Glass Transition in Polymers
Effects of confinement

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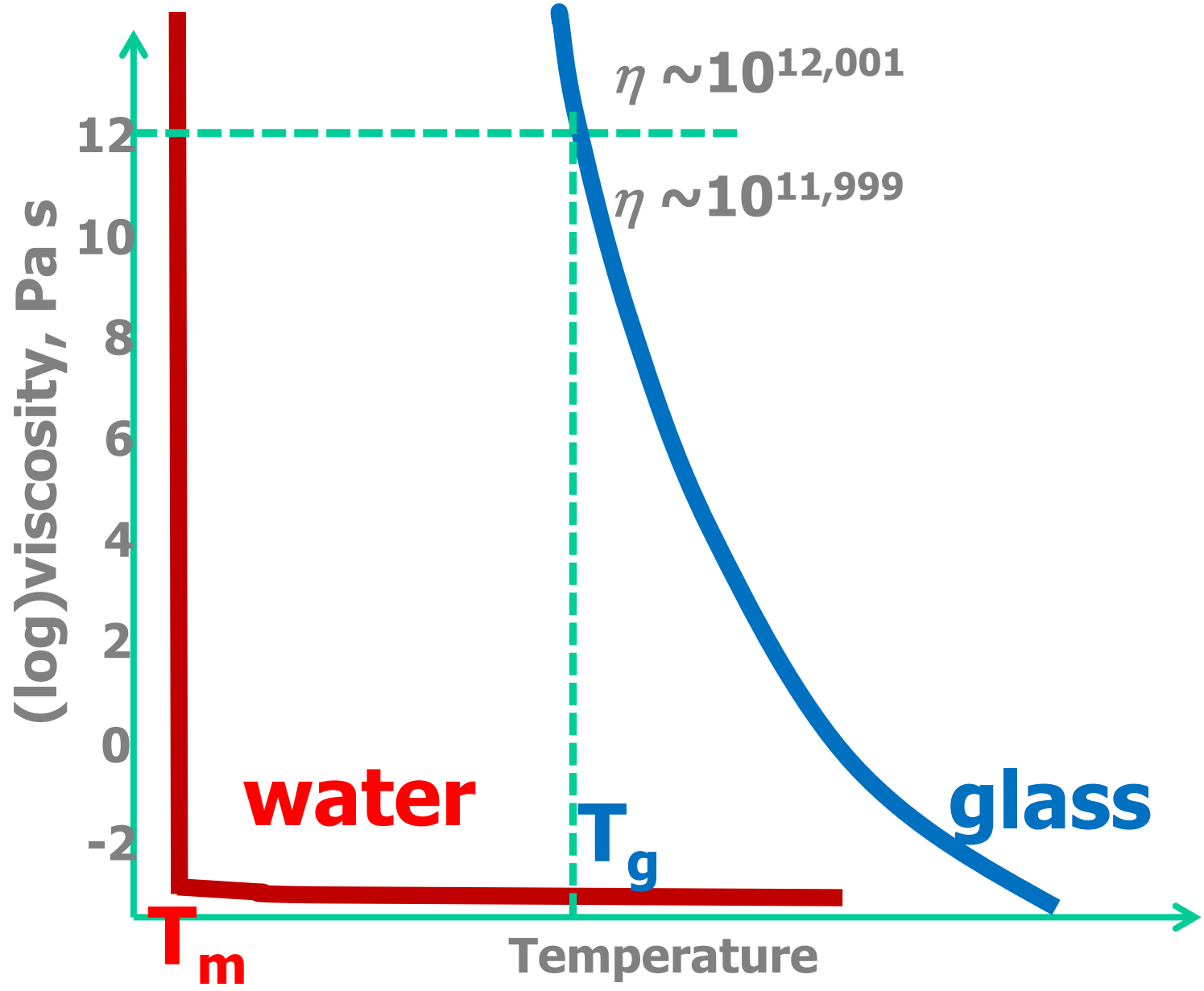
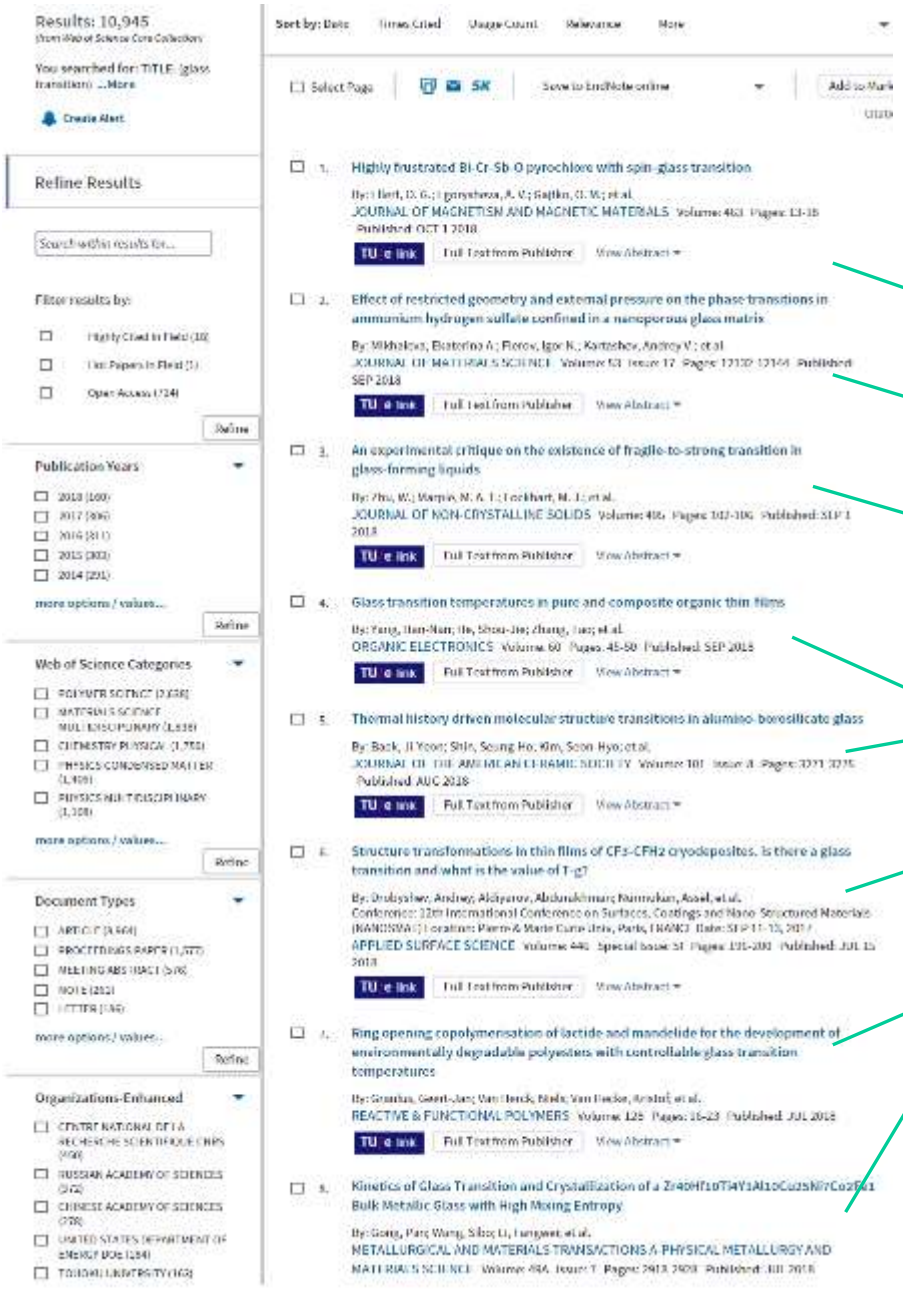
Han-sur-Lesse winter(??)school, June 13-14 2022


η ~10^12,001
η ~10^11,999
12
10
8
6
4
2
0
-2
(log)viscosity, Pa s
water
glass
T g
T m
Temperature



spin glasses

nanocomposites

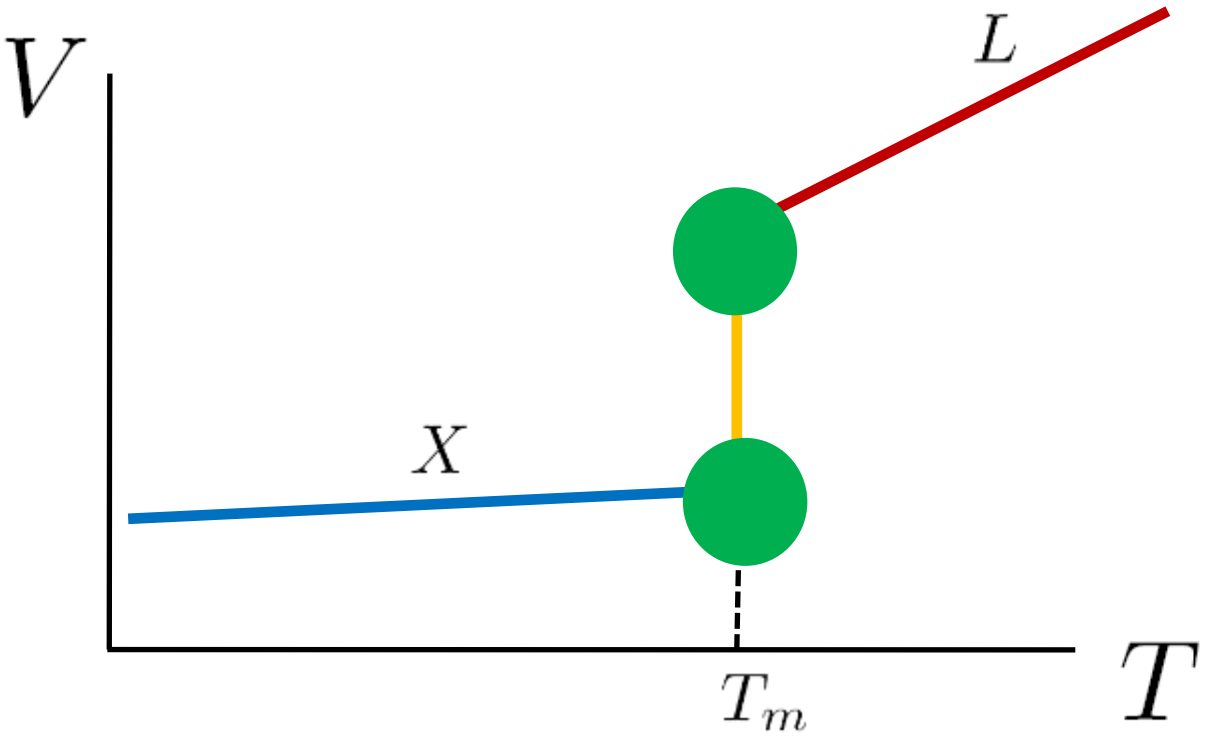
simple glass-formers

metallic glasses

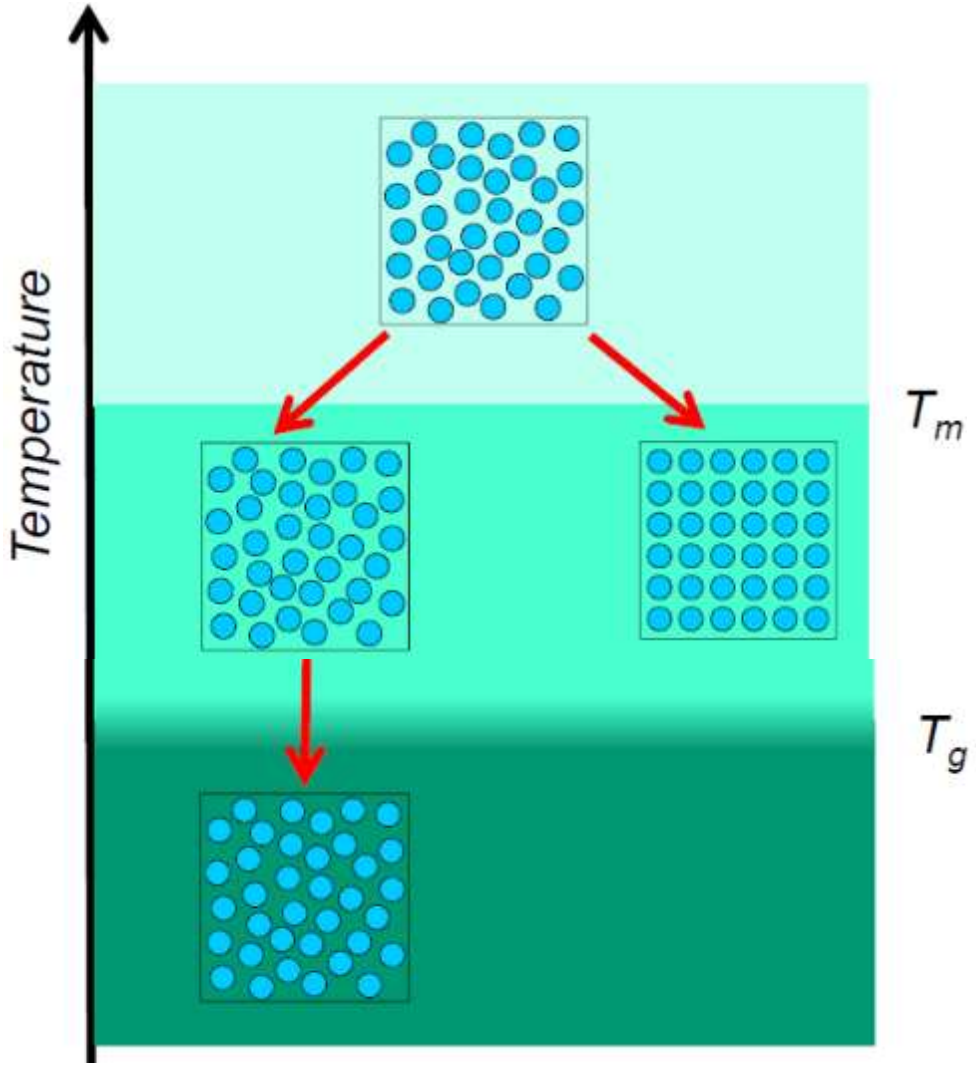
thin films

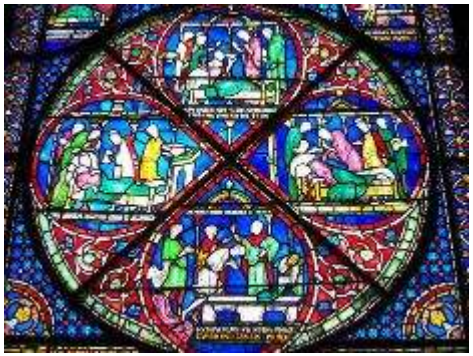
polymer glasses

What happens upon cooling?

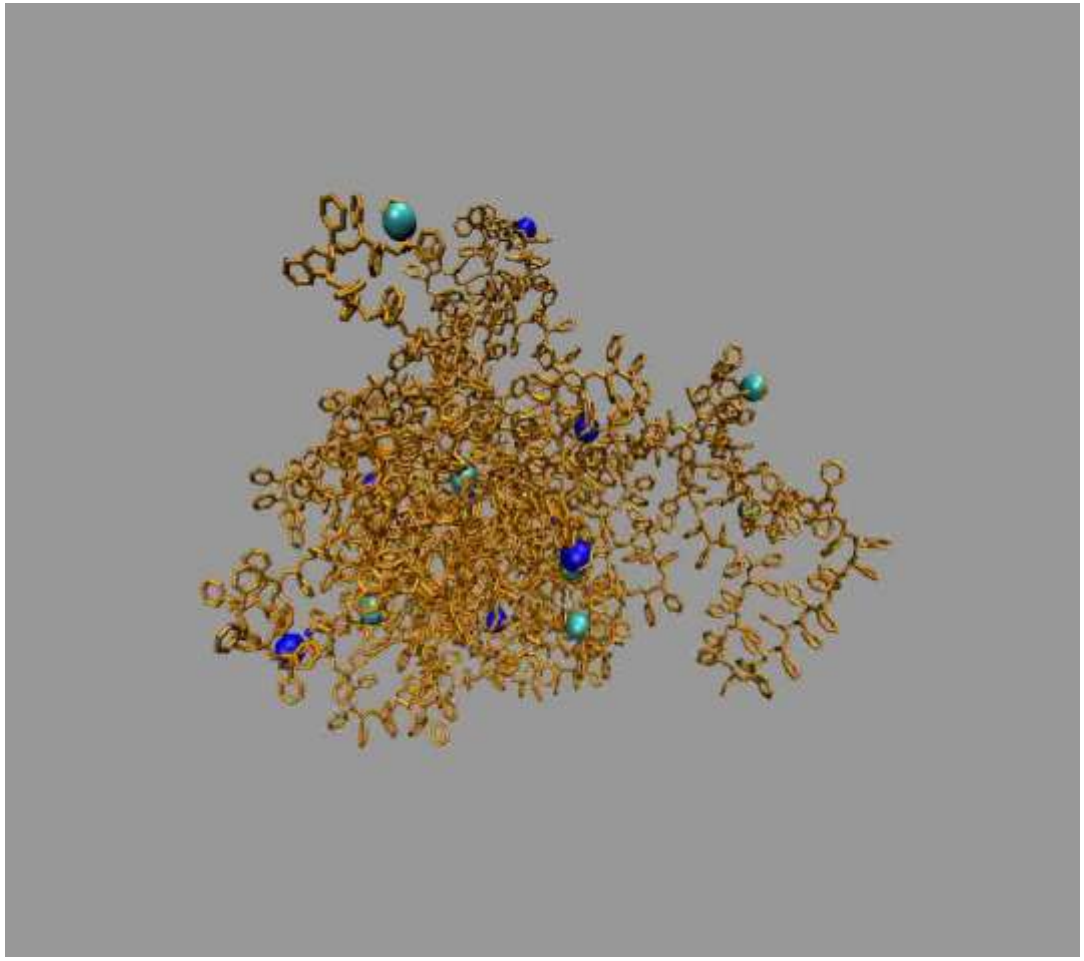


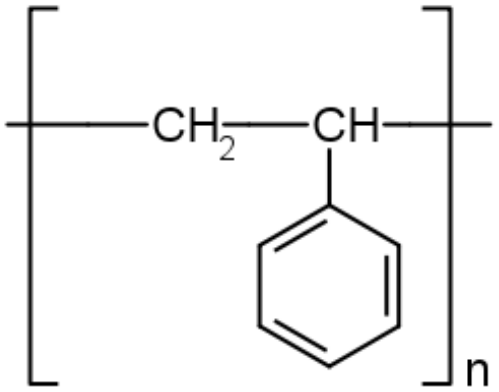
Reality





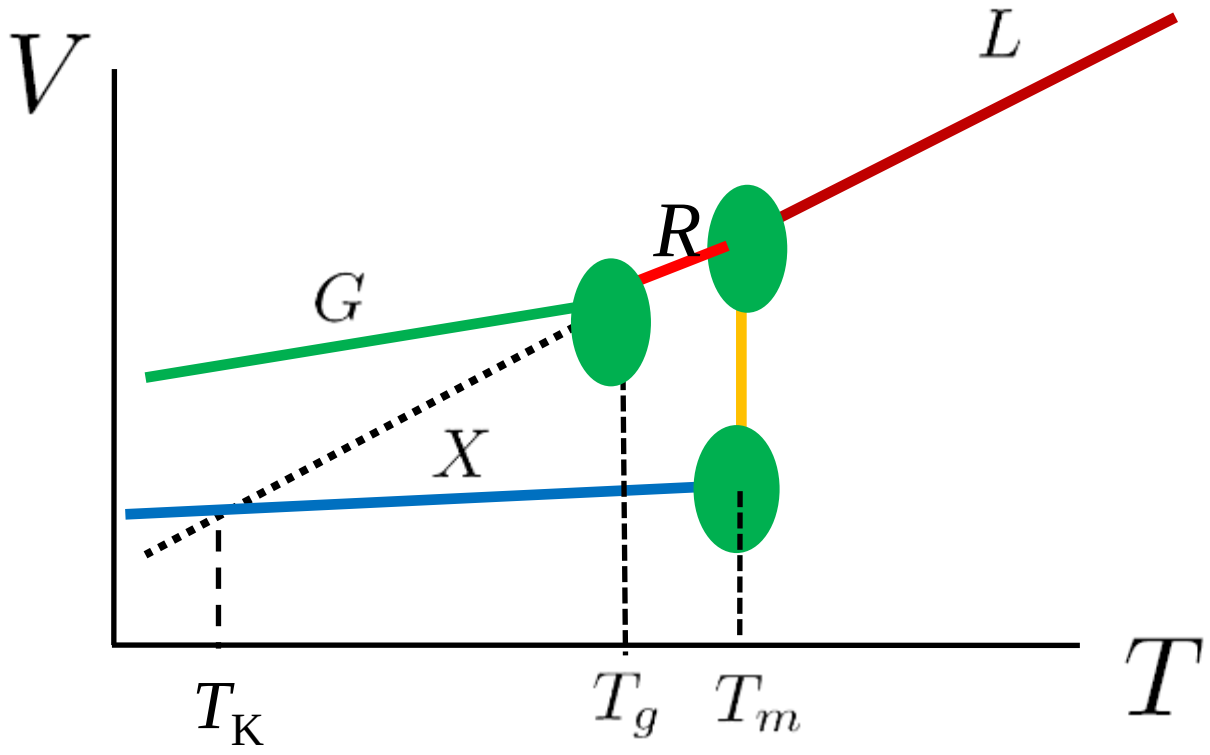
Polymer glass formers



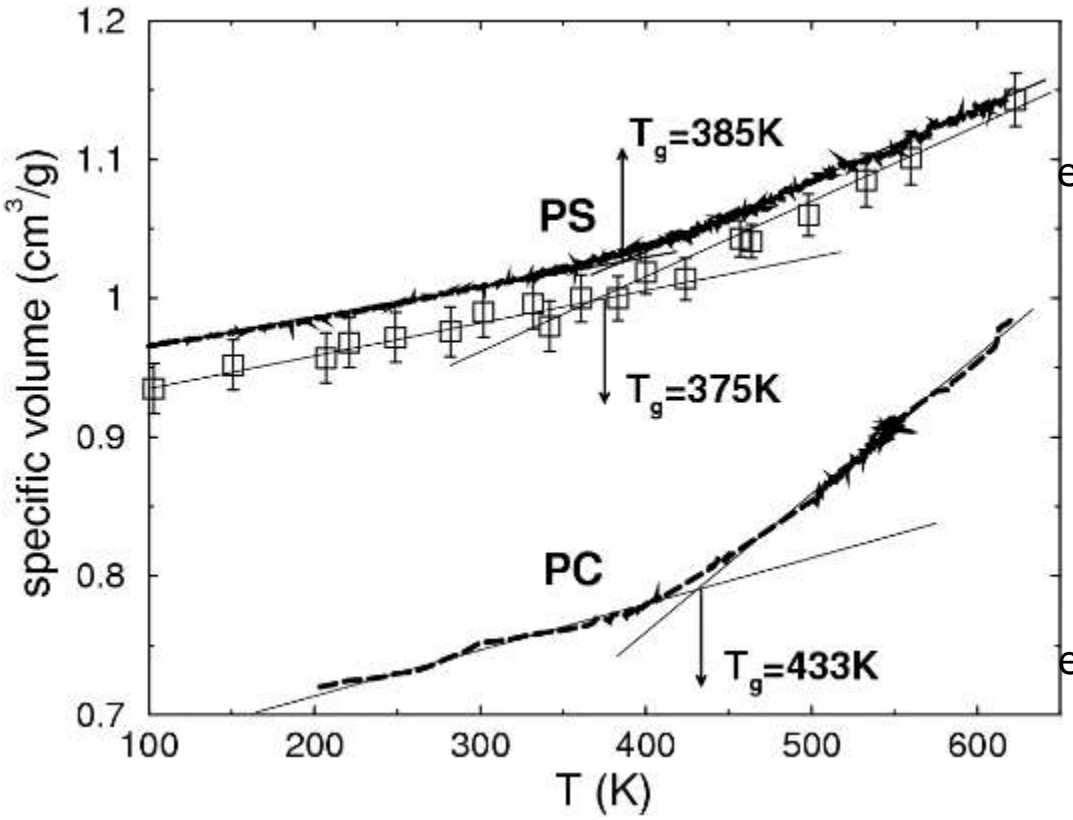


Many polymer chains

What happens when we put many polymer chains together?



MD-determined glass transition



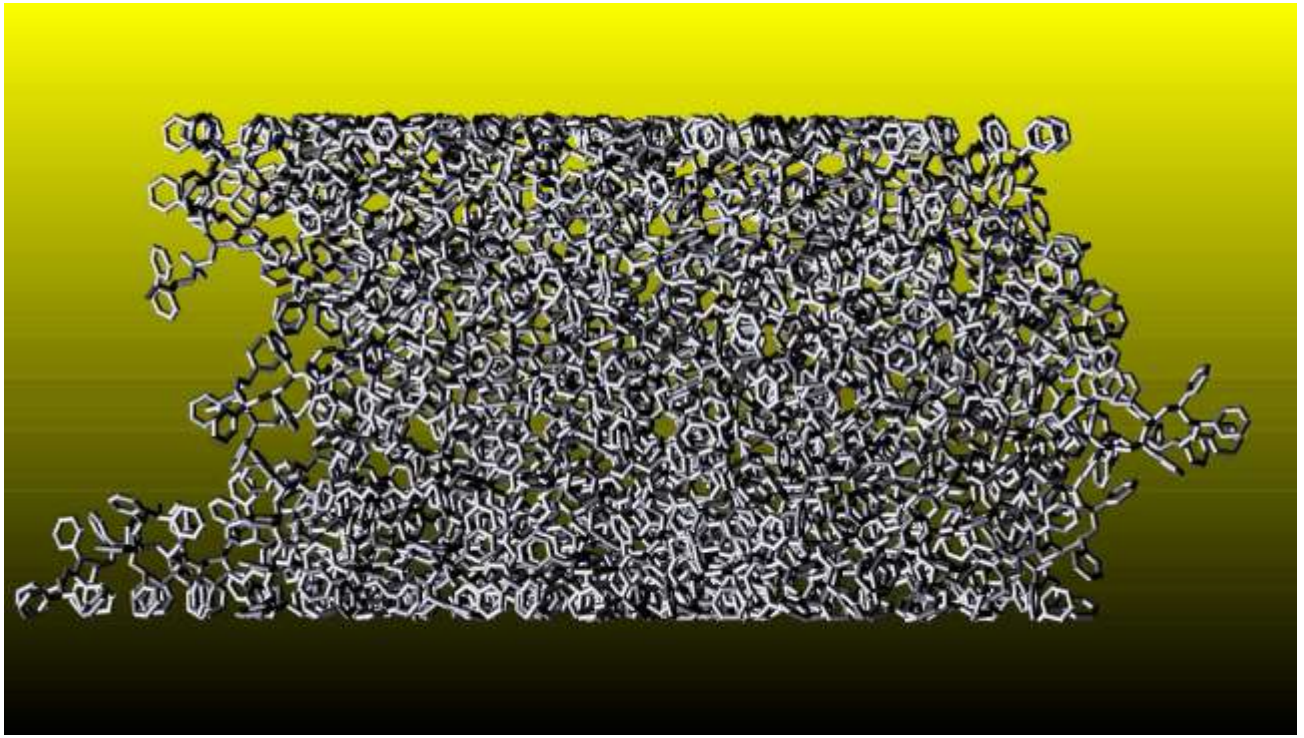
exp: ~365 K

exp: ~425 K

- MD-determined T_g is displaced upward as compared to experiment
- The value of T_g is strongly cooling-rate dependent

AVL, B. Vorselaars, M. Mazo, N. Balabaev, M.A.J. Michels, ***Europhys. Lett.*** 2005

Glass transition in thin polymer films



THE JOURNAL OF CHEMICAL PHYSICS

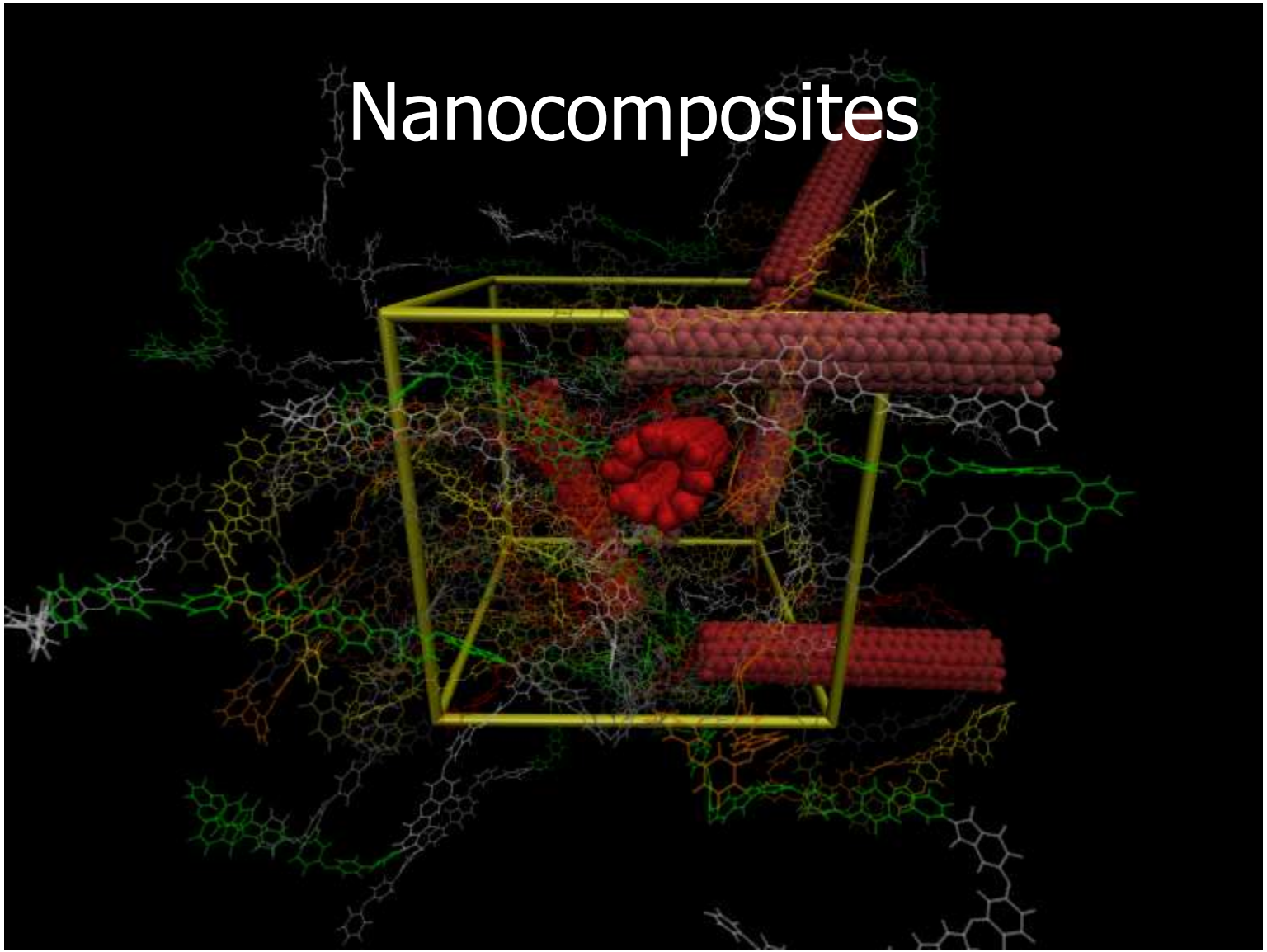
Volume 146, Issue 20, 28 May 2017

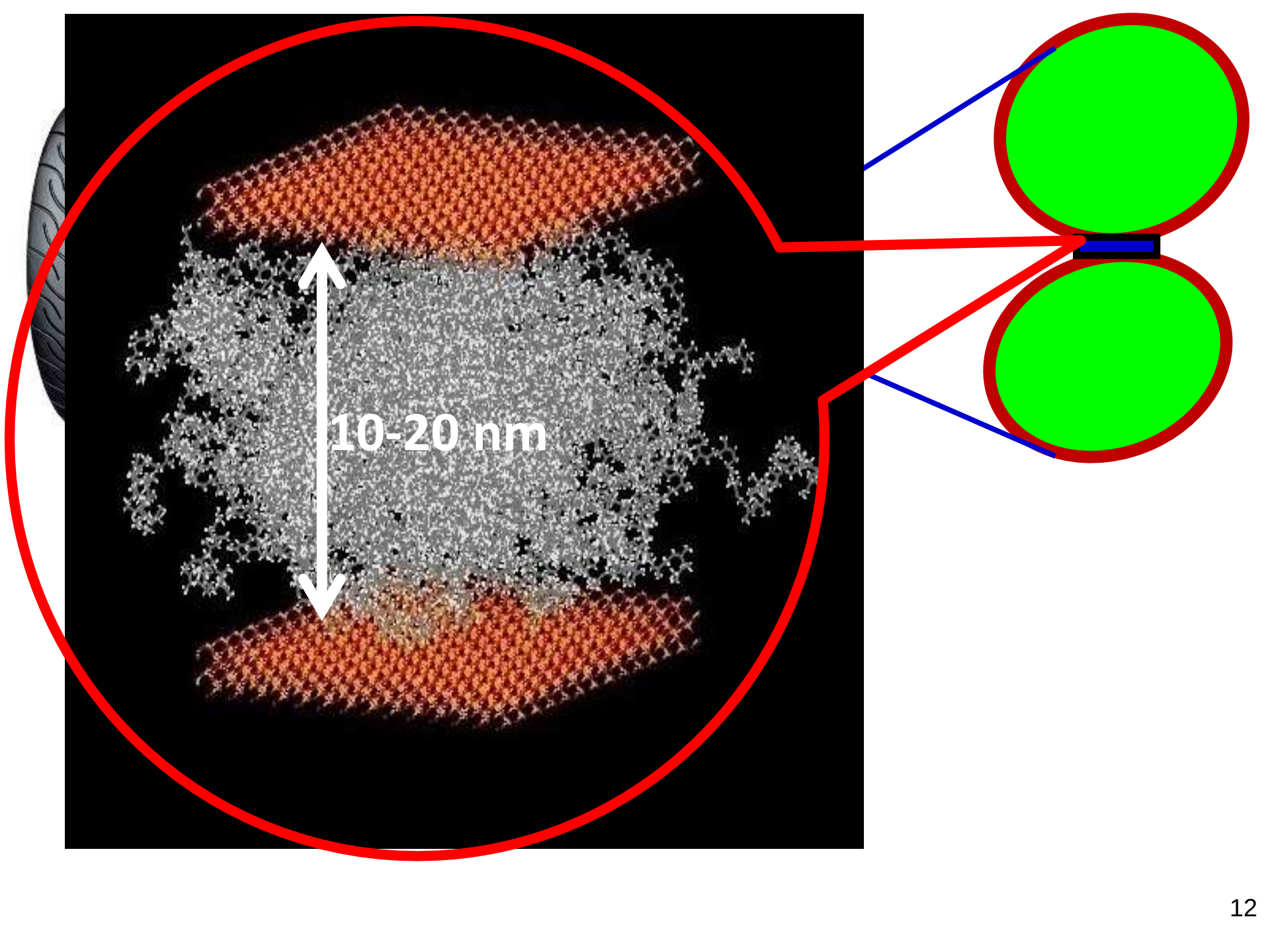
SPECIAL TOPIC:
DYNAMICS OF POLYMER MATERIALS IN THIN FILMS AND RELATED GEOMETRIES

- 26 focus articles

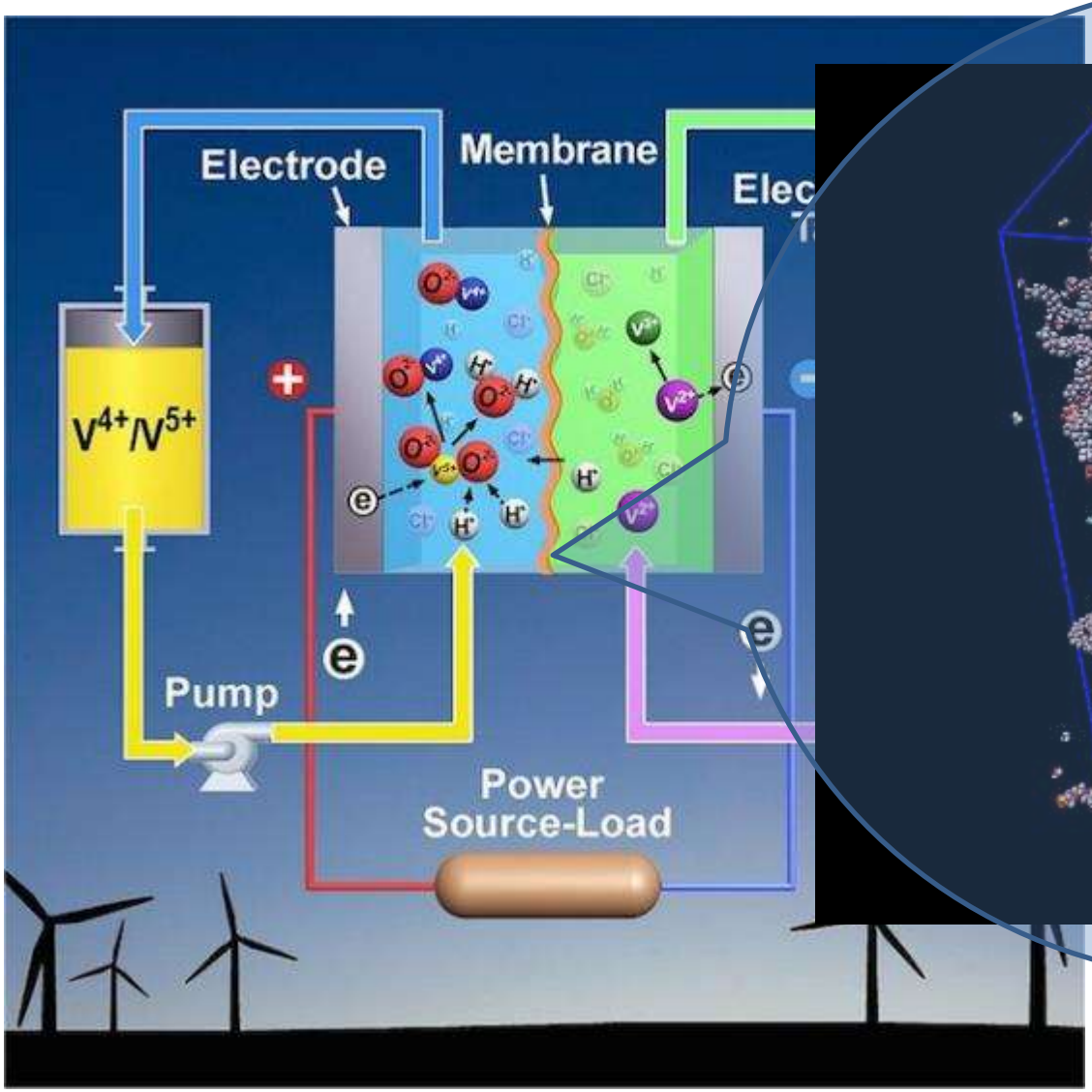
AVL, N. K. Balabaev, A. R.C. Baljon, G. Mendoza, C. W. Frank , D. Y. Yoon, ***J. Chem. Phys***., **2017**
S. Lee, AVL, C. W. Frank, D. Y. Yoon, ***Polymer,*** **2017**

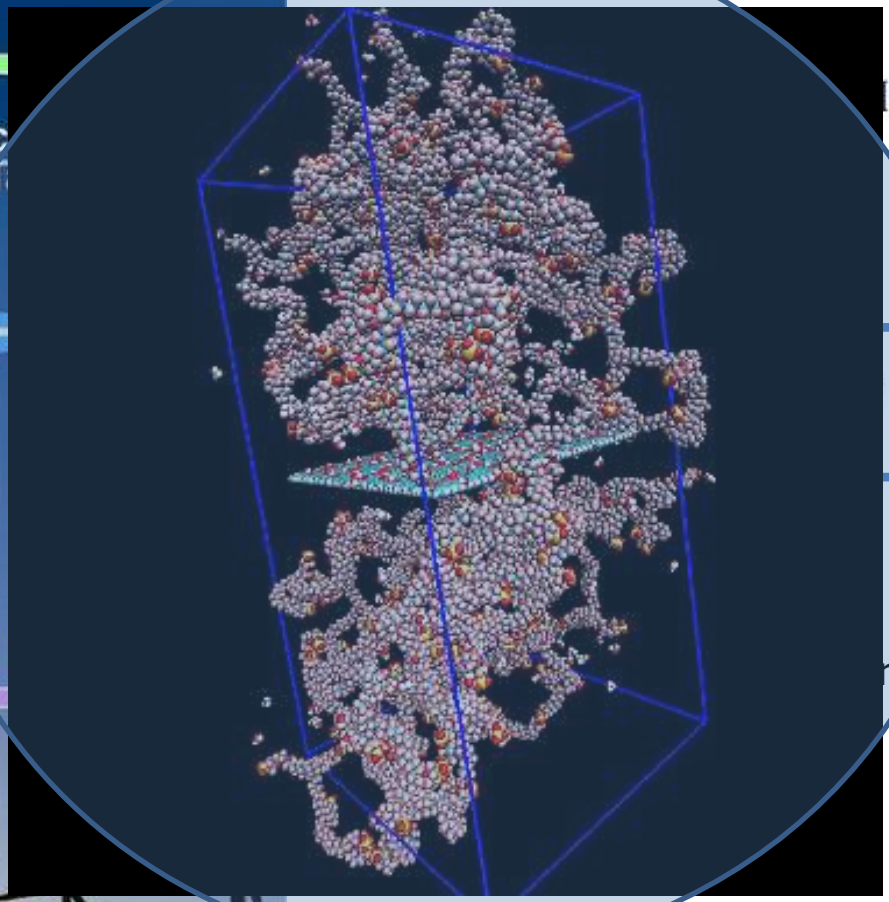
Why films?



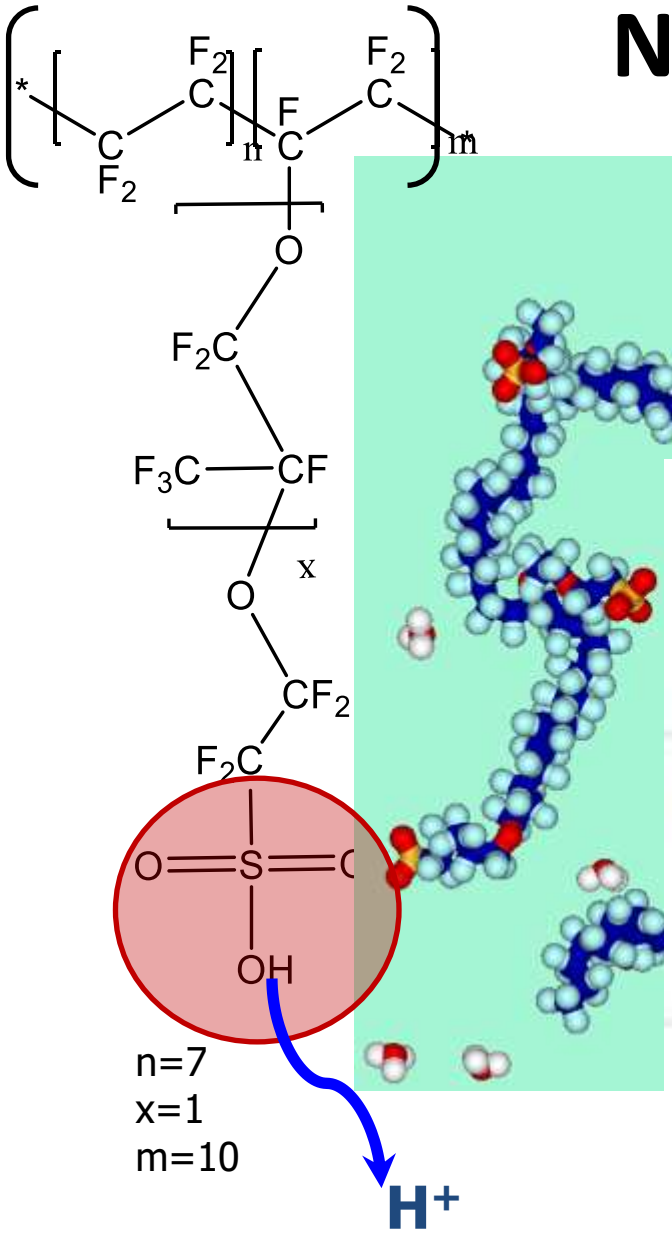

10-20 nm

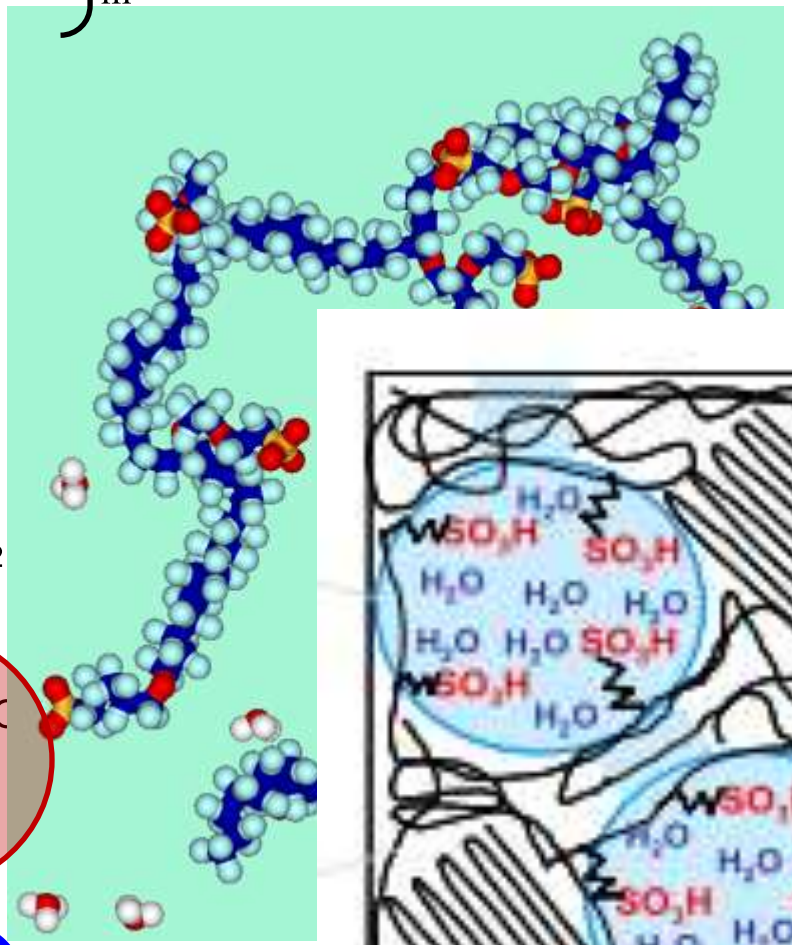
(Redox) Flow Batteries



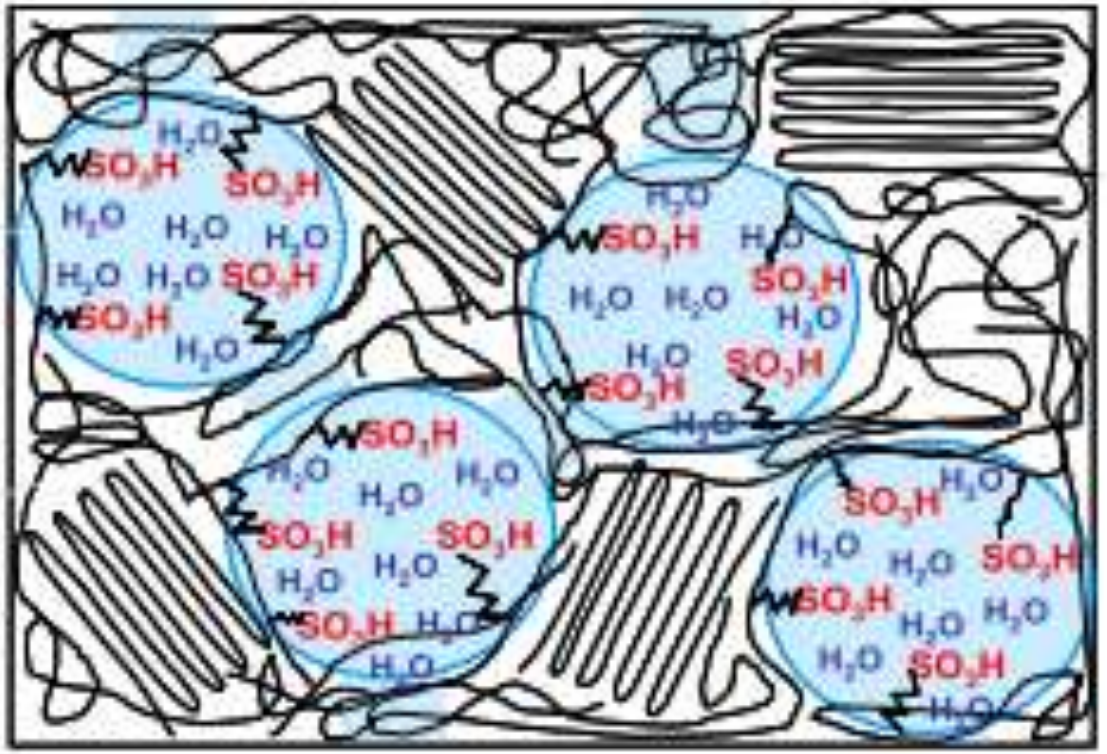


Nafion (DuPont, 1960s)

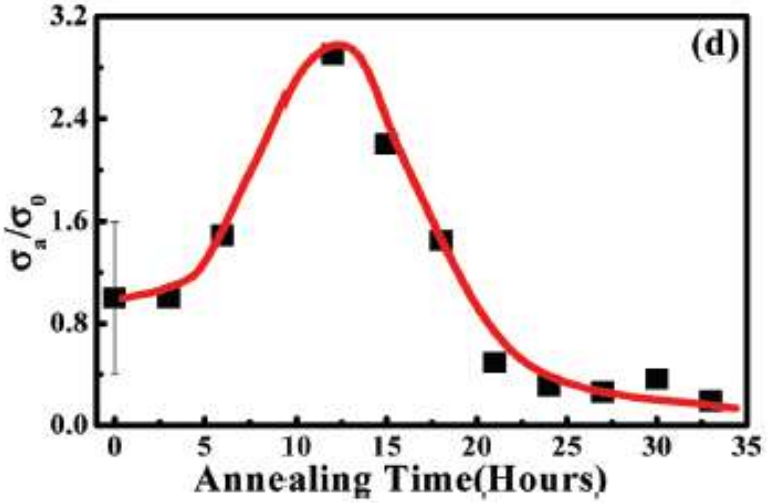




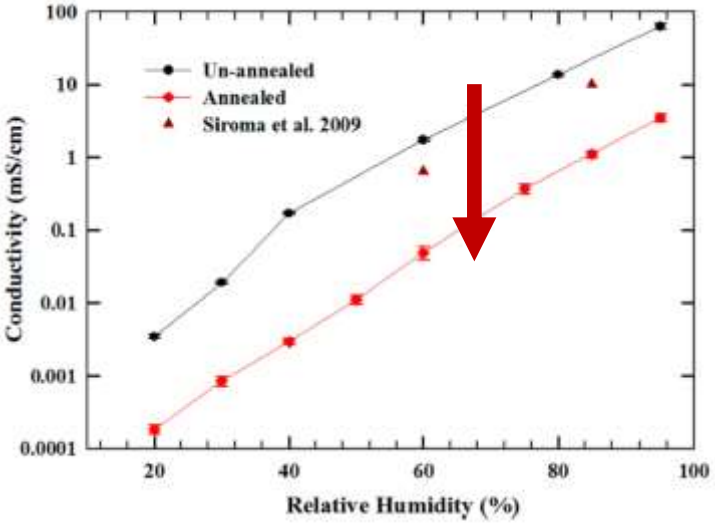
- hydrophobic backbone - **strength**
- hydrophilic side chain - **absorb water**
- high proton conductivity, **0.2 S/cm**



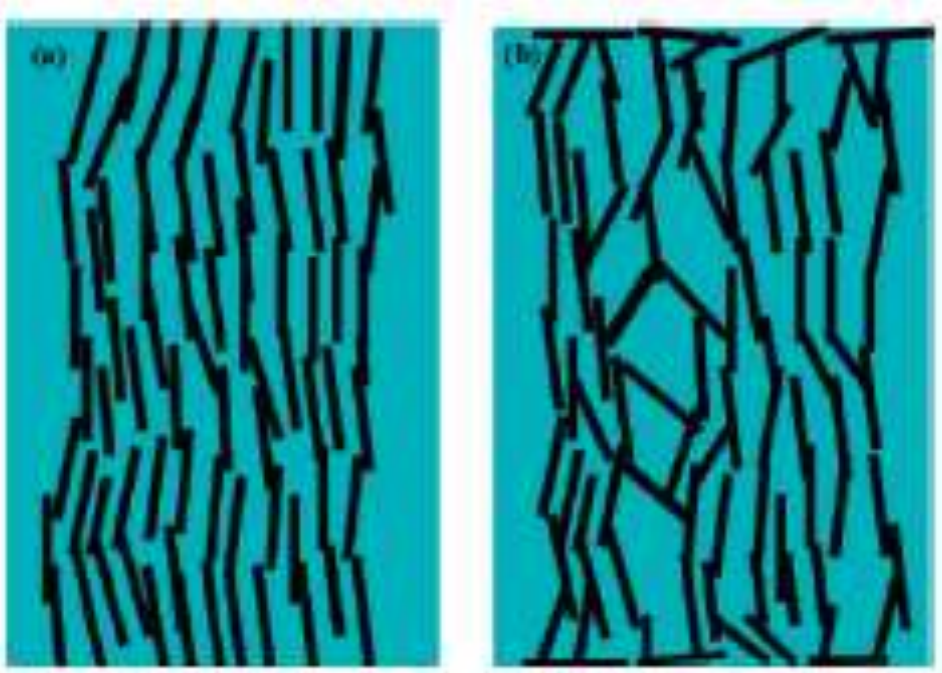
Experimental Evidence



Kwon et al., J. Phys. Chem. B, 2010, 114, 14989

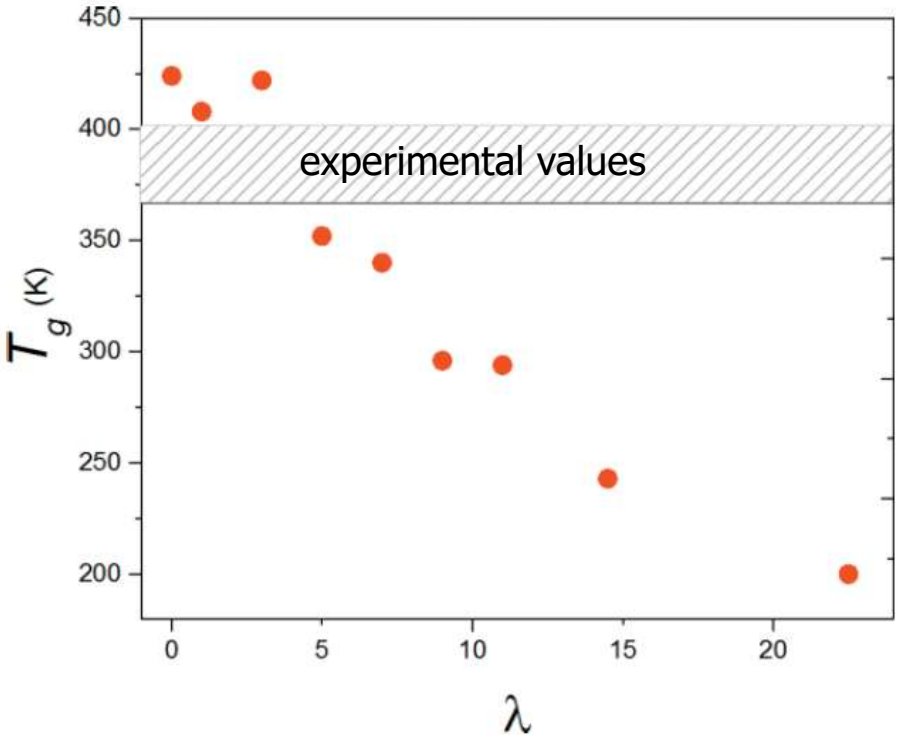


Paul et al., J. Phys. Chem. C, 2014, 118, 1828

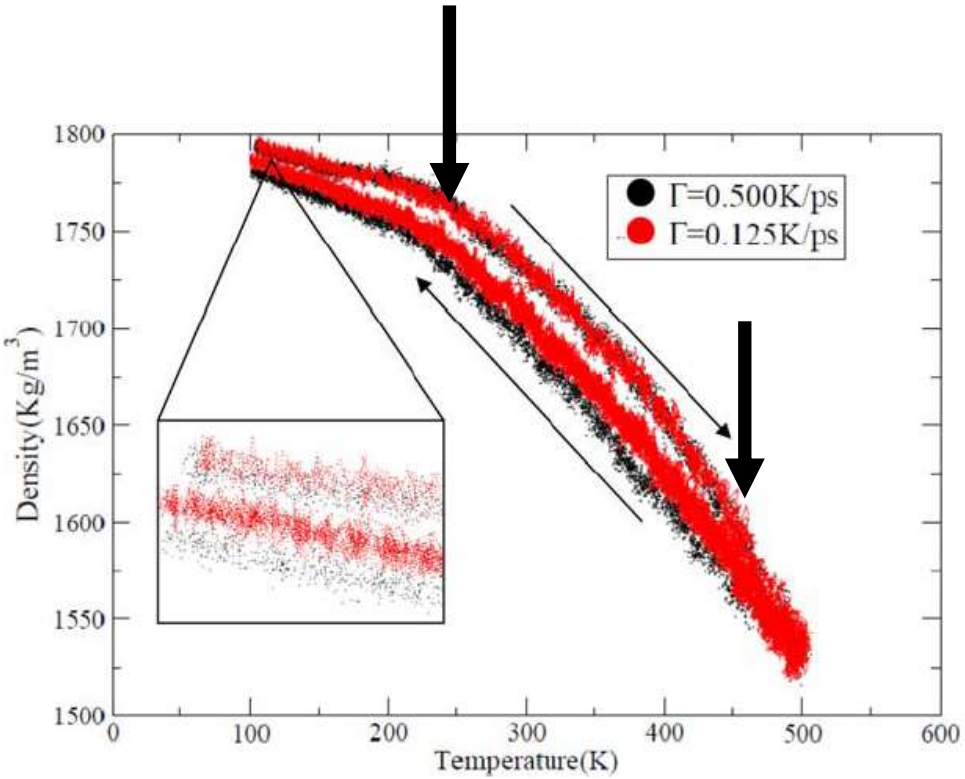


a) – pristine membrane
b) - annealed membrane

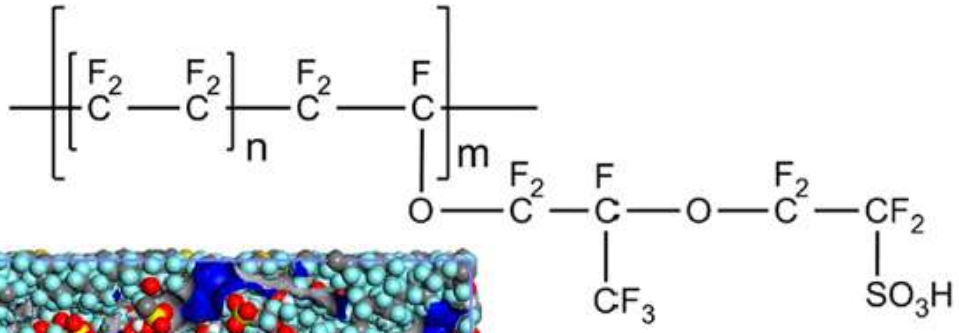
Glass Transition



Fleury et al., Fuel Cells, 2016

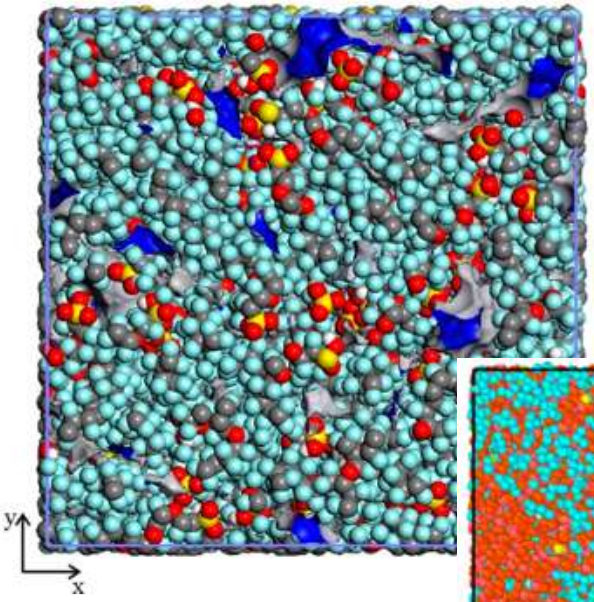


Ozmaian et al., J. Polym. Sci., Polym. Phys., 2014

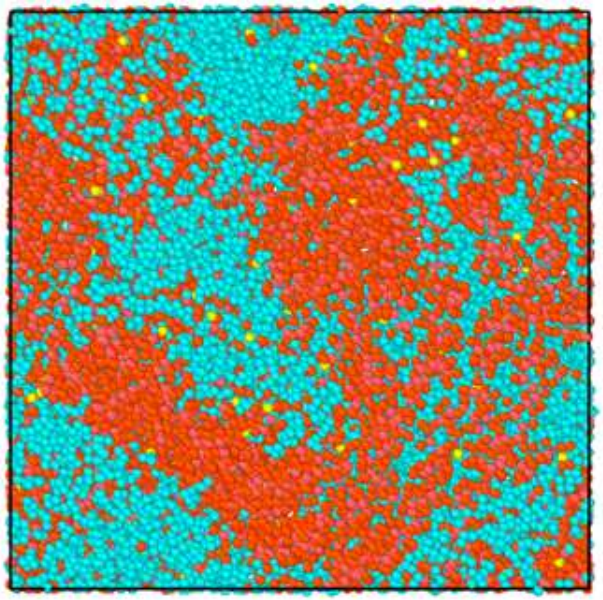


m=10, n=7, Nafion equivalent weight (EW) of 1100,

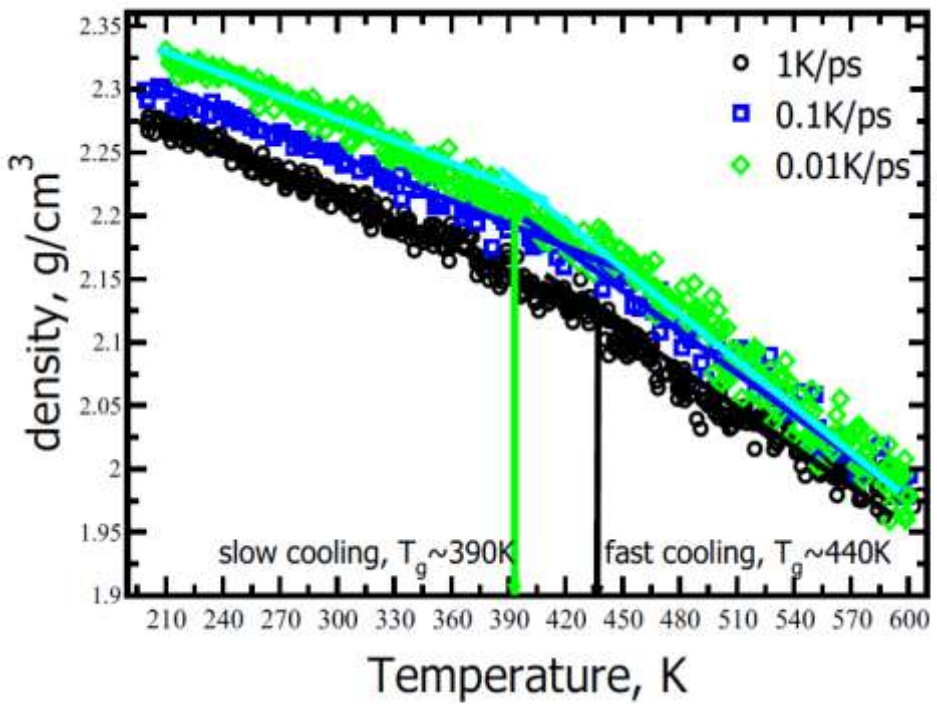
pcff + COMPASS force fields

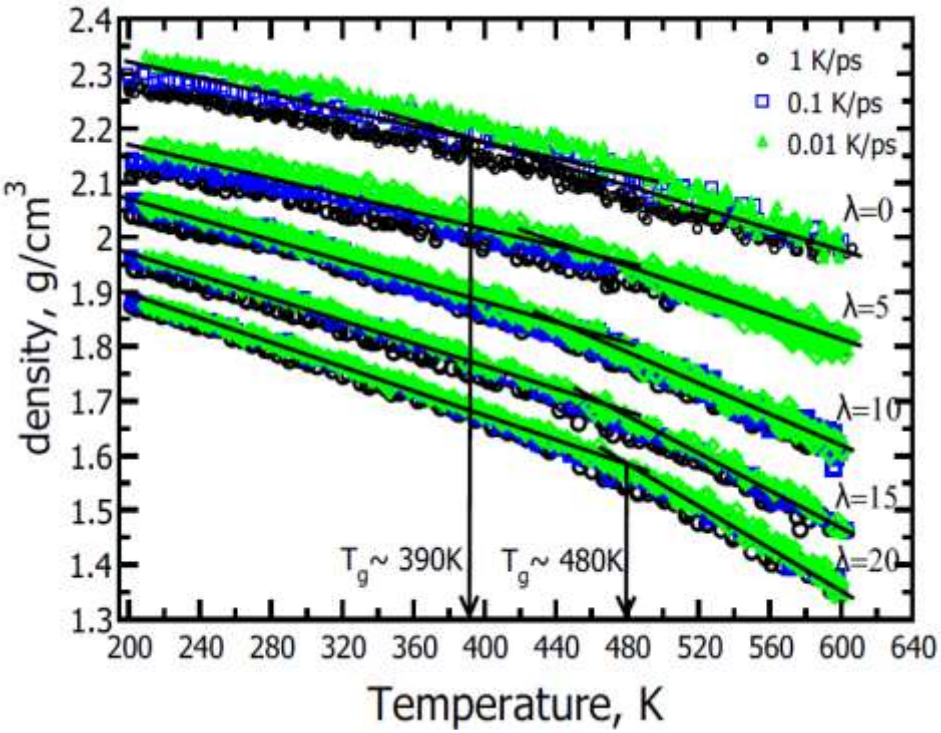


dry Nafion



hydrated Nafion (λ=15)

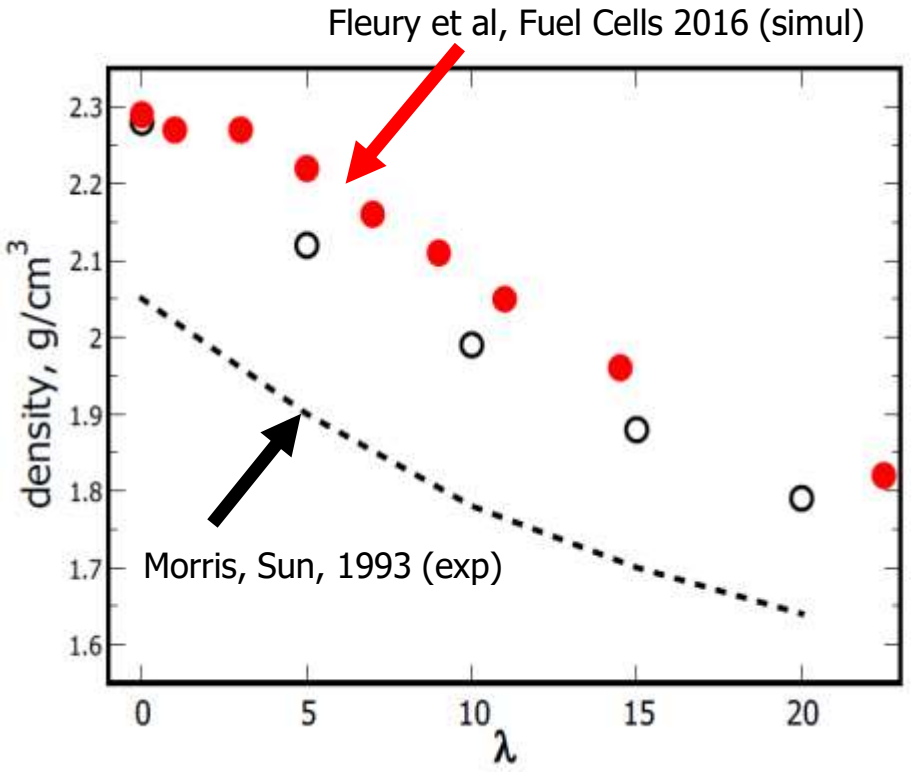


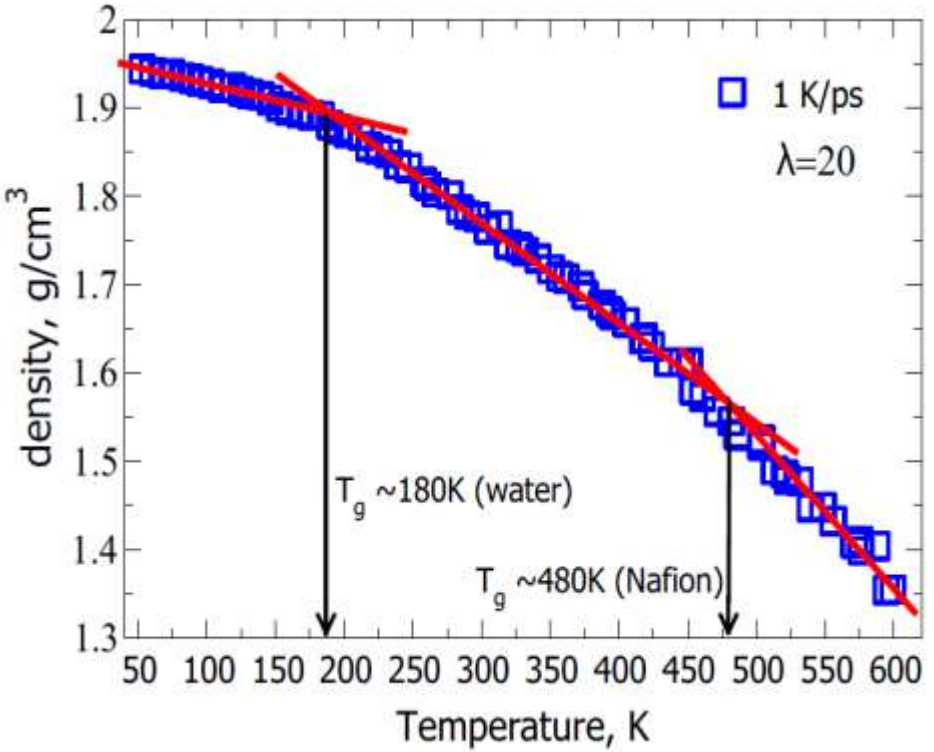


- dry Nafioin cooled down with different cooling velocities.

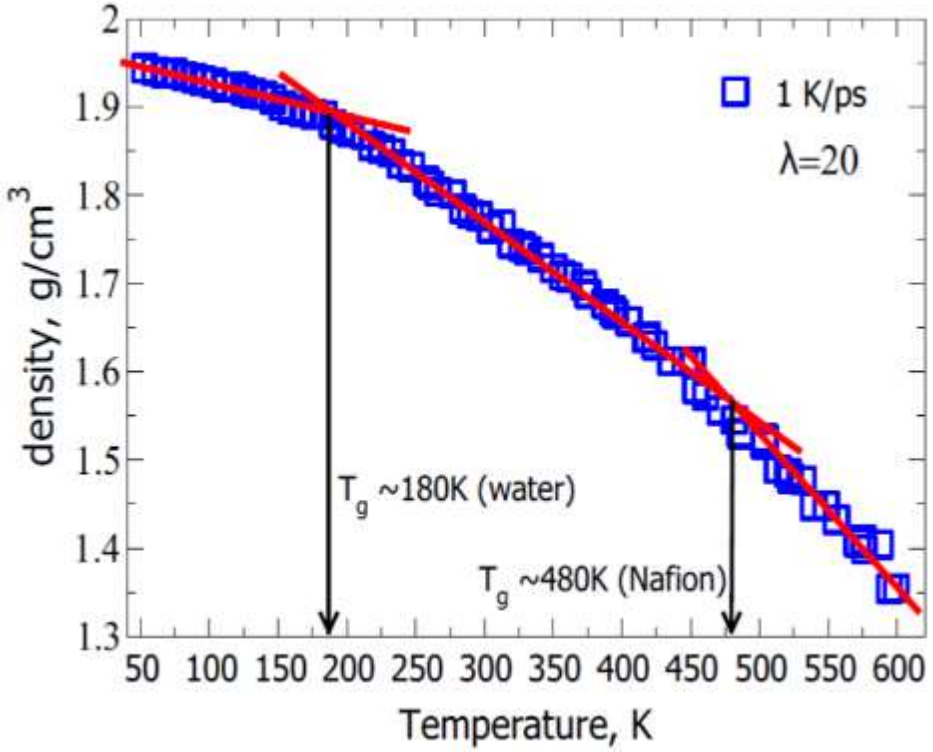
- shift of the T_g value of about 50 K is obseved for fastest cooling.

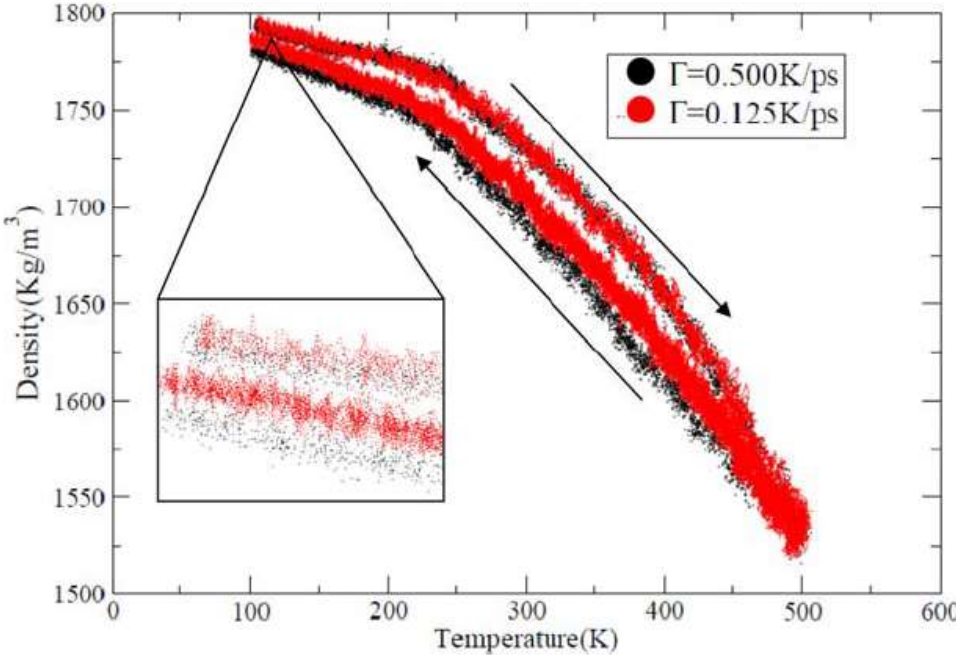
- increase of the glass-transition temperature with increasing hydration level is clearly visible





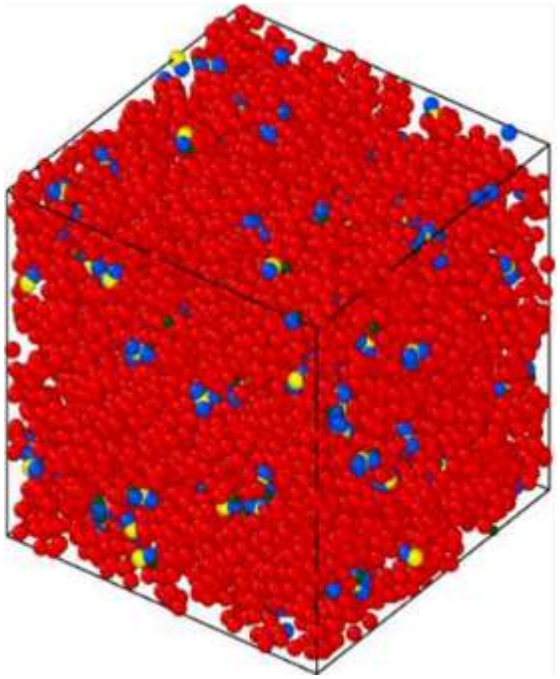
The second glass-transition temperature for water is clearly visible upon further cooling



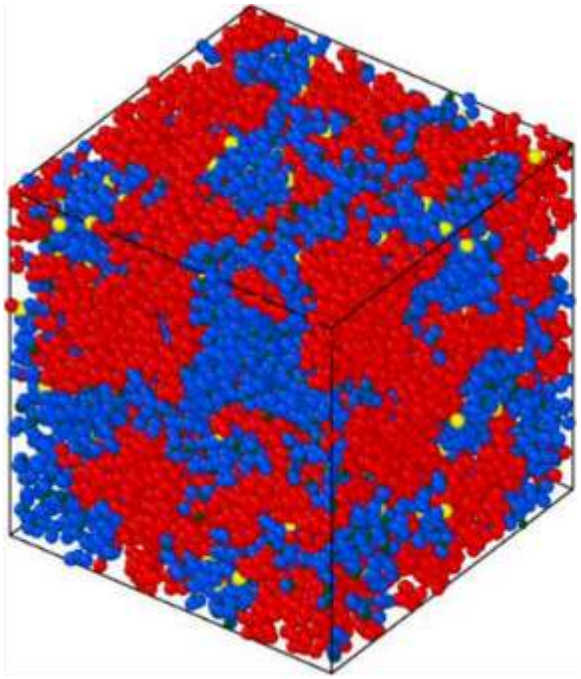


λ=14

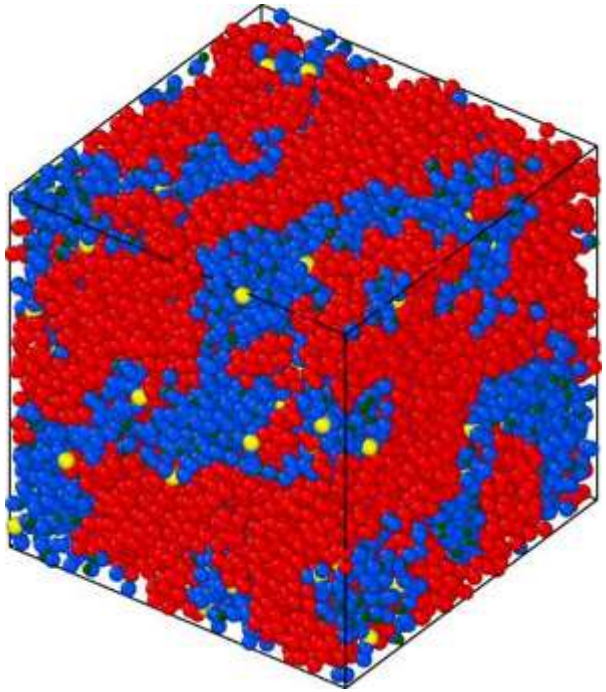
Ozmaian et al., J. Polym. Sci., Polym. Phys., 2014



dry (λ=0) Nafion, 600 K

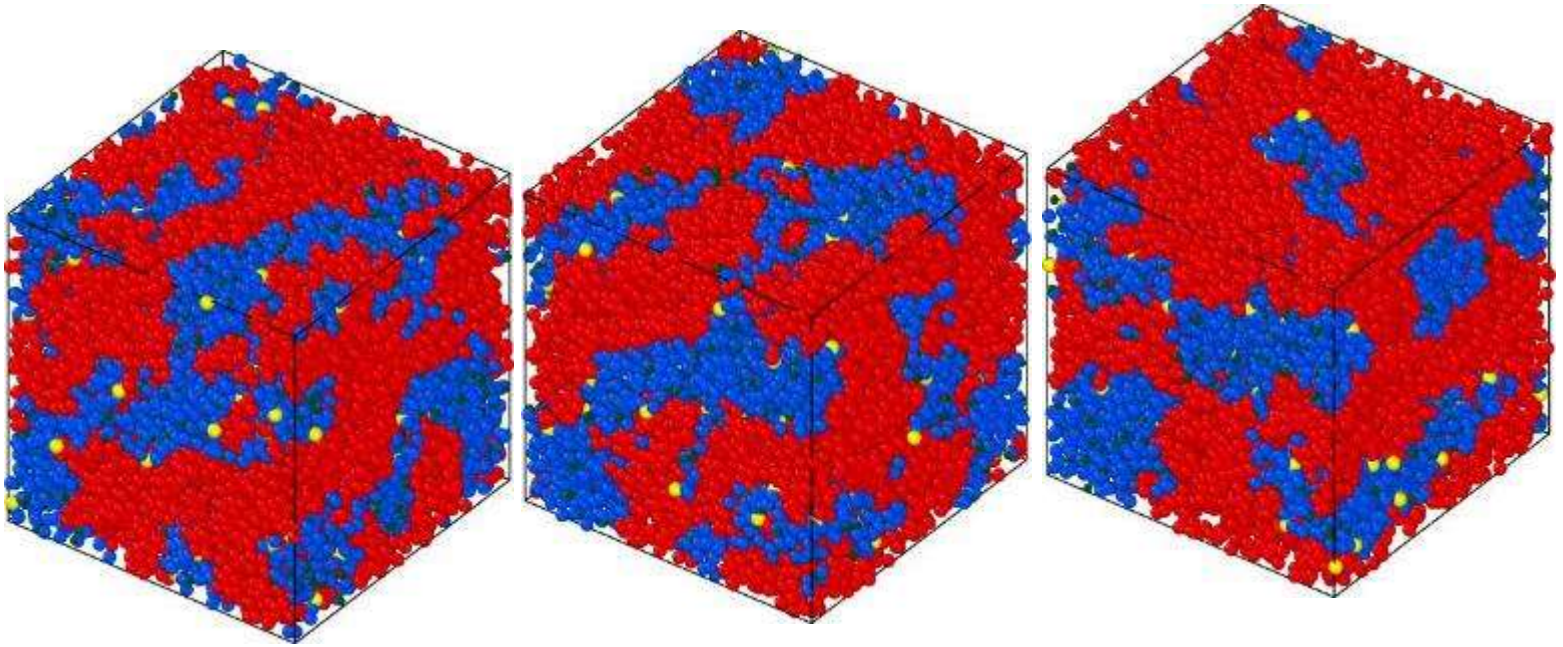


development of the percolated water cluster (blue) upon hydration (λ=15), T=600 K.



well-preserved percolated water cluster produced upon fast (cooling velocity 1K /ps) cooling of a hydrated sample from T=600 K to T=200 K, λ=15.

Slow Annealing Breaks Percolation



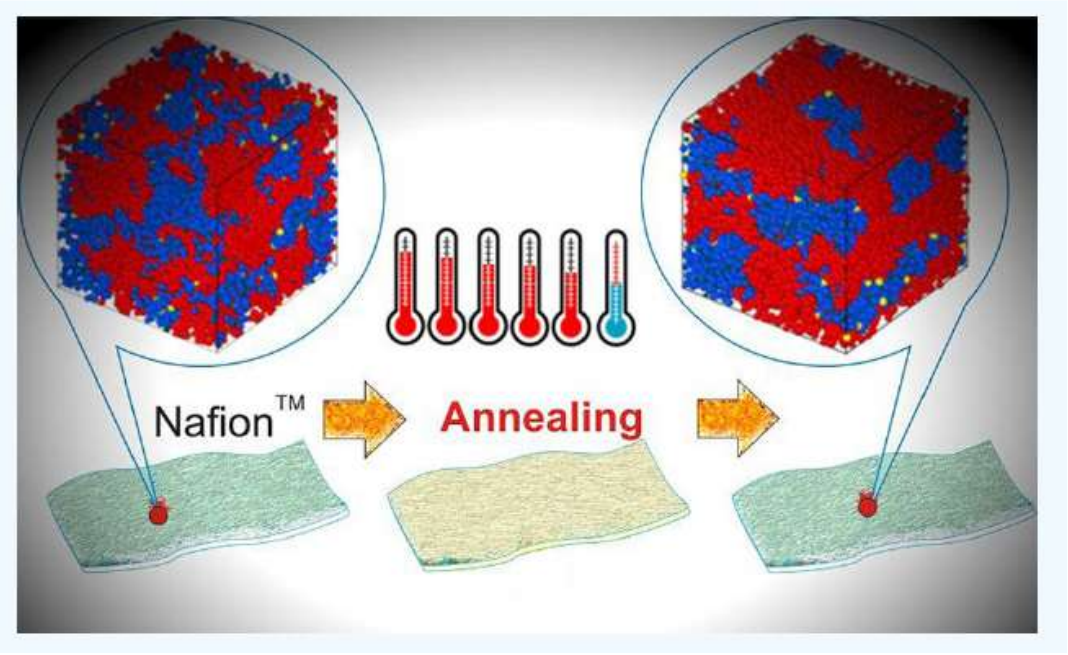
Nafion quenched from T=600 K to T=200 K by the fastest (1K/ps) cooling, λ=15

the same but 0.1K/ps cooling

percolated cluster disappears upon slow annealing (0.01K/ps).

Conclusions I

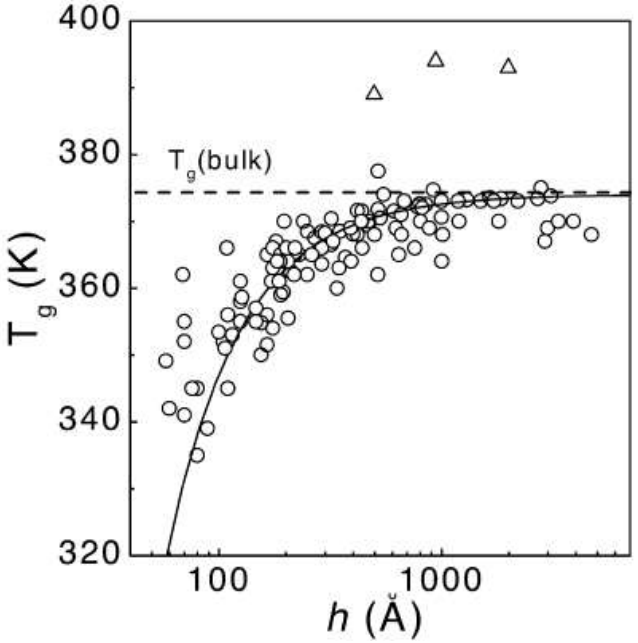
- **No** plasticization upon hydration;
- **Two** glass transitions;
- **Breaking of percolation** upon slow annealing, leading to the pronounced decrease of conductivity.



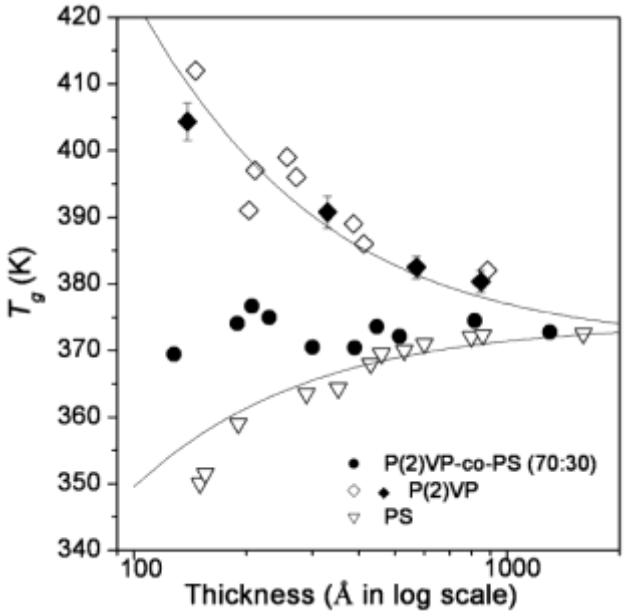
AVL, S. Sengupta, A. Varughese, P. Komarov, A. Venkatnathan, ***ACS Appl. Polym. Mater.,*** 2020, 2, 5058

Effects of Confinement

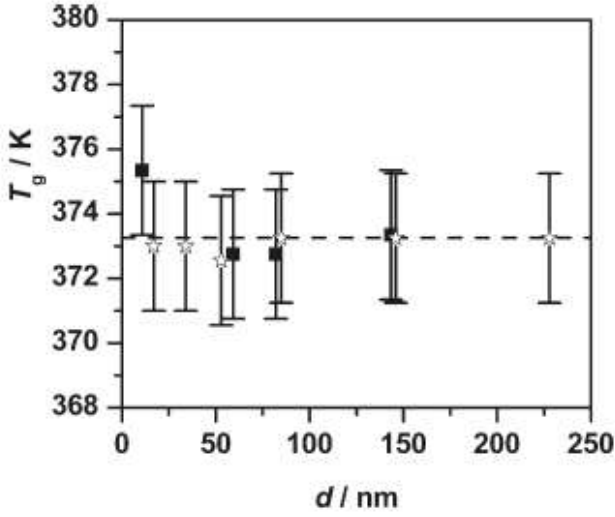
(mainly) PS, supported on silica wafers



J.A.Forrest, K.Dalnoki-Veress,
Adv. Colloid. Interface Sci, **2001**

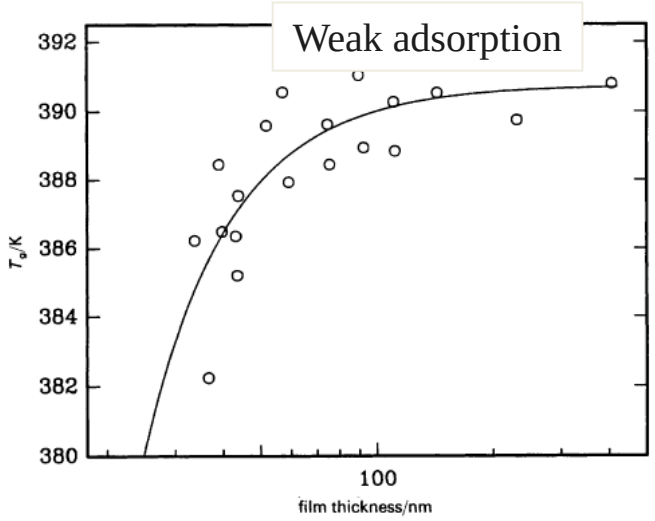


C.H. Park et al.,
Polymer, **2004**

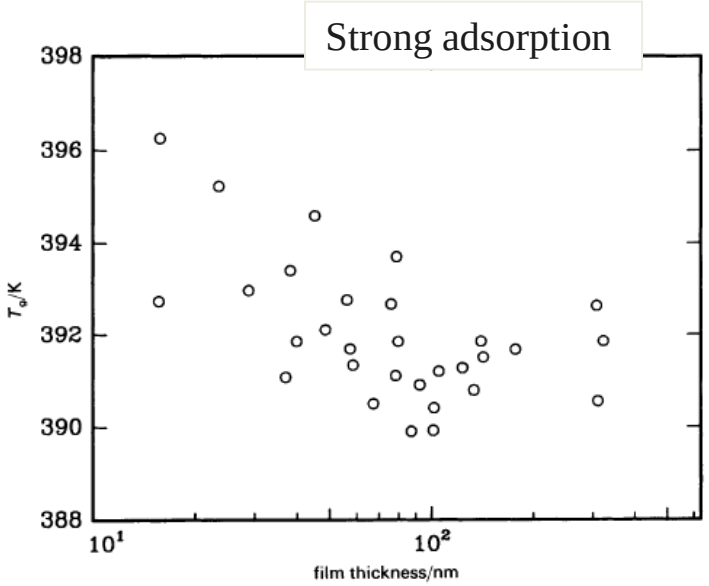


M. Tress, A. Serghei, F. Kremer et al.,
Macromolecules, **2010**

Effects of substrate

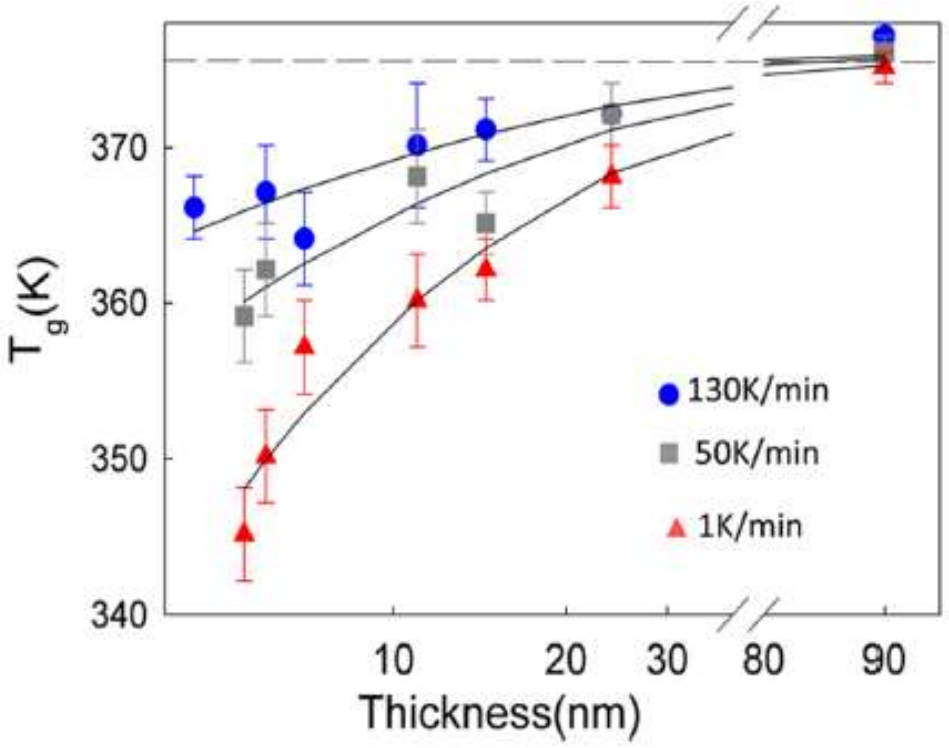


PMMA film on Au



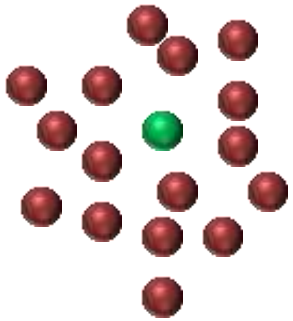
PMMA film on oxide-coated Si

J.L. Keddie et al., *Faraday Discuss*. **1994**



Z. Fakhraai, J.A. Forrest, Phys. Rev. Lett., 2005

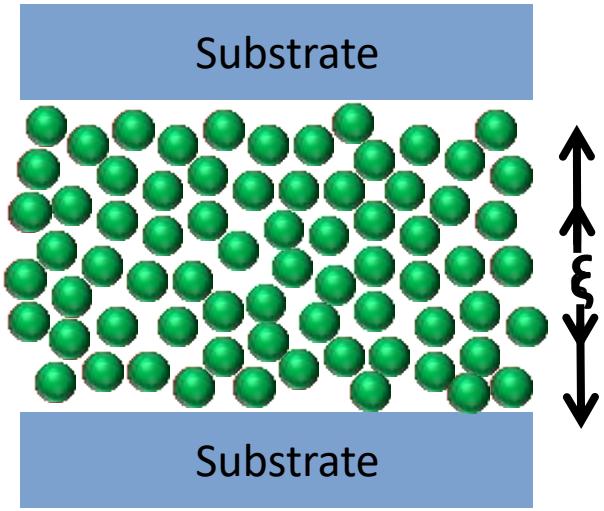
Cooperatively Rearranging Regions (CRRs)



$T \gg T_g$

Individual particle motion at high temperatures

$T \geq T_g$



Critical scaling: cluster relaxation time is $\tau_c \sim \xi^z$

Maximum cluster size at some temperature

Below this temperature → $\tau_c \sim D^z$

$D_1 > D_2 > D_3$

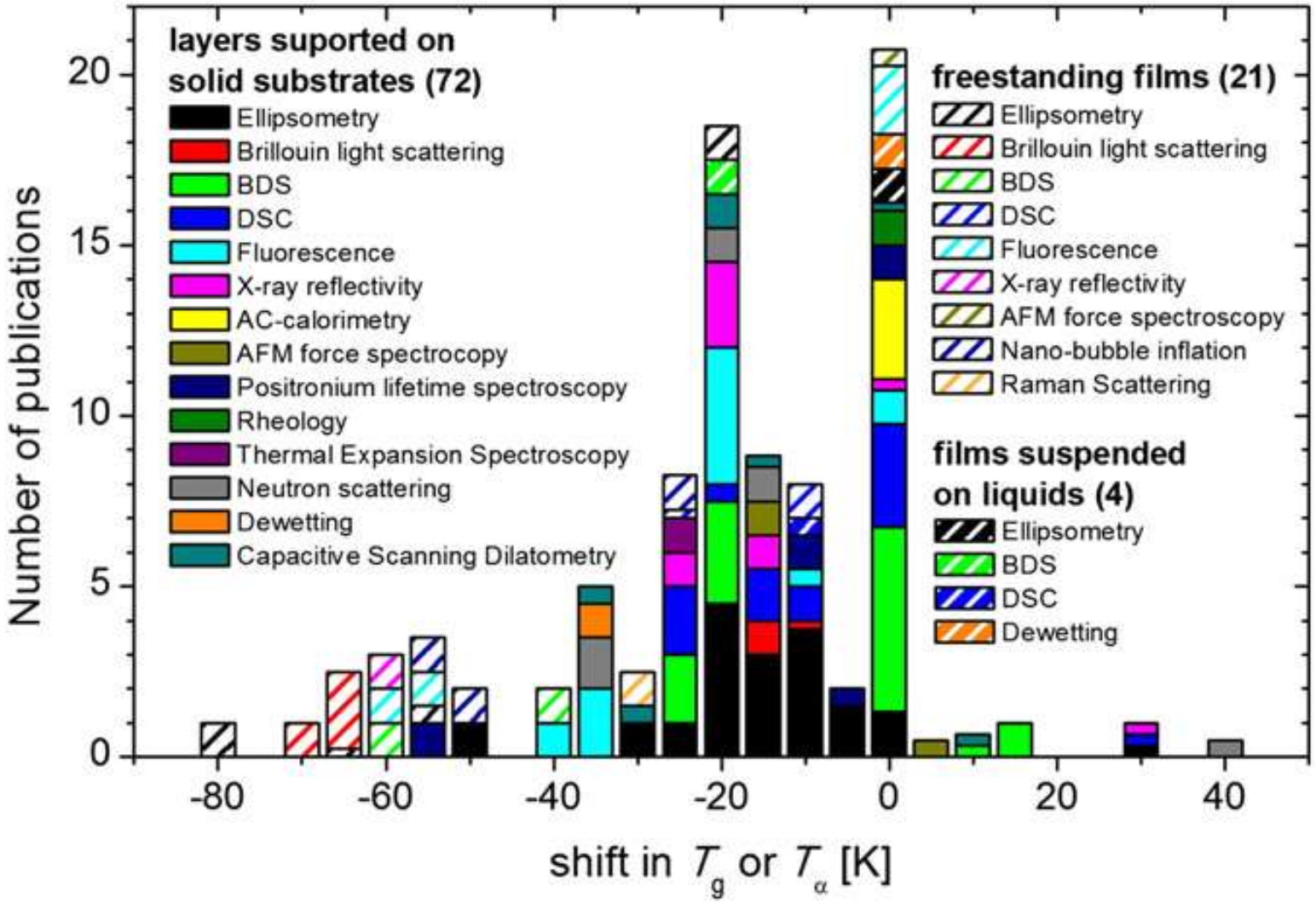
$\tau_1 > \tau_2 > \tau_3$

At low temperatures, cooperative motion of many particles, which create a cluster of size ξ

Size dependent relaxation → ***thinner films*** *exhibit* ***faster*** *dynamics*

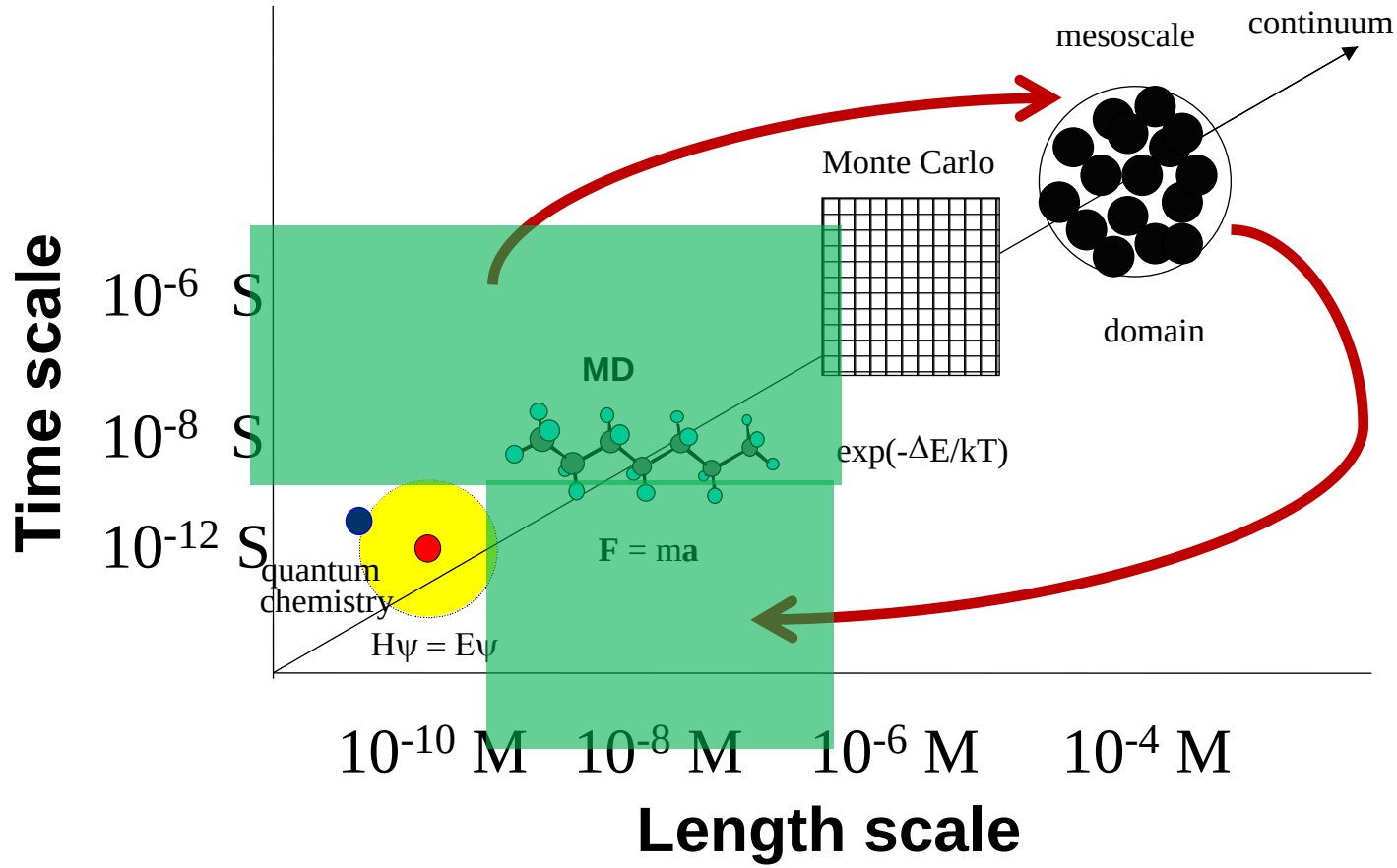
G. Adam and J.Gibbs, J.Chem. Phys, 43, 139 (1965)

F. Varnik, J.Baschnagel and K. Binder, Phys. Rev. E 65



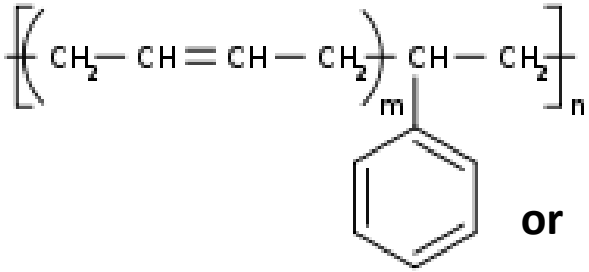
F. Kremer et al., J. Non-Cryst.Solids, 2015

What and Where

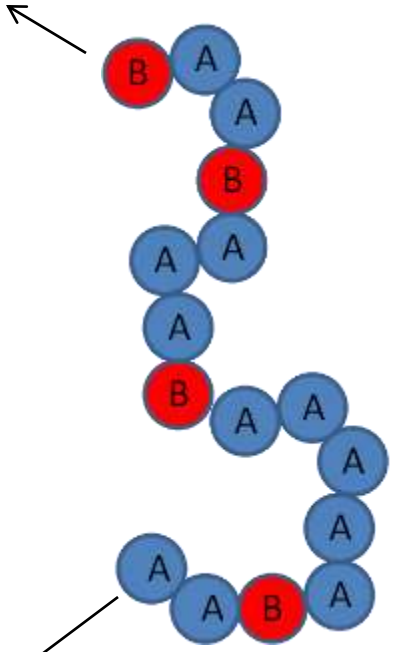


Coarse-grained SBR (NBR) rubber

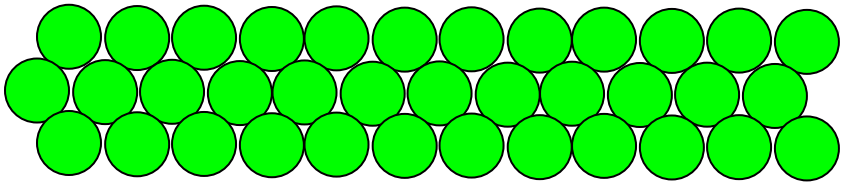
Styrene, Nitrile



or

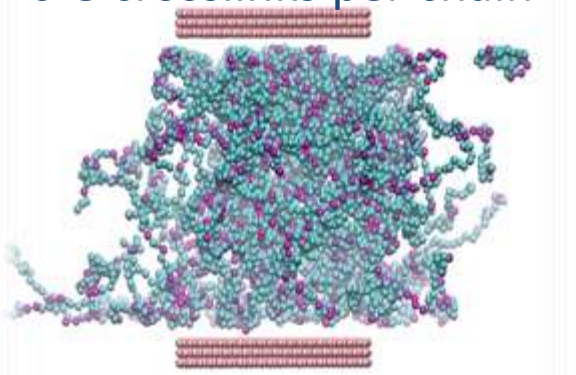


Butadiene



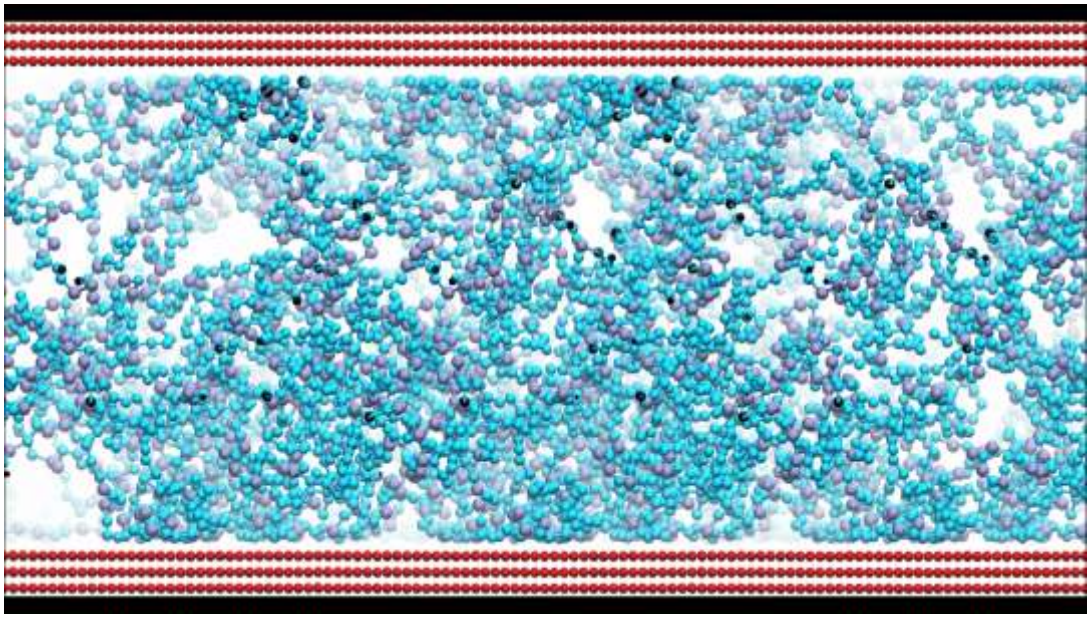
- 80% A beads, 20% B beads, 100 freely-joined LJ chains, 50 beads/chain

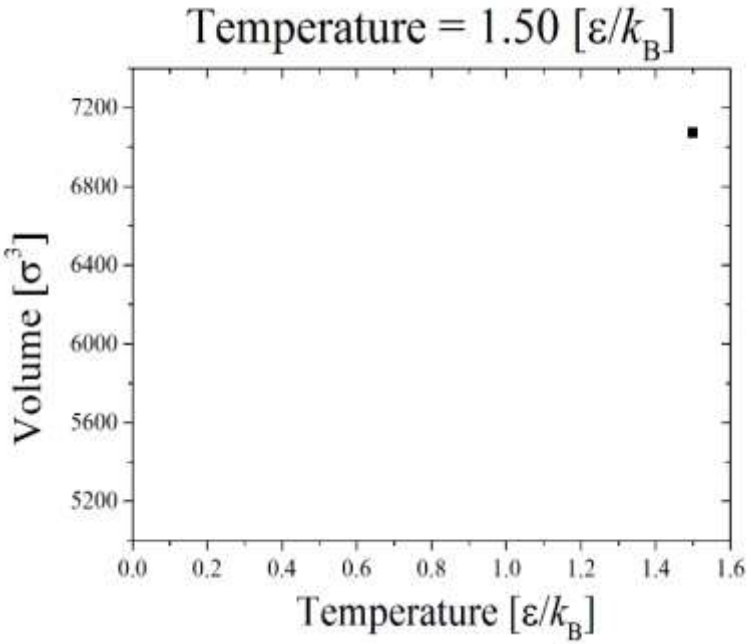
- 0-8 crosslinks per chain



C. Batistakis, AVL , M.A.J. Michels, *Macromolecules*, **2012**
C. Batistakis, M.A.J. Michels, AVL, *J. Chem. Phys.*, **2013**
C. Batistakis, M.A.J. Michels, AVL, *Macromolecules*, **2014**
T. Davris, AVL, *Polym. Composites*, **2015**
T. Davris, AVL, *J. Chem. Phys.*, **2015**
T. Davris, AVL, Macromolecules, **2016**

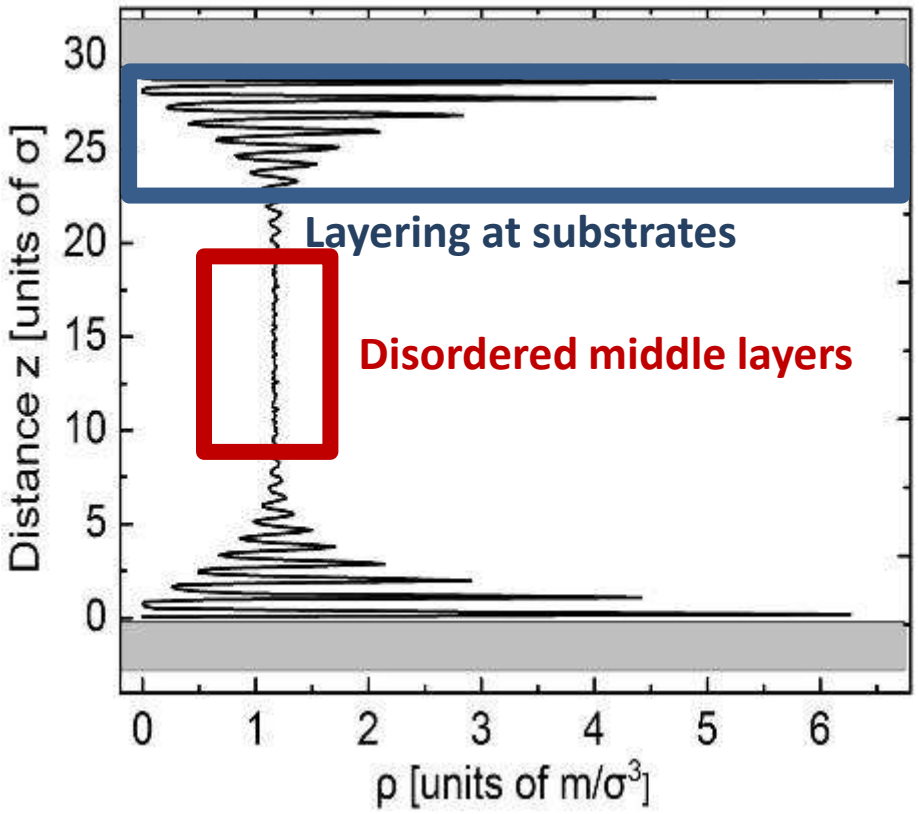
Glass-transition temperature

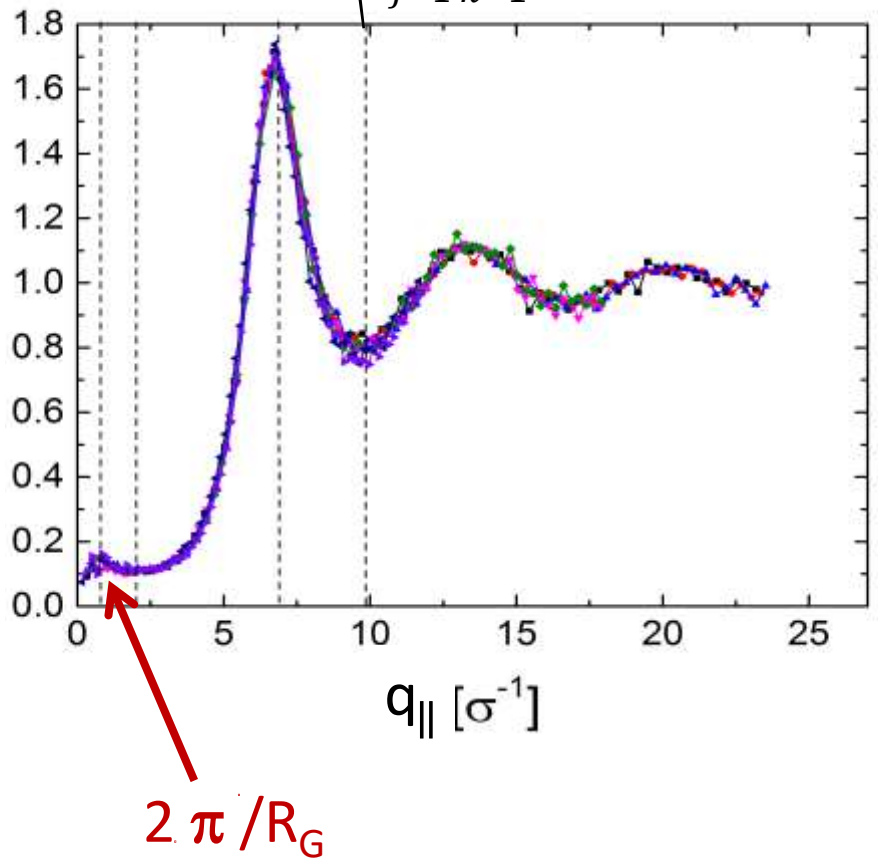




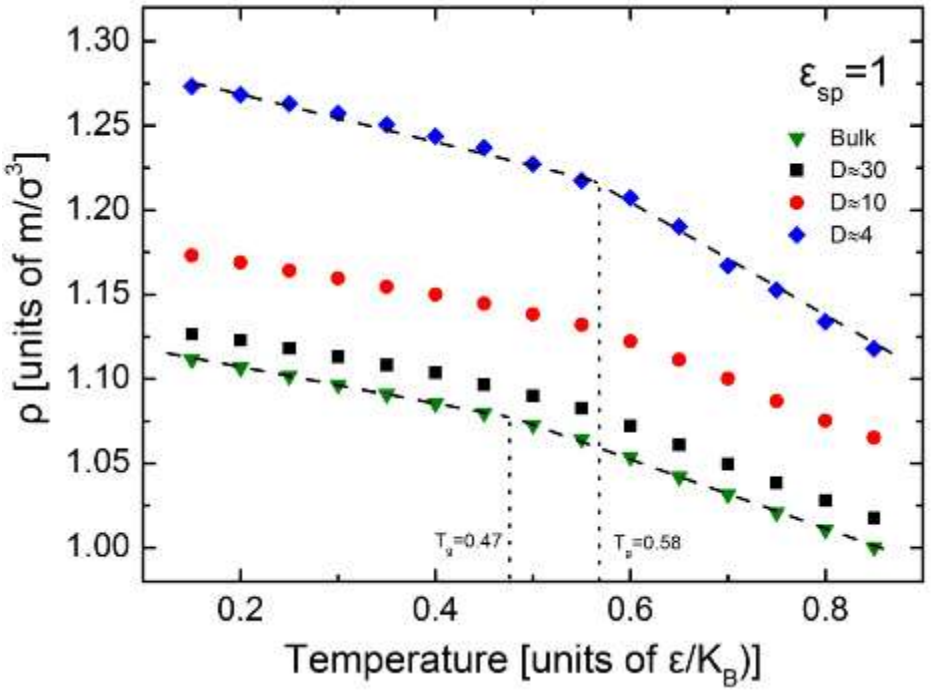
Structure

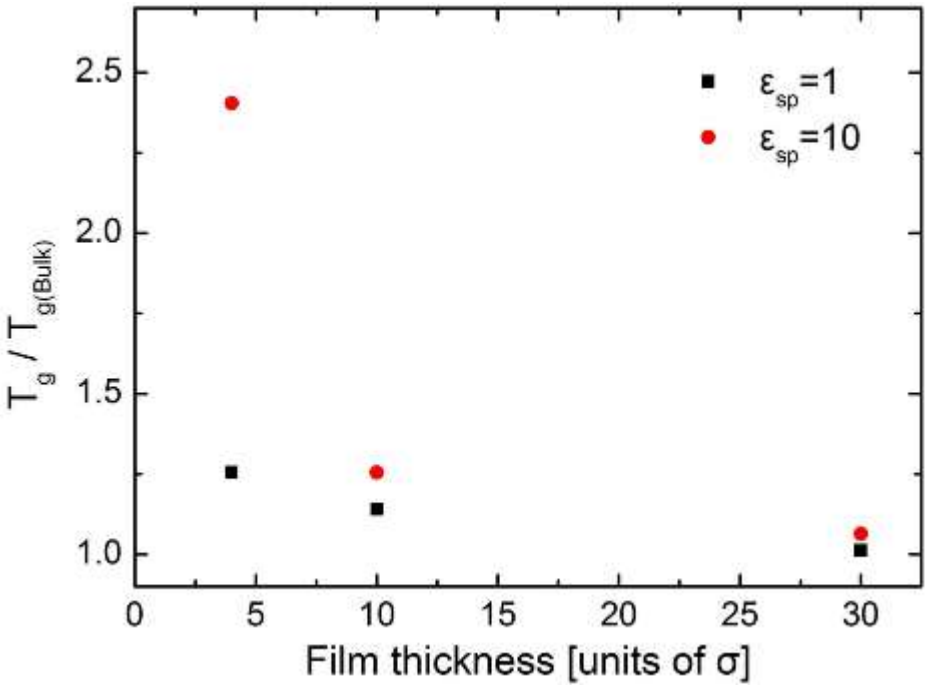
$$S(q) = \frac{1}{N}\left\langle \sum_{j=1}^{N}\sum_{k=1}^{N} \exp\{i\boldsymbol{q}\cdot(\boldsymbol{R}_j - \boldsymbol{R}_k)\} \right\rangle$$





Glass-transition temperature

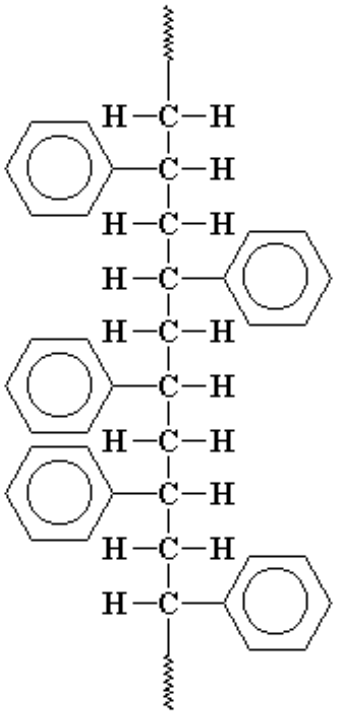


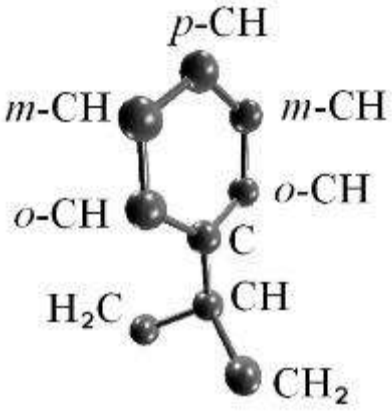


Film-averaged density and T_g :

- increase under confinement;
- increase with increasing the polymer-substrate interaction strength.

atactic polystyrene

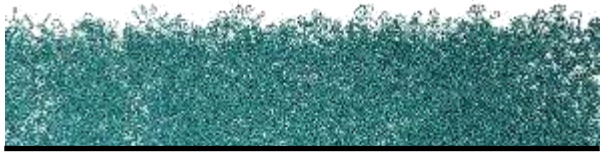




4 chains
~ 15Å

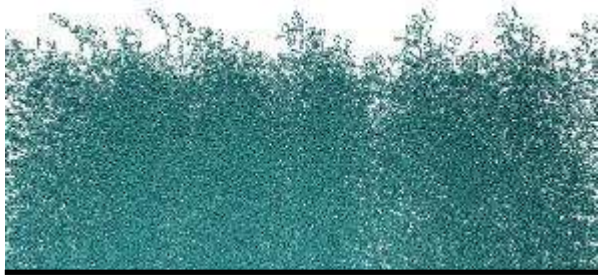
8 chains
~ 20Å

16 chains
~ 50Å



- Monomers per chain: N_{mon}=80
- Molecular weight: M ~ 9000
- Number of particles: 2564-20512

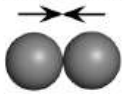
32 chains
~ 90Å



Force Field

- **Nonbonded:**

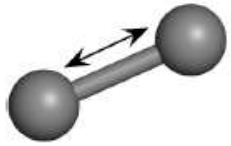
van der Waals interactions



$$V_{nonbonded}^{LJ} = \sum_{i,j} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

- **Stretching:**

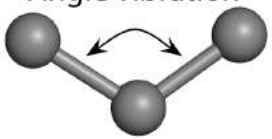
Bond vibration



$$V_{bonded} = \sum_{i,j} k_{B,ij}\left(r_{ij} - l_{ij}\right)^2$$

- **Bending:**

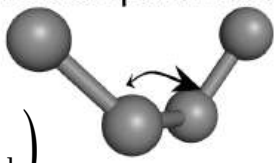
Angle vibration



$$V_{bending} = \sum_{i,j,k} k_{\theta,ijk}\left(\theta_{ijk} - \theta_{0,ij}\right)^2$$

- **Torsion:**

Torsion potentials



$$V_{pr,im} = \sum_{i,j,k,l} k_{n\phi,ijkl}\cos\left(n\phi_{\text{ijkl}}\right)$$

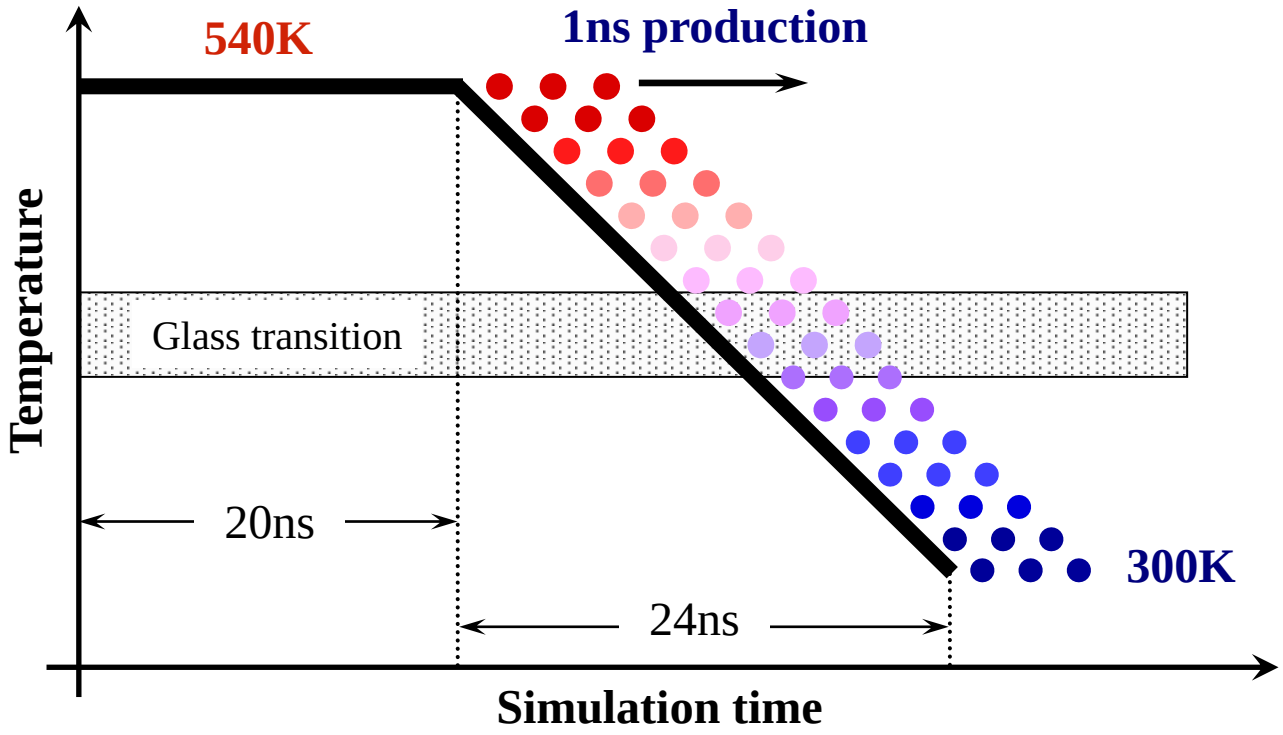
- **Substrate potential:**

$$V_{sub}(z) = \frac{1}{2}\varepsilon\left[\left(\frac{R_{\min}}{z}\right)^{9} - 3\left(\frac{R_{\min}}{z}\right)^{3}\right]$$

Strength of attraction:

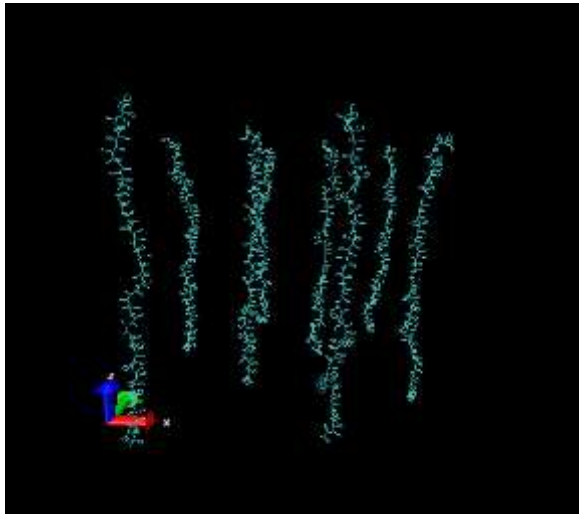
ε = 0.1 kcal/mol – 3.0 kcal/mol

Equilibration and cooling

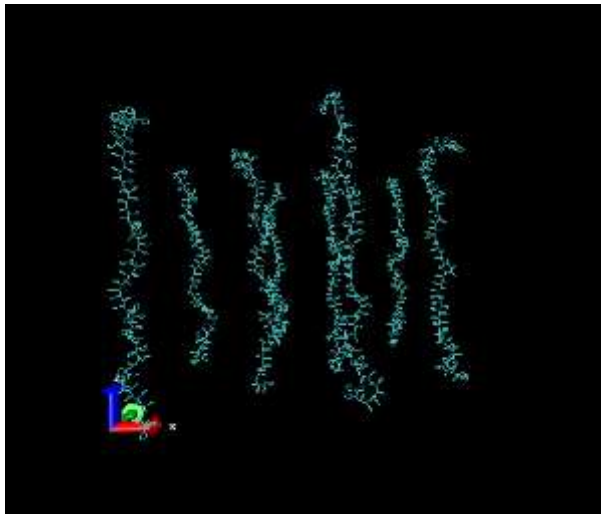


- Equilibration (20ns) at 540K;
- Cooling with constant cooling velocity (0.01K/ps);
- 1ns MD production runs for each (every 20K) intermediate temperature;

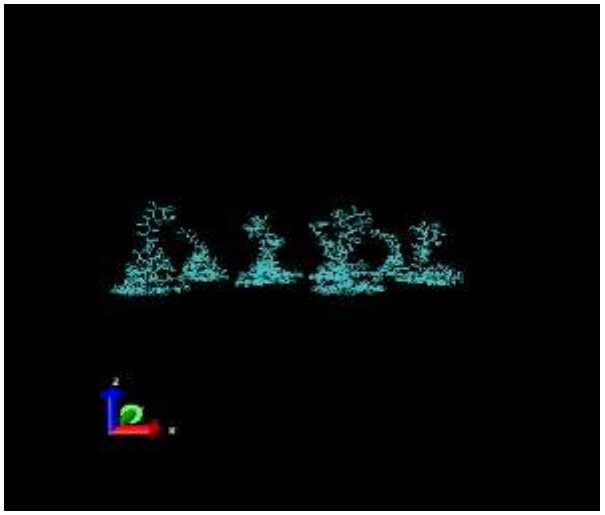
Equilibration of aPS film, 540K



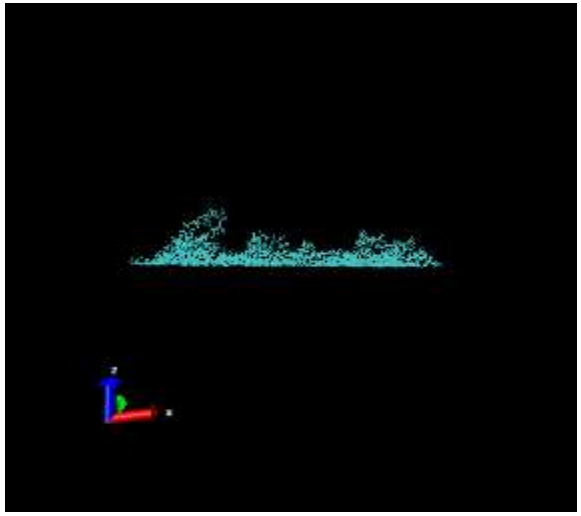
10 ps



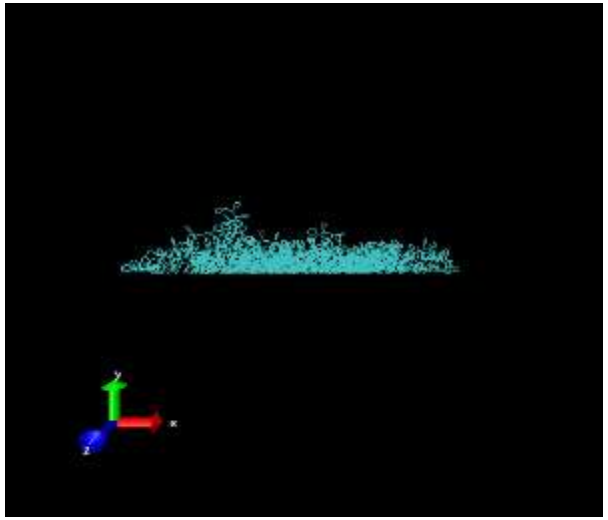
100 ps



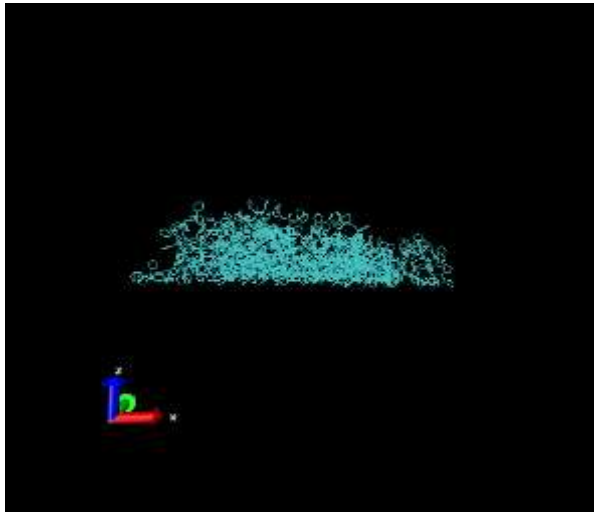
5000 ps



10 ns



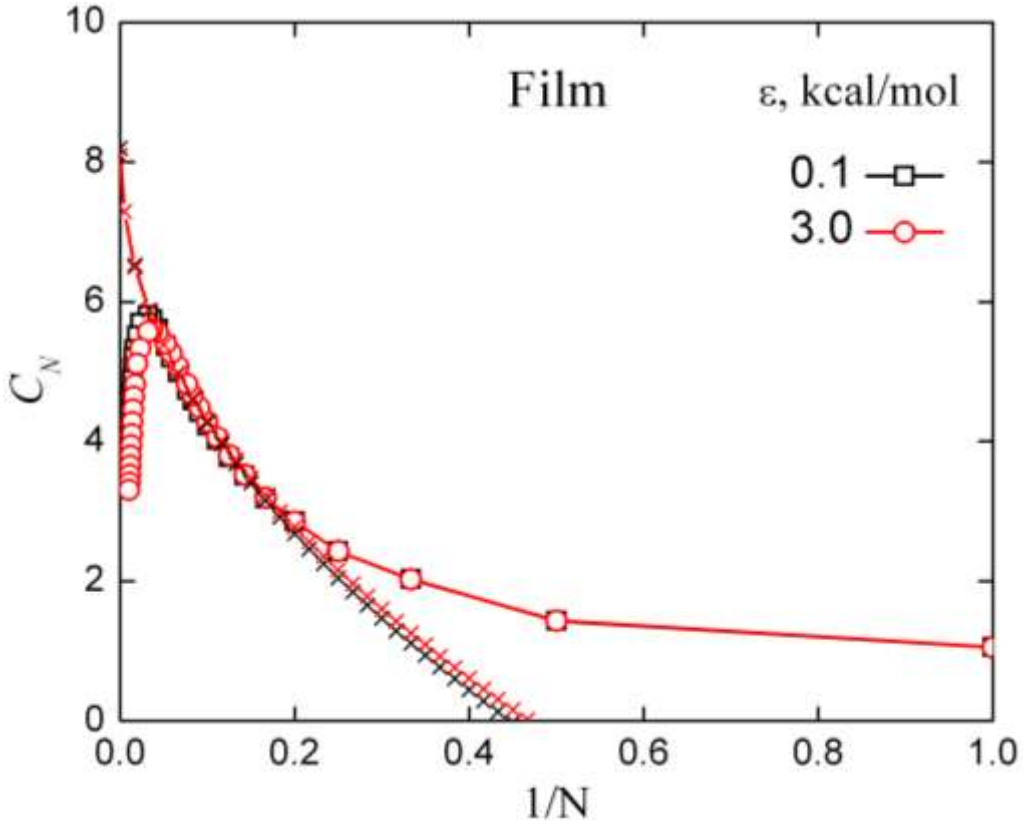
15 ns



20 ns

Characteristic ratio

$$C_N = \left\langle R^2 \right\rangle / N l_{C-C}^2$$



$$C_N = C_\infty \left(1 - \alpha N_K^{-1/2}\right)$$

$C_\infty = 8.2 \pm 0.1$

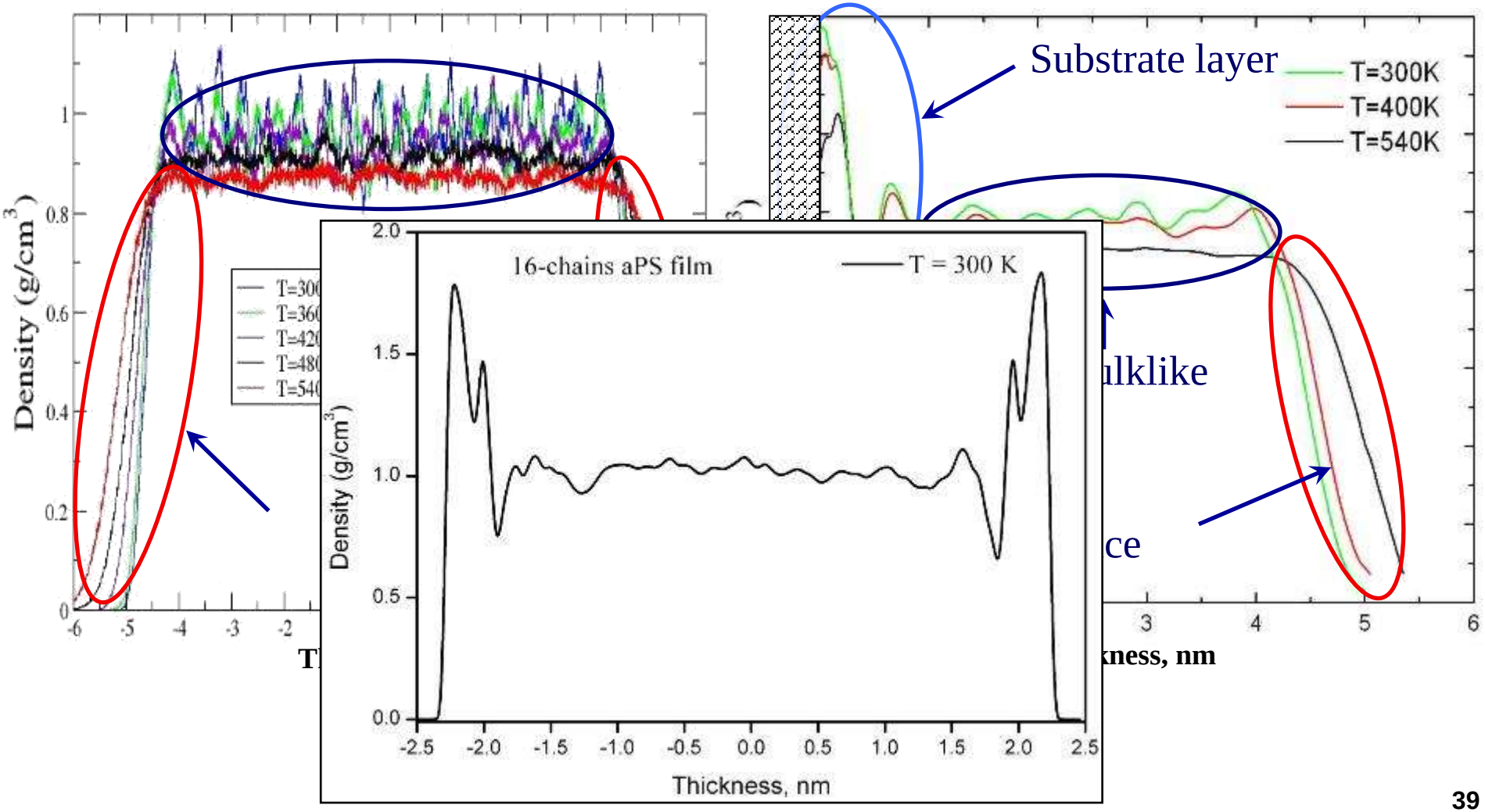
$\alpha = 0.43$ (simulations)

α=0.48 (Wittmer, Baschnagel et al., PRE, 2007)

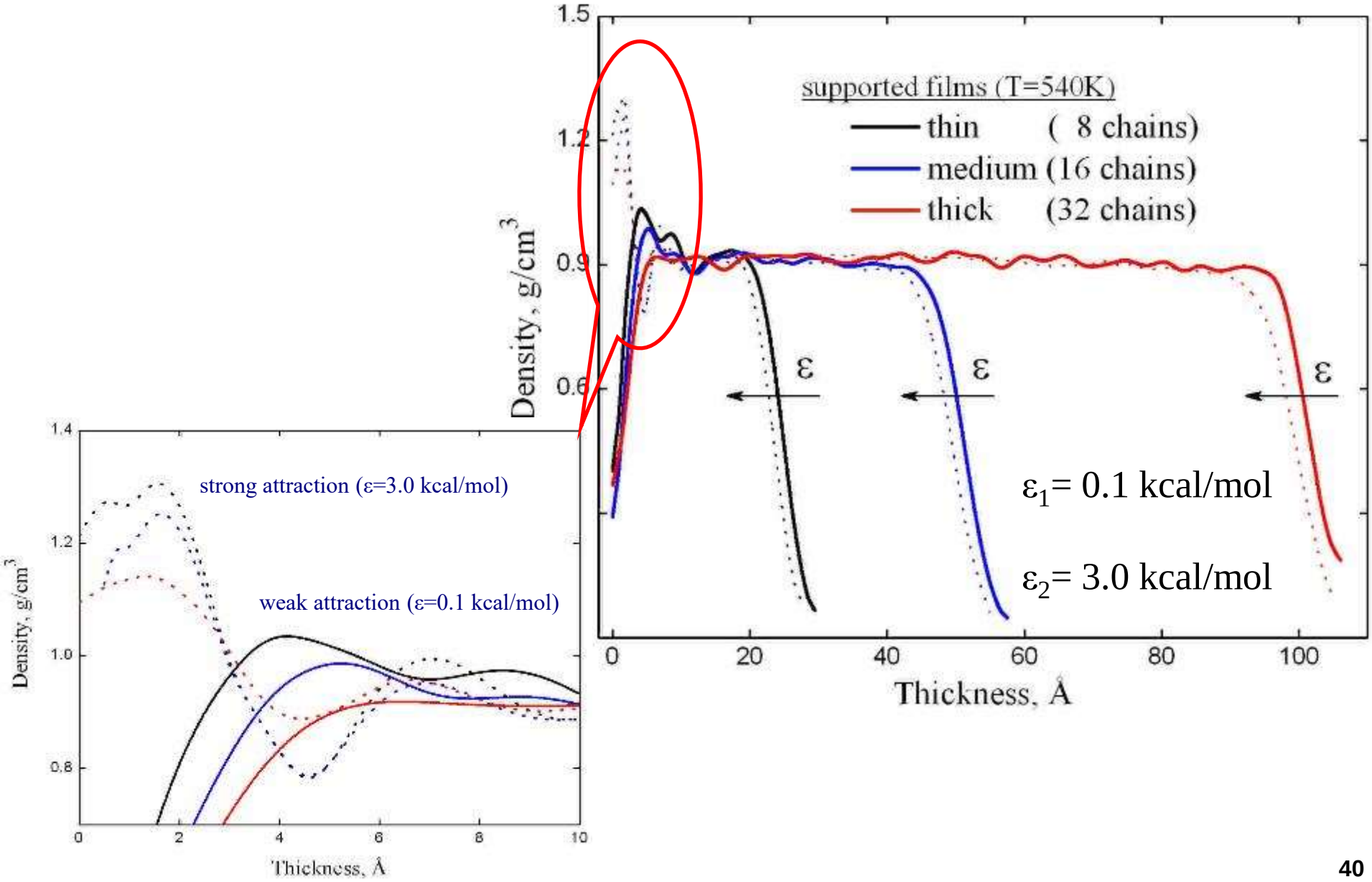
Density profile

Free-standing 32-chain film

Supported (ε=1.0 kcal/mol) 16-chain film

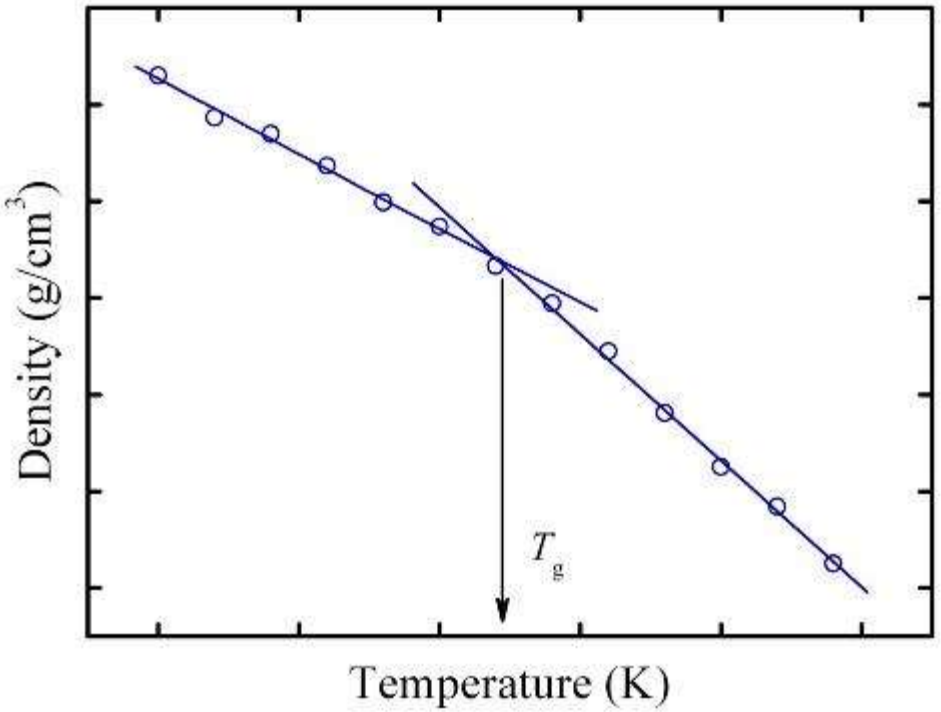


Density profile

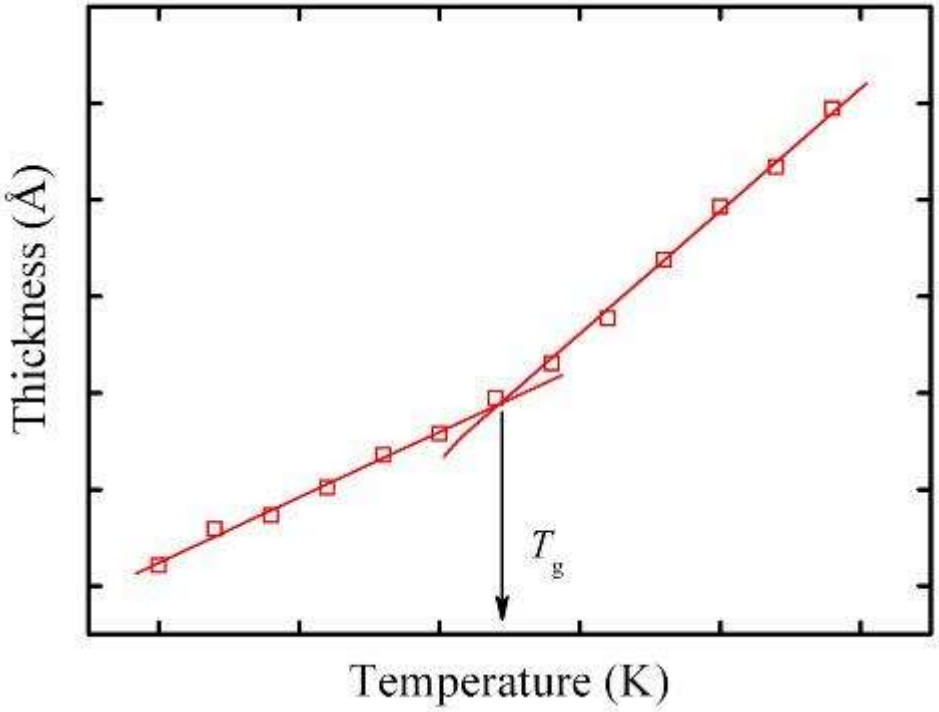


Glass transition temperature

Density measurement

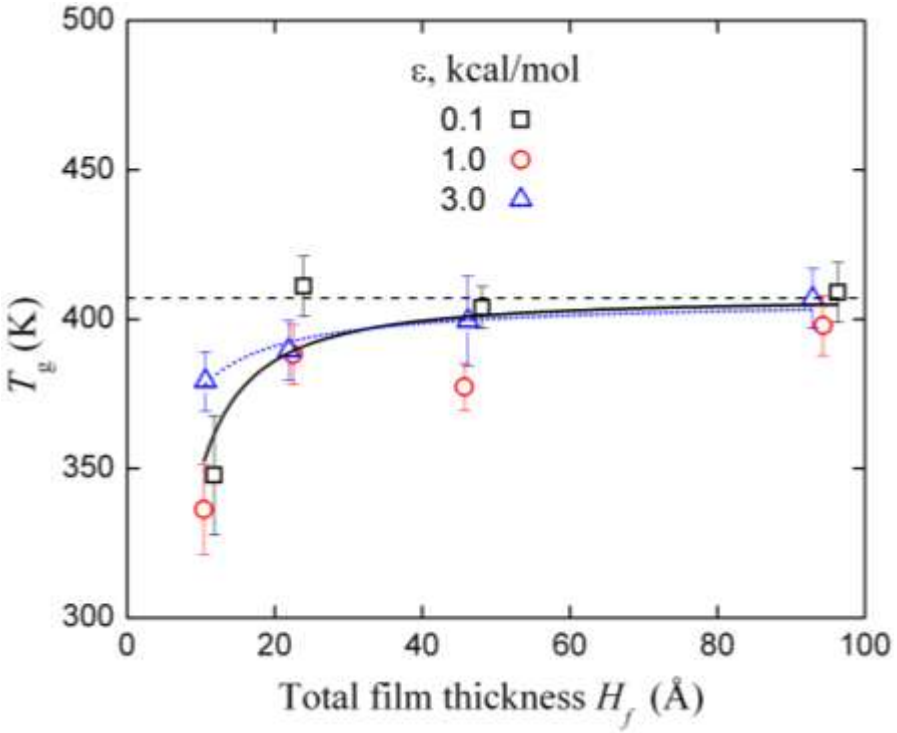


Thickness measurement



Glass transition temperature

Density measurement

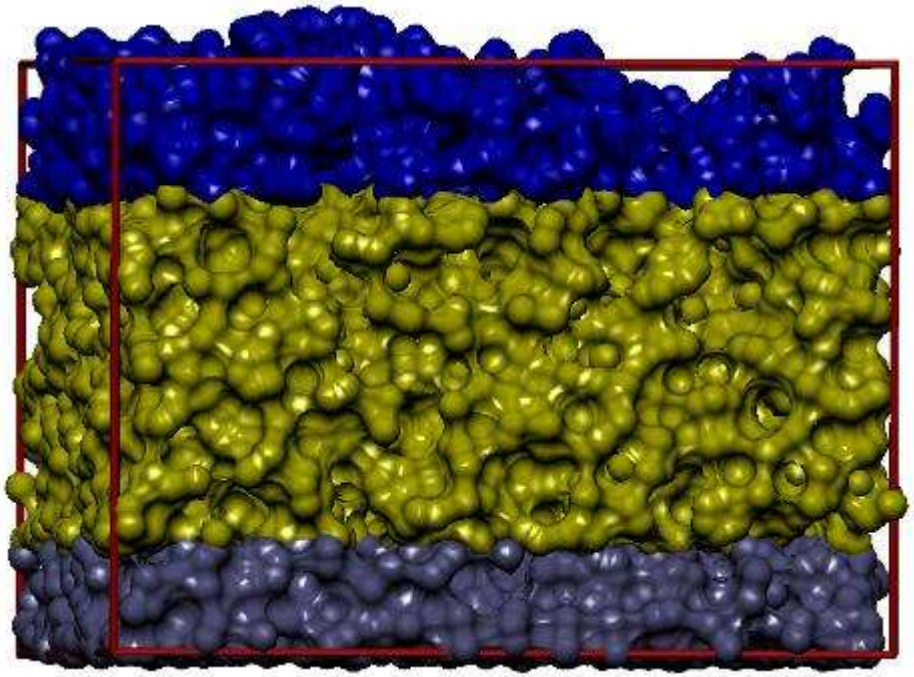


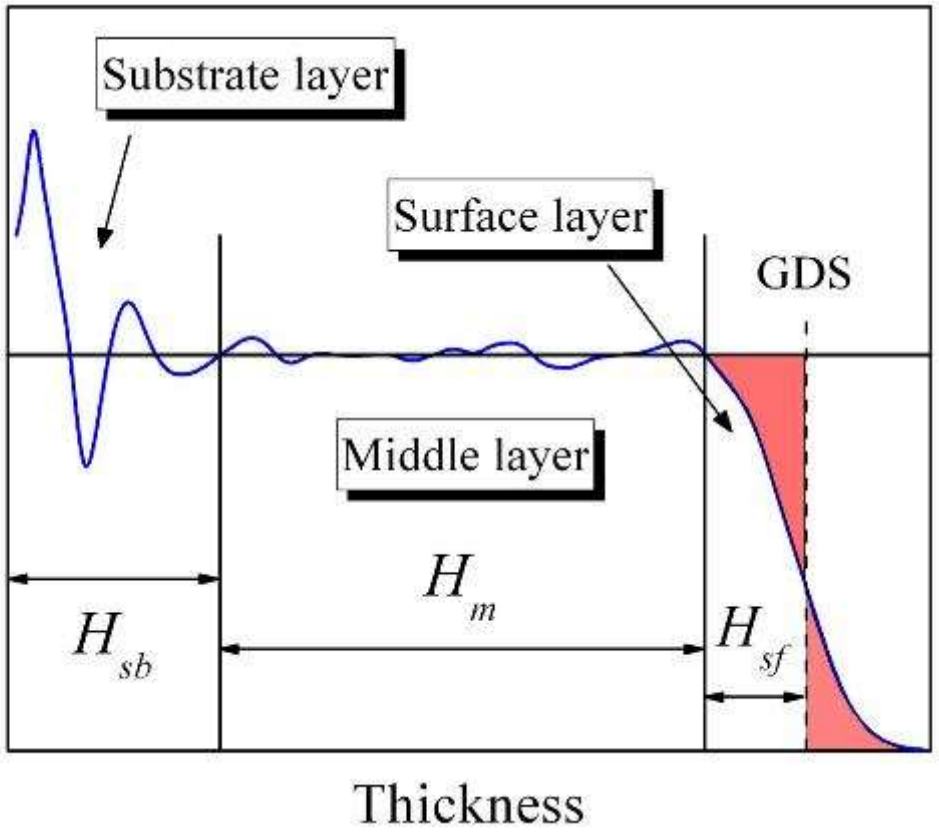
Thickness dependences of the glass transition temperature for the aPS films with weak and strong attraction to the substrate.

Solid lines represent the best fit using the equation $T_g^{film}(H_f) = T_g^{bulk}\left(1-\left(\frac{A}{H_f}\right)^{\delta}\right)$

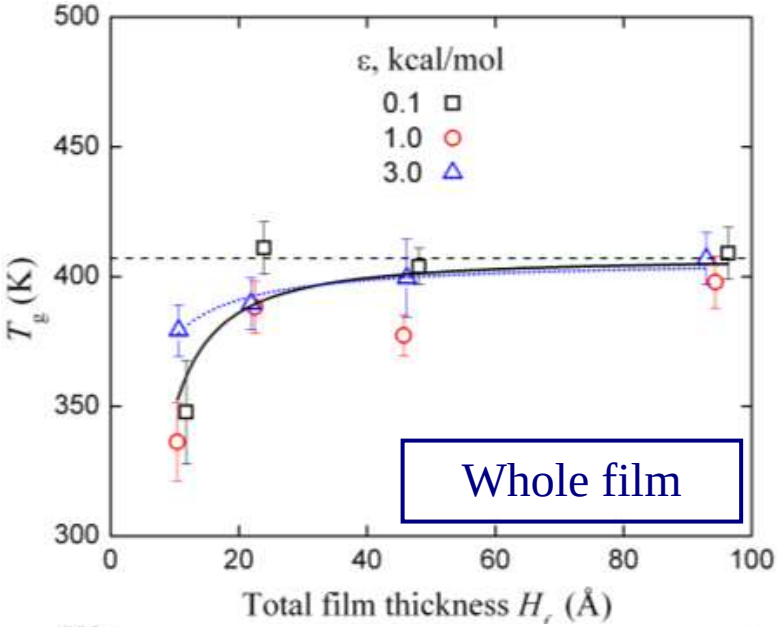
Dotted line indicates the value of T_g for the bulklike layer.

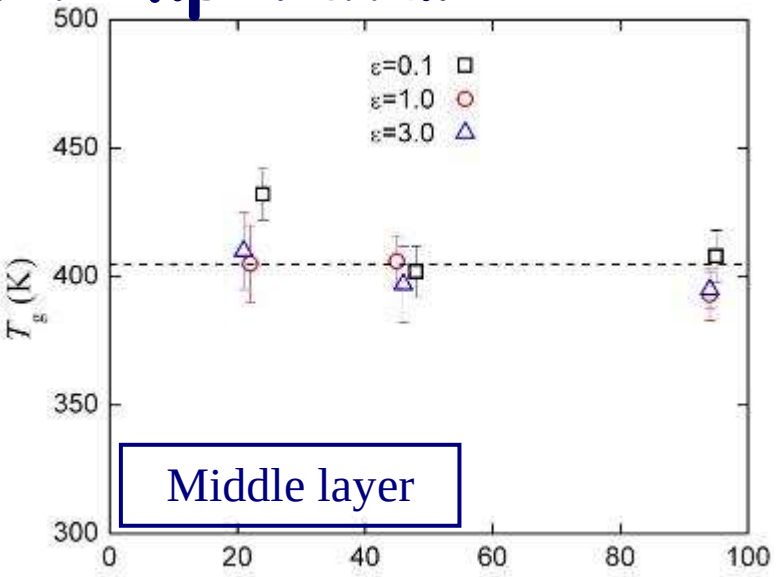
Glass transition temperature

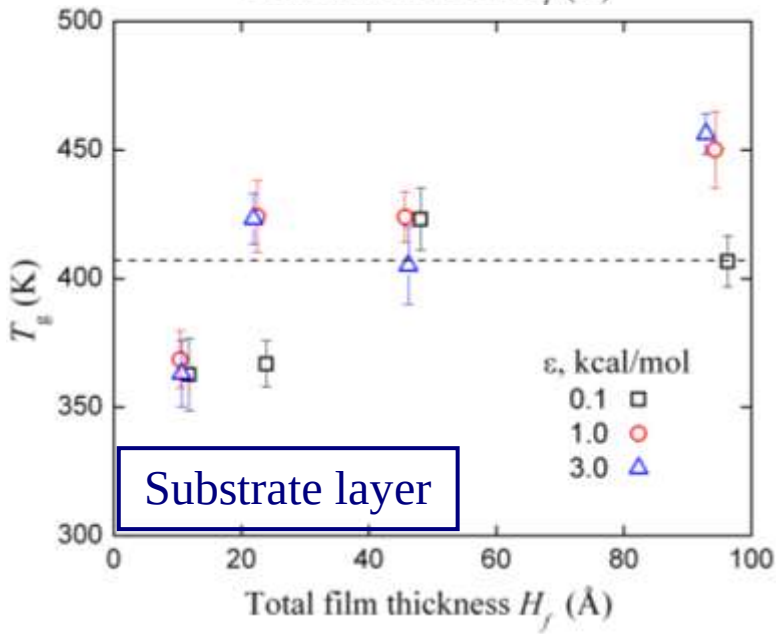


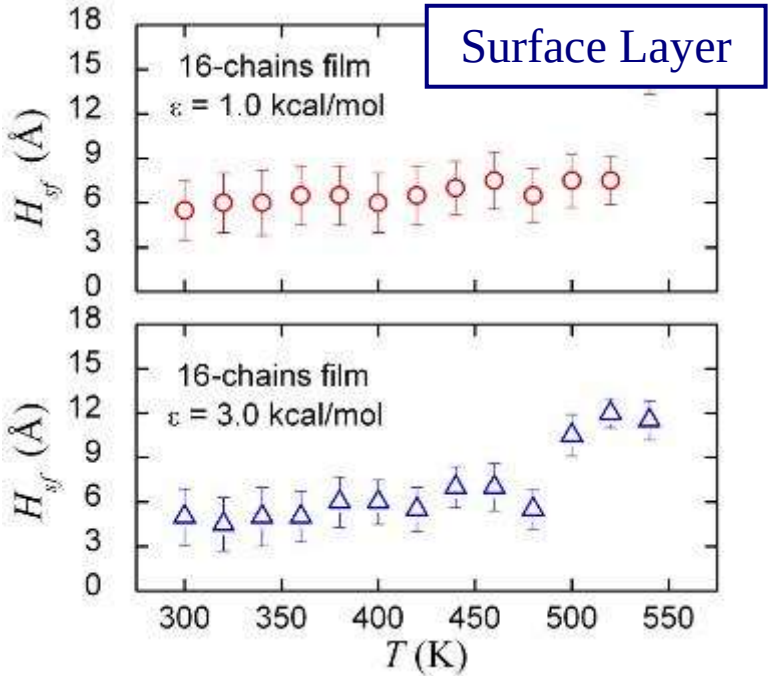


Glass transition temperature





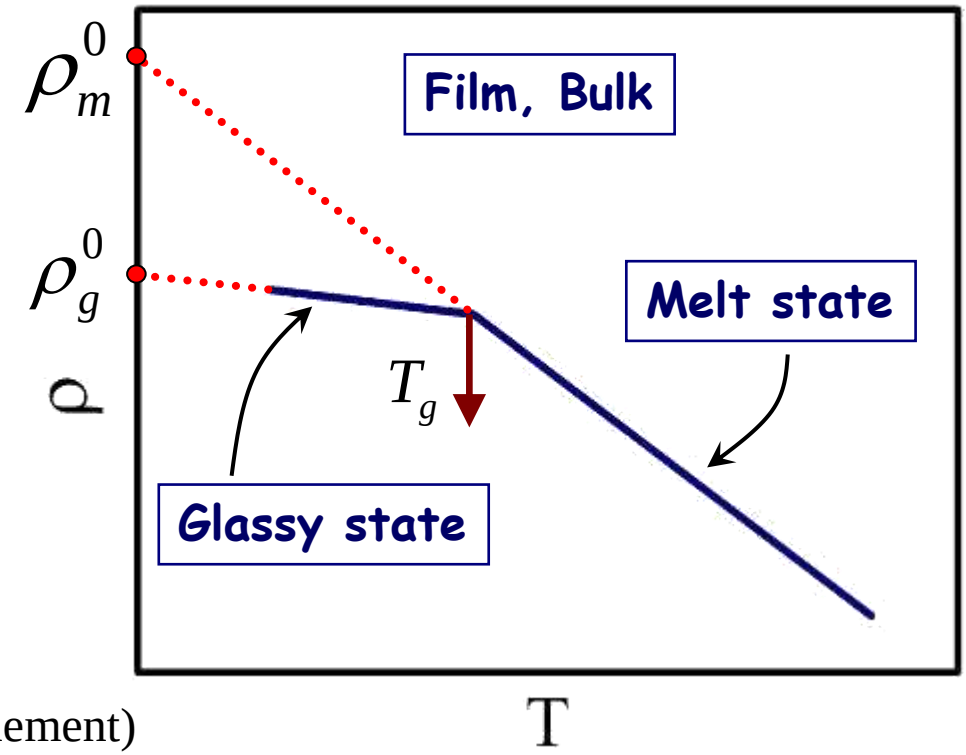




Glass transition temperature

$$\rho_{m,g}(T) = \rho^0_{m,g} + \frac{d\rho_{m,g}}{dT} T$$

$$T_g = -\frac{\rho^0_g - \rho^0_m}{\left(\frac{d\rho}{dT}\right)_g - \left(\frac{d\rho}{dT}\right)_m}$$



Valid for a bulk and a film

$$\delta\rho \equiv \rho(\text{film}) - \rho(\text{bulk})$$

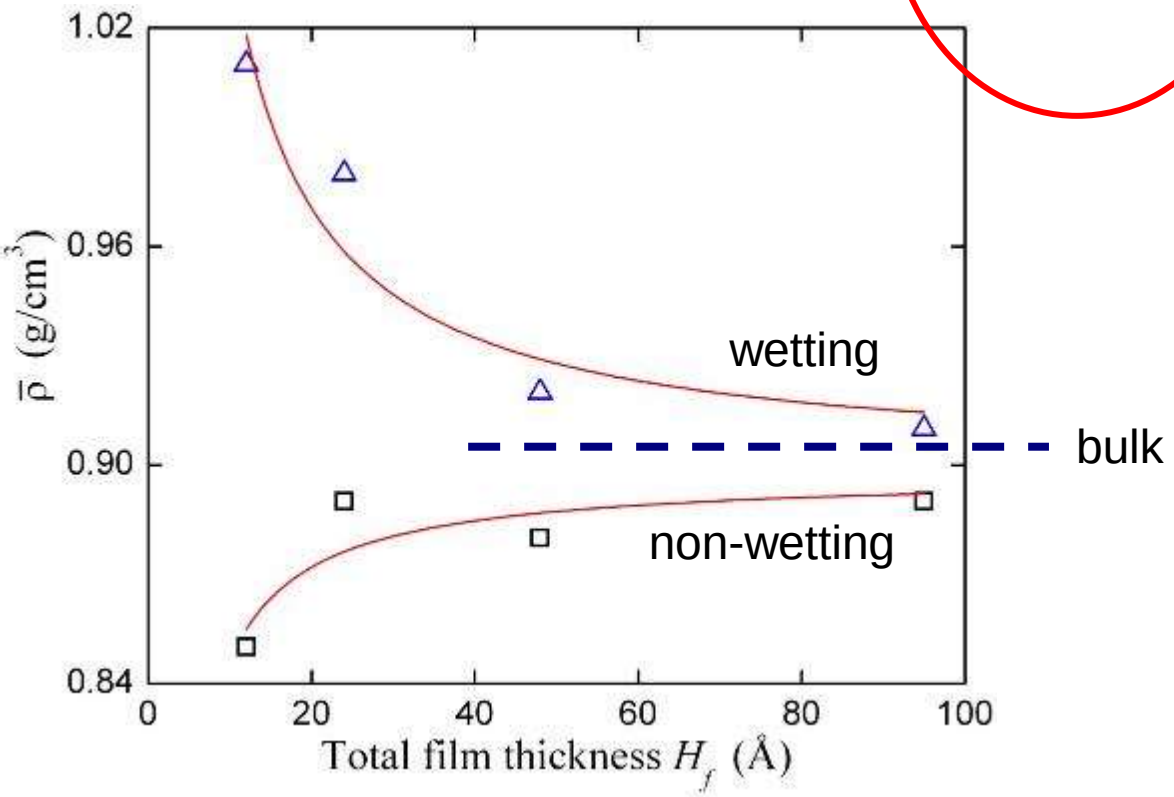
(change in average density due to the confinement)

$$\frac{T_g(\text{film})}{T_g(\text{bulk})} = \frac{1 + \frac{\delta\rho^0_g - \delta\rho^0_m}{\rho^0_g - \rho^0_m}}{1 + \frac{\frac{d}{dT}\delta\rho_g - \frac{d}{dT}\delta\rho_m}{\frac{d\rho_g}{dT} - \frac{d\rho_m}{dT}}}$$

Glass transition temperature

$$\rho(\text{film}) = \frac{1}{H_f}\left(h_{sb}\rho_{sb} + h_{md}\rho_{md} + h_{sf}\rho_{sf}\right)$$

$$\rho(\text{film}) = \rho(\text{bulk}) + \delta\rho = \rho(\text{bulk}) + \frac{h_{sb}\delta\rho_{sb} + h_{sf}\delta\rho_{sf}}{H_f} \equiv \rho(\text{bulk}) + \frac{\delta m}{H_f}$$



$$\frac{\bar{T}_g}{T_g} = \frac{1 + \dfrac{\delta\rho_g^0 - \delta\rho_m^0}{\rho_g^0 - \rho_m^0}}{1 + \dfrac{\dfrac{d}{dT}\delta\rho_g - \dfrac{d}{dT}\delta\rho_m}{\dfrac{d\rho_g}{dT} - \dfrac{d\rho_m}{dT}}}$$

In general: $\delta m = \delta m\left(H_f, T\right)$

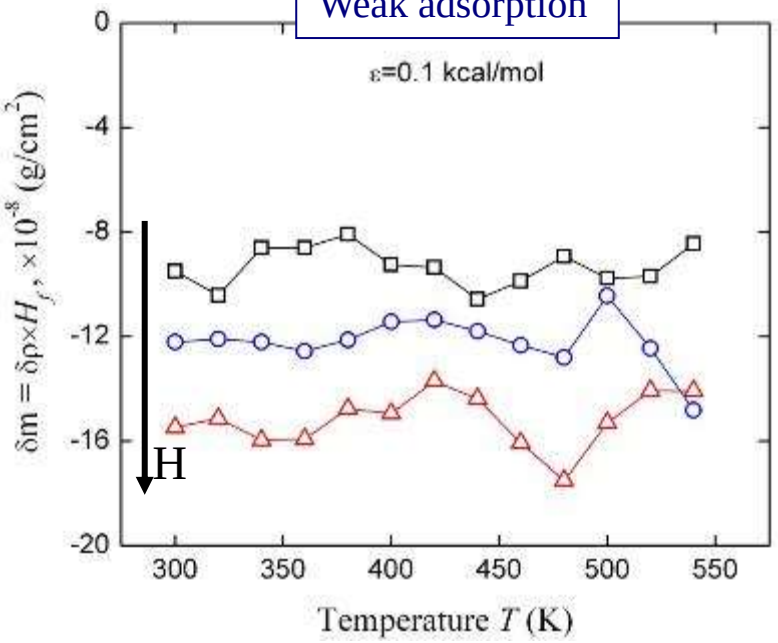
If δm is constant :

$$\boxed{\frac{\bar{T}_g}{T_g} = \frac{1 + C_1 \dfrac{\delta m}{H\left(\bar{T}_g\right)}}{1 + C_2 \dfrac{\delta m}{H\left(\bar{T}_g\right)}}}$$

$$C_1 = \frac{\left[\left(1/H\right)_g^0 - \left(1/H\right)_m^0\right] H\left(\bar{T}_g\right)}{\rho_g^0 - \rho_m^0} \neq f\left(H\right)$$

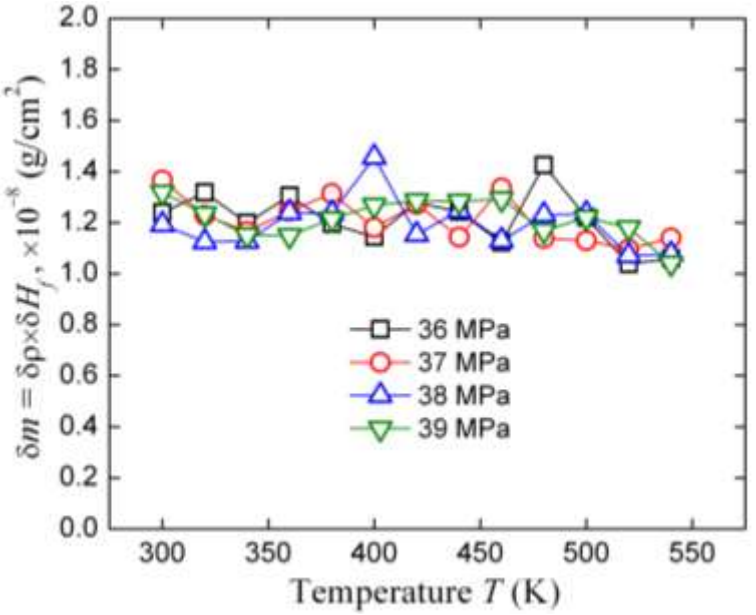
$$C_2 = \frac{1}{\rho\left(T_g\right)}\left[\frac{\bar{\alpha}_g\left(\bar{T}_g\right) - \bar{\alpha}_m\left(\bar{T}_g\right)}{\alpha_g\left(T_g\right) - \alpha_m\left(T_g\right)}\right] \neq f\left(H\right)$$

Weak adsorption



$$\delta m = \delta m(H) \quad \delta m \neq \delta m(T)$$

Strong adsorption

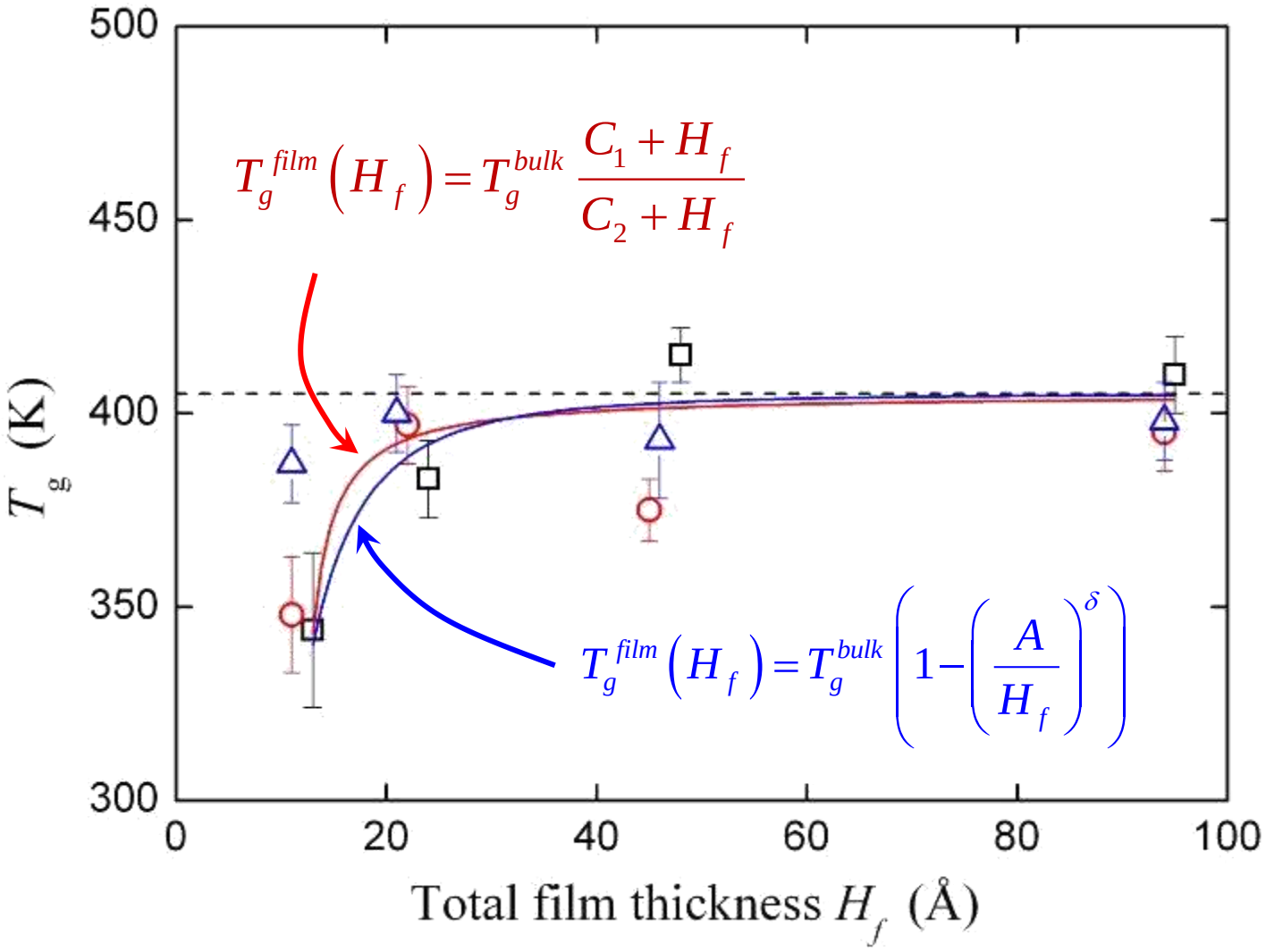


$$\delta m \neq \delta m(T)$$

$$\frac{\bar{T}_g}{T_g} = \frac{1 + C_1 \, \delta m / H(\bar{T}_g)}{1 + C_2 \, \delta m / H(\bar{T}_g)}$$

$C_1 = C_2 = -1.1 \pm 0.2$ cm^3/g

Glass transition temperature



D. Hudzinskyy, AVL et al., *Macromolecules*, 2011, **44**, 2299

Conclusions II

- The glass transition temperature:
  - remains constant for supported PS films down to ~2nm
  - decreases by ~ 50K for supported films thinner than ~2nm

- Substrate: T_g increases
- Middle: remains the same for films down to ~2nm;
- Surface: T_g decreases

- The thickness dependence of averaged film density can be used to explain the thickness dependence of T_g in films.

too complicated....

what if there are no substrates????

Free-standing films

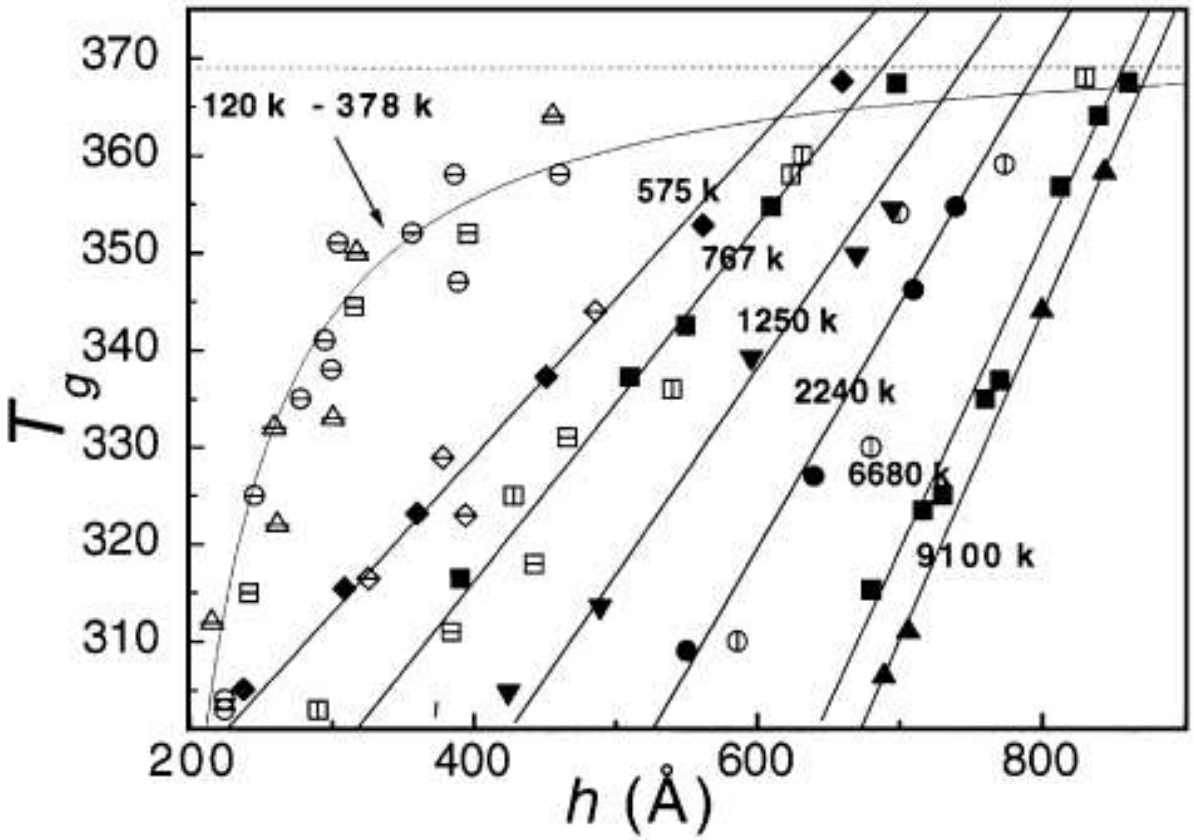


Fig. 4. Measured T_g values for free-standing polymer films. The solid symbols are obtained with ellipsometry and taken from reference [18]. The hollow symbols are obtained using BLS, with a vertical bar indicating the data from reference [24] and a horizontal bar indicating data from reference [36].

Low-M_w PS: the same effect, but larger reduction

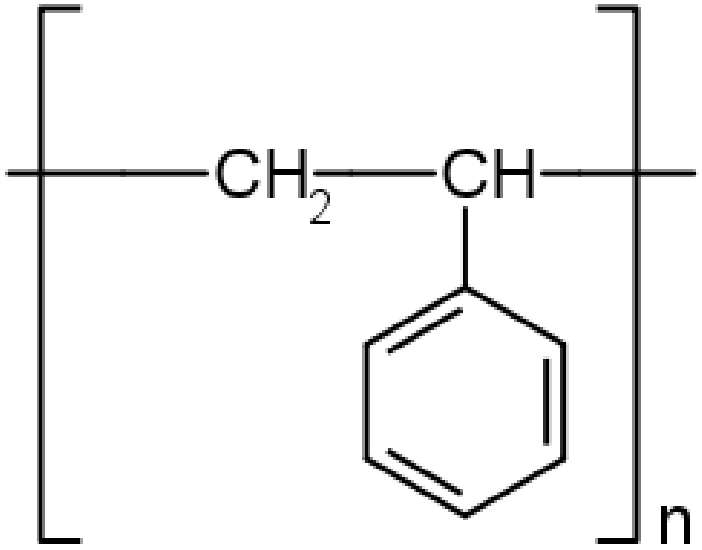
2 Hypotheses

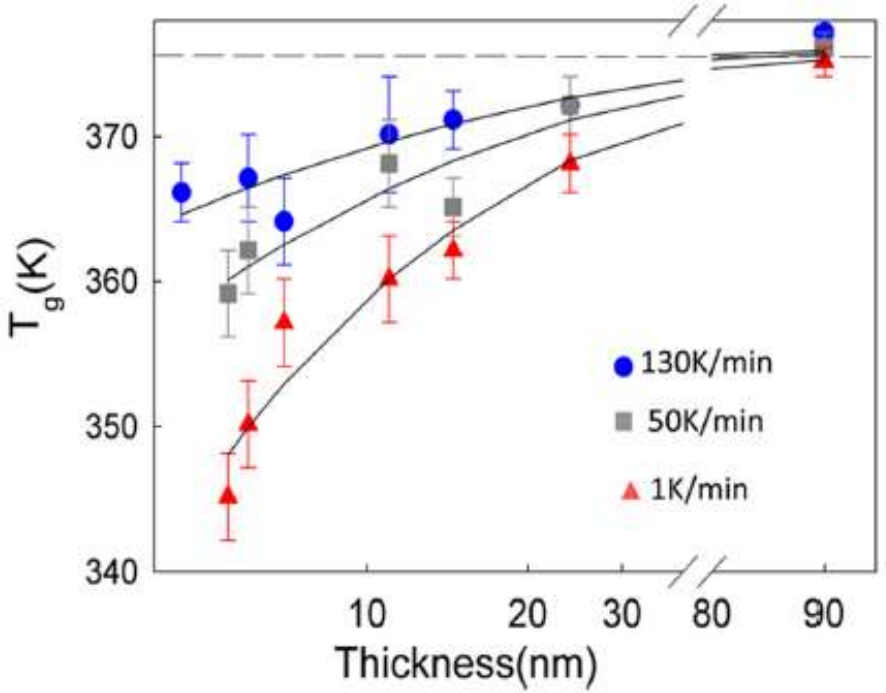
- **Chain ends**: concentrated in the interfacial layer (de Gennes), the T_g reduction for ring polymers smaller.

- **Phenyls**: concentrated and ordered at the surface –
  deficit of phenyls in the interfacial layer –
  weaker π- π interactions there –
  lower T_g there –
  lower T_g in thinner films;

linear vs. ring

(atactic) polystyrene

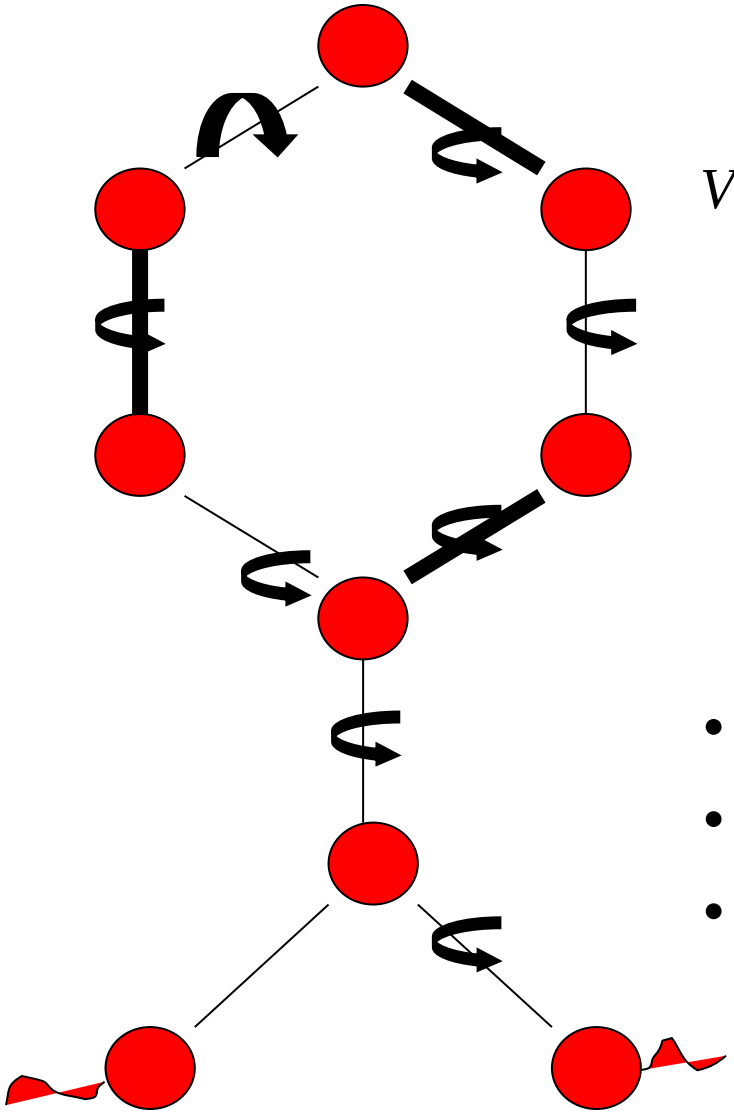




linear vs. ring

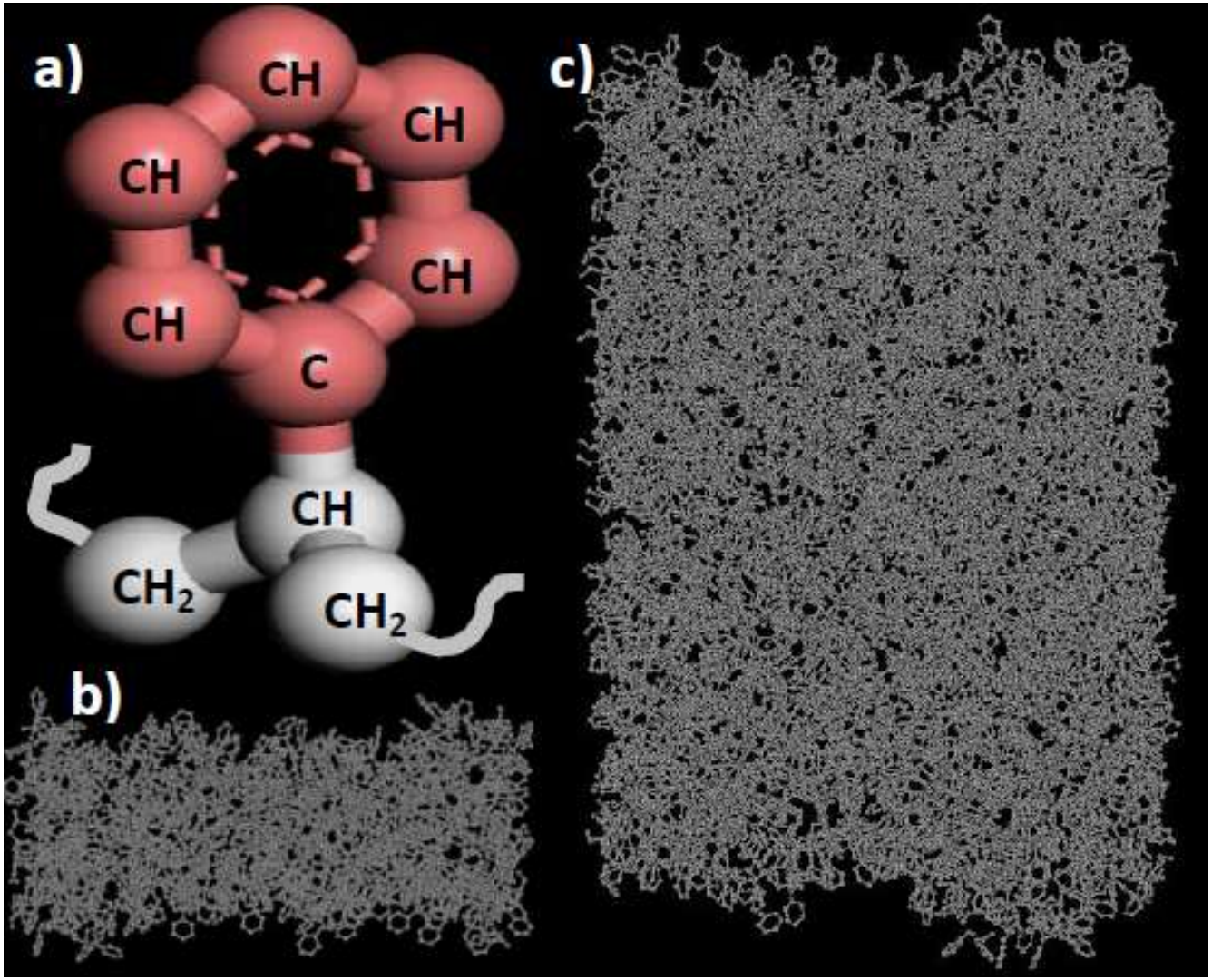
effects of cooling rate

UA model



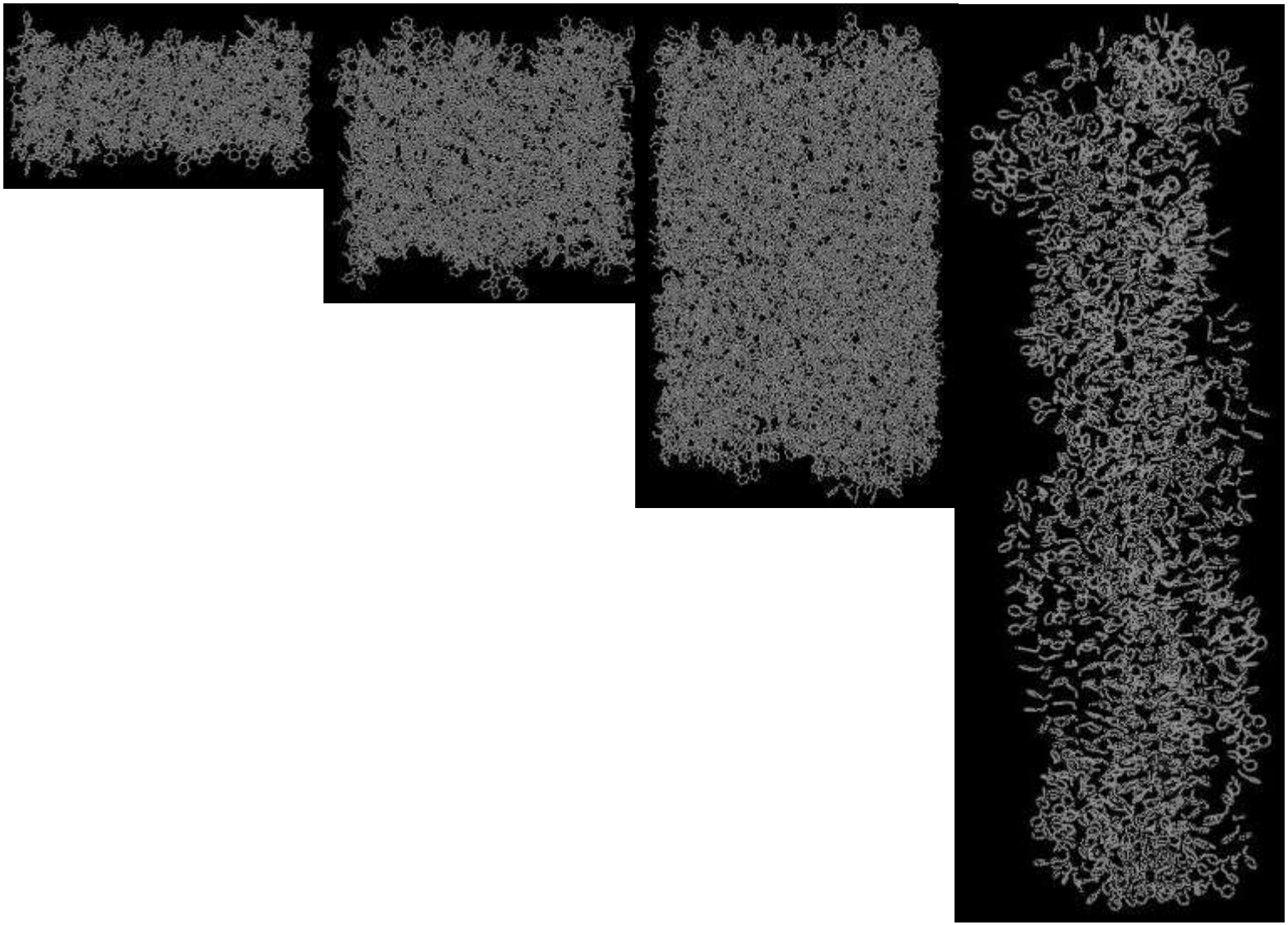
$$V_{\mathrm{PS}} = \sum_{i,j} \hat{\varepsilon}_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} \right) + \sum_{i,j} k_{B,ij} (r_{ij} - l_{ij})^2$$
$$+ \sum_{i,j,k} k_{\theta,ijk} (\theta_{ijk} - \theta_{0,ij})^2 + \sum_{i,j,k,l} k_{2\varphi,ijkl} \cos(2\varphi_{ijkl})$$
$$+ \sum_{i,j,k,l} k_{3\hat{\varphi},ijkl} \cos(3\hat{\varphi}_{ijkl})$$

- Degree of polymerization 80, M_w ~ 8400
- Temperature range 240K - 600K
- Pressure 1 bar

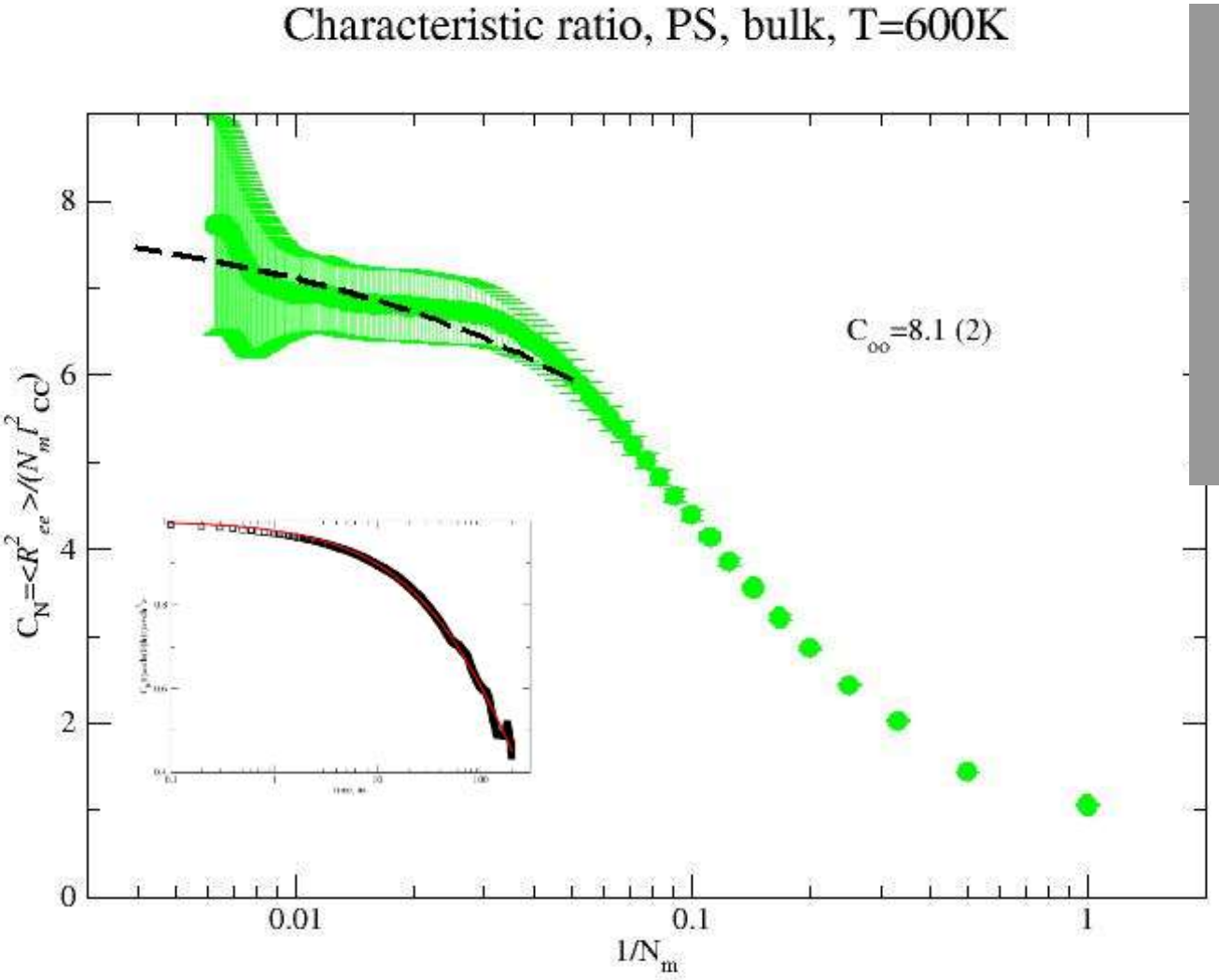

a)
CH
CH
CH
CH
CH
C
CH
CH_2
CH_2
b)
c)

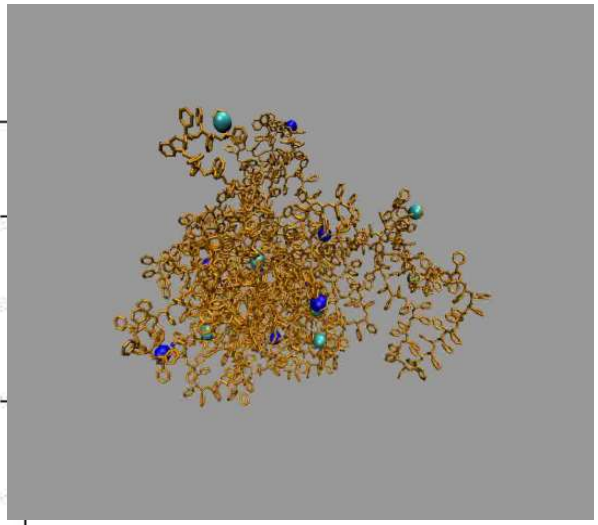
Films

8 chains, ~2.5nm 16 chains, ~ 5nm 32 chains, ~10nm 16 chains, ~20nm

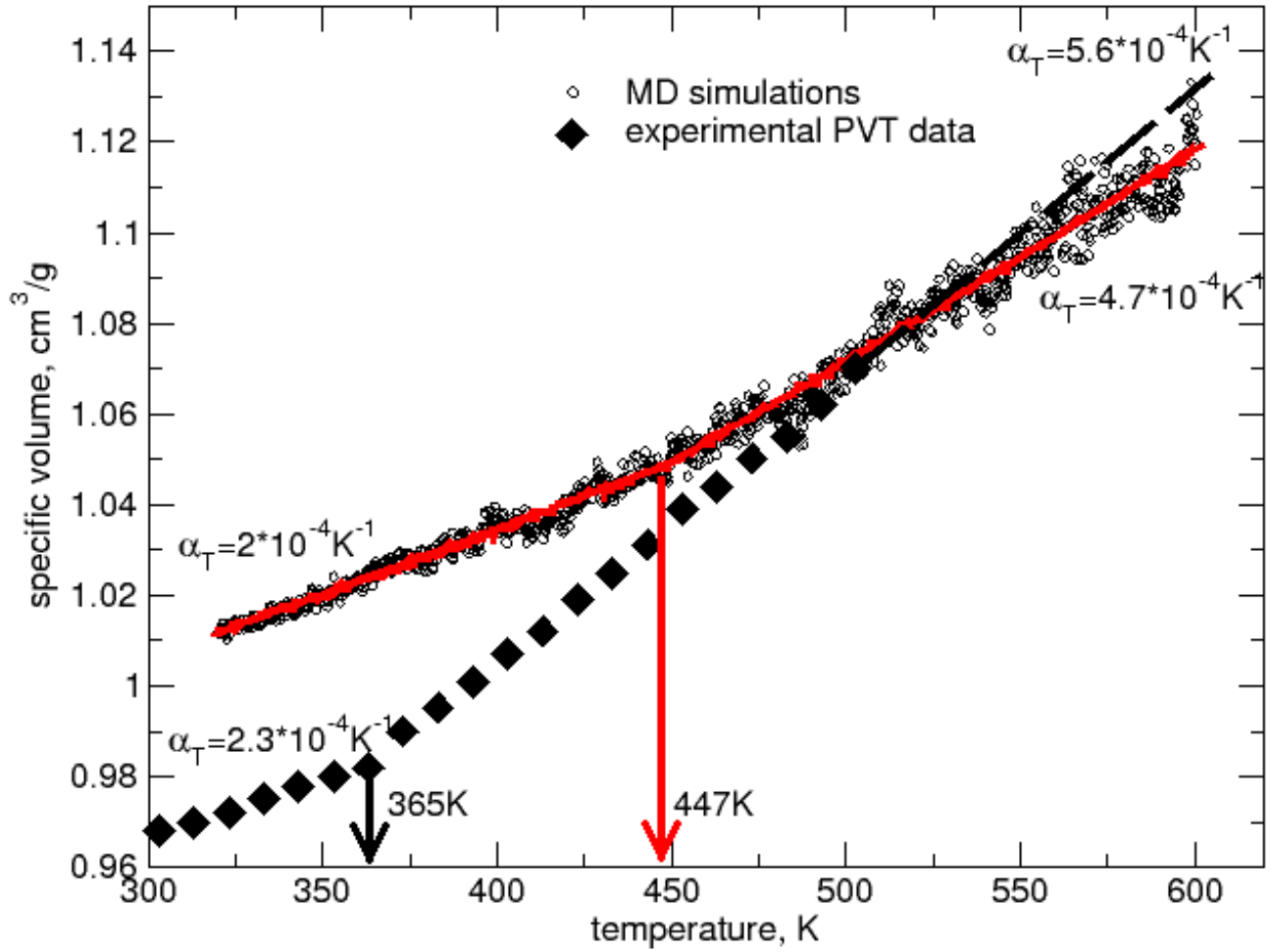


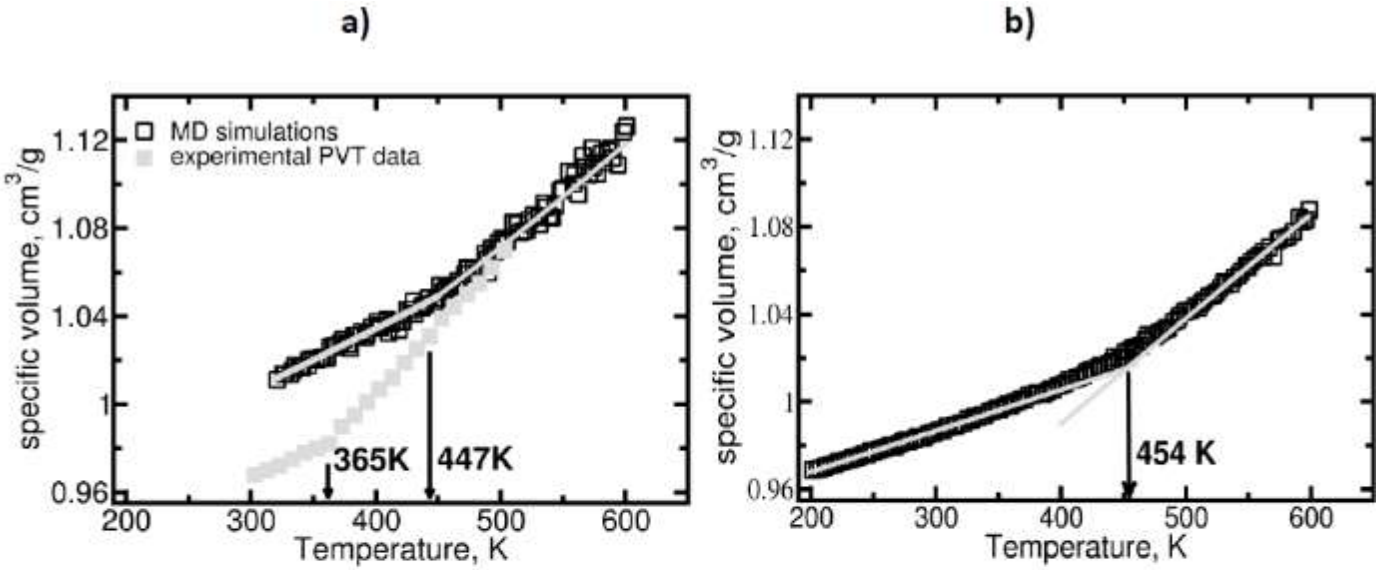
Equilibration: bulk





PS bulk vs experimental PVT data (Zoller, Walsh)





bulk aPS (a) linear and b) ring). Experimental results for linear aPS, M_w=9000.

Glass-transition temperatures: bulk

	LINEAR POLYMERS	RING POLYMERS
aPS		
bulk	447 (5)	454 (5)

Cyclic vs. linear

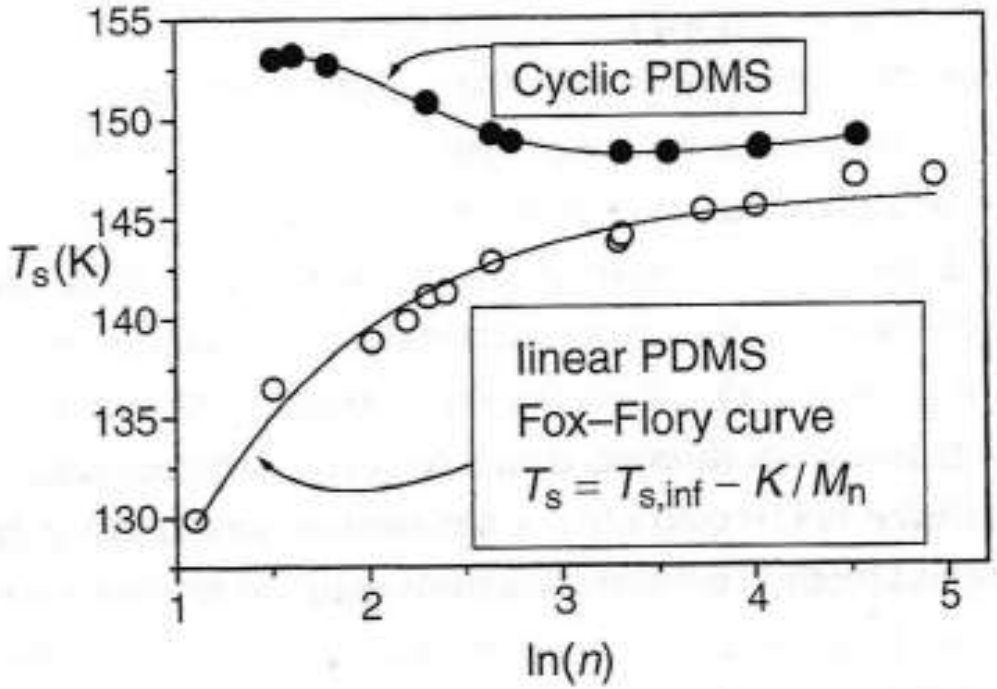
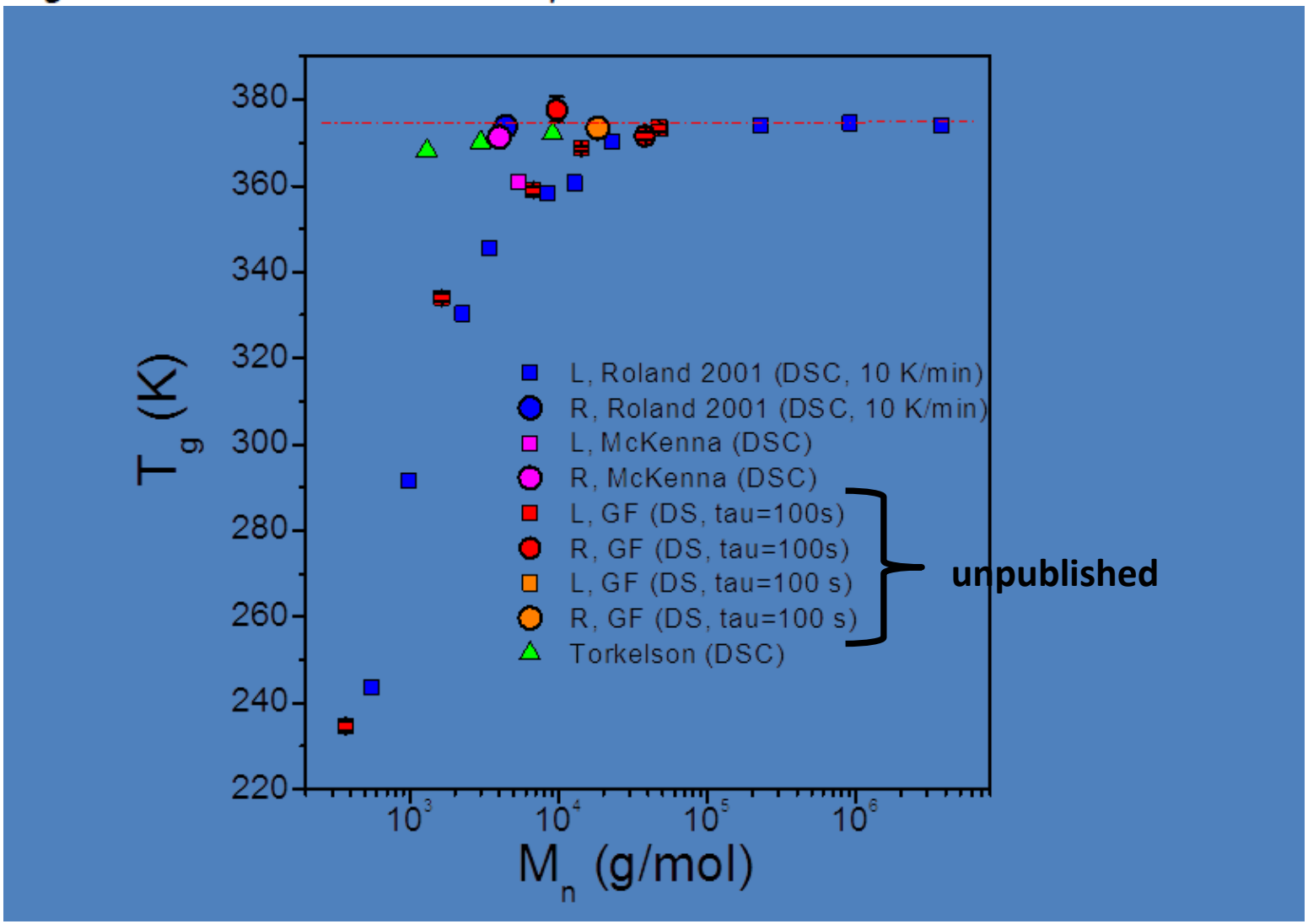


Fig. 2.13. The reference temperature T_s of the WLF equation used to fit the temperature dependence of the dielectric relaxation time τ of linear and cyclic PDMS plotted against the logarithm of the number of repeat units of PDMS. From Kirst *et al.* [86], by permission.

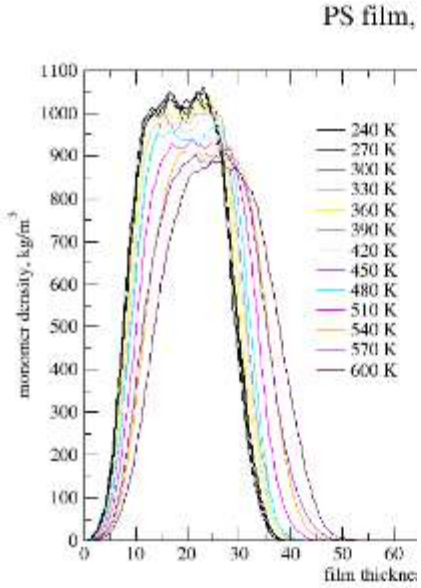
(Kirst, Kremer, Pakula, Hollingshurst, *J. Coll. Polym. Sci.* **1994**, 272, 1420)

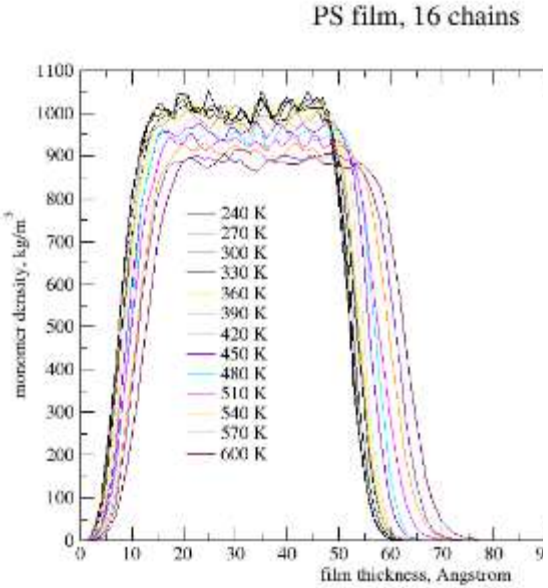
Cyclic vs. linear

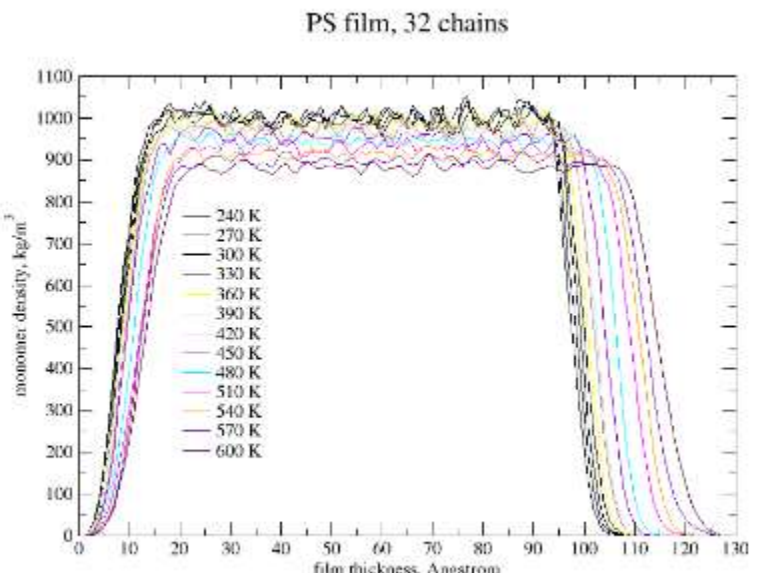
Tg - dielectric measurement by G. Floudas, 2014

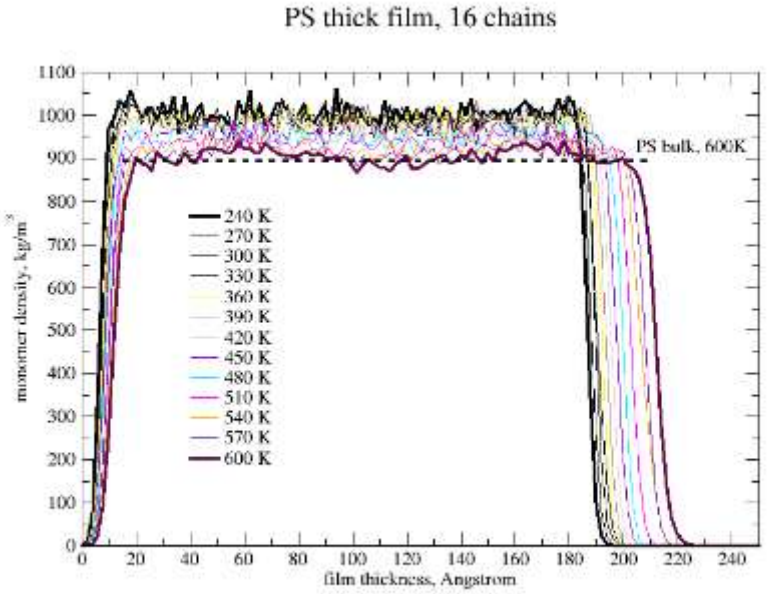


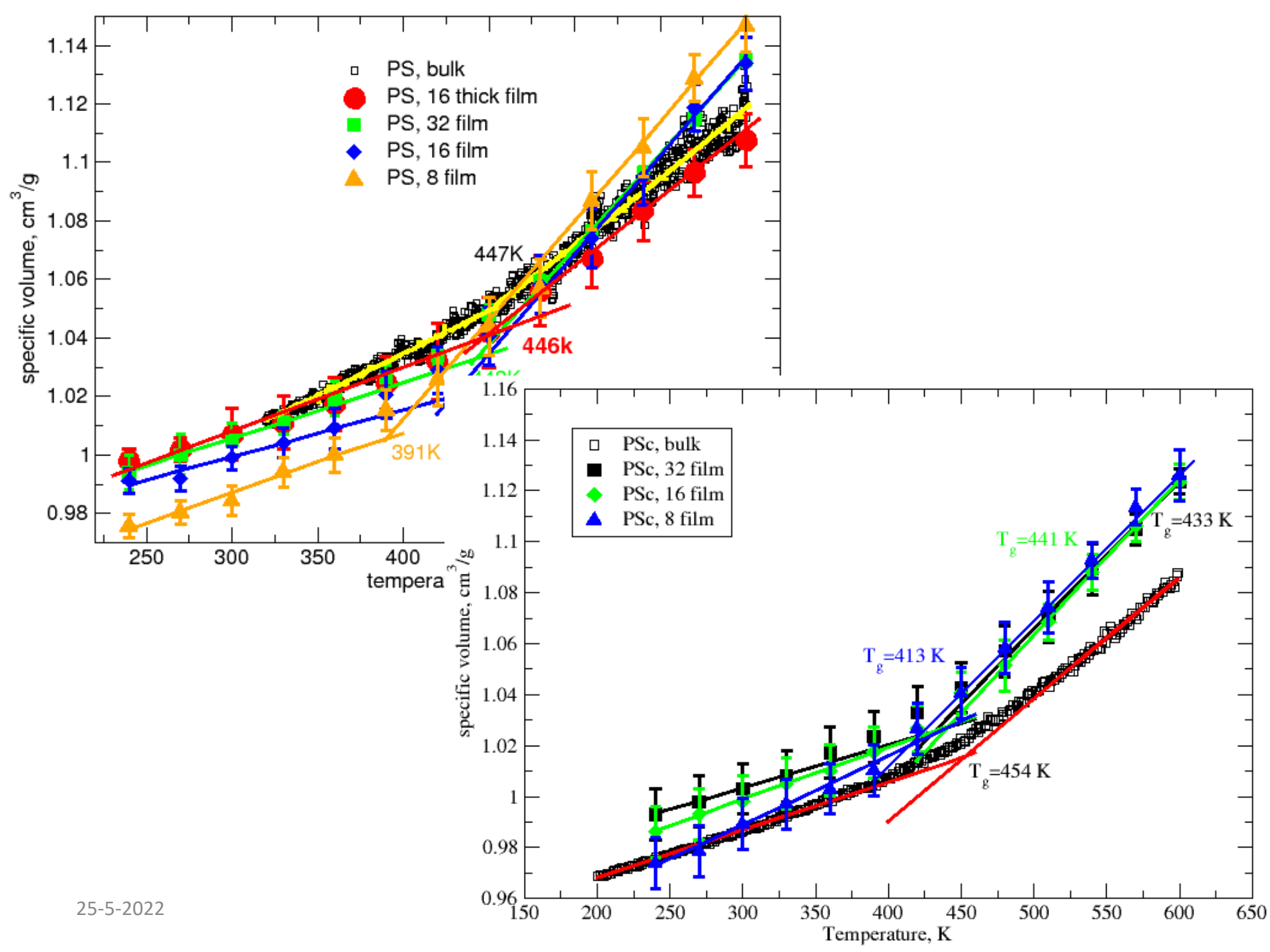
PS films


PS film,
monomer density, kg/m3
film thickne
240 K
270 K
300 K
330 K
360 K
390 K
420 K
450 K
480 K
510 K
540 K
570 K
600 K


PS film, 16 chains
monomer density, kg/m3
film thickness, Angstrom
240 K
270 K
300 K
330 K
360 K
390 K
420 K
450 K
480 K
510 K
540 K
570 K
600 K


PS film, 32 chains
monomer density, kg/m3
240 K
270 K
300 K
330 K
360 K
390 K
420 K
450 K
480 K
510 K
540 K
570 K
600 K

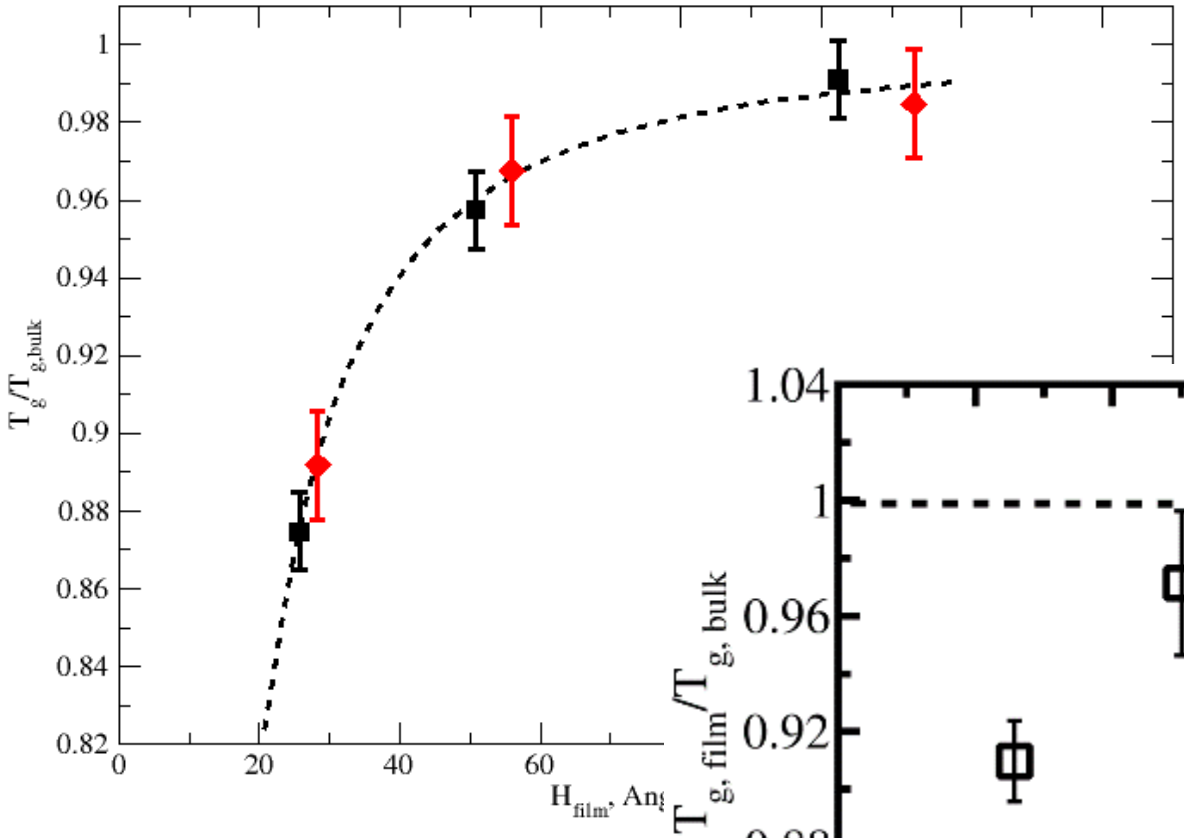

PS thick film, 16 chains
PS bulk, 600K
monomer density, kg/m3
film thickness, Angstrom
240 K
270 K
300 K
330 K
360 K
390 K
420 K
450 K
480 K
510 K
540 K
570 K
600 K

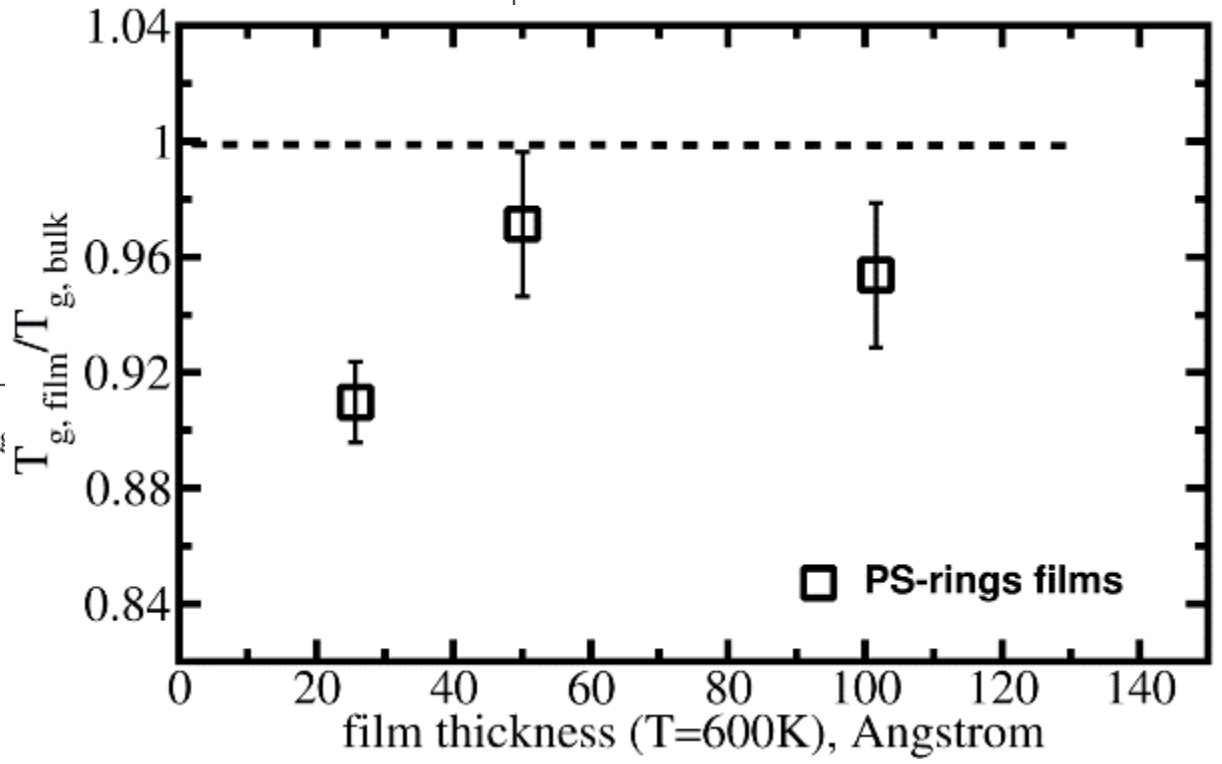

PS, bulk
PS, 16 thick film
PS, 32 film
PS, 16 film
PS, 8 film
447K
446k
391K
specific volume, cm3/g
tempera
PSc, bulk
PSc, 32 film
PSc, 16 film
PSc, 8 film
Tg=433 K
Tg=441 K
Tg=413 K
Tg=454 K
specific volume, cm3/g
Temperature, K

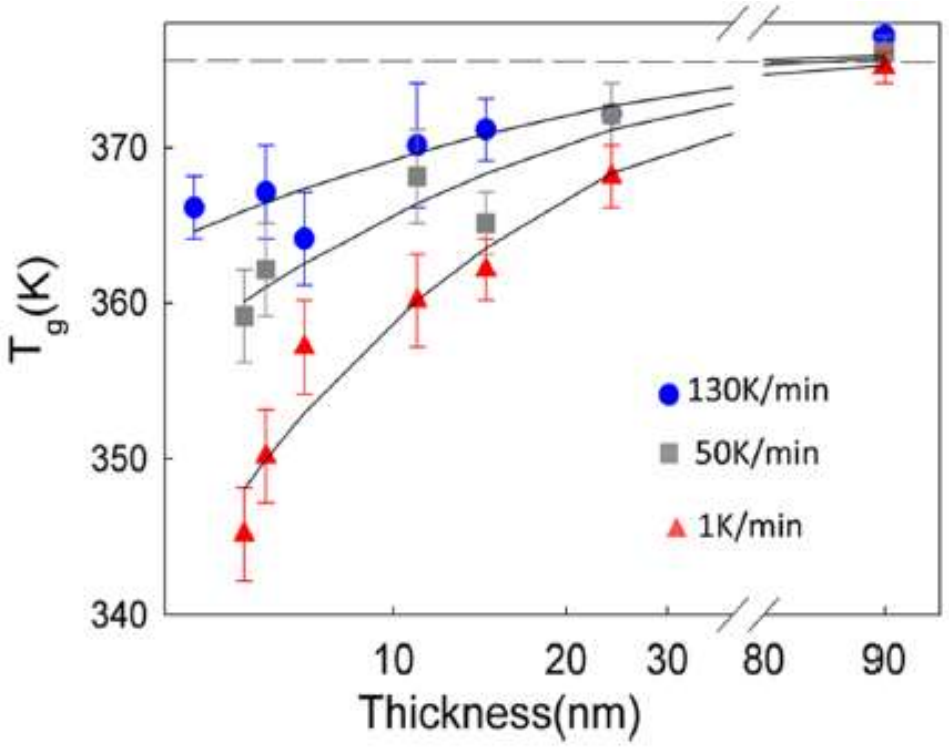
Glass-transition temperatures

	LINEAR PS	RING PS
bulk	447 (10)	454 (5)
200 Å	446 (5)	-
100 Å	443 (5)	433 (5)
50 Å	428 (5)	441 (5)
25 Å	391 (5)	413 (3)

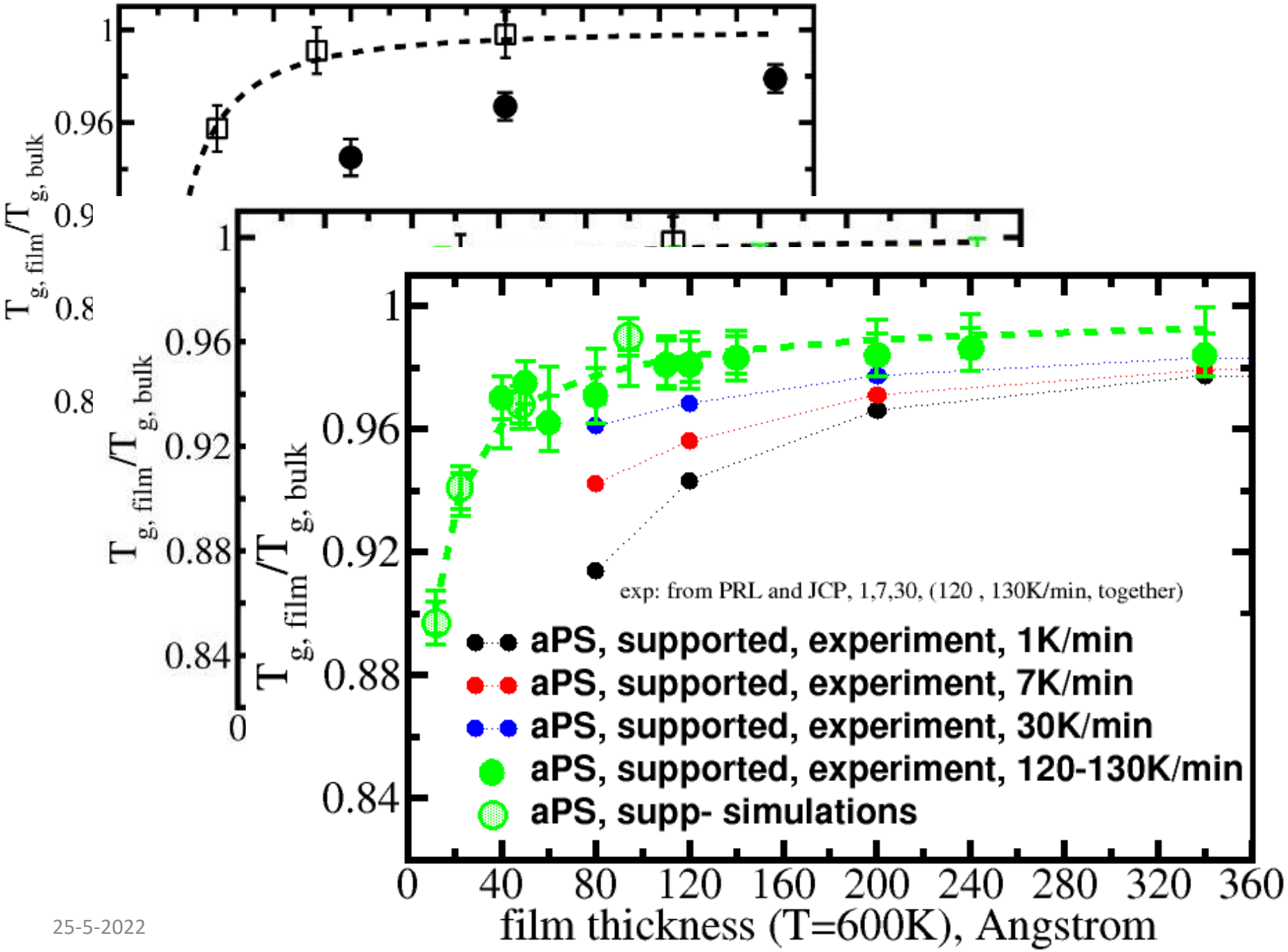
Thickness dependence



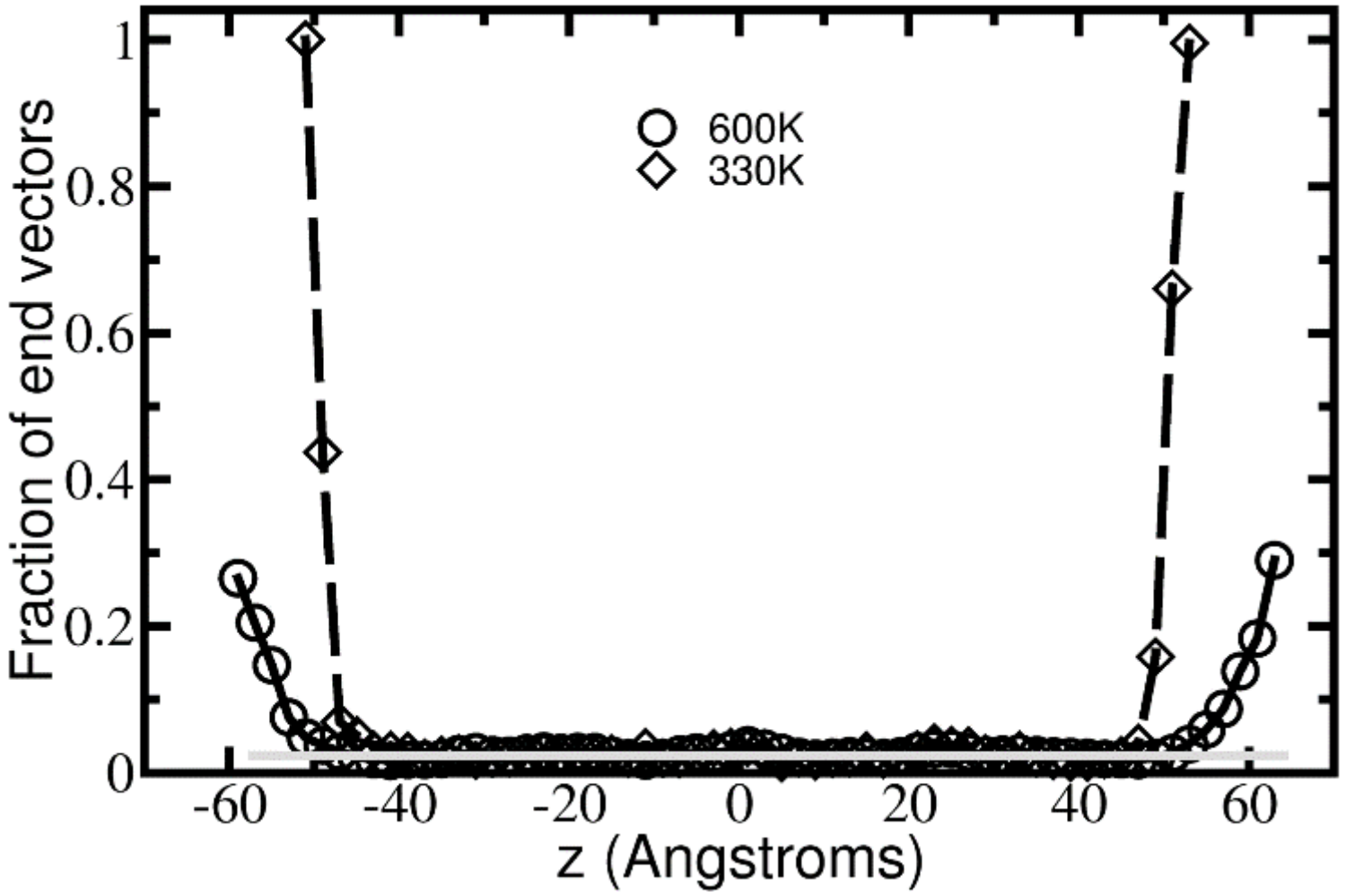




Z. Fakhraai, J.A. Forrest, Phys. Rev. Lett., 2005

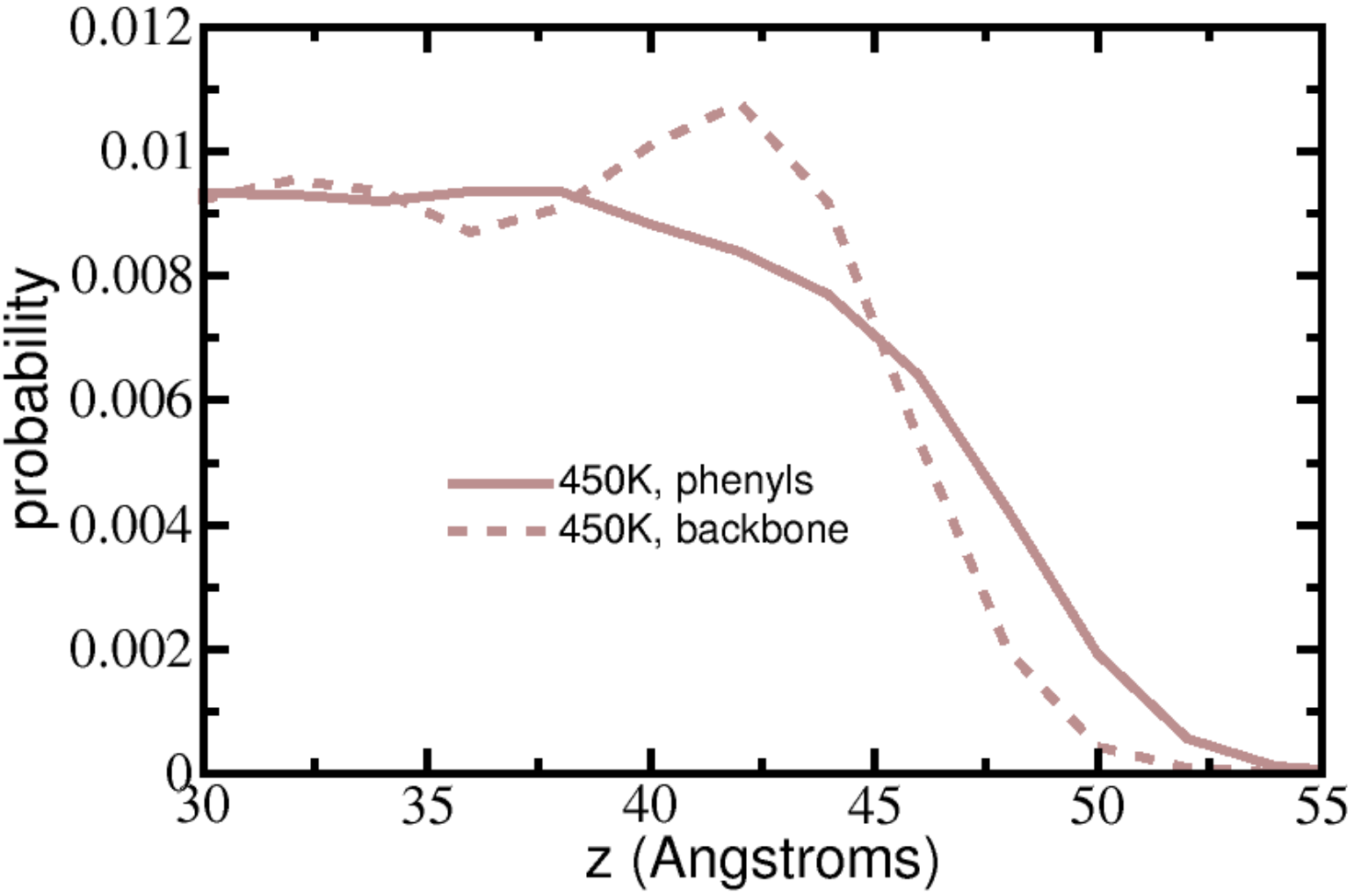

$T_{g,film}/T_{g,bulk}$
film thickness (T=600K), Angstrom
exp: from PRL and JCP, 1,7,30, (120 , 130K/min, together)
aPS, supported, experiment, 1K/min
aPS, supported, experiment, 7K/min
aPS, supported, experiment, 30K/min
aPS, supported, experiment, 120-130K/min
aPS, supp- simulations

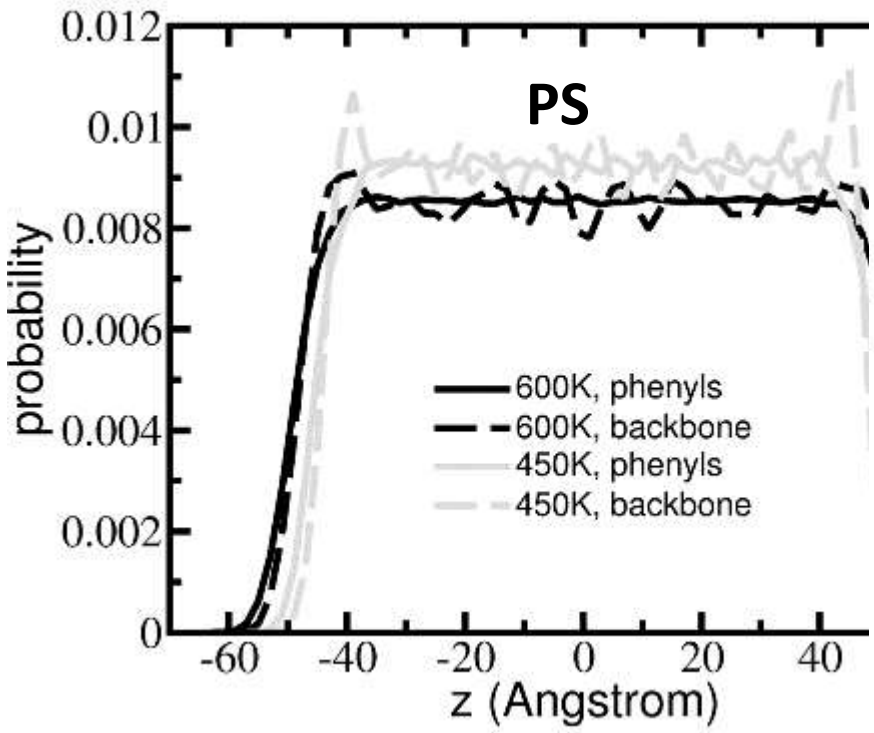
Chain ends

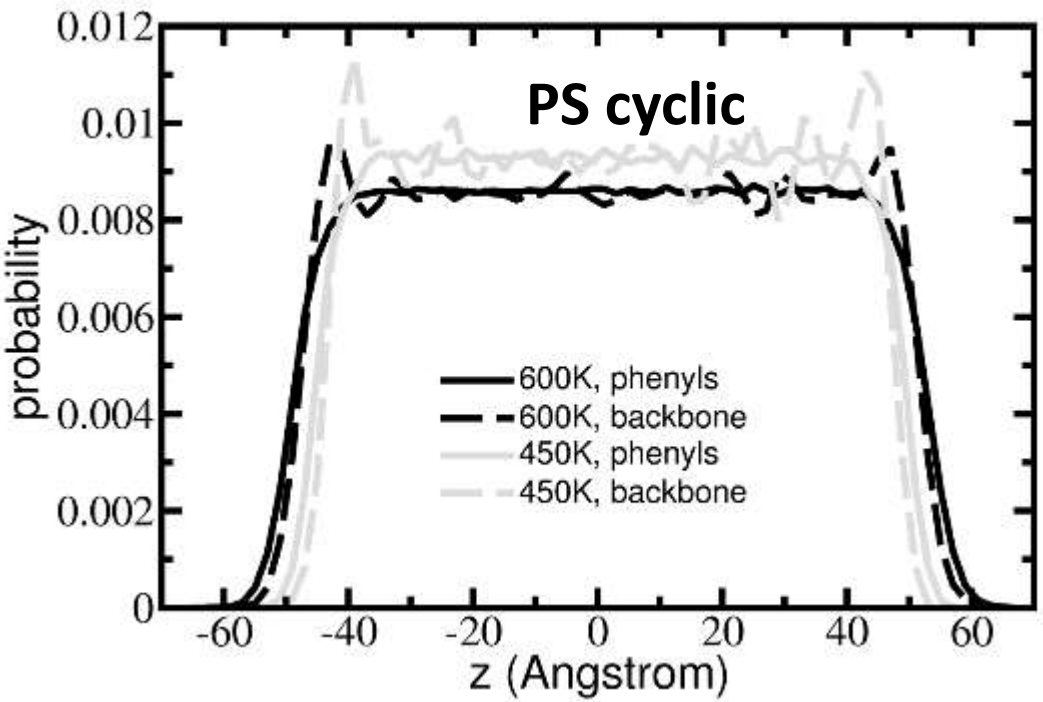


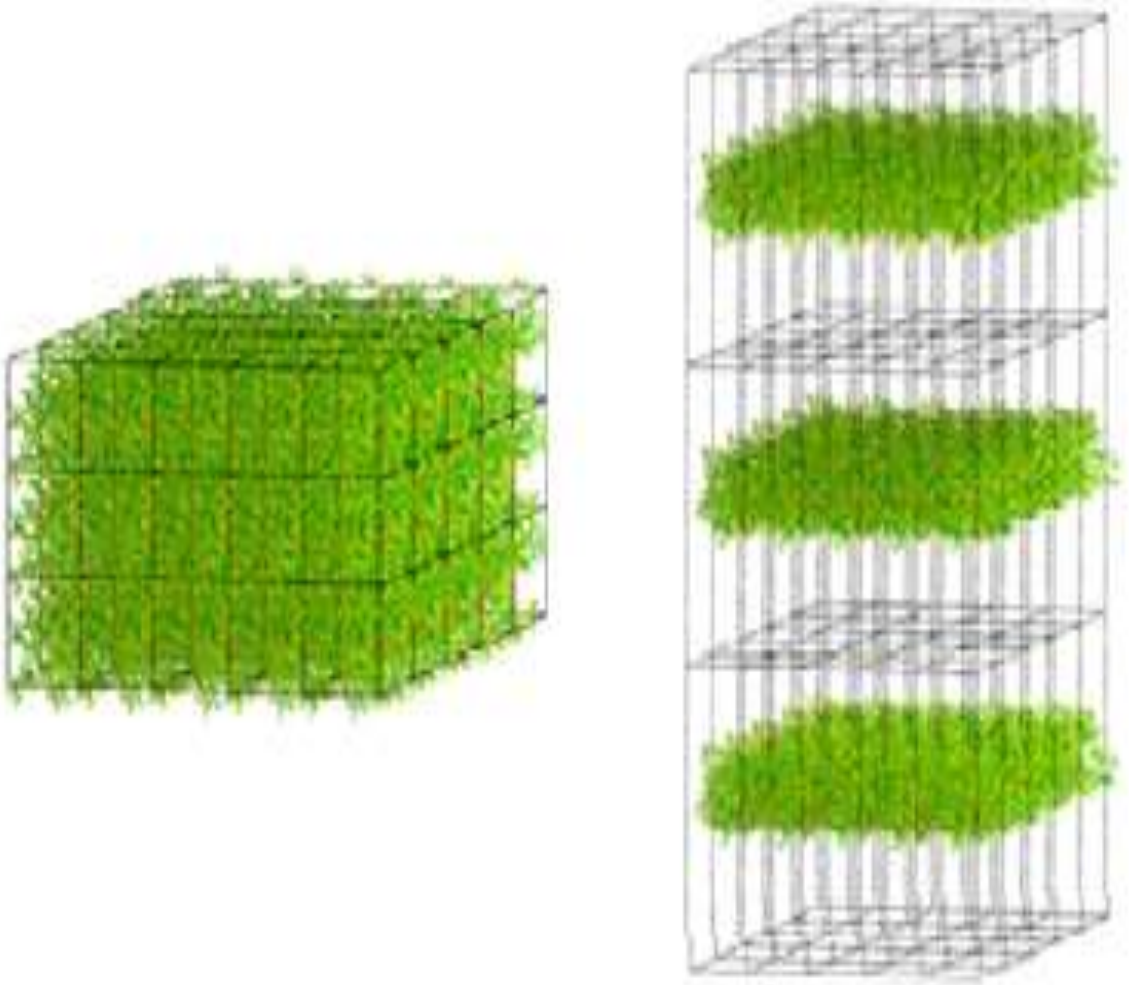
More ends are concentrated at the interface for PS film

Phenyls vs backbone



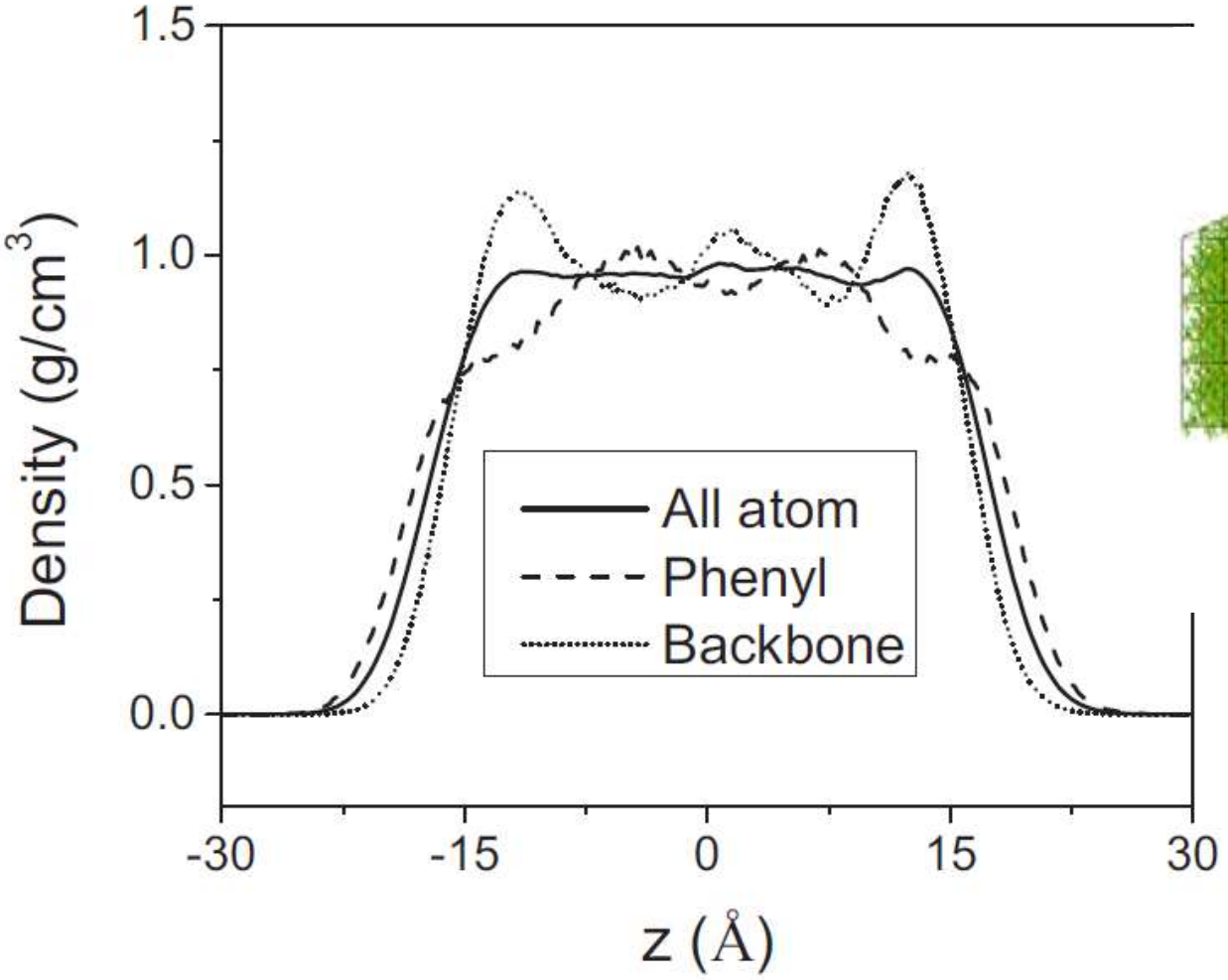

PS
probability
z (Angstrom)
600K, phenyls
600K, backbone
450K, phenyls
450K, backbone

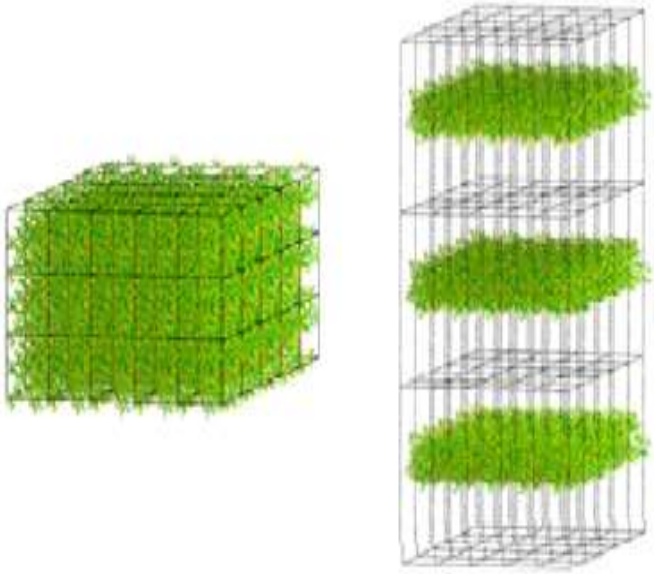

PS cyclic
probability
z (Angstrom)
600K, phenyls
600K, backbone
450K, phenyls
450K, backbone



Explicit atom force field: G.D. Smith et al., J. Phys. Chem. A 102 (1998) 4694-4702

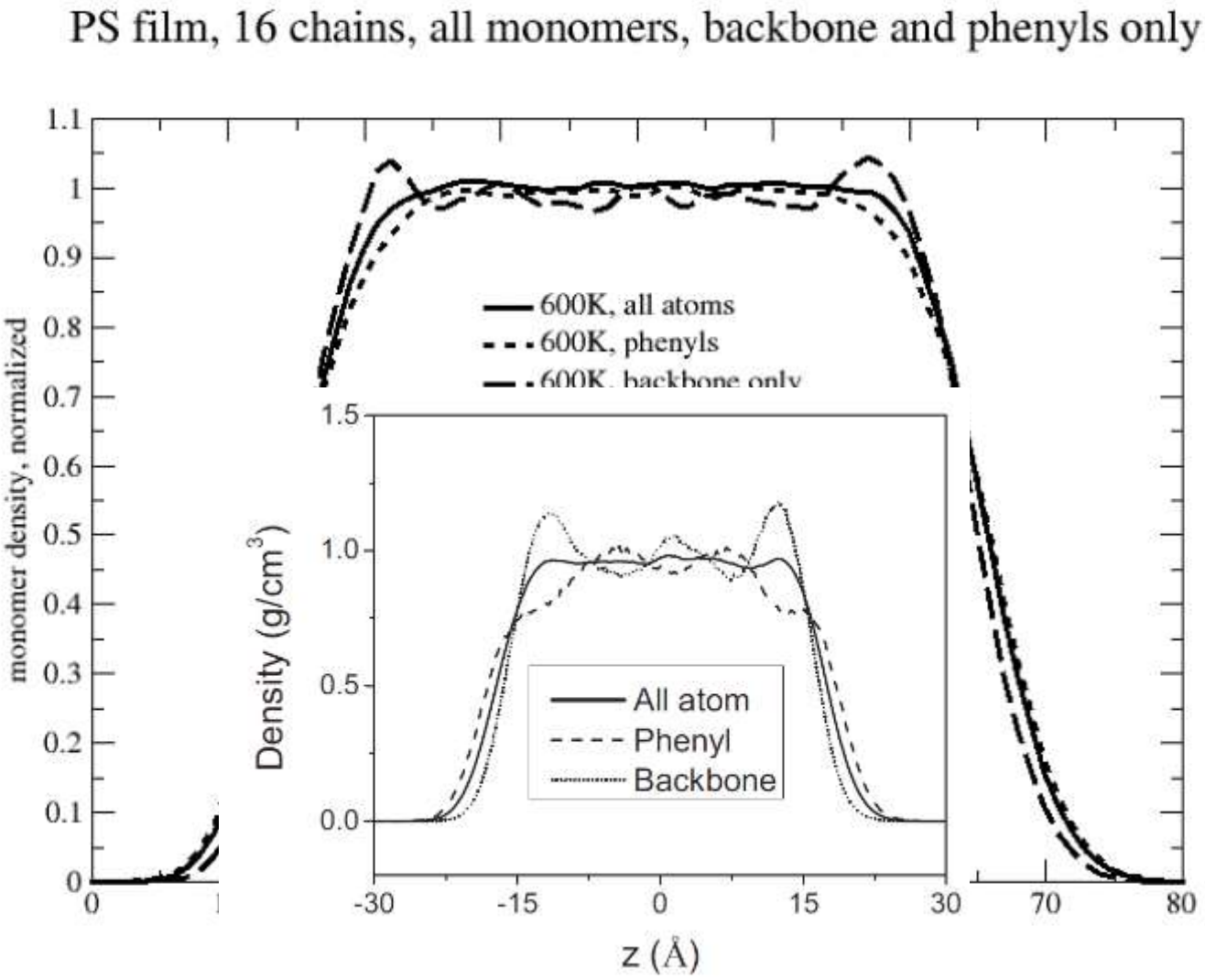
Phenyls vs backbone (all-atom model) (Sanghun Lee, Do Yoon, AVL)

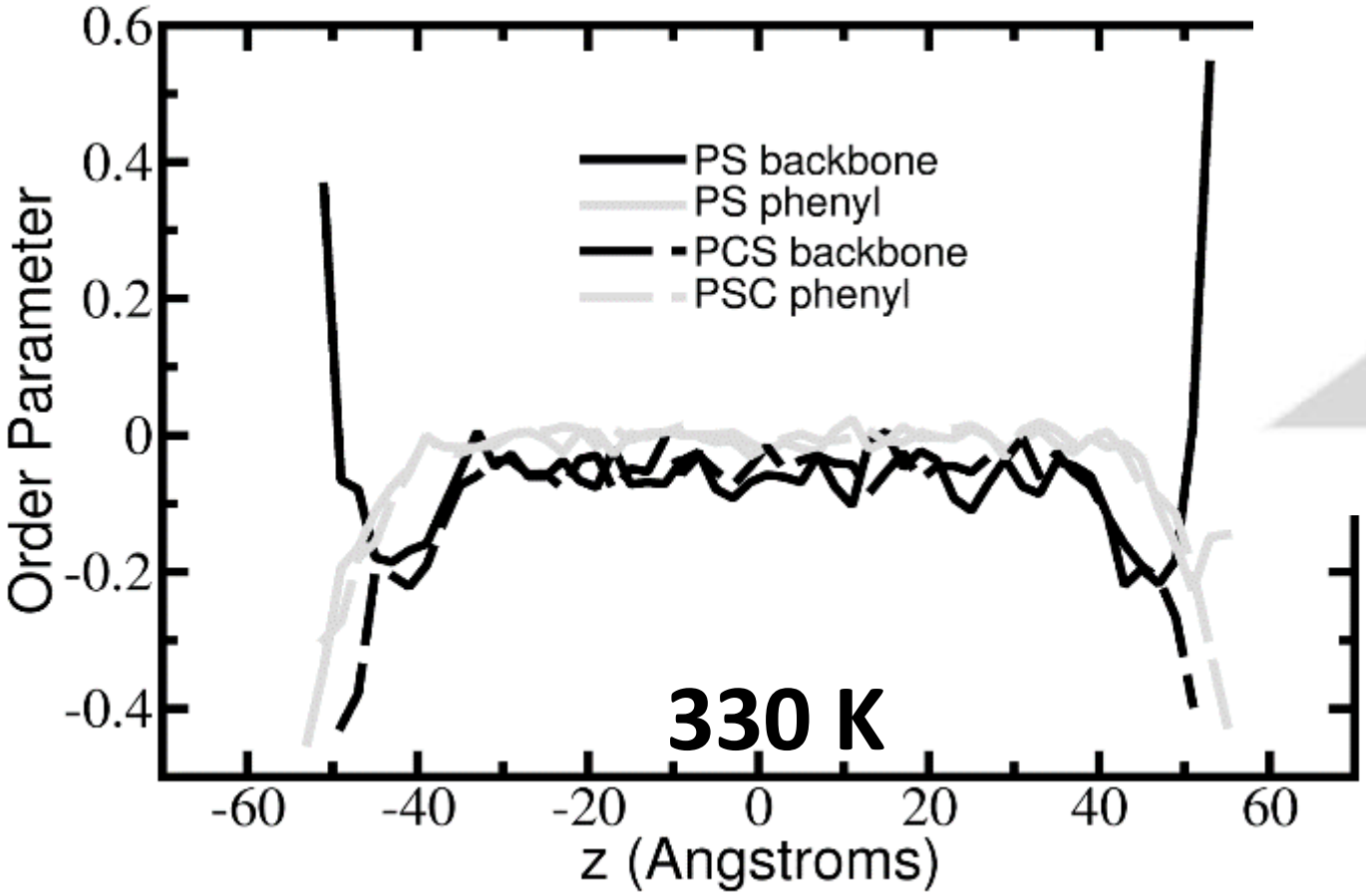


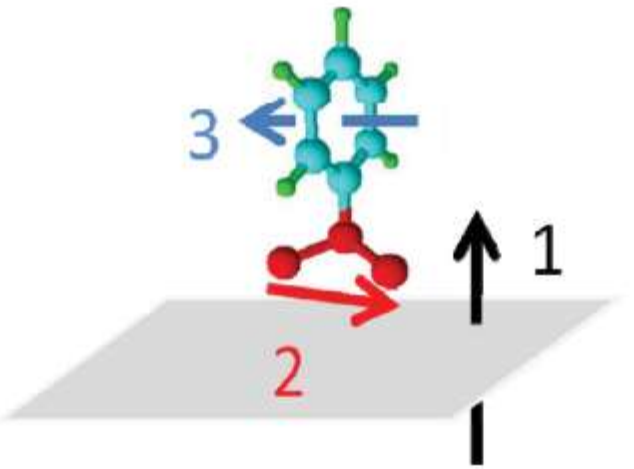


S. Lee, AVL, C. Frank, D. Yoon, Polymer, **2017**

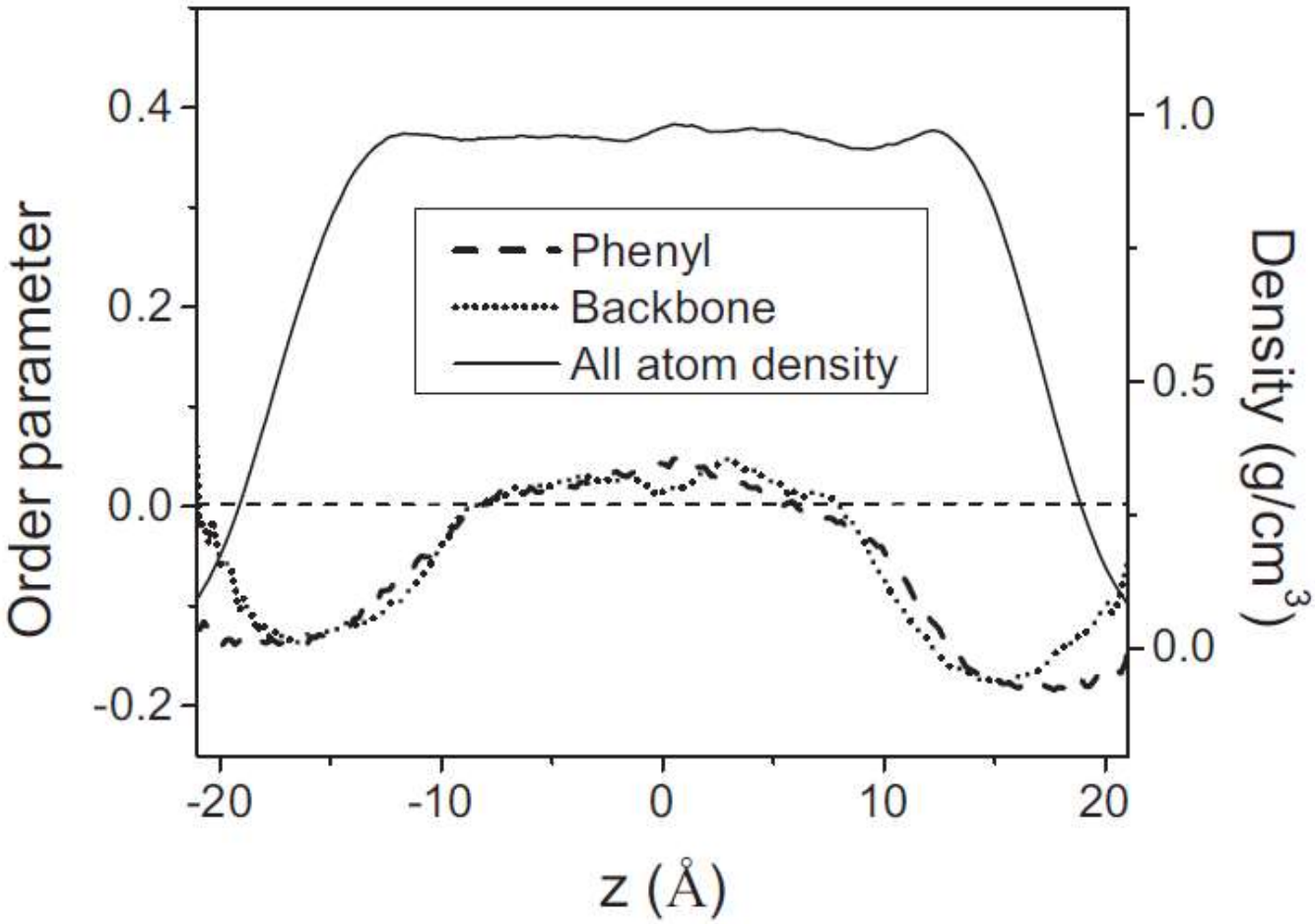
Phenyls vs backbone

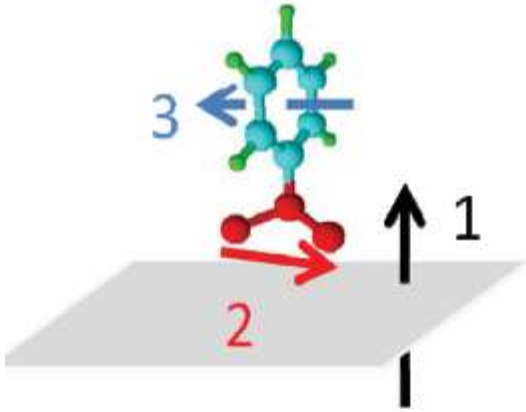



0.6
0.4
0.2
0
-0.2
-0.4
Order Parameter
PS backbone
PS phenyl
PCS backbone
PSC phenyl
330 K
-60
-40
-20
0
20
40
60
z (Angstroms)


3
1
2

Phenyls vs backbone (all-atomistic)





Conclusions

- T_g thickness dependence is (**mainly**) due to **π- π interactions** ;

- **Chain ends** also play role; interfacial layers are different for linear PS and PS cyclic;

AVL et al., J. Chem. Phys. v. 146 ***(special issue),*** **2017**
S. Lee, AVL, C. Frank, D. Yoon, Polymer, **2017**

Challenges

- Comparison of “static” T_g to that measured dynamically;
- Role of π- π interactions