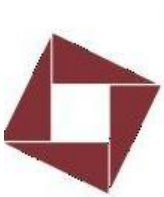


INTERNATIONAL CENTRE for THEORETICAL SCIENCES

School on glasses and glass formers

JNCASR, January 4-20 2010

Experimental Techniques -II

Ranjini Bandyopadhyay, RRI

Today's Lecture Plan

1) Dielectric spectroscopy
2) Light scattering

Dielectric Spectroscopy

- Dielectric spectroscopy measures the dielectric properties of a medium as a function of frequency.

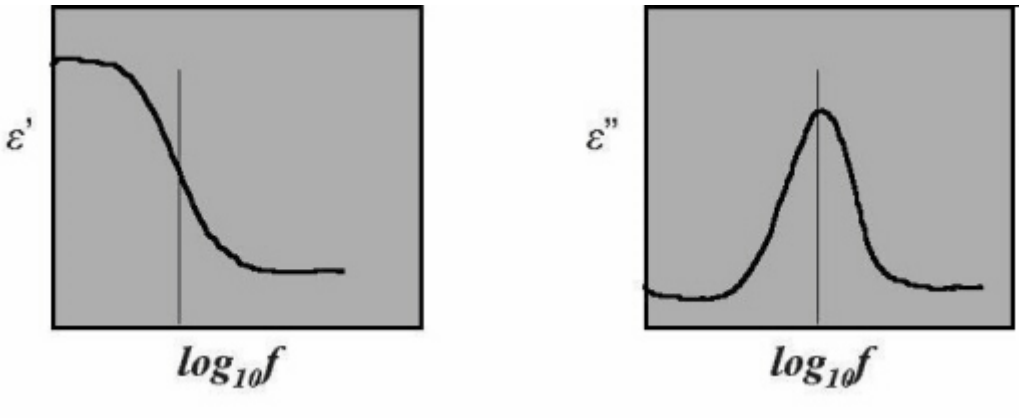
- Fluctuations in the local electric field are connected to the dynamics on a molecular scale

$D = \varepsilon_0 E + P$

In a linear, isotropic, homogeneous dielectric with an instantaneous response,

$P = \varepsilon_0 \chi E \Rightarrow D = \varepsilon_0(1+\chi)E$

$= \varepsilon E \qquad [\varepsilon = \varepsilon_0(1+\chi)]$



For linear response: P(t) = $P_\infty + \varepsilon_o \int_{-\infty}^{t} \varepsilon(t-t') \frac{d(E)}{dt'} dt'$

For $E(t)(\omega) = E_o \exp(-i\,\omega t)$,

$$P^*(\omega) = \varepsilon_o[\varepsilon^*(\omega) - 1]E^*(\omega); \varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$$

Dielectric Relaxation

- Debye relaxation: $\frac{dP(t)}{dt} = -\frac{1}{\tau_D} P(t) \Rightarrow \Phi(t) = \exp\frac{-t}{\tau_D}$
- In terms of complex permittivity: $\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+\iota\omega\tau_D}$
- Non-Debye relaxation: usually measured dielectric function is much broader than predictions of the Debye model
- KWW form: $\Phi(t) = \exp[-(\frac{t}{\tau_{KWW}})^{\beta^{KWW}}]$
- In the frequency domain, the Cole Davidson form: $\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1+\iota\omega\tau)^\beta}$
- Havriliak Negami function: $\varepsilon^*_{HN}(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1+(\iota\omega\tau)^\beta]^\gamma}$

Broadband Dielectric spectroscopy

For a capacitor C* filled with the material under study, the complex dielectric function is given by $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon'(\omega) = C^*(\omega)/C_o$, C_o is the vacuum capacitance

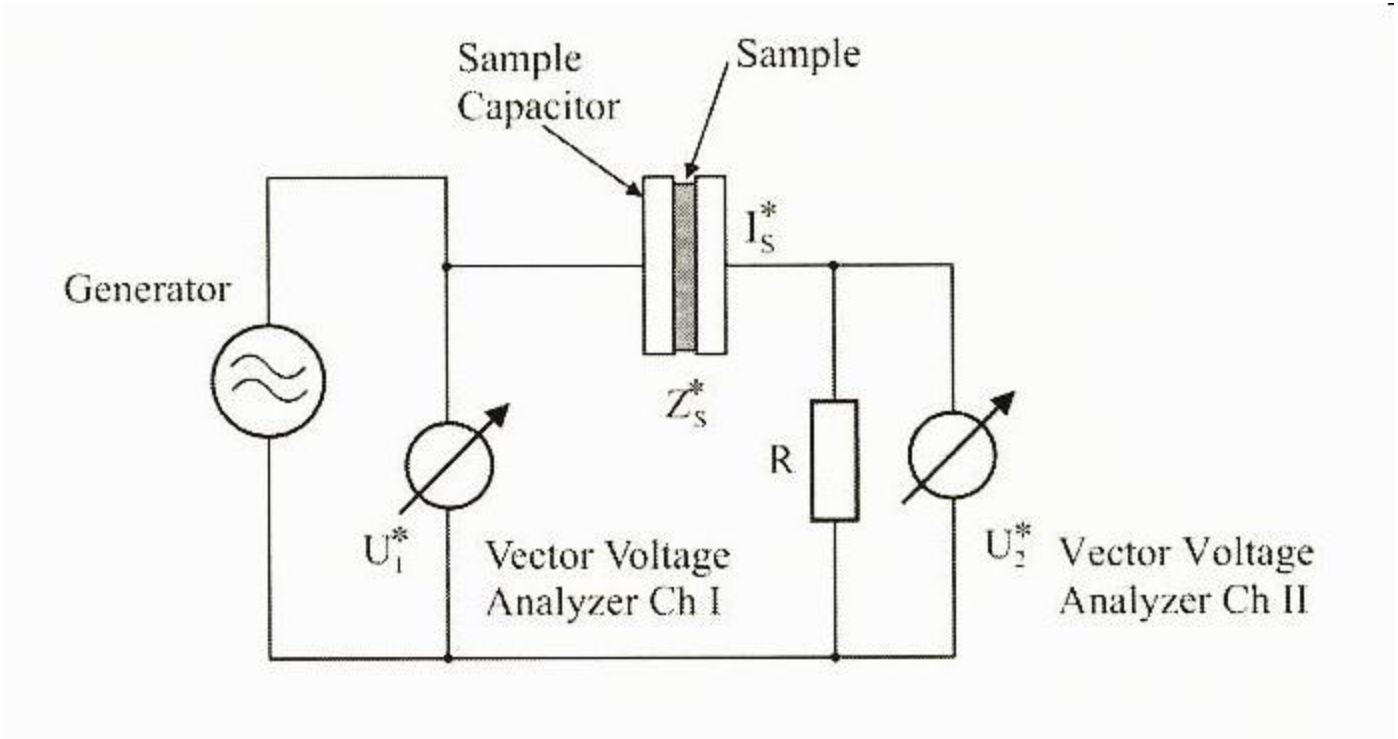
Applied electric field: $E^*(\omega) = E_o e^{i\omega t}$, with E_o small enough to be in the linear response regime:

$$\varepsilon^*(\omega) = J^*(\omega)/i\omega\varepsilon_o E^*(\omega) = 1/ i\omega\varepsilon_o Z^*(\omega)C_o$$

Different measurement techniques are used depending on the frequency range to be investigated:

1) Fourier correlation analysis in combination with dielectric converters (10^{-6} – 10^7 Hz)
2) Impedance analysis (10^1-10^7 Hz)
3) RF Reflectometry (10^6 Hz – 10^9Hz)
4) Network analysis (10^7 Hz – 10^{11} Hz)

Fourier Correlation Analysis

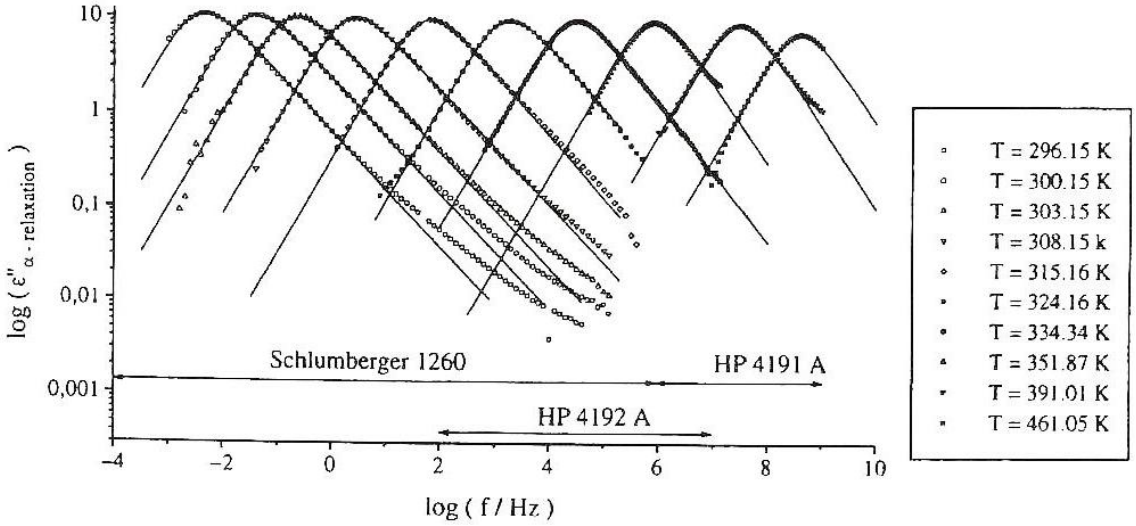


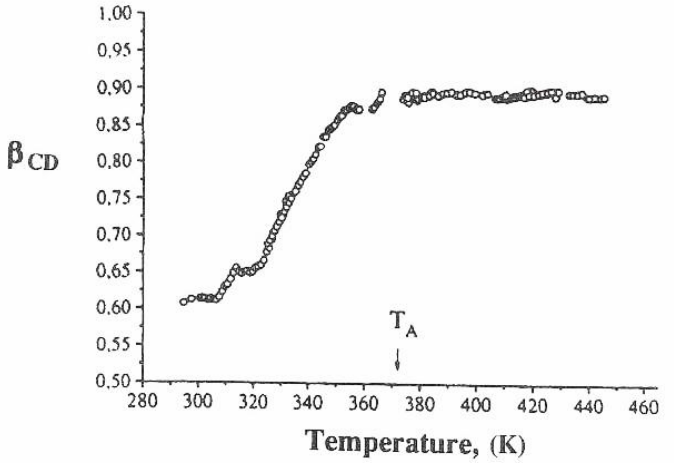
- $U_1(t)$: sine wave voltage with frequency between 10^{-6} -10^7 Hz
- R converts sample current $I_s(t)$ into a voltage $U_2(t)$
- 2 phase sensitive sine wave correlators analyze $U_1(t)$ and $U_2(t)$ in terms of the phases and amplitudes of the Fourier base waves $U_1^*(\omega)$ and $U_2^*(\omega)$
- Complex impedance $Z_s^*(\omega) = U_s^*(\omega)/I_s^*(\omega) = R[\{U_1^*(\omega)/U_2^*(\omega)\}-1]$

Relaxation time spectra

- KWW form: $M(t)/M(0) = \exp[(-t/\tau)^{\beta}]$, M(t) ~ any linearly relaxing property, $\beta = 1$ is a mono-exponential relaxation, $0<\beta<1$ implies a distribution of relaxation times.
- Cole Davidson form: $\varepsilon^* - \varepsilon_\infty = \Delta\varepsilon/(1+i\omega\tau)^{\beta_{CD}}$

Phenolphthalein Dimethylether (PDE), a simple organic glass former

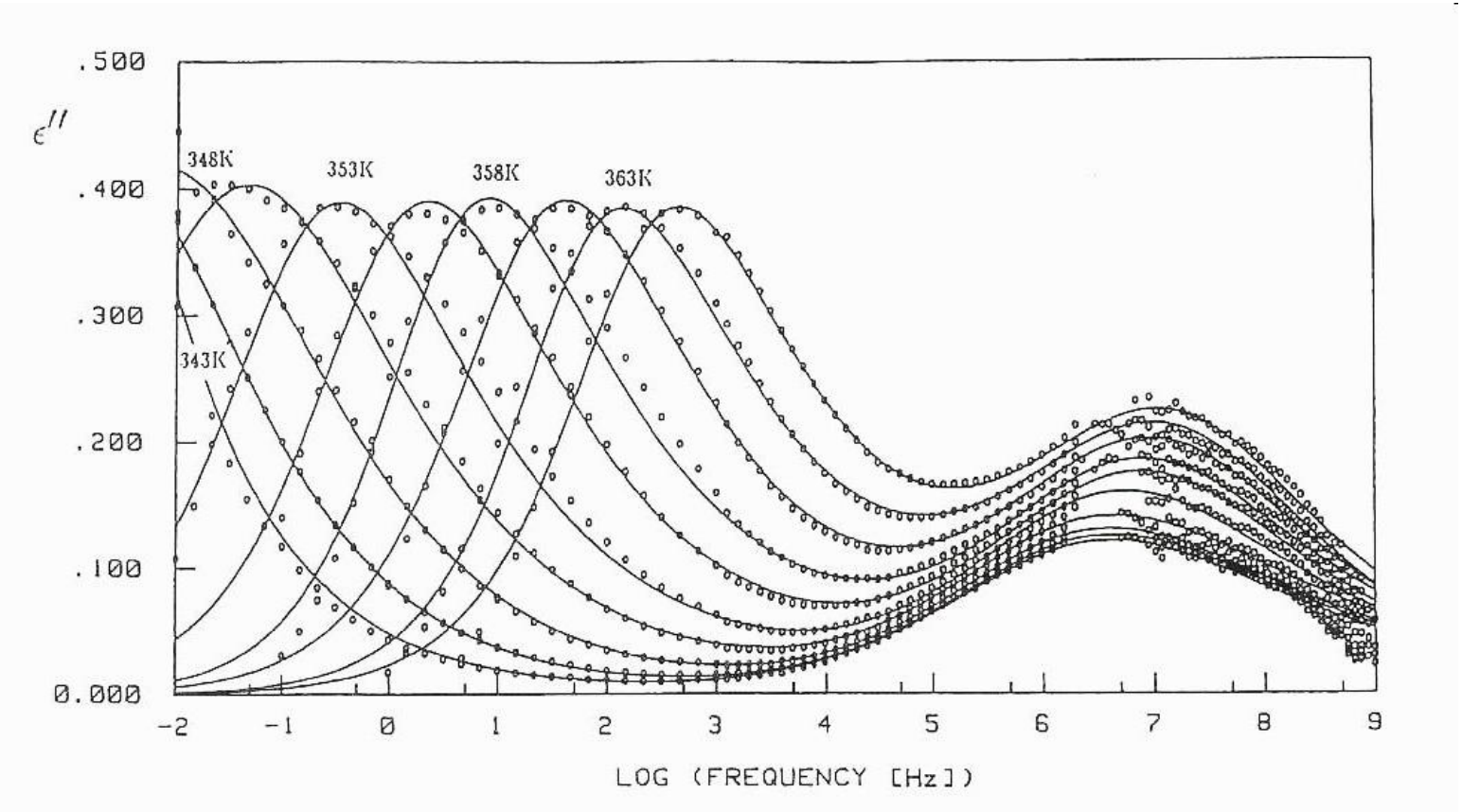




Stickel et al., Physica A (1993)

Relaxation time spectra

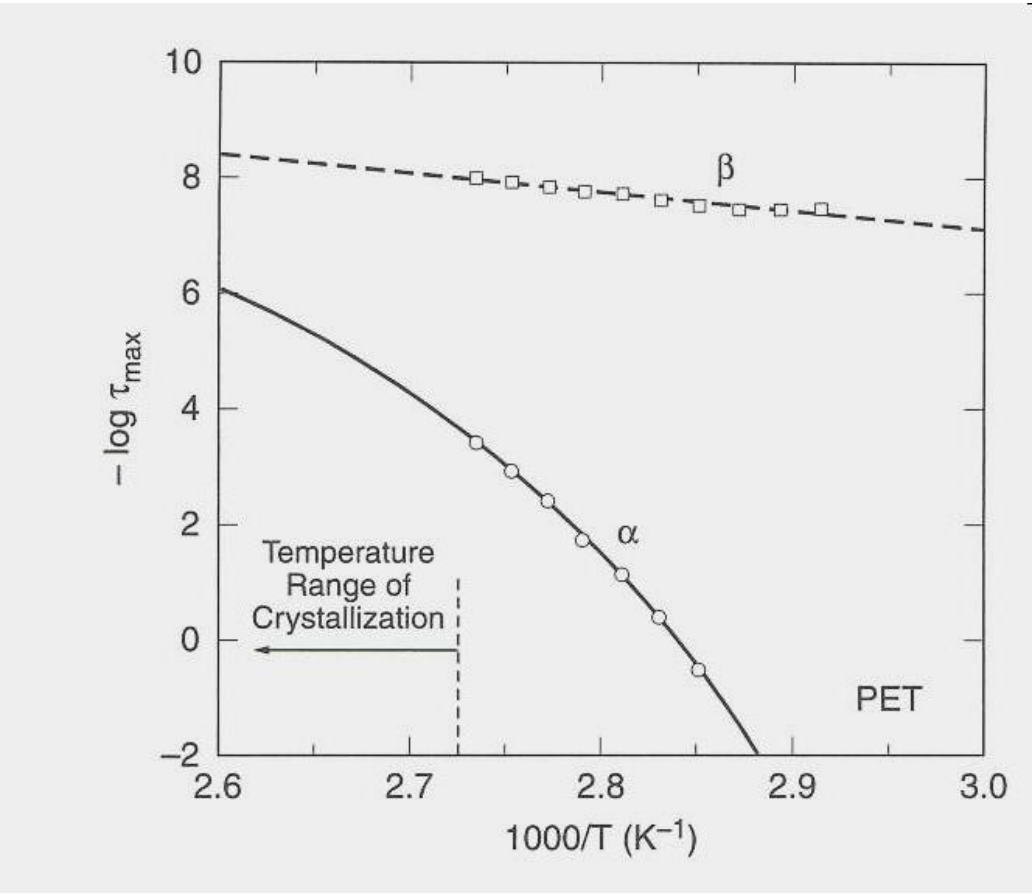
Polyethyleneterephthalate (PET) at various T and corresponding fits to Havriliak Negami functions



Hofmann et al., Physica A (1993)

Relaxation time spectra of PET (cont'd)

Relaxation times of Polyethyleneterephthalate at various T
β relaxation shows Arrhenius T-dependence, slow α mode slows down as T_g is approached



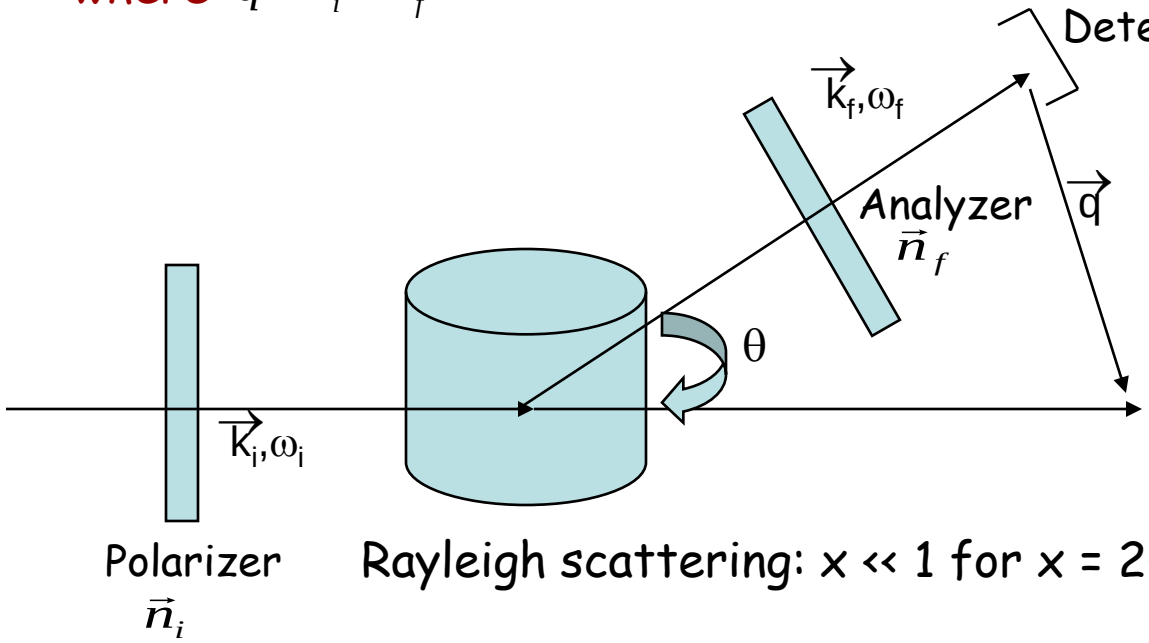
Hofmann et al., Physica A (1993)

Light scattering

- Classical theory: light scatters due to fluctuations in dielectric constant
- If a plane wave $\vec{E}_i(r,t) = \vec{n}_i E_o \exp \iota(\vec{k}_i.\vec{r} - \omega t)$ is incident on a medium with $\vec{\varepsilon}(r,t) = \varepsilon_o \vec{I} + \delta\vec{\varepsilon}(r,t)$, then

$$E_s(R,t) = \frac{E_o}{4\pi R\varepsilon_o} \exp \iota k_f R \int_V d^3r \exp \iota(\vec{q}.\vec{r} - \iota\omega_i t)[\vec{n}_f.[\vec{k}_f x(\vec{k}_f x(\delta\vec{\varepsilon}(\vec{r},t).\vec{n}_i)]$$

where $\vec{q} = \vec{k}_i - \vec{k}_f$



For an elastic scattering process,

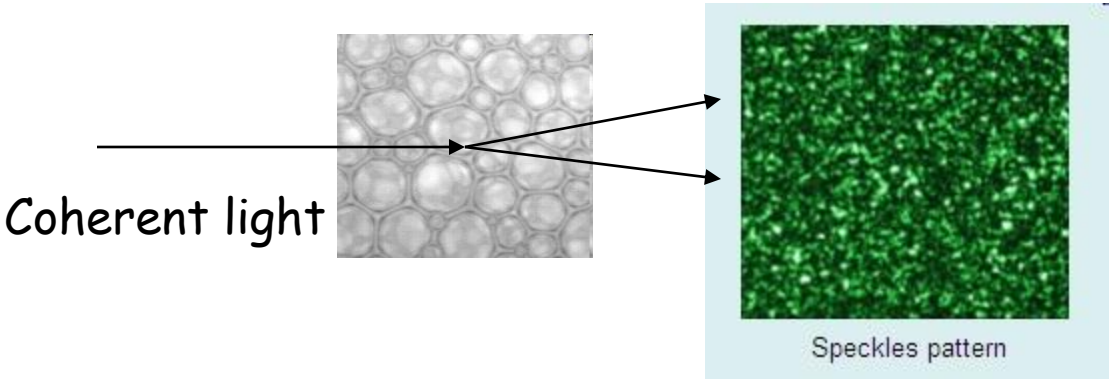
$$\left|\vec{k}_i\right| \cong \left|\vec{k}_f\right|$$

$$\Rightarrow q = \frac{4\pi n}{\lambda_i} \sin\frac{\theta}{2}$$

Rayleigh scattering: $x \ll 1$ for $x = 2\pi r/\lambda$ ($x \sim 1$, Mie theory holds)

$I = I_o [(1+\cos^2\theta)/2R^2] [2\pi/\lambda]^4 [(n^2-1)/(n^2+2)]^2 [d/2]^6$

Scattering experiments



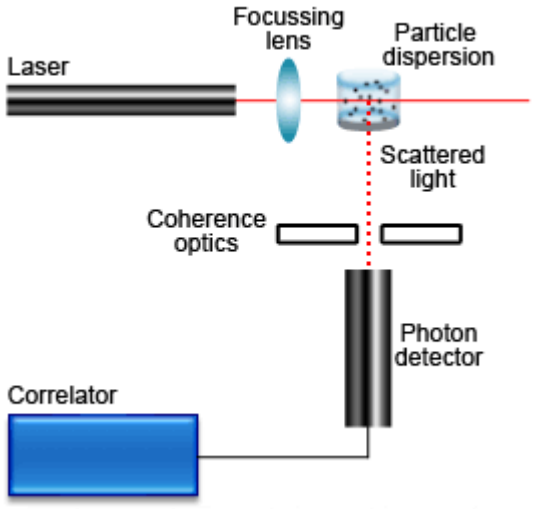
$C(\tau) = \langle I(t)I(t+\tau)\rangle_T / \langle I(t)^2\rangle_T$

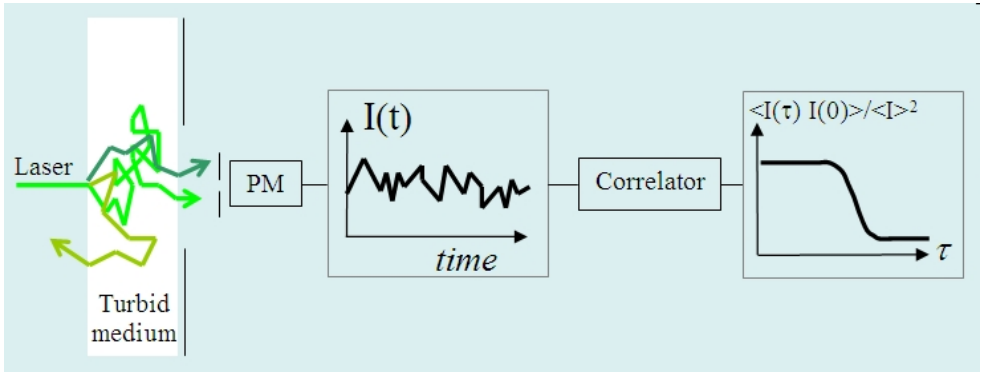
$C(\tau) = 1 + f(n_{coh}) g_1(\tau)^2$

$f(n_{coh}) = A_{coh}/A$

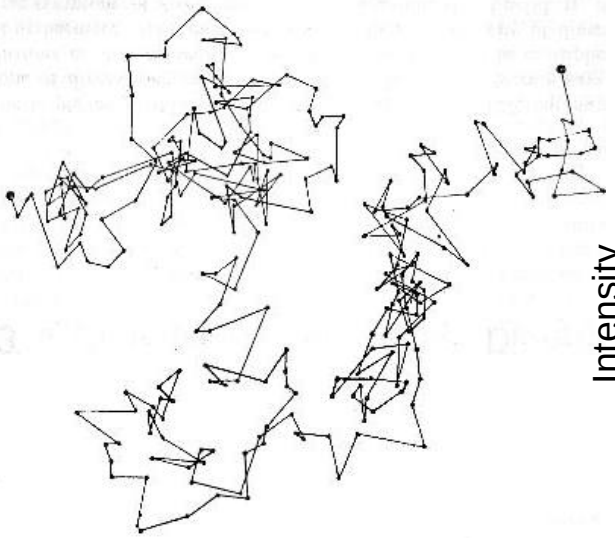
$A_{coh} = \pi b^2 = \lambda^2 R^2 / \pi a^2$

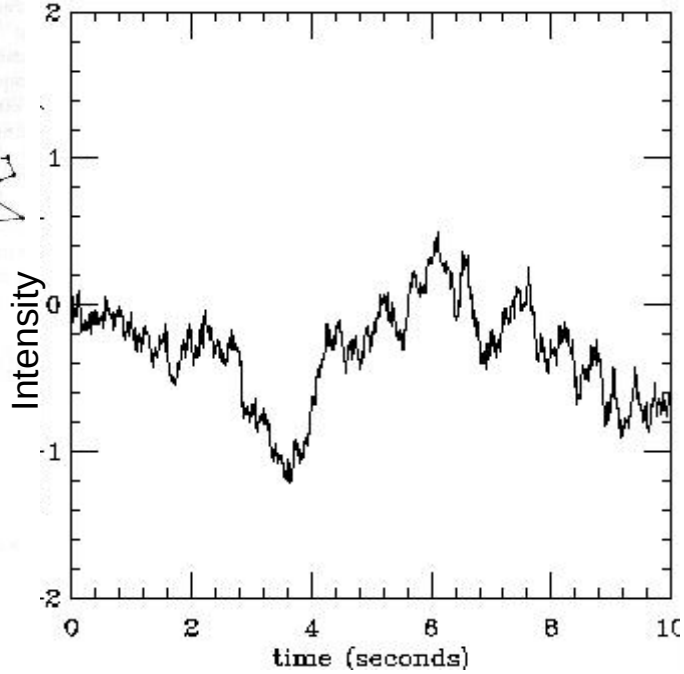
$A/A_{coh} = n_{coh}$

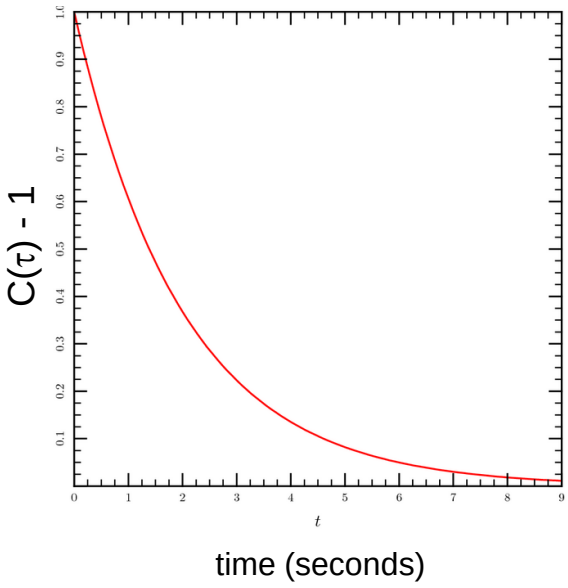




Scattering experiments :
a) Single scattering by a Brownian particle





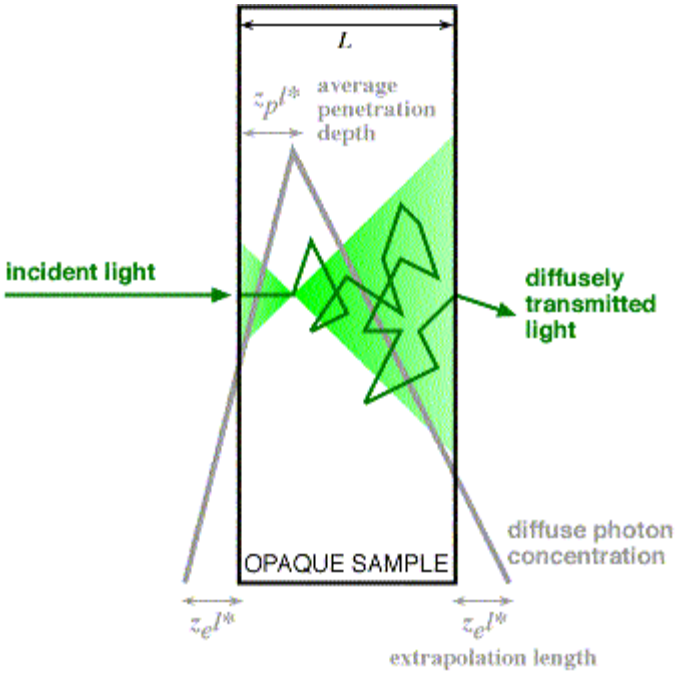


$C(\tau) = \langle I(t)I(t+\tau)\rangle_T / \langle I(t)^2\rangle_T$

$C(q,\tau) = 1 + e^{-2\tau/\tau_c}$; $\tau_c = 1/Dq^2$

$D = k_B T / 6\pi\eta r$

b) Multiple scattering: Light diffusion



$l^* \Rightarrow$ transport mean free path

$L \gg l^*$, diffusive transport

$l^* = l_s/\langle 1-\cos\theta \rangle$, $g = \langle \cos\theta \rangle$

z_p : source of diffusing photons

z_e: set by boundary reflectivity

Calculate: a) $T_d \rightarrow l^* \rightarrow$ structure

b) $g_1(x)$: $x = f(\tau_0) \rightarrow$ dynamics

Diffuse Transmission in shaving foam

Durian et al. Science (1991)

For Gillette Foamy (ε_{gas} = 0.092), measure transmission T_d and $C(\tau)$

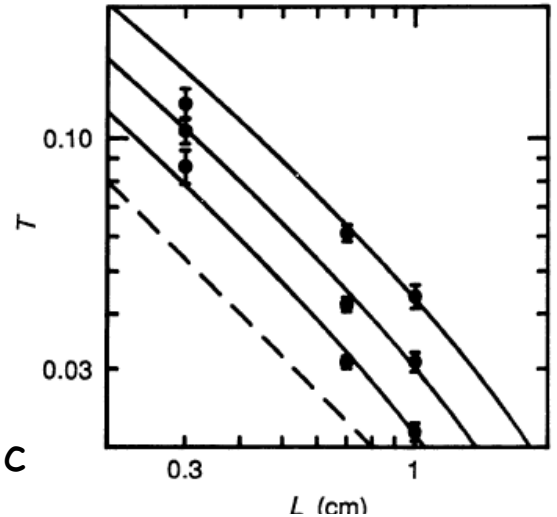
$L >> l^*$, $T_d \sim l^*/L$, $l^* \sim 3.5\, d \sim d/(\varepsilon_{liq})^{1/2}$, $d \sim t^{1/2}$

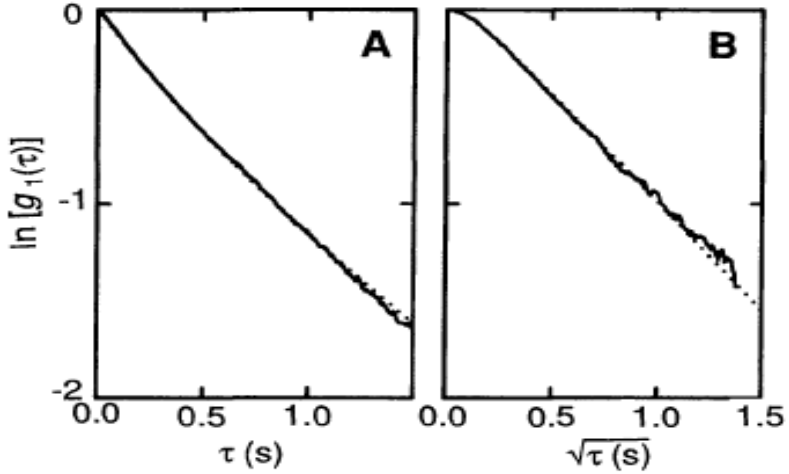
$g_{1,B}(\tau) \sim \exp[-2(6\tau/\tau_o)^{1/2}]$

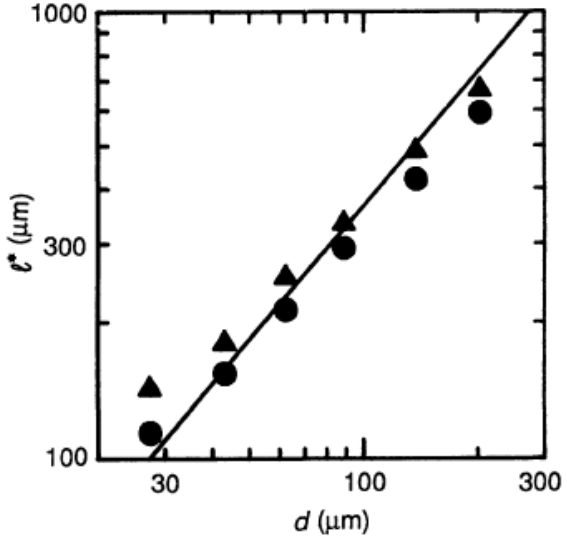
$g_{1,T}(\tau) \sim (6\Gamma_1\tau)^{1/2}/\sinh(6\Gamma_1\tau)^{1/2}$ $\Gamma_1 \sim (L/l^*)^2/\tau_o$

τ_o = time scale between rearrangements events ~ seconds

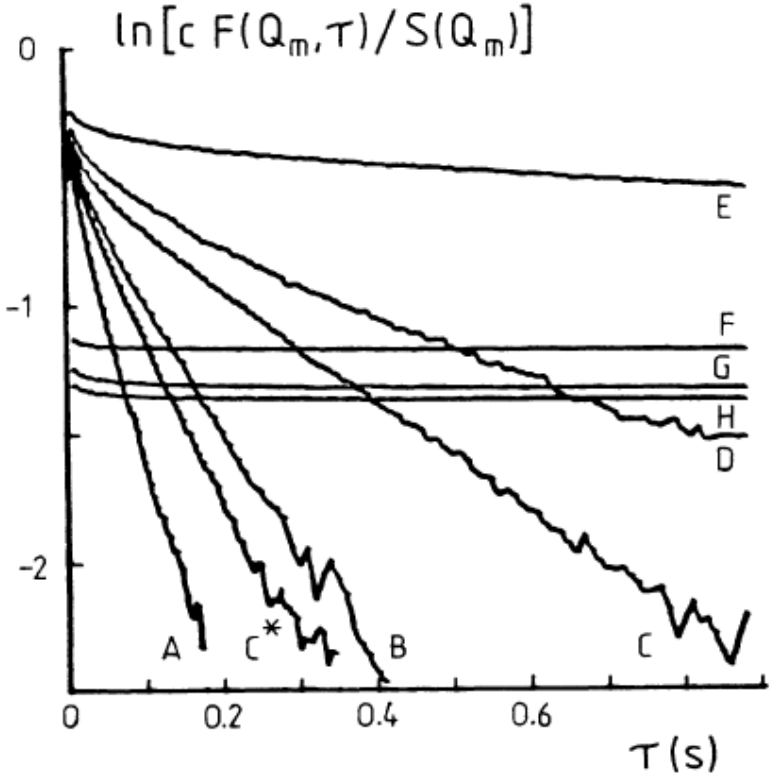
Calculate τ_o from backscattering data, obtain independent estimates of l^* from static and dynamic Transmission data. $l^* \rightarrow d$





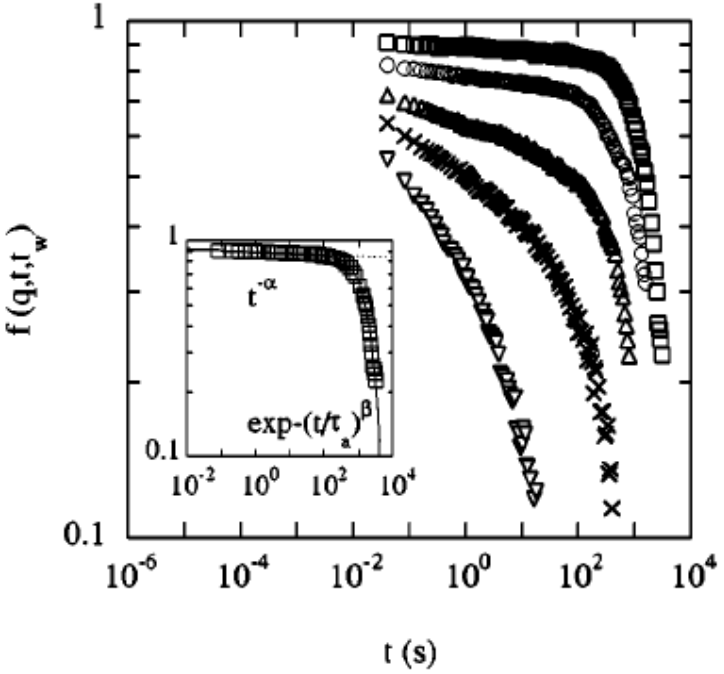


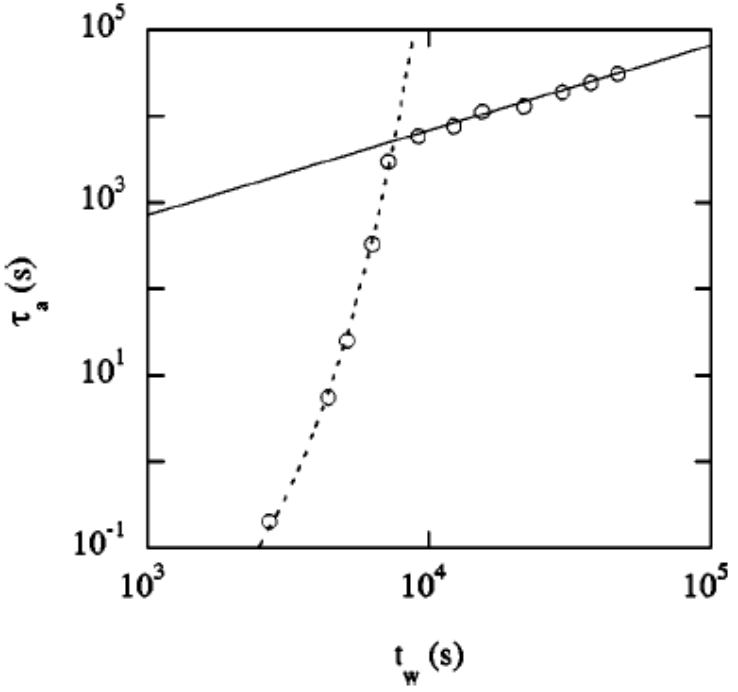
Concentrated colloidal suspensions (Pusey et al, PRL 1987)



- Initial rapid and then slow long-time decay
- Divergence of the slow decay time with concentration (A $\rightarrow$H)
- Concentration plays the role of temperature

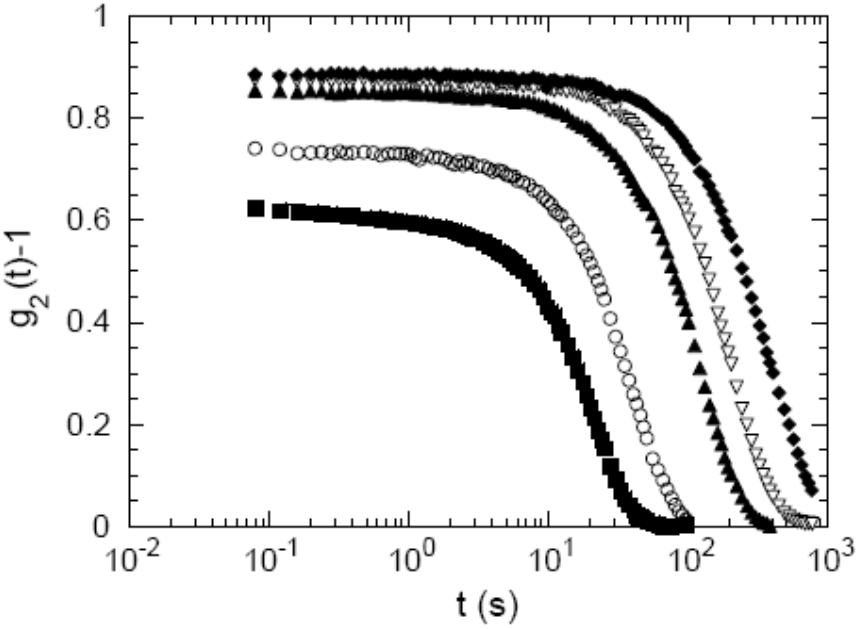
1.36% Clay suspensions Multispeckle DLS (Bellour et al, PRE 2003)

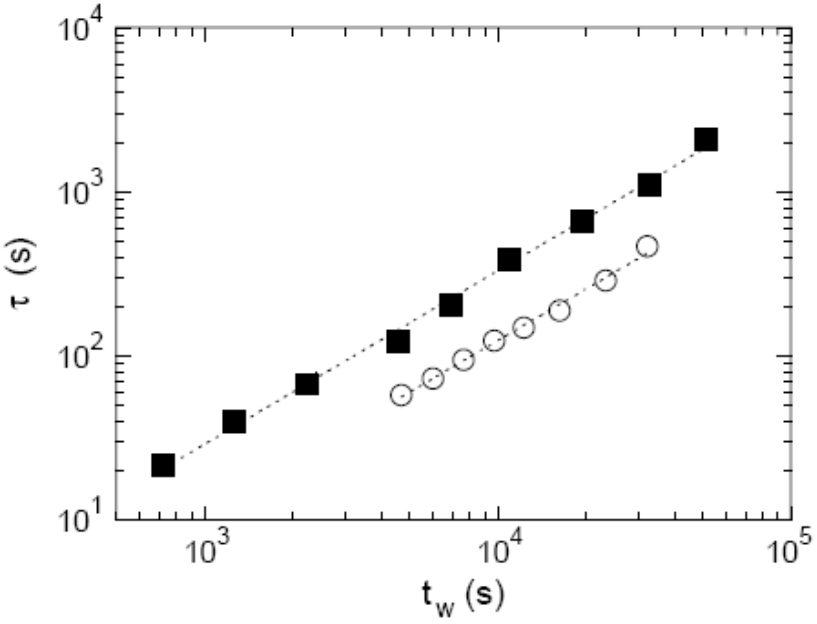


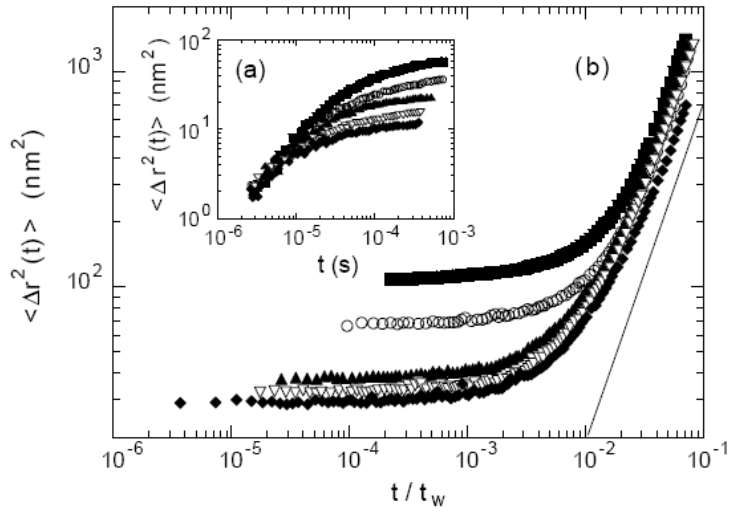


$$g_2(q,t) - 1 = At^{-\alpha}\exp[-(t/\tau_a)^{\beta}]$$

3.5% Clay suspensions Multispeckle DWS (Knaebel et al, EPL 2000)







- α-relaxation time increases as a power law with t_w.
- $\left\langle \Delta r^2(t) \right\rangle = a(\phi)\left(\frac{t}{t_w}\right)^{1.5}$

Notes

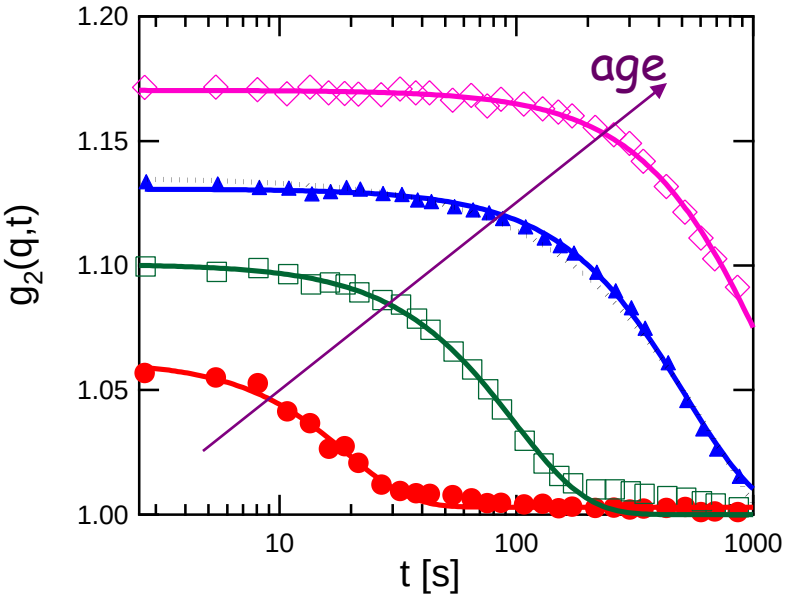
- Time Resolved Correlation (Cipelletti et al., J. Phys: Condens. Matter, 2003)
- Speckle Visibility Spectroscopy (Bandyopadhyay et al, Rev. Sci. Instrum. 2005)
- If there is time: more on the compressed exponential

XPCS: Probe of the Local Dynamics of laponite (ϕ = 0.012) as system evolves from fluid → gel → soft solid:

Bandyopadhyay et al. *PRL*, **93**, 228032 (2004)

Over wave vector Range:
0.03 nm^{-1} < q < 0.3 nm^{-1}
Motion Progressively Slows

q = 0.135 nm^{-1}



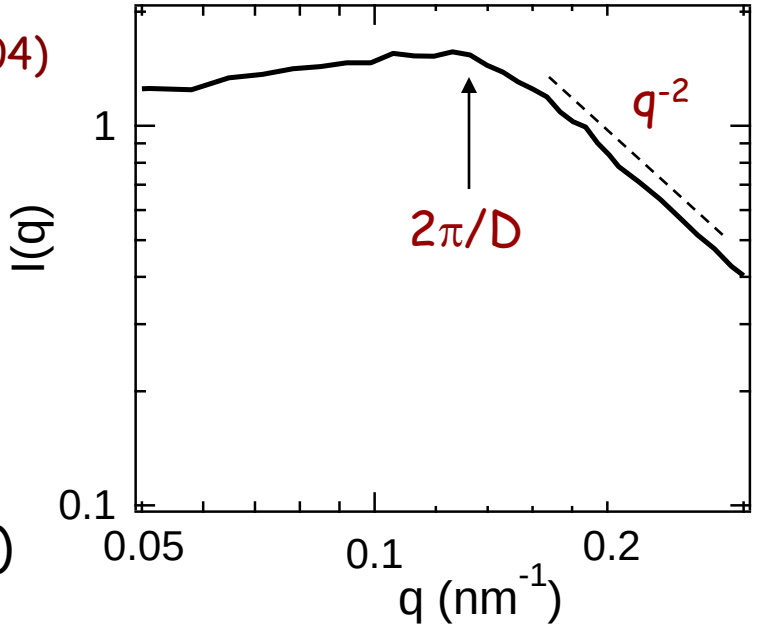
age (s)

200000

90000

30000

13000



Correlations Fit to:

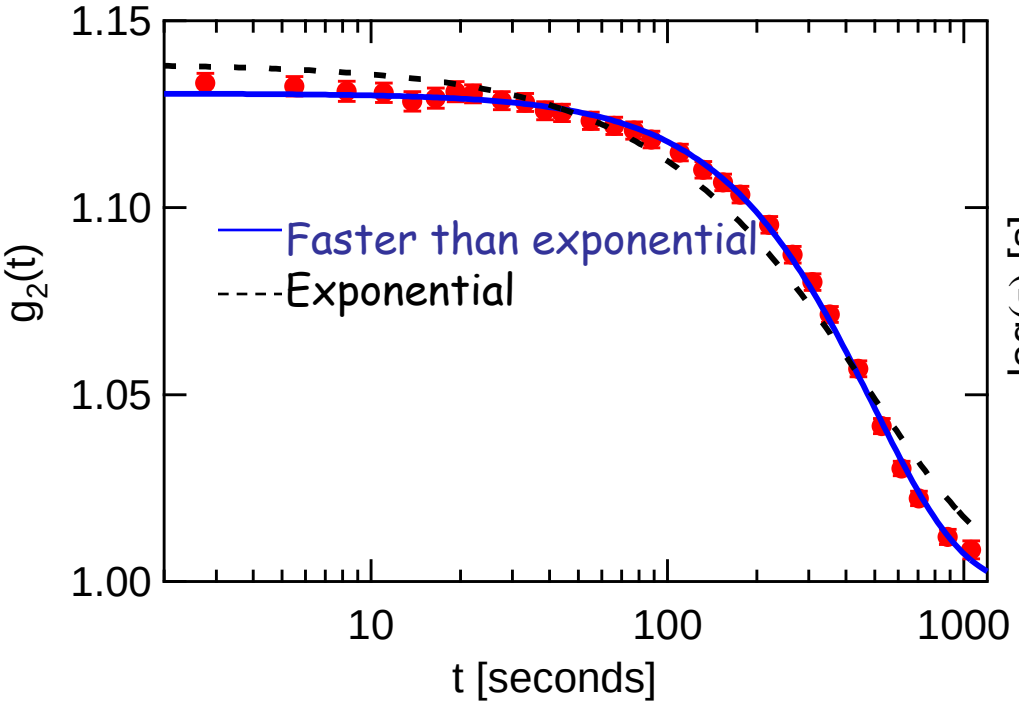
$f(q,t) = A\exp[-(t/\tau)^{\beta}]$

$g_2(q,t) = 1+b|f(q,t)|^2$

$\beta \sim 1$, early times
$\beta \sim 1.5$, late times

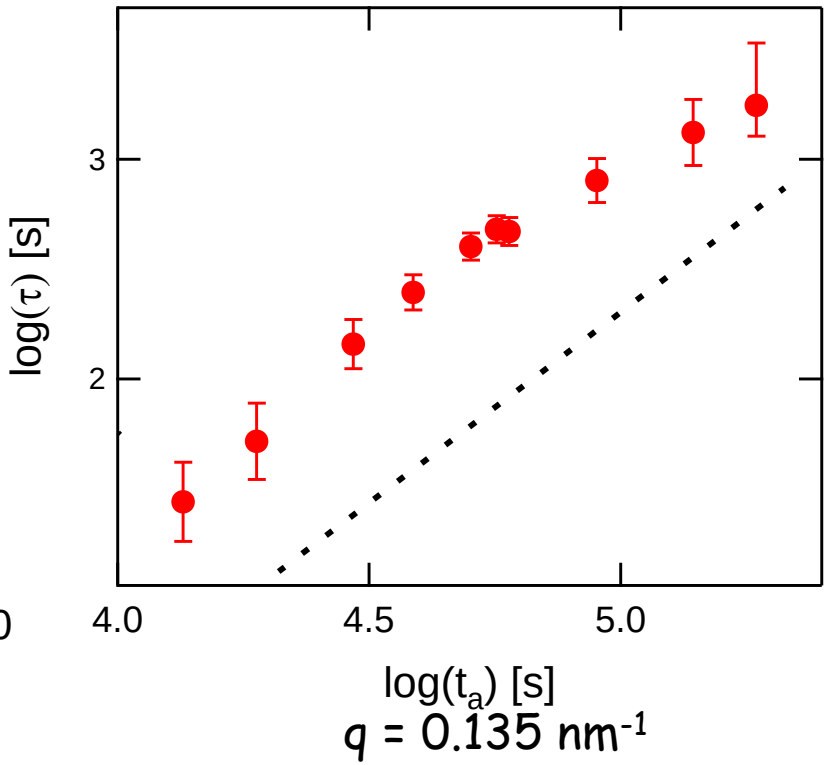
Cipelletti et al., PRL 2000,
Bouchaud and Pitard, EPJE 2001.

Faster than exponential $g_2(q,t)$



Growth of relaxation times

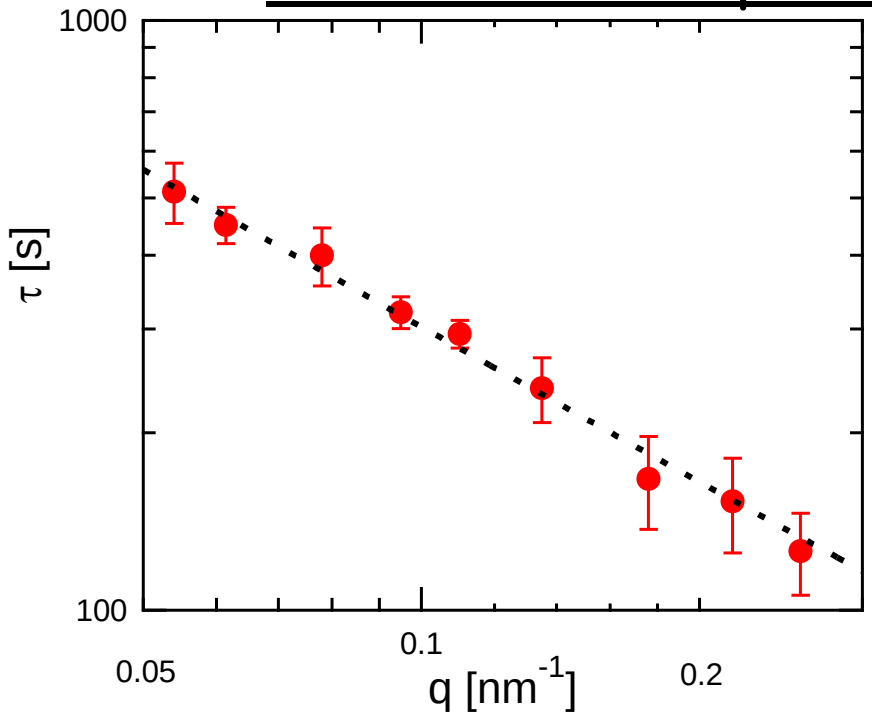
$\tau \sim t_a^{\mu}$, $\mu \sim 1.8$



Such scaling ubiquitous in aging systems

- Polymer glasses, spin glasses (both show $\mu \leq 1$).
- $\mu > 1$ in laponite (this work) and compressed microemulsions (Cipelletti, 2003).

Wave vector dependence of relaxation times



Slope of dashed line = 0.9 +/- 0.1

Compare:
$\tau \sim 1/q^{1.02+/-0.2}$ in fractal colloidal gels

age = 20,000s

Drift velocity $v_o \sim (q\tau)^{-1}$
For $q = 0.135 nm^{-1}$, $\tau \sim 100s$
$v_o \sim 0.1$ nm/sec

A compressed exponential relaxation with inverse q-dependence of relaxation times:

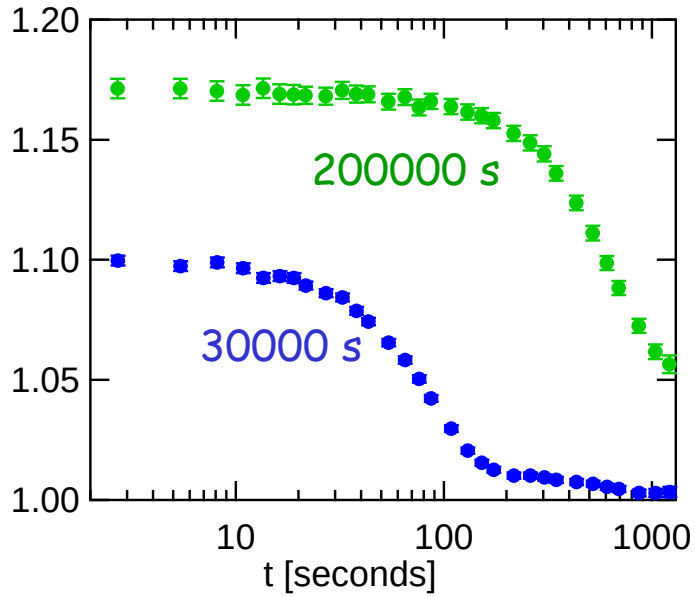
- seen in fractal gels at small q's (Cipelletti et al., PRL 2000)
- explained by random, local elastic deformation events: strain relaxation processes with a distribution of velocities (microcollapses). (Cipelletti et al, PRL 2000, Bouchaud and Pitard, EPJE, 2001)
- not conventional α -relaxation (no de Gennes narrowing).

Apparent Contrast:

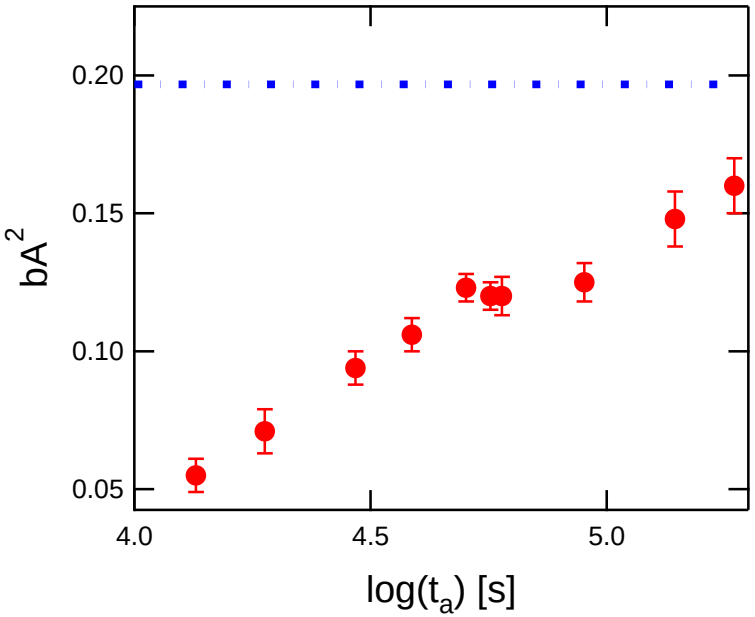
$f(q,t) = A\exp[-(t/\tau)^{\beta}]$

$g_2(q,t) = 1+b|f(q,t)|^2$

$= 1 + bA^2\exp[-2(t/\tau)^{\beta}]$



Increases quasi-logarithmically:

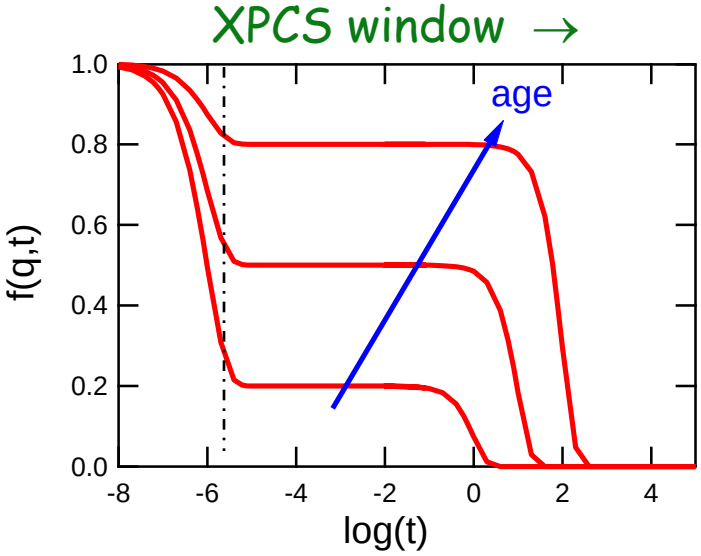


bA^2 has contributions from 2 sources:

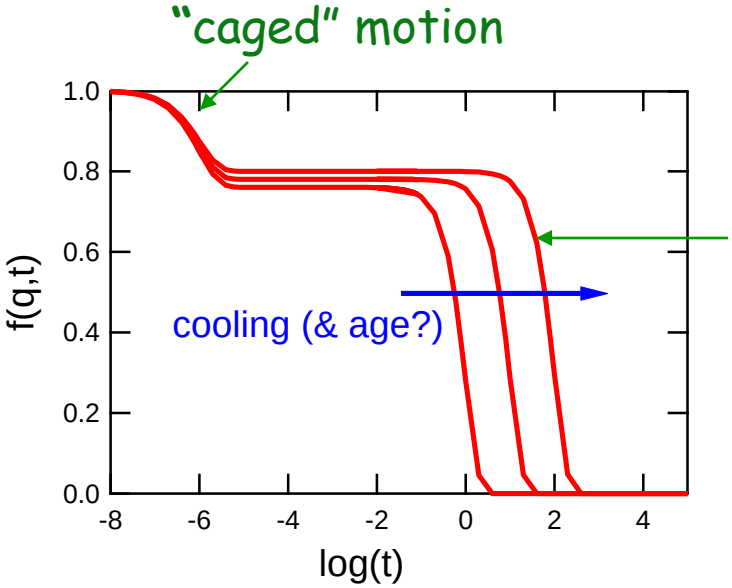
i) Instrumental ($b \approx 0.2$, measured by using aerogel)

ii) Very short time dynamics ($bA^2 < b \Rightarrow A < 1$)

Two step relaxation in laponite:



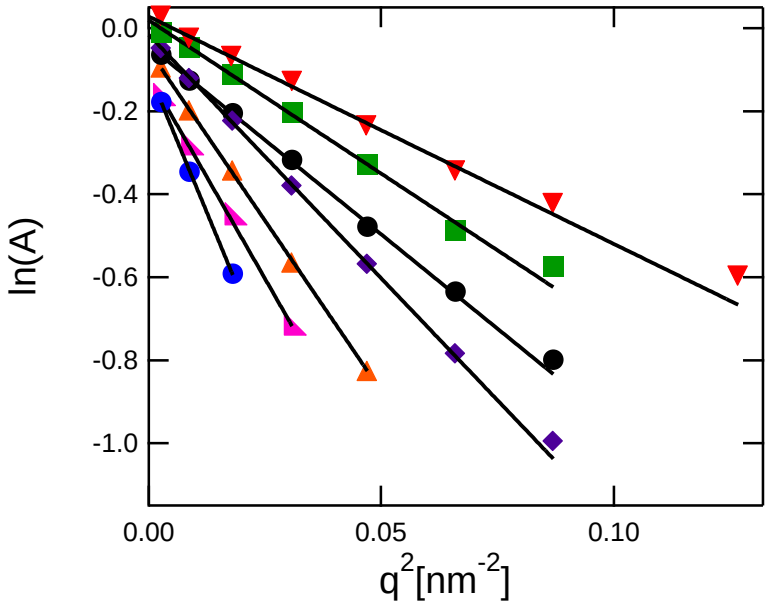
Typical Behavior for Glasses:



q-dependence of step amplitude

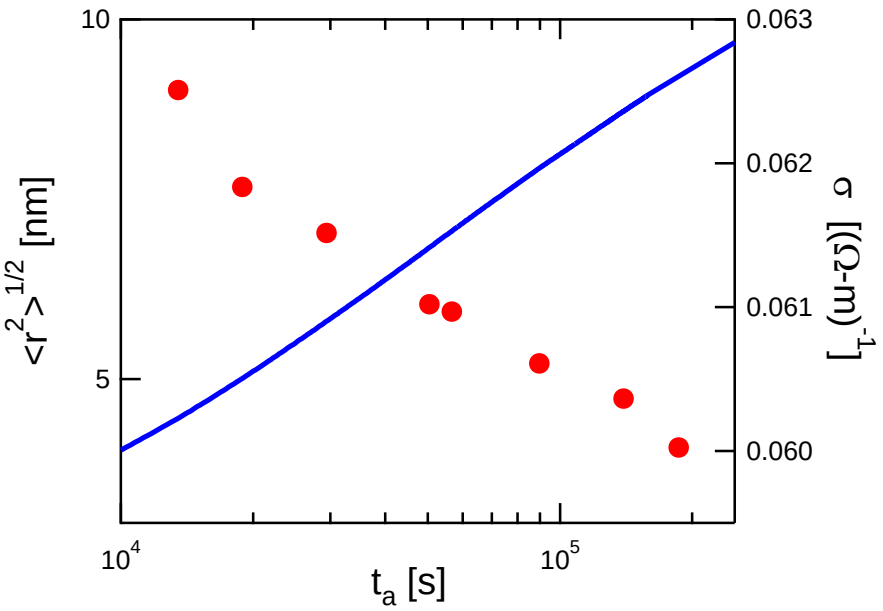
A measure of cage size

Within cage picture one can argue: $A \sim \exp(-\langle r \rangle^2 q^2/3)$



age [s]	$\langle r^2 \rangle^{1/2}$ [nm]
13000	9.0
30000	7.0
90000	5.25
200000	4.0

Sources of stress buildup in laponite:



- Growth in dc conductivity of suspension ⇒ gradual dissolution of Na^+
- Surface charge highly nonlinear function of conductivity for low conductivity solutions [1, 2]
- Evolution of interparticle potential responsible for stress buildup

- Slow dynamics → local rearrangements due to stress buildup from growth in interparticle potential
- Aging → particles trapped in increasingly deeper wells

[1] P. N. Sen, *JCP* (1987).
[2] R. Kan et al., *JCP* (1987).