NMR measurement of hydrodynamic dispersion in porous media: structure, dynamics and statistical mechanics

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Statistical Mechanics Playground

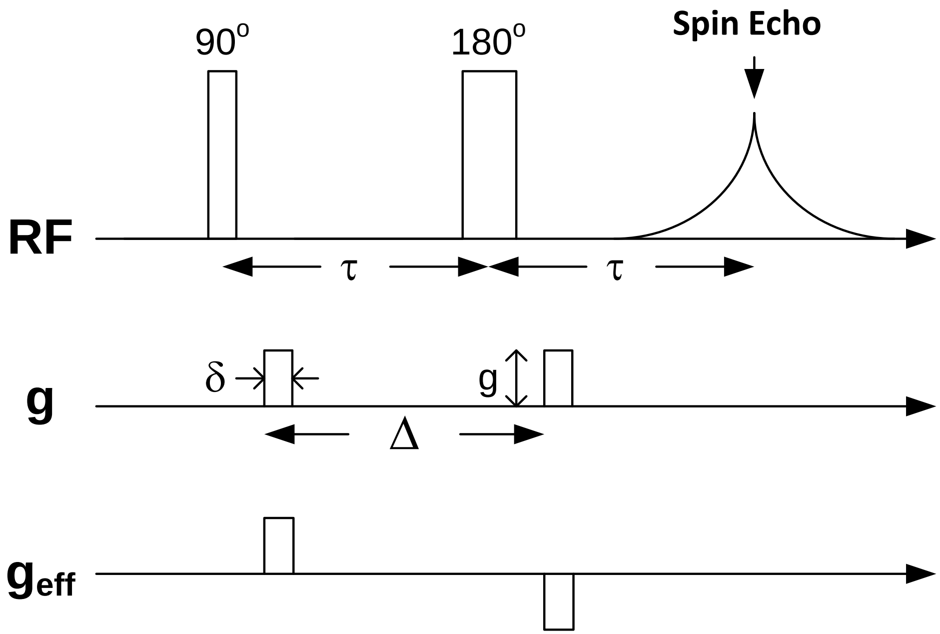
Granular Materials/Colloids - Statistical Mechanics Sandbox

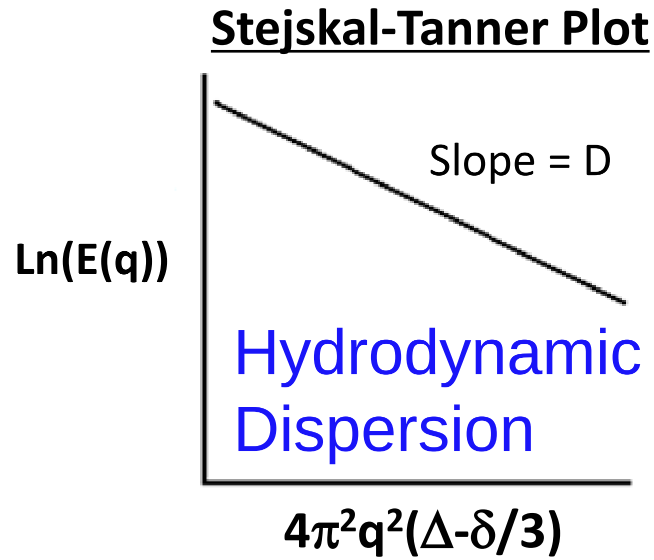
[Jaeger, Nagel, and Behringer, *RMP* **68** 1259 (1996); Seymour et al. *PRL* **84** 266 (2000); Brown et al. *PRL* **99** 240602 (2007)]

Porous Media – Statistical Mechanics Jungle Gym

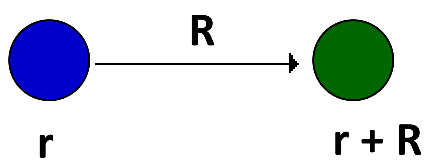
[Scheidegger, *J. App. Phys*. **25**(8): 994 (1954); Saffman, *JFM* **6** 321 (1959); Seymour and Codd, *EPJ-App. Phys* (2012)]

Pulsed Gradient Spin Echo (PGSE) NMR





$$\mathbf{q} = (2\pi)^{-1}\gamma\delta\mathbf{g} \quad [1/m]$$



Gradient (g) direction

Mean Displacement - Velocity

Phase shift ($\Delta\phi = \gamma g \delta \Delta v$)

Fourier Transform Relationship

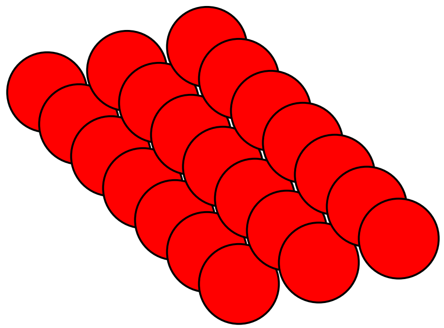
$$E(\boldsymbol{q}) = \frac{S(\boldsymbol{q})}{S(0)} = \int \langle P_S(\boldsymbol{R},\Delta)\rangle \exp(i2\pi\boldsymbol{q}\cdot\boldsymbol{R})\,d\boldsymbol{R}$$

$\Updownarrow$ **FT**

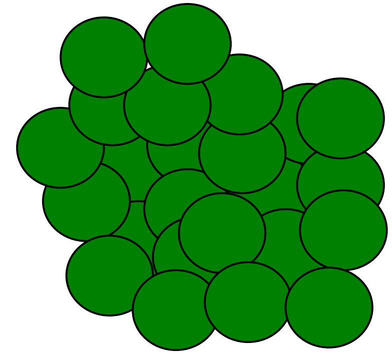
$$\langle P_S(\boldsymbol{R},\Delta)\rangle = \int E(q)\exp(i2\pi\,\boldsymbol{q}\cdot\boldsymbol{R})\,d\boldsymbol{q}$$

Structure Function Relations

Order



Disorder

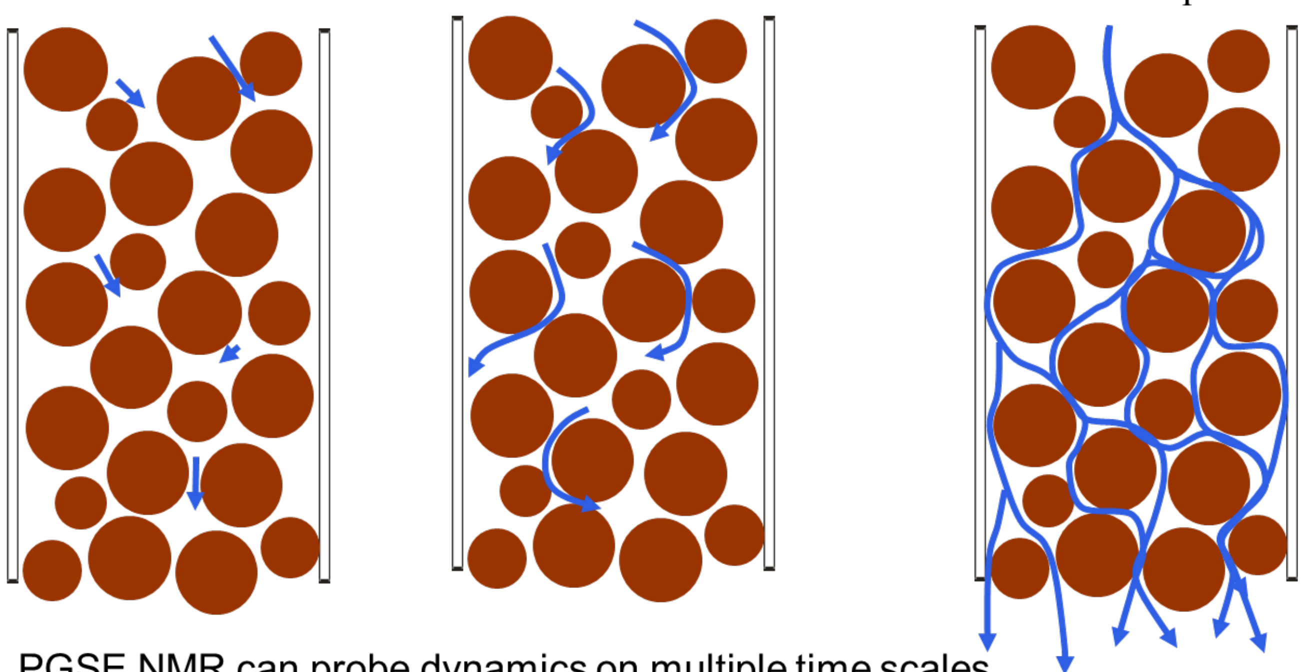


Transport

Short time
'Cauchy'-like Dispersion

Medium Time
Pore structure is sampled

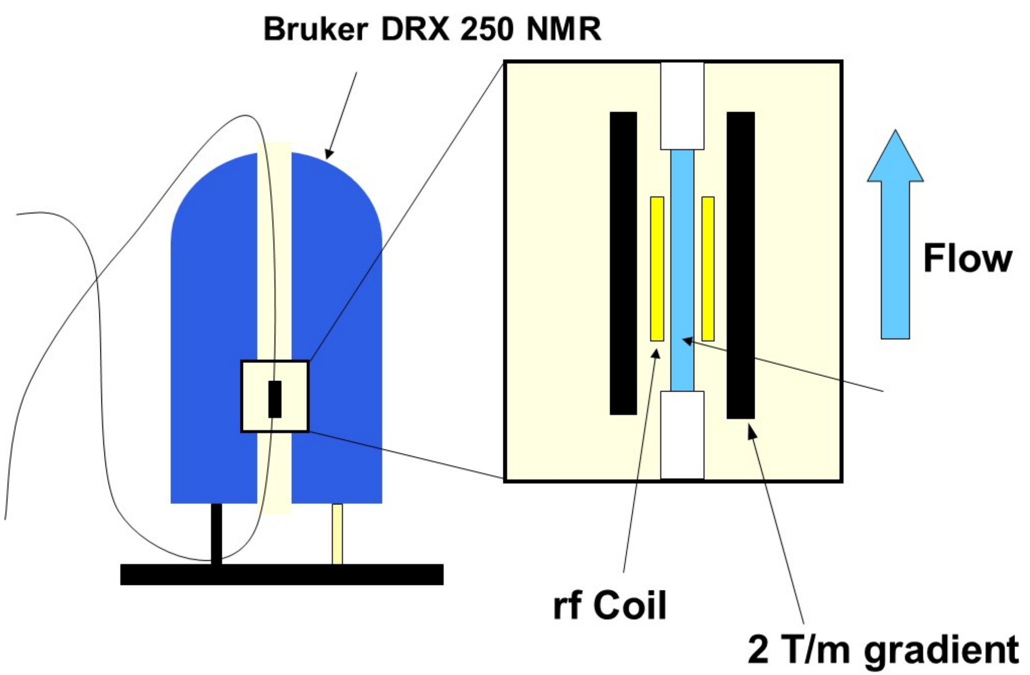
Long Time
Gaussian Dispersion

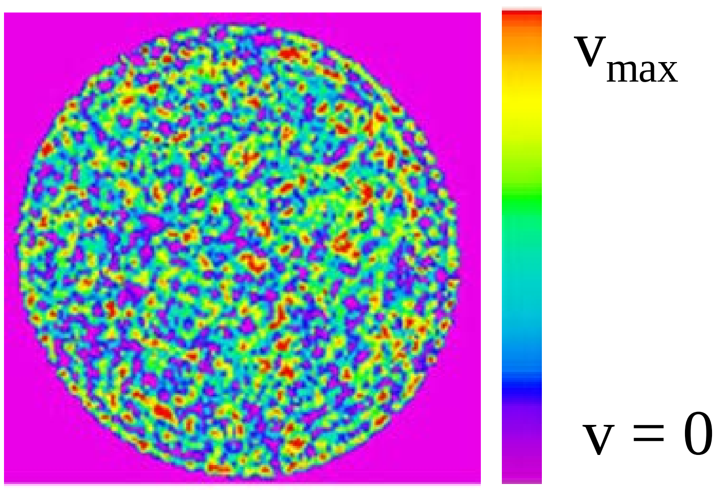


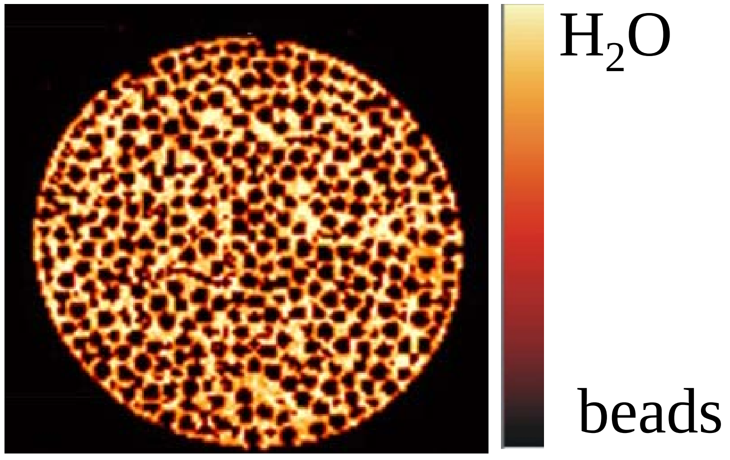
PGSE NMR can probe dynamics on multiple time scales

Flow in a Model Bead Pack

[Seymour and Callaghan, AIChE J. 1997]



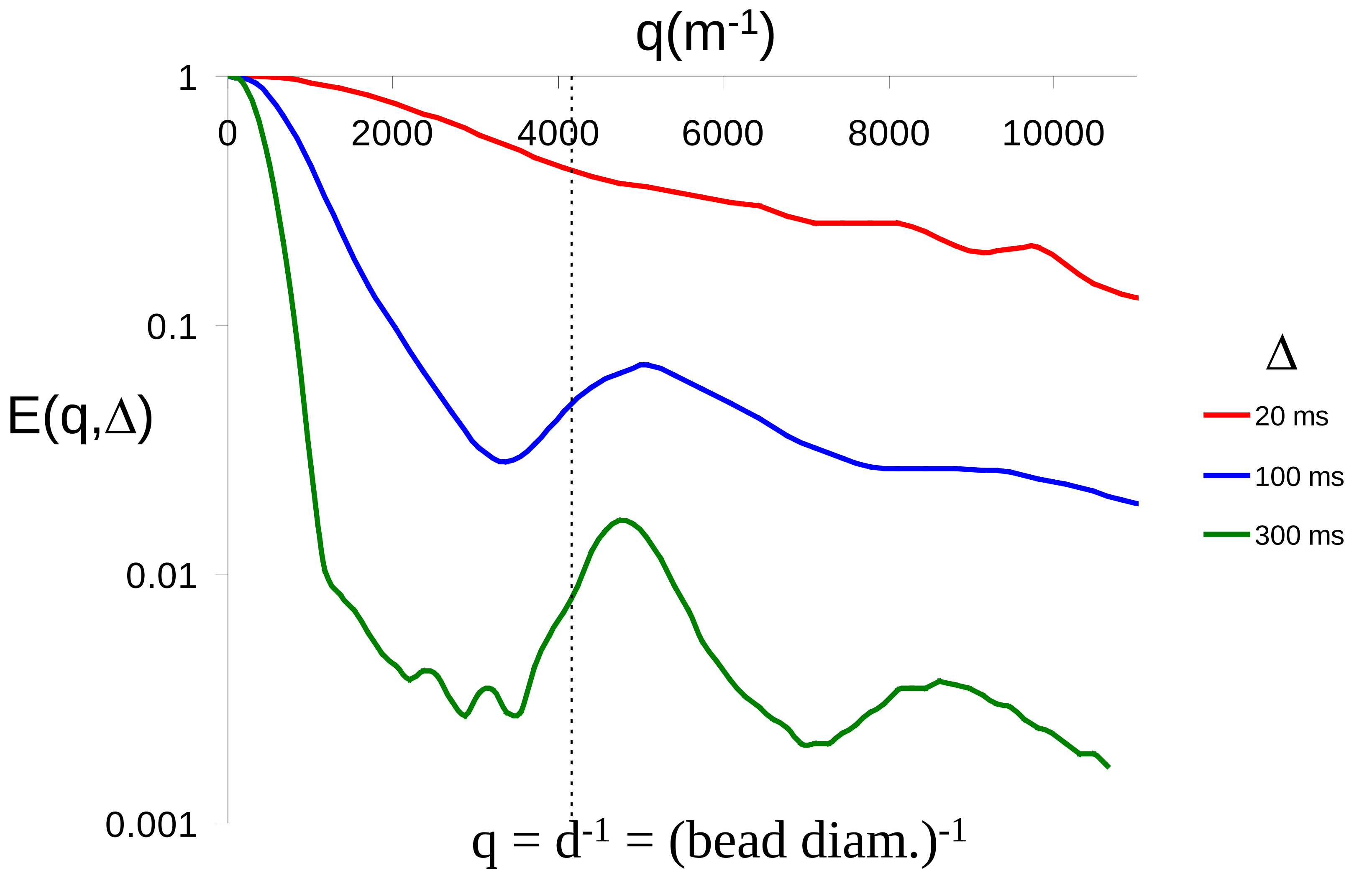




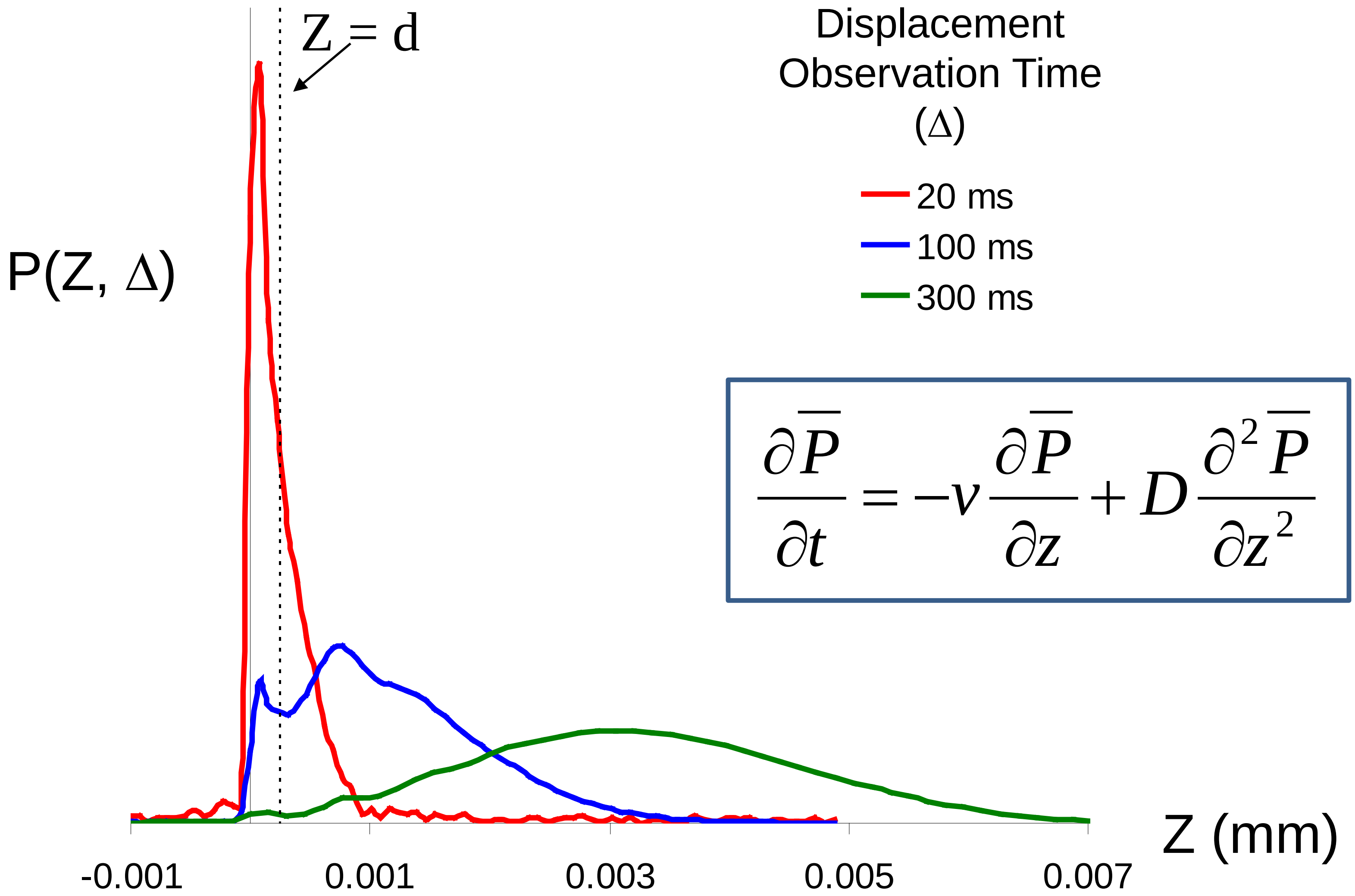
- 241 μm monodisperse beads
- 5 mm ID cylinder
- Low Re
- Range of Pe

‘Flow Diffraction’ in Monodisperse Bead Pack

[Seymour and Callaghan, JMR 1996; AIChE J. (1997); Seymour et al. PRL (2004)]



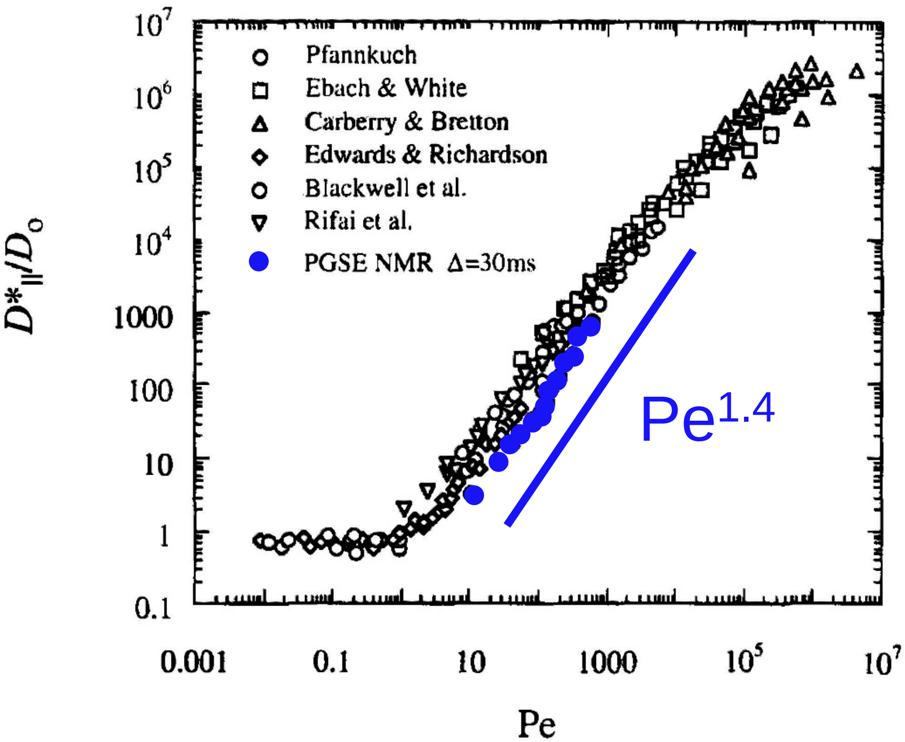
Propagator Time Evolution



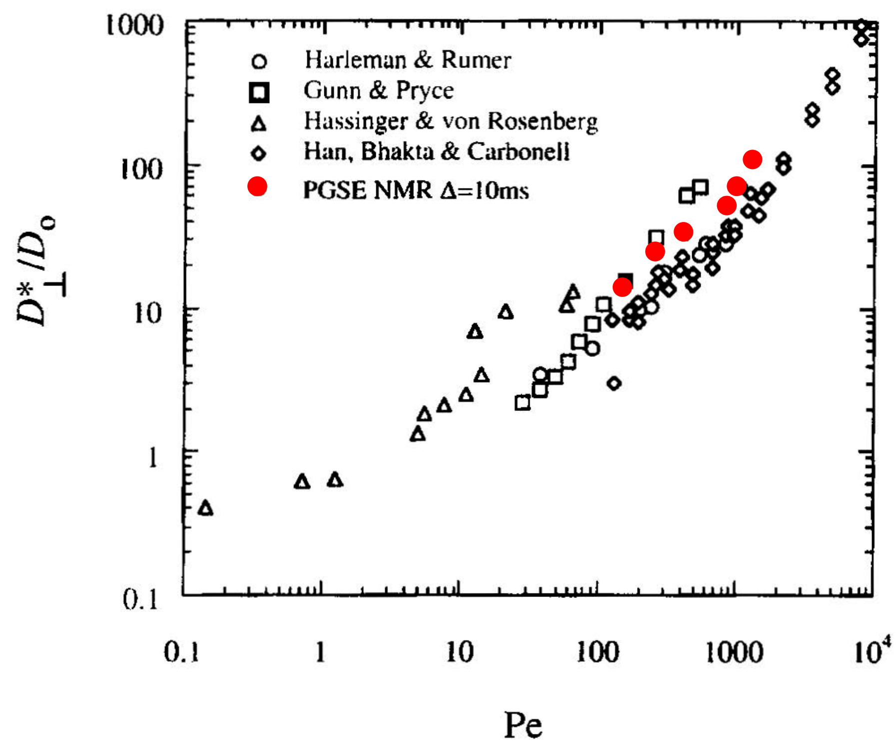
$$\frac{\partial \overline{P}}{\partial t} = -v\frac{\partial \overline{P}}{\partial z} + D\frac{\partial^2 \overline{P}}{\partial z^2}$$

Hydrodynamic Dispersion Coefficient Peclet Number Scaling

[Seymour and Callaghan, AIChE J. 1997]



$$Pe = \frac{<v>l}{D_o} = \left(\frac{\Phi}{1-\Phi}\right)\frac{<v>d_p}{D_o}$$



$D_L \sim Pe^{\alpha}$

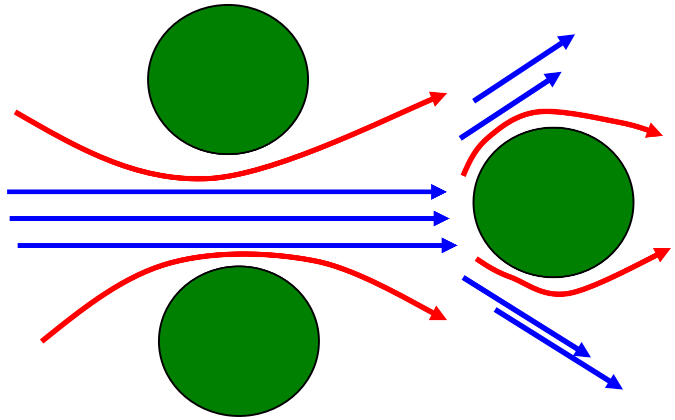
α = 2 periodic structure (Taylor dispersion)

α=1 mechanical dispersion

α~1.2 boundary layer dispersion (Pe lnPe)

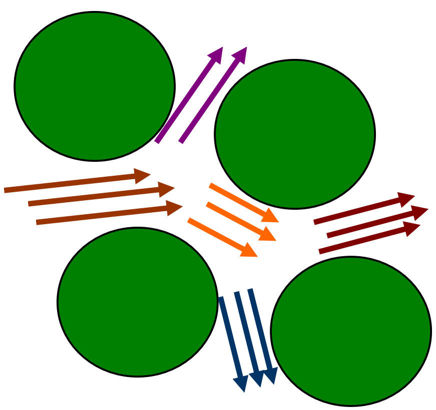
Origin of Power Law Pe^{α}

Boundary layer [P.G. Saffman, JFM, **6** 321 (1959); D.L. Koch and J.F. Brady, JFM, **154** 399 (1985)]



Interplay of diffusive and advective

Distribution of throat velocities [B. Bijeljic and M.J. Blunt, WRR **42** W01202 (2006)]



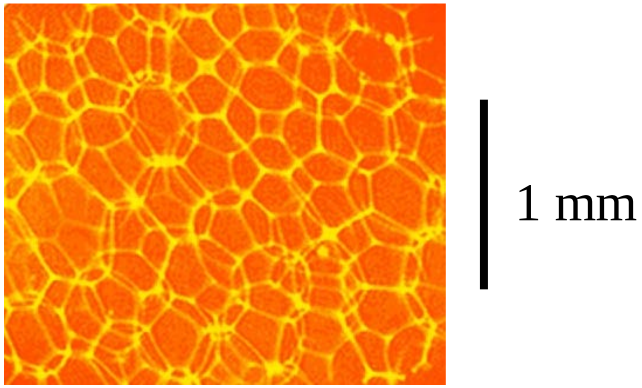
CTRW probability for time to reach next pore

$$\psi(t) \sim t^{-1-\alpha}$$

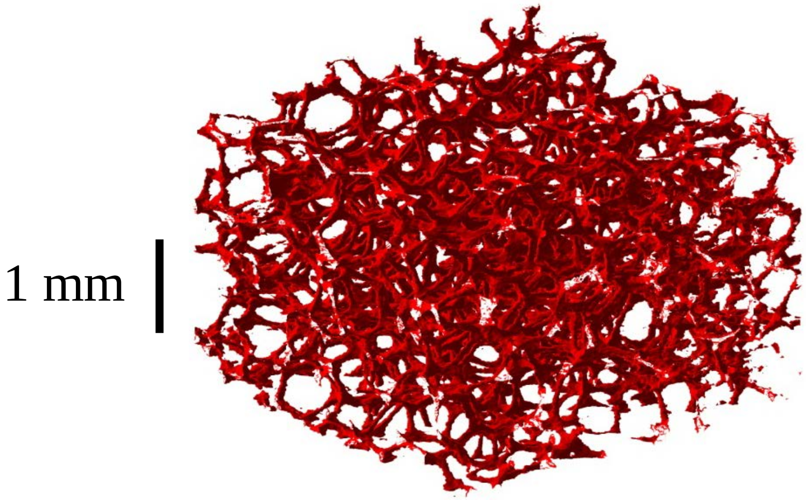
Solid cellular structures

• solid ligaments (1D) → windows (2D) → cells (3D)

• bio- & tech-structures: *e.g. bones, catalysts, filters, etc.*



2D MR image of polymer foam
(used in PGSE NMR measurements)



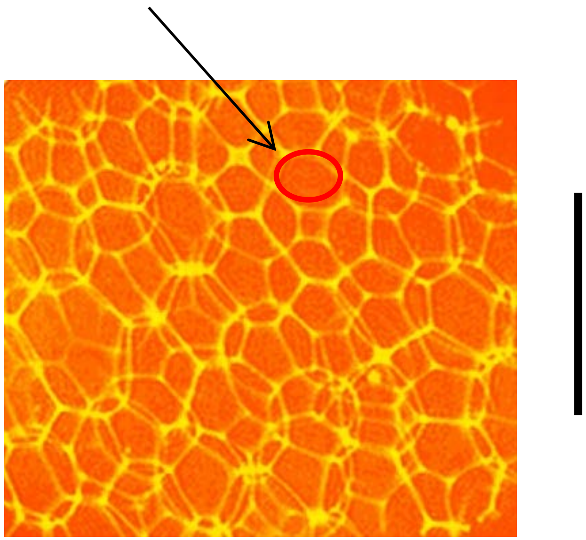
3D digitized polymer foam*
(used in LB simulations)

*structure from Montminy et. al, JCIS 2004

What is the characteristic length of a cellular structure?

- non-dimensional numbers (e.g. *Pe*, *Re*), entrance length…

mean window “diameter”



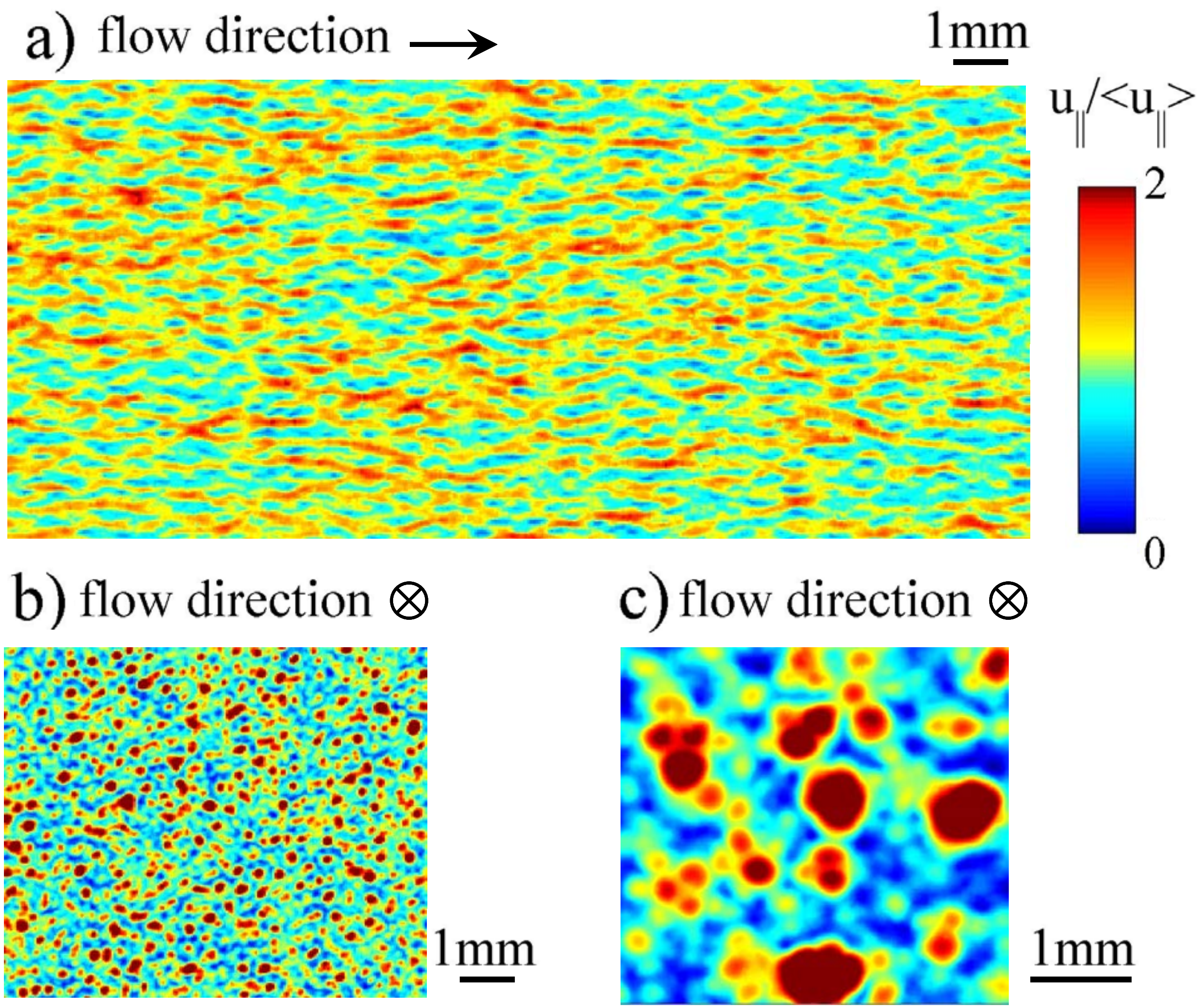
1 mm

<u>2D MR image of polymer foam</u>
(used in PGSE NMR measurements)

<u>Lord Kelvin & the Kelvin Cell</u>

tetrakaidecahedron

2D MRI Velocity Maps of water flow in polymer foam



Can we use Newtonian fluid *flow dynamics* to measure a characteristic length of cellular solids? Seymour & Callaghan, *JMR* 1996

Nonequilibrium Statistical Mechanics of Hydrodynamic Dispersion

[J. Cushman *et al. J. Stat. Phys*. **75** 859 (1994)]

$$\frac{d\Psi}{dt} = -\int_{-\infty}^{t} K(t')\Psi(t-t')\,dt'$$

Velocity autocorrelation

$$\Psi(t) = \langle u(t)u(0)\rangle$$

$$u(t) = v - \langle v\rangle$$

Green-Kubo-Taylor relation

$$D(t) = \int_{-\infty}^{t} \Psi(t')\,dt'$$

Brownian Motion O-U process

$$K(t) = \zeta\delta(t)$$

$$\Psi(t) = \langle u^2\rangle \exp(-\zeta t)$$

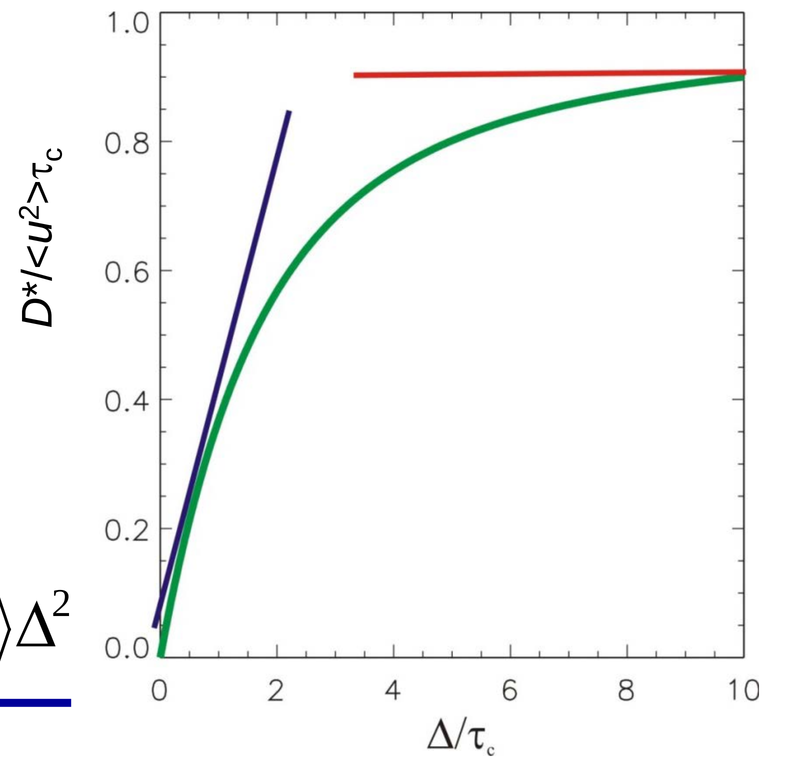
Nonequilibrium Statistical Mechanics

[R. Zwanzig Oxford Univ. Press 2001]

Brownian Motion Theory
O-U process pre-asymptotic
time dependent diffusion processes

$$\left\langle \left(Z(\Delta) - \langle Z \rangle \right)^2 \right\rangle = 2D^*(\Delta)\Delta$$

$$\boxed{D^*(\Delta) = \langle u^2 \rangle \tau_c \left[1 - \frac{\tau_c}{\Delta} \left(1 - \exp\left(- \frac{\Delta}{\tau_c} \right) \right) \right]}$$



for $\Delta << \tau_c$

$$\boxed{D^* = \tfrac{1}{2} \langle u^2 \rangle \Delta,} \quad \underline{\left\langle \left(Z(\Delta) - \langle Z(\Delta) \rangle \right)^2 \right\rangle = \langle u^2 \rangle \Delta^2}$$

for $\Delta >> \tau_c$

$$\boxed{D^* = \langle u^2 \rangle \tau_c,} \quad \underline{\left\langle \left(Z(\Delta) - \langle Z(\Delta) \rangle \right)^2 \right\rangle = 2 \langle u^2 \rangle \tau_c \Delta}$$

Memory

Infinite continued fraction

[Mori *Prog. Theor. Phys. (*1965)]

$$\tilde{\psi}(s) = \cfrac{1}{s + \cfrac{\omega_v^2}{s + \cfrac{(\omega_v^4/\omega_v^2) - \omega_v^2}{s + \cdots}}}$$

Brownian Harmonic Oscillator

2nd order truncation $\longrightarrow$ $K(t) = \omega_v^2 \exp(-t/\tau)$

[Boon & Yip *Molecular Hydrodynamics* Dover (1997)]

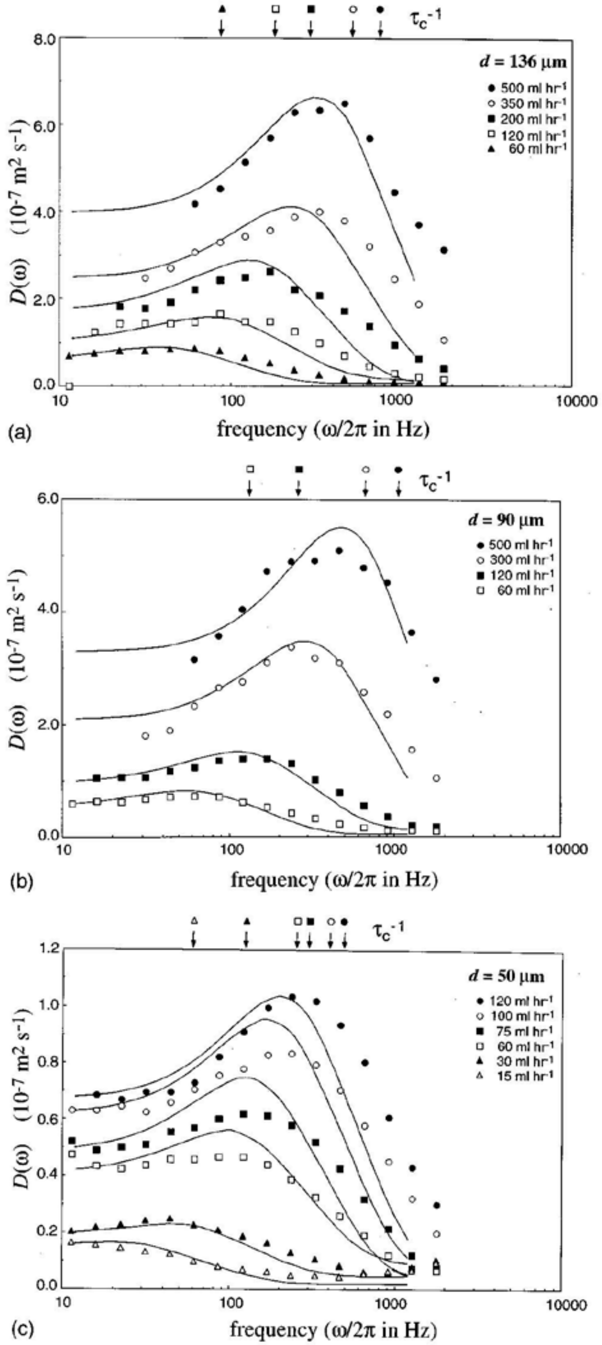
$$\omega_v^2 = \langle \dot{\mathbf{v}}^2 \rangle / \langle \mathbf{v}^2 \rangle$$

$$\boxed{D_\perp(t) = \frac{v_o^{\,2}}{\Delta}\left\{\frac{\Omega_o^2 - 1/\tau^2}{\Omega_o^4} + \frac{1}{\Omega_o^2\tau}t + \frac{e^{-t/2\tau}}{\Omega_o^4}\left[\left(\frac{1}{8\omega_2\tau^3} - \frac{3\omega_2}{2\tau}\right)\sin\omega_2 t - \left(\Omega_o^2 - \frac{1}{\tau^2}\right)\cos\omega_2 t\right]\right\}}$$

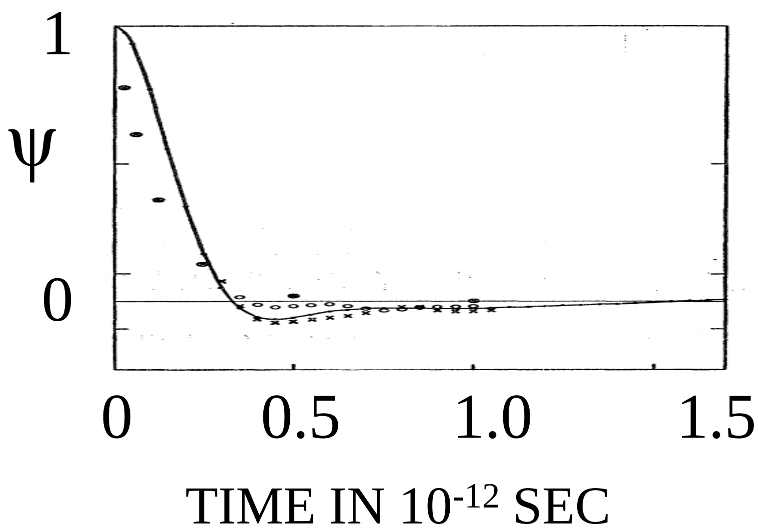
$$\omega_v^2 = \Omega_o^2 \qquad \omega_2^{\,2} = \Omega_o^2 - \frac{1}{4}\tau^{-2}$$

Transverse Dispersion in Model Bead Packs of Spheres

[Callaghan and Codd *Phys. Fluids* **13** 421 (2001); Maier *et al*. *Phys. Fluids* **12** 2065 (2000)]



Molecular hydrodynamics:

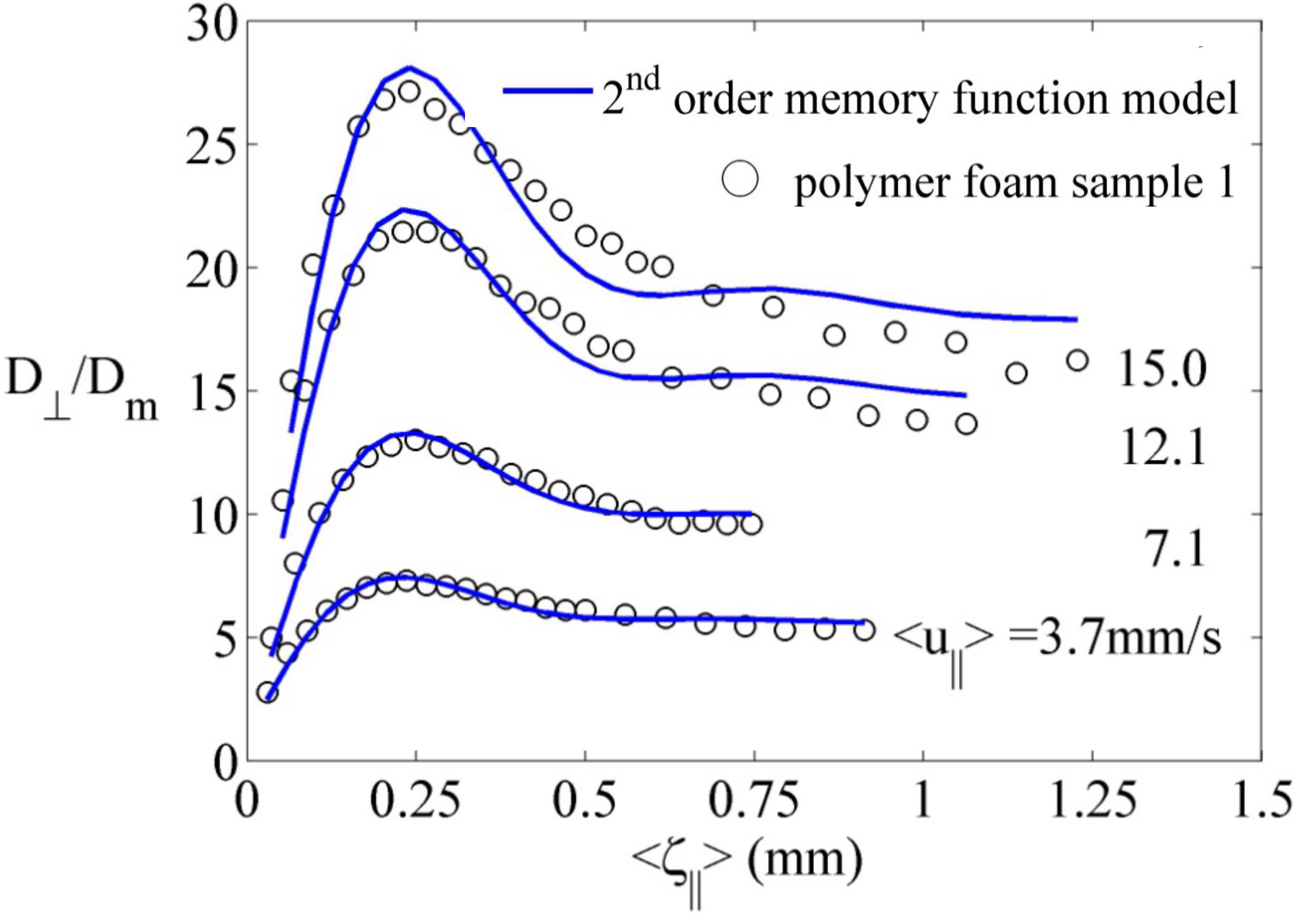


Liquid Argon - Lennard-Jones potential

[Rahman *PRL* (1964)]

Transverse Dispersion in a Polymer Foam

[T.R Brosten et al..*PRL* (2009)]



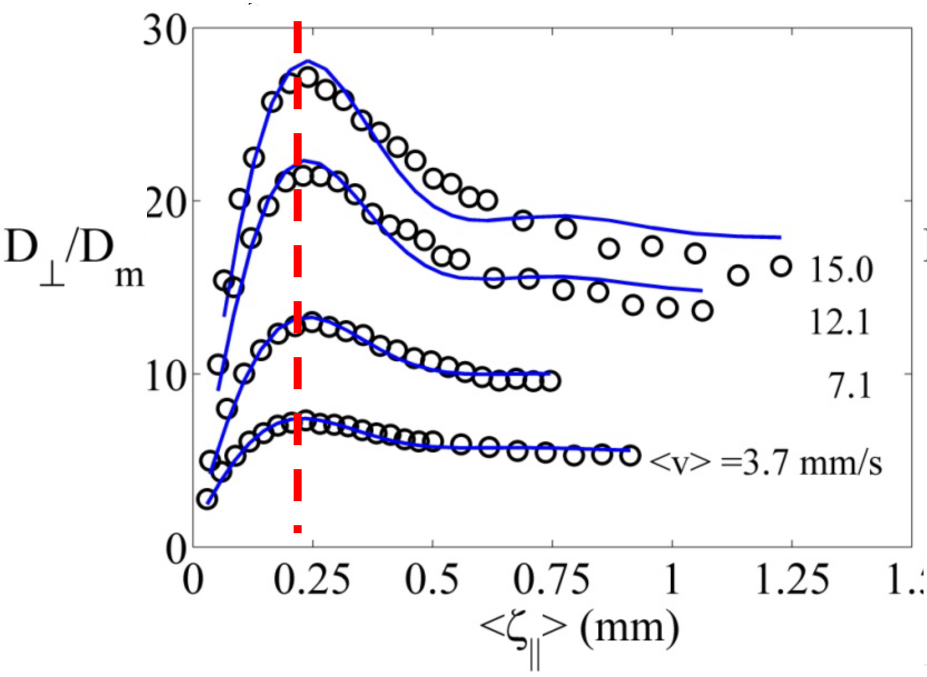
$$D_\perp(t) = \frac{v_o^{\,2}}{\Delta}\left\{\frac{\Omega_o^2 - 1/\tau^2}{\Omega_o^4} + \frac{1}{\Omega_o^2\tau}t + \frac{e^{-t/2\tau}}{\Omega_o^4}\left[\left(\frac{1}{8\omega_2\tau^3} - \frac{3\omega_2}{2\tau}\right)\sin\omega_2 t - \left(\Omega_o^2 - \frac{1}{\tau^2}\right)\cos\omega_2 t\right]\right\}$$

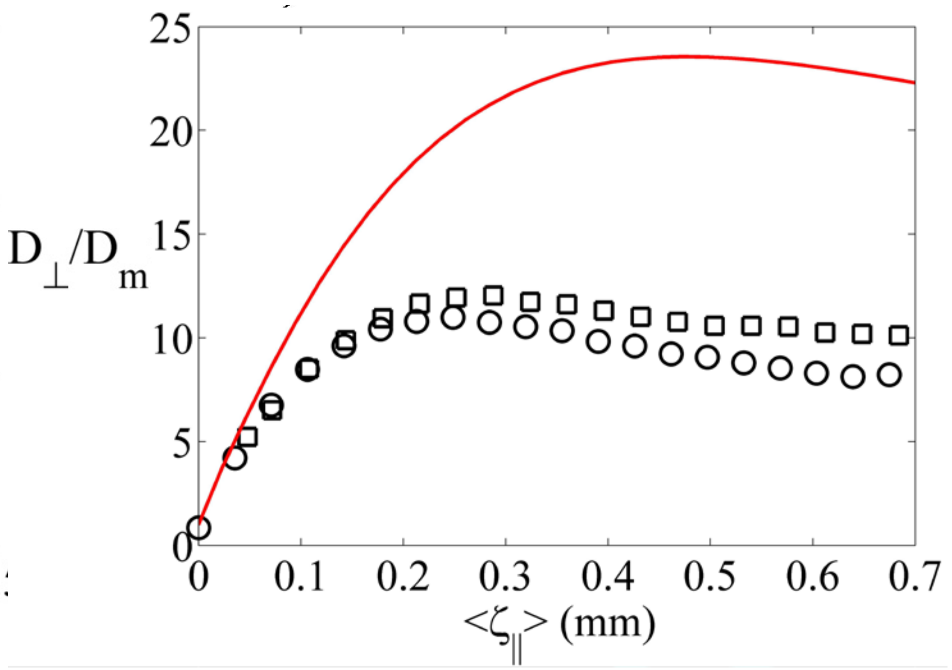
$$\omega_v^{\,2} = \Omega_o^{\,2} \qquad \omega_2^{\,2} = \Omega_o^2 - \frac{1}{4}\tau^{-2}$$

PGSE NMR Measured Transverse *Backscattering* in Cellular Foam

[T.R Brosten et al. *PRL* (2009)]

$$l = \langle \zeta_{\|} \rangle \Big|_{\frac{d D_{\perp}}{d \langle \zeta_{\|} \rangle} = 0}$$

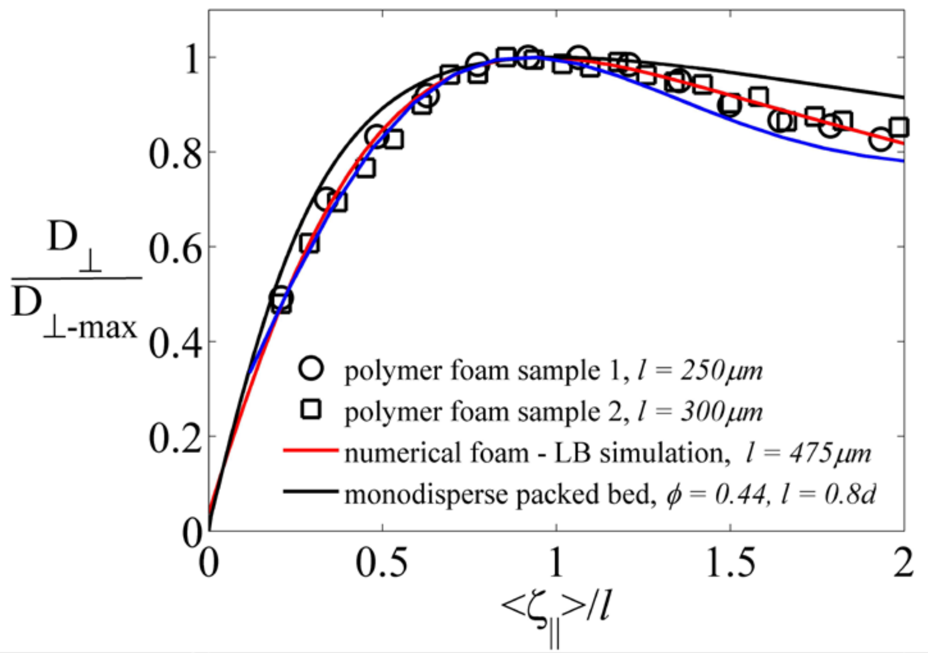


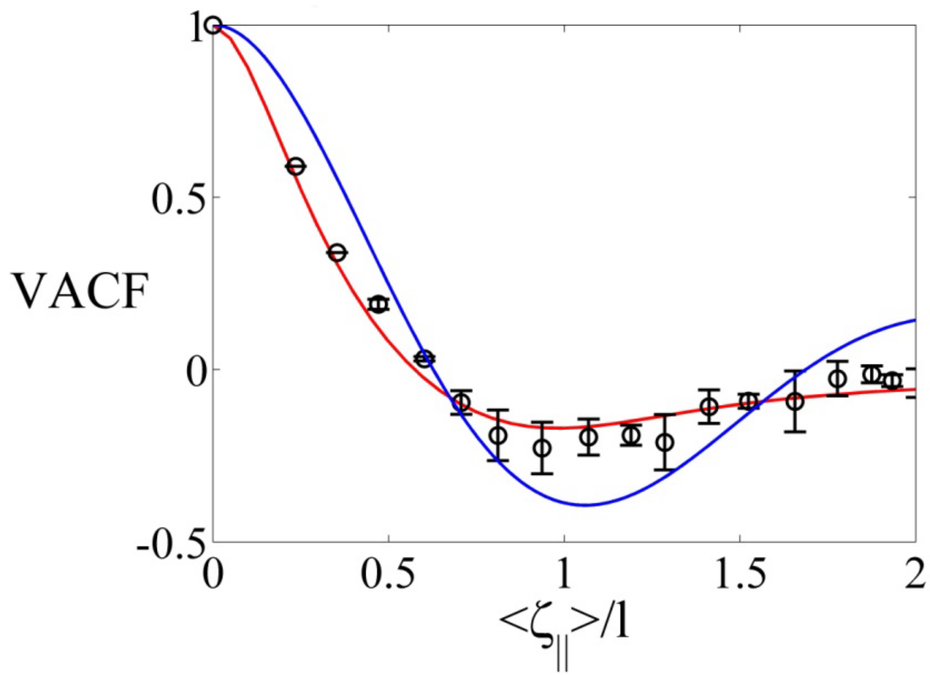


Direct measurement of transport phenomena length scale *l*

Universality of Dynamics

[T.R. Brosten *et al.* *PRL* **103** 218001 (2009)]





Conclusions

- PGSE NMR & LB simulations determine a transport length scale of cellular (foam) solids
- Introduced the memory function formalism for the short time correlations of pre-asymptotic dispersion
- Time dependent dispersion directly relates to structure and permeability

PGSE NMR and Statistical Mechanics Models

Correlate Structure and Transport

Acknowledgements

- Funding
  - US NSF Career Award CTS-0348076 (JDS)
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  - DOE OS BER ERSP DE-FG02-07 ER64416
  - Equipment Funding NSF MRI and the M. J. Murdock Charitable Trust

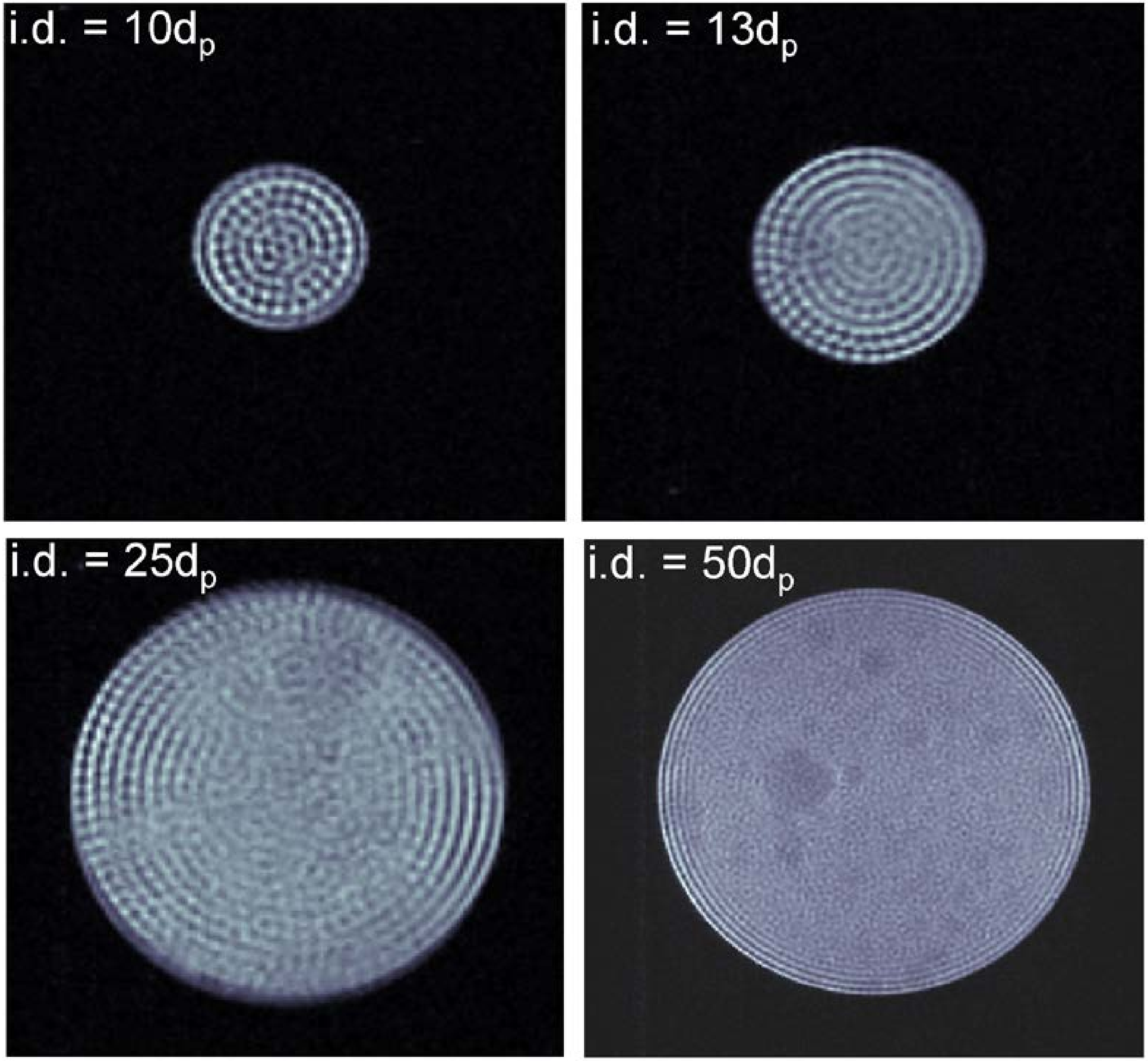
  - The late Prof. Sir Paul T. Callaghan New Zealand and H. Ted Davis Univ. Minnesota

Model Homogeneous Porous Media

d_p=100 μm

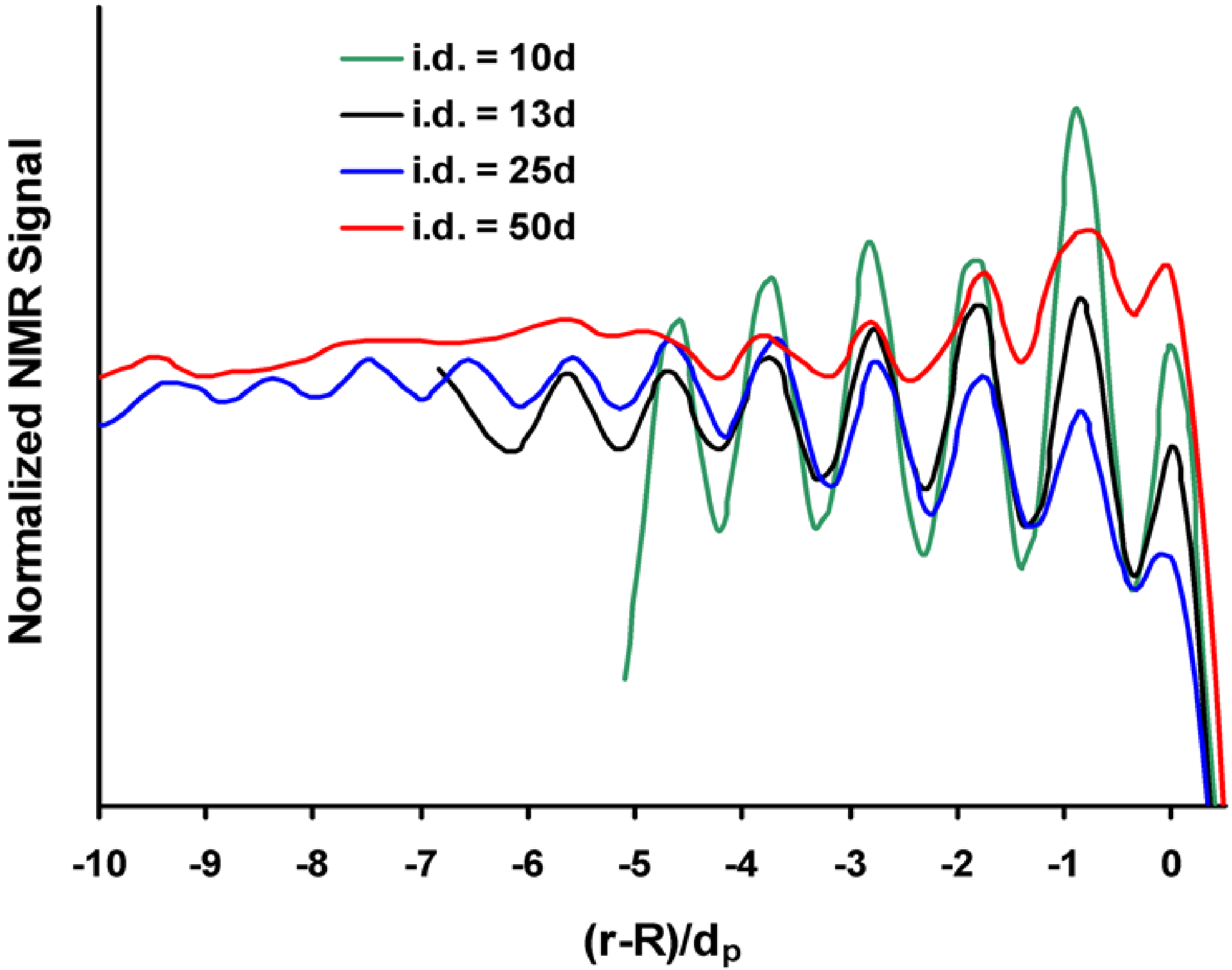
Spatial resolution 27.3 μm/pixel over a 8 mm thick slice

Slice is 80 bead diameters thick!!



Note this image 512 pts!

Radial Distribution Function



Velocity Radial Distribution Function