, t; 2)$ for a particle starting initially at $x = 2$ after a duration $t$ such that $L_D = \sqrt{2D_0 t} = 2$. The top and the bottom curves are for the reflecting and the absorbing boundary conditions respectively at a wall located at the origin. The middle curve is for free unrestricted diffusion in absence of the wall.

# Impermeable Wall





**Walkers Within a diffusion length $\sqrt{(D\,t)}$ see the walls**

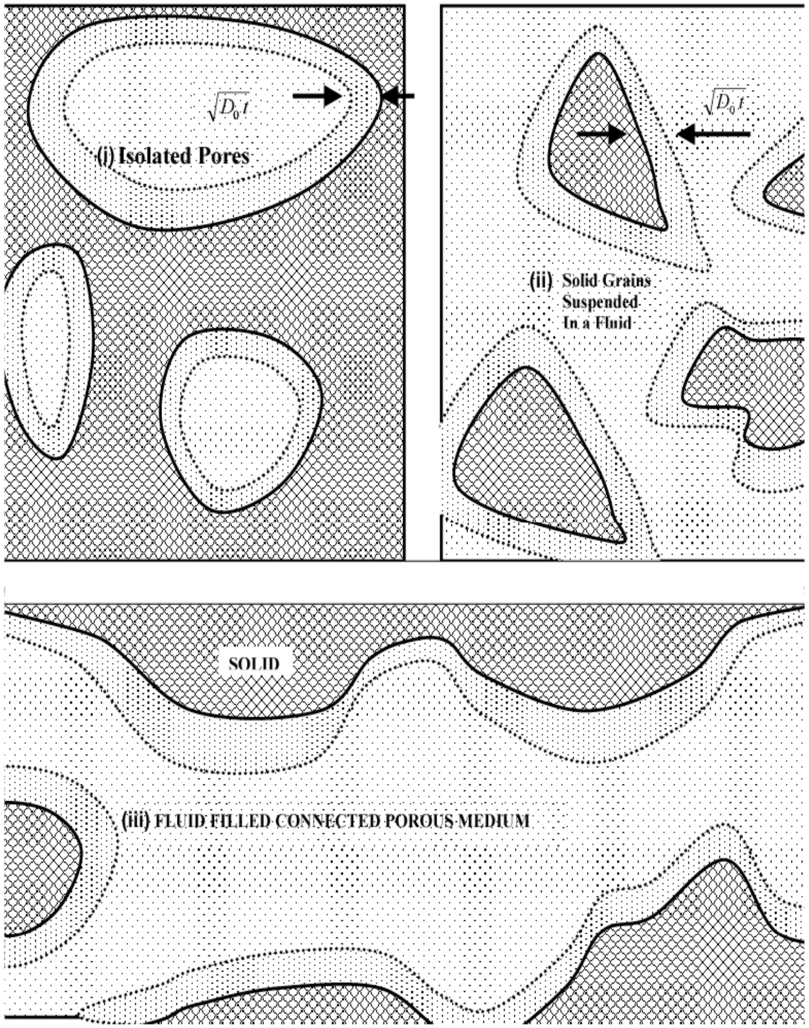
**fraction affected = $S\sqrt{(D\,t)}/V_p$**

$$\langle X^2\rangle = \text{free (far away)} + \text{restricted (near)}$$
$$= 2D_0 t \times \text{fraction of free} + 2D' t \times \text{fraction of free}$$
$$\sim 2D_0 t\,(1 - \text{Constant}\; S\sqrt{(D\,t)}/V_p)$$

$$\langle X^2\rangle = 2D(t)\,t = 2D_0 t\,(1 - \text{Constant}\; S\sqrt{(D\,t)}/V_p)$$

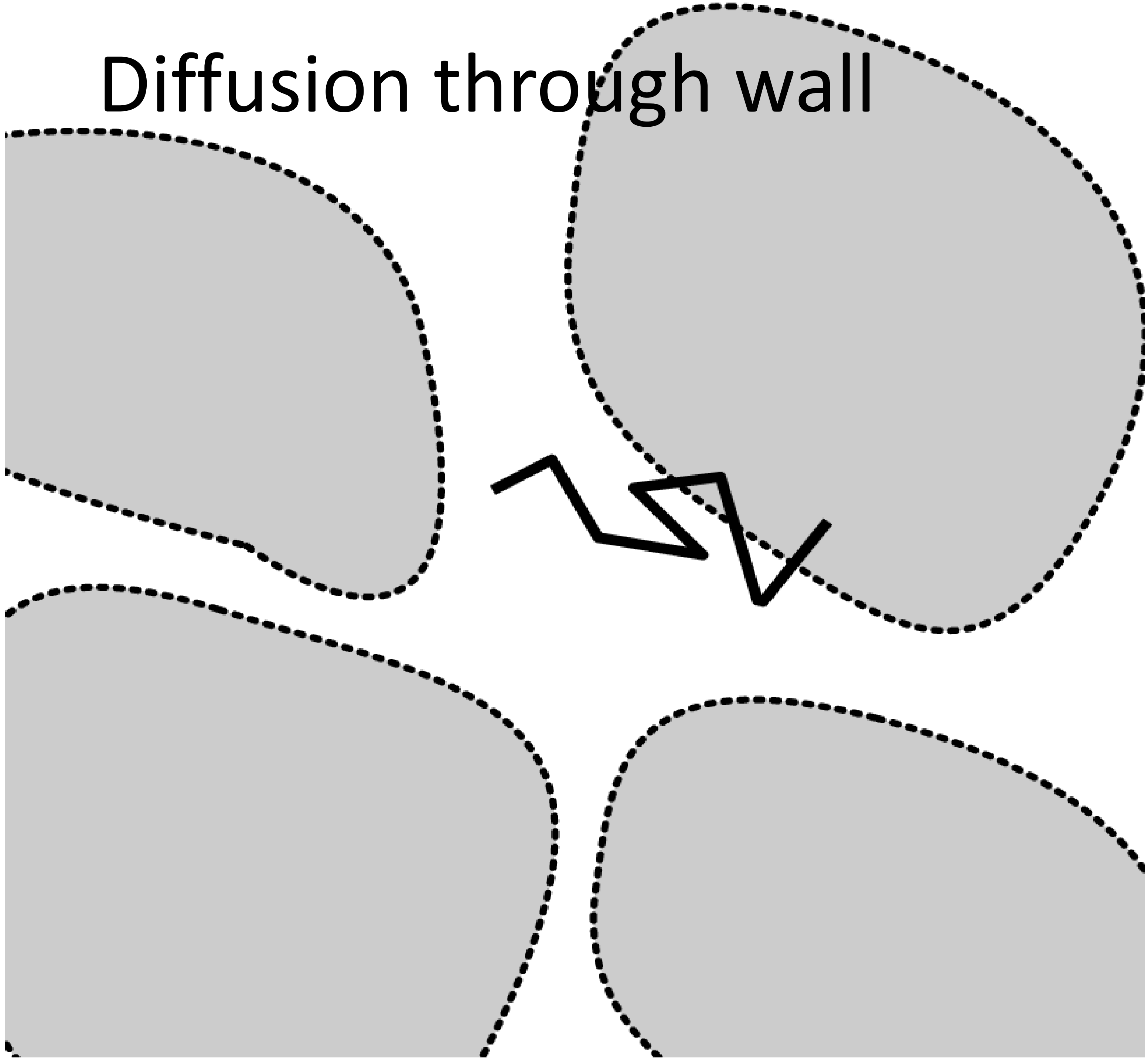
Mitra, Sen, …1992

# A Robust Result




$$D(t) = D_0\left[1 - \left(\frac{4S}{9V_p}\right)\left(\frac{D_0 t}{\pi}\right)^{1/2}\right]$$

# Diffusion through wall



# New Short-time Result with Permeability κ

P. N. Sen, J. Chem Phys. **119**, 9781, ( 2003); Ibid, **120**, 11965 (2004)

$$D_{R,eff}(t) = D_R \left[ 1 - \frac{S_R}{V_R} \left( \frac{4\sqrt{D_R t}}{9\sqrt{\pi}} - \frac{\sqrt{D_L}\left(\sqrt{D_L}+\sqrt{D_R}\right)}{6 D_R} \kappa t \right) \right] +$$

$$+ D_R \frac{S_R}{V_R} \left[ \frac{1}{6} \rho t - \frac{1}{12} D_R t \langle \frac{1}{R_1} + \frac{1}{R_2} \rangle_R \right] + \mathcal{O}\left( [D_R t]^{3/2} \right).$$

κ- correction is important for

$$t \geq \frac{16}{9\pi} \frac{D}{\kappa^2} \approx 0.06 \quad \text{sec}$$

*D =1.12 $10^{-5}$ cm$^2$/s, κ = 6.3 $10^{-3}$ cm/s*

*Latour et al. (rough, κ from long-time EMA )*

# What happens in connected pores? for Long-times $L_D$>>a

Time dependent diffusion in a disordered medium with partially absorbing walls: A perturbative approach, Jiang Qian and Pabitra N. Sen, J. Chem Phys 125, 194508 (2006).

M(t) $\rho = \infty$ stretched exponential????

[1] M. V. Smoluchowsky, Phys. Z. 17, 557 (1916).
[2] G. H. Weiss, J. Stat. Phys. 42, 3 (1986); *Aspects and Applications of the Random Walk* (North-Holland, Amsterdam, 1994).
[3] R. F. Kayser and J. B. Hubbard, J. Chem. Phys. 80, 1127 (1984).
[4] M. Fixman, Phys. Rev. Lett. 52, 791 (1984).
[5] A. R. Kansal and S. Torquato, J. Chem. Phys. 116, 10589 (2002).
P. Grassberger and I. Procaccia, J. Chem. Phys. 77, 6281 (1982).
M. D. Donsker and S. R. S. Varadhan, Commun. Pure Appl. Math. 36, 183 (1983).

Scattering Approach: Dilute $\rho = \infty$

M. Bixon and R. Zwanzig, J. Chem. Phys. 75, 2354 (1981).

T. R. Kirkpatrick, J. Chem. Phys. 76, 4255 (1982).

Scattering Approach: Dilute and periodic M(t) and D (t) finite $\rho$

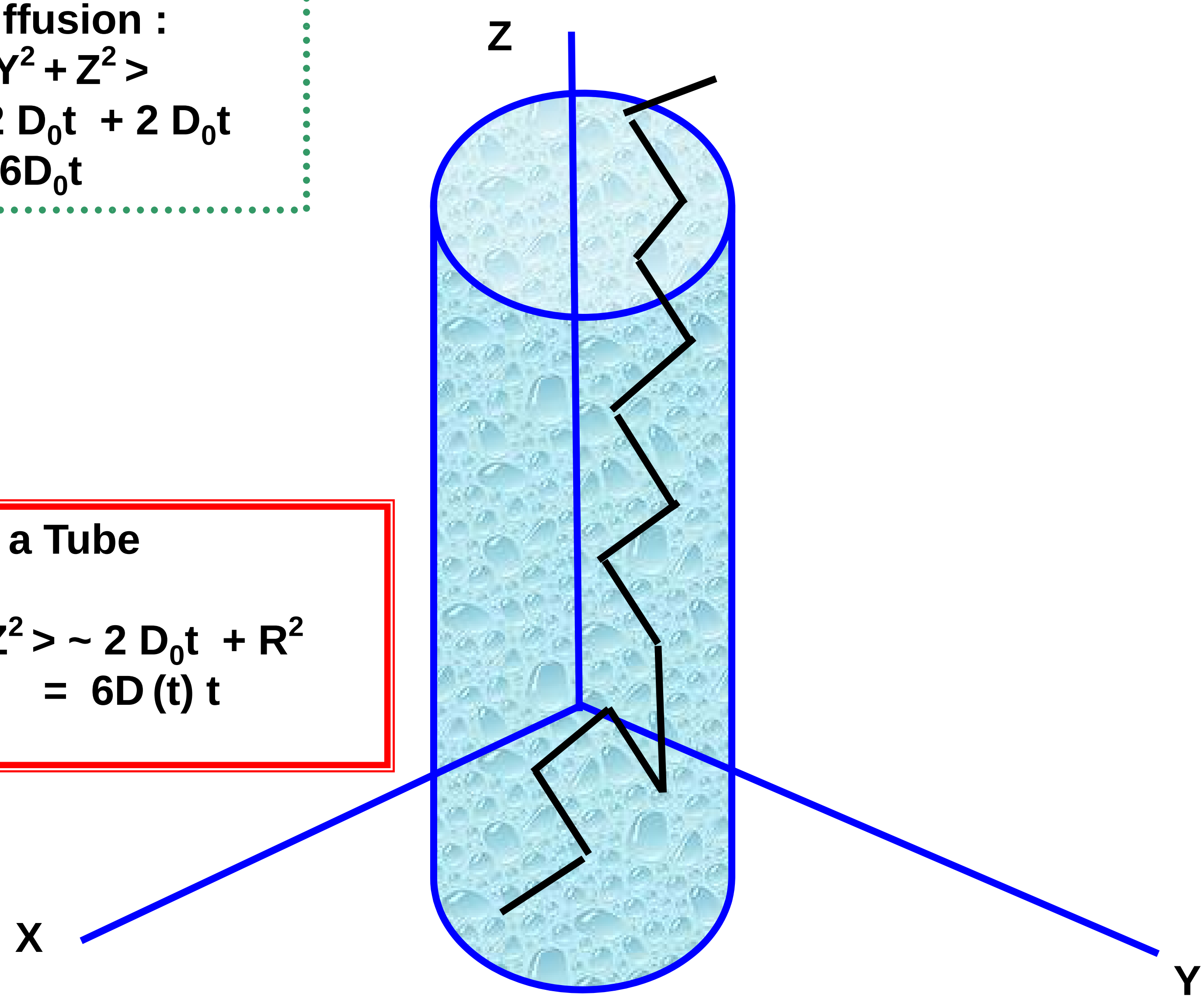
P. N. Sen, L. M. Schwartz, P. P. Mitra, and B. I. Halperin, Phys. Rev. B 49, 215 (1994).
T. M. de Swiet and P. N. Sen, J. Chem. Phys. 104, 206 (1996).

# Random Walk in a tube : Long Time

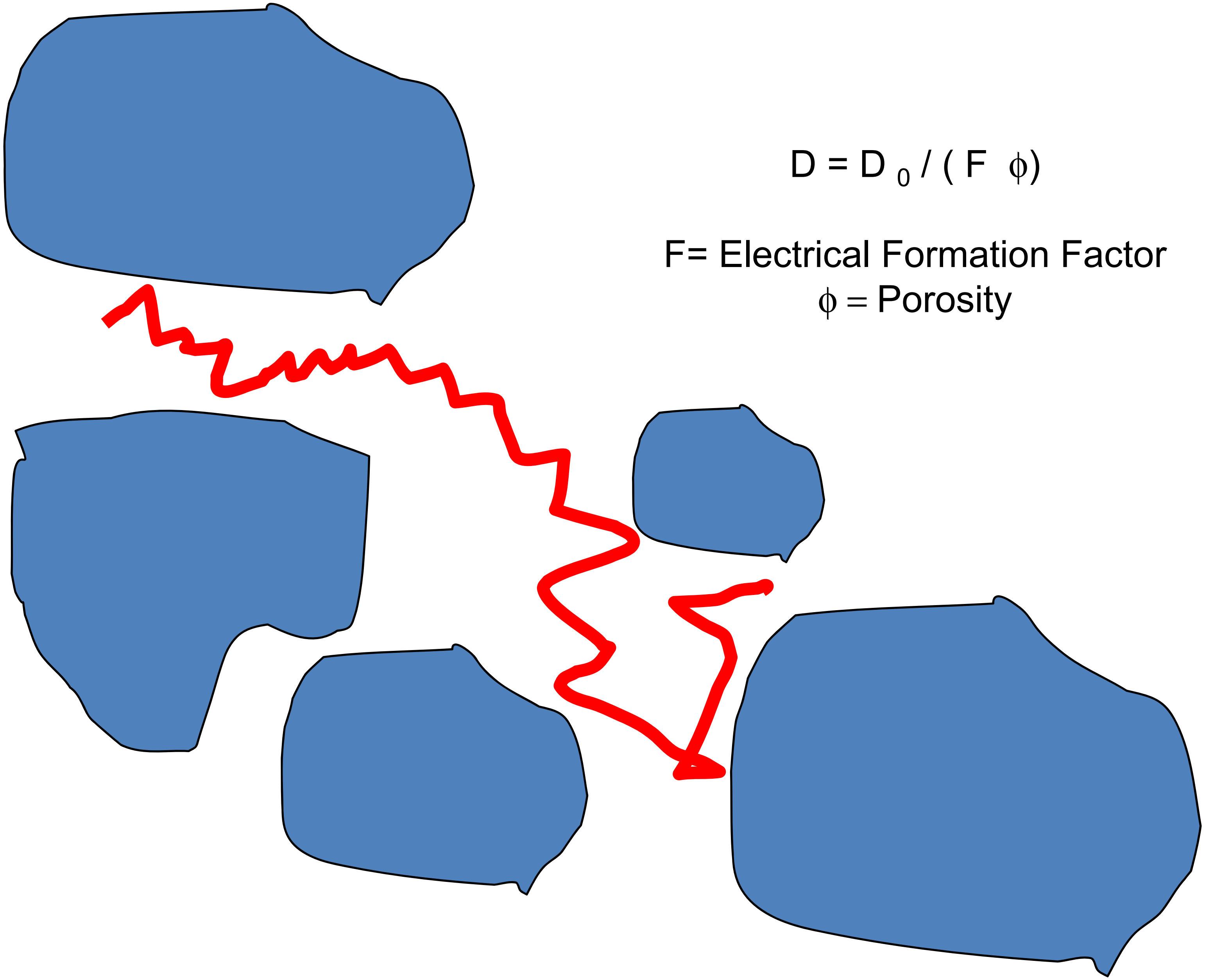
**Free diffusion :**
$<X^2 + Y^2 + Z^2>$
$= 2\ D_0t + 2\ D_0t\ + 2\ D_0t$
$= 6D_0t$

**IN a Tube**

$<X^2 + Y^2 + Z^2> \sim 2\ D_0t\ + R^2$
$= 6D(t)\ t$



# Restricted Diffusion in a porous media—Long time $\rho = 0$



$$D = D_0 / (F \phi)$$

F= Electrical Formation Factor
$\phi$ = Porosity

# Pack of Beads—Long Time

$$\frac{D(t)}{D_0} = \frac{1}{F\,\phi} + \frac{L^2}{D_0 t} + \frac{\gamma}{(D_0 t)^{3/2}} + .$$

$$\sigma = \frac{\sigma_w}{F}$$

deSwiet and Sen , J. Chem. Phys., **104**,206, 1996

# Time-Dependent Diffusion

$$D(t) = \frac{<r^2>}{6t}$$

*What we expect:*

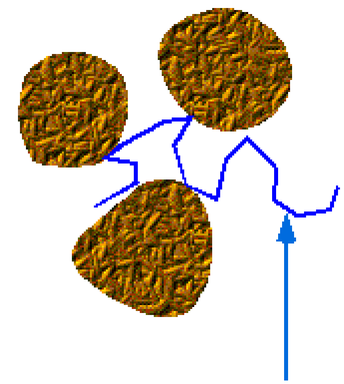
### 1. Free Diffusion

$$D(t) = D_0$$

Fluid property

### 2. Short/Early Time

$$D(t) = D_0\left[1 - \left(\frac{4S}{9V_p}\right)\left(\frac{D_0 t}{\pi}\right)^{1/2}\right]$$



Typical random walker

### 3. Long/Late Time

$$D(t) = \frac{D_0}{F\phi}\left[1 + G\,\frac{L^2_{macro}}{D_0 t}\right]$$

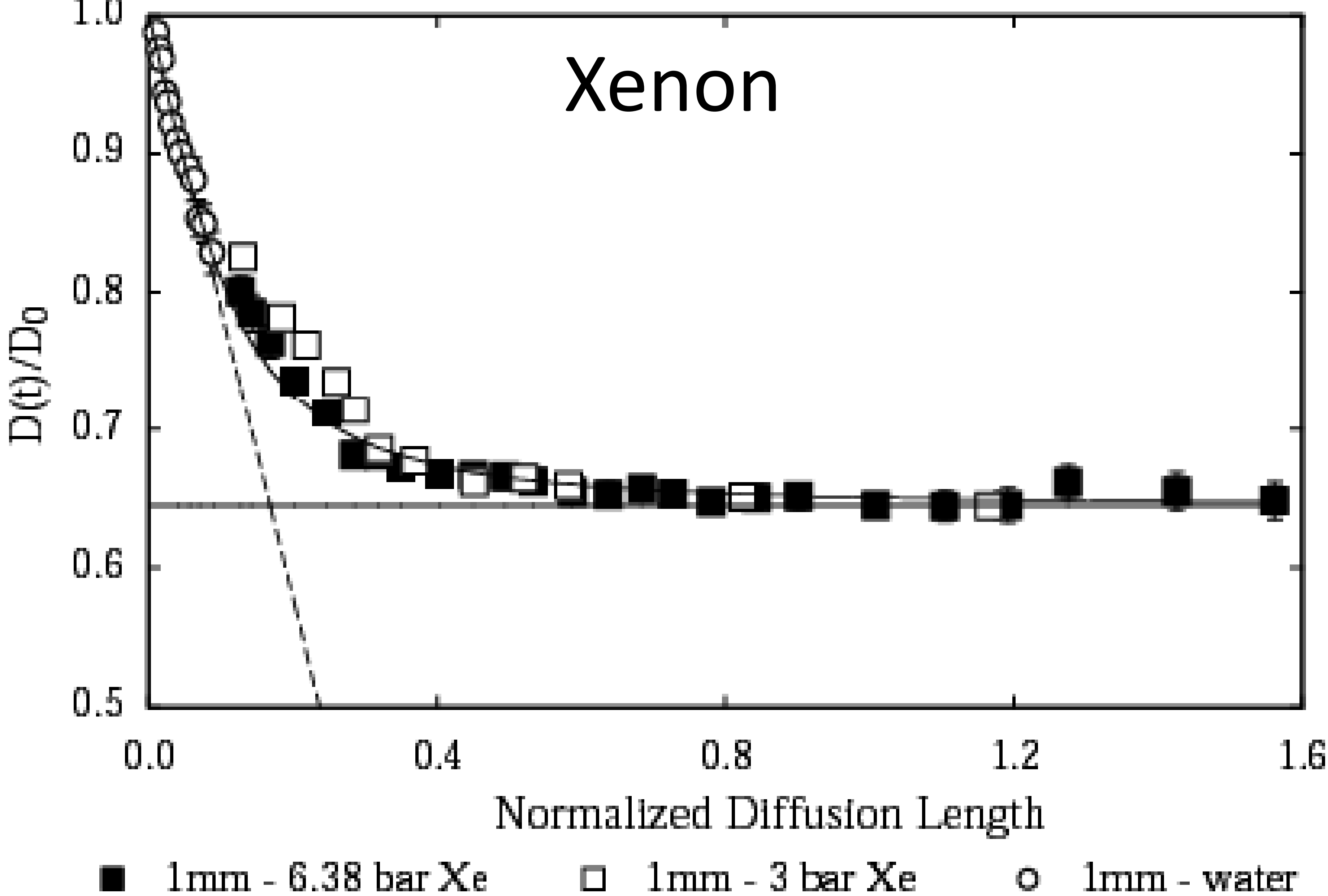
Electrical Formation Factor

Porosity

Pore size information

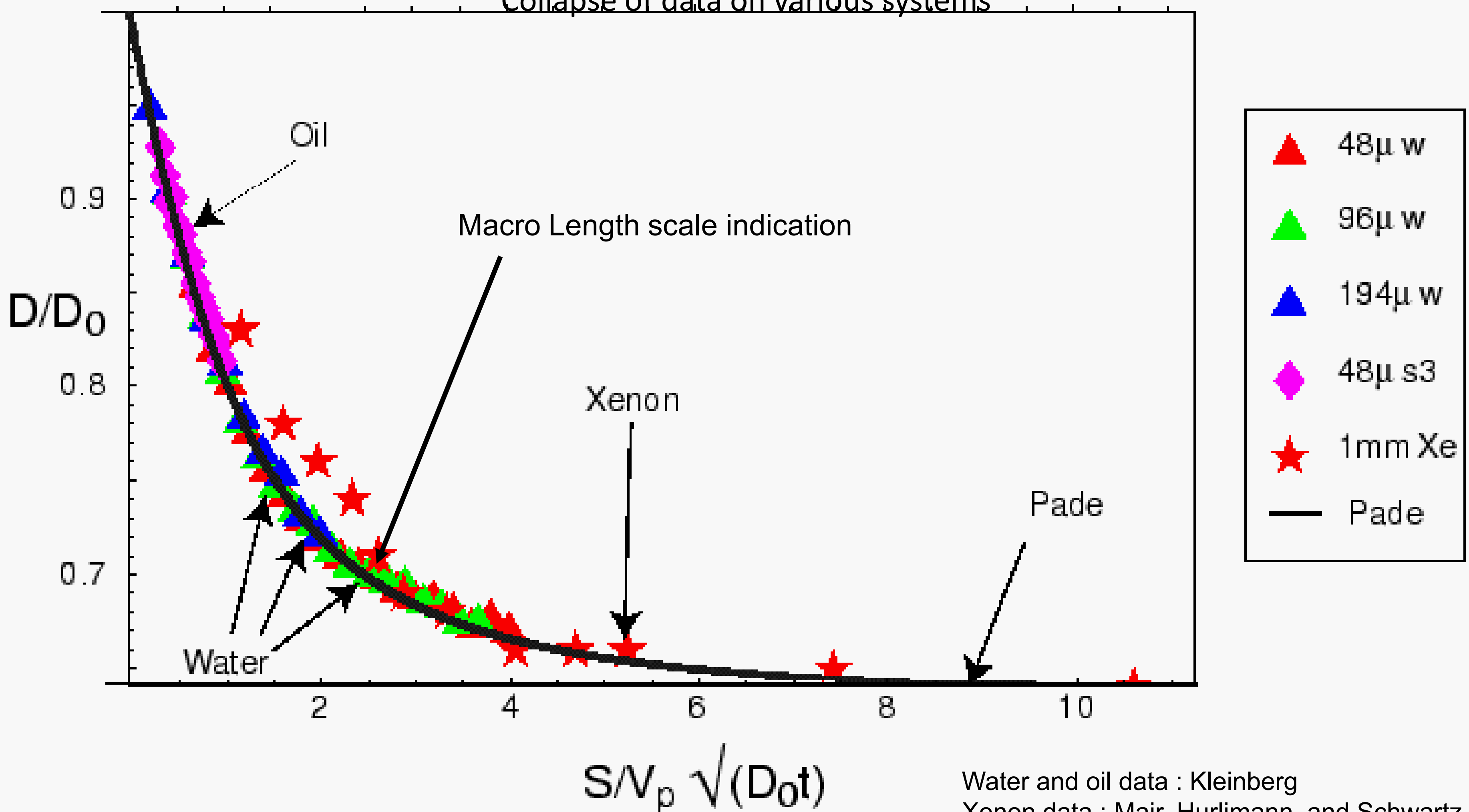
Independent of relaxivity !

Mair, Sen…., JMR 2003



# PFG Data on Beads

Collapse of data on various systems



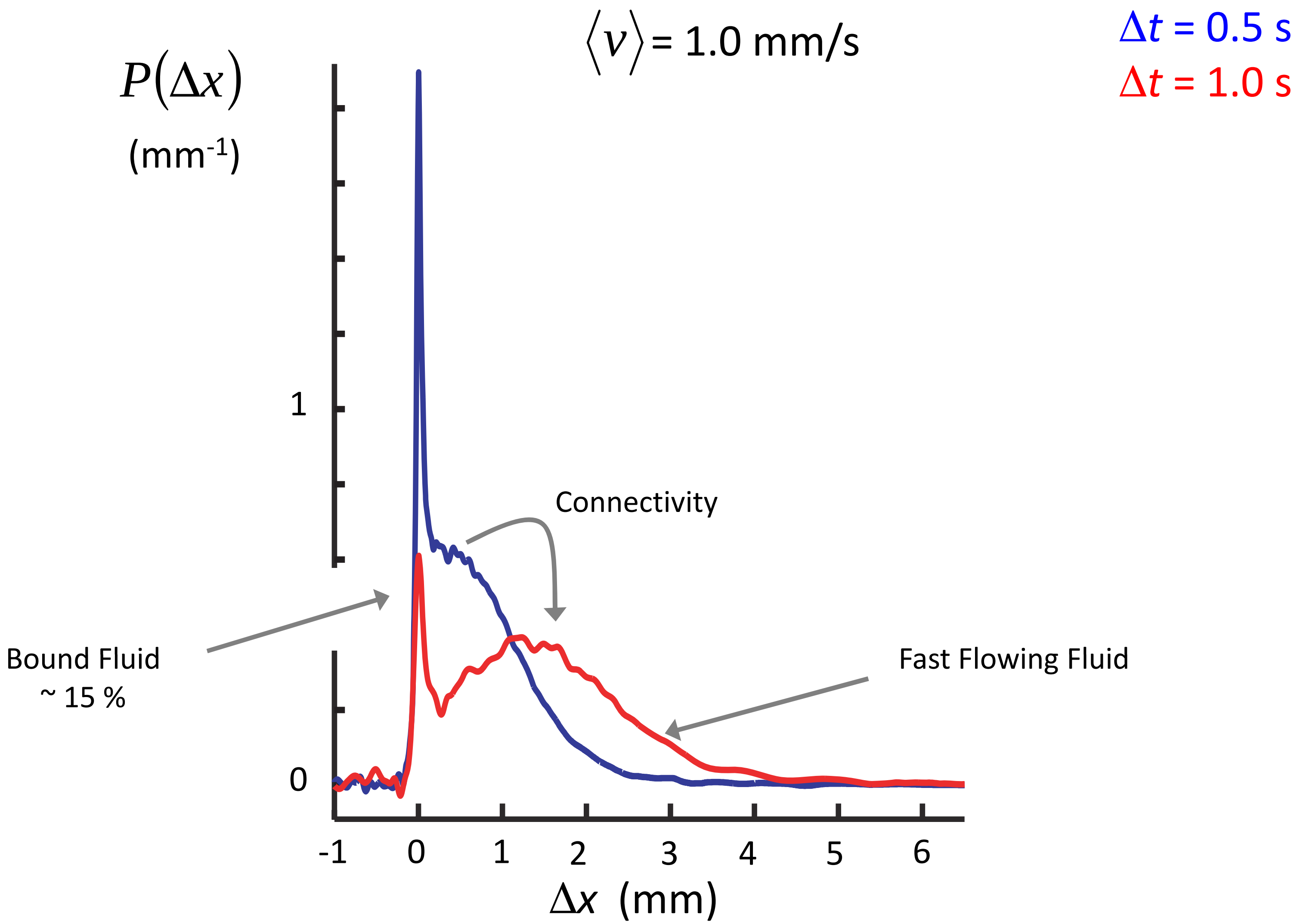

Water and oil data : Kleinberg
Xenon data : Mair, Hurlimann, and Schwartz

# Grains with Permeable Walls---Cells

1. Short-time Results

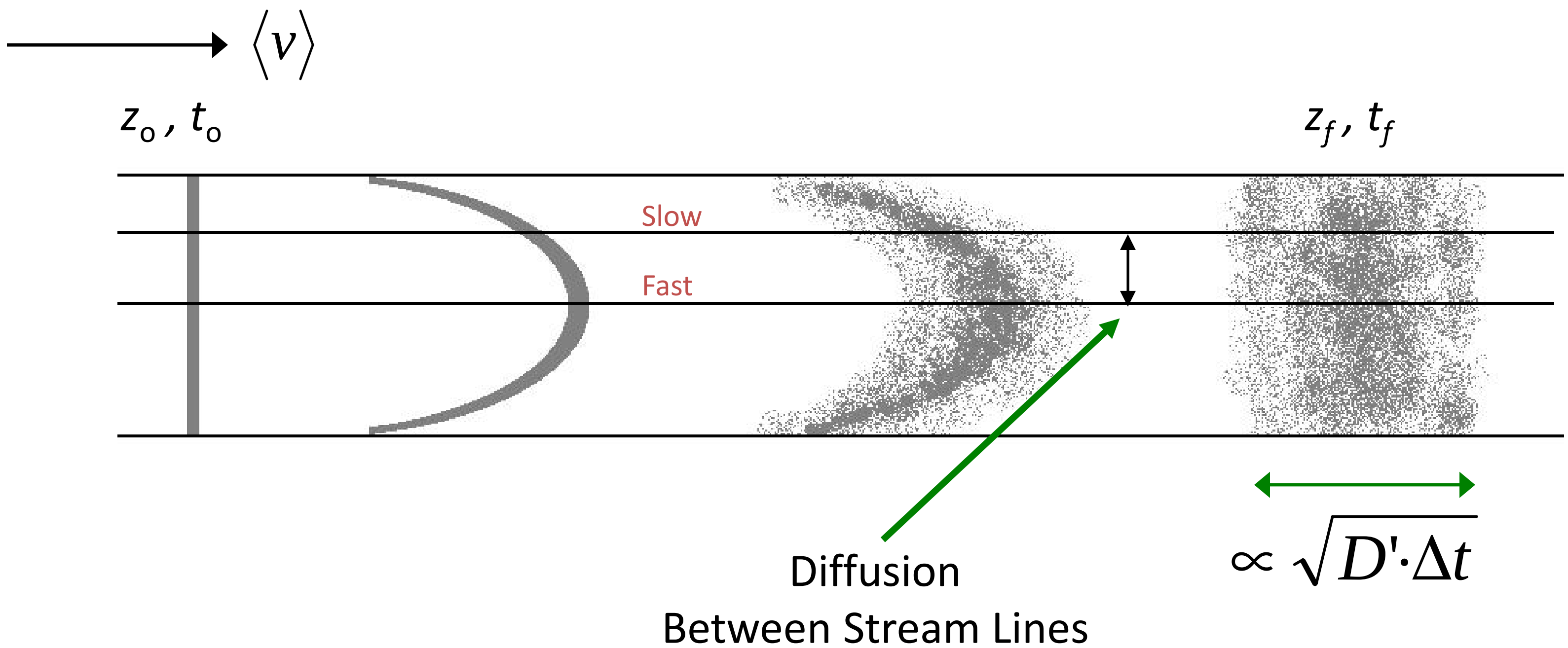
2. Long-time results

# The Propagator




Schlumberger

# Molecular Diffusion during Flow




(Taylor 1953)

$$D' = D_o\left(1 + \frac{\mathrm{Pe}^2}{48}\right) \qquad \mathrm{Pe} = \frac{\langle v \rangle a}{D_o} \approx 10 - 1000$$

Flow enhances Diffusion !

# Dispersion in a Tube with wall relaxataion

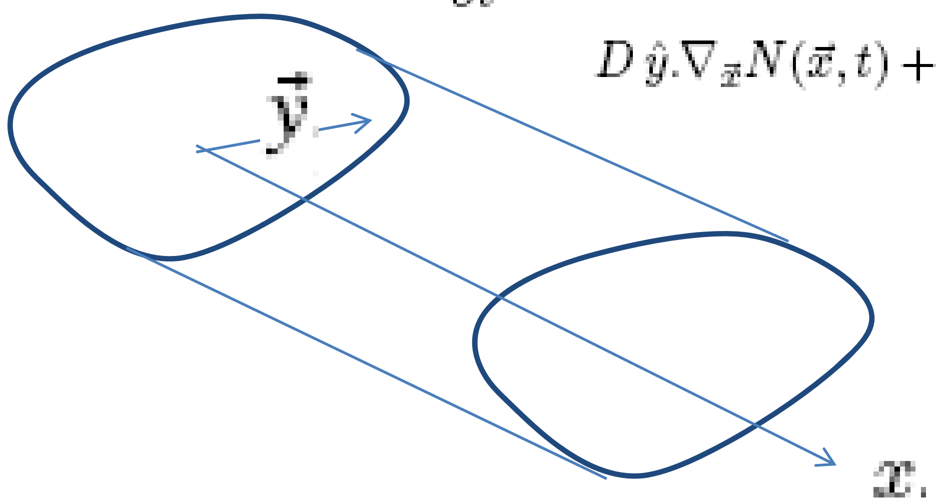
Taylor dispersion with absorbing boundaries: A Stochastic Approach, R. R. Biswas and P. N. Sen , Phys. Rev. Letters, **98**, 164501 (2007)

Concentration of Solutes, $N(\vec{x},t)$:

$\vec{x} \equiv (x, \vec{y})$

$$\frac{\partial N(\vec{x},t)}{\partial t} = D\nabla^2_{\vec{x}} N(\vec{x},t) - \vec{v}(\vec{x}).\mathbf{\nabla} N(\vec{x},t) \quad \vec{x} \in V$$

$$D\,\hat{y}.\nabla_{\vec{x}} N(\vec{x},t) + \rho N(\vec{x},t) = 0, \quad \vec{x} \in \partial V$$



# Uniform Cross-section

$$n(\vec{y},t) = \int dx\, N(\vec{x},t)$$

$$\frac{\partial n(\vec{y},t)}{\partial t} = D\, \nabla_y^2\, n(\vec{y},t) \qquad \vec{y} \in A$$

$$D\, \hat{e}.\nabla_y\, n(\vec{y},t) = -\rho\, n(\vec{y},t) \qquad \vec{y} \in \partial A$$

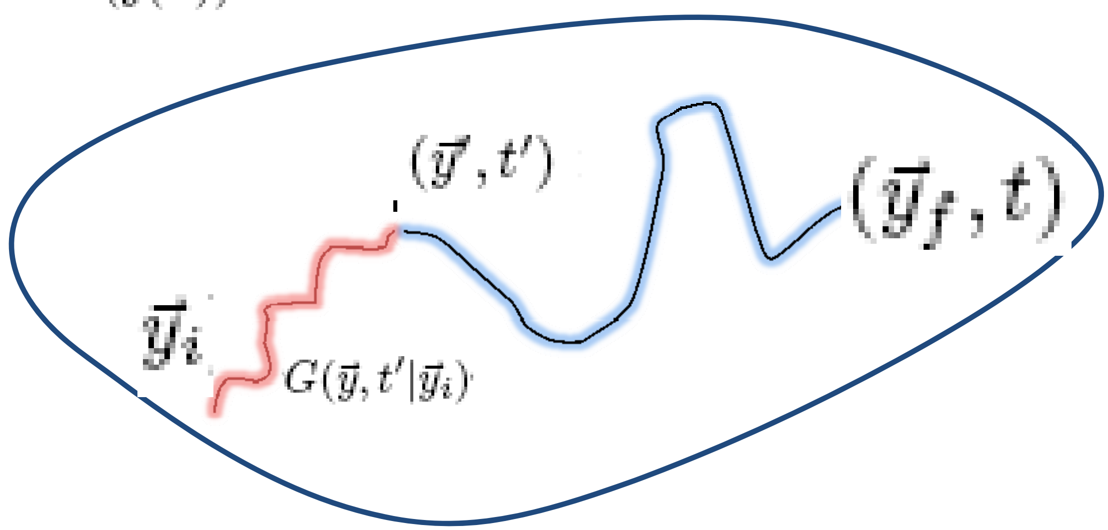
$$n(\vec{y},t) = \int_A dy' G(\vec{y},t-t'|\vec{y}')n(\vec{y}',t') \;\; t \geq t'$$

Thus, the number density of particles that pass through $(\vec{y},t')$ and *also* survive till $t$ is

$$\nu(\vec{y},t'|t) = \int_A dy_f \int_A dy_i\, G(\vec{y}_f,t-t'|\vec{y})G(\vec{y},t'|\vec{y}_i)n(\vec{y}_i,0)$$

$$\frac{dx(t)}{dt} = v(\vec{y}(t)) \;\; \Rightarrow \;\; x(t) = \int_0^t dt' v(\vec{y}(t'))$$

$$\langle x(t) \rangle = \frac{1}{N(t)} \int_0^t dt' \int_A dy\;\, v(\vec{y})\nu(\vec{y},t'|t)$$



# Taylor Dispersion between Parallel Plates

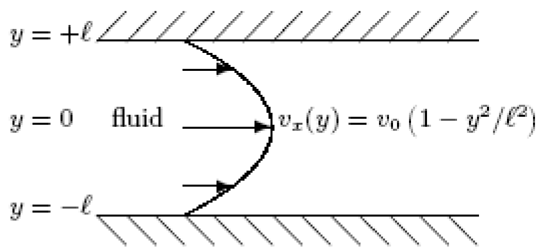



FIG. 1: Taylor dispersion between parallel plates

Time dependent diffusion in a disordered medium with partially absorbing walls: A perturbative approach, Jiang Qian and Pabitra N. Sen, J. Chem Phys **125**, 194508 (2006).

# Dispersion Cont'd: Uniform Cross Section

$$\langle (x(t))^2 \rangle = \frac{2}{N(t)} \int_{0 \le t_1 \le t_2 \le t} dt_1 dt_2 \int_{A \otimes A} dy_1 dy_2 v(\vec{y}_1) v(\vec{y}_2) \nu(\vec{y}_1, t_1 | \vec{y}_2, t_2 | t)$$

$$\nu(\vec{y}_1, t_1 | \vec{y}_2, t_2 | t) = \int_{A \otimes A} dy_i dy_f G(\vec{y}_f, t - t_2 | \vec{y}_2) G(\vec{y}_2, t_2 - t_1 | \vec{y}_1) G(\vec{y}_1, t_1 | \vec{y}_i) n(\vec{y}_i, 0)$$

$$(D \nabla_y^2 + \lambda_k) \psi_k(\vec{y}) = 0 \qquad \vec{y} \in A$$

$$(D\, \hat{e}.\boldsymbol{\nabla}_y + \rho) \psi_k(\vec{y}) = 0 \qquad \vec{y} \in \partial A$$

$$(\lambda_0 < \lambda_1 < \lambda_2 \ldots)$$

$$\int_A dy \; \psi_j(\vec{y}) \psi_k(\vec{y}) = \delta_{jk}$$

$$G(\vec{y}, t | \vec{y}') = \sum_{n=0}^{\infty} \psi_n(\vec{y}) \psi_n(\vec{y}') e^{-\lambda_n t}$$

$$\langle x(t) \rangle \xrightarrow{t \gg 2\tau} \overbrace{v_{00}}^{v_e} t + \mathcal{O}(e^{-t/\tau})$$

# Enhancement of Velocity,Reduction of Diffusion

$$v_{ij} = \int_A d\vec{y}\,\psi_i(\vec{y})\,v(\vec{y})\,\psi_j(\vec{y})$$

$$\kappa_2 = <[\delta x(t)]^2> \rightarrow 2t\sum_{k=1}^{\infty} \frac{v_{ko}^2}{\lambda_k - \lambda_0}$$

$$\kappa_3 = <[\delta x(t)]^3> \rightarrow_{\tau >> L^2/D} 6t\sum_{j=1}^{\infty}\sum_{k=1}^{\infty} \frac{v_{0j}v_{k0}(v_{kj} - \delta_{kj}v_{00})}{(\lambda_k - \lambda_0)(\lambda_j - \lambda_0)}$$

Deviations from Gaussianit y die

$$\gamma_1 = \frac{\kappa_3}{\kappa_2^{3/2}} \rightarrow \sqrt{\frac{\tau}{t}}$$

$$\gamma_1 = \frac{\kappa_4}{\kappa_2^2} \rightarrow \frac{\tau}{t}$$

$$v_e = \frac{2}{3}v_0(1 + \frac{2\alpha}{15}),\ \alpha << 1; \alpha = \rho l / D$$

$$v_e = \frac{2}{3}v_0(1 + \frac{3}{\pi^2}),\ \alpha > 1$$

$$D_{Taylor} = \frac{8v_0^2 l^2}{945\ D}(1 - \frac{4\alpha}{15})\alpha << 1; \alpha = \rho l / D$$

# Limitations and Gaps

| **Geometry** / **Time** | **Isolated** Simple | **Isolated** Complex | **Connected** Simple | **Connected Complex** ***MOTHER NATURE*** |
|---|---|---|---|---|
| Short $L_D << L_s$ | Laplace Kac | Kac | Kac | Kac |
| Long $L_D >> L_s$ | Laplace | Numerical | Periodic Bloch Floquet Numerical | Perutrbative Statistical Numerical |

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