3.2

The Amorphous State

Glasses

- **reversible response to small deformation** (no permanent stresses during a shear strain - unlike a liquid)
- **no long-range organisation**
- **high viscosity:** $\eta > 10^{11} \ Pa \ s$ (traditional definition)

coal (amorphous carbon)

silicate glasses

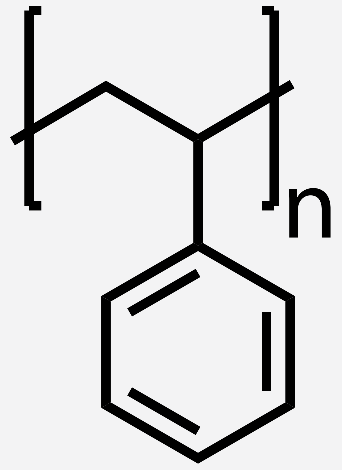
caramel

polymers

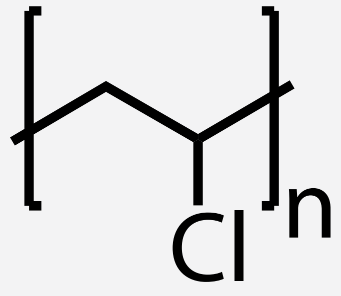
- **a glass is an amorphous and rigid solid; polymer glasses are often transparent.**

Amorphous, Glassy Polymers

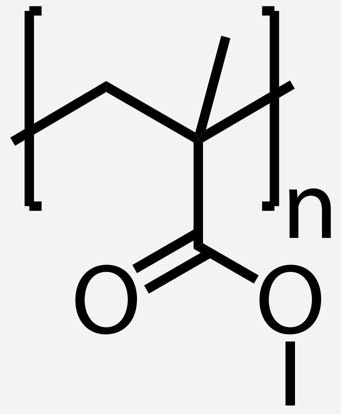
atactic polymers



PS

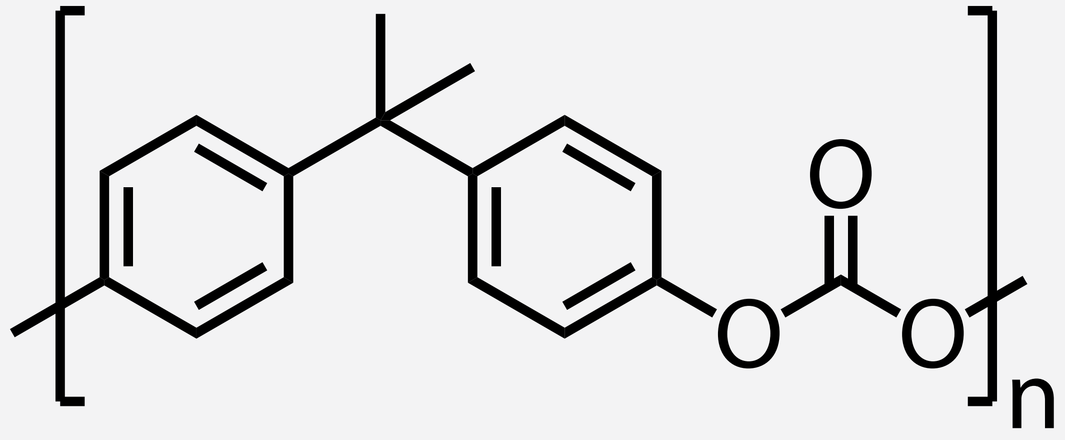


PVC

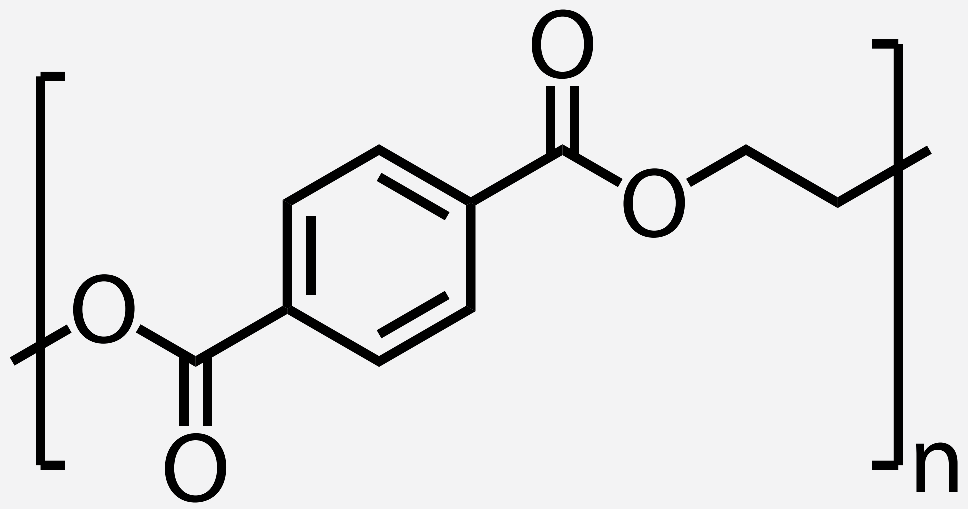


PMMA

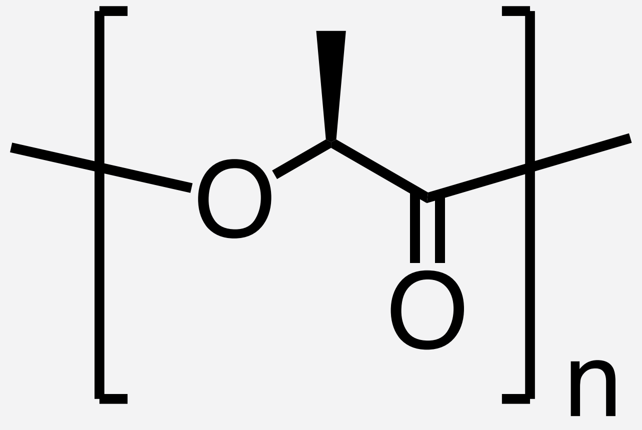
very slow crystallization



polycarbonate

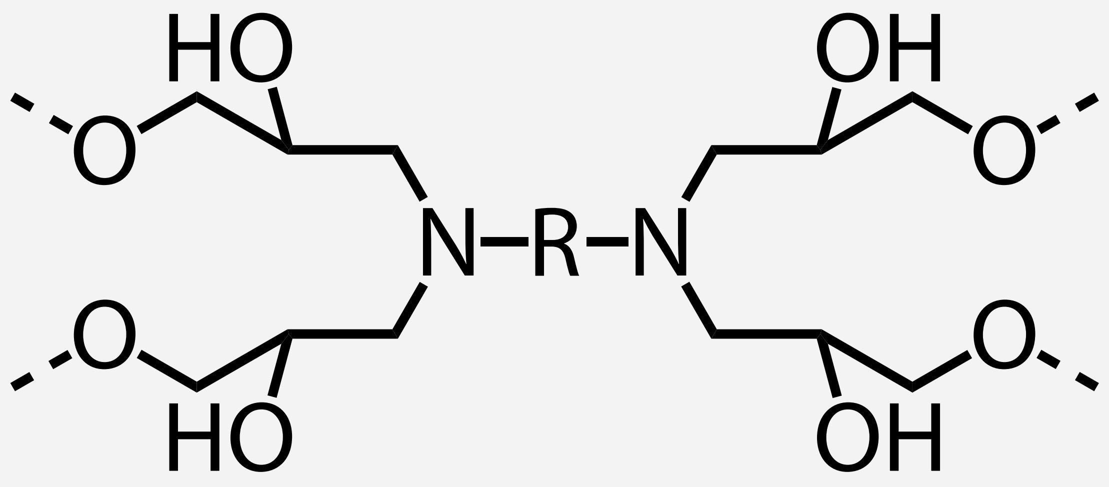


PET



PLLA

high cross-link density

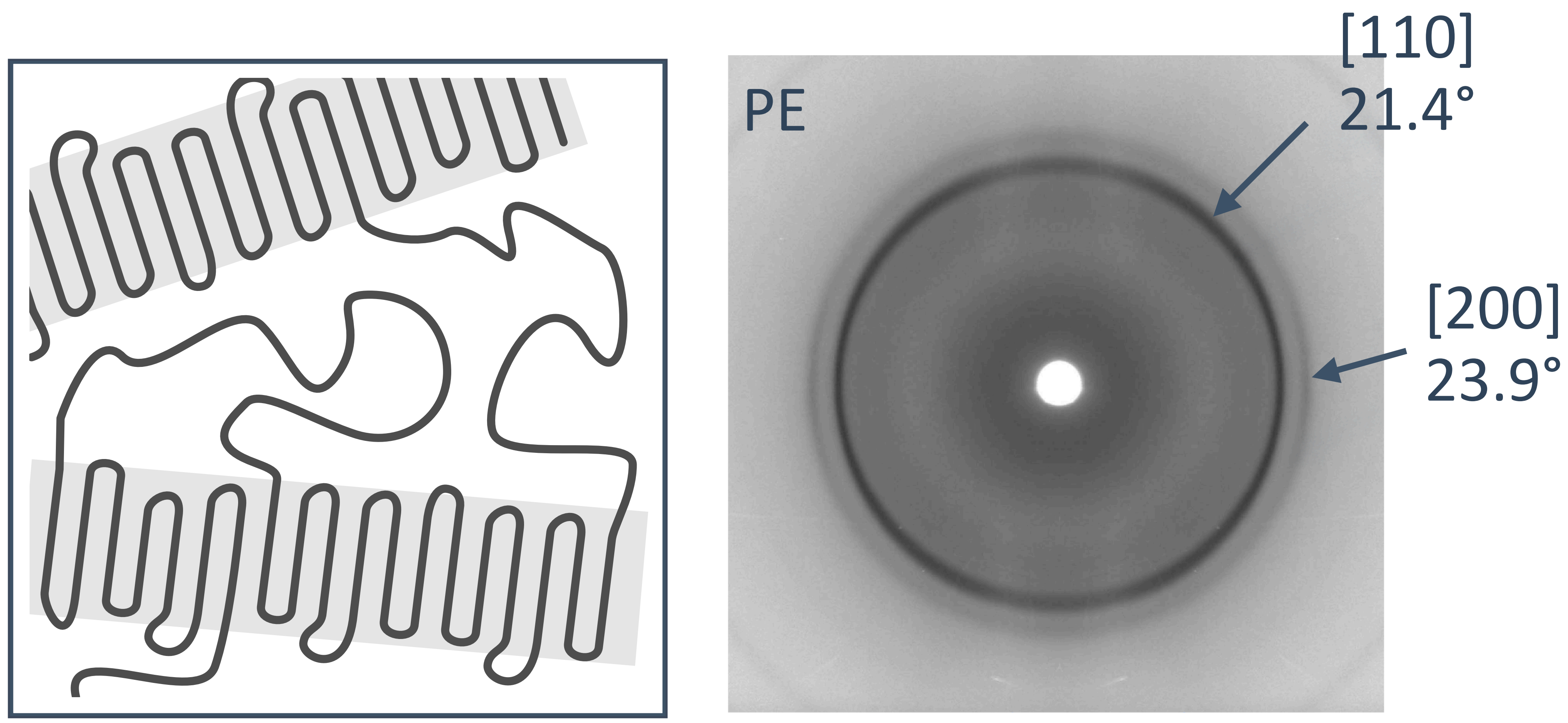


…plus various thermosets (e.g. epoxides)

The Amorphous State

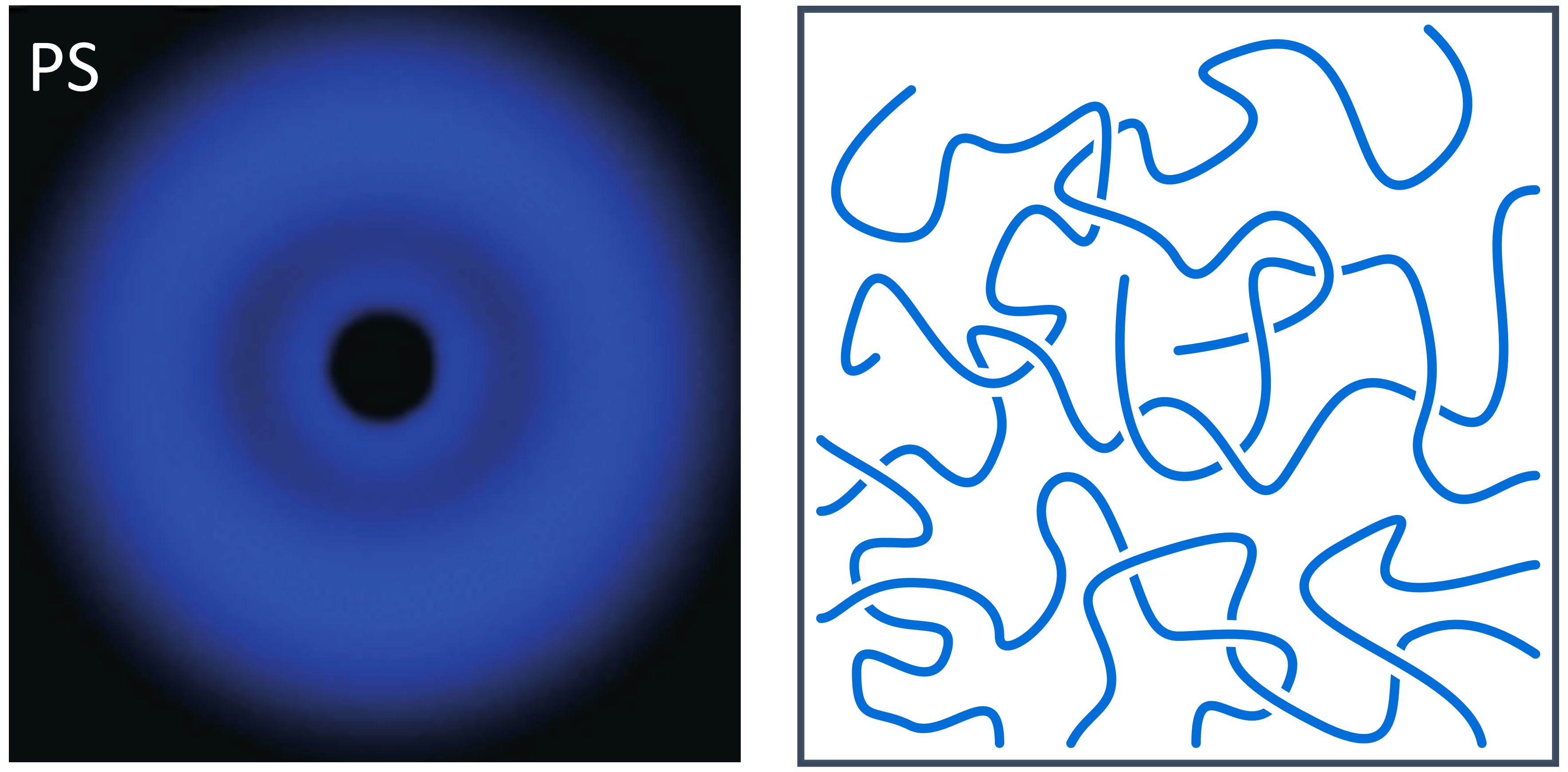
- **random distribution of polymer chains in the matrix (no ordered structures)**
- **diffuse intra- and interchain peaks in X-ray diffraction patterns**

crystalline (sharp peaks)



(unoriented sample)

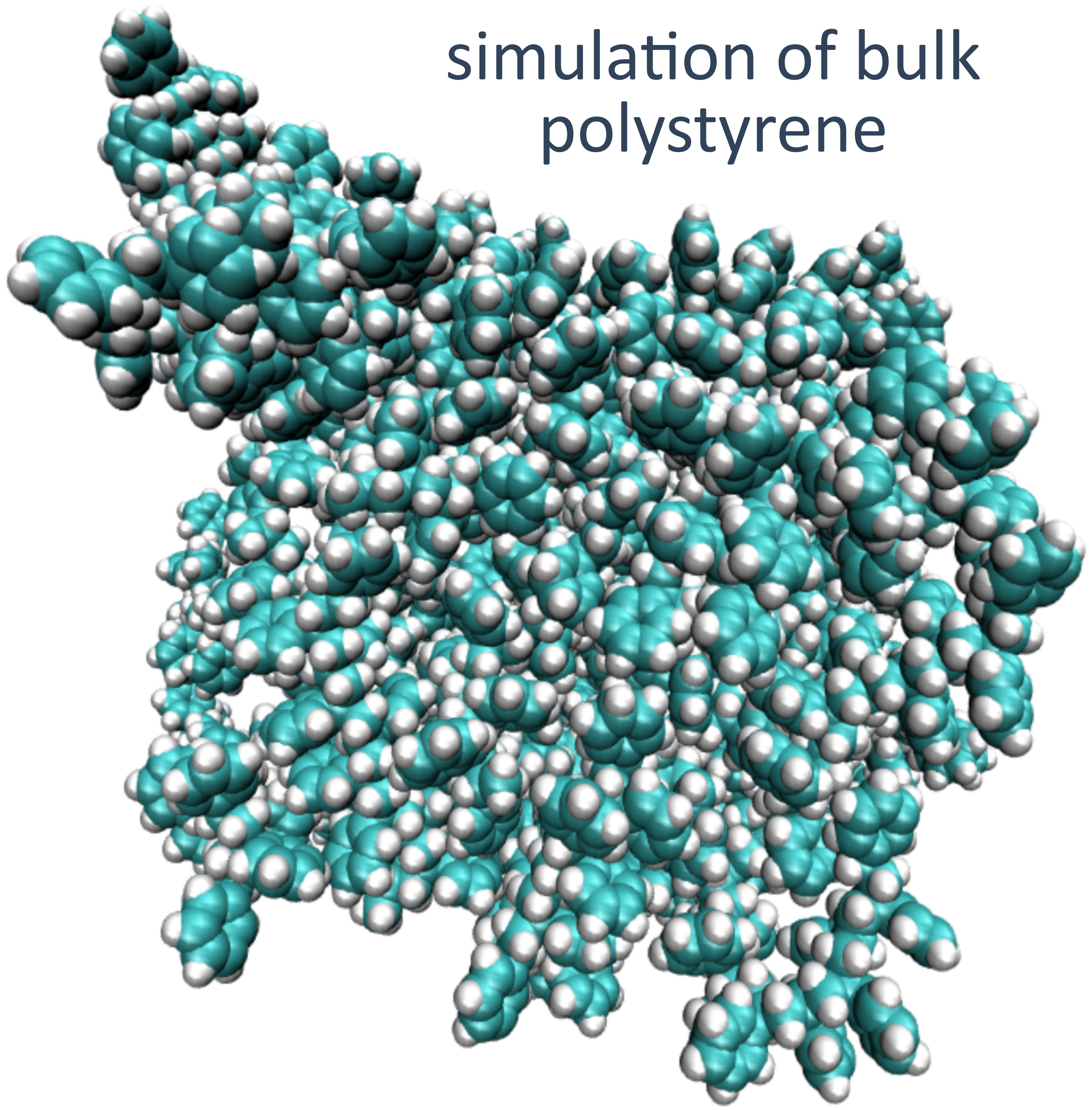
amorphous (blurry peaks)



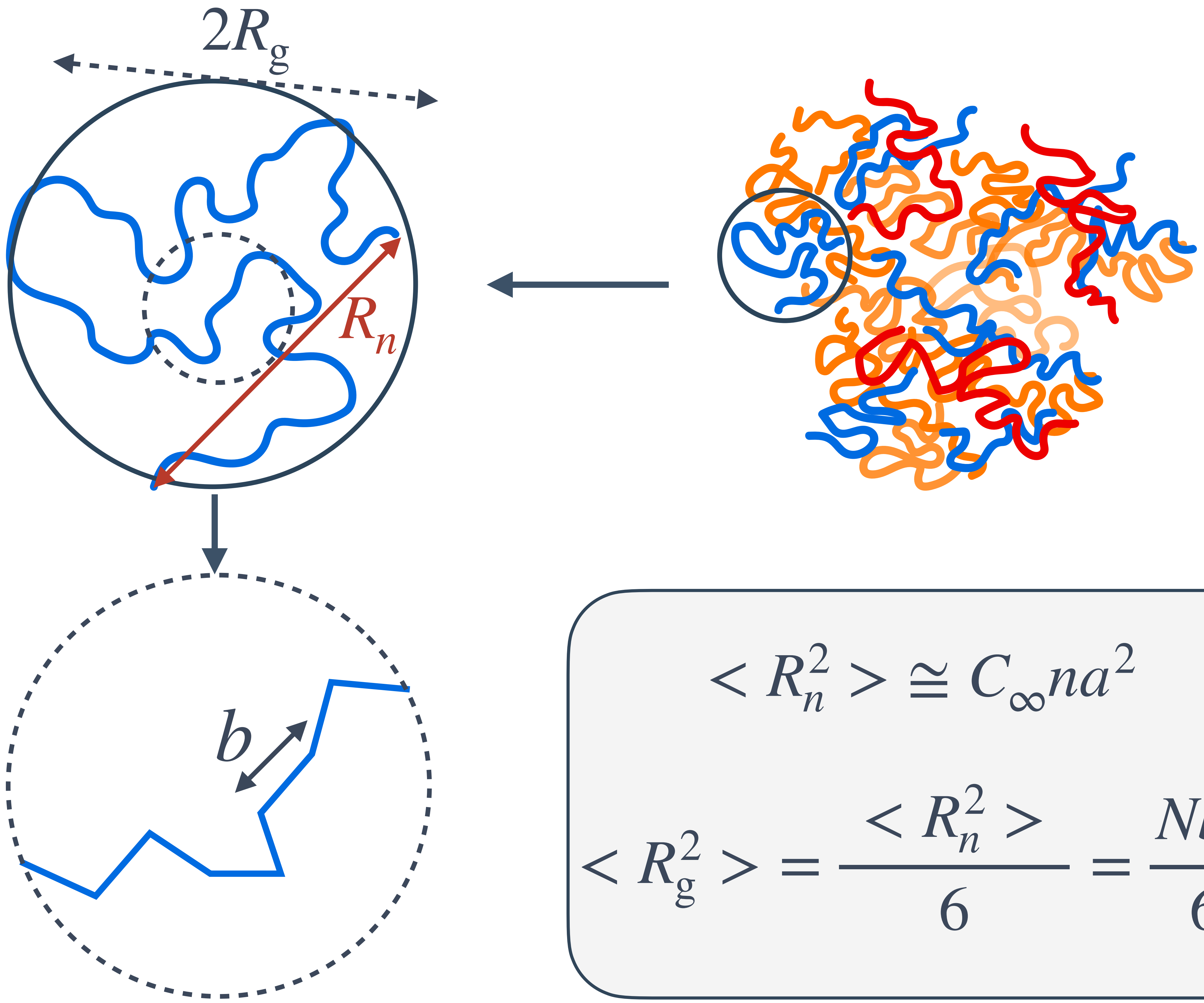
(unoriented sample)

- **local order amorphous polymers does not exceed 1-2 nm in the molten state**
  (ample evidence from wide angle X-ray diffraction, light scattering, Brillouin scattering, Raman spectroscopy, …)

Conformations in the Amorphous State



simulation of bulk polystyrene



$$< R_n^2 > \cong C_\infty n a^2$$

$$< R_g^2 > = \frac{< R_n^2 >}{6} = \frac{Nb^2}{6}$$

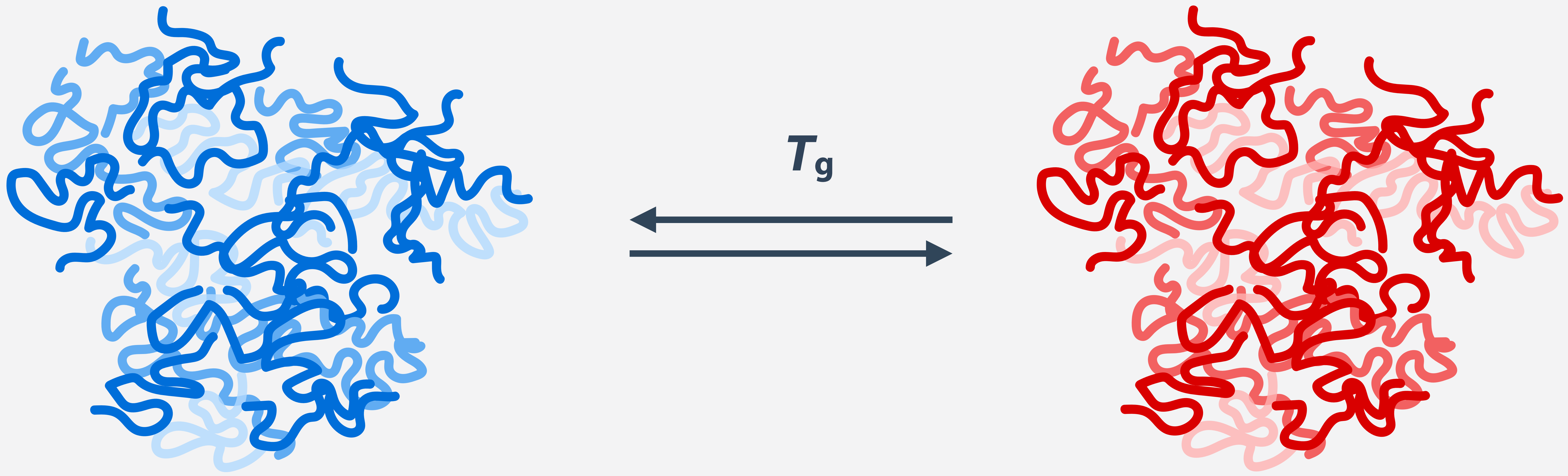
- **chains adopt “random coil” conformation of an ideal isolated chain, if chain mobility is sufficiently high**
  (experimental evidence from neutron scattering and numerical simulations)

The Glass Transition Temperature

- ***T_g*: the temperature below which the conformations stop changing (on a large scale)**
- conformations in the glassy state are “frozen” ideal chain conformations of the molten state

glassy state

rubbery or melt state



frozen conformations

rigid solid

rapid conformational changes

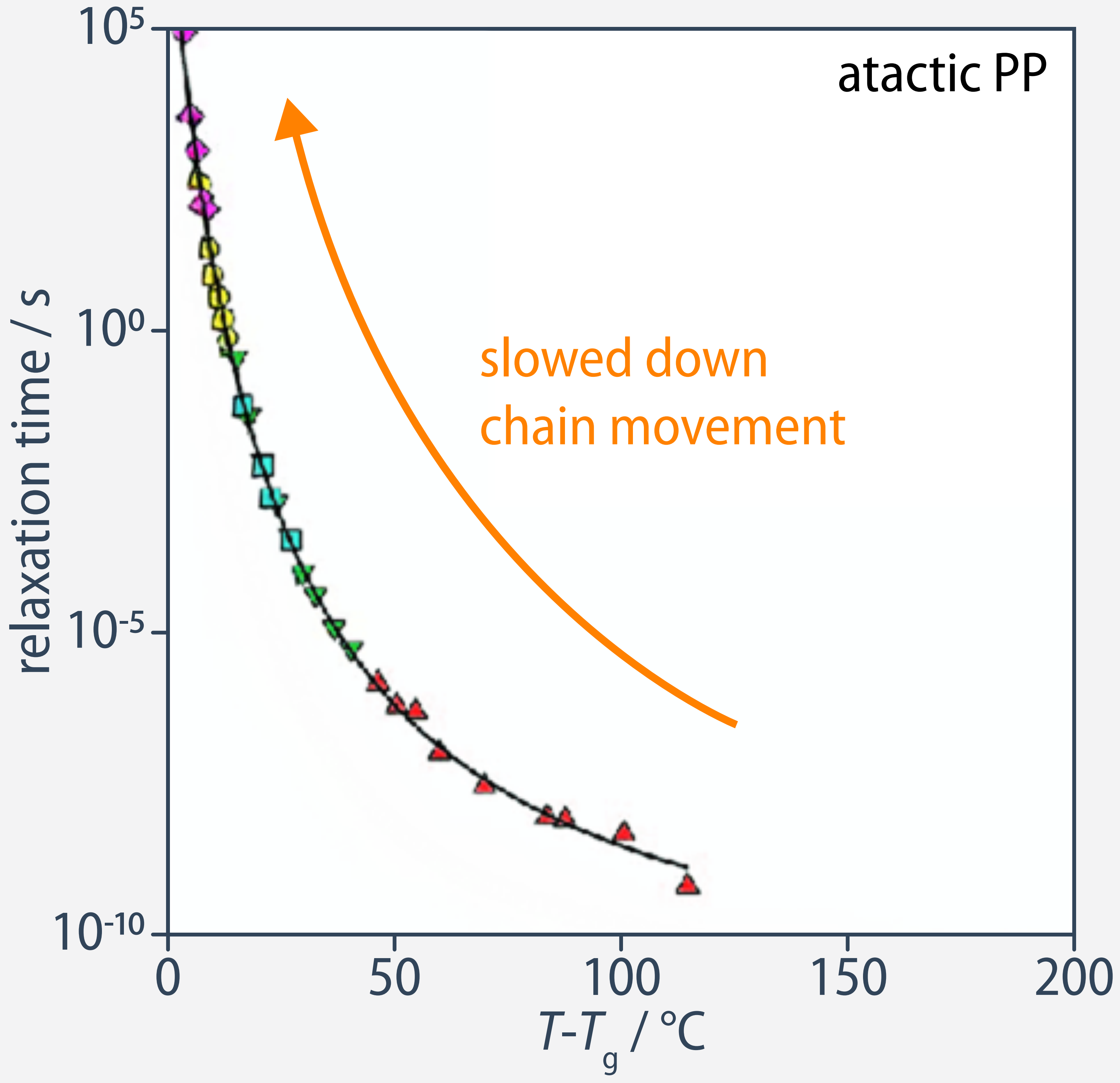
dynamic, mobile, fluidic

- **measuring techniques probing mobility changes:** thermal expansion, heat flow, specific volume, …)

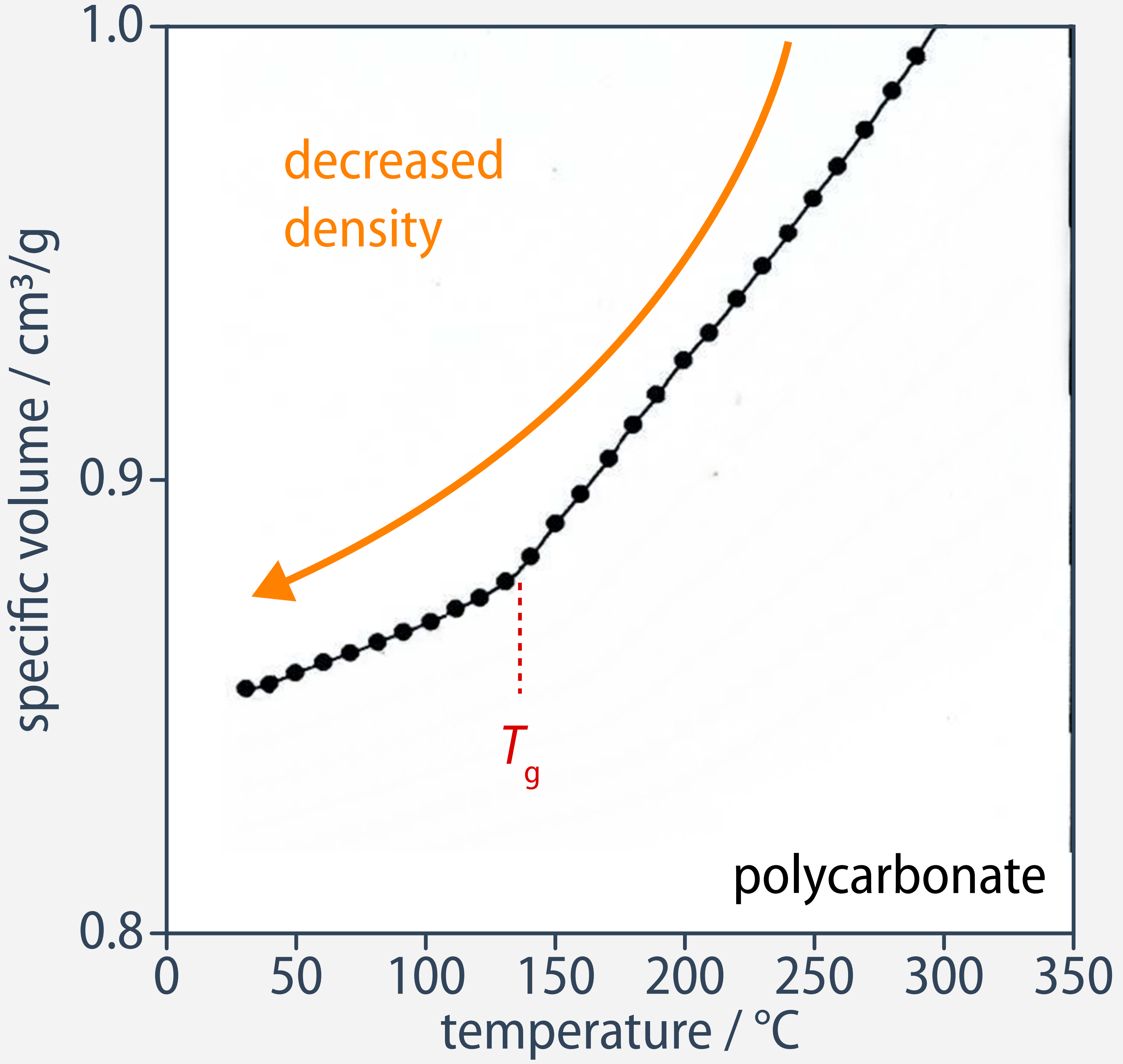
Measurement Speed

- **polymers respond to temperature changes via chain relaxations and specific volume changes**

polymer chain relaxation



specific volume



measurement speed

cooling rate: $\Theta = \frac{\mathrm{d}T}{\mathrm{d}t}$

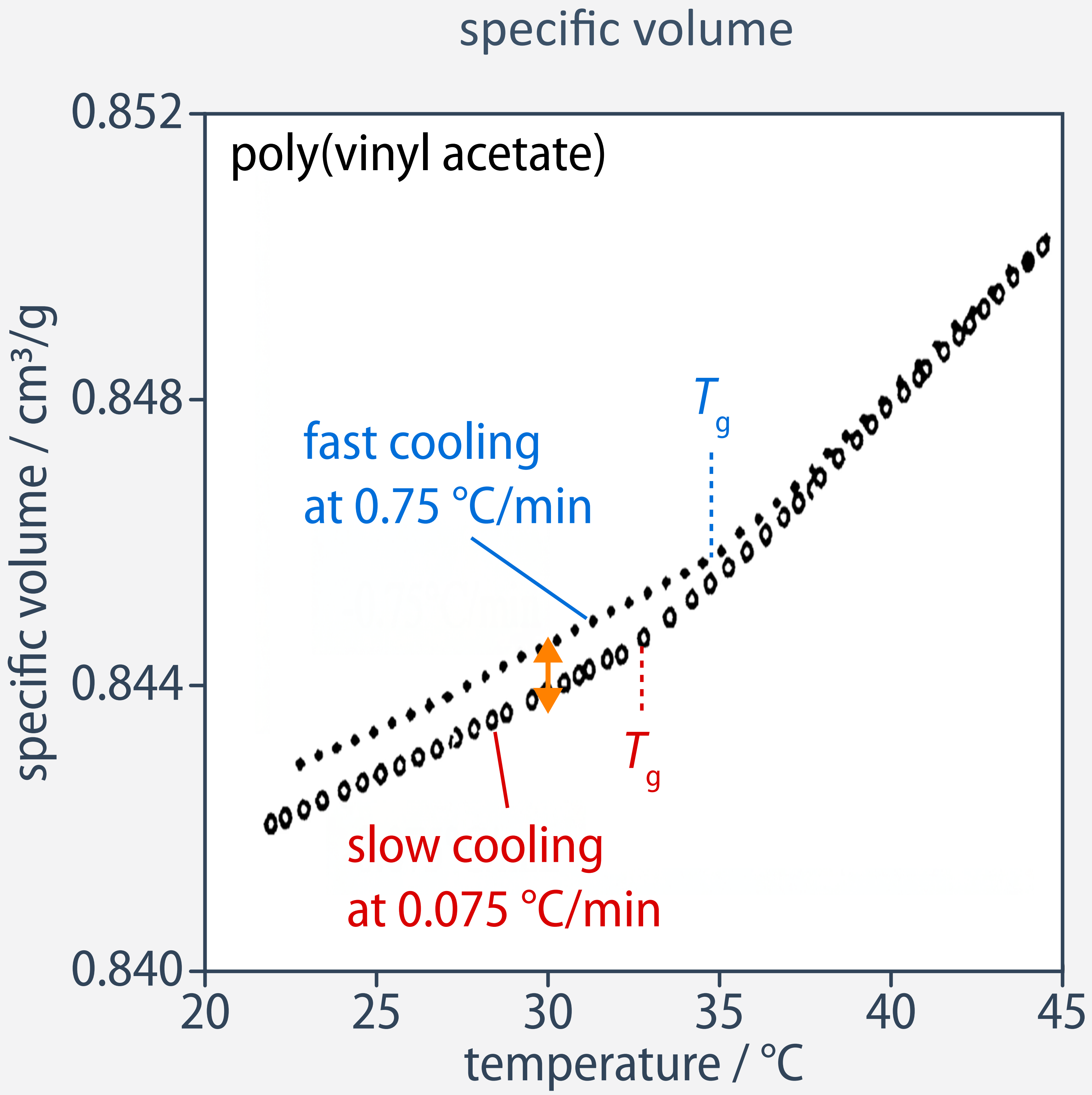
observation time: $\Delta t = \frac{T_1 - T_2}{\Theta}$

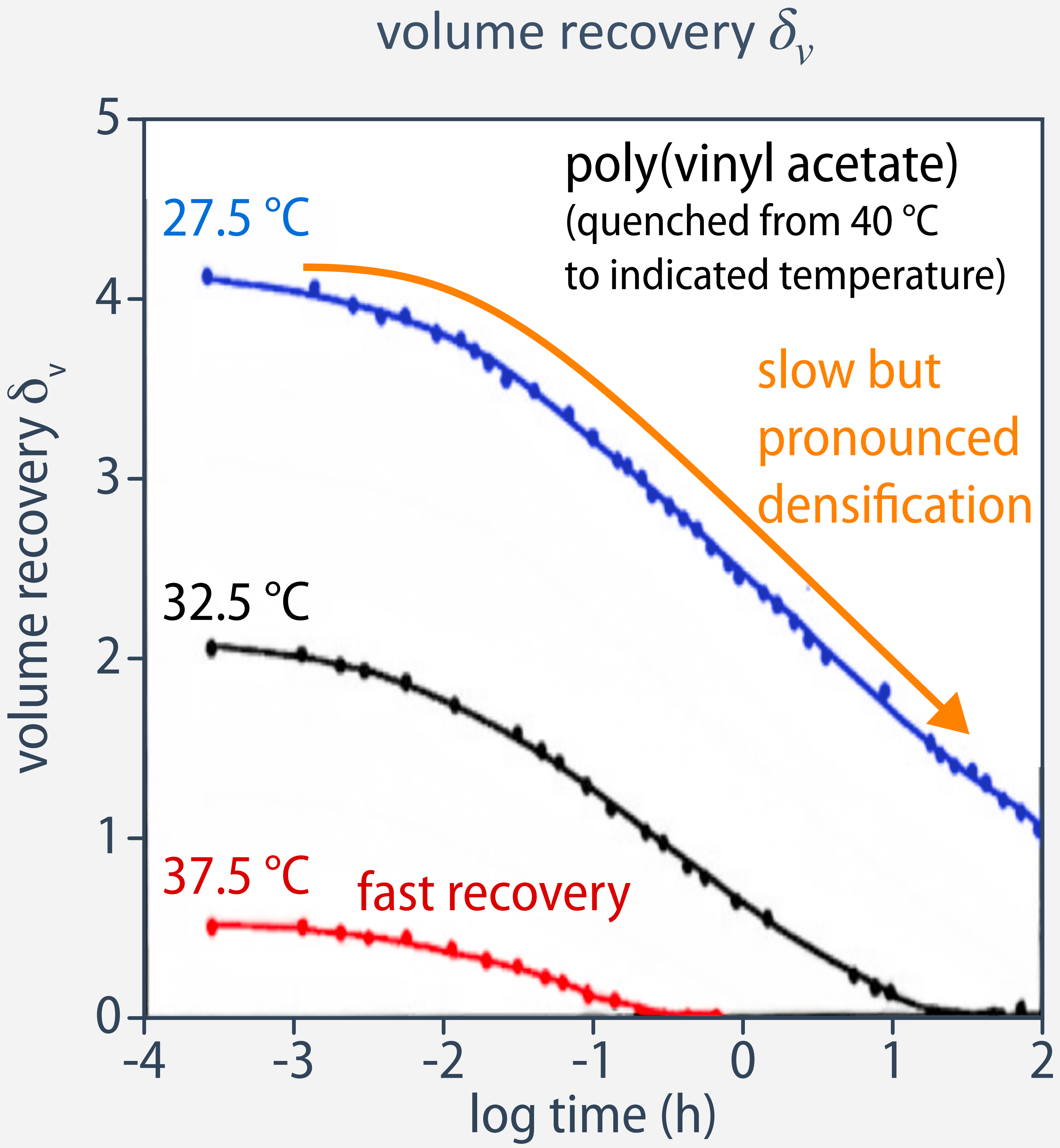
glass transition: $\tau(T) \approx \Delta t$

- **near T_g, slowed down relaxations lag behind the experimental time scale set by the scanning rate**

Physical Ageing

- isothermal volume (or enthalpy) recovery towards equilibrium on long timescales





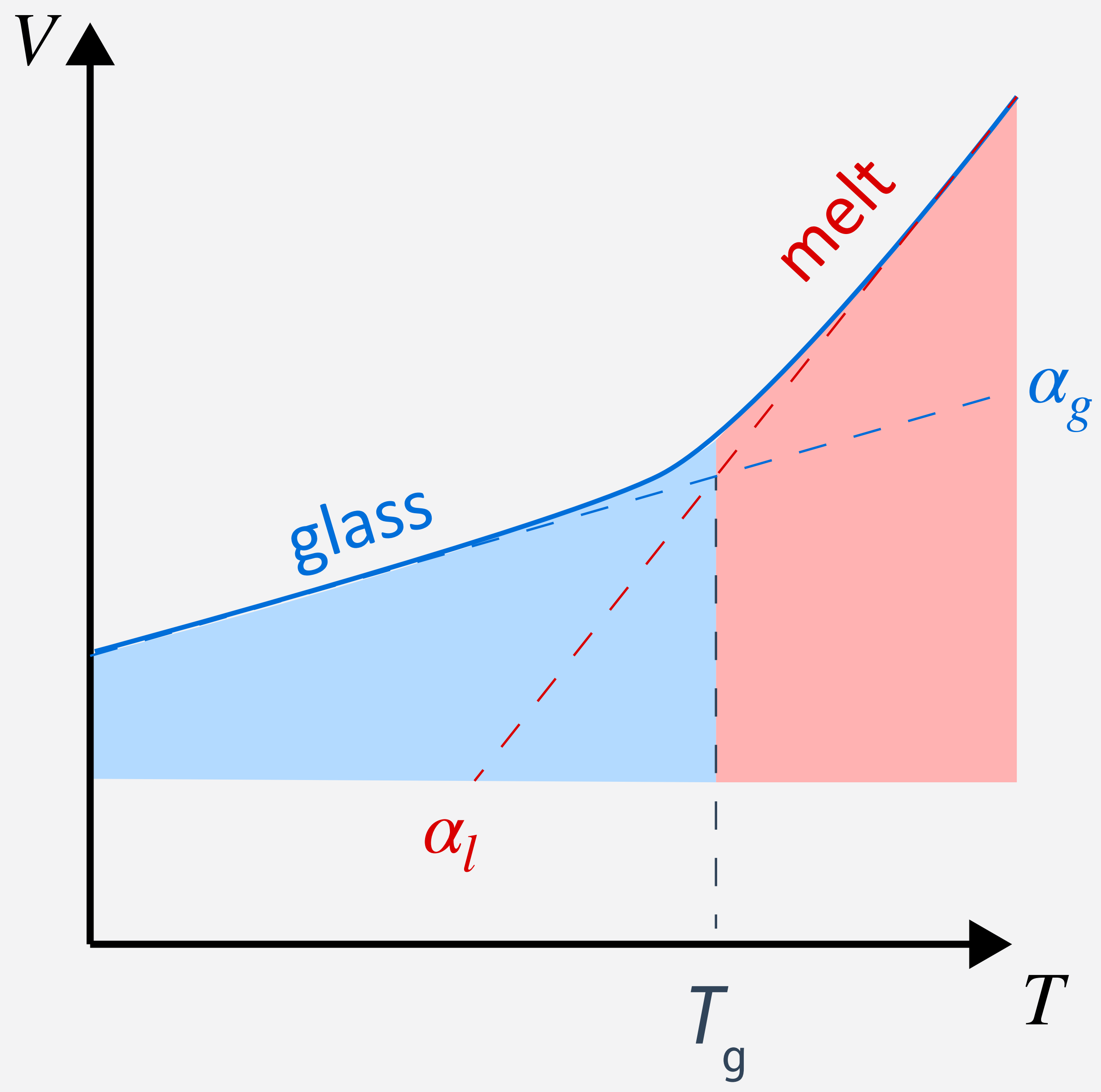
- **physical ageing as a demonstration of the out-of-equilibrium nature of the glassy state**

The Out-of-Equilibrium Nature of the Glassy State

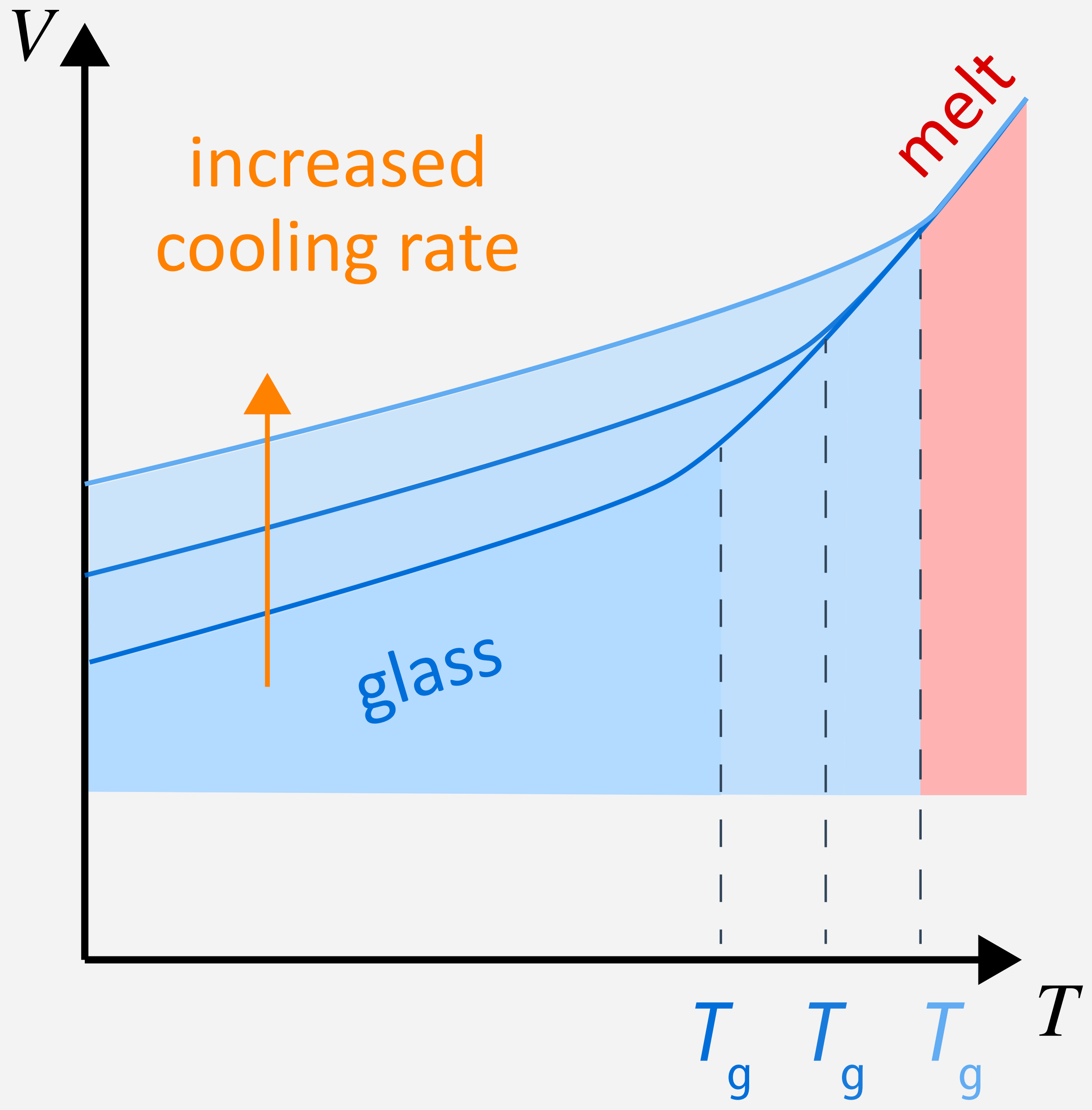
- **at T_g, sudden change in thermal expansion coefficient, α, upon cooling from the melt state**

  (measured via a dilatometer)

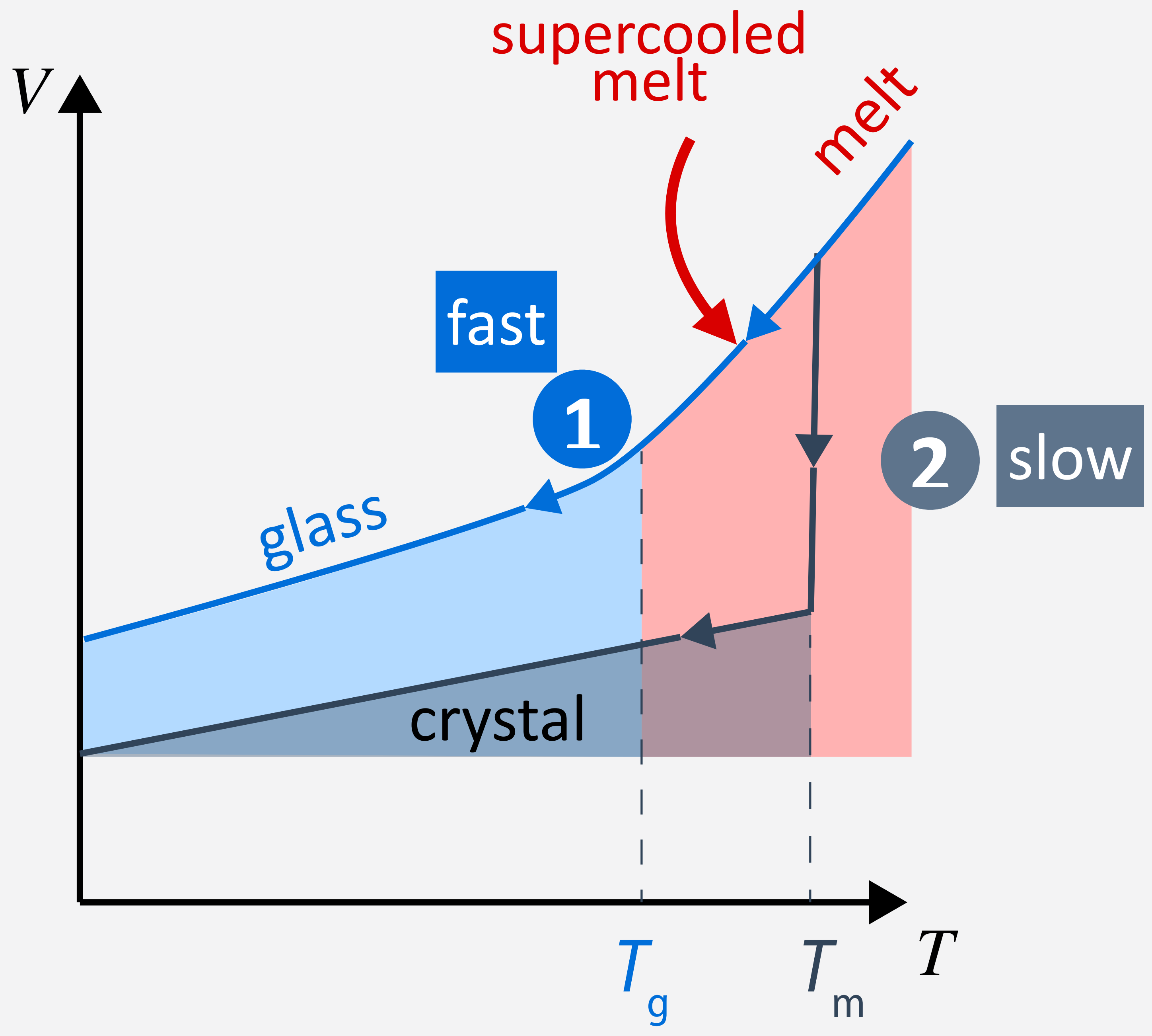
differences in α



cooling rate dependence



suppressed crystallization



- **T_g decreases with slower cooling rate (more time for chain relaxation per ΔT)**
- **T_g does not reflect thermodynamic equilibrium! The glassy state is inherently out-of-equilibrium!**

Effect of Measurement Speed

- **T_g depends strongly on measurement method and timescale**

  different standard conditions → different reported values

example: polystyrene

measurement Type	condition (rate)	T_g °C
electrical tests	1000 Hz	121
mechanical characterization	100 Hz	104
DSC	10 °C/min	100
dilatation (cooling)	2 °C/min	96
dilatation (cooling)	7×10^{-4} °C/min	82

- **T_g is a *fictive temperature*, not a fundamental thermodynamic property**

1st vs. 2nd Order Thermodynamic Transitions

$$\boxed{\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T}$$

1st partial derivatives of G:

$$V = \left(\frac{\partial G}{\partial p}\right)_T \qquad -S = \left(\frac{\partial G}{\partial T}\right)_p$$

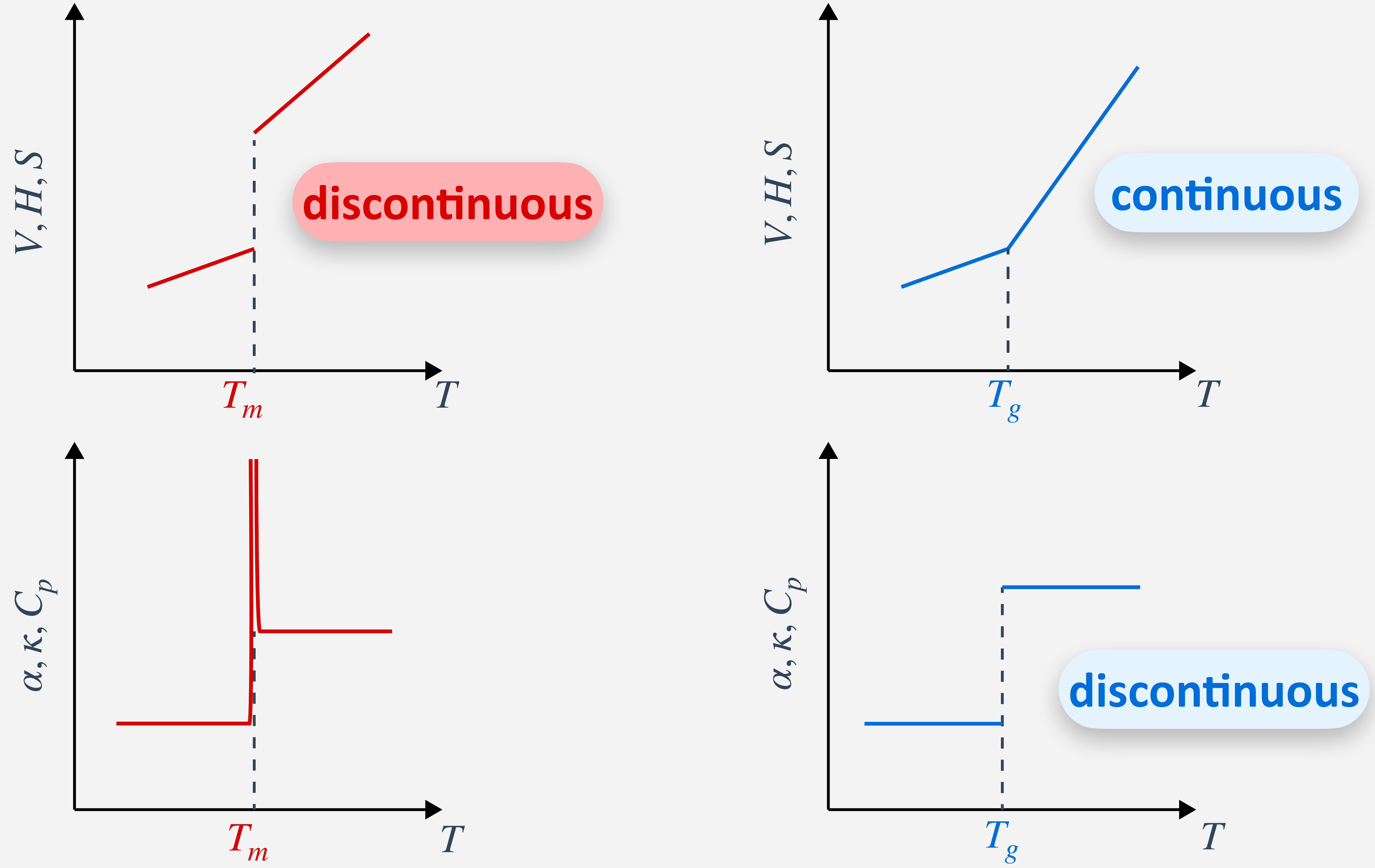
2nd partial derivatives of G:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right) = \frac{1}{V}\left(\frac{\partial^2 G}{\partial T \partial p}\right)$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right) = -T\left(\frac{\partial^2 G}{\partial T^2}\right)$$

1st order transition
(polymer crystallisation)

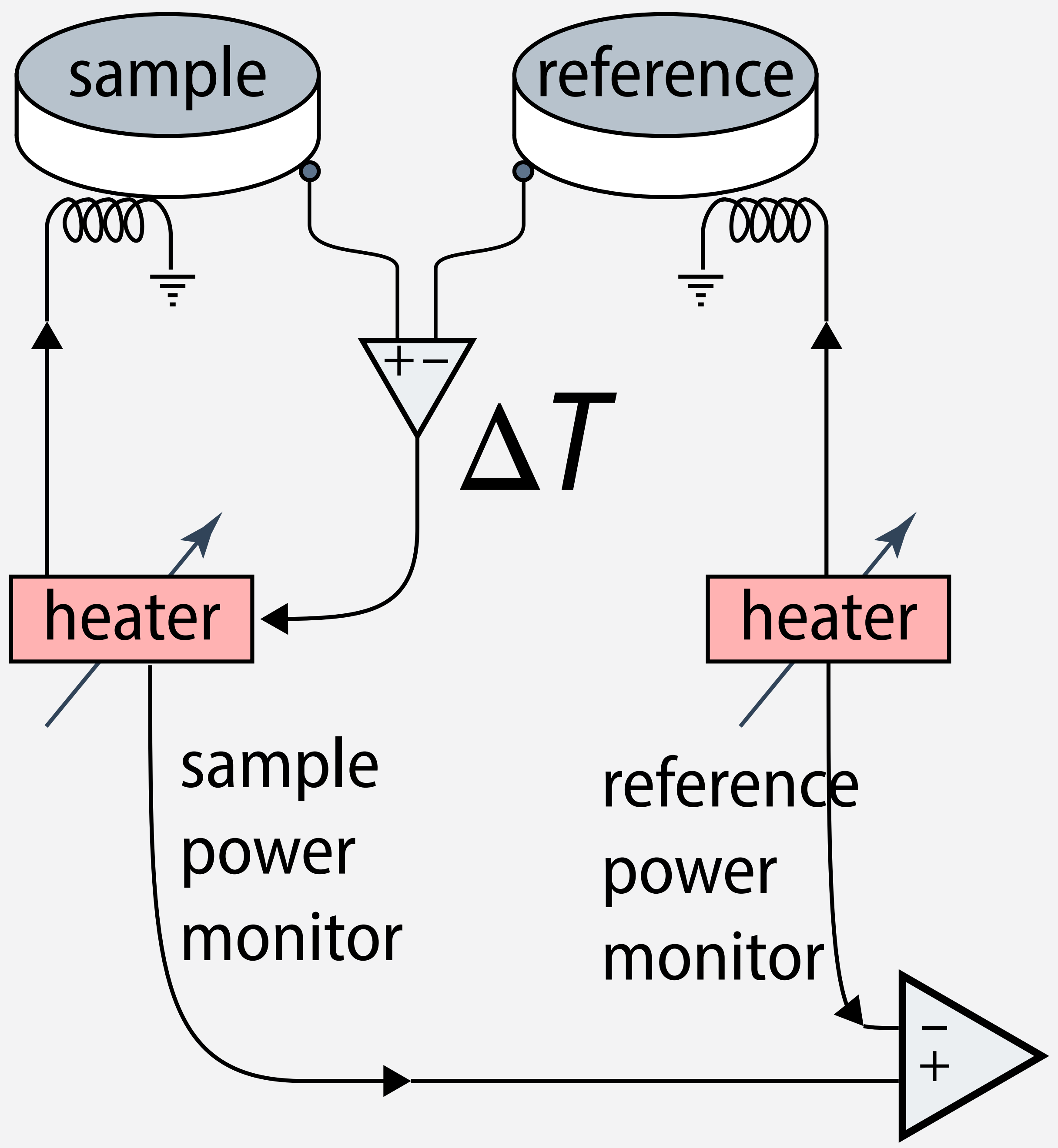
2nd order transition
(glass transition)

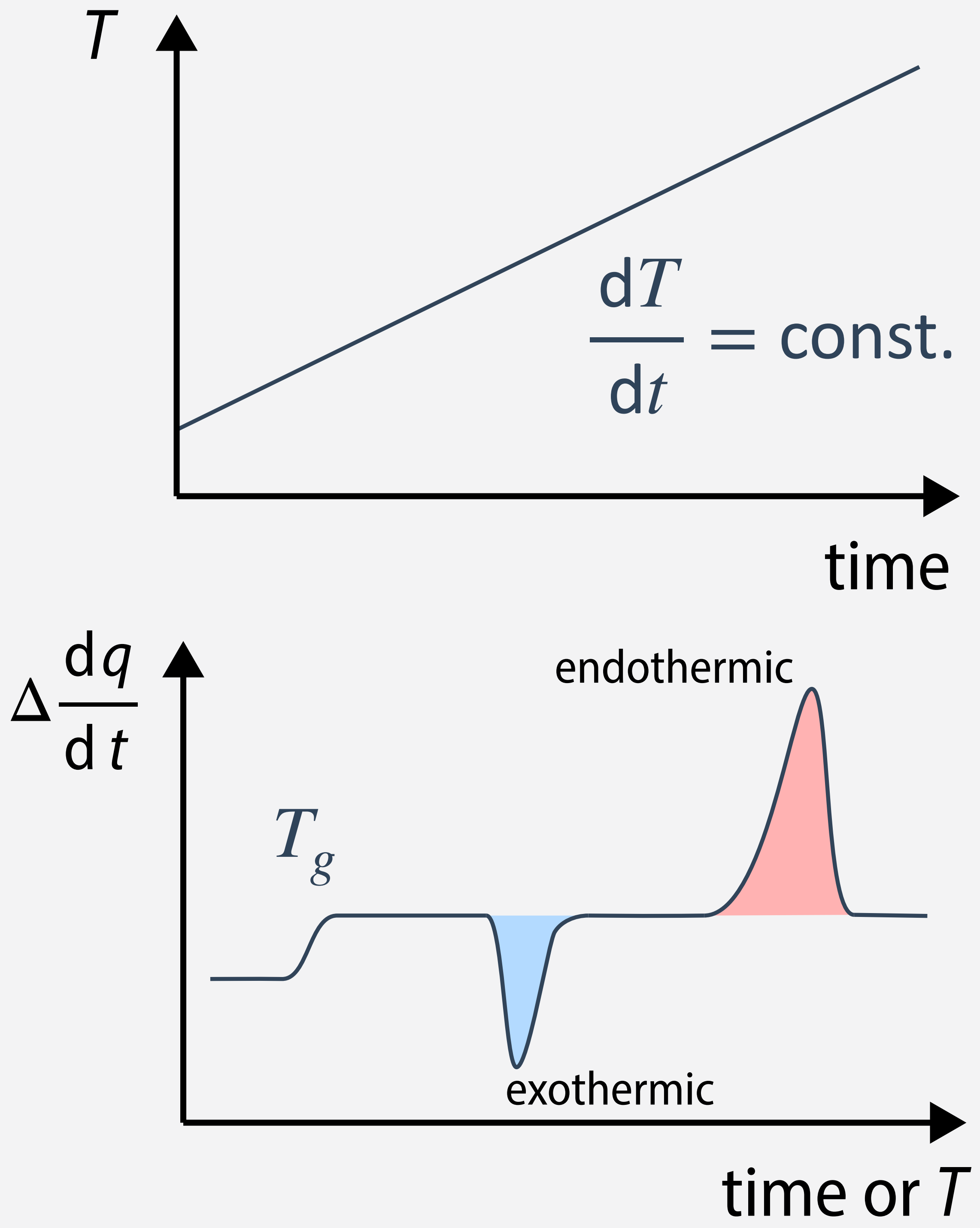


- **glass transitions: characteristics of a 2nd order transition, but NOT a true thermodynamic transition**

Principles of Differential Scanning Calorimetry (DSC)

- DSC monitors heat flow associated with phase transitions





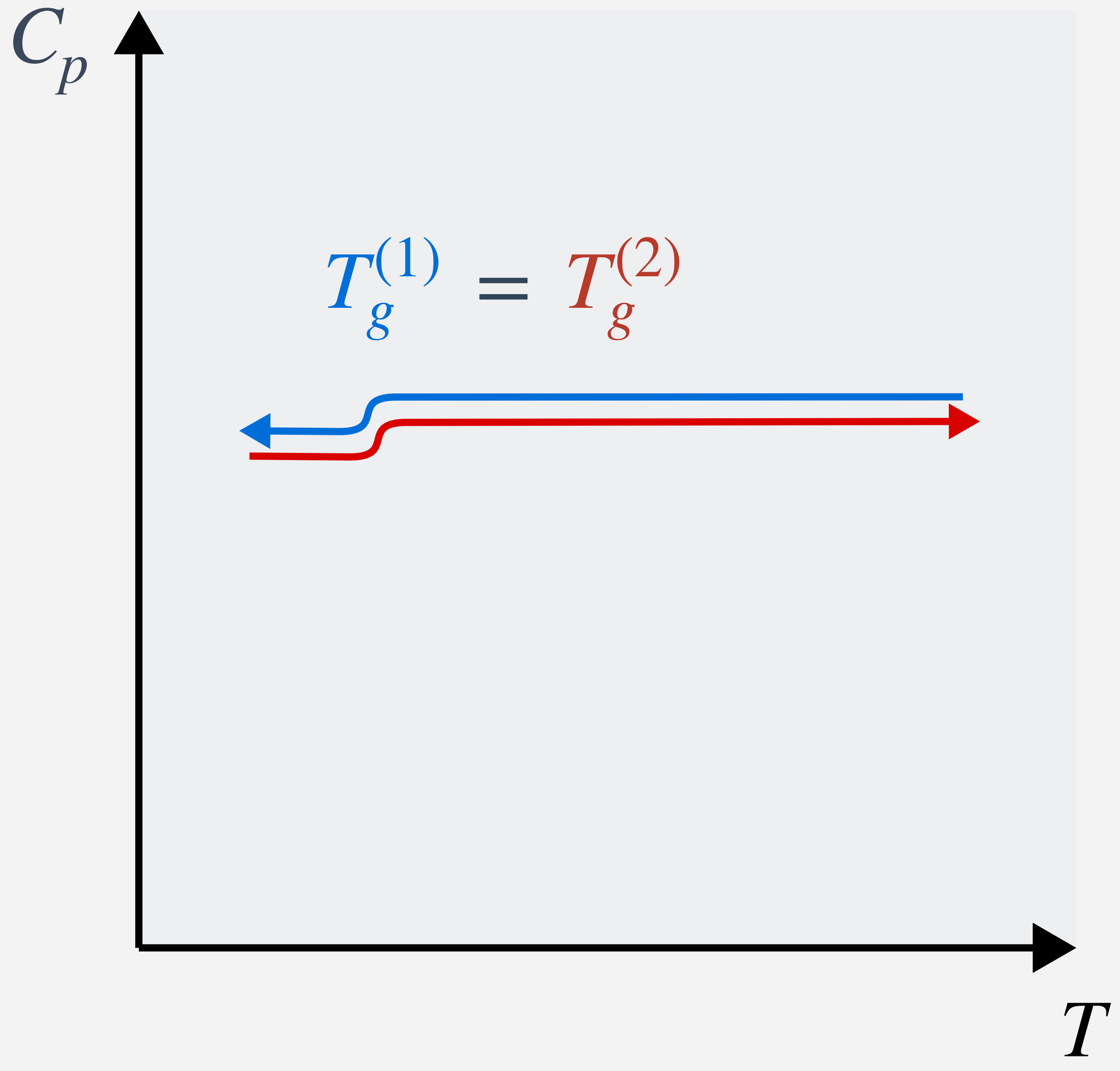
$$C_p = \frac{dQ}{dT} = \frac{dH}{dT}$$

- **endothermic processes (e.g. melting): heat is absorbed by the sample ($\Delta \mathrm{d}H/\mathrm{d}t > 0$)**
- **exothermic processes (e.g. crystallization): heat is released by the sample ($\Delta \mathrm{d}H/\mathrm{d}t < 0$)**
- **glass transition: observed as a endothermic baseline shift in the heat flow**

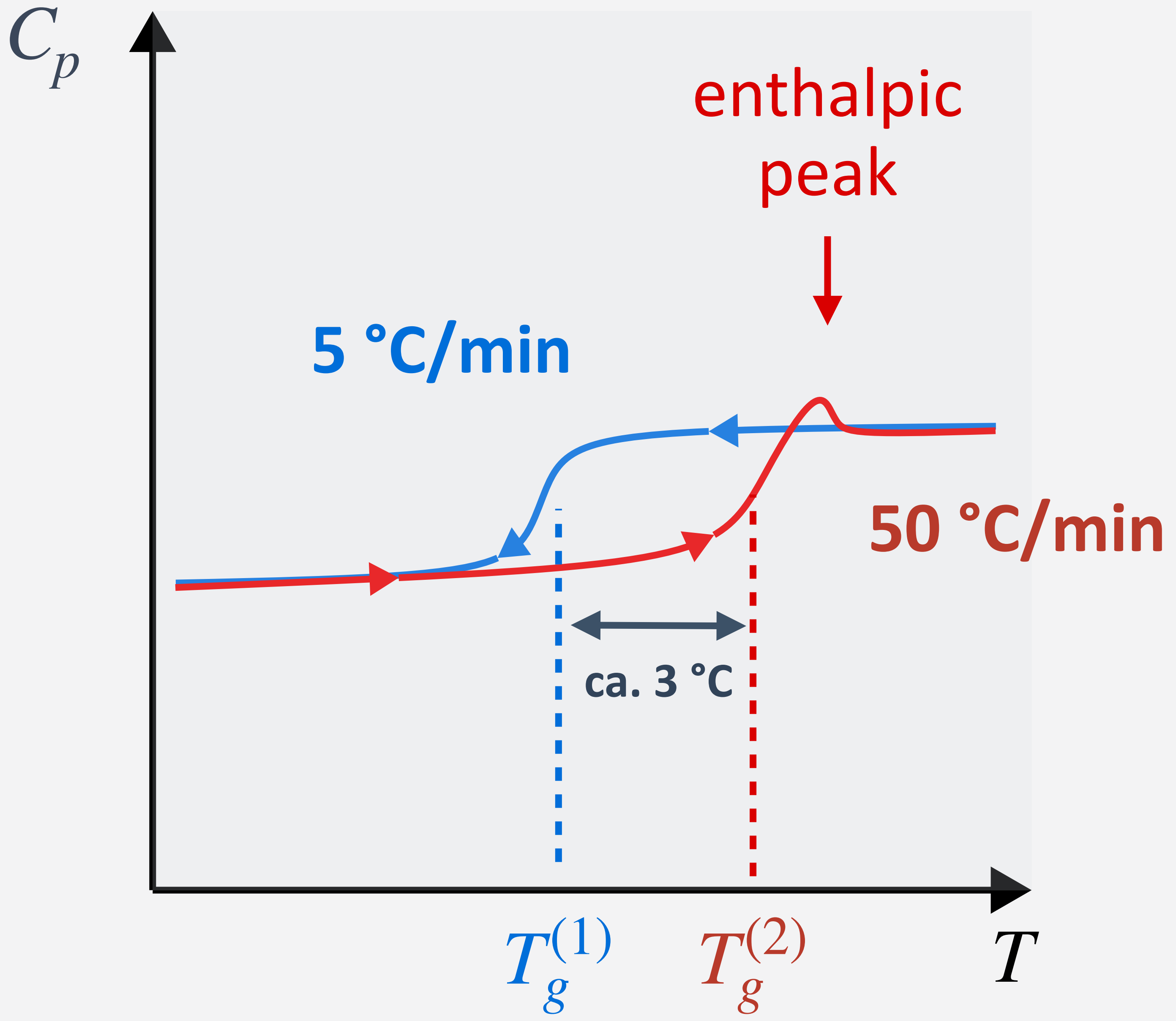
Heat Capacity Changes in DSC

- **at T_g, drop in heat capacity C_p upon cooling from the liquid state:** $C_p = \frac{dQ}{dT} = \frac{dH}{dT}$
- **during heating, enthalpy relaxation peak may appear → signature of glassy metastability**

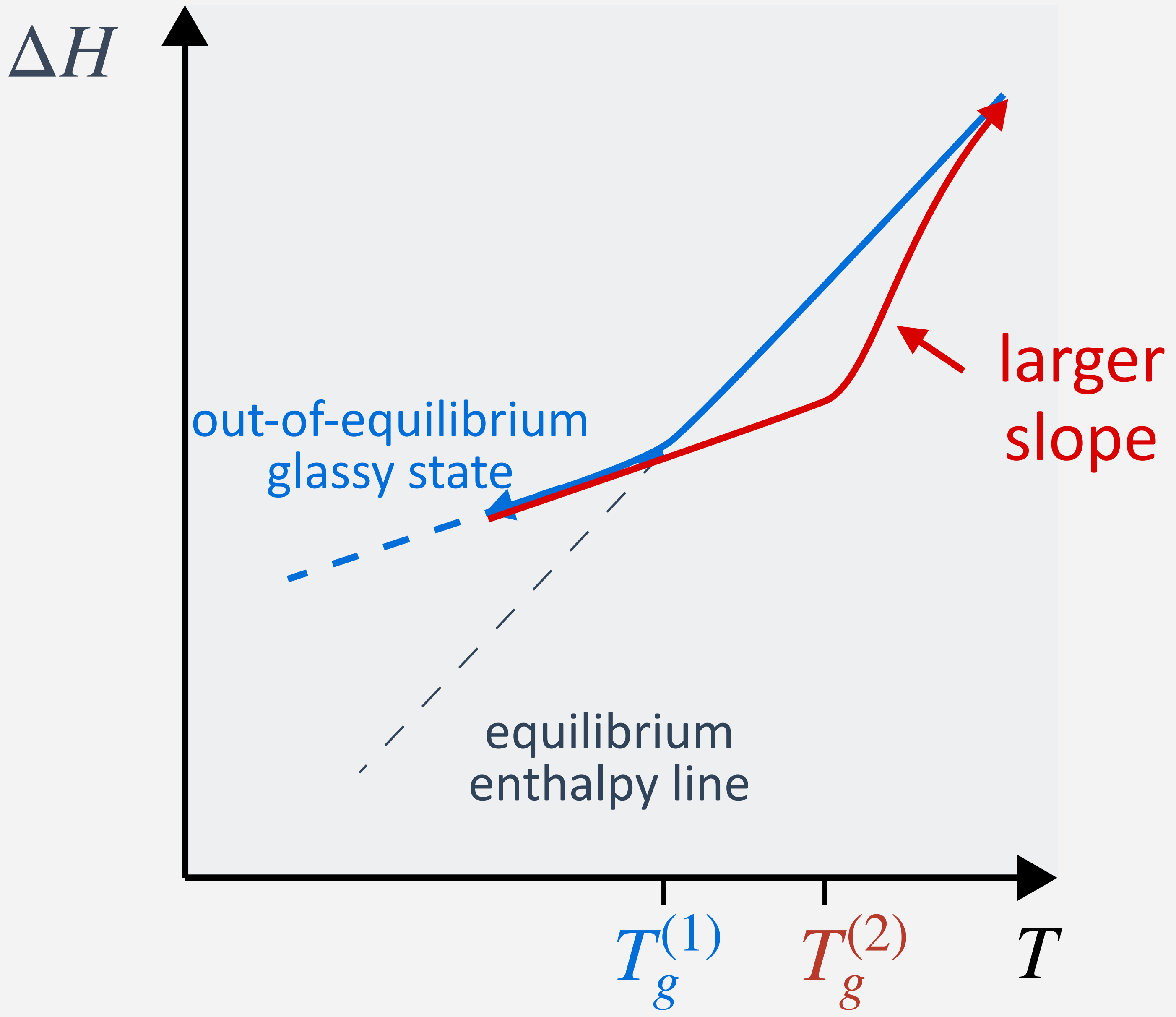
same cooling and heating rate



different cooling and heating rate



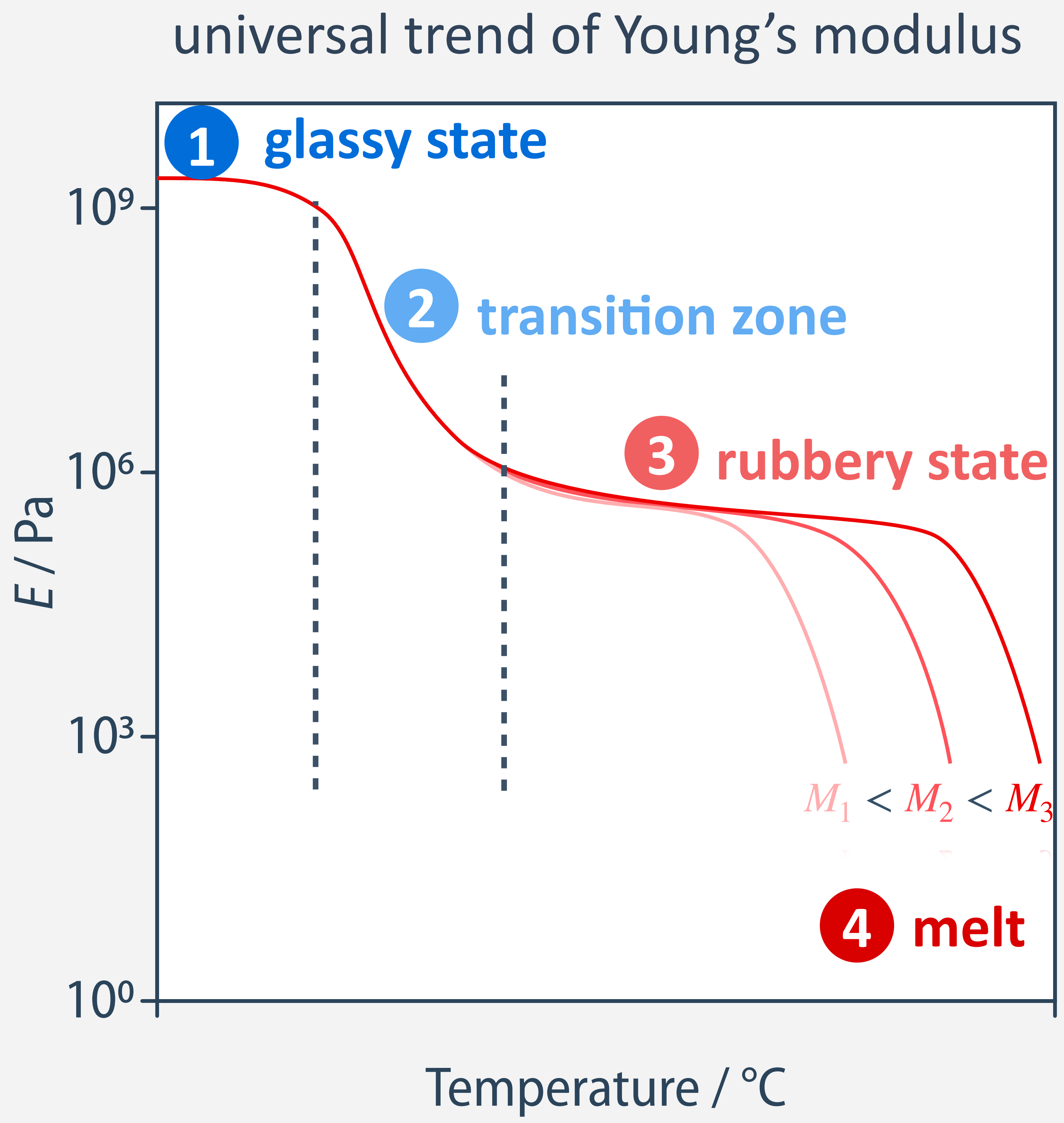
enthalpy changes

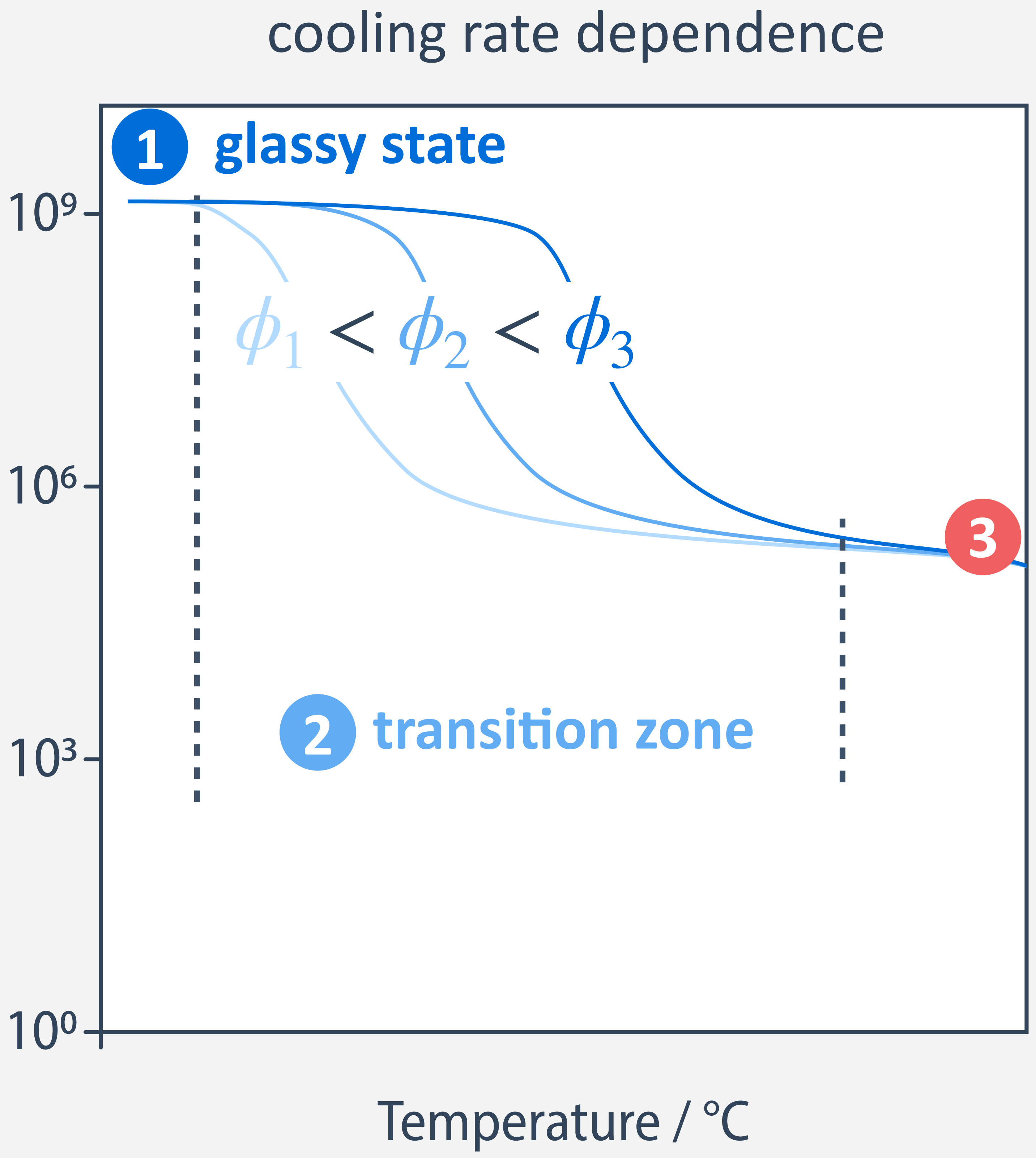


- **glassy state is out of equilibrium: chains cannot change conformation to establish equilibrium at given *T***

Mechanical Properties Across T_g

- **upon cooling through T_g, sharp increase of shear modulus** (and other elastic moduli!) **from 10^6 to 10^9 Pa**

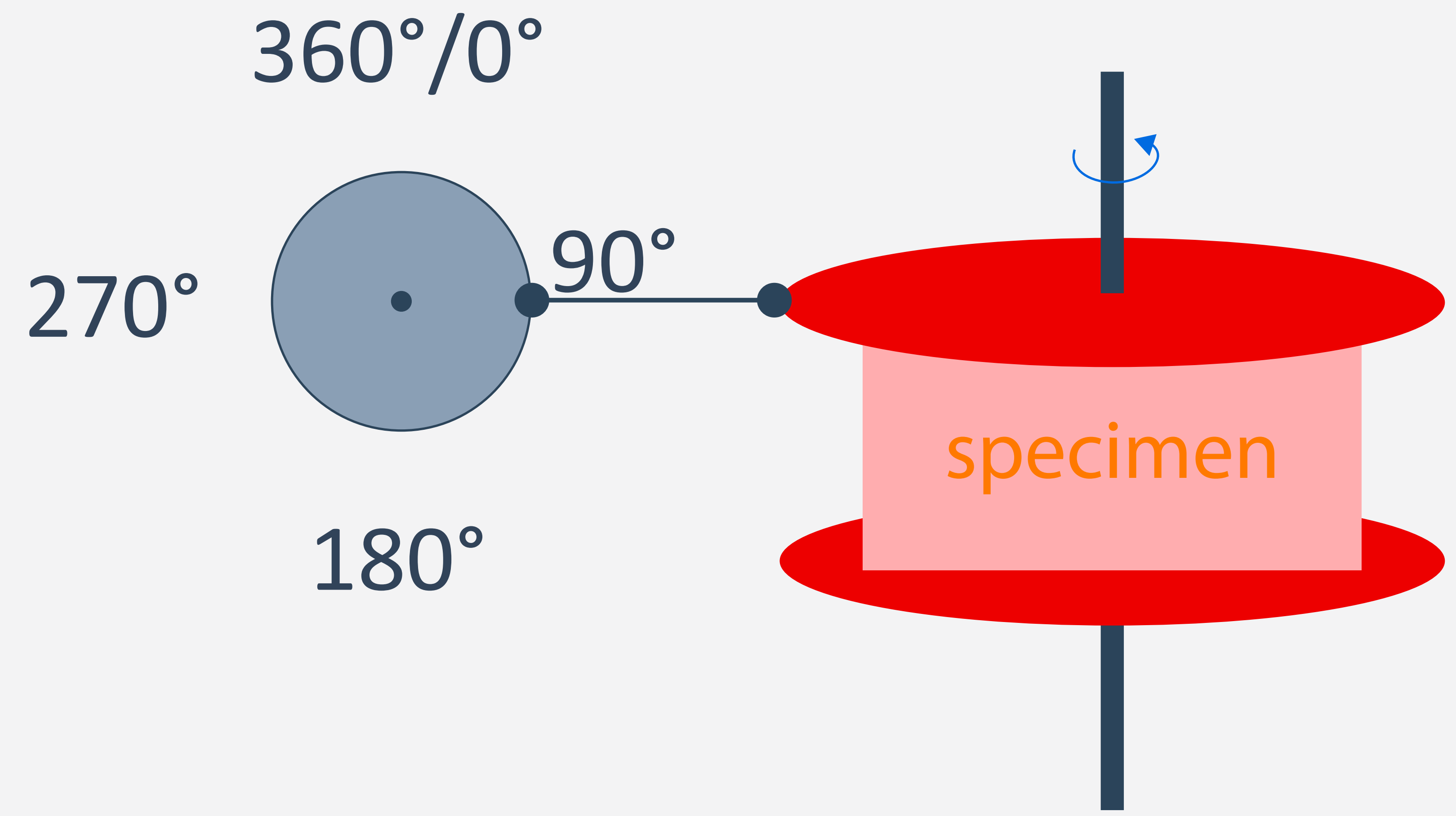




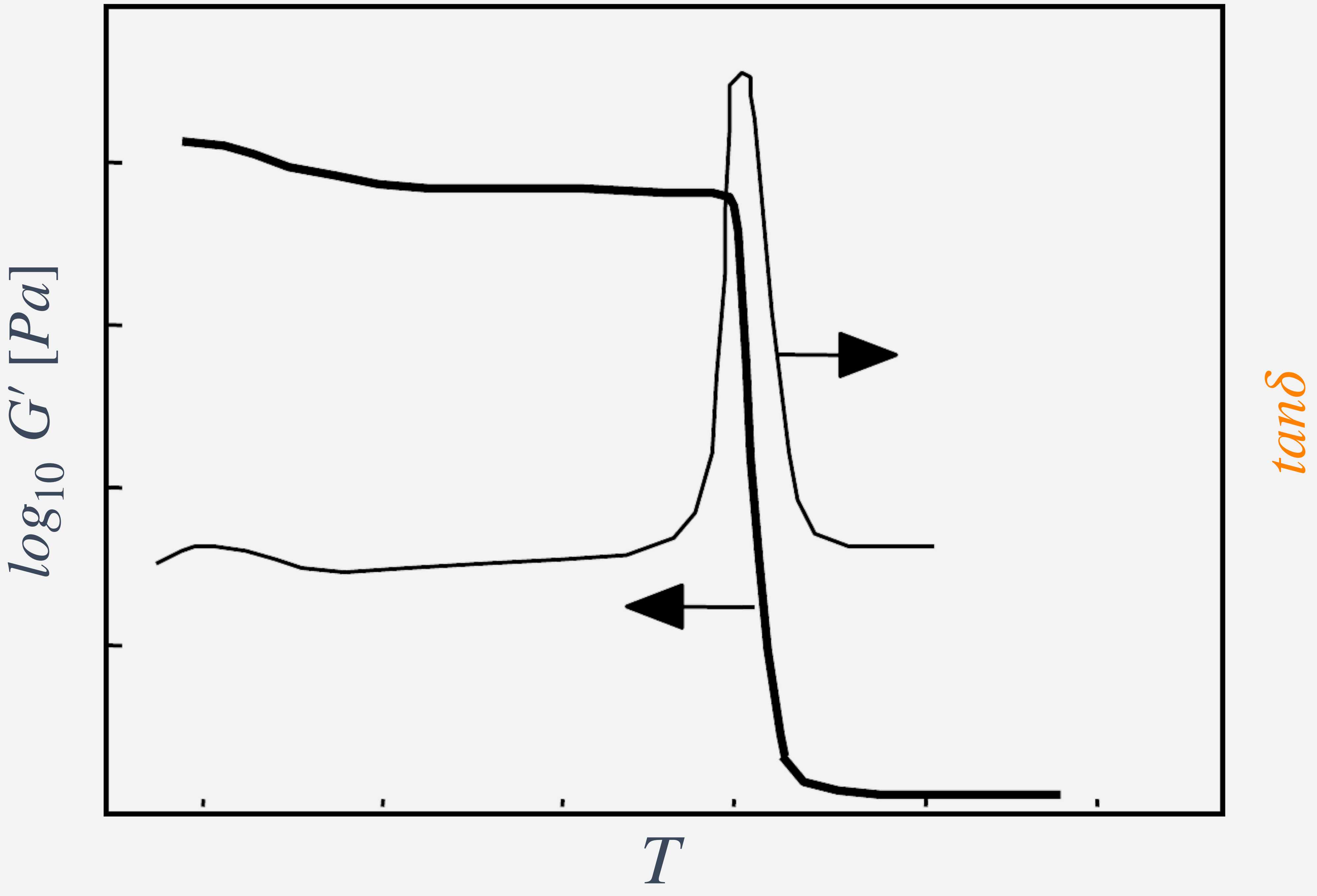
- **for long polymer chains, a rubbery regime appears at temperatures above T_g**
- **the extent of this rubbery state depends on the molar mass!** (see Chapters 4.1 and 4.2)

Dynamic Mechanical Analysis / Shear Rheology

- application of small cyclic deformations to probe stress, temperature, and frequency response
- damping ($tan\ \delta$): a measure of energy dissipation
- at T_g, a characteristic damping peak is observed



for working principle: see **Chapter 4.2**

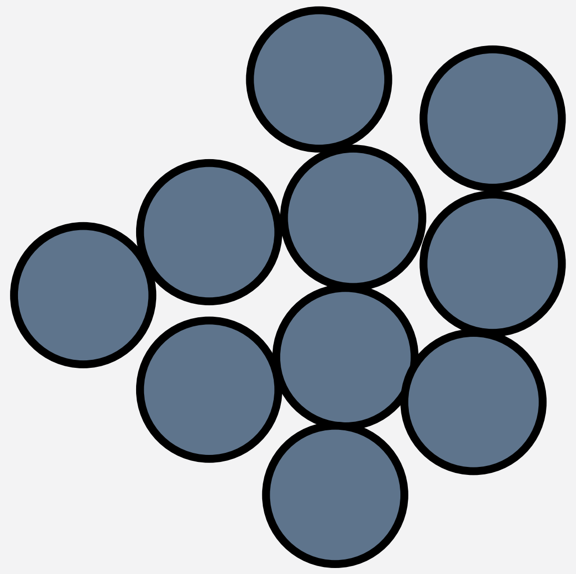


- T_g increases with increasing measurement frequency (shorter experimental time scale)

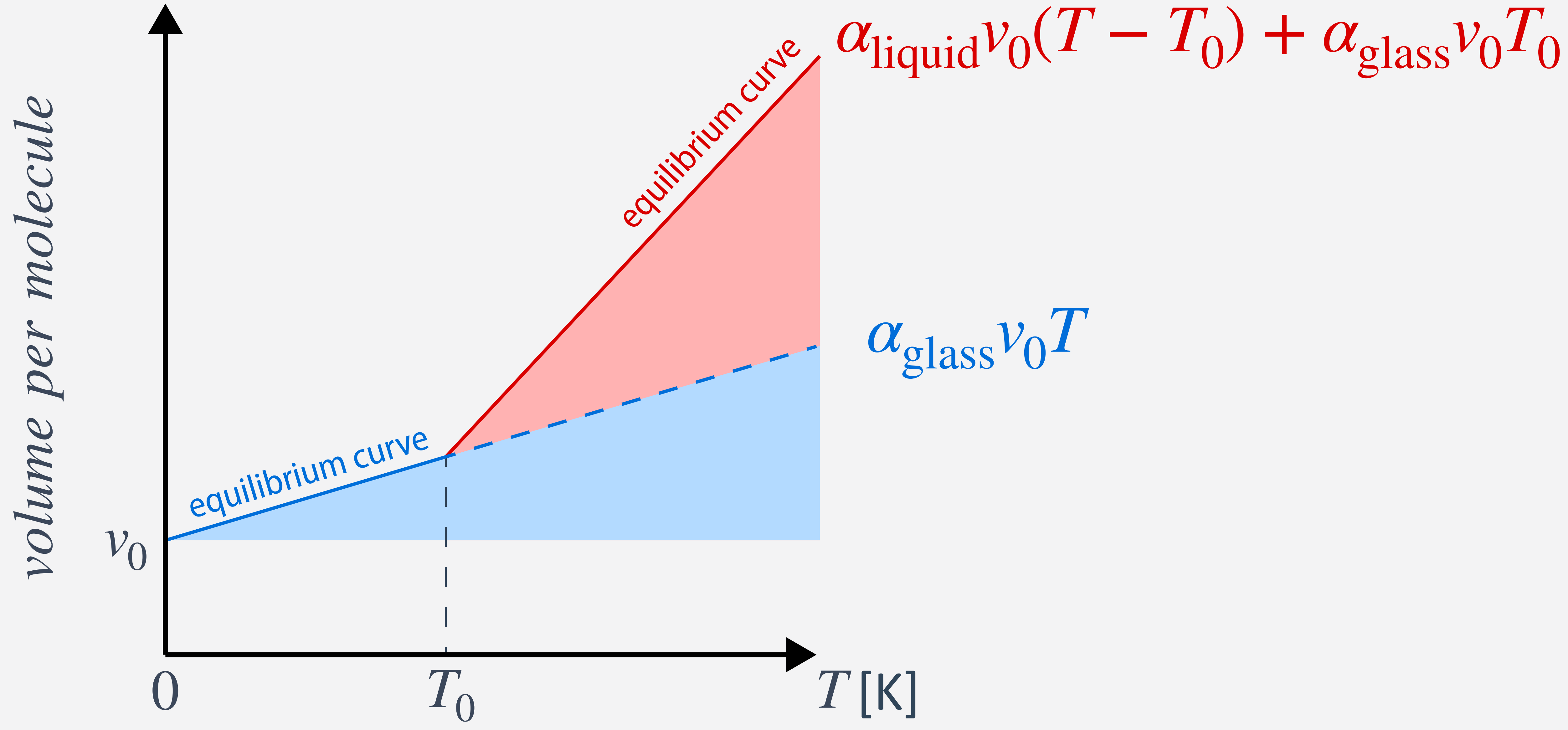
The Theory of Free Volume

- **at T_0, part of the volume created by thermal vibrations is “free”, leading to holes of size v_f**
- **movement becomes possible, if locally $v_{\mathrm{fm}} \geq v_0$** (v_0: the volume occupied by a sphere/molecule)

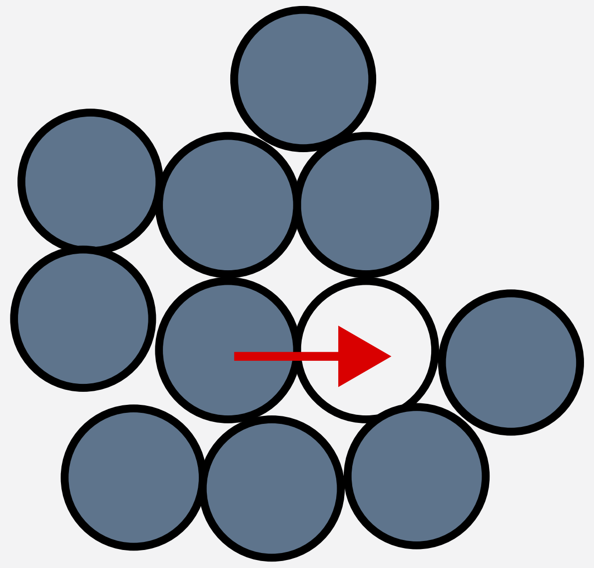
conformational changes restricted



infinitely slow cooling



conformational changes possible



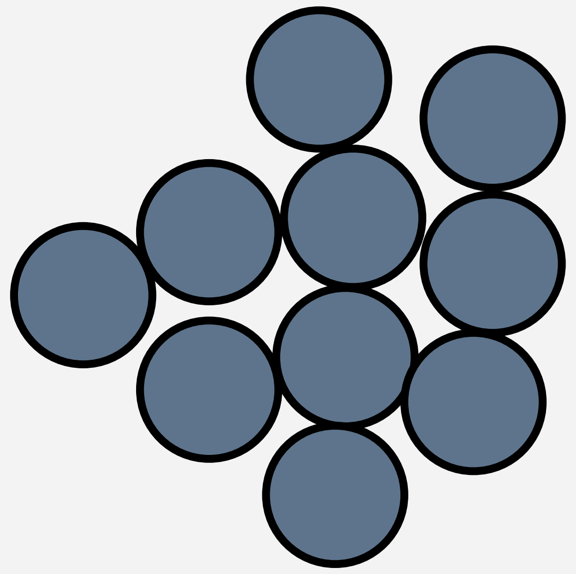
$v_{\mathrm{fm}} \geq v_0$

- **no translation & conformation changes possible below T_0** (thermodynamic glass transition temperature)

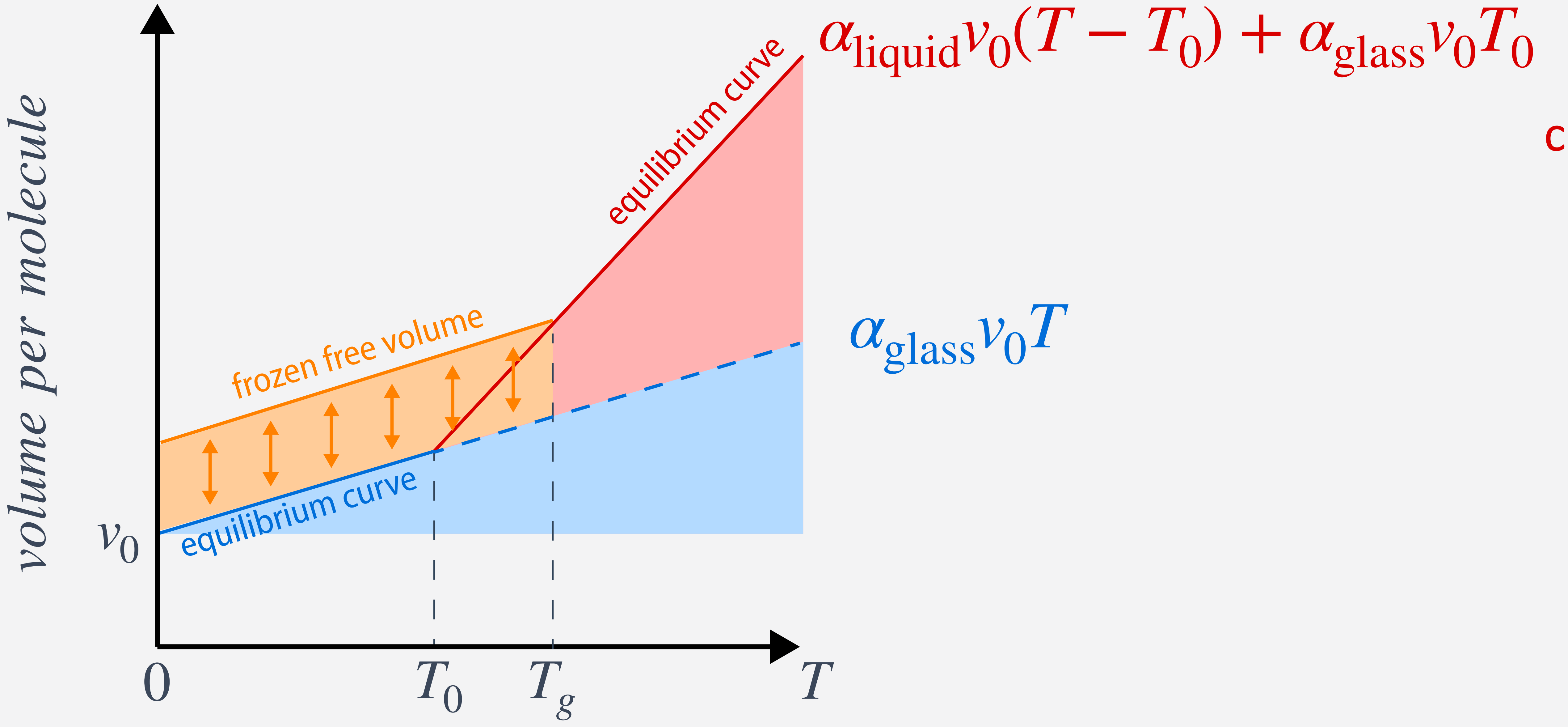
The Theory of Free Volume

- an infinitely slow cooling rate can in practice not be realized and T_0 can therefore not be measured
- free volume is hence trapped in the glassy state (**see exercise**): $v_{\mathrm{fm}} = v_0(T - T_0)\Delta\alpha$

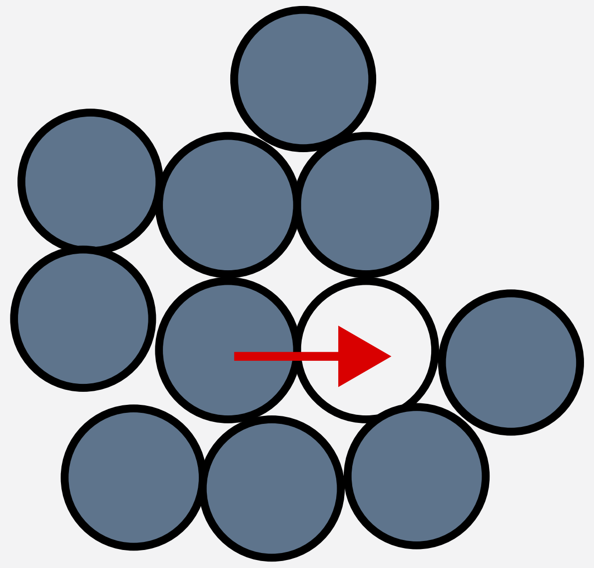
conformational changes restricted



finite cooling rate



conformational changes possible



$v_{\mathrm{fm}} \geq v_0$

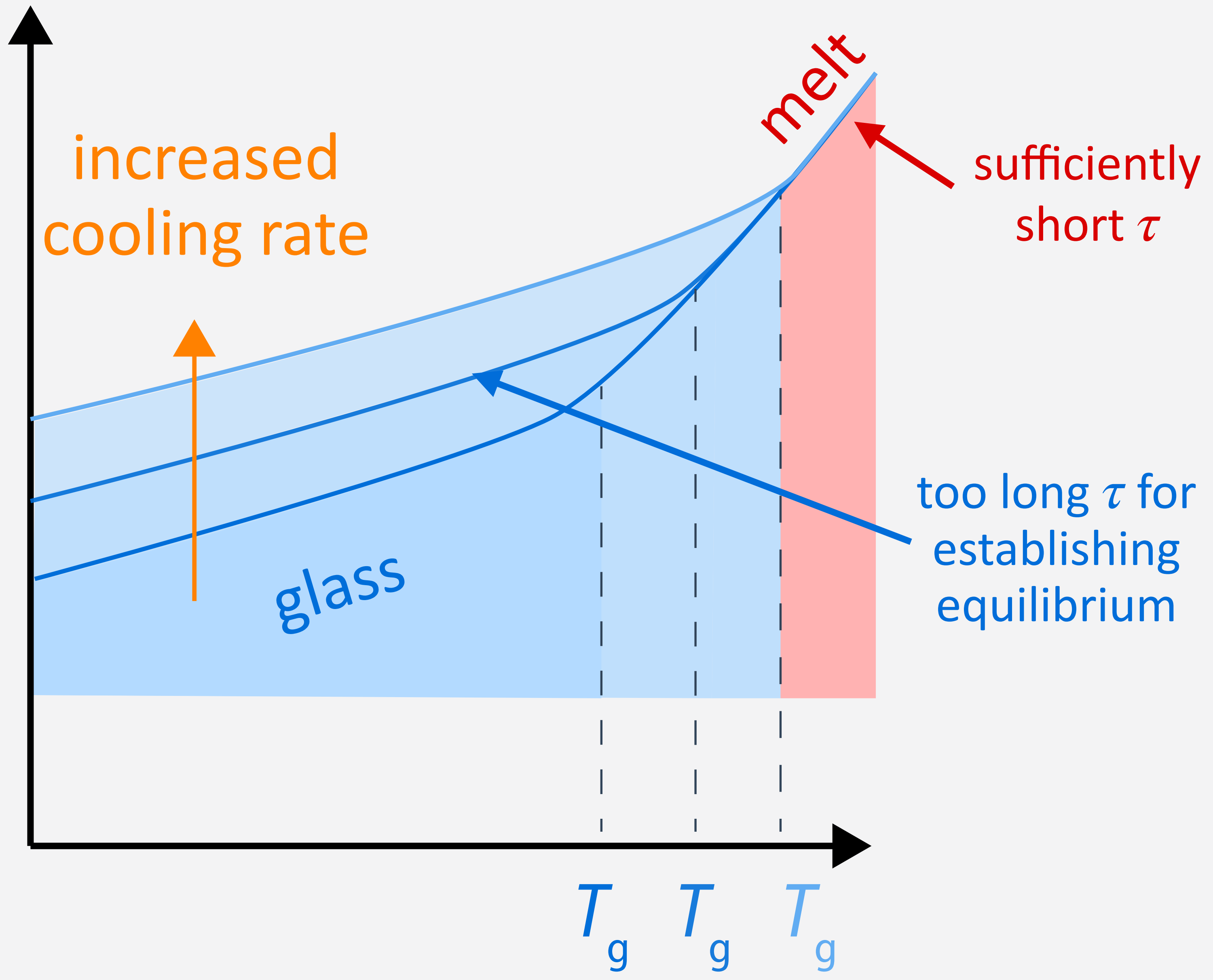
- at finite cooling rate, holes become "frozen" at a temperature $T_g > T_0$, which depends on the cooling rate

Relaxation Times and Free Volume

- **relaxation time τ needed to change conformation for equilibration**
- free volume interpretation for quantification of changes in dynamic and mechanical properties:

relaxation time τ : $\tau = \tau_0 e^{\frac{v_0}{v_{fm}}} = \tau_0 e^{\Delta\alpha^{-1}/(T-T_0)}$ $\Delta\alpha = \alpha_{liuqid} - \alpha_{glass}$

viscosity η (proportional to τ): $\eta = \eta_0 e^{\frac{v_0}{v_{fm}}} = \eta_0 e^{\frac{\Delta\alpha^{-1}}{T-T_0}}$



increased cooling rate

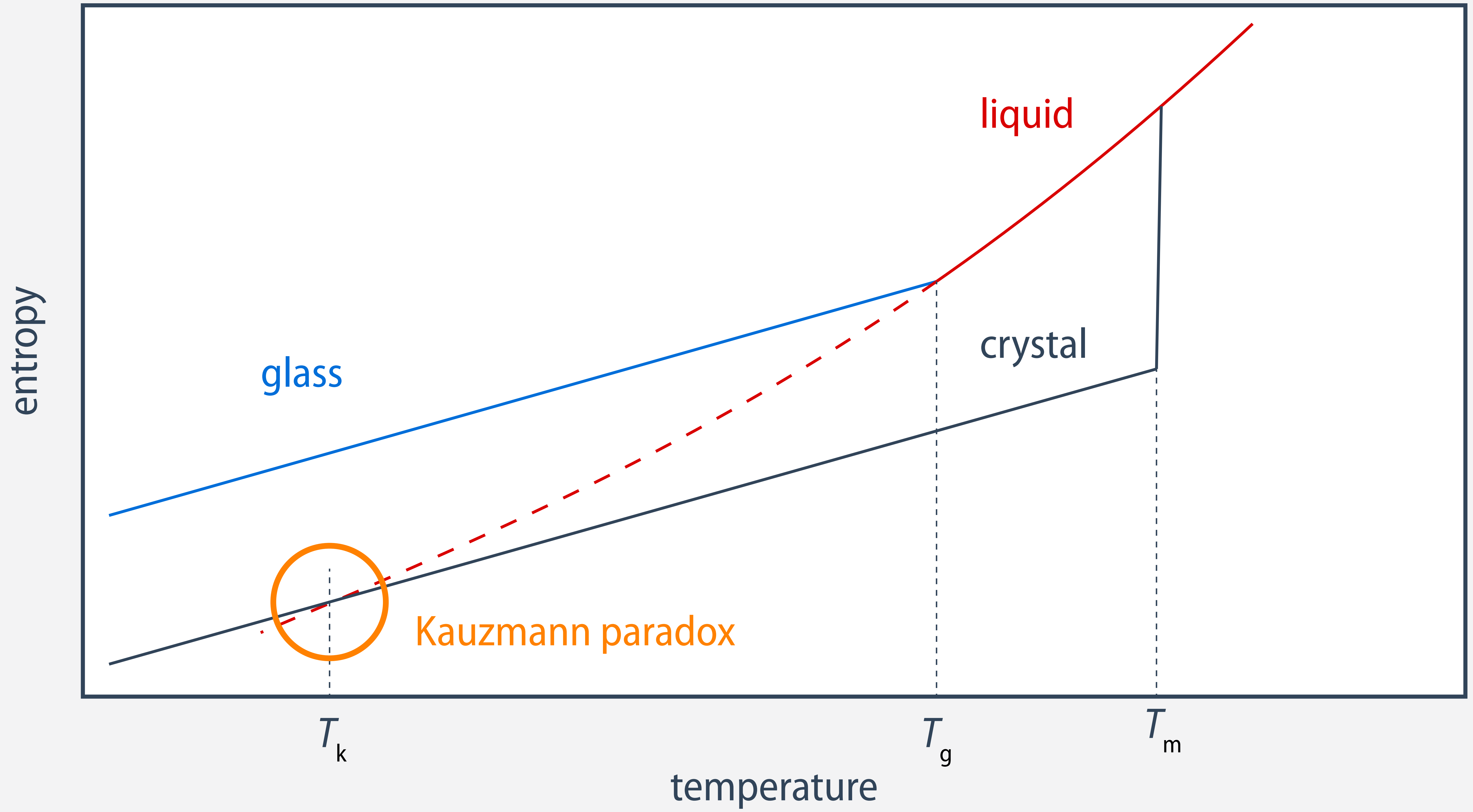
sufficiently short τ

too long τ for establishing equilibrium

- **empirically verified relationships for many glass forming systems**
- **limitations: free volume theory was founded for simple liquids** (macromolecular chain connectivity, thermal activation of chain movement, secondary interactions not considered)

Thermodynamic Theory by Gibbs-Di Marzio

- the glass transition might have an underlying thermodynamic nature, not only a kinetic one.
- transition predicted: the *conformational entropy* of the polymer chains must vanishes at T_k



Kauzmann paradox:

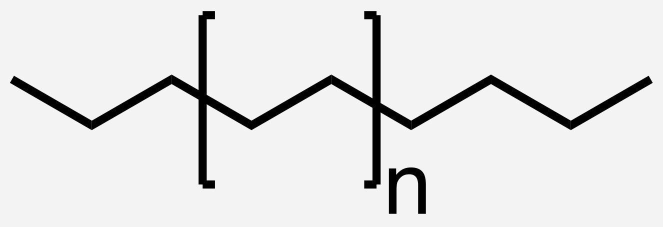
$$S_l < S_{\text{crystal}} \;\; for\ T < T_k$$

- **at T_k, a thermodynamic phase transition occurs before the paradoxical crossing** $S_l < S_{\text{glass}}$

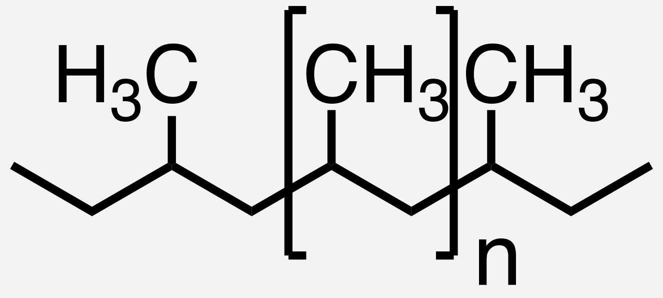
Structural Factors Impacting T_g

Chain Rigidity

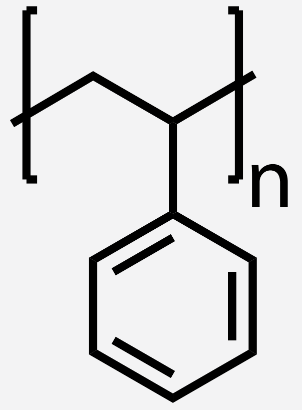
- **decreased chain mobility at increased sterically demanding (bulky) side groups**



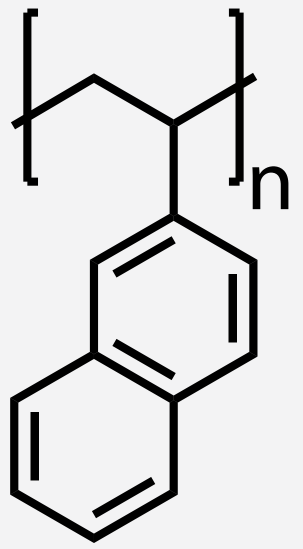
T_g = -100 °C



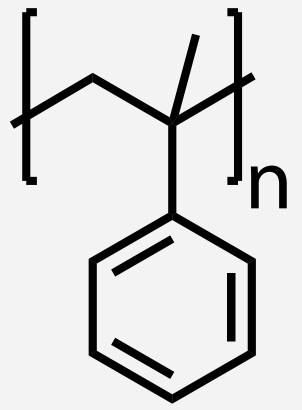
T_g = -10 °C



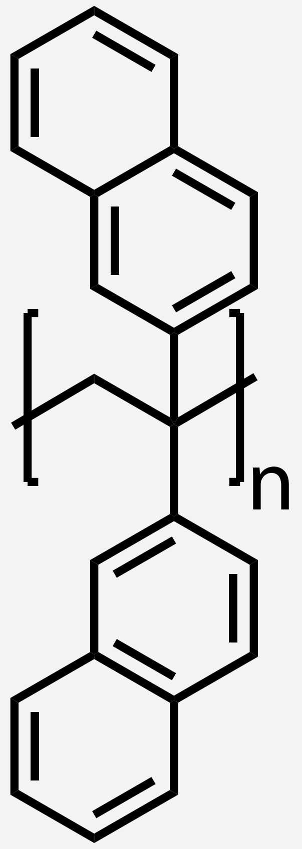
T_g = 100 °C



T_g = 135 °C



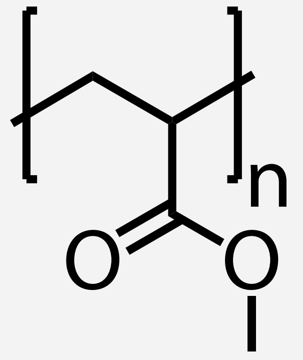
T_g = 175 °C



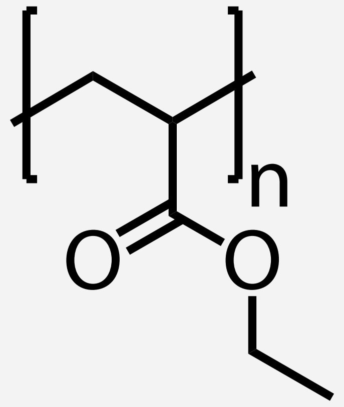
T_g = 264 °C

Plasticisation

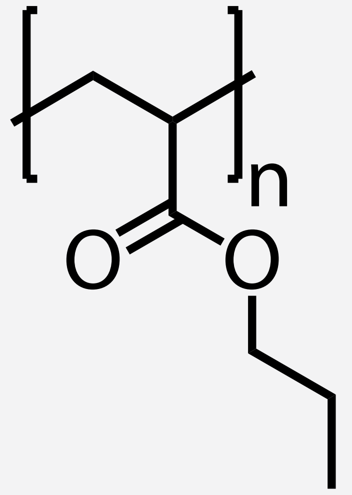
- **internal plasticisation: addition of flexible substituents reduce the T_g**
- **external plasticisation: addition of small amounts of a solvent (mainly used for PVC)**



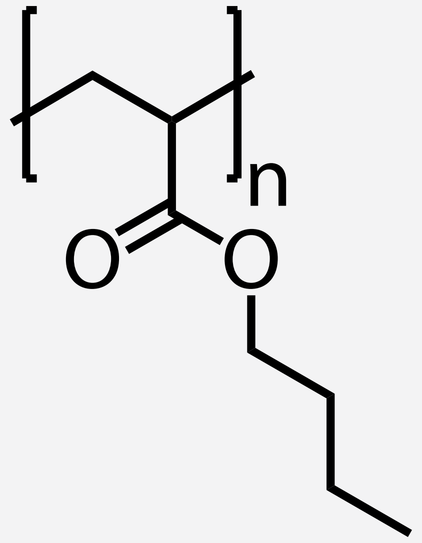
$T_g = 6$ °C



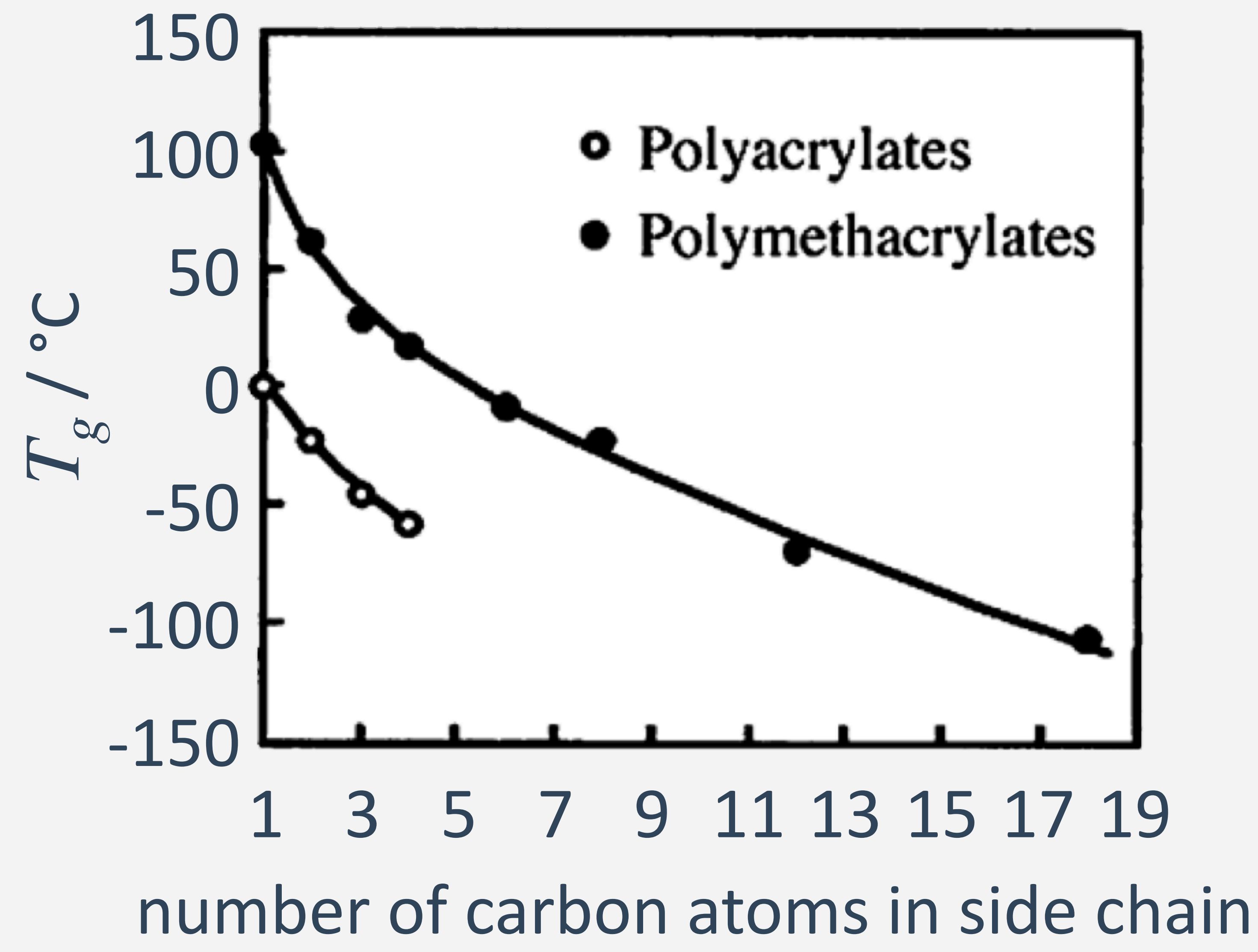
$T_g = -24$ °C



$T_g = -48$ °C



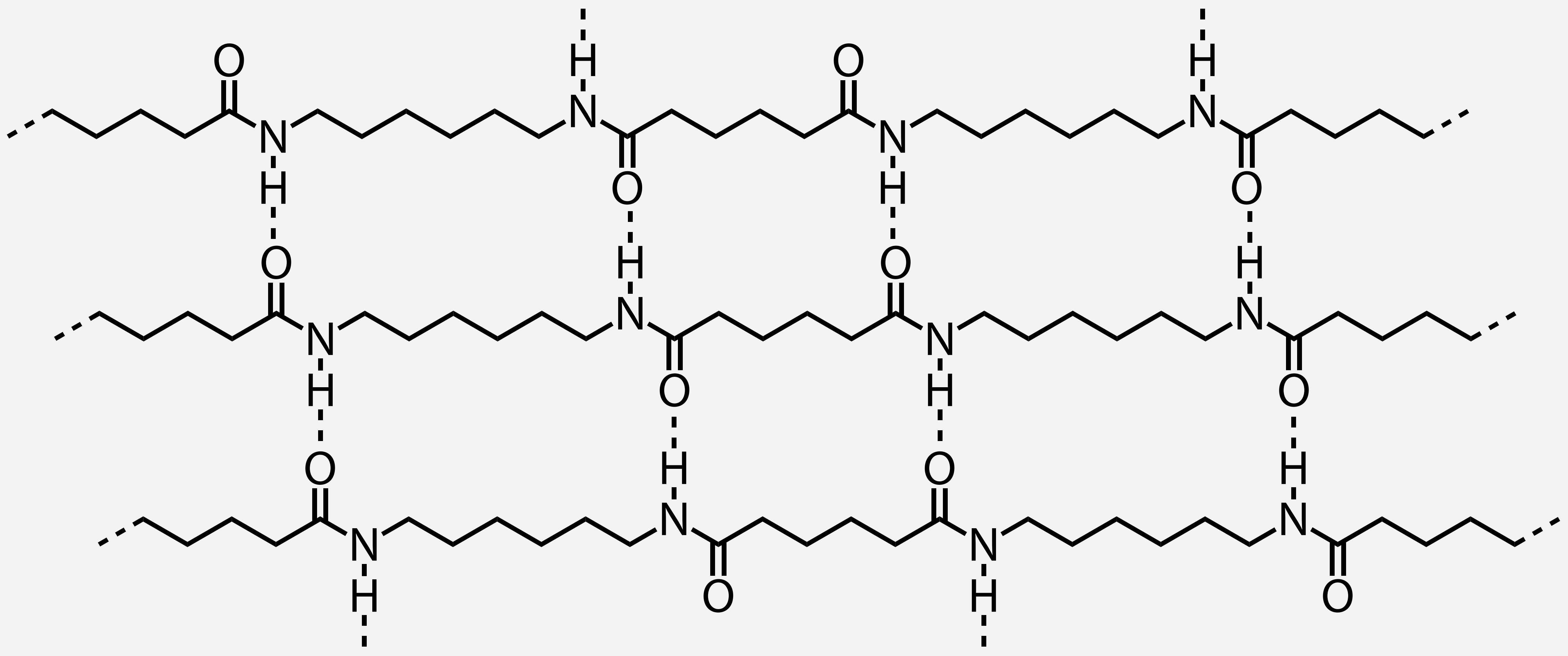
$T_g = -55$ °C

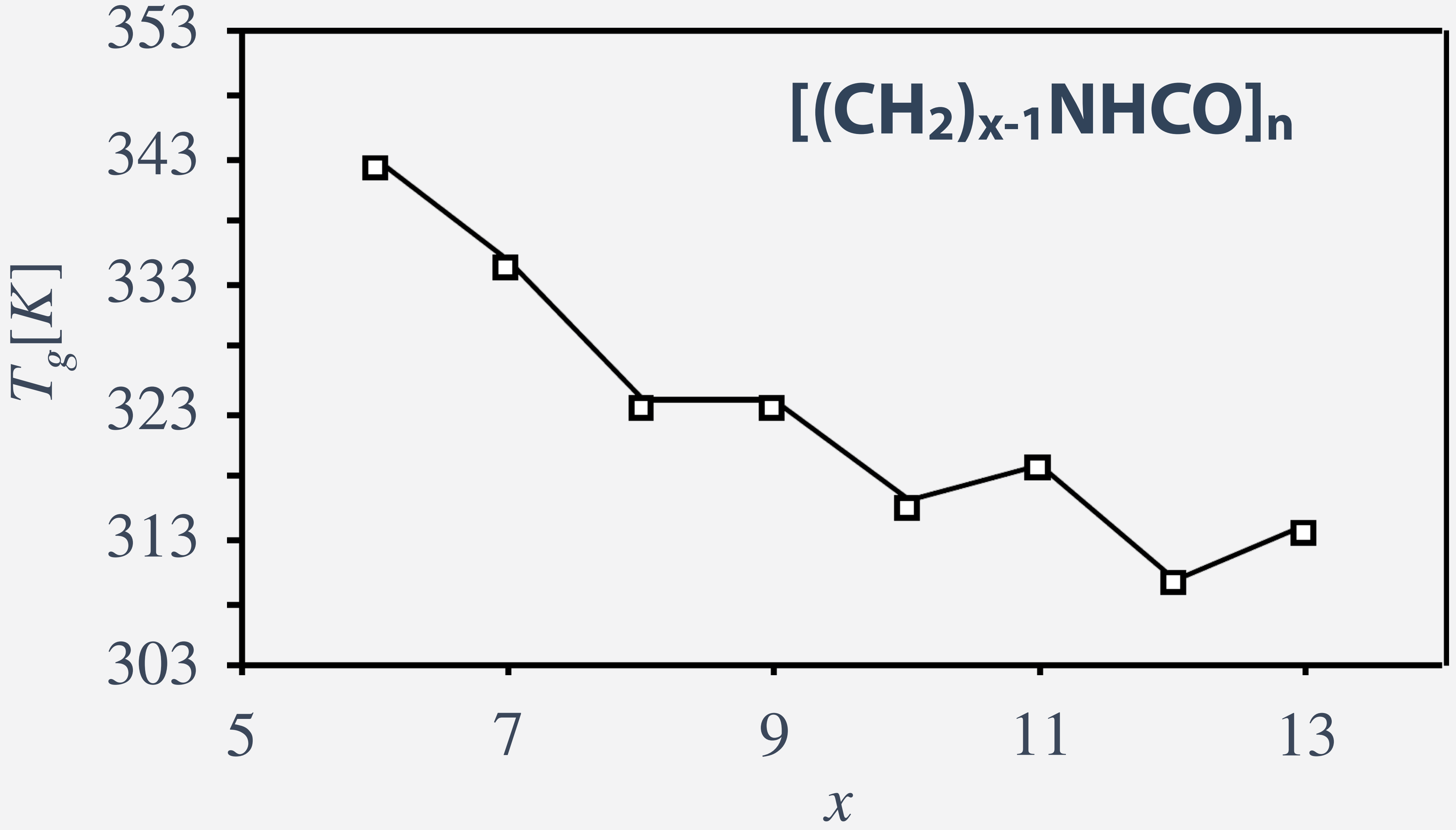


- **self-plasticisation of certain polyolefin's due to a wide distribution of the molar mass**
- **antiplasticizing effect in case of strong and specific polymer-solvent interactions**

Specific Interactions

- decreased chain mobility in case of strong inter-chain interactions, i.e. in presence of polar groups (CN, NH, C=O) and, in particular, hydrogen bonds.





- increases in T_g at increased number of amide groups in nylons.

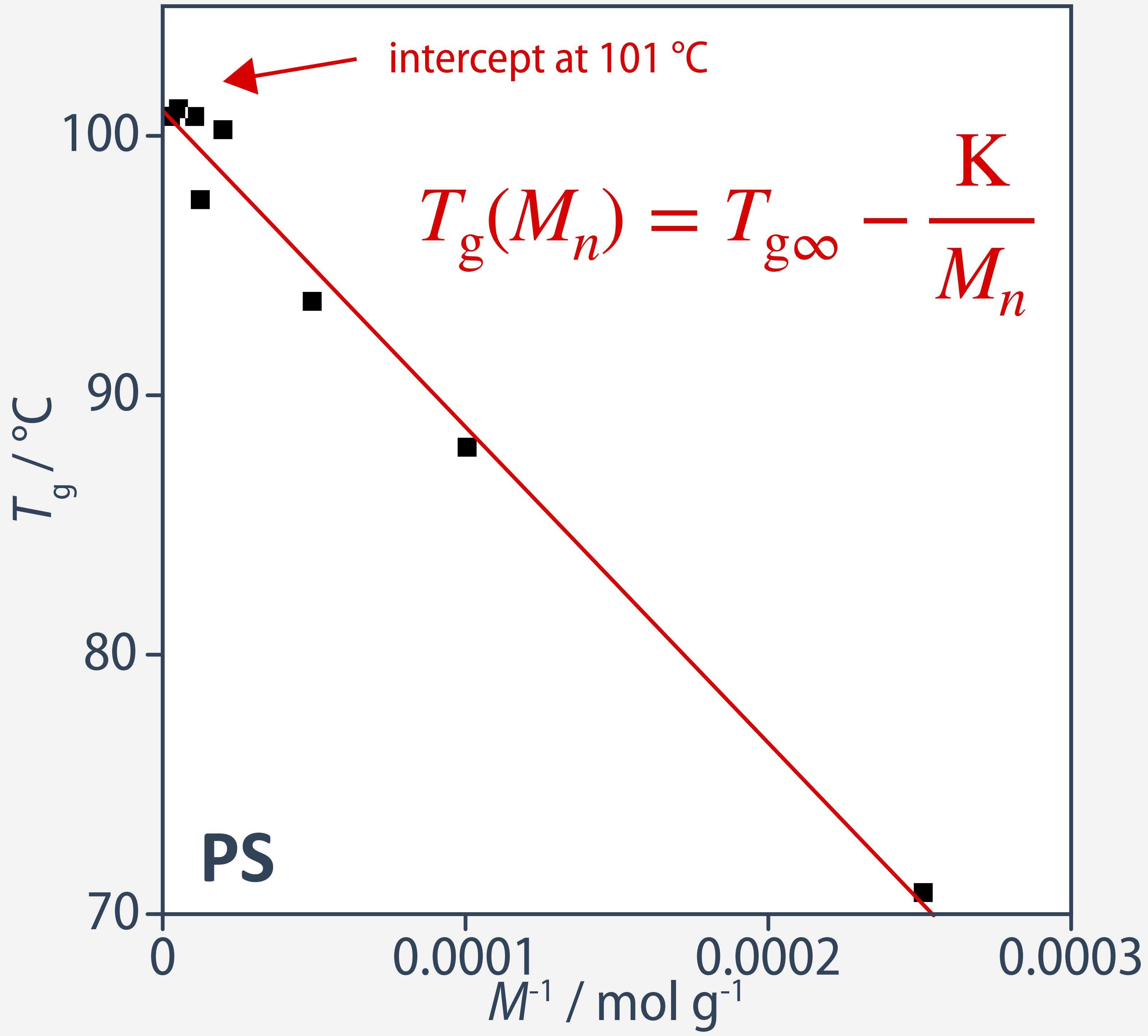
- solvents competing for hydrogen bonding interactions (i.e. H_2O) serve as plasticisers

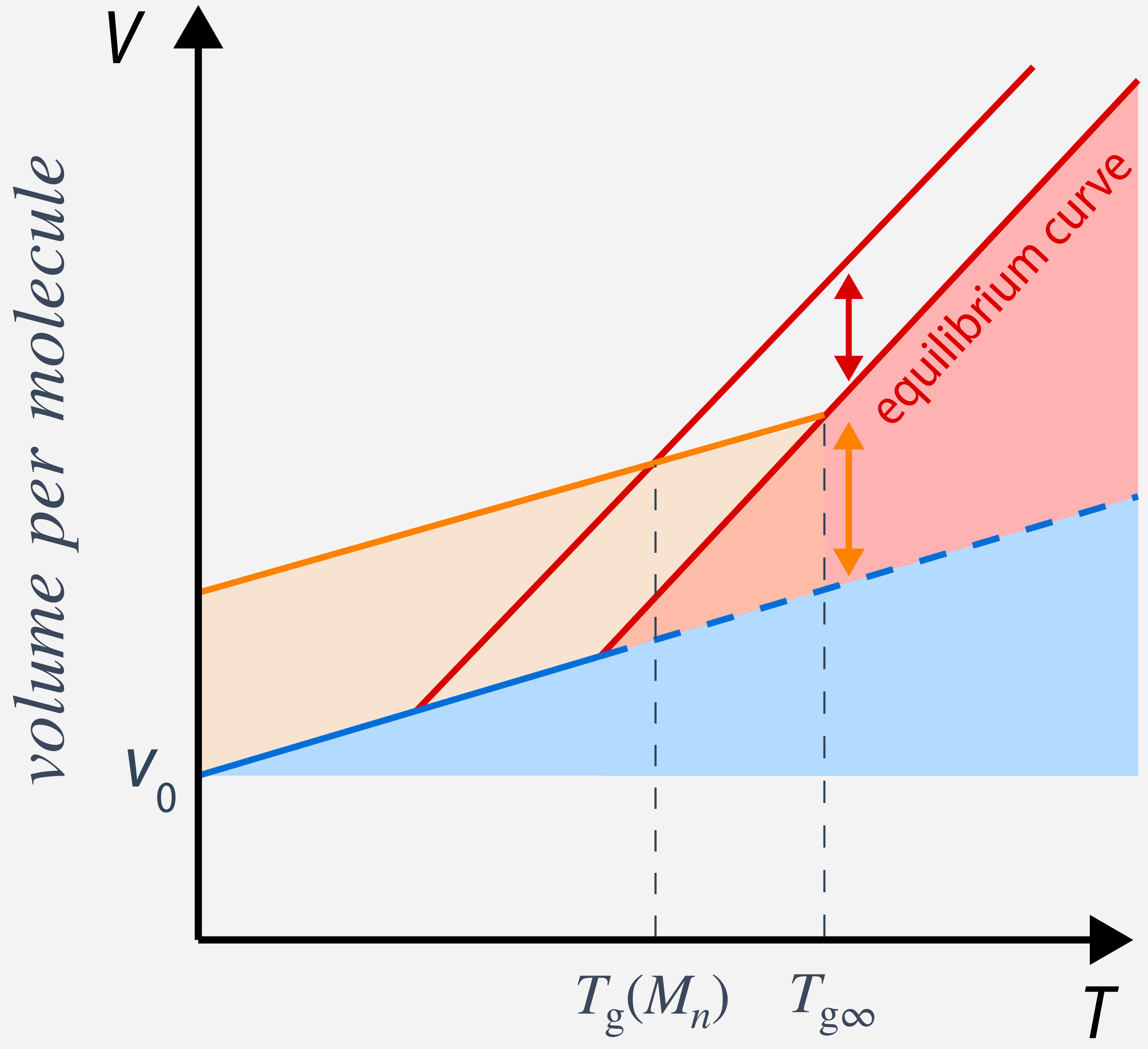
Molecular Weight Dependence

- valid for oligomers and low molar mass polymers, when end group concentration is high
- each chain end provides additional “free volume”, θ, contributing to their total fractional free volume, f_c:

$$v_{fm} = (\alpha_l - \alpha_g)v_0(T_{g\infty} - T_0) + f_c v_0 = (\alpha_l - \alpha_g)v_0(T_{g\infty} - T_0) + v_0\frac{2\rho N_A\theta}{M_n}$$

θ: additional free volume per end group





- **at finite cooling rate, holes become "frozen" at a temperature $T_g > T_0$, which depends on the cooling rate**

see also Exercise Sheet

Superglue

- working principle: strong adhesive nature of cyanoacrylates and quick polymerization (glass formation!)

The History of Superglue

1942

Cyanoacrylates discovered during WWII search gun sight plastics. Stick to everything, so discarded

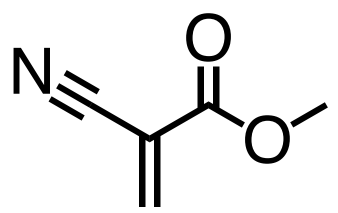
1951

Cyanoacrylates rediscovered during research looking for polymers for jet canopies

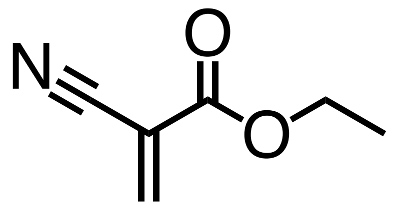
1958

Their potential finally realised: cyanoacrylates are developed into a glue which eventually becomes available commercially in 1958. Numerous other manufactures follow suit.

Cyanoacrylates



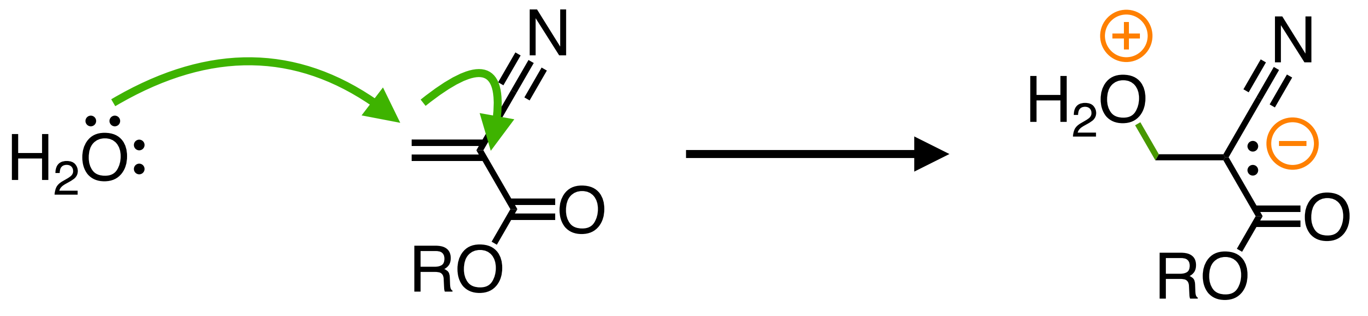
methyl cyanoacrylate



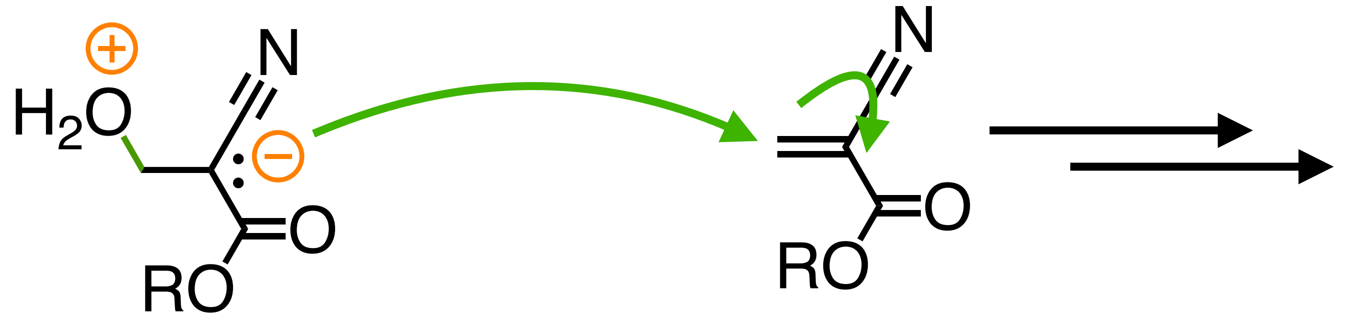
ethyl cyanoacrylate

Most common: ethyl cyanoacrylate, but others can also be used. Medical grade cyanoacrylates such as 2-octyl cyanoacrylate can be used to close up wounds

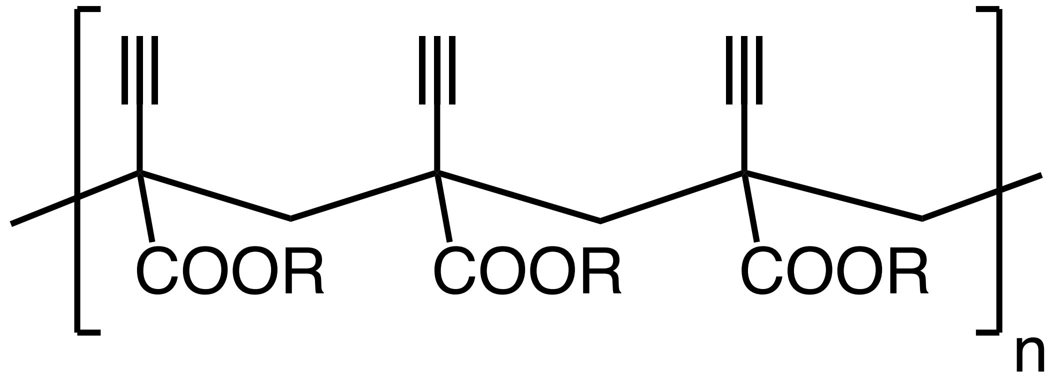
Mechanism



Cyanoacrylates 'cure' in the presence of water. Only a small amount of water is required to kick of the reaction - even the water vapour in air is enough.

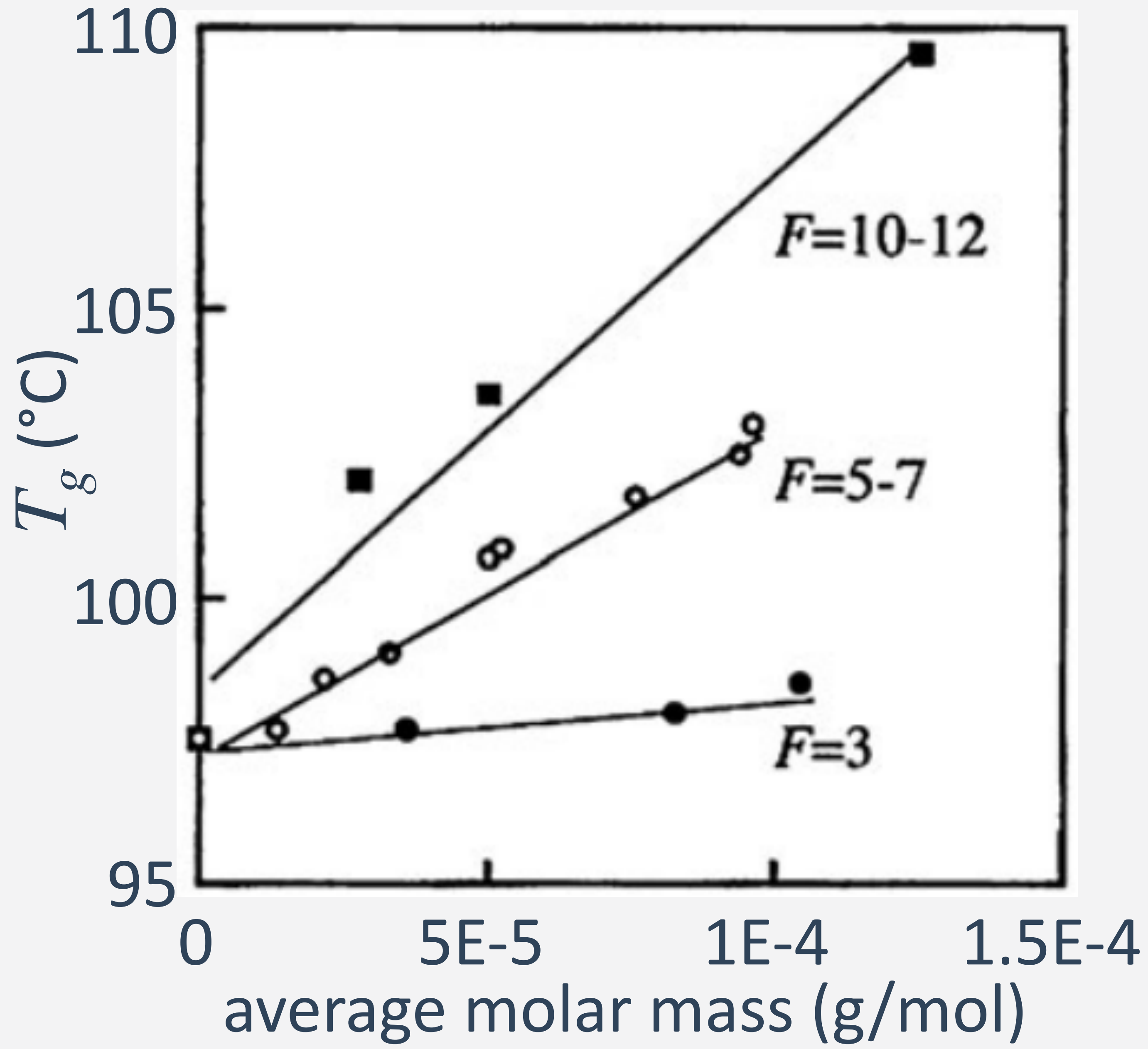


The reaction produces an anion which can add to more of the original cyanoacrylate, a process that repeats to form the adhesive polymer chains

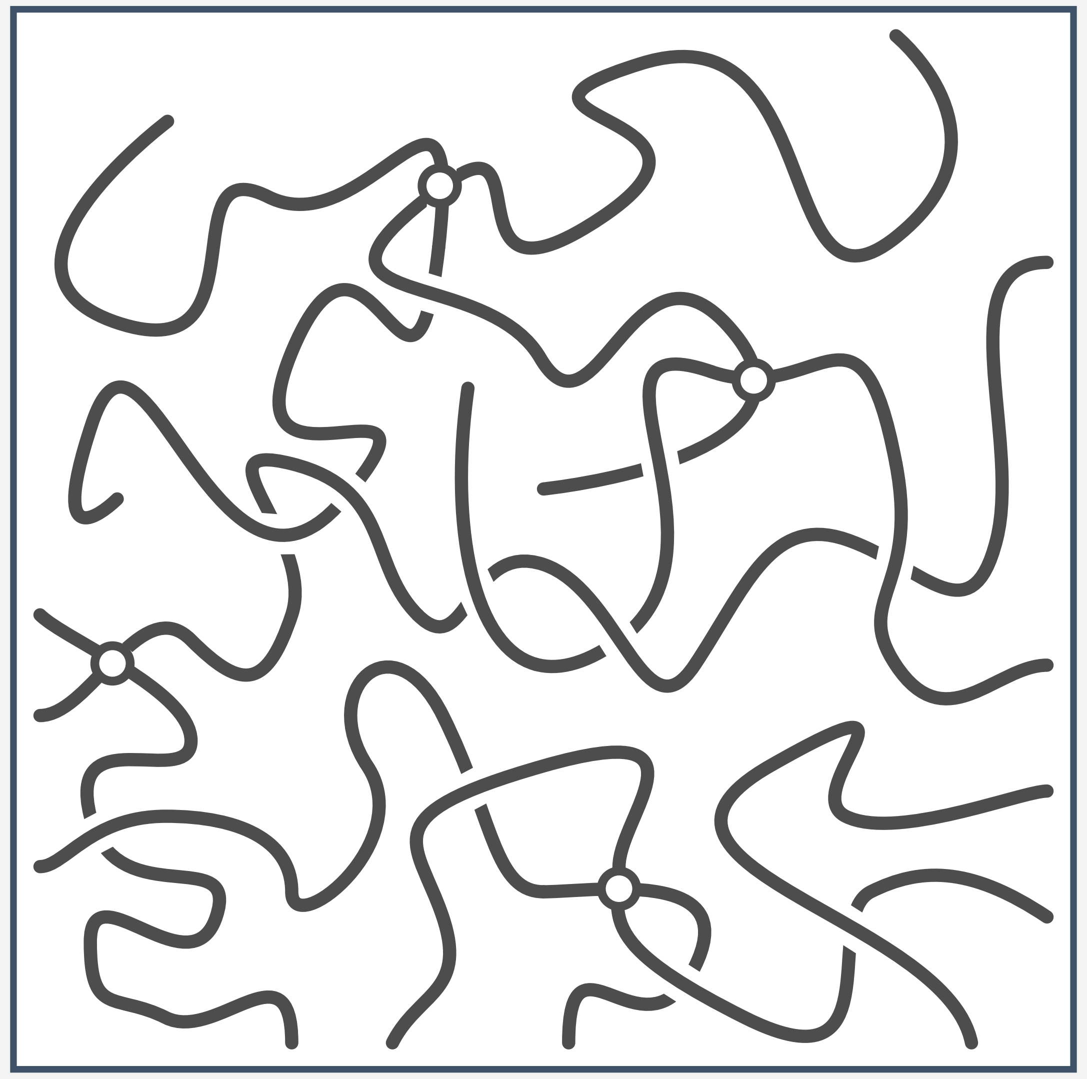


Cross-Linking

- **low cross-linking density: discussed relations hold true, in particular molecular weight dependence**
- **high cross-linking density: the sterical demand of catenary connections may lead to an increase in T_g**

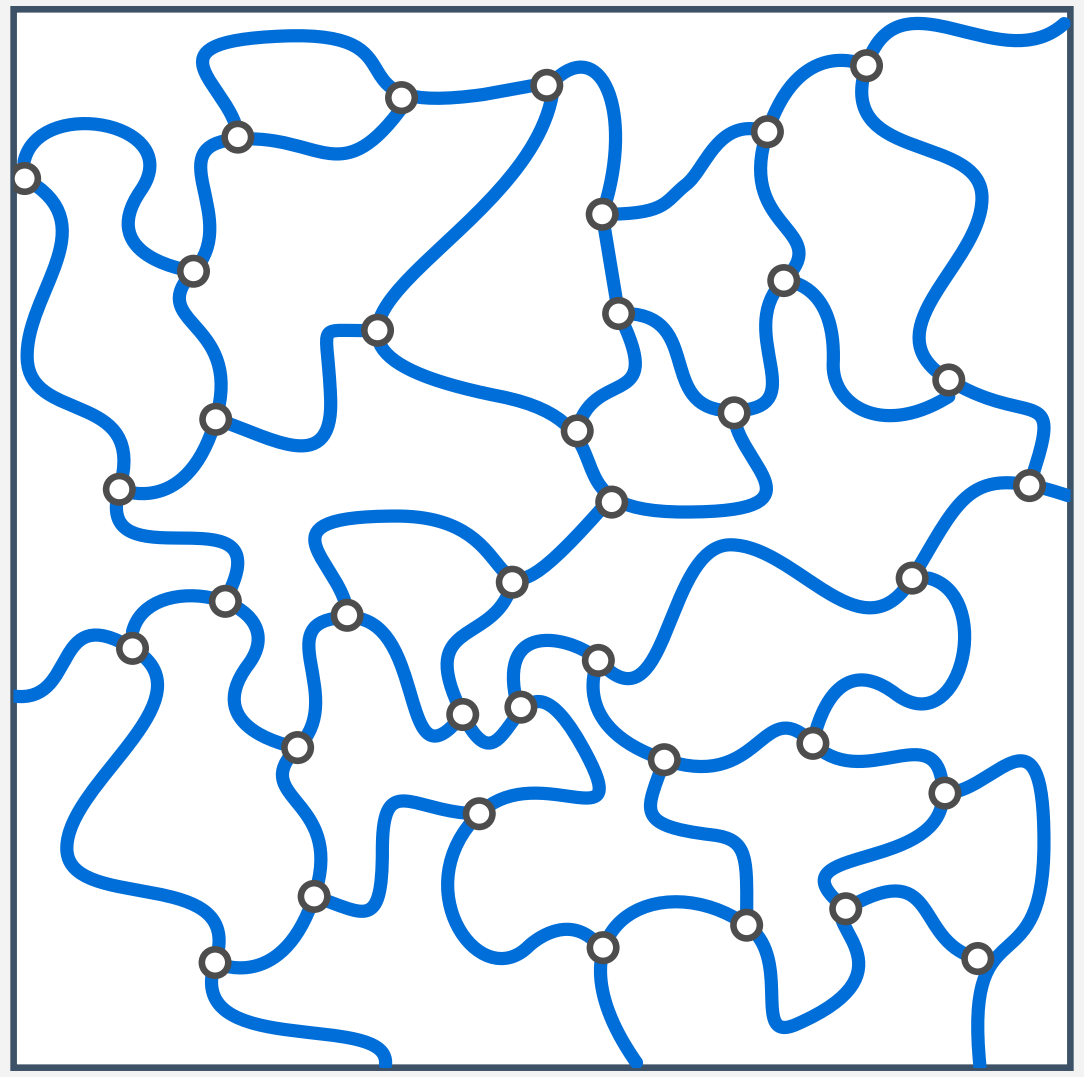


elastomers



T_g < room temperature

thermosets



T_g > room temperature

- **increased cross-linking density increases the T_g of thermosets**
- **impact: as thermoset fabrication proceeds, gradually decreased mobility can slow down synthesis**
  (hence, the need to cross-link at high *T* in some cases)

Copolymers

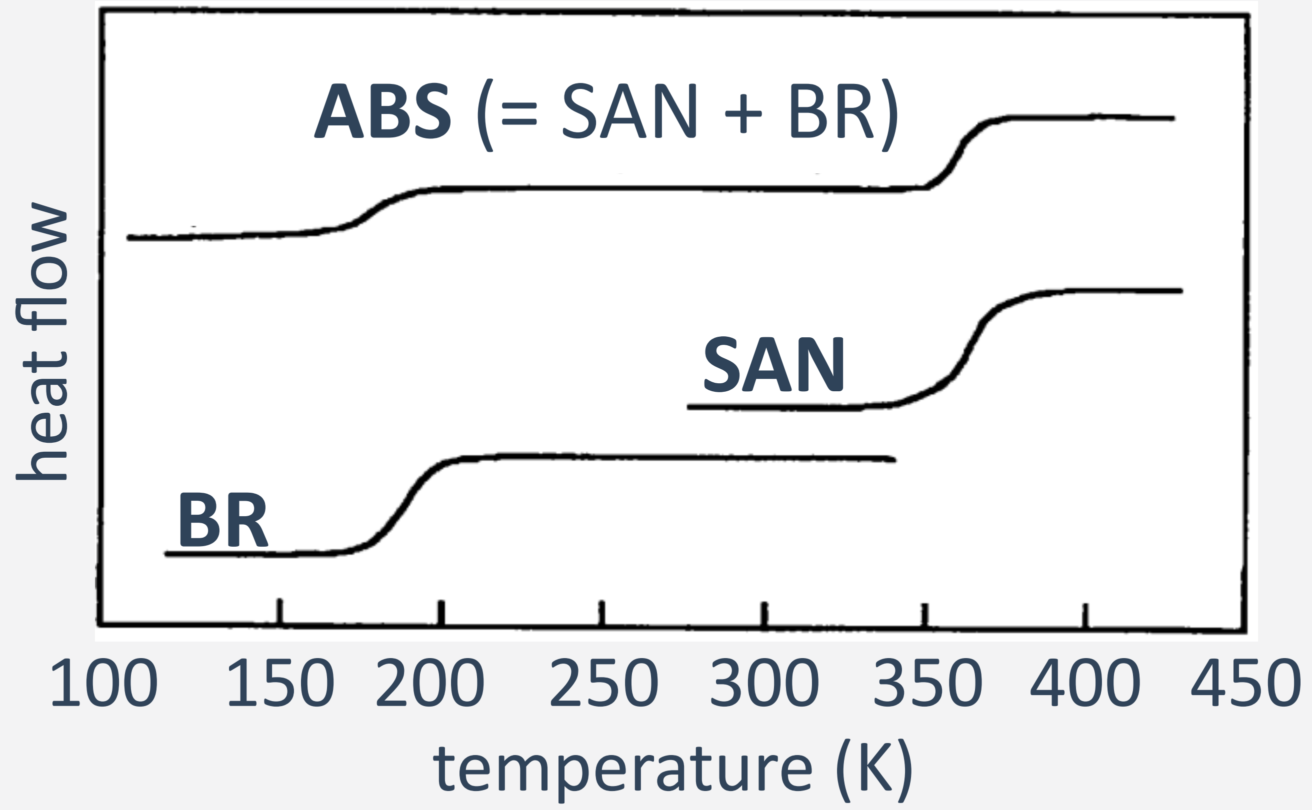
- **random copolymers, likewise homogeneous polymer mixtures, display a single T_g**

simple, empirical law of mixing:

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

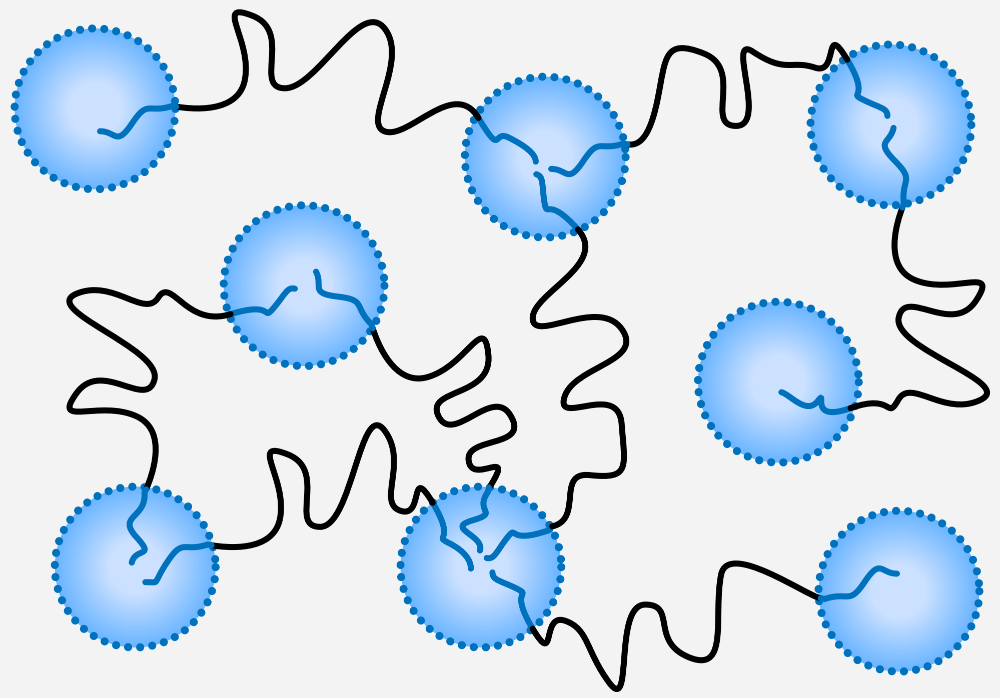
w_i: mass proportion of each component

- **several glass transitions in block copolymers depending on the number of components**



(also phase separated mixtures of polymers, Chapter 5)

- **thermoplastic elastomers: cross-links from glassy domains from one block at operating temperature**



glassy, hard physical cross-links
∅ 10 – 100 nm

soft matrix: low T_g

Overview of Glass Transition Temperatures in Linear Polymers

Polymer Type **[CH$_2$-CHR]$_n$**	**Substituent R**	T_g [°C]	**Trend Rational**
polyethylene	H	-80	increasingly bulky substituents ↓
polypropylene	CH_3	-20	
polystyrene	Ph	100	
polybutene	C_2H_5	-24	**internal plasticisation:** increasingly flexible substituents ↓
polypentene	C_3H_7	-40	
Polyhexene	C_4H_9	-50	
poly(methylacrylate)	$COOCH_3$	5	**internal plasticisation**
poly(ethylacrylate)	$COOC_2H_5$	-20	
poly(propylacrylate)	$COOC_3H_7$	-48	
poly(butylacrylate)	$COOC_4H_9$	-55	
polyvinylalcohol	OH	85	**polar groups**
polyvinylchloride	Cl	81	
polyacrylonitrile	CN	105	
polyvinylacetate	$C(O)CH_3$	28	

Poly(methyl methacrylate) [CH$_2$-CCH$_3$R]$_n$	**Substituent R**	T_g [°C]	**Trend Rational**
PMMA (isotactic)	$COOCH_3$	145	**tacticity** for disubstituted repeat units
PMMA (atactic)	$COOCH_3$	105	
PMMA (syndiotactic)	$COOCH_3$	115	

Learning Outcome

- **in the amorphous state, polymer chains adopt their ideal random walk conformations. These become “frozen in” at temperatures below the glass transition temperature**

- **determination of T_g by dilatometry, calorimetry, static mechanical tests, and dynamic measurements**

- **the out-of-equilibrium nature of the glassy state, like the strong dependence on measurement speed and provided experimental time can be rationalised by the theory of Free volume**

- **high T_g values are favoured by high M_n, chain stiffness, strong interchain forces (specific interactions)**

- **if necessary, plasticisers can be used to reduce the T_g**