Theory of nonlinear creep under large deformation in polymer glasses

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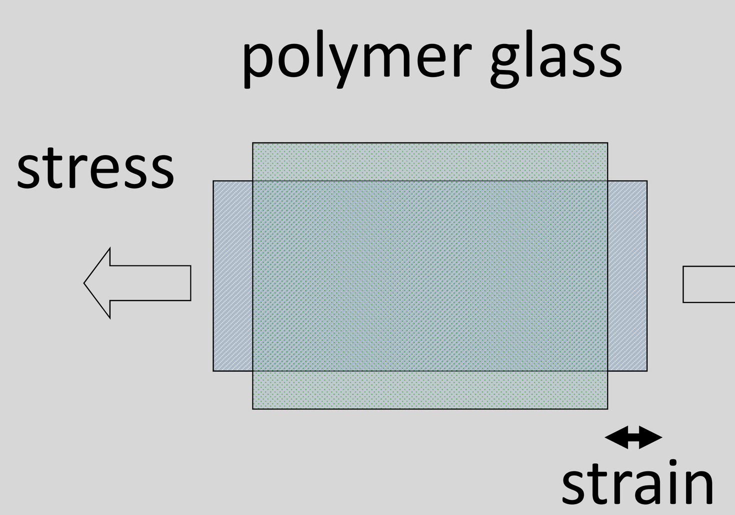
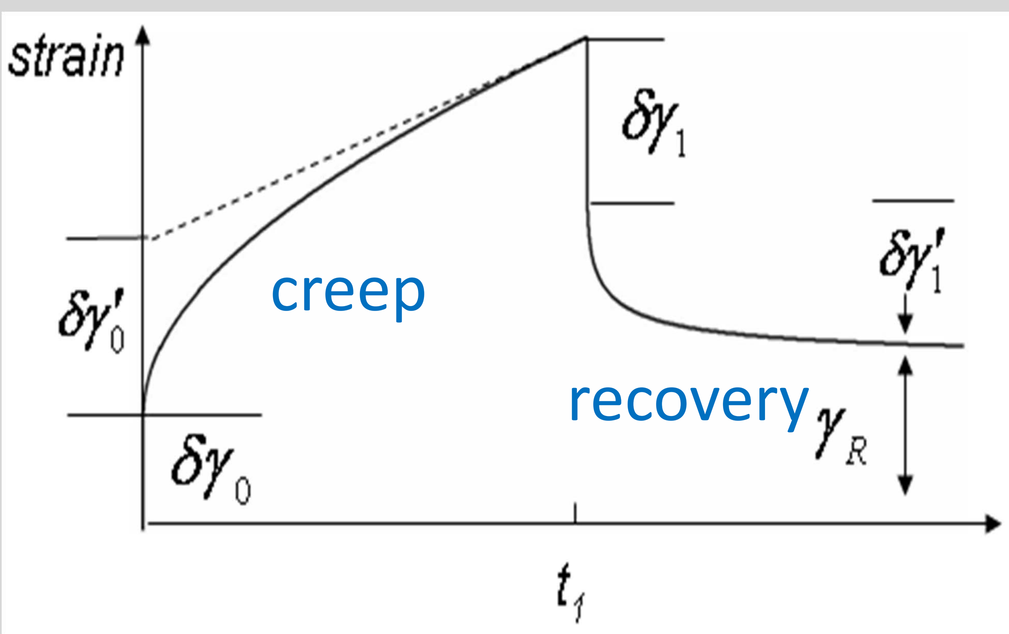
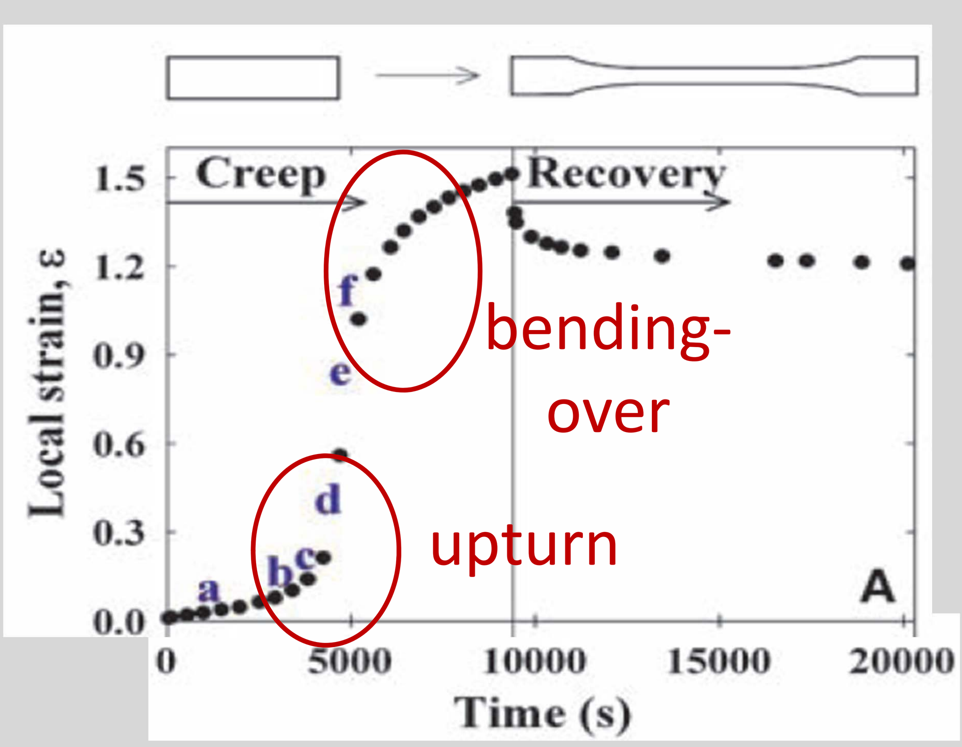
Goal



- Creep is defined by the time dependence of strain at constant stress



- At low stress, the typical ideal creep curve grows monotonically and gradually bends down approaching the steady flow state (constant strain rate) after an instantaneous jump

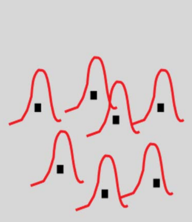


- But, at large stress and/or deformation, a dramatic upturn occurs, and followed by a bending-over at very large strain
  - What's the origin of the upturn and bending-over?
  - What causes the dynamics change during these processes?
  - How to model the creep response?

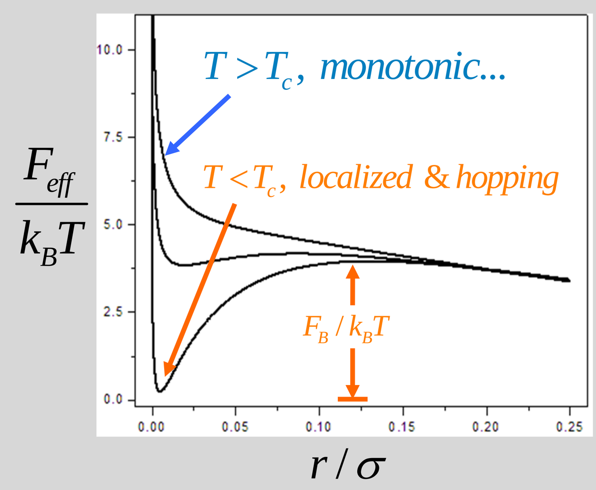
Microscopic theory of glassy dynamics

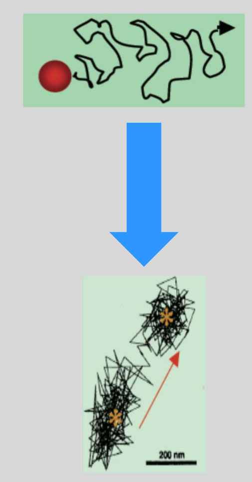
- Dynamical "free energy" for single-segment movement:

$$\zeta_s \frac{\partial r(t)}{\partial t} = -\frac{\partial}{\partial r} F_{eff}(r(t)) + \eta(t)$$



$$F_{eff}(r) = -3k_BT\ln(r) - k_BT\int \frac{d\vec{q}}{(2\pi)^3}\rho C^2(q)S(q)\left[1+S^{-1}(q)\right]^{-1} e^{-q^2r^2[1+S^{-1}(q)]/6}$$





- **State variable** under Gaussian thread model

$$S_0 = S(q=0)$$

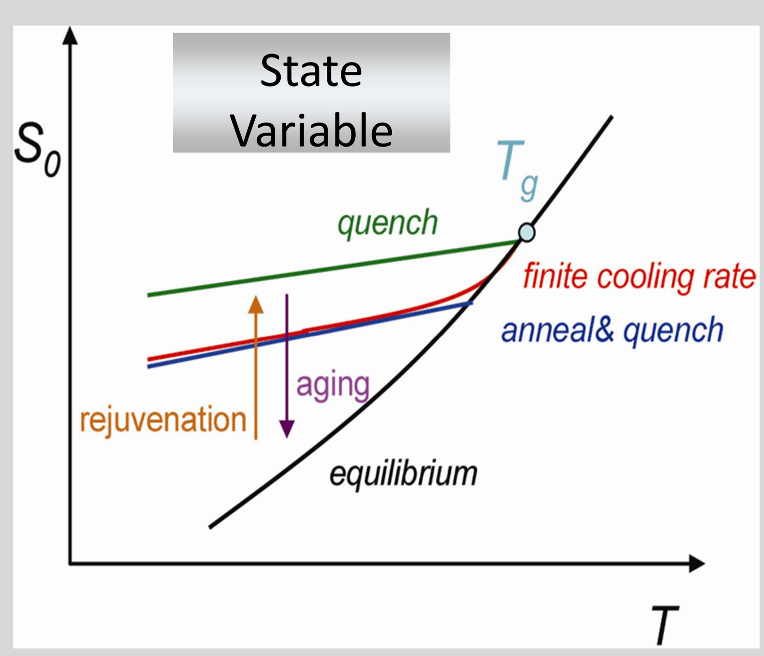
determines

Mechanical and Dynamical properties:

Elastic modulus: E'

Alpha relaxation time: $\tau_\alpha(T) = \tau_0(T)e^{a_c F_B/k_BT}$

Model of aging and rejuvenation



aging | rejuvenation

$$\frac{dS_0}{dt} = -\frac{S_0 - S_{0,l}}{\tau_\alpha(S_0,0)} + \psi(S_{0,g} - S_0)\cdot\tau\cdot\frac{\tau}{E'(S_0,\tau)\tau_\alpha(S_0,\tau)}$$

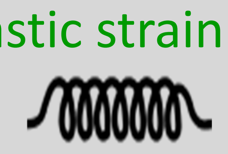
plastic strain rate

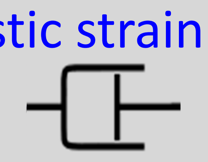
Constitutive equation of nonlinear mechanical response

- Generalized Maxwell Model:

$$\dot{\gamma} = \frac{d\tau}{dt}\frac{1}{E'(\tau)} + \frac{\tau}{E'(\tau)\tau_\alpha(\tau)}$$

elastic strain rate | plastic strain rate





- Nonexponential decay:

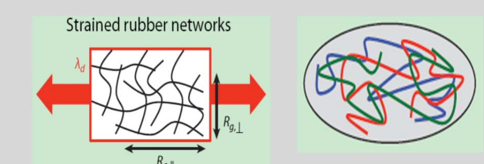
$$\tau(t) = \int_0^t dt' E'(\tau(t'))e^{-\left[\int_{t'}^t dt''\tau_\alpha^{-1}(\tau(t''))\right]^{\beta_K}}\dot{\gamma}(t')$$

β_K : related to heterogeneity

- Strain hardening at large deformation

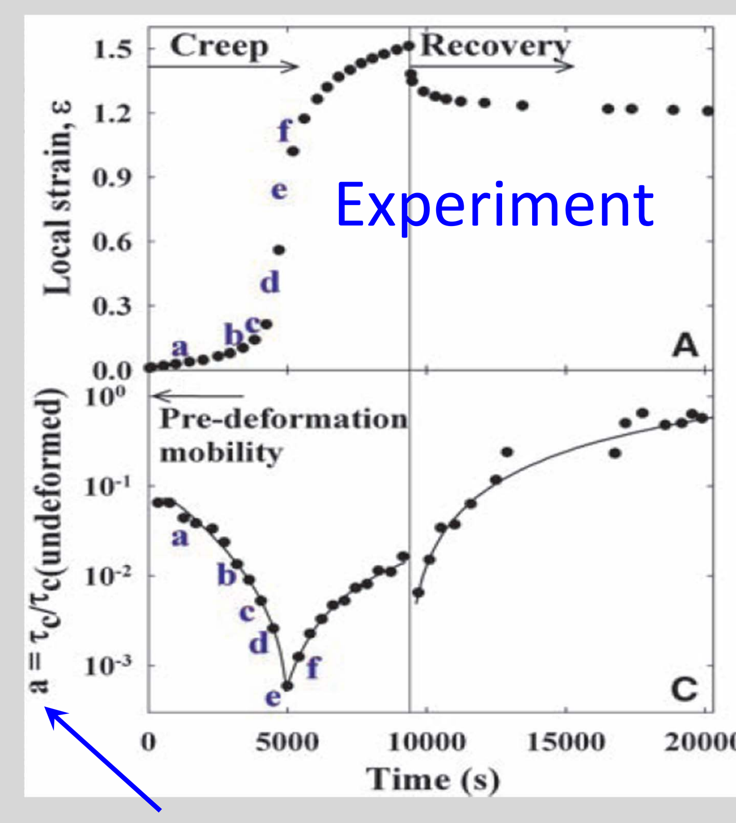
State variable decreases for stretched chain

$$\frac{S_{0,eff}}{S_0} \simeq \frac{1}{1+\sqrt{\frac{S_0}{N_x}}\frac{1}{4}(\lambda^2+\frac{2}{\lambda}-3)}$$

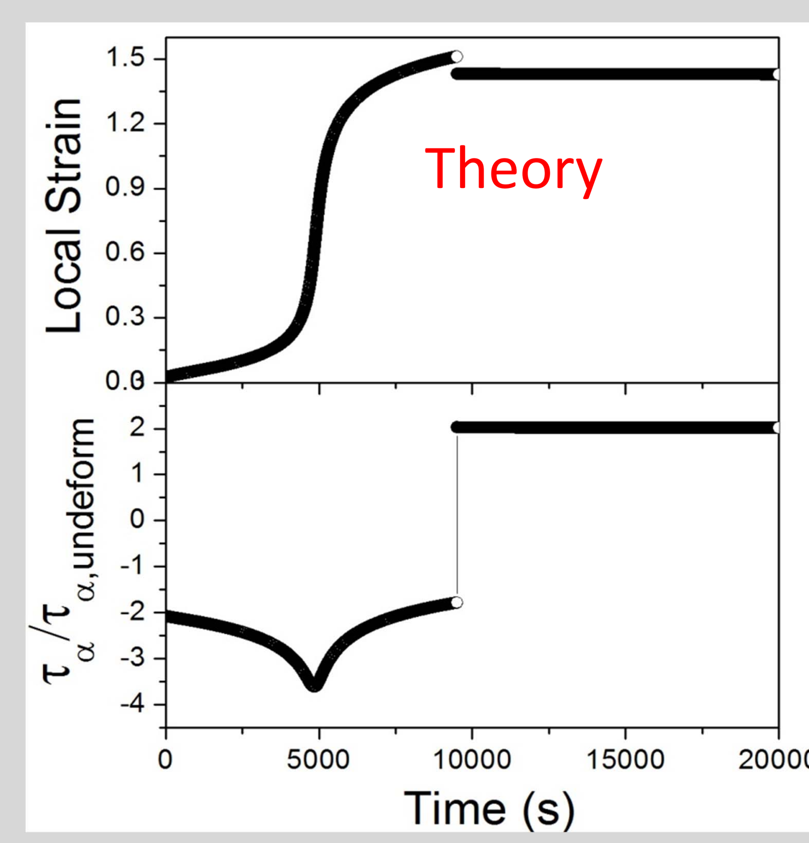


$$\lambda = e^\gamma$$

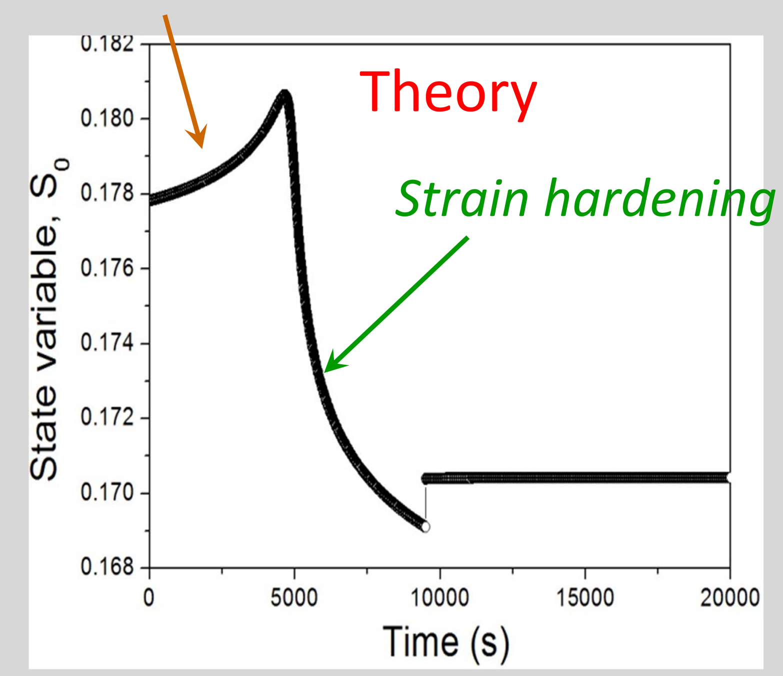
Results: Creep at large stress



Shift factor (relaxation time)



rejuvenation



Conclusion

- The *upturn* behavior is caused by *rejuvenation* process.
- The *bending-over* happening at very large deformation is due to *strain hardening*.
- Strain response and relaxation time are well predicted except for the recovery process because of the lack of relaxation mechanism of stretched chain in the theory.