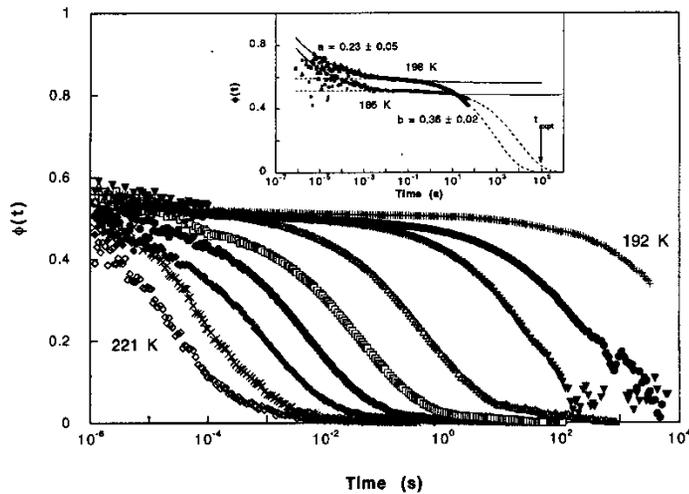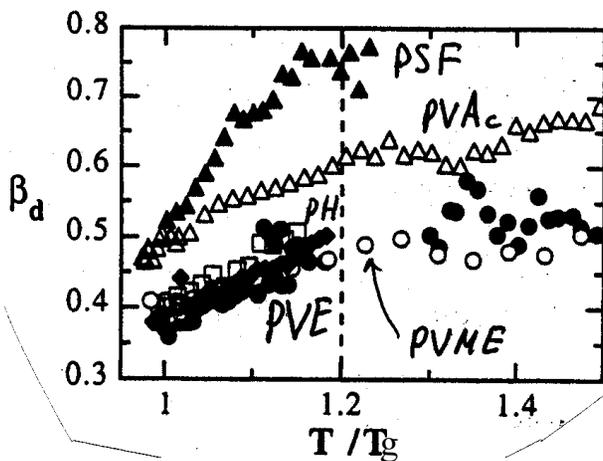# *Segmental Relaxation (α-process)*

The main structural relaxation in polymers is the segmental, so-called α-relaxation. It controls diffusion and viscosity, rotation of monomers. The α-process is the relaxation on time scale shorter than the rubbery plateau and the Rouse modes. It is responsible for the transition region and is associated with the glass transition.

It is usually ascribed to micro-Brownian motion of chain segments. Most authors agree that the α-process is related to conformational changes (like gauche trans transition). Because the glass transition is directly related to the α-relaxation, both, Tg and segmental relaxation (the α-process), show the same dependence on M_w and crosslinking.
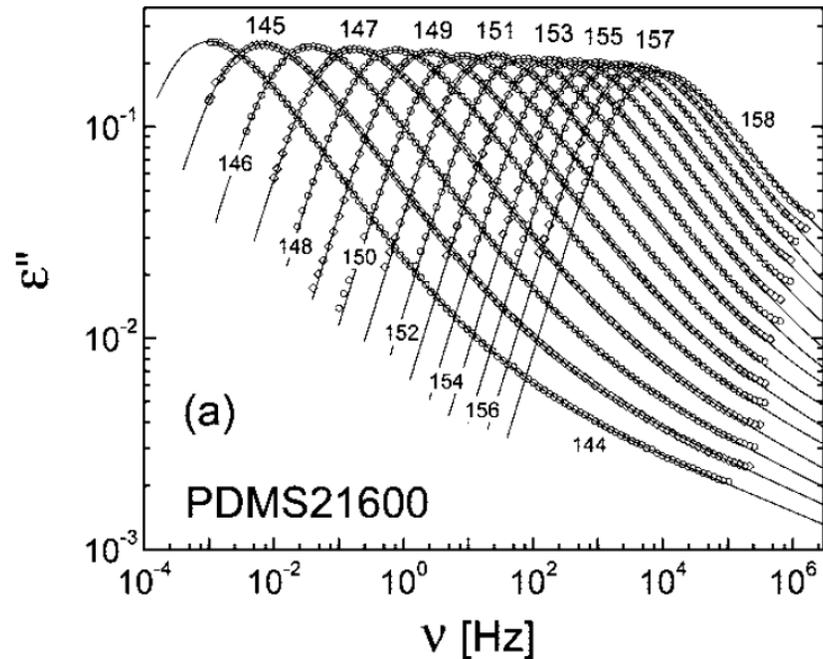
Many similarities between the glass transition in low-weight molecular systems and in polymers suggest that the chain connectivity is not required for this process.

Intermediate scattering function $\phi(t)$ in PPG [Bergman, et al. **Phys.Rev.B 56**, 11619 (1997)] shows strong stretching of segmental relaxation.

Dielectric relaxation spectra in PDMS are also stretched [Hintermeyer, et al. **Macromolecules 41**, 9335(2008)].

The shape parameter depends on the system and varies with temperature. However, at higher T the temperature variations of β_{KWW} is weak.

Stretching parameter for different polymers [Colmenero, et al. **JPCM 11**, A363 (1999)].

There are two basic reasons for the stretched spectrum:
1. The process corresponds to a weighted sum of elementary processes each having a correlation function that may be exponential in time. E.g. it may be equivalent to a distribution of relaxation times
2. The process has a natural non-exponential dependence.

Temperature Dependence of Segmental Relaxation

The characteristic relaxation time of the segmental process, τ_α, demonstrates strongly non-Arrhenius temperature dependence in all polymers. It is usually described using Williams-Landel-Ferry (WLF) equation:
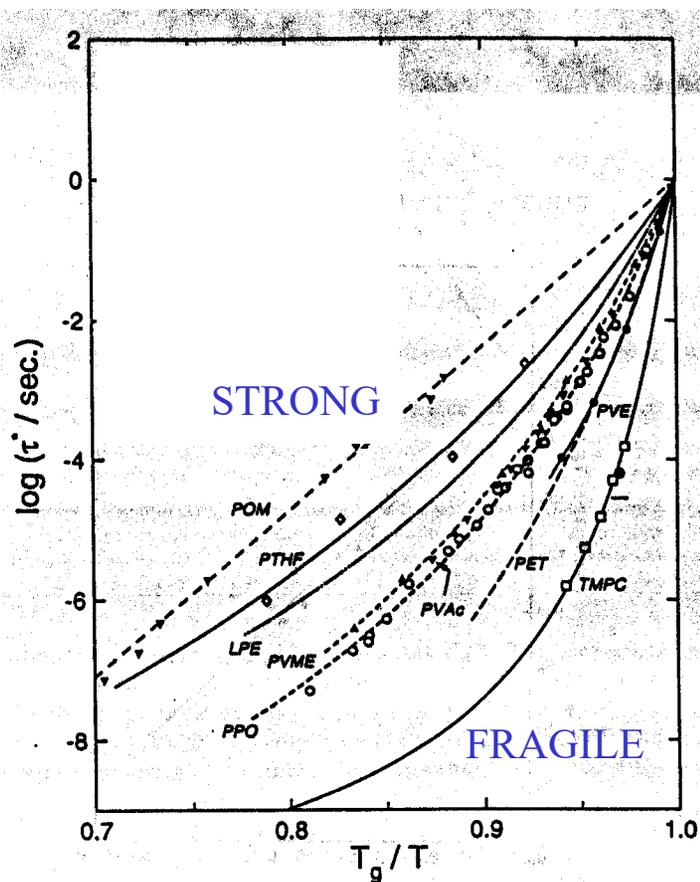
$$\log a_T = \log[\tau(T^*)/\tau(T)] = \frac{C_1(T - T^*)}{T - (T^* - C_2)}$$

Here T* is some reference temperature, often T*~Tg.

The same temperature dependence in non-polymeric systems is usually described by the Vogel-Fulcher-Tammann (VFT) equation:

$$\tau = \tau_0 \exp\left[\frac{B}{T - T_0}\right]$$

The equations are equivalent: $C_2 = T^* - T_0$; $2.3 C_1 C_2 = B$, $C_1(T^*) = \log[\tau(T^*)/\tau_0]$.

Different polymers show stronger or weaker deviations of τ_α from the Arrhenius behavior. The classification on strong and fragile systems has been suggested by Angell [in: Relaxation in Complex Systems, NRL, Washington, Eds.K.Ngai, G.Wright, 1984, p.3]. The systems that show Arrhenius-like temperature dependence of τ_α were called strong, strongly non-Arrhenius – fragile.

Degree of fragility can also be related to an apparent activation energy E_a around Tg (just a slope of $\ln(\tau_\alpha)$ vs $1/T$ around T~Tg). $E_a \sim B/(Tg - T_0)$ for some polymers can be large than the binding energy for C-C bond and has therefore no physical or chemical meaning. It reflects some cooperativity in motion.
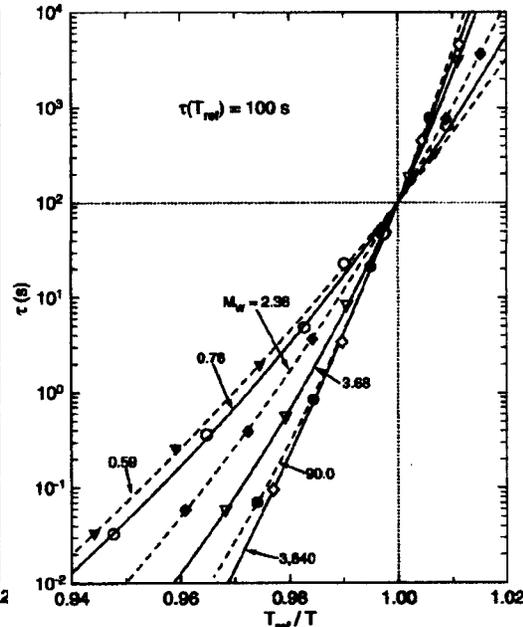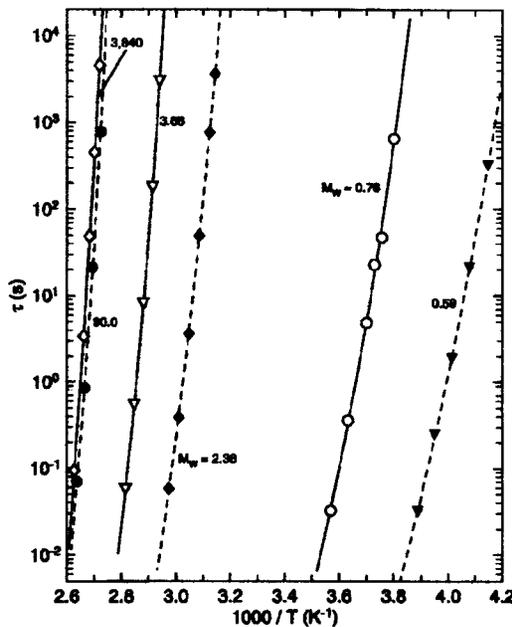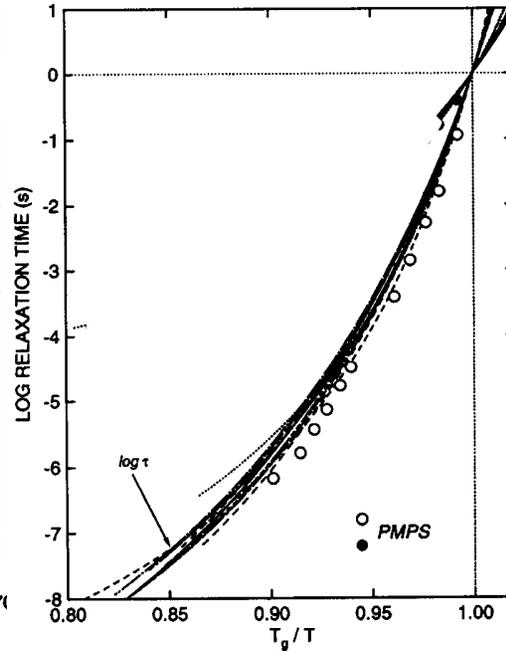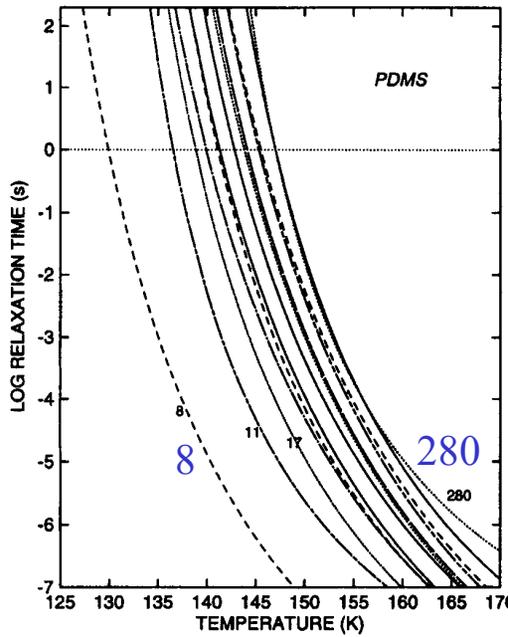
τ_{α} of segmental relaxation depends on molecular weight of a chain: the lower is Mw the shorter is τ_{α}. This effect might depend on end groups of the chain. Traditional explanation is based on free volume ideas (will be discussed later).

Relaxation time in PDMS with different degree of polymerization (shown by numbers on the left) [Roland, Ngai, **Macromolecules 29**, 5747 (1996).]. In the case of PDMS, the temperature variations of τ_{α} for all molecular weights scale well with Tg (right) suggesting no change in fragility.

Similar results are presented for PS [Santangelo, Roland, **Macromolecules 31**, 4581 (1998)]. However, the fragility of PS chain appears to be dependent on Mw.

Recent ideas relate fragility to a rigidity of backbone and side groups. Rigid chains frustrate packing and increase fragility.

Mode-coupling Theory Approach

Mode-coupling theory (MCT) for structural relaxation has been developed during last 15 years. It considers density-density correlation function

$\phi_q(t) = \langle \rho_q(t) * \rho_q \rangle / S_q$. It is analyzed in framework of the Zwanzig-Mori formalism:

$$\partial_t^2 \phi_q(t) + \Omega_q^2 \phi_q(t) + \Omega_q^2 \{ i\gamma_q \partial_t \phi_q(t) + \int_0^t m_q(t-t')\partial_{t'}\phi_q(t')dt' \} = 0 \qquad (6)$$

This is a standard approximation that takes into account memory effects. The main achievement of the theory is calculation of the memory kernel on a microscopic basis. The memory kernel is related to fluctuating forces F_q coupled to the density fluctuation ρ_q. The fluctuating force is coupled to an infinite set of relaxation modes:

$$F(r,t) = \int dr' \nabla V(r-r')\rho(r,t)\rho(r',t) \qquad (7)$$
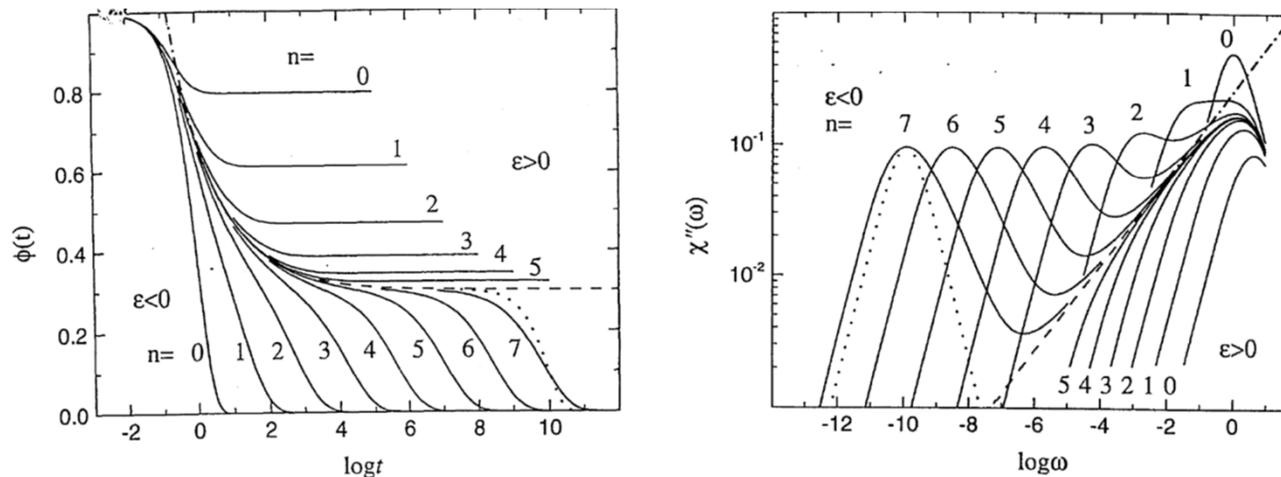
MCT predicts tow step relaxation scenario, particular critical behavior of structural relaxation and existence of crossover T at which dynamics change qualitatively. MCT provides good qualitative description of dynamics at high T.

Shoving (elastic) model

Shoving model [J.C. Dyre, **Rev. Mod. Phys. 78**, 953 (2006)] assumes that the relaxation event in supercooled liquids happens as in elastic solids, i.e. require some deformation:

$$\log\left[\frac{\tau_\alpha(T)}{\tau_0}\right] = \frac{G_\infty(T)V_0}{T}$$

Here $G_\infty(T)$ is the high-frequency elastic modulus and V_0 is some volume.

(a)
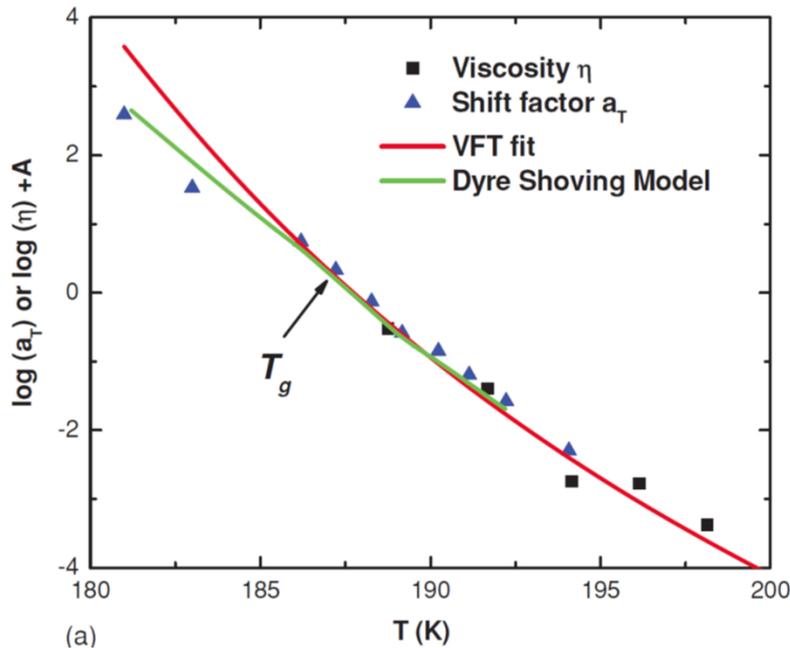
Indeed, it has been demonstrated for many glass-forming liquids that this approach describes well the temperature dependence of $\tau_\alpha(T)$ upon approaching Tg.

Example for m-toluidine (symbols) where Shoving model provides better description than VFT [Xu, McKenna, **JCP 134**, 124902 (2011)].

Elastic collective nonlinear Langevin equation (ENCLE) theory [Mirigian, Schweizer, **Macromolecules 48**, 1901 (2015)] combines MCT at higher T and shoving model at lower T with additional entropic barrier in the crossover region. It describes $\tau(T)$ for many systems in a broad temperature range without additional adjustable parameters.

Glass Transition
Phenomenon of the Glass Transition

Glass transition is usually defined as a transition from a liquid state to a solid state. It appears as a sharp change of temperature dependence for many properties, including volume (density), entropy, elastic constants. The temperature where the change happens is called the glass transition temperature Tg.
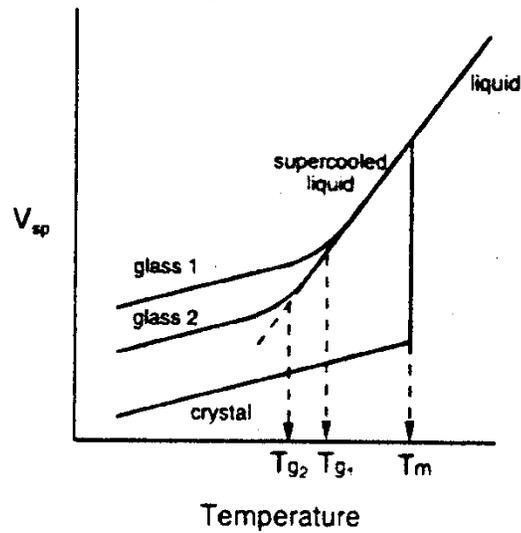
Temperature variations of volume. Tg depends on cooling rate.
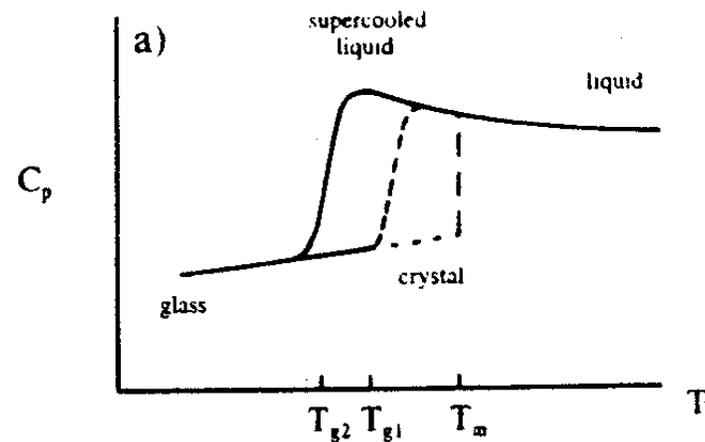
Change in specific heat at temperatures around Tg.

However, Tg is an ill-defined quantity. It depends on a cooling or heating rate. Due to that reason also another definition of Tg is accepted: Tg is a temperature where segmental relaxation time $\tau \sim 100$ sec. *There is no phase transition of any kind at Tg.*

The nature of the glass transition phenomenon remains a subject of discussions. However, the basic event of the observed transition from a liquid to a solid is a kinetic phenomenon. Glass transition is a freezing of segmental relaxation.
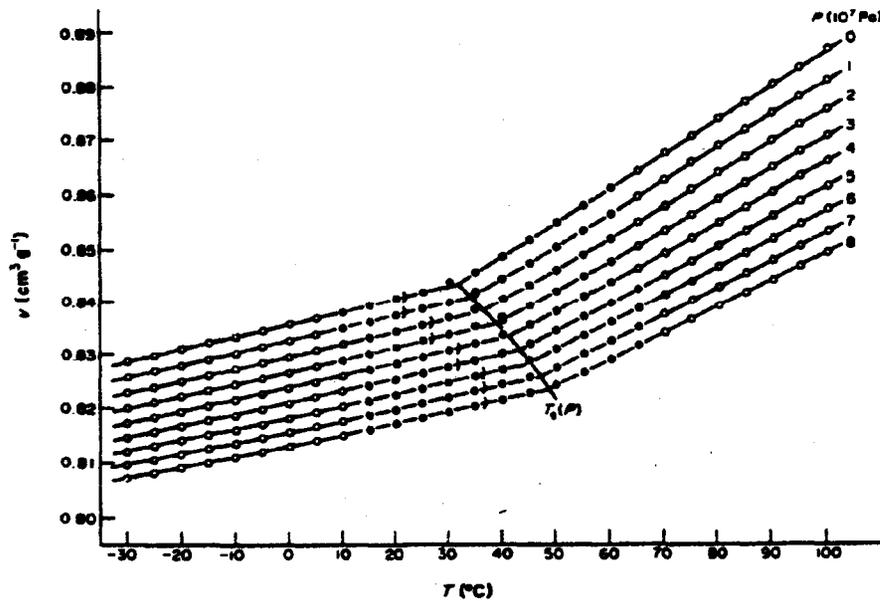
Glass transition depends on pressure: increase in P leads to increase in Tg of polymers. dTg/dP is different for different polymers.

This effect might be important for polymer processing where polymer melt is usually under some pressure.

The Kauzmann paradox

Considering changes of entropy, S, during cooling of a liquid state, Kauzmann paid attention [Kauzmann, **Chem.Rev. 43**, 219 (1948)] that extrapolated S of supercooled liquids may become lower than entropy of a crystal. That should happen at some temperature T_K.

That does not violate any thermodynamic law. However, it is difficult to expect that the entropy of a disordered state will be below the entropy of an ordered state.

T_K has been found close to T_0 VFT. That leads to speculation on existence of a real thermodynamic transition at $T \sim T_K \sim T_0$, that is avoided because the system falls out of equilibrium at Tg.
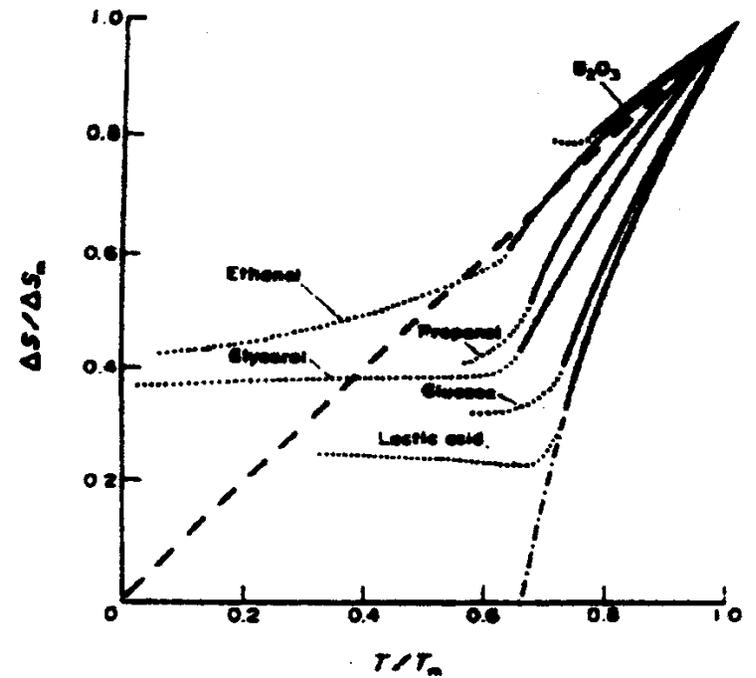
Several models were proposed to explain VFT or WLF equations for τ and to describe the glass transition:

-The free volume approach, assumes that the fractional free volume becomes 0 at $T \sim T_0$;

-Thermodynamic approach (Adam and Gibbs theory, Gibbs DiMarzio theory) treats the glass transition as a cooperative process, the degree of cooperativity increases when temperature decreases.

However, all the models are phenomenological, have some problems and the nature of this temperature dependence remains unclear.

Free Volume Approach

The basis is the Doolittle's viscosity equation:

$$\eta = a \exp(bv/v_f) \tag{1}$$

Here v_f is the free volume and v is the total volume. The same relation can be written for the relaxation time. The free volume is defined as $v_f = v - v_0$. Here v is the total macroscopic volume and v_0 is the actual molecular volume. The fractional free volume is usually assumed to vary with T:

$$f = v_f / v = f_g + \alpha_f (T - T_g) \tag{2}$$

f_g is the fractional free volume frozen at Tg and a_f is the thermal expansion coefficient of the free volume. Substituting eq.2 in eq.1:

$$\log a_T = \log \frac{\eta}{\eta_g} = \frac{b}{2.3}\left(\frac{1}{f} - \frac{1}{f_g}\right) = -\frac{b}{2.3 f_g} \frac{T - T_g}{f_g / \alpha_f + T - T_g} \tag{3}$$

Thus we have an equation similar to WLF equation, with T*=Tg, $C_1 = b/2.3 f_g$; $C_2 = f_g / \alpha_f$. In that case one can relate the model parameters and WLF parameters: $f_g = b/2.3 C_1$ and $\alpha_f = b/2.3 C_1 C_2$. However, because the constant b is an arbitrary parameter, no direct estimates of the free volume fraction can be obtained.
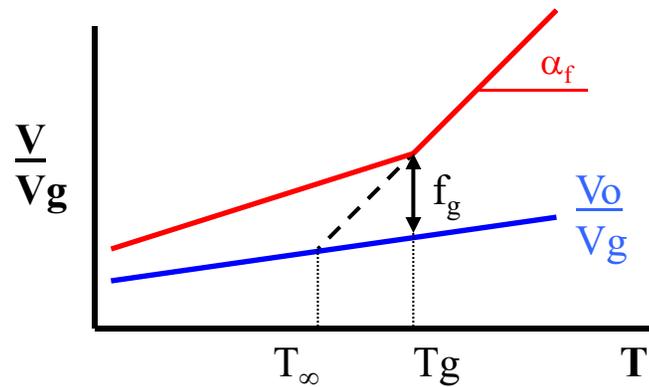
A simple picture behind the free volume approach is based on the assumption that an empty (free) volume is needed for molecular motion. This free volume decreases with decrease in T. That leads to slow down of the motion. Relaxation time at Tg crosses the experimental time scale and freezing of the structure (including free volume) occurs. It gives frozen free volume f_g. If one would cool the sample down with infinitely slow rate, $f_g=0$ will be reached at T_∞ that would be equivalent to T_0 of VFT equation.

When one considers b~1, the value for the free-volume fraction at Tg for many polymers falls in the range f_g~0.013-0.034. WLF proposed a "universal" value f_g~0.025. Later, another relation was also suggested: $f_g=10^{-4}*Tg+0.07$ [Boyer, Simha, **J.Polym.Sci.Polym.Lett. 11**, 33 (1973)]. It was further modified: f_g is not frozen at Tg; one should distinguish fractional empty free volume or dynamic free volume from total free volume.

Free volume approach has been extended to include pressure effects:

$$\log a_T = -\frac{b}{2.3 f_0} \frac{T - T_0 - \Theta(P)}{f_0/\alpha_f + T - T_g - \Theta(P)} \qquad (4)$$

Here f_0 is f at $T=T_0$. $\Theta(P)$ is a function that depends on the pressure-dependent coefficient of thermal expansion of the free volume, $\alpha_f(P)$. It has been shown that the equation 4 describes reasonably well T- and P- dependencies for some polymers.

Nevertheless, the free-volume approach has been criticized for many problems. In some cases unreasonable parameters of the free volume should be assumed in order to describe data for some materials. It has been also demonstrated that holding free volume constant (by varying simultaneously P and T) leads to different viscosity, suggesting that not only density, but also temperature play role in the glass transition.

The influence of molecular weight on Tg, chain-end free volume approach

Tg for many polymers depends on molecular weight Mn. At not very low Mn, Fox-Flory empirical equation describes reasonably well the molecular weight dependence of Tg:

$$T_g(M_n) = T_g(\infty) - \frac{K}{M_n} \tag{5}$$

Free volume approach explains the Fox-Flory equation, assuming that chain ends contribute an excess free volume. In that case, decrease in Mn leads to increase of chain ends concentration and increase of free volume. Increase in free volume leads to decrease in Tg.

Let's assume that chain end has a free volume θ. Then the free volume per unit volume is $2\theta\rho N_A/Mn$, where ρ is density, N_A is Avogadro's constant. Assuming that f_g is independent of Mn, the excess free volume introduced by chain ends should be compensated by the thermal contraction:

$$2\theta\rho N_A / M_n = \alpha_f [T_g(\infty) - T_g(M_n)] \quad \text{Then} \quad T_g(M_n) = T_g(\infty) - \frac{2\theta\rho N_A}{\alpha_f M_n} \tag{6}$$

The Fox-Flory equation is obtained with the constant $K = 2\theta\rho N_A/\alpha_f$.
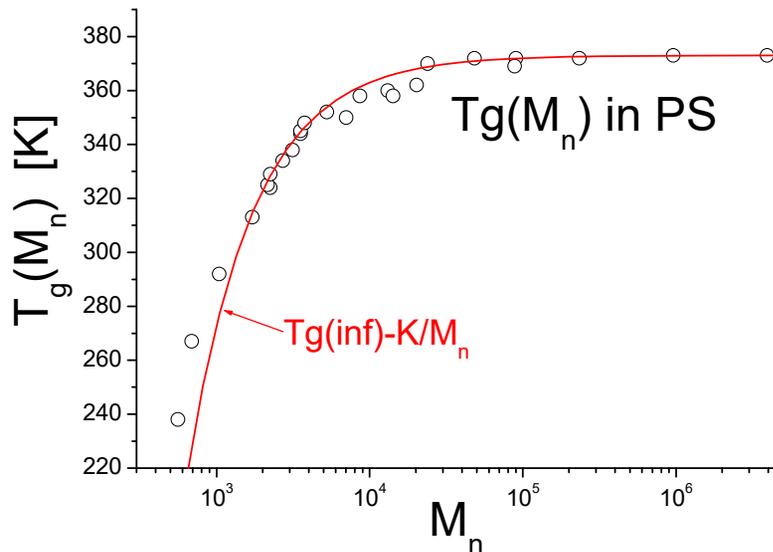
Thus, chain-end free volume idea describes well the molecular weight dependence of Tg. However, it is known that the free volume is not universal at Tg. Also, a simple free volume approach can not explain the behavior of Tg in ring polymers (will be discussed later.

Thermodynamic Approach

Any conformational changes require some cooperative motion of a few molecules (cooperative domain). Domain consists of z conformers, each has c_1 number of states. The conformational entropy for 1 mole of conformers in which there are N_z domains consisting of z conformers: $S_c = N_z k \ln c_1$

$$z = \frac{N_A}{N_z} = \frac{N_A k \ln c_1}{S_c} = \frac{s*}{S_c}$$

here s* is the conformational entropy of one mole of conformers where each conformer relaxes independently. At high T>T* when there is no cooperativity $s*=S_c$. At T<T* S_c drops faster than s*, assumption

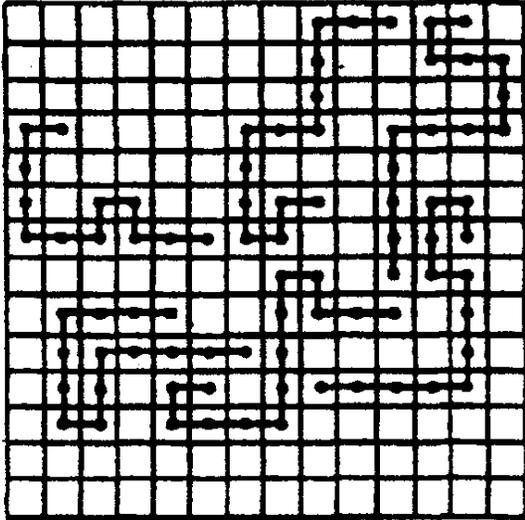$$S_c = \frac{T*}{T*-T_0}\frac{T-T_0}{T}s*; \qquad\qquad \tau = \tau_0 \exp\left(\frac{C}{TS_c}\right)$$
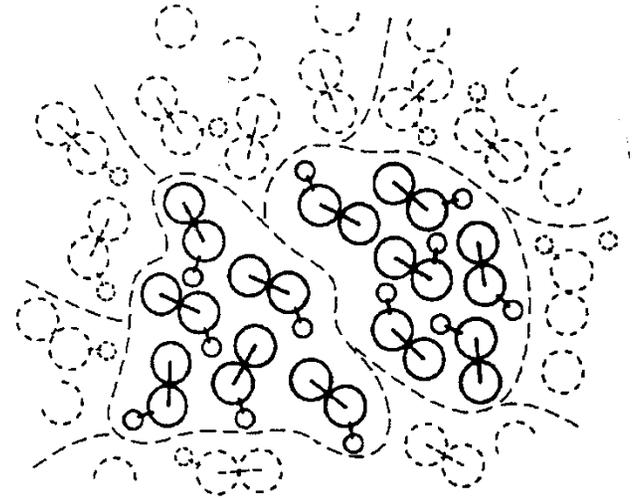
An equation for relaxation time (Δμ is the energy barrier for one conformer to relax):

$$\ln(\tau/\tau*) = \frac{\Delta\mu}{k}\left[\frac{z}{T} - \frac{1}{T*}\right] = \frac{\Delta\mu}{k}\left[\frac{s*}{TS_c} - \frac{1}{T*}\right] = -\frac{\Delta\mu}{kT*}\frac{T-T*}{T-T_0} \qquad (7)$$

The eq.7 is equivalent to WLF or VFT equations.

Gibbs – DiMarzio theory

The theory is based on application of the lattice model of a polymer system to the glass transition problem. The polymer chains of degree of polymerization X have many configurations which fit onto the lattice of coordination number Z. Each chain has the lowest energy shape. Deviation of each bond from the lowest energy shape cost energy $\Delta\varepsilon$. The number of flexed out bonds is f. There are also n_0 vacant sites (holes) on the lattice. It results in additional hole energy per intermolecular bonds broken by introduction of the vacancies into the lattice (bond energy α).
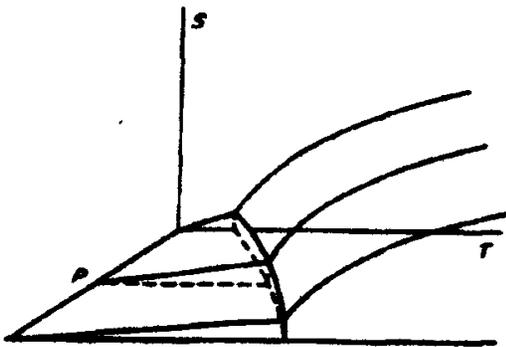

The lattice model predicts the existence of a true second-order transition at a temperature T_2. The number of allowed arrangements of the molecules decreases with decreasing T because: (i) the number of holes decreases; (ii) the configurational entropy of the molecules deceases because the chains favor low-energy states at lower T. The T(P) transition line defines the point $T_2(P)$ where the total configurational entropy first becomes 0. In that respect, the T(P) line represents the thermodynamic glass transition in experiments of long time-scale.

Gibbs DiMarzio theory gives rather complicated prediction for the molecular weight dependence of Tg [McKenna, **Compreh.Polym.Sci. 2**,311 (1989)]:

$$\frac{x}{x-3}\frac{\ln v_0}{1-v_0}+\frac{1+v_0}{1-v_0}\ln\left[\frac{(x+1)(1-v_0)}{2xv_0}+1\right]+\frac{\ln 3(x+1)}{x}=\frac{-2\dfrac{\Delta\varepsilon}{kT_g}\exp\left(-\dfrac{\Delta\varepsilon}{kT_g}\right)}{\left(1+2\exp\left(-\dfrac{\Delta\varepsilon}{kT_g}\right)\right)}-\ln\left[1+2\exp\left(-\frac{\Delta\varepsilon}{2kT_g}\right)\right] \qquad (8)$$

Here x is twice the degree of polymerization and v_0 is the volume fraction of holes, Tg is the glass transition temperature T_2. The eq.8 describes well Tg(Mn). It even describes the deviation from the Fox-Flory equation at smaller Mn.

The theory also makes an interesting prediction for ring polymers. It has been observed that Tg increases with decrease in Mn in ring PDMS. This behavior has been described qualitatively using the eq.8.
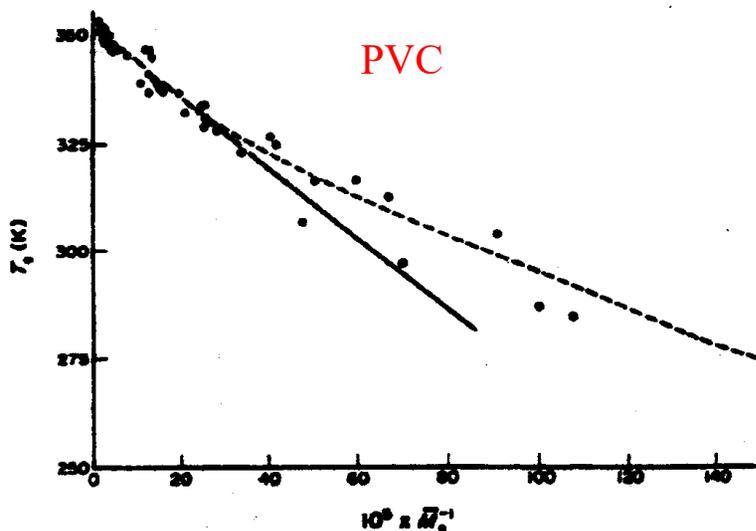
Tg vs 1/M in PVC. Solid line shows Fox-Flory relationship. The dashed lines shows Gibbs DiMarzio model predictions (eq.8) [from Pezzin, et al. **Eur.Polym.J. 6**, 1053(1970)].
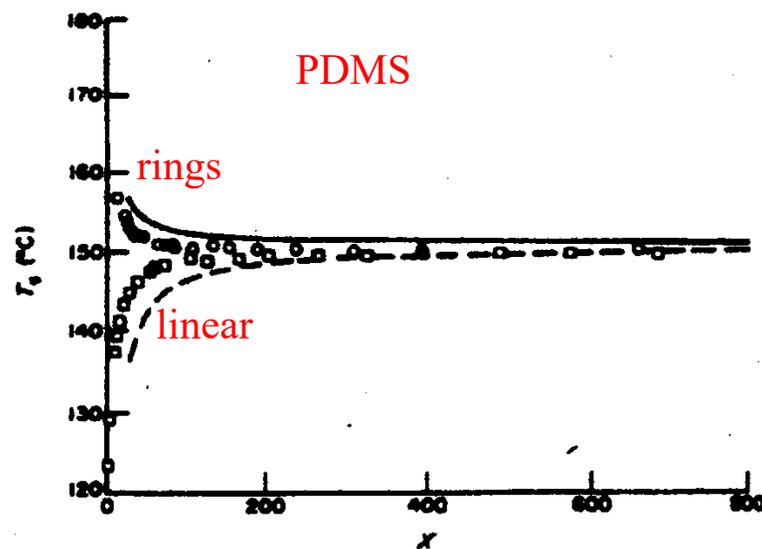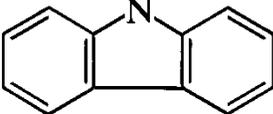
Tg in ring and linear PDMS compared to predictions of Gibbs-DiMarzio theory [from Guttman, DiMarzio, **Macromolecules**, 1988]

Influence of Molecular Structure and Architecture on Tg

Flexibility of the main-chain. Flexible group (for example, ether link) will enhance main-chain flexibility and reduce Tg. Inflexible group (for example, terephthalate) will increase Tg.
Si-O-Si is a very flexible link. As a result, PDMS has one of the lowest Tg known for polymers.

Influence of side groups. Bulky, inflexible side groups increase Tg .
Rigid and flexible side groups:

Polymer	R	Transition temperature in °C at ~1 Hz
Polypropylene	CH_3	0
Polystyrene	C_6H_5	116
Poly-N-vinylcarbazole		211

Increasing the length of flexible side groups reduces Tg, mostly due to increase in free volume.

Polymer	R_1	Transition temperature in °C at ~1 Hz
Polyvinyl n-butyl ether	$CH_2CH_2CH_2CH_3$	−32
Polyvinyl isobutyl ether	$CH_2CH(CH_3)_2$	−1
Polyvinyl t-butyl ether	$C(CH_3)_3$	+83

Configuration of the chain also plays important role:
➢Tacticity: Example of syndiotatctic vs isotactic and atactic, e.g. PMMA
➢Microstructure: Example of 1,2-PB and 1,4-PB
➢Positional isomerism: Example hhPP, or ht-PP
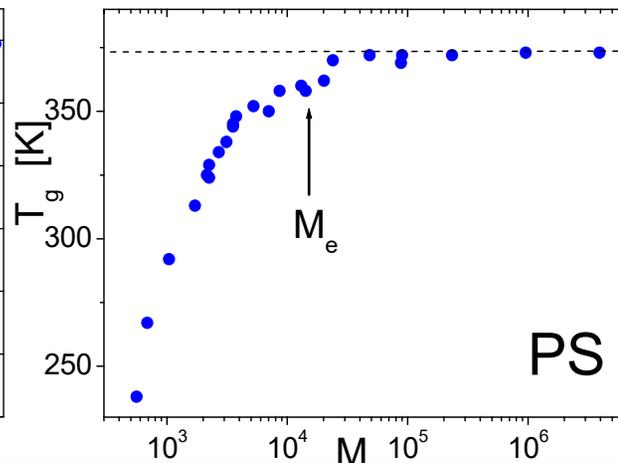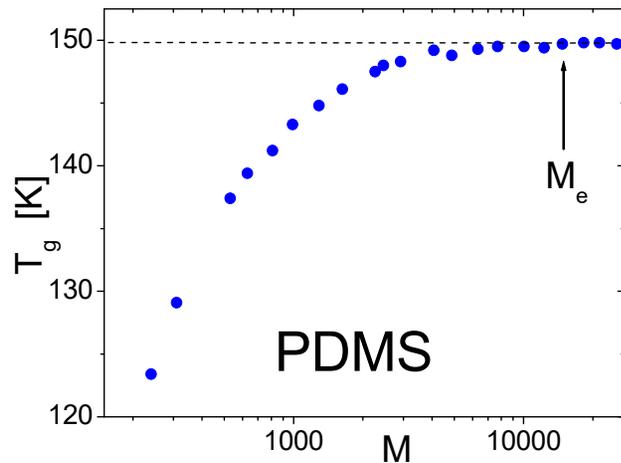
It is important to emphasize that the molecular weight dependence of Tg does not correlate with molecular weight between entanglements, M_e.

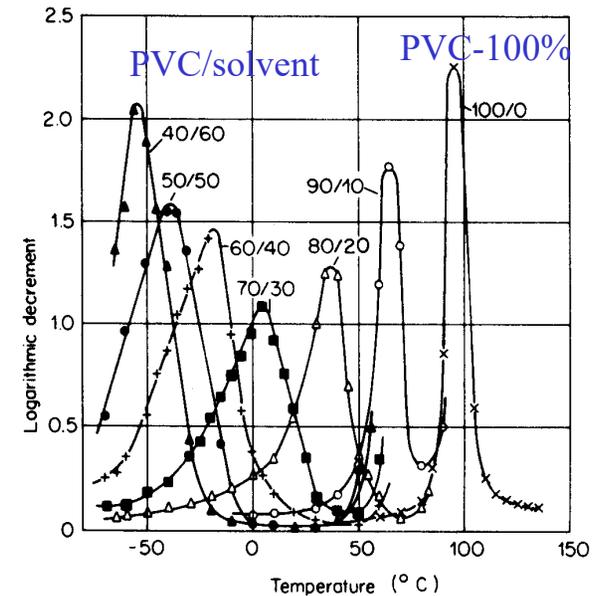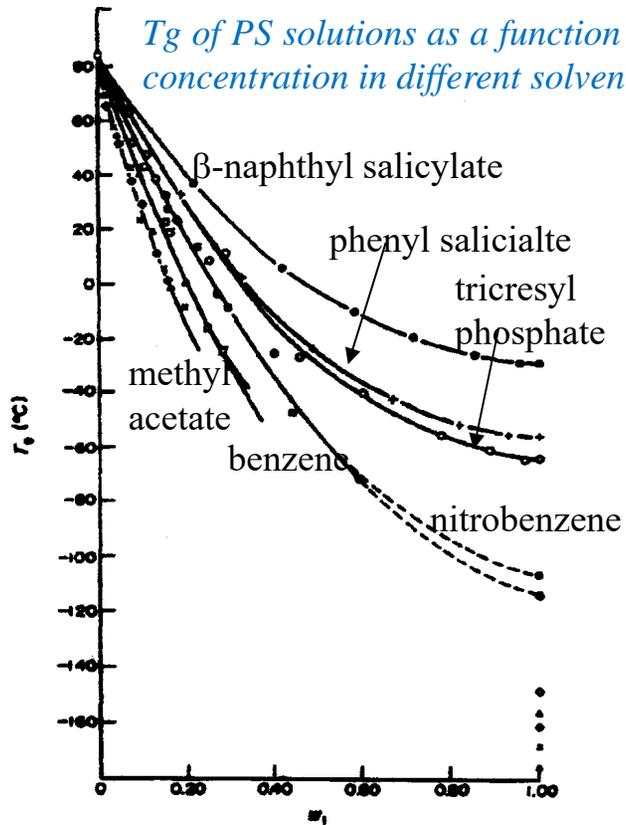PDMS and PS have similar M_e but differ strongly in the molecular weight dependence of Tg.

<u>Influence of end groups.</u> We already discussed the idea of chain-end free volume approach that explains the molecular weight dependence of Tg. We also discussed that ring polymers (no ends) have different dependence of Tg on Mn.

It is possible to change direction of the molecular weight dependence of Tg by changing end groups. The stronger are interactions of the end groups the stronger will be increase of Tg with decrease in Mn.

Dependence of Tg on chain length (x_M – number of monomers) in PFB polymer with different end groups [Danusso, et al. **Polymer 34**, 3687(1993)]: ■ - CH_2OCH_3 ; □ - $CH_2OSi(CH_3)_3$ o – CH_2OCOCF_3 ; ● - CH_2OH ; + - CH_2OK.
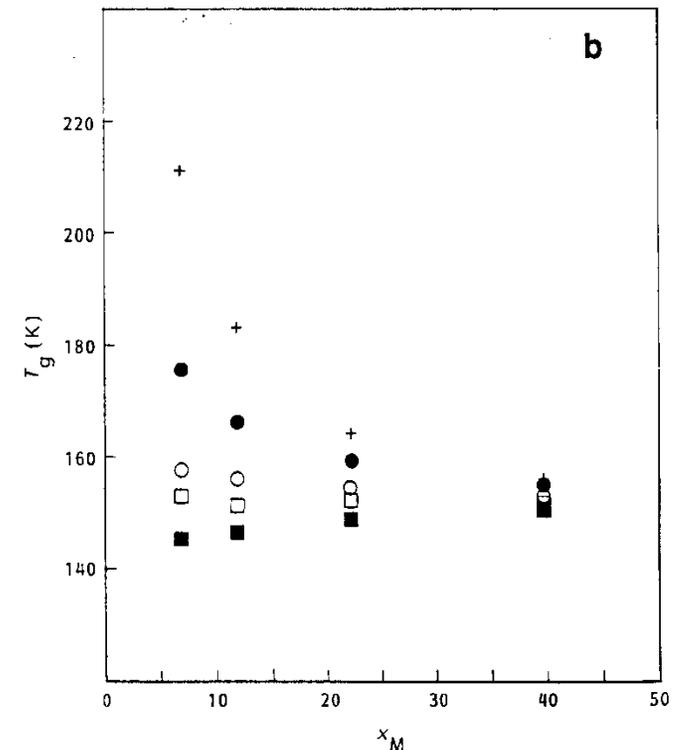
Glass transition depends strongly on composition of polymer solutions, on a solvent used. Adding a solvent to a polymer usually leads to plasticization (decrease of Tg). The figure shows PVC plasticized with various amounts of di(ethylhexyl)phthalate.

Tg of PS solutions as a function of solvent concentration in different solvents.

β-naphthyl salicylate

phenyl salicialte

tricresyl phosphate

methyl acetate

benzene

nitrobenzene

Tg varies non-linear with concentration of solvents. One of the explanation is based on the free-volume approach. Fractional free volume of the solvent f_s is higher than that of the polymer f_p (solvent has lower Tg). Assuming that the fractional free volumes are not additive, the total fractional free volume:

$$f = v_s f_s + v_p f_p + k_v v_s v_p \qquad (11)$$

Here v_s and v_p are volume fractions, k is a negative constant $\sim 10^{-2}$. Eq.11 assumes that occupied volumes are additive and that agrees with measurements of density. Assuming iso-free-volume state at Tg the following dependence is predicted [McKenna]:

$$T_g(v_s) = \frac{v_s \alpha_s T_{gs} + v_p \alpha_p T_{gp} + k_v v_s v_p}{v_s \alpha_s + v_p \alpha_p} \qquad (12)$$

Here α is the thermal expansion coefficient of the fractional free volume. The eq.12 describes the data well with reasonable parameters.

Free volume ideas were also used for description of Tg in co-polymers [Gordon, Taylor, **J.Appl.Chem. 2**, 493 (1952)]:

The simplest approximation, although not the most accurate, is the Fox equation for Tg of random copolymers:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

(13)

Here w_1 and w_2 are weight fraction of the copolymers 1 and 2, respectively.
It is based on considering entropy of the mixtures, and particular assumptions on changes at Tg of the copolymer.
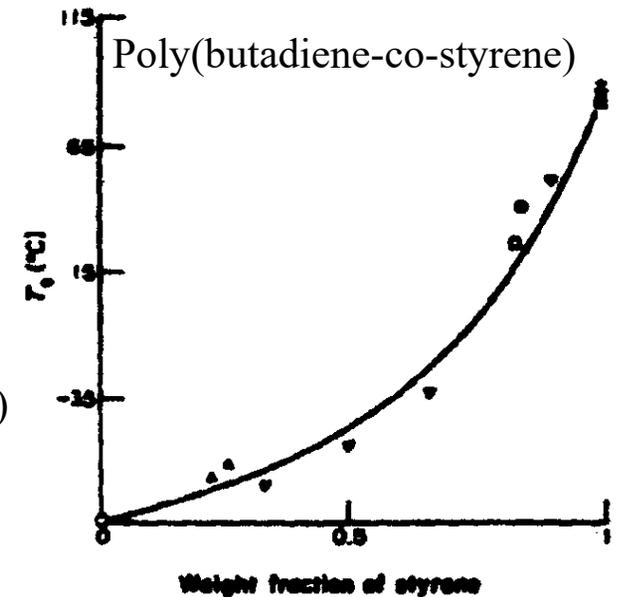
In the case of polymer blends there are two situations:

Immiscible blends show separate Tg for each of the components (2 Tg's for binary blends). Example of shear modulus and logarithmic decrement in blend of PS and styrene-butadiene co-polymer.
Separated Tg's will be observed also in block co-polymers of immiscible blocks.

Poly(butadiene-co-styrene)
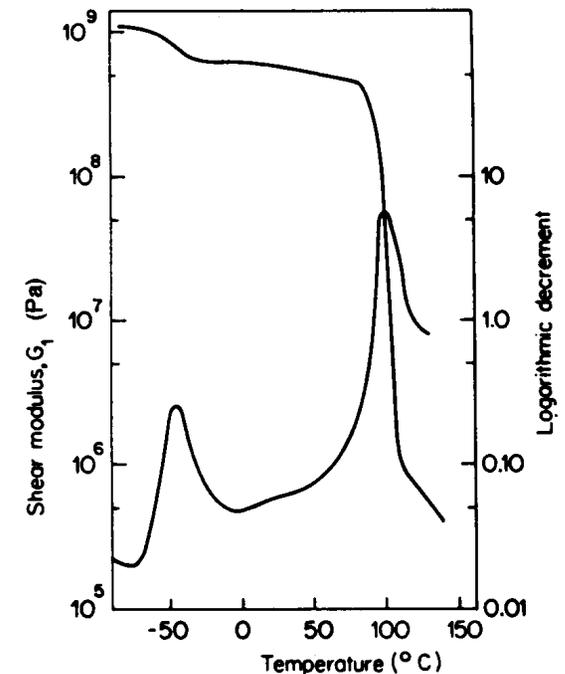
A single Tg appears in DSC of miscible blends. It appears in between Tg's of the mixed components and the transition broadens. However, each component has its own relaxation time, and τ of the fast component slows down less than τ of the slow component speeds up. One can analyze it as Tg^{eff}.
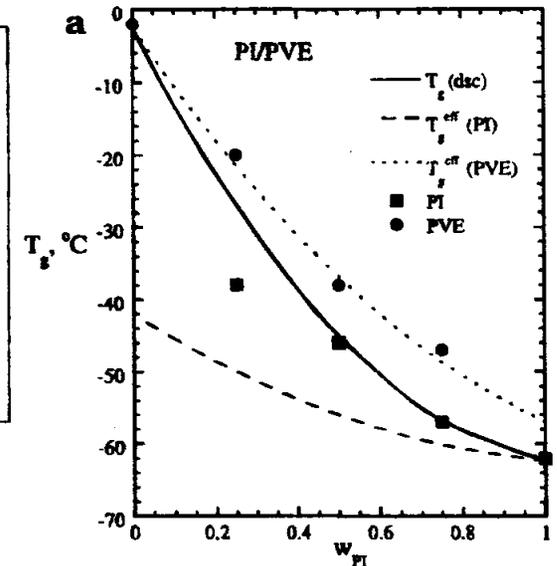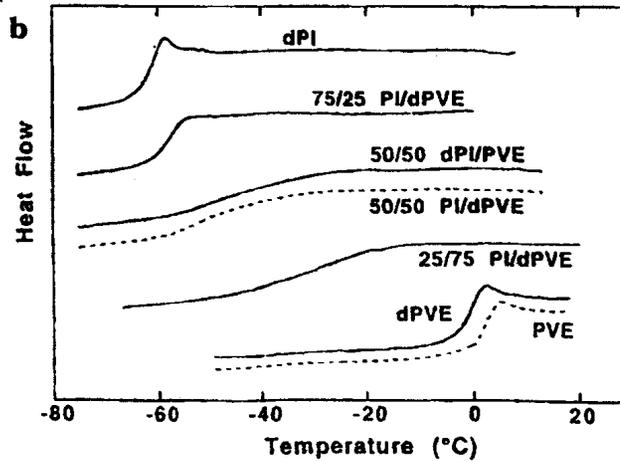

There are a few models proposed for the description of Tg in miscible polymer blends. One of the ideas was proposed by Lodge and McLeish [**Macromolecules 33**, 5278 (2000)], and takes into account effective concentration of monomers A and B around a typical monomer A: $\phi_{eff} = \phi_S + (1-\phi_S)\phi$

Where ϕ is the volume fraction of A component and ϕ_S is the "self-concentration" term:

$$\phi_S = \frac{C_\infty m_0}{n_0 \rho N_A V} \qquad (14)$$

Here m_0 is mass of a monomer, n_0 is the number of backbone bonds per monomer, ρ is the density, V is a volume that influences the relaxation of a monomer. It is assumed to be V~l_K^3 (l_K is the Kuhn length).The main idea is that the monomer A experience higher concentration of A because of its connectivity. As a result, you have a distribution of ϕ_{eff}. The model explains many characteristic properties of relaxation and Tg in miscible blends, even gives good quantitative predictions for some systems. However, it fails for some other systems.
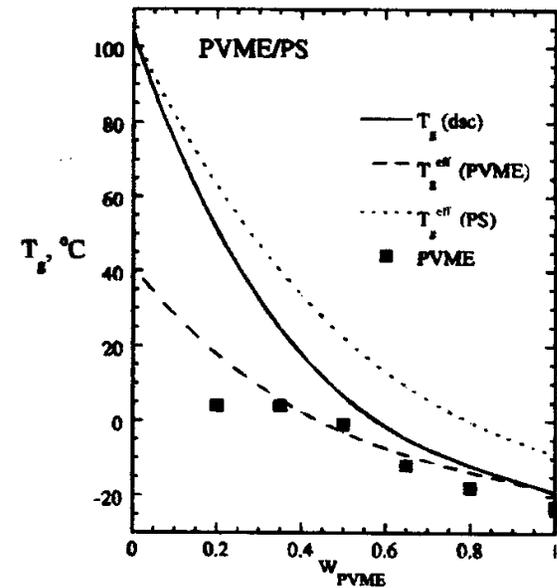
<u>Glass transition in thin polymer films:</u> Developments in nano science and nano technology leads to decrease of characteristic size of elements. Qualitative difference appears when we approach length scales ~5-50 nm.

One example of that is variation of Tg in thin polymer films [review by Forrest, Dalnoki-Veress, **Adv.Coll.Interf.Sci. 94**, 167 (2001)]. It has been observed that Tg of polymer films drops with decrease in film thickness h. The best polymer analyzed is PS. Various techniques show drop of Tg ~30-50K when h ~10 nm. Drop of Tg depends on substrate, suggesting importance of a polymer-substrate interactions. In particular, it has been shown that for polymer physically grafted to substrate Tg can increase with decrease in h.

Another example: PMMA on Au -> Tg decreases with decrease in h, while PMMA on SiO_2 -> Tg increases with decrease in h.
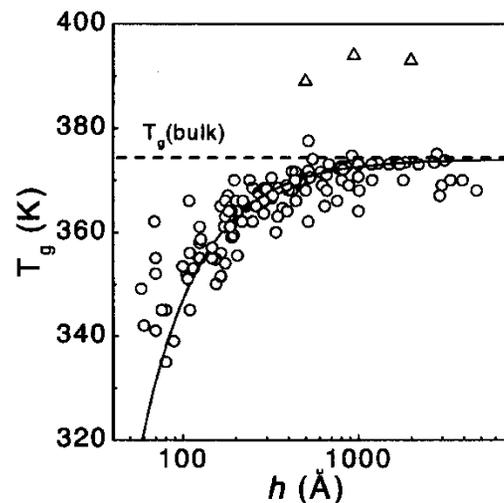
Tg in thin PS films as a function of thickness h.
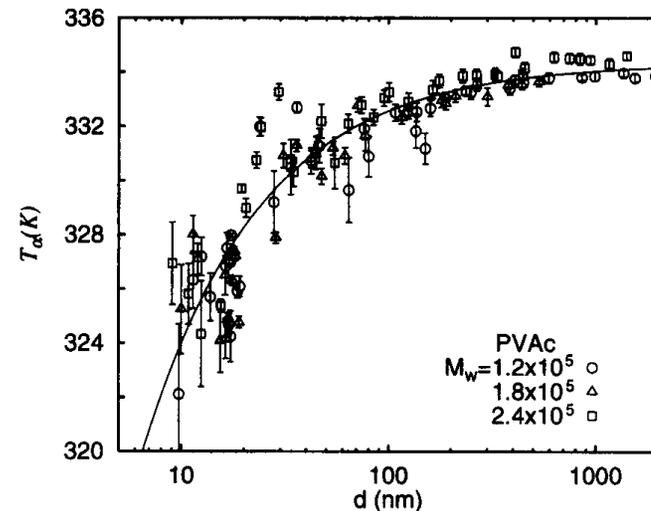
Tg in thin PVAc films [Fukao, et al., **J.Non.Cryst.Sol. 307-310,** 517 (2002)].

No significant dependence of the effect on Mw has been observed in thin supported films. Tg(h) is usually described by an equation:

$$T_g(h) = T_g^{bulk}\left[1 - \left(\frac{a}{h}\right)^{\delta}\right]$$

Even stronger effect has been reported for thin free standing films (no substrate). In that case, strong dependence of the effect on molecular weight has been observed. There are two regimes: lower M_w (for PS~120,000 – 370,000), and higher M_w (>370,000).

Effect at lower M_w is similar to the effect in supported films but is ~2 time stronger.

Much stronger dependence appears at higher M_w, it starts to deviate from the bulk behavior at h~R_{EE} (end-to-end distance).
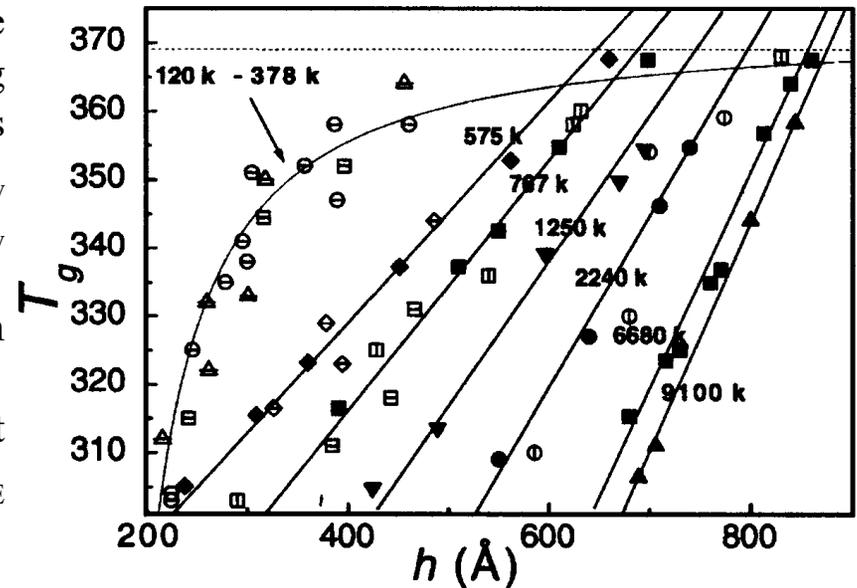
Traditional picture for these variations is related to a surface layer that is assumed to have higher mobility than the bulk polymer. Of course, if it interacts strongly with a substrate, it might have lower mobility. The thickness of the layer might be different for different polymers and for PS is estimated to be ~3.5-4 nm. Decreasing the thickness of the film enhances the influence of the layer on the film properties.
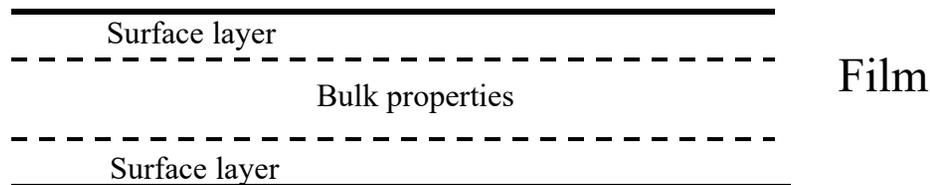
This idea explains why the effect appears to be stronger in free-standing films. There are many microscopic models that try to explain details of the effect, in particular, for free-standing films with high Mw polymers. However, no one of them can describe all the data consistently.

Concluding remarks

1. Spectral shape of segmental relaxation is always stretched (non-exponential). Stretching of the relaxation spectrum is a characteristic feature for relaxations in complex systems. The mechanism of the stretching (dynamic heterogeneity or intrinsically non-exponential process) remains unclear, although there are many indications of heterogeneous dynamics at time scale shorter than segmental relaxation time.

2. Segmental relaxation exhibits non-Arrhenius temperature dependence that is usually approximated by WLF or VFT equations. Steepness of temperature dependence of segmental dynamics (fragility) depends on chain rigidity.

3. Glass transition in polymers is "freezing" of segmental relaxation. Tg is an ill-defined quantity. It corresponds to the temperature at which segmental relaxation time becomes comparable to the laboratory time scale (cooling rate).

4. Microscopic mechanism of the glass transition remains a topic of active research. It seems that different mechanisms dominate at different temperature ranges.

5. Chemical structure, chain length and architecture of macromolecules affect their glass transition temperature.

6. Confinement effect leads to variation of Tg in thin polymer films. Detailed microscopic mechanism of these variations remains unclear.