Title: Using Î²-NMR to Solve Hard Problems in Soft Condensed Matter

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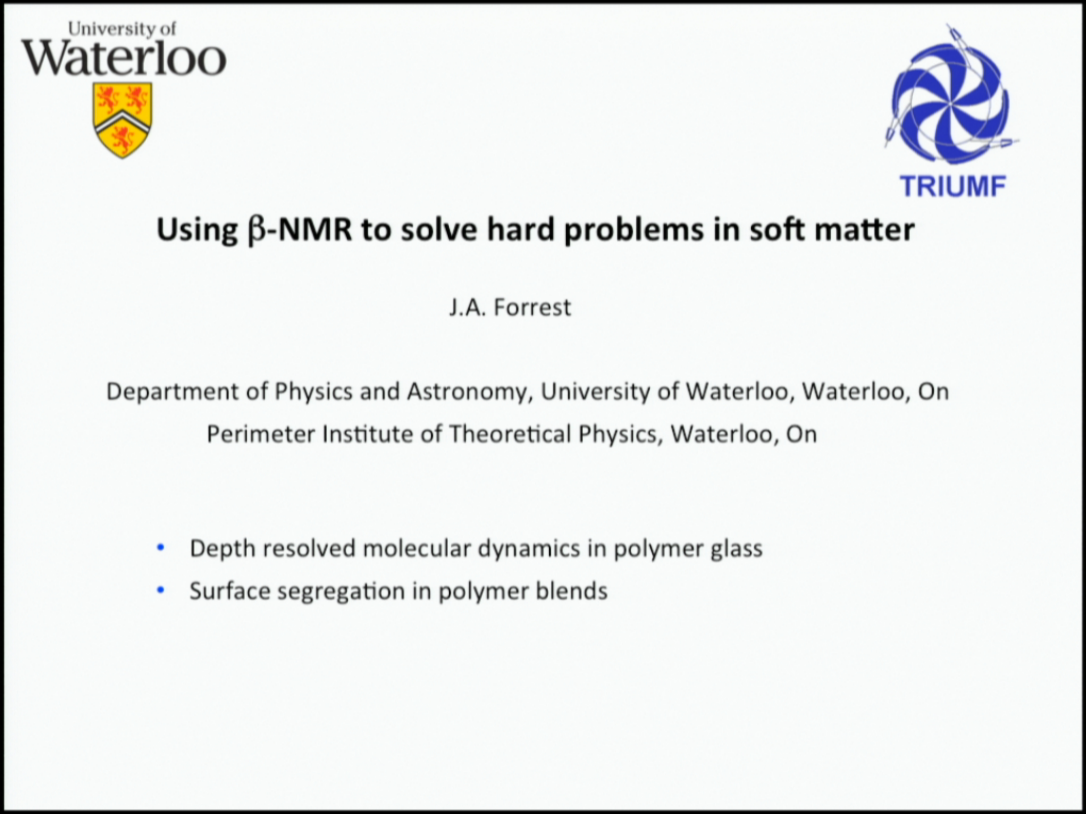
Abstract: <span>Beta-detected nuclear spin relaxation of 8Li+ has been used to study important problems in polymer physics. In the first case we probe the depth dependence of molecular dynamics in high- and low-molecular-weight deuterated polystyrene (PS-d8). The average nuclear spin-lattice relaxation rate, 1/T1 avg, is a measure of the spectral density of the polymer dynamics at the Larmor frequency (41MHz at 6.55Tesla). The mean fluctuation rate decreases approximately exponentially with distance from the free surface, returning to bulk behavior for depths greater than ~10nm and the effective thickness of the surface region increases with increasing temperature. These results present challenges for the current understanding of dynamics near the free surface of polymer glasses. In the second case, we use the technique to make the first quantitative measurements of surface segregation in samples that are blends of two chemically identical polymers with different degrees of polymerization.</span>



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# Using β-NMR to solve hard problems in soft matter

J.A. Forrest

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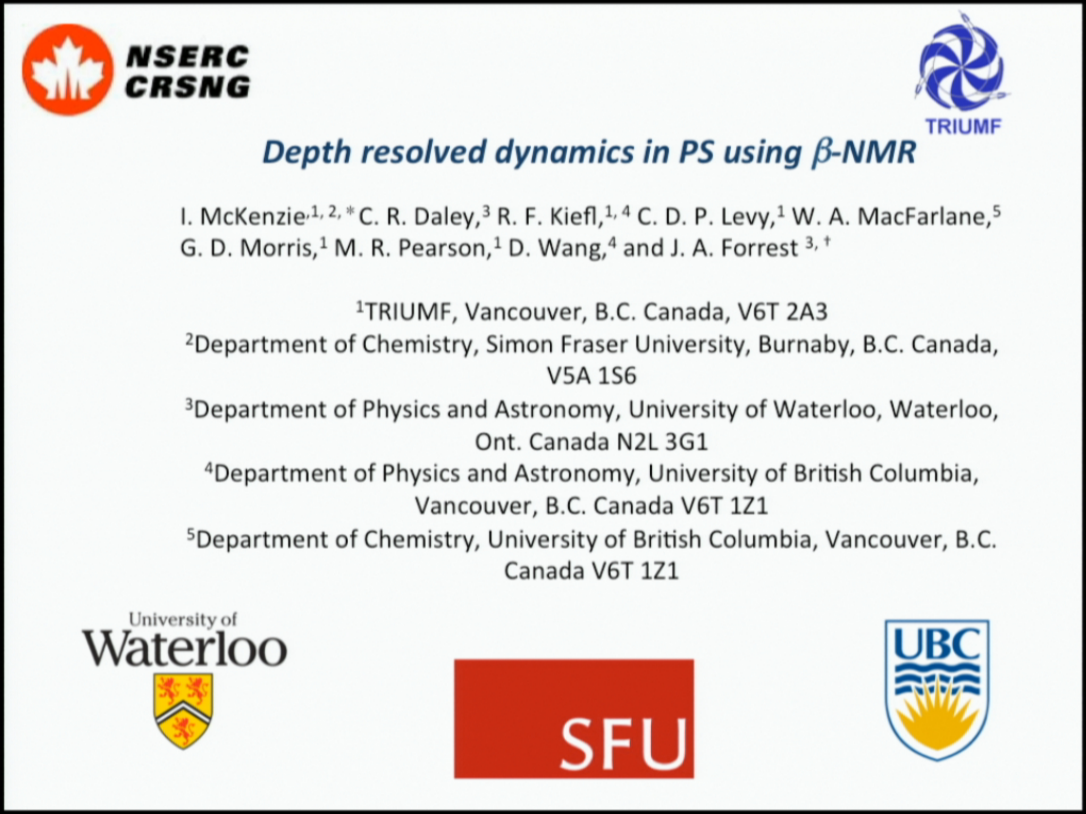
Perimeter Institute of Theoretical Physics, Waterloo, On

- Depth resolved molecular dynamics in polymer glass
- Surface segregation in polymer blends


= ⊕ S
= ⊕ T
D = Σ GSO
= ⊕_b C_b^{2D}
compact
⊕(G, ω_3)
⊕ 2D (toric code Z_N)
⊕ 2D (d.s. Z_N)
ω_3
3! = 6



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# Depth resolved dynamics in PS using $\beta$-NMR

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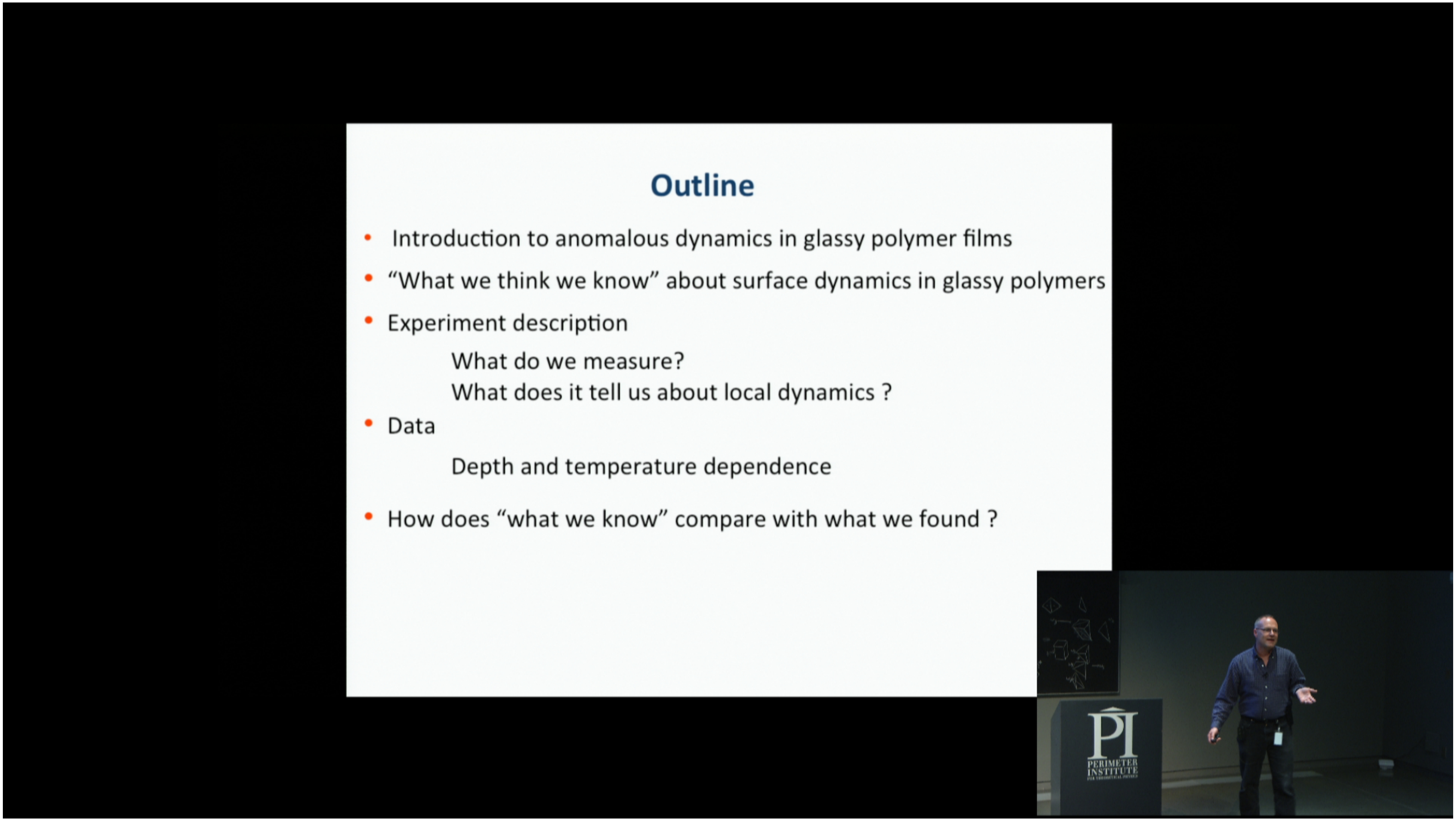
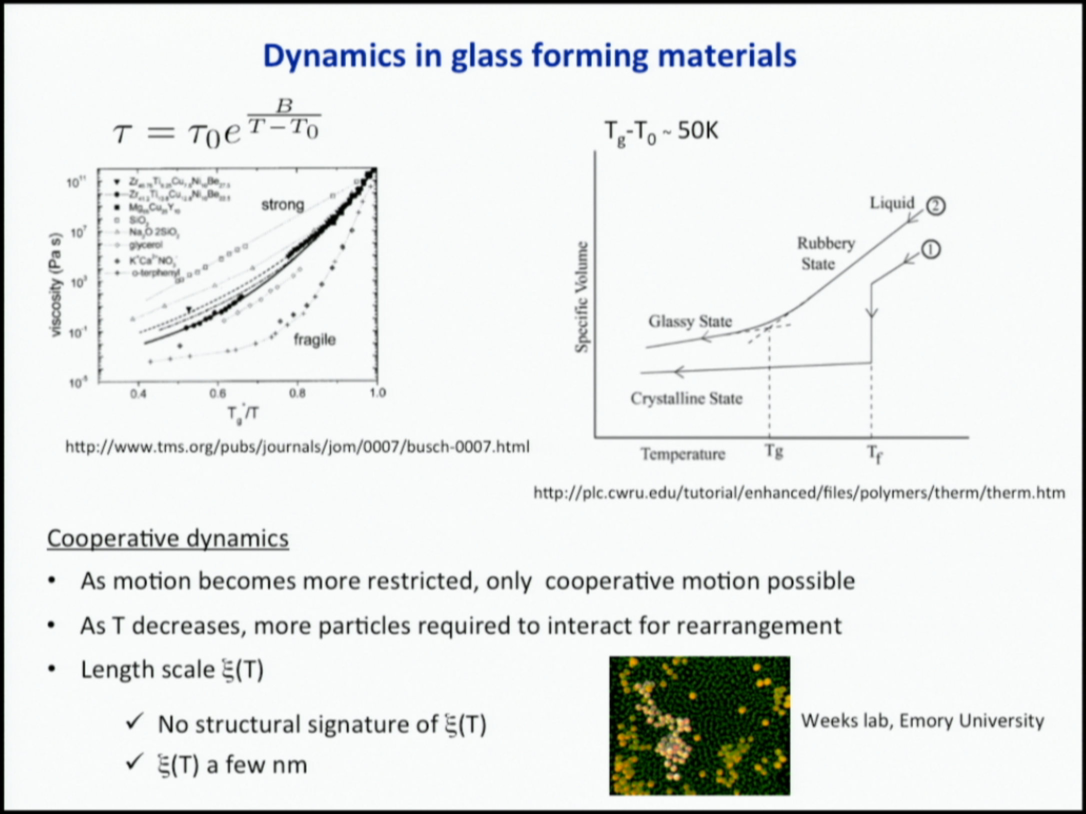


## Outline

- Introduction to anomalous dynamics in glassy polymer films
- “What we think we know” about surface dynamics in glassy polymers
- Experiment description
  - What do we measure?
  - What does it tell us about local dynamics ?
- Data
  - Depth and temperature dependence
- How does “what we know” compare with what we found ?



# Dynamics in glass forming materials

$$\tau = \tau_0 e^{\frac{B}{T - T_0}}$$

http://www.tms.org/pubs/journals/jom/0007/busch-0007.html

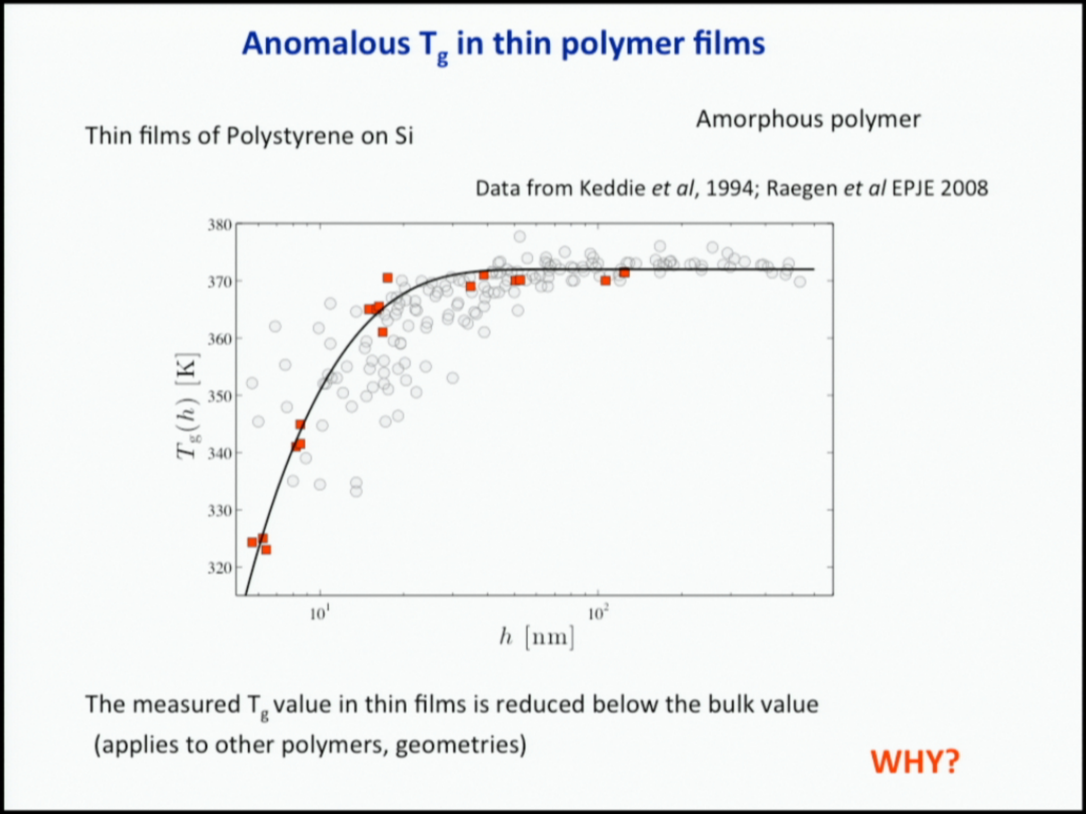
$T_g$-$T_0$ ~ 50K

http://plc.cwru.edu/tutorial/enhanced/files/polymers/therm/therm.htm

Cooperative dynamics

- As motion becomes more restricted, only cooperative motion possible
- As T decreases, more particles required to interact for rearrangement
- Length scale ξ(T)
  - ✓ No structural signature of ξ(T)
  - ✓ ξ(T) a few nm

Weeks lab, Emory University



## Anomalous $T_g$ in thin polymer films

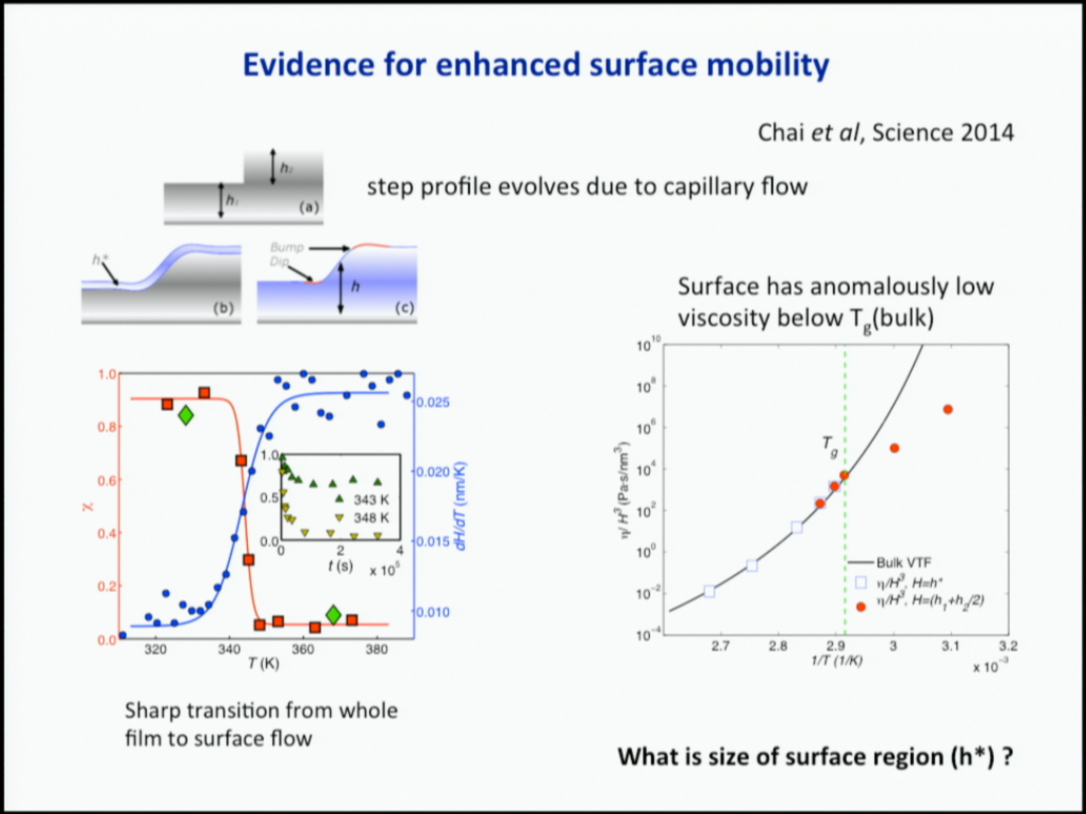
Thin films of Polystyrene on Si

Amorphous polymer

Data from Keddie *et al*, 1994; Raegen *et al* EPJE 2008

The measured $T_g$ value in thin films is reduced below the bulk value
(applies to other polymers, geometries)

**WHY?**



# Evidence for enhanced surface mobility

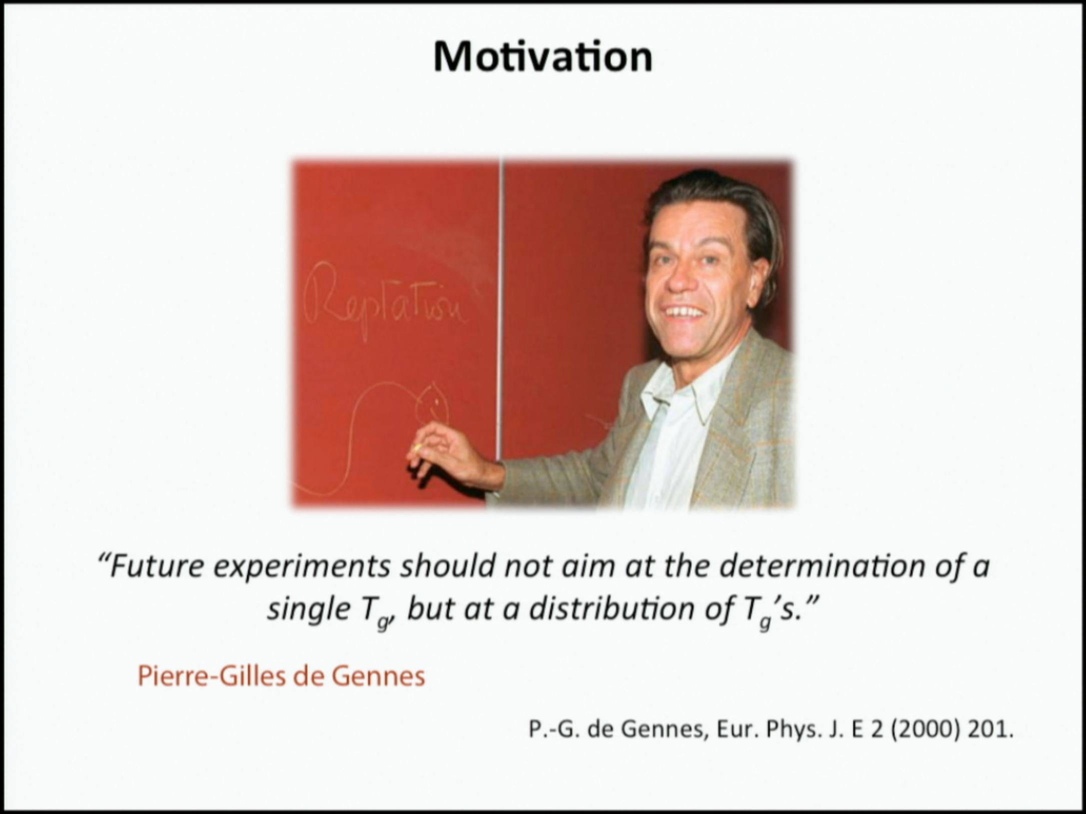
Chai *et al*, Science 2014

step profile evolves due to capillary flow

Surface has anomalously low viscosity below $T_g$(bulk)

Sharp transition from whole film to surface flow

**What is size of surface region (h*) ?**

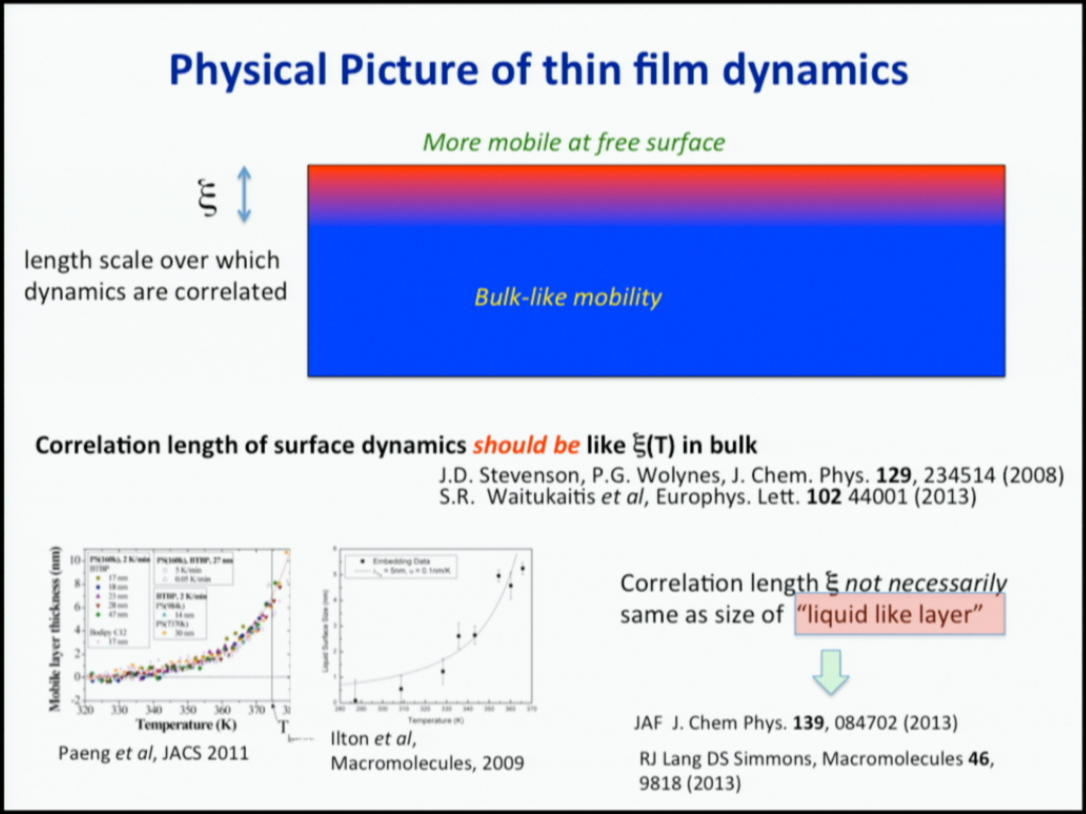


# Motivation

*“Future experiments should not aim at the determination of a single $T_g$, but at a distribution of $T_g$’s.”*

Pierre-Gilles de Gennes

P.-G. de Gennes, Eur. Phys. J. E 2 (2000) 201.



# Physical Picture of thin film dynamics

*More mobile at free surface*

ξ

length scale over which dynamics are correlated

*Bulk-like mobility*

**Correlation length of surface dynamics *should be* like ξ(T) in bulk**

J.D. Stevenson, P.G. Wolynes, J. Chem. Phys. **129**, 234514 (2008)
S.R. Waitukaitis *et al*, Europhys. Lett. **102** 44001 (2013)

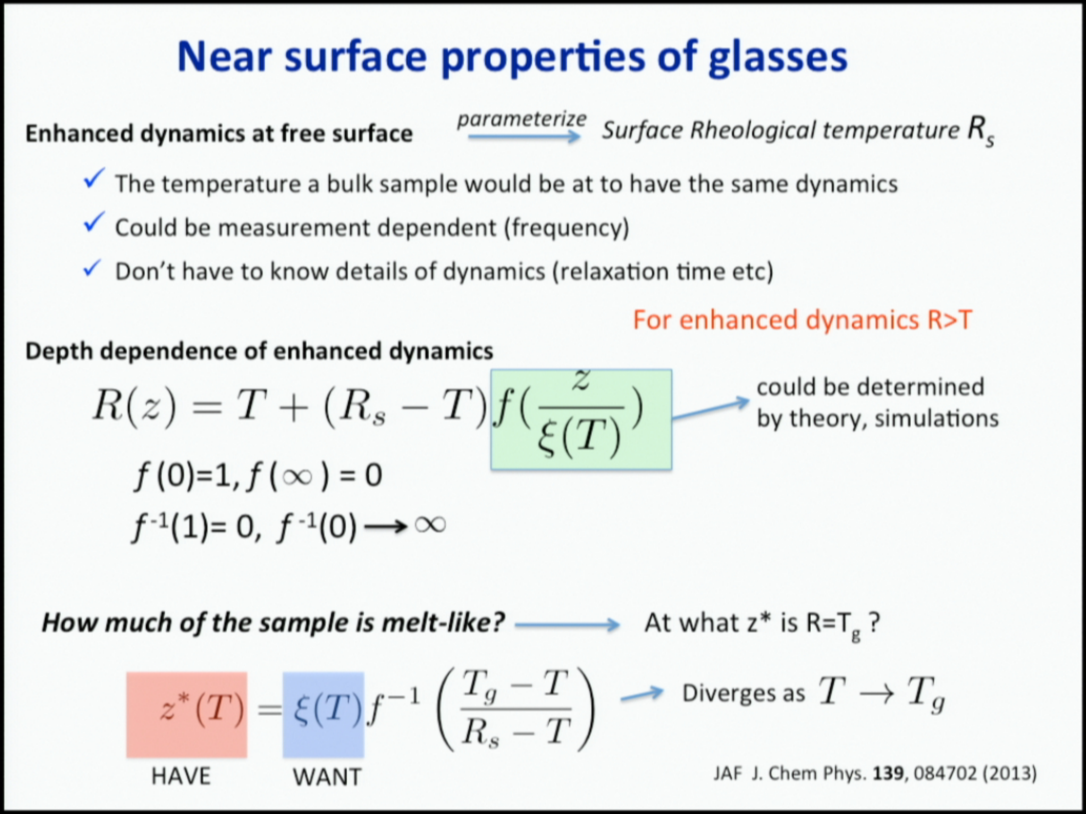
Paeng *et al*, JACS 2011

Ilton *et al*,
Macromolecules, 2009

Correlation length ξ *not necessarily* same as size of "liquid like layer"

JAF J. Chem Phys. **139**, 084702 (2013)

RJ Lang DS Simmons, Macromolecules **46**, 9818 (2013)



# Near surface properties of glasses

**Enhanced dynamics at free surface** $\xrightarrow{\textit{parameterize}}$ *Surface Rheological temperature* $R_s$

- ✓ The temperature a bulk sample would be at to have the same dynamics
- ✓ Could be measurement dependent (frequency)
- ✓ Don't have to know details of dynamics (relaxation time etc)

For enhanced dynamics R>T

**Depth dependence of enhanced dynamics**

$$R(z) = T + (R_s - T)\boxed{f(\frac{z}{\xi(T)})}$$

→ could be determined by theory, simulations

$f(0)=1, f(\infty) = 0$

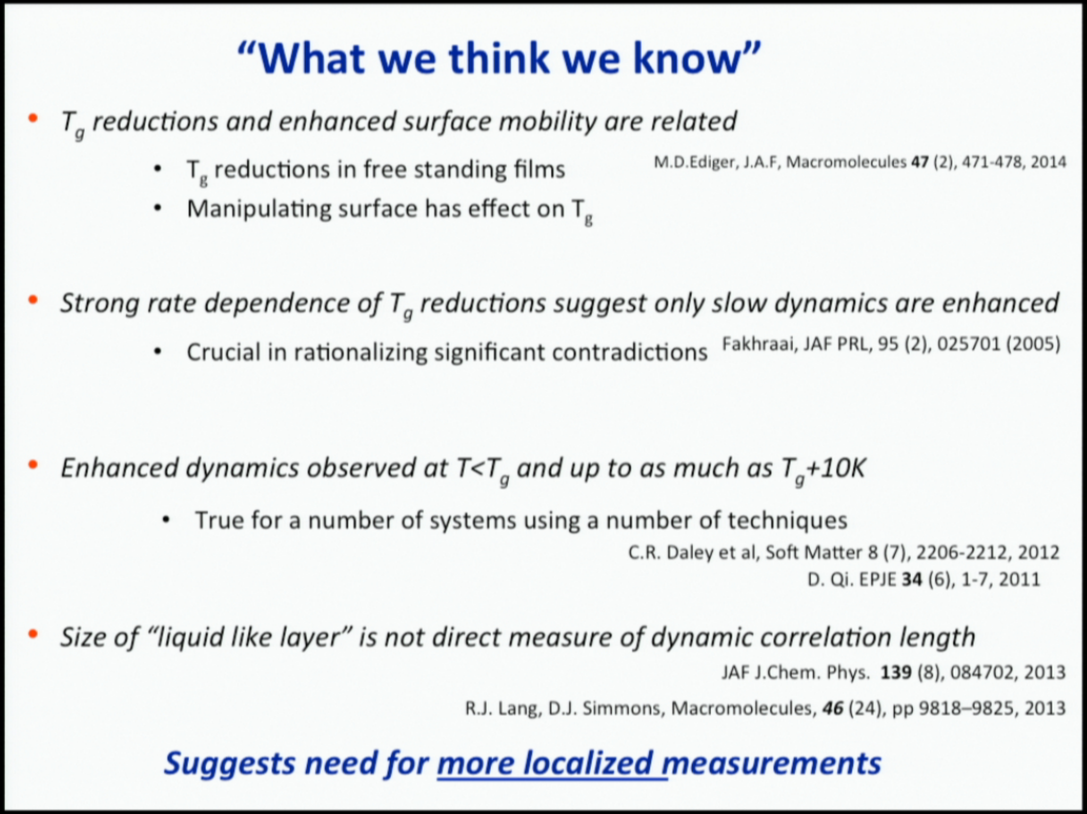
$f^{-1}(1)= 0,\ f^{-1}(0) \longrightarrow \infty$

***How much of the sample is melt-like?*** → At what z* is $R=T_g$ ?

$$\underset{\text{HAVE}}{\boxed{z^*(T)}} = \underset{\text{WANT}}{\boxed{\xi(T)}}\, f^{-1}\left(\frac{T_g - T}{R_s - T}\right)$$

→ Diverges as $T \to T_g$

JAF J. Chem Phys. **139**, 084702 (2013)



# "What we think we know"

- *$T_g$ reductions and enhanced surface mobility are related*
  - $T_g$ reductions in free standing films M.D.Ediger, J.A.F, Macromolecules **47** (2), 471-478, 2014
  - Manipulating surface has effect on $T_g$
- *Strong rate dependence of $T_g$ reductions suggest only slow dynamics are enhanced*
  - Crucial in rationalizing significant contradictions Fakhraai, JAF PRL, 95 (2), 025701 (2005)
- *Enhanced dynamics observed at $T<T_g$ and up to as much as $T_g+10K$*
  - True for a number of systems using a number of techniques

C.R. Daley et al, Soft Matter 8 (7), 2206-2212, 2012
D. Qi. EPJE **34** (6), 1-7, 2011

- *Size of "liquid like layer" is not direct measure of dynamic correlation length*

JAF J.Chem. Phys. **139** (8), 084702, 2013
R.J. Lang, D.J. Simmons, Macromolecules, ***46*** (24), pp 9818–9825, 2013

***Suggests need for more localized measurements***

# Samples

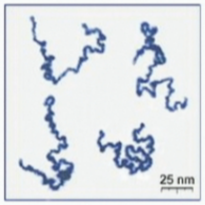
*h* ~ 180 nm     Sample on Sapphire substrates

All polymer from Polymer Source Inc.

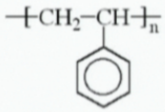
d-PS with $M_w$= 980 g/mol     $T_g$=280K

d-PS with $M_w$ = 627,000 g/mol     $T_g$=370K

Annealed at $T_g$+ 15-25 K for 24 hours in $N_2$



n= polymerisation index

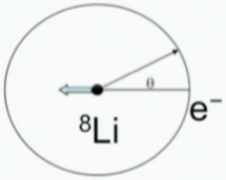


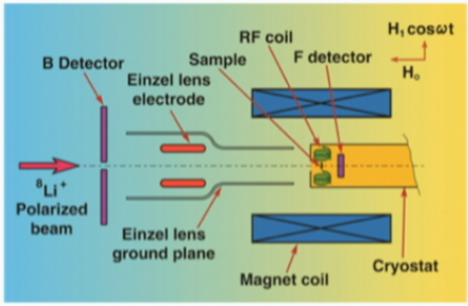
$-\!\!\left[CH_2-CH\right]\!\!-_n$

## Beta NMR

Polarization = 70%

Lifetime = 1.2s





$$\frac{1}{T_1} = \frac{7\omega_Q^2}{50}\left(1+\frac{\eta^2}{3}\right)\left[\frac{\tau_c}{1+\omega_L^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_L^2\tau_c^2}\right]$$

*Experiment is sensitive to fluctuations in the electric Quadrupole field at a frequency of $10^7$ Hz*

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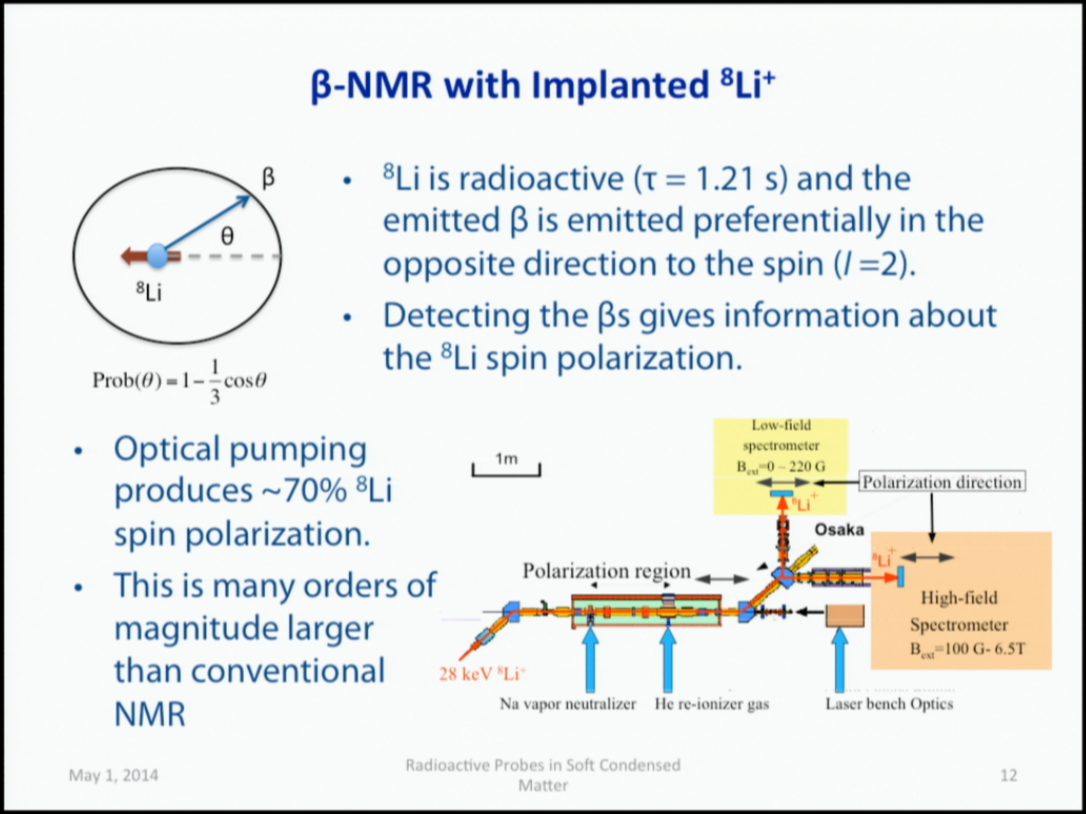
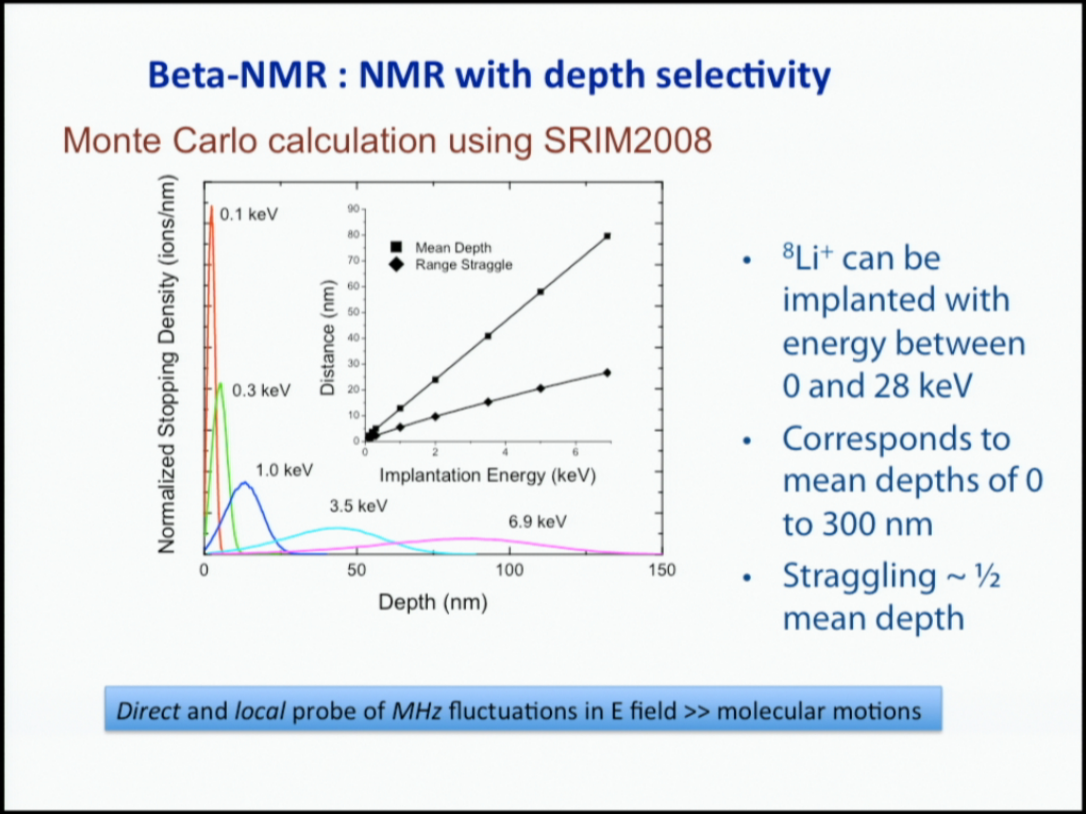


# β-NMR with Implanted $^8Li^+$

$$\mathrm{Prob}(\theta) = 1 - \frac{1}{3}\cos\theta$$

- $^8$Li is radioactive ($\tau$ = 1.21 s) and the emitted β is emitted preferentially in the opposite direction to the spin ($I$ =2).
- Detecting the βs gives information about the $^8$Li spin polarization.

- Optical pumping produces ~70% $^8$Li spin polarization.
- This is many orders of magnitude larger than conventional NMR

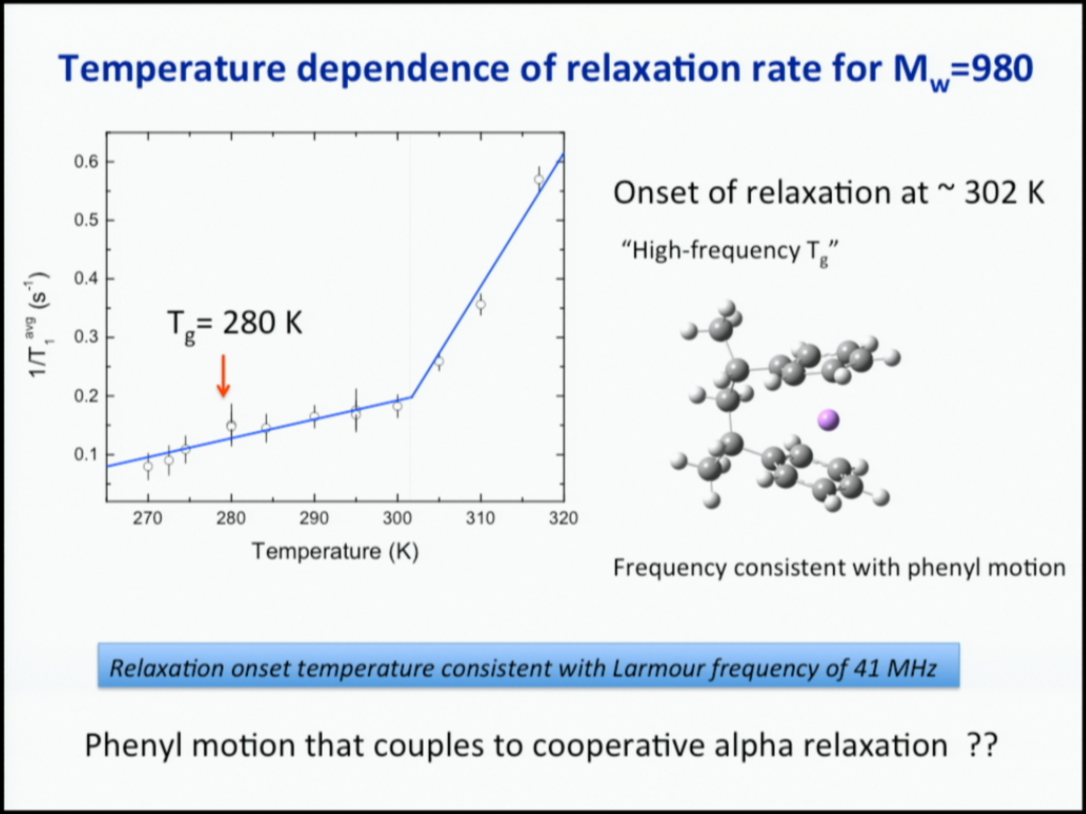


# Beta-NMR : NMR with depth selectivity

## Monte Carlo calculation using SRIM2008

- $^8Li^+$ can be implanted with energy between 0 and 28 keV
- Corresponds to mean depths of 0 to 300 nm
- Straggling ~ ½ mean depth

*Direct* and *local* probe of *MHz* fluctuations in E field >> molecular motions



## Temperature dependence of relaxation rate for $M_w$=980

Onset of relaxation at ~ 302 K

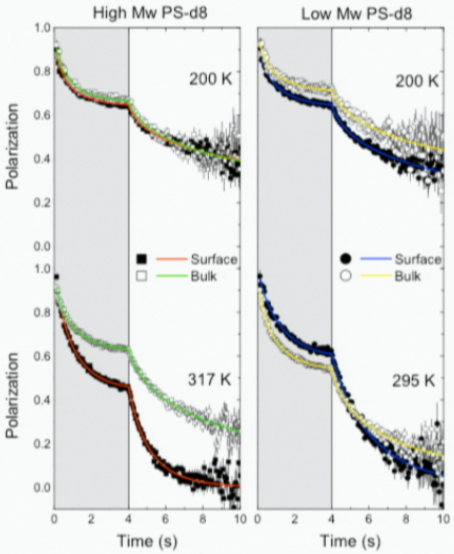
"High-frequency $T_g$"

Frequency consistent with phenyl motion

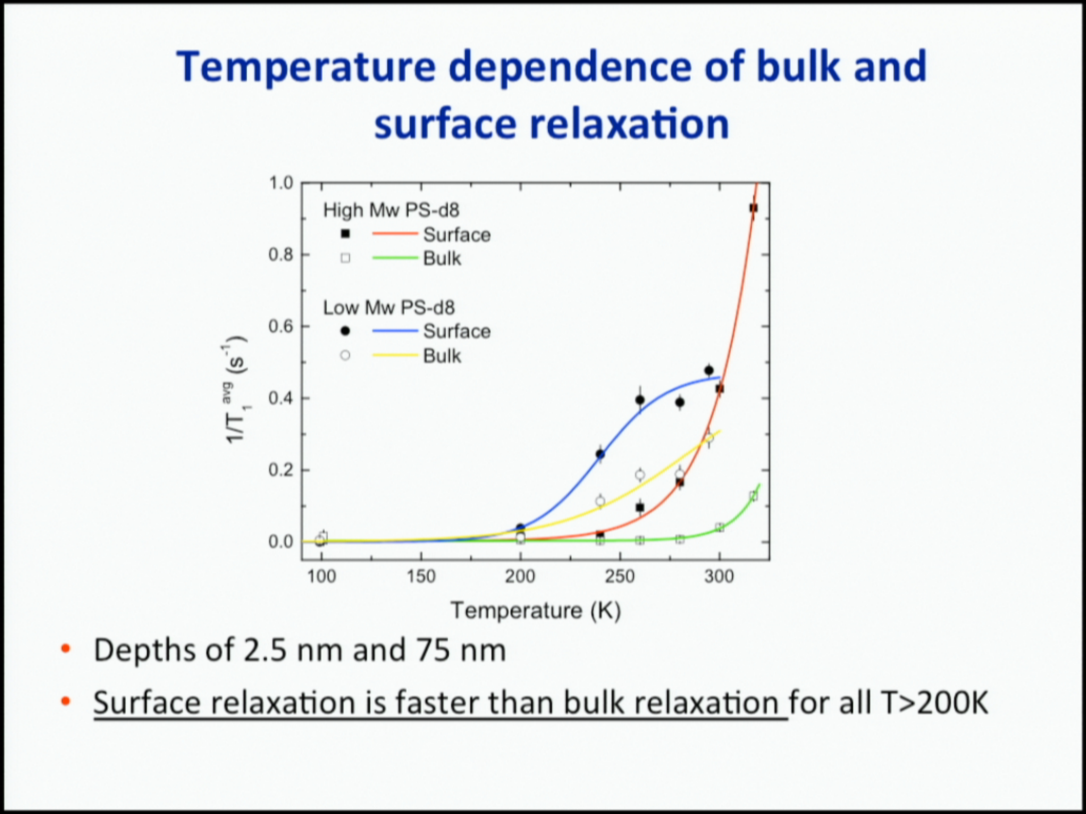
*Relaxation onset temperature consistent with Larmour frequency of 41 MHz*

Phenyl motion that couples to cooperative alpha relaxation ??

# Surface and bulk relaxation



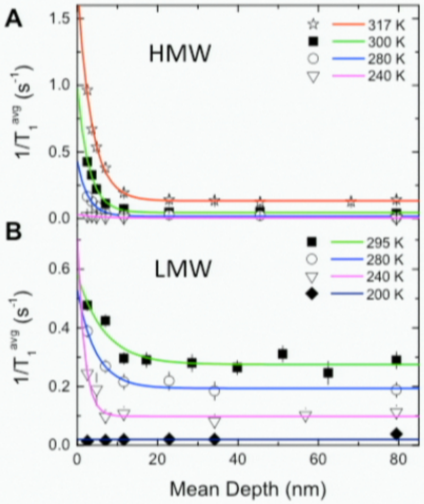
- Depths of 2.5 nm and 75 nm
- Relaxation rate at surface is faster than that in the interior of the sample



# Temperature dependence of bulk and surface relaxation

- Depths of 2.5 nm and 75 nm
- Surface relaxation is faster than bulk relaxation for all T>200K

# Depth dependence of enhanced relaxation



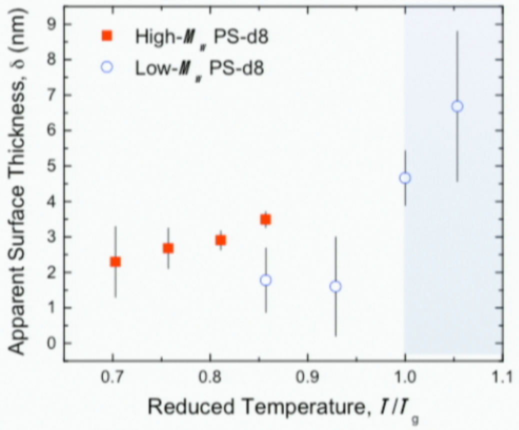
- Vary depth by varying energy of Li probe
- Expect to probe reasonable narrow range

- Relaxation rate R(z) monotonically approaches bulk value as distance from free surface increases

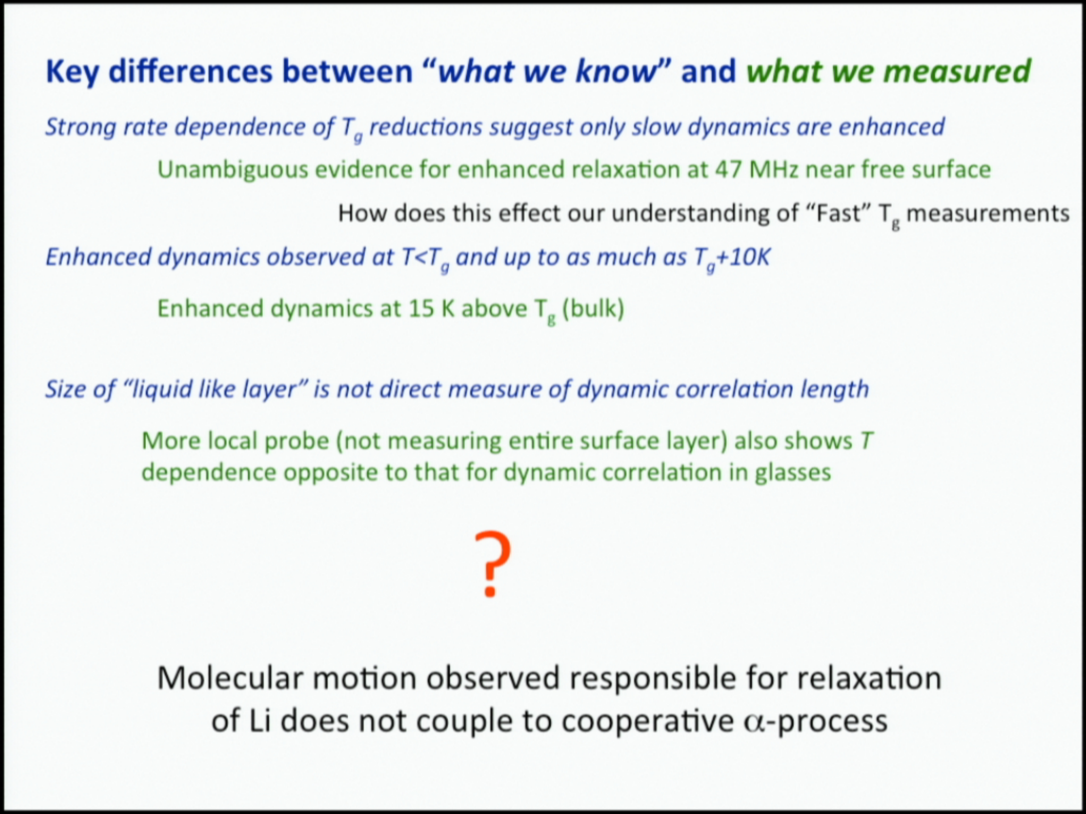
- Local probe, NOT liquid layer

$$R(z) = R(bulk) + (R(0) - R(bulk))e^{-\frac{z}{z*}}$$

# Temperature dependence of z*



- Surface correlation length similar to observations of surface liquid layer
- Z* increases with temperature
- Surface enhancement of dynamics even in the liquid above $T_g$



## Key differences between "*what we know*" and ***what we measured***

*Strong rate dependence of $T_g$ reductions suggest only slow dynamics are enhanced*

Unambiguous evidence for enhanced relaxation at 47 MHz near free surface

How does this effect our understanding of "Fast" $T_g$ measurements

*Enhanced dynamics observed at $T<T_g$ and up to as much as $T_g$+10K*

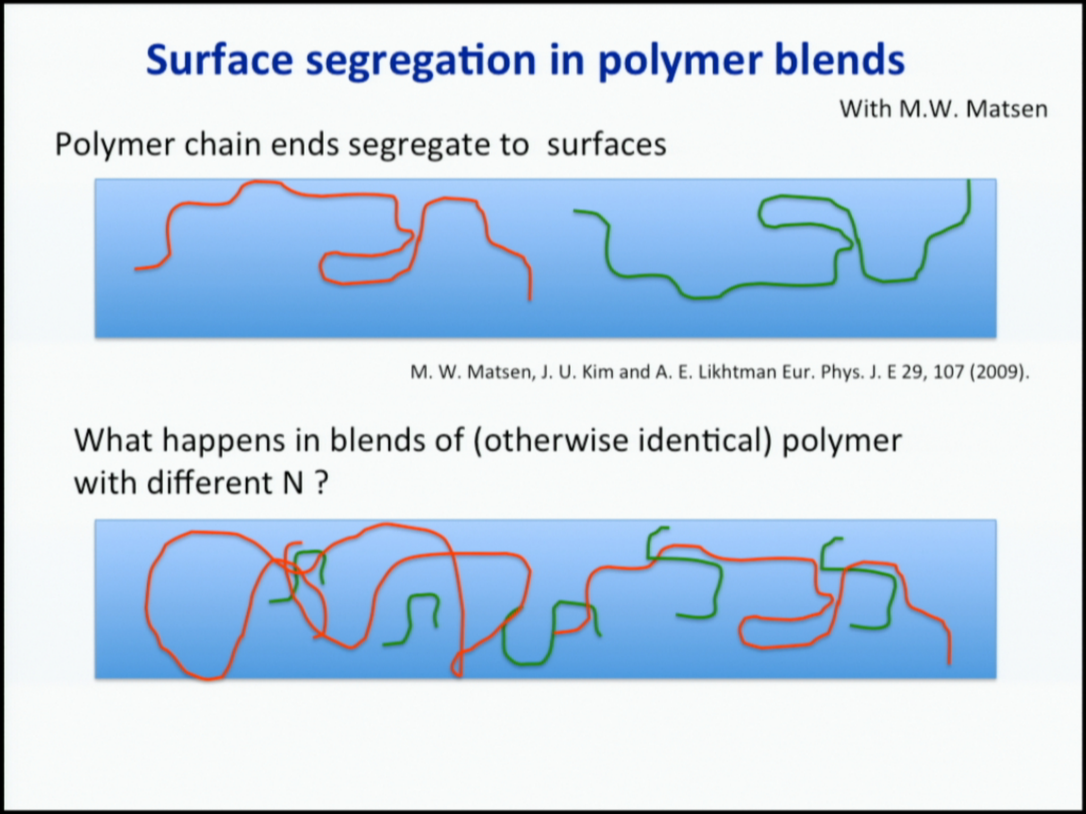
Enhanced dynamics at 15 K above $T_g$ (bulk)

*Size of "liquid like layer" is not direct measure of dynamic correlation length*

More local probe (not measuring entire surface layer) also shows *T* dependence opposite to that for dynamic correlation in glasses

?

Molecular motion observed responsible for relaxation of Li does not couple to cooperative $\alpha$-process



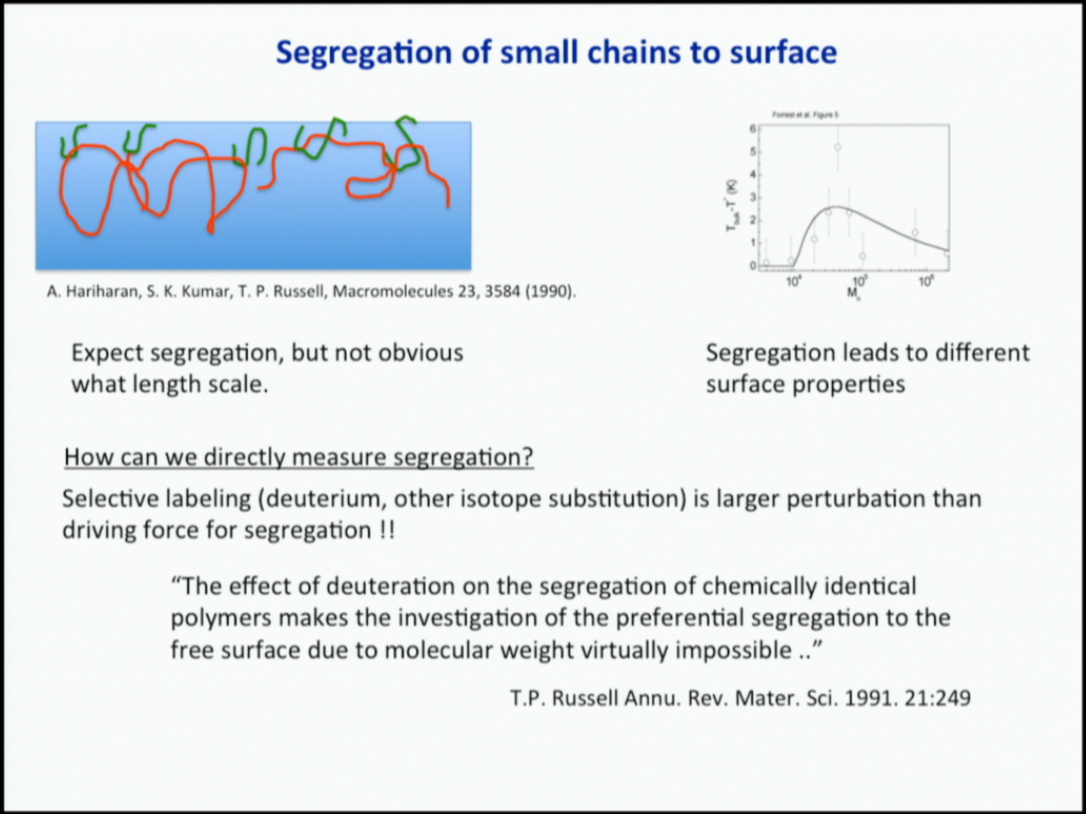
## Surface segregation in polymer blends

With M.W. Matsen

Polymer chain ends segregate to surfaces

M. W. Matsen, J. U. Kim and A. E. Likhtman Eur. Phys. J. E 29, 107 (2009).

What happens in blends of (otherwise identical) polymer with different N ?



# Segregation of small chains to surface

A. Hariharan, S. K. Kumar, T. P. Russell, Macromolecules 23, 3584 (1990).

Expect segregation, but not obvious what length scale.

Segregation leads to different surface properties

How can we directly measure segregation?

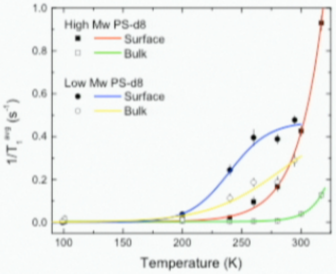
Selective labeling (deuterium, other isotope substitution) is larger perturbation than driving force for segregation !!

> "The effect of deuteration on the segregation of chemically identical polymers makes the investigation of the preferential segregation to the free surface due to molecular weight virtually impossible .."

T.P. Russell Annu. Rev. Mater. Sci. 1991. 21:249

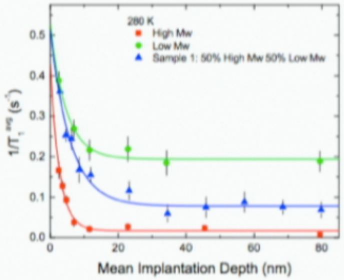
# Impossible?

Notice difference between relaxation rate for LMW and HMW



Introduces a depth dependent ***natural contrast mechanism*** between LMW and HMW polymers

Can look at segregation of LMW polymer in blends of LMW and HMW

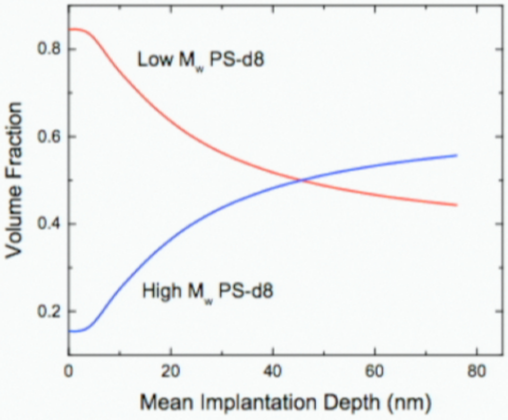


- At small depth relaxation rate is same as LMW
- At large depth relaxation rate ~ average

New method for measuring segregation of LMW chains in binary blends

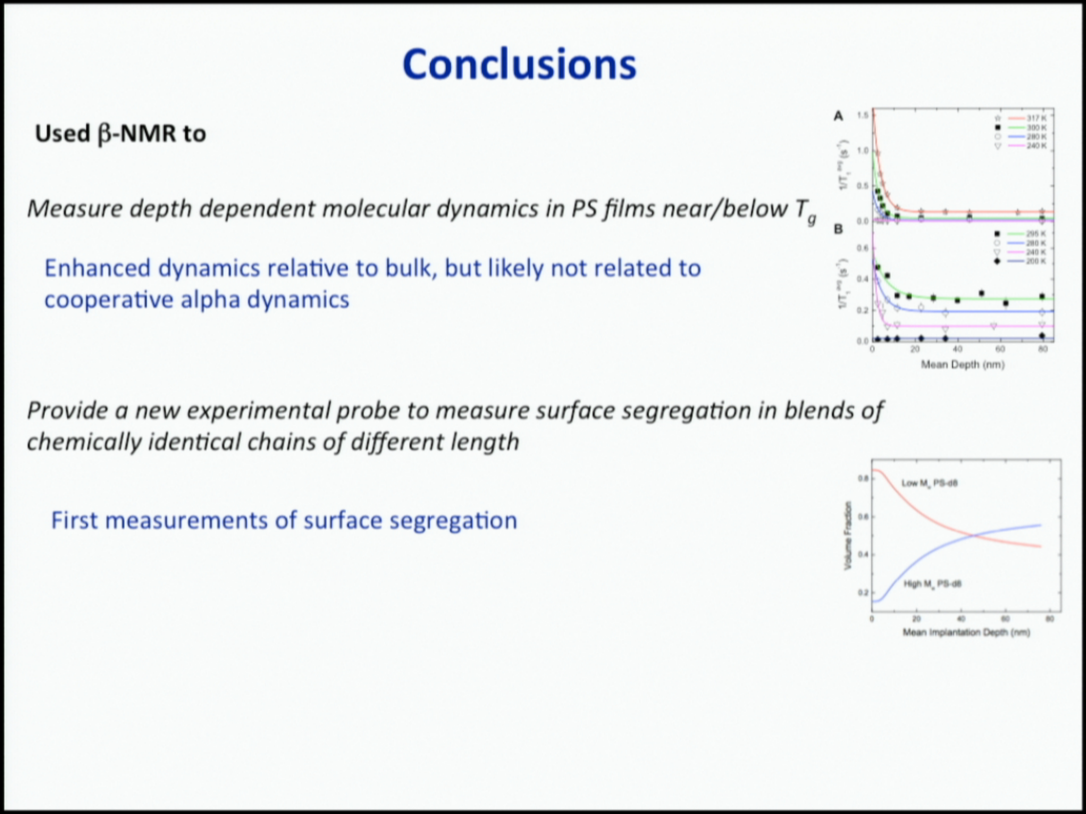
# Quantifying segregation

$$T^{-1}(z) = \alpha_L(z) T_L^{-1}(z) + (1 - \alpha_L(z)) T_H^{-1}(z)$$



*First quantitative measurements of segregation in blends of same polymers with different N*

Full experiment scheduled for August 2014!



# Conclusions

**Used β-NMR to**

*Measure depth dependent molecular dynamics in PS films near/below $T_g$*

Enhanced dynamics relative to bulk, but likely not related to cooperative alpha dynamics

*Provide a new experimental probe to measure surface segregation in blends of chemically identical chains of different length*

First measurements of surface segregation


EXIT
RESERVED
RESERVED
RESERVED
RESERVED