Simulations of Thin Polymeric Films

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Students

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Collaborators

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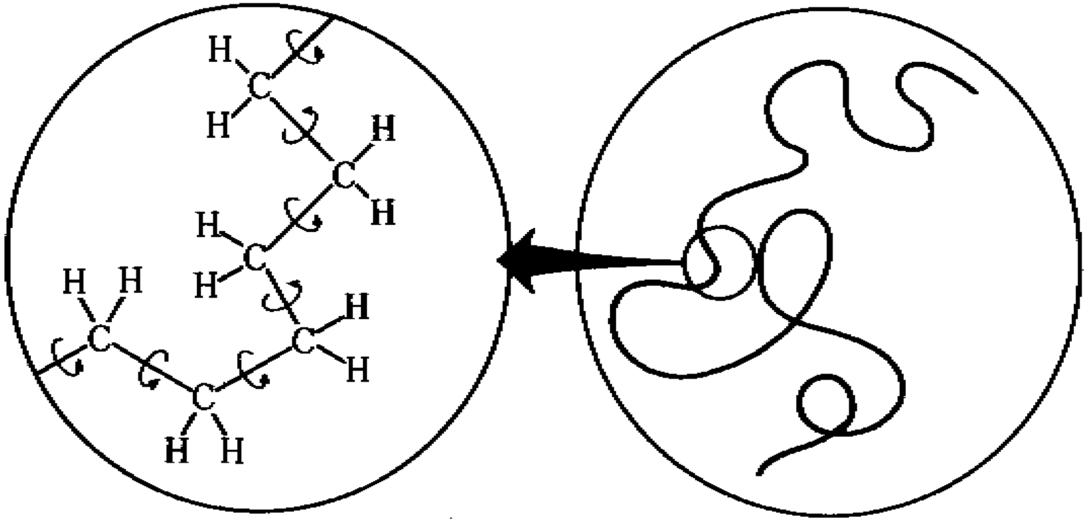
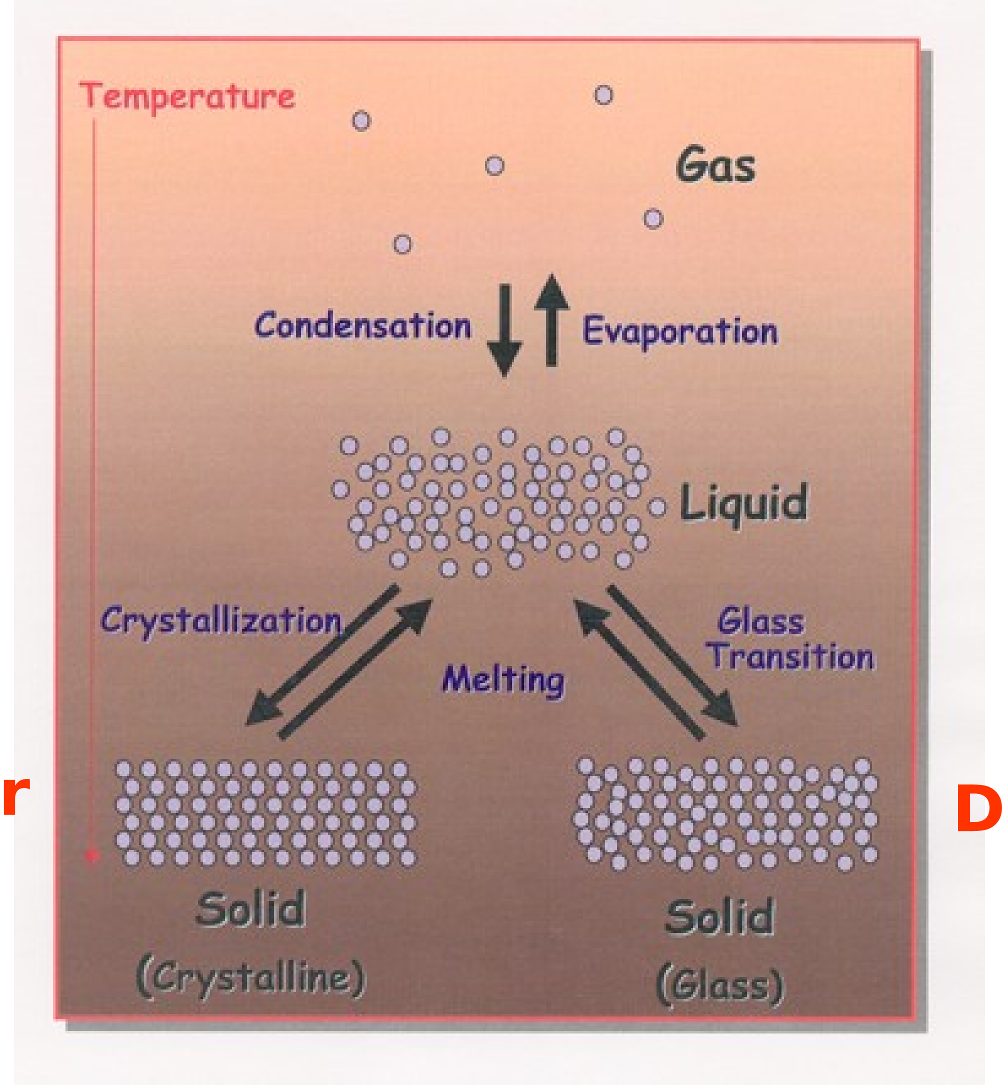
Polymers

Polyethylene



- [Random Walks in Space]
- [Rheology: Viscoelastic]
- [Cooling: Glass Transition]

Glass Transition



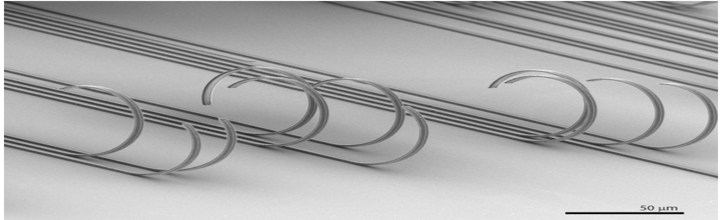
Order

Disorder

Fall 2009 or Spring 2010

Take as Elective Chemistry/Physics 538

Polymer Science

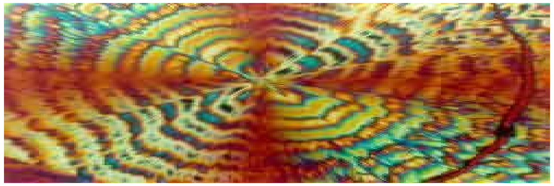


Silicon Microhooks: Image of fine silicon ribbons coated on one side with a photocurable polymer. Residual thermal stress in the overlying polymer causes the ribbons to bend upwards into hook-like structures. Courtesy: M. Meitl

Mechanics of Gels and Cells

Instructor: Arlette Baljon

(abaljon@mail.sdsu.edu)



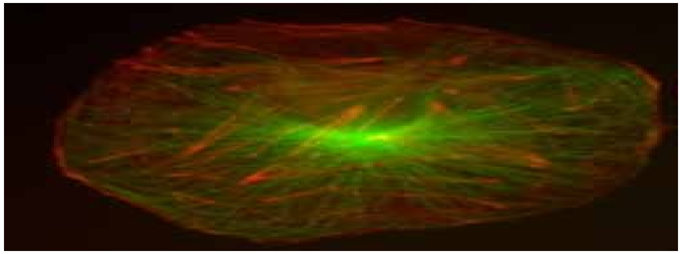
Biodegradable plastics: Image of polymer crystals spiraling out from a central point forming beautiful spherulites. Courtesy: J. Hobs

Comments by previous students:

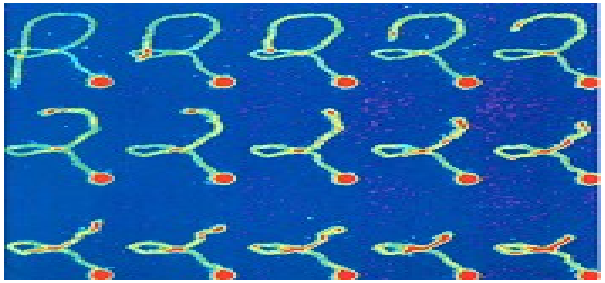
- This was a very fascinating course.
- The novel structure of this course, especially the talk sessions are most useful for students.
- I loved the use of software packages and internet content to supplement the lecture material.
- The problem sessions really facilitate understanding of the more challenging problems.
- The animations in biophysics were really interesting.
- This was useful considering that quantitative Biology is the next big thing.
- I'd certainly suggest other students to take Dr. Baljon's class.

For students of

- Physics
- Chemistry
- Bioengineering
- Mechanical Engineering
- Chemical Physics
- Bioinformatics



Cytoskeleton: This image show the distributions of microtubules (green) and actin filaments (red) in cultured epithelial cells. Courtesy: ITG



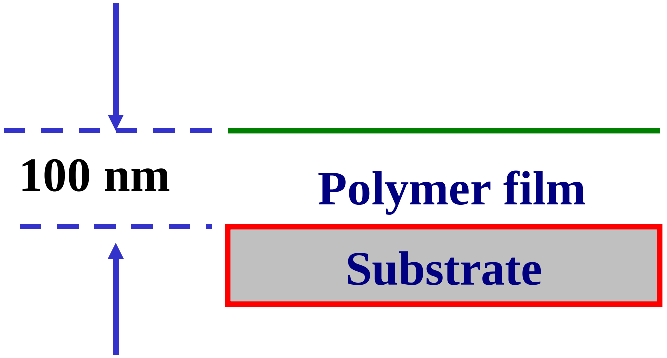
Viscoelastic motion: Images of tube-like relaxation of a single, fluorescently labeled (light blue) molecule of DNA in an entangled polymer solution (not shown). DNA is attached with one end to a (red) bead. Courtesy: T. Perkins, D. Smith, and S. Chu.

Info and Course Syllabus

www.sci.sdsu.edu/~abaljon/syllabus538.html

Thin Films of Polymers

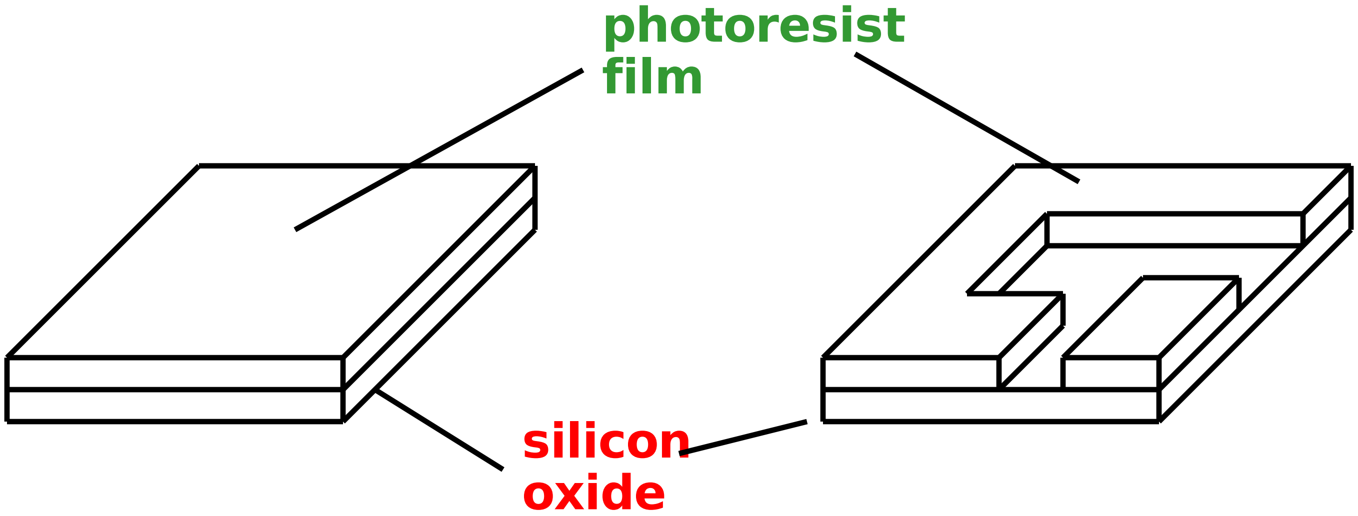
Ultra thin polymer films find applications in microelectronics industry



- Lithography
- Millipede Data Storage
  Technology

Tune properties (stable at room temperature)

Polymer Films for Lithography

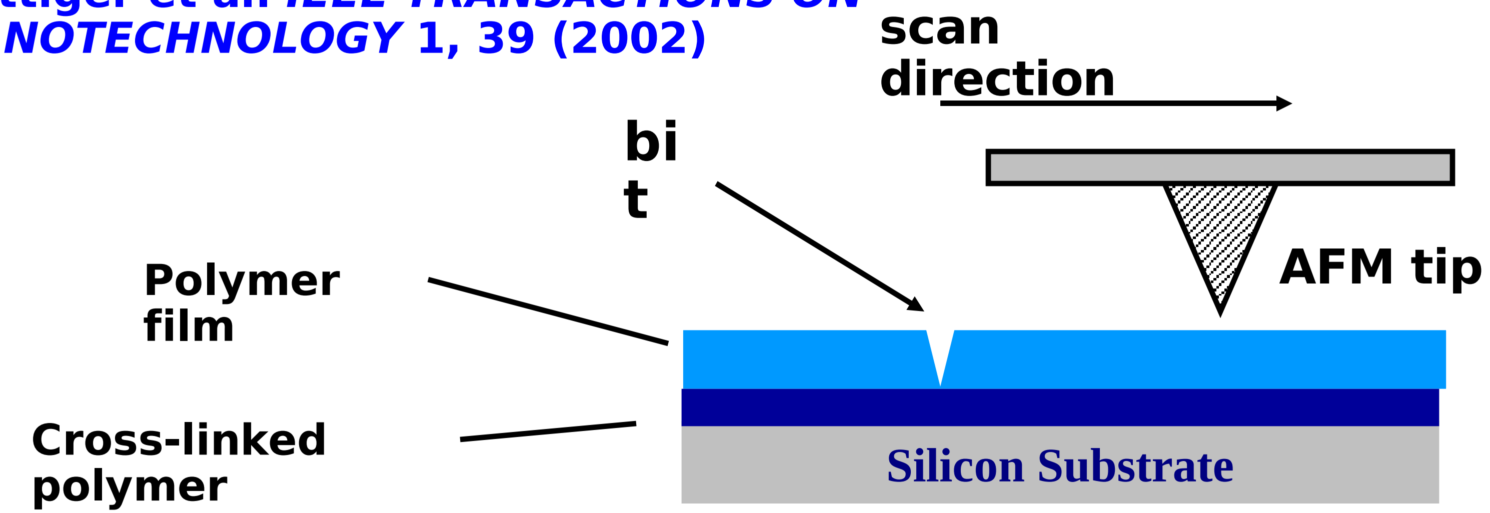


- **Nanoscale circuit → Imprint → Chip**

- **Important consideration:**
  Mechanical stability of films

Millipede Data Storage Technology

Vettiger et al. *IEEE TRANSACTIONS ON NANOTECHNOLOGY* 1, 39 (2002)



scan direction

bit

AFM tip

Polymer film

Cross-linked polymer

Silicon Substrate

- Thermomechanical read/write process in nanoscale polymer films using AFM-like tip
- A “bit” is written by heating the polymer film above its glass transition temperature and then creating an indentation in it using an AFM-like tip
- Polymer film used should be easily deformable for bit writing, written bits should be stable and it should be possible to repeatedly erase and rewrite the bits

Glass Transition Behavior of Thin Films

Increasing the T_g of thin polymer films:

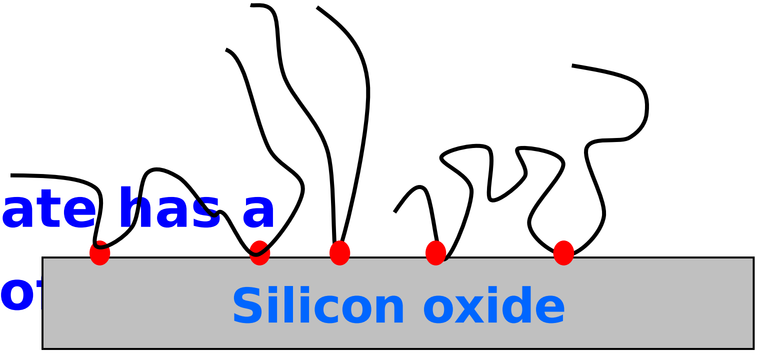
- **Increase the strength of attractive polymer-surface interactions**
- **Use grafted (chemically bonded to the surface) polymer films**

Experimental data:

- **Fryer et al. (2001):** **Tuning the interfacial energy changes the T_g by about 10-15 deg C for both PS and PMMA (100 nm thick) films**
- **Tate et al. (2001):**

  Chain grafting to the substrate has a significant effect on the T_g of (100 nm thick) polymer films:

  55 deg C increase for PHS



Free Standing Films

- **Supported thin film:**

  Glass transition temperature higher than that of bulk

- **Free standing thin film:**

  Glass transition temperature lower than that of bulk

- Electronic Transistors
- Gas separation membranes

Flexible Polymer Transistors

- (PhysOrg.com) -- Computer and television displays made using flexible, bendable polymer materials are technologies of the future, promising roll-up computer monitors and other innovations. Scientists are making progress toward bringing these technologies into our homes and offices.

WHAT'S HOT IN CHEMISTRY…

Polymer Promise: One Day IT Will All Be Organic

Science watch (2000)

- An all-polymer semiconductor sounds almost like a contradiction in terms because we generally think of plastics as being completely non-conducting as far as electricity is concerned–hence their everyday use as insulation for cables, casings, and sockets. An all-polymer visual display unit sounds equally implausible, since the stimulated emission of light is the province of inorganic materials such as doped metal phosphors.
- Yet some polymers can conduct and some can emit light, and what paper #2 reports is their bringing together to create the first all-polymer device. It is the work of Richard Friend, Henning Sirringhaus, and Nir Tessler of the Cavendish Laboratory at the University of Cambridge, England, and it brings the "organic" computer of the future one step closer.
- The paper describes an organic semiconductor integrated optoelectronics device which consists of a high-mobility conjugated polymer transistor driving a polymer light-emitting diode (LED). (Polymer LEDs were discovered by Friend and fellow chemist Andy Holmes in 1989.) The other component, a so-called field-effect transistor (FET), was made from poly(hexylthiophene), which consists of linked five-membered sulfur-containing thiophene rings, each with a hexyl group attached. What is special about this polymer is the way in which it has been produced so that all these hexyl groups are orientated in the same direction.
- The performance of the FET approaches that of an inorganic thin-film silicon FET with field-effect mobilities up to 0.1 cm2 per volt and ON-OFF current ratios in excess of a million. Paper #2 explains how the LED and FET were integrated into a working device mounted on a silicon dioxide substrate, and it clearly demonstrated that the high-mobility FET has sufficient driving current to switch a polymer LED. Moreover, it was easy to make and robust in operation, albeit relatively crude, and while it does not address the complex issue of integrating a full pixel–which would require the use of a polymer insulator–it points the way forward.

Quantum Mechanics

- electrons

….

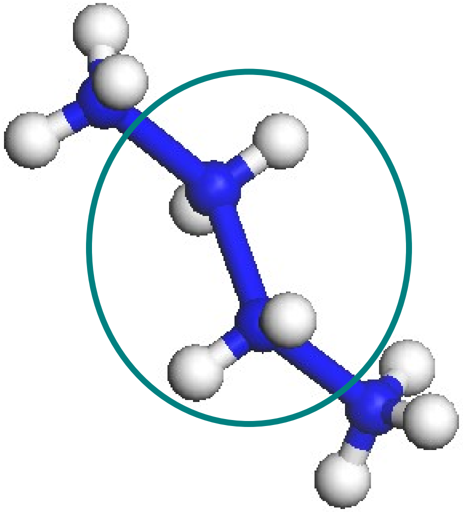
< few nm

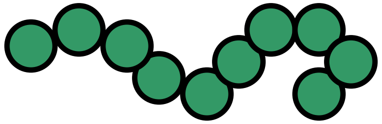
Molecular Modeling

- Atoms to coarse grained collections of atoms that can be treated as discrete entities

Models

- Atomistic
- United atom
- bead-spring





Continuum Mechanics

- Piecewise continuity of materials
- Constitutive equations

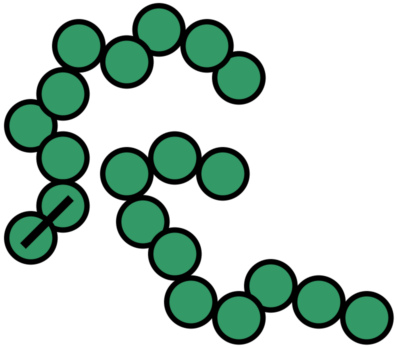
> μm

Molecular Modeling

- **Bead-spring model:**

Polymer: Bead-spring chain

40 chains, chain length = 100



Lennard-Jones Potential $V_{LJ}(r)=4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]$

Anharmonic Spring $V_S(r)=0.5kR_o^{2}\ln[1-(\frac{r}{R_o})]$

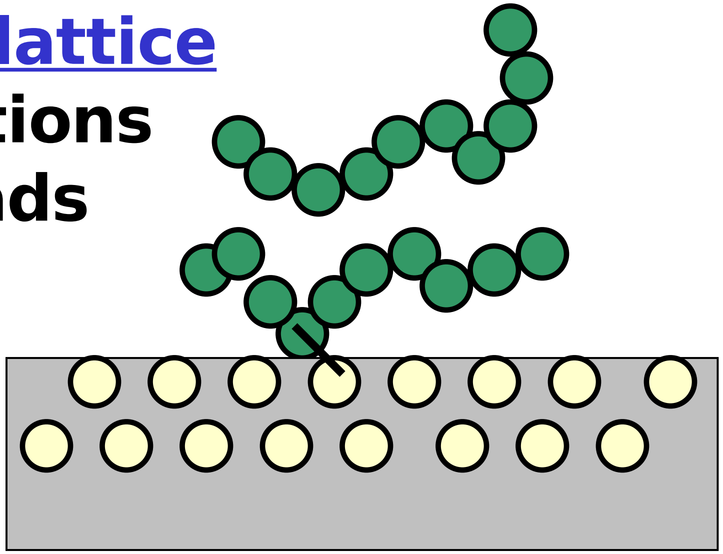
$$\tau=\sqrt{m\sigma^{2}/\varepsilon}$$

All quantities are reported in reduced Lennard-Jones units

$\sigma\approx 0.5nm$ $\varepsilon\approx 30meV$ $\tau\approx 5ns$

- **Substrate: atoms on a lattice**

  Lennard-Jones interactions between the chain beads and surface beads



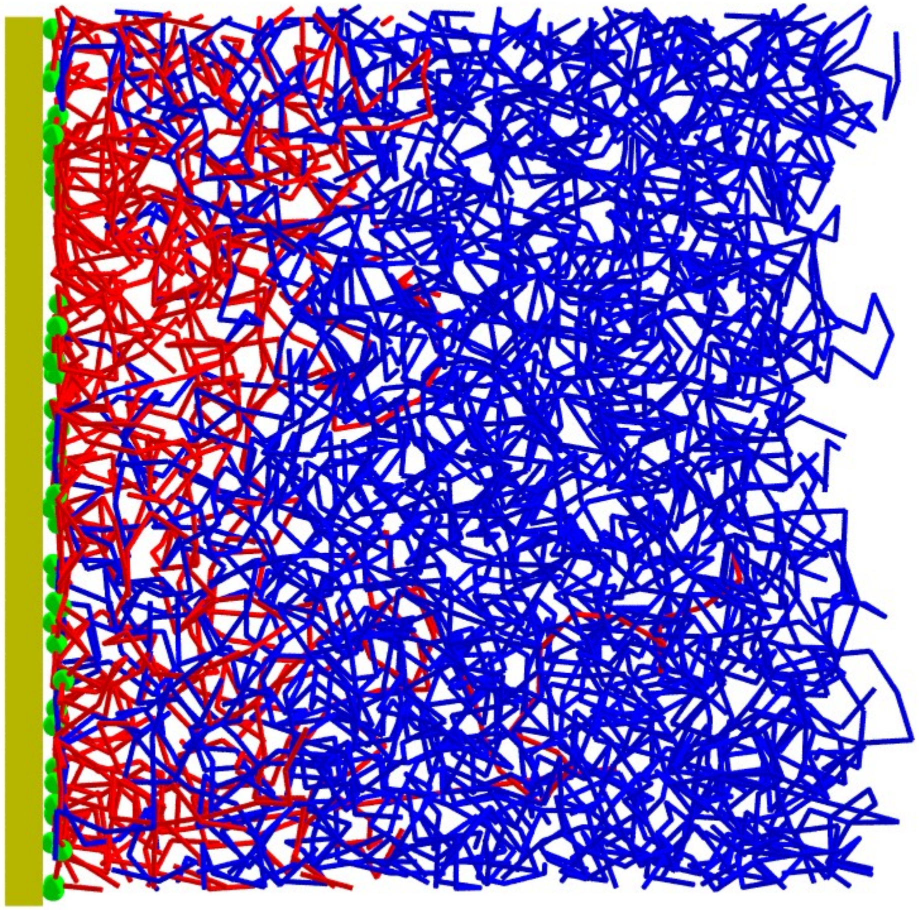
$\sigma_{ps}=0.9\sigma$

$\varepsilon_{ps}=\varepsilon$ or $\varepsilon_{ps}=0.1\varepsilon$

- **Chain grafting on substrate: On 10 chains 5% of the beads are connected by anharmonic springs to the substrate atoms**

Constant temperature

Model Film



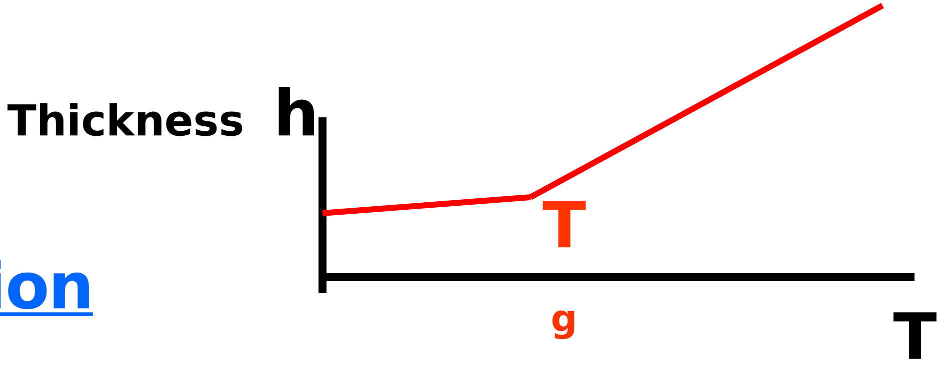
— Ungrafted chain

— Grafted chain

Substrate

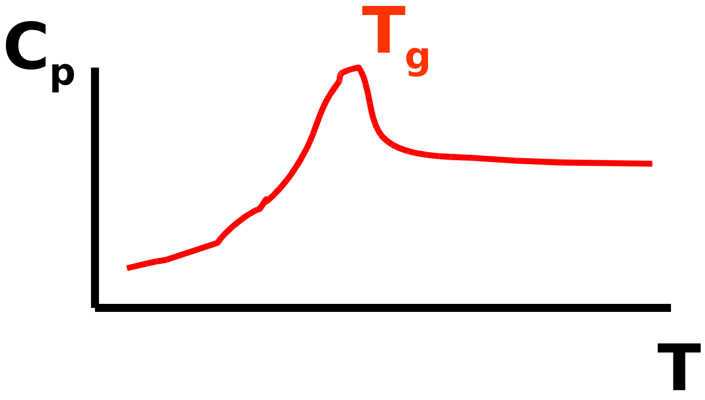
Polymer film

Determination of Glass Transition



- Thermal expansion

  - Temperature dependence of film thickness

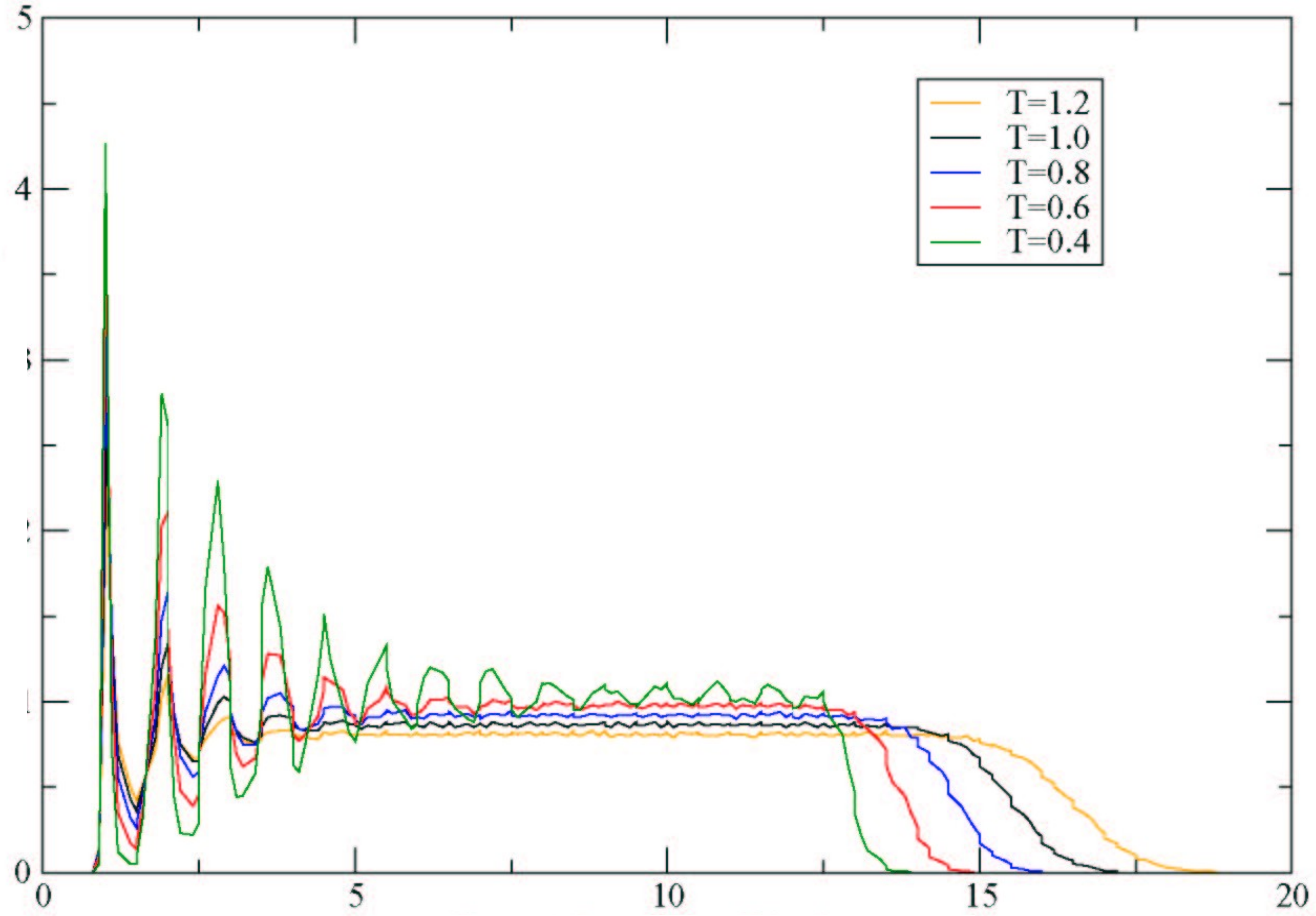


- Heat capacity

  - Energy fluctuations (calorimetric method)

Film Thickness: Bead distribution in an ungrafted film

Number density

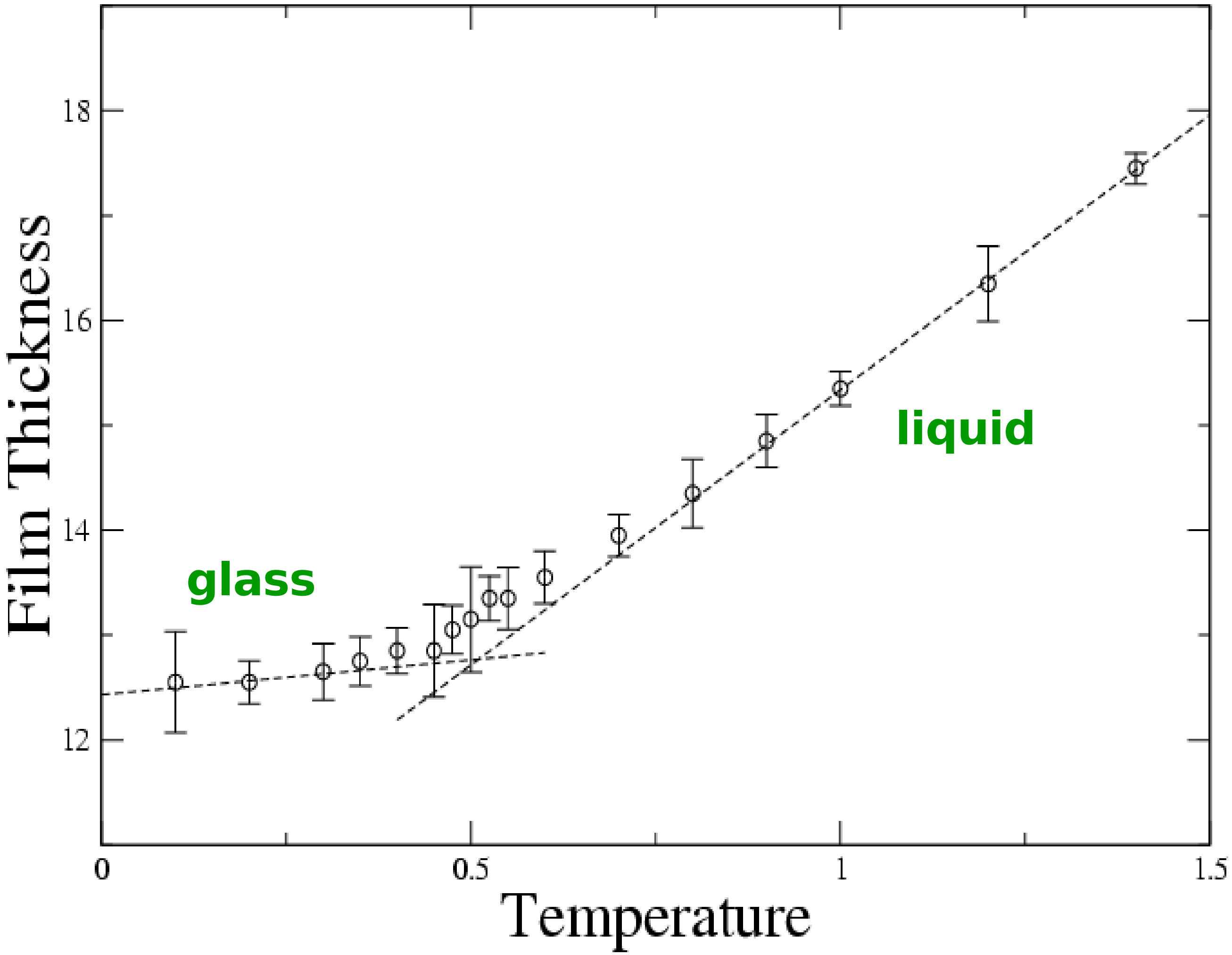


Z(distance)

$\boldsymbol{\varepsilon_{ps}=\varepsilon}$

Decrease in thickness at low temperature

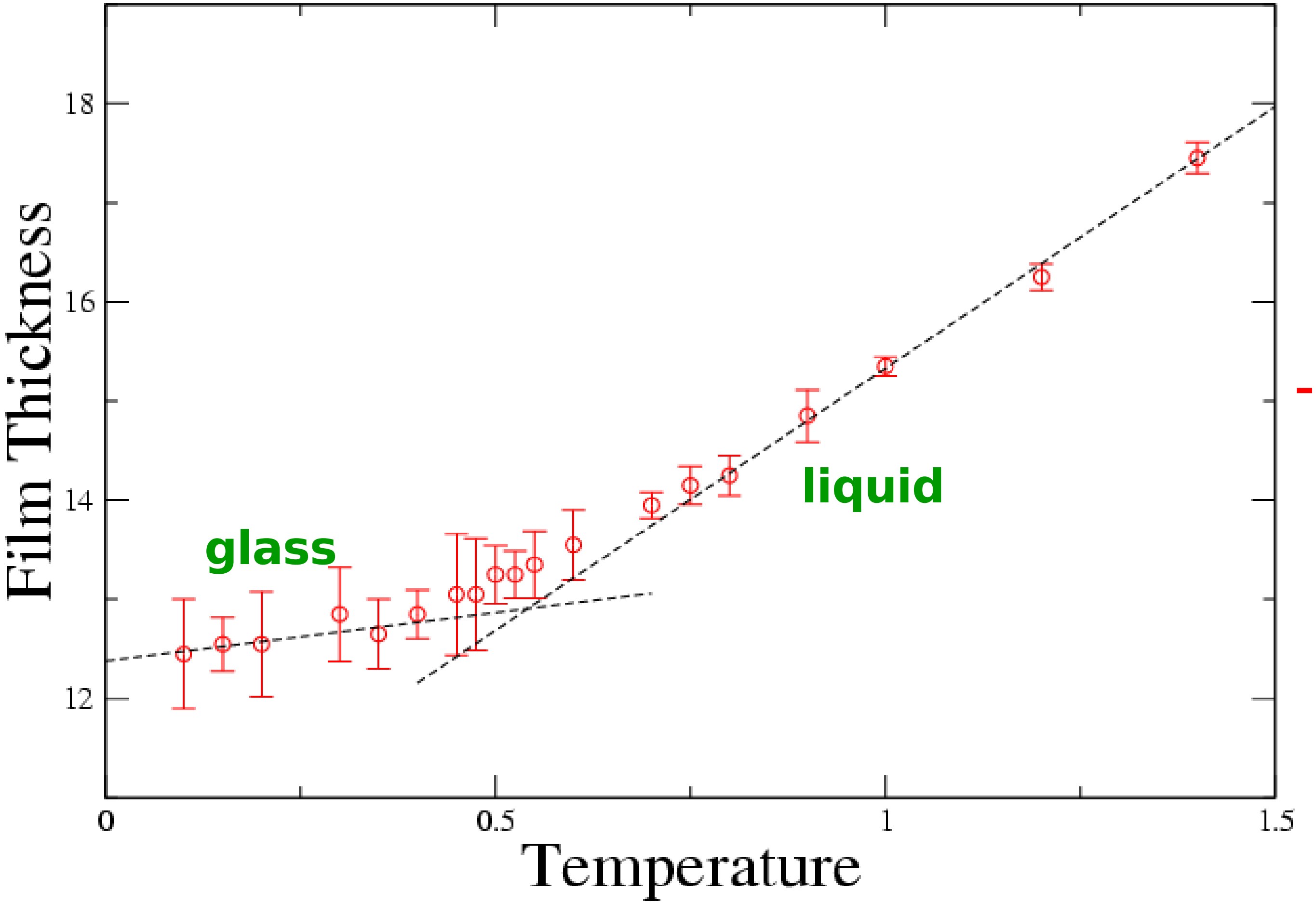
T_g of the Ungrafted Film



***T_g* = 0.51**

Temperature dependence of film thickness

Effect of Grafting



Ungrafted

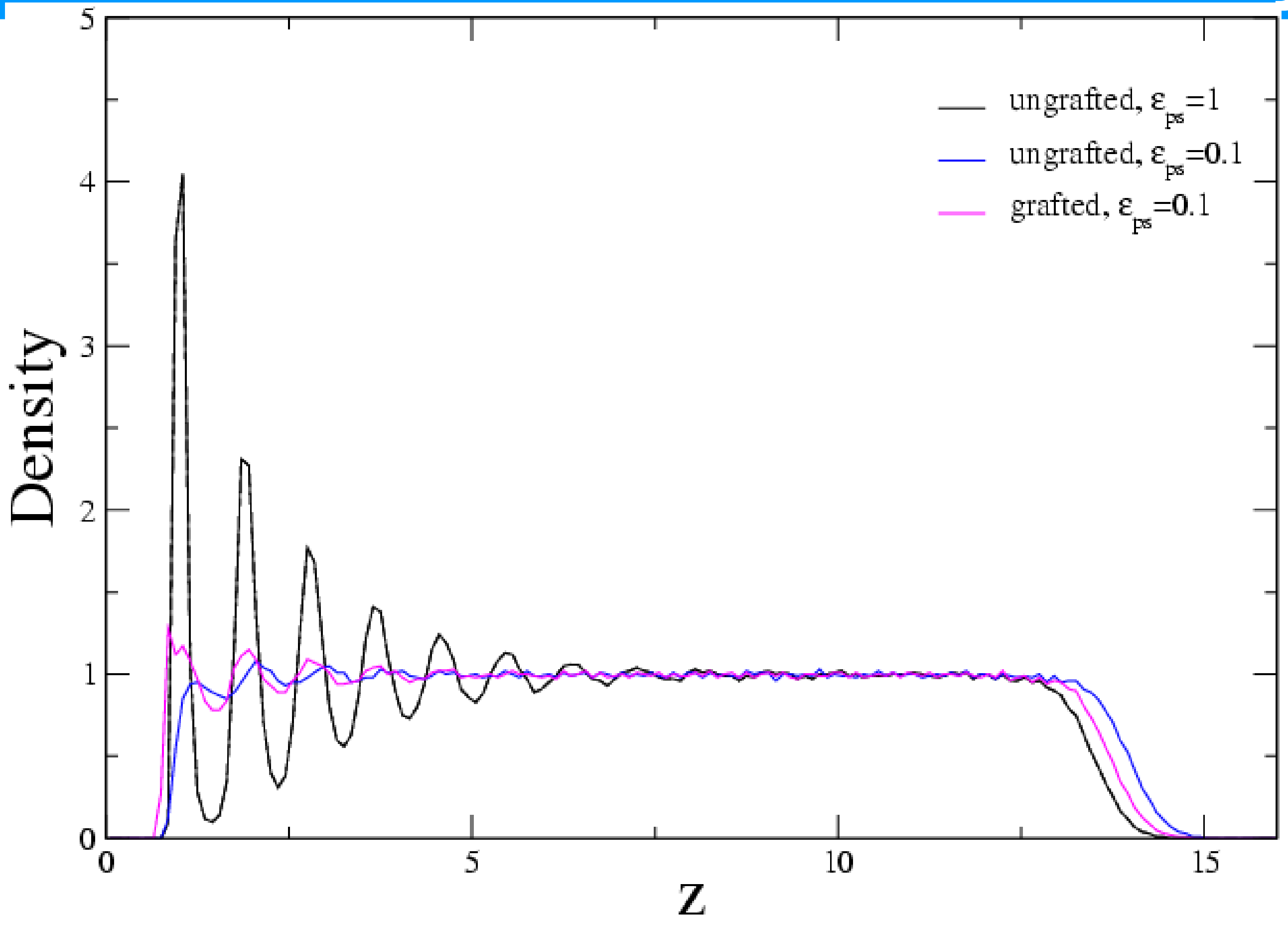
T_g=0.51

- Grafted

T_g=0.54

Grafting has some effect on T_g

Effect of Substrate-Polymer Interaction on Bead Density



ε_{ps}=0.1

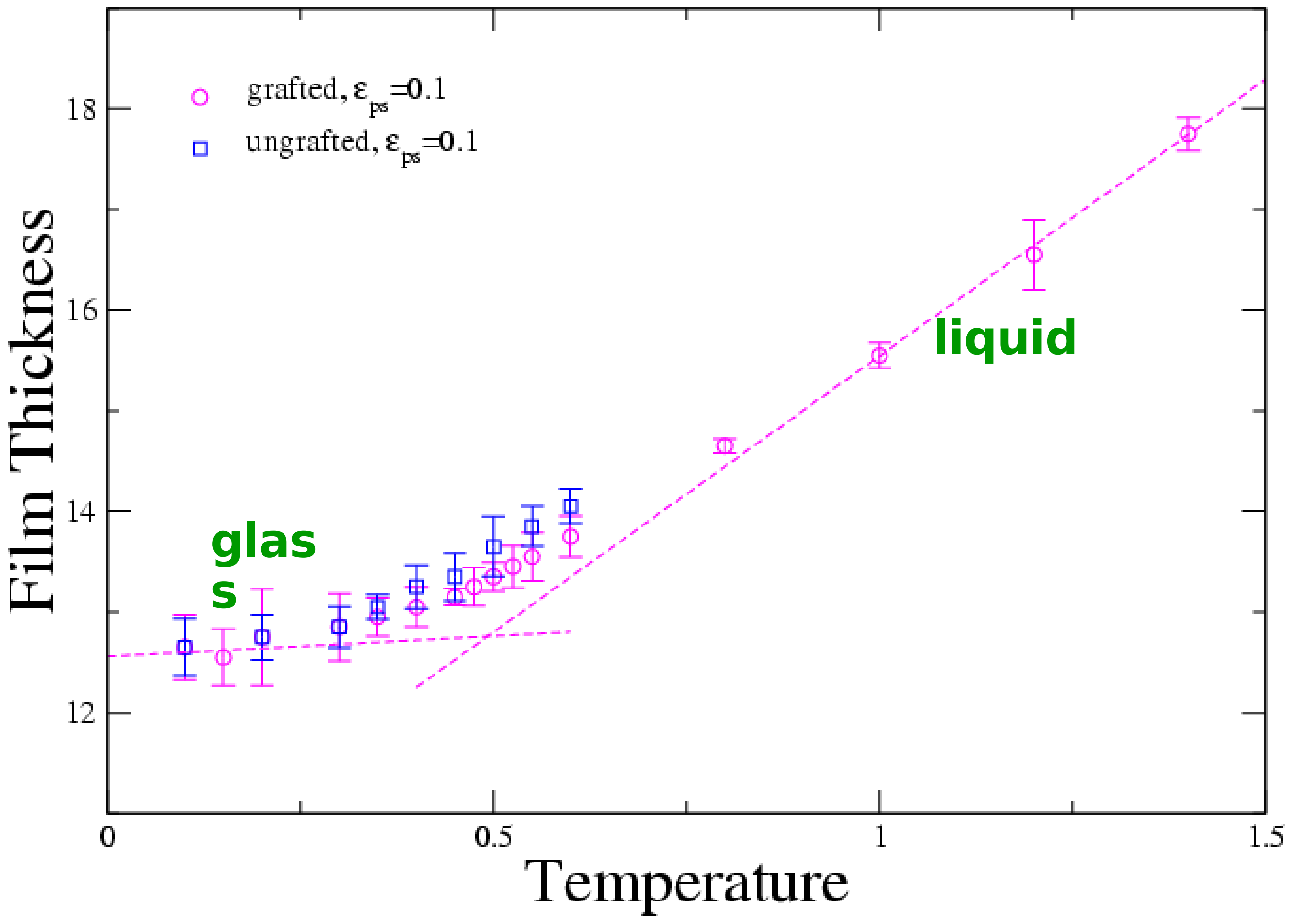
Ungrafted

Grafted

T=.55

Strength of the polymer-substrate interaction has a significant effect on bead layering near the substrate surface

Effect of Substrate-Polymer Interaction on Glass Transition



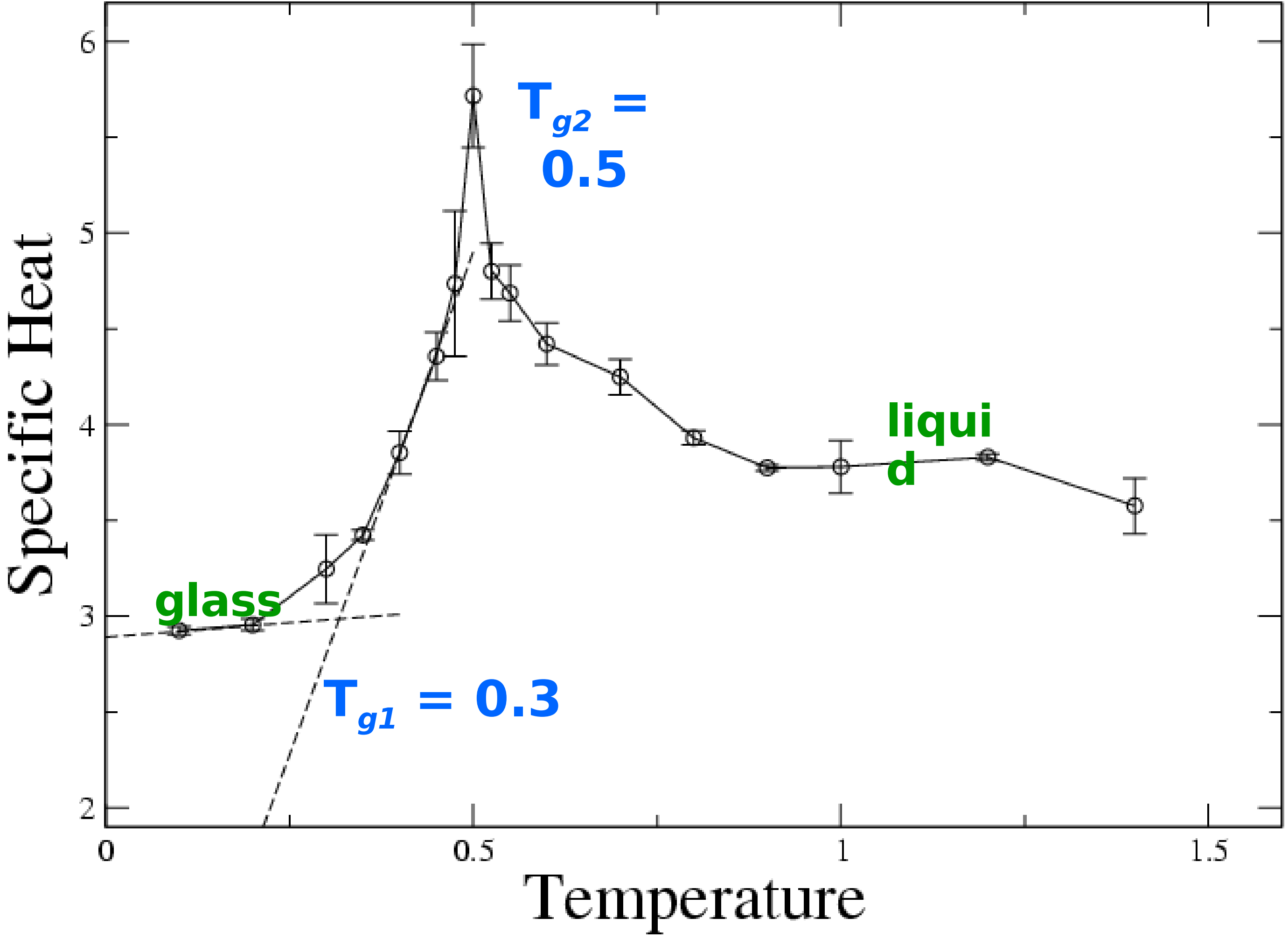
ε_{ps}=0.1

Ungrafted

Grafted

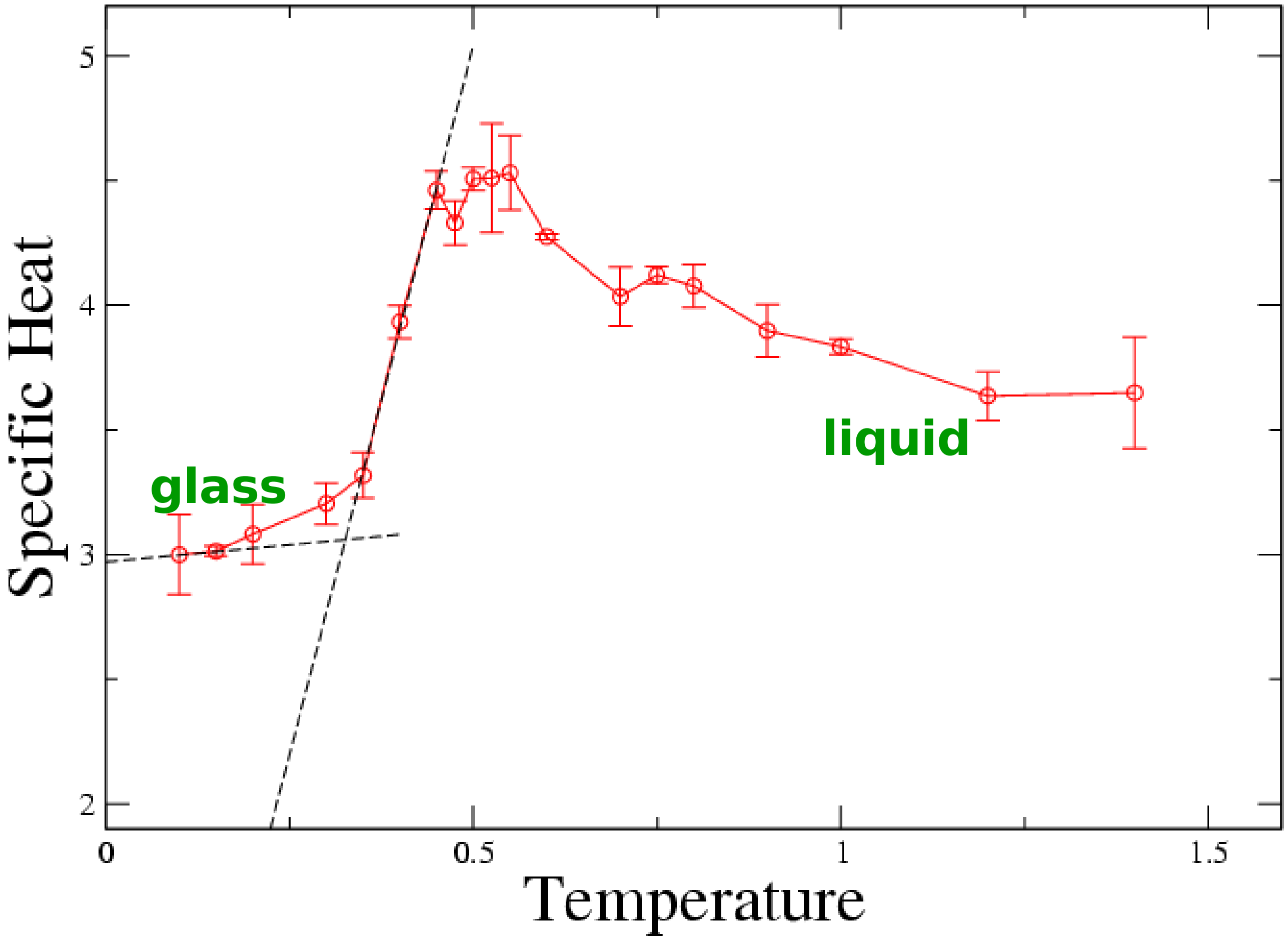
T_g=0.49

Heat Capacity: Ungrafted Film



$$c_p = \frac{\left\langle (\Delta E)^2 \right\rangle}{NT^2}$$

Heat Capacity: Grafted Film

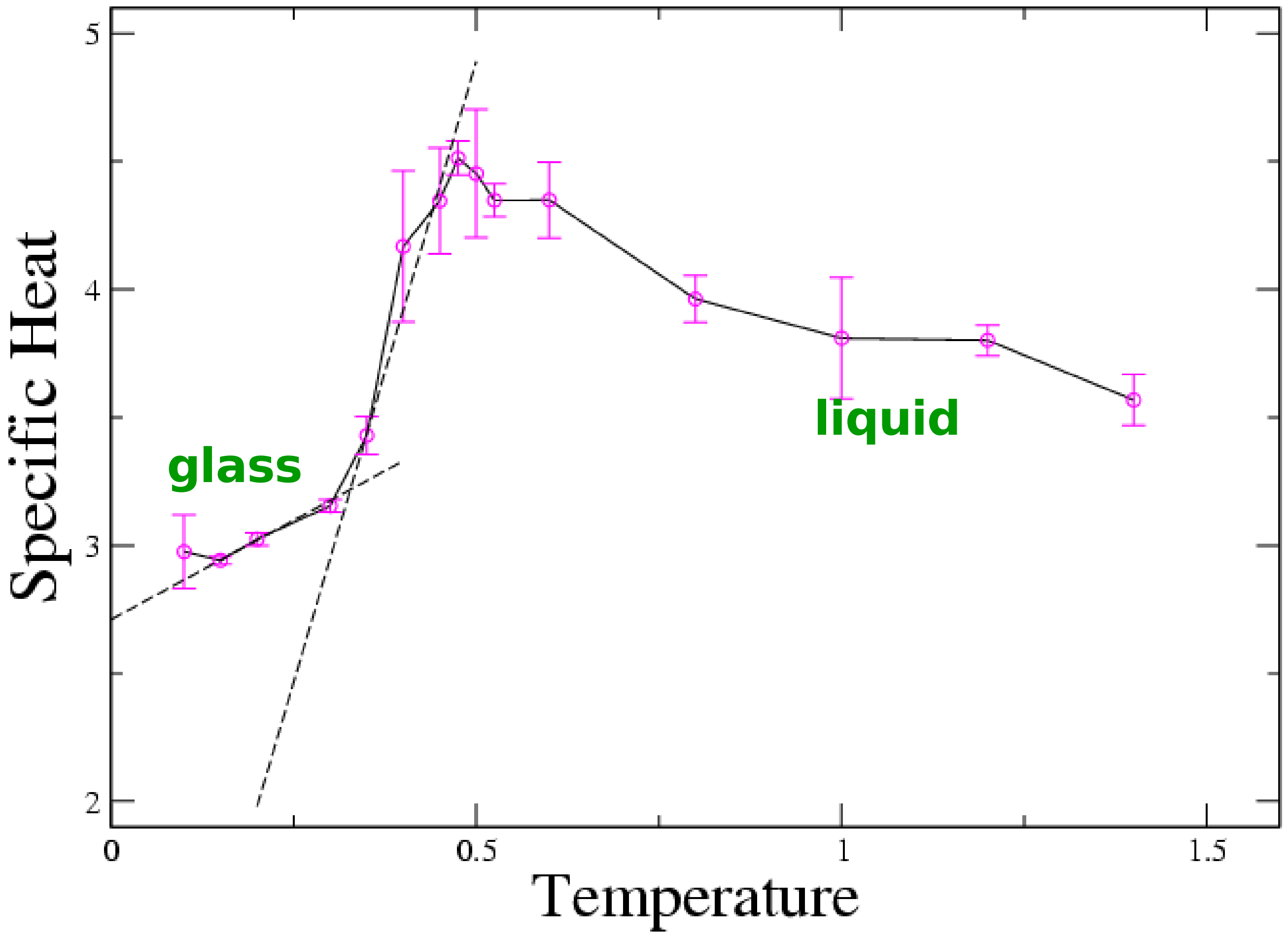


T_{g1} = 0.33

T_{g2} = 0.55

Grafting has a small effect on glass transition temperature

Heat Capacity: Effect of Surface Interaction



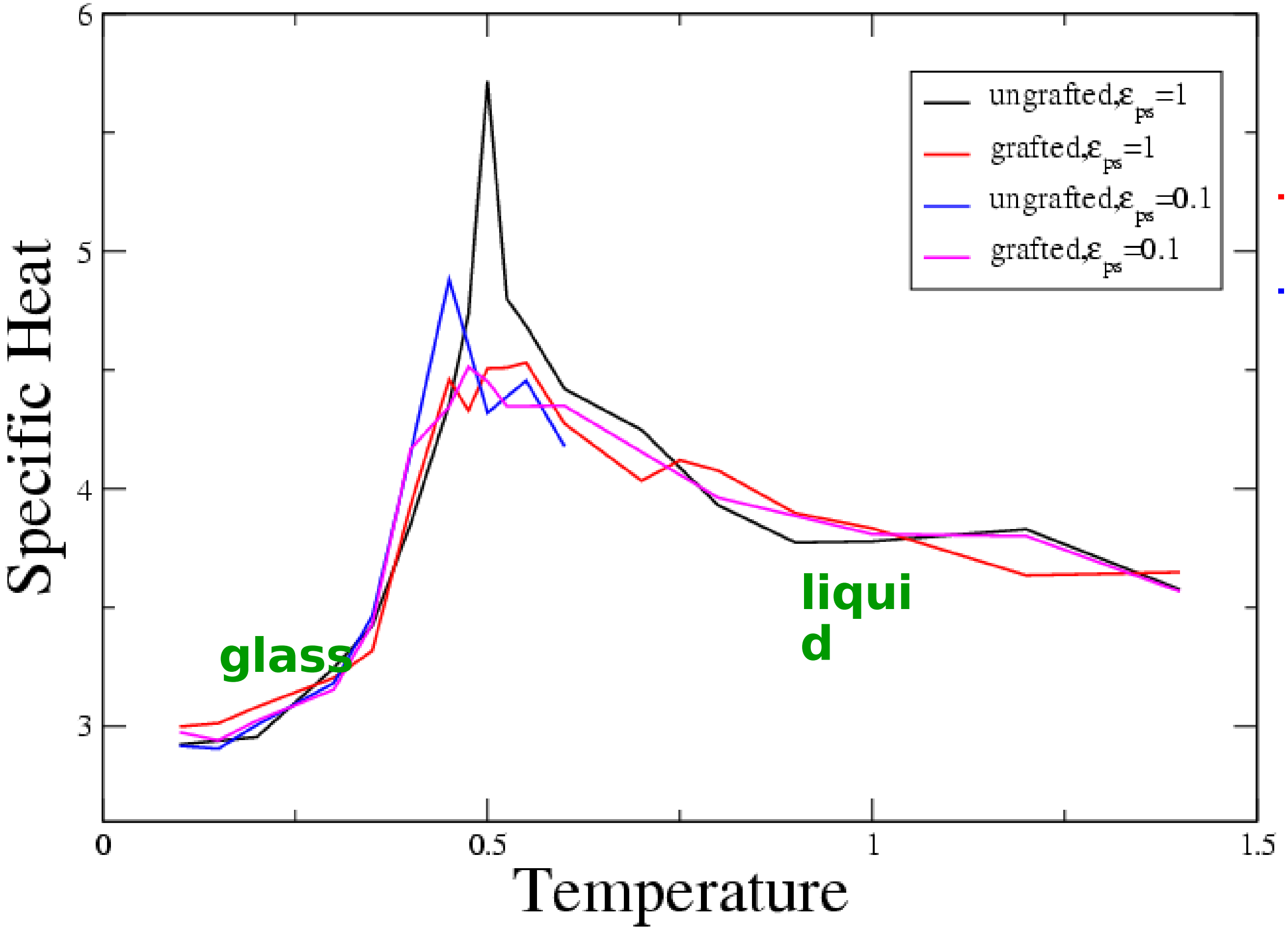
ε_{ps}=0.1

Grafted

T_{g1} = 0.33

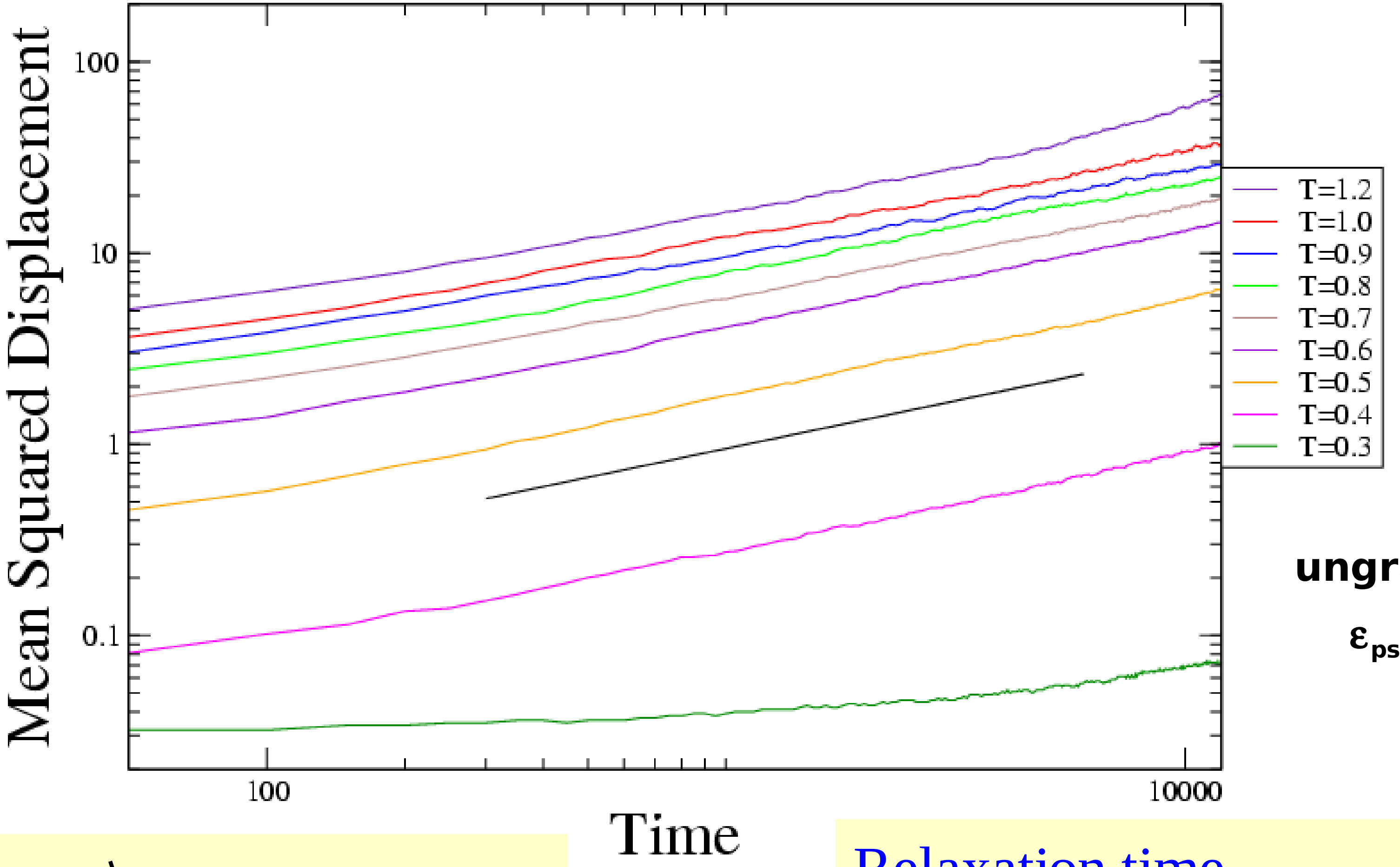
T_{g2} = 0.49

Heat Capacity: Comparison



Ungrafted films show a sharp peak

Bead Diffusion



ungrafted

ε_{ps}=1

$$\left\langle \Delta r^2(t) \right\rangle \approx (D(T)t)^{0.5}$$

Relaxation time

$$\tau(T) = 1/D(t)$$

Glass Transition: Comparison

	T_g: Film Thickness	T_{g1}	T_{g2}	T_{MCT}
Ungrafted $\varepsilon_{ps}=1$	0.51	0.3	0.5	0.36
Grafted $\varepsilon_{ps}=1$	0.54	0.33	0.55	0.36
Ungrafted $\varepsilon_{ps}=0.1$	-	0.32	0.45	-
Grafted $\varepsilon_{ps}=0.1$	0.49	0.33	0.49	-

Fragility

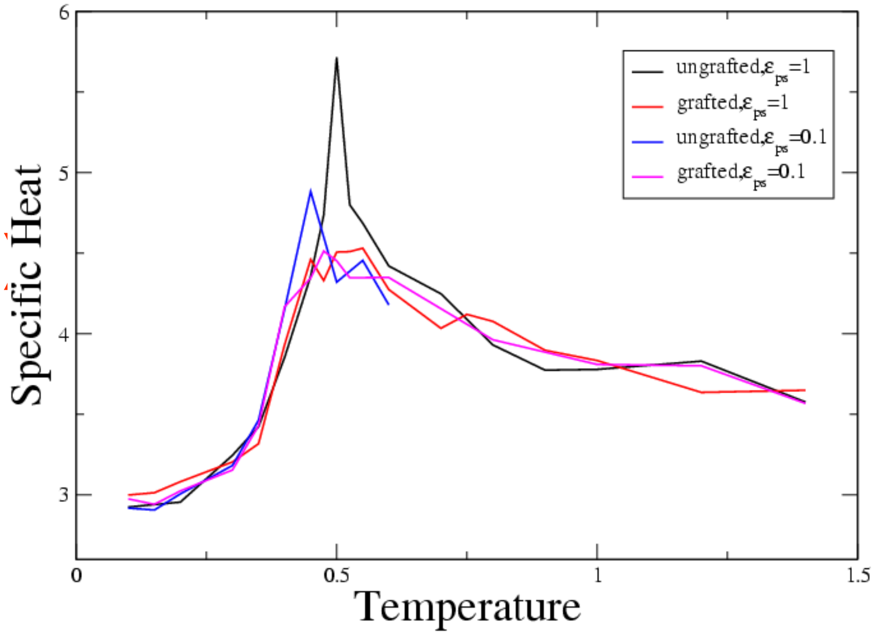
Structural Change: **T_{g2} - Film Thickness**

Dynamic Arrest: **T_{g1} - MCT**

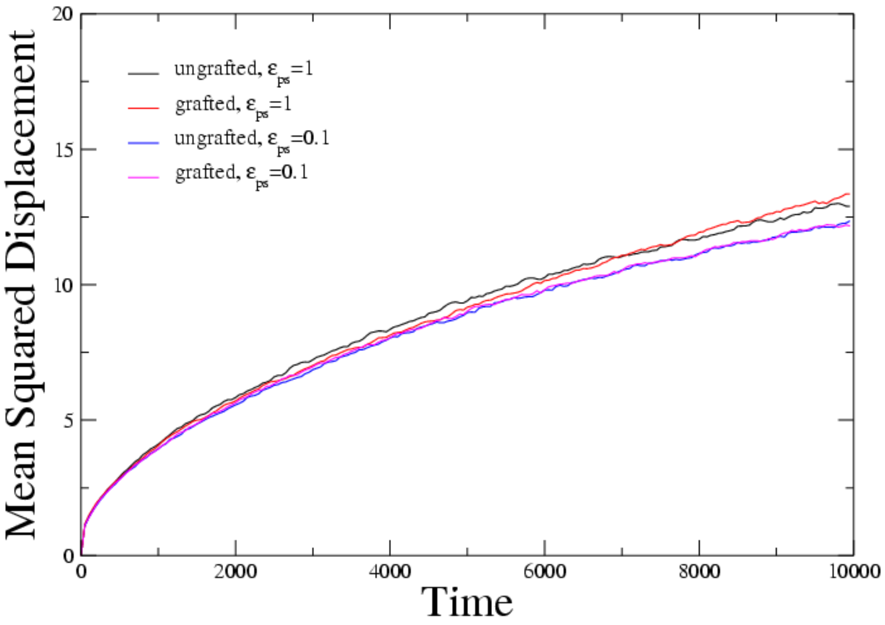
Fragility parameter = T_{g2}-T_{g1}

Related to the amount of (local) structural order

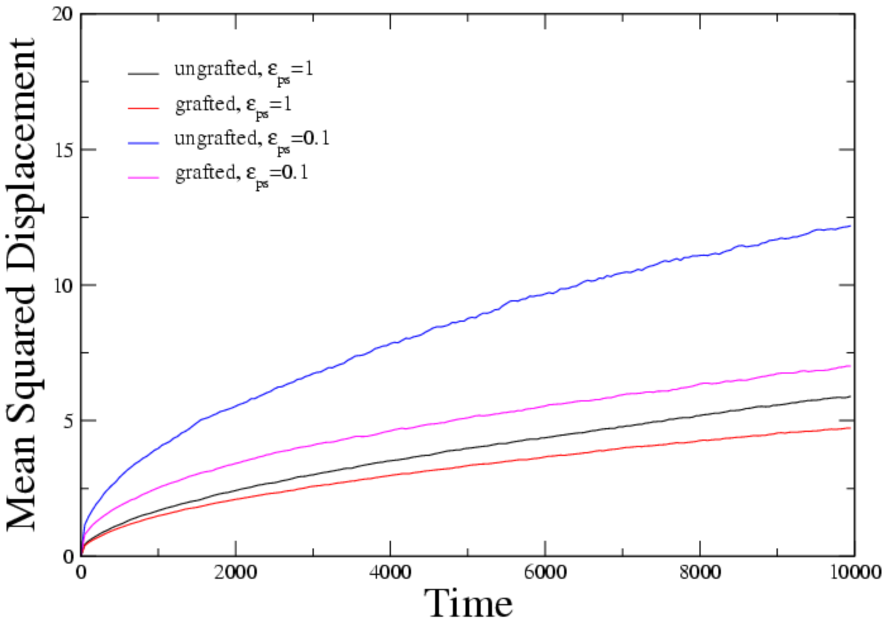
fragile $T_{g2} \approx T_{g1}$



Dynamic Heterogeneities near T



Layer near free surface



Layer near substrate

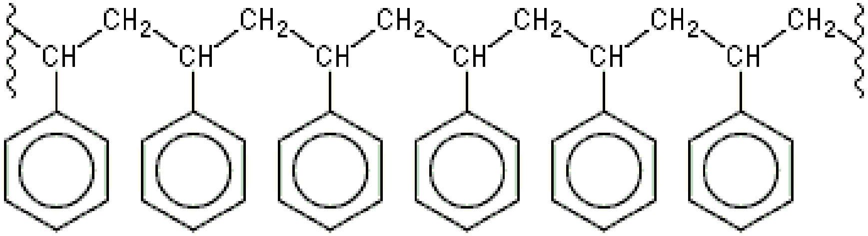
T=0.55

Layering

Summary Supported films

- **Measurements of T_g using thermal expansion and heat capacity yield similar results**
- **Chain grafting has a small effect on the glass transition temperature (15-25 deg C)**
- **Polymer-substrate interaction effects fragility (T_{g2}-T_{g1}) and shape of T-C_p plot**

Polystyrene

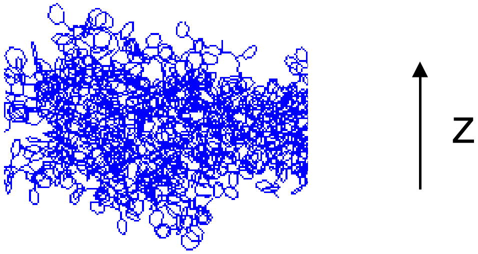


Atactic Polystyrene

United Atom Model

Free Standing Films

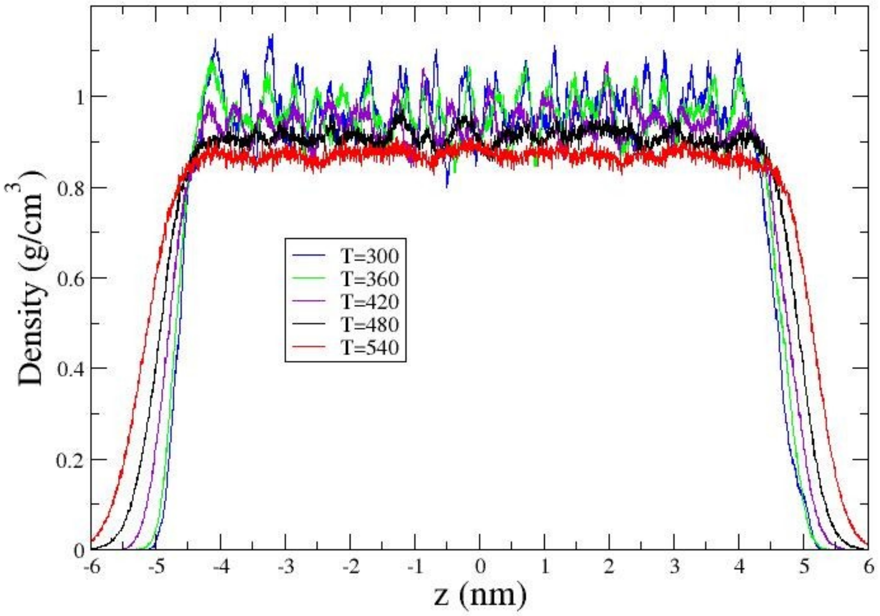
MD Simulations

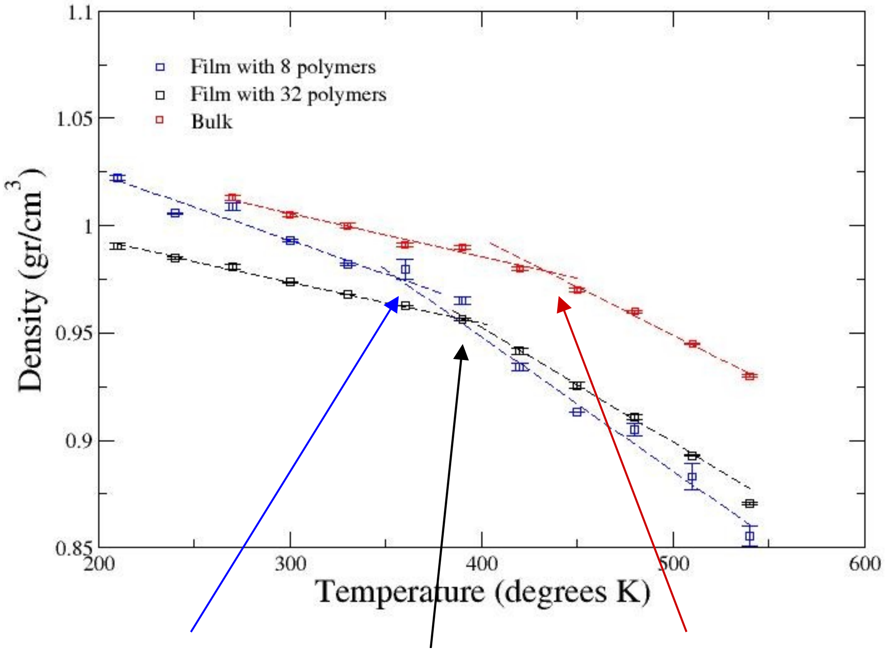


- Free standing films
  - 8 or 32 polymer chains (4 nm/12 nm)
  - 80 monomers per chain
  - united atom model
  - periodic boundary conditions in xy-directions
- Bulk
  - 8 polymer chains

Temperature varies between 300 and 450 degrees

Density





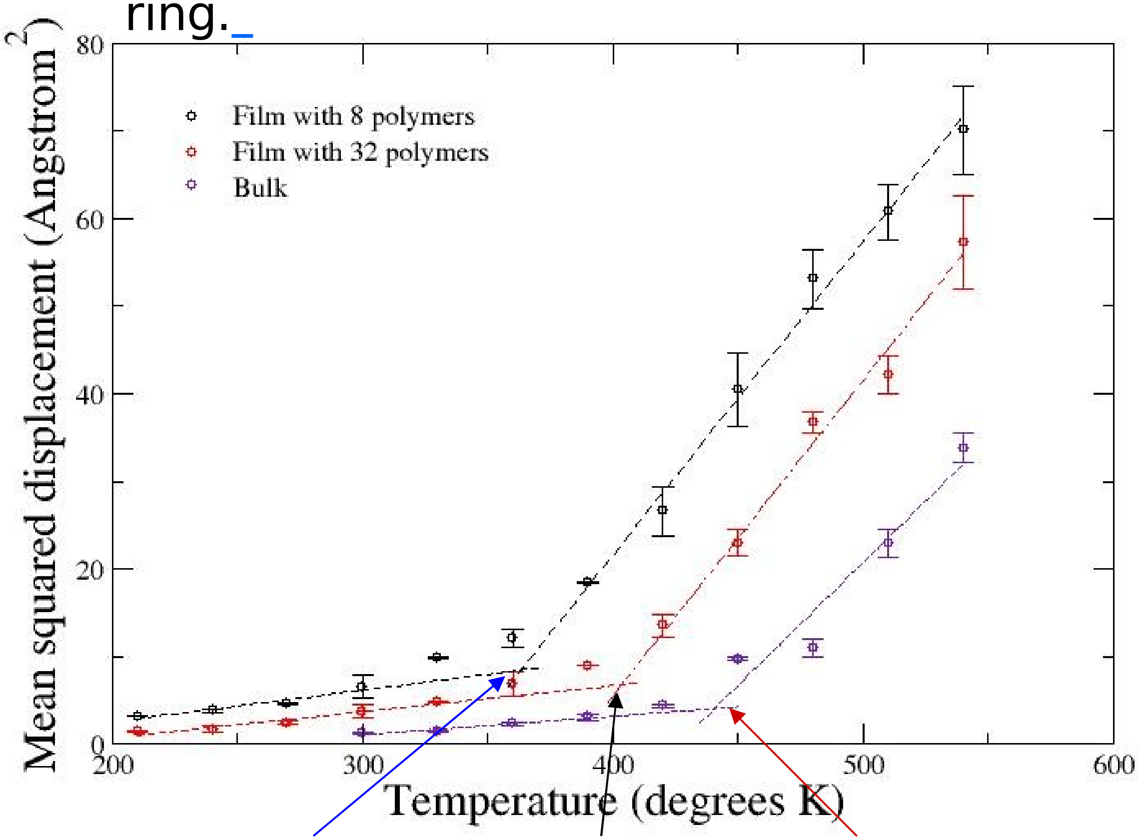
T_g=362 T_g=392 T_g=447

4 nm 12 nm bulk

Glass transition temperature decreases with film thickness

Doi Method

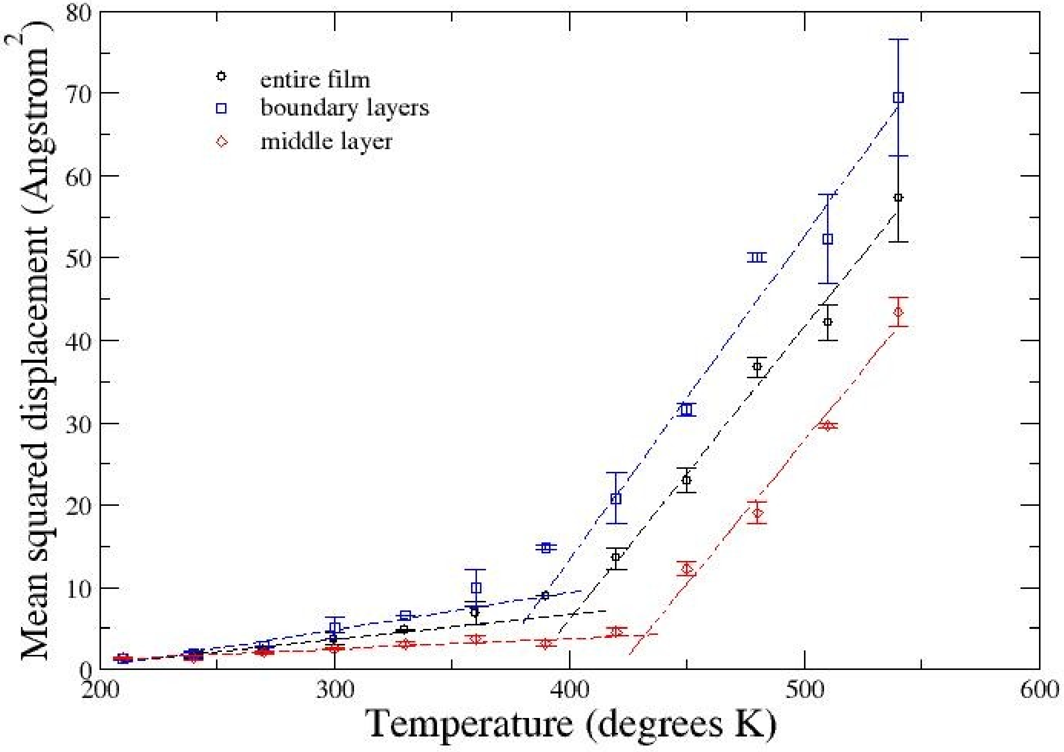
Mean squared displacement of beads in the side groups at the chain ends after 400 ps. The data are obtained by averaging over all six groups in the phenyl ring._



T_g=363 T_g=403 T_g=440

4 nm 12 nm bulk

Layering 32 polymer film



entire film (12 nm)

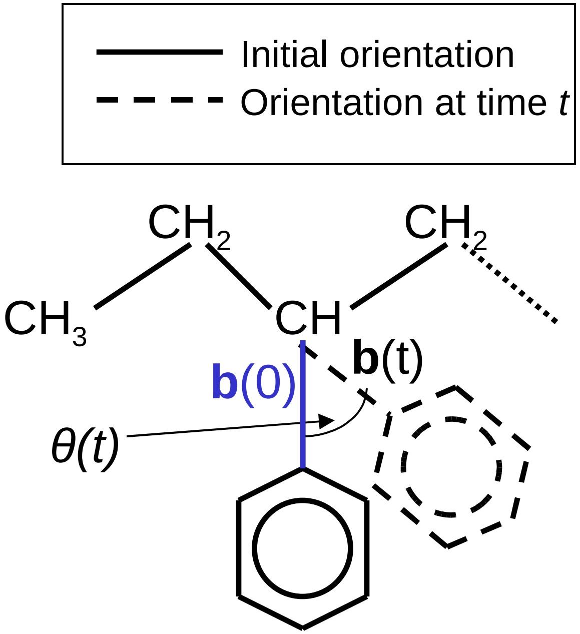
middle (5 nm)

boundary

Relaxation time

Orientational mobility of the end CH-Phenyl bonds

$$P_2(t)=\left\langle \frac{3}{2}(\vec{b}(0)\vec{b}(t))^2-\frac{1}{2}\right\rangle$$



Measure for amount of relaxation

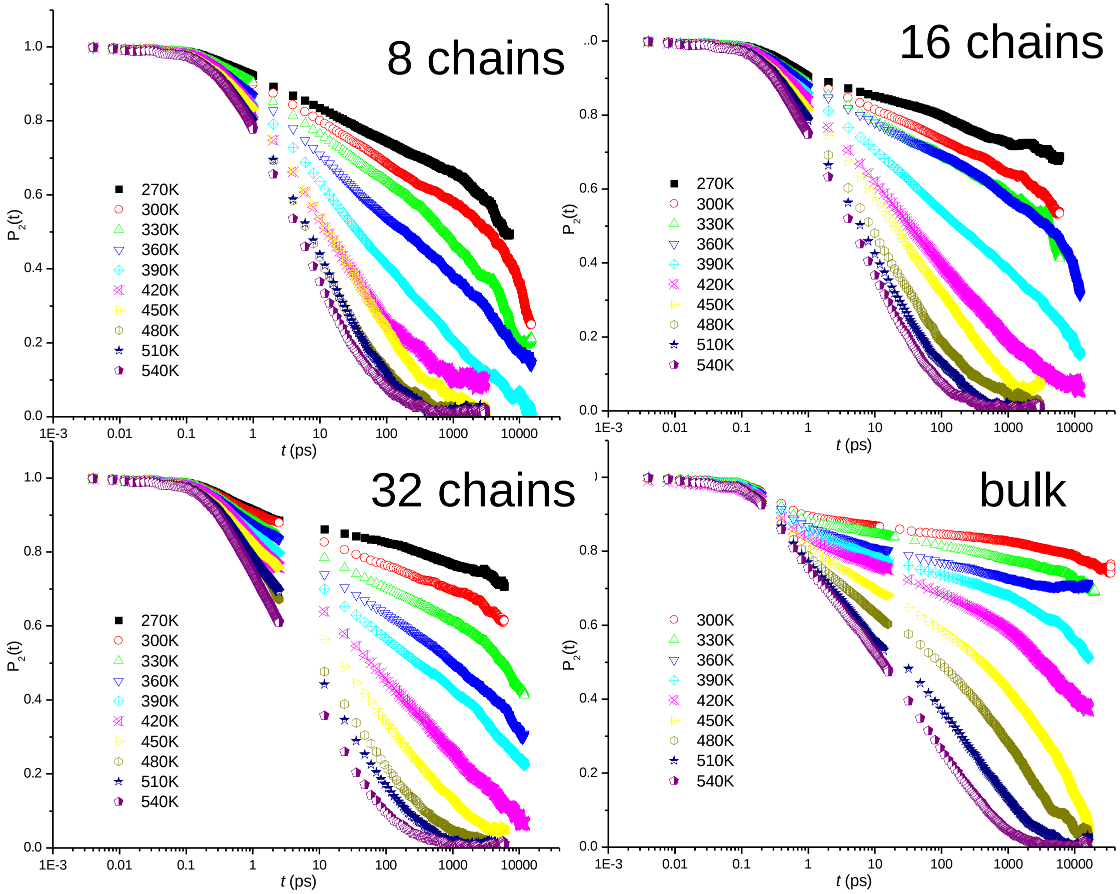
Multiple relaxation processes

Only monomers at end of chain

T -> 0 $P_2(t)=1$

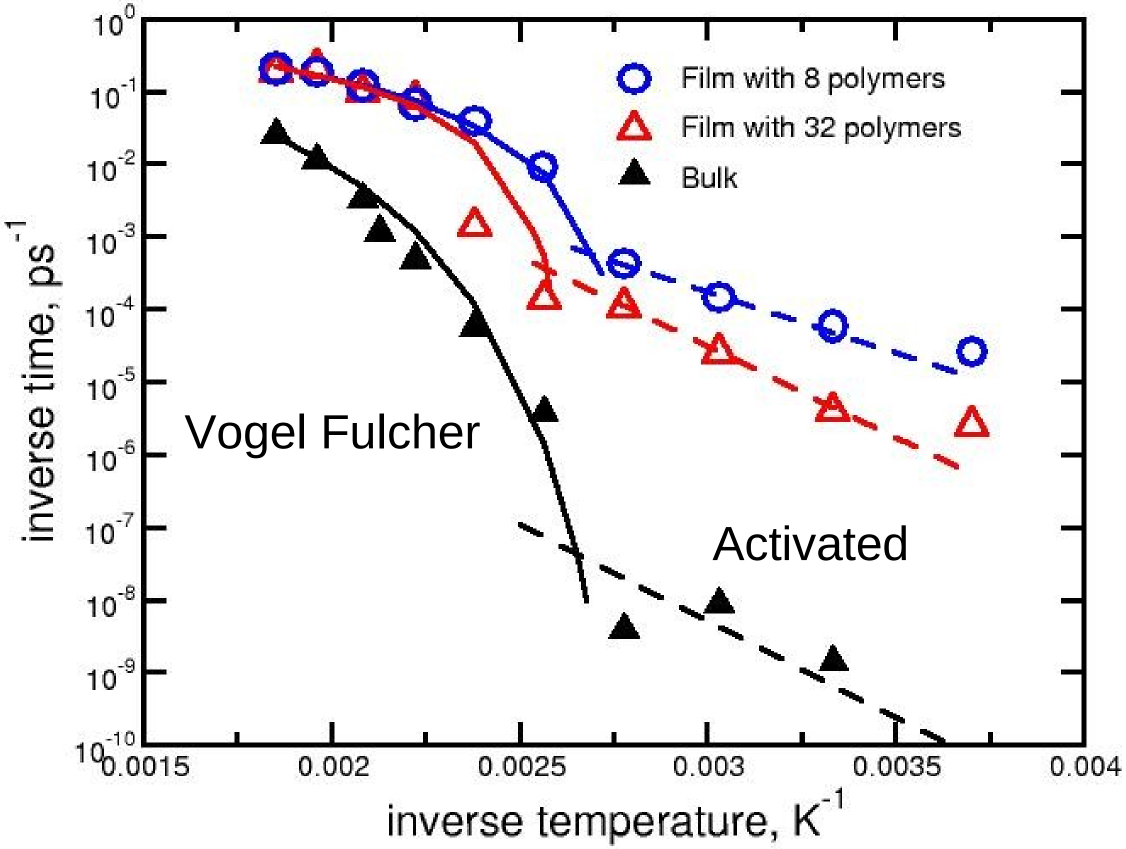
T -> ∞ $P_2(t)=0$

P_2 orientational autocorrelation function



Fit to $P_2(t) = a_0 \exp-(t/\tau_0)^{\beta}$ obtain relaxation time τ_0

Dependence of relaxation time on temperature



Activated

$$\tau = \tau \quad \exp\frac{U_{act}}{k_B T}$$

Vogel Fulcher

$$\tau = \tau \quad \exp\frac{U_{act}}{k_B (T - T_0)}$$

T_g=352 T_g=396 T_g=402

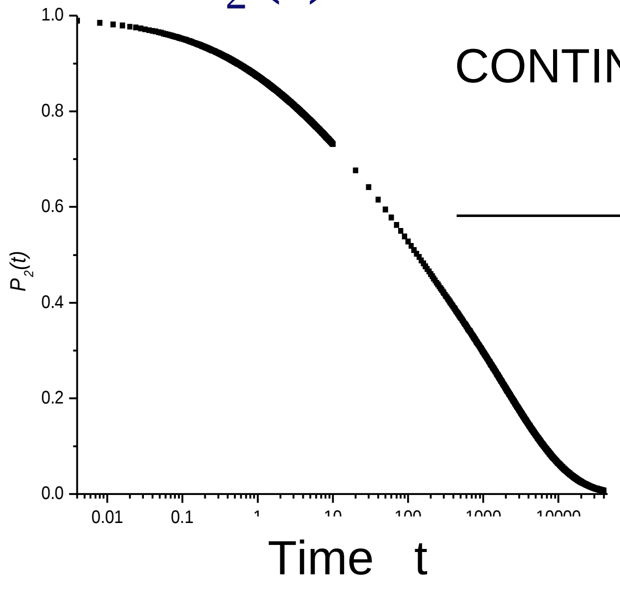
Multiple relaxations

Laplace transform: spectral density g(τ)

CONTIN software program

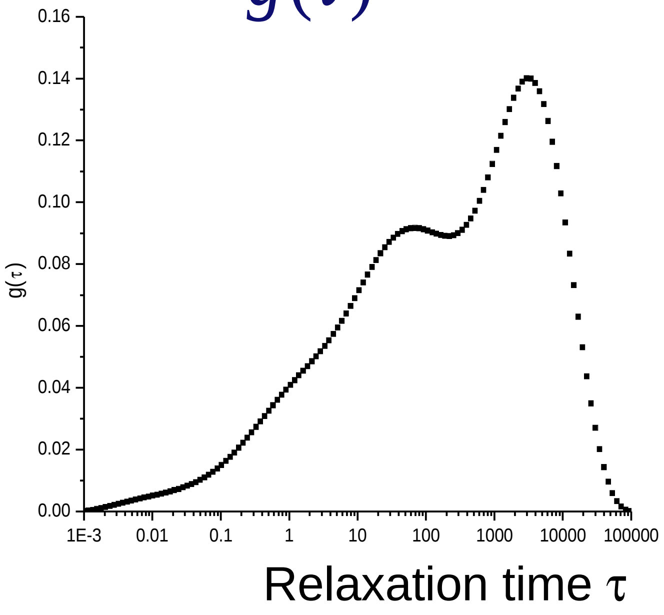
$$P_2(t) = \quad g(\tau)\exp(-t/\tau)d\tau$$

$P_2(t)$

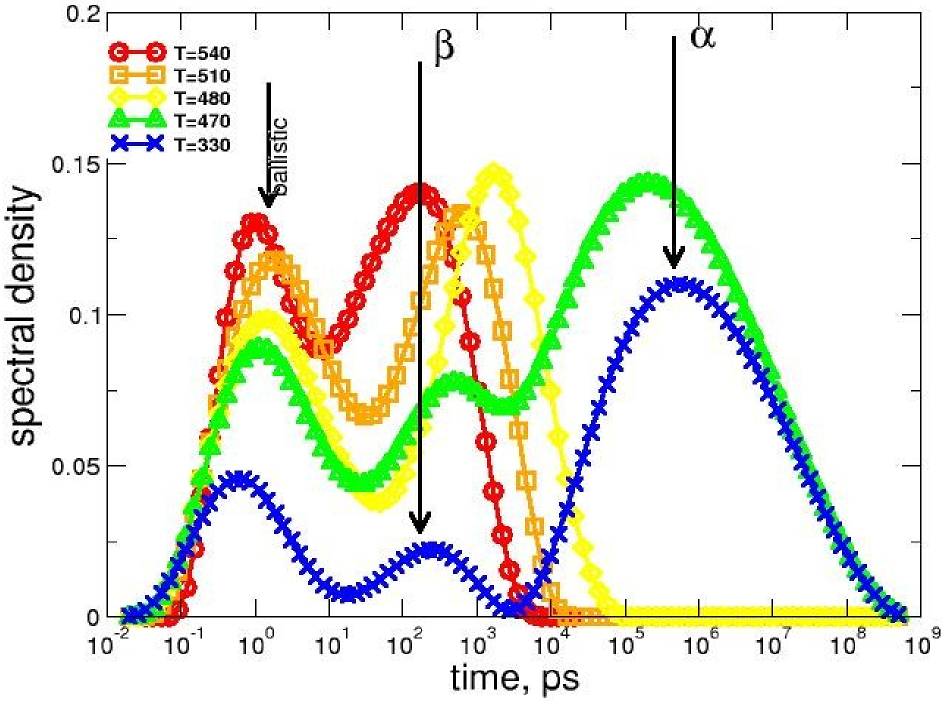


CONTIN

$g(\tau)$



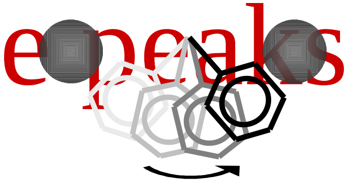
Bulk



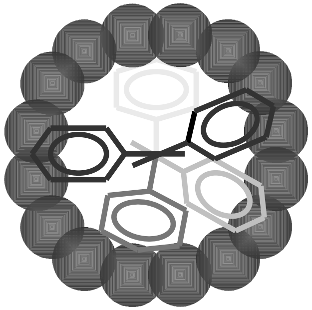
Relaxation time increases with decreasing temperature

Interpretation of multiple peaks

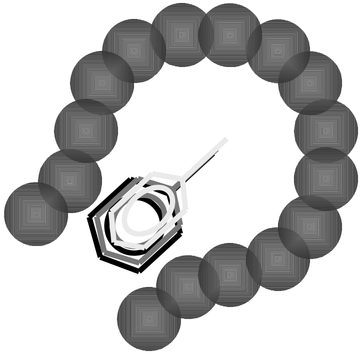
- First peak: Transient relaxation
  - Relaxation due to ballistic motion between collisions
  - Very fast
- Second peak: β-relaxation
  - ‘Cage’ effect; Local structural relaxation
- Third peak: α-relaxation
  - Final relaxation; cooperative rearrangements



Transient relaxation



Relaxation within cage

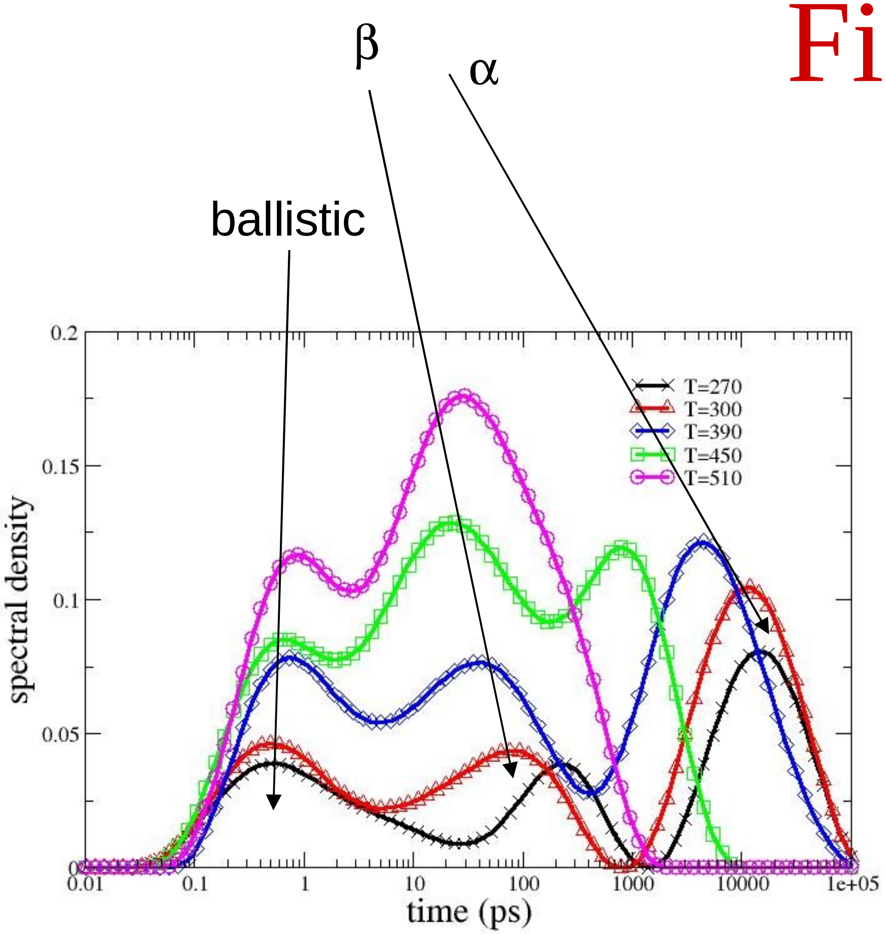


Final *α*-relaxation

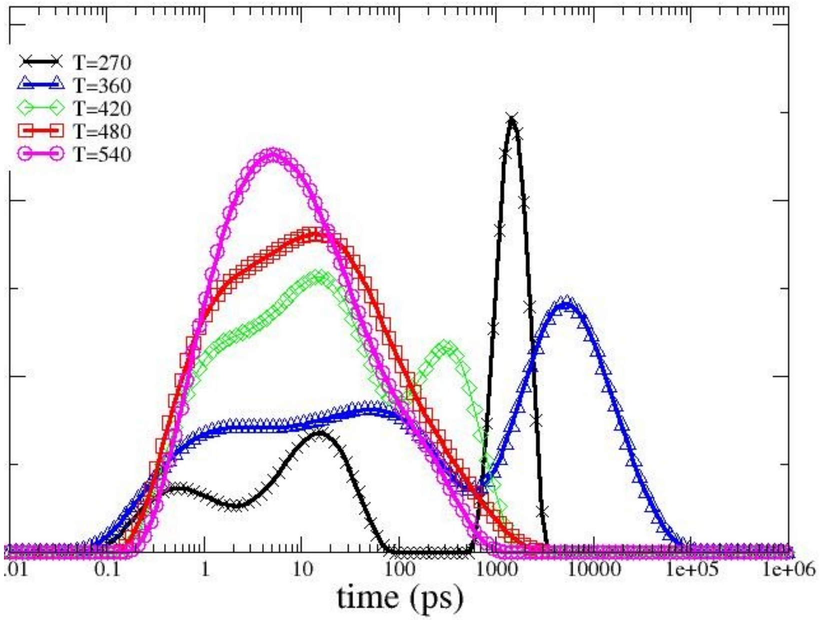
Film

Relaxation time increases with

decreasing temperature

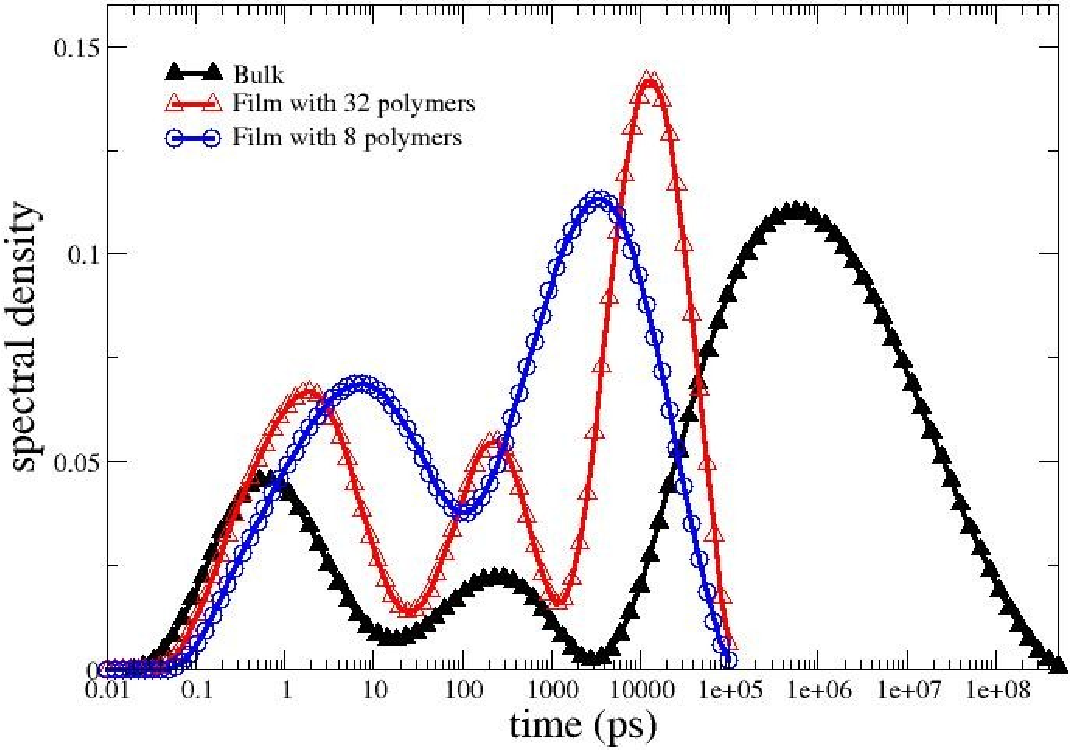


32 chains – 12 nm



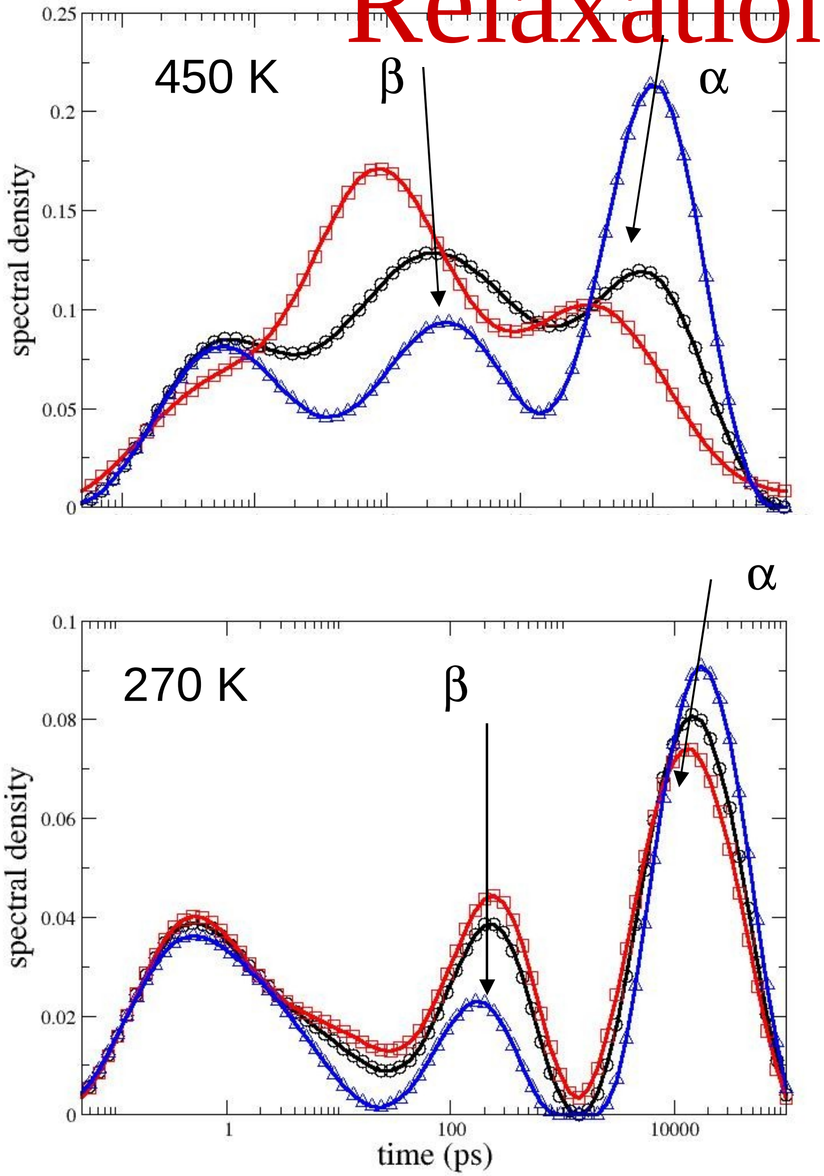
8 chains – 4 nm

Comparison at 330 K



α relaxation time depends on film thickness
β relaxation time depends **not** on film thickness

Relaxation layer by layer



32 polymers

entire film (12 nm)

boundary

middle (5 nm)

α relaxation stronger in middle of film
β relaxation stronger near boundary

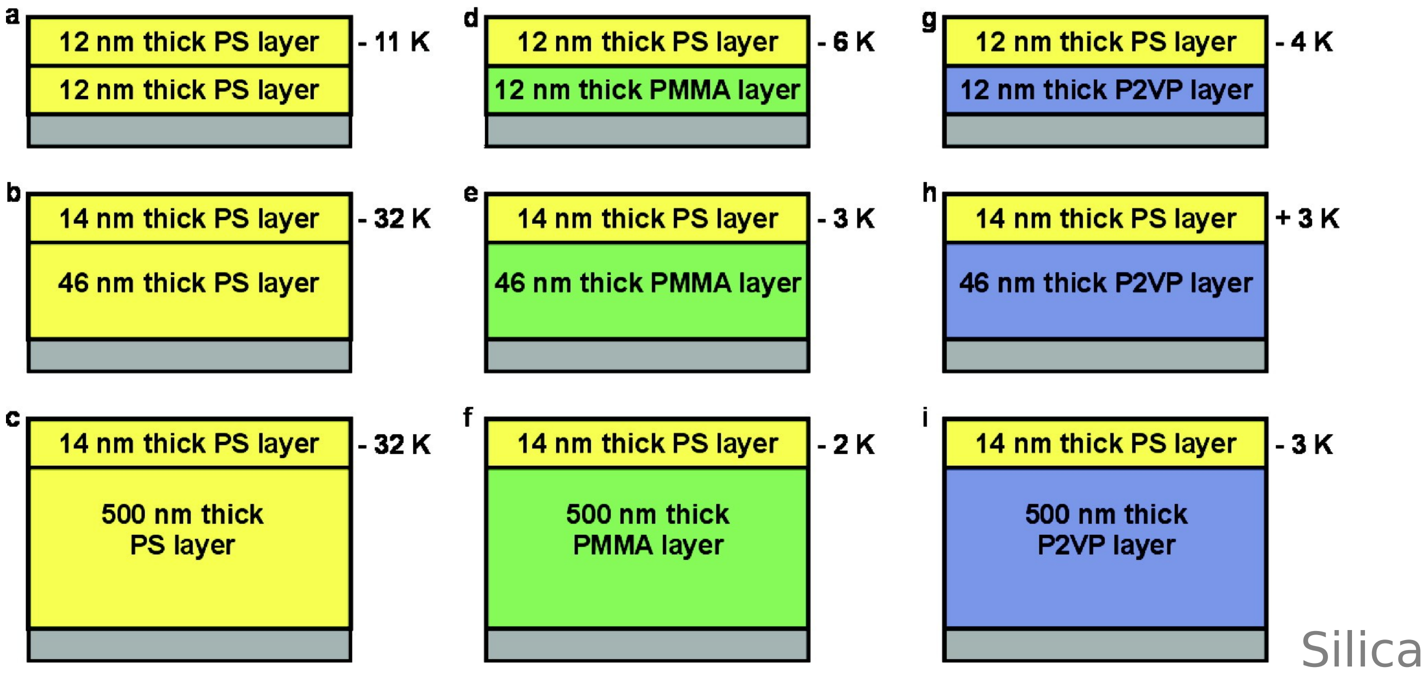
α relaxation time longer in middle of film
β relaxation time independent of position
in film at low T

Conclusions Polystyrene

- Glass transition temperature slightly higher than that for bulk PS experimentally: 375 degrees K.
- Glass transition temperatures in these free standing polystyrene films decrease with film thickness
- Confinement:
  - strong influence on alpha relaxation time
  - not much effect on beta relaxation time
- Layering:
  - alpha relaxation time shorter near boundary (but everywhere much faster than bulk)
  - beta relaxation time independent of position in film (similar to bulk)

Interfaces affect α-and β-relaxation dynamics in different ways.

Chemistry


a
12 nm thick PS layer
12 nm thick PS layer
- 11 K
b
14 nm thick PS layer
46 nm thick PS layer
- 32 K
c
14 nm thick PS layer
500 nm thick PS layer
- 32 K
d
12 nm thick PS layer
12 nm thick PMMA layer
- 6 K
e
14 nm thick PS layer
46 nm thick PMMA layer
- 3 K
f
14 nm thick PS layer
500 nm thick PMMA layer
- 2 K
g
12 nm thick PS layer
12 nm thick P2VP layer
- 4 K
h
14 nm thick PS layer
46 nm thick P2VP layer
+ 3 K
i
14 nm thick PS layer
500 nm thick P2VP layer
- 3 K
Silica

Outlook

- Study the relations between peak positions and temperatures
  - Change temperatures more gradual
  - Longer simulation runs
  - Allows more insight in the relaxation processes
- Study the influence of film thickness more in-depth
  - Simulate more films to find relaxation-time to thickness relation
  - Find origin: Density or boundary or something else?
- Compare simulation and experiment

Monte Carlo Simulations of the Glass Transition in Polyethylene

Orestis Alexiadis[1], Vlasis Mavrantzas[1], Arlette Baljon[2] and Rajesh Khare[3]

[1]University of Patras (Greece), [2]San Diego State University

and [3]Texas Tech University

Simulation Details

- **Novel End-bridging Monte Carlo Simulation**

Monte Carlo moves used:

30%	End-bridging (EB)
25%	Concerted rotation (CONROT)
15%	Reptation
10%	Configuration bias (CCB)
10%	End rotation
10%	Flip

- **Bulk and Thin film systems**

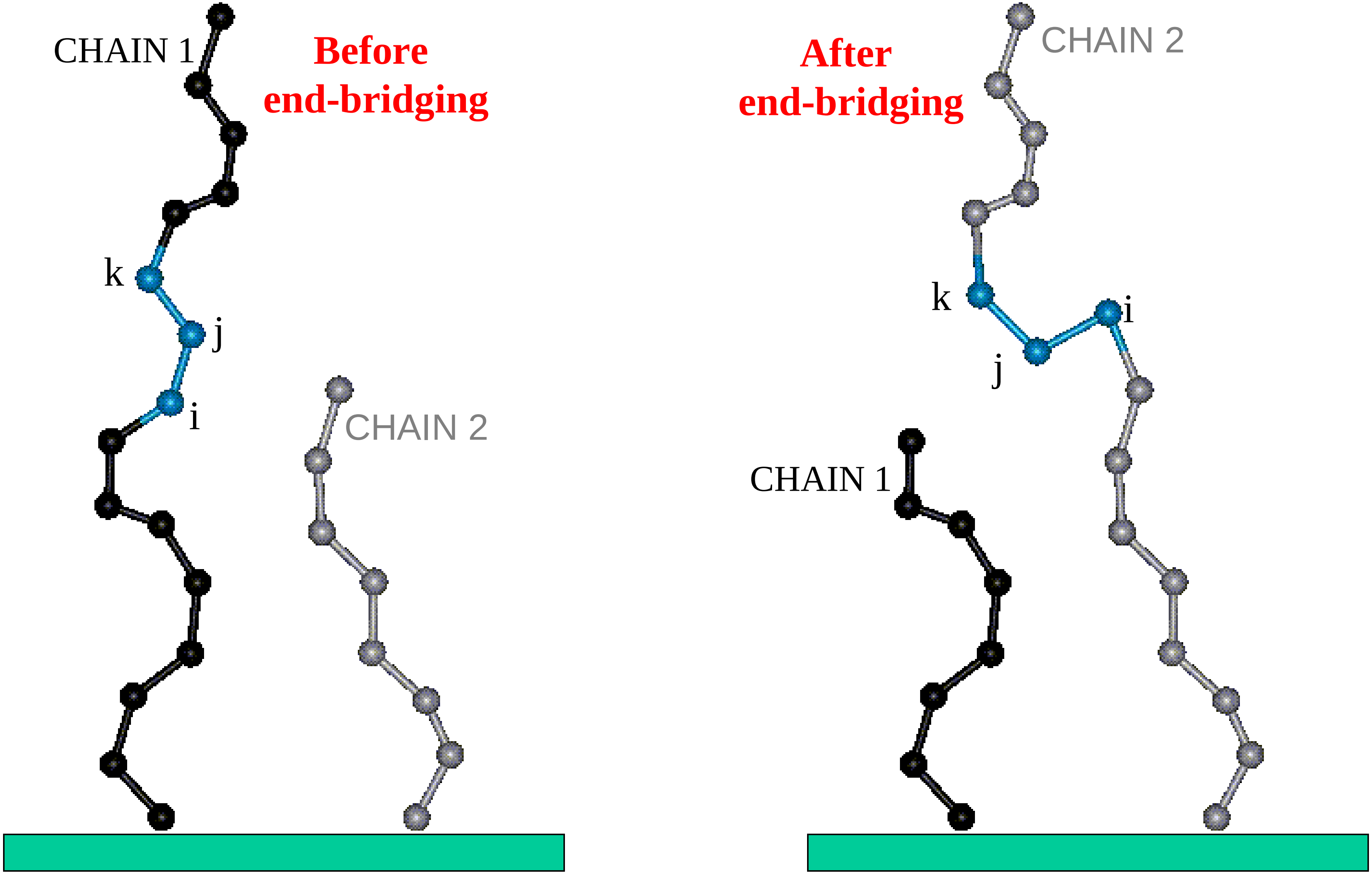
C_{156} , 80 chains

Polydispersity Index = 1.27

In thin film simulations all chains are grafted on a hard surface of area A ~ 70 Å x 70 Å

END BRIDGING (EB)

[Pant & Theodorou, 1995; Mavrantzas et al., 1999]



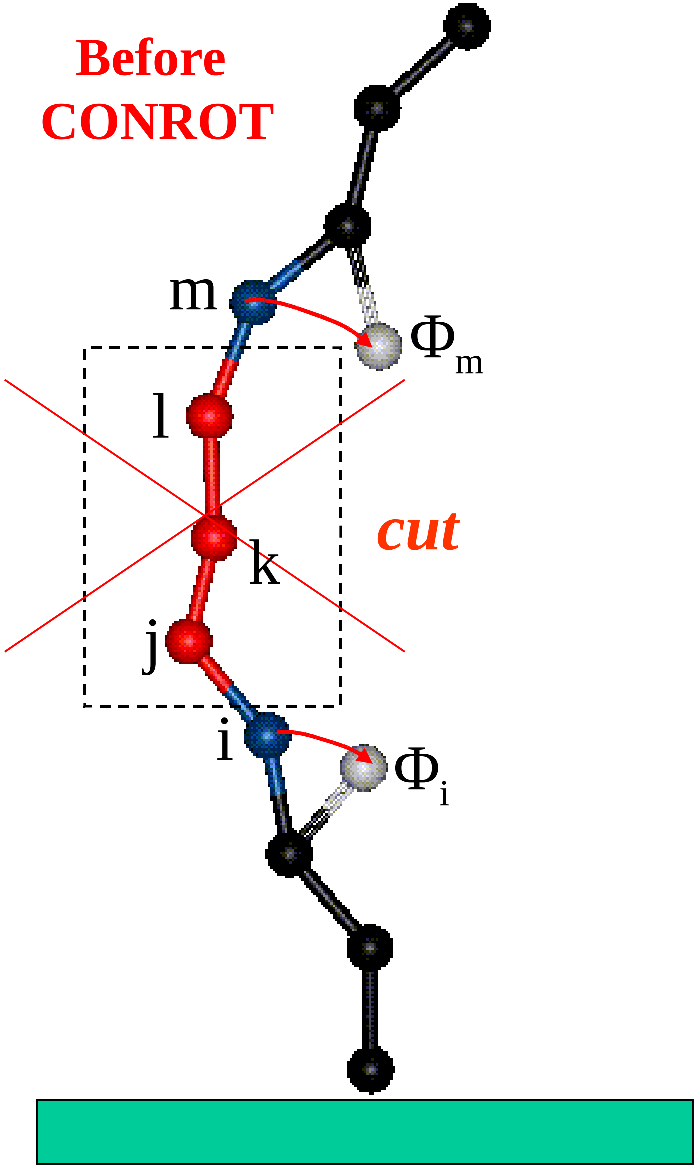
Before end-bridging

After end-bridging

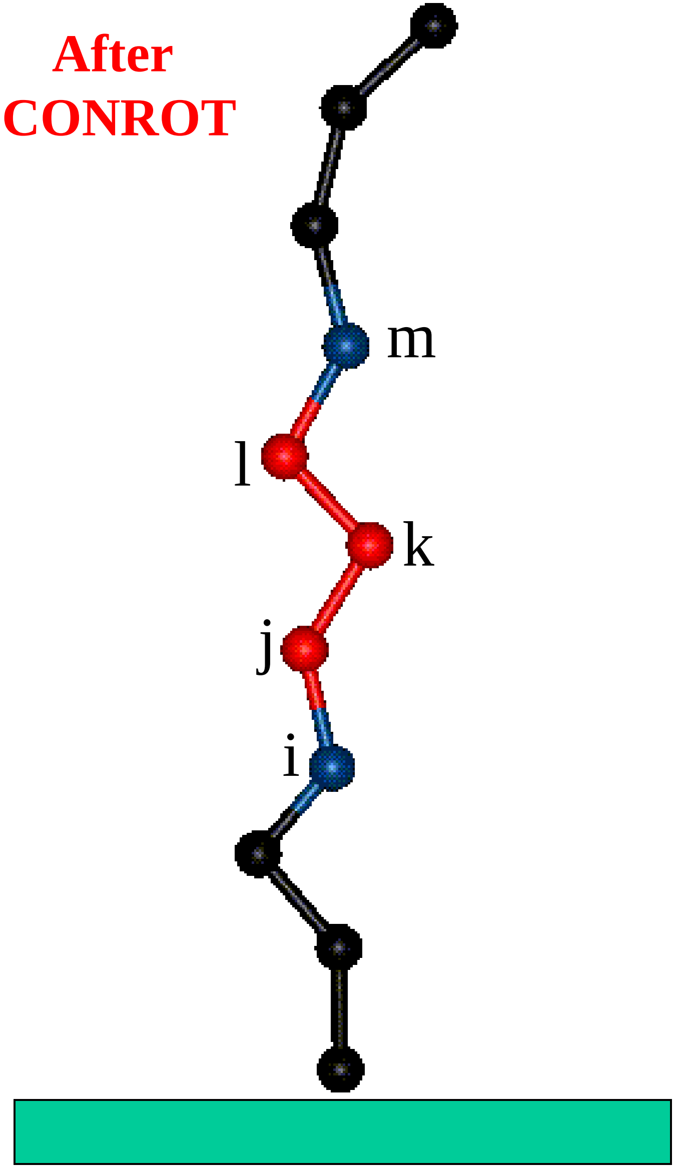
CONCERTED ROTATION (CONROT)

[Dodd et al., 1993]

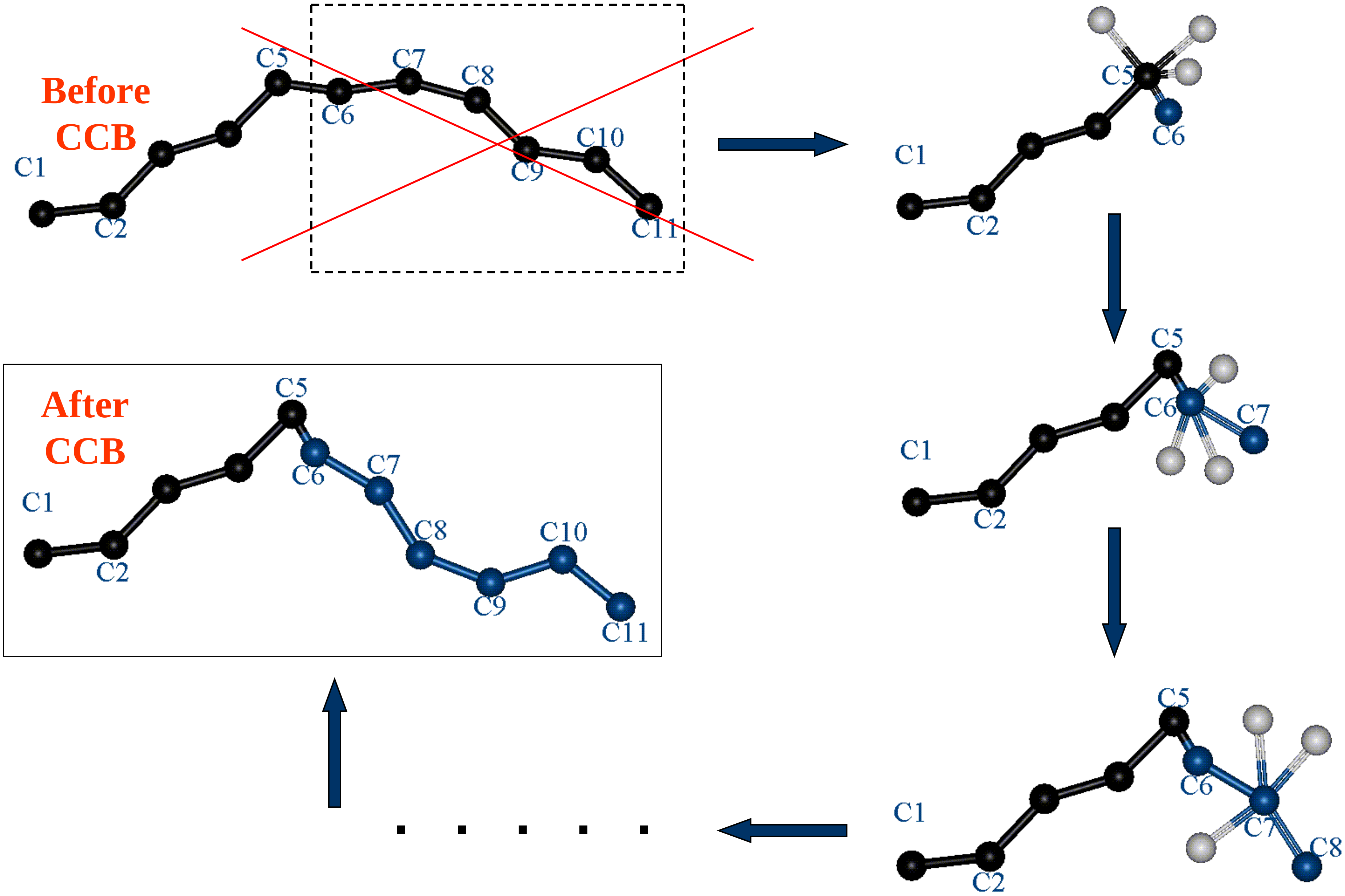
Before CONROT



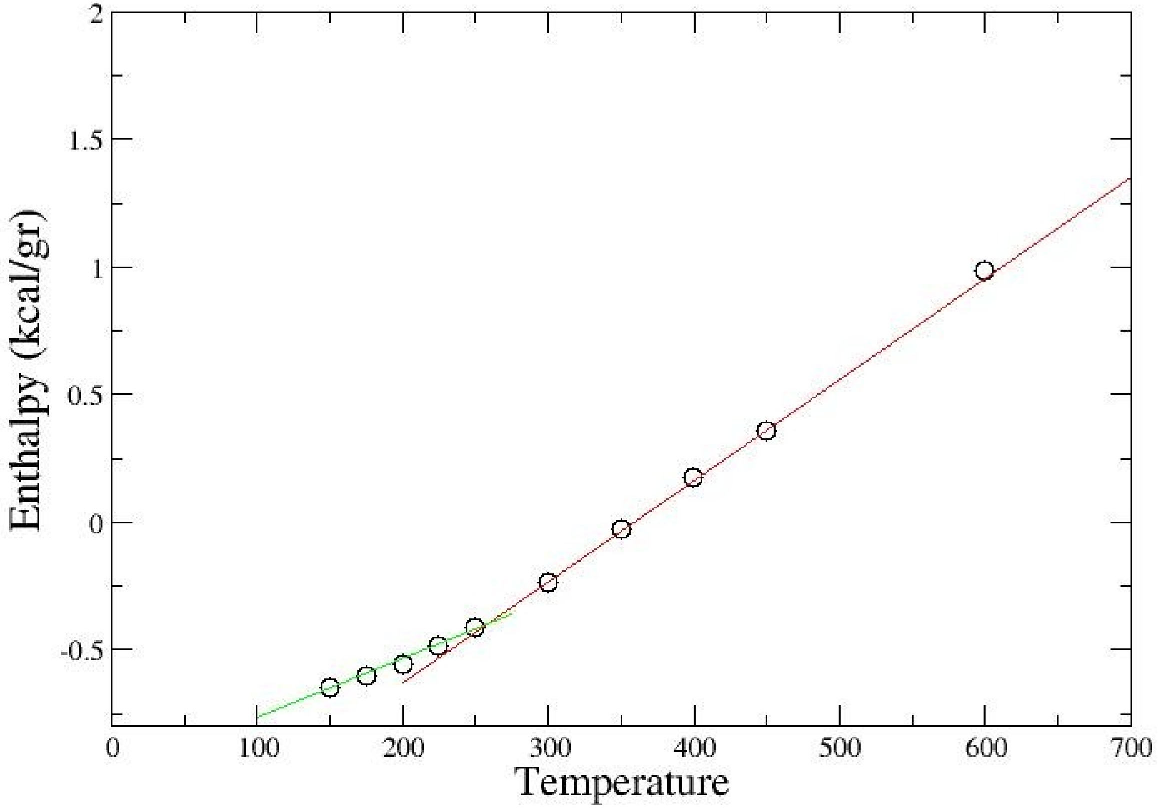
After CONROT



CONFIGURATIONAL BIAS (CCB)



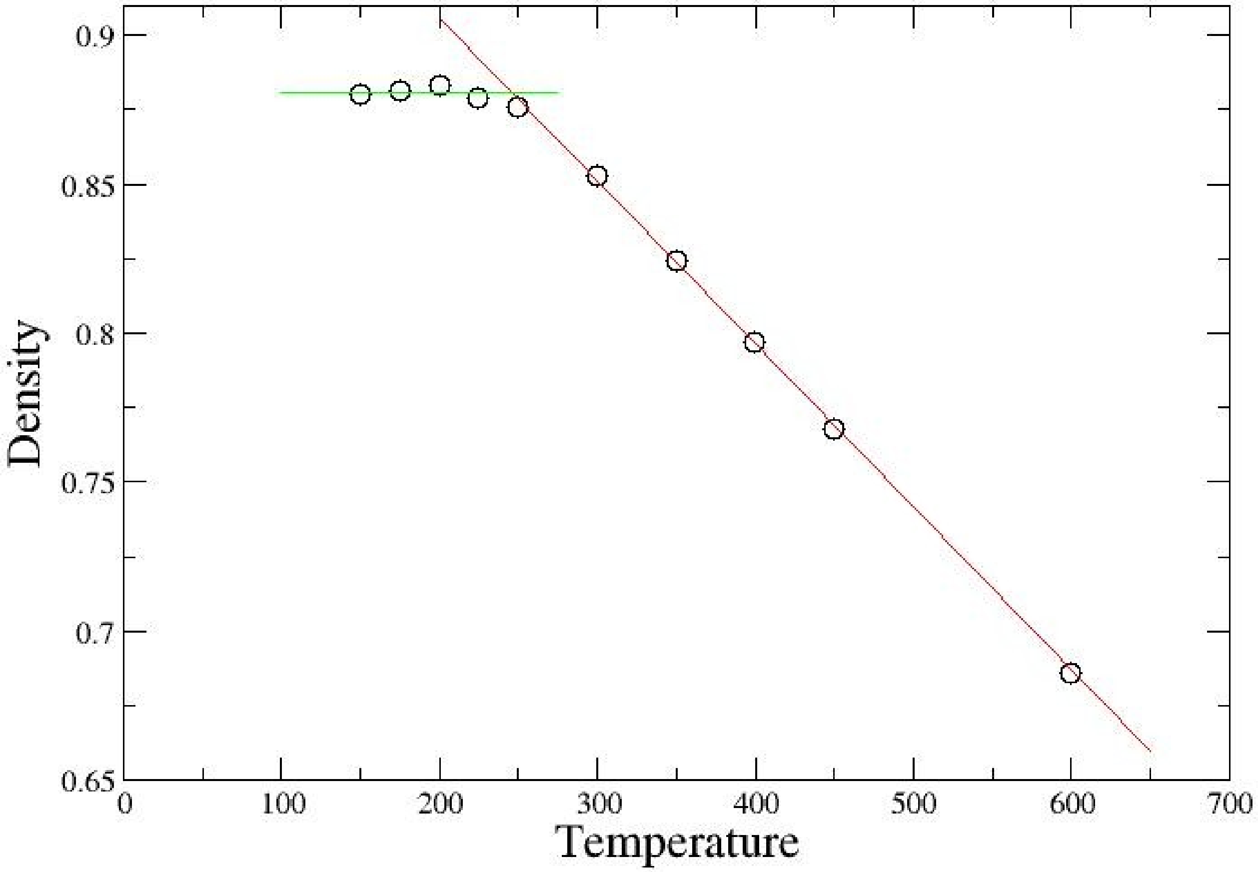
Bulk: glass transition



Simulated glass transition temperature ~ 246 K

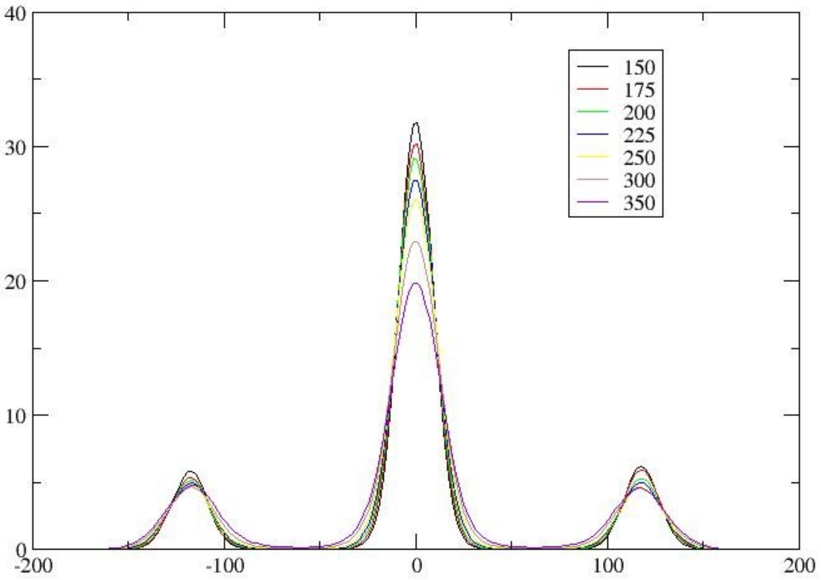
Experimental value: ~ 231 K (Davis and Eby, J. Appl. Phys., 1973)

Determination of T_g from Density



Simulated glass transition temperature ~ 245 K

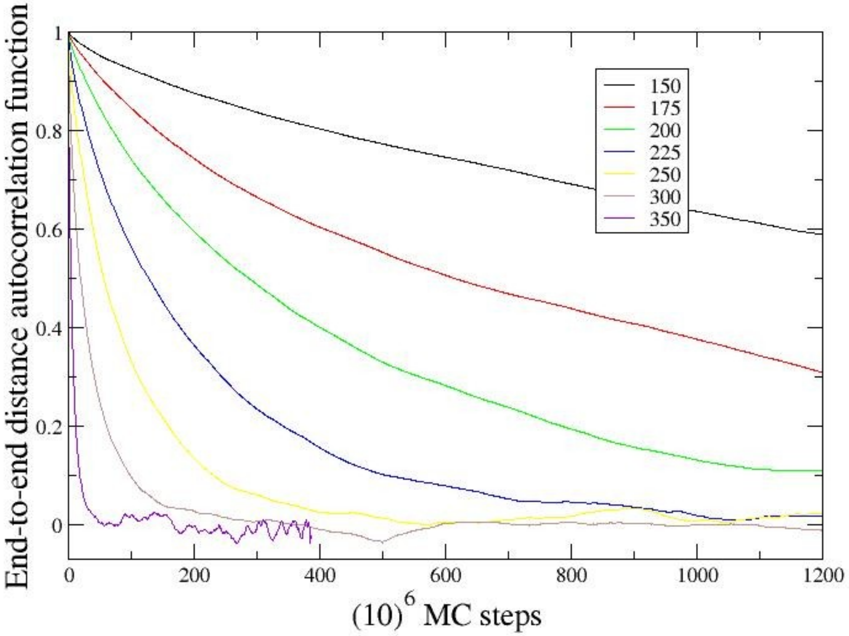
System Equilibration



g^- t g^+

Distribution of torsional angles

% trans increases as temperature decreases



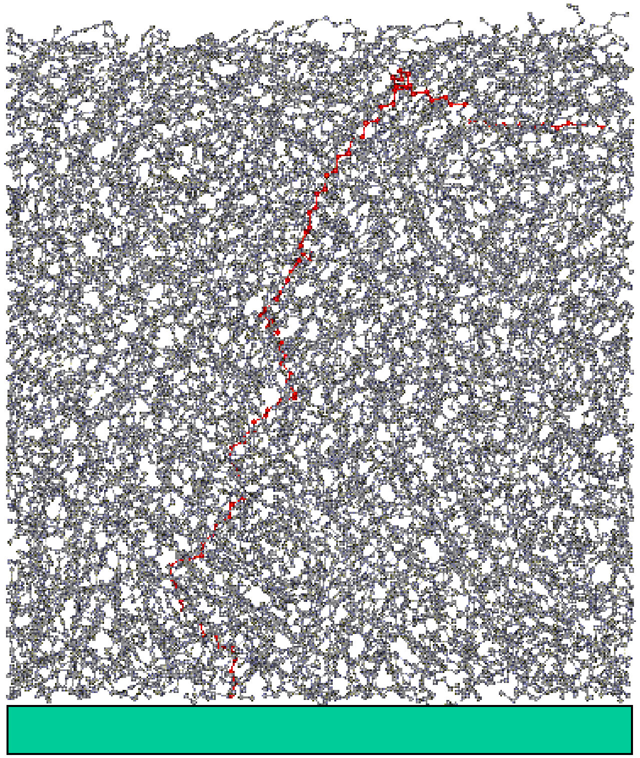
End-to-end autocorrelation function

ACF does decay to zero at T=225 K

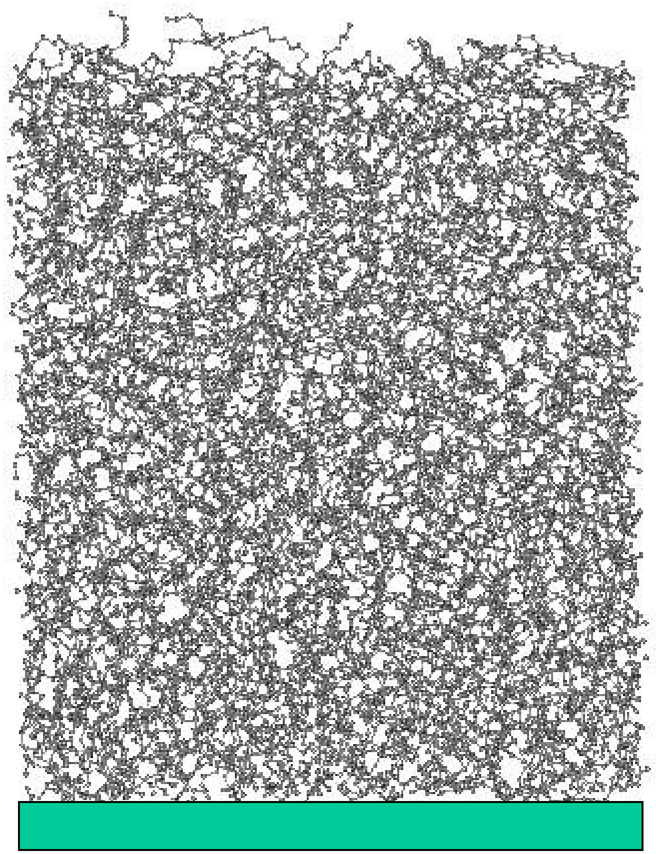
Acceptance Rate of EB-moves

Temperature	% accepted
150	0.00014
180	0.0003
200	0.0007
220	0.0013
240	0.003
270	0.006
300	0.014
350	0.04
400	0.09

Thin Films: Grafted System
80 chains of C_{156}

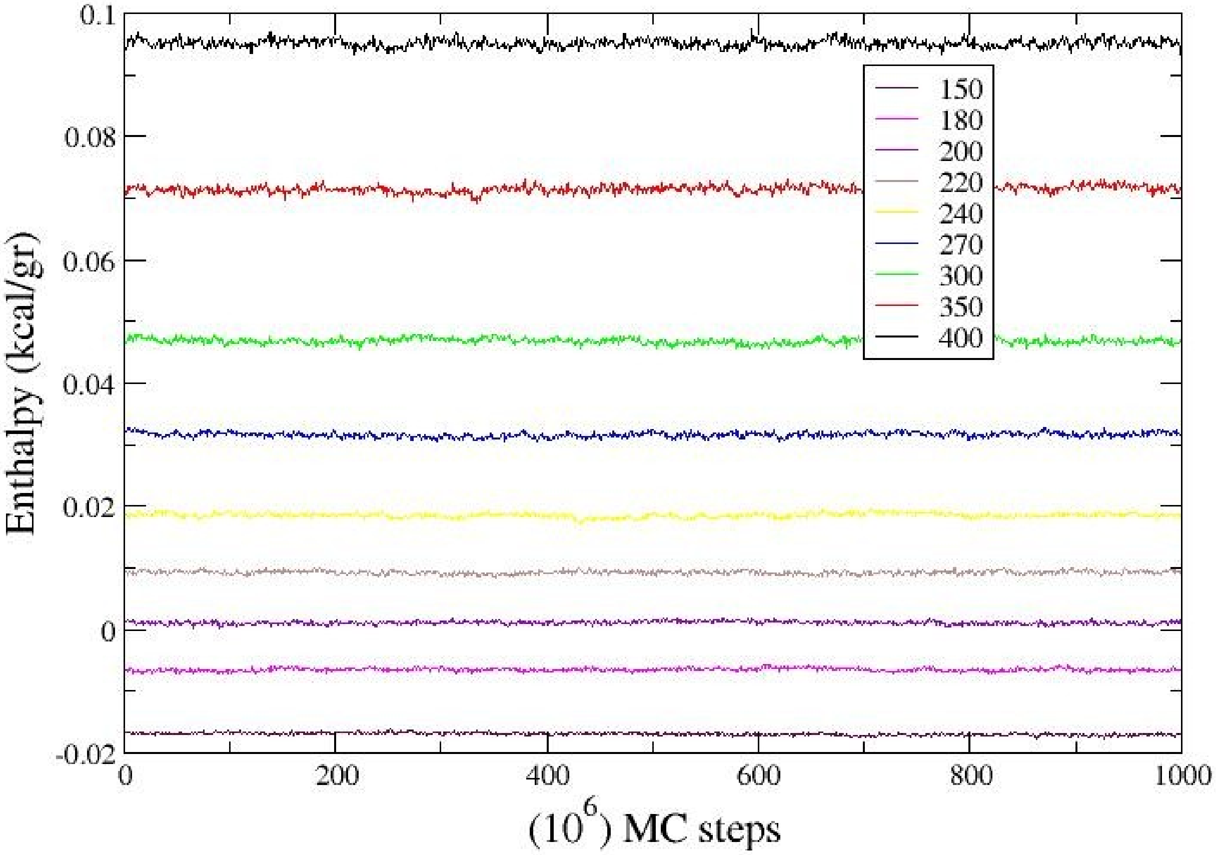


T=200K



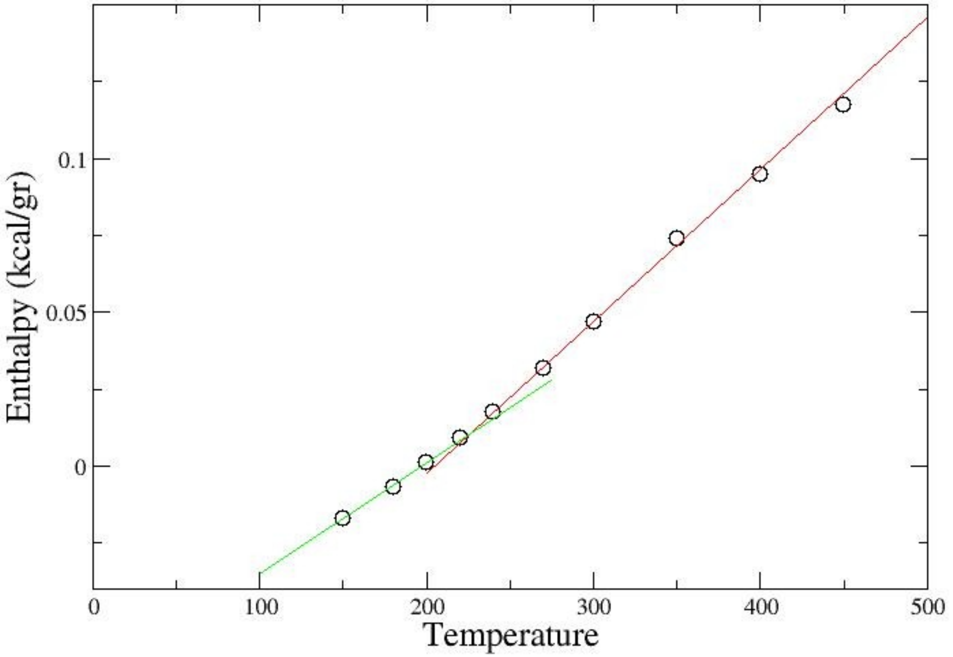
T=400K

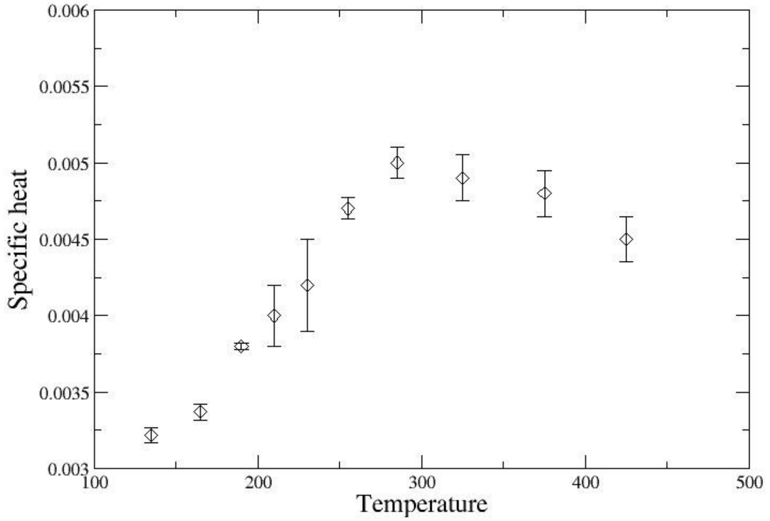
Enthalpy Traces



Enthalpy and Specific Heat

T determination from enthalpy:



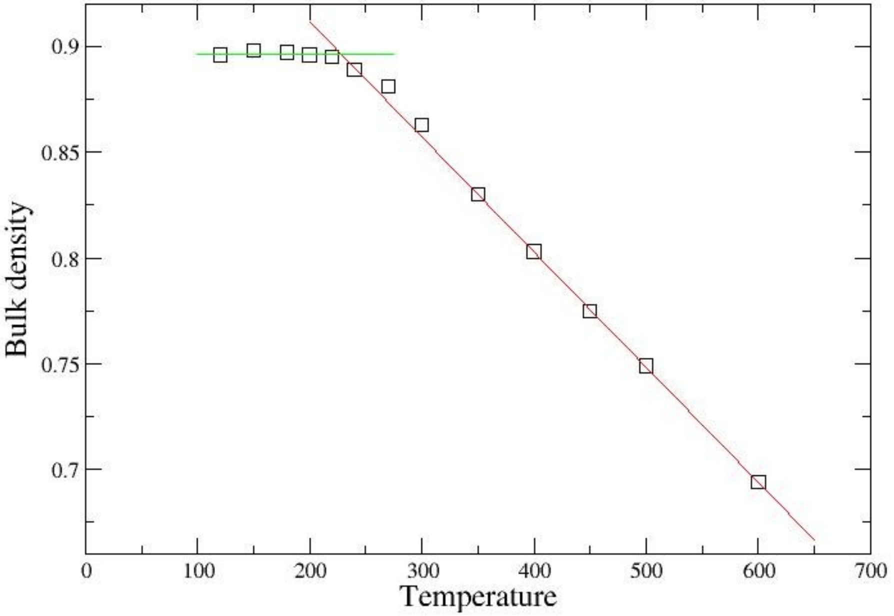


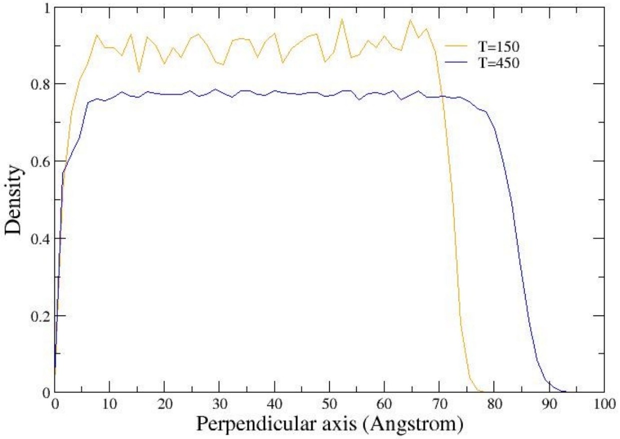
Simulated glass transition temperature ~ 227 K

<u>Note</u>: Chain grafted on a hard surface

Thin Films with Grafted Chains: T_g Determination

T_g determination from density:





Simulated glass transition temperature ~ 228 K

Note: **Chain grafted on a hard surface**

Summary

- Novel Monte Carlo moves used for simulating polyethylene both above and below the glass transition temperature
- Simulations capable of “equilibrating” the system for some temperatures below $T_{g.}$
- T_g of grafted film found to be lower than that of the bulk sample

  Considerations: chain-surface interactions, grafting

- Future Work:

  Realistic surface model, other chemistries