RPK B "POLYMER PHYSICS"

Register Polymeerkundige

Glass Transition in Polymers
II. Theories and Computer simulations

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Outline

- Supercooled liquids and glass transition
- Theoretical approaches
- Simulations of glass transition

part II

- Glass transition in thin polymer films

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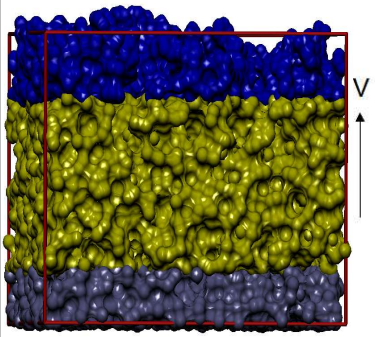
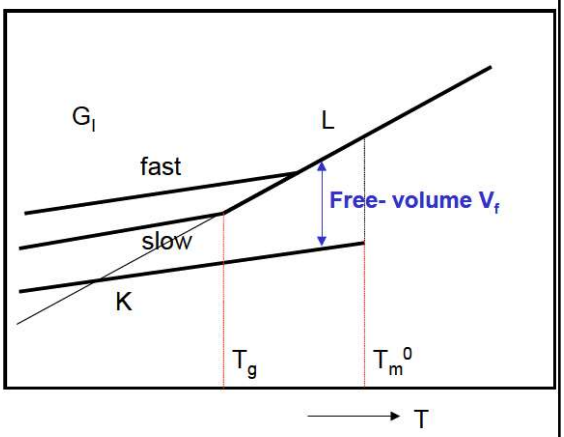
II. Theoretical Approaches

A: Free volume theor(ies)





Assumption: liquid contain free volume that permits segmental motion

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Main result: relation between diffusion coefficient and free volume

no diffusion, D=0, unless the free volume exceeds some critical value v*

$$D \sim \exp(-\gamma v^* / v_f)$$

how to get it??

Empirical Doolittle equation for fluidity: $\varphi \sim \exp(-bv / v_f)$

$$\eta = a \exp\left(\frac{bv}{v_f}\right)$$

where (using Stokes-Einstein relation): $D = \frac{kT}{6\pi r}\varphi$

$$D \sim \eta^{-1} \sim \exp(-bv / v_f)$$

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Temperature dependence of free volume

$$f = \frac{V_f}{V} = f_g + (T - T_g)\alpha_f$$

$$\alpha_f = \alpha_L - \alpha_g$$

- linear function of temperature
- v : sample volume
- v_f: free volume
- f_g: fraction free volume at T_g
- α_f: difference in thermal expansions between liquid and glass

f_g = 0.025 = 2.5 %, α_f = 4.8 10^{-4} K^{-1} typical values

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free-volume equations

$$\eta = a \exp\left(\frac{bv}{v_f}\right)$$

$$f = \frac{V_f}{V} = f_g + (T - T_g)\alpha_f$$

Williams-Landel-Ferry (WLF) equation

$$\ln\left(\frac{\eta_T}{\eta_{T_0}}\right) = \frac{-C_1(T - T_g)}{C_2 + T - T_g} = \ln a_T$$

(exercise)

Vogel-Fulcher-Tammann (VFT) equation

$$\eta = A \exp\left(\frac{B}{T - T_V}\right)$$

(exercise)

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T_g: molecular weight dependence

- Associated with each chain end is a certain extra mobility and extra free volume
- The concentration of chain ends is proportional to M^{-1}
- The fractional free volume (f) at a specified temperature below T_g is

$$f = f_{M=\infty} + C_2 / M$$

- linear temperature dependence of free volume

$$f \sim C_0 + C_1 T + C_2 / M$$

Fox-Flory equation: $T_g \sim T_{g,M=\infty} - C_3 / M$

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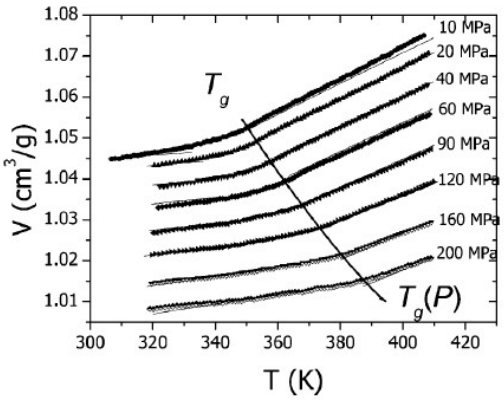
Useful features and drawbacks

- recovers WLF and VFT equations
- role of free volume confirmed by positron annihilation lifetime spectroscopy (PALS)



- "free volume" is badly defined parameter;
- Tg does not increase indefinitely, but tends to level off at high pressures;
- wrong pressure dependence of viscosity and characteristic relaxation times.

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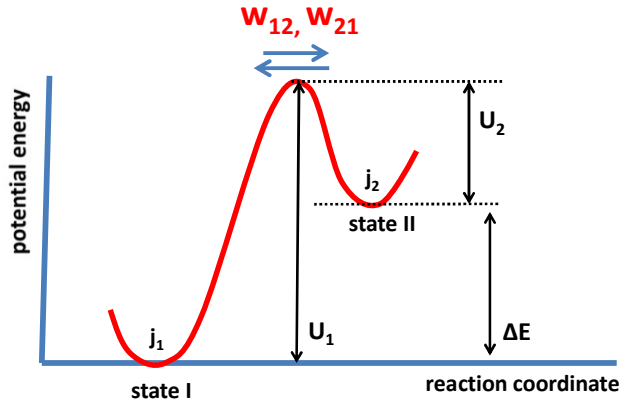
B. Kinetic theor(ies)

(Volkenstein, Ptitsyn, 1956)



exercise:

$\Delta E \ll u_1, u_2 = u$ - Arrhenius dependencies → $\tau \sim \exp\frac{u}{k_B T}$, $v - v_{eq} \sim j_2 - j_{eq} \sim \exp(-\frac{t}{\tau})$

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Main drawback: no cooperativity

(Gotlib, Ptitsyn, 1961)

$u \neq \text{const}, \quad u = f(j_2)$

$\tau_{j_2,T} \sim \exp(-\alpha j_2)$

$$j_{2,eq} = \frac{A\exp(-\frac{\Delta E}{k_B T})}{1 + A\exp(-\frac{\Delta E}{k_B T})}$$

$$\ln\left[\frac{\tau(T)}{\tau(T_{ref})}\right] = \underbrace{\frac{U(T - T_{ref})}{k_B T_{ref}^2}}_{\text{Arrhenius}} - \underbrace{\frac{C_1(T - T_{ref})}{C_2 + (T - T_{ref})}}_{\text{WLF}}$$

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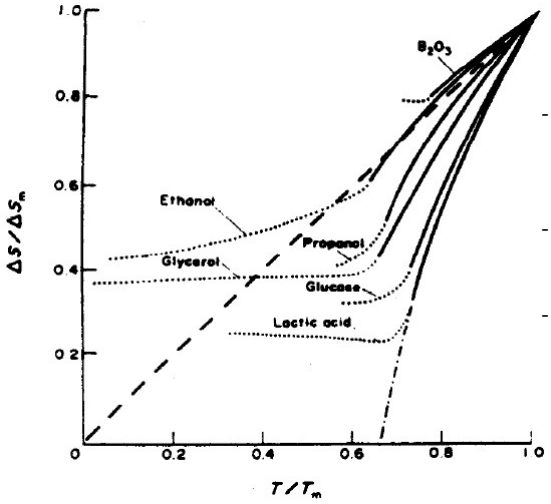
C. Thermodynamic approaches
Kauzmann paradox



- diference in entropy between supercoole d liquid and crystalline phase for different glass-formers.
- shown as fraction of entropy of fusion
- temperature expressed as fraction of melting temperature

W. Kauzmann, Chem. Rev., 1948, 43, 219

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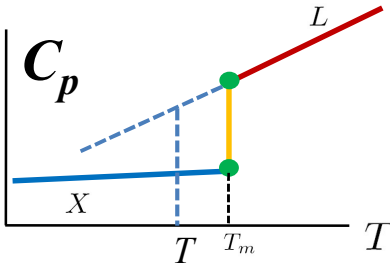
C. Thermodynamic approaches
Kauzmann paradox



$$S_{liquid,T_m} = S_{liquid}(T) + \int_{T}^{T_m} \frac{c_{p,liquid}}{T} dT$$

$$S_{crystal,T_m} = S_{crystal}(T) + \int_{T}^{T_m} \frac{c_{p,crystal}}{T} dT$$

$$S_{liquid}(T) - S_{crystal}(T) = S_{liquid,T_m} - S_{crystal,T_m} - \int_{T}^{T_m} \frac{c_{p,liquid} - c_{p,crystal}}{T} dT$$

Kauzmann temperature: $S_{liquid}(T_K) = S_{crystal}(T_K)$

$$\Delta S_m = S_{liquid,T_m} - S_{crystal,T_m}$$

$$\Delta S_m = \int_{T_K}^{T_m} \frac{c_{p,liquid} - c_{p,crystal}}{T} dT$$

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T_g always > T_K , i.e. T_K is not attainable experimentally

Gibbs, Di Marzio, 1958

the observed glass transition is a kinetic phenomenon, the underlying true transition can possess equilibrium properties;

based on a lattice model of a similar type to that in the Flory-Huggins theory for polymer solutions;

second-order transition;

$\Delta\alpha$ is the volumetric thermal expansivity associated with the transition;

Δk is the change in compressibility.

$$\left[dT / dP\right]_{tr} = \Delta k / \Delta\alpha$$

(exercise)

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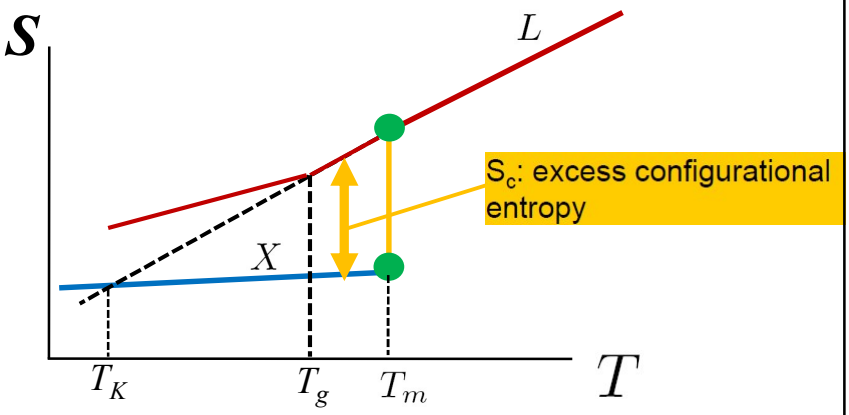
Excess configurational entropy



- The excess configurational entropy Sc is that part of the entropy associated with the freedom of the liquid molecules to adopt new conformations.
- It can be estimated as the difference in entropy between the supercooled liquid and the crystalline state.

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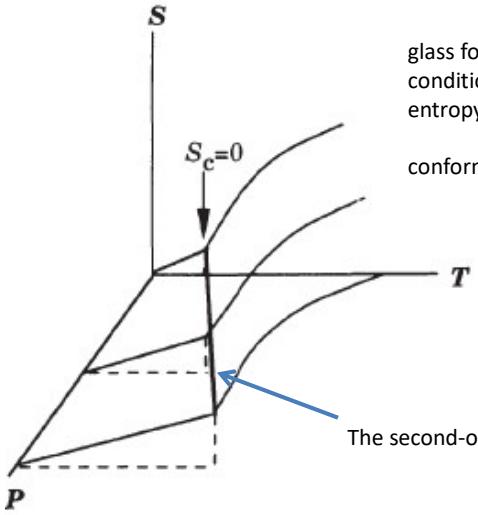

glass formation at $T=T_g$ is associated with the condition $S_c = 0$, where S_c is the conformational entropy

conformational entropy decreases with T decrease

The second-order transition is marked with a thick line.

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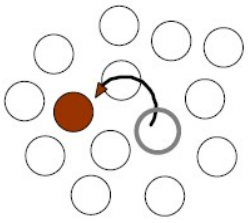
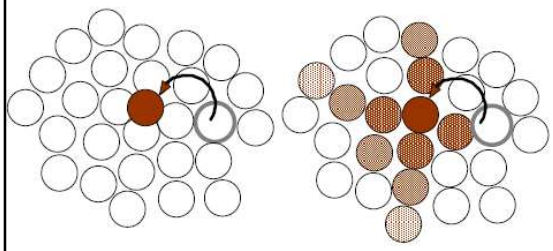
Adam, Gibbs: concept based on **cooperativity**



• High temperature - configurational rearrangement takes place via **individual** hopes



• Low temperature – cooperative motion of many units to allow a configurational rearrangement to take place.

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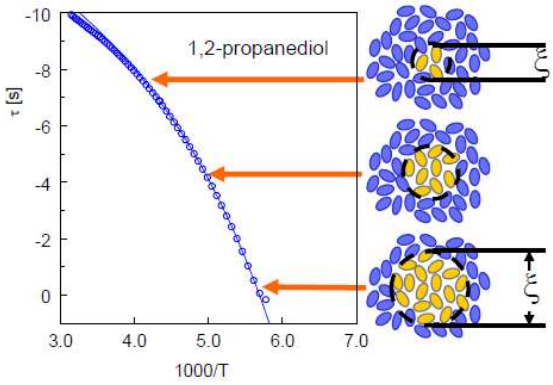
Adam-Gibbs theory

• Cooperatively rearranging region (CRR) - the minimum number of molecules which must cooperatively move to permit rearrangement.

• Size of the cooperatively rearranging regions increases with decreasing temperature.



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what about relaxation times?

• Energy barrier for single molecule to move: Δμ
• Number of molecules in CRR: *z**

$$\tau^{-1} \sim \nu_0 \exp\left(-\frac{z^* \Delta\mu}{k_B T}\right)$$

exercise :

The non-Arrhenius behaviour is a direct consequence of the increasing size of the CRR at low temperature

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assume the size of the CRR $z^* \sim (S_c)^{-1}$

$$\tau^{-1} \sim \nu \exp\left(-\frac{C}{S_c T}\right)$$

S_c vanishes at the Kauzmann temperature, this implies that τ diverges at T_K.

With $T_K = T_0$ we recover the VFT equation

$$\tau = \tau_0 \exp\left(\frac{E}{T - T_0}\right) \quad \text{(exercise)}$$

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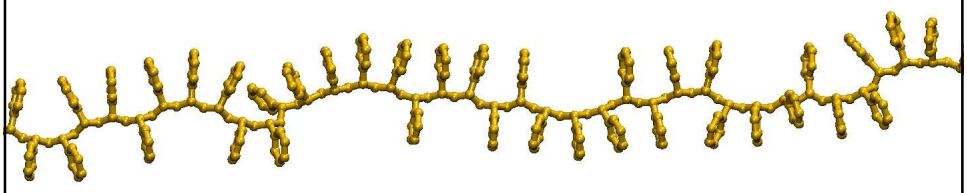
III. Simulations of glass transition



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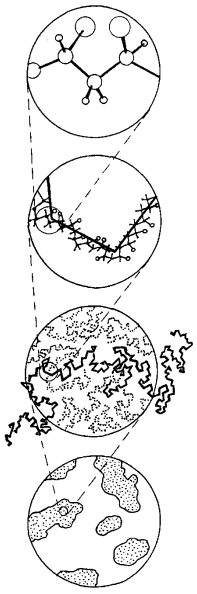
Length and time scales in polymers

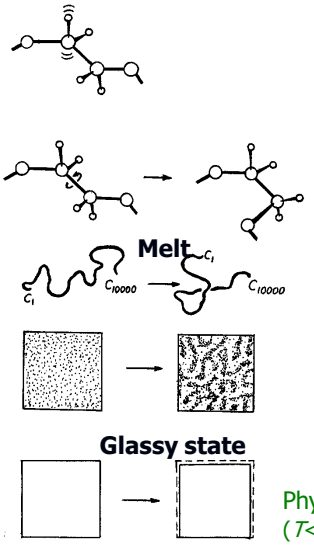


Bond lengths, atomic radii ~0.1 nm

Statistical (Kuhn) segment length *b* ~ 1 nm

Chain radius of gyration ~10 nm

Domain size in phase-separated material ~1 μm



Bond vibrations $\geq 10^{-14}$ s

Conformat. transitions $\geq 10^{-11}$ s

Longest relaxation time $\geq 10^{-3}$ s

Phase/ microphase separation ≥1 s

Physical ageing ($T < T_g$-20°C)≥1yr

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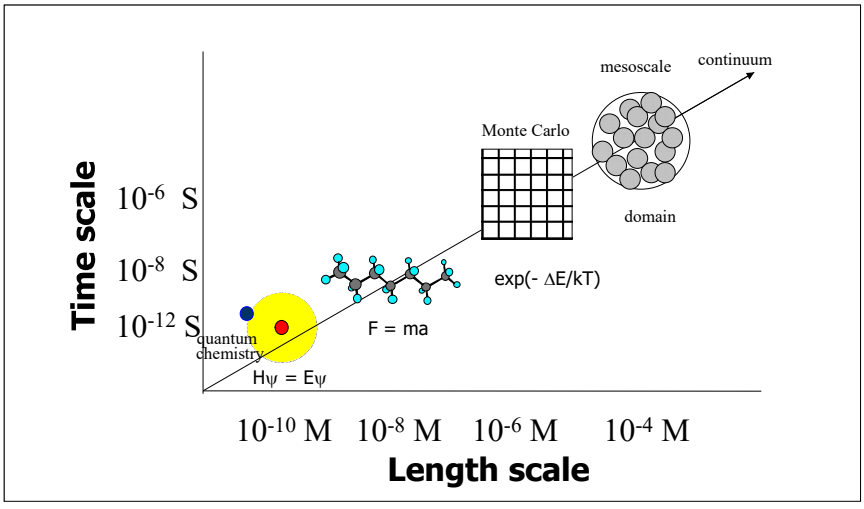
What and Where: Scales in Simulations



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$$H(\vec{r}_1,...,\vec{r}_N;\vec{p}_1,...,\vec{p}_N) = T(\vec{p}_1,...,\vec{p}_N) + U(\vec{r}_1,...,\vec{r}_N)$$

$$U(\vec{r}_1,...,\vec{r}_N) = \sum_i v_1(\vec{r}_i) + \sum_i \sum_{j>i} v_2(\vec{r}_i,\vec{r}_j) + \sum_i \sum_{j>i} \sum_{k>j>i} v_3(\vec{r}_i,\vec{r}_j,\vec{r}_k) + ...$$

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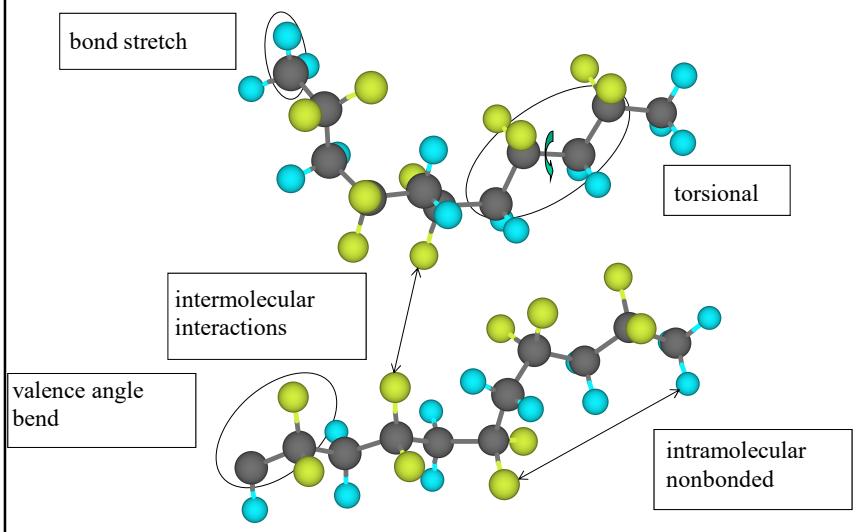
The Force Field



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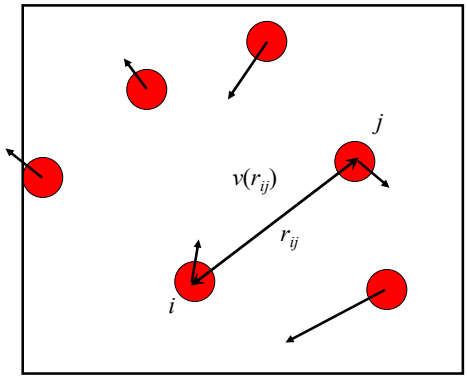
Molecular Dynamics



Very simple in principle: solution of classical Newton equations!

$$m_i \ddot{\vec{\mathbf{r}}}_i = m_i \vec{\mathbf{a}}_i = \vec{\mathbf{F}}_i = \sum_{j \neq i}^{N} \vec{\mathbf{F}}_{ij}$$

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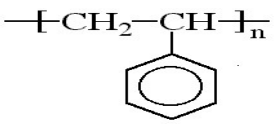
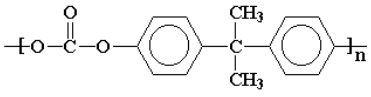
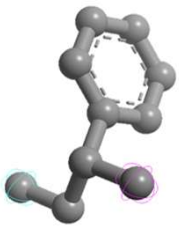
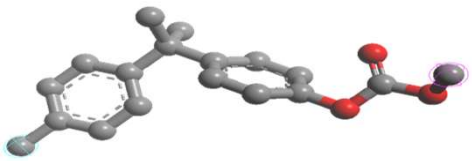
PS vs PC as model amorphous polymers









- PS fails brittle, PC tough
- **What is the relation with molecular structure and chain dynamics ?**

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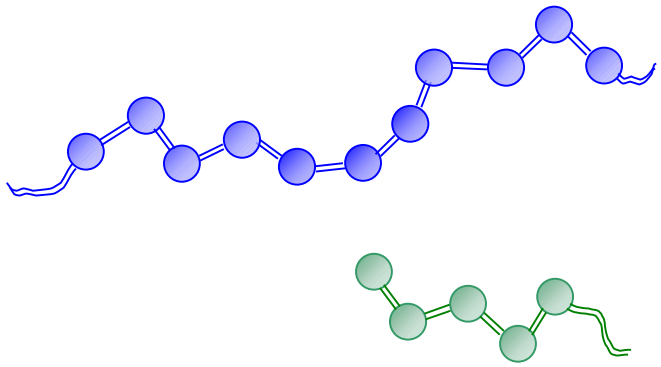
End-Bridging Monte Carlo



P.V.K. Pant & D.N. Theodorou, *Macromolecules* **28**, 7224 (1995)

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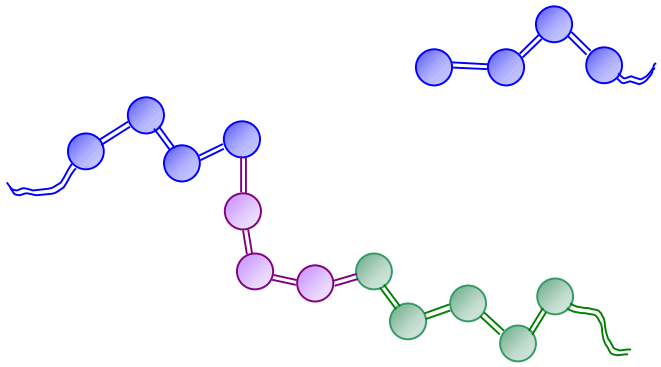
End-Bridging Monte Carlo



P.V.K. Pant & D.N. Theodorou, *Macromolecules*, **28**, 7224 (1995)

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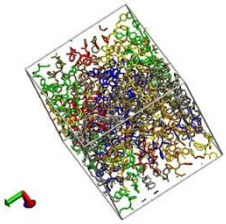
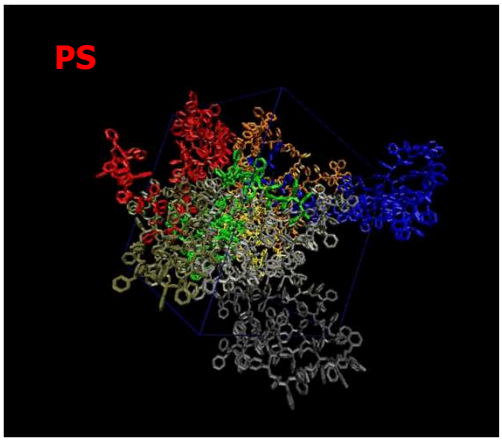
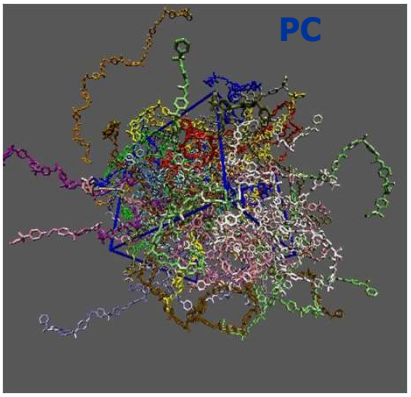
Equilibration

$T \sim T_g$ $P = 1$ atm







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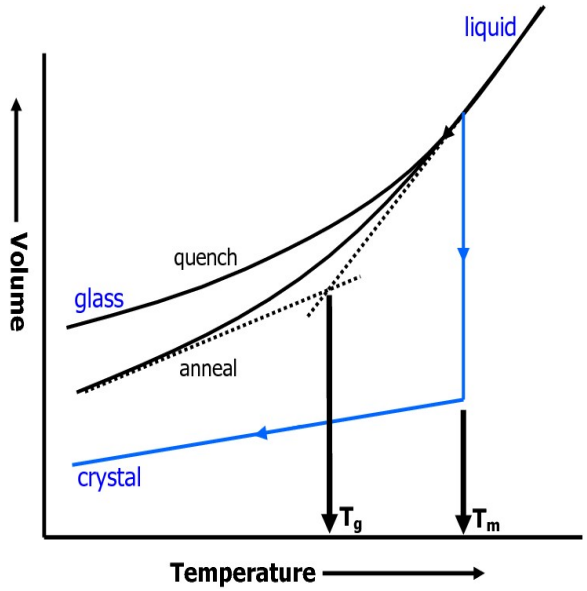
PVT measurement



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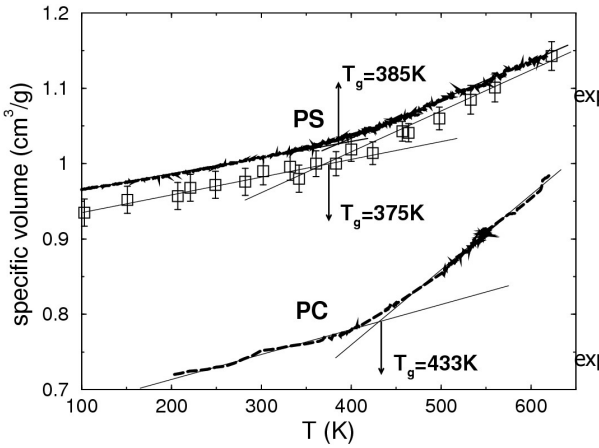
MD-determined glass transition



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 31

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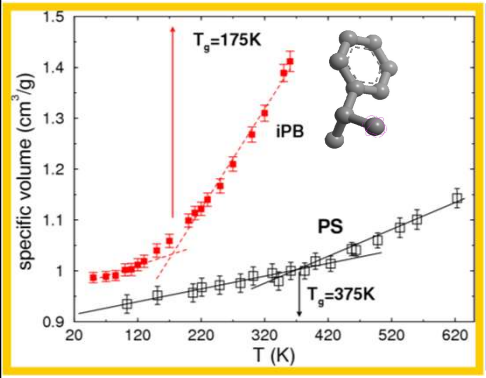
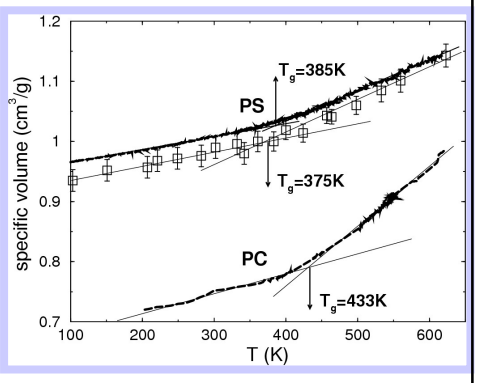
MD-determined glass transition





•MD-determined T_g is displaced upward in T as compared to experiment

•The value of T_g is strongly cooling-rate dependent

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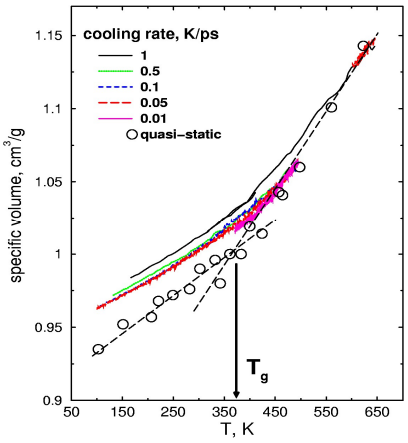
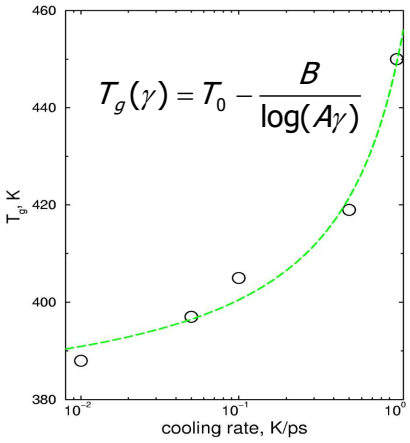
Cooling-rate dependence of T_g





T_g logarithmically increases with cooling rate

AVL, N. K. Balabaev, M.A.J. Michels, ***Macromolecules***, 36, 8574 (2003)

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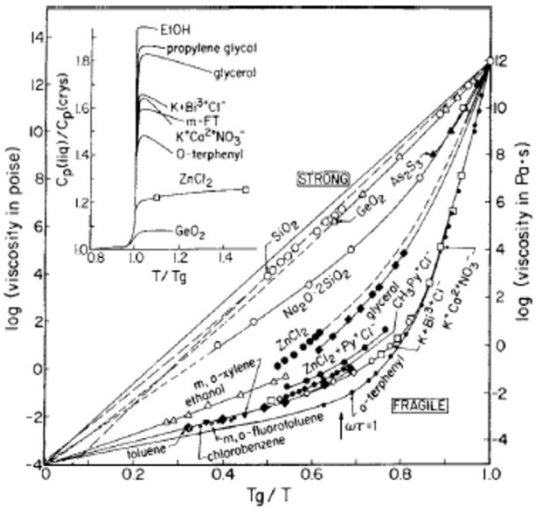
Slowing down of dynamics



$\tau = \tau_0 \exp\left(\frac{\Delta E}{k_B T}\right)$ Arrhenius law

$\tau = \tau_0 \exp\left(\frac{A}{T - T_0}\right)$ Vogel-Fulcher-Tammann law

The C.A. Angell (1985) plot

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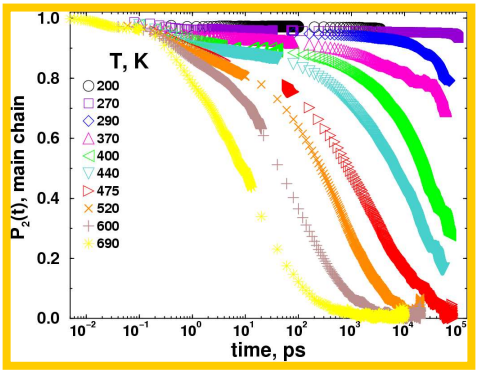
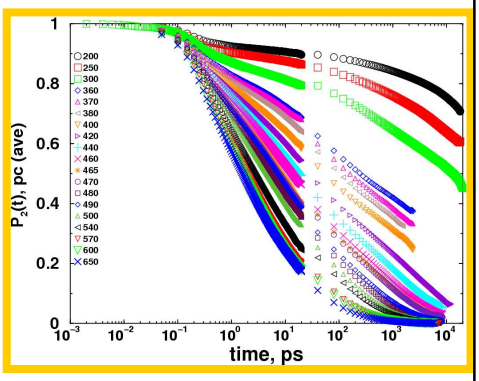
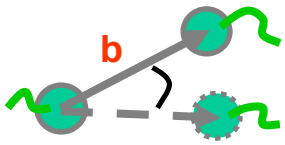
Orientational mobility

polystyrene



polycarbonate





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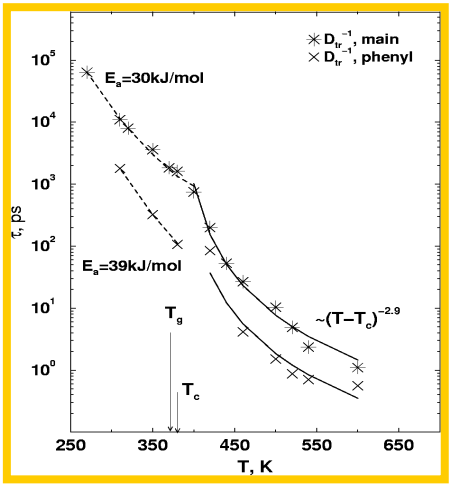
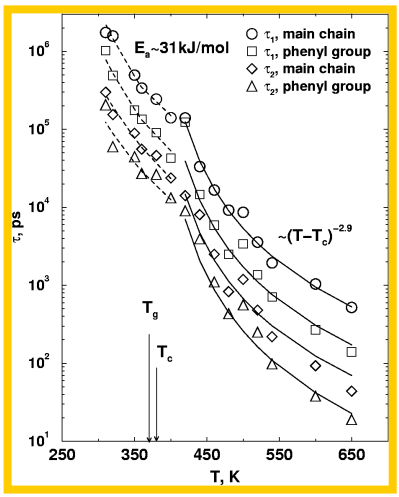
PS: orientational relaxation





- $T > T_g$: universal algebraic (VFT) behaviour
- $T < T_g$: similar activated behaviour

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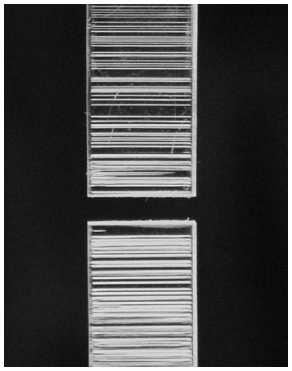
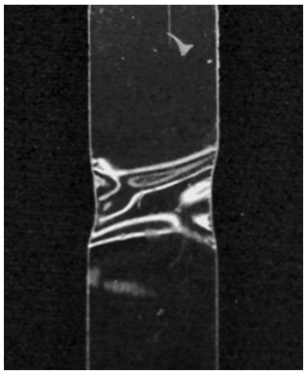
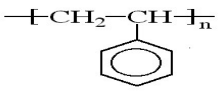
- **Brittle vs. Tough**

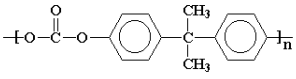




Polystyrene



Polycarbonate



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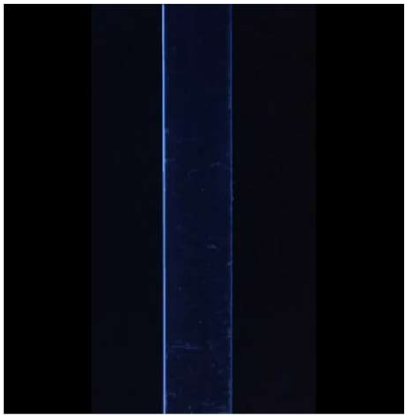
Mechanical rejuvenation



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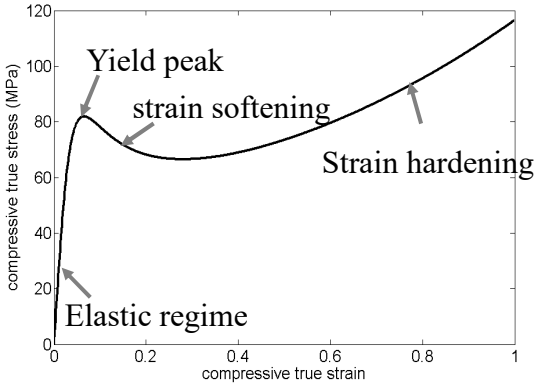

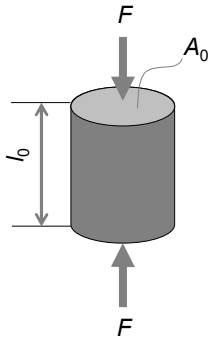

$$\sigma = F / A$$

$$\varepsilon = l / l_0 - 1$$

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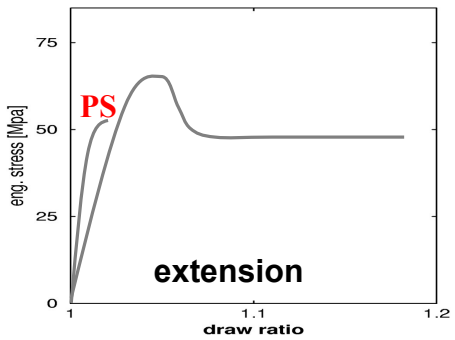
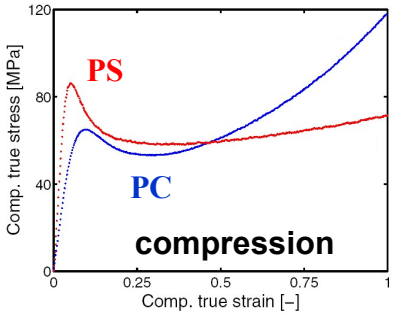
Stress-strain behaviour





- Intrinsic microscopic response vs chemical structure unclear
- *(e.g. H.E.H. Meijer et al., TU/e and DPI)*

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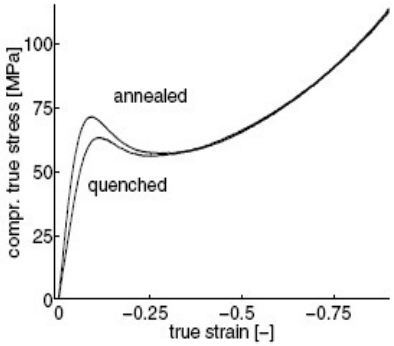
Thermal rejuvenation

- **Thermal**: heating up above T_g, then quenching



H.G.H. van Melick, PhD thesis, Eindhoven, 2002

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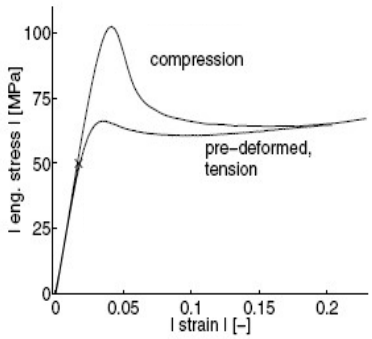
Mechanical rejuvenation

- **Mechanical**: deformation above the yield point, then compression



H.G.H. van Melick, PhD thesis, Eindhoven, 2002

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Thermal and mechanical rejuvenation

- **Thermal**: heating up above T_g, then quenching
- **Mechanical**: deformation above the yield point, then compression

Bulk mechanics similar

Microscopically the same ????

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Relevant experimental time scales

- thermal aging (hours – years)
- mechanical deformation (seconds – minutes)
- intrinsic segmental relaxation (ms – hours)

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Relevant simulated scales

Segmental dynamics in non-deformed bulk

Mechanical rejuvenation and overaging

0.1 ps – 100 ns

50 Å – 100 Å

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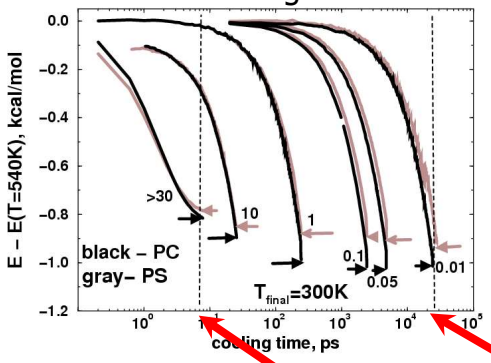
Cooling down below T_g



- Cooling time, τ_c

10 ps (quenched)

25 ns (annealed)

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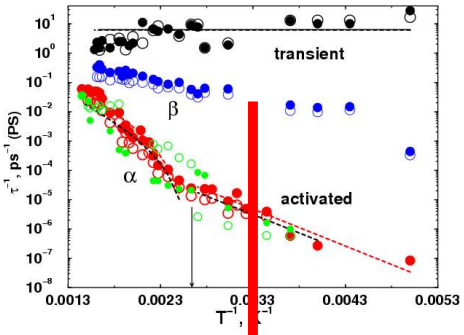
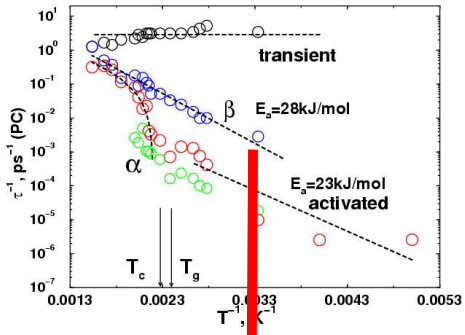
Temperature dependence of P_2 relaxation times

polystyrene



polycarbonate



T = 300K

$\tau_\beta \sim 50$ ps << $\tau_\beta \sim 500$ ps

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segmental β relaxation

PS: 50 ps PC: 500 ps

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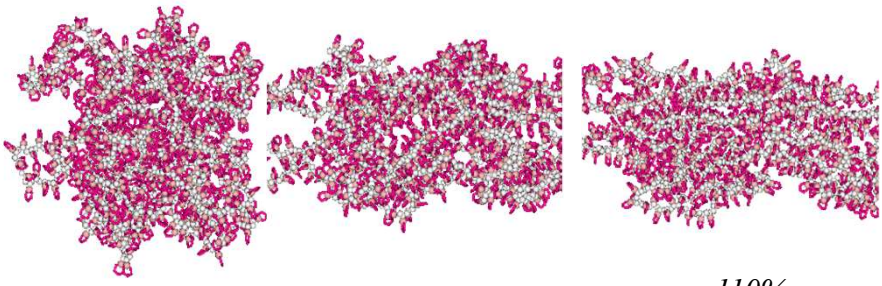
Uniaxial extension



γ_L=0 γ_L=65% γ_L=110%

$\dot{\gamma} = 0.005\ Å/ps \quad \tau_y = 1000\,ps$

- PS: 4 chains x N=160, 8 chains x N=80
  : 64 chains x N=10, 8 chains x N=80

AVL, N.K. Balabaev, M.A. Mazo, M.A.J. Michels, *Macromolecules* **2004**
AVL, M.A.J. Michels, *Phys. Rev. Lett.*, **2007**

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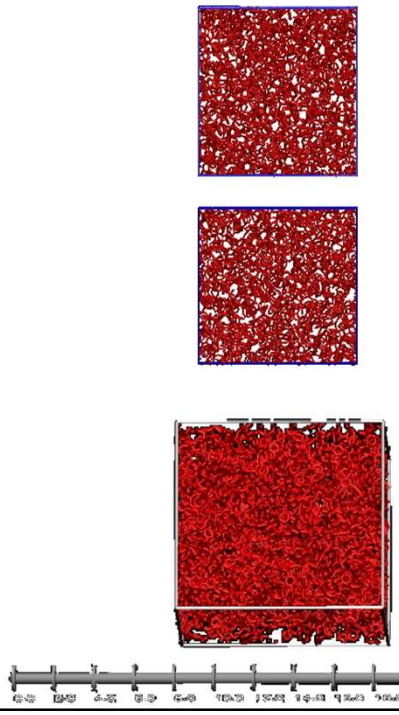
PS:

$T << T_g$

PC:



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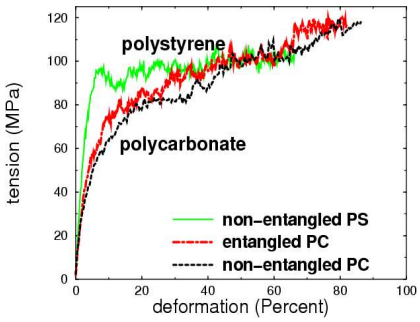
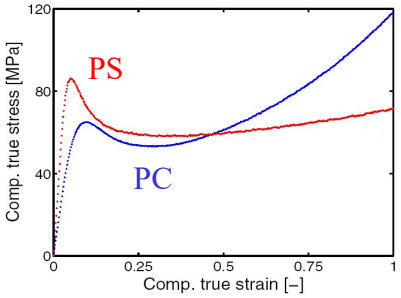
Simulation vs. experiment





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

H.G.H. van Melick et al., Polymer **2003**

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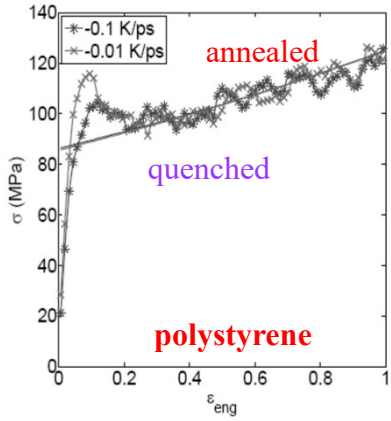
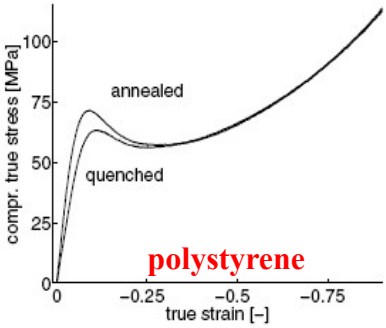
Simulation vs. experiment





AVL, M.A.J. Michels, *Phys. Rev. Lett.*, **2007**
B. Vorselaars, PhD, **2008**

H.G.H. van Melick, PhD thesis, Eindhoven, **2002**

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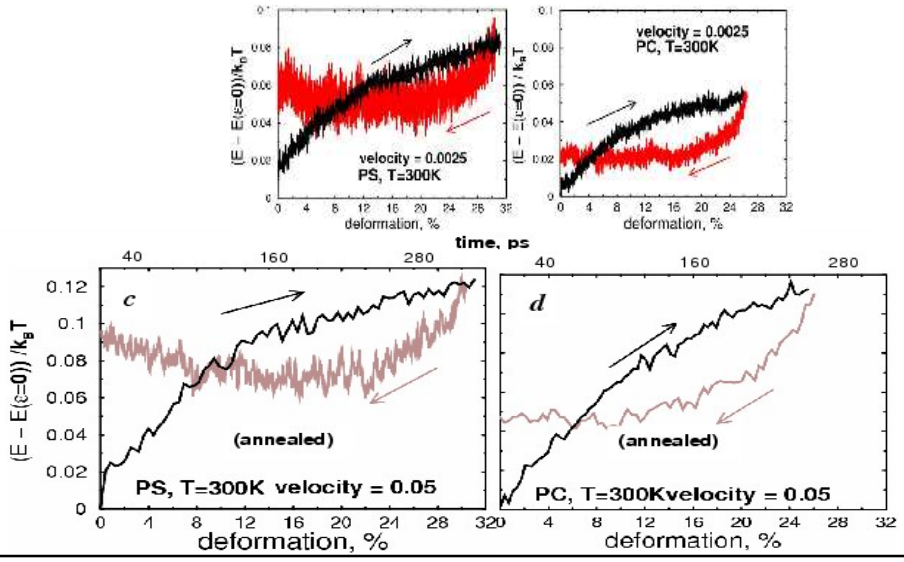
Stretching - compression loop: annealed samples



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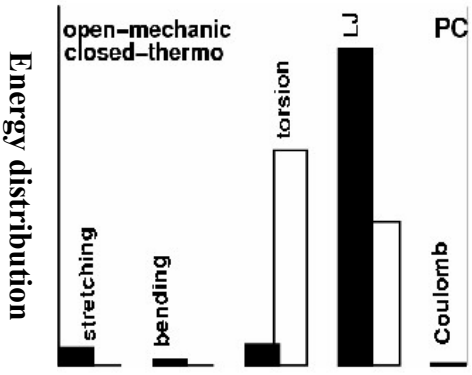
Energy partitioning



- mechanically rejuvenated glass is different from thermally rejuvenated glass

AVL, M.A.J. Michels, *Phys. Rev. Lett.*, 2007

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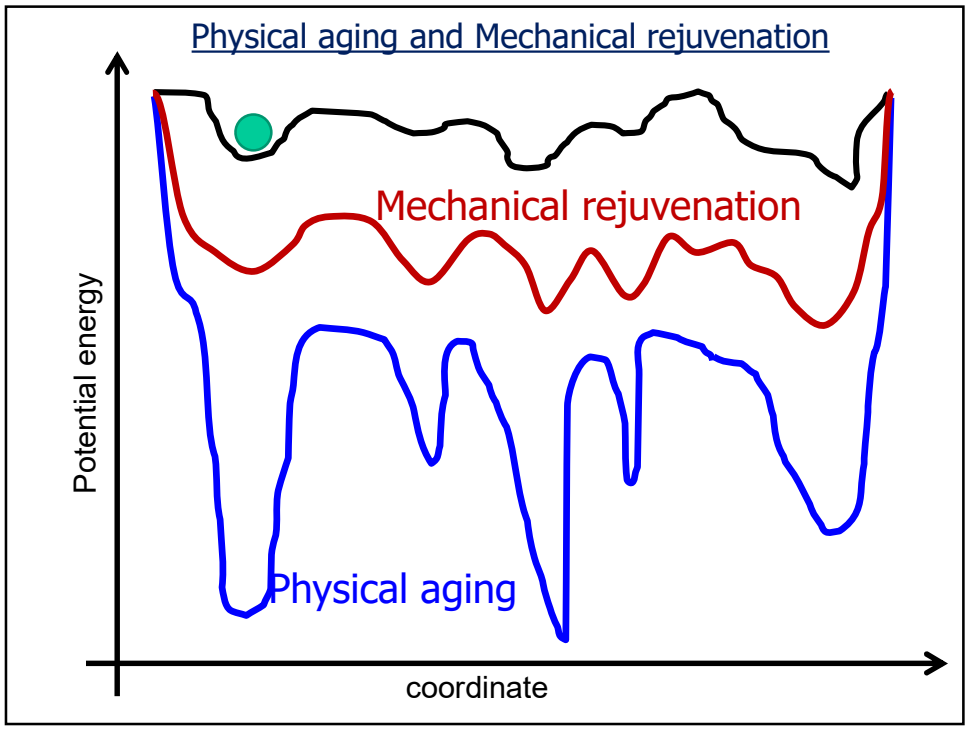

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Summary

- Asymptotic glass-transition T_g reproduced well;
- Slowing down of cage escape is collective. Below T_g universal
- activated segmental motion;
- Overaging and rejuvenation for typical polymer glasses can be
- simulated;
- Key factors are ratios between three time scales:
- - β relaxation;
- - cooling time;
- - deformation time;
- Thermal and mechanical rejuvenation are microscopically different;

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