A microscopic view of physical aging and plastic deformation in amorphous solids

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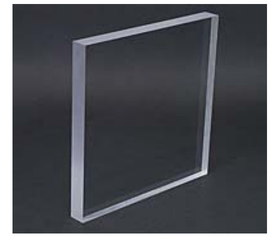
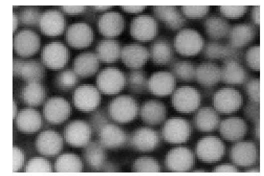
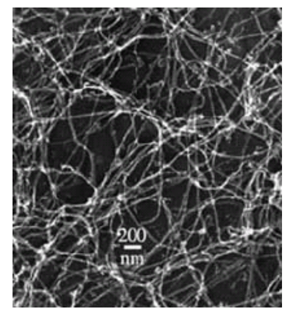






KITP workshop "Glasses 2010"

Collaborators:
Mya Warren (now UCSD) and Amy Liu (now Lumerical Solutions)

Nonequilibrium relaxations (physical aging)

- Below T_g, glasses do not equilibrate, material can only slowly explore configuration space, α-relaxation time τ increases
- Material properties depend on waiting time t_w since the glass was formed and time t at which external conditions (stress) are changed
- Almost all glasses age:

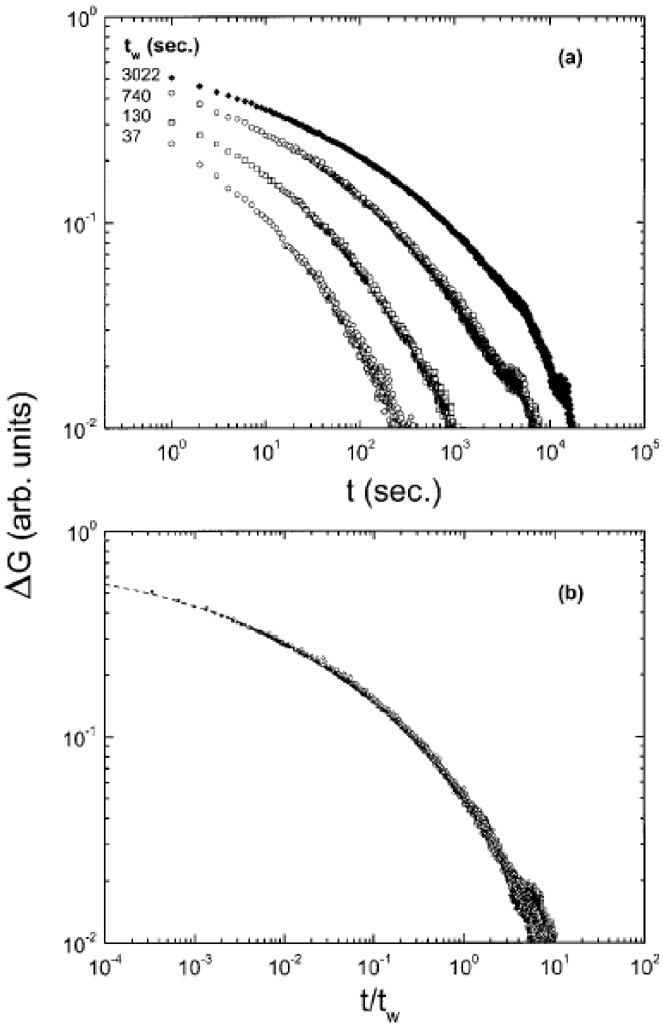
→ thermodynamic quantities (energy, density) ~ log t_w

→ correlation functions $C(t,t_w) \sim C_{fast}(t) + C_{age}(t/t_w^m)$

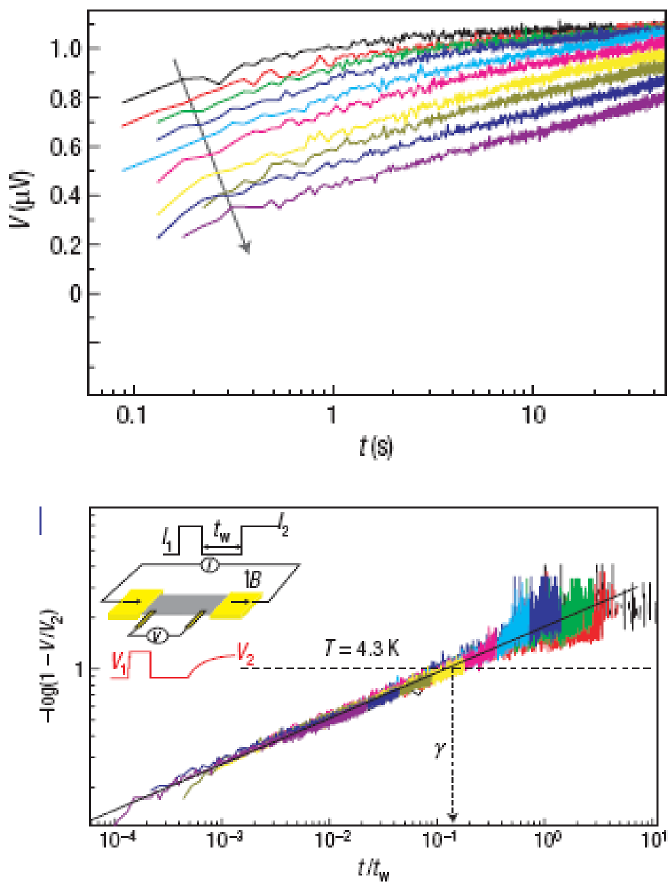
- In structural glasses, aging changes the mechanical properties such as creep compliance and yield stress.

Aging is ubiquitous…

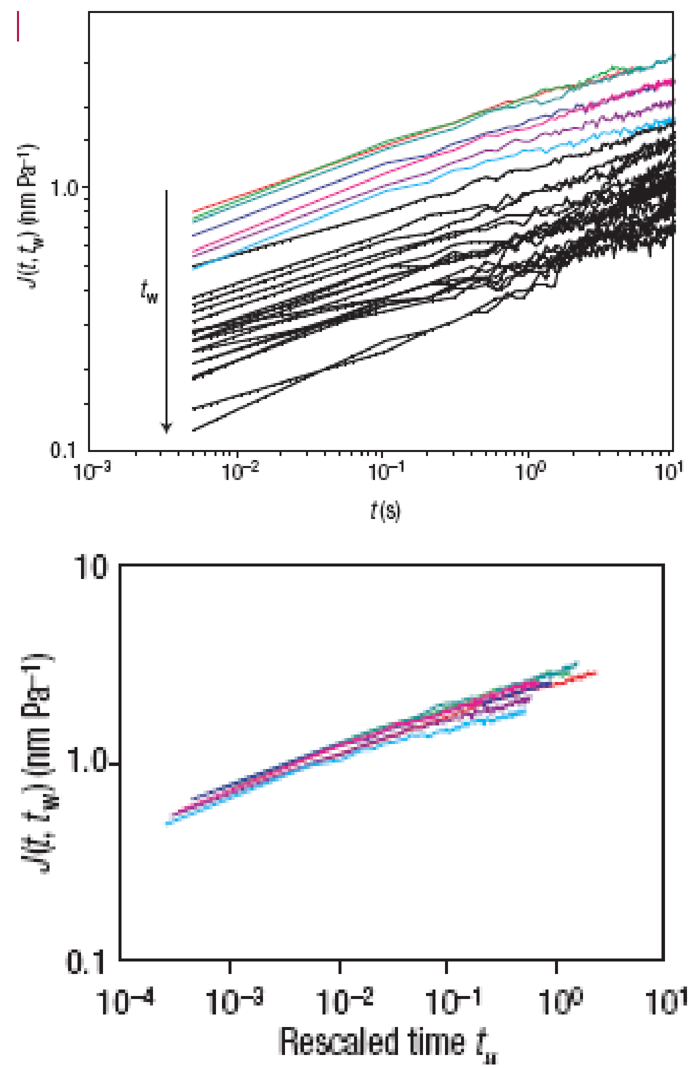
Electron glass



Vortex glass



Cytoskeleton



PRL **84**, 3402 (2000) Nature Physics **3**, 111 (2007) Nature Materials **4**, 557 (2005)

Questions:

- How are the macroscopic physical aging effects related to molecular level processes?

- How does plastic deformation interact with physical aging?

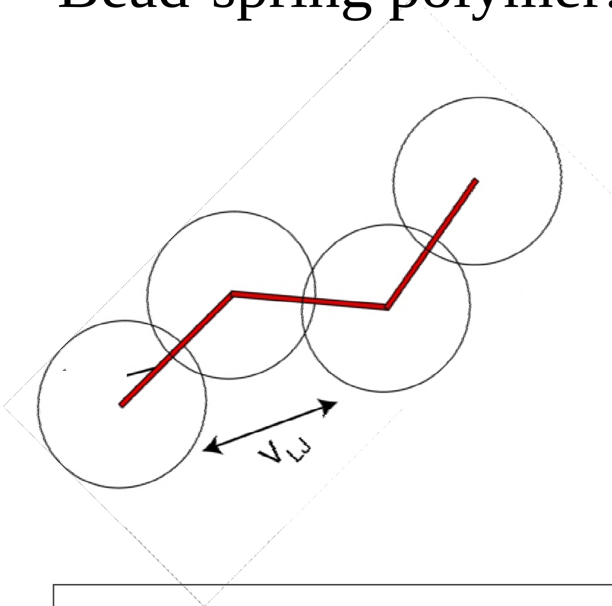
- What is the molecular level origin of physical aging in structural glasses?

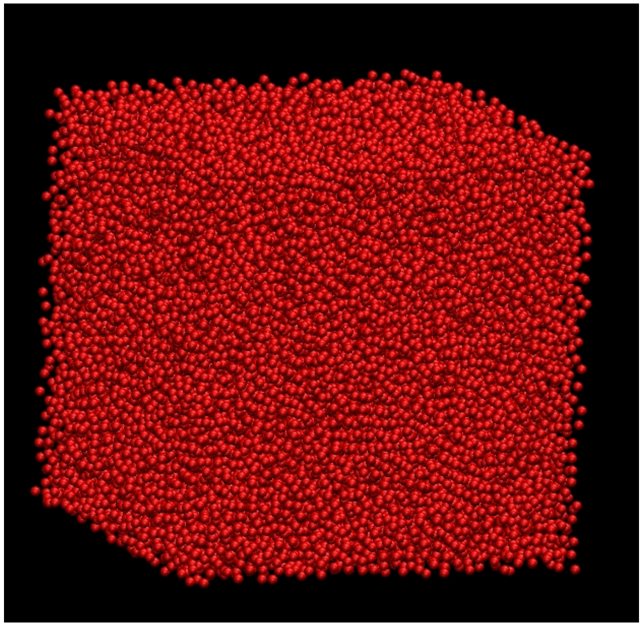
- How does active deformation accelerate segmental dynamics?

Molecular dynamics

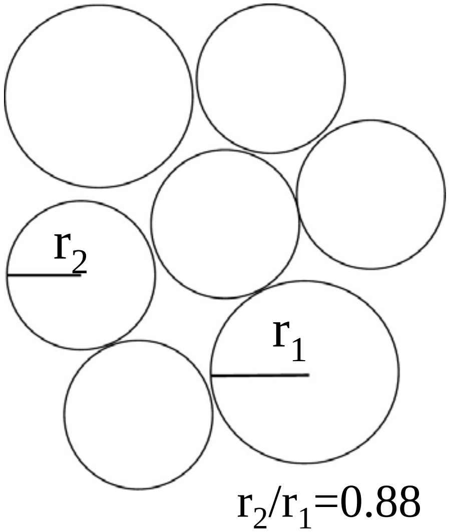
- Our approach: minimalistic molecular models that capture generic physics of structural glasses

Bead-spring polymer:





Binary LJ mixture:

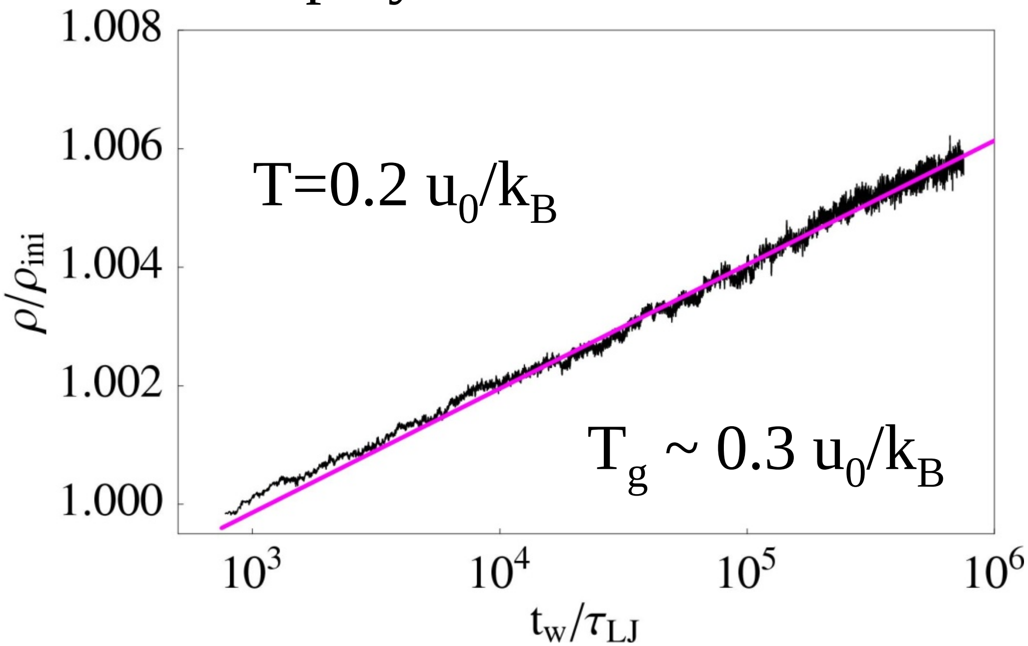


- Lennard-Jones (LJ) potential $V_{LJ} \rightarrow$ van der Waals interaction, energy $u_0 \sim$ meV, length d ~ nm, time ~ ps

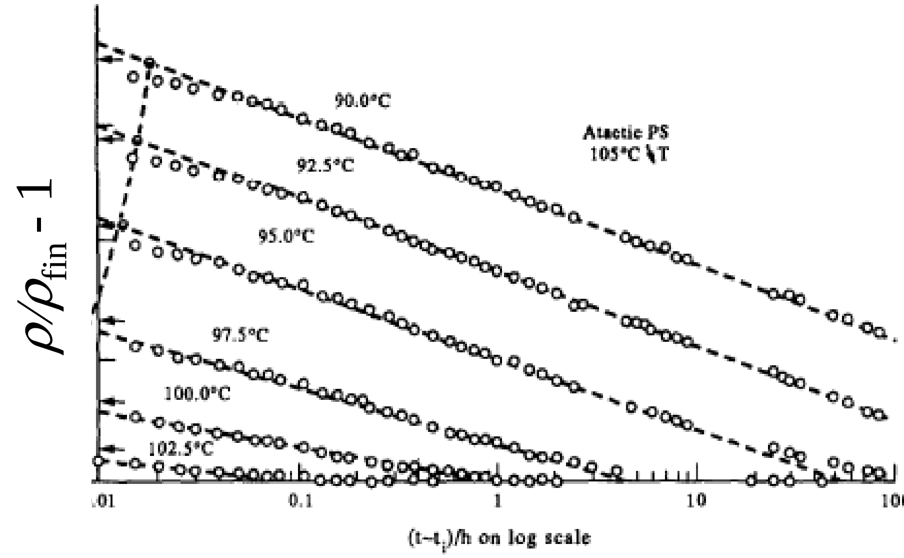
- Covalent bonds, 2 different sphere sizes prevent crystallization
  → computer glass transition to amorphous solid

Aging of thermodynamic variables

polymer simulation



atactic polystyrene

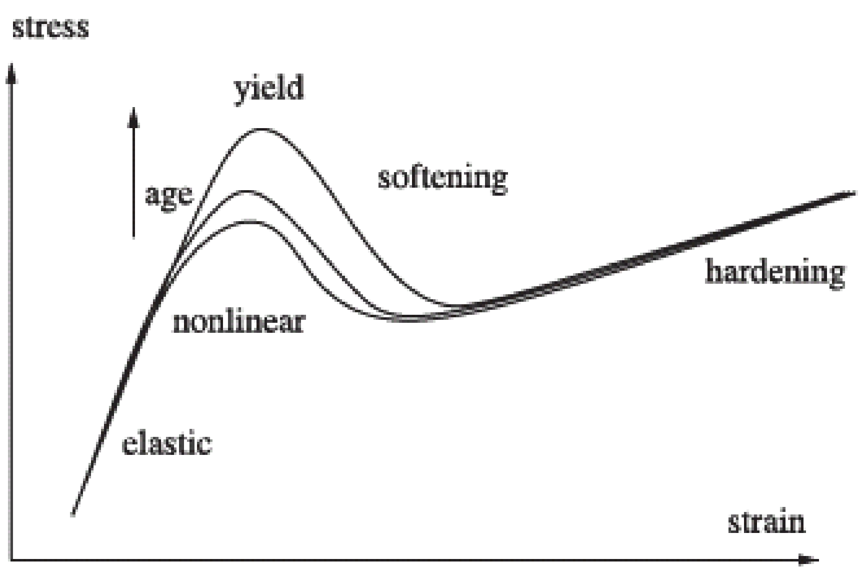


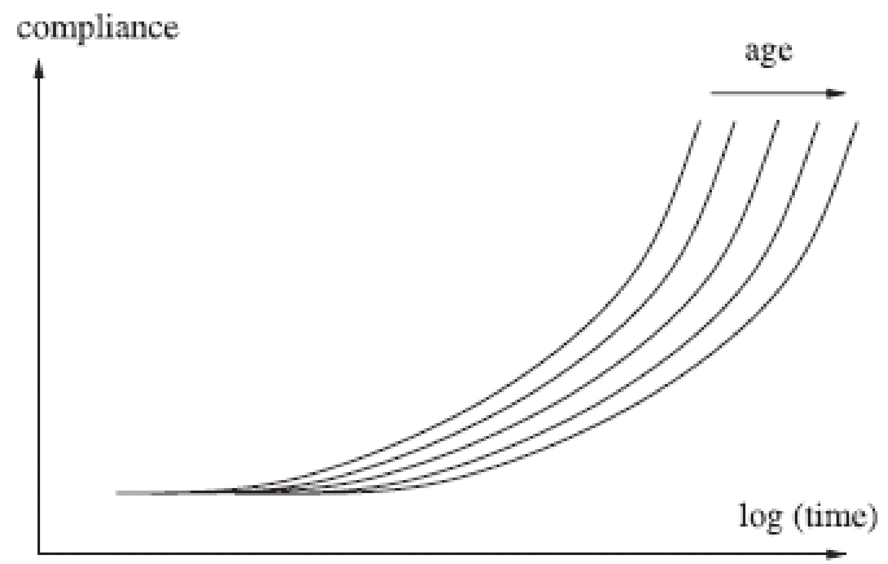
J. Hutchinson, Prog. Poly. Sci. (1995)

- Glass compactifies logarithmically in absence of deformation when maintaining zero hydrostatic pressure
- physical aging rate $r_v = -\frac{1}{V_0}\frac{dV}{d\log t}$

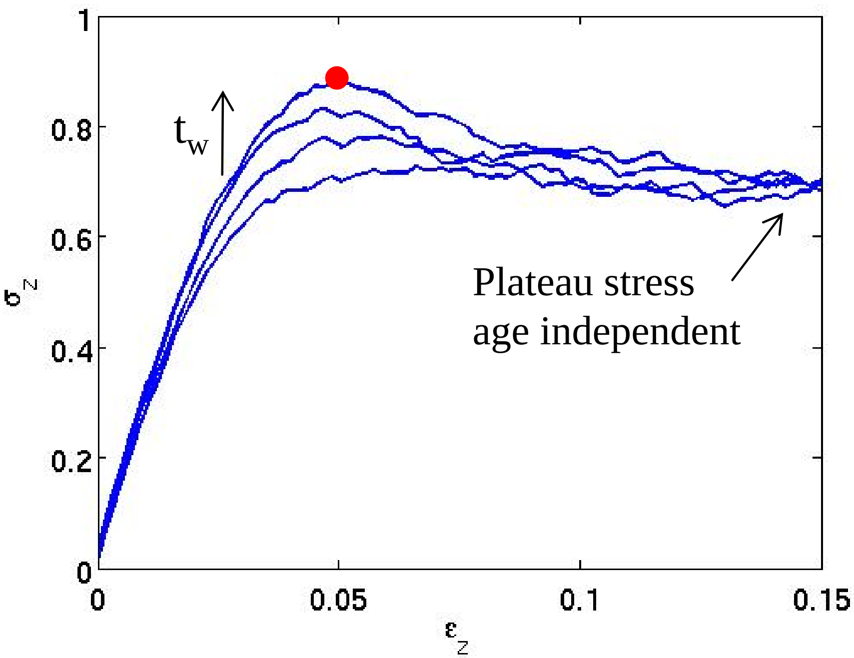
Physical aging and mechanical properties

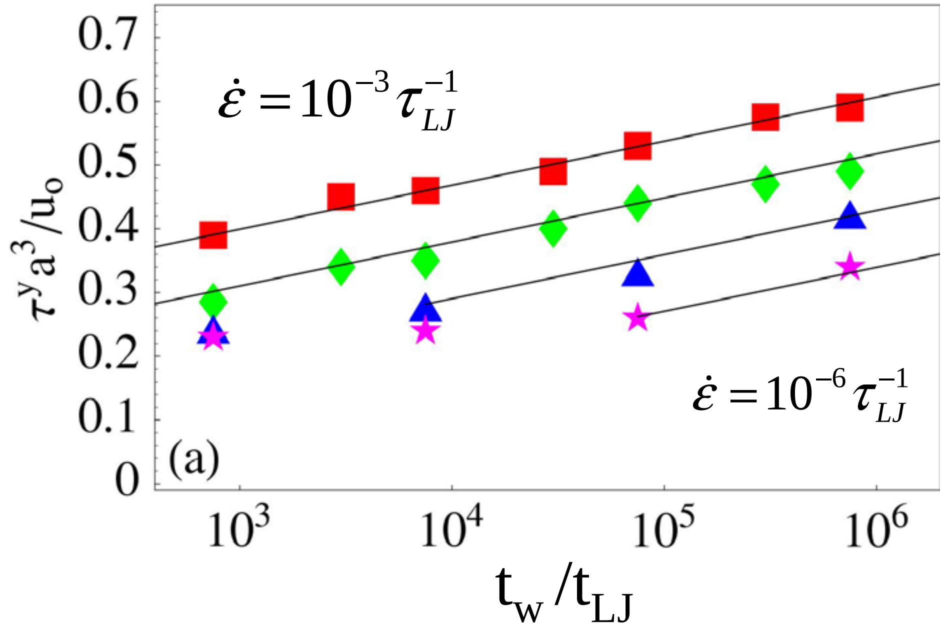
- Almost all polymer glasses undergo slow structural relaxations in the glassy state
- density, enthalpy change with waiting time elapsed since the glass was formed
- mechanical properties change with age: compliance decreases, yield stress increases

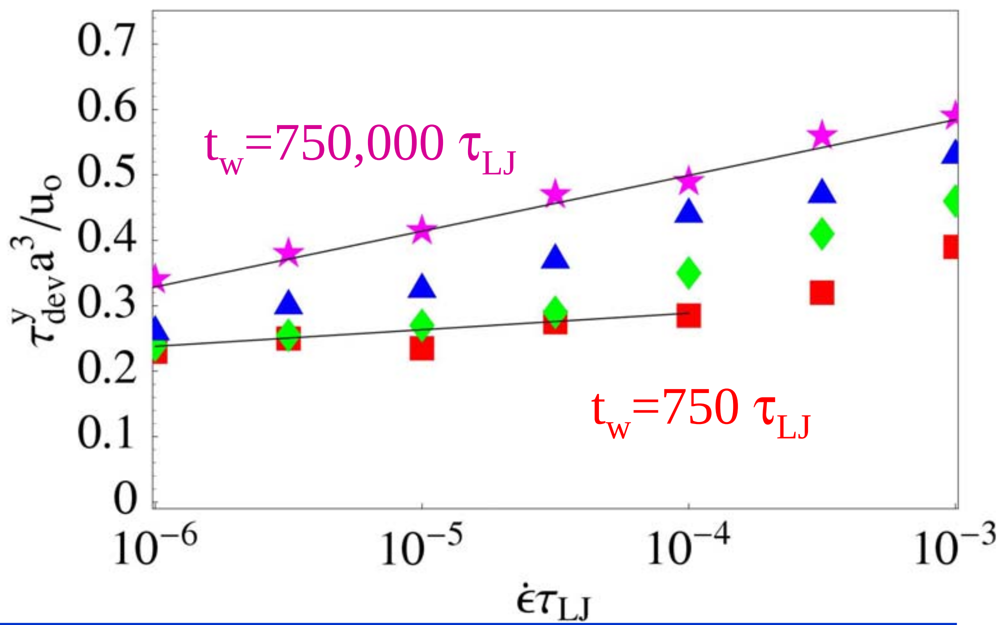




Yield (overshoot) stress





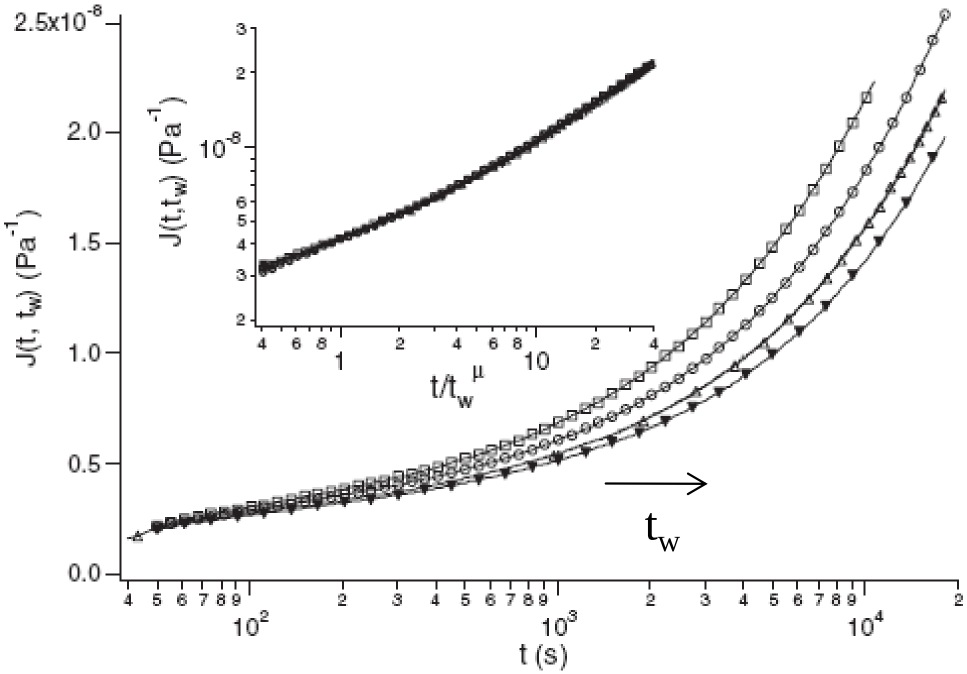


- Age for t_w after down-quench, deform at constant strain rate

Overshoot stress

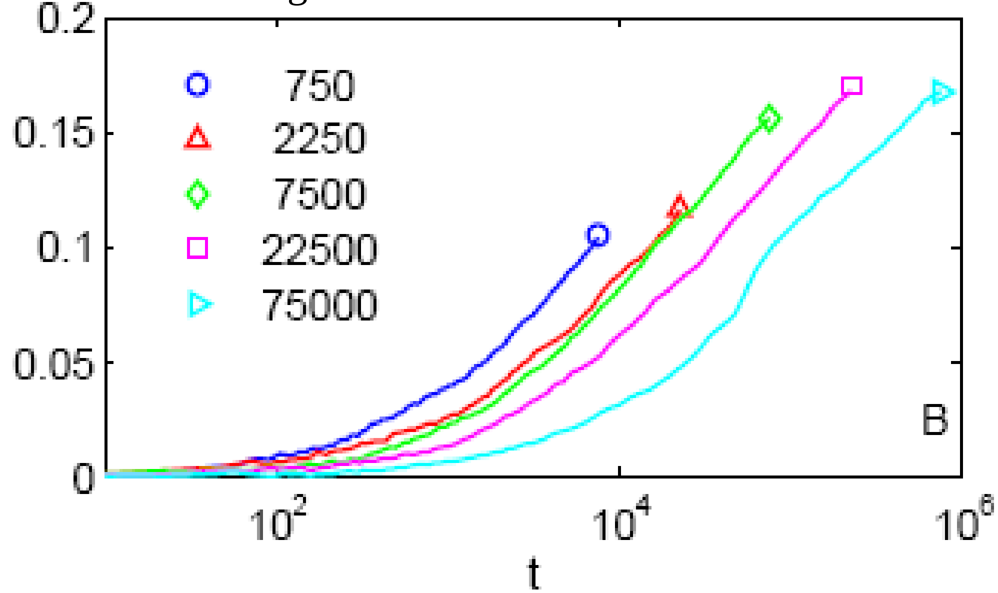
- grows ~ log (t_w)
- grows ~ log (strain rate)

Creep compliance



Montes et al, J. Stat. Mech., P03003 (2006)

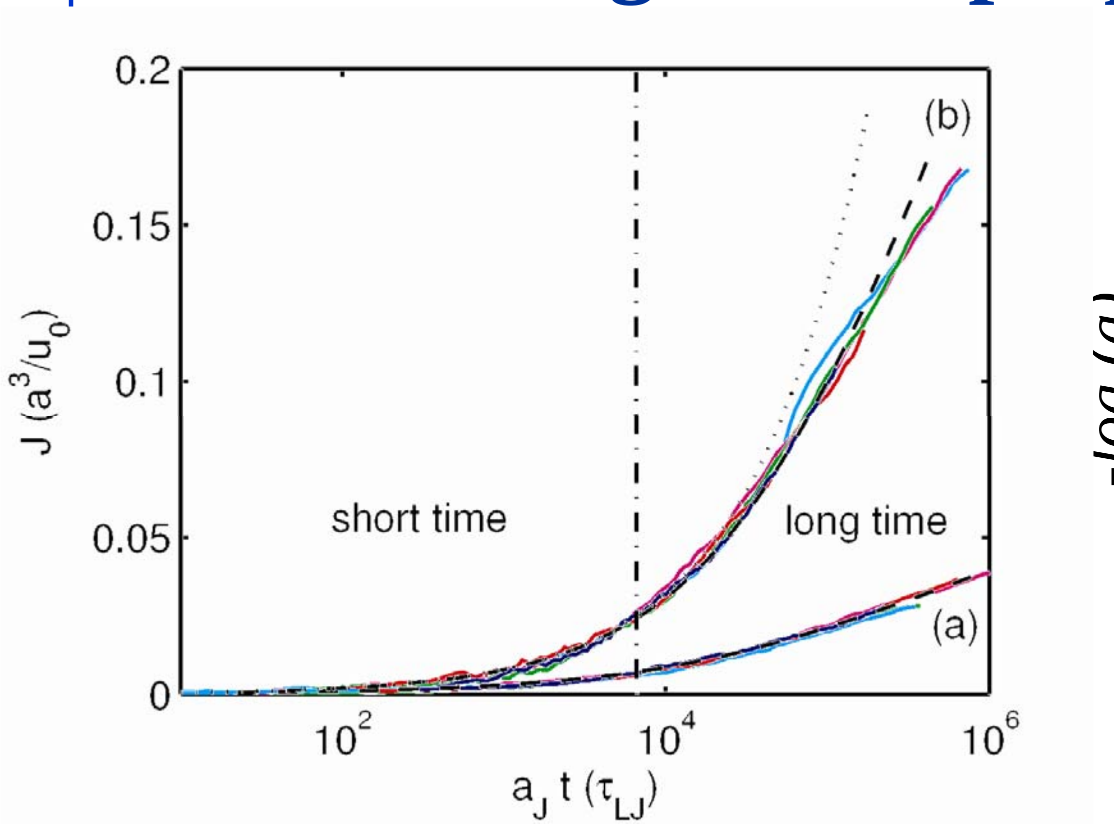
From molecular dynamics:



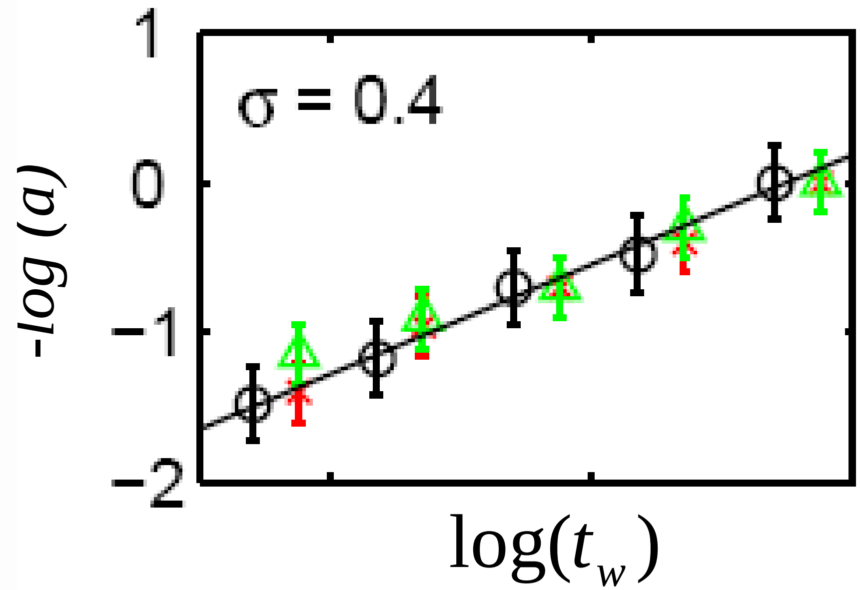
Warren and JR, PR E **76**, 031802 (2007)

- Age for t_w after simple down quench.
- Apply constant load, measure time-dependent strain → $J(t,t_w)=\varepsilon(t,t_w)/\sigma$
- Compliance shifts to longer times with increasing t_w, → polymer stiffens

Time-waiting time superposition



Shift factor vs waiting time:



$a_J : t_w^{-m}$

- As in experiments, compliance curves overlap after shifting time by $a_J(t_w)$

aging exponent μ=μ(T,σ) < 1:
→subaging

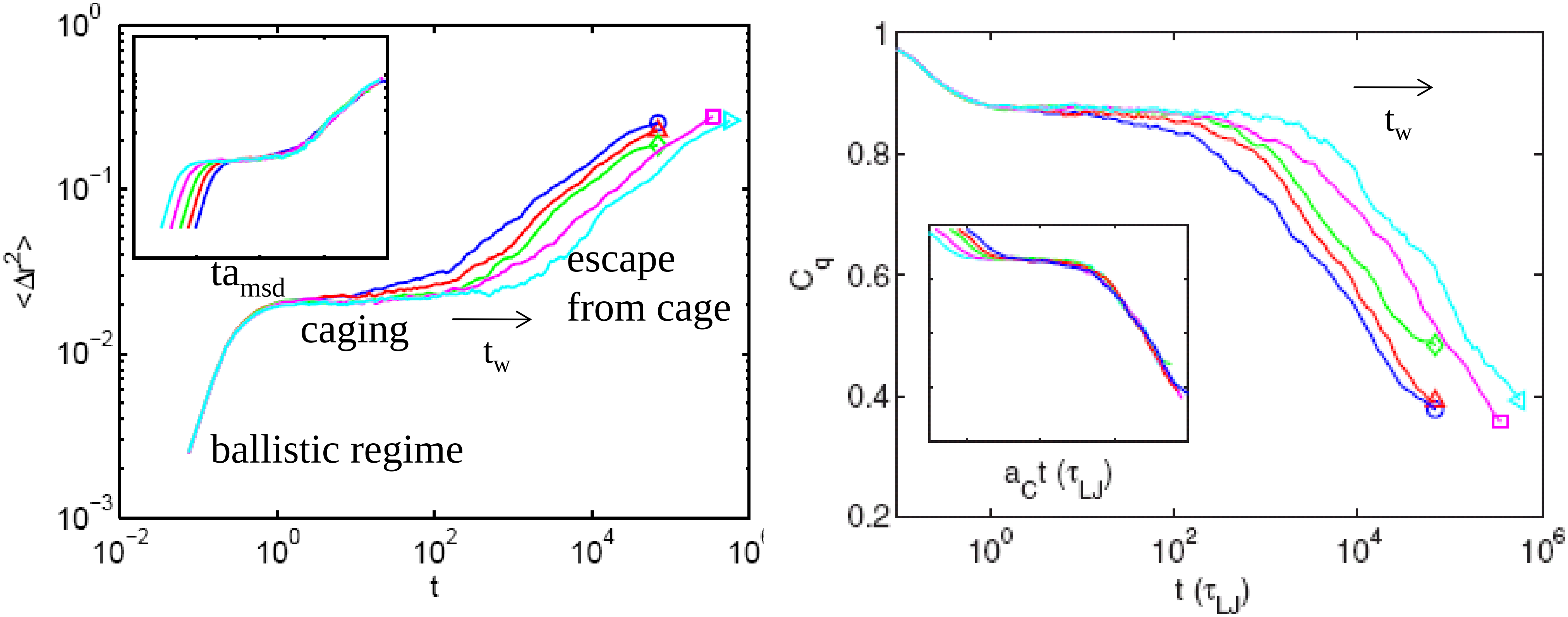
- μ(T) from microscopic theory (segmental hopping):

Chen & Schweizer PRL **98**, 167802 (2007)

Molecular mobility controls mechanical response

- the mechanical shift factor $a_J(t_w)$ is related to atomic mobility

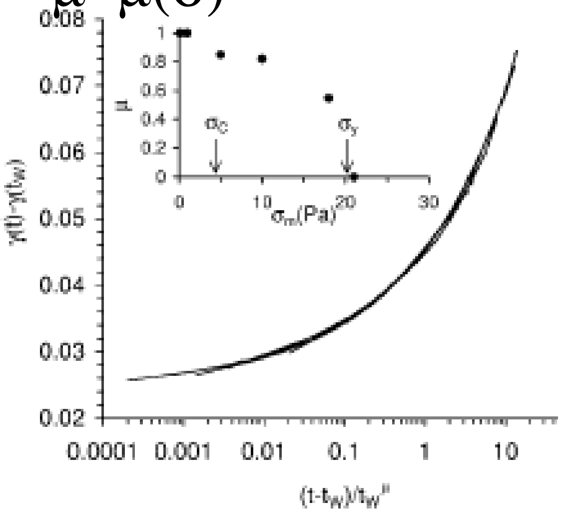
mean-squared displacement　　　　intermediate scattering function



- time to escape from local cages increases with t_w; superposition by shifting with factor a_{msd} We find: $a_{msd} \sim a_C \sim a_J$

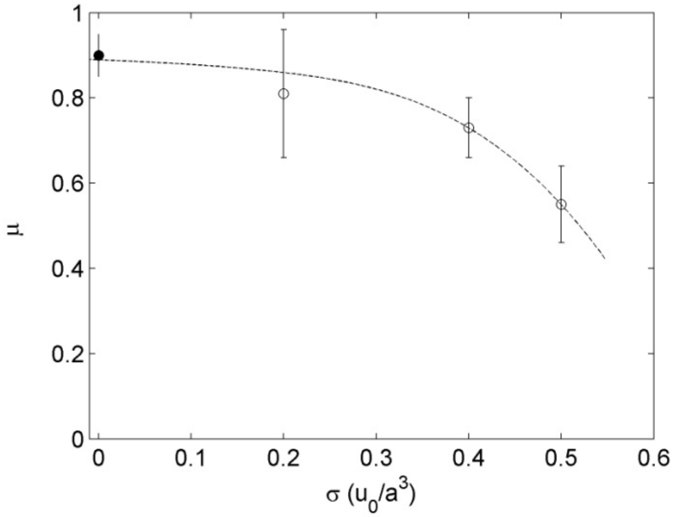
Aging and rejuvenation

- Age for t_w, then apply stress σ and measure aging exponent $\mu=\mu(\sigma)$



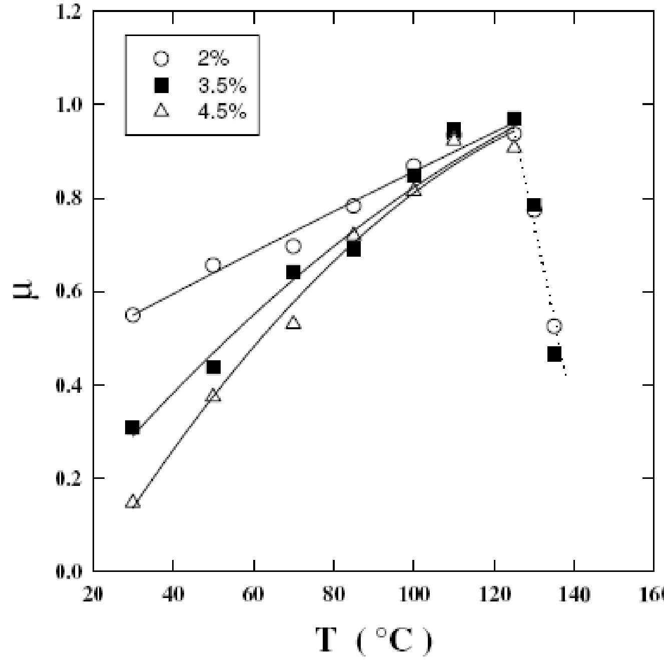
microgel paste

Cloitre et al., PRL (2000)



polymer simulation

Warren and JR, PR E **76**, 031802 (2007)



polycarbonate

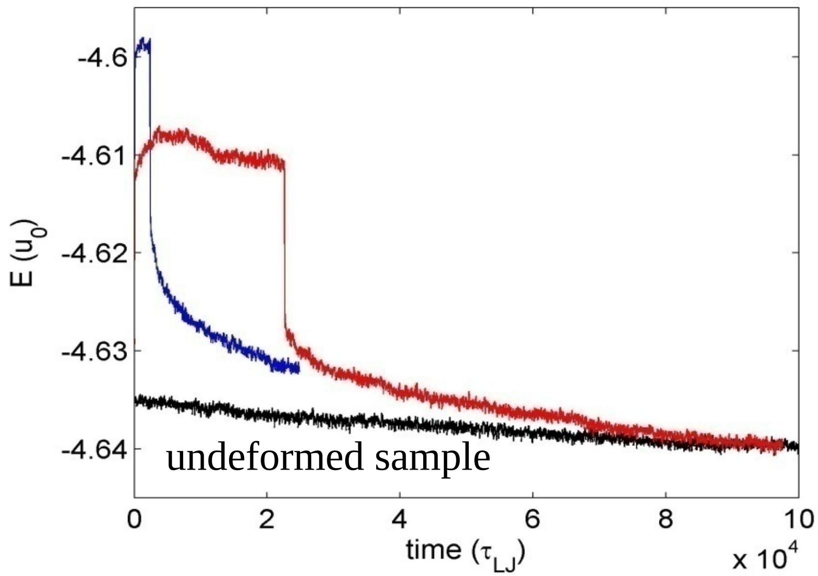
McKenna, J. Phys Condens Mat. (2003)

- μ decreases, relaxation times increase more slowly:
  → system "looks younger" at larger stresses: mechanical rejuvenation?

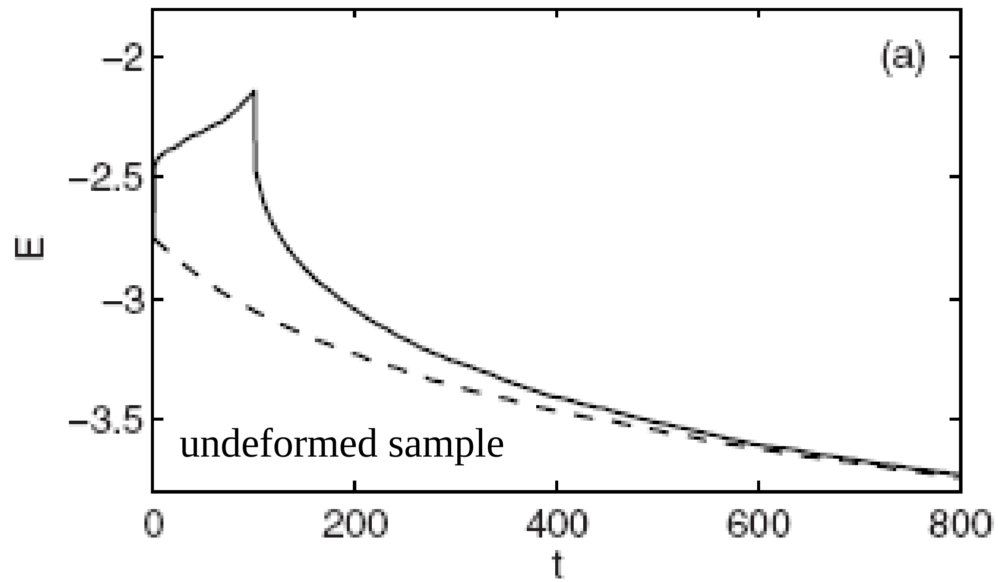
Aging and rejuvenation

- Compare relaxation of unstressed and rejuvenated sample
- Energy of rejuvenated sample decreases faster after stress release

Molecular dynamics

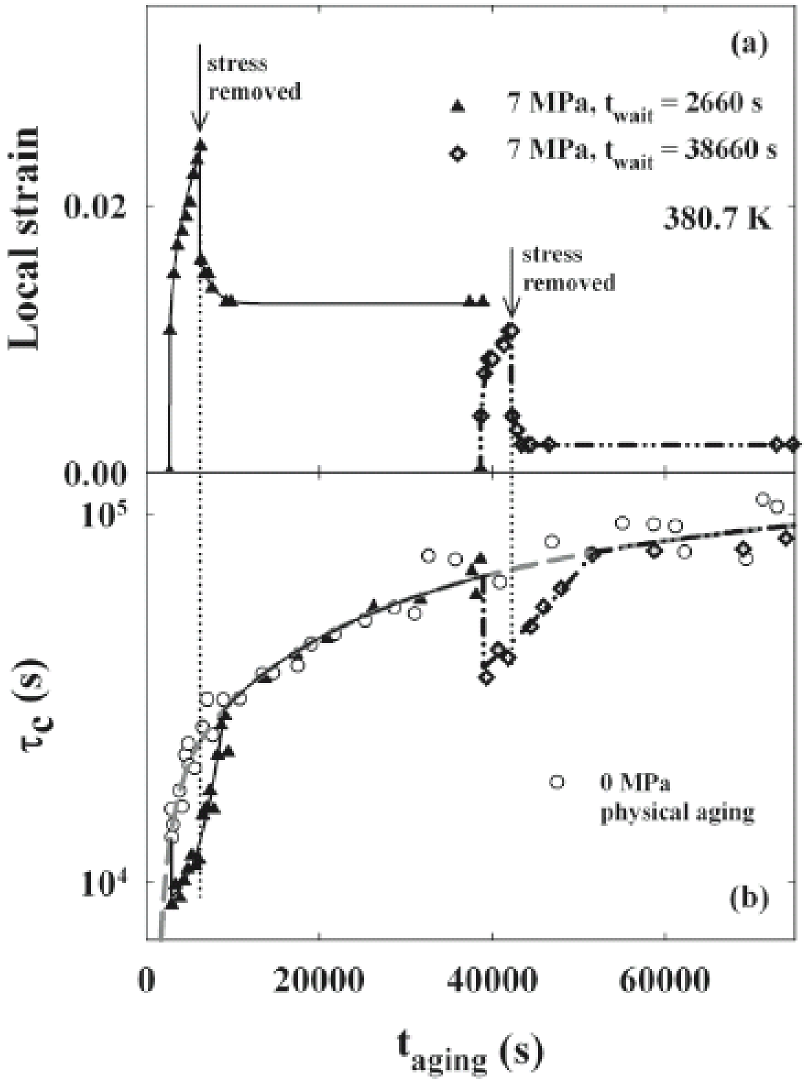


Soft glassy rheology (SGR)



- But the time to reach equilibrium is unchanged!
  Is the system really “rejuvenated”?
- Emerging picture: small (subyield) stress only lead to transient acceleration of dynamics, full erasure only after plastic flow.

Experiments on PMMA

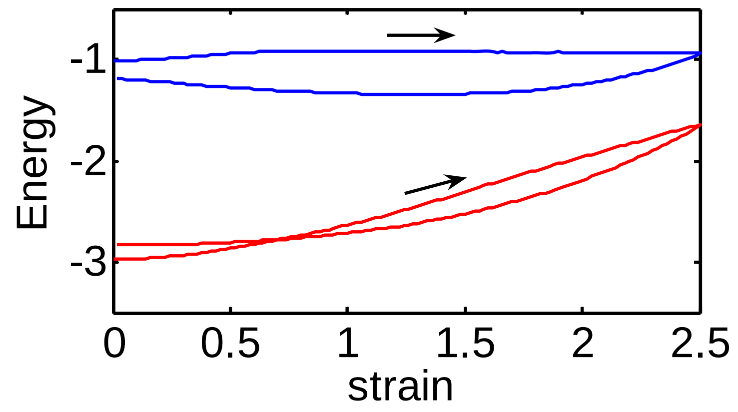


Lee and Ediger (submitted)

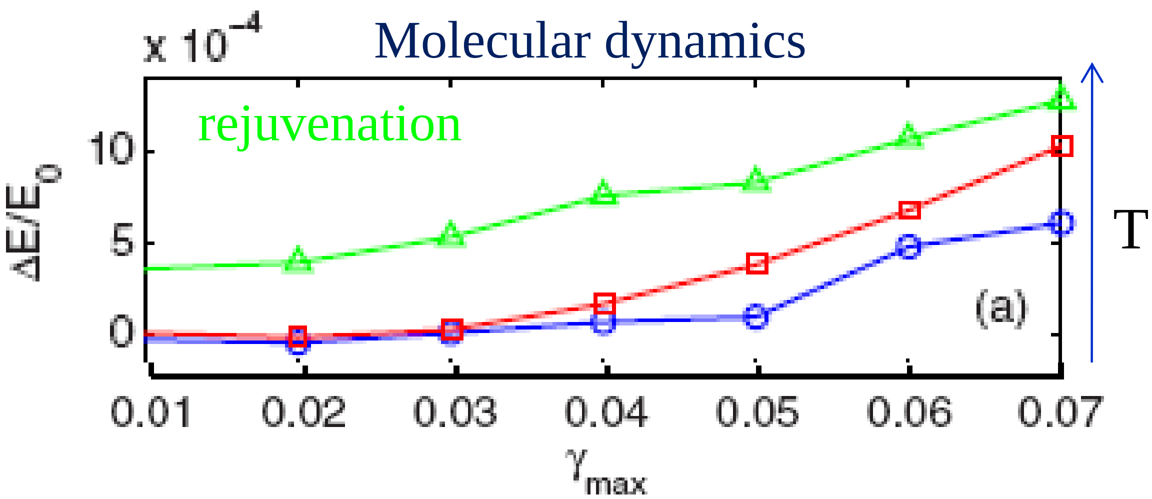
- direct measurement of segmental relaxation via local probe molecules
- extract relaxation times from decay of autocorrelation function
- stresses in the pre-flow regime perturb the aging dynamics only transiently

Rejuvenation in a strain cycle

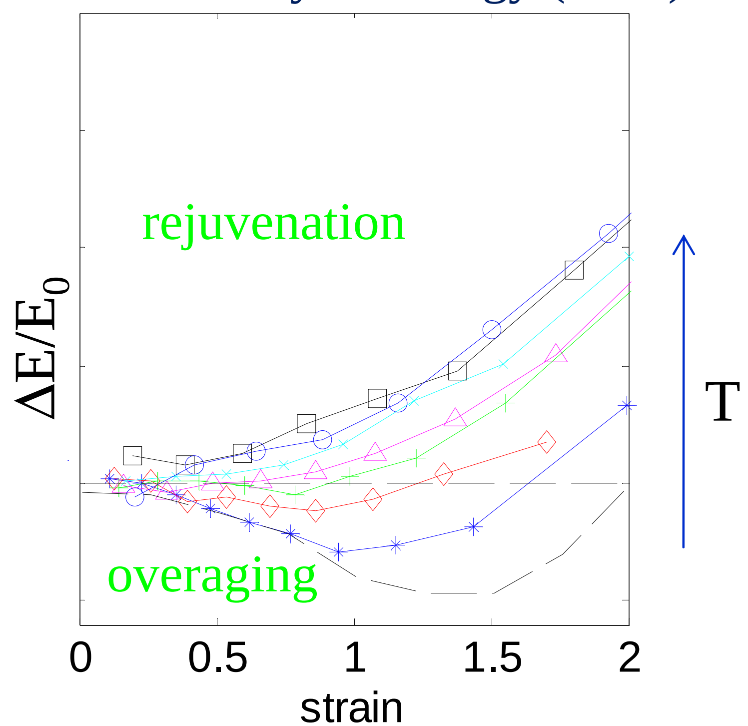
- Cycle strain, record energy after unloading
- Find regions of increased (rejuvenated) and decreased (overaged) energy states
- Within SGR model, find regime of overaging for low noise temperature and small strains



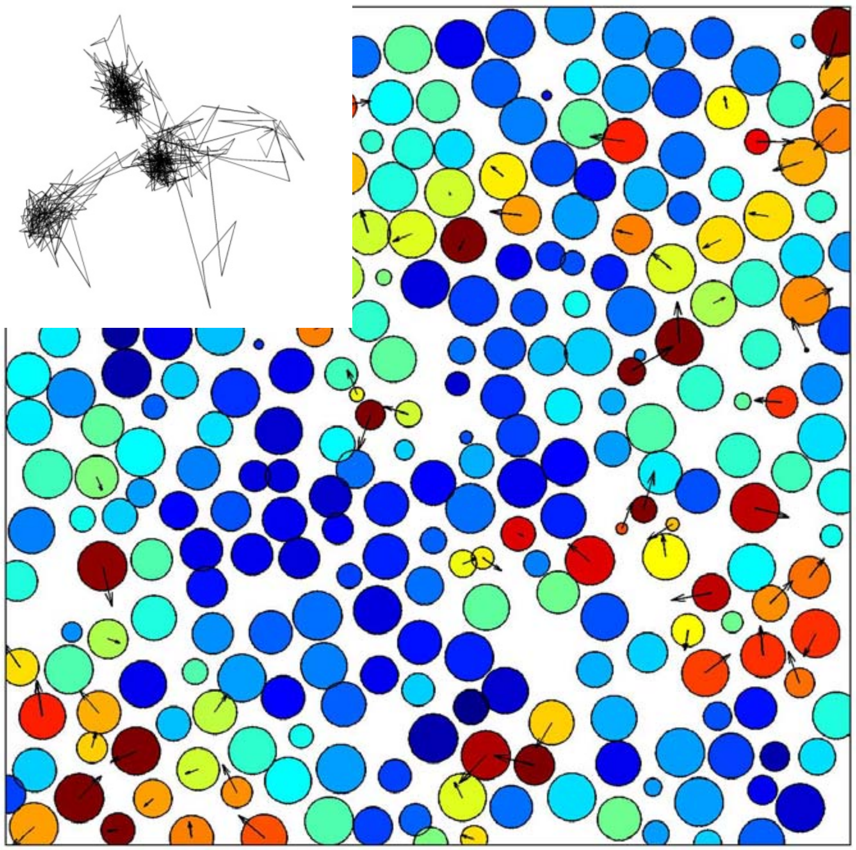
Soft Glassy Rheology (SGR)



Warren and JR, PR E **78**, 041502 (2008)

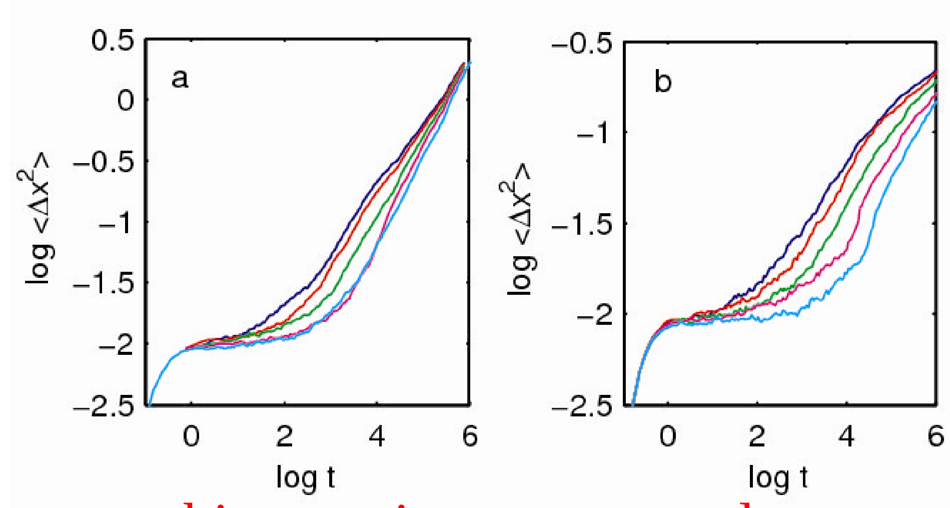


Atomistic features of glassy dynamics



2D slice through a polymer glass

Red = highly mobile
Blue = immobile



binary mixture polymer

- Structural relaxations are
  - Collective
  - Spatially heterogeneous
  - Temporally intermittent
- Trajectories are well described as a series of hops between long lived caged states

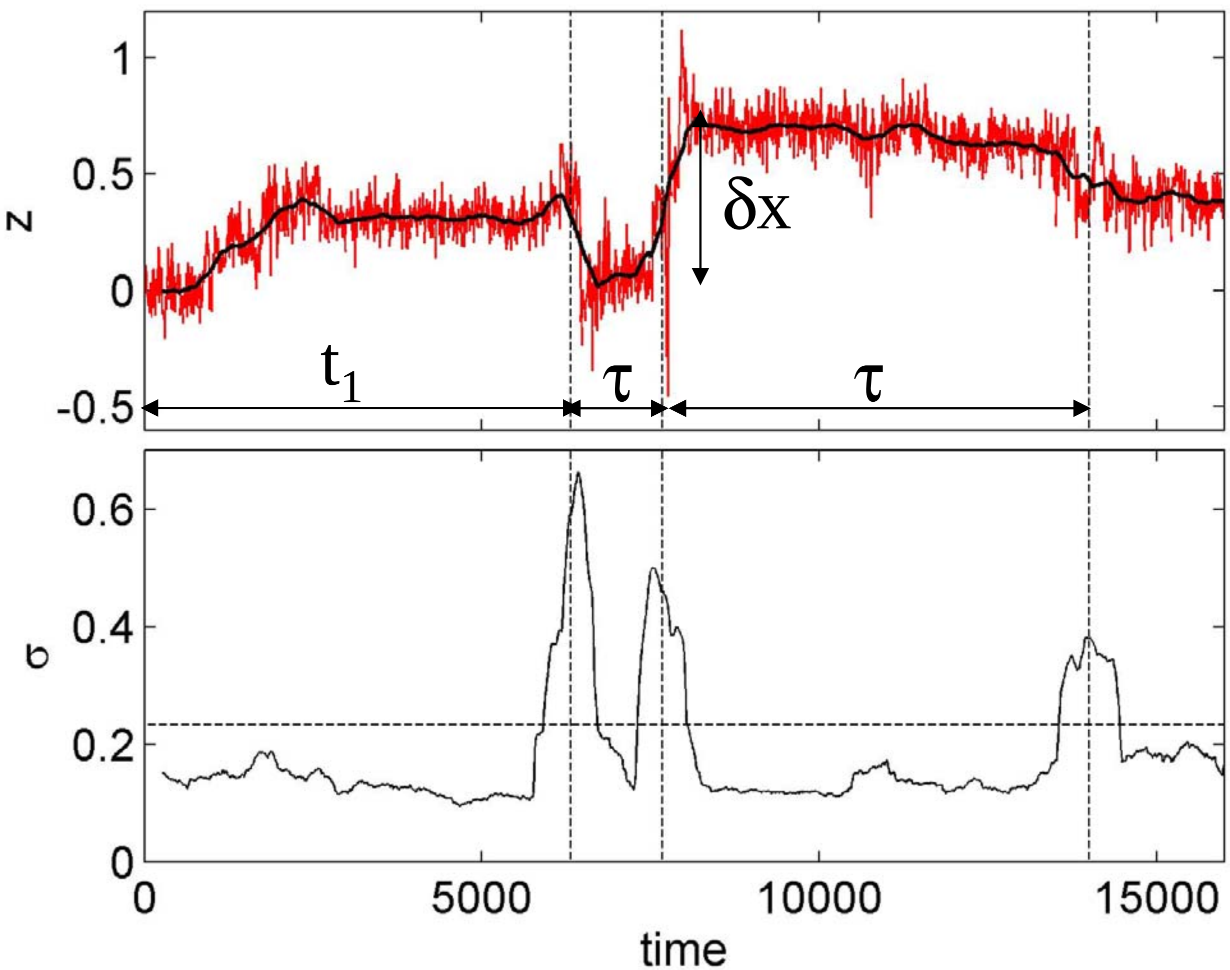
Analysis of particle (segmental) trajectories

Record particle trajectories

Calculate running average and standard deviation σ

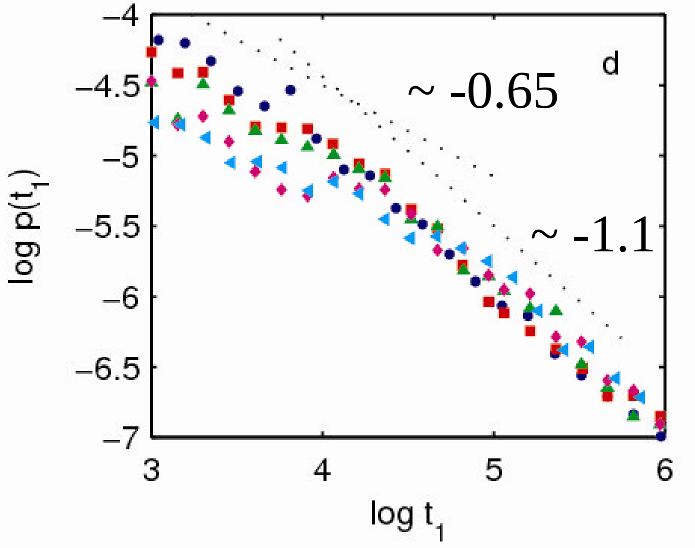
Hops identified through a threshold in σ, i.e. through their activity

Find hop times and displacements



Hop times and displacements – polymer glass

First hop time



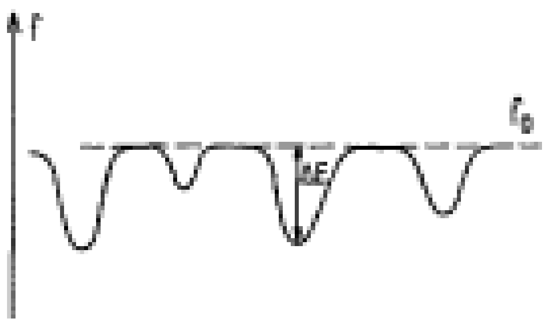
- Age-dependent
- Two power laws, tail moves to longer times with increasing age, likelihood of small t_1 decreases

- Persistent times and displacements age-independent
- Pure power law for persistent time
- As in trap model of glassy dynamics: trap energies redrawn from stationary potential energy landscape

Warren and JR, EPL (2009)

Aging in an energy landscape picture

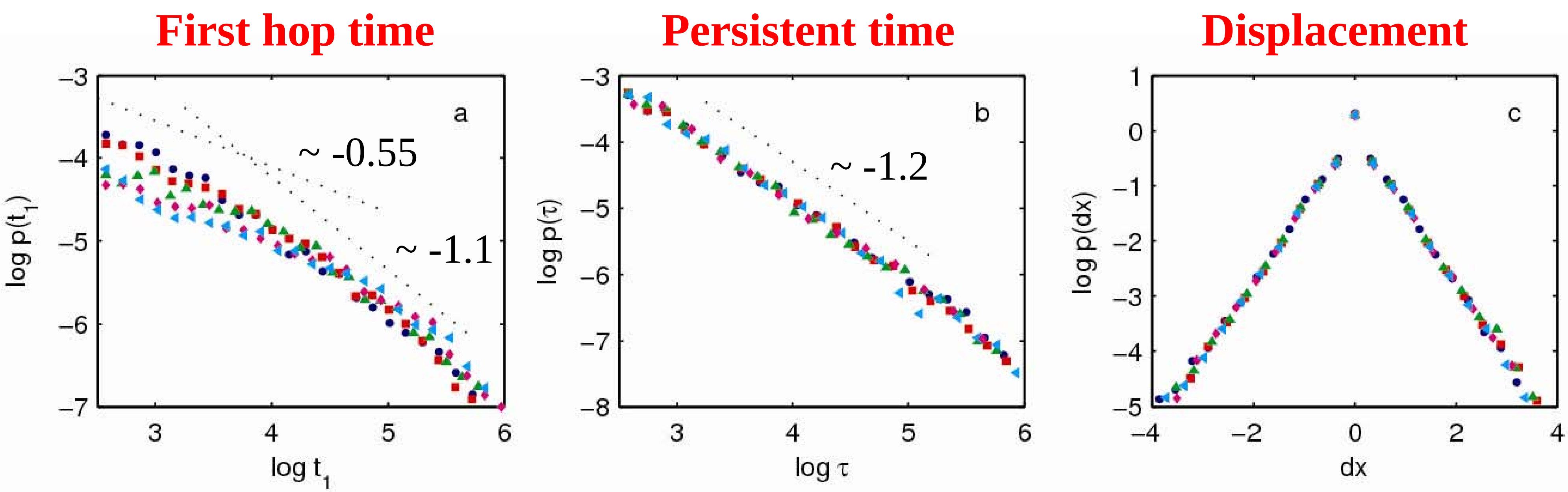
- Consider activated hops in a random energy landscape:
- Escape rate: $w \sim \exp[-\beta E]$
- Distribution of trap depths: $\rho(E) \sim \exp[-\beta_g E]$
- Energy drawn anew after every jump (annealed disorder)



(Bouchaud 1992, Monthus and Bouchaud 1996)

- For $T < T_g$, the dynamics becomes nonstationary and "ages"
- System does not equilibrate due to the presence of very deep traps
- predicts distribution of trapping times $P(t) \propto t^{-(1+T/T_g)}$
- mean trapping time infinite → aging

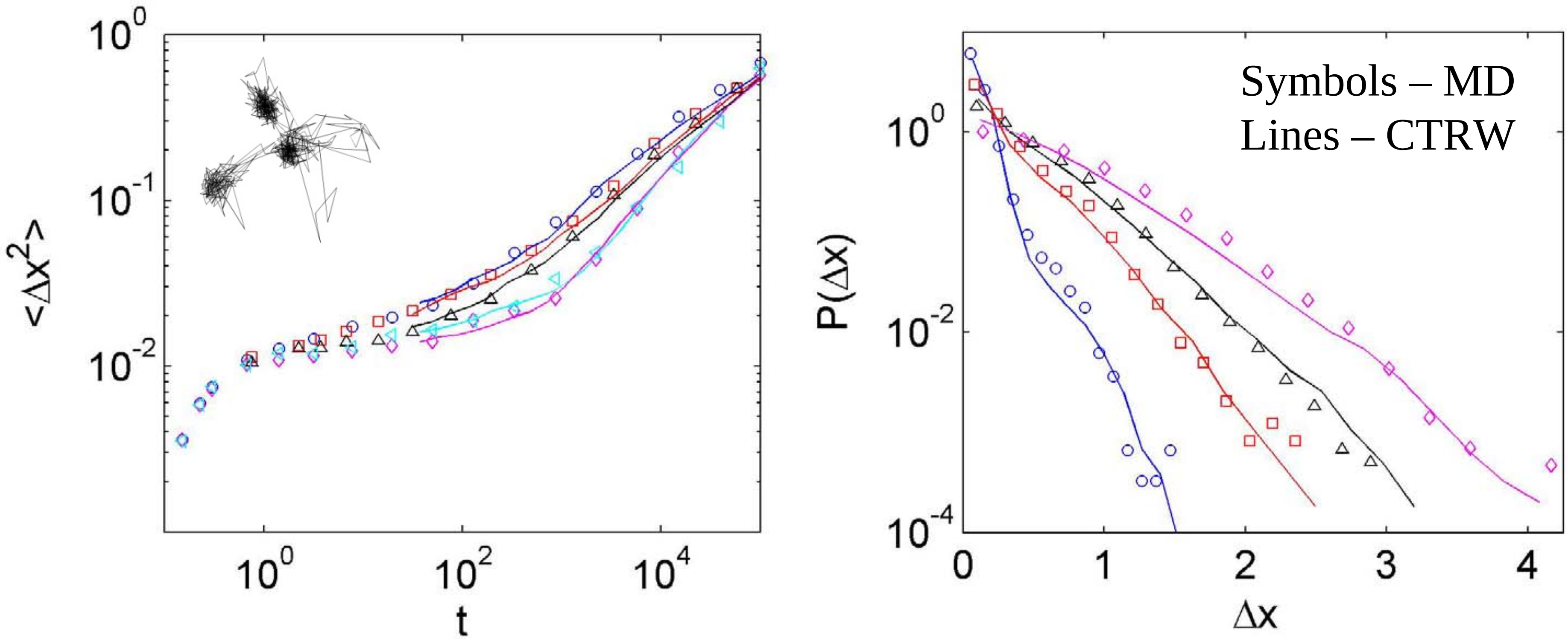
Hop times and displacements – binary mixture



- Hop time and persistence time distributions unchanged
- Displacement distribution purely exponential, no Rouse regime

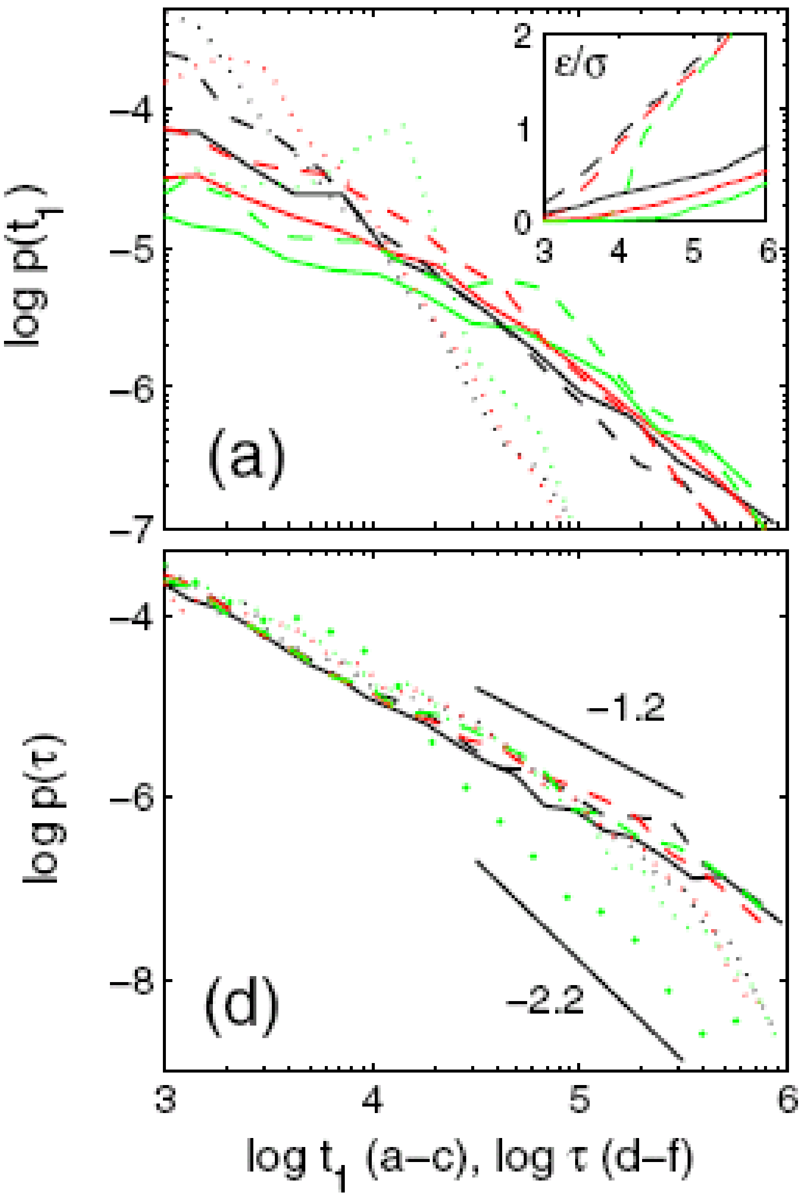
→ Findings are general for structural glasses, not polymer specific.

Continuous time random walk



- Particle dynamics are modeled using a continuous time random walk (CTRW) with measured hop statistics (no adjustable parameters).
- Aging is self-generating!
- All of the important physics has been captured

Accelerated dynamics: constant stress (creep)



• three different t_w and three stresses σ=0 (solid), σ=0.4 (dashed) and σ=0.5 (dotted)

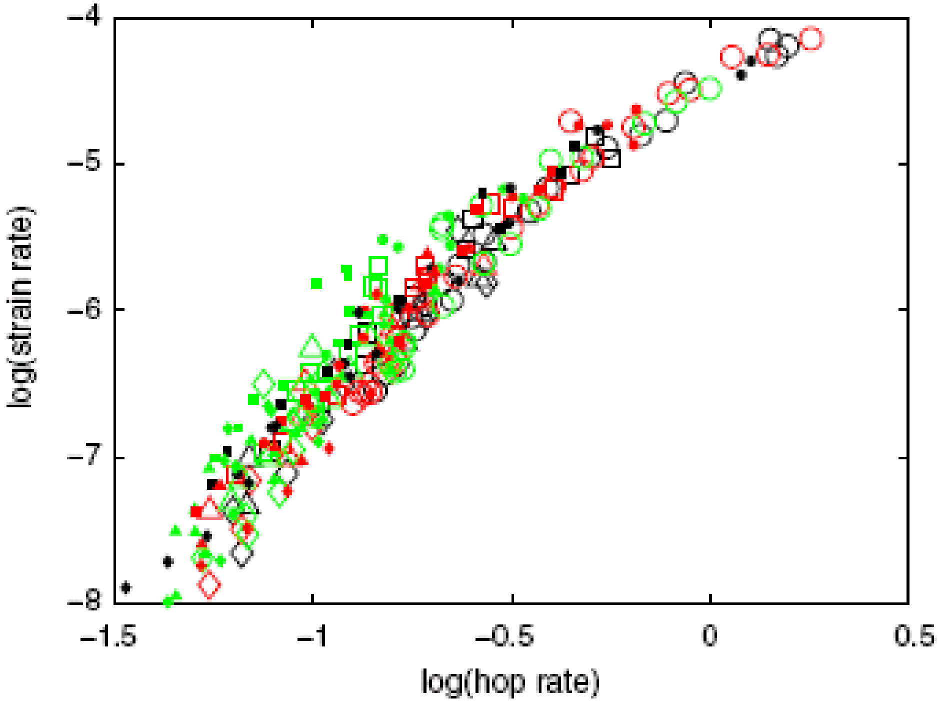
• first hop time dist. narrows with increasing stress, power law tail steepens (see expts. Ediger group)

• persistence time distribution modified for large times

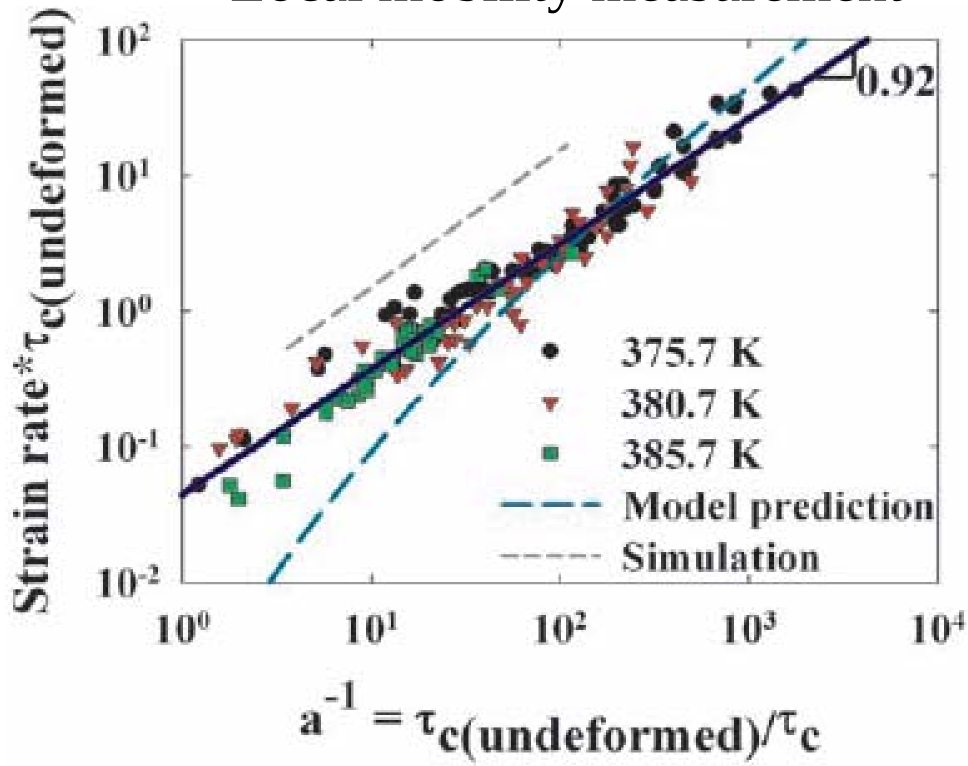
• power law exponent decreases below -2 → aging is stopped

Average hop rate and mobility

Simulation



Local mobility measurement



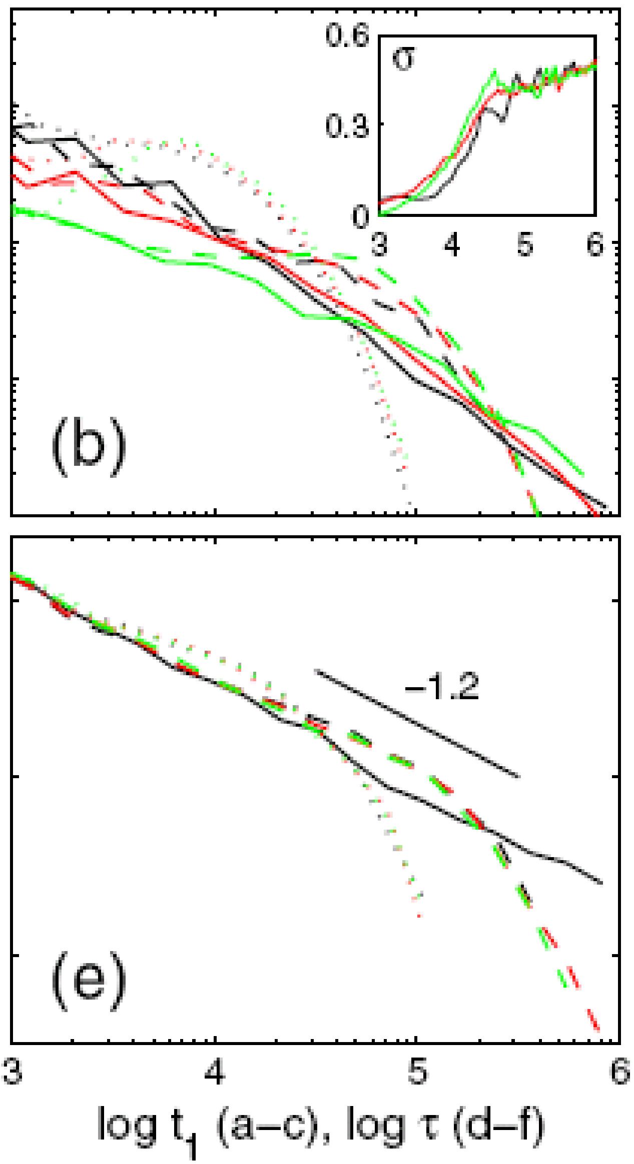
(Lee et al., Science (2009))

- strain rate is a universal function of hop rate

- data collapse for different stresses and ages

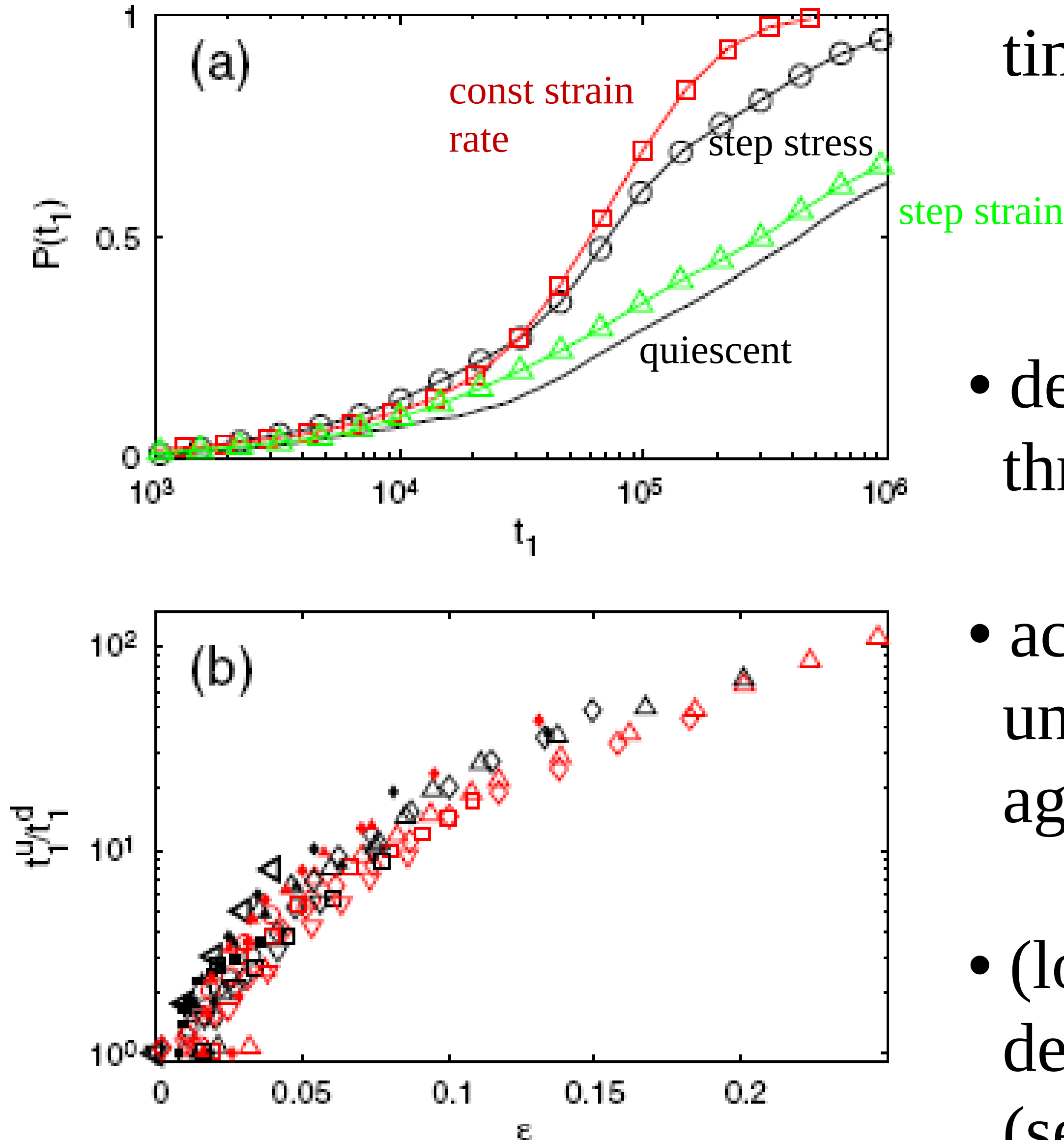
- qualitatively similar relationship observed in recent experiments

Accelerated dynamics: constant strain rate



- three different t_w and three strain rates $\dot{\varepsilon}$
- distributions "cut off" at times ~ $0.1/\dot{\varepsilon}$ but no change at small times
- aging stopped due to truncation of persistence time distribution

Acceleration ratio



Warren and JR, PRL (2010)

- describe transformation of hop time dists through cumulatives

$$P(t) = \int_0^t p(t_1)dt_1$$

- define an acceleration ratio through times when $P_u(t_1^u) = P_d(t_1^d)$

- acceleration ratio collapses onto universal curve when plotted against total strain

- (local) strain is good variable to describe accelerated dynamics (see also SGR model)

Summary

• Simulations reproduce mechanical behavior typical of glasses.
Slow relaxation (aging) changes yield stress and creep compliance.

• Molecular mobility controls mechanical response

• Reduction of aging exponent under subyield stress, but glass returns to original aging trajectory; erasure of aging only through plastic flow

• Robust picture of activated hopping dynamics with broad distribution of relaxation times
- only first hop time waiting time dependent
- particle/segment 'forgets' its age after one hop
- supports picture of annealed disorder as assumed in trap model

• Accelerated dynamics: narrowing of relaxation time spectrum
universal dependence of acceleration on strain

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