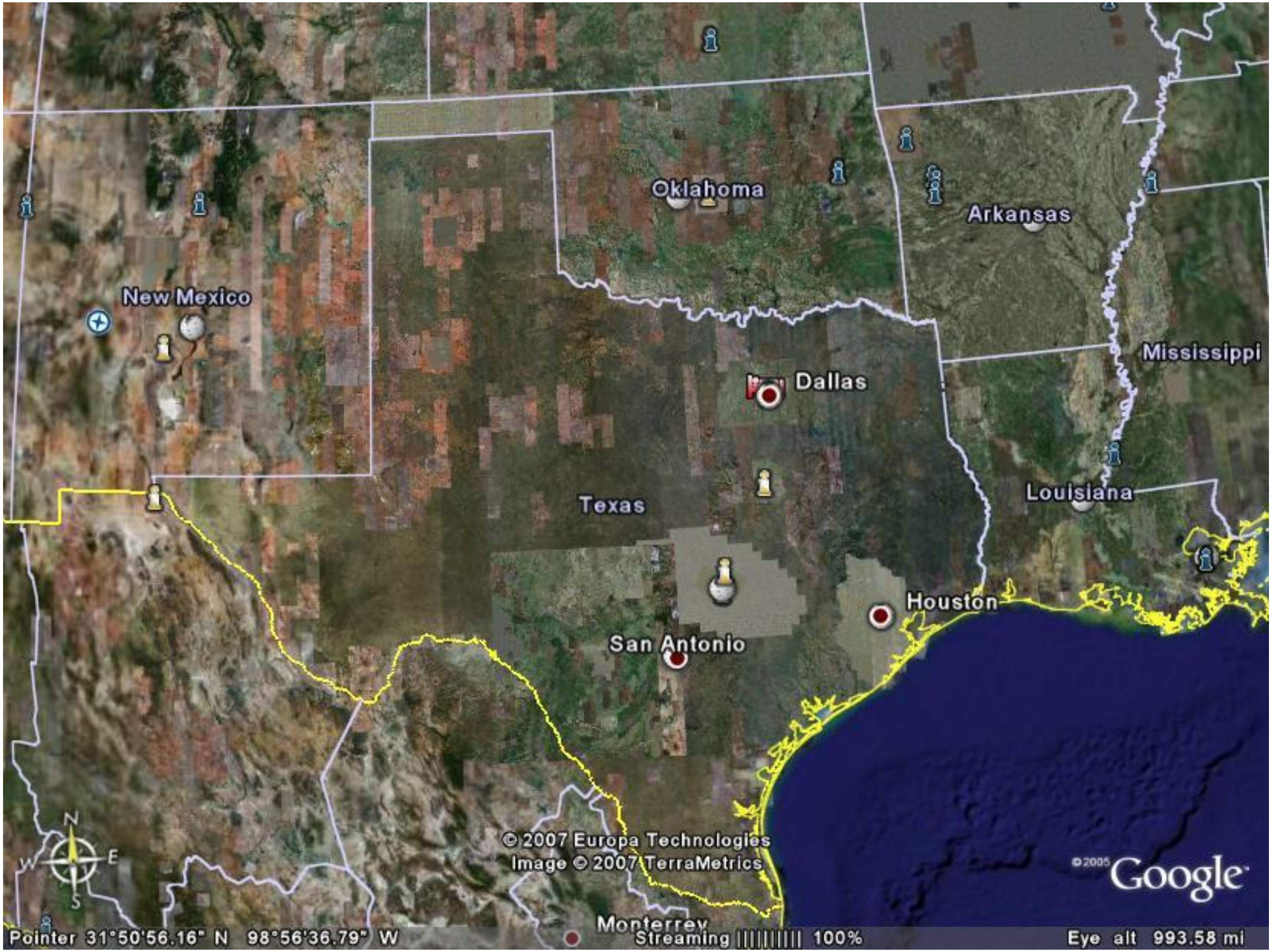
TEXAS TECH UNIVERSITY
Edward E. Whitacre Jr.
College of Engineering

Structural Recovery in Glasses: Phenomenological Descriptions and Anomalous Behaviors

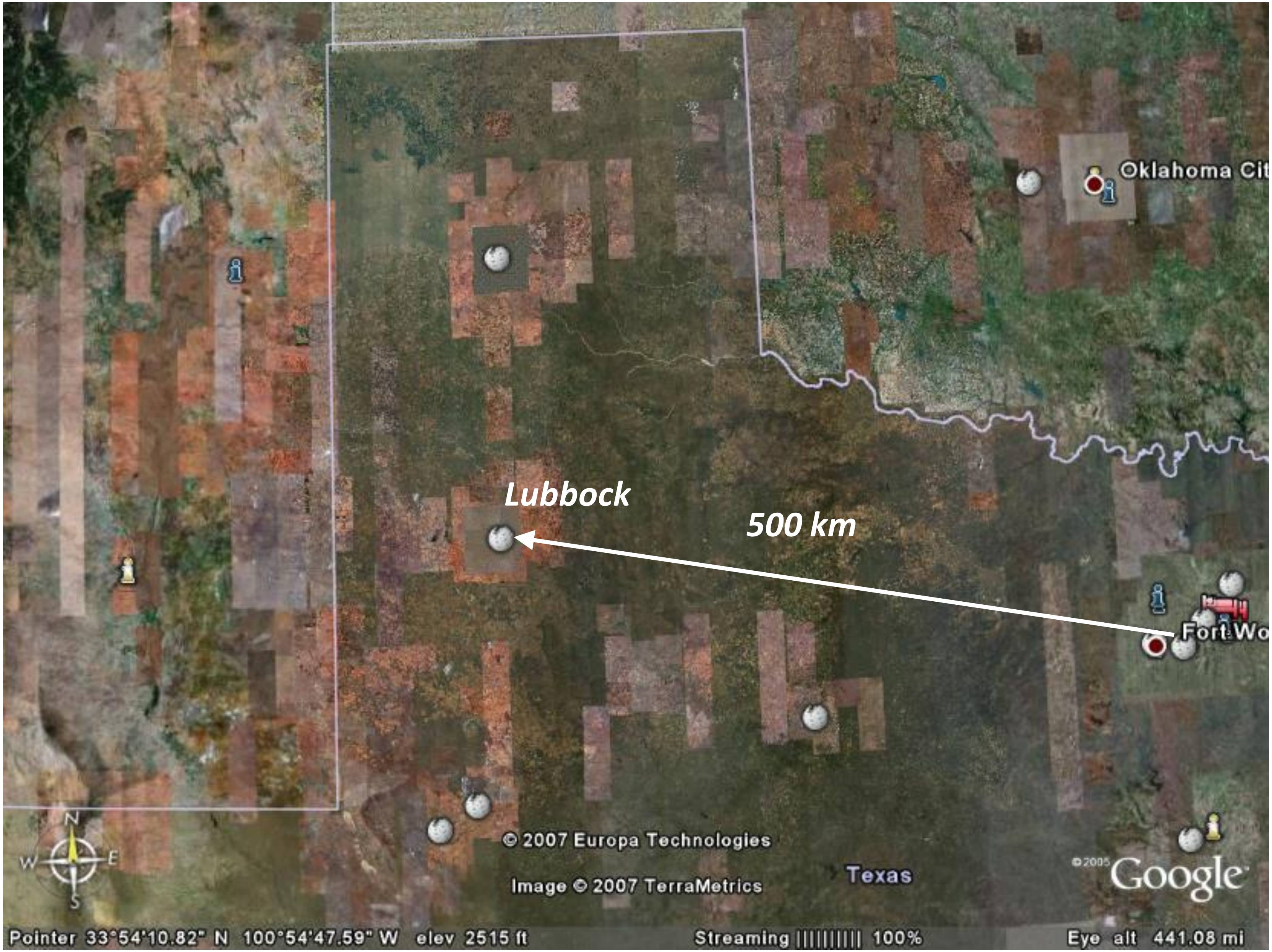
Gregory B. McKenna
Department of Chemical Engineering
Texas Tech University
Lubbock, TX USA
Greg.McKenna@ttu.edu

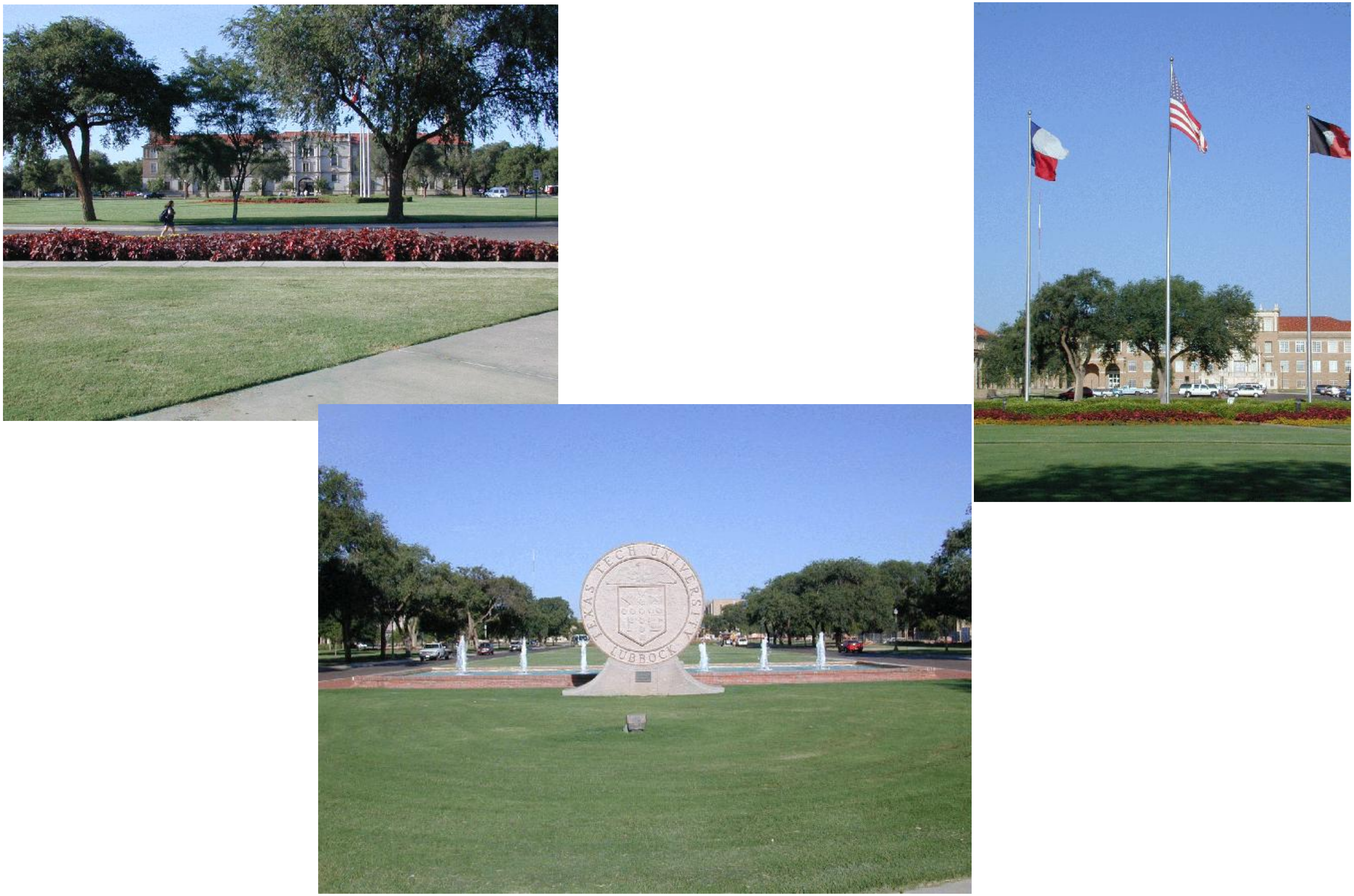
School on Glass Formers and Glasses
JNCASR, Bengaluru, India
January 4-20, 2010


N
W
E
S
© 2007 Europa Technologies
Image © 2007 TerraMetrics
Image © 2007 NASA
Google
Pointer 38°57'33.84" N 95°15'55.44" W
Streaming |||||||||| 100%
Eye alt 3958.94 mi

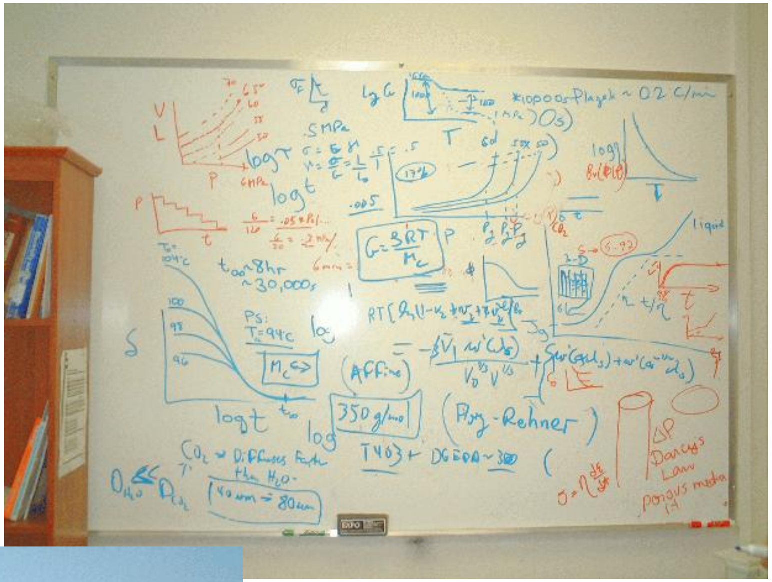


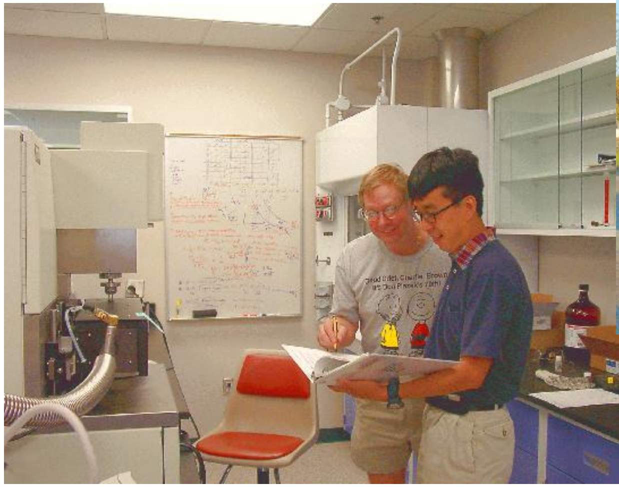
Oklahoma
Arkansas
New Mexico
Mississippi
Dallas
Texas
Louisiana
Houston
San Antonio
© 2007 Europa Technologies
Image © 2007 TerraMetrics
©2005 Google
Monterrey
N
E
S
W
Pointer 31°50'56.16" N 98°56'36.79" W
Streaming |||||||||| 100%
Eye alt 993.58 mi


Oklahoma Cit
Lubbock
500 km
Fort Wo
© 2007 Europa Technologies
Image © 2007 TerraMetrics
Texas
©2005 Google
N
W
E
S
Pointer 33°54'10.82" N 100°54'47.59" W elev 2515 ft
Streaming |||||||||| 100%
Eye alt 441.08 mi



Texas Tech University





Polymers in Chemical Engineering at TTU

Outline

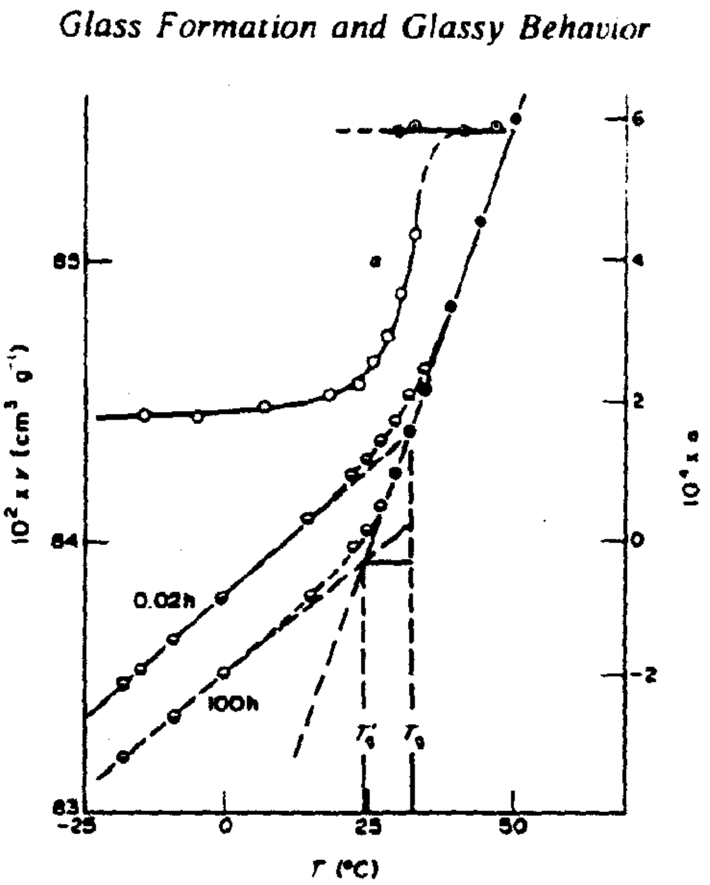
- Some Background
- The Temperature Jump Experiments
  - Structural Recovery
    - Intrinsic Isotherms
    - Asymmetry of Approach
    - Memory Effects
- The models
  - TNM or KAHR
- Other Structural Recovery paths
  - The Chemical Activity Jumps
    - Relative Humidity Jump
    - CO_2 Jump
  - Isochoric Recovery in Nanopores

The measured glass transition is path and measurement method dependent

The glass transition is path-dependent

The glass transition is path-dependent

Tg depends on rate or time



Path dependence of Tg and pressure effects on Tg

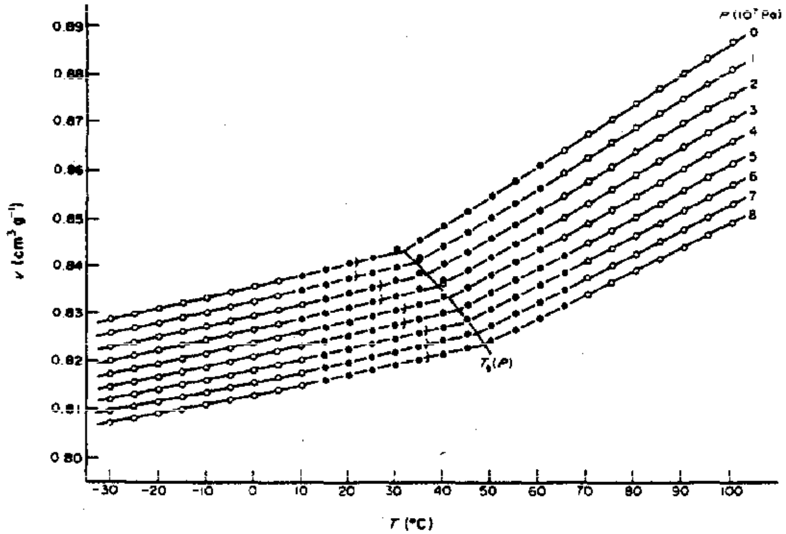


Figure 7 Specific volume v of poly(vinyl acetate) *vs.* temperature T at different pressures, as indicated, for variable-formation glass; note definition of $T_g(P)$ for this type of glass (after ref. 37, with permission)

318 *Glass Formation and Glassy Behavior*

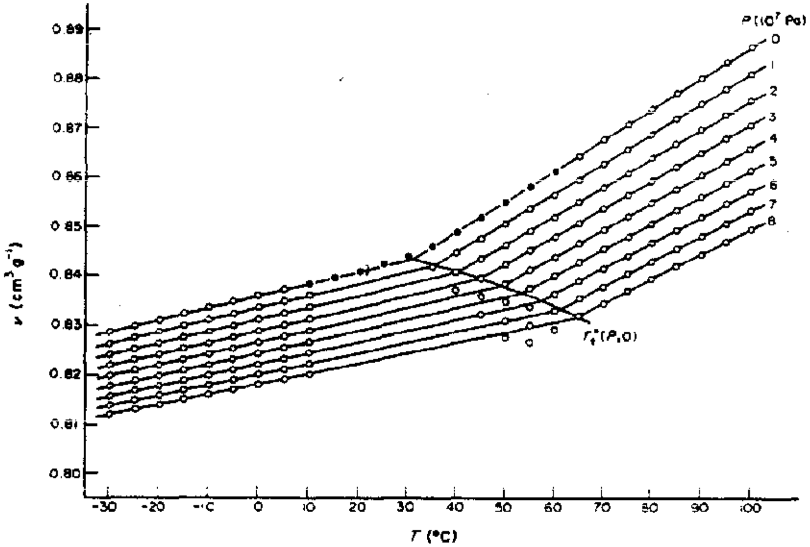


Figure 8 Specific volume v of poly(vinyl acetate) *vs.* temperature T at different pressures, as indicated, for isobaric glass formed at 1 atm; note definition of $T_g^*(P, 0)$ for this type of glass (after ref. 37, with permission)

The glass transition is path-dependent

Pressure dependence depends on path of glass formation

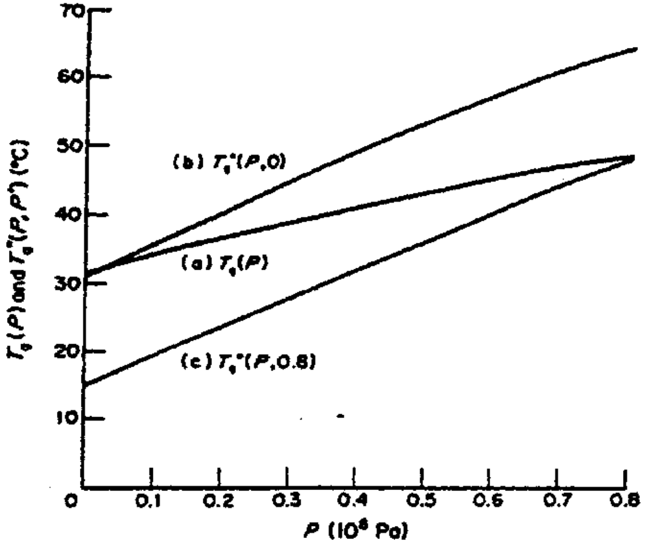
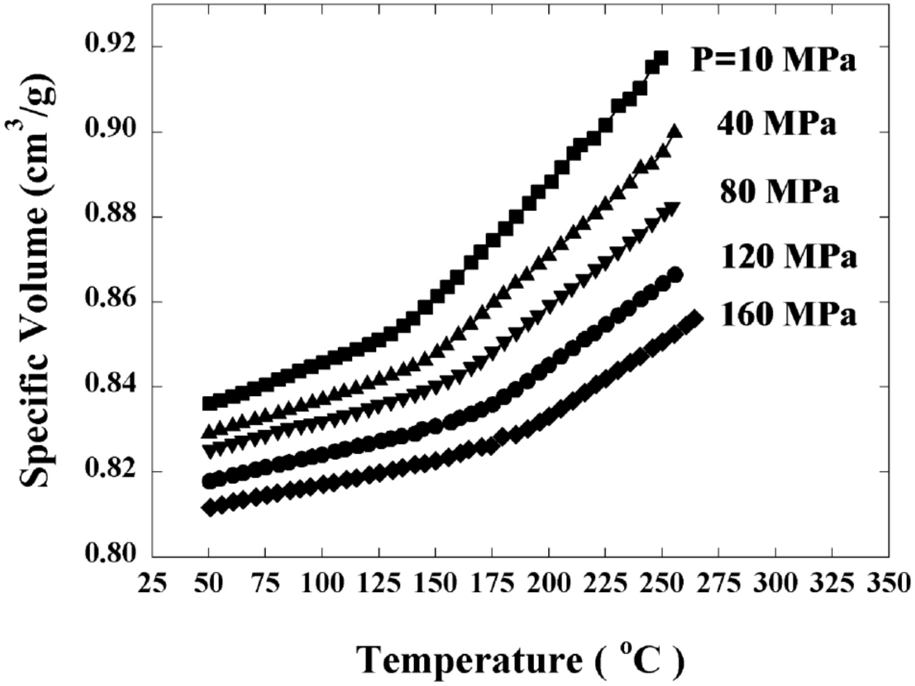
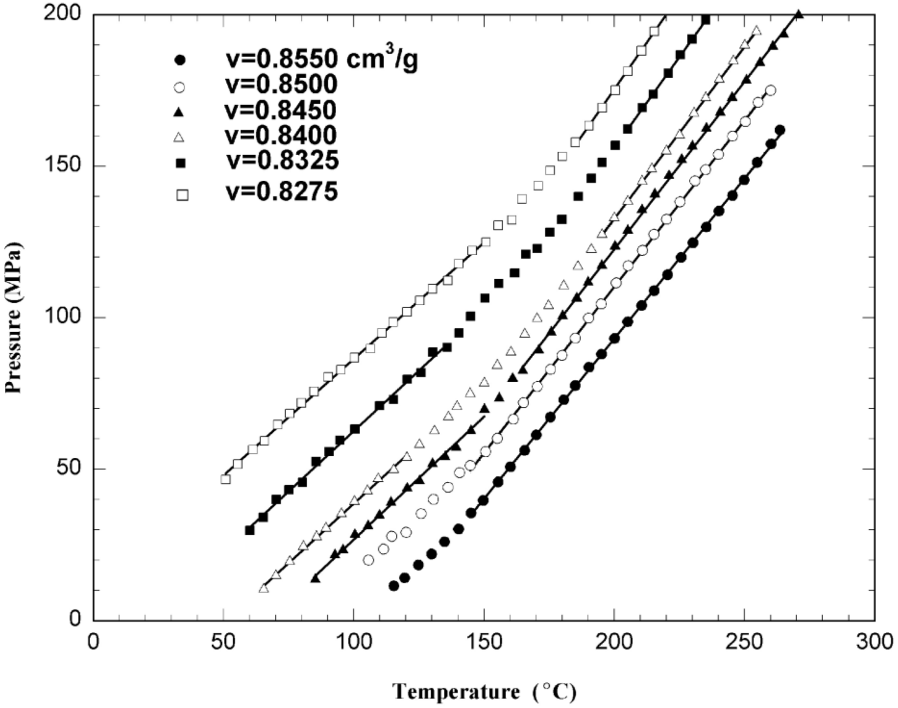


Figure 9 Transition map showing T_g and T_g^* *vs.* pressure P for different formation histories: (a) variable formation ($P' = P$), as in Figure 7; (b) isobaric glass formed at 1 atm ($P' = 0$), as in Figure 8; and (c) isobaric glass formed at 800 bar ($P' = 0.8$ kbar). Note that $\mathrm{d}T_g(P)/\mathrm{d}P < \mathrm{d}T_g^*(P,0)/\mathrm{d}P \approx \mathrm{d}T_g^*(P,0.8)$ (after ref. 37, with permission)

After McKinney and Goldstein, 1974



Isobaric measurements

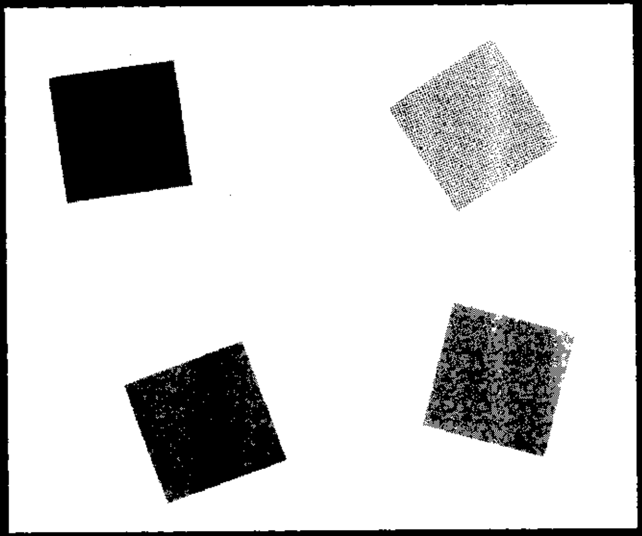


Isochoric measurements

Colucci et al, JPSB (1997)

The glass transition depends on the measurement technique

Assignment of the Glass Transition



Rickey J. Seyler, editor

ASTM

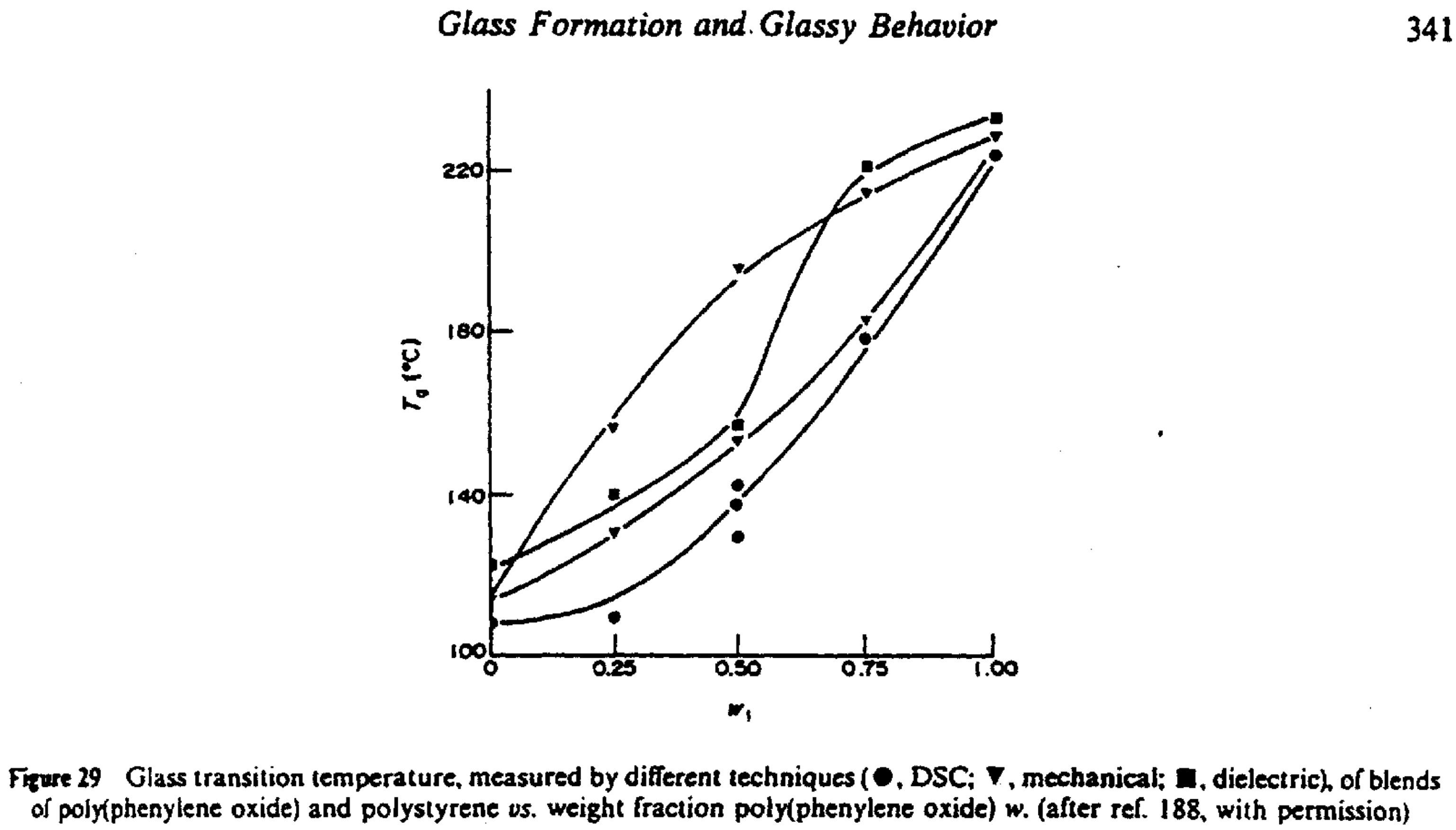
STP 1249

The glass transition depends on measurement technique.

- "The differences in assigned values of Tg were greater between measurements for a given thermomechanical history than between thermomechanical histories for a given measurement."

M.J. Moscato and R.J. Seyler, "Assigning the Glass Transition Temperature in Oriented Poly(ethylene terephthalate)," in *Assignment of the Glass Transition, ASTM STP 1249,* R.J. Seyler, ed., ASTM, 1994, pp. 239-252.

The glass transition depends on the measurement technique



Glass Formation and Glassy Behavior 341

Figure 29 Glass transition temperature, measured by different techniques (●, DSC; ▼, mechanical; ■, dielectric), of blends of poly(phenylene oxide) and polystyrene *vs.* weight fraction poly(phenylene oxide) *w.* (after ref. 188, with permission)

After McKnight, et al, 1971

The Glass Transition is a Kinetic Phenomenon as Measured in the Laboratory

***Structural Recovery:** The evolution of the non-equilibrium state (or structure) of the glass towards equilibrium.*

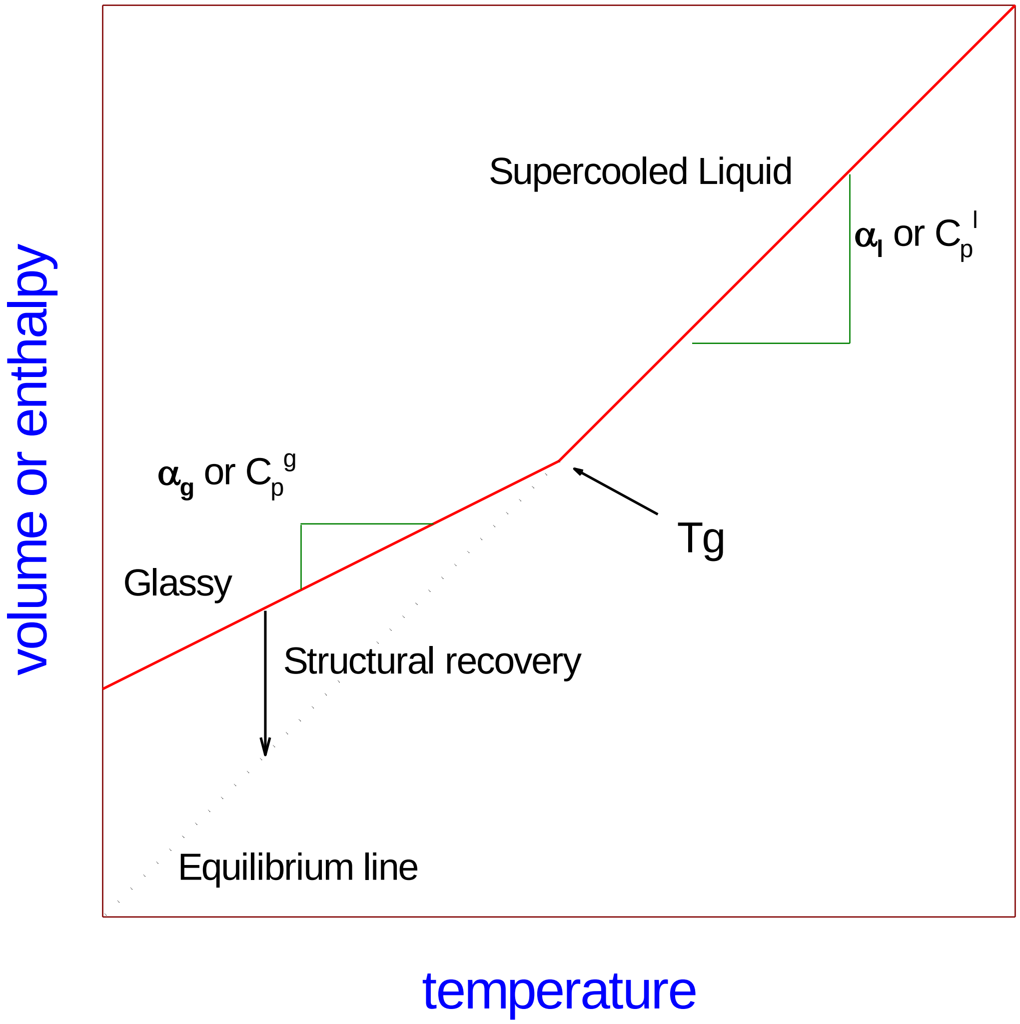
Physical aging is the response of mechanical (or other) property to the changing structure of the glass.

The glass transition kinetics

Structural Recovery

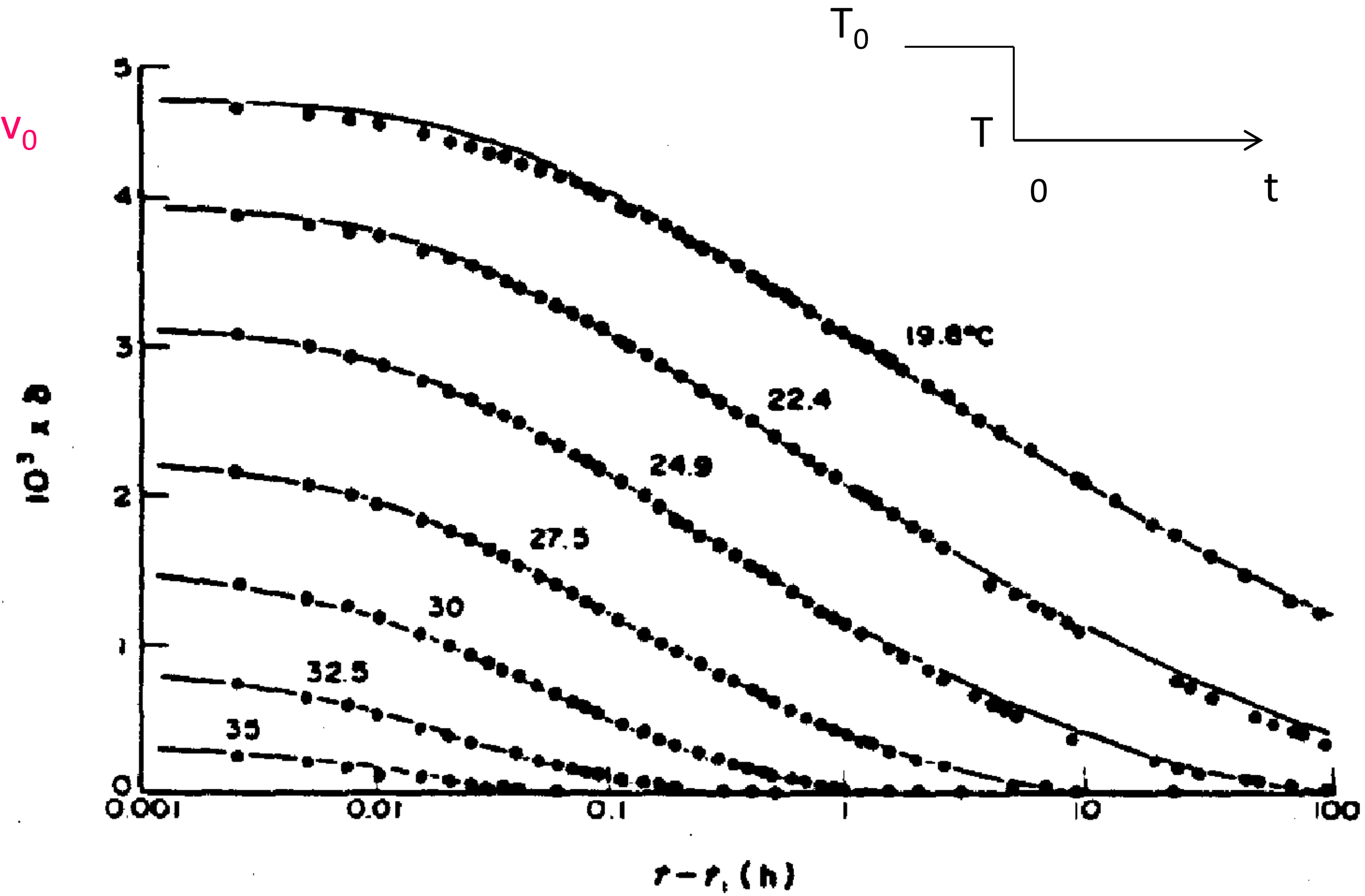
- Must explain:
  - Intrinsic isotherms (Nonexponential)
  - Asymmetry of approach (Nonlinear)
  - Memory (or crossover) effects (History dependent)

Down-jump experiments: Intrinsic Isotherms



Intrinsic isotherms

$\delta = (v-v_0)/v_0$



After A.J. Kovacs, 1964

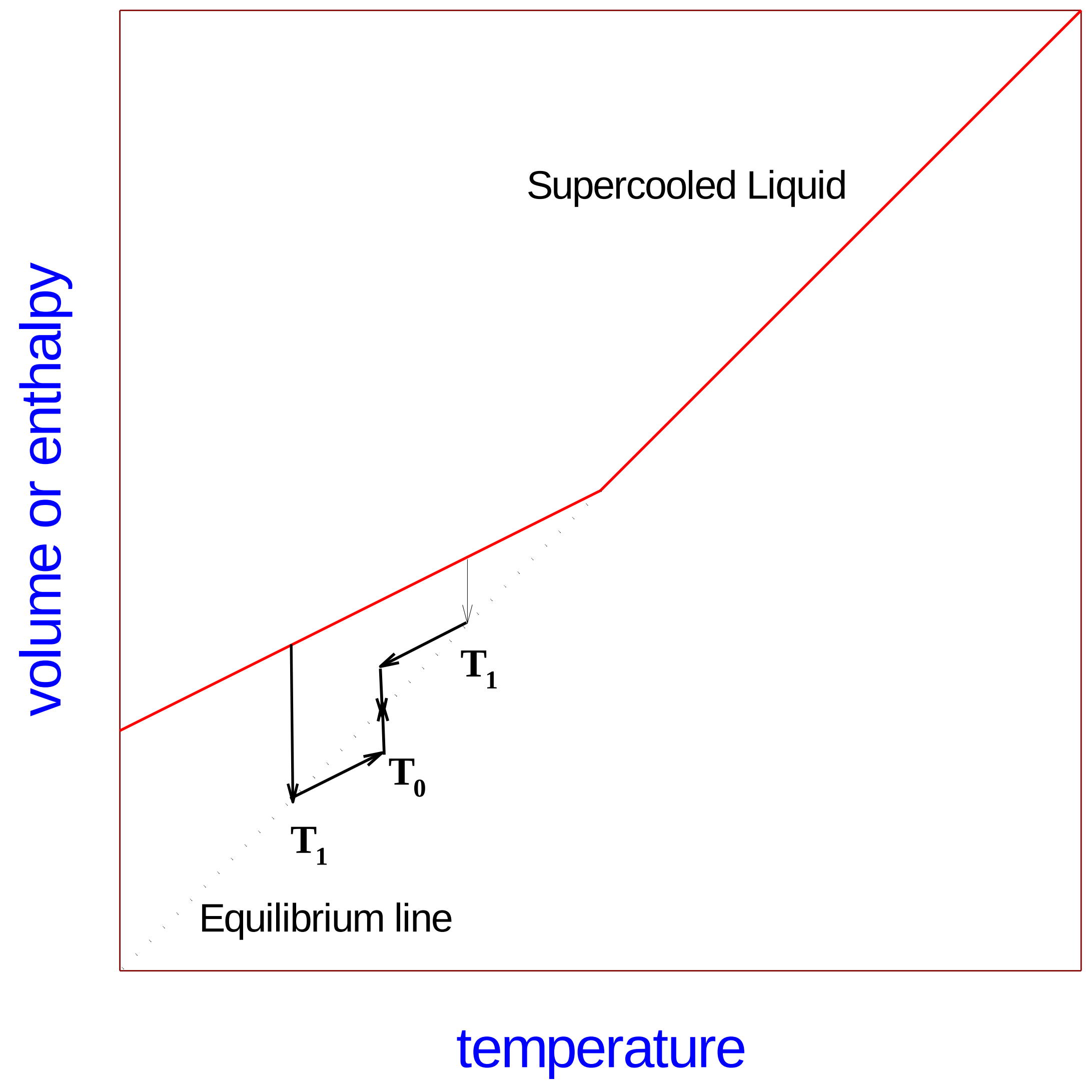
Intrinsic isotherms

Empirically, the intrinsic isotherms can be described
by a stretched exponential expression with an exponent that
depends on the magnitude of the T-jump from T_0 to T.

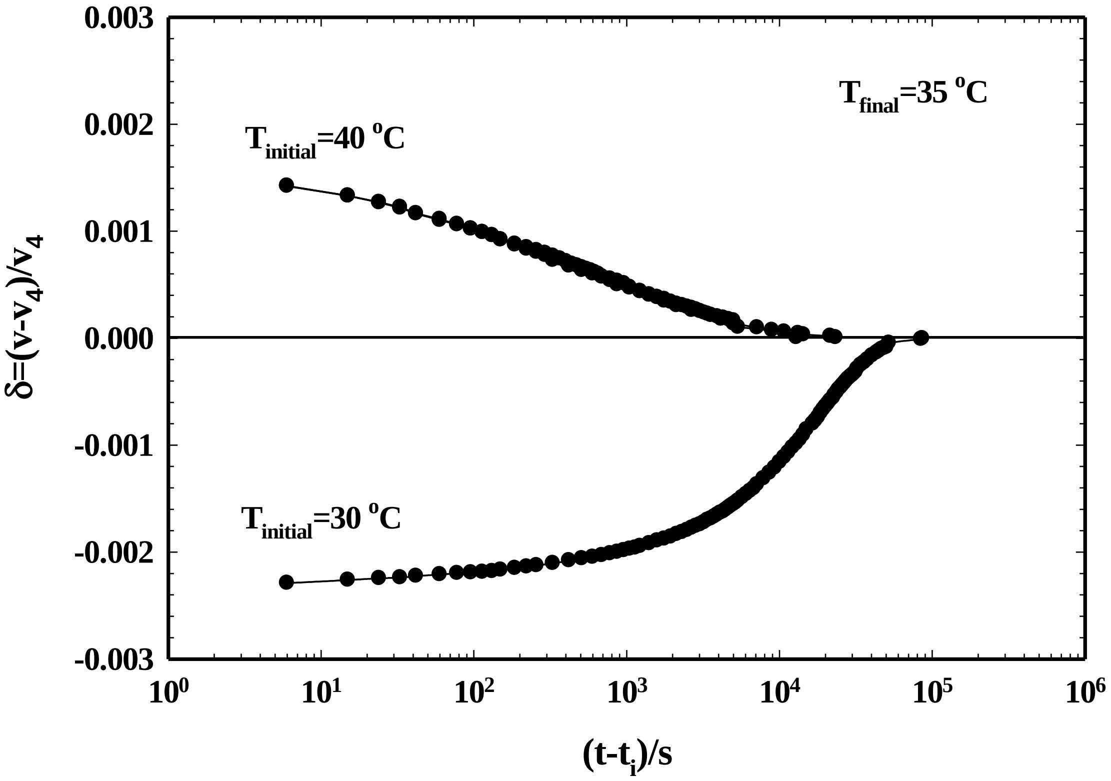
$\delta = \delta_0 \exp[-(t/\tau)^\beta]$

Indicates a non-exponential decay, but data are insufficient to establish this definitively.

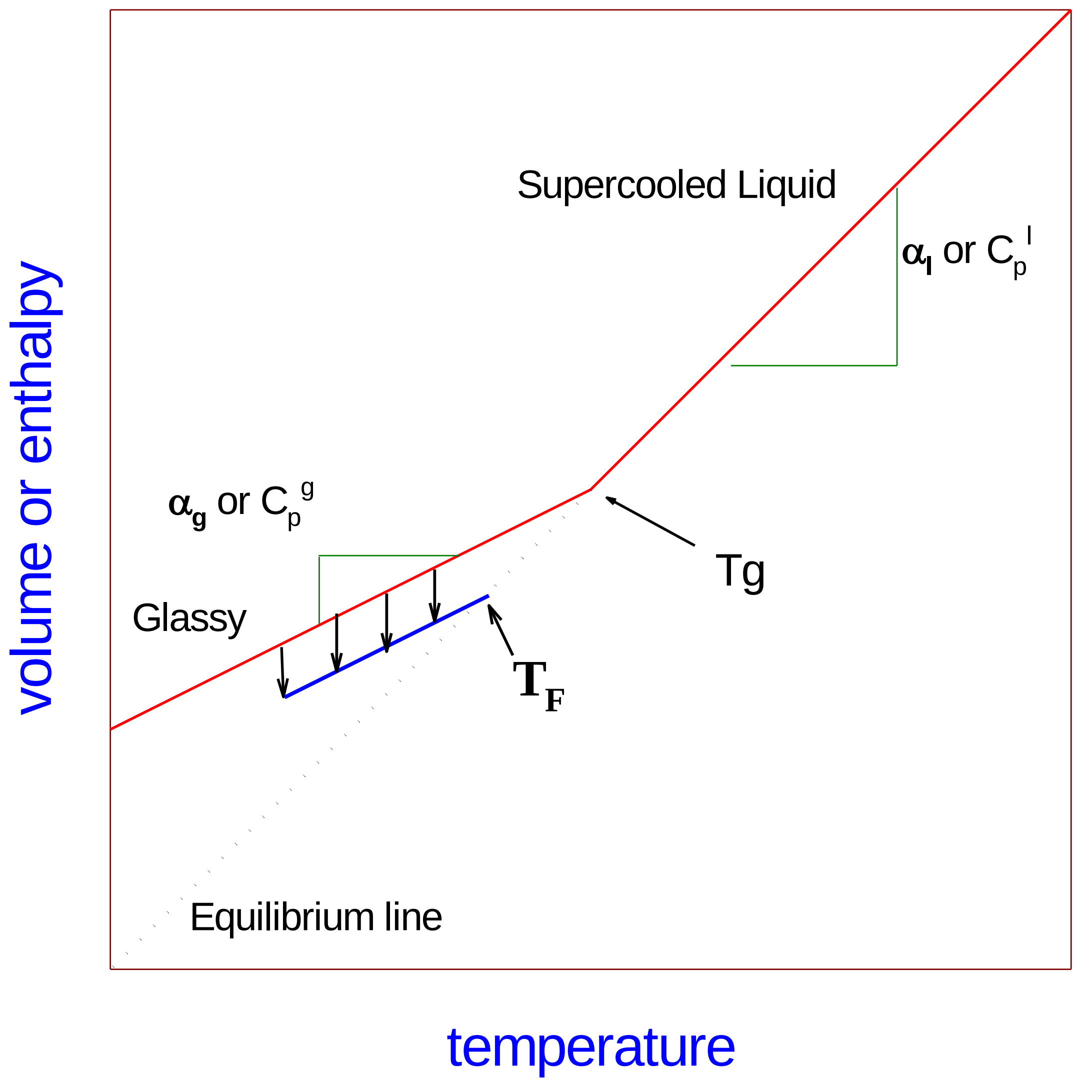
Asymmetry of Approach:
Demonstration of Nonlinearity



Asymmetry of Approach



Memory Experiment: 2-step T-jump



Memory Experiment: Requires more than a single relaxation time or a non-exponential relaxation function

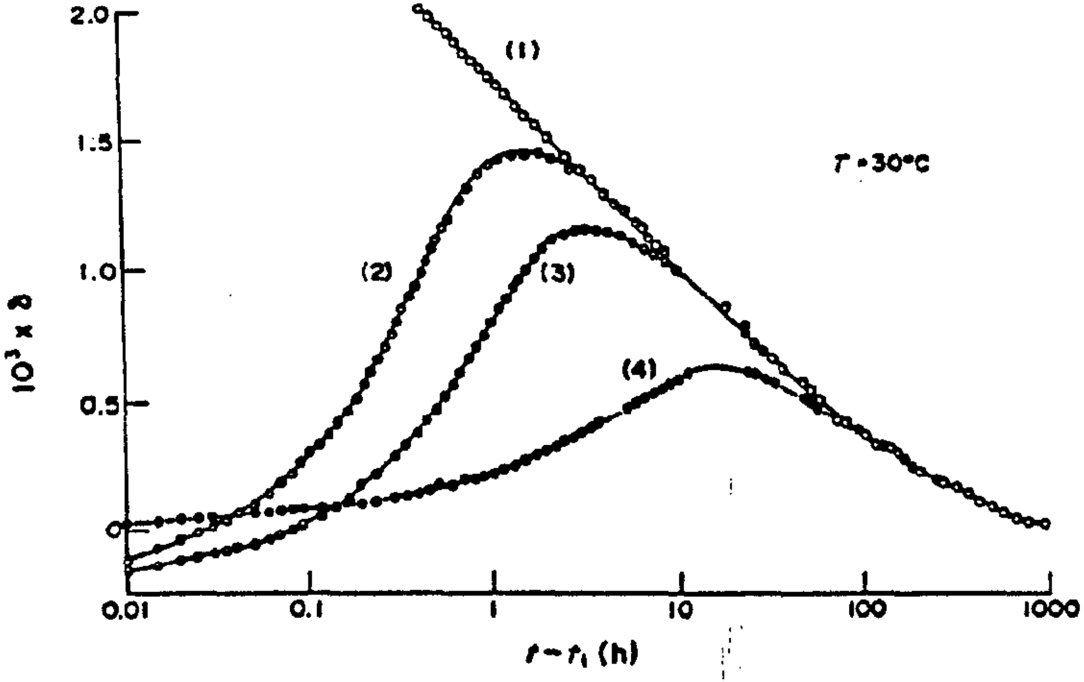


Fig. 6. Isothermal evolution at $T_0 = 30$ °C for poly(vinyl acetate) showing memory effect: (1) quench from 40 °C to 30 °C; (2) quench from 40 °C to 10 °C for 160 h followed by up-jump to 30 °C; (3) quench from 40 °C to 15 °C for 140 h followed by up-jump to 30 °C; (4) quench from 40 °C to 25 °C for 90 h followed by up-jump to 30 °C. Note that at short times $\delta \approx 0$. (After Ref. 1, with permission.)

After A.J. Kovacs, 1964

The Tool-Narayanaswamy-Moyninhan (TNM) or Kovacs, Aklonis, Hutchinson, Ramos (KAHR) Models

- **Non-exponential decay**
  - Sum of exponentials (KAHR)
  - Stretched exponential (TNM)
- **Nonlinearity**
  - Relaxation time depends on structure (time-temperature-structure superposition)
    - Fictive temperature T_F (TNM)
    - Departure from equilibrium δ (KAHR)
- **History Dependent**
  - Boltzmann linear superposition in “reduced time”

The TNM-KAHR Models of Structural Recovery

The Constitutive Equation:

$$\delta(z) = -\Delta\alpha \int_{0}^{z} R(z - z')\frac{dT}{dz'}dz'$$

Reduced Time:

$$z = \int_{0}^{t} \frac{d\xi}{a_T a_\delta} \qquad \text{or} \qquad z = \int_{0}^{t} \frac{d\xi}{a_T a_{T_F}}$$

(KAHR) *(TNM)*

The TNM-KAHR Models of Structural Recovery

Retardation (relaxation) functions:

$$R(z) = \sum g_i e^{-t/\tau_i} \qquad \textit{or} \qquad R(z) = R_0 e^{-(t/\tau)^{\beta}}$$

(KAHR)

(TNM)

The TNM-KAHR Models of Structural Recovery

The Temperature Functions:

$$\frac{\tau_i(T,\delta)}{\tau_{i,r}} = a_T a_\delta = e^{-\theta(T-T_r)} e^{-\frac{(1-x)\theta\delta}{\Delta\alpha}}$$

(KAHR)

$$\frac{\tau(T,T_F)}{\tau_r} = a_T a_{T_F} = e^{\frac{x\Delta h}{R}\left(\frac{1}{T}-\frac{1}{T_r}\right)} e^{\frac{(1-x)\Delta h}{R}\left(\frac{1}{T_F}-\frac{1}{T_r}\right)}$$

(TNM)

x is a partition parameter $0<x<1$
Δh is an activation energy
$\Theta = E_a/RT_g^2$

The TNM-KAHR Models of Structural Recovery

The TNM differential form:

$$\frac{dT_F}{dT} = 1 - e^{\left[-\left(\int_0^t \frac{dt}{\tau}\right)^{\beta}\right]}$$

Determination of the Fictive Temperature

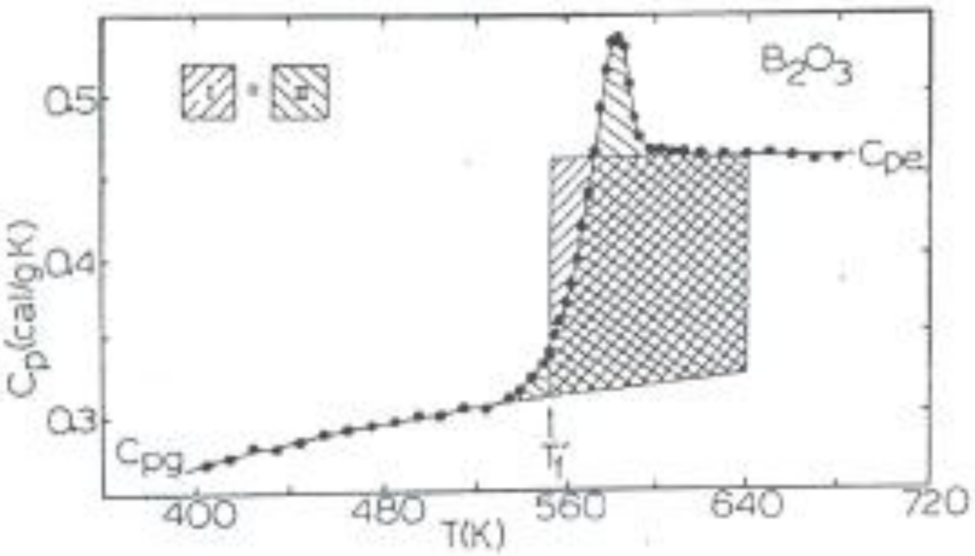


Fig. 27. Determination of the fictive temperature T_f from a DSC scan in which there is an annealing peak present. (Reprinted with permission of C.T. Moynihan. From Moynihan, C.T., Lee, S.-K., Tatsumisago, M. and Minami, T. (1996), Reference 93).

The TNM-KAHR Models of Structural Recovery

How well do the models work?

↓

Reproduce the asymmetry of approach

↓

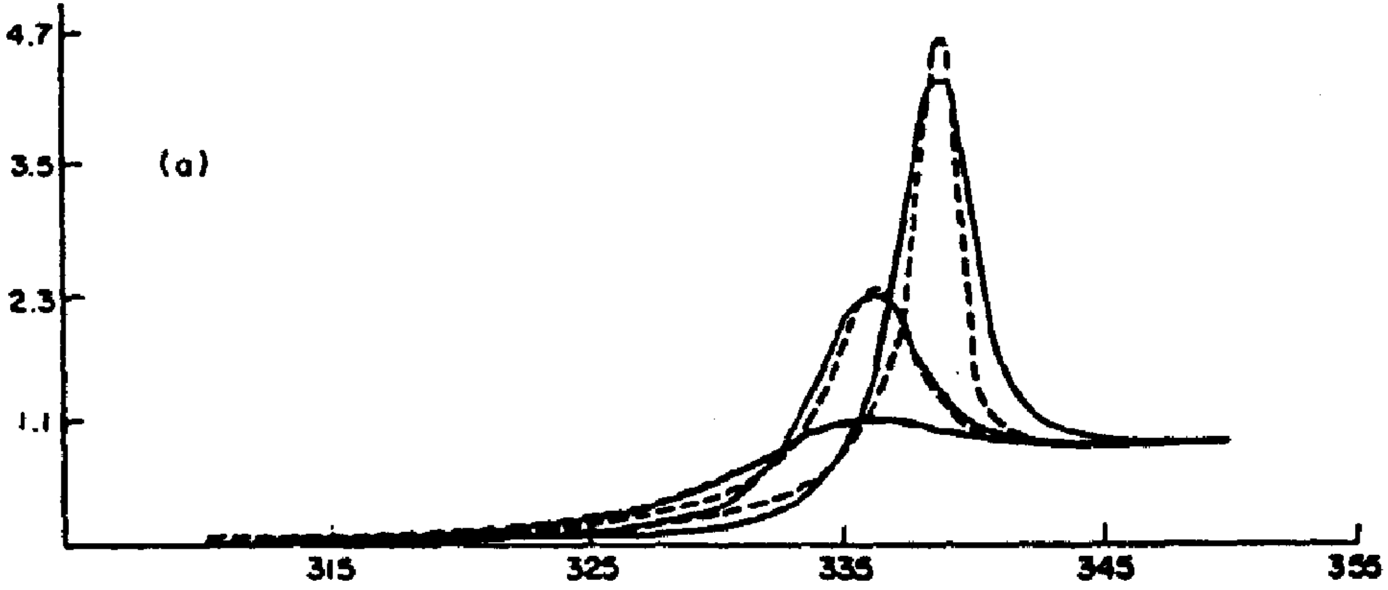
Reproduce the memory or cross-over experiment

↓

Capture enthalpy overshoot in DSC experiments

The TNM-KAHR Models of Structural Recovery

PMMA in DSC experiments



After J.J. Tribone, J.M. O'Reilly and J. Greener, Macromolecules, 1986

The TNM-KAHR Models of Structural Recovery

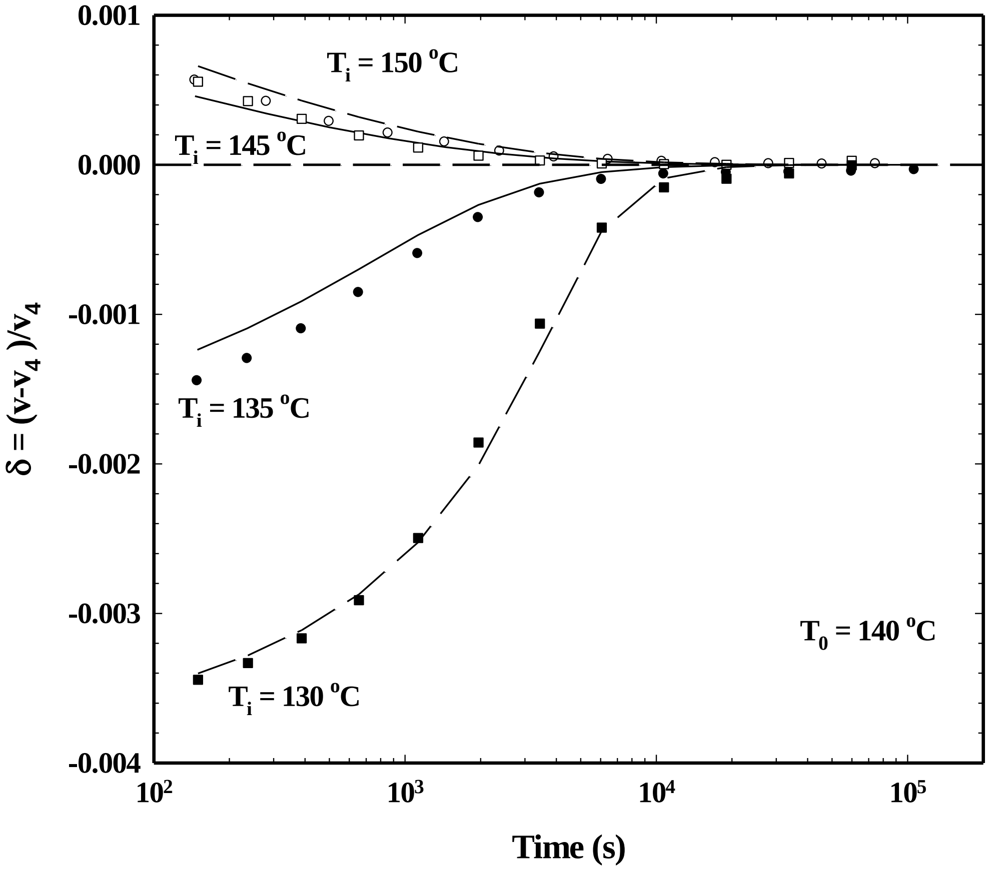


Figure 5. Plot of asymmetry of approach experiments in a polycarbonate material aged into equilibrium at temperatures T_i and then jumped to a final test temperature of T_0 = 140 °C. Points are for experimental data and lines represent KAHR-model description of the data. See text for discussion. (Data after reference 19.)

C.R. Schultheisz and G.B. McKenna, 1997

The TNM-KAHR Models of Structural Recovery

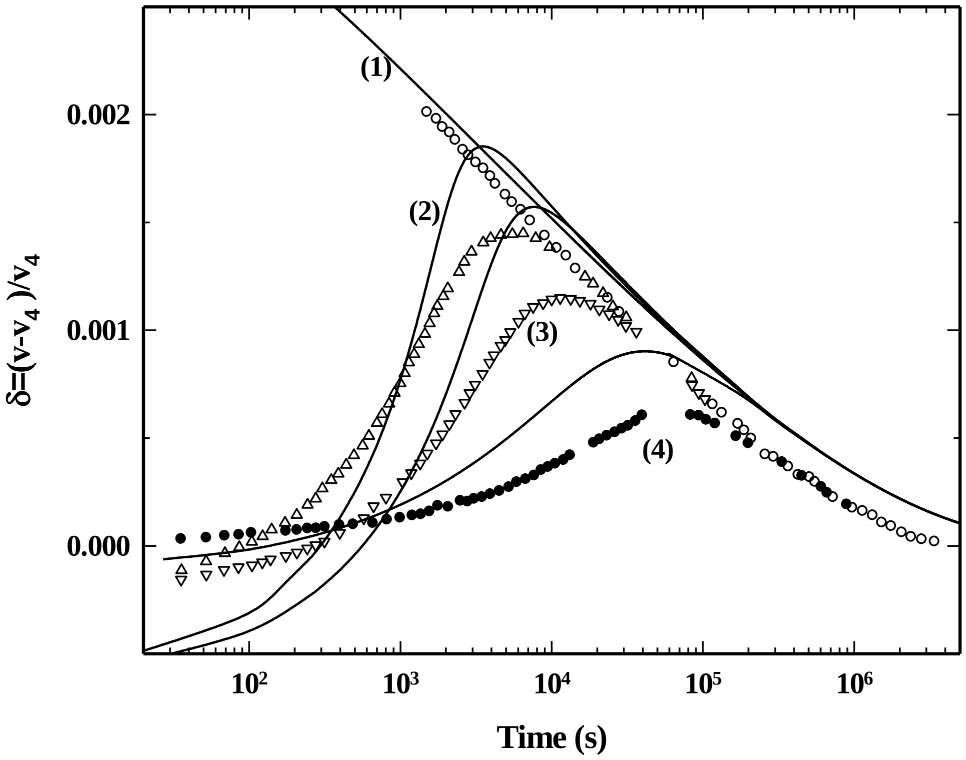


Figure 6. Comparison of KAHR-model calculations (lines) with the Kovacs memory experiment data depicted in Figure 4. Note that the time axis is for time after the beginning of the quench rather than the end as in Figure 4. Curve numbers have same meaning as in Figure 4. (Calculations after C.R. Schultheisz, ref. 20).

The TNM-KAHR Models of Structural Recovery

- *Models are good representations of the kinetics of structural recovery, but do not capture all behaviors*
  - *Material parameters change as temperature range changes*
  - *Fits not good for deep quenches (> 25-30 °C in some experiments)*
  - *Pressure-jumps are problematic as well*
  - *However, these models are really the current paradigm for describing structural recovery*

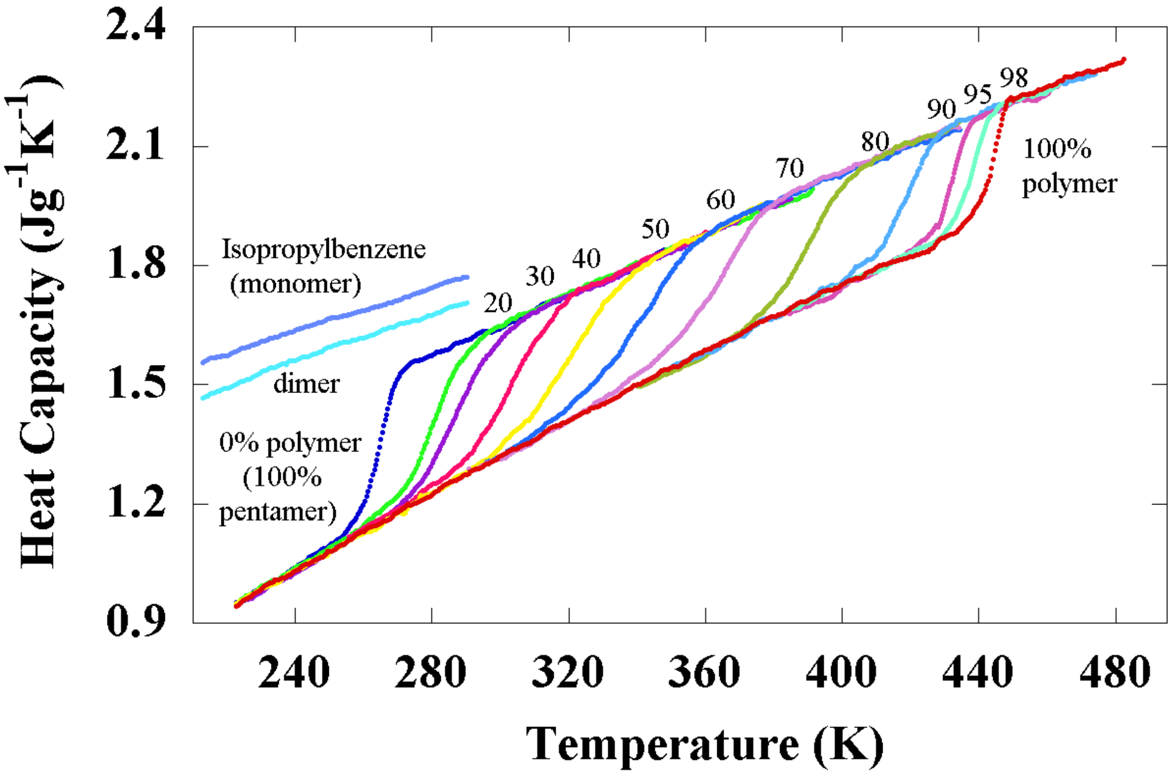
Another Path of Structural Recovery: Experiments made possible by the plasticizing effect in polymers.

What is plasticization?

- **According to free volume or configurational entropy models of Tg, addition of small molecules of low glass transition to a polymer leads to a decrease in the Tg of the mixture. If the small molecules are volatile, we can take advantage to 'rapidly dry' the sample through the concentration glass transition and search for the same signatures as when one changes temperature rapidly. In what follows it is shown that glasses subjected to such 'chemical activity' or plasticizer jumps are only qualitatively like temperature glasses. Another strong instance of the path dependence of the glassy structure.**

Examples of Plasticization

Poly-α-methyl styrene and its oligomer at different concentrations



Examples of Plasticization

Glass Formation and Glassy Behavior 339

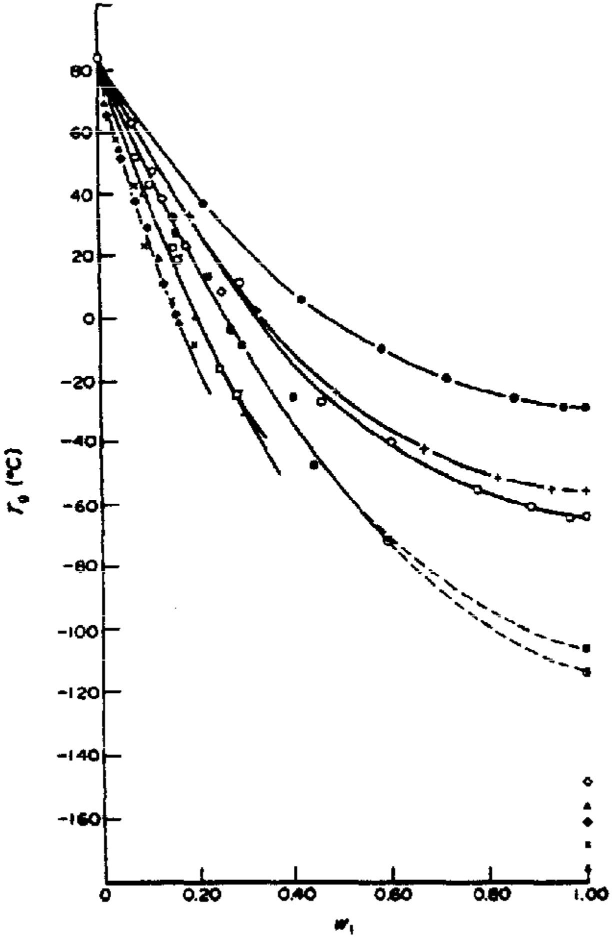
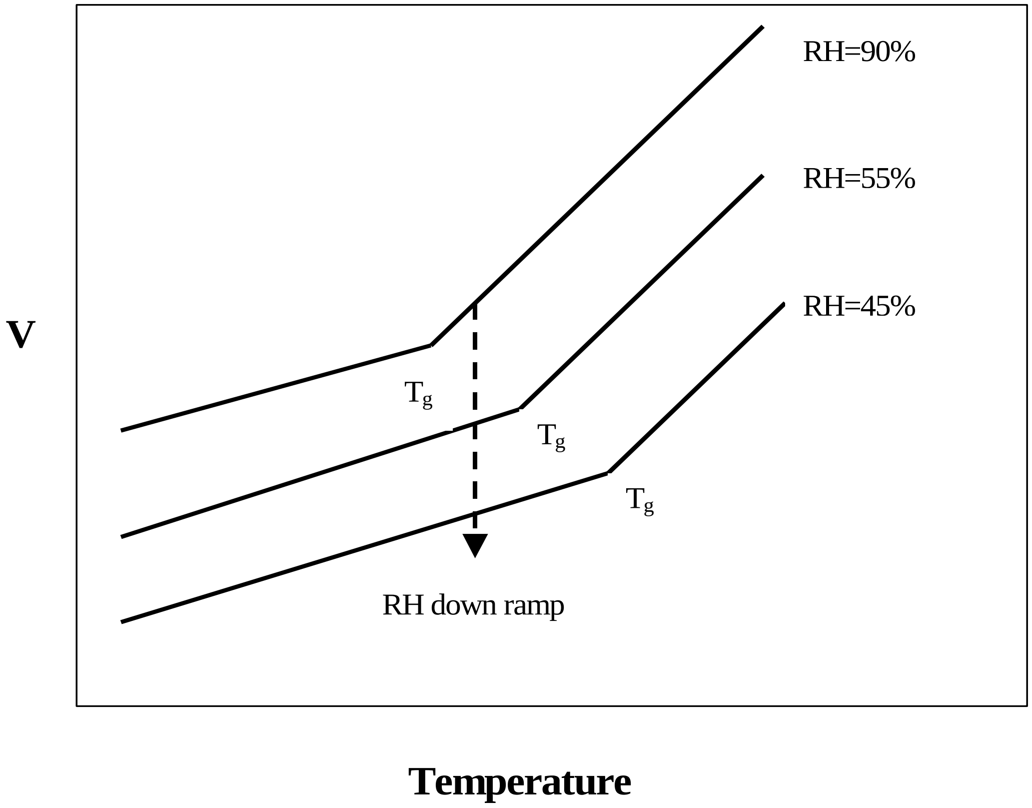
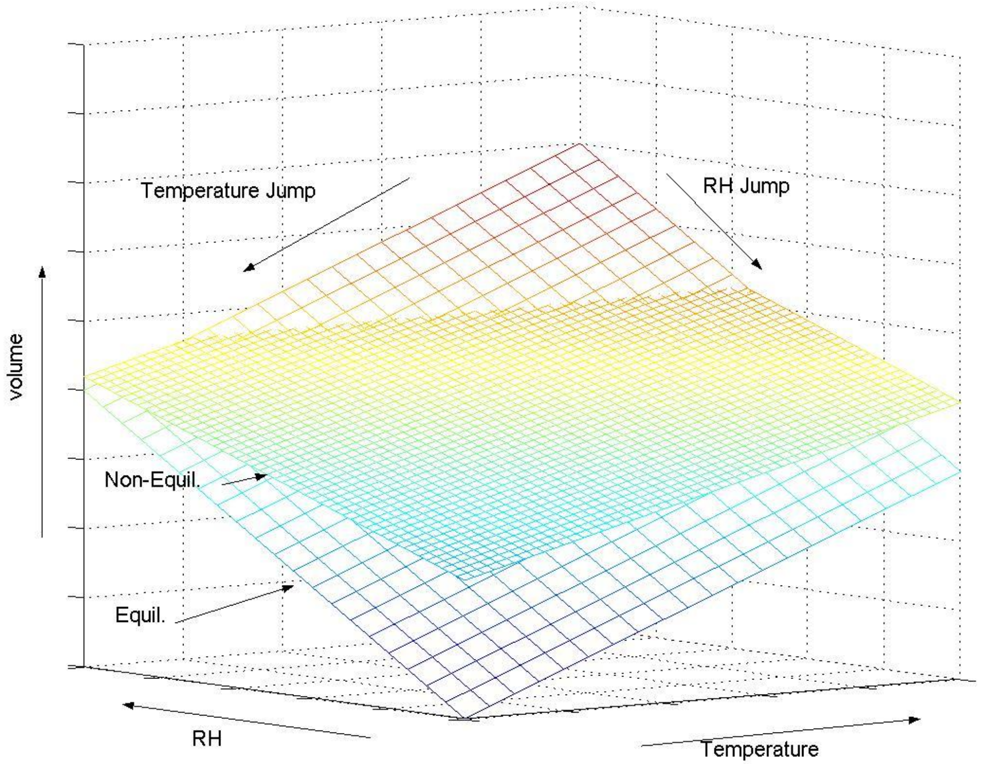


Figure 27 Glass transition temperatures of polystyrene solutions with various low molecular weight diluents: ●, β-naphthyl salicylate; +, phenyl salicylate; ○, tricresyl phosphate; ⊙ methyl salicylate; ■, nitrobenzene; ◇, chloroform; ×, methyl acetate; ◆, ethyl acetate; ▲, carbon disulfide; □, benzene; ⌀, toluene; △, amyl butyrate (after ref. 181, as cited in ref. 57, with permission)

The Chemical Activity Jump (RH example)

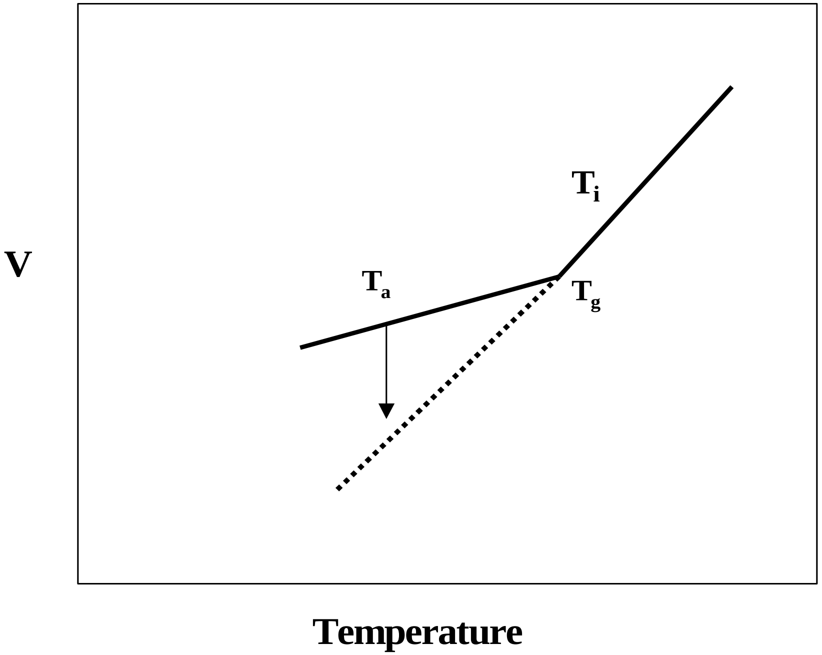


Fundamental Hypothesis

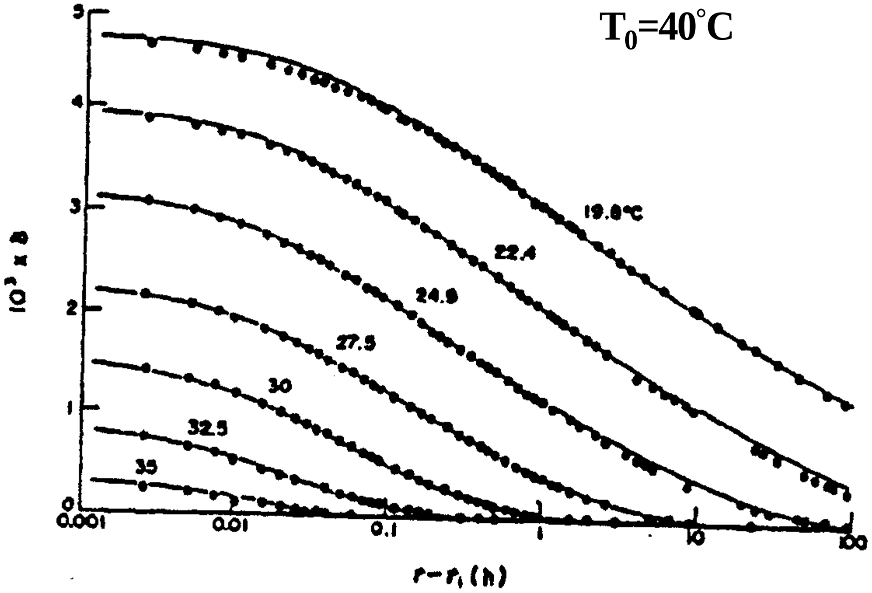


The change of relative humidity (or CO_2 pressure) has a similar effect to temperature changes on the structural recovery and physical aging.

Review of Kovacs' Thermal Experiments

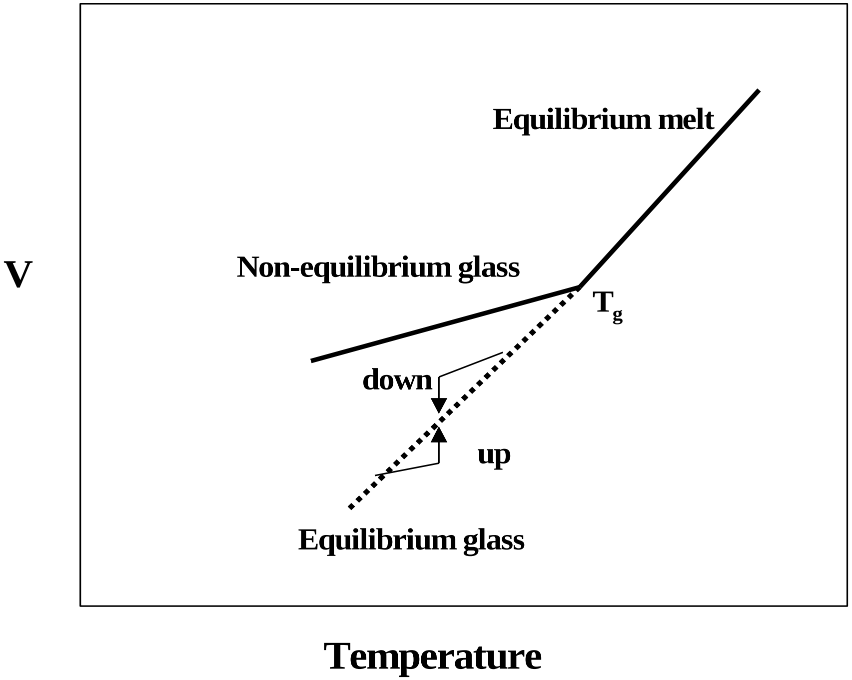


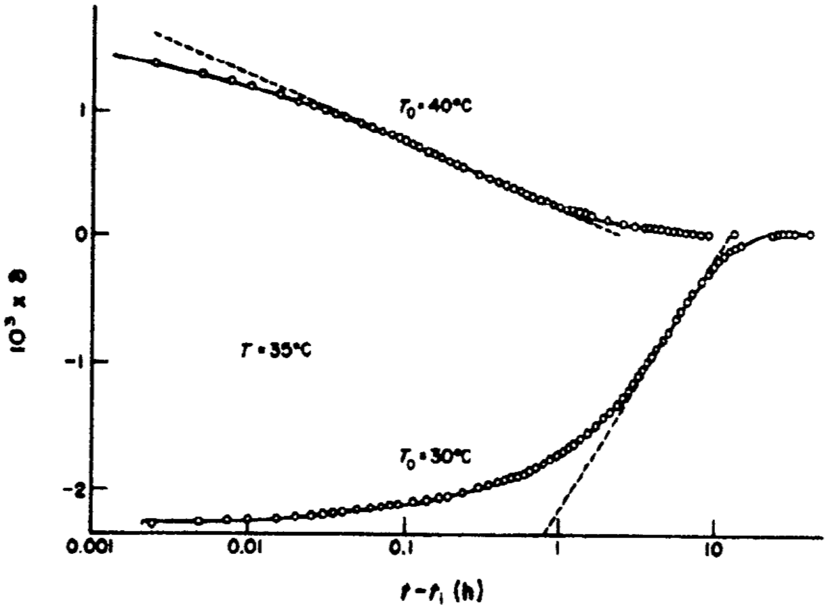
Intrinsic isotherms



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

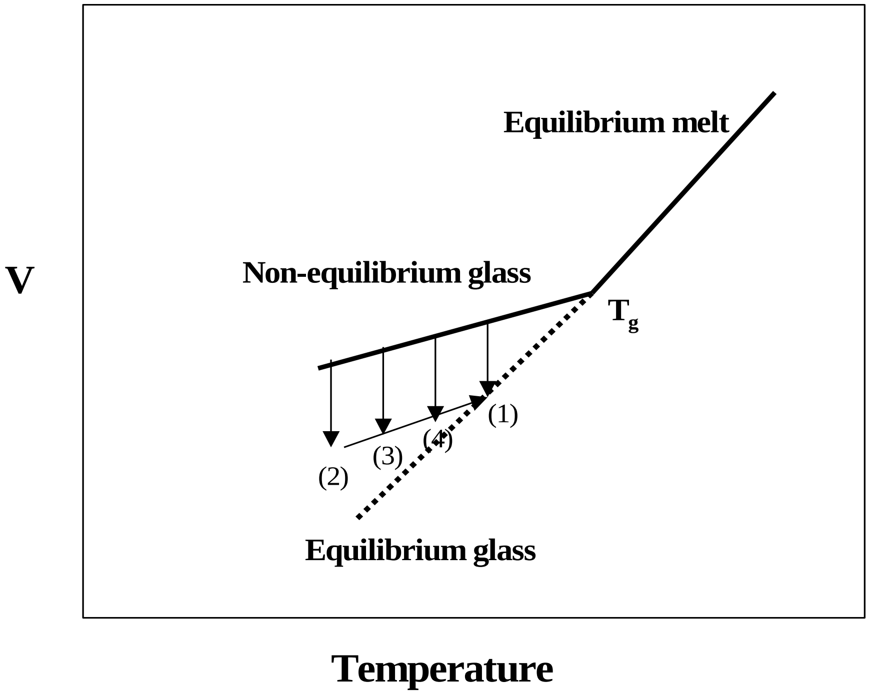
Asymmetry of Approach Experiments



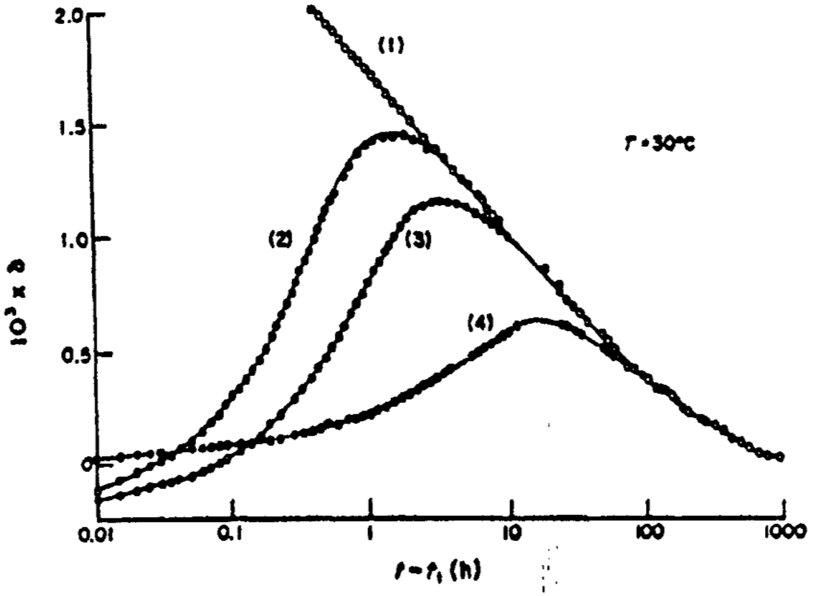


- Asymmetry of approach needs a temperature up-jump and a temperature down-jump.
- Both jumps have the same magnitude and the same final temperature.
- The volume response after a down-jump and the volume response after an up-jump approach the equilibrium volume asymmetrically.
- The reason for the asymmetry of approach is because the structural relaxation is dependent on the current structure. (Non-linear kinetics)

Memory Effect (Cross Over)

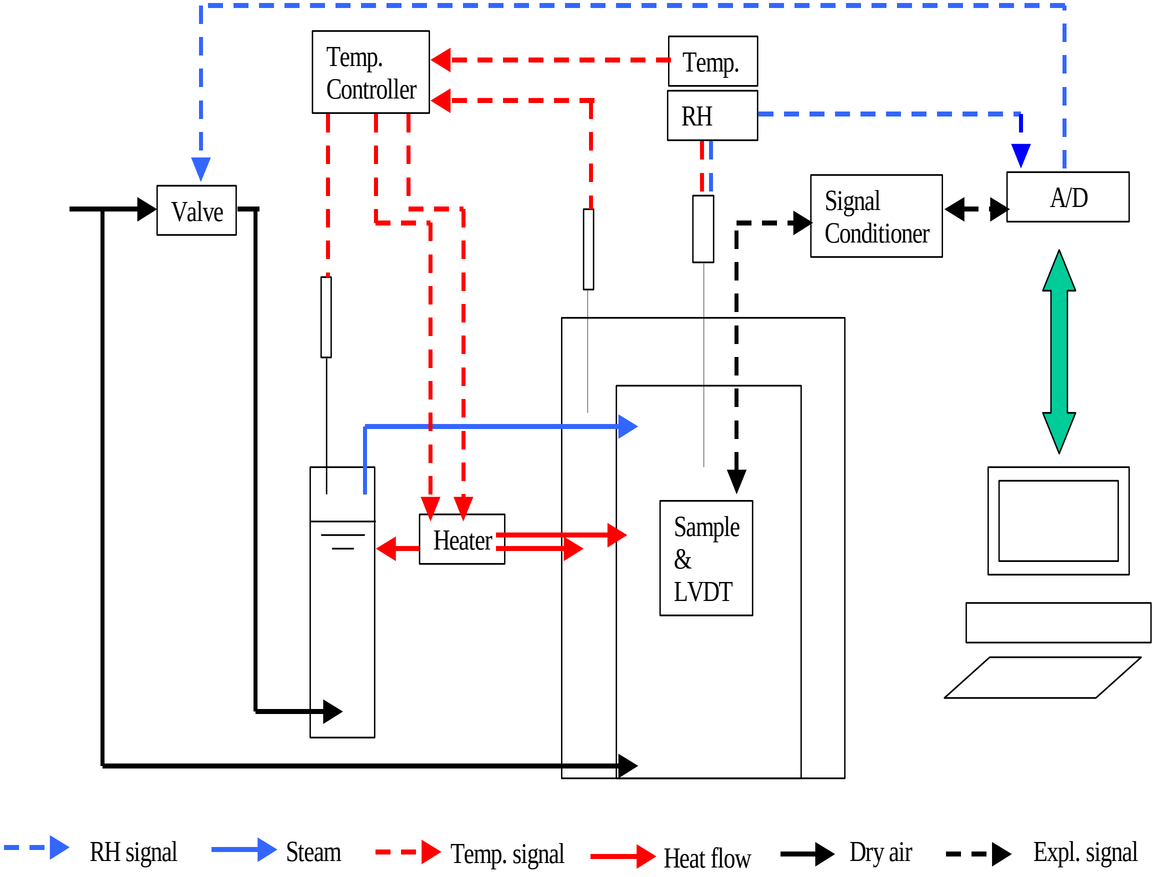


- Sample relaxes at a temperature below T_g and is then heated up.
- The relaxation is controlled such that the volume of the sample after heating to the final temperature is equal to the equilibrium volume



- After reheating, the sample will first increase in volume and then pass through a maximum and finally join the intrinsic isotherm to reach the equilibrium volume.
- This is due to a distribution of relaxation times. (Non-exponential kinetics)

Experimental Set-up for RH-jumps



The sample is epoxy Terminated DGEBA (Dow Chemical) fully curedwith amine terminated PPO (Huntsman).

$T_{g\infty\ dry}$=72 C .

Films of approximately 40 µm thickness

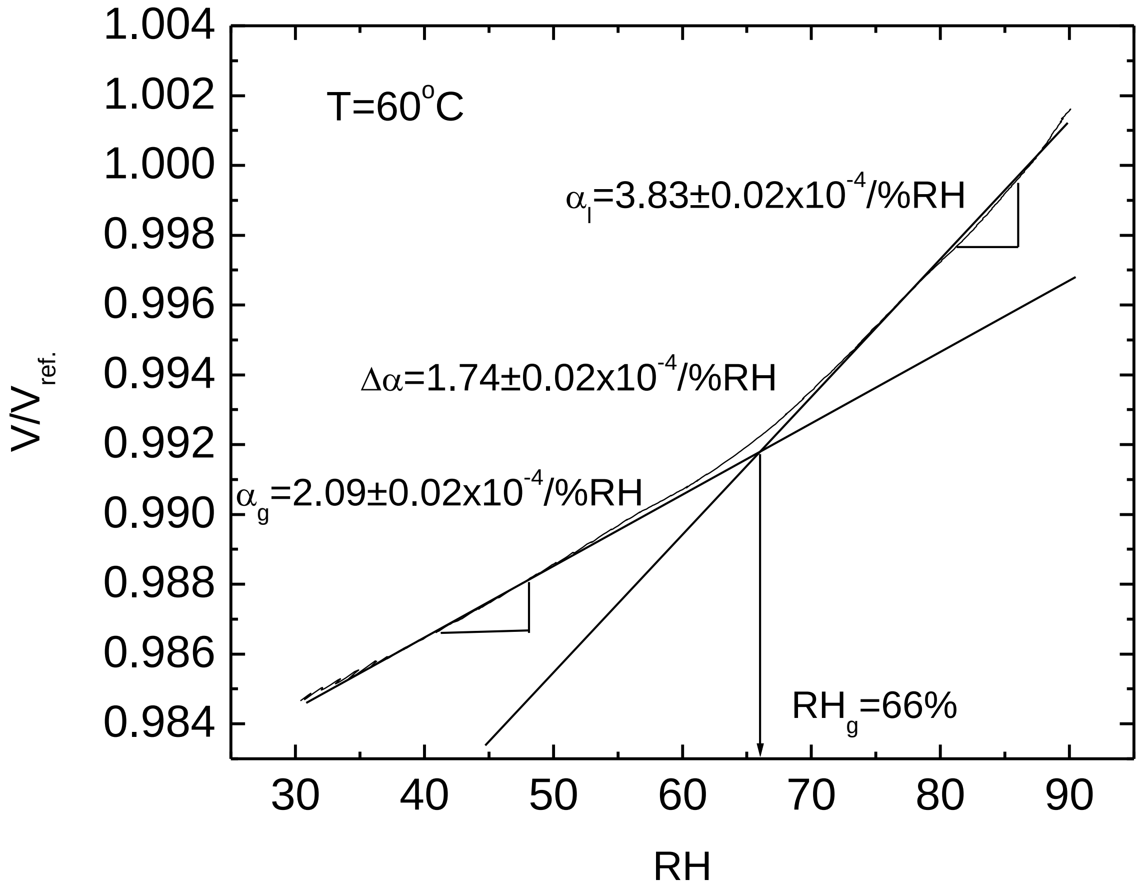
Structural Recovery Experiments after Plasticizer Jumps

- Intrinsic Isopiestics
- Asymmetry of approach
- Memory experiment
- Comparison between intrinsic isopiestic and intrinsic isotherms—Anomalous kinetics
- Volume overshoot—anomalous behavior

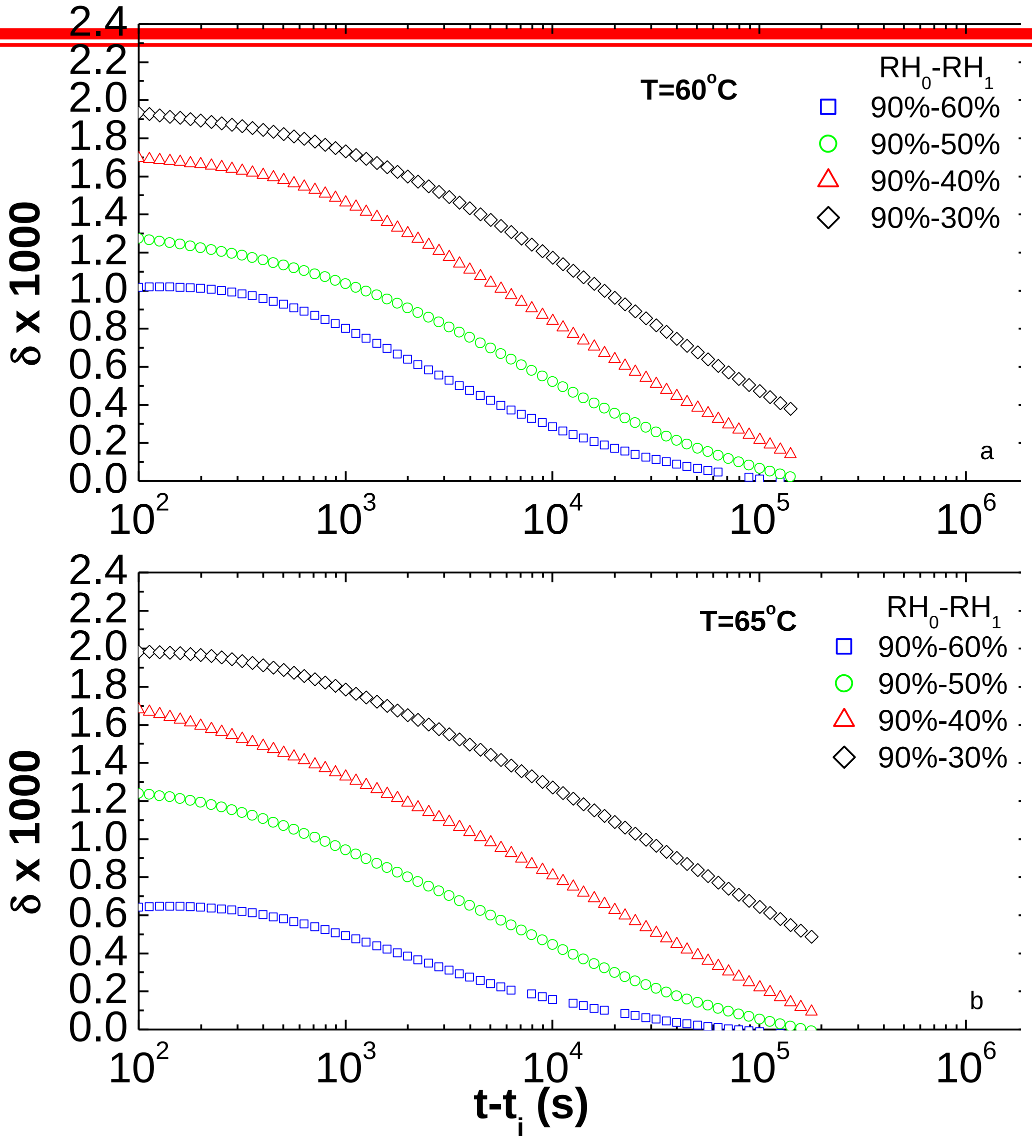
Volume Measurement

- Measurement of length change
- Sample is isotropic
- Volume is calculated based on length
- A stress of 0.1MPa is added on the sample

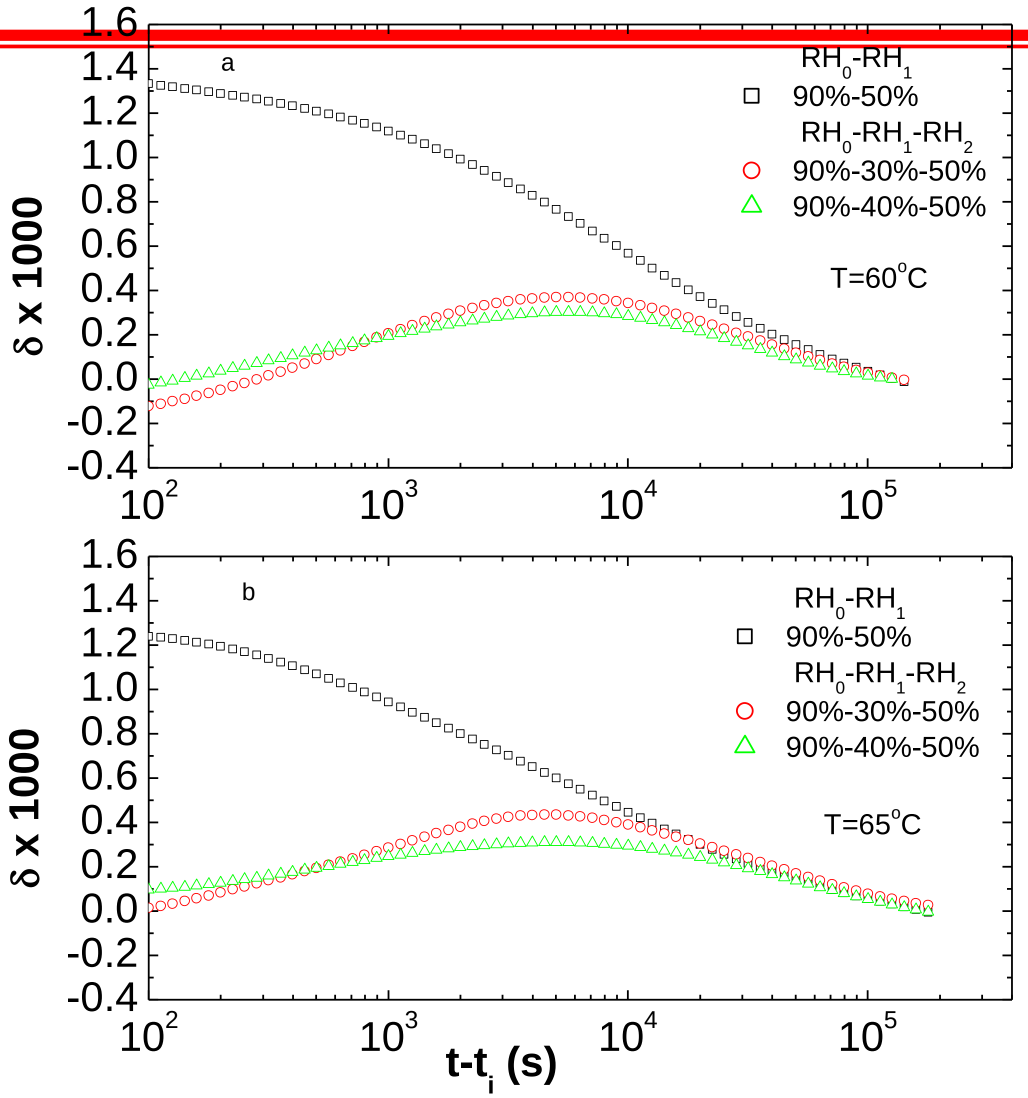
Humidity Ramps : Volume Change during RH Ramp



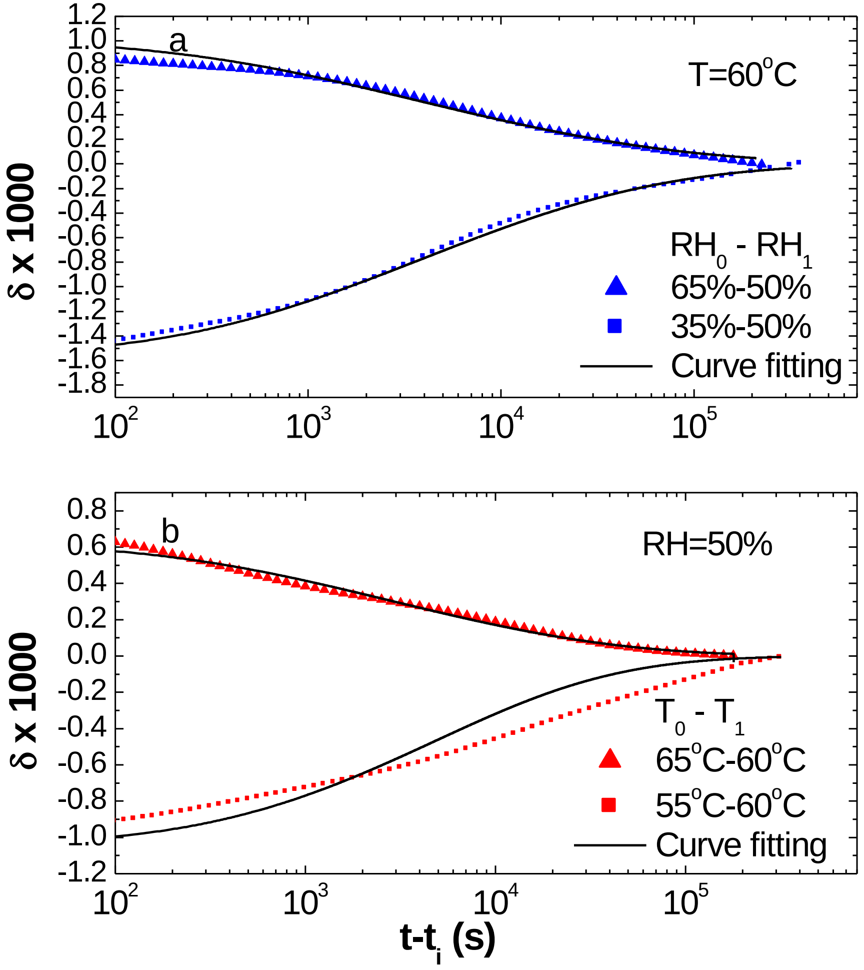
Structural Recovery: Intrinsic Isopiestics



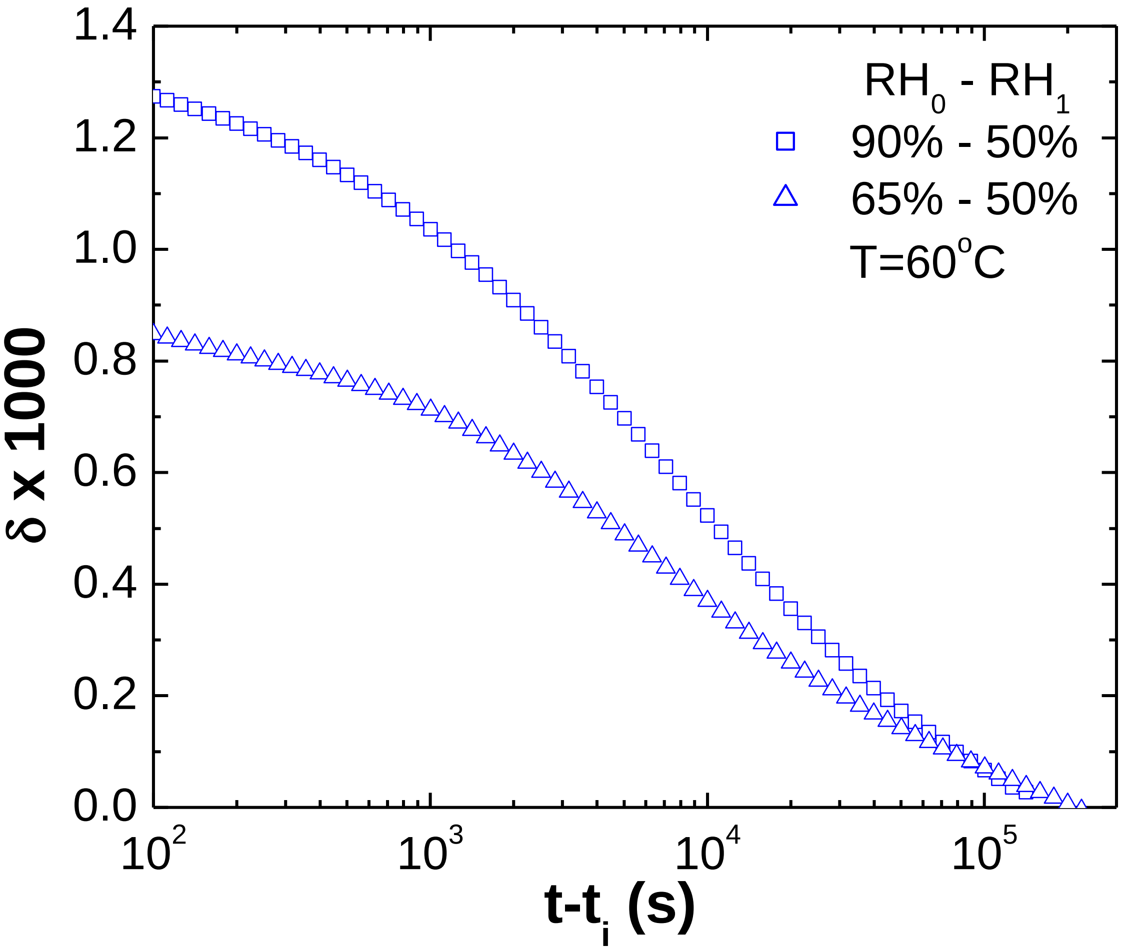
Structural Recovery: Memory Effect



Asymmetry of Approach

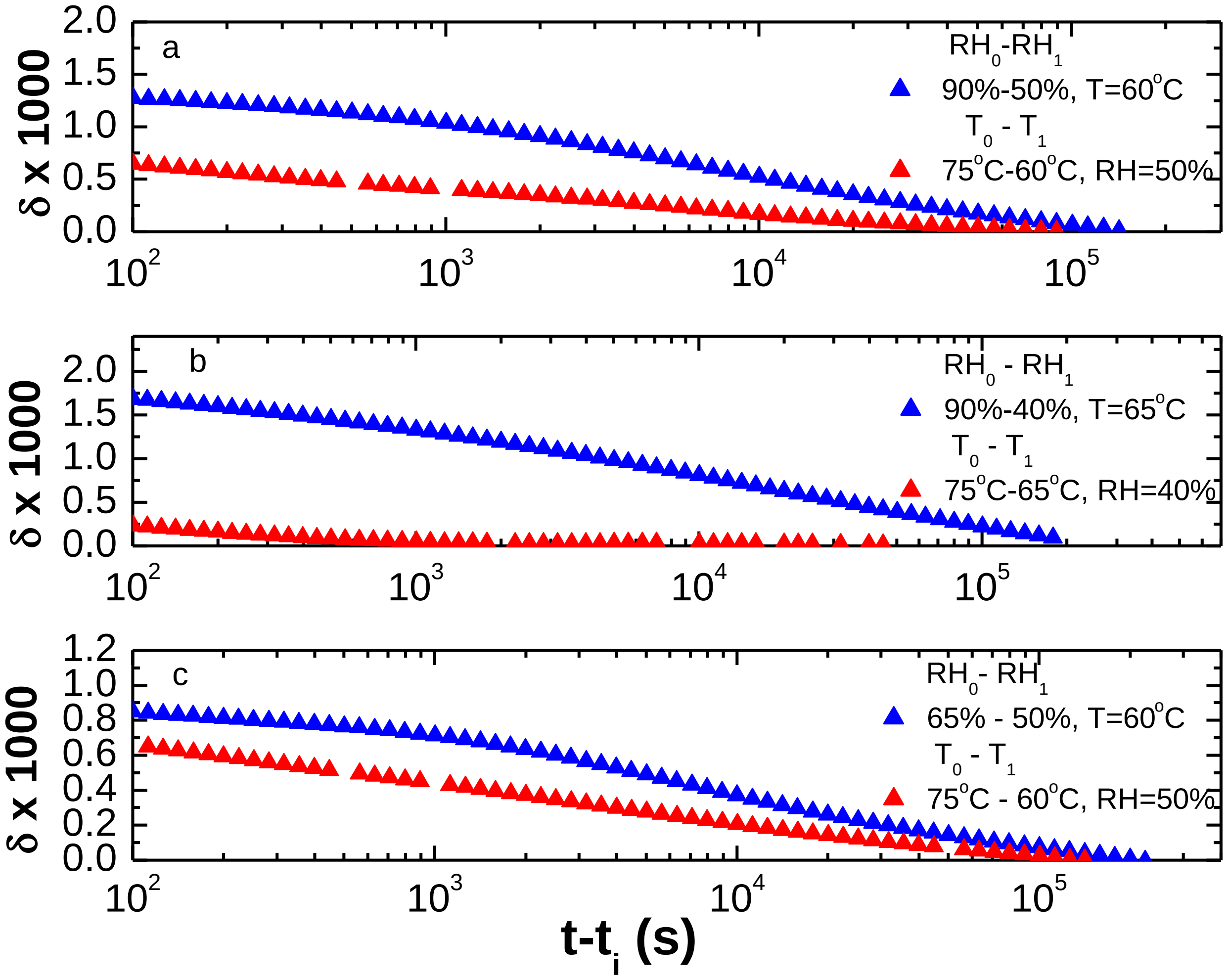


Structural Recovery: RH-Jump



RH-Jump vs. T-Jump

to the same final state



$\delta_{0RH} > \delta_{0T}$

$\delta_{0RH} > \delta_{0T}$

$\delta_{0RH} = \delta_{0T}$

Extended TNM-KAHR Model

- Boltzmann Superposition

$$\delta(t) = -\Delta\alpha_T \int_0^t \exp(-(\frac{t-t'}{\tau})^\beta)\frac{dT}{dt'}dt'$$

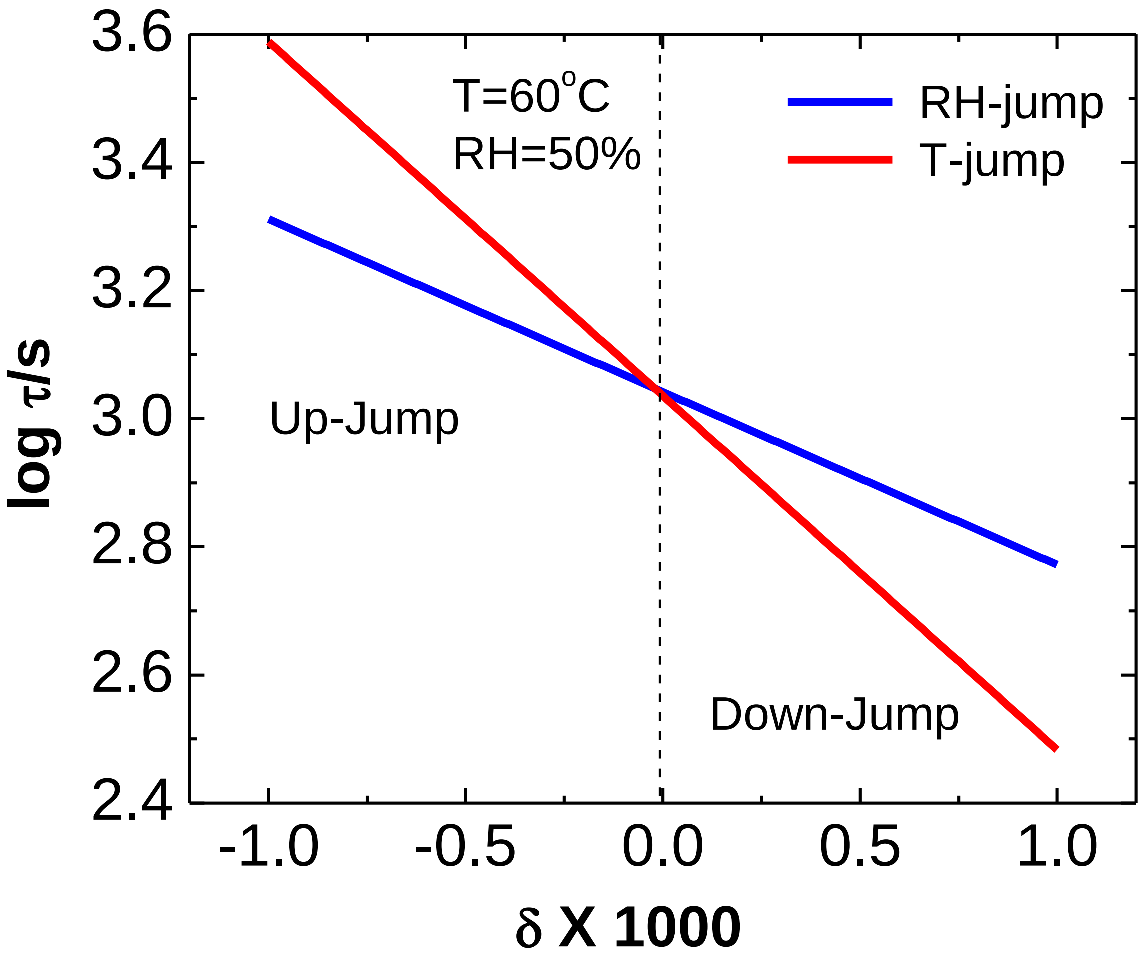
- Temperature structure dependent relaxation time

$$\mathbf{ln}\,\tau(\boldsymbol{T},\delta) = \mathbf{ln}\,\tau_0 - \theta_{\boldsymbol{T}}(\boldsymbol{T}-\boldsymbol{T}_{\boldsymbol{r}}) - (1-\boldsymbol{x})\theta_{\boldsymbol{T}}\delta/\Delta\alpha$$

The model is extended to the RH experiments by replacing T,T$_r$ θ$_T$ and Δα$_T$ with RH, RH$_r$ θ$_{RH}$ and Δα$_{RH.}$

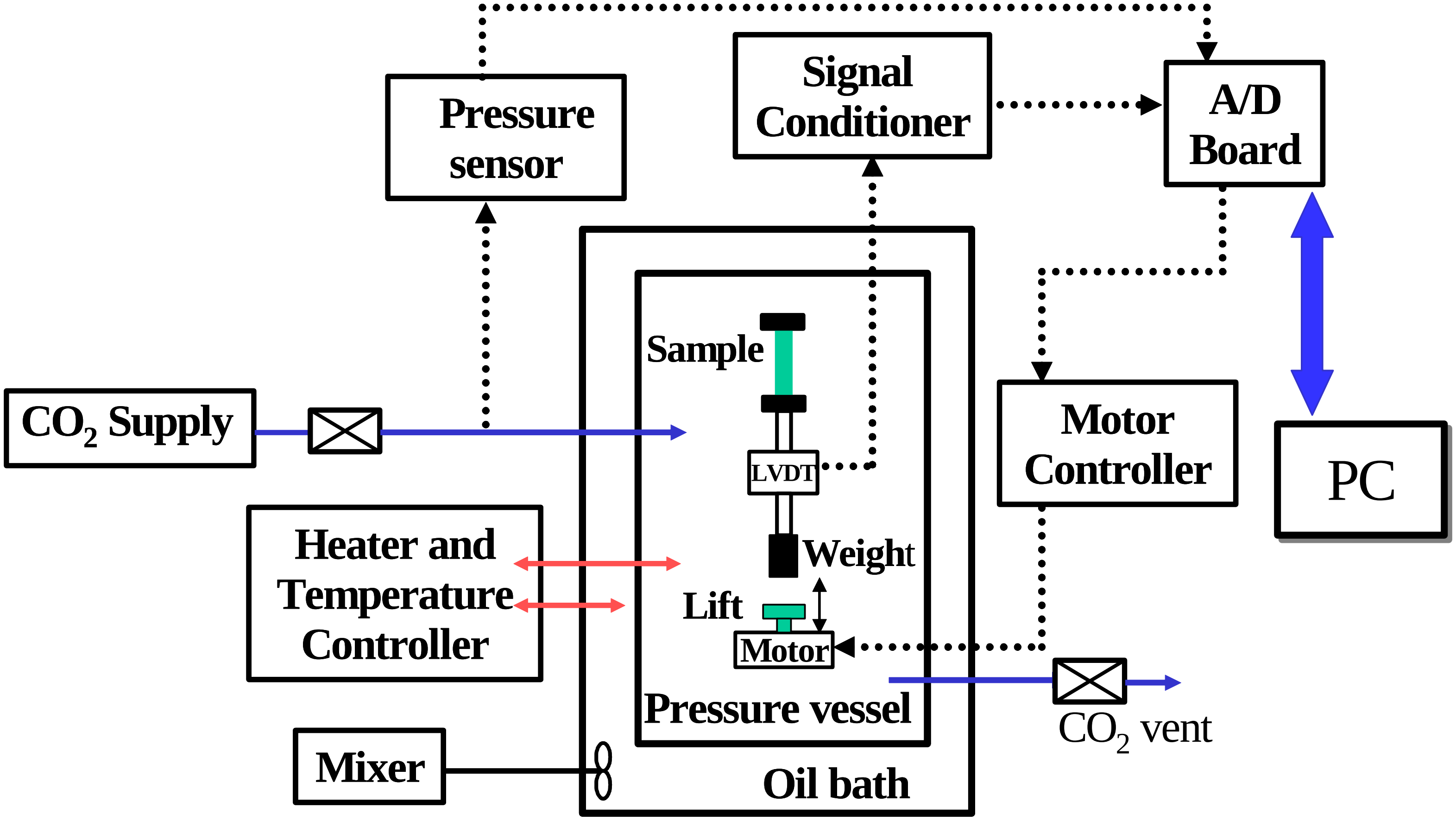
Comparison of Asymmetry Results:

T-jump and RH-jumps to same final conditions

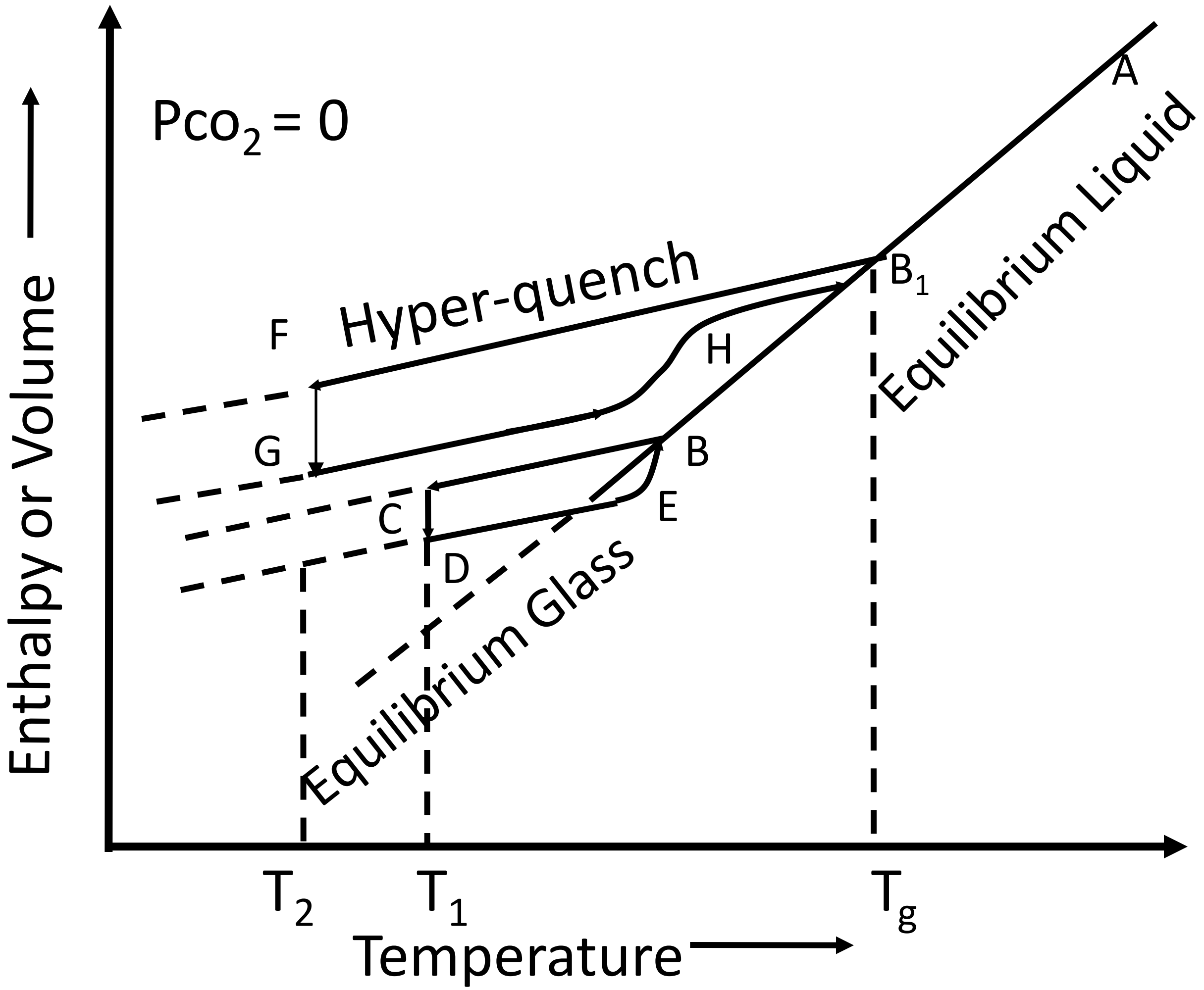


Physical Aging and CO_2 Pressure Jump Experiments

Experimental system



Hyper-Quench vs Plasticzer-Quench: are they equivalent?

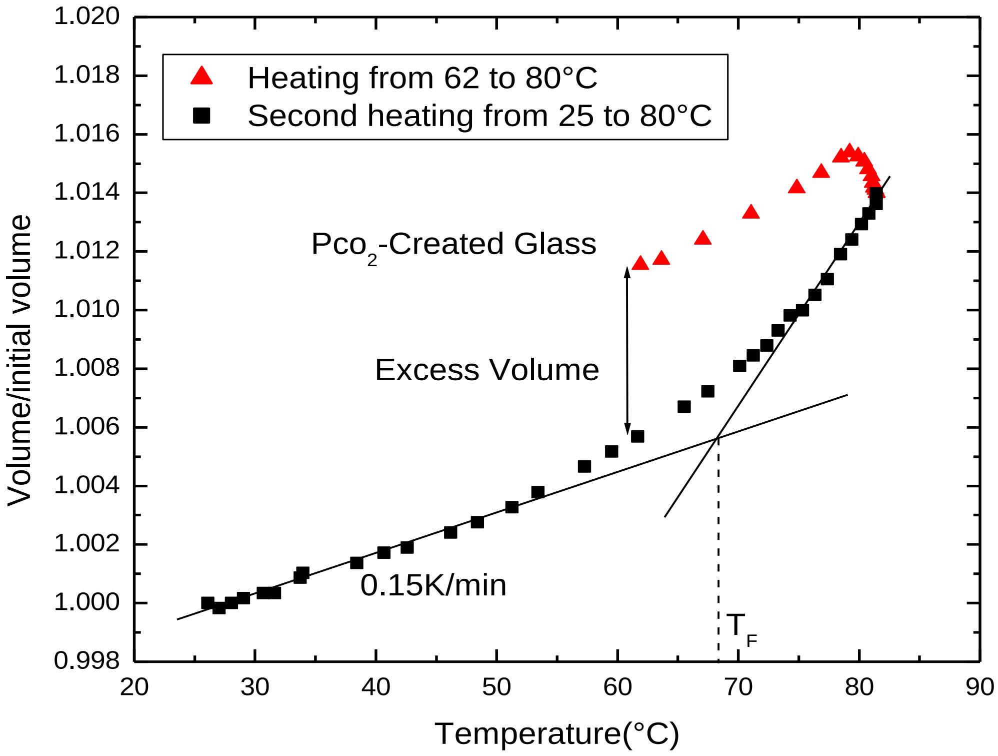


- **Both Hyper-Quench and Pco_2-Quench have excess volume.**

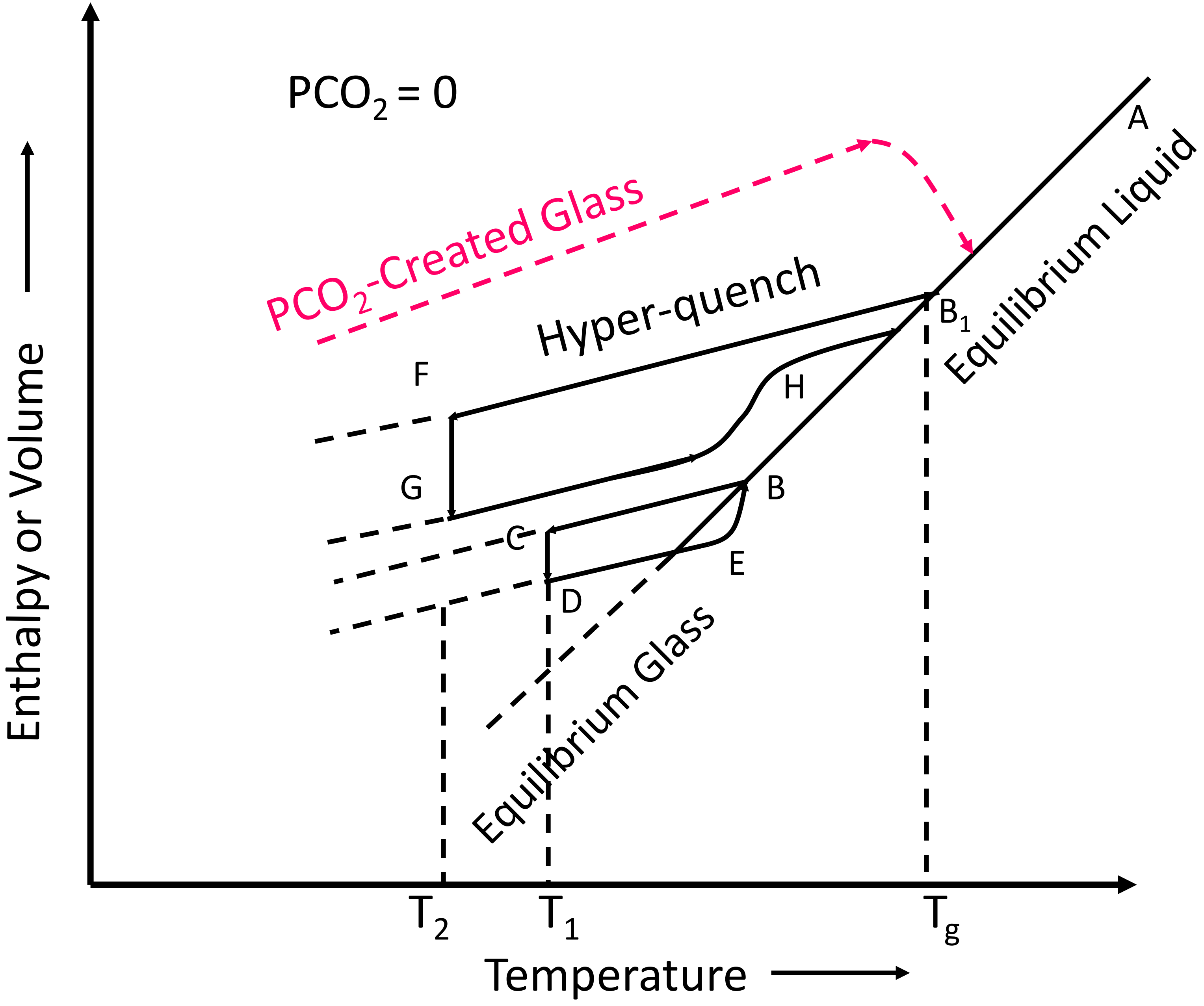
- **Vapor preswelling and rapid thermal quenching seem to have nearly identical effects on the development of enthalpy relaxations during aging of PVC at 30°C and 0.5 MPa.**

After: A. R. Berens and I. M. Hodge, *Macromolecules*, **15,** 756 (1982).
Based on DSC experiments.

Hyper-Quench vs Plasticzer-Quench: are they equivalent?



- The glass created by PCO$_2$-jump is different from that created by T-Jump.


PCO₂ = 0
PCO₂-Created Glass
Hyper-quench
A
Equilibrium Liquid
B₁
F
H
G
B
C
E
D
Equilibrium Glass
Enthalpy or Volume
T₂
T₁
Tg
Temperature

Structural Recovery after PCO_2-jumps

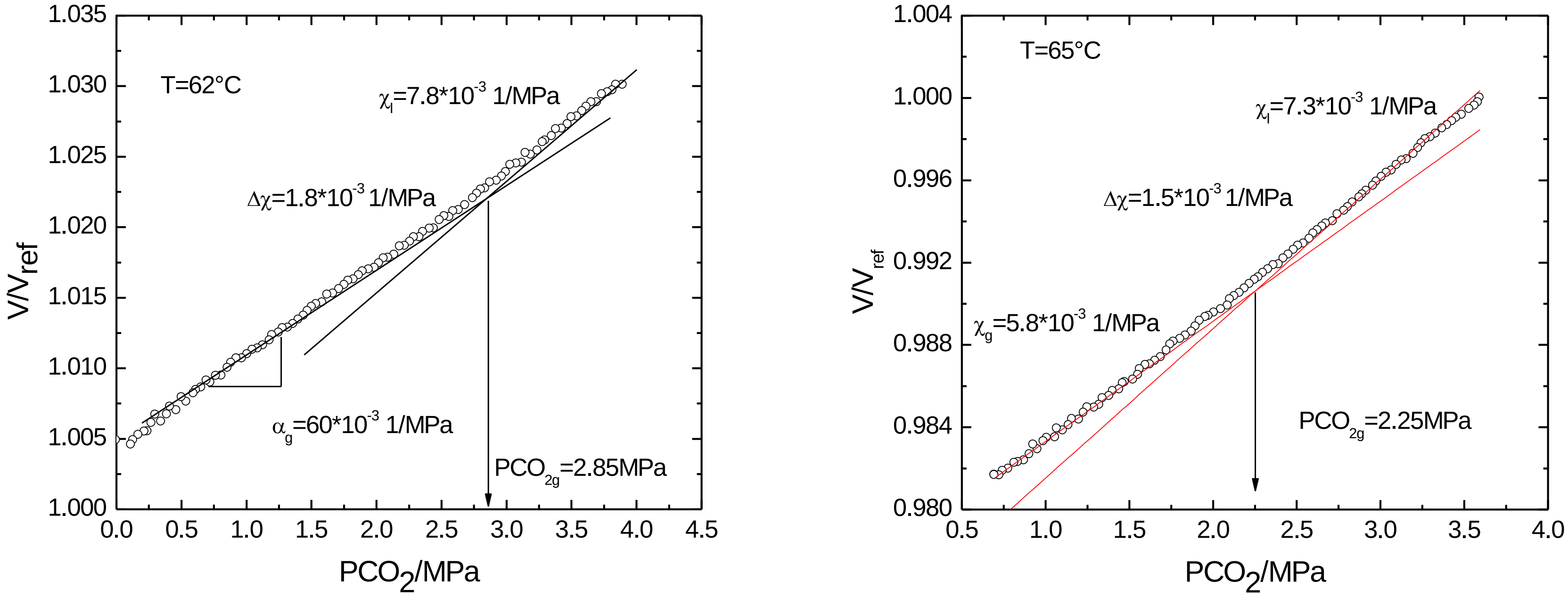
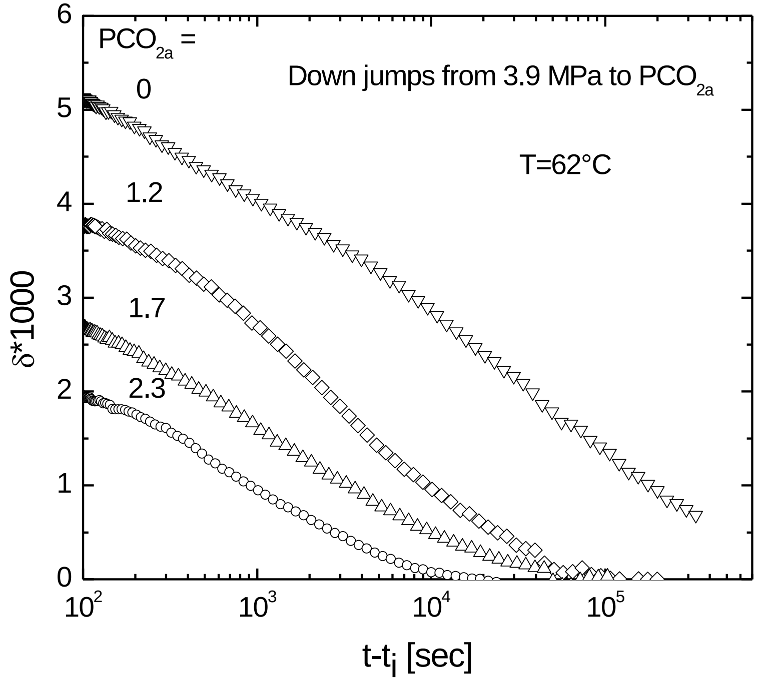
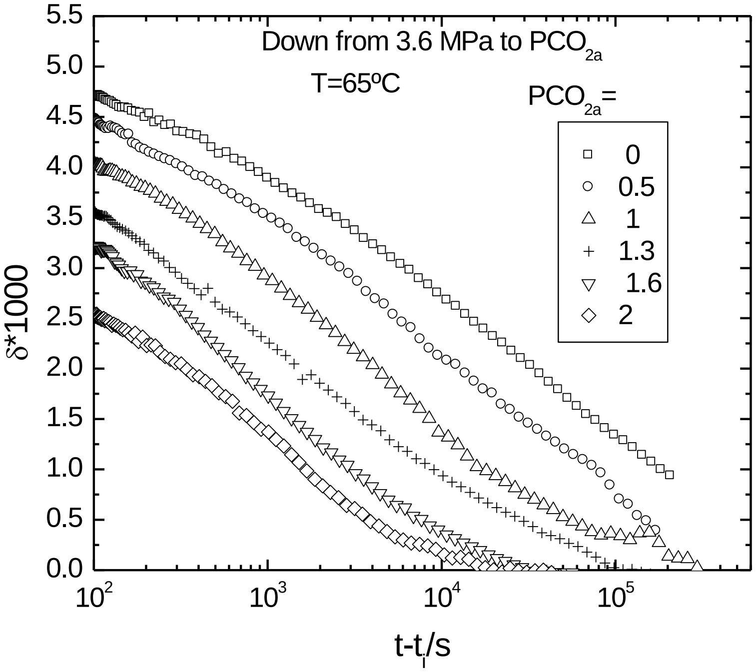


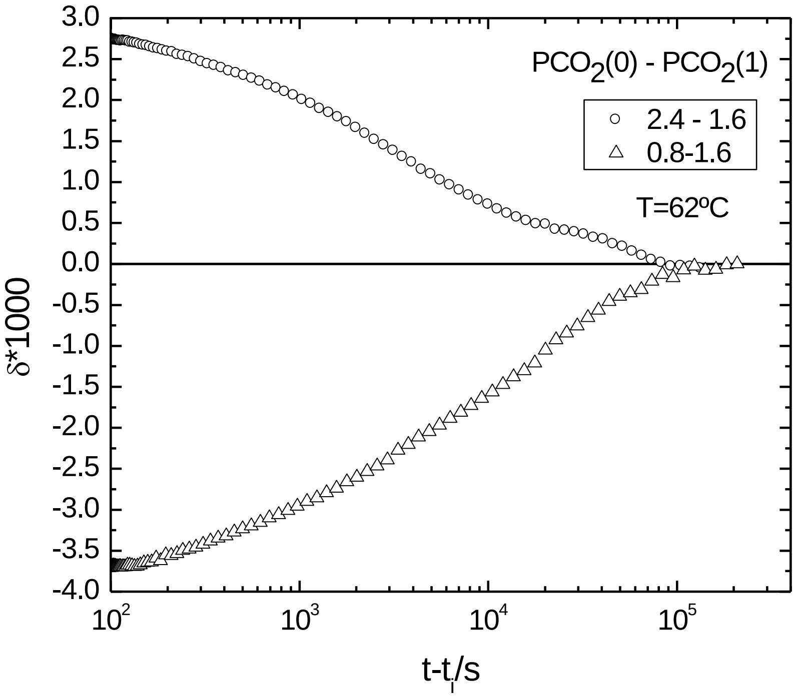
Figure 5: Volume versus PCO2 at (a) 62°C and (b) 65°C for the epoxy resin during the depressurization step. Figures 5a and 5b confirm that the epoxy/CO2 system shows a glass transition in CO2 concentration.

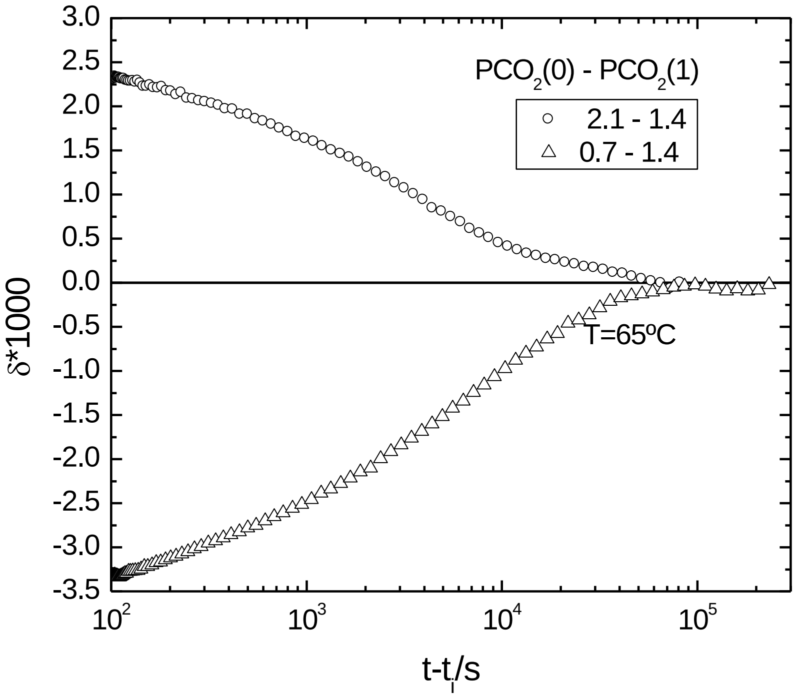
Intrinsic Isopiestics



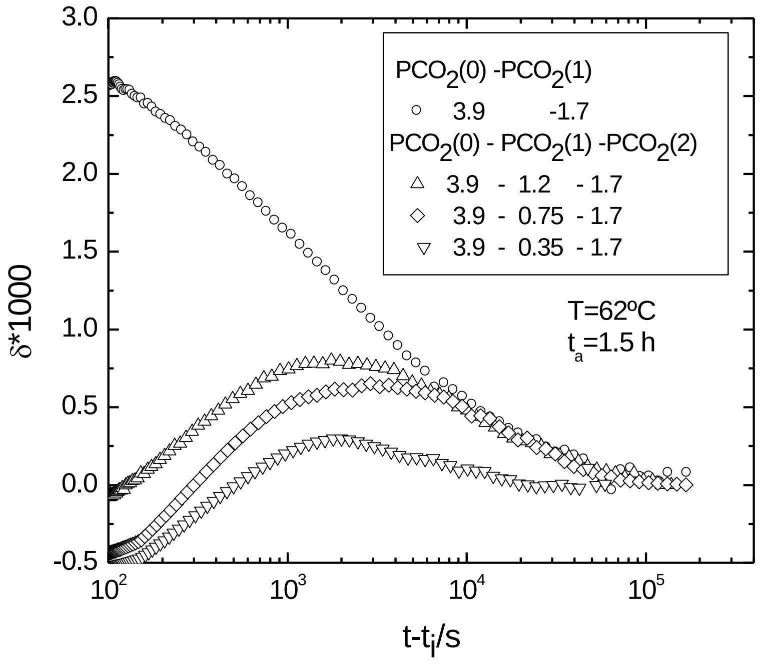


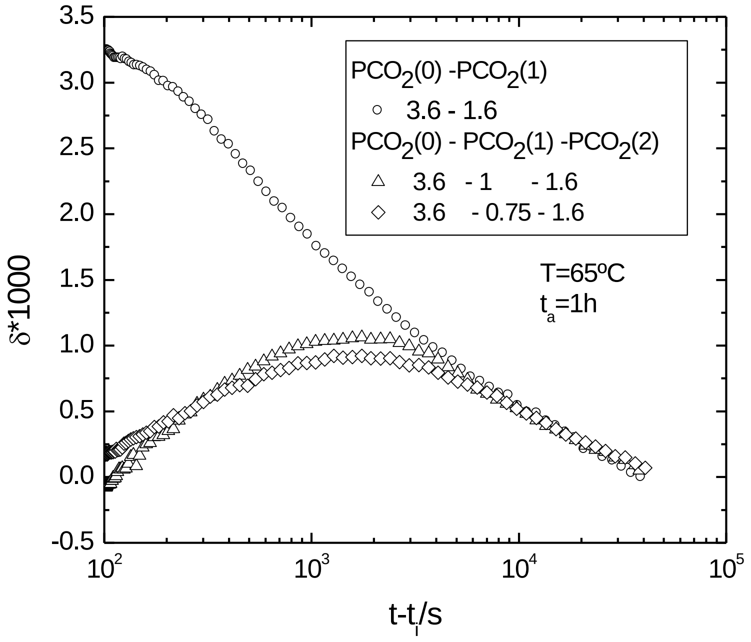
Assymetry of Approach





Memory or Crossover Effect





Enthalpy Recovery after PCO_2-Jumps

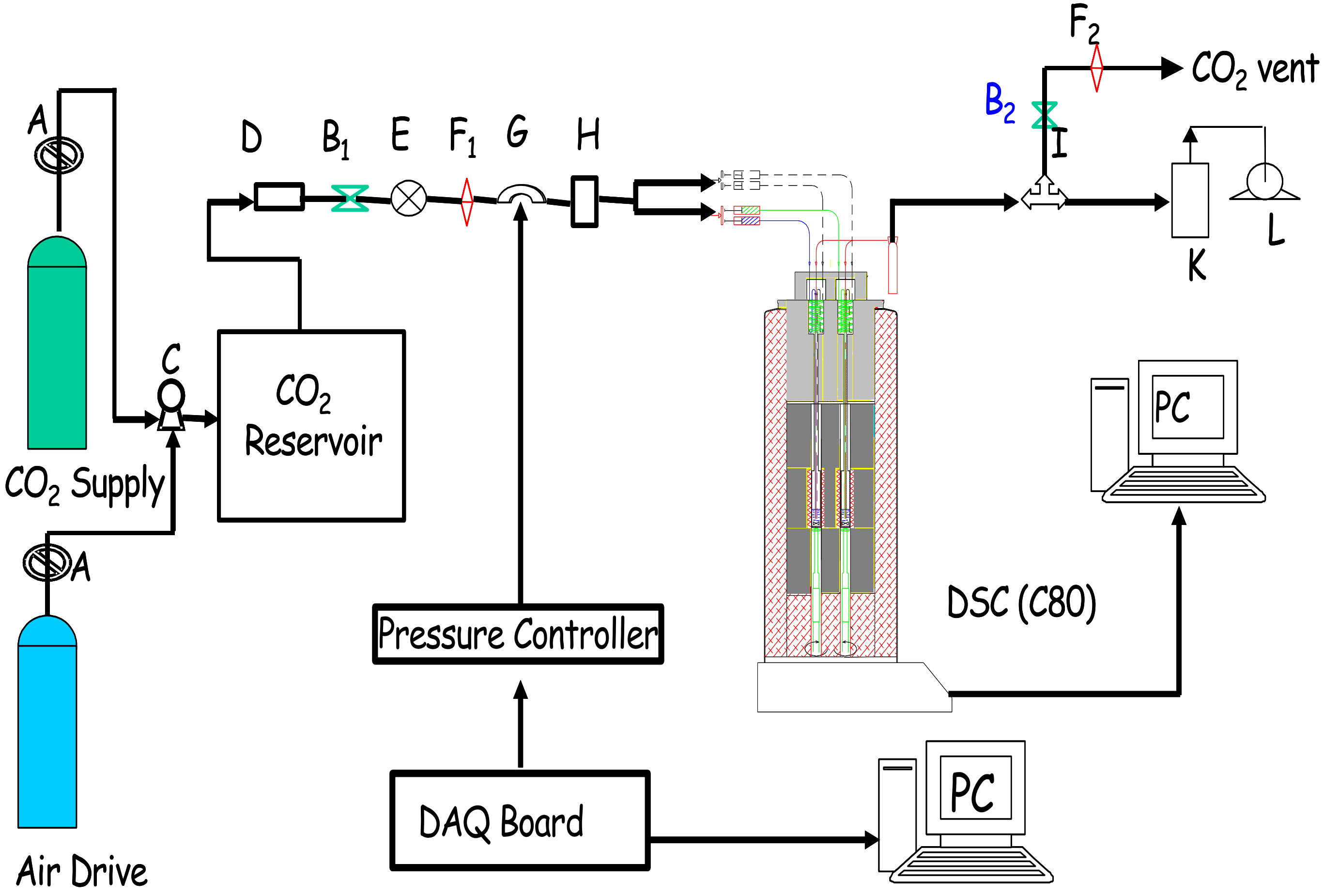
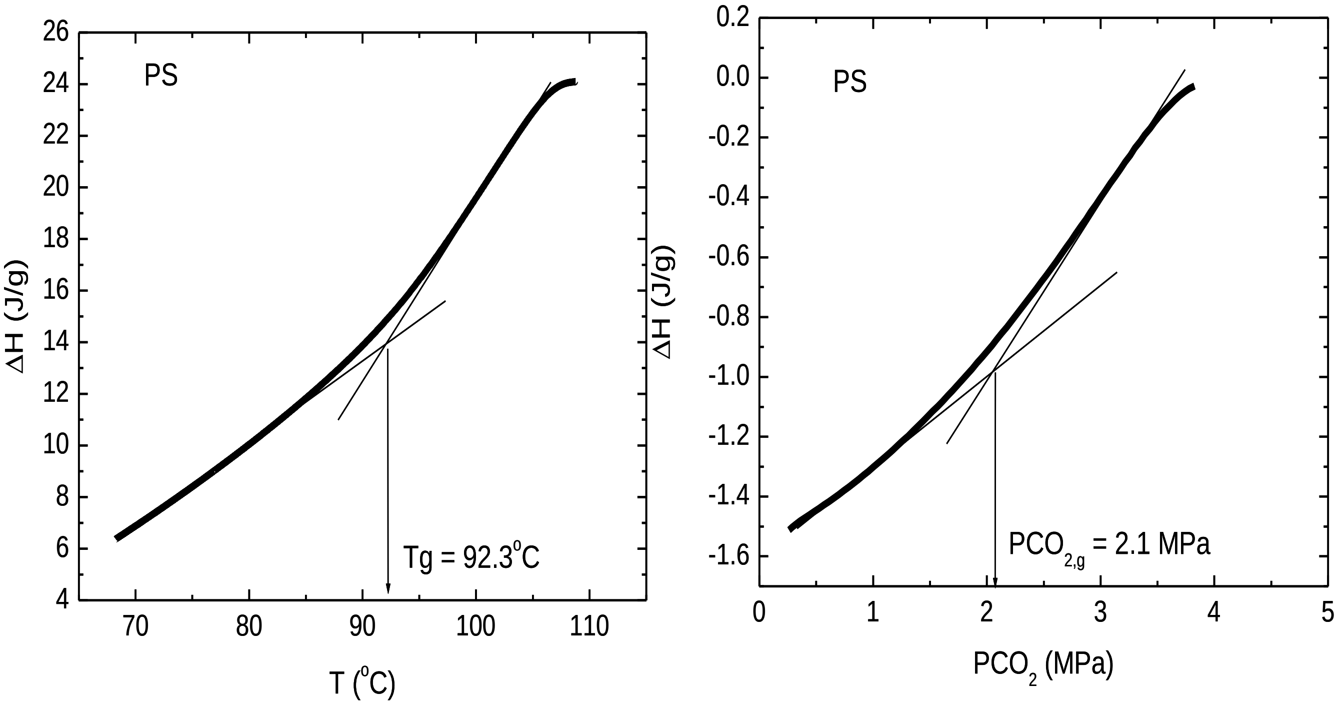


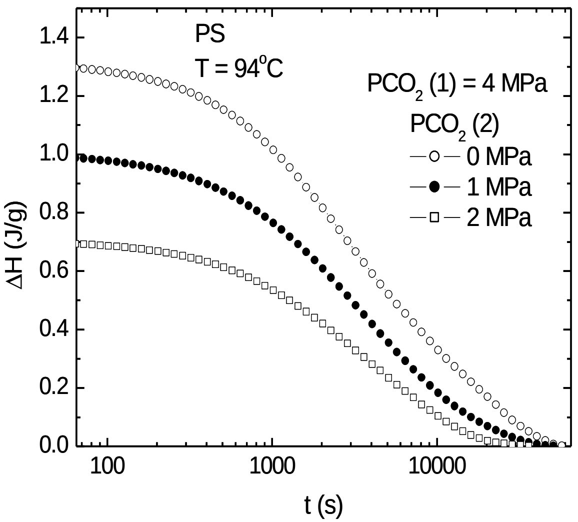
Figure 1 Schematic of the modified Setaram C80 calorimeter. A) Regulator B1) Inlet automatic valve B2) Outlet automatic valve C) High pressure pump D) Filter E) Safety valve F1) Inlet needle valve F2) Outlet needle valve G) Pressure sensor H) One way valve I) Three-way valve K) Cold trap L) Vacuum pump

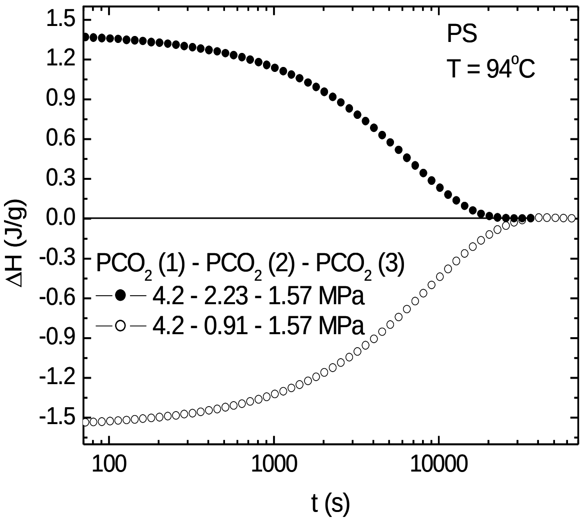
Temperature decrease and Pressure decrease



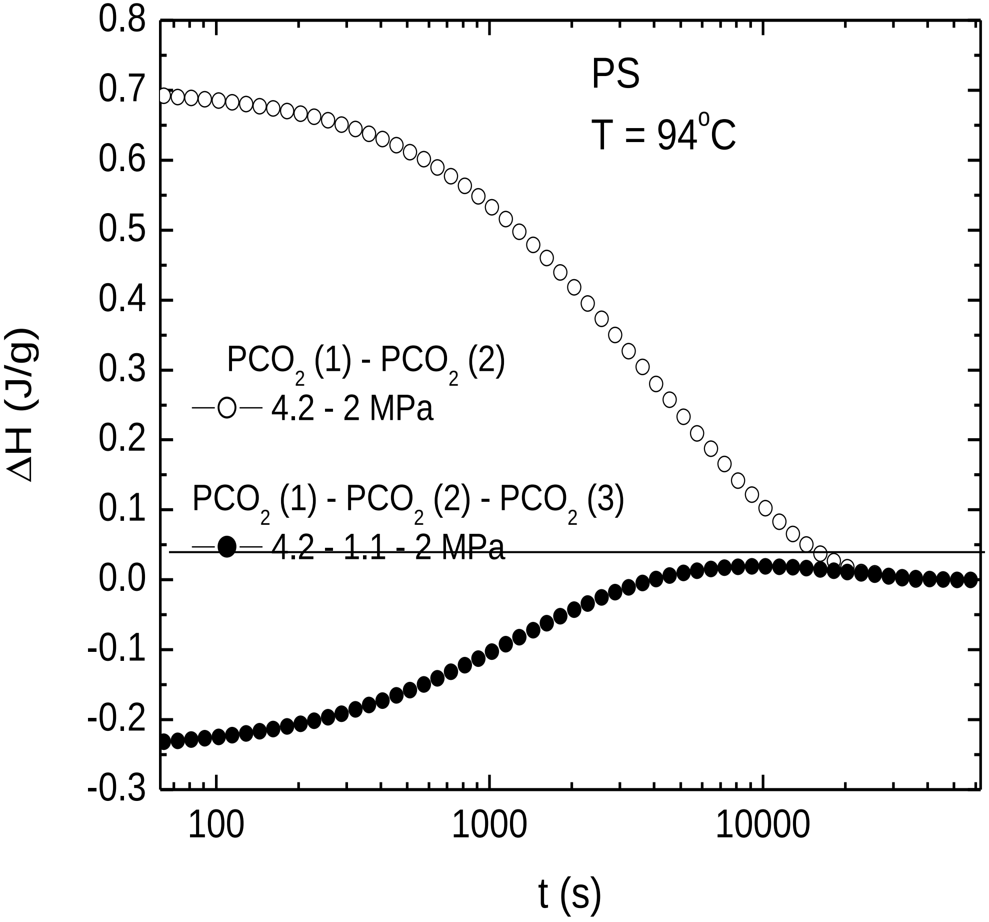
Figures 2 (a) Glass transition temperature for the polystyrene obtained on cooling after annealing at 104˚C for 2 h and (b) carbon dioxide pressure glass transition obtained on depressurization after equilibrating the sample at 4 MPa

Intrinsic Isopiestic   Assymetry of Approach





Memory


PS
T = 94°C
PCO2 (1) - PCO2 (2)
4.2 - 2 MPa
PCO2 (1) - PCO2 (2) - PCO2 (3)
4.2 - 1.1 - 2 MPa
ΔH (J/g)
t (s)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
100
1000
10000

Summary

- Chemical activity jumps (RH or P_{CO2}) exhibit similar behavior to temperature jumps.
  - RH-jumps exhibit intrinsic isopiestics similar to intrinsic isotherms of Kovacs in down-jump conditions
  - RH-jumps exhibit asymmetry of approach
  - RH-jumps exhibit memory

Summary

- Chemical activity jumps (RH or P_{CO2}) exhibit similar behavior to temperature jumps.
  - – PCO_2-jumps exhibit intrinsic isopiestics similar to intrinsic isotherms of Kovacs in down-jump conditions
  - – PCO_2-jumps exhibit asymmetry of approach
  - – PCO_2-jumps exhibit memory

Summary, con't

- Even though the structural recovery after relative humidity jumps looks similar to that after temperature jumps, their underlying kinetics are quite different.
  - Both the total time to reach equilibrium and the instantaneous volume relaxation times for RH-jump conditions are longer than those from the T-jump experiment for down-jump conditions.
  - Similar results pertain for the PCO_2-jump experiments.
- V-T measurements after PCO_2-jumps show quantitative differences from the temperature "hyperquench".
- Have shown the first enthalpy recovery after PCO_2–jumps.
  - Intrinsic isopiestic
  - Assymetry
  - Memory

Structural Recovery at the Nanometer Size Scale

Simon, Park, McKenna, EPJE(2002)

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:
  11.6 nm
  25.5 nm
  47.9 nm

Organic Liquids Confined to Nanoscale Pores

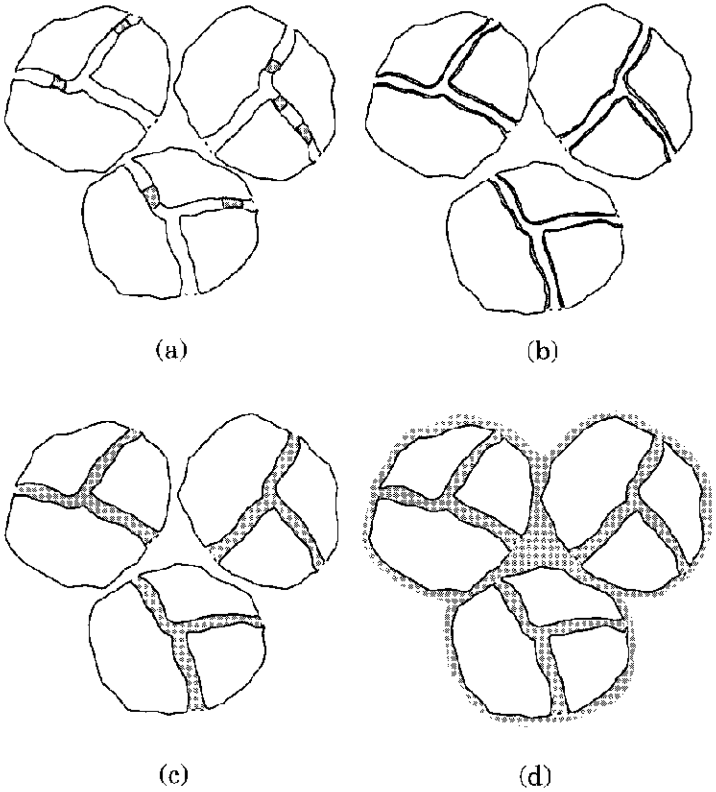
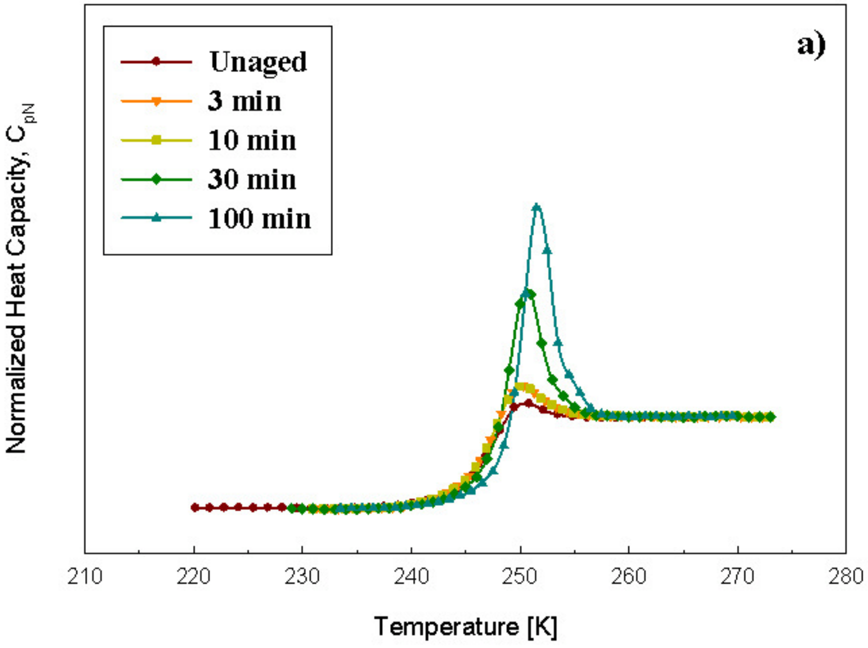
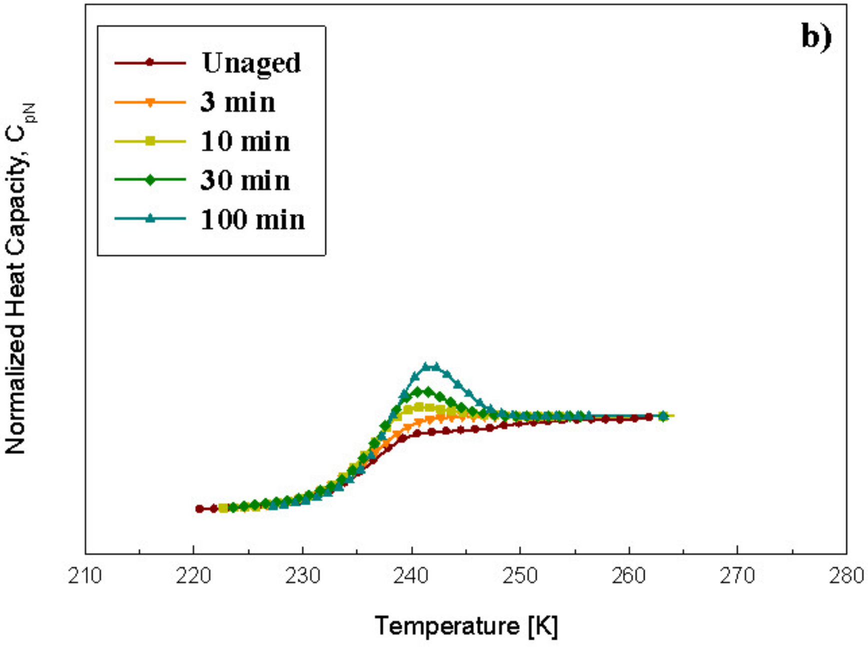


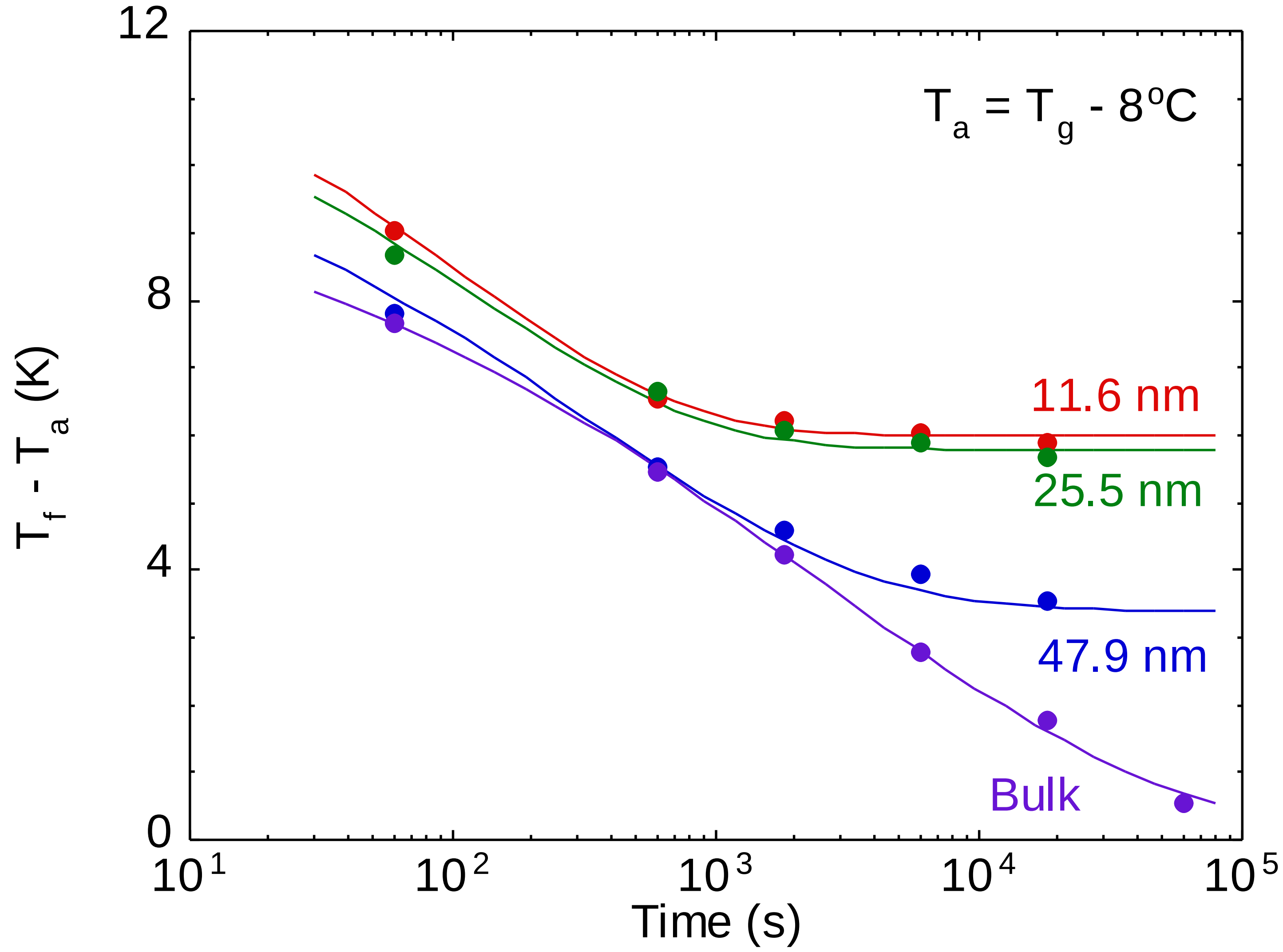
Figure 1. Schematic illustration of pore filling in CPG materials, where three small grains of porous glass are grouped together for illustrative purposes. As the CPG comes into contact with a liquid and its vapor, (a) poor wetting—the liquid enters the smallest diameter pores and form "plugs", (b) good 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.

Comparison of structural recovery in bulk and in pores (with S.L. Simon and J.Y. Park)



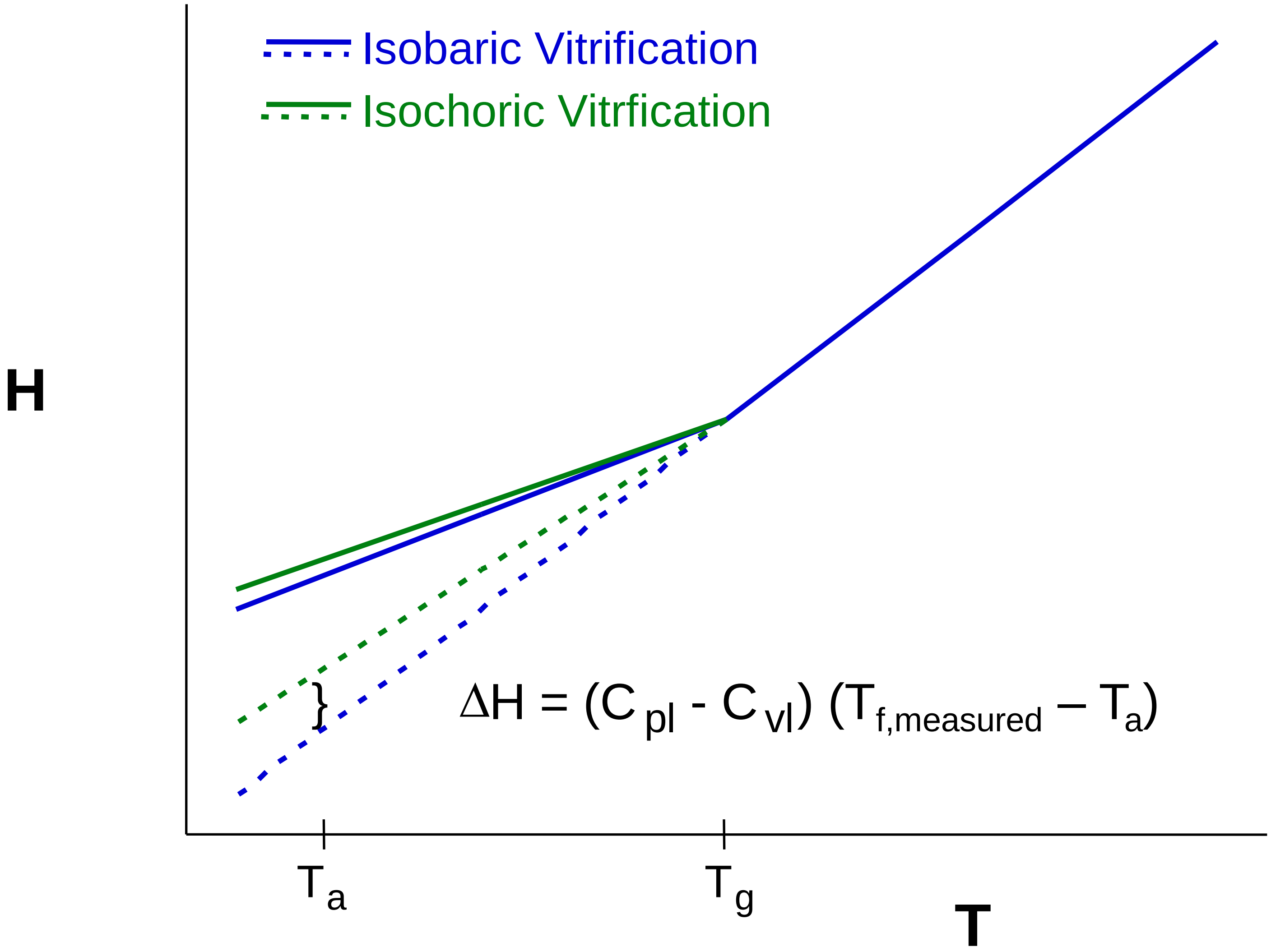


Enthalpy Recovery for o-TP in the bulk and in nanopores



Note that T_F-T_a>0 for material confined to pores

Isochoric vs Isobaric Vitrification



$$\Delta H = (C_{pl} - C_{vl})\ (T_{f,measured} - T_a)$$

Evidence of isochoric glass formation

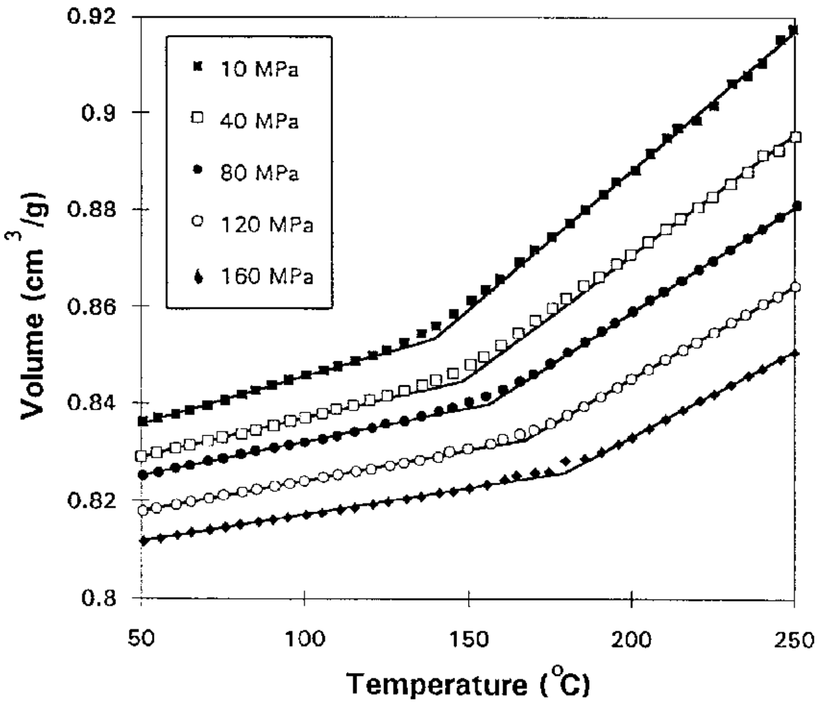


Figure 1. Isobaric PVT results. Symbols are the experimental data, while solid lines are the linear regression results. Legend denotes pressures.

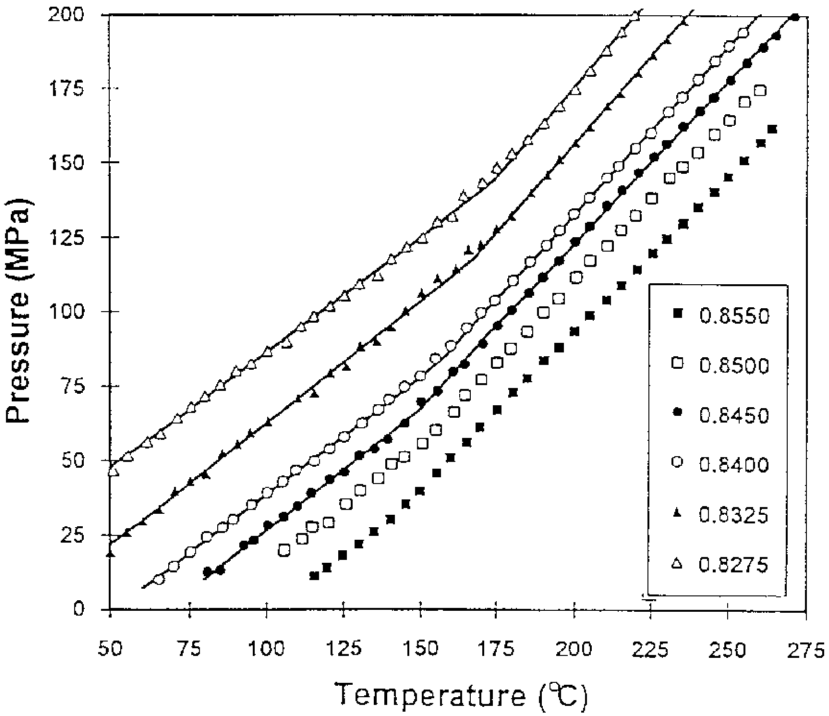


Figure 2. Isochoric PVT results. The symbols represent the experimental data obtained at different isochoric volumes in cm^3/g as defined in the legend. The solid lines are the result of linear regression of the data above and below the expected transition.

Colucci, McKenna et al (1997)

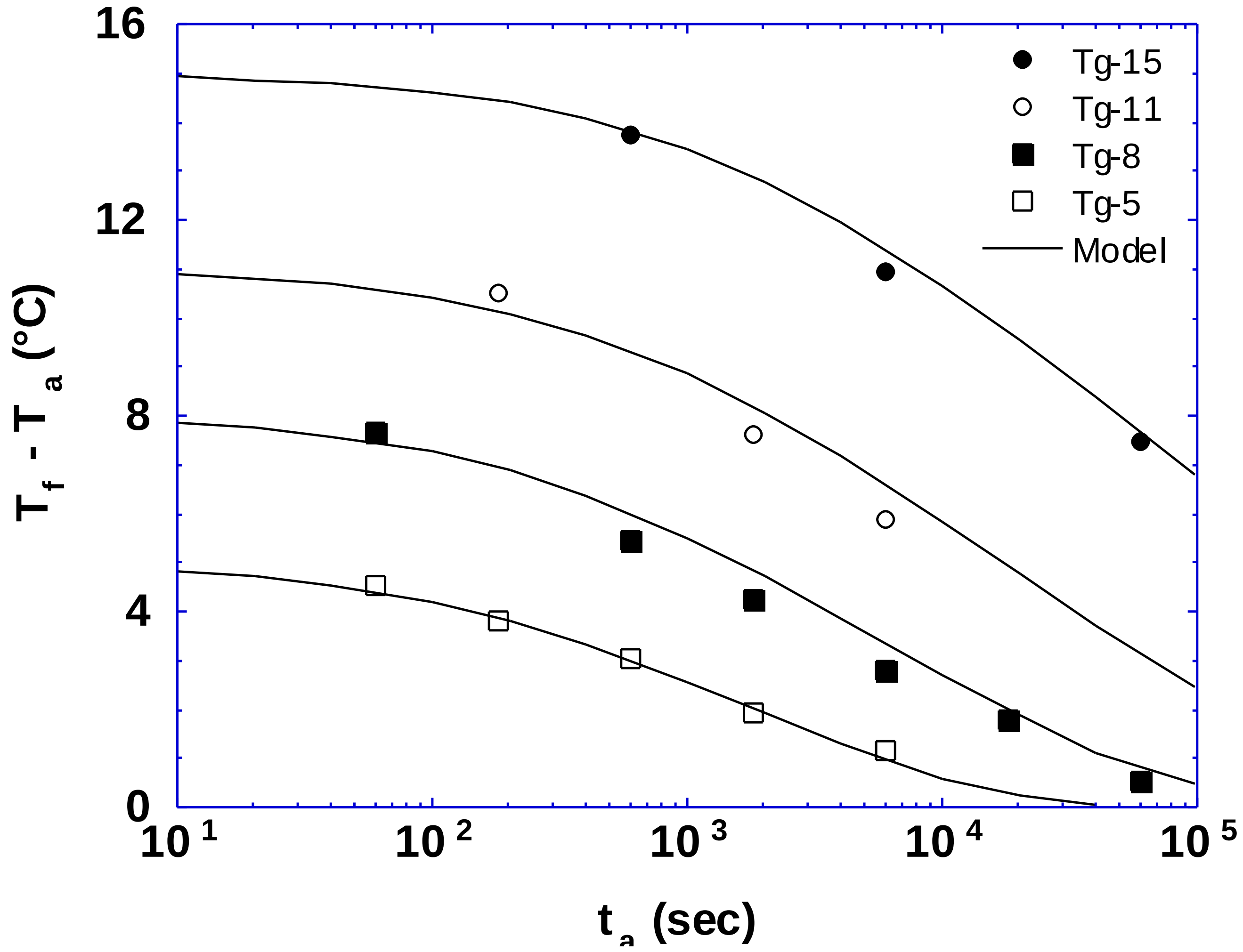
Bulk Structural Recovery (TNM model)-cast in terms of δ rather than T_F

$$\delta = \delta_o \, e^{-\left(\int \frac{dt}{\tau}\right)^{\beta}}$$

$$\ln \tau = \ln \tau_{ref} - \theta_T (T - T_{ref}) - (1 - x)\theta_T \delta / \Delta C_p$$

$$T_f = T_a + \delta/\Delta C_p$$

TNM model calculations for bulk o-TP



TNM model extended to isochoric aging and subsequent return to 1 bar upon heating

$$\ln\tau \;=\; \ldots \;+\; \theta_P(P-P_{ref})$$

$$P_o \;=\; P_{ref} \;+\; \alpha_g K_g \Delta T$$

$$P_{eq} \;=\; P_{ref} \;+\; \alpha_l K_l \Delta T$$

$$T_f - T_a \;=\; \Delta H/\Delta C_p \;=\; \{-(C_{pl} - C_{vl})\Delta T + \delta\}/\Delta C_p$$

$$\big\uparrow$$

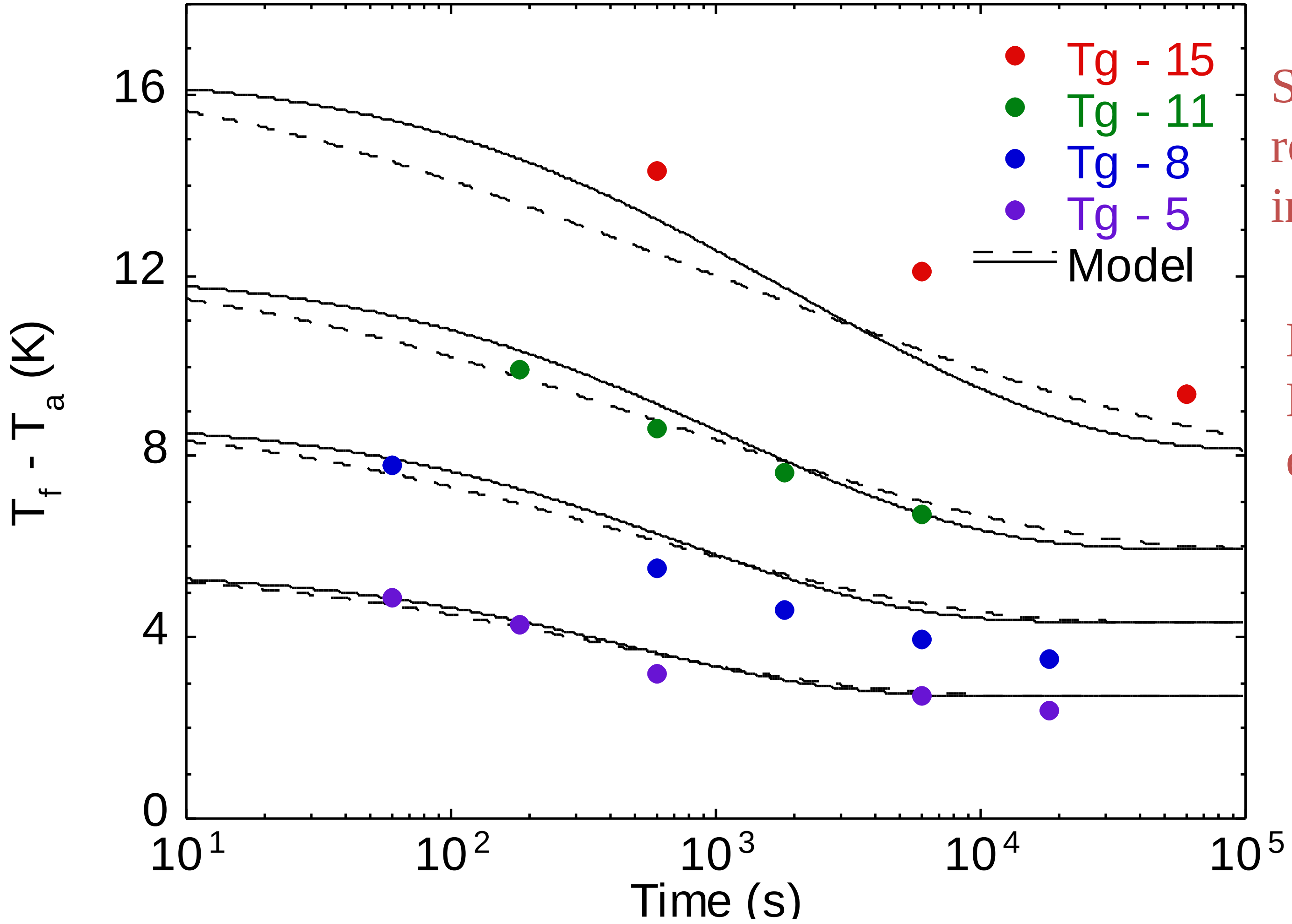
$T_f - T_a \neq 0$ as $\delta \longrightarrow 0$

Assumptions used to model nanopore aging data

- **Model parameters which describe the bulk recovery should describe the recovery in the nanopores**
- **Two additional adjustable model parameters are needed: θ_P and $T_{constraint} \approx T_g$ of material in nanopores**
- **Values of material parameters needed for the calculations (C_{pl}, ΔC_p, α, $\Delta\alpha$, K, ΔK, V_g) are obtained from the literature with $C_v = C_p - V_g T_g \alpha^2 K$**
- **Pressure relaxation is a) instantaneous or**

  b) it relaxes at the same rate as the enthalpy

Enthalpy Recovery for o-TP in 47.9 nm Pore

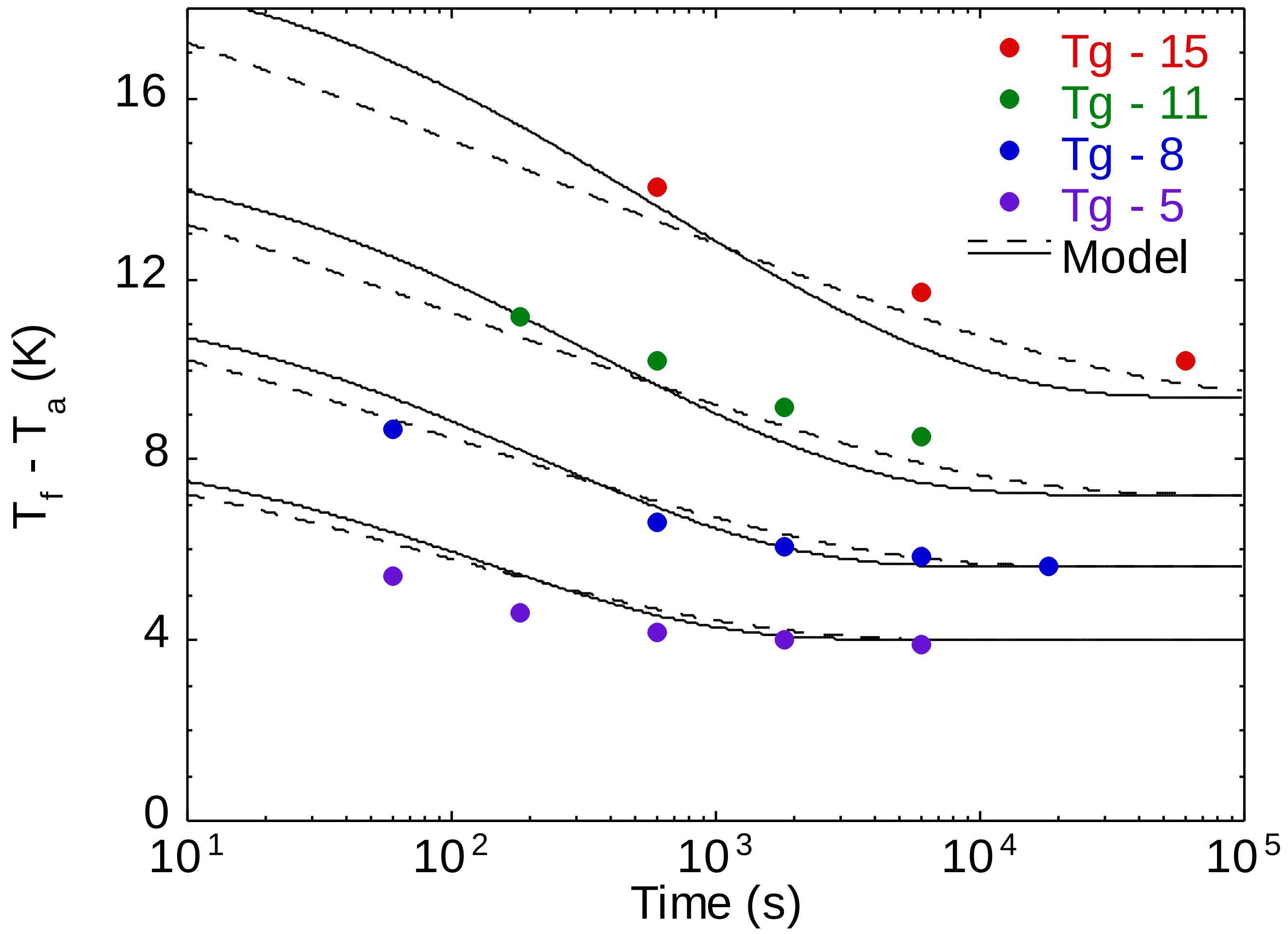


Solid: pressure relaxes instantaneously

Dashed: pressure Relaxes at rate of enthalpy

$T_{g,constraint} = T_g$

Enthalpy Recovery for o-TP in 25.5 nm Pores



Solid: pressure relaxes instantaneously

Dashed: pressure Relaxes at rate of enthalpy

$T_{g,constraint} = T_g + 2.5\ K$

Values of the model parameters used for fitting the enthalpy recovery of o-TP

Parameter	Value	Values from literature for fitting the bulk response
Δh^* (kcal/mol)	75	75
X	0.45	0.04 - 0.05
β	0.70	0.67 - 0.75
$\ln \tau_{ref}/s$	5.5	5.8 - 6.2
θp (bar^{-1})*	0.017	Not Applicable
θp (bar^{-1})**	0.022	Not Applicable

* Pressure relaxes during aging at the same rate as the enthalpy

** Pressure relaxes to equilibrium value during quench

Literature values used in the model calculations of enthalpy recovery

Parameter	Value	Ref.
ΔC_p (cal g^{-1} K^{-1})	0.13	Jackson and McKenna
C_{pl} (cal g^{-1} K^{-1})	0.342	Chang and Bestul
α_l (10^{-4} K^{-1})	7.34	Naoko and Koeda
α_g (10^{-4} K^{-1})	2.57	Naoko and Koeda
K_l (GPa)	2.56	Naoko and Koeda
K_g (GPa)	3.70	Naoko and Koeda
V_g (cm^3 g^{-1})	0.893	Naoko and Koeda

Discussion

- $dT_g/dP = 0.26$ K MPa^{-1}

- ΔP needed to obtain the reduction in T_g observed would range from -22 to 36 MPa and the corresponding temperature at which constraints set in would be 10 - 40 K above T_g which is inconsistent with our analysis

- Isochoric vitrification cannot be the reason for the reduction in T_g for materials confined to nanopores

- Hence, the results of the current work are consistent with the original idea that the reduction of Tg in nano-pores is an ***intrinsic*** size effect

Summary

- **Enthalpy recovery for o-TP in nanopores levels off at $T_{f,measured} > T_a$**
- **The time to reach equilibrium is shorter than for the bulk for aging a given distance below T_g**
- **The data can be quantitatively explained using the TNM model assuming isochoric vitrification near the reduced T_g**
- **Isochoric vitrification affects aging or structural recovery but it is not the cause of the reduced T_g. The reduction in T_g is due to an *intrinsic* size effect**

Acknowledgements

- NIST
- NSF
- ARO
- ACS-PRF
- S.L. Simon
- P.A. O’Connell
- D. Colucci