TEXAS TECH UNIVERSITY
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Free volume, configurational entropy and other aspects of the glass transition: Perspectives from an engineering/experimental view

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Are Glasses Important?

- Search Term: ‘Glass’
  - 90 363 from 1987 to 2000
  - 65,301 from 2001 to 2005
  - 65,698 from 2006 to 2010
- **=221,362 hits vs. 938,000,000 Yahoo**

- Search Term: ‘Polymer Glass’
  - **24,899** from 1987-2010 vs. **12,800,000 Yahoo**

The Simple Free Volume Model: Doolittle and Ferry

- Doolittle

$$\text{Ln}\ \eta = \ln A + B(v-v_f)/v_f$$

$v_f = v - v_0$ free space or free volume

$v_0 =$ ‘limiting specific volume’ (modern is occupied volume)

→ describes simple liquids

The Simple Free Volume: Ferry and Williams, Landel and Ferry

- The WLF equation

  $v_f = v_g\,[0.025 + \Delta\alpha(T-T_g)]$

  Where v_f is the free volume and it is linear in temperature from a 'critical value' at T_g to temperature T.

- For polymers (and more generally other materials) the reduced viscosity (temperature shift factor) can be written as:

  $a_T = [\eta(T)T_{ref}\,\rho(T)/\eta_{ref}T\rho_{ref}$

Ferry/WLF con't.

$\log a_T = \log [\eta(T)/\eta_{ref}] + \log [T_{ref}\, \rho_{ref}/T\rho(T)]$

And they found that the data could be fit very well with an equation of the form:

$\log a_T = -C_1(T-T_{ref})/(C_2+T-T_{ref})$

and if $T_g = T_{ref}$

$\log a_T = -C_1(T-T_g)/(C_2+T-T_g)$

Ferry / WLF con't.

Ferry defined the fractional free volume f as

$f = f_0 + \alpha_f\,(T - T_{ref})$

Combining with the Doolittle equation for free volume, the temperature dependence of free volume and the definitions of the shift factor for viscosity (reduced viscosity) WLF found:

$\log a_T = -[(B/(2.303f_0))(T-T_{ref})]/(f_0/\alpha_f + T-T_{ref})$

Ferry / WLF con't.

Relating free volume parameters to WLF equation parameters:

$C_1 = B/(2.303f_0)$
$C_2 = f_0/\alpha_f$

If the reference condition is the glass temperature, then the free volume at the T_g is

$f_g = B/(2.303C_1^g)$

Ferry / WLF Con’t.

- Relations between WLF and VFT parameters

$C_1^g = B/[2.303(T_g – T_0)]$

$C_2^g = T_g – T_0$

Why are we interested in free volume theory and why does it have such 'staying' power?

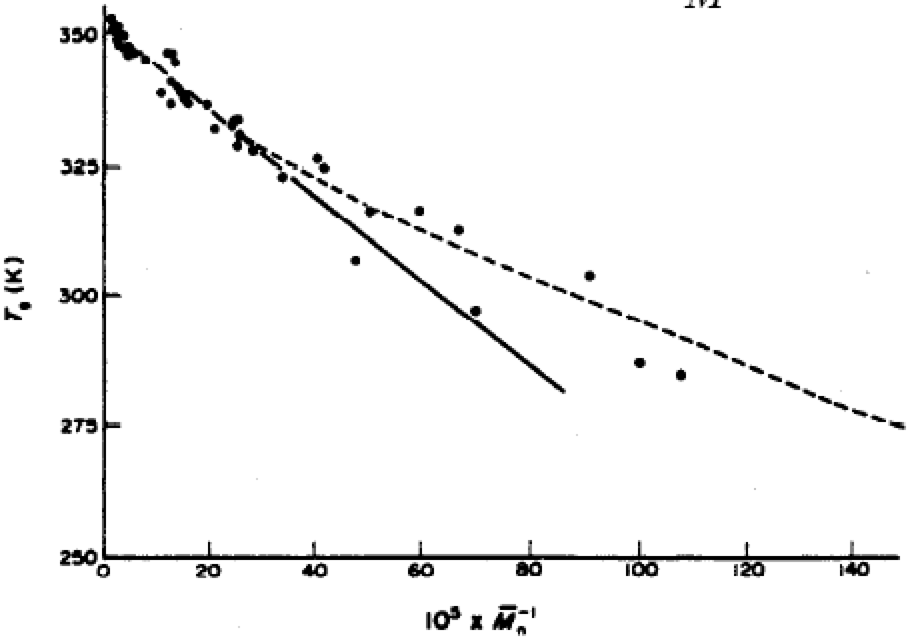
- It is at a minimum descriptive of experimental observations of interest to scientists and, especially, engineers.
  - Effect molecular weight on T_g
  - Temperature dependence of viscosity
  - Composition dependence of T_g
  - Effect of pressure on T_g

Free volume ‘predictions’

- Effect of molecular weight on T_g

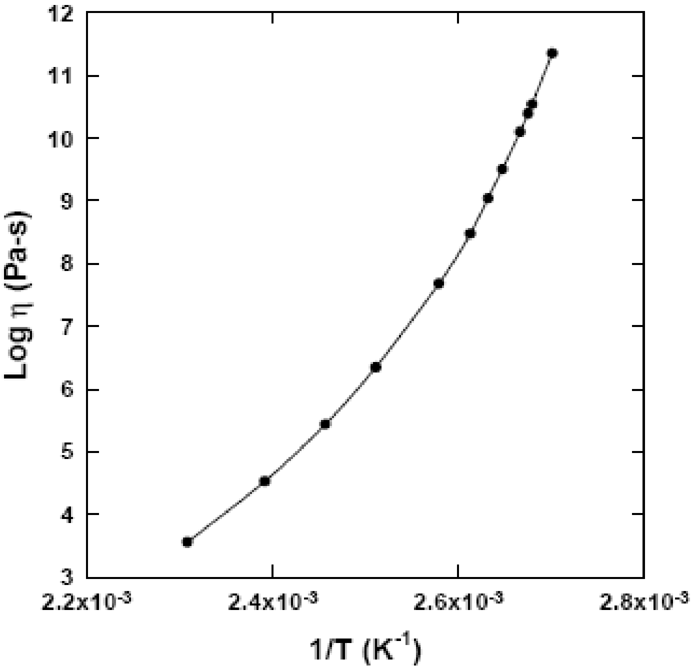
Chain ends are sites of higher free volume and T_g is predicted to vary as $1/M_n$

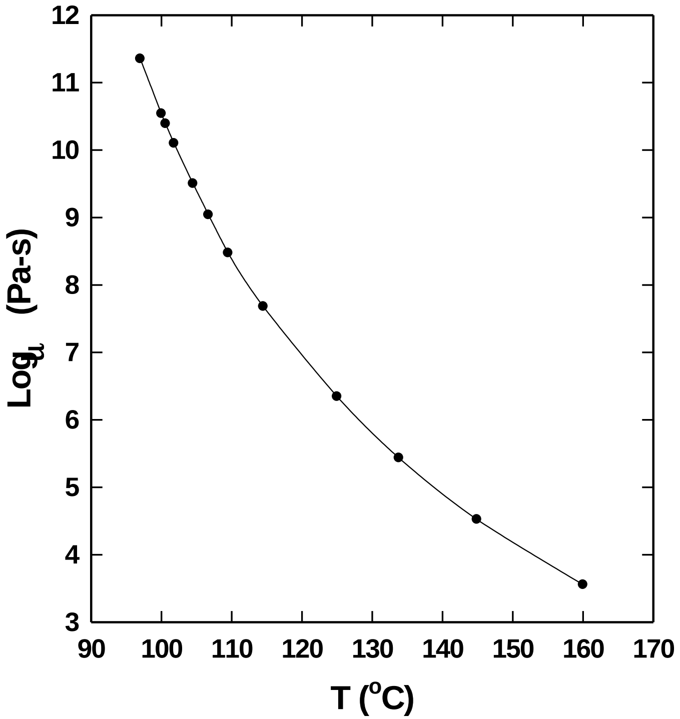
Fox-Flory Equation $$T_g(M) = T_g(\infty) - \frac{K}{M}$$



Free volume ‘predictions’

- Temperature dependence of viscosity



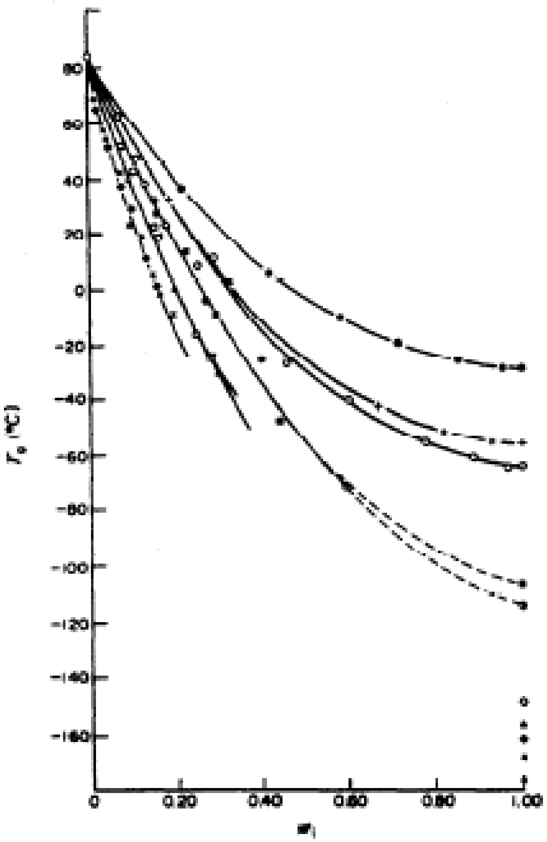


Free volume ‘predictions’

In the presence of a diluent. Subscripts d and p refer to diluent and polymer, respectively

Interaction parameter

$$T_g(v_1) = \frac{v_1 \alpha_{r1} T_{g1} + v_2 \alpha_{r2} T_{g2} + k'_v v_1 v_2}{v_1 \alpha_{r1} + v_2 \alpha_{r2}}$$



Free volume ‘predictions’

- T_g is predicted to increase as pressure increases due to compression of free volume. But, if the dT_g/dP is pressure dependent, which T_g should be used?

Free volume ‘predictions’

- Entropy part of ‘thermodynamic surface’ is poorly predicted—at least by the Simha-Somcynsky cell model (a free volume theory).

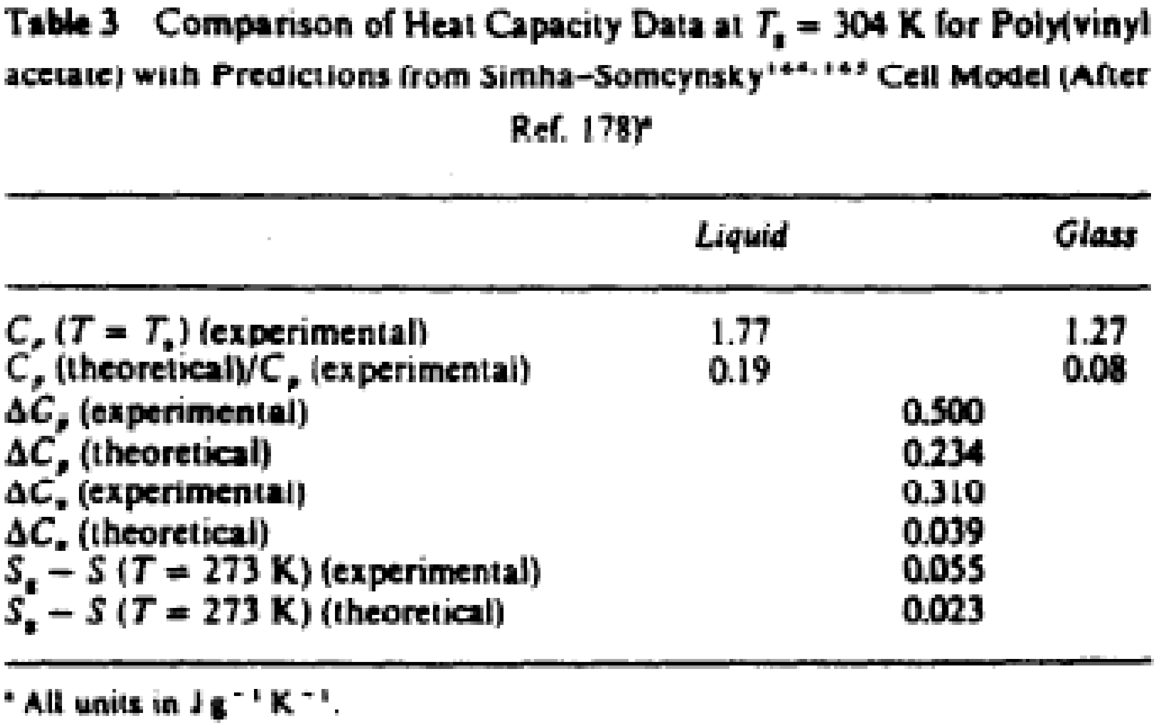


Table 3 Comparison of Heat Capacity Data at $T_g = 304$ K for Poly(vinyl acetate) with Predictions from Simha–Somcynsky[144,145] Cell Model (After Ref. 178)[a]

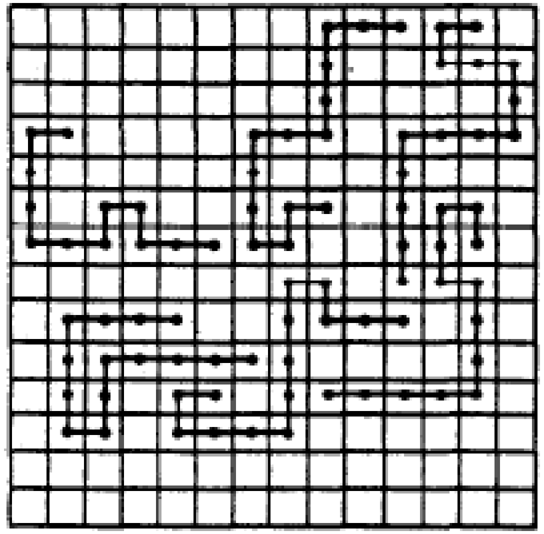
	Liquid		*Glass*
C_p ($T = T_g$) (experimental)	1.77		1.27
C_p (theoretical)/C_p (experimental)	0.19		0.08
ΔC_p (experimental)		0.500	
ΔC_p (theoretical)		0.234	
ΔC_v (experimental)		0.310	
ΔC_v (theoretical)		0.039	
$S_g - S$ ($T = 273$ K) (experimental)		0.055	
$S_g - S$ ($T = 273$ K) (theoretical)		0.023	

[a] All units in $J\,g^{-1}\,K^{-1}$.

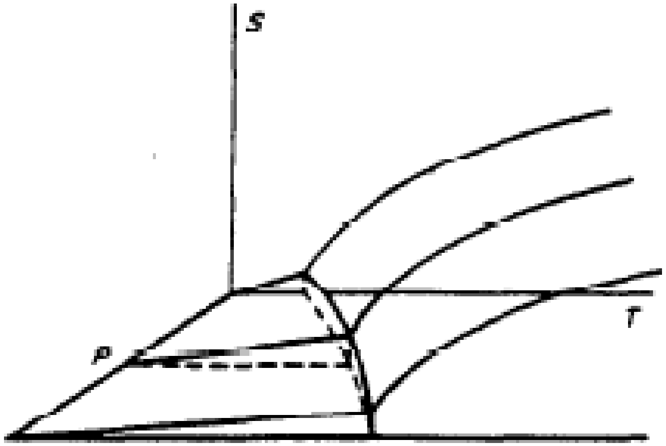
Configurational entropy model of Gibbs and DiMarzio

- Based on the Flory-Huggins lattice model with addition of hole energy and bond-flex energy.
  - Originally the GD work found that there may be an ideal glass transition at T_2, which they found was the point of zero configurational entropy.
  - Then from the lattice model, one has the tools to calculate the change of T_g with molecular weight, composition, etc.
- Later, Adam and Gibbs made the ansatz that the relaxation time should vary inversely with the configurational entropy giving an equation similar to the VFT equation.
- Interestingly, the GD equation, which includes a free volume term (emty site fraction) gives a fractional free volume of 0.025 at the T_g.

Gibbs-DiMarzio



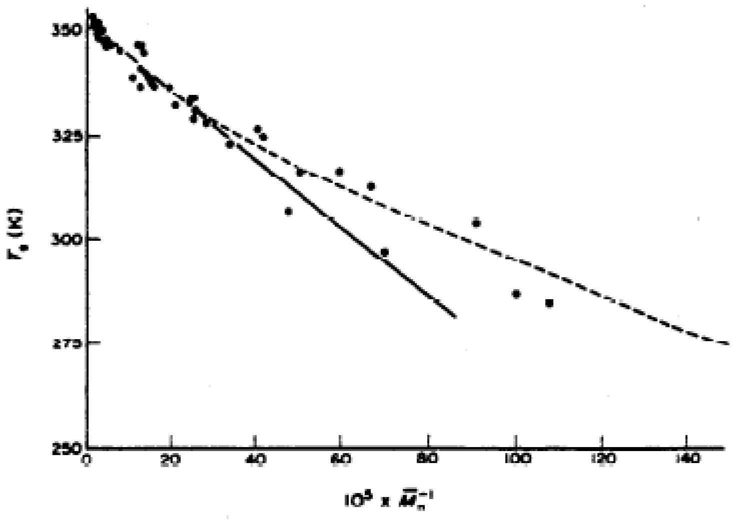
Flory-Huggins extended lattice model



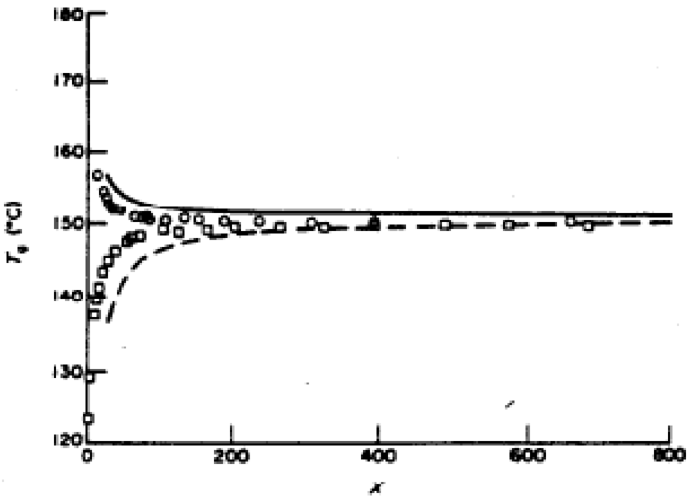
Second order thermodynamic transition in the Ehrenfest sense.

Gibbs-DiMarzio predictions

- Molecular weight and architecture dependences:



Linear chains



Rings and linear chains

Gibbs-DiMarzio Predictions

- Composition dependence of T_g

$$T_g(x) = \frac{x T_{g1} + (1 - x) T_{g2} (\Delta C_{p2} / \Delta C_{p1})}{x + (1 - x)(\Delta C_{p2} / \Delta C_{p1})}$$

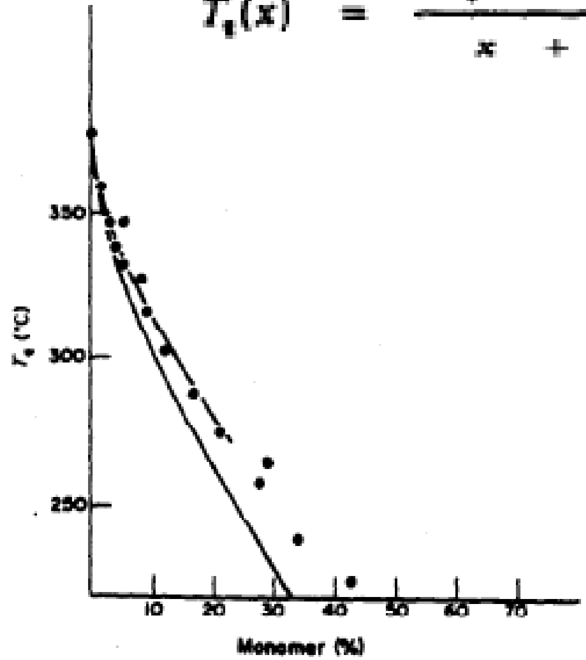
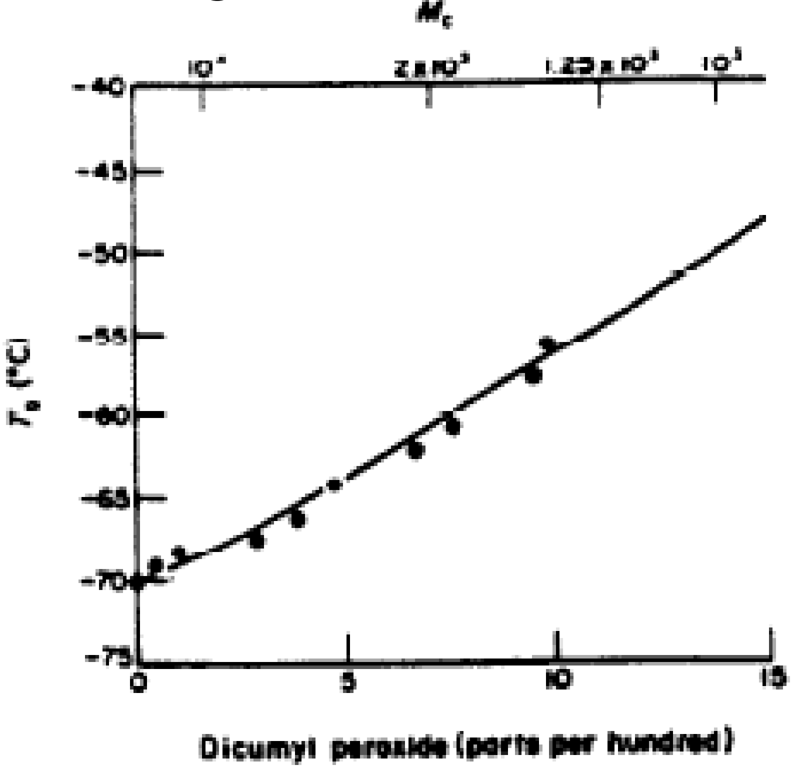


Figure 19 Variation of glass transition temperature with composition for solutions of polystyrene in styrene monomer. The lines represent calculations from the Gibbs–DiMarzio lattice model: upper line calculation allows for 'holes' while the lower one does not (after ref. 25, with permission)

Gibbs-DiMarzio predictions

- Crosslink dependence of T_g

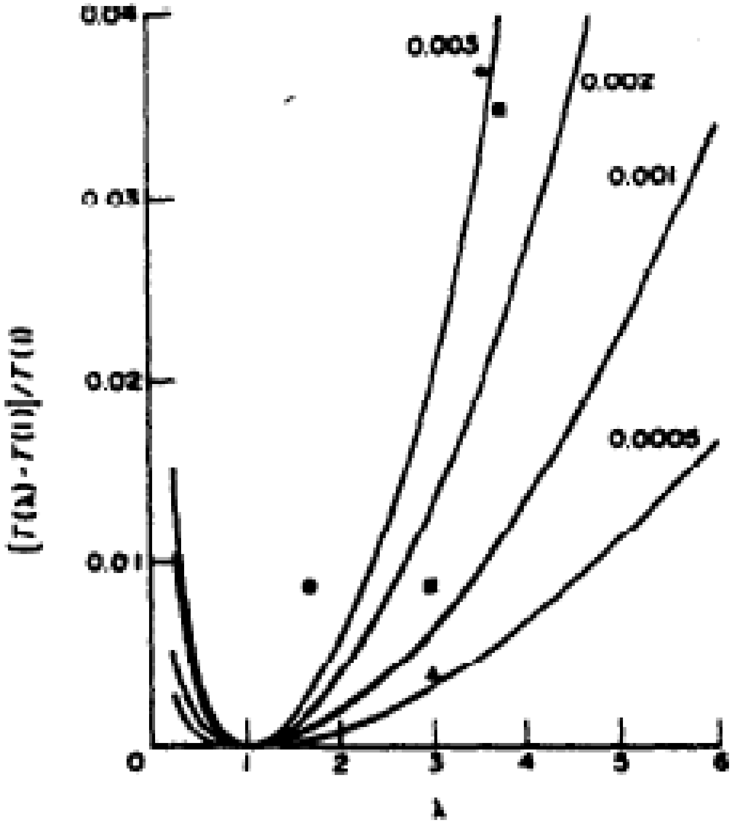
$$\frac{T(\chi) - T(0)}{T(0)} = \frac{K M \chi/\gamma}{1 - K M \chi/\gamma}$$



Gibbs-DiMarzio predictions

- Deformation dependence of T_g

$$\frac{T(\lambda)}{T(1)} = \exp\left[\frac{G}{2\Delta C_p T_0}[I_1 - 3]\right]$$



Gibbs-DiMarzio predictions

- Heat capacity change at T_g .

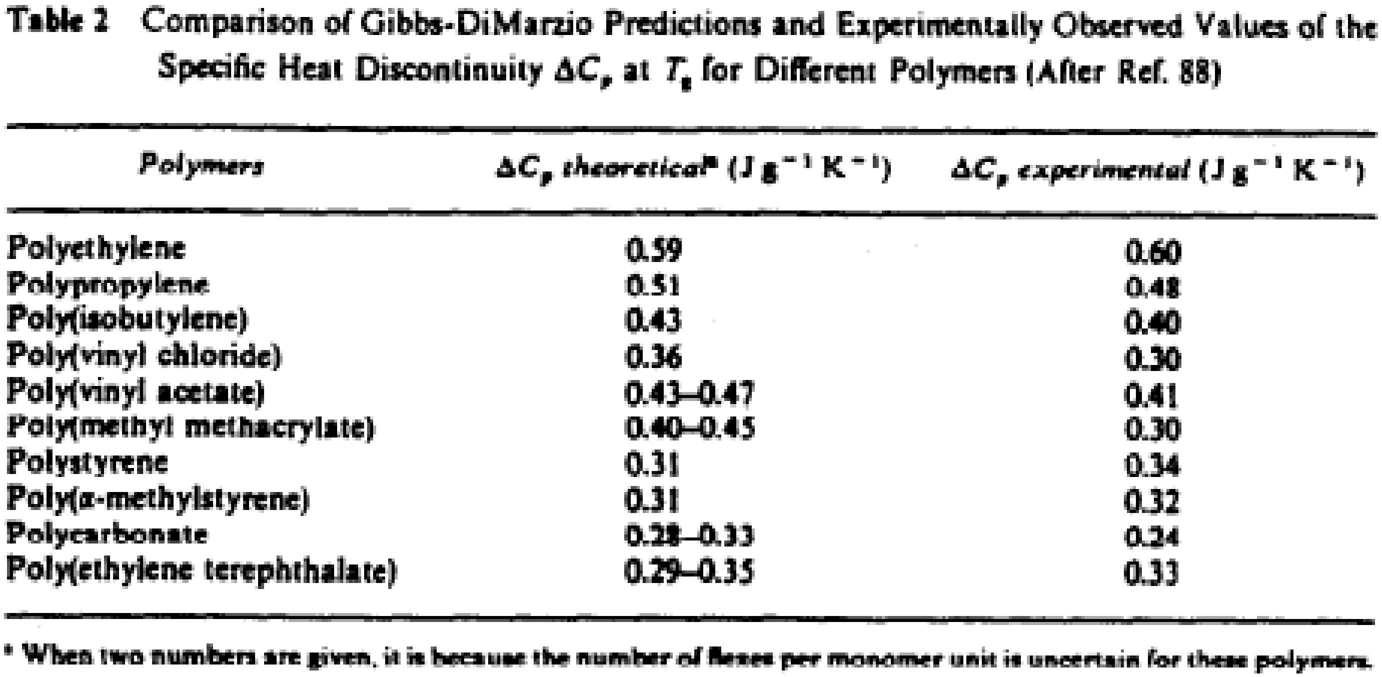


Table 2 Comparison of Gibbs-DiMarzio Predictions and Experimentally Observed Values of the Specific Heat Discontinuity ΔC_p at T_g for Different Polymers (After Ref. 88)

Polymers	ΔC_p *theoretical*[a] ($J\,g^{-1}\,K^{-1}$)	ΔC_p *experimental* ($J\,g^{-1}\,K^{-1}$)
Polyethylene	0.59	0.60
Polypropylene	0.51	0.48
Poly(isobutylene)	0.43	0.40
Poly(vinyl chloride)	0.36	0.30
Poly(vinyl acetate)	0.43–0.47	0.41
Poly(methyl methacrylate)	0.40–0.45	0.30
Polystyrene	0.31	0.34
Poly(α-methylstyrene)	0.31	0.32
Polycarbonate	0.28–0.33	0.24
Poly(ethylene terephthalate)	0.29–0.35	0.33

[a] When two numbers are given, it is because the number of flexes per monomer unit is uncertain for these polymers.

A bit of summary/conclusion

- The ability to make predictions or descriptions of the glass transition behavior of polymers is a very useful feature of both free volume models and the Gibbs-DiMarzio model. Their ‘correctness’ in this sense is not an issue as is the fact that they are very useful. They are clearly not the definitive answer to what the nature of glass formation and glassy behavior are.

A pot-pourri of other issues

- Some thoughts on dynamic fragility

Dynamic Fragility

- The temperature dependence of the viscosity or segmental relaxation time as T_g is approached.
- Here, we use the dynamic fragility m.

$$m \equiv \left. \frac{d \log \tau}{d(T_g / T)} \right|_{T=T_g} = \frac{BT_g}{(T_g - T_\infty)^2}$$

Does m really correlate with the heat capacity jump at T_g?

Inorganic Liquids: m vs $C_{p,l}/C_{p,c}$

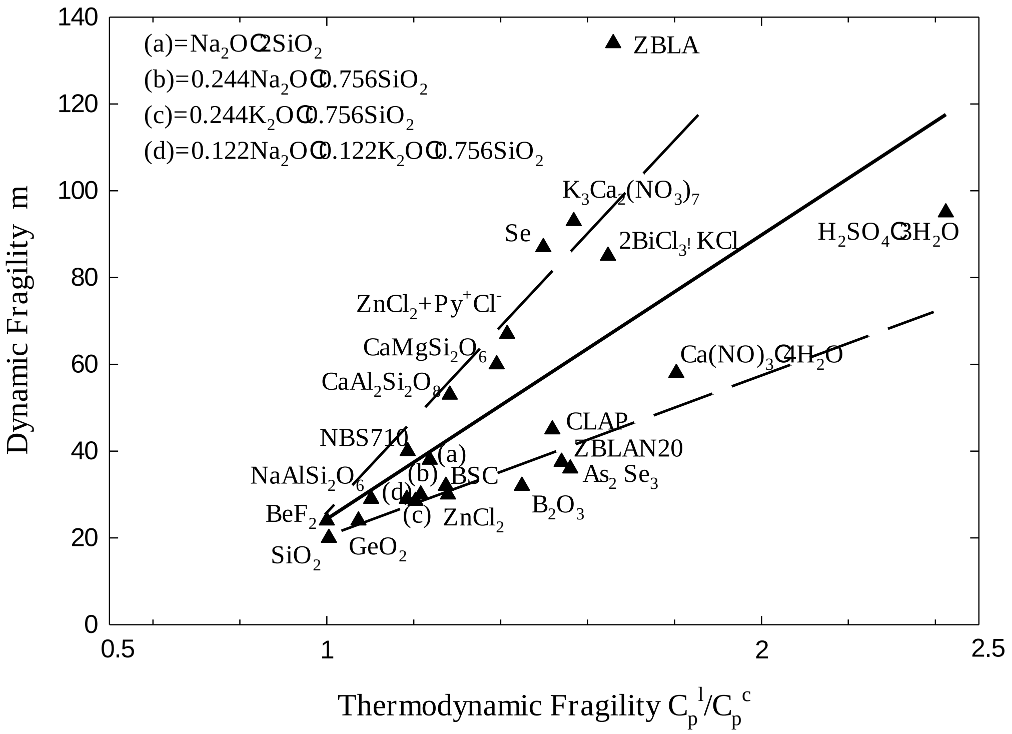


Figure 6. Huang and McKenna

Does m really correlate with the heat capacity jump at T_g?

Polymers: m vs $C_{p,l}$/ $C_{p,g}$

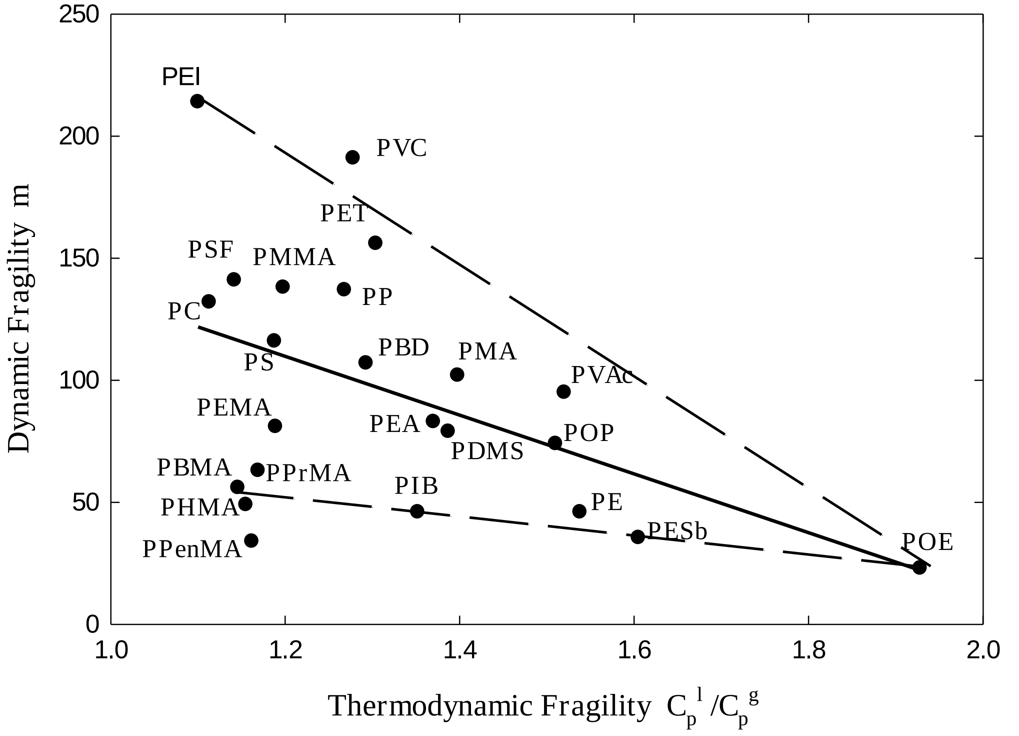


Figure 3. Dynamic fragility vs. thermodynamic fragility for 23 glass forming polymer liquids. Center line is linear regression on the data. Top and bottom lines suggest bounds on behavior--as guide to eye.

Huang and McKenna

Dynamic fragility and the glass temperature*

*Q. Qin and G.B. McKenna, J. Non-Crystalline Solids, 352, 2977-2985 (2006)

$$\text{For the WLF equation: } \log a_T = \frac{-C_1(T - T_{\mathrm{ref}})}{C_2 + T - T_{\mathrm{ref}}} \tag{6}$$

$$m = \left(\frac{\mathrm{d}\log a_T}{\mathrm{d}(T_{\mathrm{g}}/T)}\right)_{T=T_{\mathrm{g}}} = \frac{C_1^g T_{\mathrm{g}}}{C_2^g} \tag{7}$$

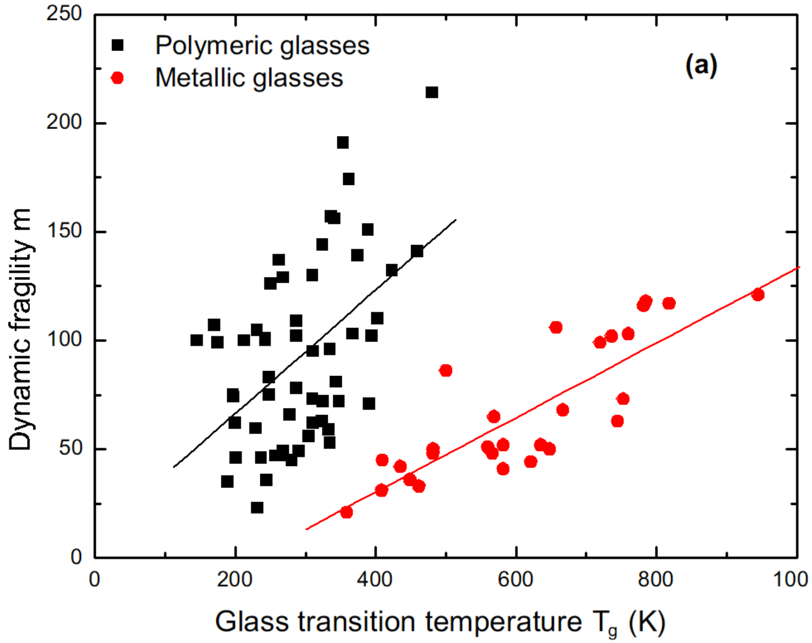
$$E_g = \ln 10 R \frac{C_1^g}{C_2^g} T_g^2 \tag{8}$$

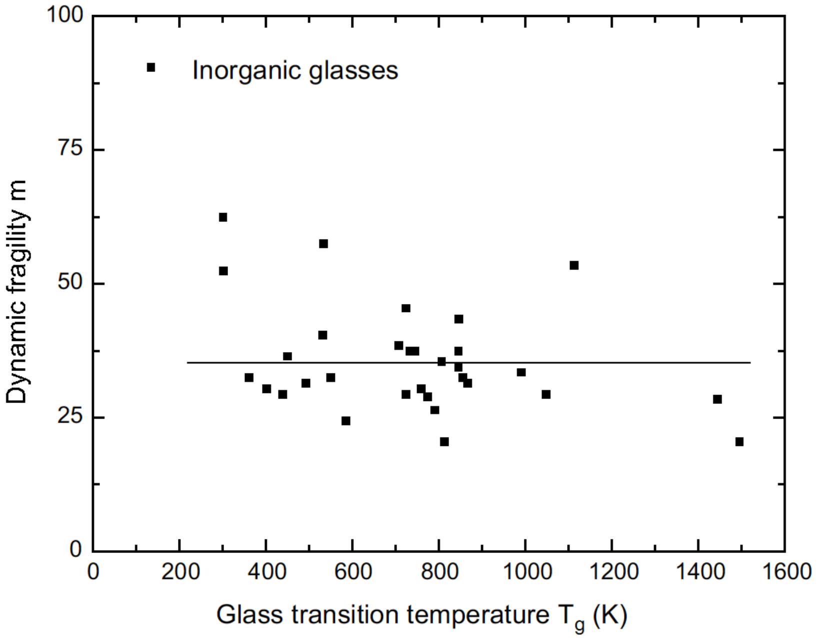
→ m should be linear in T_g and
E_g should vary as T_g^2

Remarks: WLF and VFT are equivalent
At VFT T_0 $m=\infty$ for all systems

Based on Eq. (7), the WLF equation suggests that m should be nearly linear in T_{g}. If the ‘universal’ WLF parameters for polymers are used $(C_1^g = 17.44, C_2^g = 51.6\ \mathrm{K}$ [24]), a simple relation would be achieved theoretically as $m \approx 0.34T_{\mathrm{g}}$. We examine this result subsequently.

Dynamic fragility vs. Glass temperature



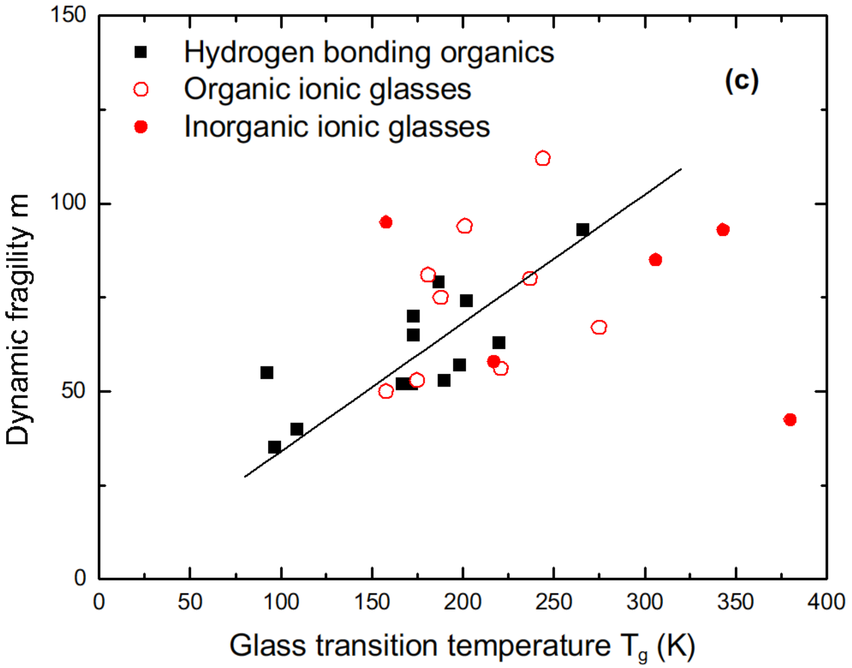


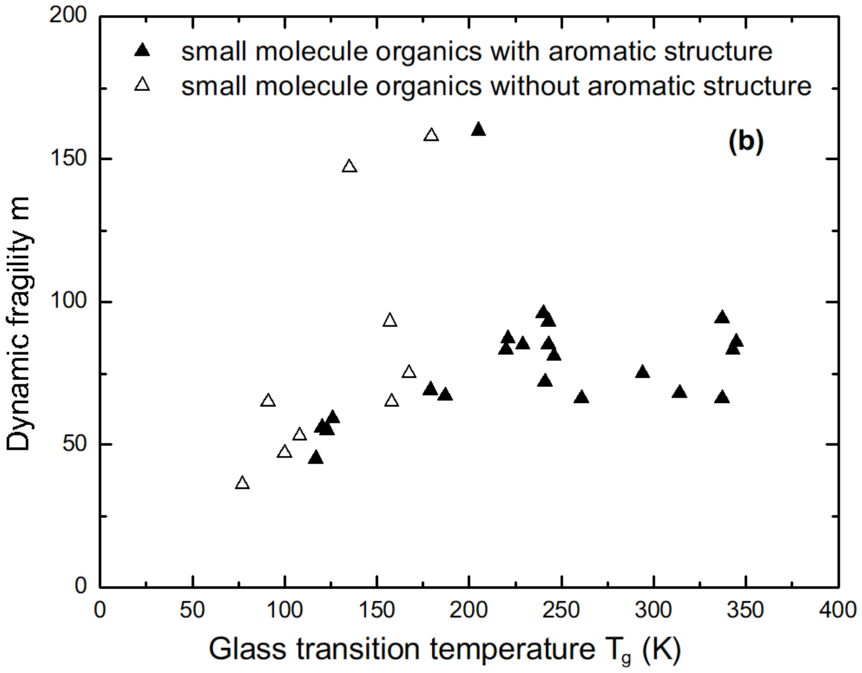
Slope_{poly} =0.28+/-0.07

Slope_{met} =0.17+/-0.02

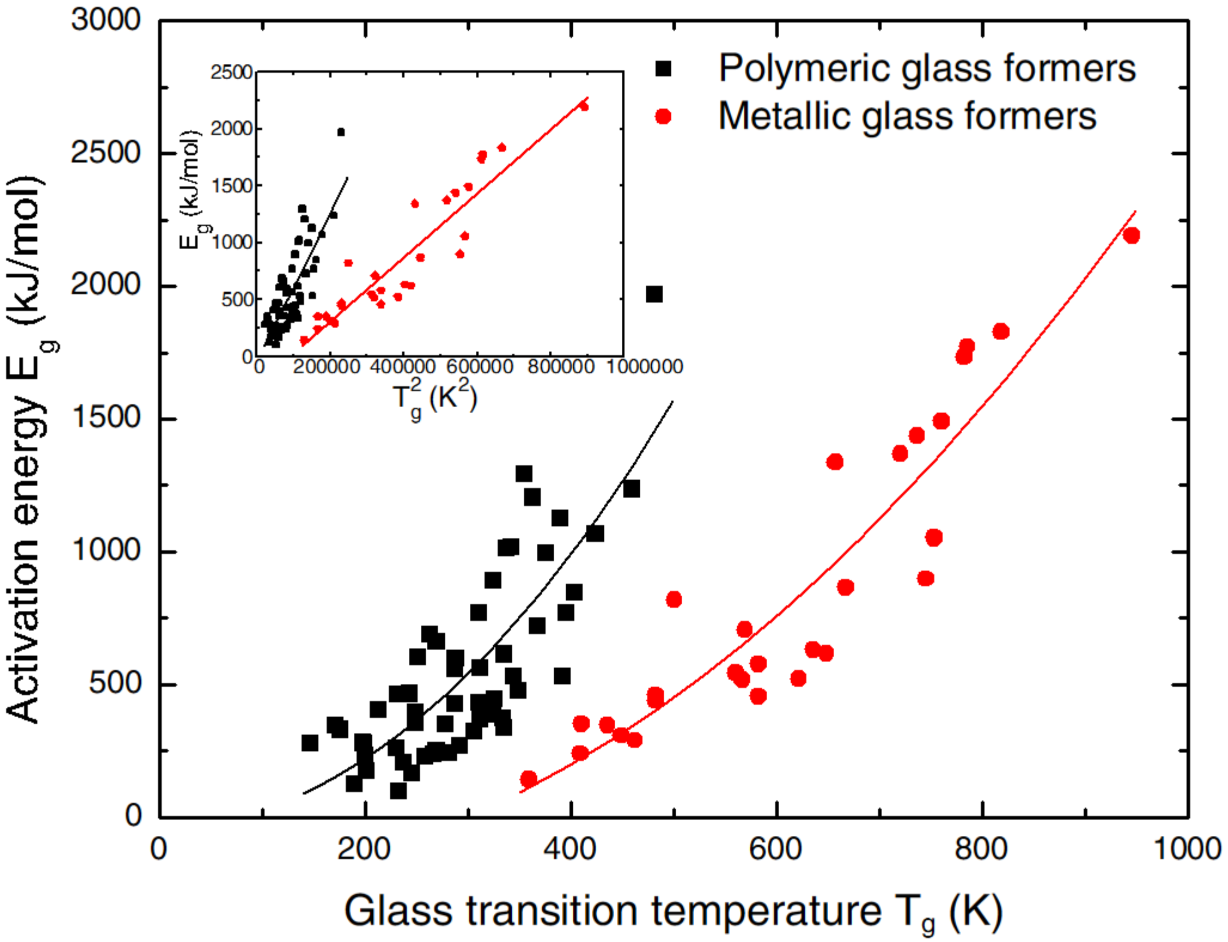
Slope_{inor} =0

Dynamic fragility vs. Glass temperature



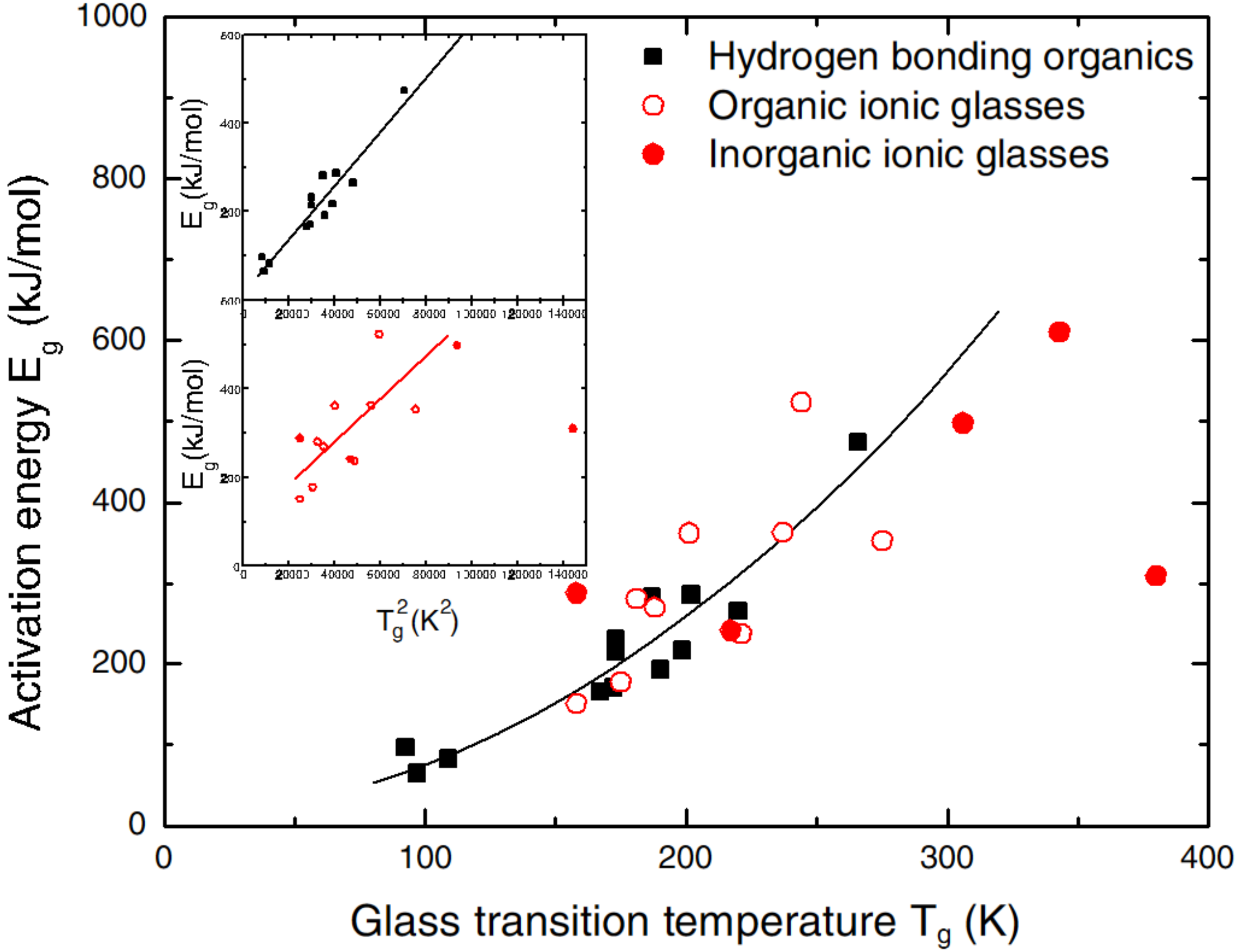


$\text{Slope}_{\text{H-bond}} = 0.25 +/- 0.06$

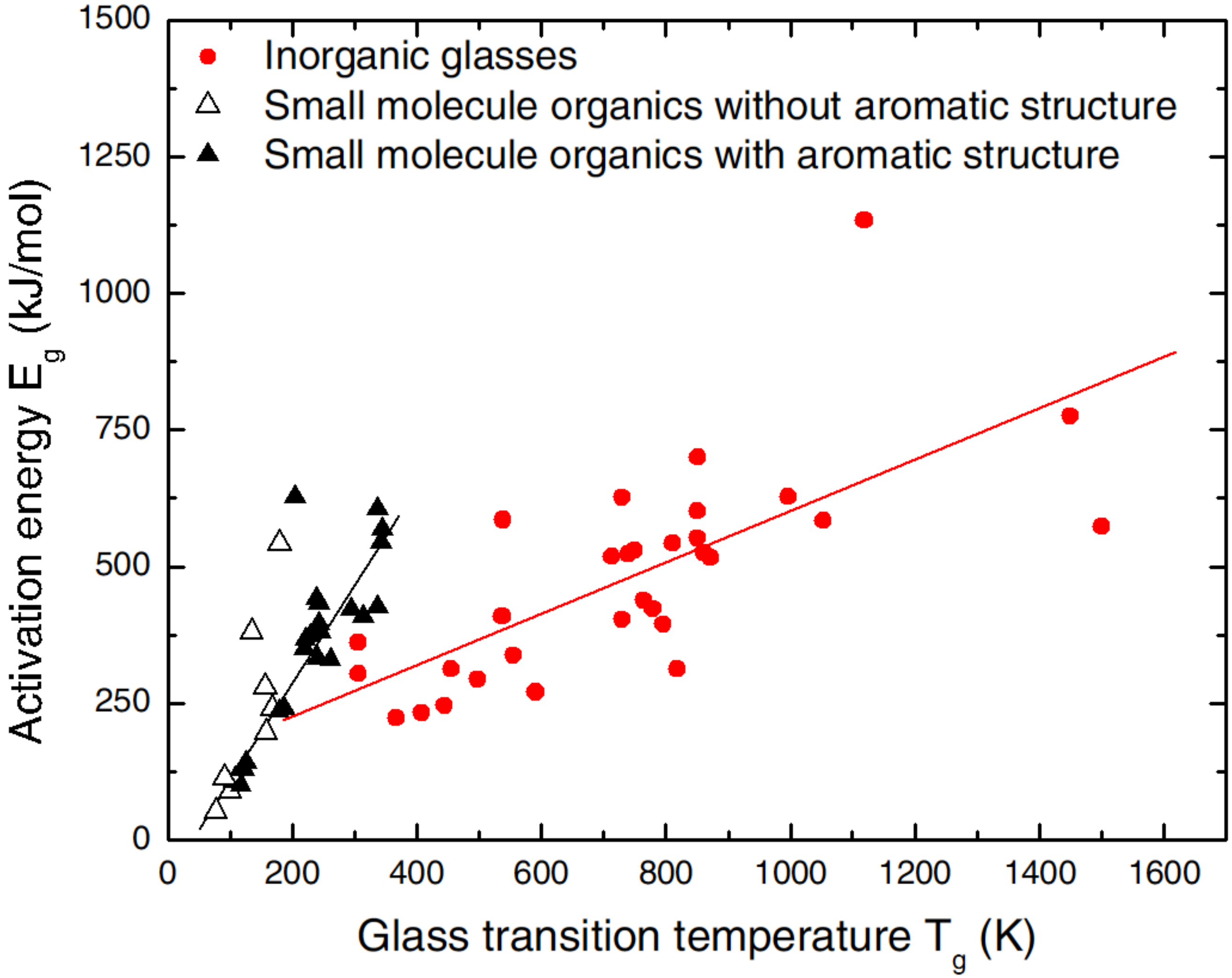


Polymer and Metallic glass-formers follow WLF-prediction very well:

E_g varies as T_g^2



Hydrogen bonding organic and ionic glass-formers follow WLF-prediction very well: E_g varies as T_g^2



Inorganic glass-formers and non-hydrogen bonding small molecule Organics do not follow WLF-prediction: E_g varies linearly in T_g

Summary and Conclusions

- ***m varies linearly in T_g and E_g varies as T_g^2 for polymeric, metallic, ionic, and hydrogen bonding organic glass-formers.***
- ***m is nearly independent of T_g and E_g varies linearly in T_g for inorganic and non-hydrogen bonding organic glass-formers.***

Summary and Conclusions

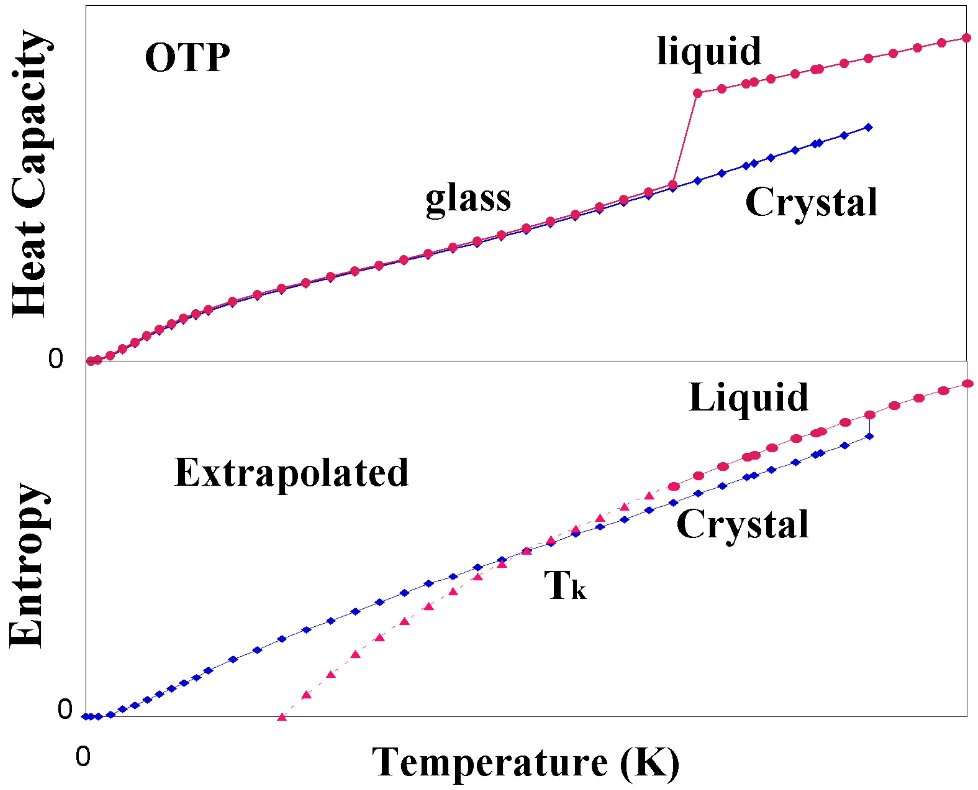
- ***Dynamic fragility is not a true descriptor of the temperature dependence or super-Arrhenius behavior of glass-forming liquids. It seems to "work" for the inorganic and non-hydrogen bonding organics because E_g is linear in T_g for these systems.***
- ***A better descriptor of the temperature dependence of glass-forming liquids is the apparent activation energy E_g at T_g.***
  - ***Remark: E_g should reflect both bond strengths and 'cooperativity' of the dynamics.***

Is there an ideal glass transition? Kauzmann paradox is not essential for understanding the glass transition.

Heat Capacity Measurements on Mixtures of Poly(α-methyl styrene) and its Pentamer

*D. Huang, S.L. Simon and G.B. McKenna, J. Chem. Phys., 119, 3590-3593 (2003).

Kauzmann Paradox



- When $T<T_k$, $S_{liq} < S_{cryst}$ — violates the third law of thermodynamics
  - This "paradox" is often considered as a fundamental problem in molecular glass-formers
- W. Kauzmann, Chem. Rev. 43, 219 (1948)

Kauzmann’s Plot, 1948

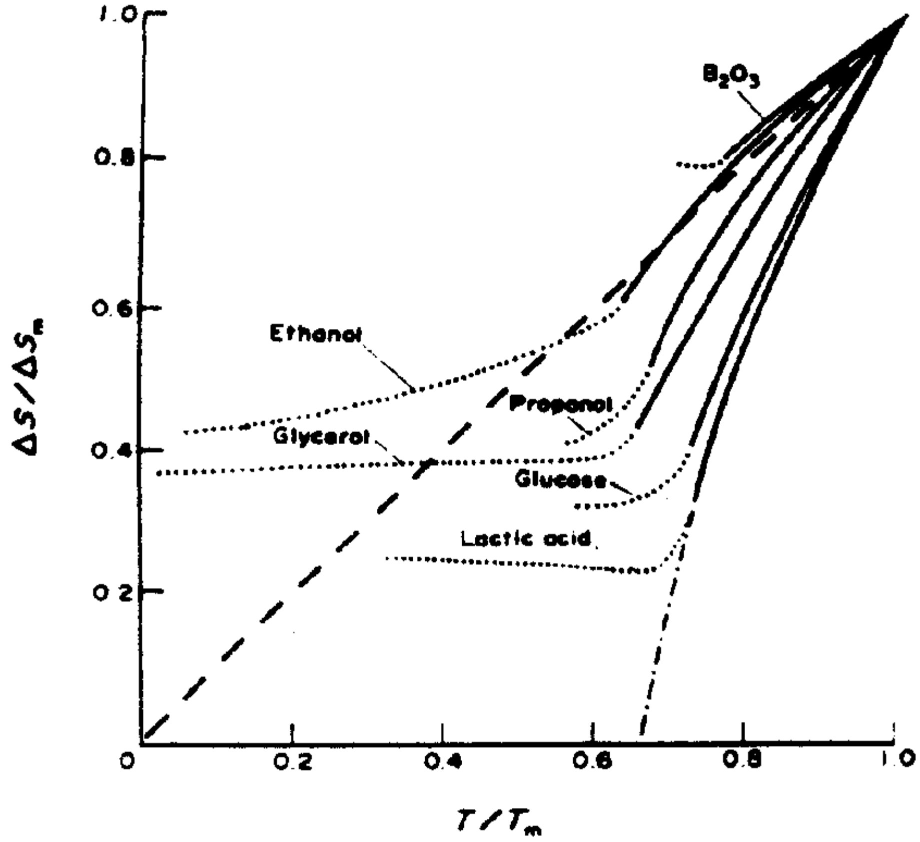


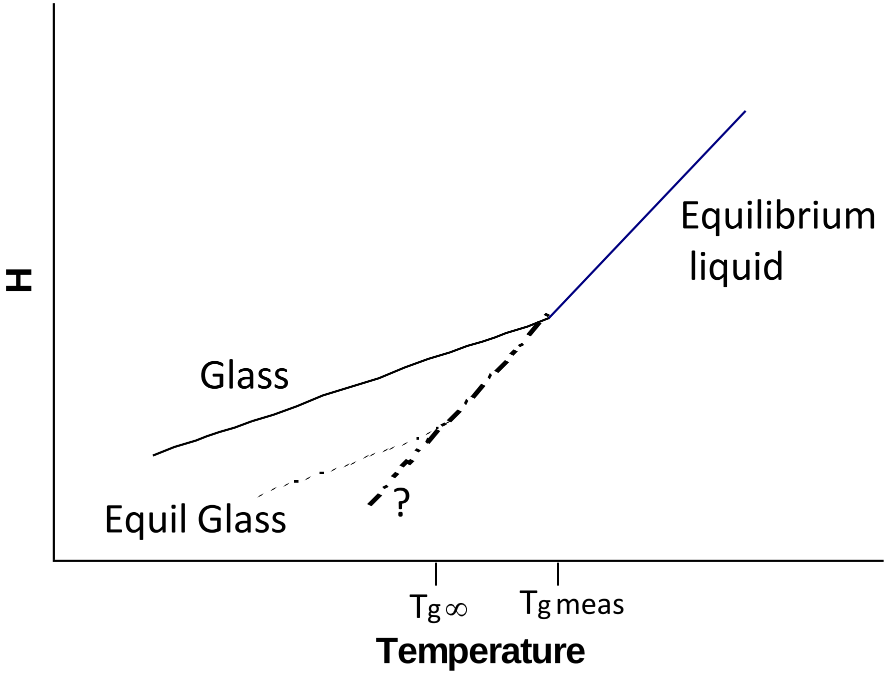
Figure 5 Differences in entropy between supercooled liquid and crystalline phases for different glass-forming materials, as indicated. $\Delta S/\Delta S_m$ = difference in entropy expressed as fraction of entropy of fusion; T/T_m = temperature expressed as fraction of melting temperature (after ref. 22)

Possible Resolution of Kauzmann Paradox

- Gibbs-DiMarzio theory:

$$S_c(T) - S_c(Ts) = \Delta Cp \ln T/Ts$$

$$S_c(Ts) = \Delta Cp \ln Ts/T_2$$



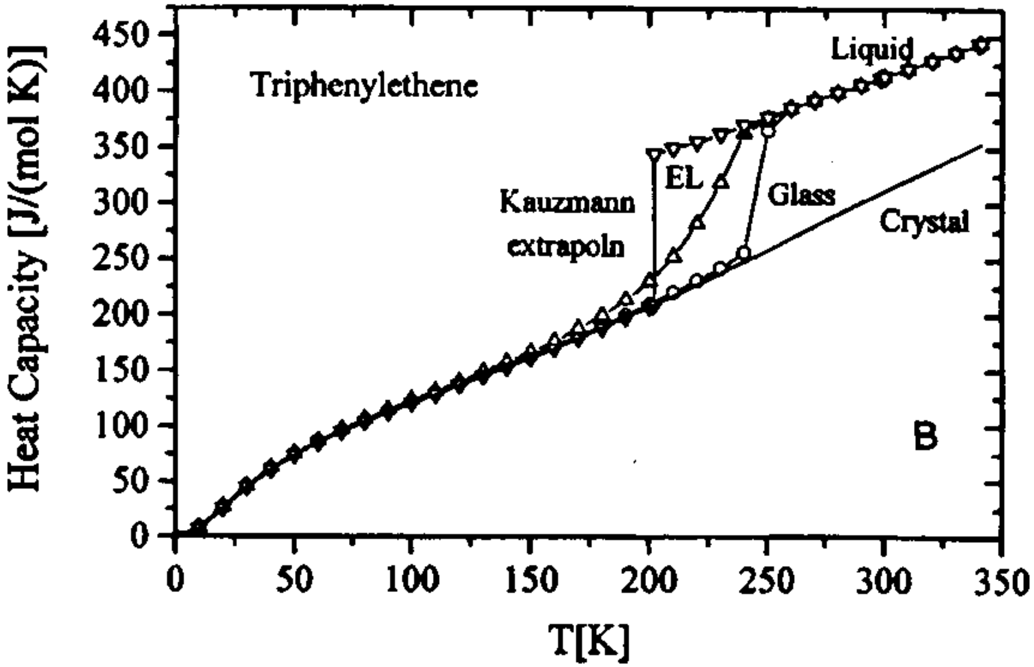
Tg, as measured, is a kinetic transition

Is there a thermodynamic Tg?

- E. A. DiMarzio and J. H. Gibbs, J. Chem. Phys. 28, 807 (1958)

Possible Resolution of Kauzmann Paradox (cont')

- Johari's interpolation method

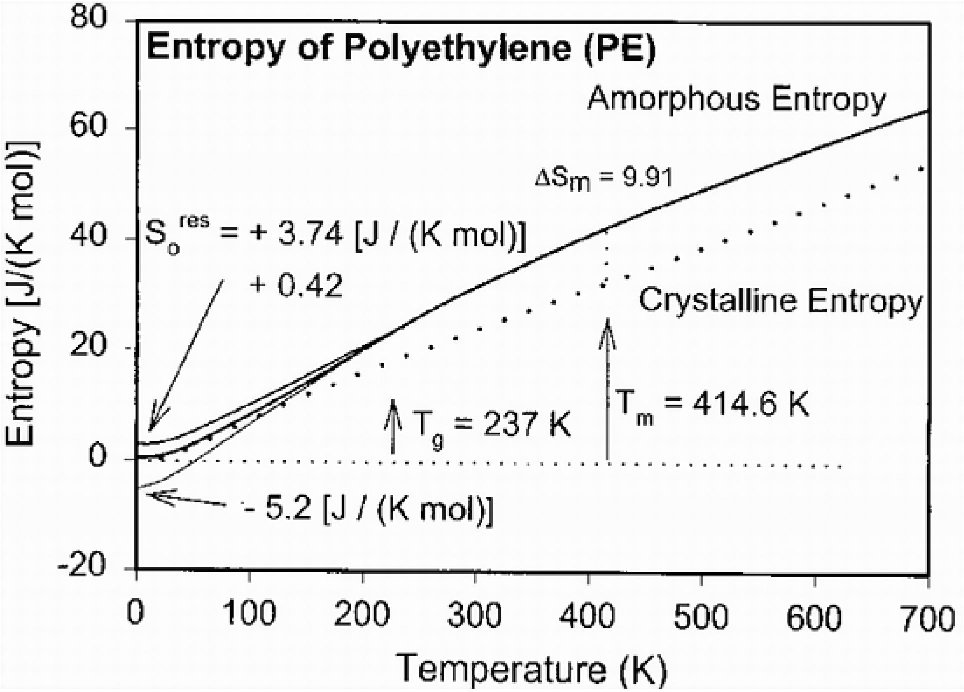


•A smooth decrease of heat capacity without invoking a thermodynamic phase transition should occur.

•G. P. Johari, J. Chem. Phys. 113, 751 (2000)

Possible Resolution of Kauzmann Paradox (cont')

- Pyda and Wunderlich's model



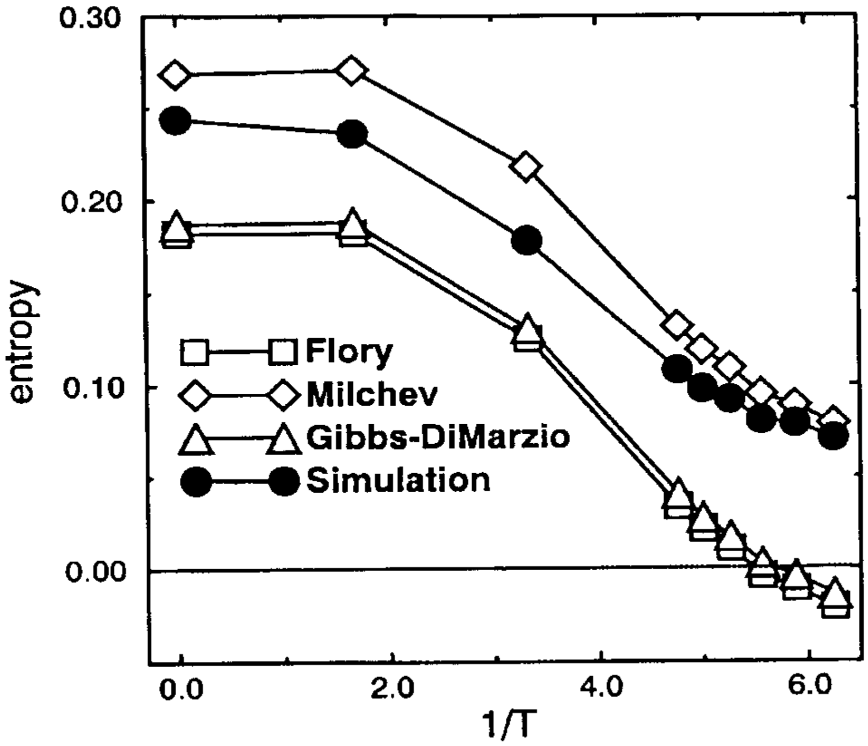
$$Cp = Cv + TV\frac{\alpha^2}{\kappa}$$

$$\approx C_{vib} + C_{conf} + C_{ext}$$

- M. Pyda and B. Wunderlich, J. Polym. Sci. Part B: Polym. Phys. 40, 1245 (2002)

Possible Resolution of Kauzmann Paradox (cont')

- Wolfgardt et al.'s simulation



The computer simulation showed always positive entropy near 0K.

Note: G-D gives negative Entropy, not zero.

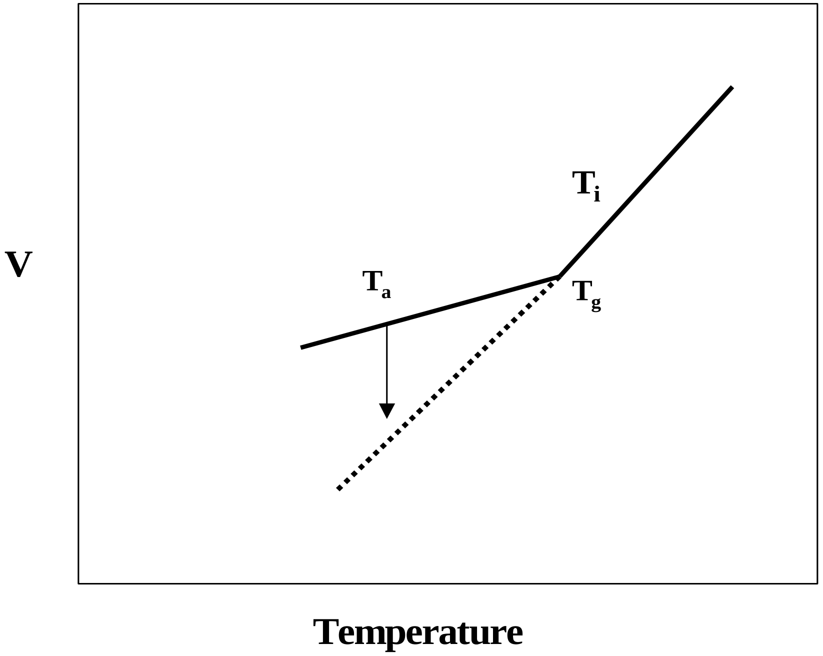
- M. Wolfgardt, J. Baschnagel, W. Paul, and K. Binder, Phys. Rev. E 54, 1535 (1996)

The problem with testing the Kauzmann paradox:

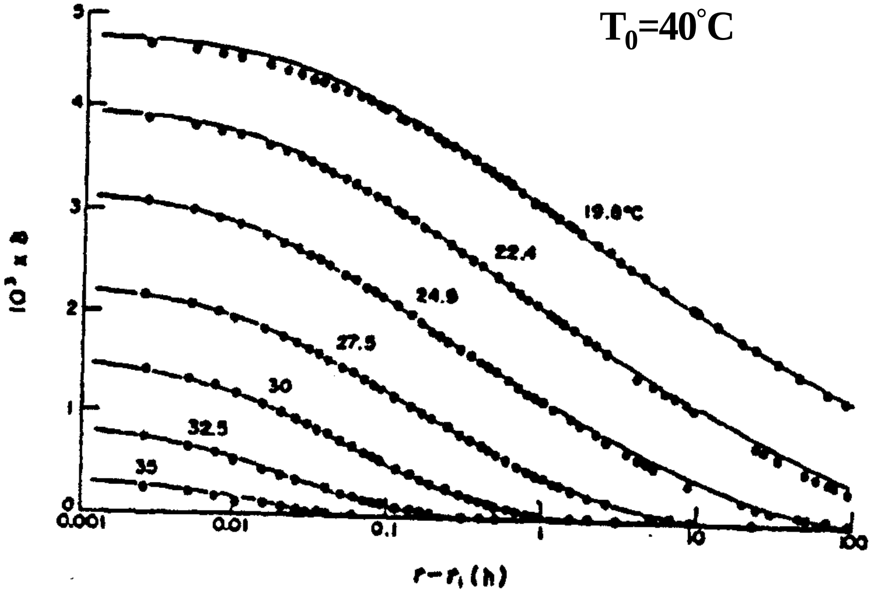
Extremely slow kinetics below T_g

NB: T_k is approximately 50-100 K below T_g

Review of Kovacs’ Thermal Experiments



Intrinsic isotherms



- A measure of structure is δ (δ =(V-V_∞)/ V_∞, V_∞ is the equilibrium volume).
- Equilibrium is approached asymptotically
- The time to reach equilibrium increase as T decreases

Objective

- In this study we introduce a new experimental method to extrapolate equilibrium heat capacity from above T_g to T_k-130 K in order to determine if there is a phase transition below T_g.

⇒ Measure the equilibrium heat capacity of polymer/ oligomer mixtures at varying concentrations and extrapolate to 100% polymer.

Methodology

- Measure absolute value of Cp(l) of mixtures of poly(α-methyl styrene) with pentamer above their T_g.

- Extrapolate to zero concentration diluent to get Cp(l) for poly(α-methyl styrene) below its T_g and also below T_k .

- Integrate to obtain enthalpy H and entropy S at temperature from above T_g to T_k-180 K.

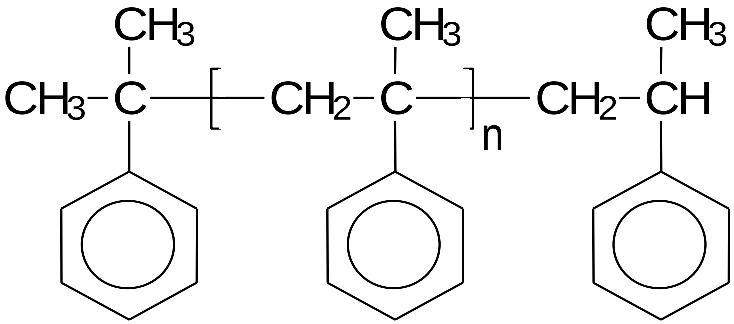
$$H = \int_{T_1}^{T_2} C_p(T)dT$$

$$S = \int_{T_1}^{T_2} C_p(T)d(\ln T)$$

$\Rightarrow$ We need accurate values of Cp(l)

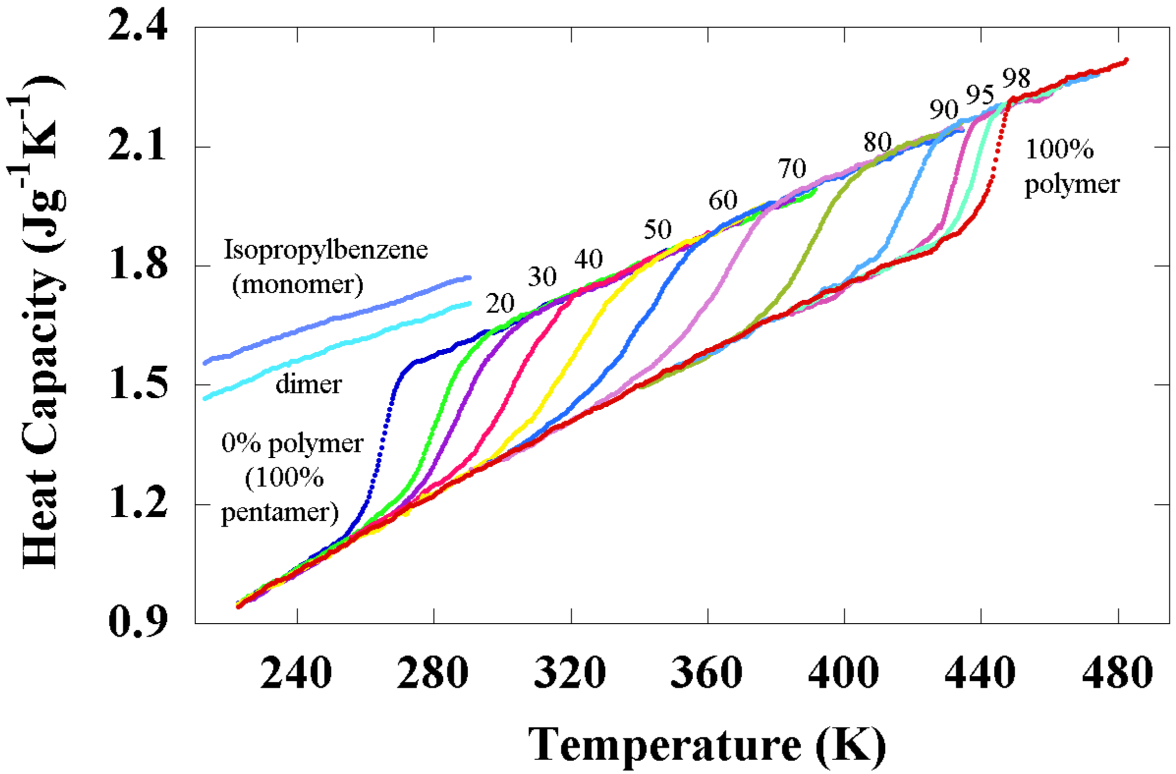
Materials

- Poly(α-methyl styrene) and its oligomers:
  - Can be synthesized by anionic polymerization
  - Do not contain initiator groups at the chain ends.

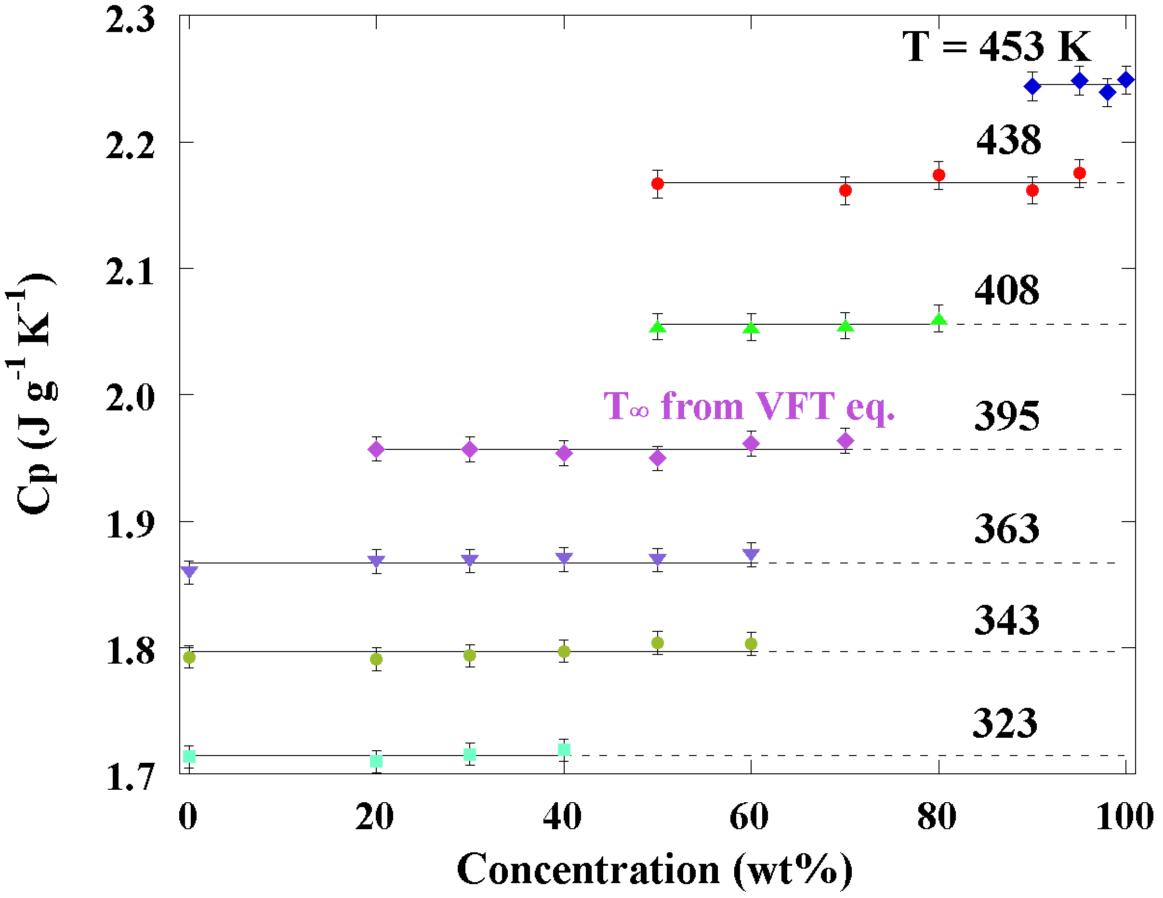


Material	Molecular Weight	T_g (K)	T_k (K)
Poly(α-methyl styrene)	$1.08\ \ 10^5$	444	394
Pentamer (n=3)	586	265	215

Results:
Heat capacity of poly(α-methyl styrene)/pentamer mixtures



Heat Capacity of poly(α-methyl styrene)/pentamer mixtures as a function of concentration at different temperatures



Relative excess configurational entropy and the relative entropy of the equilibrium liquid state for poly (α-methyl styrene) as a function of T and 1/T.

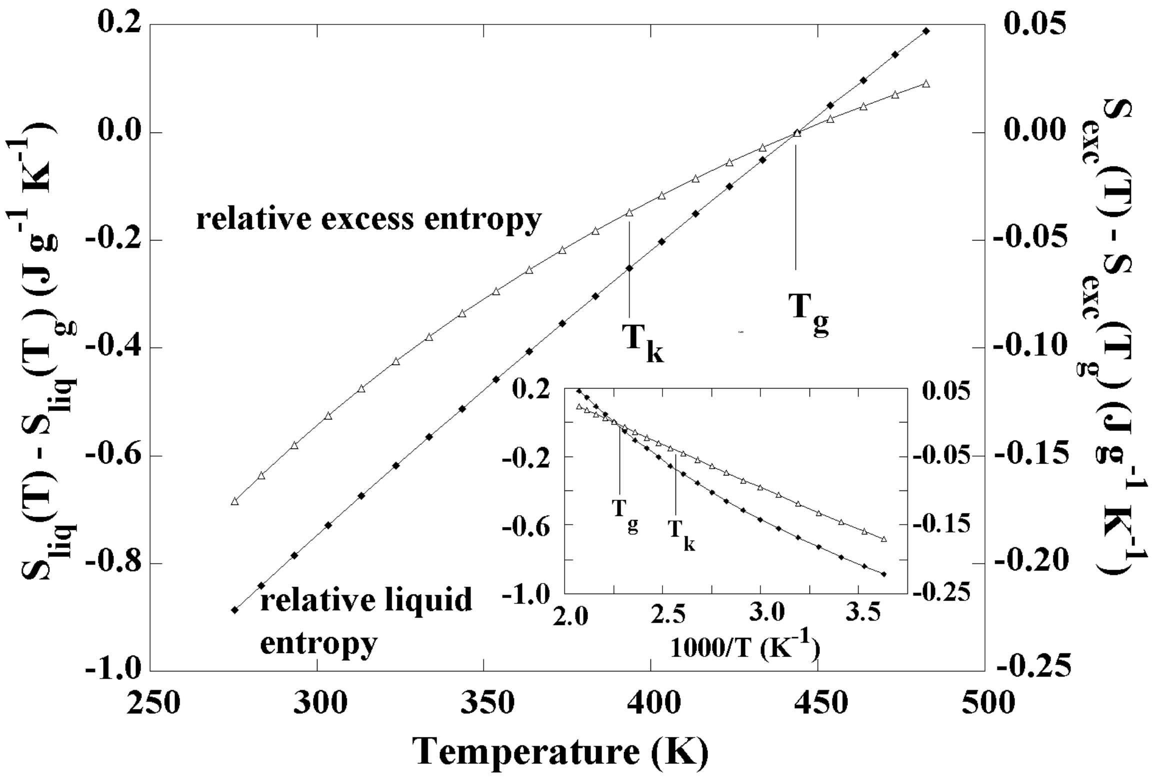
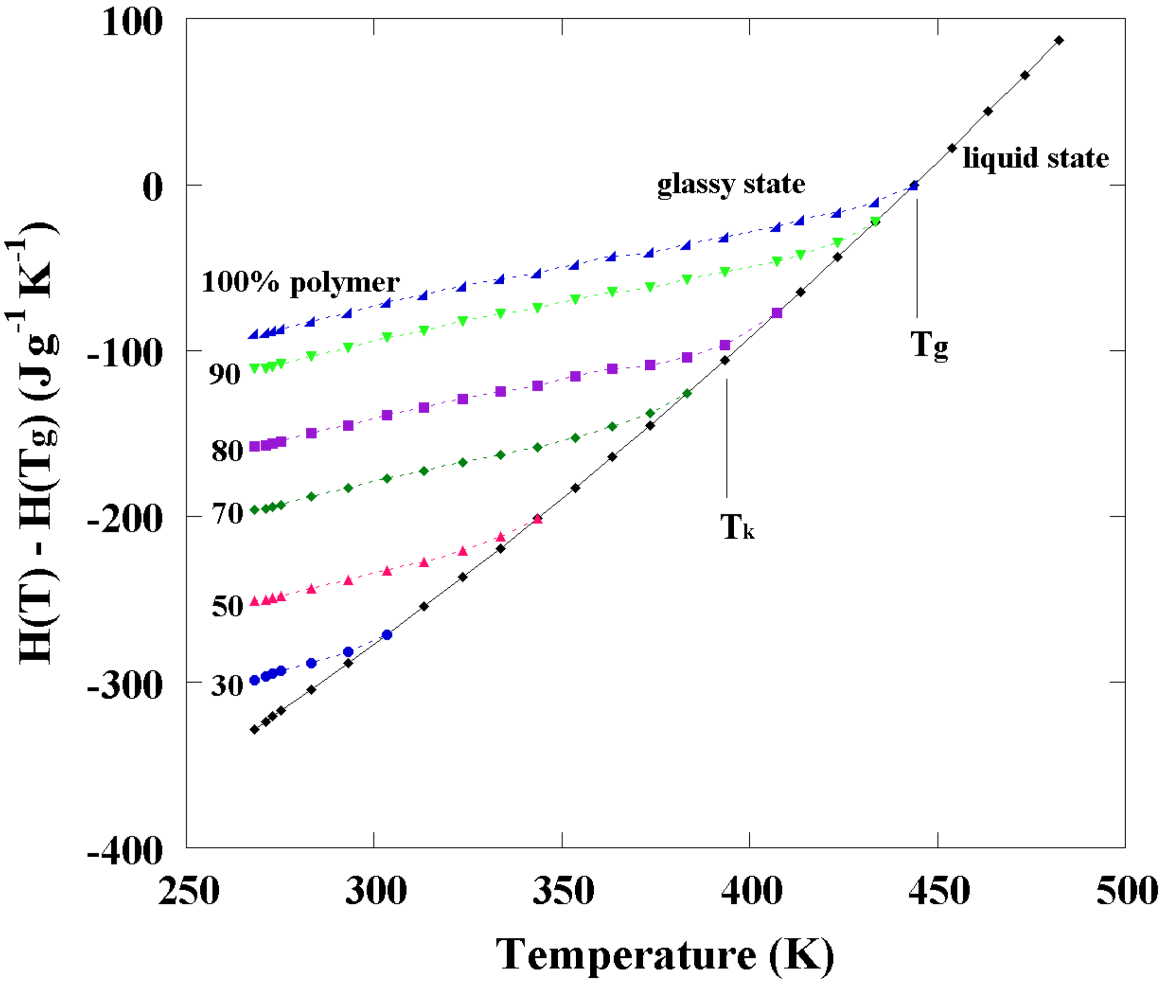


Figure 3

Enthalpy-Temperature plot for poly(α-methyl styrene) and mixtures with the pentamer



Intermediate Summary

- C_p(l) for the oligomeric α-methyl styrene asymptotes rapidly to the value for the polymer with increasing X_n, consistent with Wunderlich's hypothesis that rotational and translational degrees of freedom are not important for heat capacity of polymers.
- C_p(l) of poly(α-methyl styrene)/pentamer mixtures is independent of concentration at all temperatures and concentrations investigated, C_p(l) is a linear function of T from above T_g to T_k–130 K.
- The results suggest that a thermodynamic transition does not occur even far below the Kauzmann temperature.

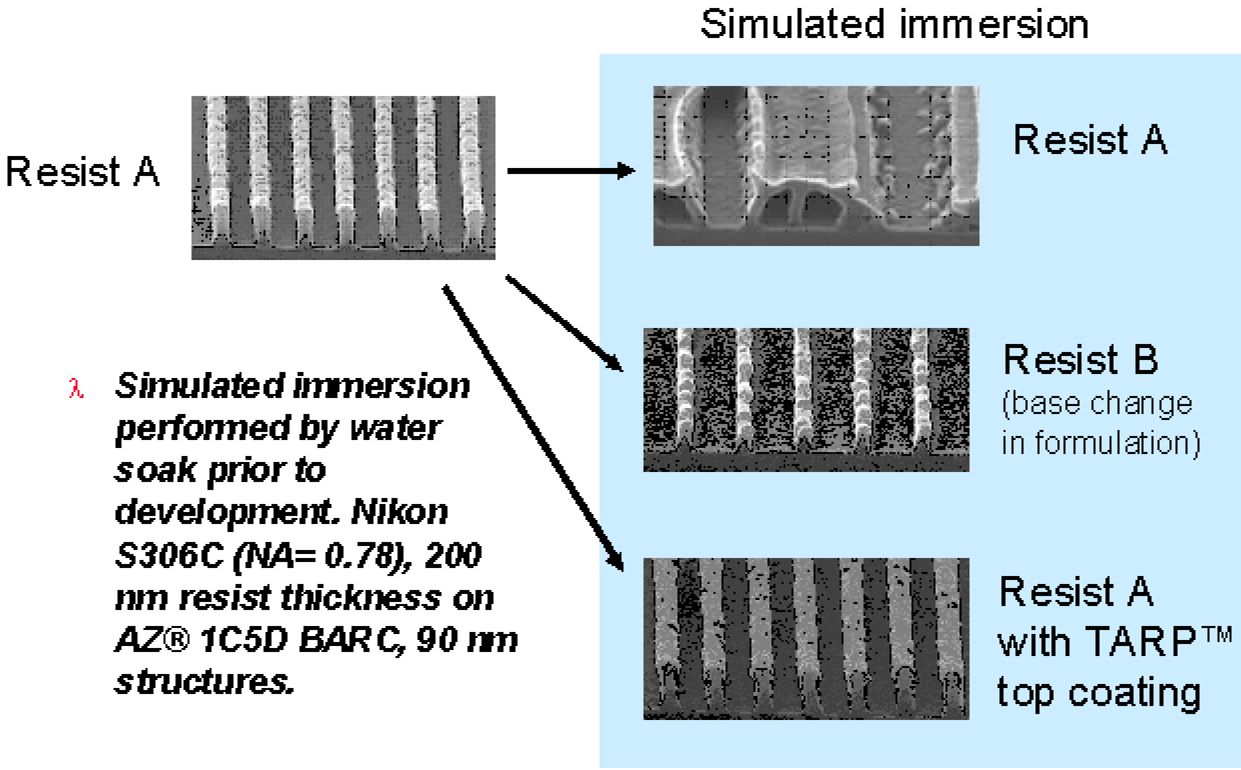
Intermediate Summary, con't.

- The results are not consistent with proposed resolutions of the Kauzmann paradox
  - Gibbs-DiMarzio second order thermodynamic transition
  - Johari's interpolation method
- The results may be consistent with:
  - Wolfgardt et al's computer simulations
  - Pyda and Wunderlich's extrapolation/modeling work on polyethylene

The glass transition at the nanoscale:

Why is it important?

Instability of nanolithographic structures

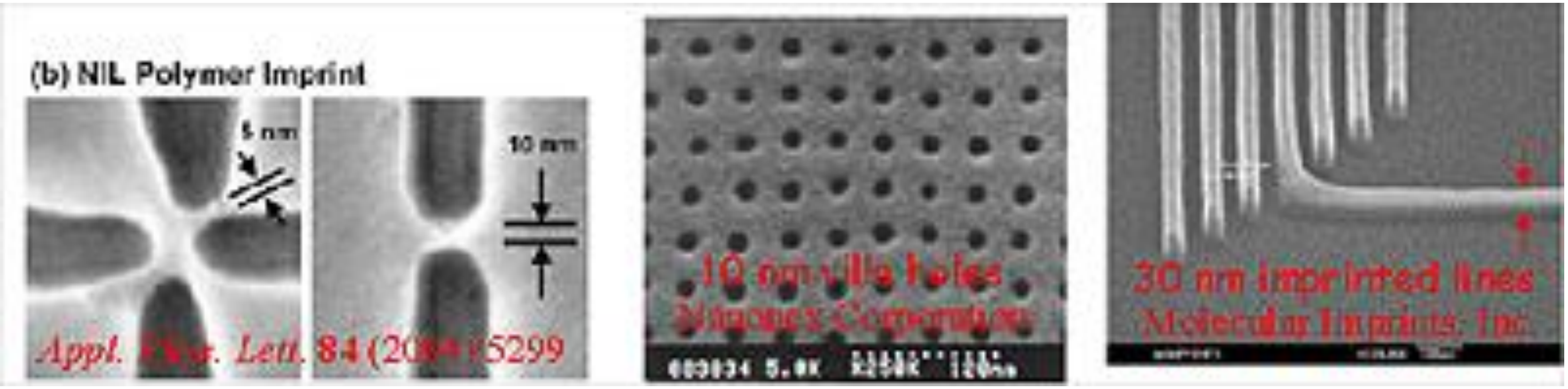


- ***Simulated immersion performed by water soak prior to development. Nikon S306C (NA= 0.78), 200 nm resist thickness on AZ® 1C5D BARC, 90 nm structures.***

http://polymers.msel.nist.gov/researcharea/electronics/image05/Resists_immersion_Lithography02.gif

Pattern transfer and stability

1. **Nanoimprint lithography (NIL) has demonstrated the ability to pattern features as small as 5 nm**
2. **Widespread use of NIL as a robust nanofabrication method requires well-controlled pattern fidelity**
3. **The stability of nanoscale patterns is critical to the use of NIL to pattern functional materials**



Examples of nanoimprint patterns and resolution

http://polymers.msel.nist.gov/researcharea/electronics/Pattern_Transfer_Stability.cfm

Stability at the nanoscale

- Depends on mechanical properties of polymers
  - Do mechanical properties change?
- In the bulk, polymer properties are very sensitive to the glass transition temperature and the fact that the glass is a non-equilibrium material
  - Importantly polymers are used at a very high proportion of the Tg
    - E.g. polycarbonate has a T_g of 140 ^oC = 413 K
      - » $T_{ambient}/T_g = 0.72$

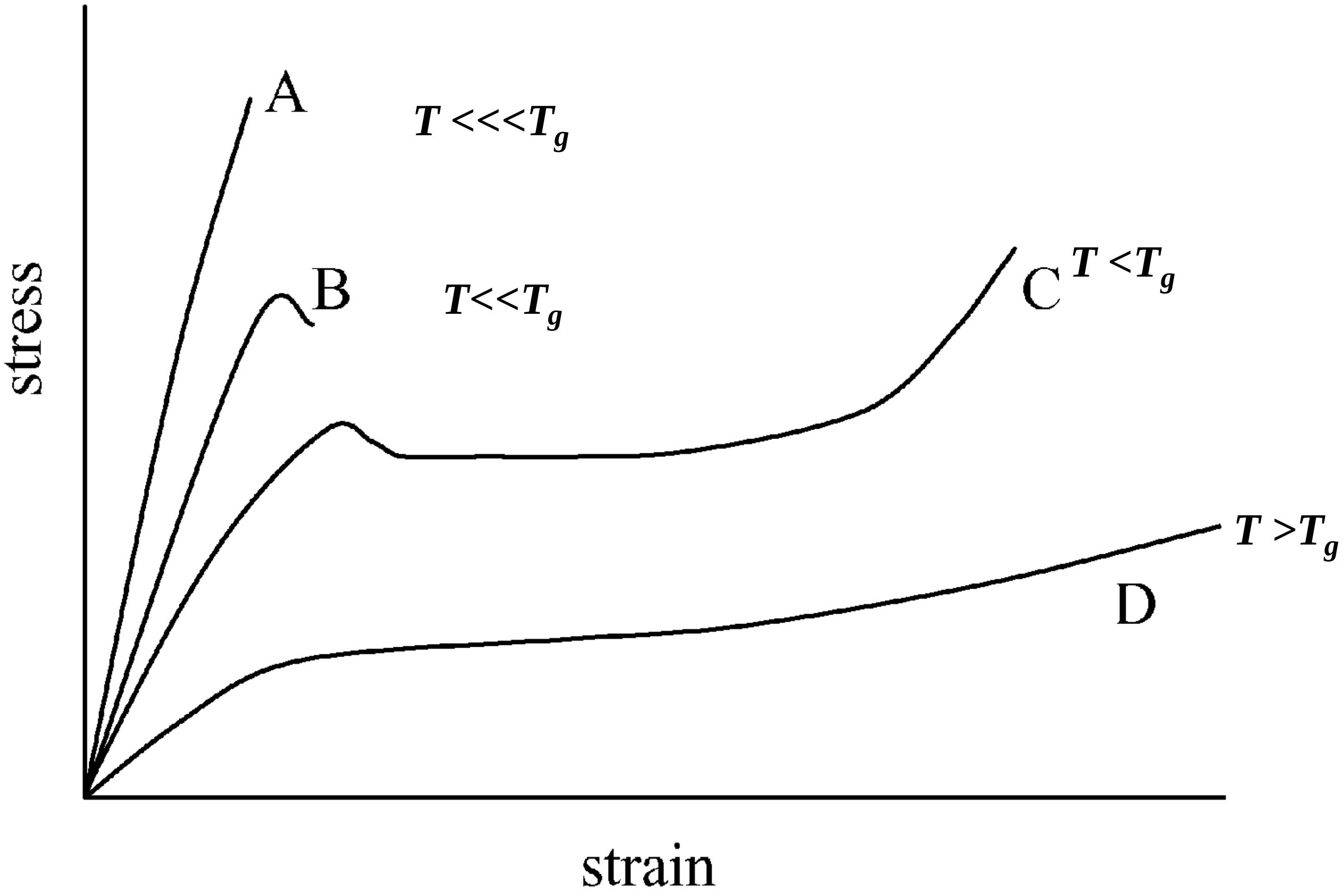


Fig 1. Typical engineering stress – strain curves for an amorphous polymer as a function of temperature or strain rate. (After O'Connell and McKenna, 2004)

Controlled Pore Glass:

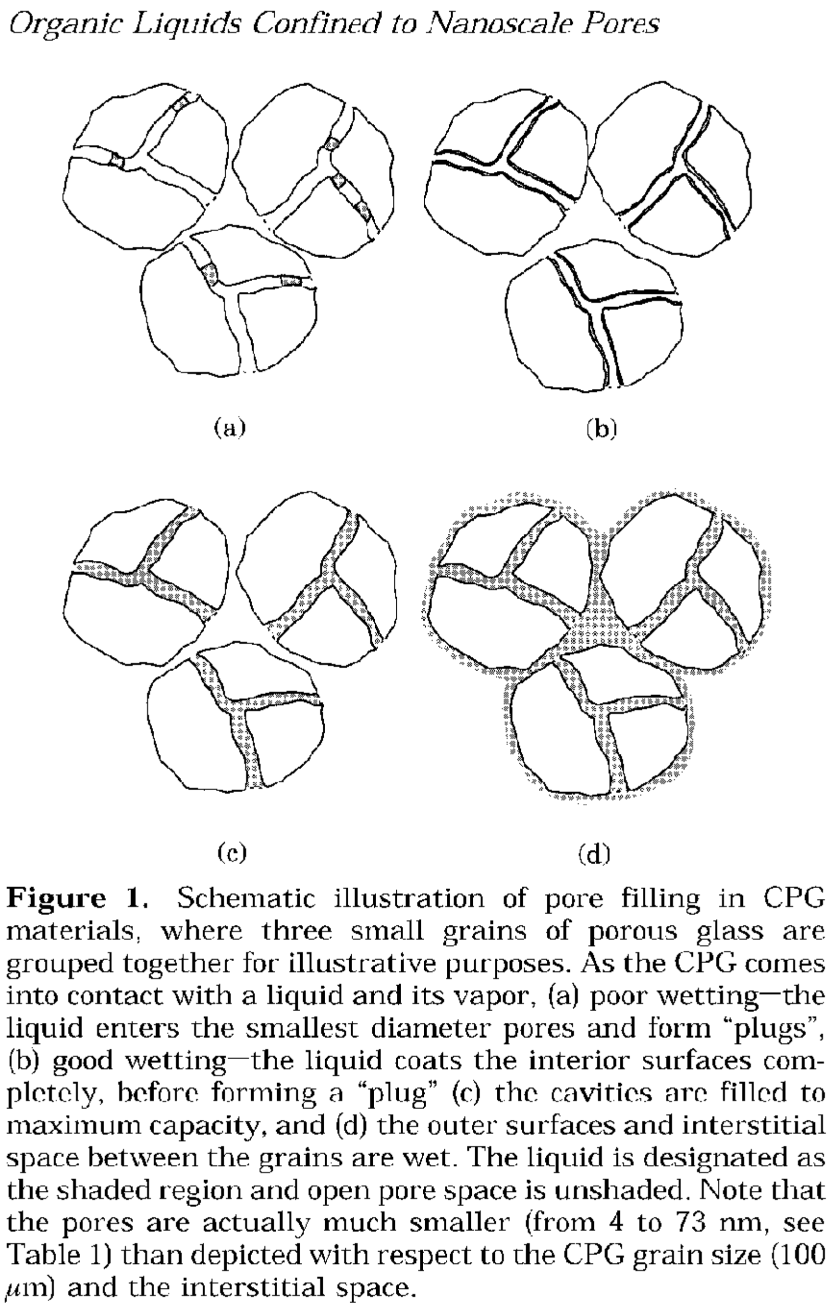
A means of nano-confinement

A Typical Nano-geometry/Experiment

- Ortho-terphenyl
  $T_g \approx 245$ K (bulk)

- Imbibed into CPG matrix at 80°C

- CPG Matrix (Wolfgang Haller, NIST)
  Treated with hexamethyldisilazane
  CPG diameters:
  4 nm-73 nm



Organic Liquids Confined to Nanoscale Pores

Figure 1. Schematic illustration of pore filling in CPG materials, where three small grains of porous glass are grouped together for illustrative purposes. As the CPG comes into contact with a liquid and its vapor, (a) poor wetting—the liquid enters the smallest diameter pores and form "plugs", (b) good wetting—the liquid coats the interior surfaces completely, before forming a "plug" (c) the cavities are filled to maximum capacity, and (d) the outer surfaces and interstitial space between the grains are wet. The liquid is designated as the shaded region and open pore space is unshaded. Note that the pores are actually much smaller (from 4 to 73 nm, see Table 1) than depicted with respect to the CPG grain size (100 μm) and the interstitial space.

Glass Transition at the nano-scale

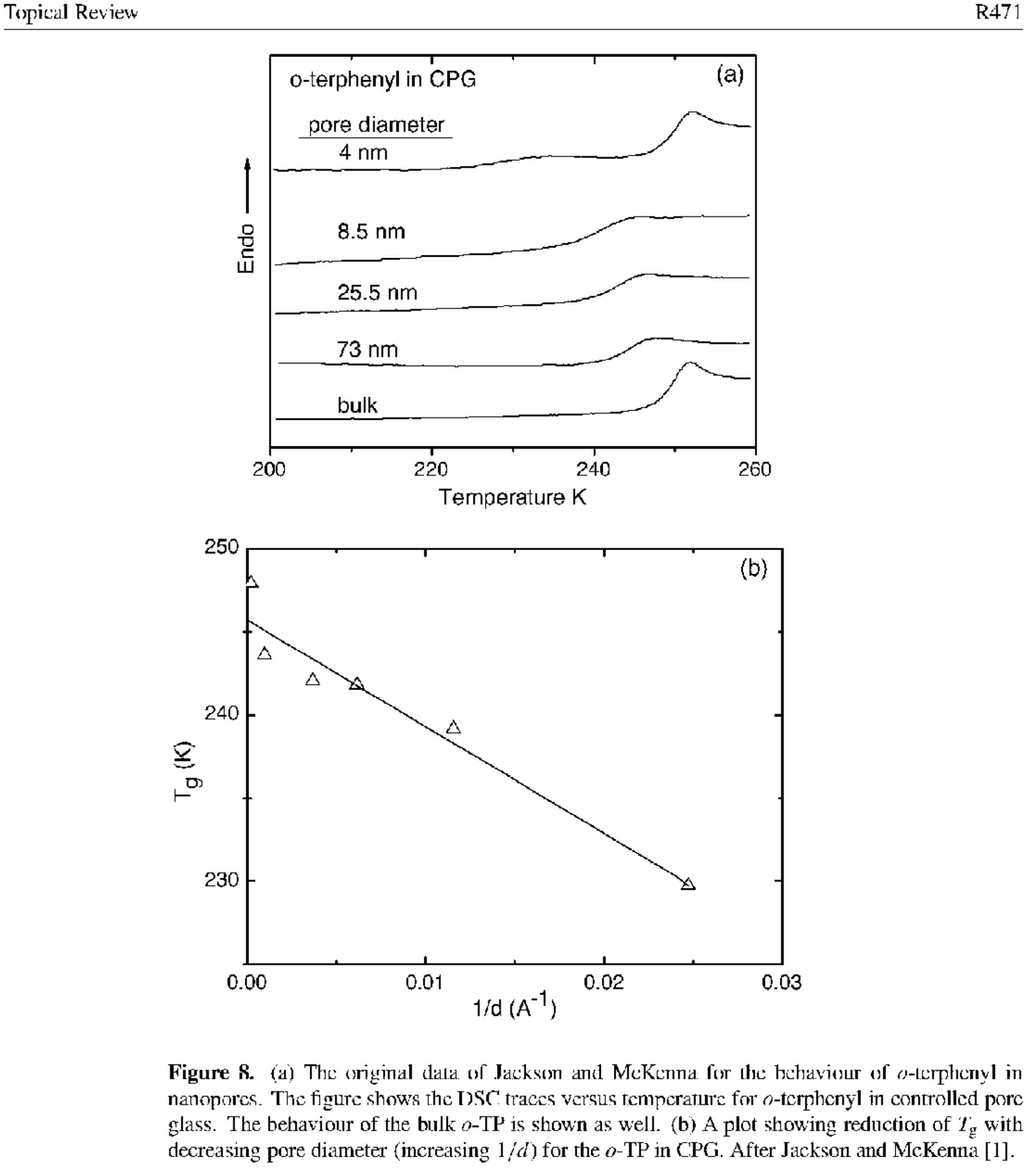


Figure 8. (a) The original data of Jackson and McKenna for the behaviour of *o*-terphenyl in nanopores. The figure shows the DSC traces versus temperature for *o*-terphenyl in controlled pore glass. The behaviour of the bulk *o*-TP is shown as well. (b) A plot showing reduction of T_g with decreasing pore diameter (increasing $1/d$) for the *o*-TP in CPG. After Jackson and McKenna [1].

Tg in thin, free-standing Polystyrene films

K. DALNOKI-VERESS *et al.*

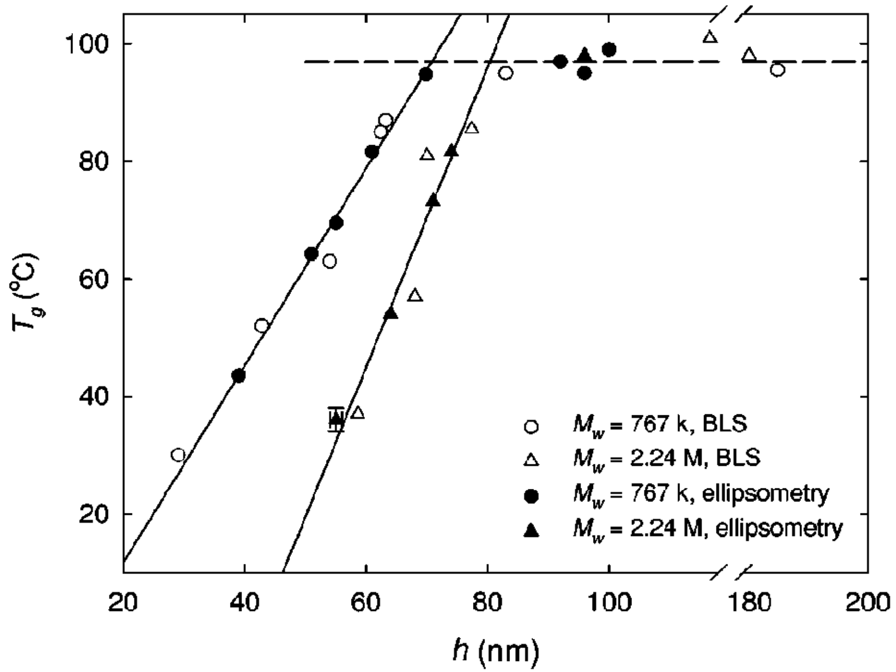


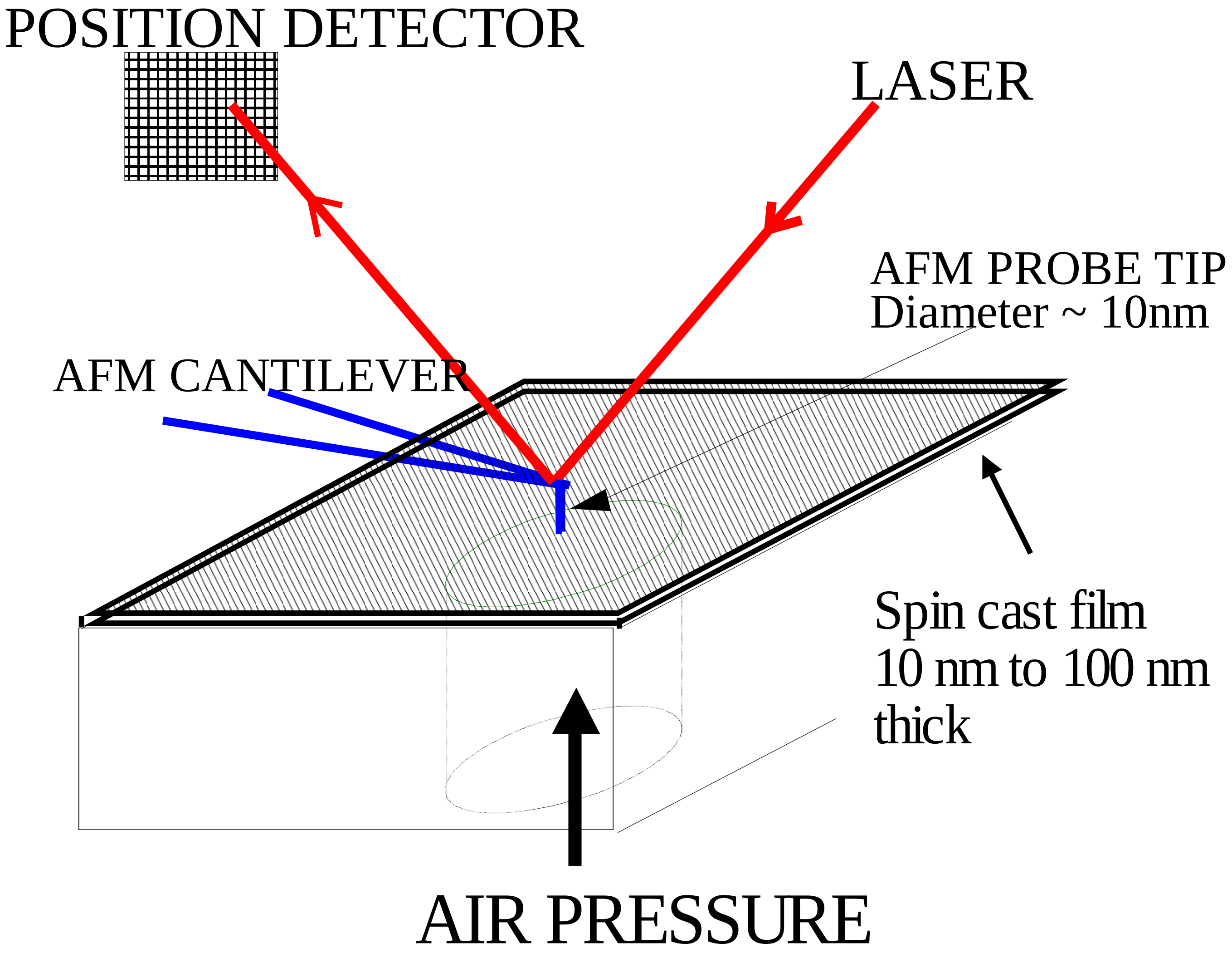
FIG. 3. Plot of T_g versus film thickness h for freely standing PS films with $\bar{M}_w = 767 \times 10^3$ and $\bar{M}_w = 2240 \times 10^3$. Two sets of data are shown: previous BLS data (open symbols) [6], and the transmission ellipsometry data obtained in the present study (solid symbols).

Viscoelasticity at the nanoscale (measurements of the dynamics of the glass transition):

a new nanorheological measurement technique

(with P.A. O'Connell)

Experimental



POSITION DETECTOR

LASER

AFM PROBE TIP
Diameter ~ 10nm

AFM CANTILEVER

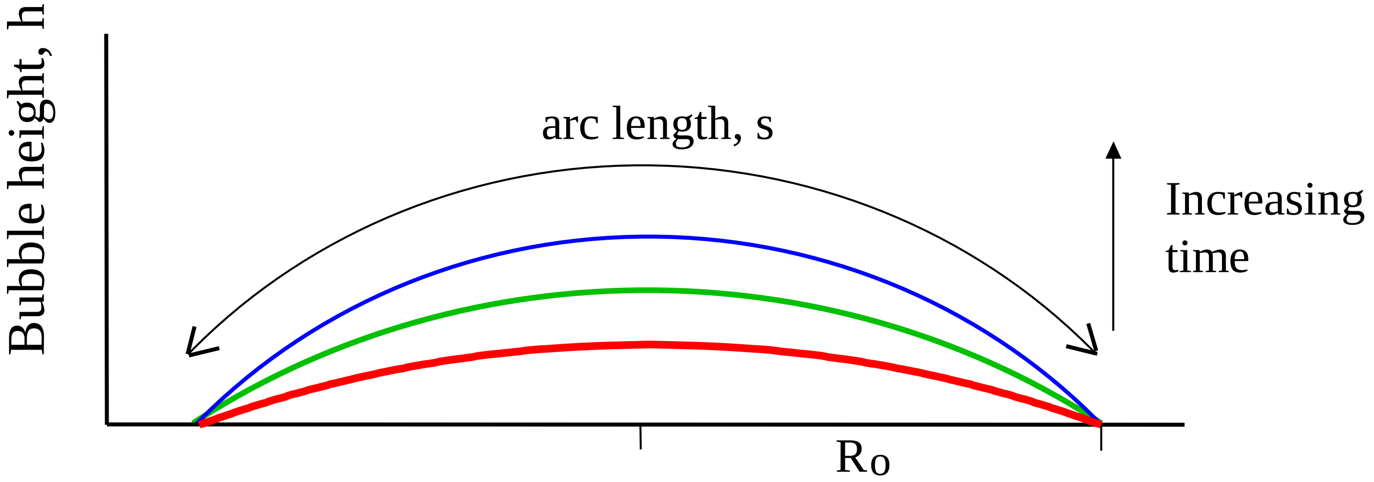
Spin cast film
10 nm to 100 nm
thick

AIR PRESSURE

O'Connell and McKenna, Science, March 18, 2005

Experimental cont’d

BUBBLE PROFILE



[*] stress, $\sigma = \frac{PR}{2t_o}$

strain, $\varepsilon = \frac{s}{2R_o}$

where $R = \frac{h^2 + R_o^2}{2h}$

$s = R_o \sin^{-1}(R_o / R)$

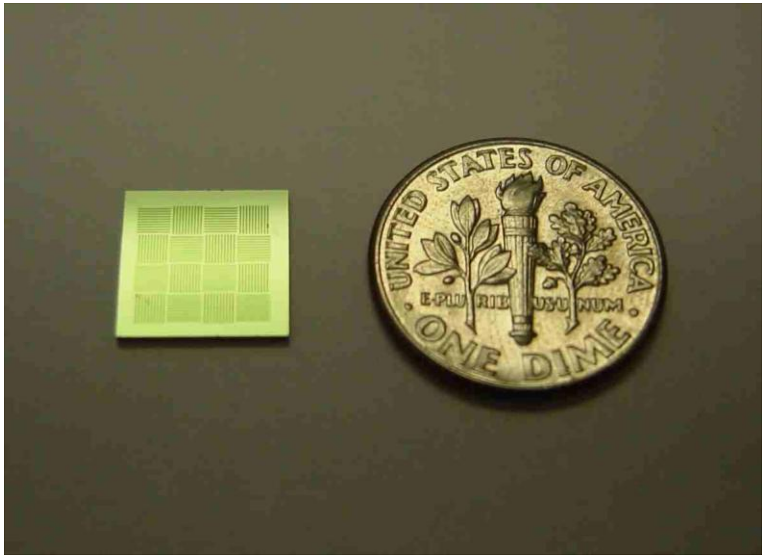
so $D(t) = \varepsilon(t) / \sigma(t)$

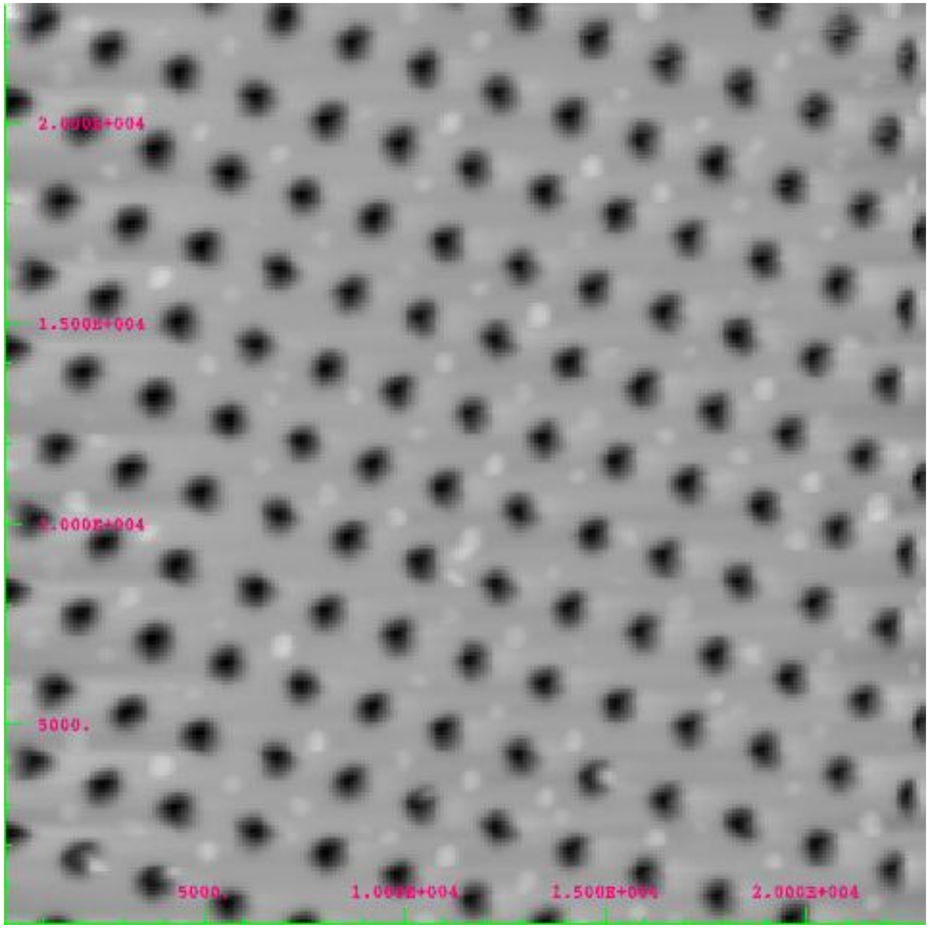
[*] A.E. Green, J.E. Adkins, *Large Elastic Deformations*, Oxford University Press, London (1970)

Experimental Conditions

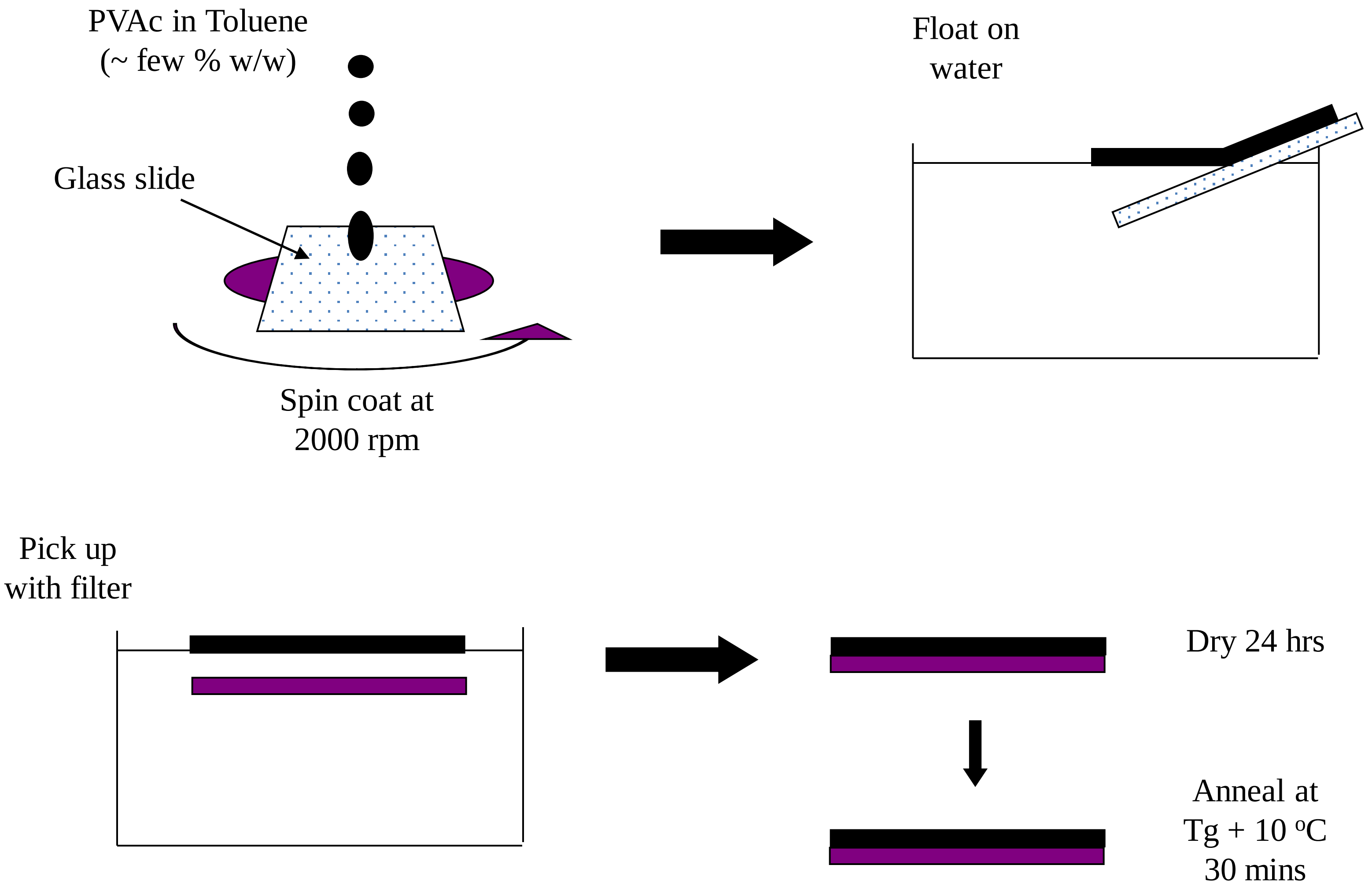
- ***Polymers***
  - ***PVAc with M_w=170,000 daltons***
  - ***PS with M_w=1,200,000 daltons***
- ***T_{gPVAc}=303.8 K (30.6 ^oC);T_{gPS}=98.8 ^oC (cooling at 10 K/min)***
- ***Spin coated and films floated onto silicon nitride "membranes"***
  - ***Initial concentration determines the film thickness***
    - ***Film thickness measured by AFM***
- ***Pressure apparatus built to fit in Molecular Imaging PicoSPM atomic force microscope***

Clean Filter : 22 micron square





Sample preparation



PVAc in Toluene
(~ few % w/w)

Glass slide

Spin coat at
2000 rpm

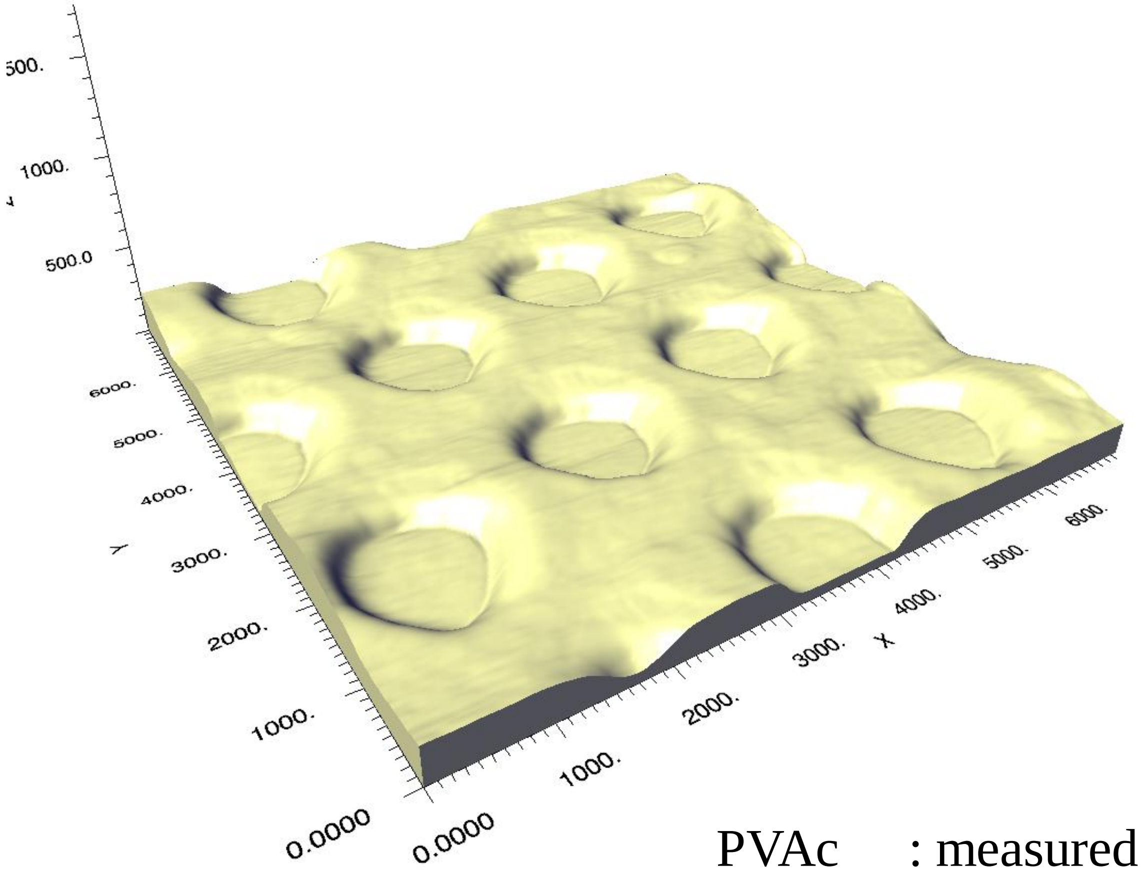
Float on
water

Pick up
with filter

Dry 24 hrs

Anneal at
Tg + 10 ^{o}C
30 mins

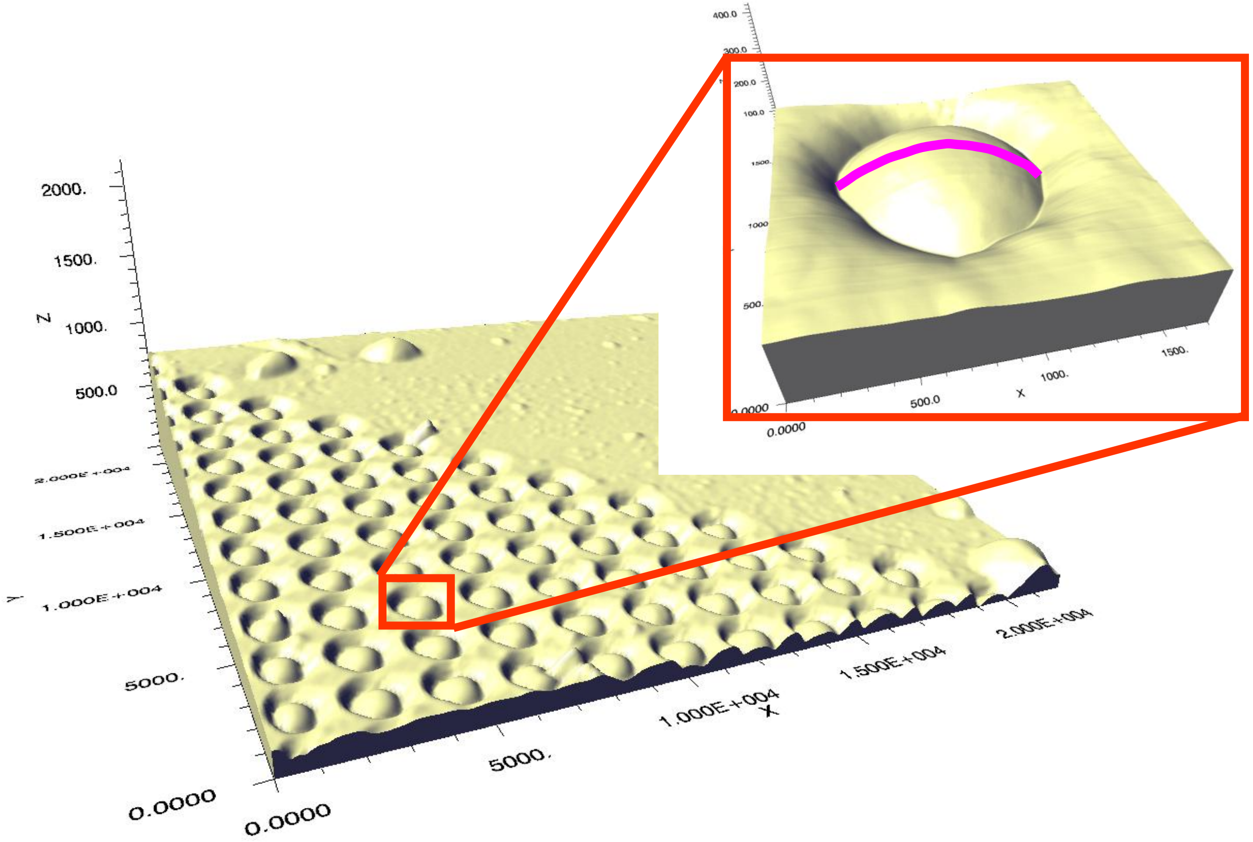
3-D Image of a Coated Filter



PVAc : measured Tg = 30.6 ^{o}C

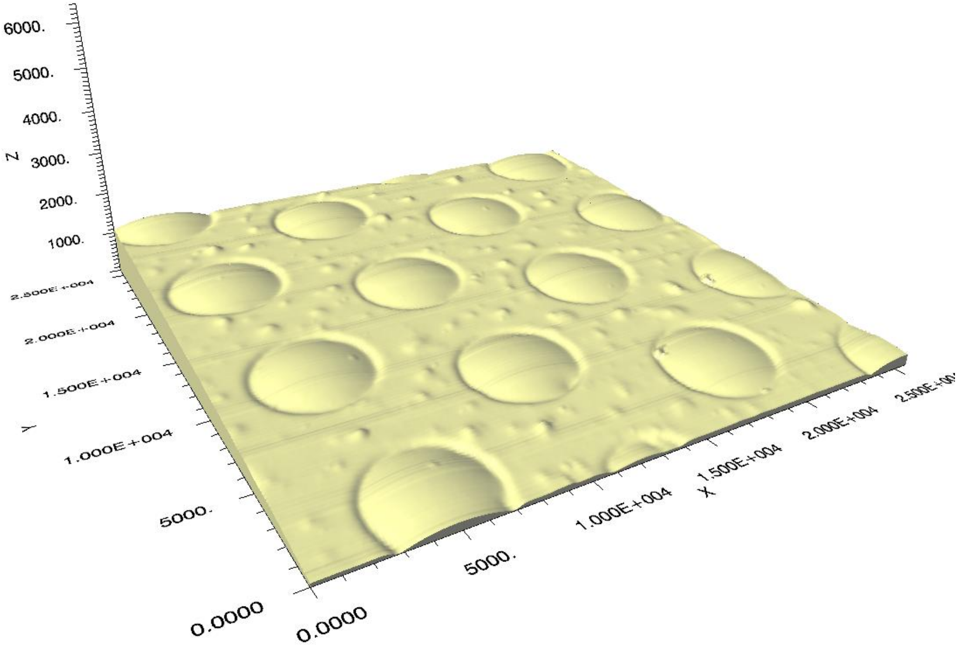
: 27nm thickness

: M_W = 170 000

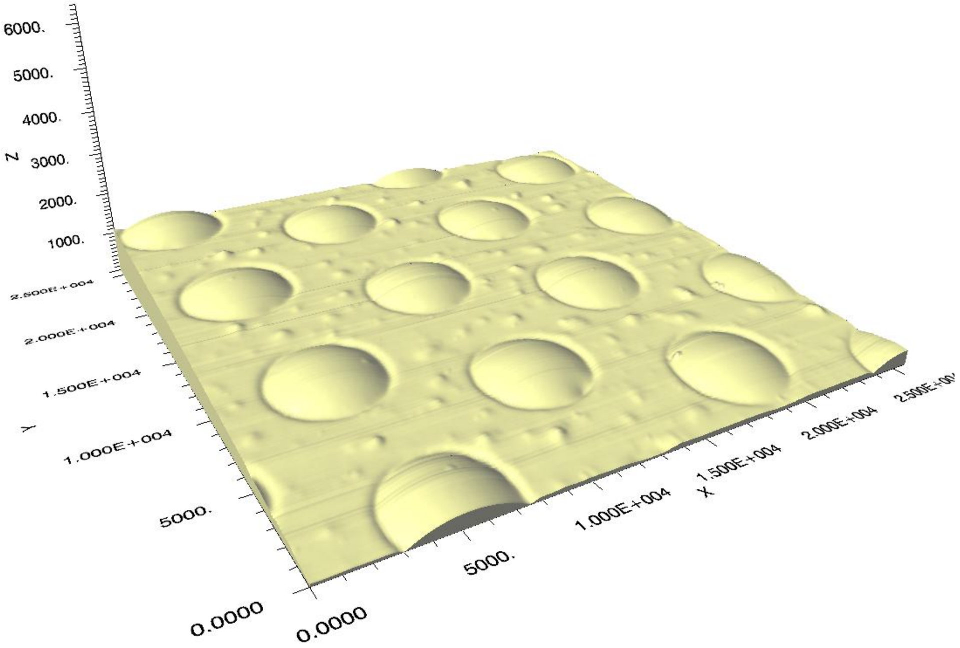


O'Connell and McKenna, Science, March 18, 2005

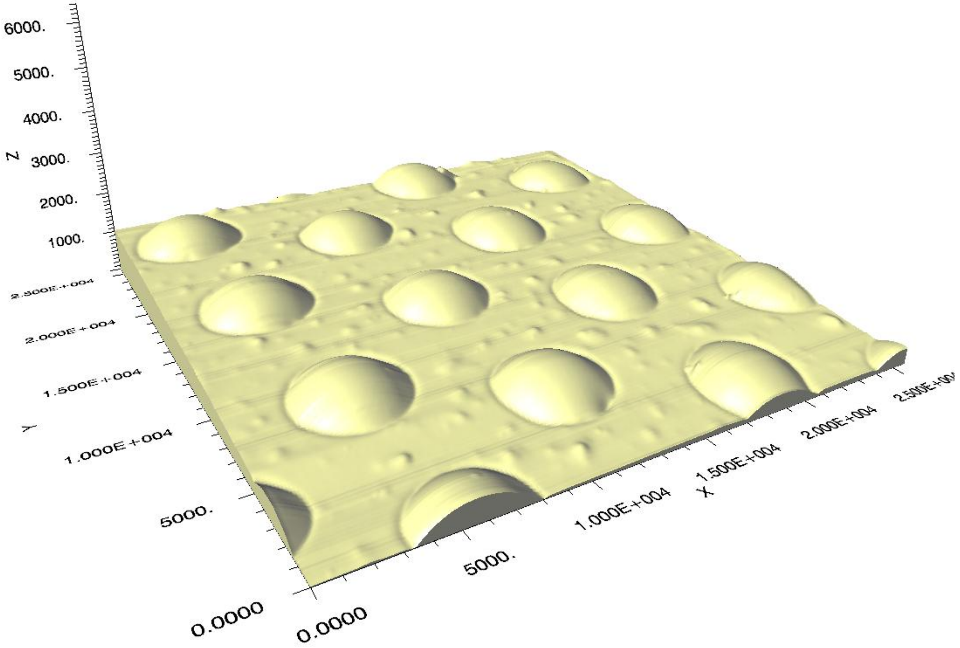
PVAc : 40 ^{o}C : 150nm : 2psi : 5 μm diameter



PVAc : 40 ^{o}C : 150nm : 3psi : 5 μm diameter



PVAc : 40 °C : 150nm : 5psi : 5 μm diameter



PVAc : 40 ^{o}C : 150nm : 7psi: 5 μm diameter

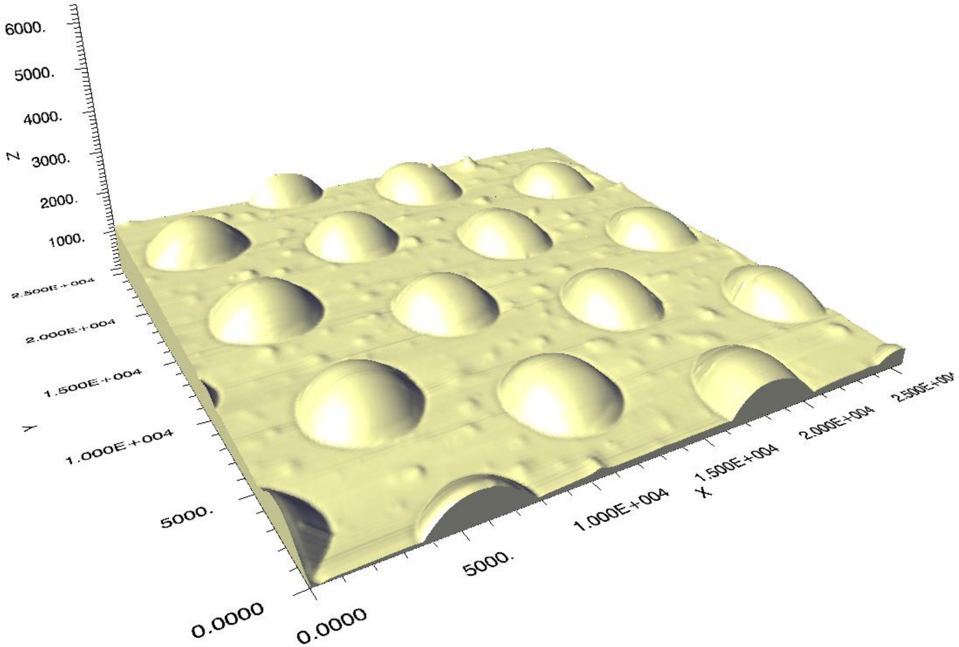
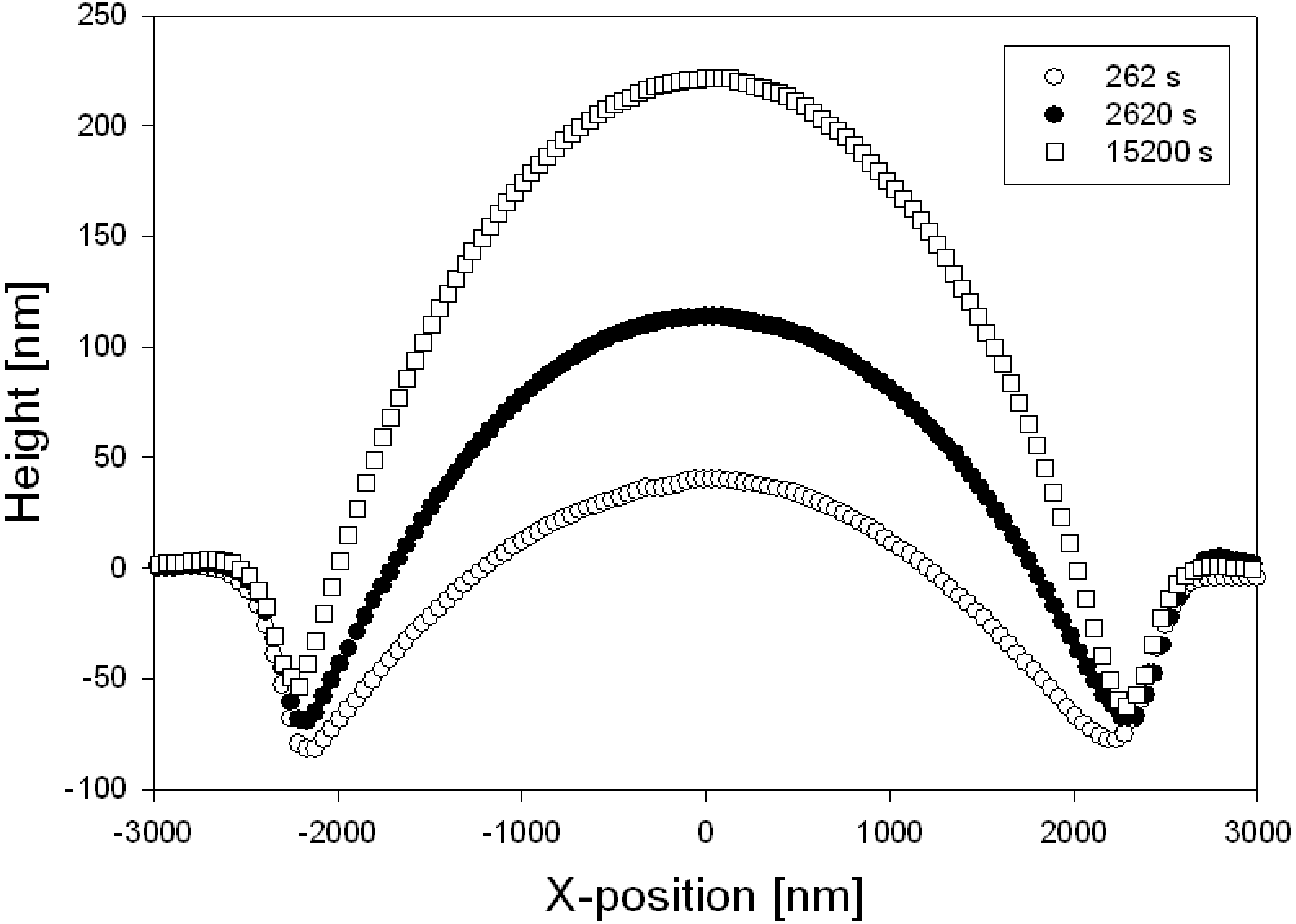
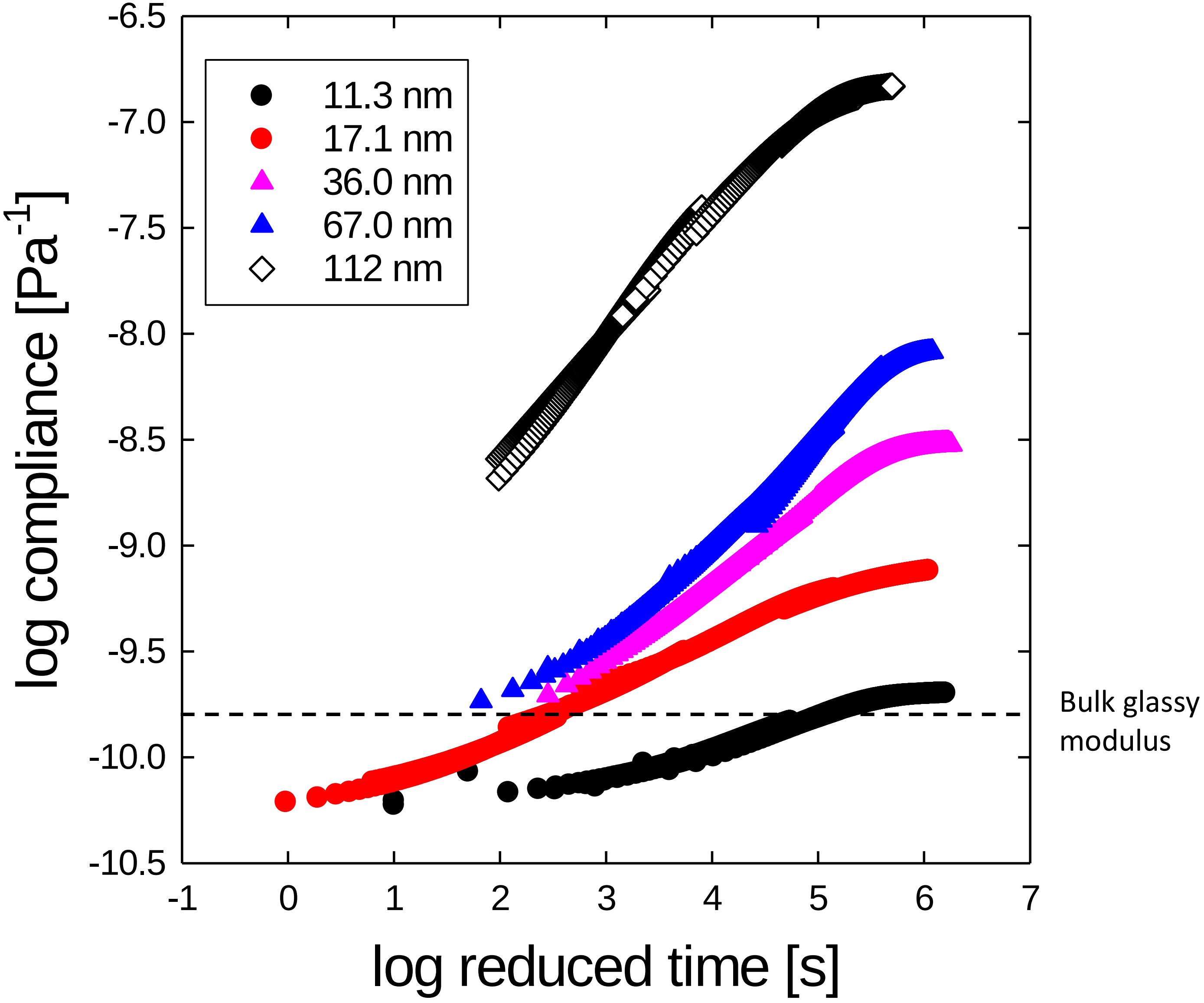


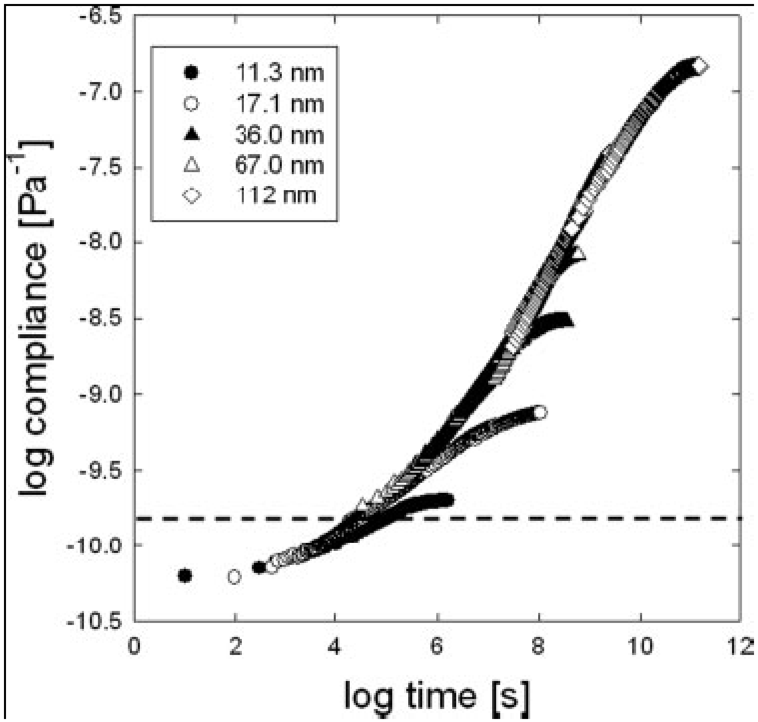
FIG 11


Height [nm]
250
200
150
100
50
0
-50
-100
X-position [nm]
-3000
-2000
-1000
0
1000
2000
3000
○ 262 s
● 2620 s
□ 15200 s

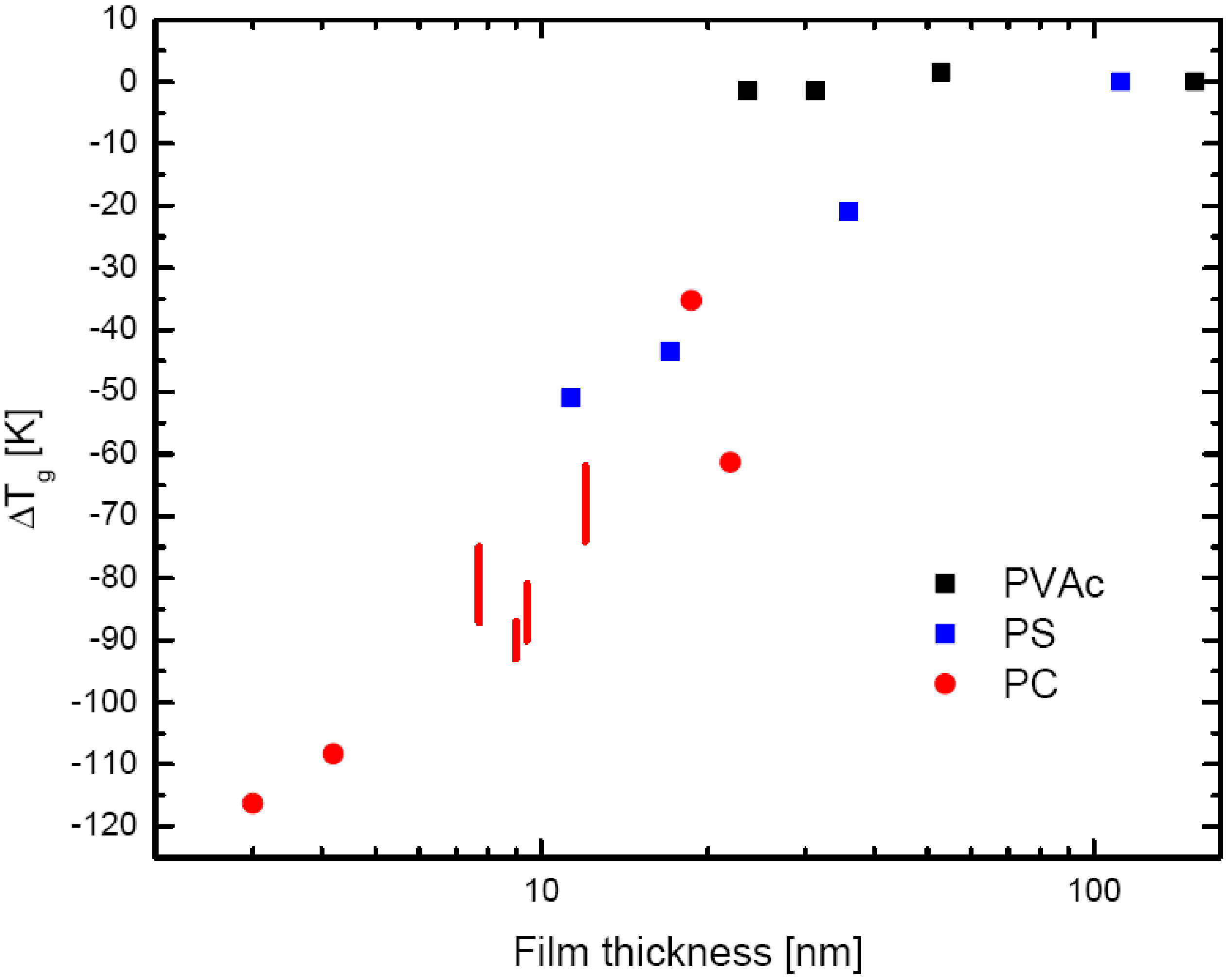
PS : master curves at different thicknesses



Polystyrene thin film master curves at $T_{ref}=T_g$ (this is the reduced T_g of the system).



T_g reductions at the nanoscale in thin polymer films can be very large, but they seem to not be universal.



The glass transition remains an important and fascinating subject

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The End