Entanglements and Mechanical Failure of Polymer Glasses

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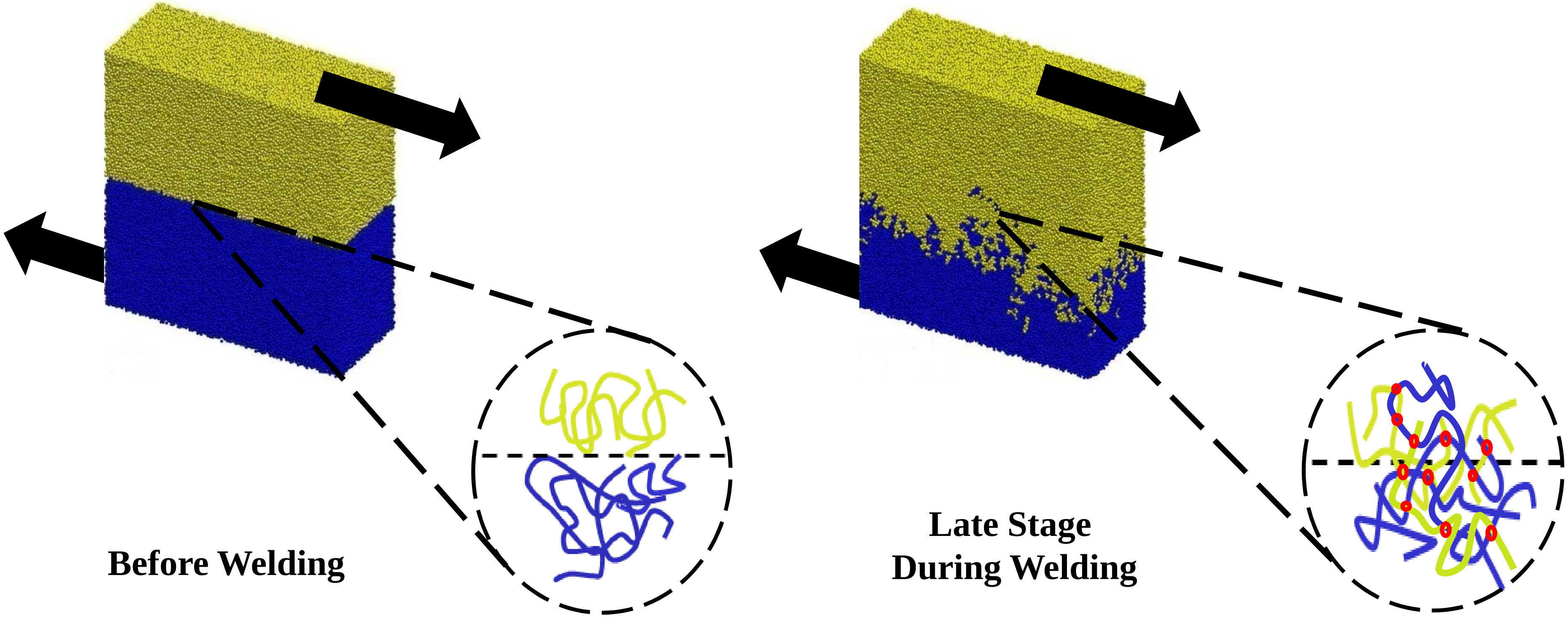
Development of Interfacial Strength and Entanglements During Welding of Polymers

How does the interfacial strength develop during welding?
How does the development correlate with
the evolution of interfacial structure?

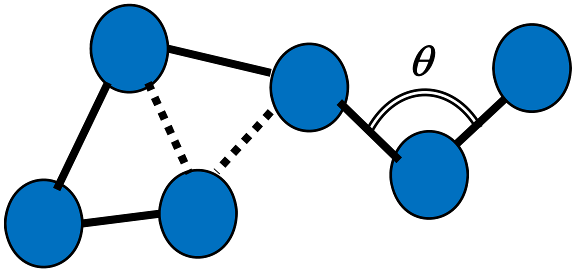


Before Welding

Late Stage
During Welding

Thermal welding is a common means to join polymer parts together and integrate polymers into effective device.

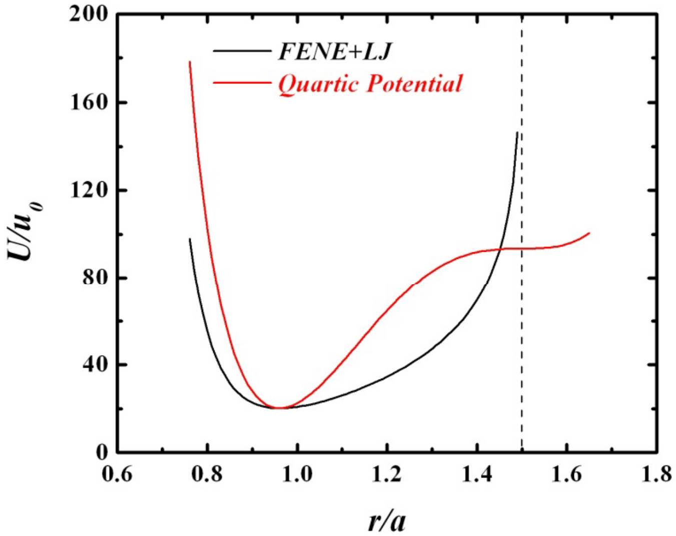
Coarse-grained Bead-Spring Model of Polymers

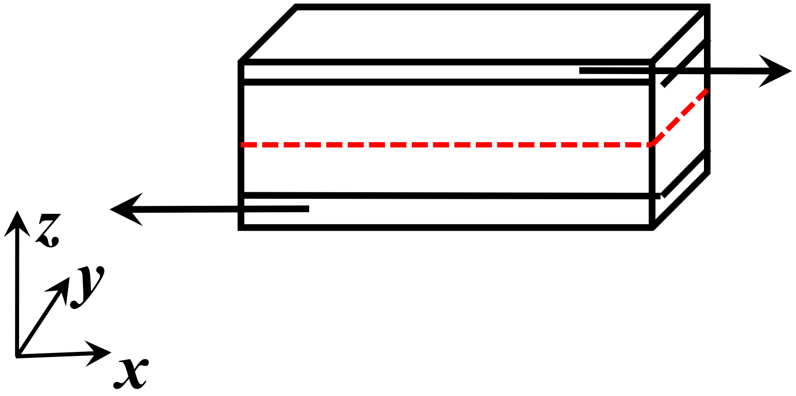


- Neighboring beads along the chain are connected via finitely extensible nonlinear elastic (FENE) potential *(Kremer& Grest, 1990)*
  - —— $U_{FENE} = -0.5kR_0^2 \ln[1-(r/R_0)^2]$

  or breakable quartic bond potential
  - —— $U_{Quartic} = K(r-R_0)^3(r-R_1)$
- All beads interact via *Lennard-Jones* (LJ) potential
  - - - - - $U_{LJ} = 4u_0[(a/r)^{12}-(a/r)^6-(a/r_c)^{12}+(a/r_c)^6]$
- Bond bending potential between adjacent bonds
  - ═══ $U_{bend}=k_{bend}(1+\cos\theta)$
  - ➡ vary entanglement length N_e
- u_0~3kJ/mol=30meV, a~0.5nm, $\tau=(m/u_0)^{1/2}a$~5ps

Simulation on Welding and Shear Testing





Nonequilibrium molecular dynamics (MD) simulation

- Chain length $N=500$, entanglement length $N_e=85\pm7$
  Welding at $T=1.0u_0/k_B$ above $T_g\approx0.35u_0/k_B$
  States at different welding times t_w were quenched to $T=0.2u_0/k_B<T_g$

- Switch to breakable bond potential for mechanical test
  ratio of the forces at which the covalent and
  van der Waals bonds break ~ 100

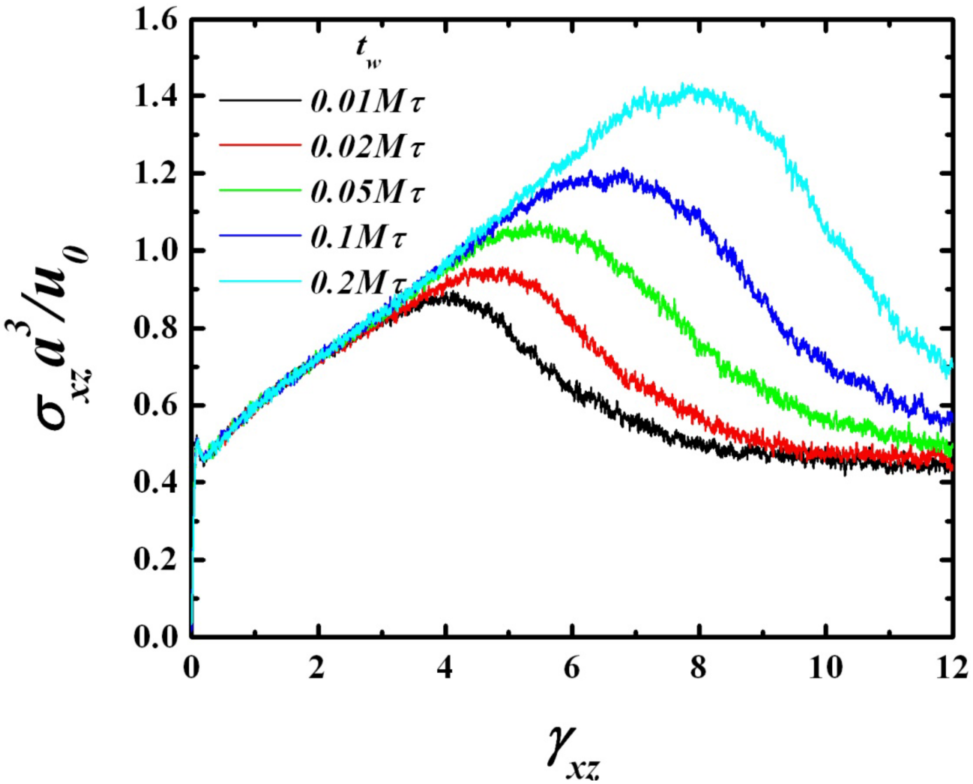
- Simple shear *constant strain rate* $d\gamma_{xz}/dt = 2\times10^{-4}$
  Periodic boundary conditions within the shear plane
  Temperature control using a Langevin thermostat

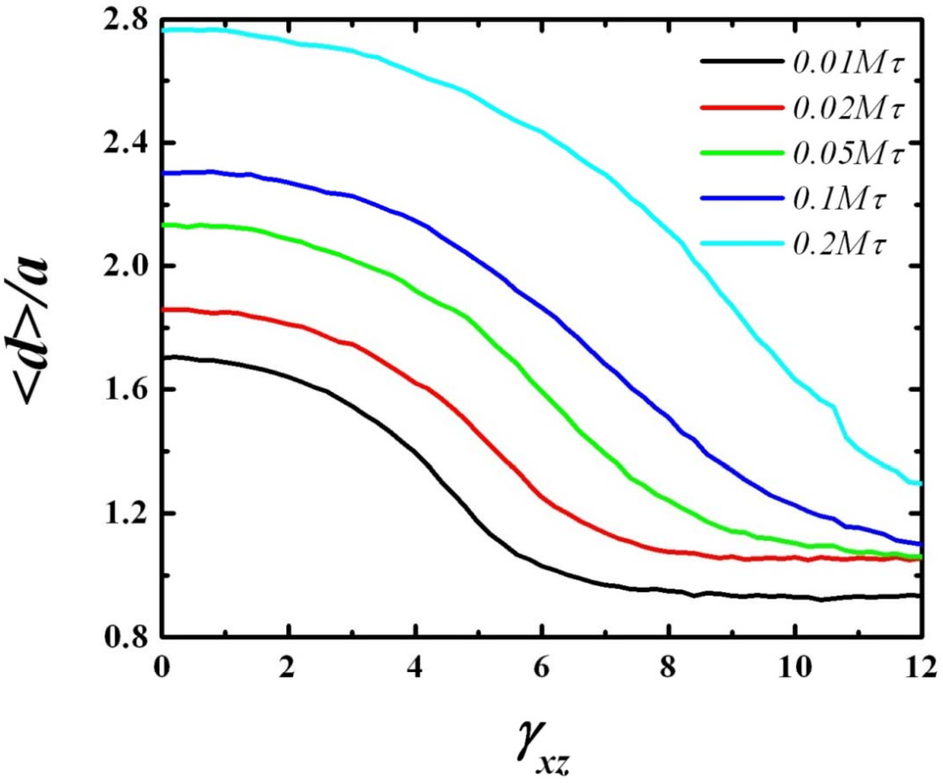
Interface fails by pure chain pullout at small t_w

- **Average interpenetration depth of beads that have diffused across the interface <*d*> decreases with shear strain γ_{xz}**
- **At steady state, shear stress σ_{xz} is uniform across the interface along *Z***

  Strain hardening in the entangled regions away from the interface

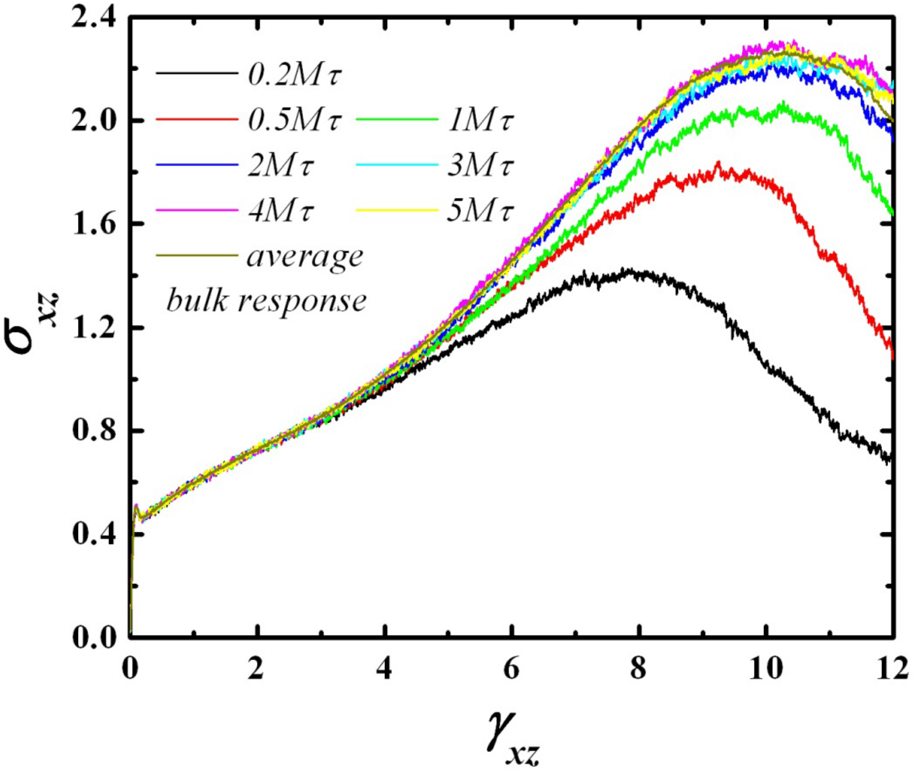
  ➡ *Strain localization near the interface*
- **Universal final <*d*> and σ_{xz} ➡ *corresponds to friction between polymer pieces***

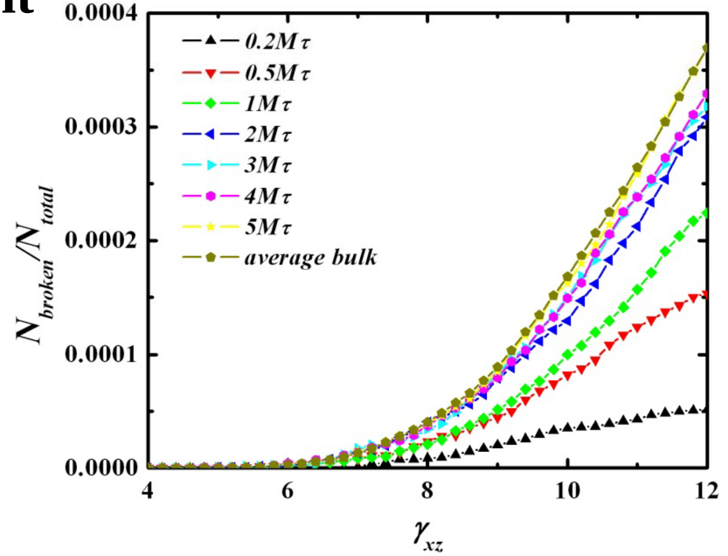


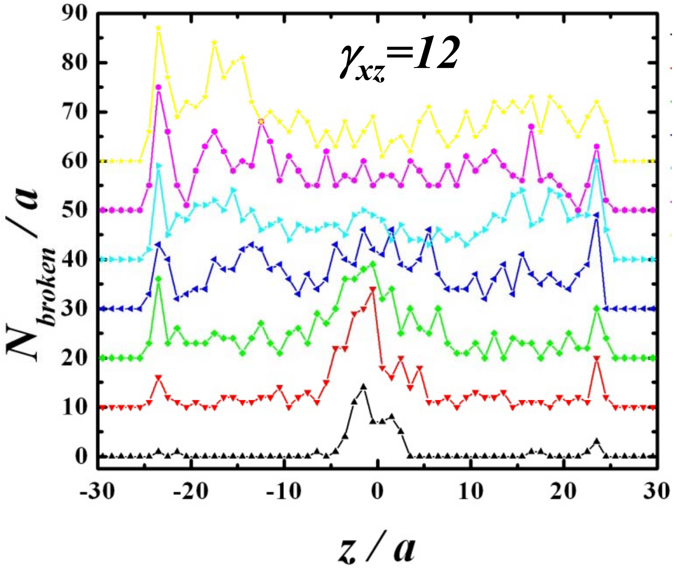


Interface fails by chain scission at large t_w and in bulk states

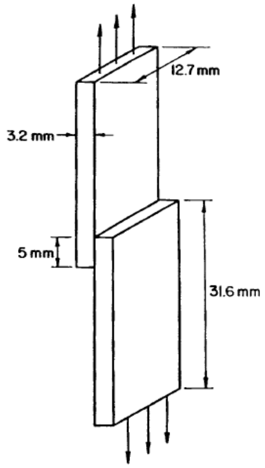
- Chain scission sets in at large t_w, and the stress-strain behavior starts to saturate towards average bulk result
- Broken bonds show up around the interface initially, but at late stage can be anywhere across the sample



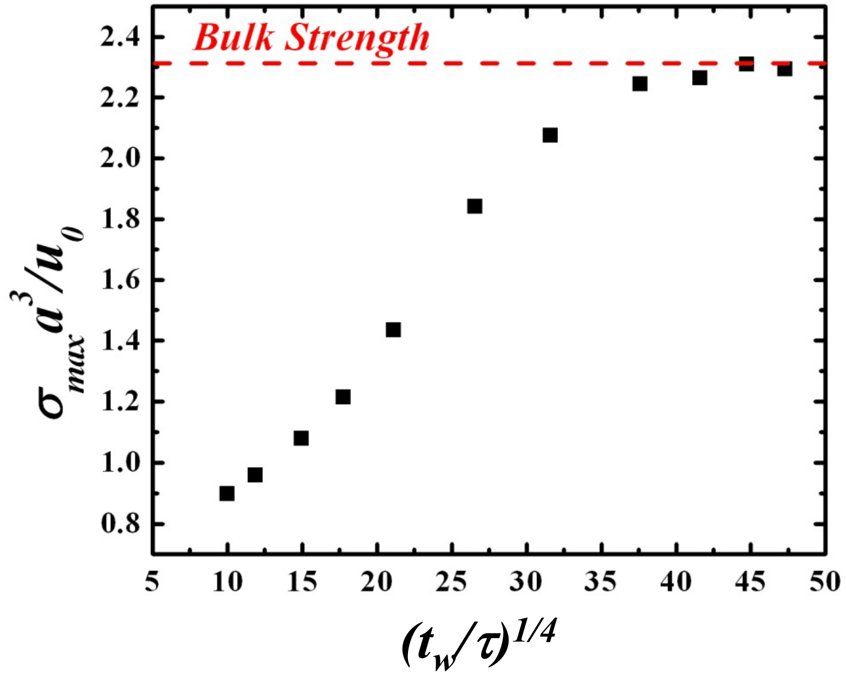


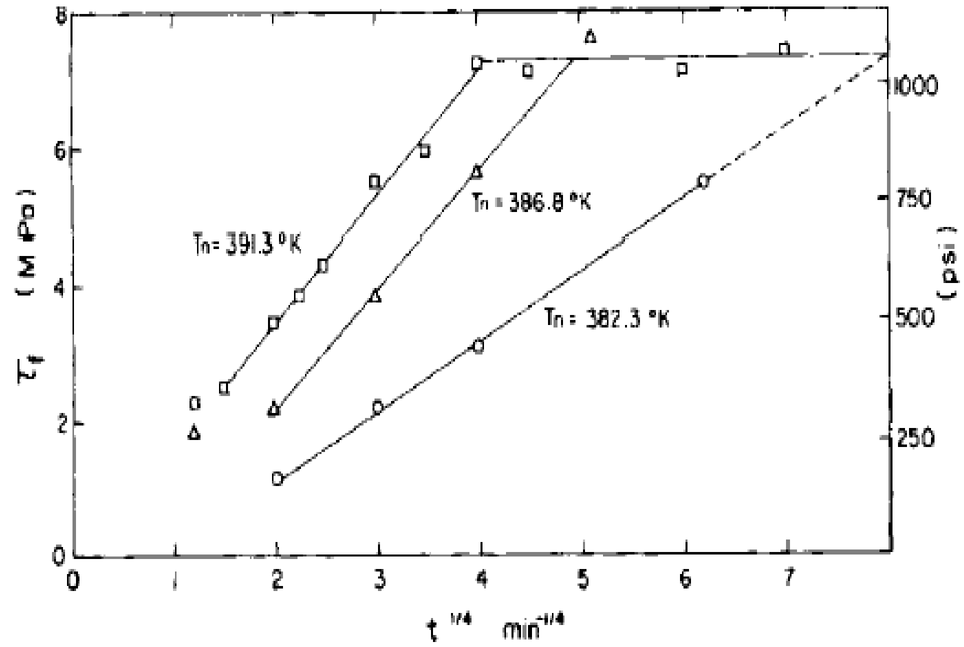


Time Dependence of the Maximum Shear Stress before Failure



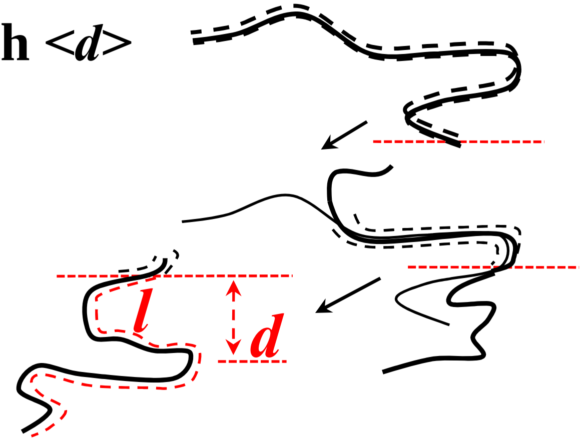
- **$t_w^{1/4}$ scaling law in the intermediate time regime**
- **After more chain scission sets in, σ_{max} saturates towards the bulk**
- **Agree with the experimental results by the *Lap-Shear Joint Method***



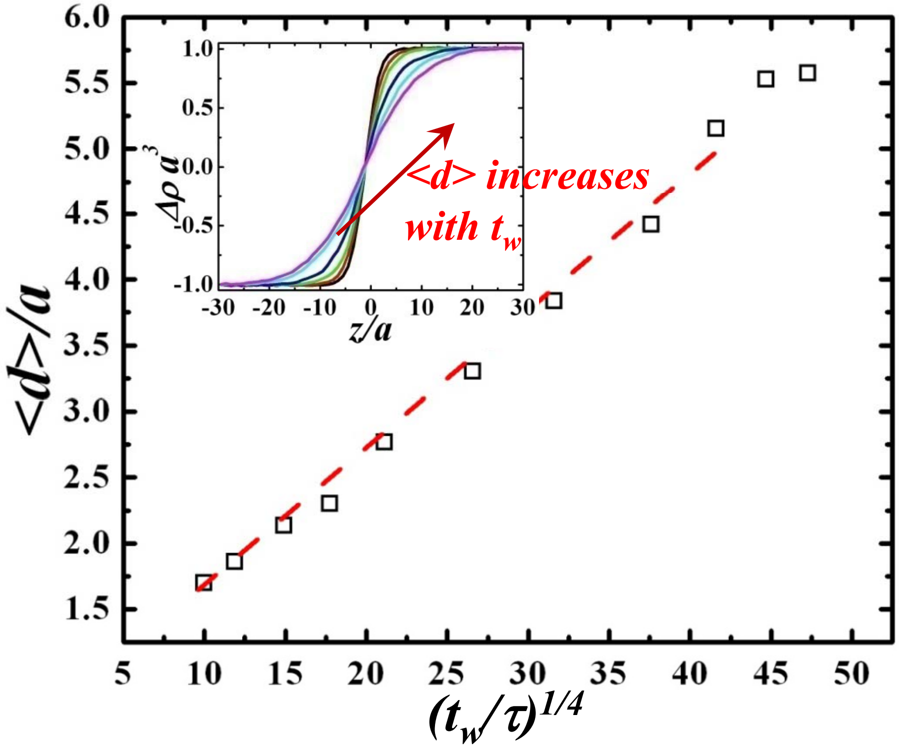


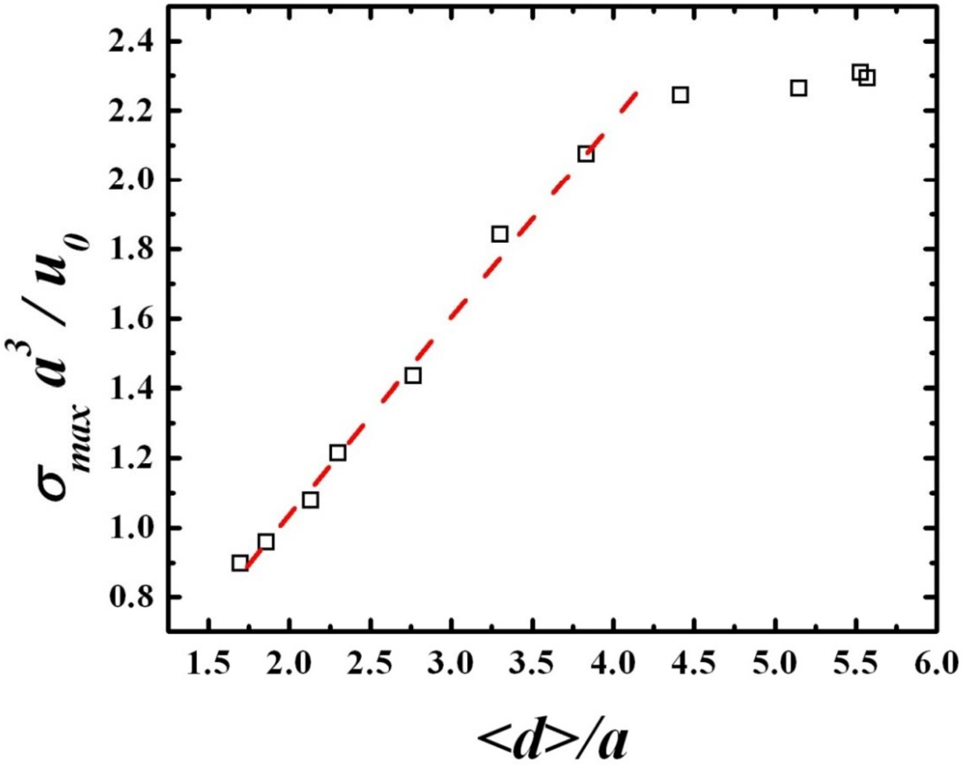
***D.B.Kline & R.P.Wool* (1988)**

σ_{max} Correlates with <*d*> before Saturation

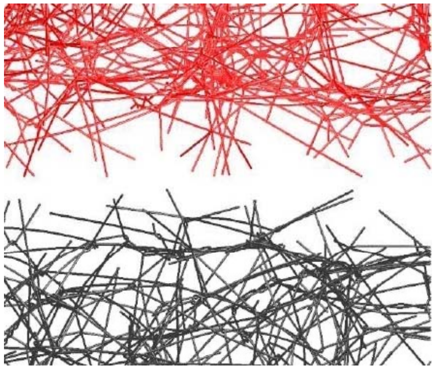


- **$t_w^{1/4}$ scaling law of the average interpenetration depth <*d*>**
  Consistent with theoretical predictions based on reptation dynamics (Doi & Edwards)
  The average contour length <*l*> of chain segments that have diffused across the interface scales as $t_w^{1/2}$
  $<d> \sim <l>^{1/2} \sim t_w^{1/4}$
- **Before saturation σ_{max} correlates well with <*d*>**
  No saturation in <d> with t

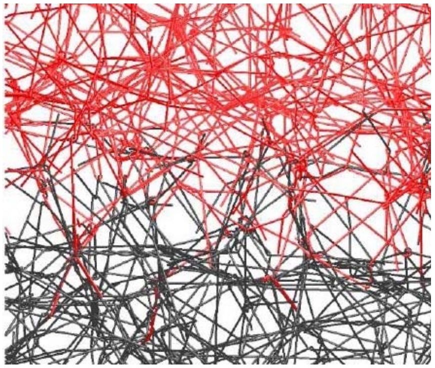




Identify Entanglements



PPs before welding



PPs at late stage during welding

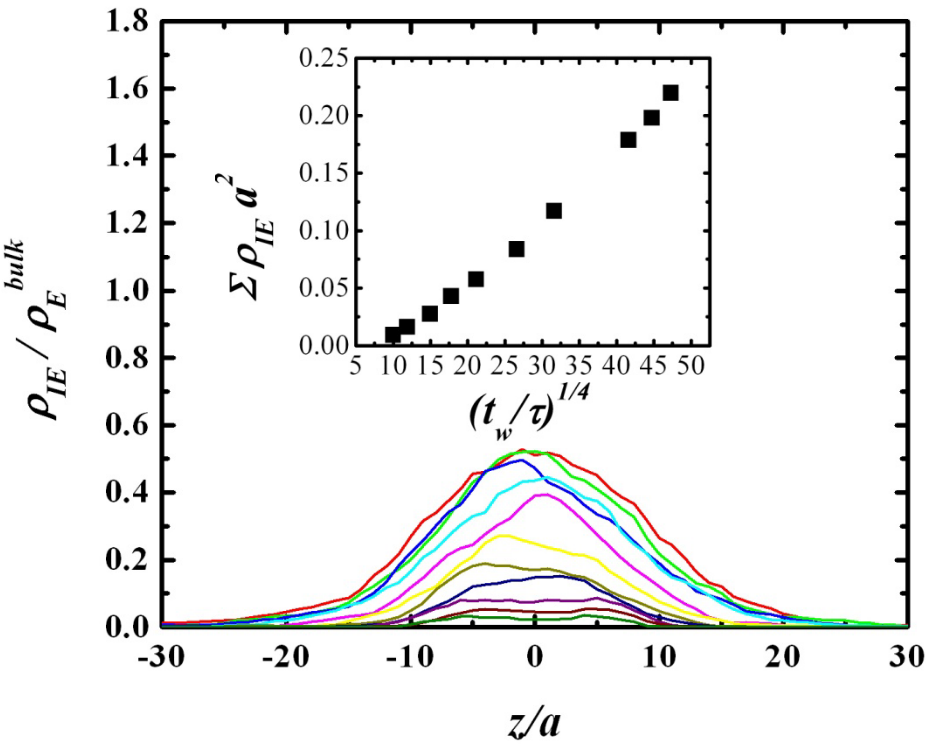
Primitive Path Analysis (PPA) (*Everaers et al. 2004*)

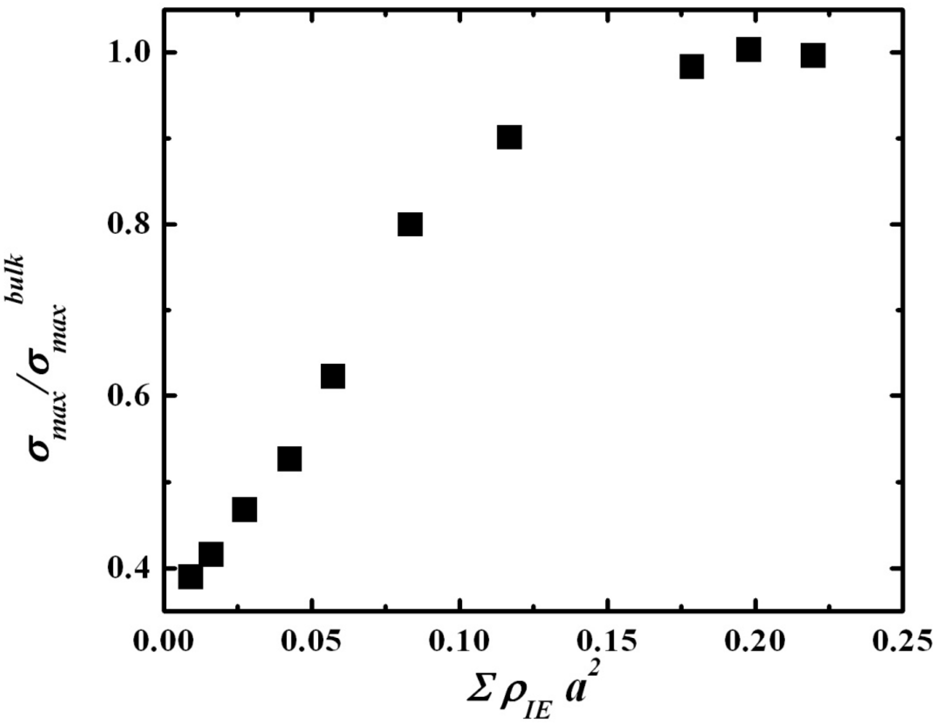
- Fix chain ends
  Deactivate intrachain excluded-volume interactions
  Retain interchain excluded-volume interactions
- *Minimize energy by cooling the system down to* ***T~0***
- Bond forces try to reduce the bond length to zero
  and pull chains taut
- Insert extra beads ***(Hoy & Grest, 2007)***
  to reduce the effects due to chain thickness
- Contacts of PPs ⟺ Entanglements

σ_{max} Correlates with Areal Density of Interfacial Entanglements before Saturation

- **Interfacial Entanglements (IEs) form between chains from the opposite sides**
  $\Sigma\rho_{IE}$ obeys $t_w^{\,1/4}$ scaling law
- $N_{IE} \sim \langle d \rangle A \Rightarrow \Sigma\rho_{IE} = N_{IE}/A \sim \langle d \rangle \sim t_w^{1/4}$ **consistent with reptation dynamics**
- ***No saturation in $\Sigma\rho_{IE}$ with t_w either***

Entanglements between chains from opposite sides





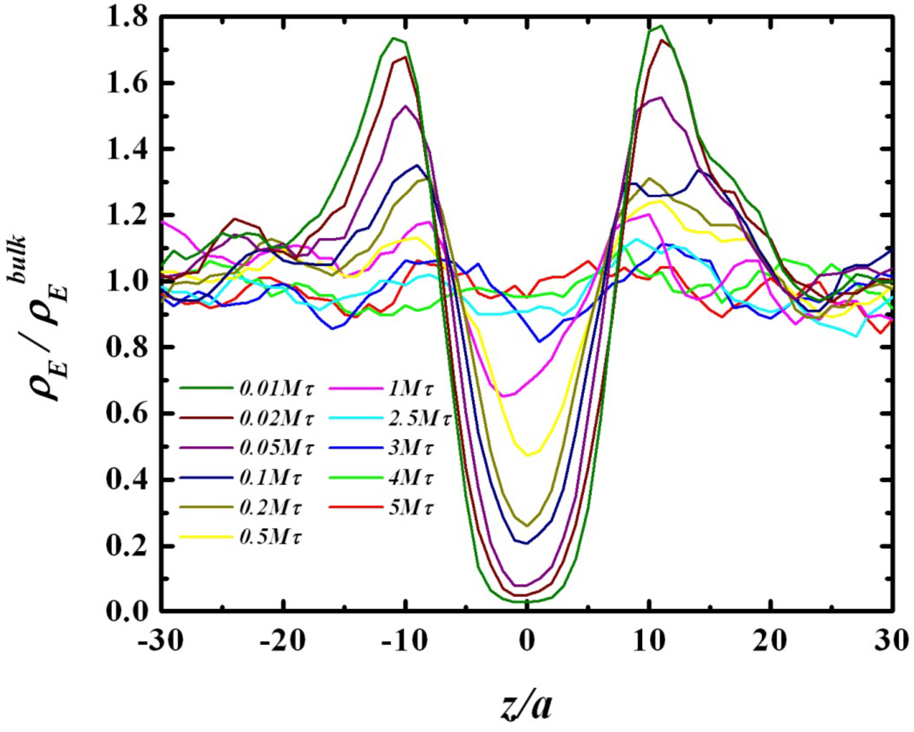
Bulk Response is Recovered as Entanglement Density Profile Approaches the Bulk Result

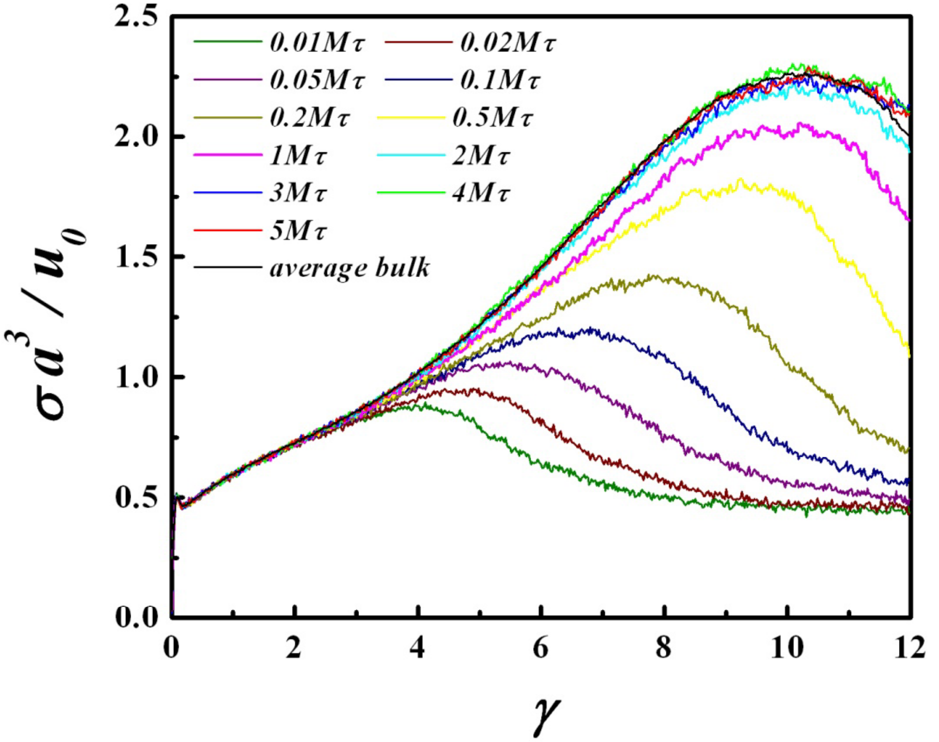
- **Bulk shear strength is fully recovered when entanglement density ρ_E equals its bulk value across the whole sample**

  ρ_E saturates at ρ_E^{bulk}

- **A sufficient number of entanglements can survive disentanglement via chain ends during shearing and effectively anchor chains to the opposite sides**

Entanglements between chains from any side





Conclusions for welding

Power law dependence of interfacial shear strength on welding time

- σ_{max} rises with welding time as $t_w^{1/4}$, in agreement with experiment and theory of reptation dynamics.

- At small t_w , the interface fails via pullout of chain ends.
  At large t_w and for the bulk, shear failure is through chain scissions.

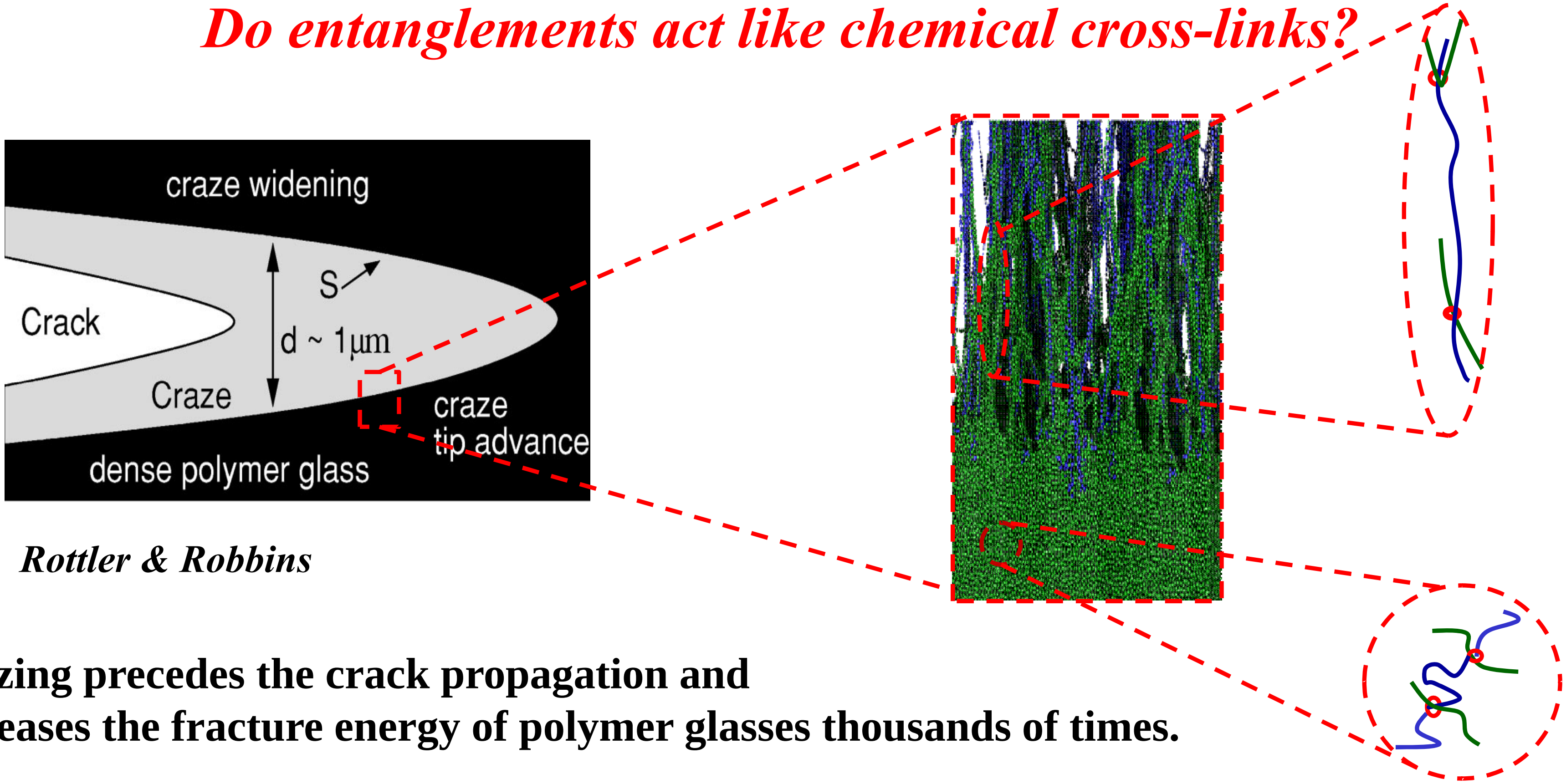
Correlation of interfacial strength with interfacial structure

- Before saturation σ_{max} correlates with the interpenetration depth $<d>$ and areal density of interfacial entanglemnts $\Sigma\rho_{IE}$ that both increase as $t_w^{1/4}$.

- The crossover to bulk strength coincides with the evolution of ρ_E to its bulk distribution.

Evolution of Entanglements During Craze Formation in Glassy Polymers

Do entanglements act like chemical cross-links?



Rottler & Robbins

Crazing precedes the crack propagation and increases the fracture energy of polymer glasses thousands of times.

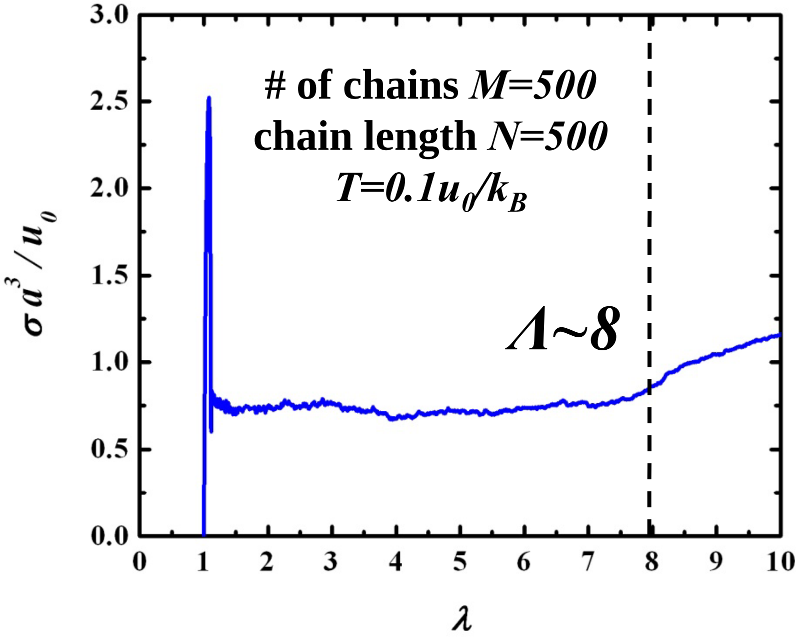
Theoretical Arguments

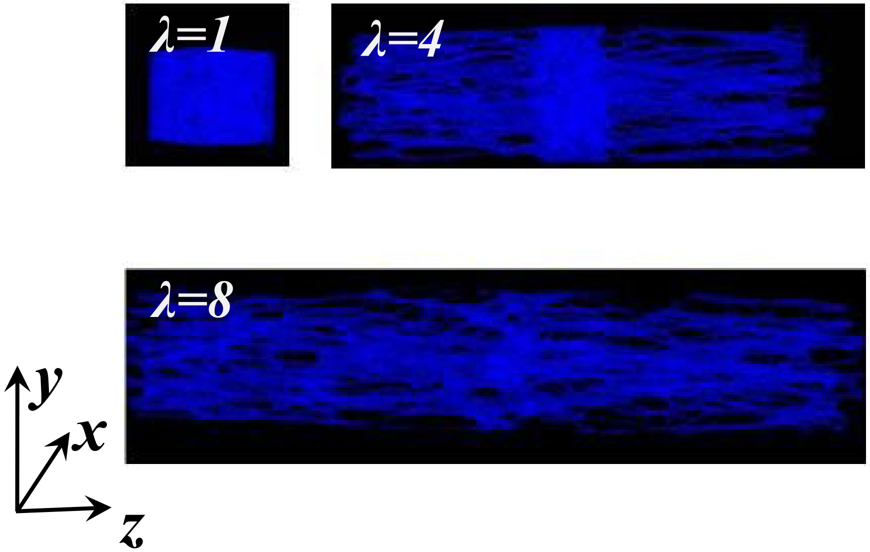
Assume entanglements act like permanent chemical cross-links

Tautening of chain segments between entanglements determines the volume expansion ratio $\Lambda = V_f / V_i = \rho_i / \rho_f$

$$\Lambda = N_e l_0 / (N_e l_p l_0)^{1/2}$$
$$= (N_e l_0 / l_p)^{1/2}$$

Simulation on Crazing

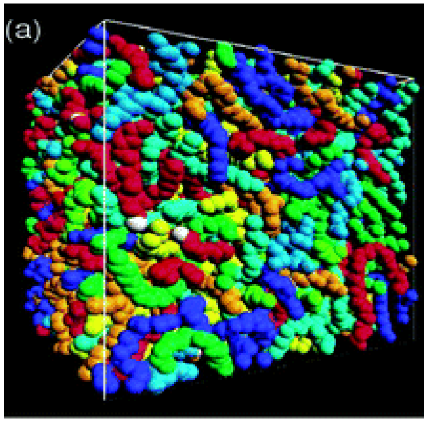


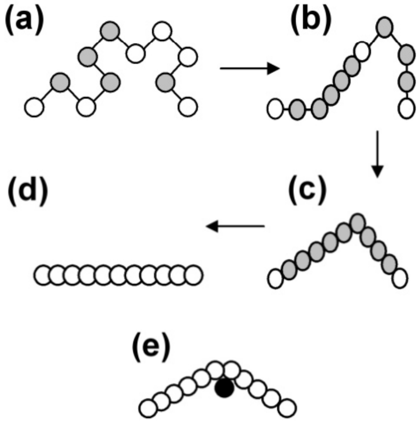


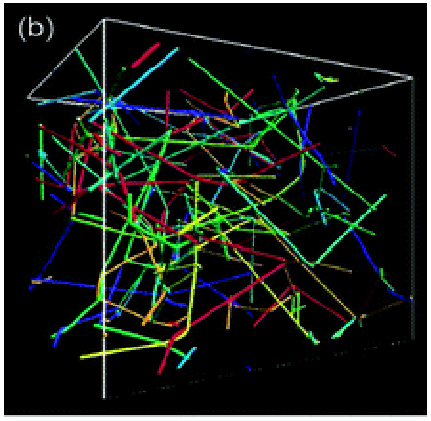
Nonequilibrium molecular dynamics (MD) simulation

- Bead-Spring Model (Kremer & Grest, 1990)
- Bond-bending potential
  $N_e=85, 39$ *and* 26 *for* $k_{bend}/u_0=0, 0.75$ *and* 1.5
- Uniaxial expansion with constant velocity until $\lambda = L_z/L_{z0}$ equals Λ
  3- D periodic boundary conditions
  Temperature control using a Langevin thermostat

Identify Entanglements







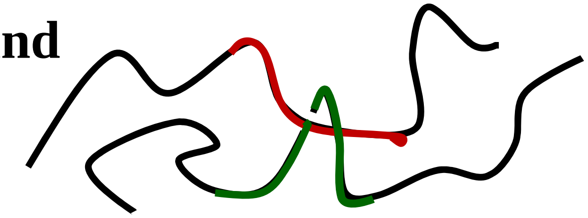
Contour Reduction Topological Analysis (CReTA)

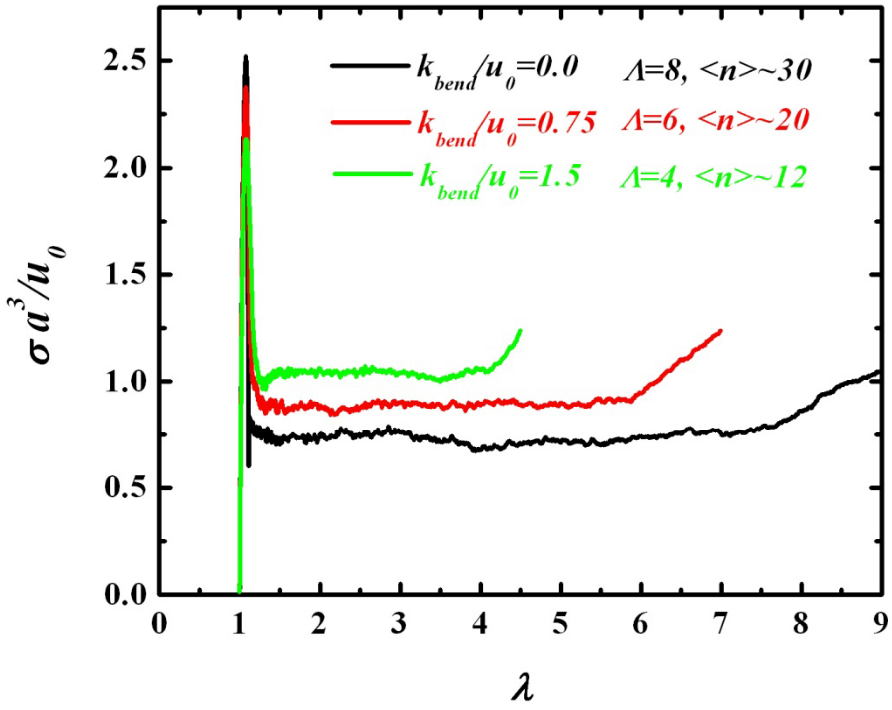
- Follow entanglements based on the idea of Primitive Path in the tube model of melt dynamics
- Fix beads at chain ends, minimize contour length without allowing chain crossing
- Contacts of Primitive Paths ⟺ Topological Constraints (TCs)
- Map TCs to pairs of interchain beads
  Distribution of TCs along the chain

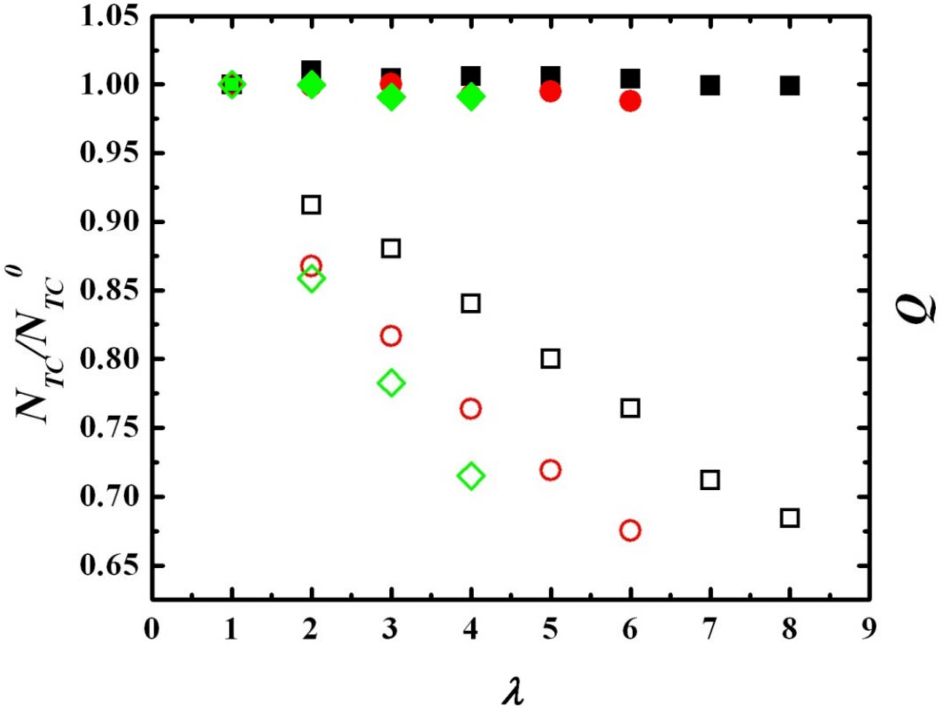
No significant change in the number of TCs

Most TCs remain between the same chain segments

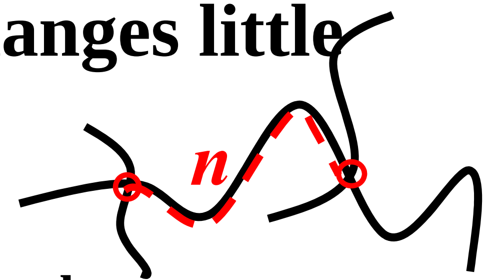
- *N_{TC}* varies by less than *3%* of *N_{TC}^0* in the undeformed glass, *error ~ 0.5% N_{TC}^0*
- Average distance between TCs along the chain <*n*> changes little
- *Q~70%* TCs are between the same pairs of chains, and move less than <*n*> along the chain



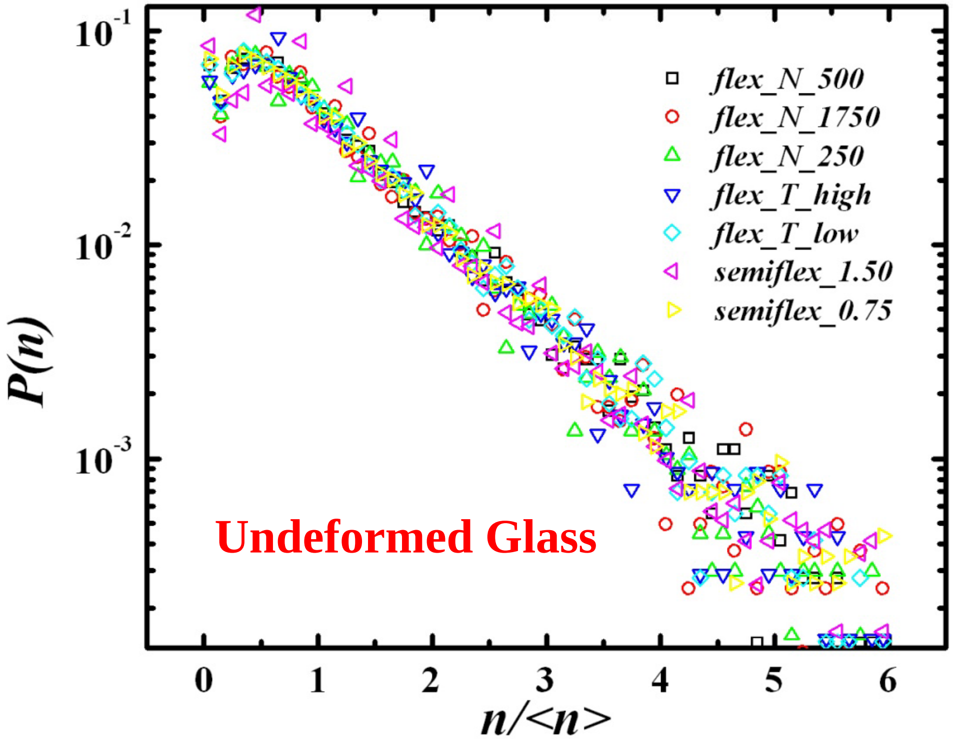


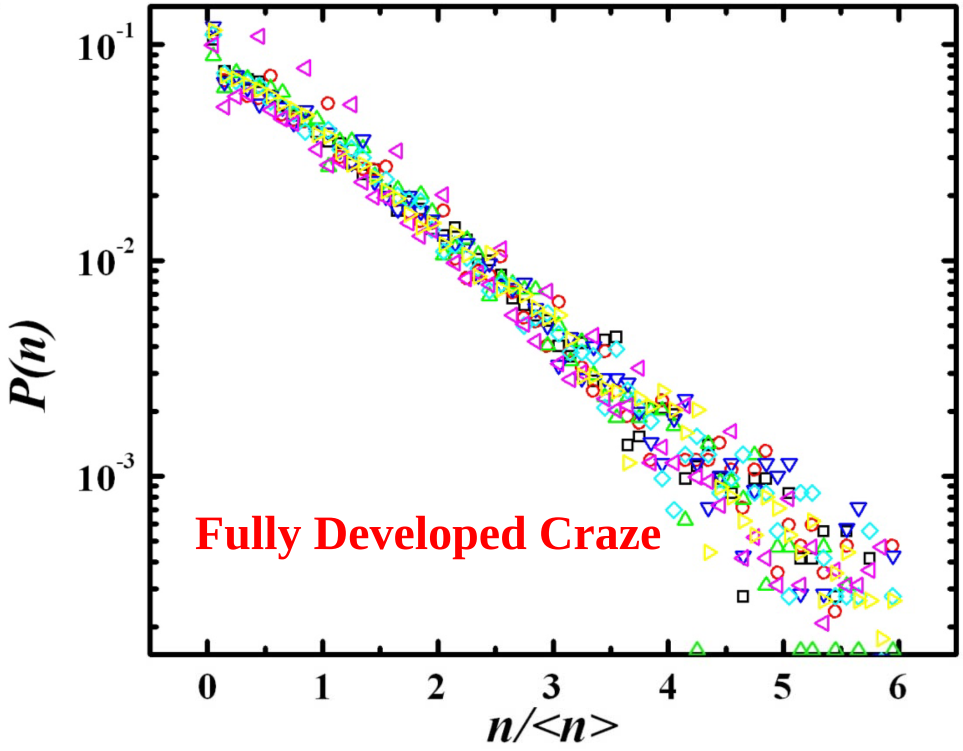


Distribution of TCs along the chain changes little



- **Tail of the distribution of n fits $exp(-n/n_c)$ with $n_c \sim \langle n \rangle$**
- **$\langle n \rangle$, n_c, and $P(n)$ change little during crazing**
- **In systems with different chain lengths, chain stiffness , and temperature, distributions of n normalized by $\langle n \rangle$ collapse**
- **$\langle n \rangle / N_e \sim 0.4$, where N_e is the entanglement length in rheological measurements**

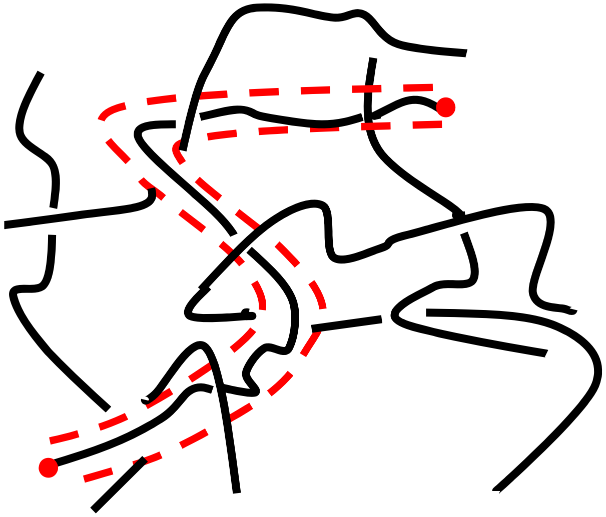


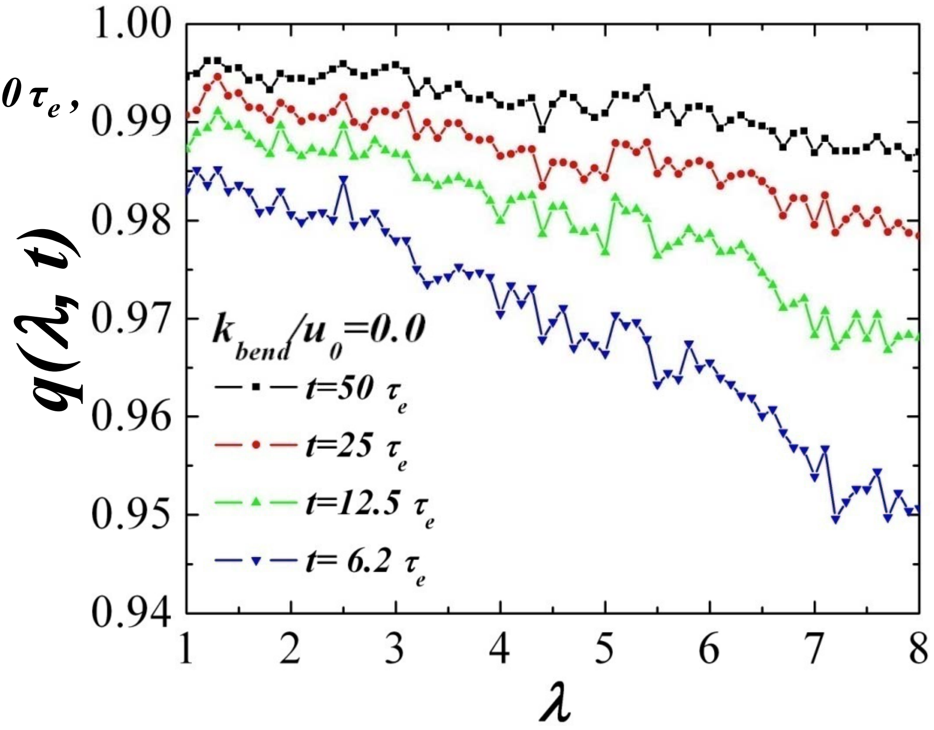


New TCs are from the same tubes

- **Lost initial TCs ($1-Q \sim 30\%$) are replaced by TCs with different chain segments**
  Not predominantly distributed near chain ends
  Can't explain as disentanglement through chain ends
- **Almost all mate chains come from the chain's tube in the undeformed glass**
  Initial tubes are explored by end-constrained dynamics at a melt temperature
  $q(\lambda, t)$ shows the portion of mate chains encountered by λ
  that belong to the tube chains explored by t

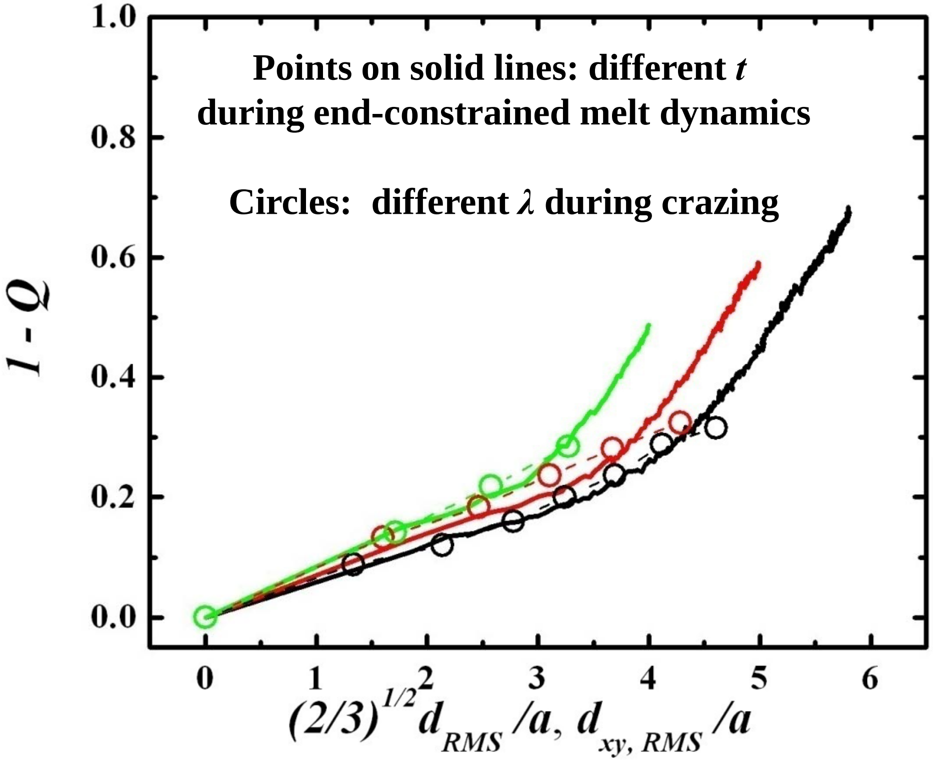
With chain ends frozen, the glass is heated up and maintained at $T=1.0u_0/k_B>T_g$ for $t=50\,\tau_e$, where τ_e is the entanglement time.

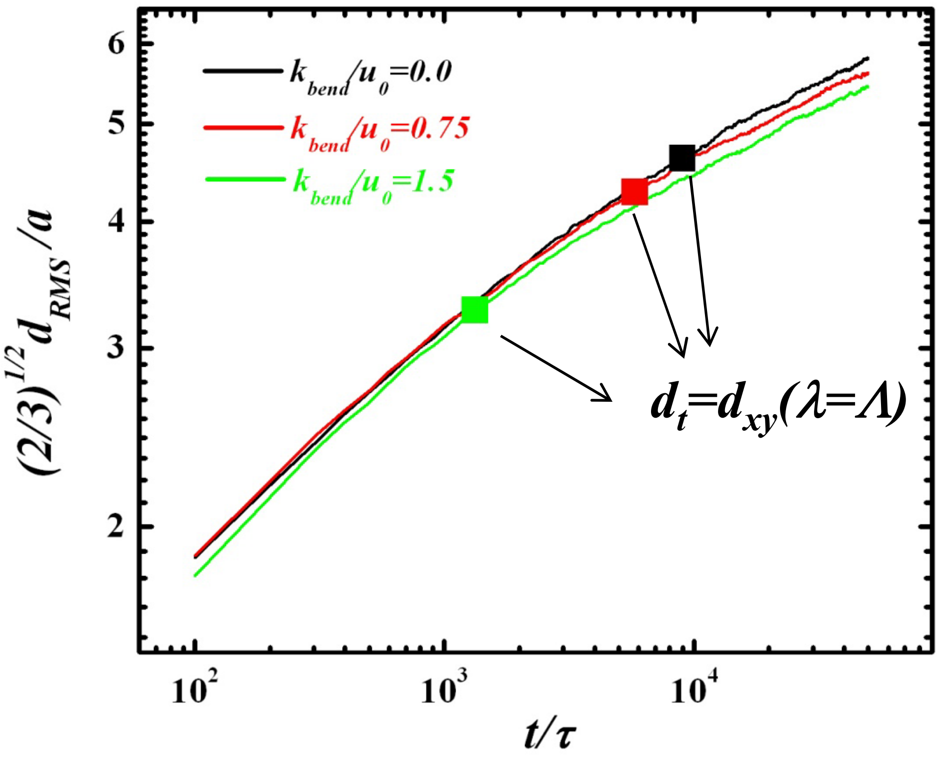




New TCs arise from deformation activated diffusion

- Displacement d_{xy} within the plane normal to the stretching direction reflects the subtle changes associated with drawing atoms into fibrils
- The same d_{xy} and lateral displacement d_t during end-constrained melt dynamics lead to the same degree of changes in the identity of TCs
  $d_t=(2/3)^{1/2}d_{RMS}$
- d_{xy} at the end of craze formation is on the order of tube diameter





Conclusions for craze formation

During craze formation, entanglements do not act like chemical cross-links
But on the tube level they are preserved

- Total number of TCs remains almost unchanged during crazing.
- Distribution of TCs along the chain changes little
- Most (~***70%***) TCs remain between the same chain segments
- The rest (~***30%***) are replaced by TCs with chains from the same tubes
- Variation in the identities of TCs arises from deformation activated diffusion within the tube, in a manner similar to thermal diffusion in melt dynamics