Dynamic arrest in multicomponent glass forming alloys

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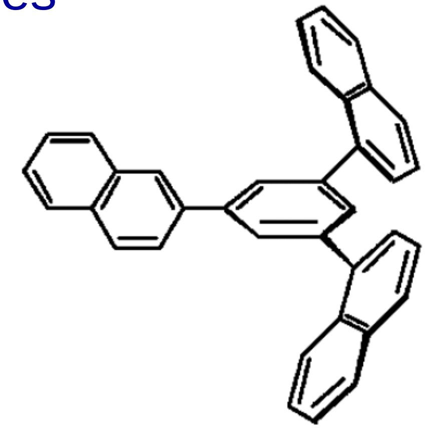
Outline

- Strategies for glass forming ability
- Diffusion in simple liquids
- Dynamic arrest and glass transition
- Radiotracer technique
- Pd alloys: - *D* of all components including Pd
  - Comparison with η and SE eq.
- Zr alloys
- Conclusions

- Directed covalent bonding
  oxide glasses, amorphous SCs, ….

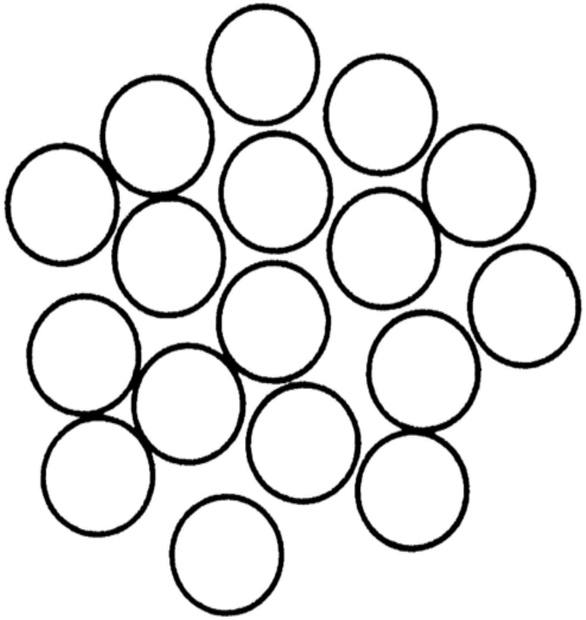
- Structural asymmetry and complexity
  single component molecular glasses

TNB



- Dynamic asymmetry (size disparity, short range order, …)
  multicomponent metallic glasses

Diffusion in simple liquids



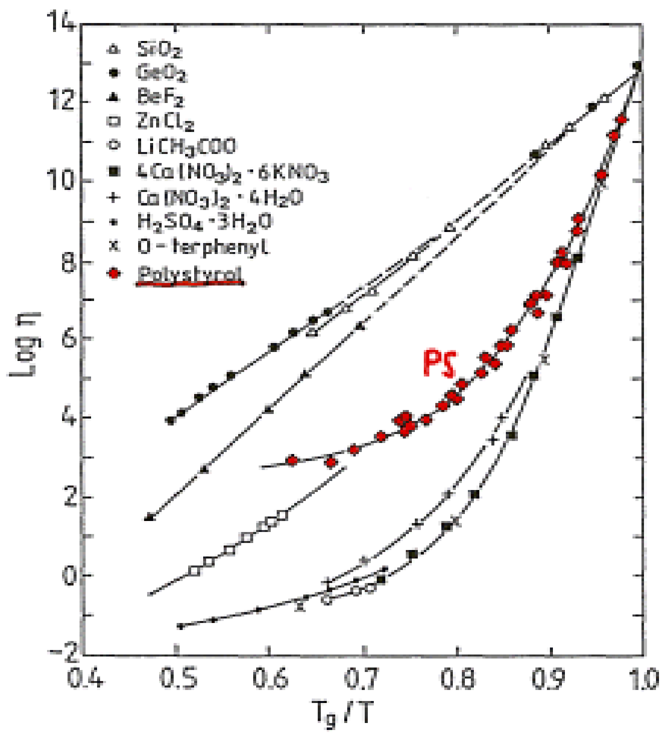
High *T*: "gas-like diffusion"

$$D \propto \lambda \bar{v}$$

$$\bar{v} \propto 1/\sqrt{m}$$

$$\text{Stokes–Einstein:} \quad D(T) \propto \frac{1}{d}\frac{T}{\eta(T)}$$

Dynamic arrest and glass transition



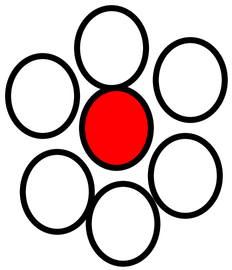
Uncorrelated collisions

⬇

correlation

⬇

cage effect



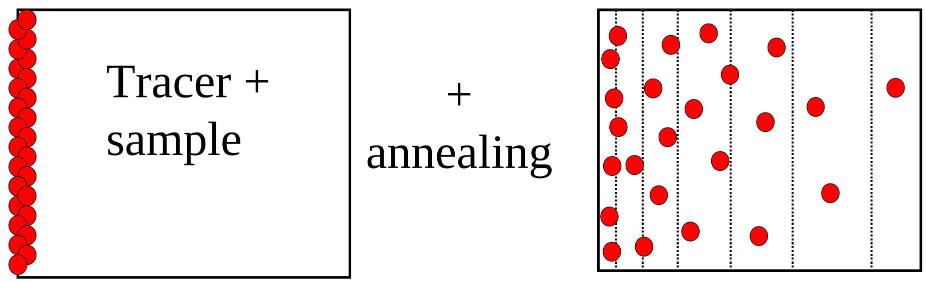
$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right)$$

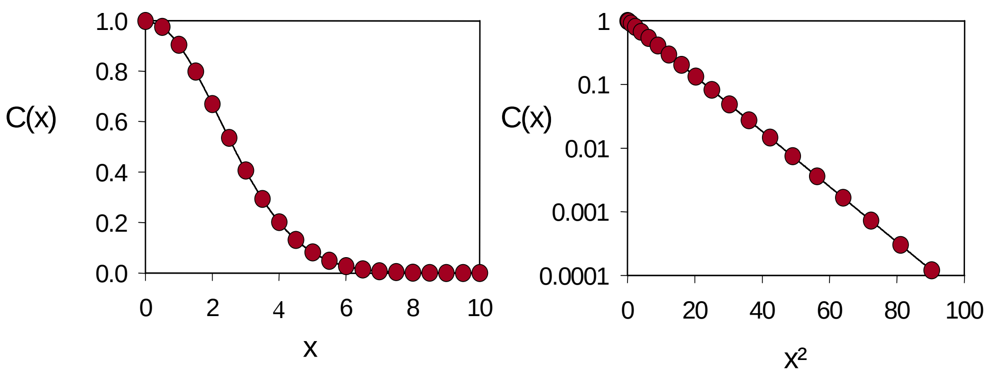
Breakdown of SE eq. ⇔ dyn. heterogeneity

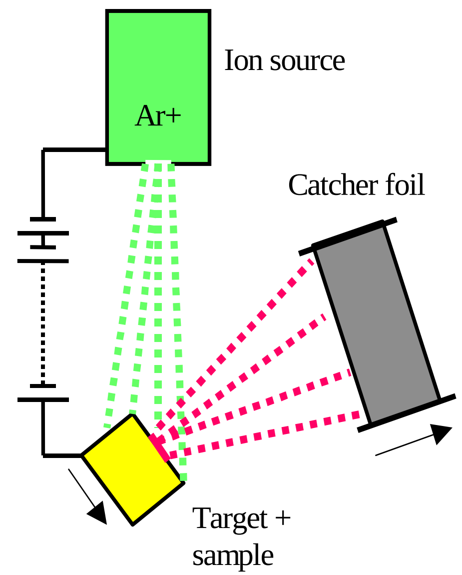
Mode coupling theory (Götze, Sjoegren)

- Cage effect ⇒ liquid-like motion freezes in at $T_c > T_g$
- $T < T_c$: only “medium assisted highly collective hopping”

Radiotracer technique







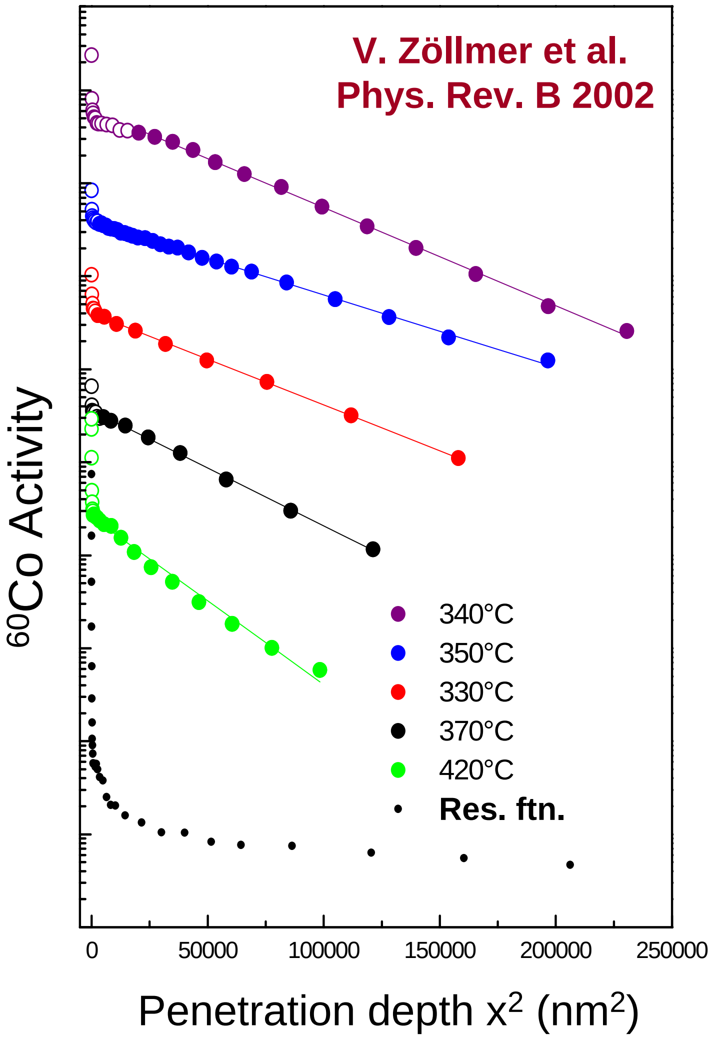
Faupel et al. J. Vac. Sci. Tech. 1992

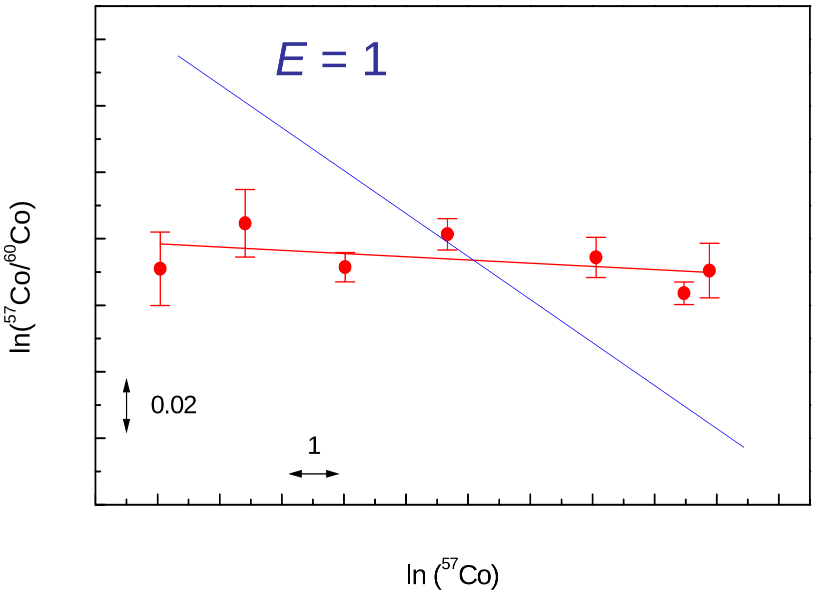
µm range: grinding

Thin film solution: $c(x,t) = \frac{I_0}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right)$

Diffusion profiles and isotope effect

$Pd_{40}Cu_{30}Ni_{10}P_{20}$ glass

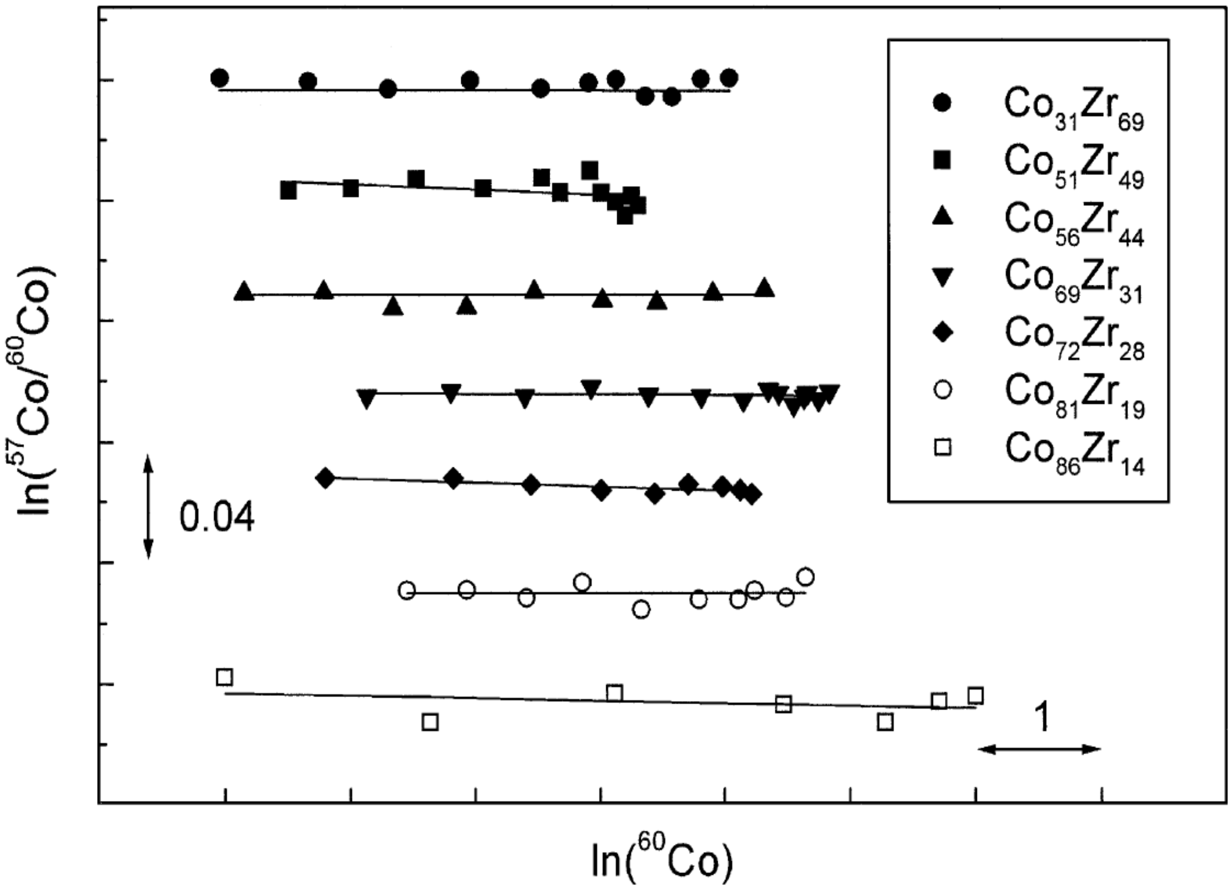




$$\ln\left(\frac{c_a}{c_b}\right) = const. - \left(\frac{D_a}{D_b} - 1\right)\ln c_a$$

$$E = \left(\frac{D_a}{D_b} - 1\right)\left(\sqrt{\frac{m_b}{m_a}} - 1\right)^{-1}$$

Co isotope effect in Co-Zr glasses



Heesemann, Zöllmer, Rätzke, Faupel, Phys. Rev. Lett. 84, 1467 (2000)

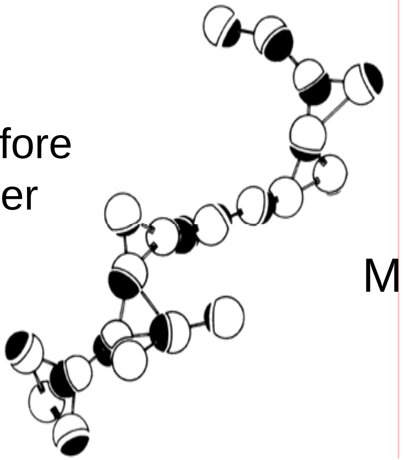
Mass dependence - isotope effect *E*

Isotope effect: $$E = \left(\frac{D_a}{D_b} - 1\right)\left(\sqrt{\frac{m_b}{m_a}} - 1\right)^{-1}$$

Ideal single jump: $$D \propto \upsilon_0 \propto \frac{1}{\sqrt{m}}$$ → *E* = 1

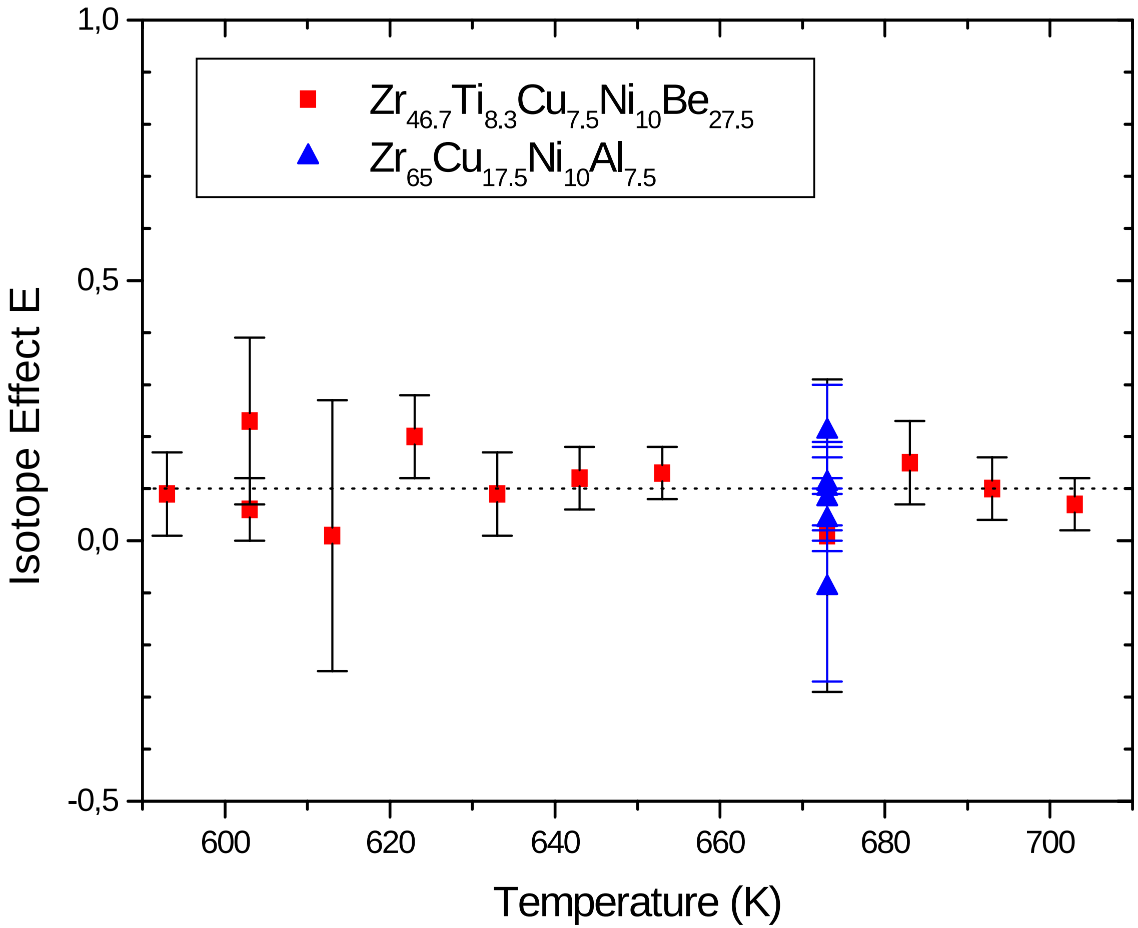
Collectice hopping: $$\upsilon_0 \propto \frac{1}{\sqrt{M}}$$ → *E* << 1

O before
● after



MD simulations: Schober et al., Teichler et al, ...

Co in Zr-based systems melt below T_c



Ehmler, Heesemann, Rätzke, Faupel, Geyer, Phys. Rev. Lett. 80, 4919 (1998)

Diffusion in Pd-Cu-Ni-P alloys

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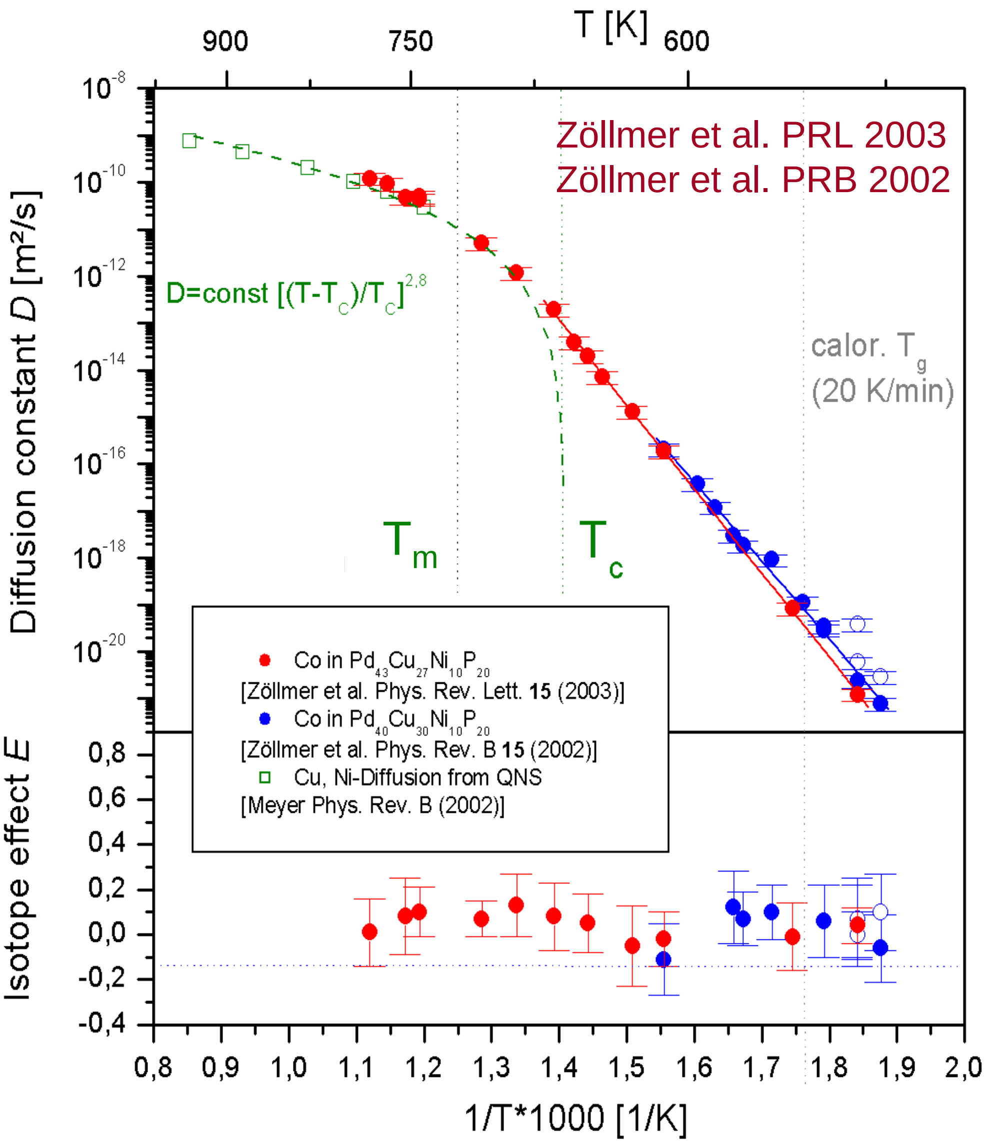


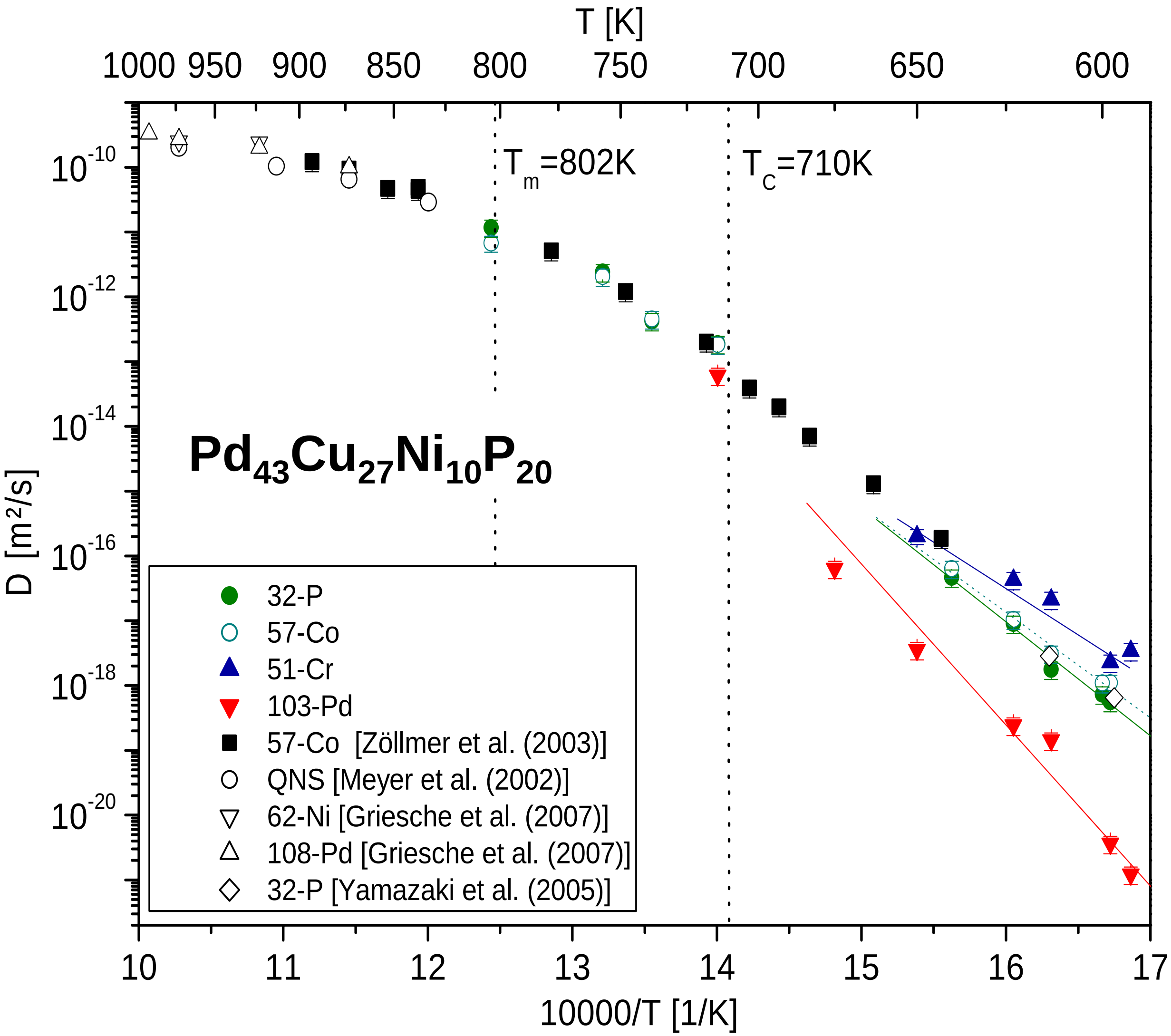
Isothermal glass transition
no change in $E \Rightarrow$
no change in mechanism

$T < T_c$
collective hopping

$T > T_c$
Barriers decay $\Rightarrow$
onset of liquid-like motion

Equilibrium melt
$E \approx 0 \ \Rightarrow$ far from binary collisions
highly viscous melt

Decoupling of component diffusivities

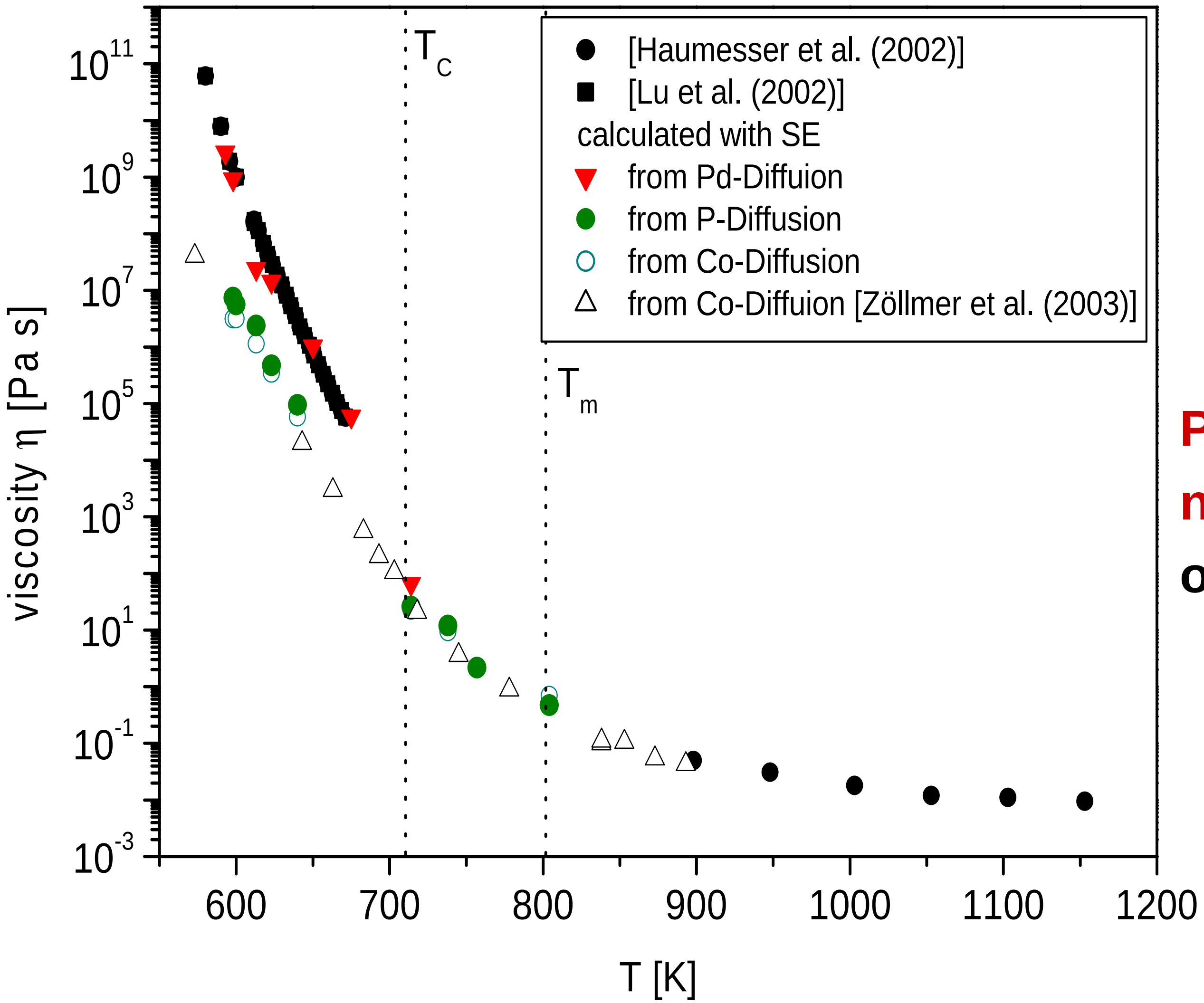


Small components:
little decoupling

Pd:
strong decoupling
- 10^4 at T_g
- onset close to T_c

Bartsch, Rätzke, Meyer, Faupel, Phys. Rev. Lett. 104, 195901 (2010)

Test of Stokes Einstein equation



$$D = \frac{k_B T}{6\pi\eta r}$$

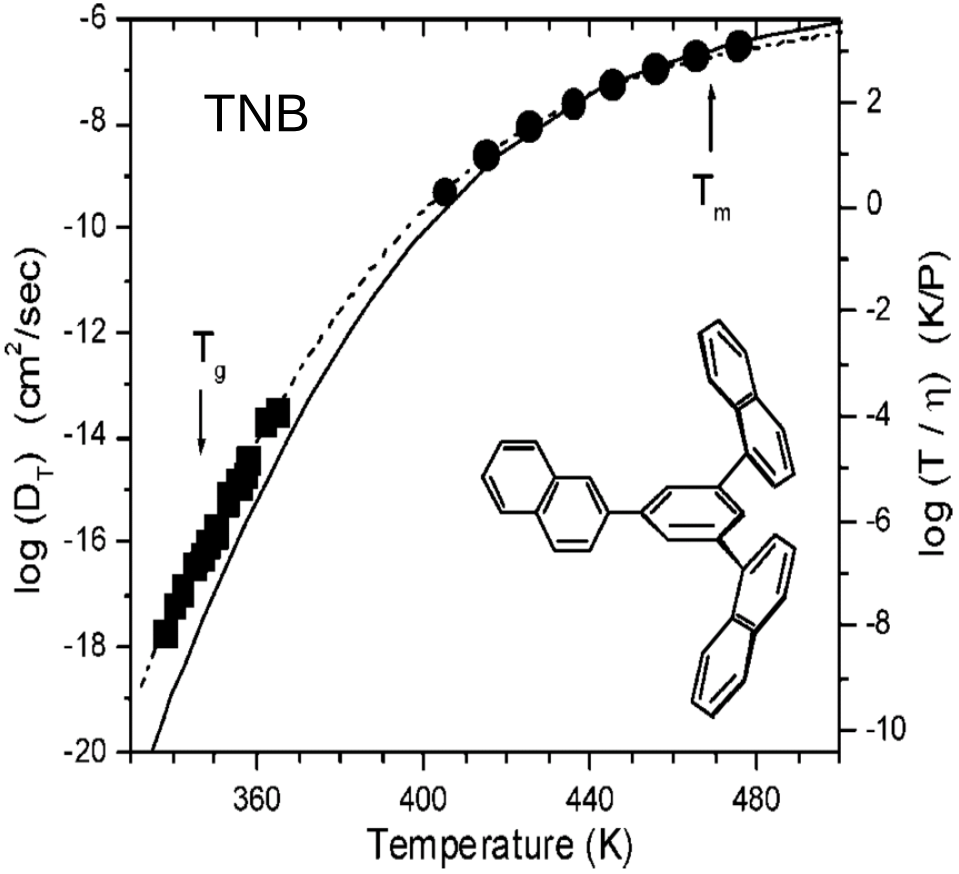
Pd:

no viscous decoupling

over 14 orders of magn.

Bartsch, Rätzke, Meyer, Faupel, Phys. Rev. Lett. 104, 195901 (2010)

Single comp. molecular glass formers

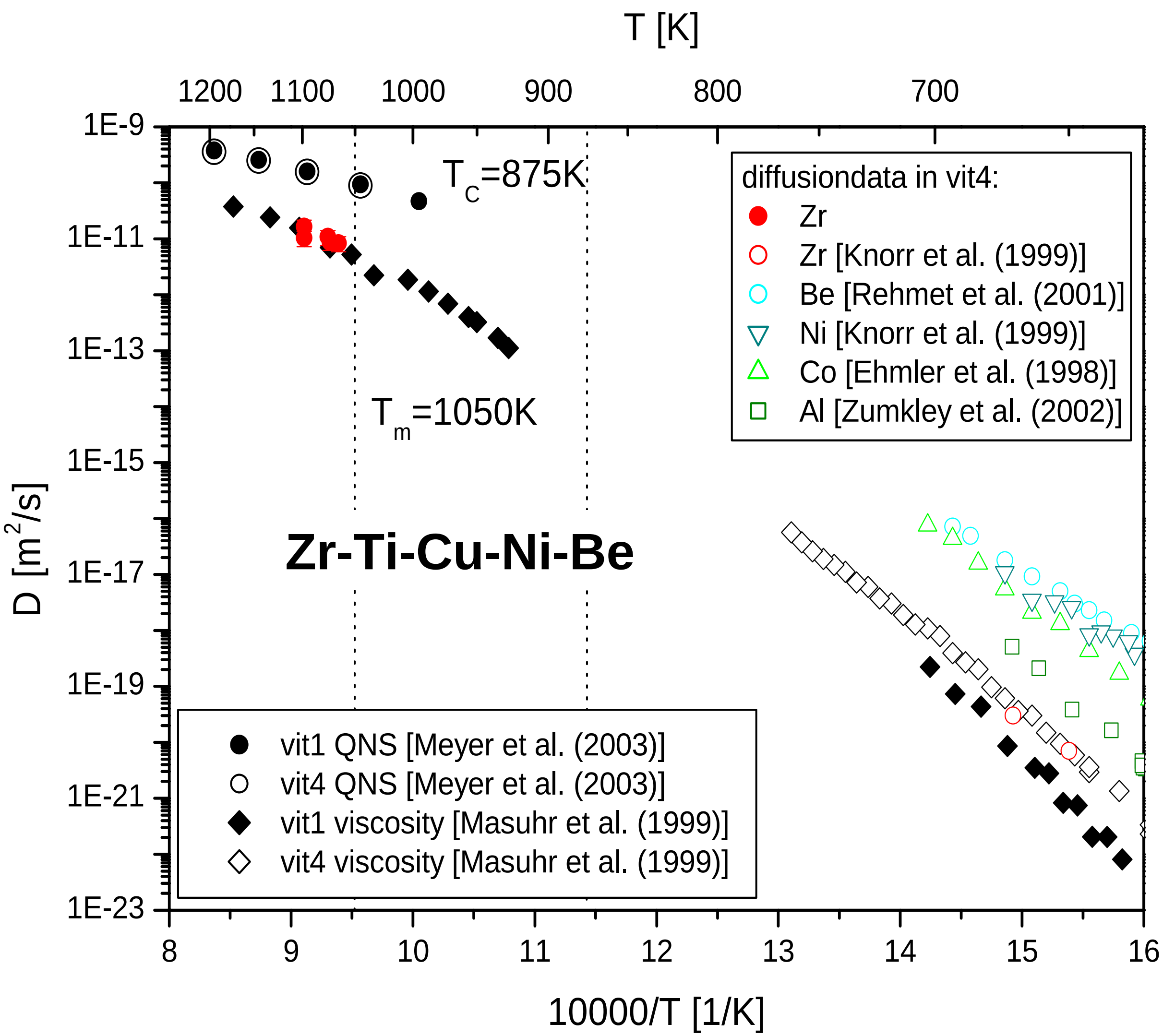


Swallen,…, Ediger, J. Phys. Chem. B 113, 4600 (2009)

Interpretation

- Pd forms slow subsystem
- Subsystem has to rearrange for viscous flow
- No covalent bonds: only SRO and size disparity
- Hard sphere MD simulations* $\Rightarrow$ size disparity sufficient

*e.g., Kumar et al., J. Chem. Phys. (2004)



- **Component decoupling also above T_c**
- **SE valid only for Zr? (η only for vit1)**

⇓

Slow Zr subsystem even in equilibrium melt?

Conclusions

- Little component decoupling of D_i for small components
- Strong decoupling large/small
- No viscous decoupling for large component

  $\Rightarrow$ slow subsystem key to GFA
- Subsystem without covalent bonds

  - size effects
  - sort range order

Earlier work: Faupel, Frank, Mehrer, Schober, Teichler et al., Review Modern Physics 75, 237 (2003)