Local fluctuations and responses in glassy polymers

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Outline

Experiments probing nanodielectric response and fluctuations

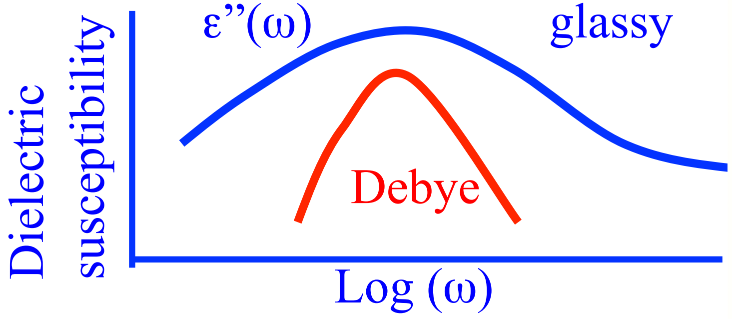
- Search for a dynamical correlation length using noise fluctuations
- Local FDR in a fragile structural glass.
    - Spatio-temporal images of fluctuations and responses
    - Violation factor X(C) *suggests* continuous replica symmetry breaking

Signatures of glassy materials:

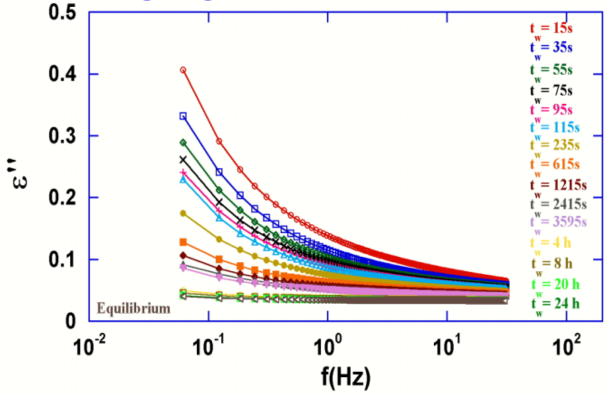
Slow- nonexponential relaxation.

$\exp[-(t/\tau)^{\beta}]$

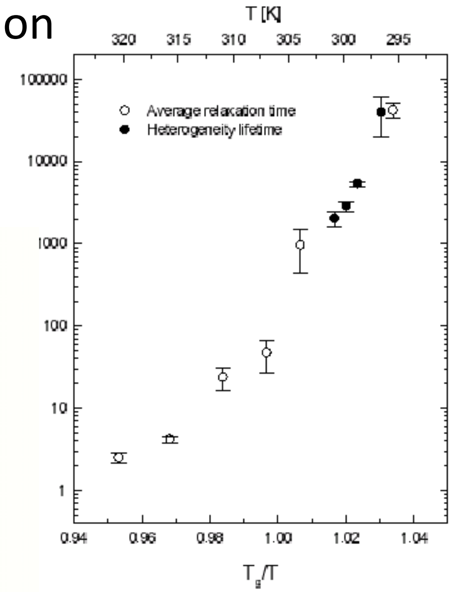
Broadened response



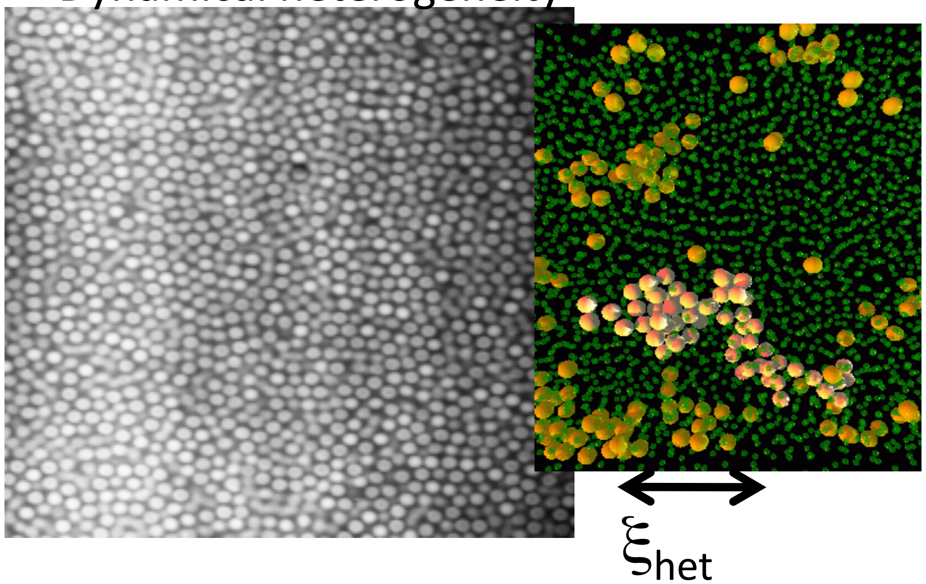
Aging after T-quench



Diverging relaxation times below T_g (fragile glasses)



Dynamical heterogeneity



Jamming

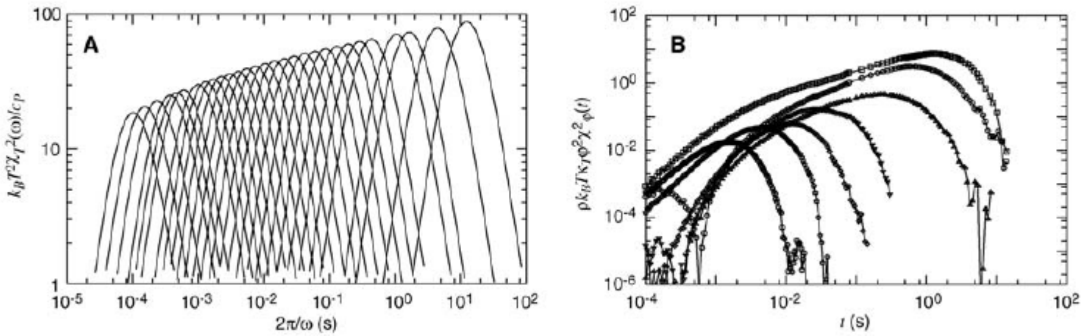
Key (yet unproven) idea:

Dynamical correlation length, ξ ~ 1-3 nm determines behavior near the glass transition (N_{corr} ~ 100 molecules)

- Grows slowly or rapidly on approach to glass transition?
- Behavior tests competing theories
  - Random first-order transitions (RFOT) (Wolynes)
  - Kinetically constrained models (Garrahan and Chandler)

Simulations and colloidal experiments: 4th order correlation function measures number of correlated molecules $N_{corr} = \chi_4(t) = N < \delta C(t)^2 >$

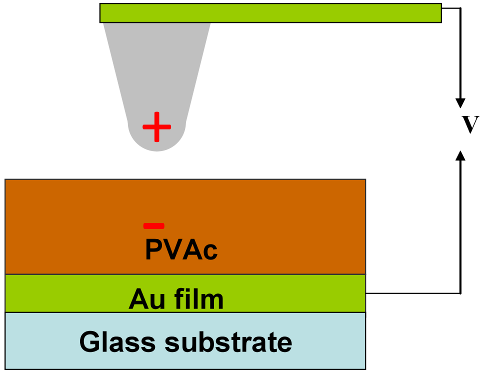
Indirect exp. evidence for weak growth from *dynamic susceptibilities*

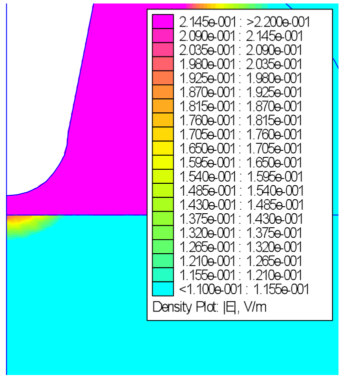


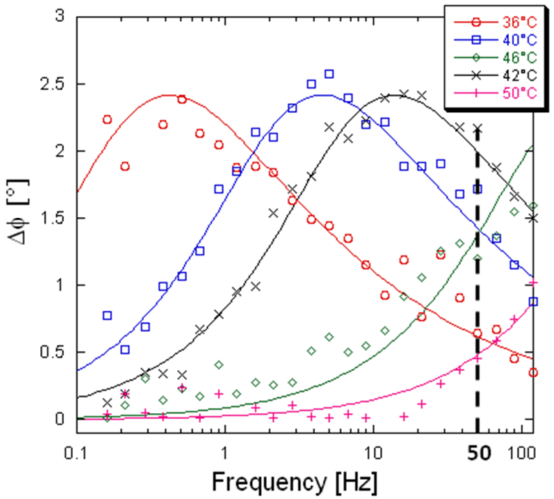
$$\chi_4(t) \geq \frac{k_B}{c_P} T^2 \chi_T^2(t)$$

Berthier et. al. *Science 2005*

Nanodielectric spectroscopy







$$F = -dU/dz = -\frac{1}{2}\frac{\partial C_{\text{tip}}(\varepsilon)}{\partial z}\,V^2$$

$$f_{res} = \left(\frac{k - {dF}/{dz}}{m}\right)^{1/2}$$

Measure local ac susceptibility using response of f_{res} to applied ac voltages

$$V = V_0 \sin \omega t$$

$$\delta f_{res} = \frac{1}{8k}\frac{\partial^2 C}{\partial z^2}(V_0 - V_P)^2 f_{res}$$

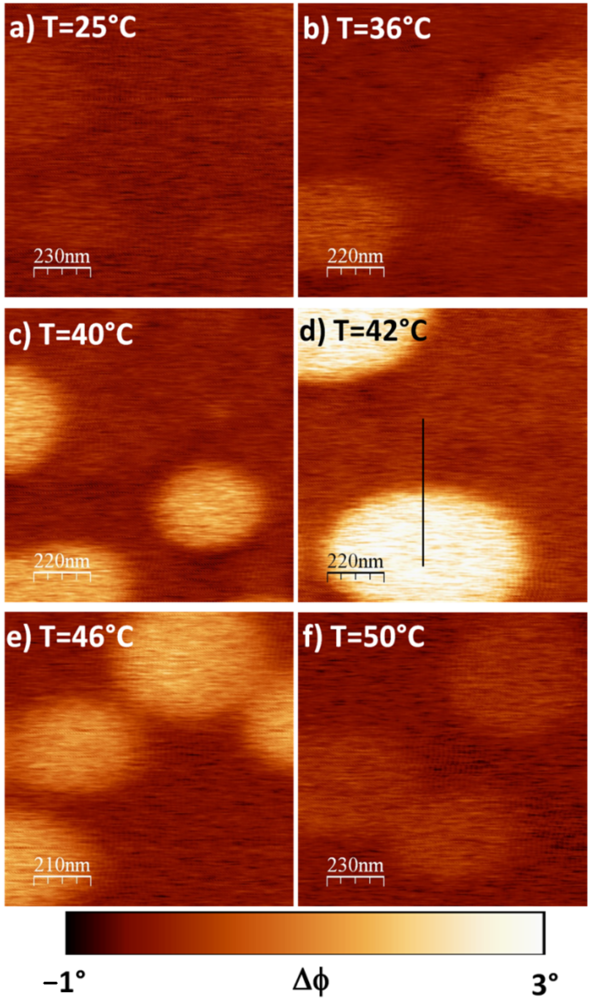
Offset voltage V_p arises from dc polarization

Crider, et. al. *NanoLett* 2006, *APL* 2007, *J. Chem. Phys* 2008; Riedel et. al. APL 2010

Nanodielectric spectroscopy of polymer blend

PVAc has glass transition at 32 C

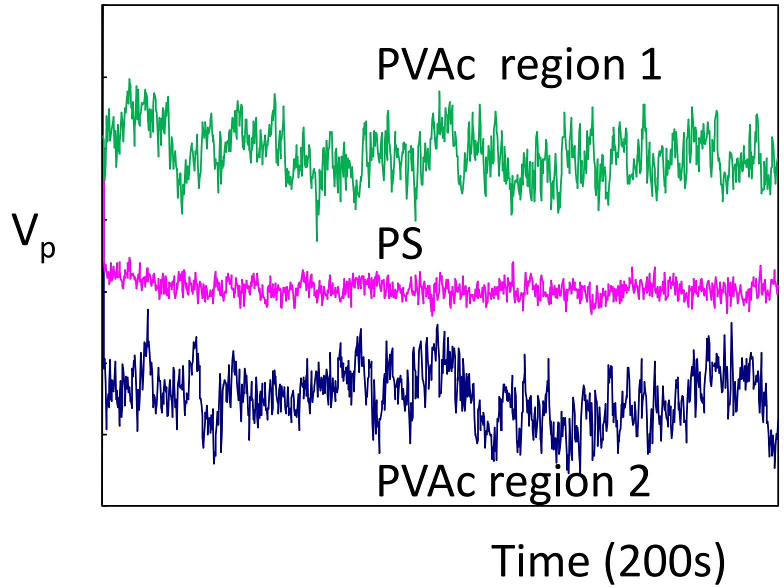
Phase in PS/PVAc blend @ 50Hz



Local noise spectroscopy

$$<\delta P^2>=\frac{k_B T\chi(t)}{V}$$

Polarization noise in PVAc/PS



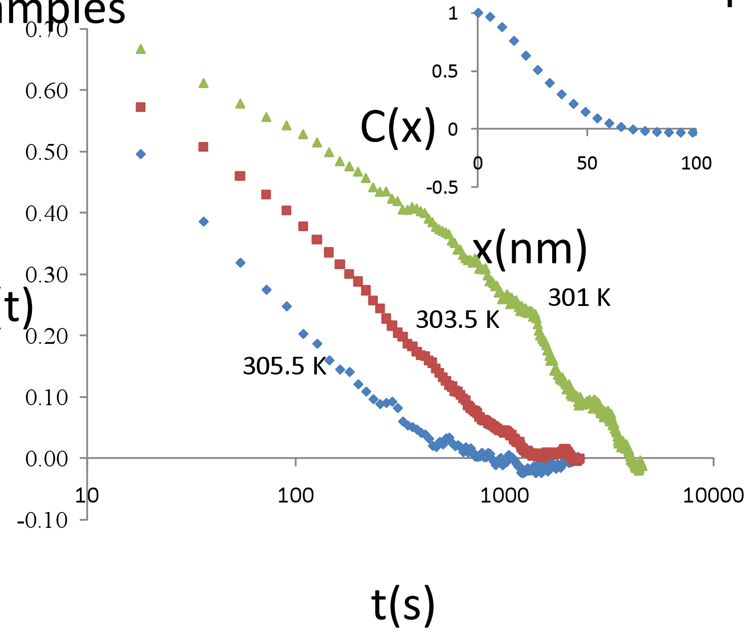
Imaging spatio-temporal noise near T_g

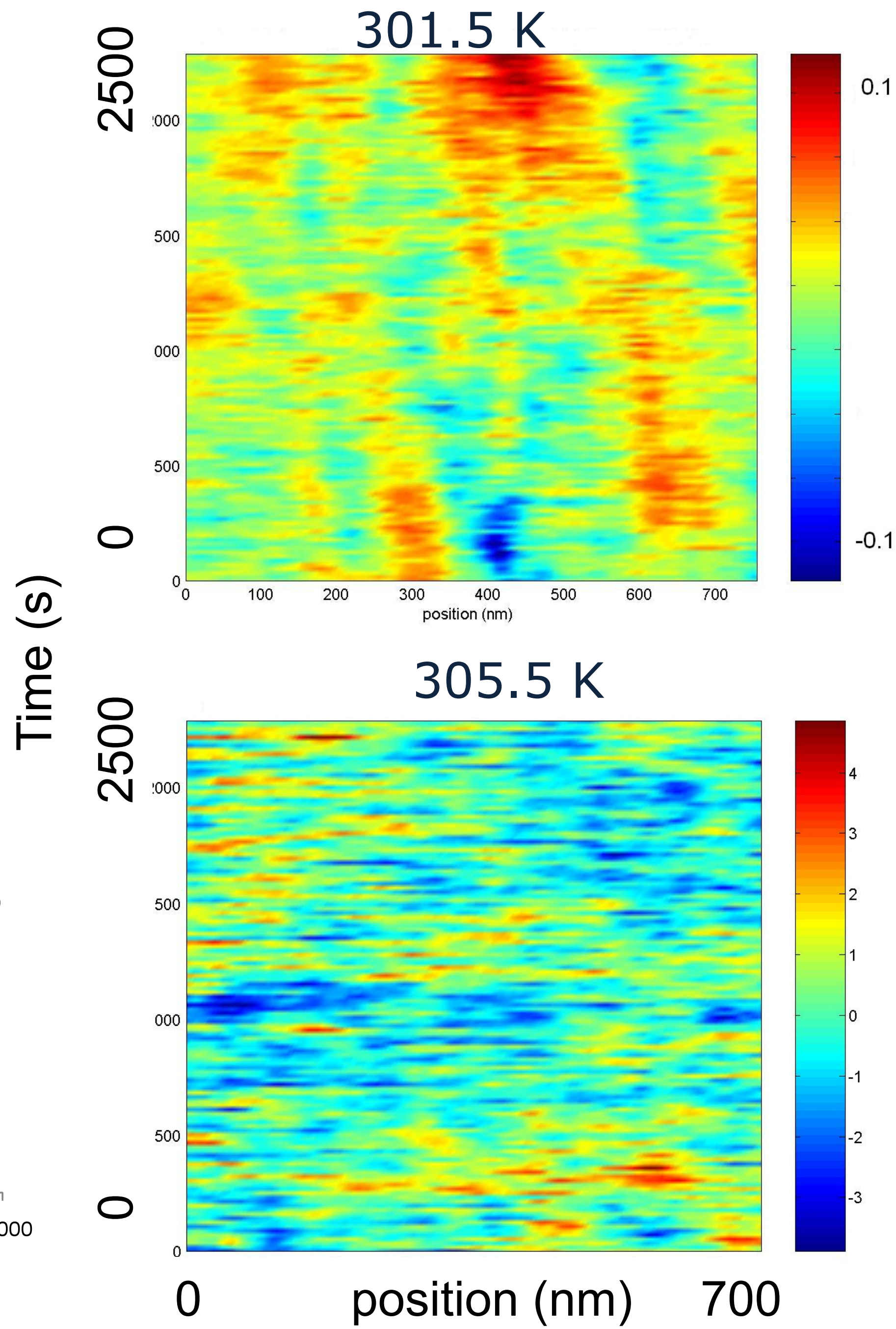
Can study various correlation functions C(x,t)

e.g. global C(t) averaged over x

$C(t) = \langle\langle V_p(t') V_p(t'+t) \rangle_{t'} \rangle_x$

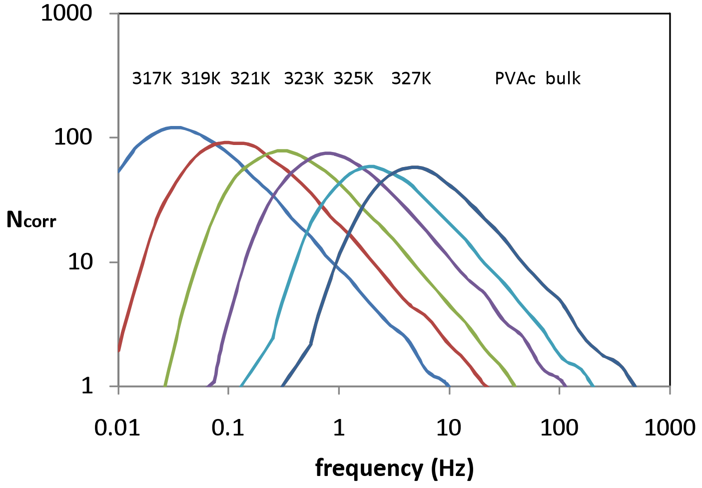
Effectively many independent samples





Detect dynamic correlations with fluctuations in noise power?

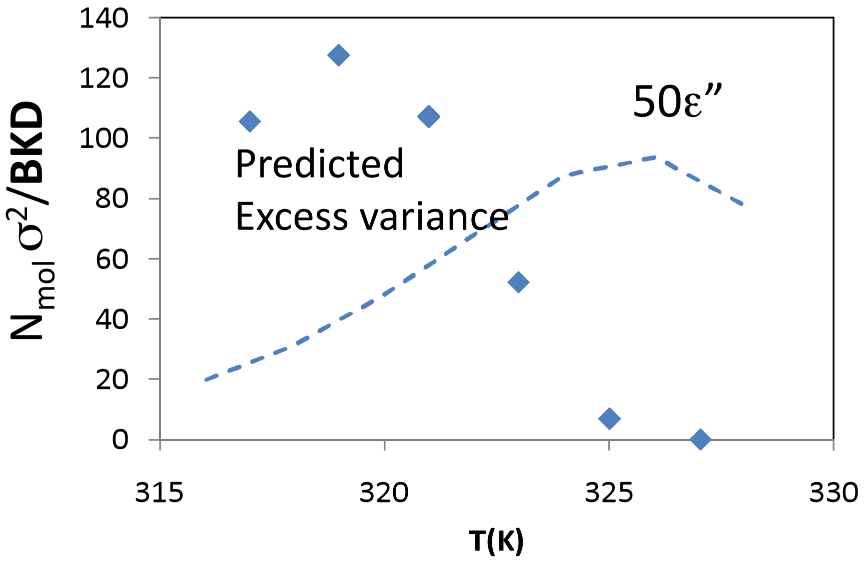
χ_4 from dynamic susc

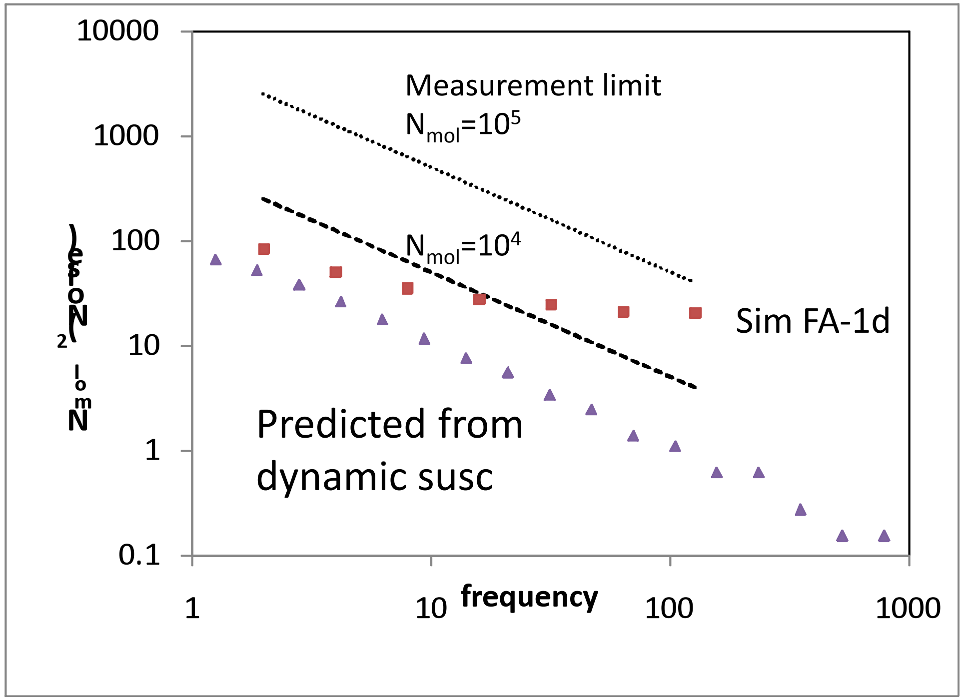


Predicts noise variance

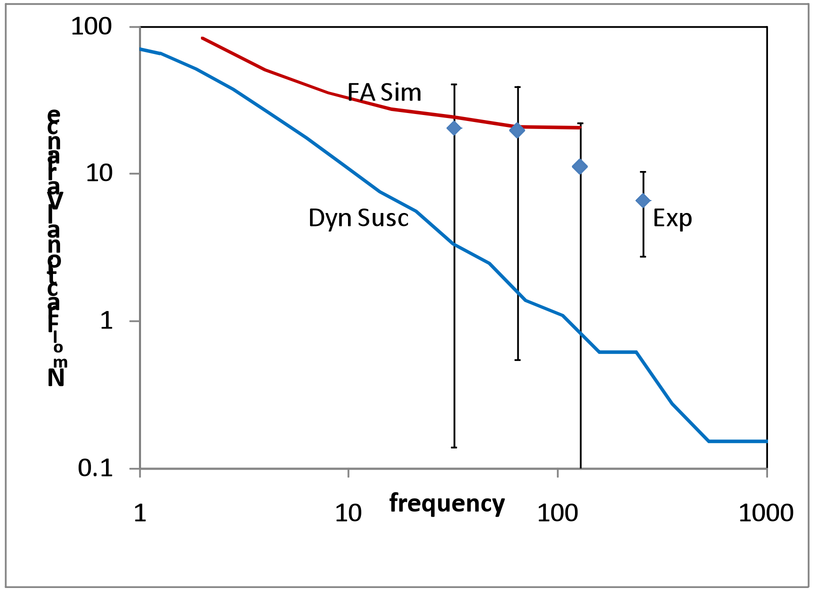
$$N_{mol}\frac{<S(f)^2>}{<S(f)>^2} = N_{corr}(f)\exp(-(t_{obs}/\tau_{het})^{\beta})$$

Gaussian background: $$N_{mol}\frac{<S(f)^2>}{<S(f)>^2}_{BKD} = \frac{N_{mol}t_{obs}}{f}$$



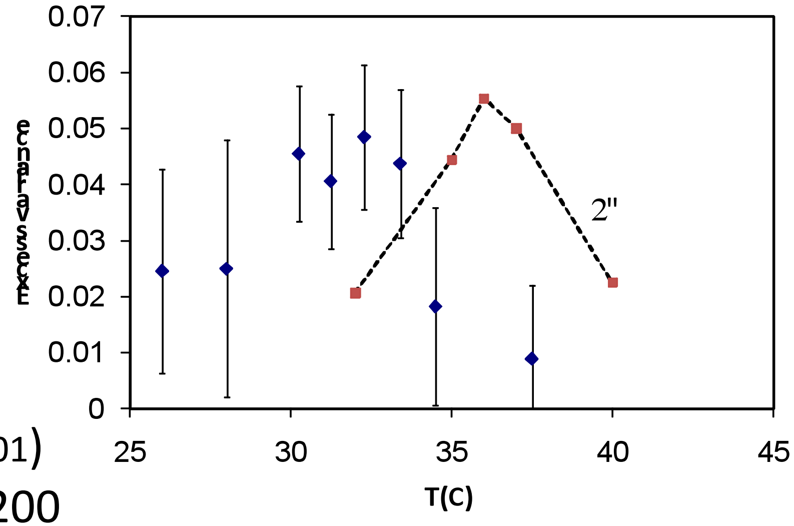


Excess noise variance in ultrathin (30 nm) PVAc single-position spectra



Effective volume: $(2\pm1) \times 10^3$ nm^3

$N_{mon} \sim (2\pm1) \times 10^4$ monomers



Qualitative agreement in T dependence, but

requires $350 < N_{corr} < 1050$

Note that heterogeneity scale at T_G +10K (Reinsberg, 2001) gives $70 < N_{corr} < 550$ at T_g would be $150 < N_{corr} < 1200$

Fluctuation-Dissipation Relations (FDR)

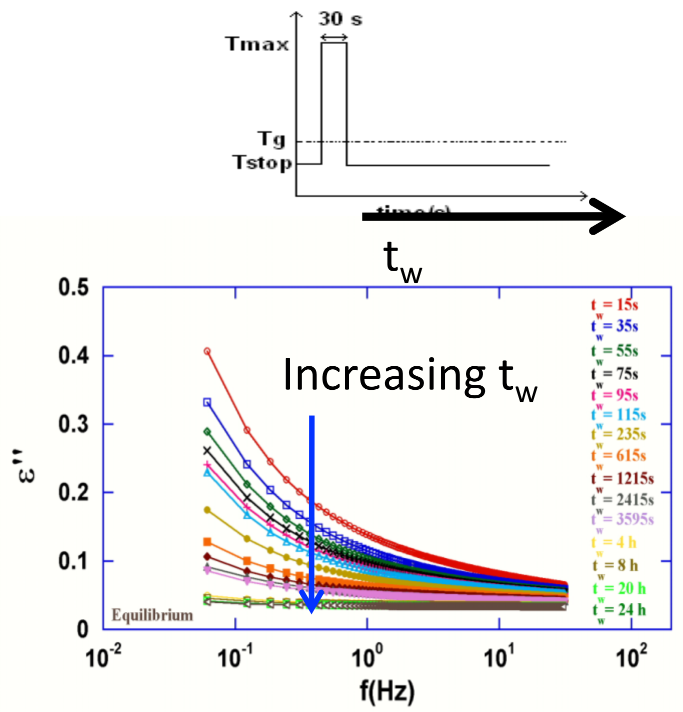
Stokes-Einstein Relation
$D = k_B T / 6\pi\eta_0 r$

Diffusion constant scales inversely with viscosity (1906)

Nyquist Relation
$S_I = 4k_B T/R$

Current noise scales inversely with resistance (1928)

Violations expected in systems far from equilibrium

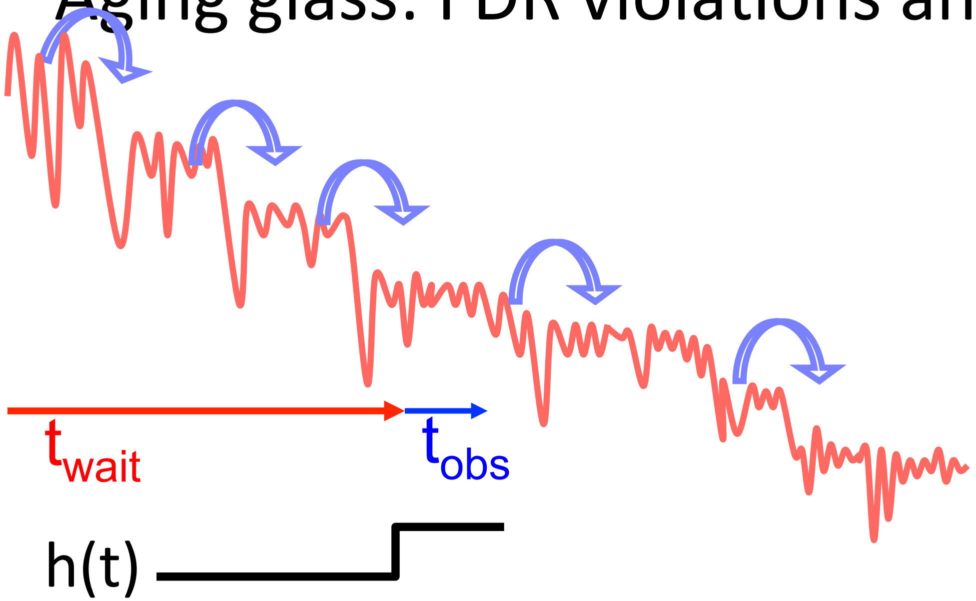


Aging glass: ideal system to study *non-equilibrium* FDR Cugliandolo and Kurchan, PRL 1993, PRE 1997, …MFT

Proposed: $T_{eff} = S_I R/4k_B$

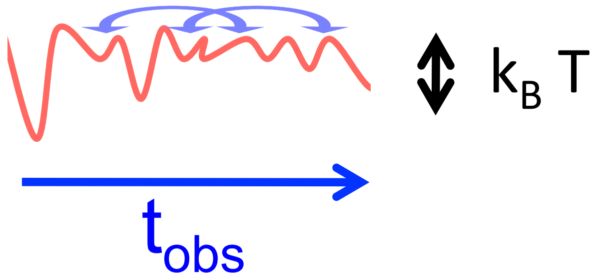
- T_{eff} behave like a real temperature?
- Universality in the violations?
- Model-dependent scaling?

Aging glass: FDR violations and effective temperature



For $t_{obs} << t_w$ looks like equilibrium

FDR holds $T_{eff} = T$

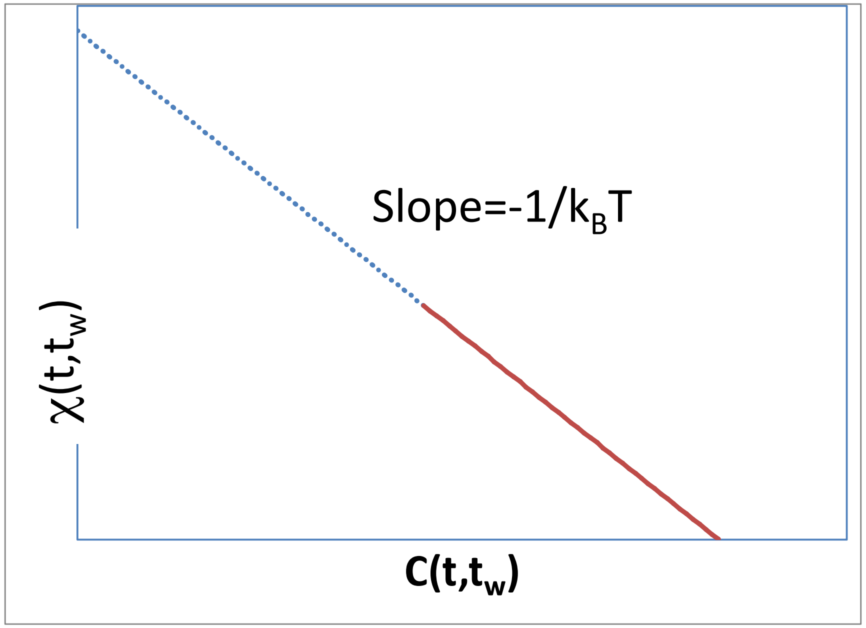


$t = t_w + t_{obs}$

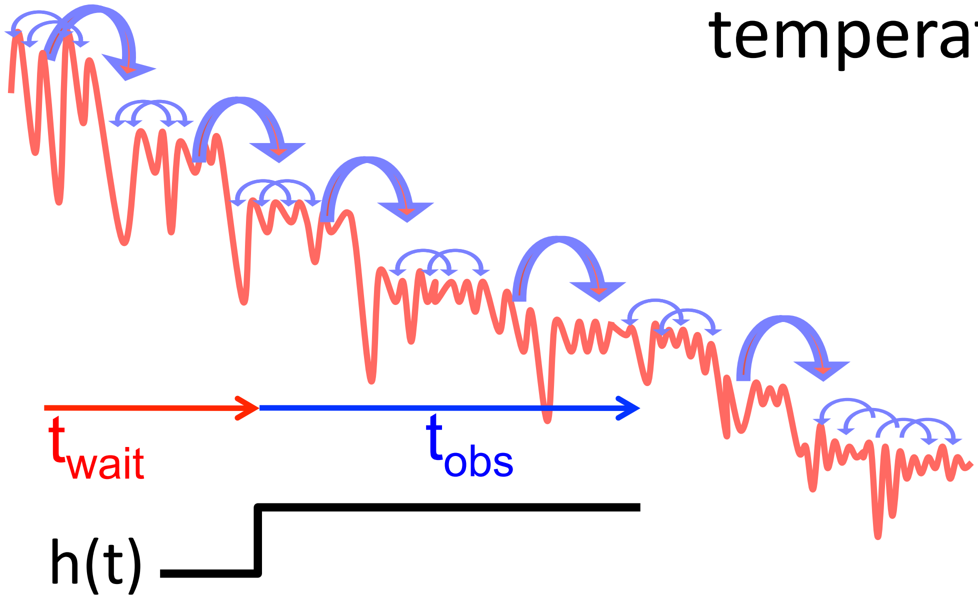
$C(t,t_w) = <O(t_w)O(t)>$ noise

$\chi(t,t_w) = O(t)/h(t_w)$ susceptibility

$\chi(t,t_w) = [1/k_B T][C(t_w,t_w) - C(t,t_w)]$

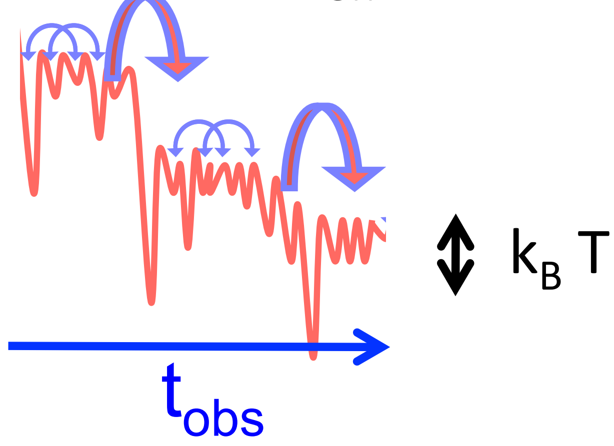


Time-dependent FDR violations and effective temperature



For $t_{obs} \geq t_w$ looks non-equilibrium

FDR fails $T_{eff} > T$

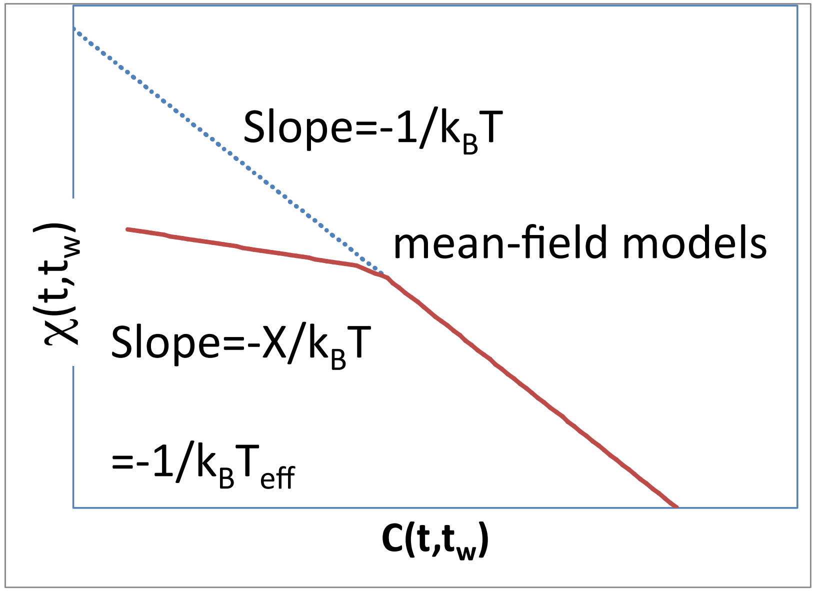


$t = t_w + t_{obs}$

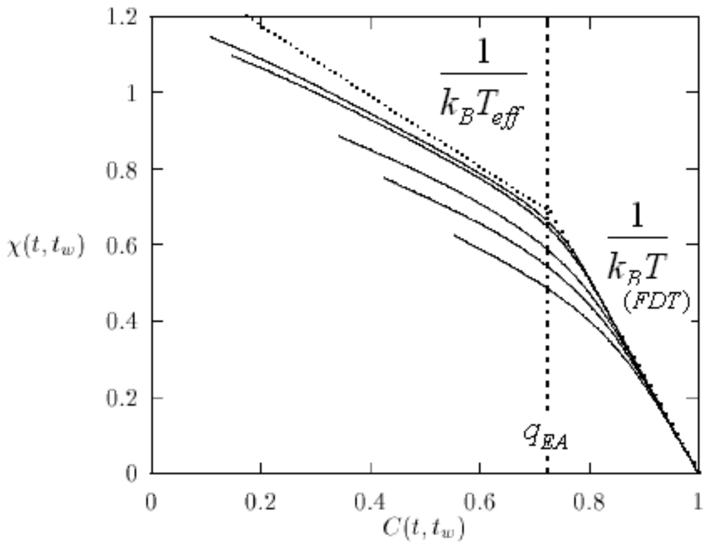
$C(t,t_w) = \langle O(t_w)O(t)\rangle$ $\quad \chi(t,t_w) = O(t)/h(t_w)$

$\chi(t,t_w) = X/k_B\,T[C(t_w,t_w) - C(t,t_w)]$

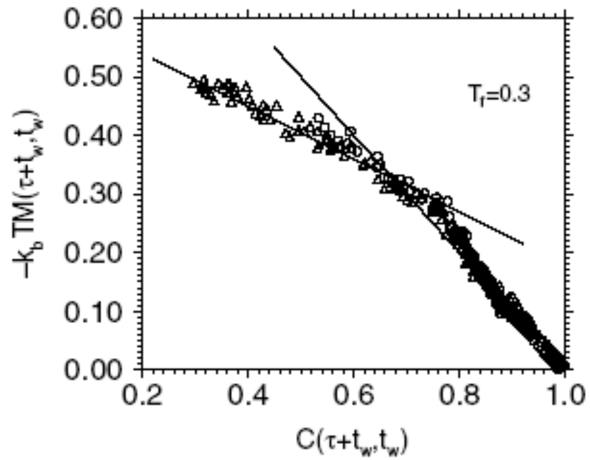
$X = T/T_{eff}$ is deviation of slope from FDR



MFT and simulations: does $X(t,t_w)$ approach a universal function $X(C)$?

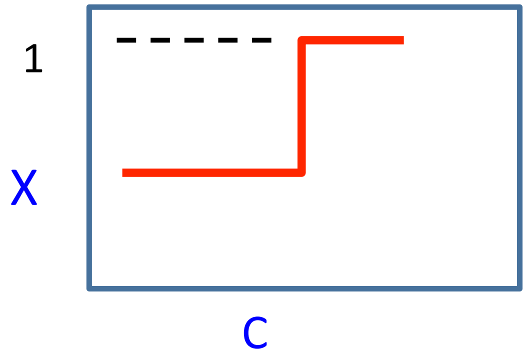


p-spin Ising model
Cugliandolo, Kurchan, 1997

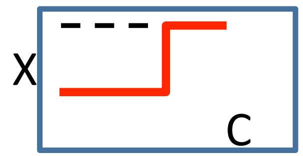


Lennard-Jones
Barrat, Kob 1998

$X = kT \cdot$ slope of χ vs. C

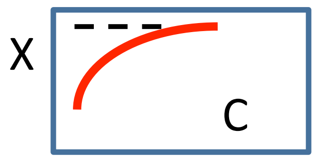


• X(C) reflects glass order parameter distribution(Parisi 1997)



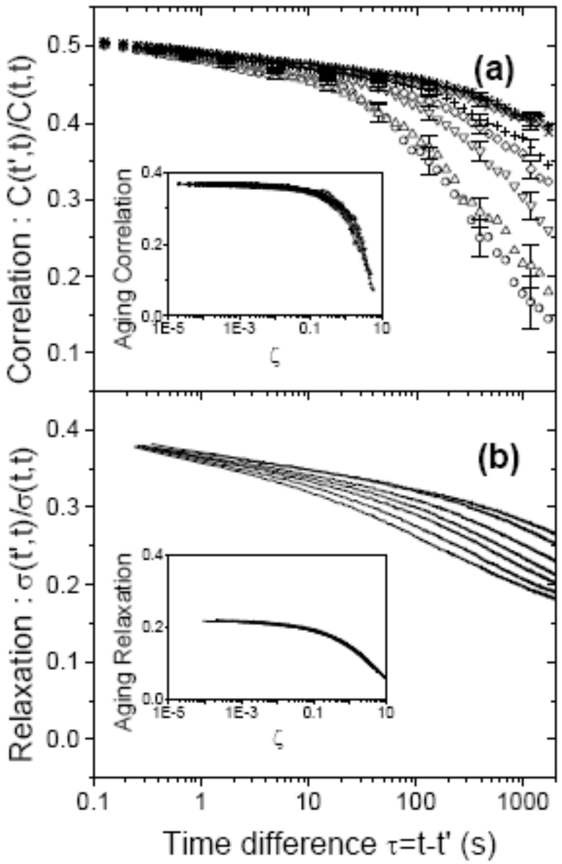
•X(C) is *discontinuous* in MFT of one-step replica symmetry (RSB) breaking models *and* RFOT theory of structural glasses.

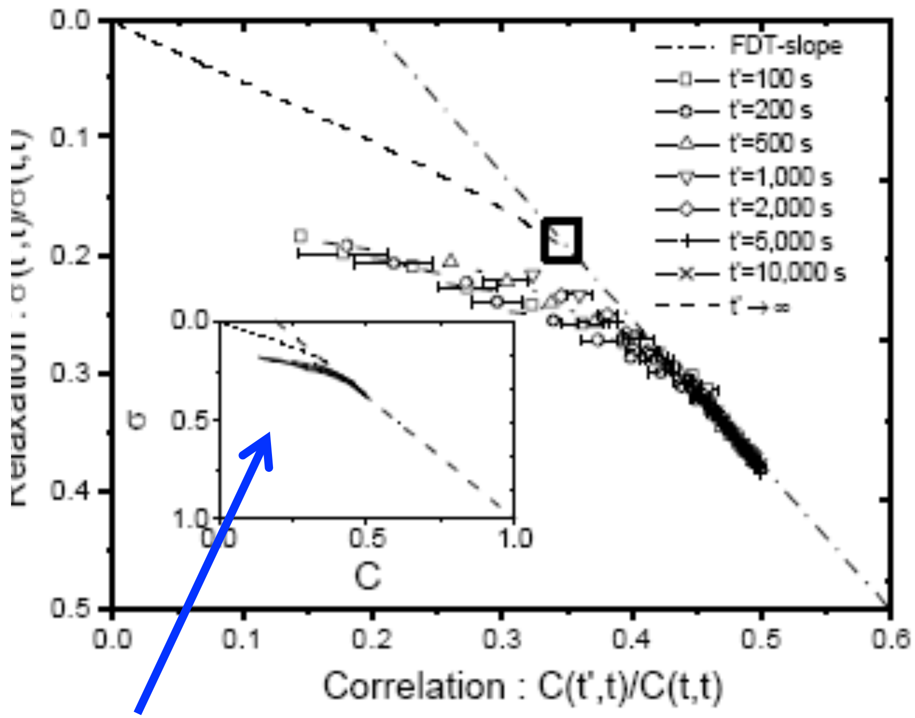
•X(C) is continuous in continuous RSB models such as Sherrington-Kirkpatrick spin glass models



FDR violations observed in spin glasses

Only experiment thus far in strong aging regime with $t\text{-}t_w > t_w$





Appropriate scaling leads to collapse to X (C)
Similar to MFT

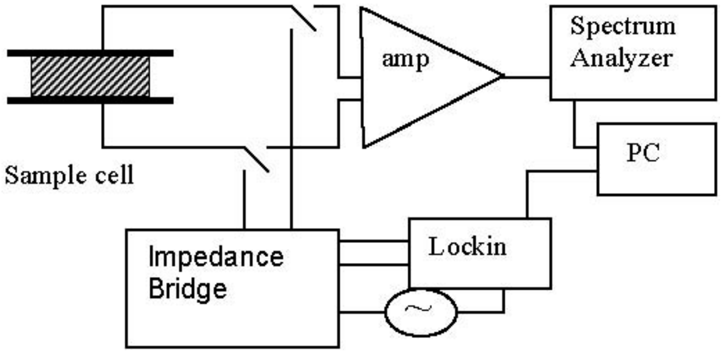
Herisson and Ocio PRL 2002

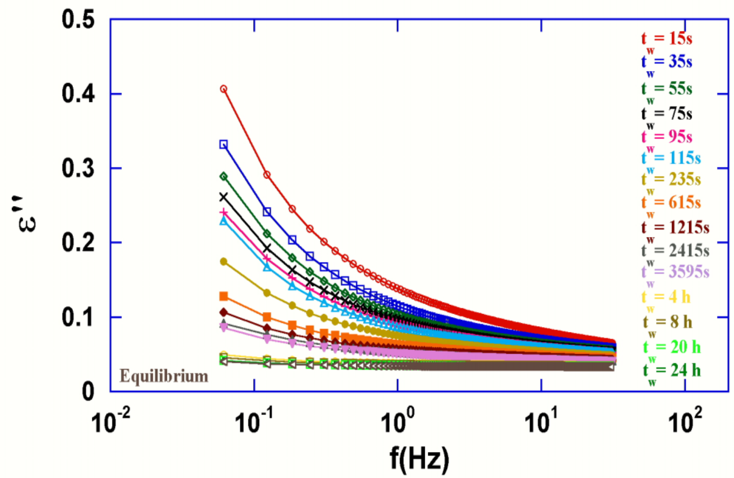
Structural glasses: Conventional macro approach:

measure dielectric susceptibility and current noise $\varepsilon(\omega)=\varepsilon'(\omega)+i\varepsilon''(\omega)$

(voltage)

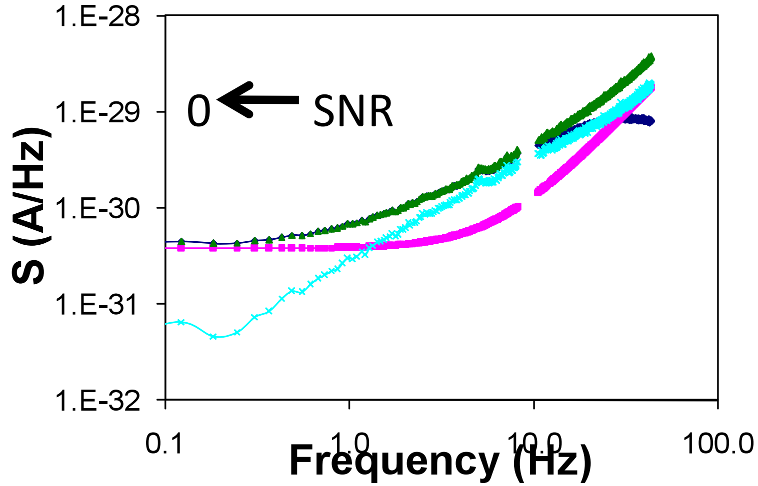
FDR: $S_i = 4k_bTC_0\omega\varepsilon''$





But instrumentally and statistically challenging to measure in *strong* aging regime $t-t_w > t_w$ or $ft_w < 1$

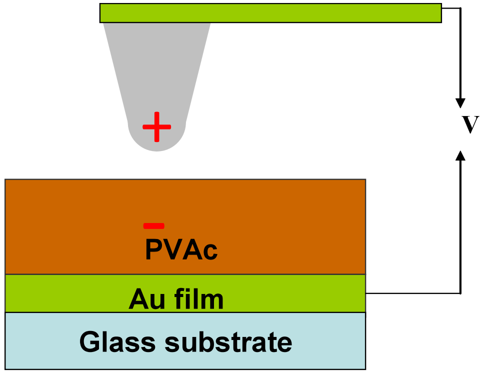
Experiments thus far focused on Weak aging quasi-equilibrium regime

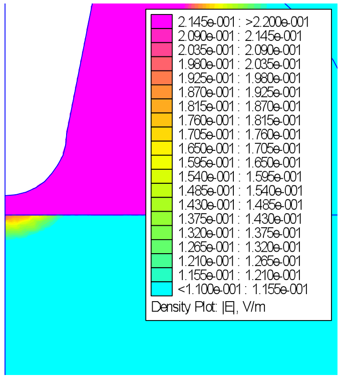


Summary of experimental results structural/colloidal glasses

Material	Property	FDR violations?	$(t-t_w)/tw$	Ref.
Glycerol	electrical	small	< 1	Grigera, 1999
Laponite	electrical	large	< 1	Buisson, 2003
Laponite	rheological	none	< 1	Buisson, 2004
“	“	large	<< 1	Abou, 2004
“	“	large	<< 1	Strachan, 2006
“	“	large	<< 1	Bartlett, 2006
“	“	none	<< 1	Jabbari-Farouji, 2007
Poly-carbonate	electrical	large	<1	Buisson, 2005

Nanodielectric spectroscopy





$$\mathrm{F} = -\mathrm{dU}/\mathrm{dz} = -\frac{1}{2}\frac{\partial C_{\mathrm{tip}}(\varepsilon)}{\partial \mathrm{z}}\ \mathrm{V}^2$$

Detect with shift in f_{res}

$$\delta f = \frac{1}{8k}\frac{\partial^2 C_{tip}}{\partial z^2} V^2 f_{res}$$

Polarization produces surface potential , V_p , which offsets applied voltage

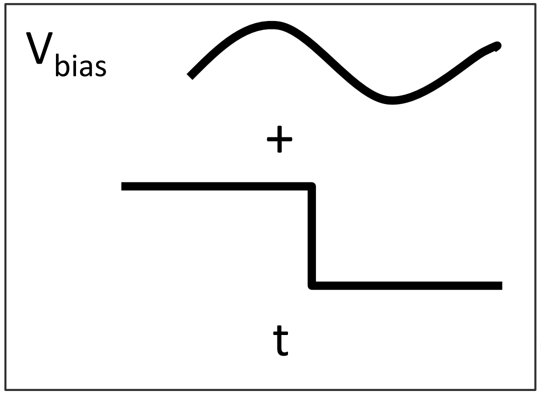
Response to ac or dc voltages.

$$\delta f = \frac{1}{8k}\frac{\partial^2 C}{\partial z^2}(V_0 - V_P)^2 f_{res}$$

$$\mathrm{V} = \mathrm{V}_{\mathrm{dc}} + \mathrm{V}_0 \sin \omega t$$

Crider, et. al. *NanoLett* 2006, *APL* 2007, *J. Chem. Phys* 2008

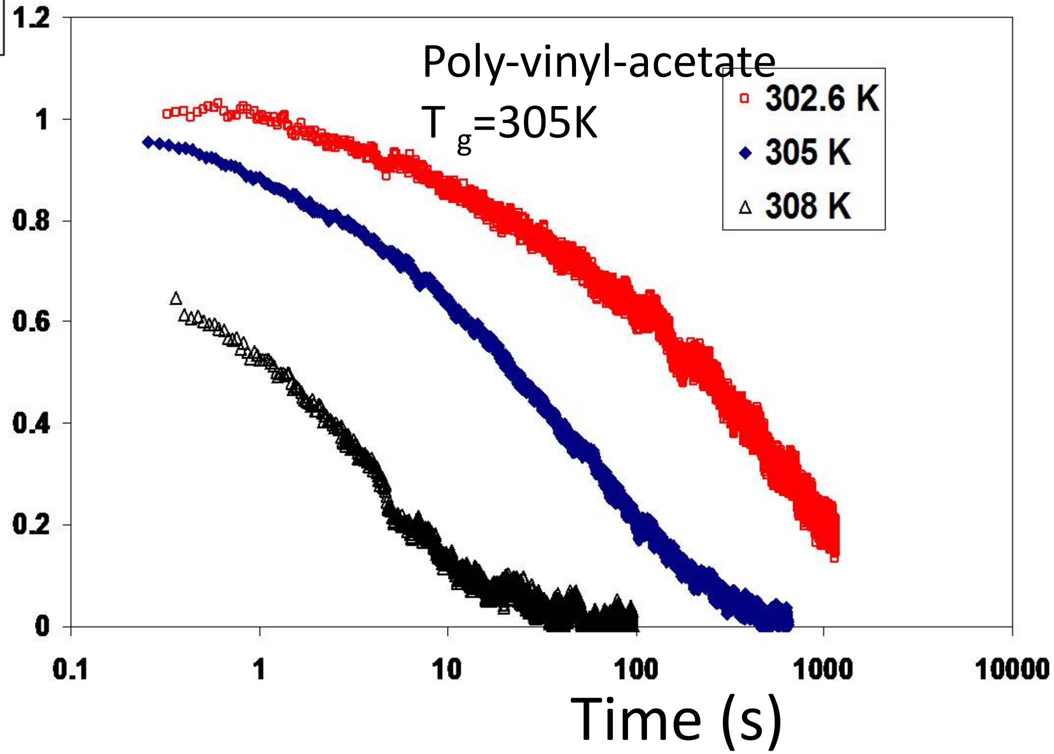
Apply ac + dc bias step----measure polarization relaxation



$$V = V_{dc} + V_0 \sin \omega t$$

$$\delta f_\omega = \frac{f_0}{2k}\frac{d^2C}{dz^2} V_0 V_P(t) \sin\omega t$$ lock-in detection

$$1 - \chi(t) = V_P / V_{dc}(0)$$



FDR: Expect polarization fluctuations $< \delta P^2 >= k_B T\chi / \Omega$ Ω is volume probed

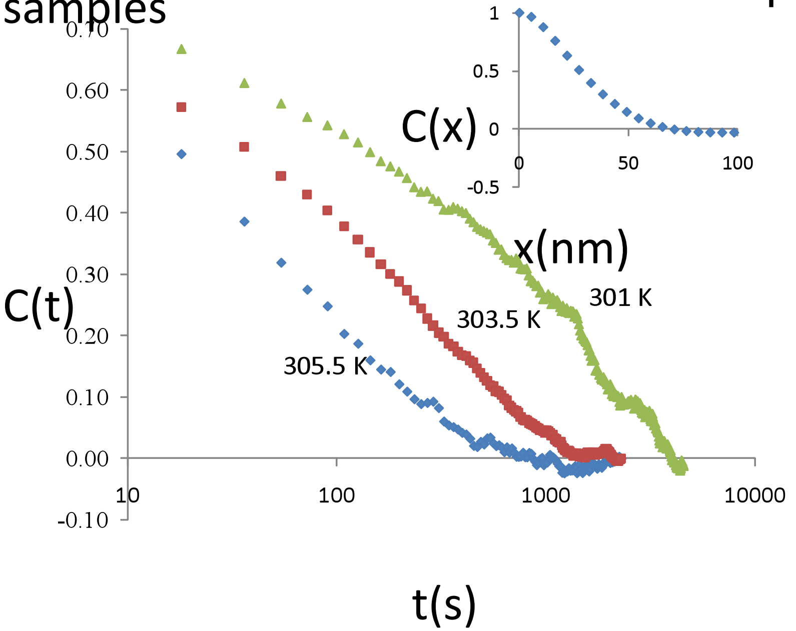
Imaging spatio-temporal noise near T_g

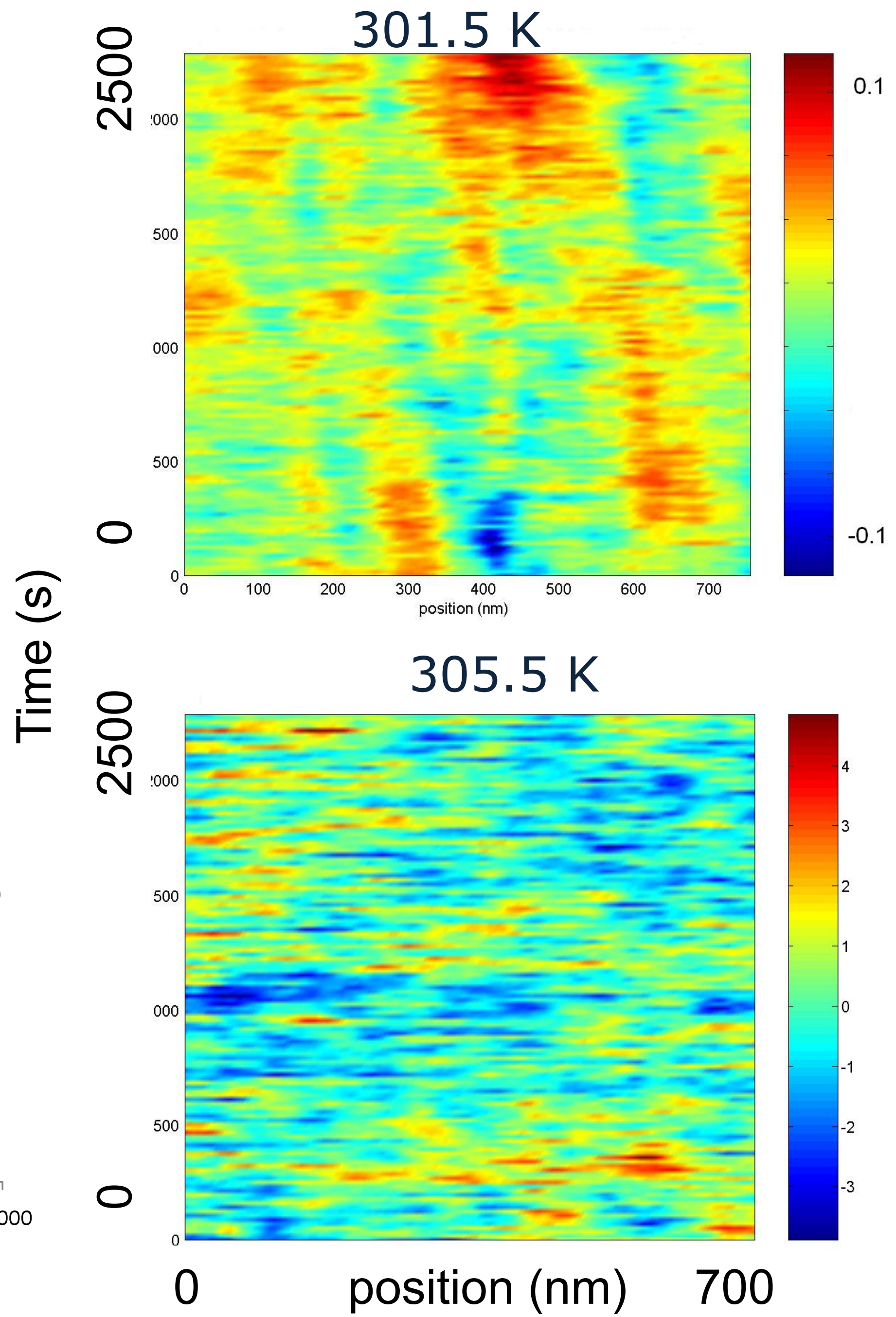
Can study various correlation functions $C(x,t)$

e.g. global $C(t)$ averaged over x

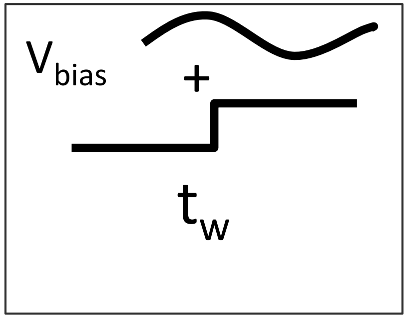
$C(t) = \langle\langle V_p(t') V_p(t'+t) \rangle_{t'} \rangle_x$

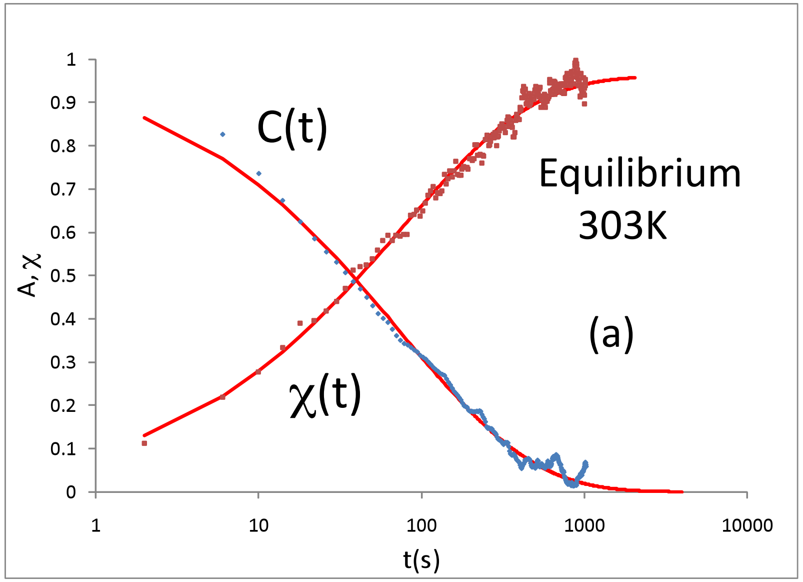
Effectively many independent samples





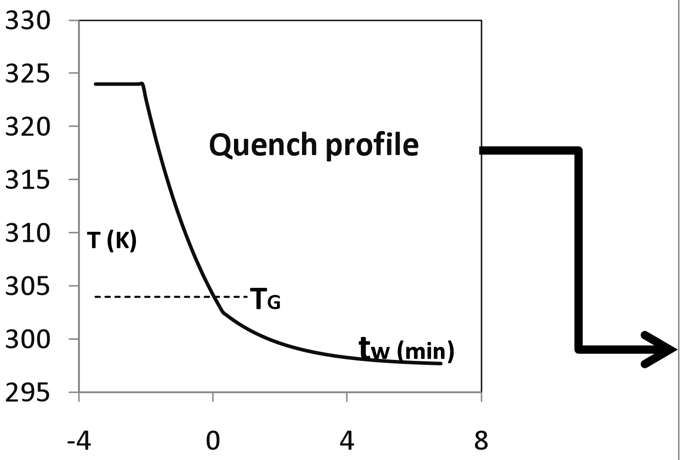
Relaxation and correlation: equilibrium and aging

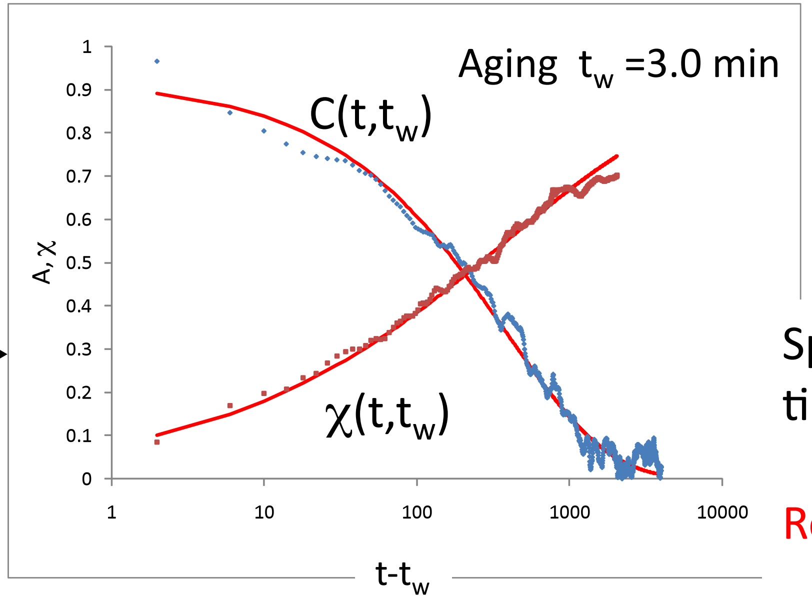




$\beta_\chi = \beta_C$
$= 0.53$

Response and noise agree on dynamic spectrum





$\beta_\chi = 0.4$

$\beta_C = 0.65$

Spectrum of relaxation times according to:

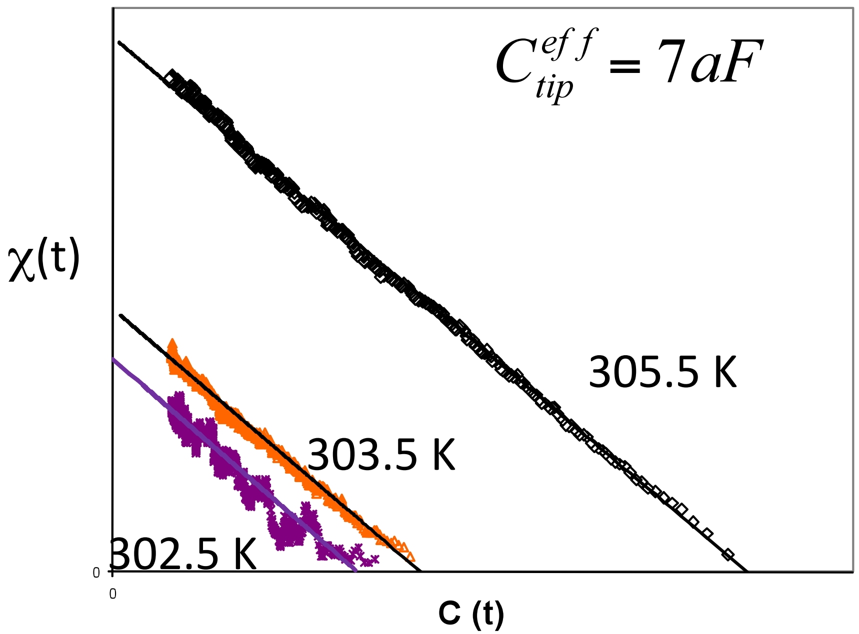
Response: stretched

Noise: compressed

FDR for this measurement:

has the form:

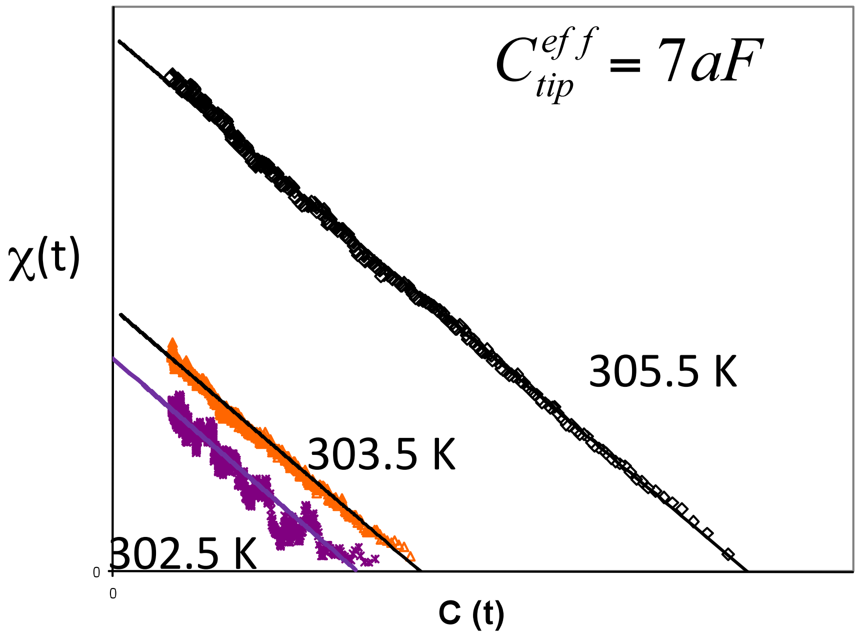
$$\chi_{ex}(t) = \frac{C_{tip}^{eff}}{k_B T}[C(0) - C(t)]$$



FDR for this measurement:

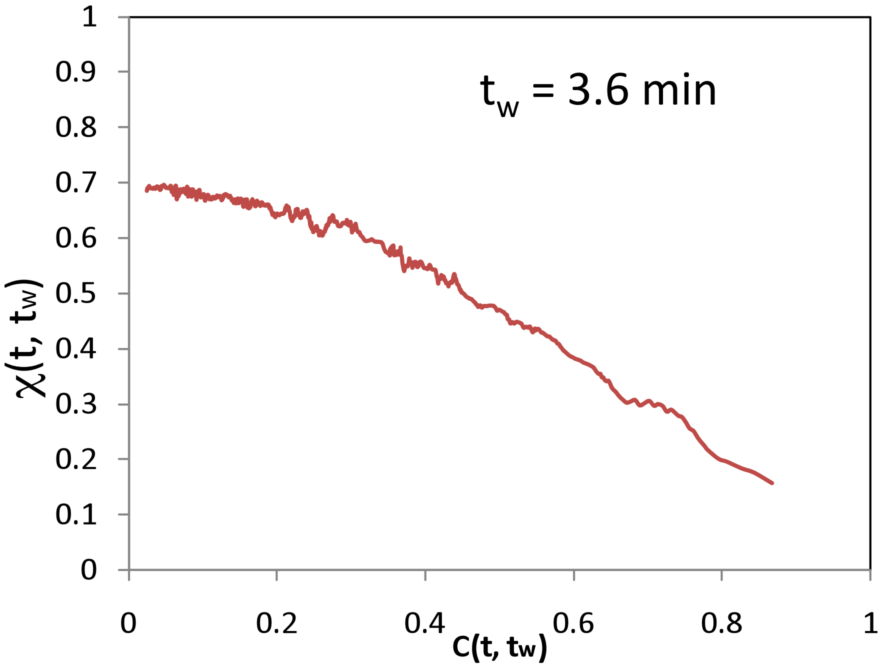
Equilibrium

$$\chi_{ex}(t) = \frac{C_{tip}^{eff}}{k_B T}[C(0) - C(t)]$$

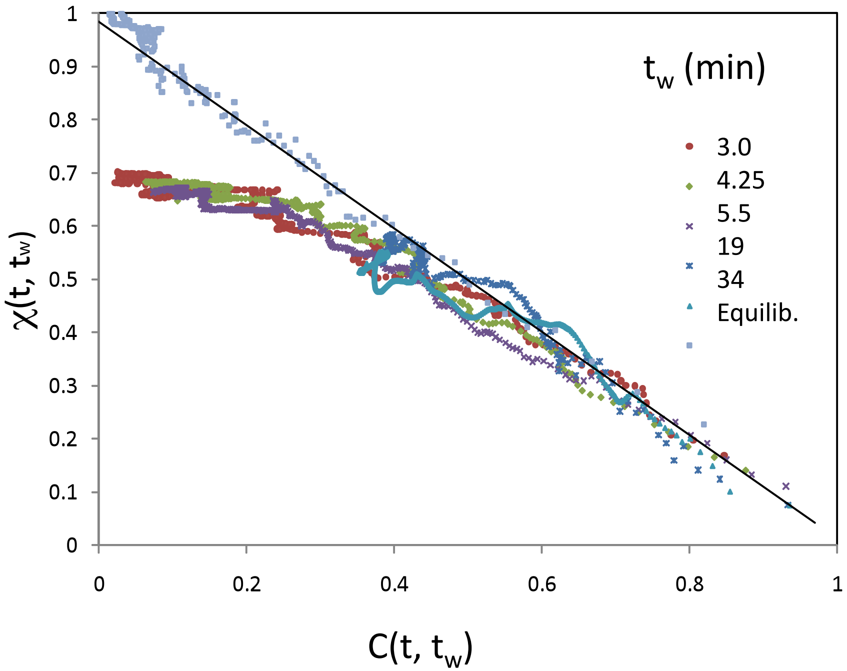


Aging 298K

$$\chi_{ex}(t, t_w) = \frac{C_{tip}^{eff}}{k_B T}[C(t_w, t_w) - C(t, t_w)]$$



Collapse of FDR violations

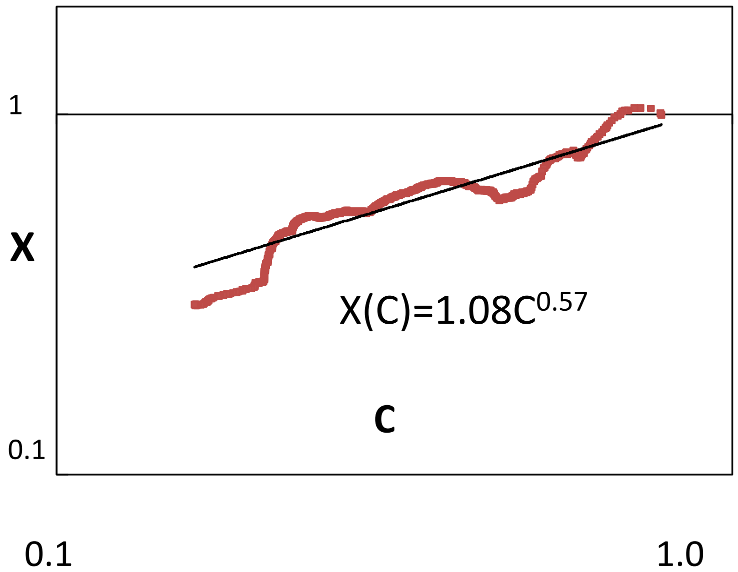


Violation factor

$X = -\text{slope} \ = T_{eff} / T$

$X(t,t_w) \rightarrow X(C)$ continuous

X(C) is a power-law similar to SK model of continuous RSB



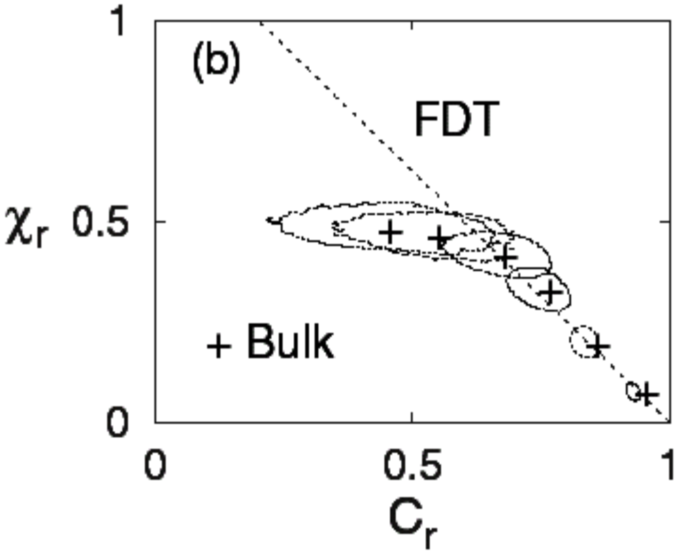
Disagrees with single-step RSM Models and RFOT

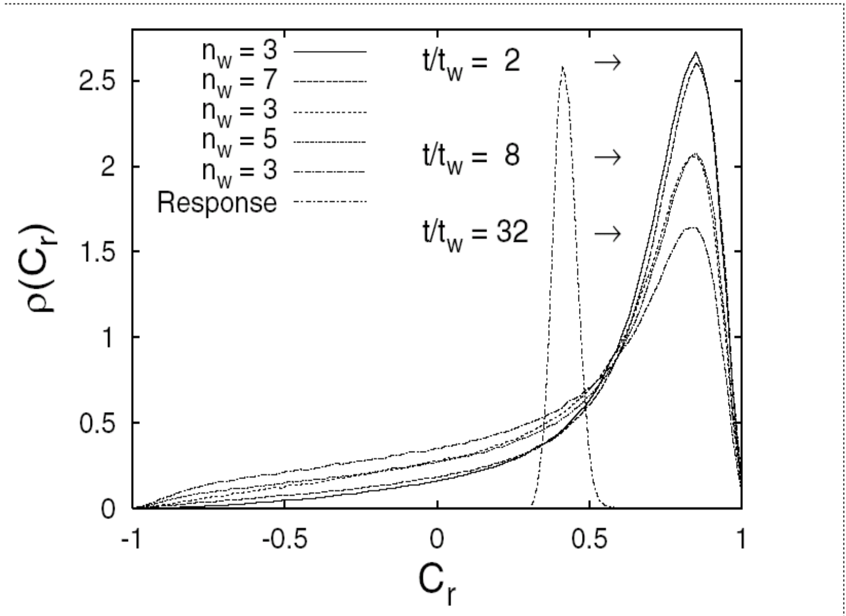
Oukris, Israeloff *Nature Physics* (2010)

Local aging is heterogeneous in a model spin glass

Castillo, Chamon, Cugliandolo, Kennett *PRL* 2002

Castillo, Parsaeian, *Nature Physics* 2007





Fluctuations are heterogeneous but single T_{eff} found

RFOT theory (Wolynes) predicts local variations in T_{eff}

C_r is correlation function (noise)

χ_r is response function

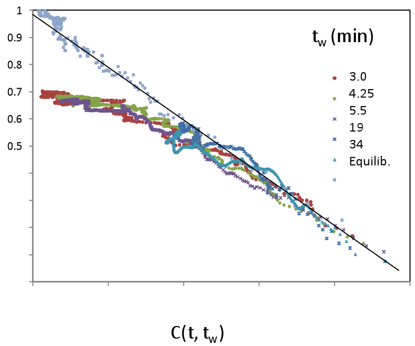
Local experiments can answer this question

FDR violations in aging structural glass

Summary

•Aging relaxation-time spectrum is stretched for relaxation, compressed for noise in strongly aging polymer glass. Also true for rapid cooling regime.

• Produces FDR violations which collapse to a single scaling function X(C).



•FDR violation factor $X(t,t_w)$ → X(C) ~ power-law , consistent with continuous RSM.

•Why is $T_{eff} >> T_{initial}$? Is this a property of fragile glasses?

•Need deeper quenches

Thanks to:

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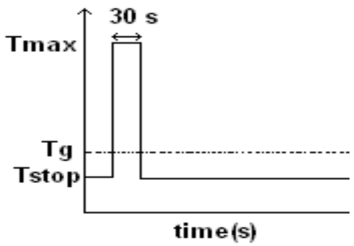
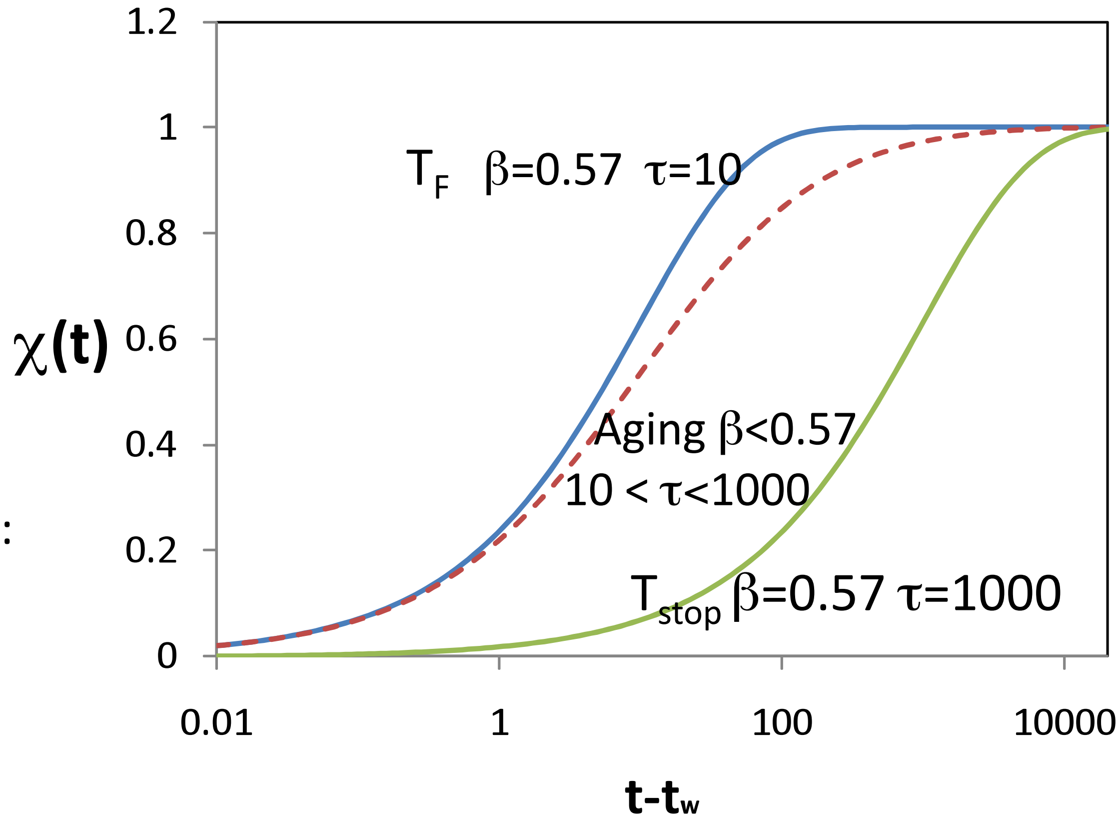
NSF-DMR

Aging in structural glasses –shallow quench

Evolution of relaxation time from short to long (but finite)



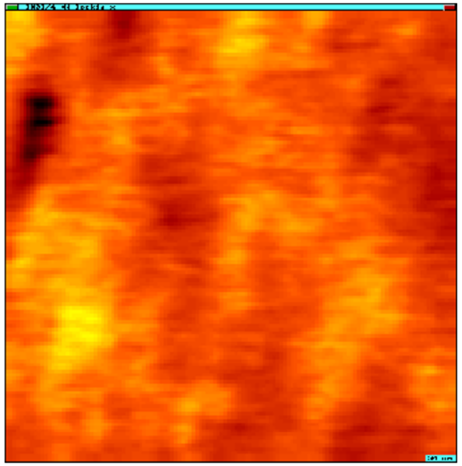


deep quenches or SG:

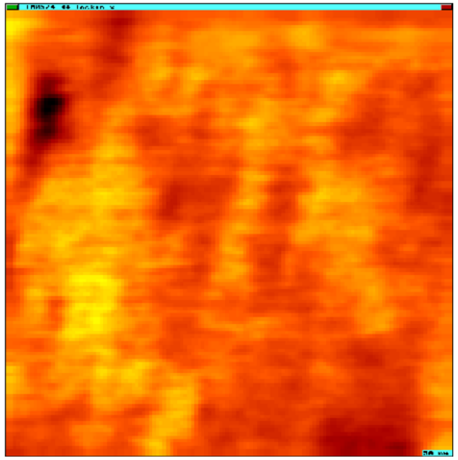
Evolution to infinite relaxation time

Aging model from Lunkenheimer, PRL 2005
Relaxation rate evolves from value at T_F to T_{Stop}

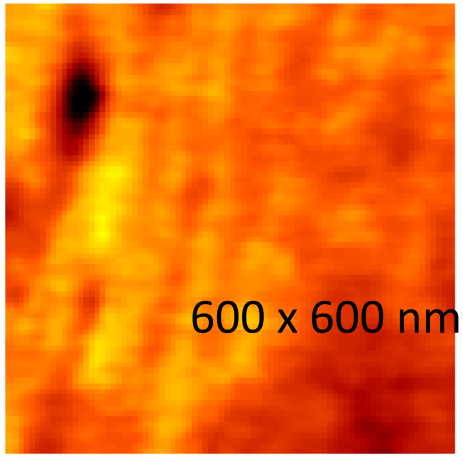
Polarization fluctuations images in PVAc near T_g



t=0



t=17 min



t= 48 min

$$< \delta V_P^{\ 2} >= k_B T / C_{tip}^{eff}$$

Measure rms <δV_P > = 25±4 mV $C_{tip}^{eff} = 6.5 \pm 2aF$