Structure and Properties of Polyethylene Nanofibers from Molecular Dynamics Simulations

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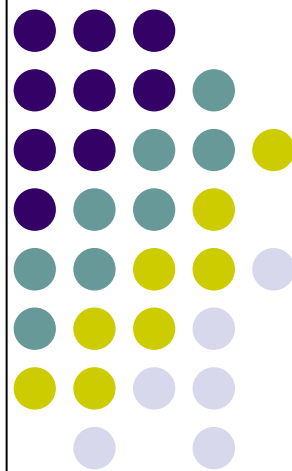
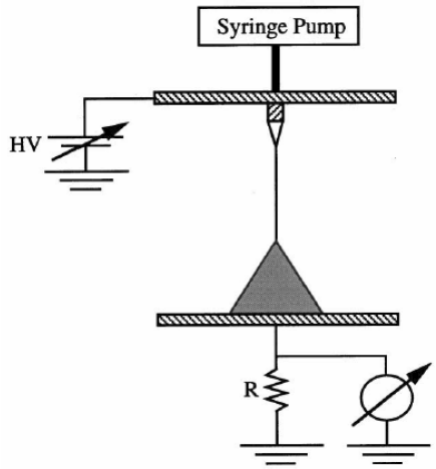
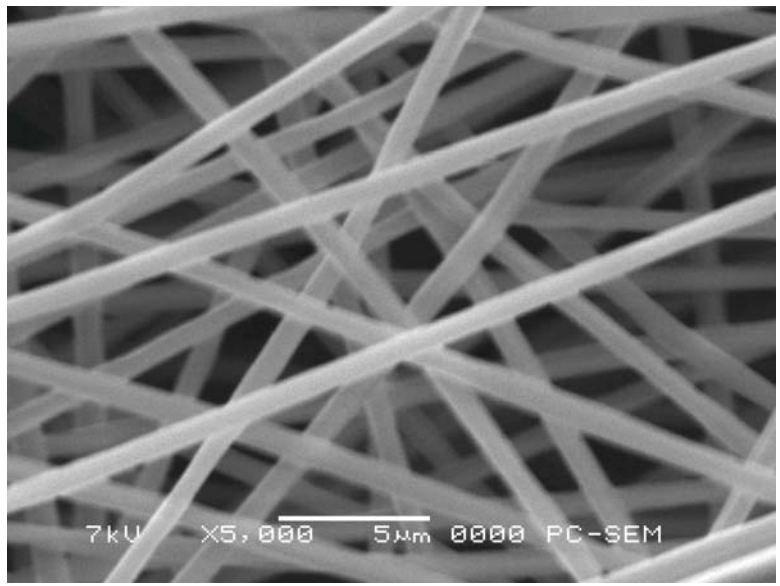


Introduction

- Electrospinning: A versatile method to produce fibers with diameters in the *nano* range
- Advantages
  - Small diameters (3 nm-10 μm)
  - High surface area (1-100 m^2/g)
  - High porosity (ca. 90%)
  - Small fiber-to-fiber distance



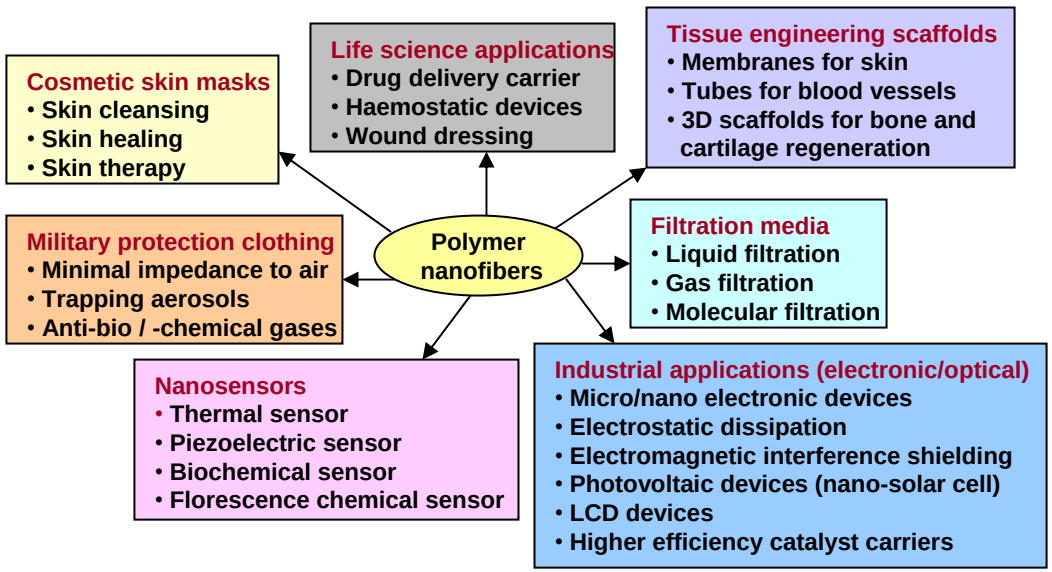


Courtesy of Jian Yu

Motivation

- Numerous applications postulated for nanofibers, but little fundamental investigation of the *nanofiber* properties

- Difficulty of characterization on the nanoscale

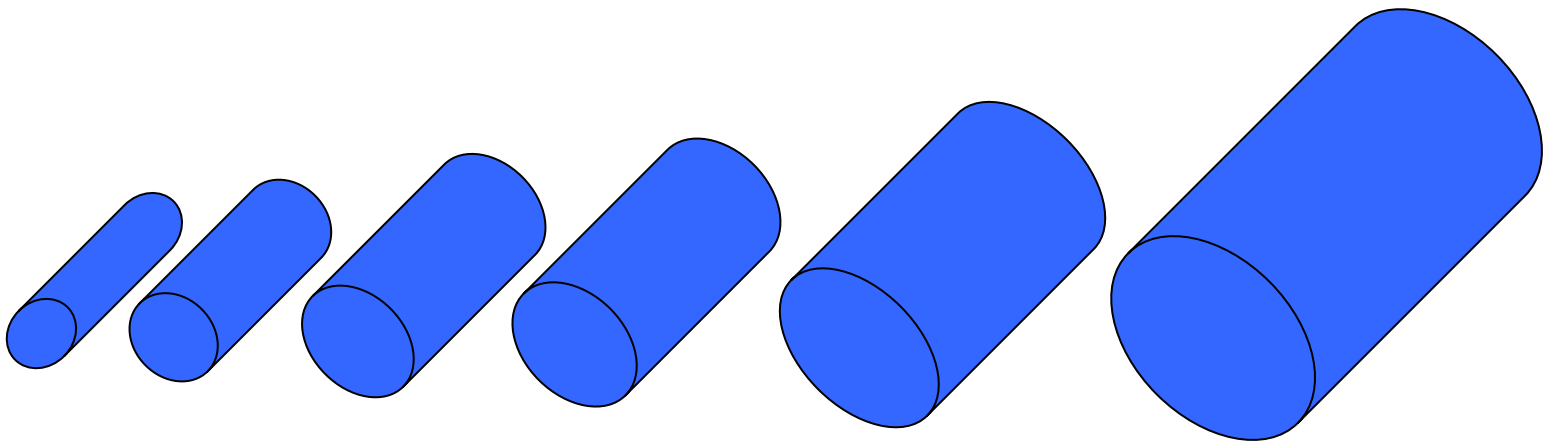


Burger C, Hsiao BS, Chu B, Annu. Rev. Mater. Res. 2006, 36, 333

Objectives

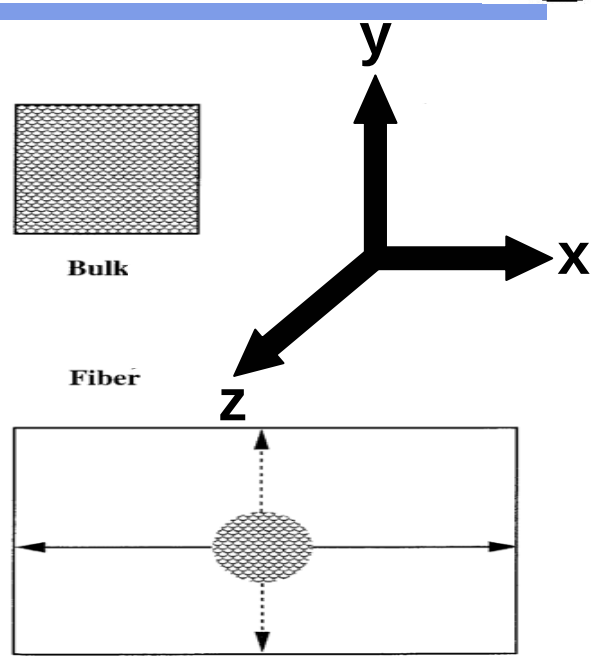
- Evaluate the fiber properties (including structural, mechanical, thermal) at the molecular level as a function of fiber size

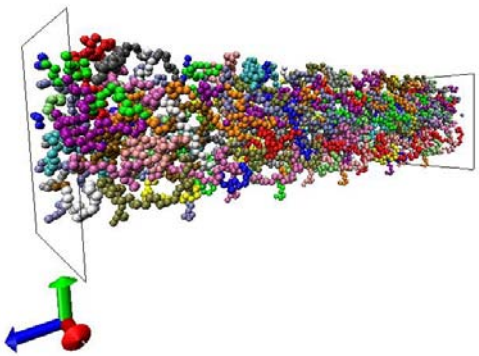
- Understand the origin of transition from bulk-like behavior to nanomaterial behavior: How small is “nano”?

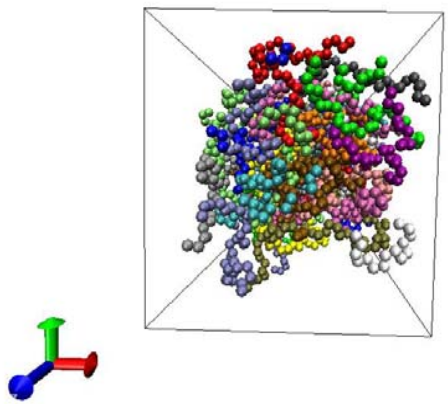


Approach

- **Constructing the simulation**
  - Step I: Equilibrium simulation in bulk using Periodic Boundary Conditions
  - Step II: Increase box size in 2 directions. The system remains periodic only in Z-dimension







Molecular Dynamics Simulation

- Polyethylene: the prototypical chain-like molecule (C50-C300)
- Total system size: 200 to 150,000 C atoms
- Compute engine: LAMMPS *from Sandia National Laboratory*
- Structural characterization
  - NVT ensemble, 495 K

Radial density profiles

- Radial density profile is obtained by:

$$\rho(r) = \frac{n(r)}{\pi(\delta r)^2 L}$$

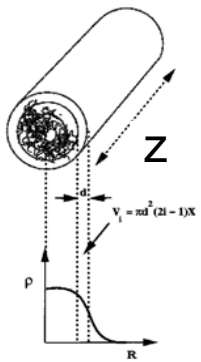
- Where

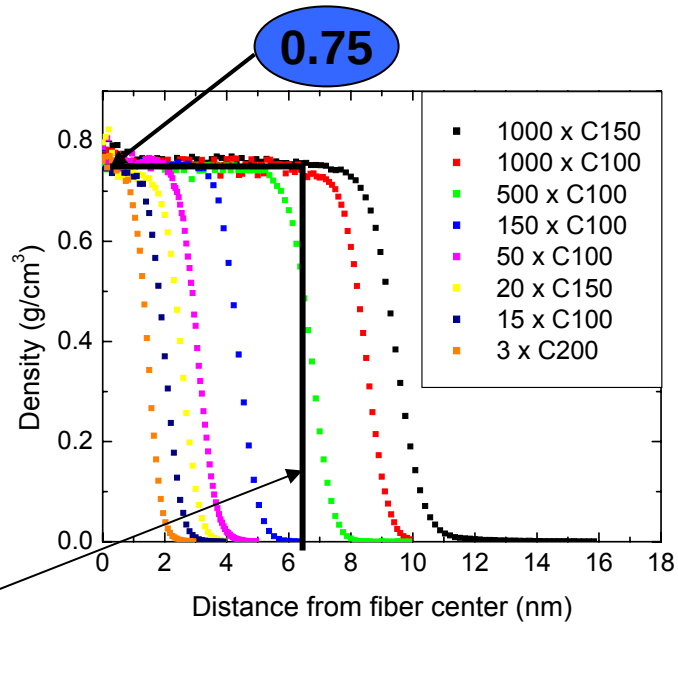
$$n(r) = \sum_{i=1}^{N} \int_{r}^{r+\delta r} \delta(r_i - r) dr$$

- Fiber radius calculated by Gibbs dividing surface method

$$2\pi \int_0^{\infty} \left[\rho(r) - \rho^{step}\left(r \middle| r_{GDS}\right)\right] \cdot r dr = 0$$

Diameters from **2.0** to **23** nm





Interfacial thickness: Distance over which density decreases from 90% of its bulk value to 10%:~ 0.78-1.39 nm

Increases slightly with fiber size*

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Interfacial Excess Energy

- Gibbs Dividing Surface applied to energy profile
- Calculate interfacial excess energy

$$E_{int} = \left[E_{total} - E_{GDS}\right] / \left[2\pi r_{GDS} L\right]$$

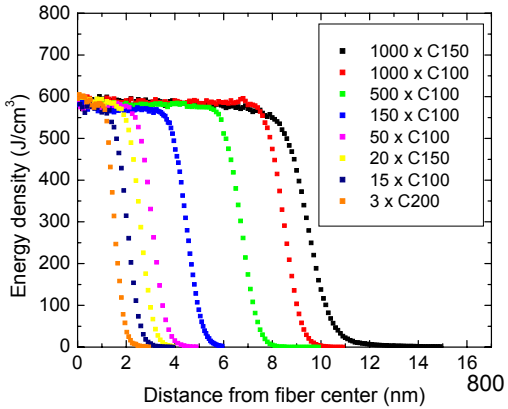
$$E_{total} = 2\pi L \int_0^\infty E(r) r dr$$

$$E_{GDS} = E_{core} \pi r_{GDS}^2 L$$

- E_{int}=0.022±0.002 J/m^2

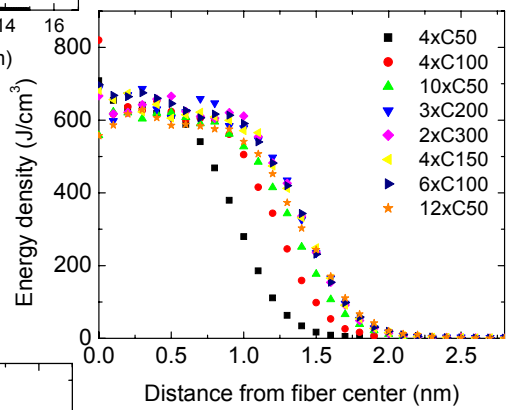
(similar to thin film PE simulations[1] and experiments[2])

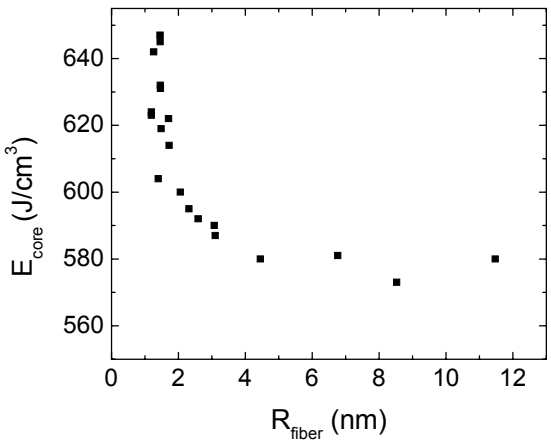
- E_{int} **NOT** dependent on fiber size*



R_{fiber} > 2 nm

R_{fiber} < 2 nm





Ecore depends on fiber size!!!

[1] *He D,Reneker DH, Mattice WL, Comp. Th. Poly. Sci.. 1997, 7, 19*

[2] *Polymer Handbook, Wiley 1999, 4th edition.*

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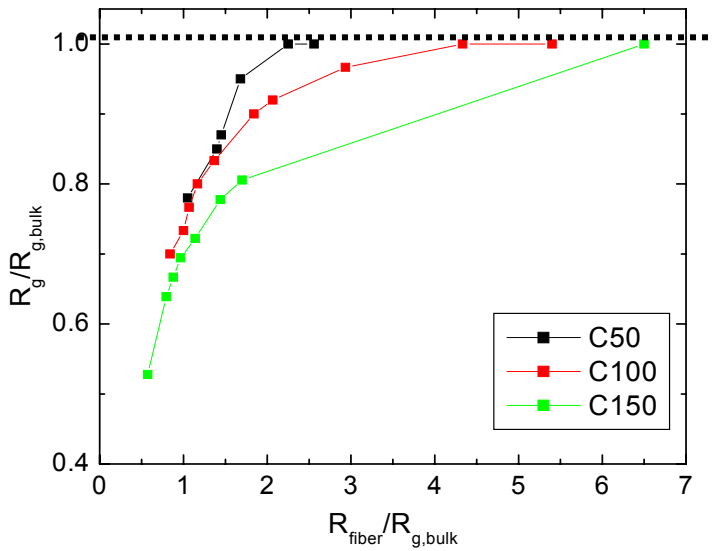
Molecular Conformations

- Measure of chain size: Radius of gyration
- Chains are confined*
- Confinement increases as
  - Fiber size decreases
  - Molecular weight increases
  - Effect notable up to 2-4xRg



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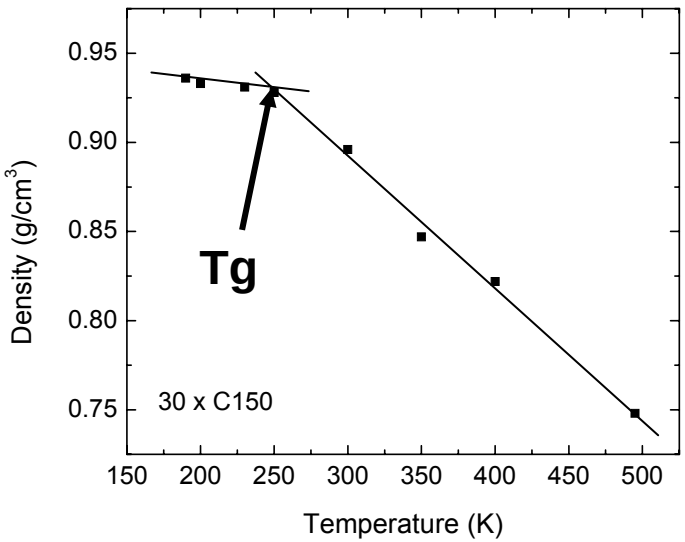
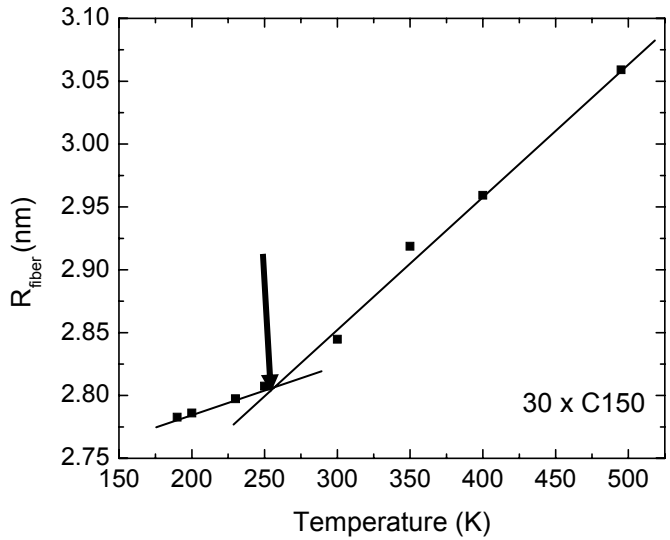
Glass Transition Temperature (Tg)

- Determination
  - Slow cooling (effective rate =1.97x10^{10} K/s) from 495 K down to 100 K
  - Re-equilibrate at several temperatures to determine fiber radius and core density vs T*





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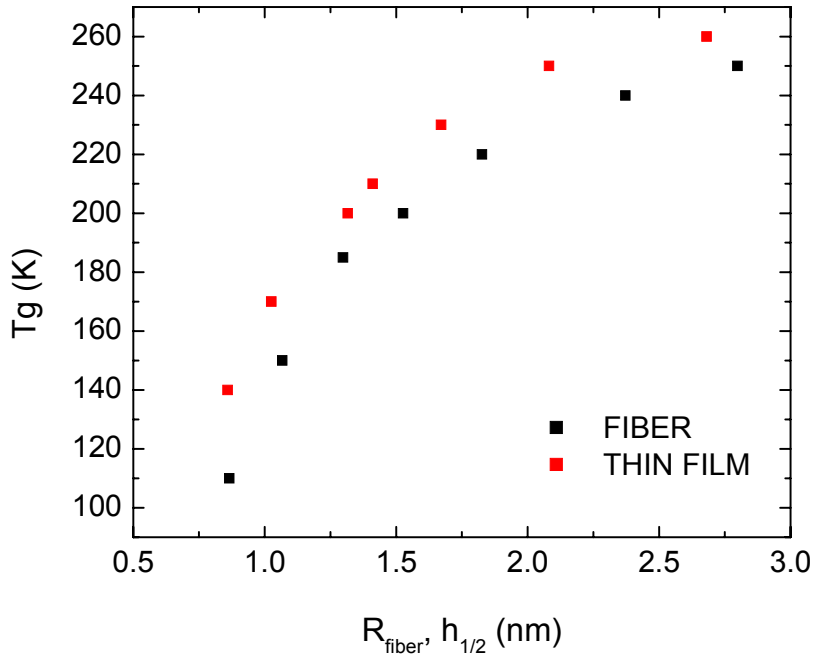
Fiber vs film Tg's

- T_g depends significantly on fiber radius or thin film thickness
- Observed in amorphous thin films experimentally and theoretically[1-4]
- T_g more depressed for nanofiber than the thin film*



[1] *Keddie JL, Jones RAL,Cory RA Europhysics Letters 1994, 27, 59*

[2] *Fukao K, Miyamoto Y, Phys.Review E 2000, 61, 1743*

[3] *Ellison CJ, Torkelson JM, Nature Materials 2003, 2, 695*

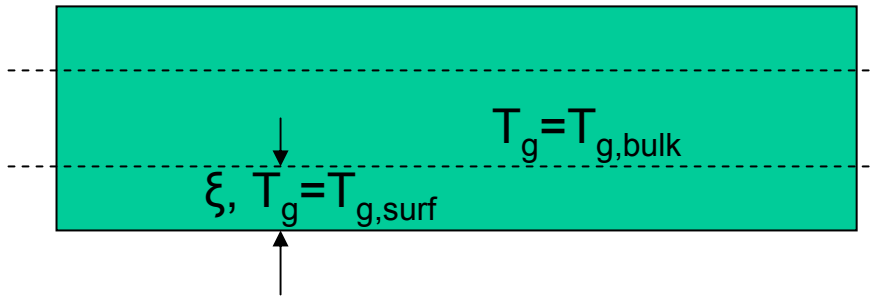
[4] *Fryer DS, Nealy PF,de Pablo J, J.Journal of Vac. Sci. Tech 2000, 18, 3376*

*Manuscript submitted to Macromolecules

Modeling of Tg depression in nanofibers

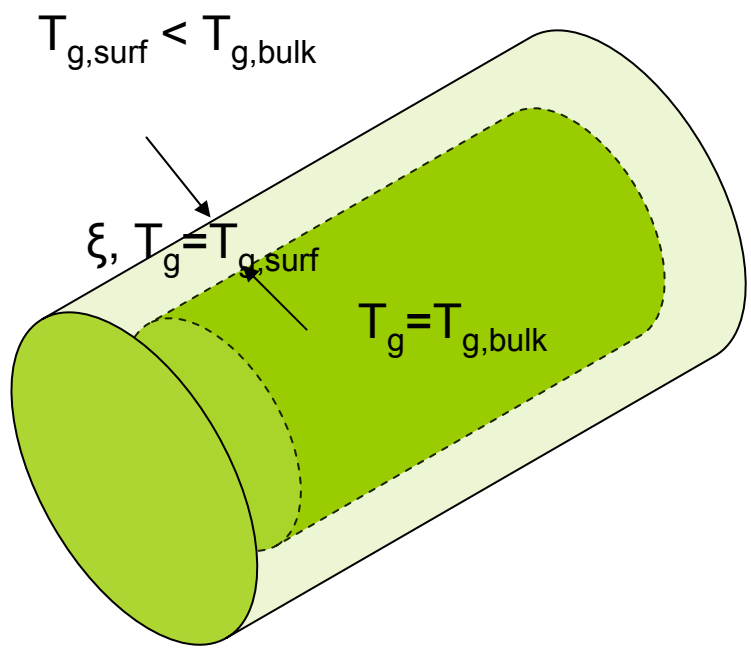
- Layer model[1]: A volume-averaged formulation for thin films

$$T_g = T_{g,bulk} - \frac{\xi(T_g)}{h_{1/2}}\left(T_{g,bulk} - T_{g,surf}\right)$$



- Derivation of formula for nanofibers*:
  - Surface material with thickness ξ(T) and $T_g=T_{g,surf}$
  - Core material with $T_g=T_{g,bulk}$

$$T_g = T_{g,bulk} - \left[\frac{2\xi(T_g)}{R} - \left(\frac{\xi(T_g)}{R}\right)^2\right]\left(T_{g,bulk} - T_{g,surf}\right)$$



[1]*Forrest JA, Mattsson J, Phys Rev. E., 2000, 61, R53.*

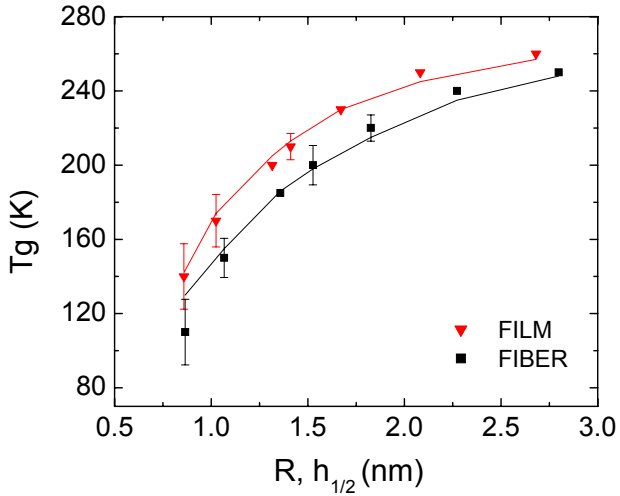
*Manuscript submitted to Macromolecules

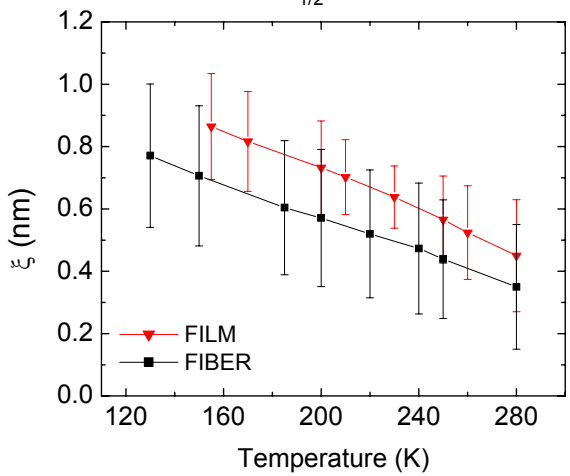
Cooperativity Length Scale

- Cooperativity length scale ξ(T) with decreasing temperature is given by

$$\xi(T) = \xi(T_{ref}) + \sigma(T_{ref} - T)^{\gamma}$$

- where $T_{ref}=T_{g,bulk}=280$ K[1]
- Thin film*:
  - Tg,surf=155±5K
  - ξ ($T_{g,bulk}$) = 0.45 ± 0.18 nm
- Nanofiber*
  - Tg,surf=150±7K
  - ξ ($T_{g,bulk}$) = 0.35 ± 0.2 nm
- Statistically indifferent ξ in nanofibers and thin films
- Single ξ~ 4 nm regardless of geometry, compared to CRR=0.46 nm [2]





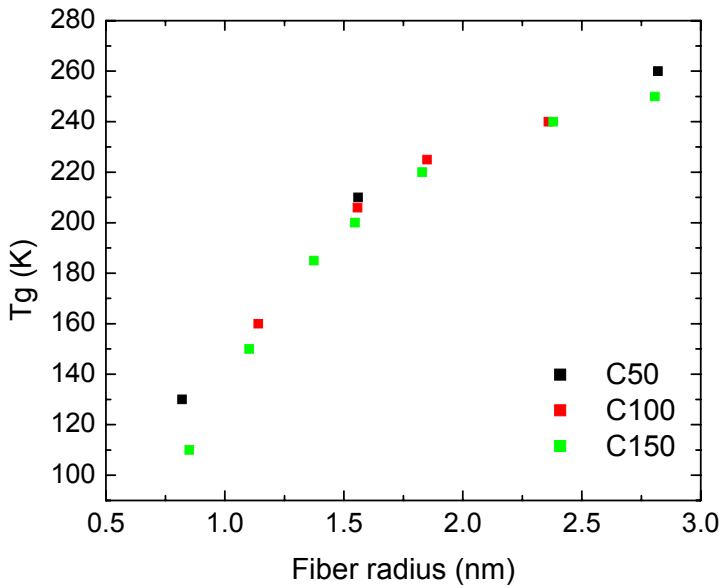
[1]*Capaldi FM, Boyce MC,Rutledge GC, Polymer., 2004, 45, 1391.*

[2]*Solunov CA, European Polymer Journal, 1999, 35, 1543.*

*Manuscript submitted to Macromolecules

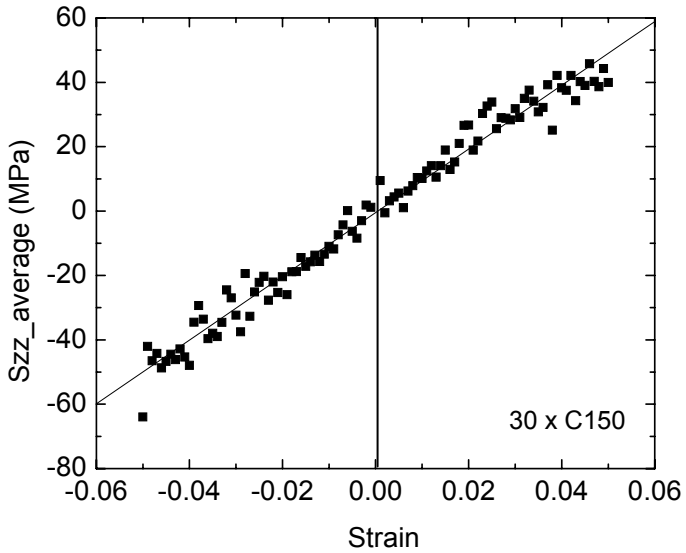
Molecular Weight Dependence of T_g

- 3 different molecular weights (MW)
  - C150, MW = 2100 g/mol
  - C100, MW = 1400 g/mol
  - C50, MW = 700 g/mol
- Depression in Tg **NOT DEPENDENT** on Molecular Weight
- Agreement with amorphous thin polymer films of low to moderate molecular weight
- Layer theory VALID for this molecular weight range



Mechanical Properties

- Determination of Young's modulus (E)
  - Apply constant strain rate up to a predetermined strain along the long axis of the fiber (compression and tension, small elongation ±5%)
  - Noise in stress data, stress is averaged for several different initial configurations using weighted least squares method
  - Calculate Young's modulus as initial slope to stress-strain curve

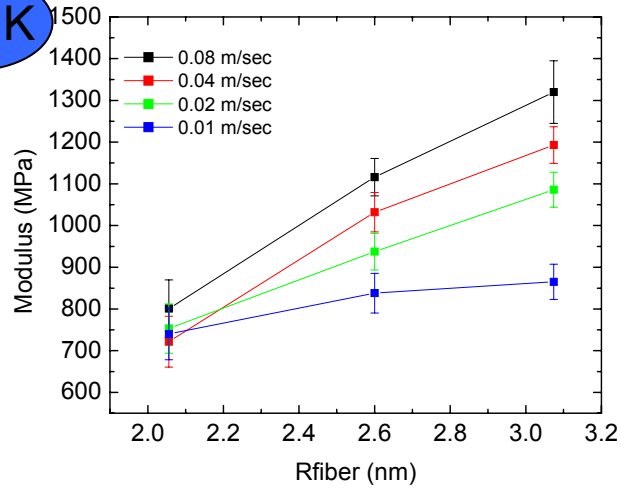


- Displacement rate = 0.049 m/sec
- Fiber diameter = 6.148 nm

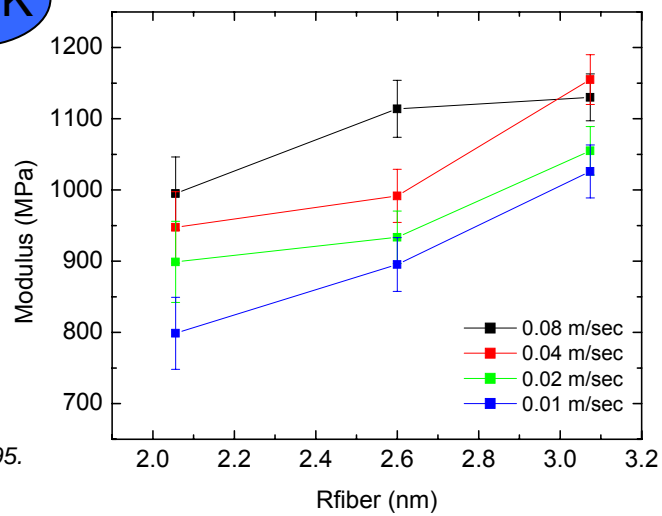
Dependence of E on fiber radius

- Simulation temperatures: Well below Tg
- Modulus decreases with decreasing fiber size at 150K and 100K
- Similar results found in experimental studies of thin films[1]

150 K



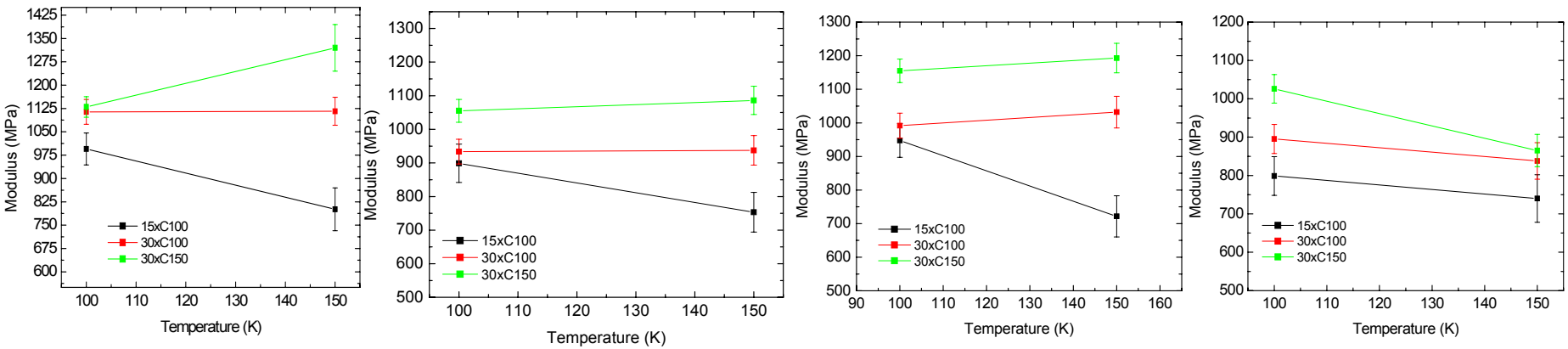
100 K



[1]*Stafford CM, Vogt BD,Harrison C, Julthongpiput D, Huang R Macromolecules, 2006, 39, 5095.*

Strain rate vs. Temperature

- Modulus decrease due to the action of relaxation processes which
  - Speed up at high temperature
  - Rendered irrelevant by high strain rates
- Surface relaxations faster than bulk (Small fibers are more “surface” than bulk)
- Small fibers: Temperature effect wins (despite high strain rates)
- Large fibers: Temperature competing against high strain rates



Strain rate **decreasing**

Conclusions

- Structural characterization
  - Bulk-like behavior at center
  - Confined chains towards the surface
  - No dependence of interfacial excess energy on fiber size
- Thermal characterization
  - Tg depression as fiber size decreases (similar to thin films)
  - Single cooperativity length scale at $T_{g,bulk}$ (~ 4 nm)
- Mechanical characterization
  - Young's modulus decreases as fiber size decreases
  - Temperature and strain rate are competing for large fibers

Acknowledgements

- Rutledge and Van Vliet groups at MIT
- Dupont-MIT Alliance