Deformation and Fracture of Glassy Polymers

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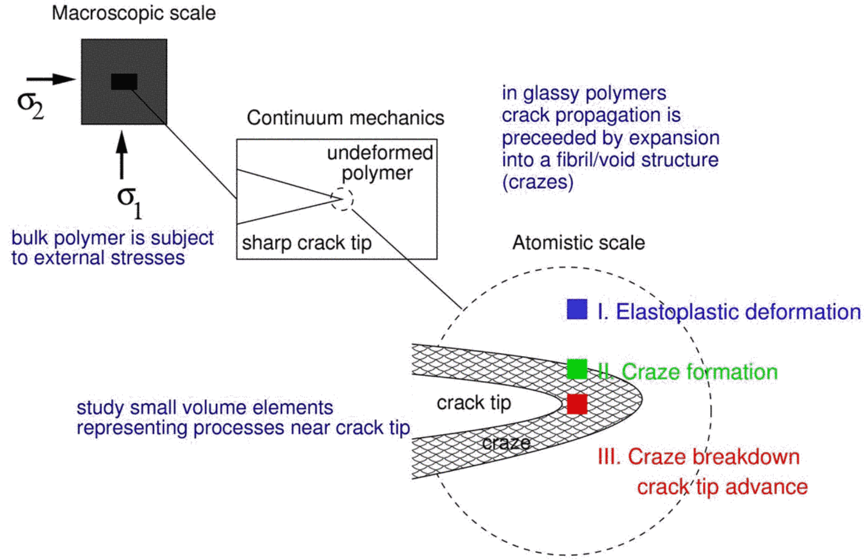
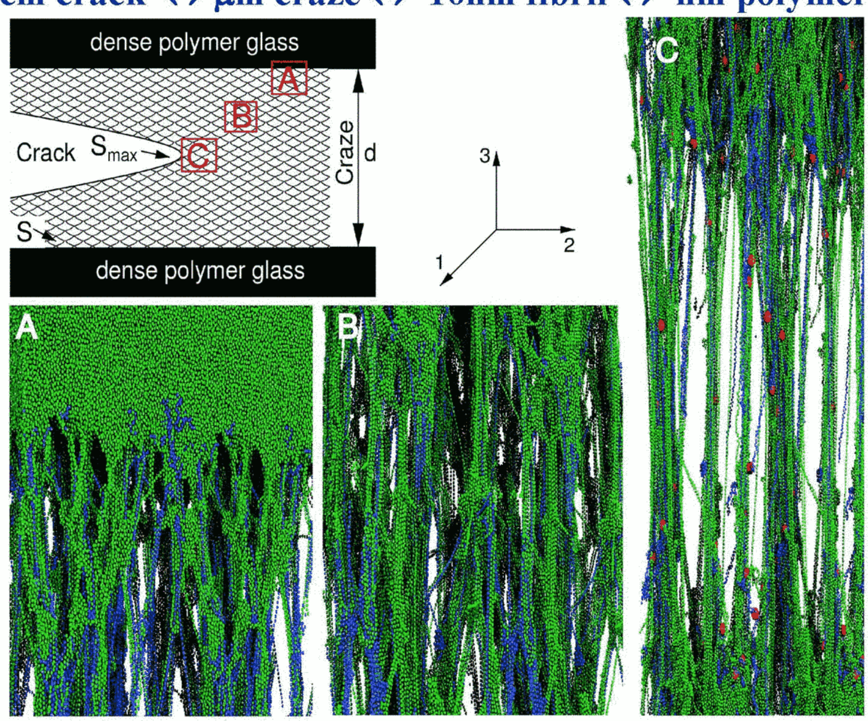


IV. From molecular simulations to the macroscopic fracture energy

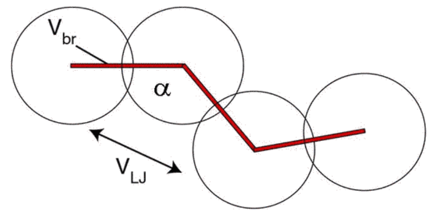
Craze formation: a multiscale problem

cm crack ↔ µm craze ↔ 10nm fibril ↔ nm polymer



A simple model for polymer glasses

Beads and springs → length N:



- Lennard-Jones (LJ) potential V_{LJ} → van der Waals interaction, energy u_0 ~ meV, length d ~ nm, time ~ ps, max force f_{LJ}
- Covalent bonds V_{br} → breaking force $f_c = 100\ f_{LJ}$
- presence of bonds prevents crystallization: glass transition $T_g \sim 0.3\ u_0/k_B$
- Angle forces V_α → flexible/semiflexible → vary entanglement length N_e

- Molecular dynamics: $\ddot{\mathbf{r}}_i = \sum_{i \neq j} \mathbf{F}_{i,j} / m_i$
  integrate classical equations of motion of many-particle system
- Follow particle motion, measure local or integrated response of system

Important length scales in polymer glasses

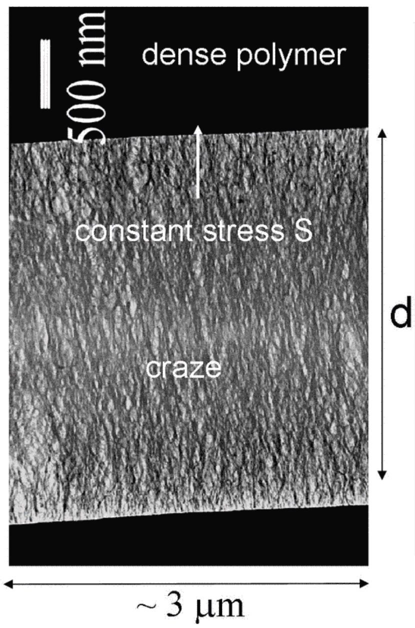
persistence length N_p
(length to change direction)

total length N
(# of repeat units)

entanglement length N_e determined from plateau modulus $G=4\rho RT/5M_e$
(topological constraints from other chains)

- many polymer properties scale with dimensionless ratios N/N_p, N/N_e
- can use relatively simple coarse-grained models like bead-spring chains

Craze fracture in experiments

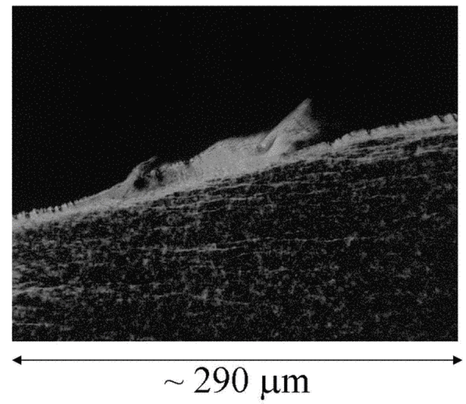


Courtesy of E. Kramer et al., UCSB

Experimental craze growth parameters:

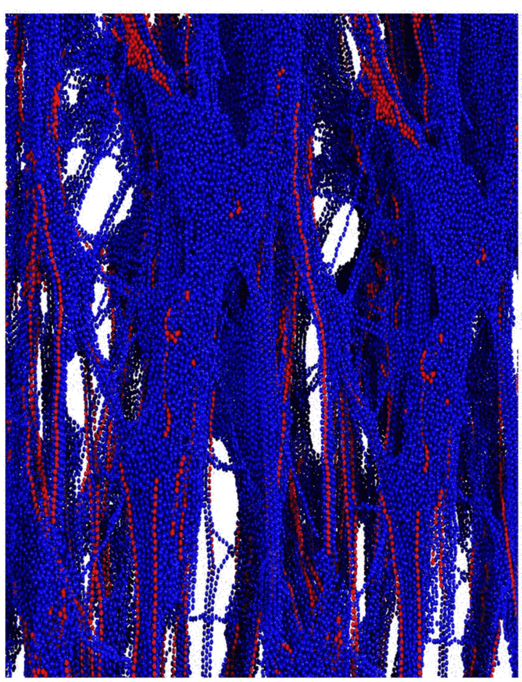
- extension ratio $\lambda = \rho_i/\rho_f \sim 2\text{-}6$
- drawing stress $S \sim 40\text{-}70$MPa
- fibril diameter $D \sim 5\text{-}30$ nm
- craze width $d \sim 3\text{-}20\mu m$

HDPE-copolymer (semicrystalline)



Courtesy of F. Lapique
J. Appl. Poly. Sci. **77,** 2370 (1999)

Craze fracture in simulations



- chains bundle and form fibrils, oriented in widening direction
- frequent branching and cross-ties
- structure depends on molecular parameters, temperature
- some chains carry a large amount of stress (red)

Simulations reproduce key experimental features!

When and how does a solid yield?

- energy-based yield criterion: $F_{shear} \sim \tau_{dev}^2 = const.$

  $$\tau_{dev} = \frac{1}{3}\left[(\sigma_1-\sigma_2)^2+(\sigma_2-\sigma_3)^2+(\sigma_3-\sigma_1)^2\right]^{1/2}$$

- in friction: τ ~ normal load/area, suggests dependence on $p = -(\sigma_1+\sigma_2+\sigma_3)/3$
- pressure-modified von Mises criterion

  $$\tau_{dev}^y = \tau_0 + \alpha p$$

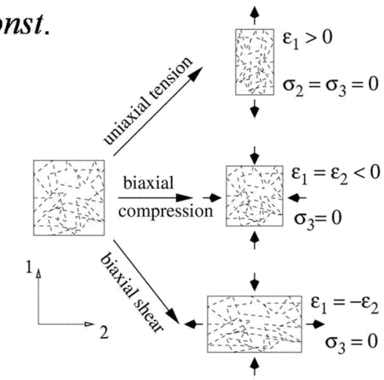
  Assumes complete isotropy/delocalization
- other criteria if shear localizes:

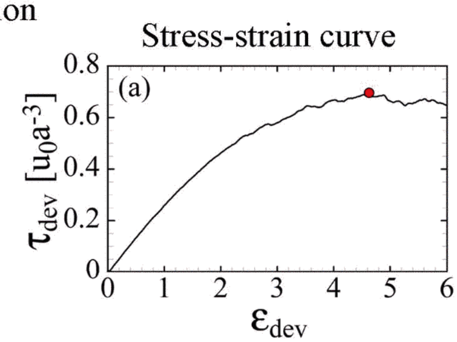
  pressure-modified Tresca criterion:

  $$\tau_{\max} = \frac{1}{2}|\sigma_i - \sigma_j|_{\max} = \frac{3}{\sqrt{2}}(\tau_0 + \alpha p)$$

  Mohr-Coulomb criterion:

  $$\tau_y = \tau_0 - \sigma_n \tan\Phi$$

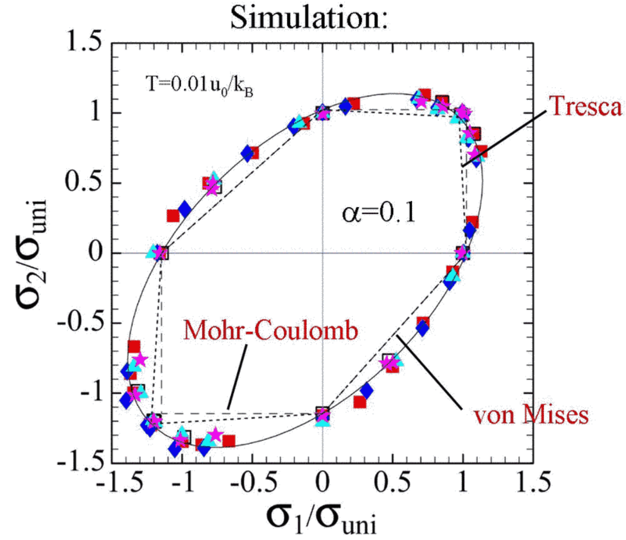




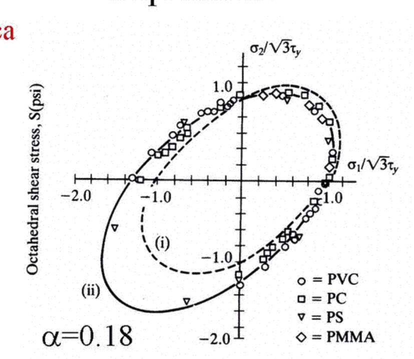
Shear yield criteria for polymer glasses

Biaxial stress states only, many different polymers:

Simulation:



Experiments:

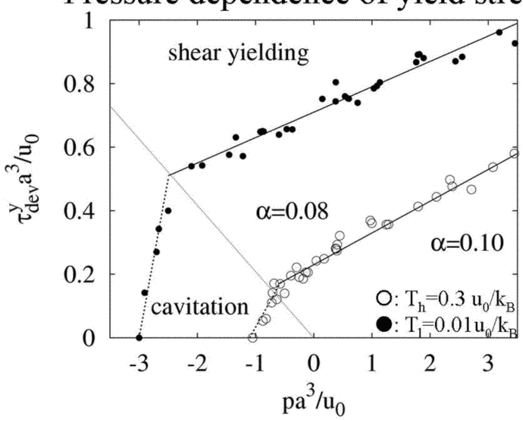


From: T.H.Courtney, Mechanical Behavior of Materials

- von Mises: $\tau_{oct}^y = \tau_0 + \alpha p \rightarrow$ elliptical yield surface, good fit
- Tresca: $\tau_{\max} = \frac{3}{\sqrt{2}}(\tau_0 + \alpha p) \rightarrow$ polygonal yield surface

Conditions for craze initiation

Pressure dependence of yield stress

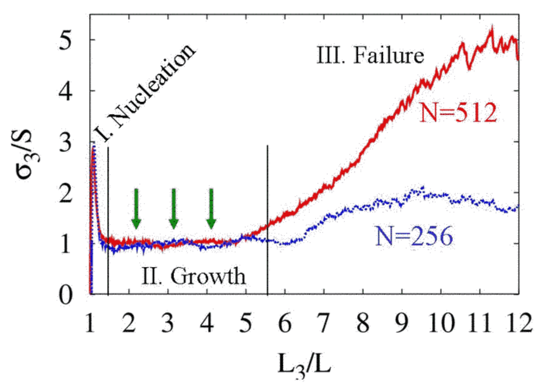


- von Mises criterion $\tau^y_{dev} = \tau_0 + \alpha p$ holds for multiaxial shear deformation
- periodic boundary conditions prevent localization
- triaxial stress leads to cavitation and initiates craze formation
- here enforce by increasing volume, occurs near defects in real polymers

J. Rottler, M. O. Robbins, Phys. Rev. E **64**, 051801 (2001)

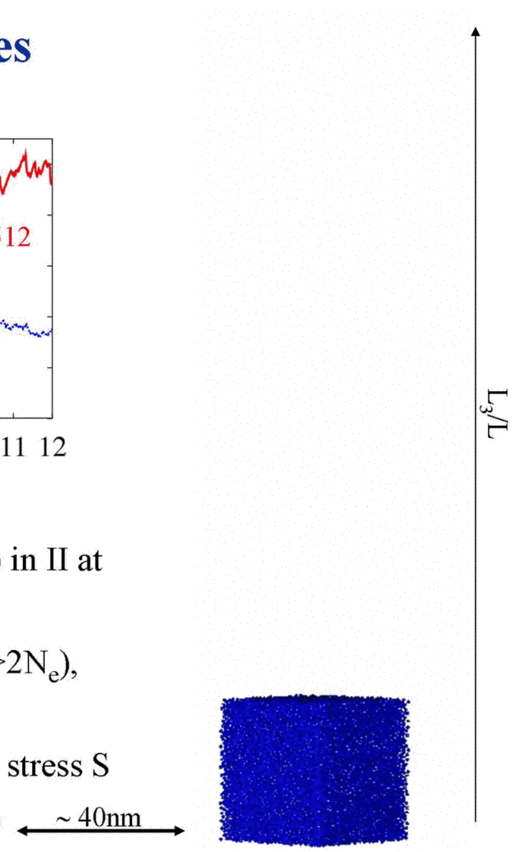
Craze growth regimes

Stress-strain curve



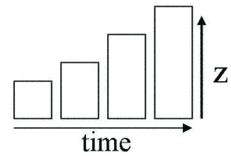
- Cavitation in I, growth (fibril drawing) in II at constant stress S, failure in III
- I and II independent of N (but need $N>2N_e$), not so III
- Two phases coexist at constant normal stress S

J. Rottler, M. O. Robbins, Phys. Rev. E **68**, 011801 (2003)

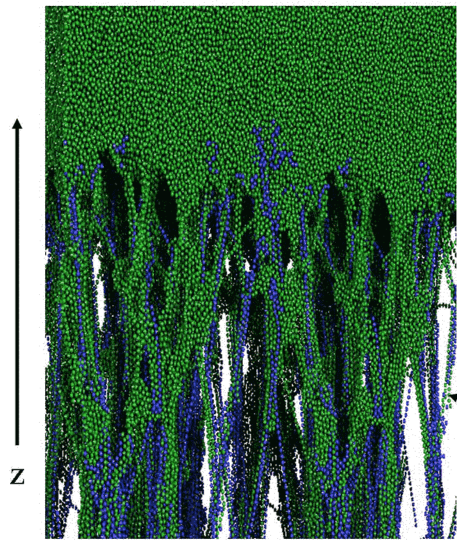


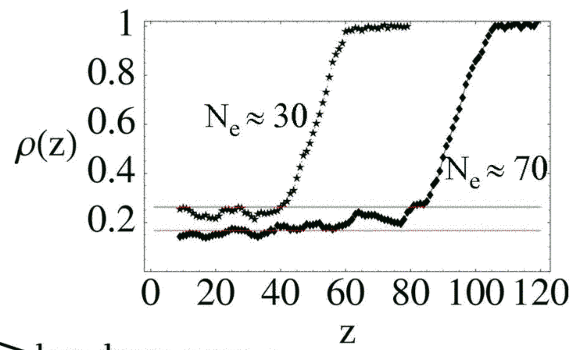
The extension ratio

- expand simulation cell in one direction at constant velocity:



- dense polymer is expanded at interface by extension ratio $\lambda = \rho_i/\rho_f$

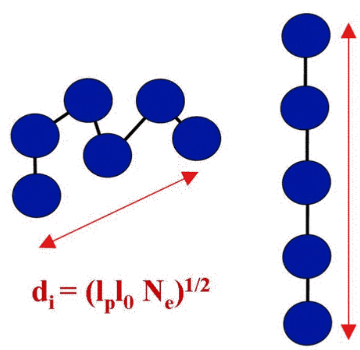




$N_e \approx 70$ (flexible):	$\lambda_{fl} \approx 6.0 \pm 0.6$
$N_e \approx 30$ (semiflexible):	$\lambda_{sfl} \approx 3.6 \pm 0.3$

What limits λ?

Simple model (E. J. Kramer): Stretch segments of length N_e until taut



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

$d_f = \lambda d_i = N_e l_0$

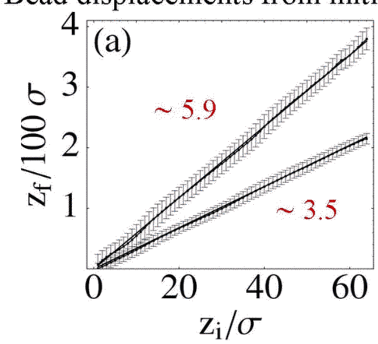
$$\lambda_{max} = d_f/d_i = (N_e l_0/l_p)^{1/2}$$

- agrees with observed values of λ
  flexible polymers: $\lambda_{max} \approx 6.5$, $\lambda \approx 6.0$
  semiflexible: $\lambda_{max} \approx 3.5$, $\lambda \approx 3.6$
- but average straight segment only $N_e/3$ since only expand z-component of $d_{iz} = \cos(\Theta_z)\, d_i$
- would have $\lambda = \sqrt{3}\lambda_{max}$ if pulled fully straight

→ System "jams" through a small fraction of entanglements that are initially aligned with z and become fully stretched!

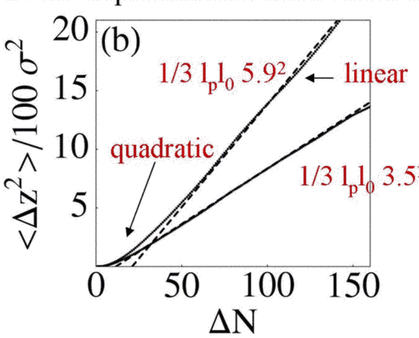
Analyzing the chain deformations

Bead displacements from initial positions:



- $z_f = \lambda\, z_i$: Expansion nearly affine along z ($\sim\pm N_e/3$)
- Smaller lateral deviations allow chains to gather in fibrils at initial density to minimize surface area

Bead displacements from chain center:

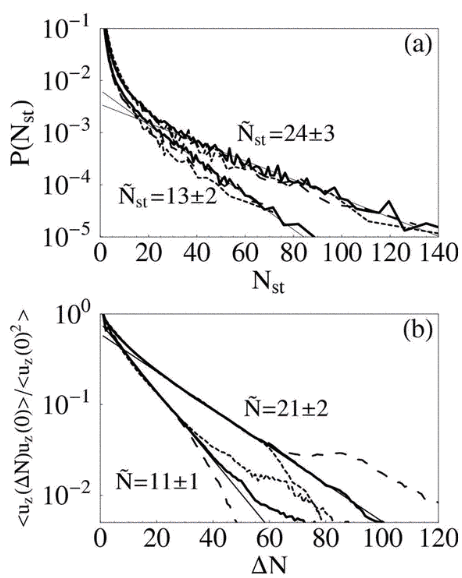


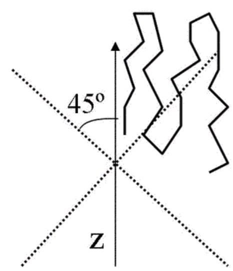
- before def.: $<\Delta z^2>_{ini} = l_p l_0 \Delta N/3$
- after def.: long scales $<\Delta z^2> = \lambda^2 <\Delta z^2>_{ini}$
  short scales $<\Delta z^2> = (l_0 \Delta N)^2$
  ~ no change in Δx and Δy

→ anisotropic random walk on large scales, straight segment on short scales

Characteristic length scale in craze

- obtain typical length of straight segments from crossover: $\tilde{N}_{st} = 1/3\, \lambda^2 l_p / l_0$
- inserting $\lambda_{(s)fl} \rightarrow \tilde{N}_{st} = 21$ or $\tilde{N}_{st} = 12$



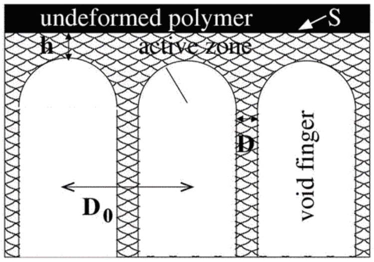


- Bond points up (down) if angle Θ_z within 45° of z (-z) axis
- Measure number N_{st} of consecutive up (down) steps
- Distribution develops exponential tail, fit to $P(N_{st}) \propto \exp(-N_{st}/\tilde{N}_{st})$

$$\tilde{N}_{st} = 24 \approx 70/3 = N_e/3$$
$$\tilde{N}_{st} = 13 \approx 30/3 = N_e/3$$

- similar length scales from decay of bond-bond autocorrelation function

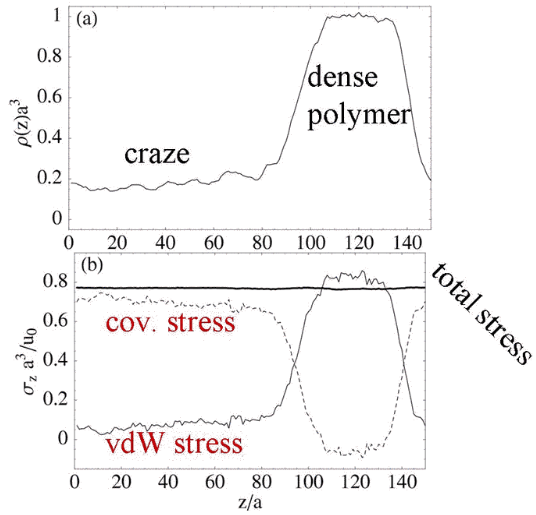
Capillary model for craze widening



- treat polymer at interface as viscous fluid
- void cylinders propagate into dense polymer
- stress carried by energy at interface: $S \sim \Gamma/D_0$ (Laplace pressure)

incorrect, find instead:

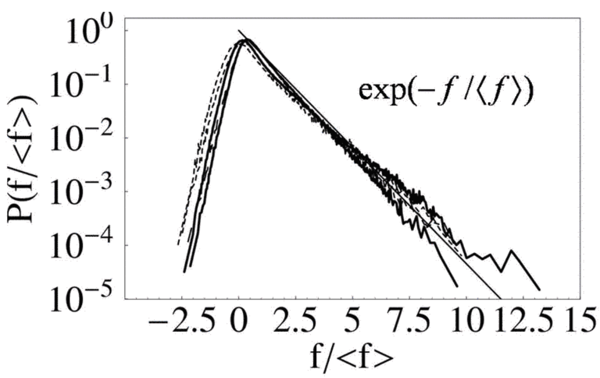
$S\lambda = S_0 = \text{const.}$



- stress transfer at interface from vdW to cov. bonds
- 60-90% of stress carried by covalent bonds in craze
- 80% of work dissipated!

Force distribution in polymer crazes

- compressive (negative) forces: gaussian distribution
  tensile (positive) forces: exponential distribution



- force tail universal, independent of N, T, r_c.
- data collapse after normalization by average force $\langle f\rangle$
- exp. force dist. is hallmark of jammed, granular matter

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Jamming under Tension in Polymer Crazes

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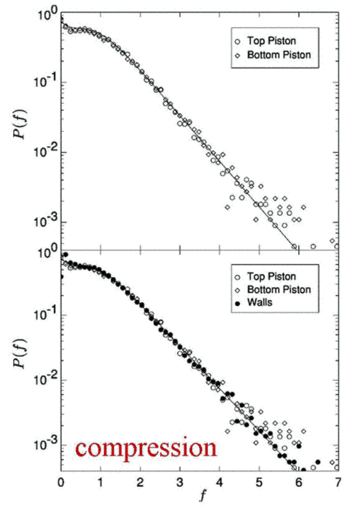
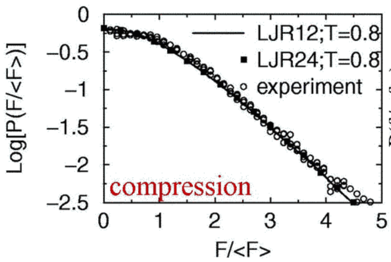
Force distribution in jammed systems

Granular media



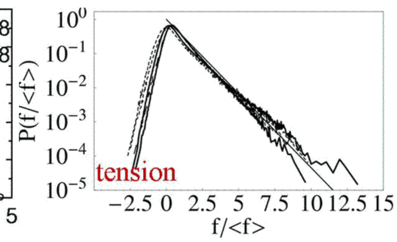
Mueth *et al.*, PRE **57**, 3164 (1997)

Lennard-Jones beads



O'Hern *et al.*, PRL **86**, 111 (2001)

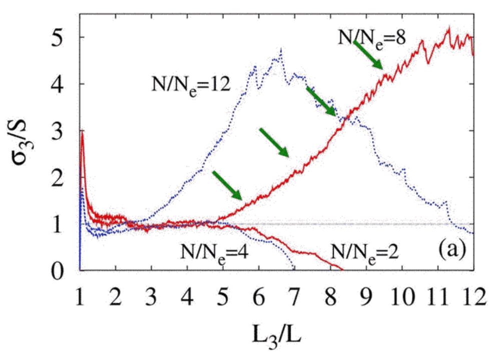
Polymer craze



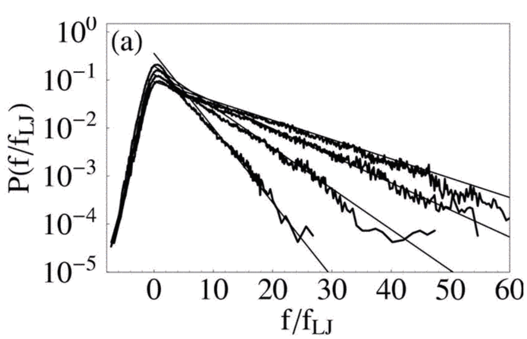
Rottler and Robbins, PRL **89**, 195501 (2002)

- conventional jamming mechanism: reduction of free volume
- jamming under tension: frictional forces prevent chains from sliding past each other at entanglement points

Craze breakdown



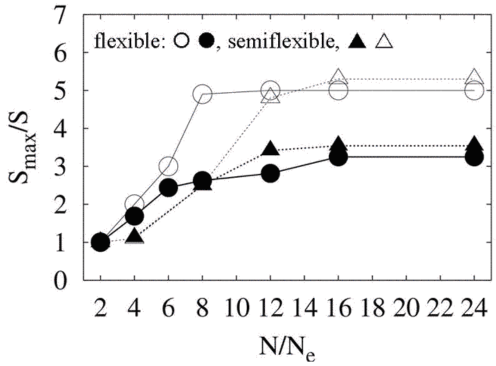
- short chains $N/N_e = 2$ (flexible) or $N/N_e = 4$ (semiflexible) disentangle
- stress rises from S to S_{max} as N ↑
- S_{max} limited by chain scission

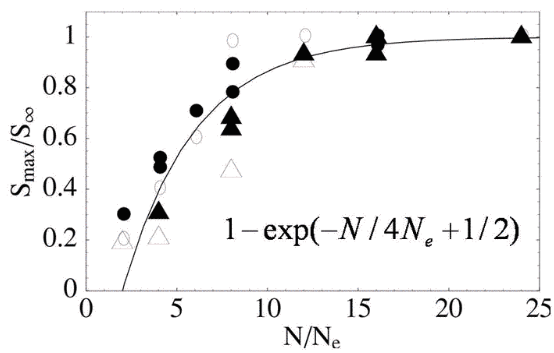


- $P(f/f_{LJ}) \sim \exp(-f/<f>)$ for tensile forces, with $<f>= 3 - 11$
- scission at $P(f>f_c)\ n \sim 1$, where n # of strands
- simple estimate: $F_{max}/f_c=n$
  but exp. dist. yields: $F_{max}/f_c=n/\ln(n)$

→ fibrils are much weaker!

Fibril failure stress S_{max}





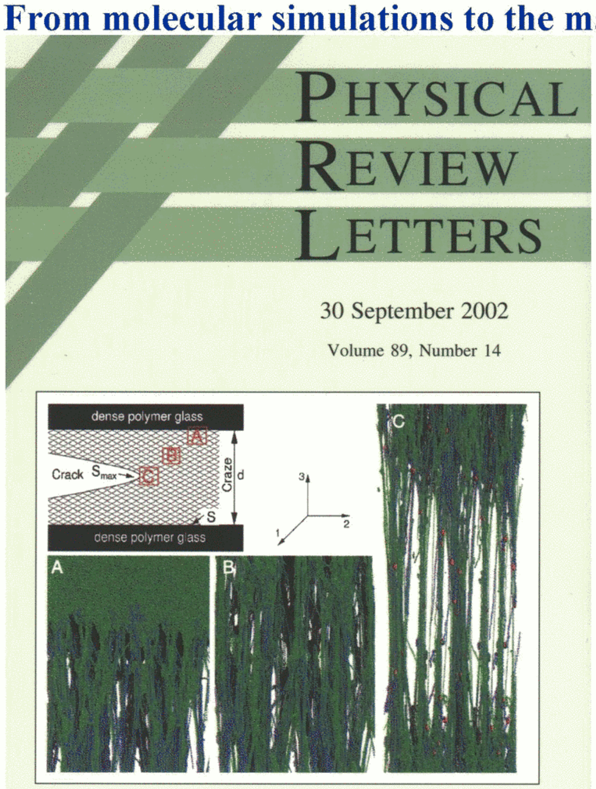
- S_{max}/S saturates between $N/N_e = 8 – 16$
- experimental polymers: saturation between $N/N_e = 6 - 12$

S_{max}/S=3.4-3.8 for T=0.1 u_0/k_B
S_{max}/S=5.0-5.3 for T=0.3 u_0/k_B

- data collapses when normalize by S_∞ (long chain limit)
- "Master curve":
  - typical distance entanglement-chain end: N/4
  - typical scale for disentanglement: N_e

  → disentanglement probability ~ $\exp(-N/4N_e)$, set to 1 for $N = 2N_e$

From molecular simulations to the macroscopic fracture energy



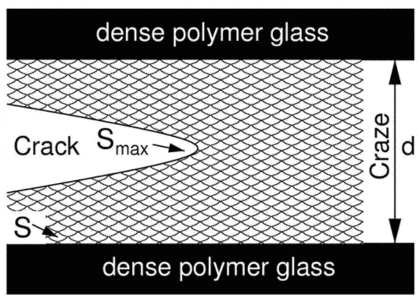
- How does crazing in front of the crack tip determine the macroscopic material strength?
- fracture energy G_c = work to propagate crack through unit area
- Lower bound: $G_{eq}=2\Gamma$ (interfacial free energy change), any excess dissipated
- G_c/G_{eq} ~ 1 for brittle materials
  $<10^3$ for metals
  ~ 10^3 to 10^4 for glassy polymers due to craze formation

Calculating the fracture energy…

Craze grows from d/λ to d under constant stress S →

$$\frac{G_c}{G_{eq}} = \frac{SD_0}{2\Gamma}\frac{d}{D_0}(1-1/\lambda)$$

What limits craze width d?



Continuum model by H. R. Brown (1991):

- Stress equals S at boundary, but stress concentration near crack tip breaks fibrils when stress reaches S_{max}
- Stress at distance r from the crack tip diverges as $r^{-1/2}$
- Divergence cut off at fibril spacing D_0
- Stress varies from S_{max} to S as r varies from D_0 to d

$$d/D_0 = 4\pi\kappa(S_{max}/S)^2$$

Elastic prefactor κ and S_{max}/S not known, determine with simulations

J. Rottler, S. Barsky and M. O. Robbins, PRL **89**, 148304 (2002)

How does the model compare to real polymers?

dimensionless ratio

$$d/D_0 = 4\pi\kappa(S_{max}/S)^2$$

Multiscale model:		**Experiments:**
flexible chains:	d/D_0 = 290-890	d = 3-20 μm, D_0 = 20-30 nm
semiflexible chains:	d/D_0 = 200-600	d/D_0 = 100-1000

enhancement of fracture energy

$$\frac{G_c}{G_{eq}} = \frac{SD_0}{2\Gamma}\frac{d}{D_0}(1-1/\lambda)$$

Multiscale model :		**Experiments:**
flexible chains:	G_c/G_{eq}=1300-4300	PMMA: G_c/G_{eq}~ 2500
semiflexible chains:	G_c/G_{eq}=1200-3500	PS: G_c/G_{eq}~ 5000

- In both model and experiments large toughness enhancement over 2Γ
- Toughness drops with decreasing temperature
- Chain scission is more prominent at lower temperatures

Conclusions

- Bead-spring polymer model reproduces key elements of craze growth and failure in nanoscale regions
- Following cavitation, crazes form at constant fibril drawing stress S that depends on T, adhesive interactions, chain friction
- Entanglements limit macroscopic extension ratio $\lambda_{max} = (l_0/l_p N_e)^{1/2}$, but microscopic extension of chains only ~ $N_e/3$ on average!
- Exponential force distribution as in conventional "jammed" systems
- Chain length determines craze breakdown stress S_{max} through competition between chain disentanglement and scission
- Parametrize continuum fracture model with elastic constants c_{ij} and fibril breaking stresses $S_{max} \rightarrow$ macroscopic toughness G_c