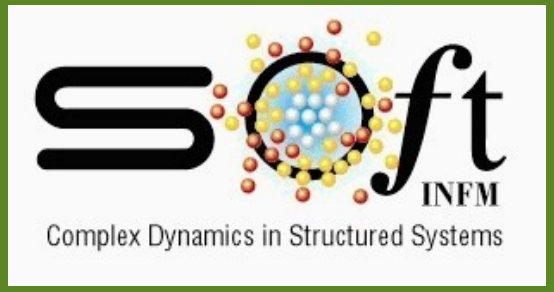

Universal Scaling Between Relaxation And Caged Dynamics In Glass-Forming Liquids, Polymers And Mixtures

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[3] INFM-CNR CRS SOFT, Roma, Italia

Outline

- Background
- Numerical Simulations
- Comparison with experiments
- Conclusions

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An old idea still intriguing: relaxation vs. vibrations

The idea that structural relaxation and vibrational dynamics are connected despite to the enormous time scale separation, had old roots [Tobolsky(1943)] ...

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$\approx 10^{-12}$ s

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$$\tau \stackrel{?}{=} f\left(\langle u^2 \rangle\right)$$

$\approx 10^{-12}$ s

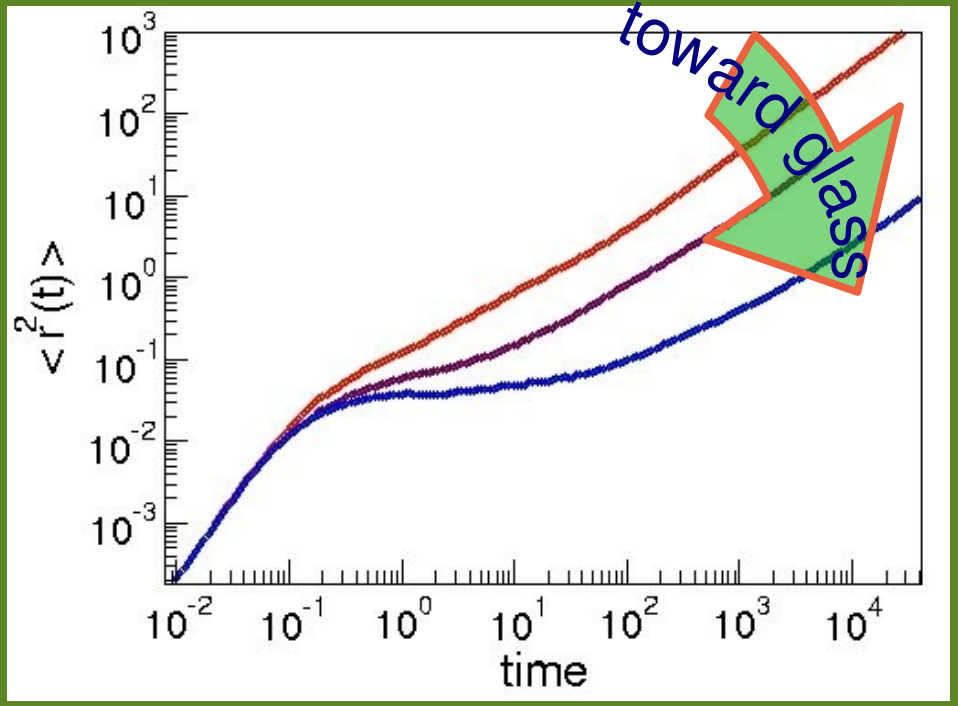
$\approx 10^{2}$ s @ Tg

...but it is still intriguing

[Nemilov(1978), Brawer(1984), Dyre(1996), Scopigno(2003),.....]

Focusing on the cage effects

MSD exhibits different regimes:
ballistic caging relaxing



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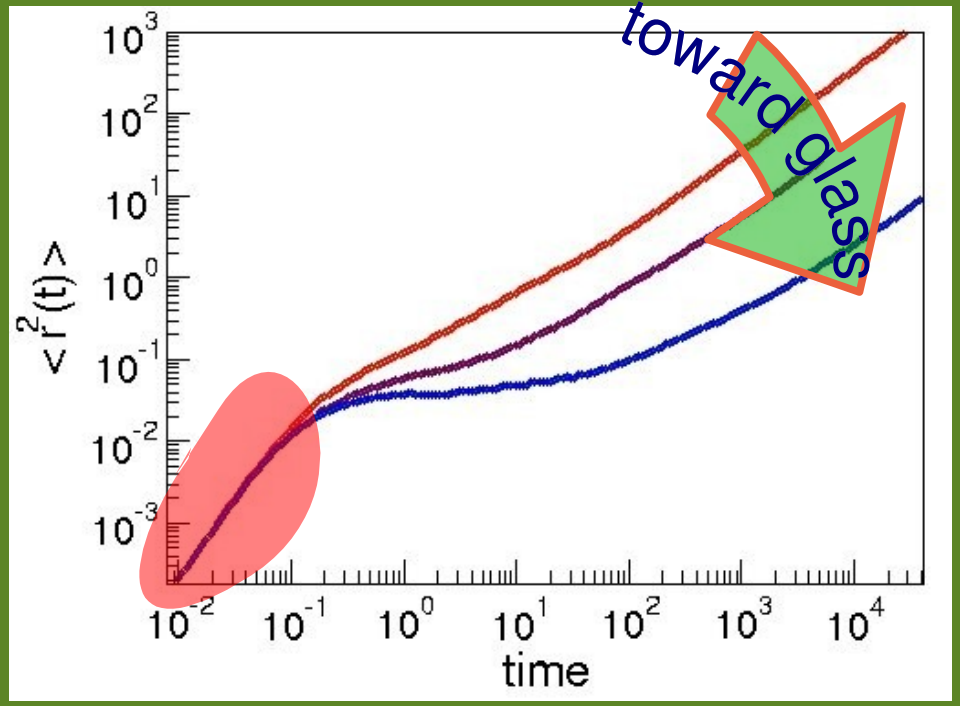

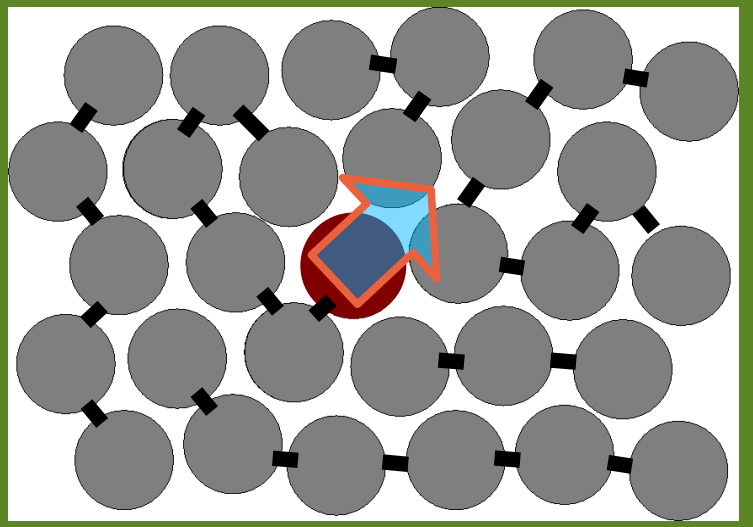

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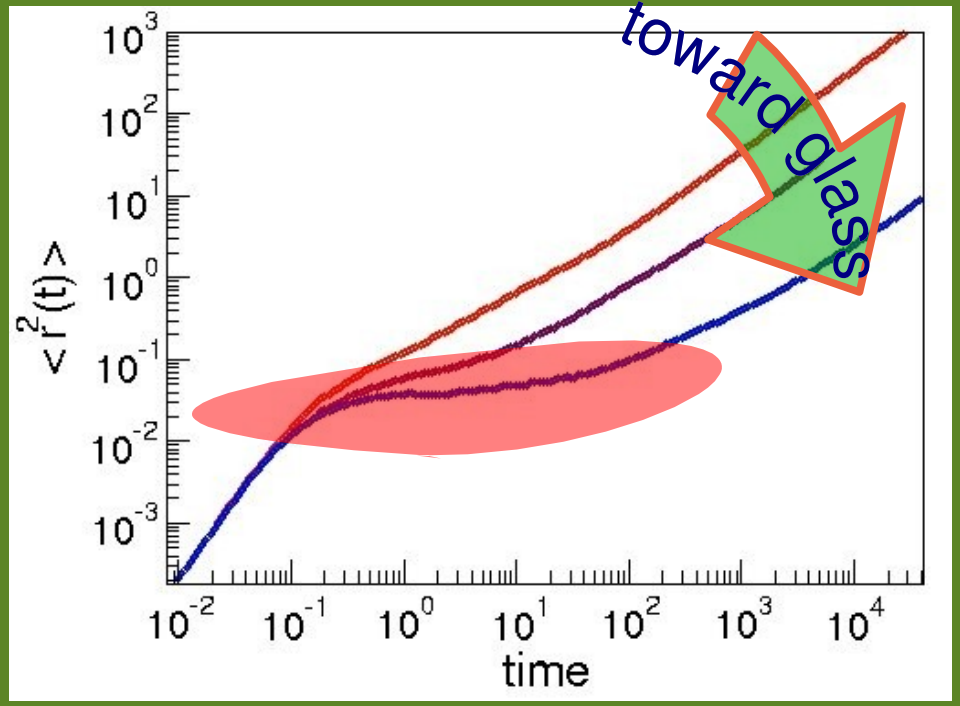

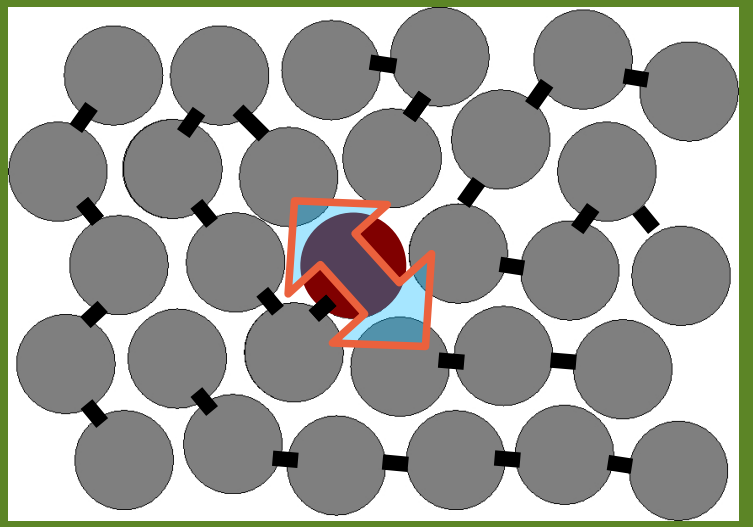

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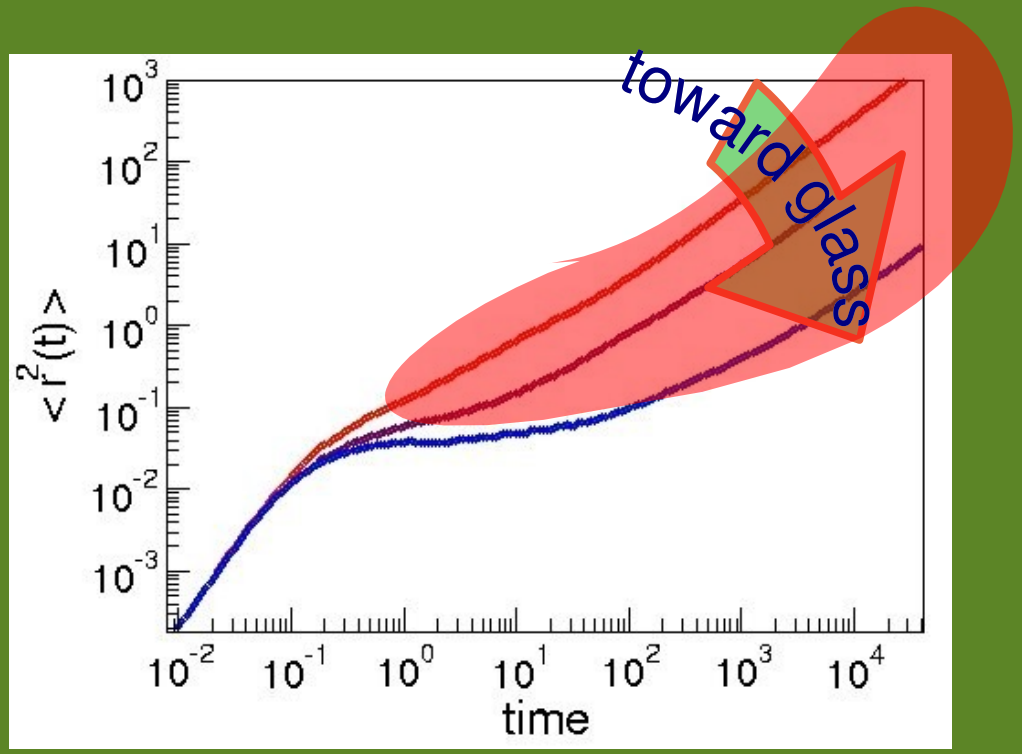

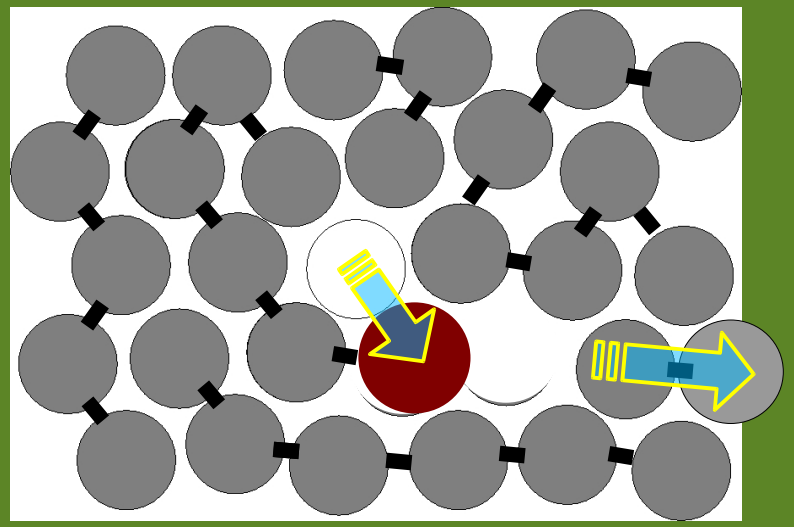

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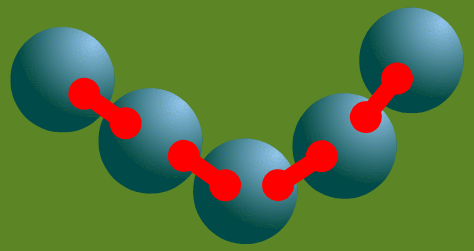
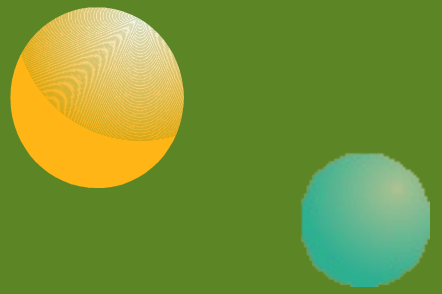
Models:

a) Bead-spring flexible polymer melt

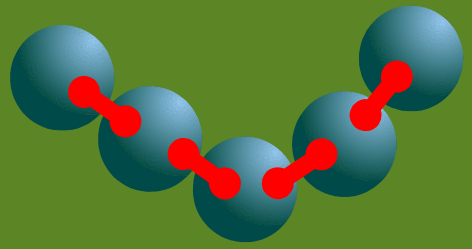


b) Modified Kob-Andersen Binary Mixture

- **80 : 20**
- **σ_B / σ_A = 0.88**
- **σ_{AB} / σ_A = 0.8**
- **m_B / m_A = 1**

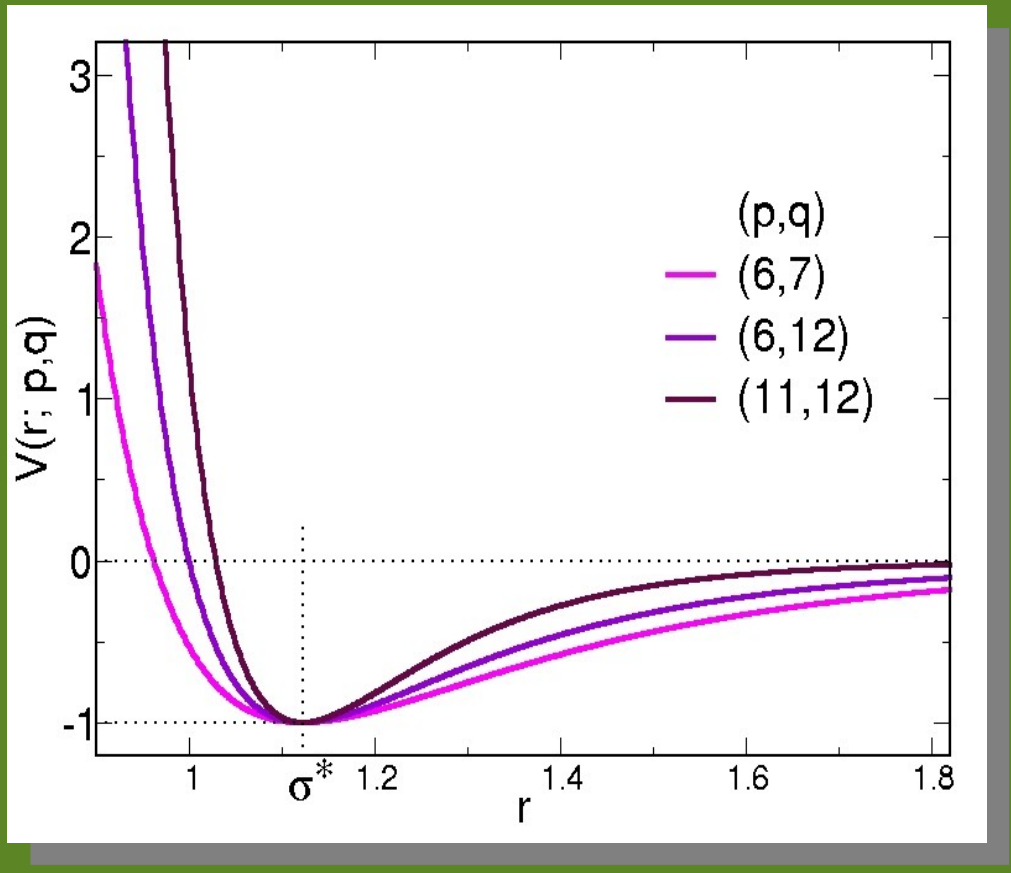


Models : control parameters



$$V_{LJ}(r;p,q) = \frac{\epsilon}{q-p}\left(p\left(\frac{\sigma}{r}\right)^q - q\left(\frac{\sigma}{r}\right)^p\right).$$

- Density *ρ*
- Temperature **T**
- Chain length **M** (polymer)
- Potential softness: **q** and **p** exponents

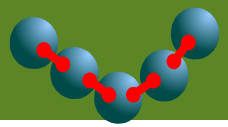


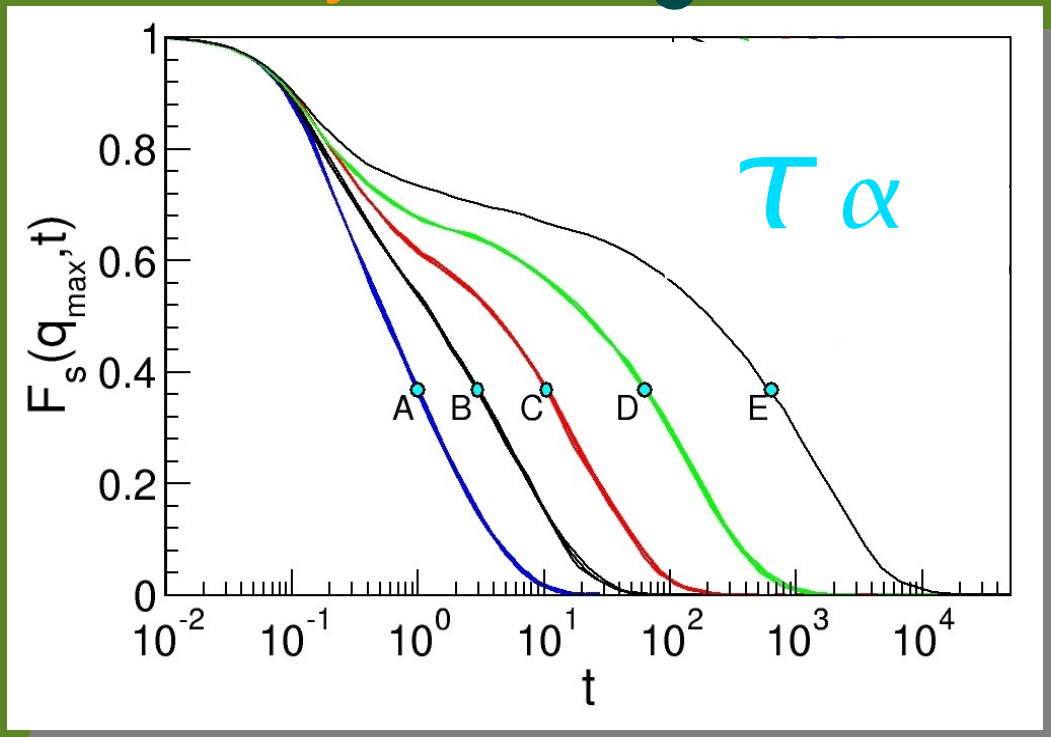
Equivalent ISF States

DIFFERENT STATES RELAX IN THE SAME WAY!!!

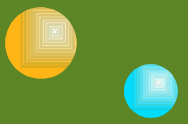
They define EDM (Equivalent Dynamics Multiplets)

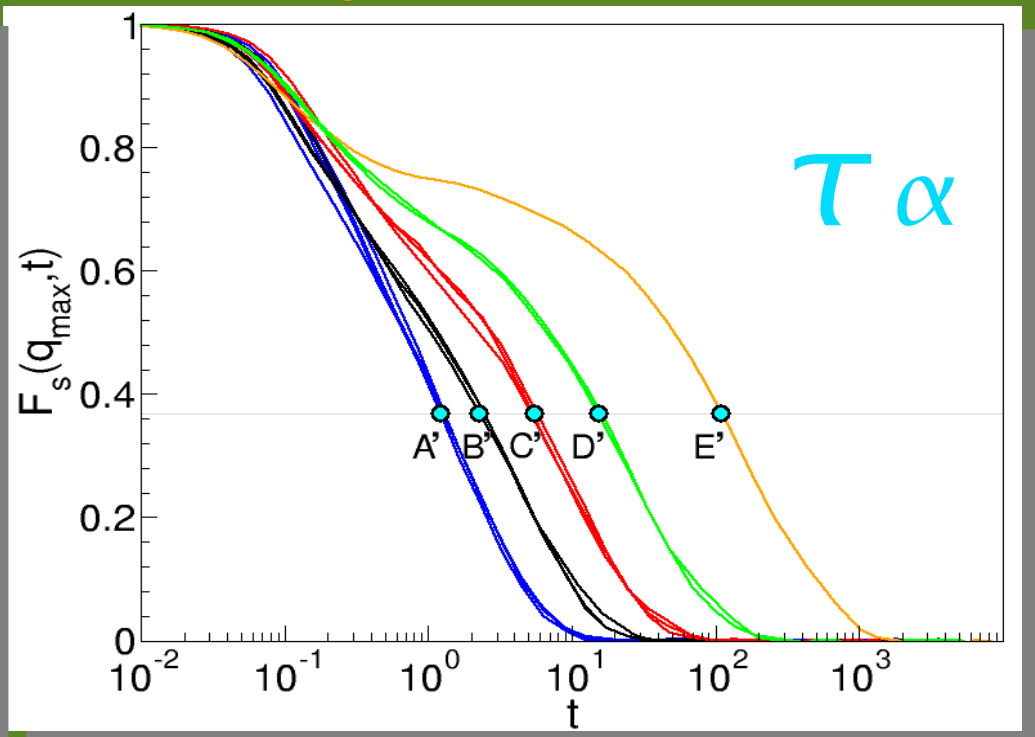
Polymers





Binary Mixture





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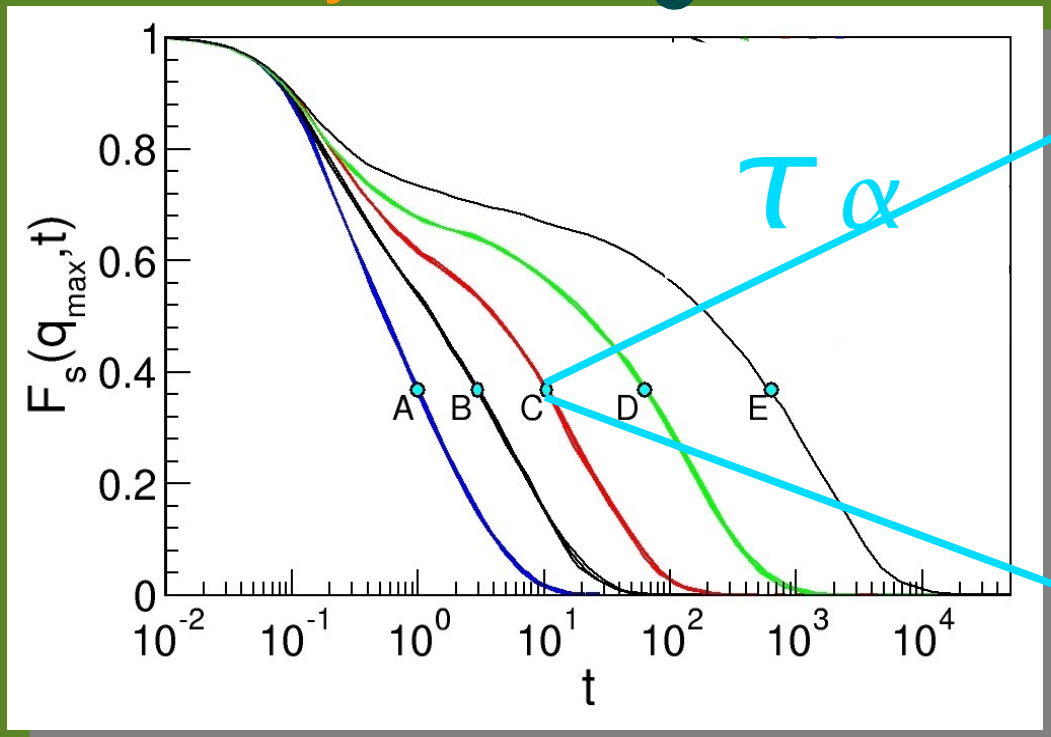

{ M, ρ, T, q, p}

{ 2, 1.033, 0.5, 10, 6}
{ 3, 1.056, 0.7, 12, 6}
{ 5, 1.033, 0.6, 12, 6}
{10, 1.056, 0.7, 12, 6}

Equivalent ISF States

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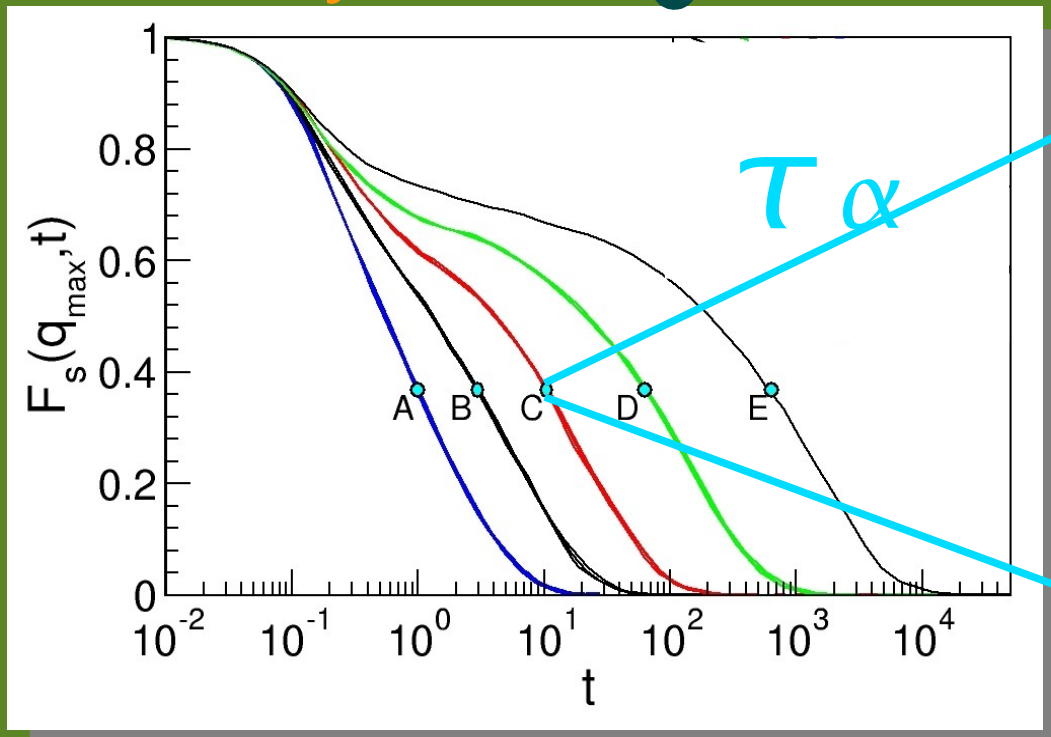

τ_α

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{ 2, 1.033, 0.5, 10, 6}
{ 3, 1.056, 0.7, 12, 6}
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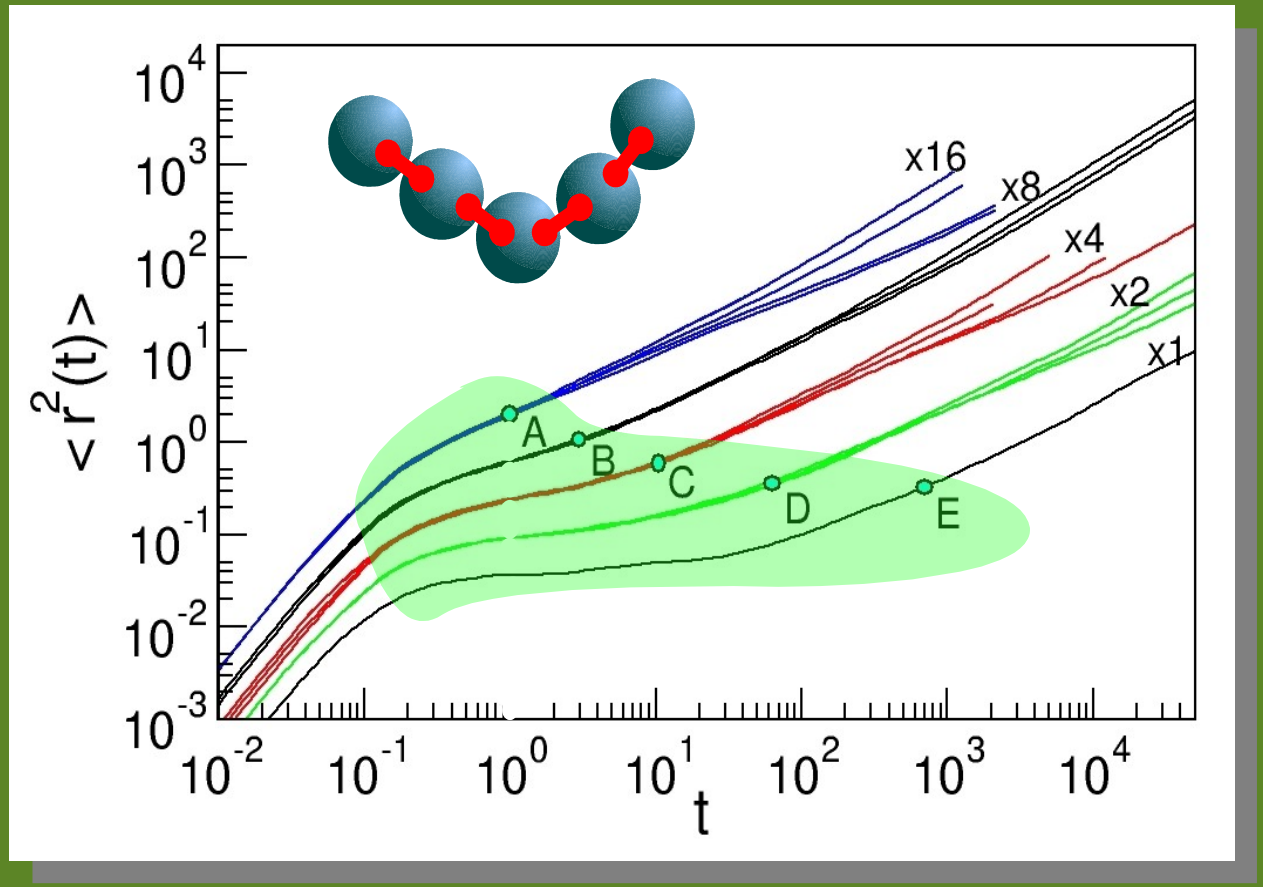
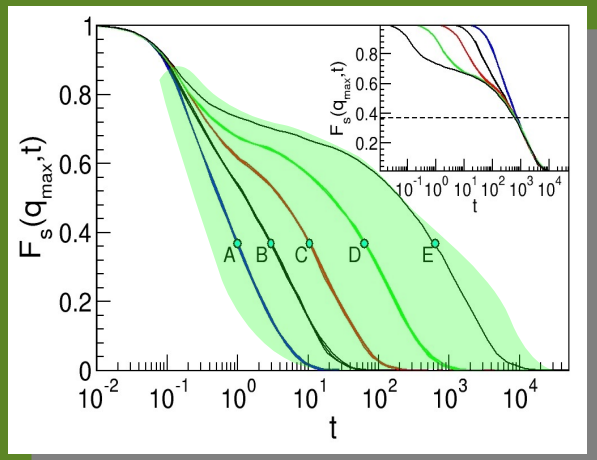
{10, 1.056, 0.7, 12, 6}

Then τ_α tags the α-relaxation of EDM (Equivalent Dynamics Multiplets)

Monomer displacement for EDMs





States with coincident α-relaxation time exibit coincidence in MSD from the end of ballistic until the relaxation time (in Polymeric Liquid)

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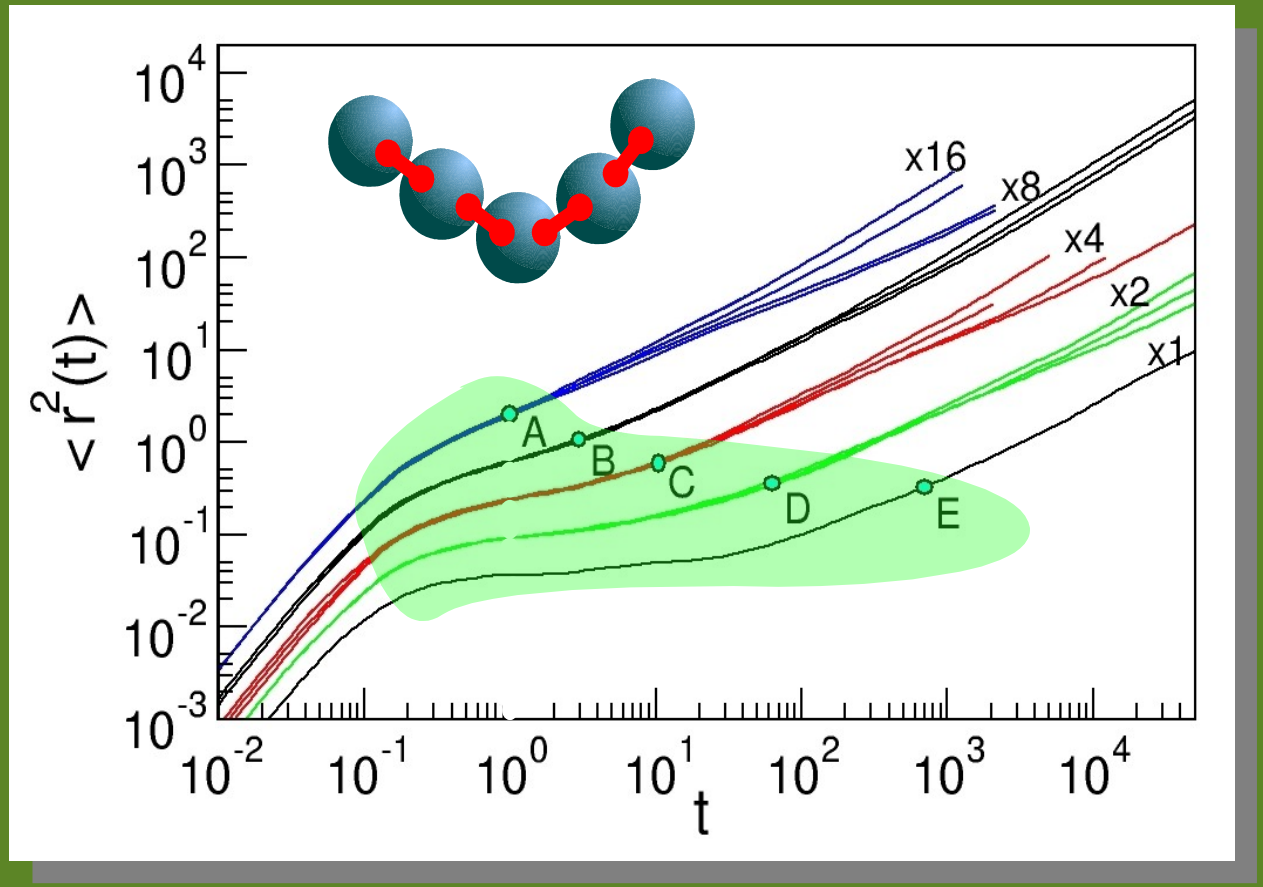
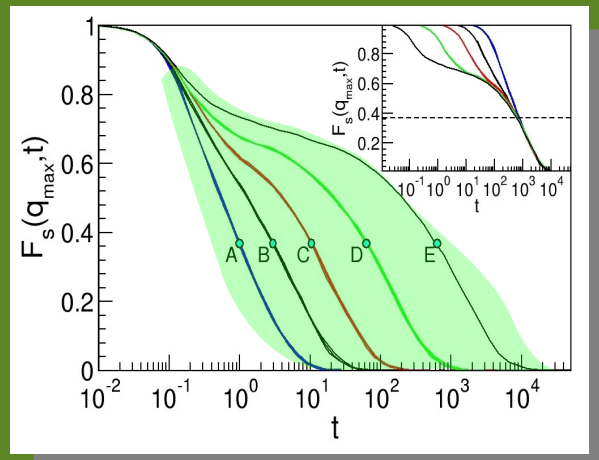
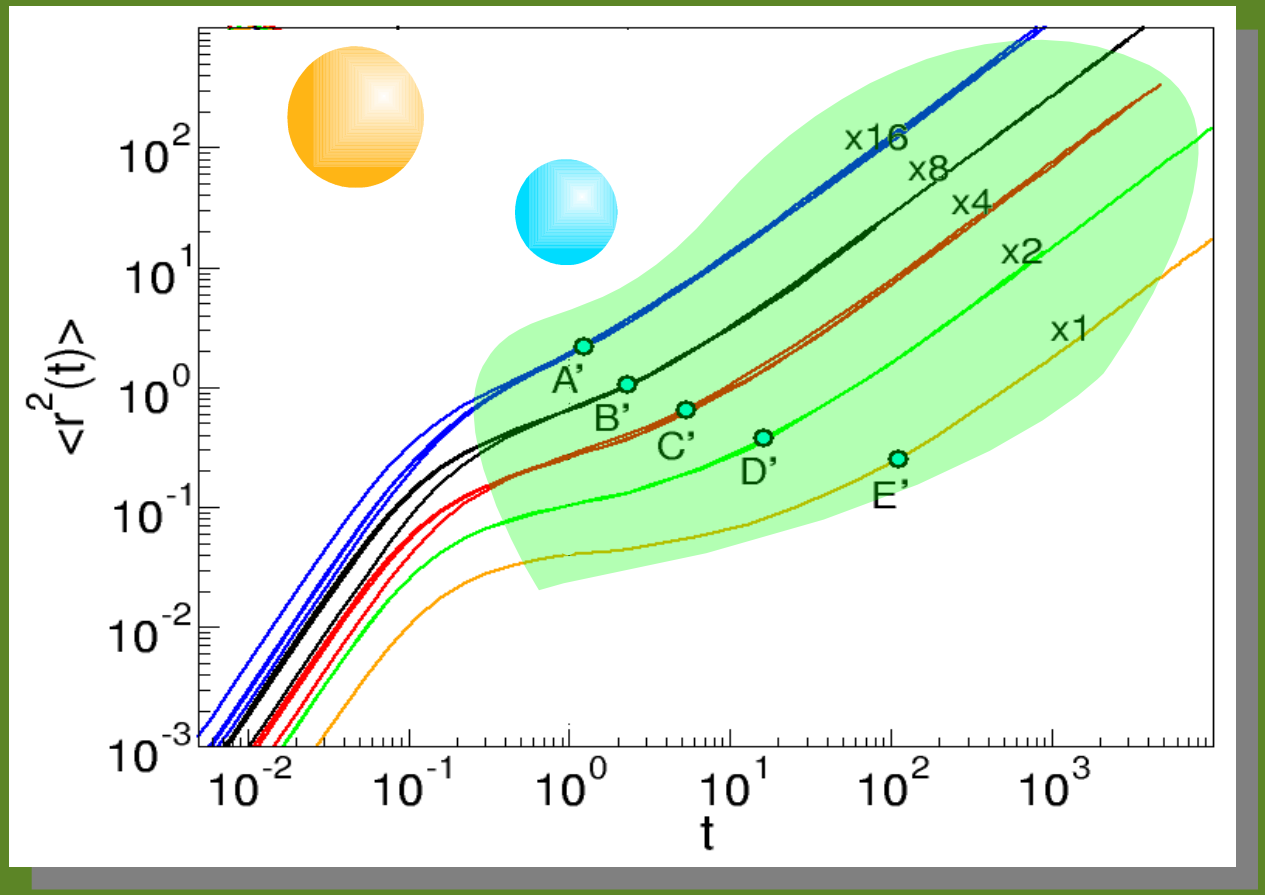


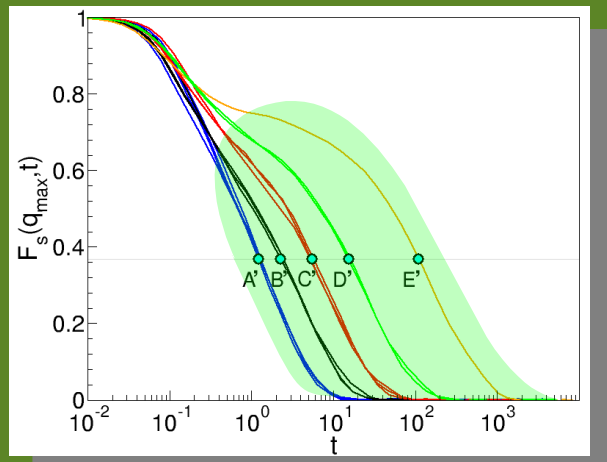


States with coincident α-relaxation time exibit coincidence in MSD from the end of ballistic until the relaxation time (in Polymeric Liquid)

VIBRATIONAL AND RELAXATION DYNAMICS ARE STRONGLY CORRELATED !!!

... more over for Binary Mixtures

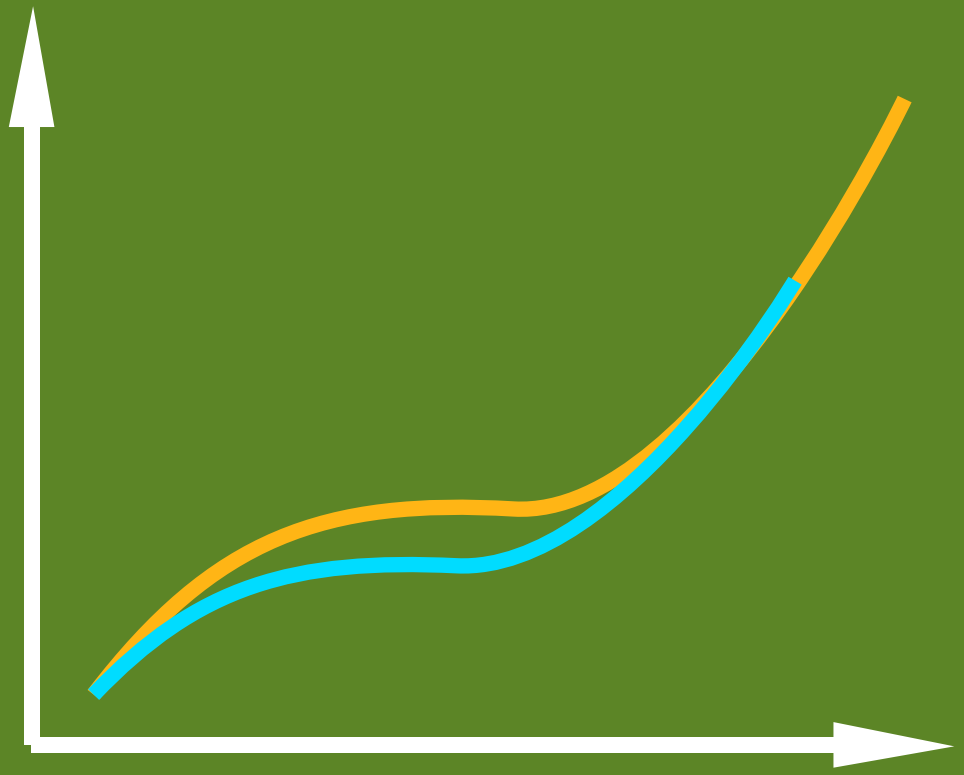




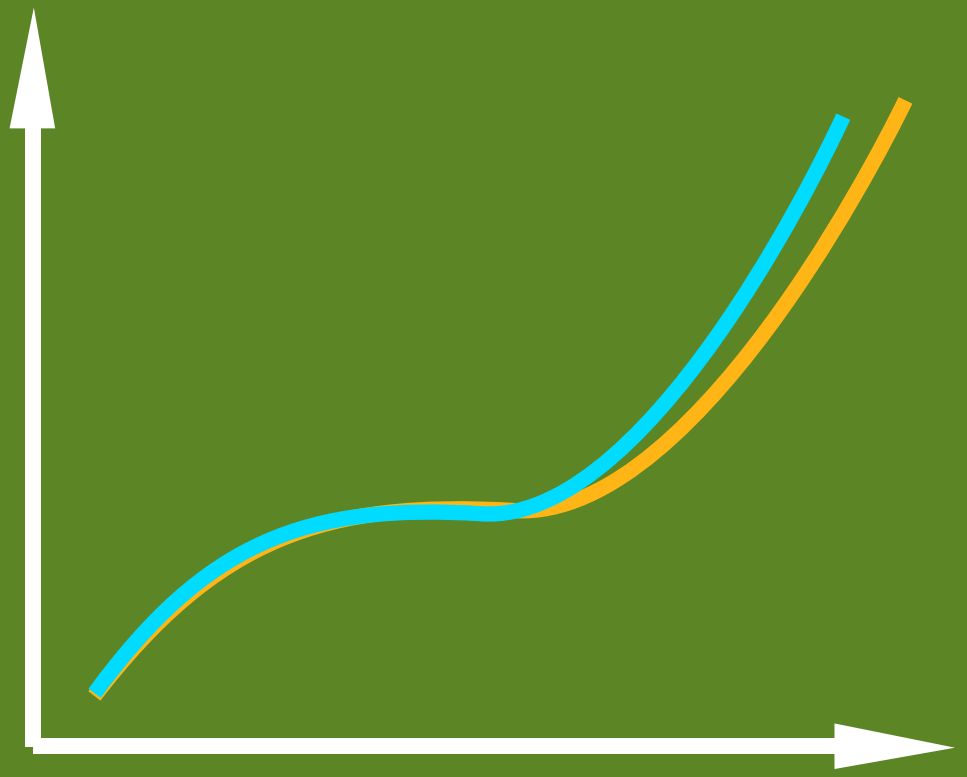
States with coincident α-relaxation time exibit coincidence in MSD from the end of ballistic onwards (in Binary Mixtures)

VIBRATIONAL AND DIFFUSIONAL AND RELAXATION DYNAMICS ARE STRONGLY CORRELATED !!!

Why do we care about EDMs ?



MSD



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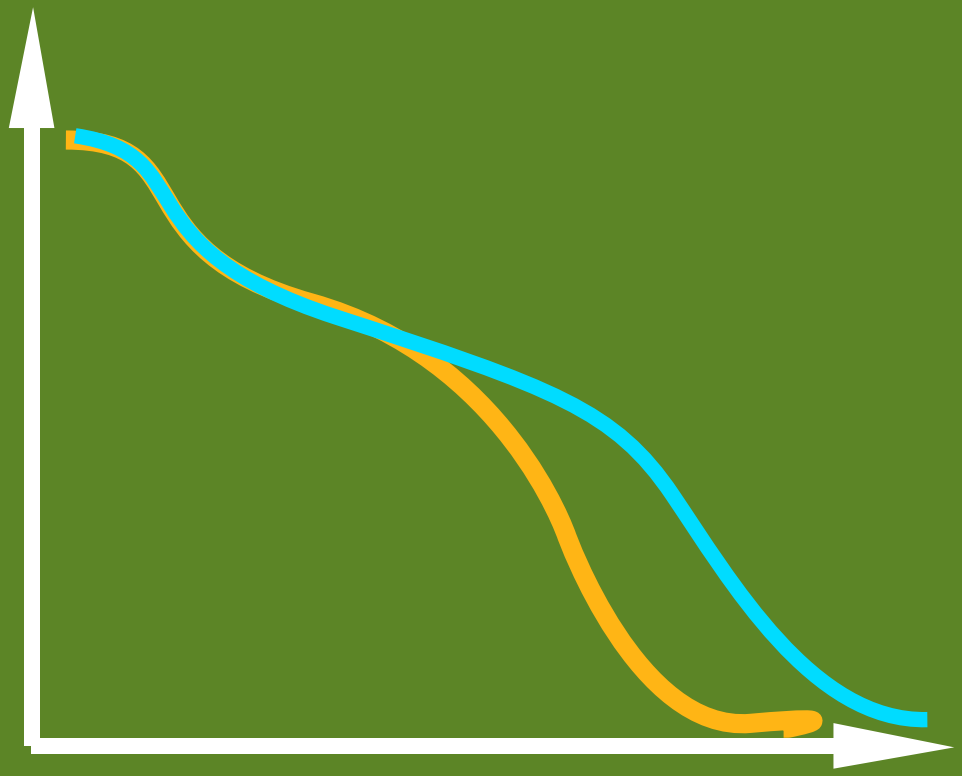
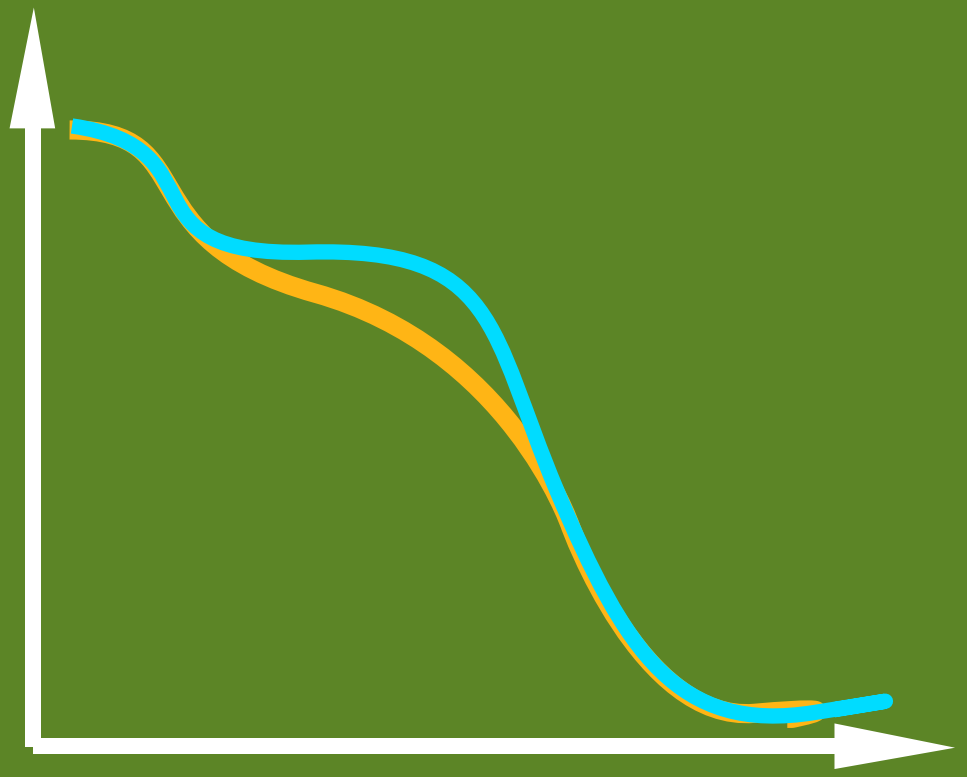


ISF



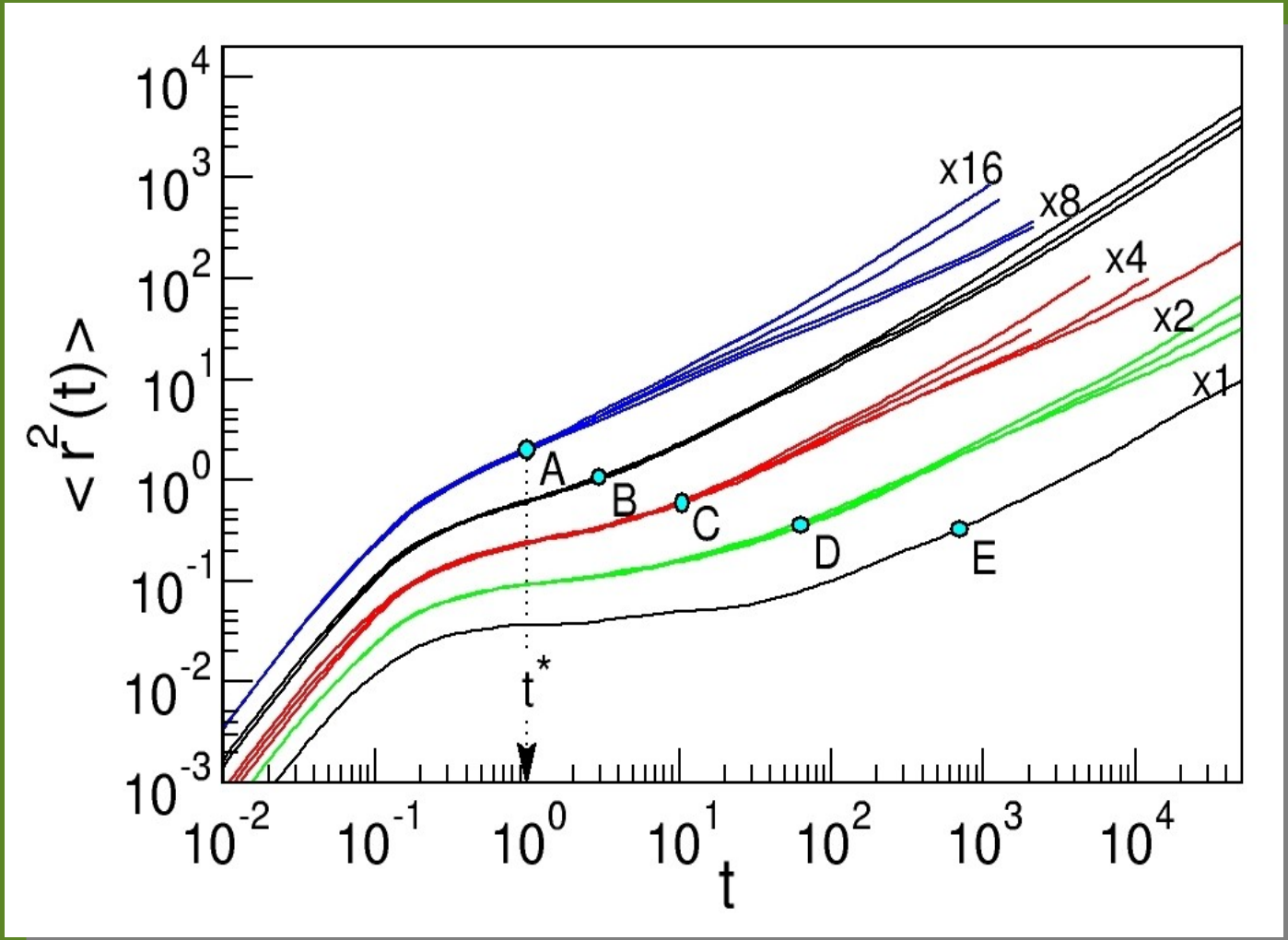
Why do we care about EDMs ?

ISF

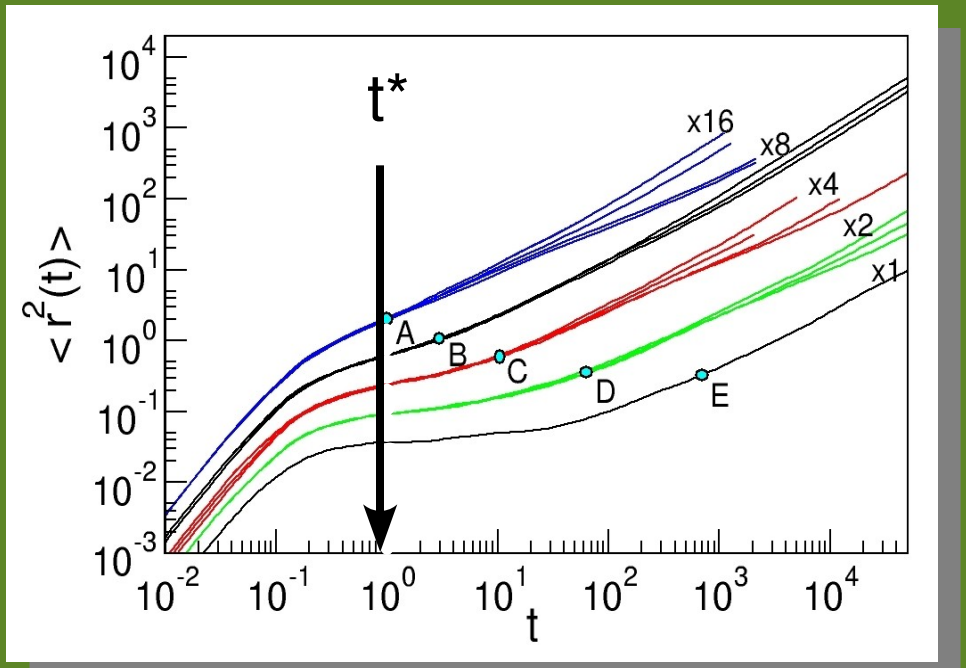
A tag for MSDs

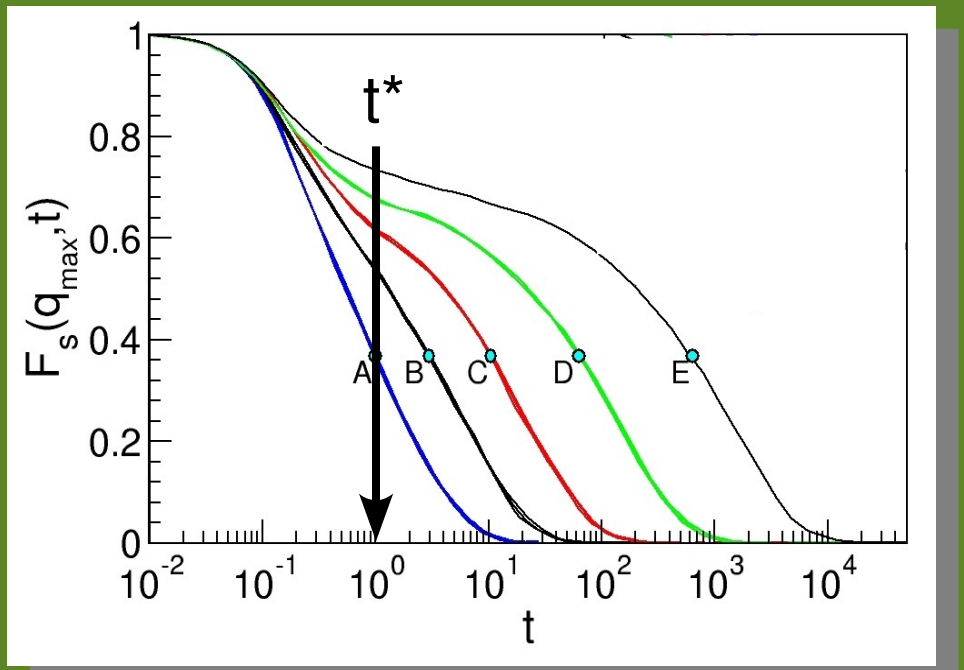
Vibrational dynamics is tagged by square amplitude of vibrations:

$$\langle u^2 \rangle = \langle \Delta r^2 (t = t^*) \rangle$$



Inflection points in MDS and ISF coincide





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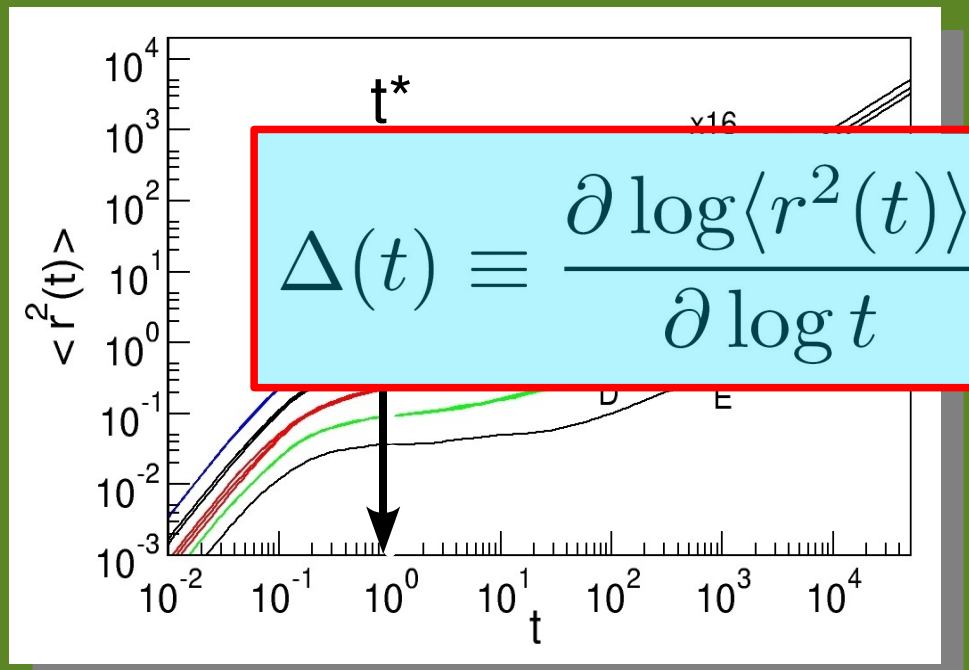
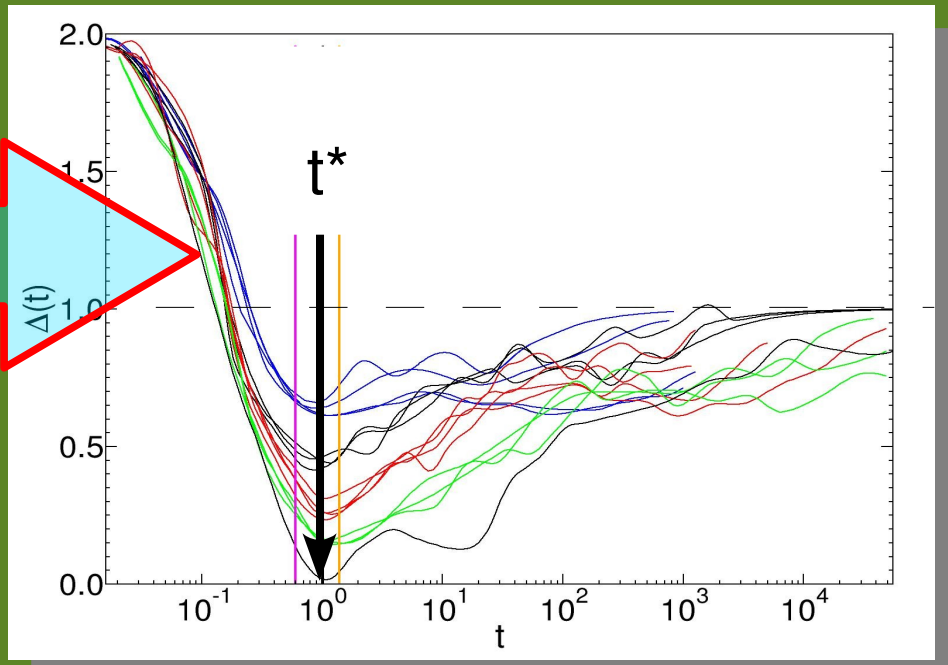
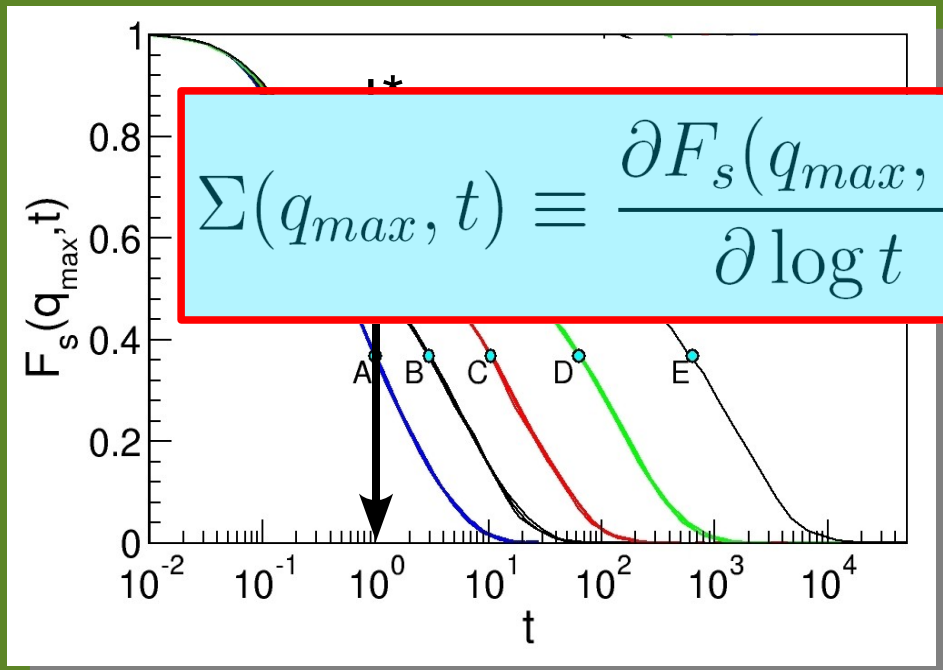
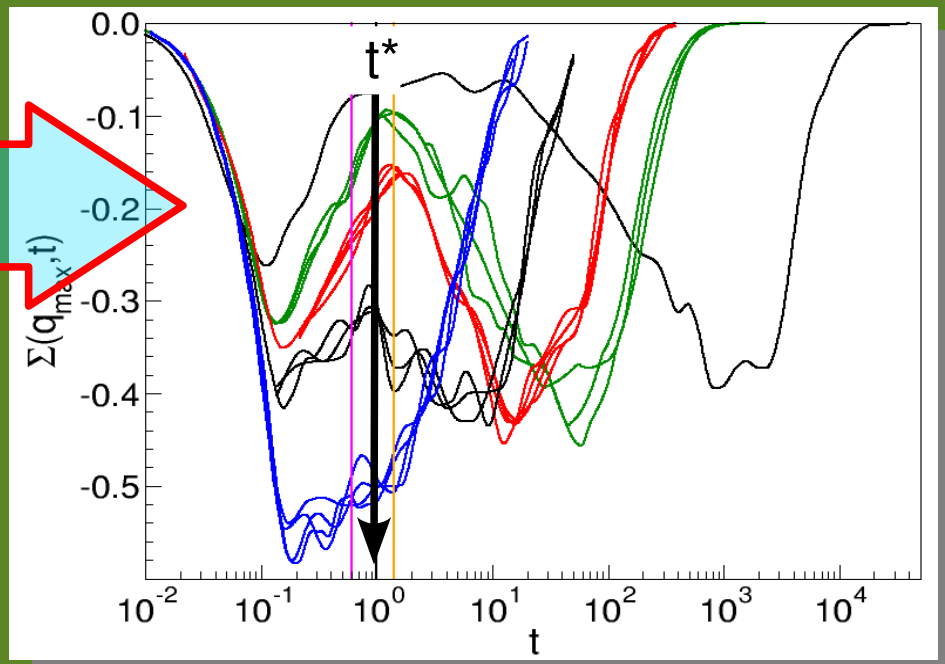


$$\Delta(t) \equiv \frac{\partial \log \langle r^2(t) \rangle}{\partial \log t}$$





$$\Sigma(q_{max}, t) \equiv \frac{\partial F_s(q_{max}, t)}{\partial \log t}$$



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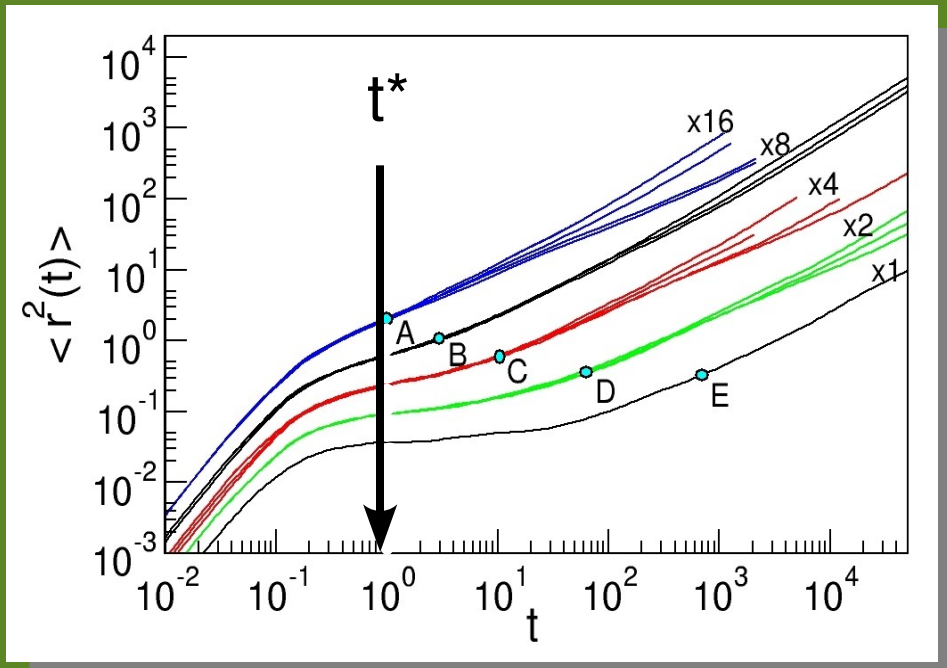
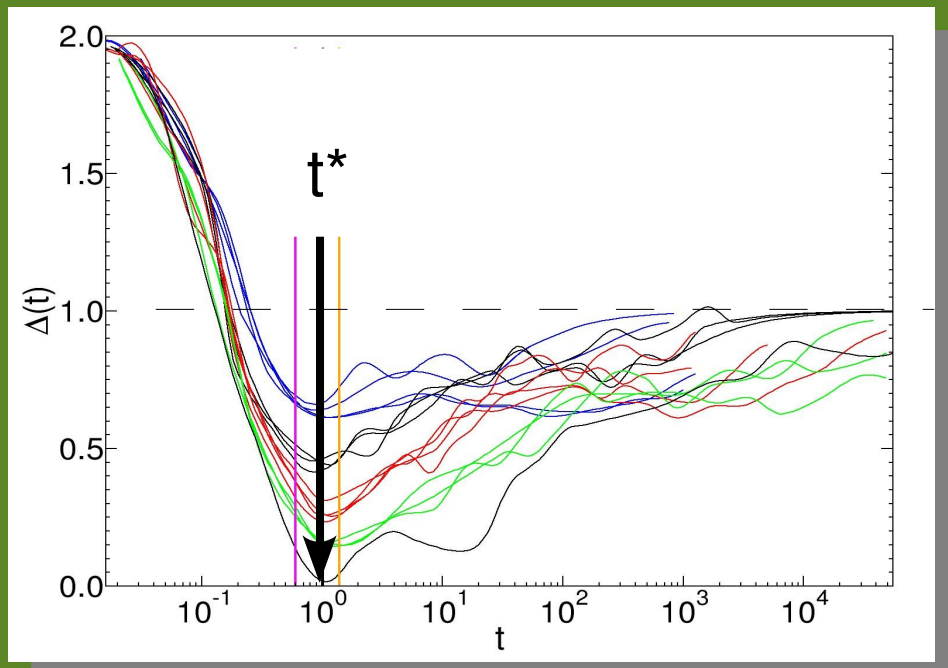
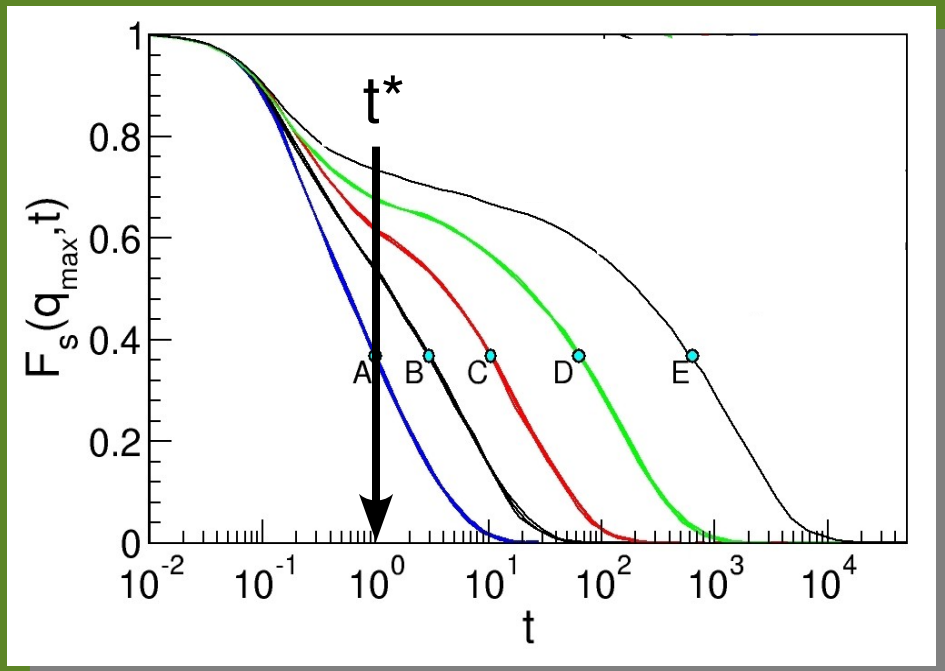
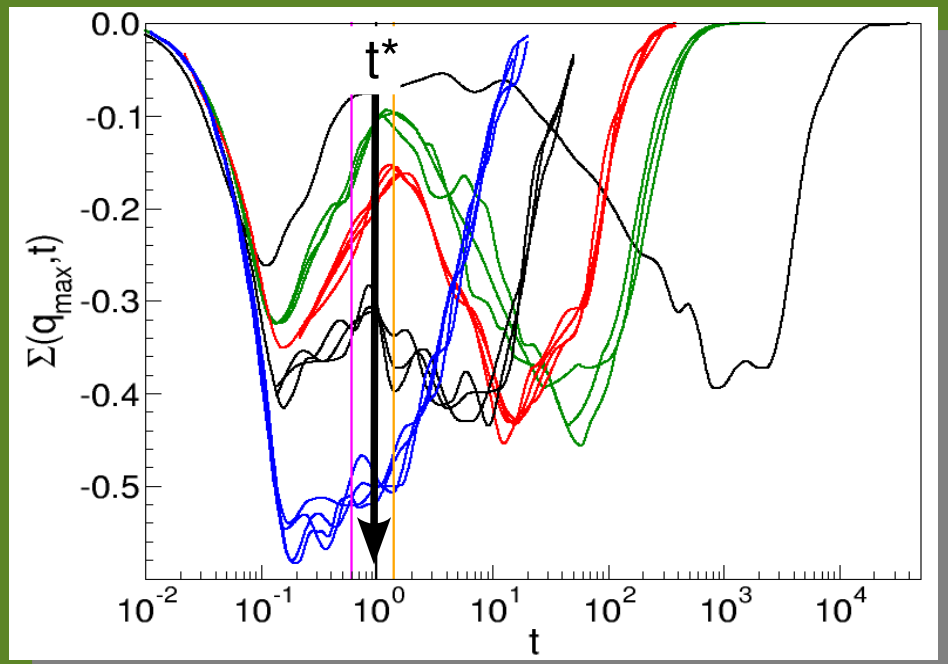


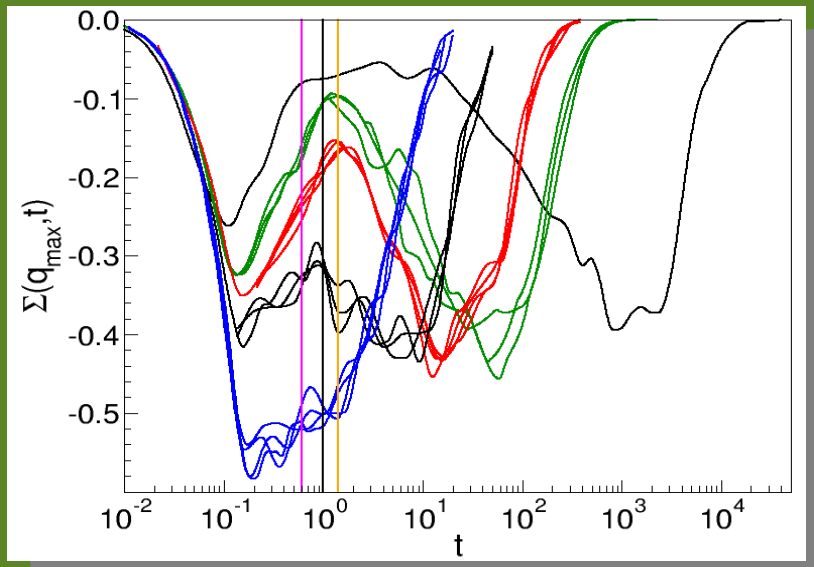


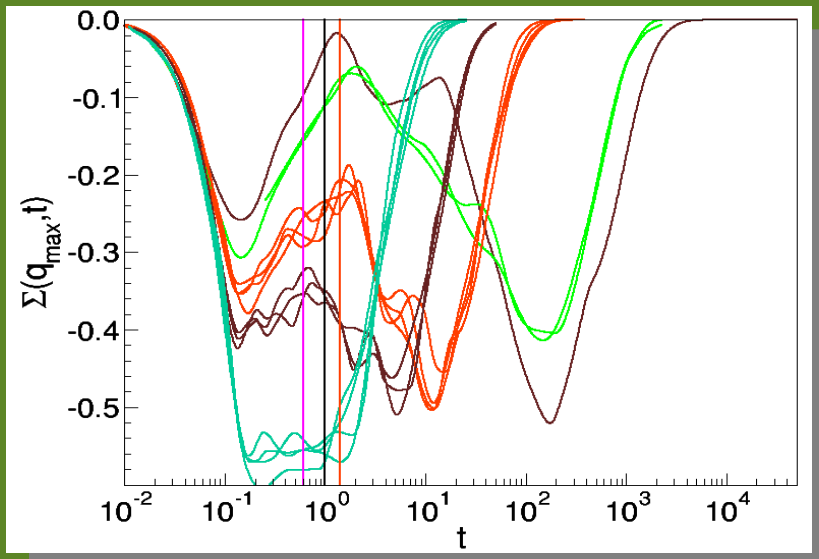




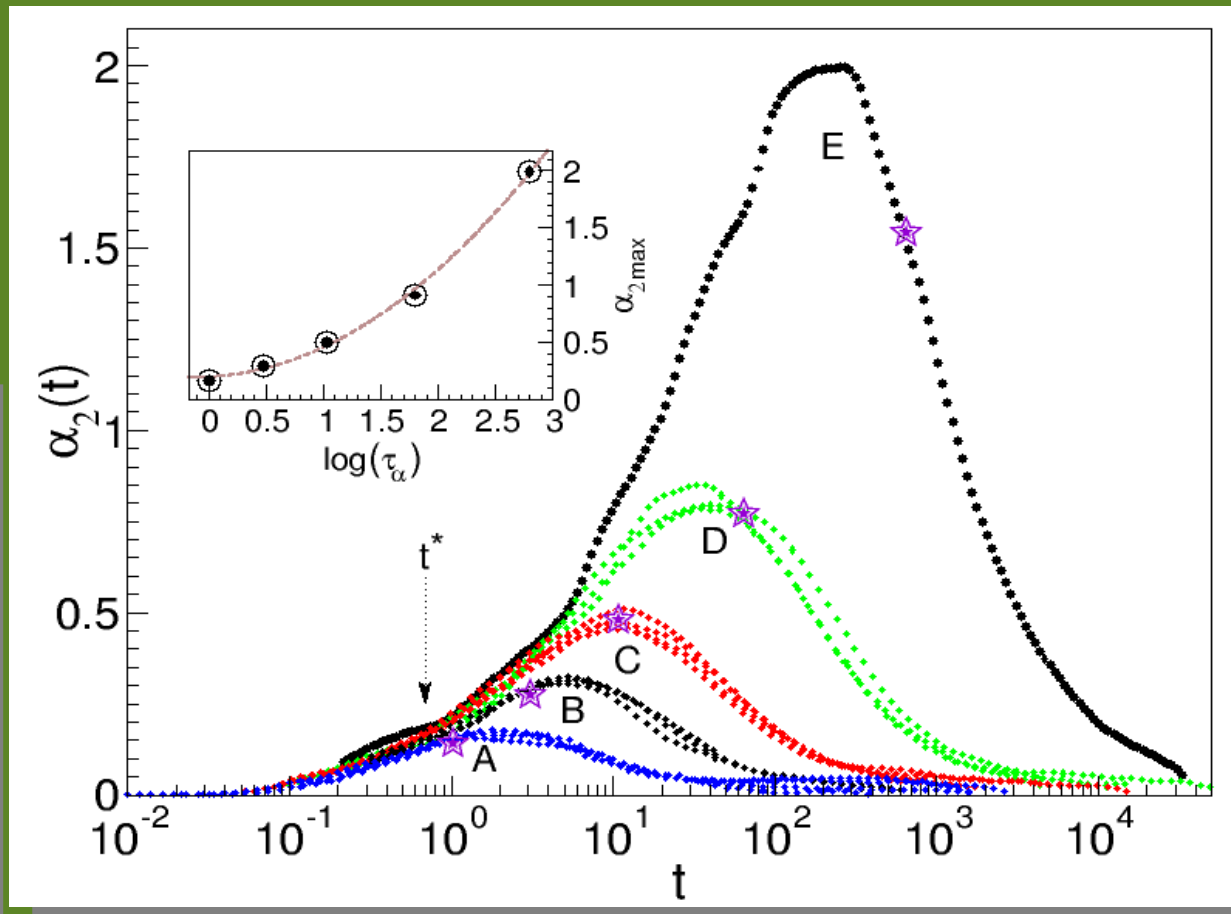
Heterogeneous dynamics growth

Heterogeneous Dynamics still negligible at t*
and modify strongly the structural relaxation only after





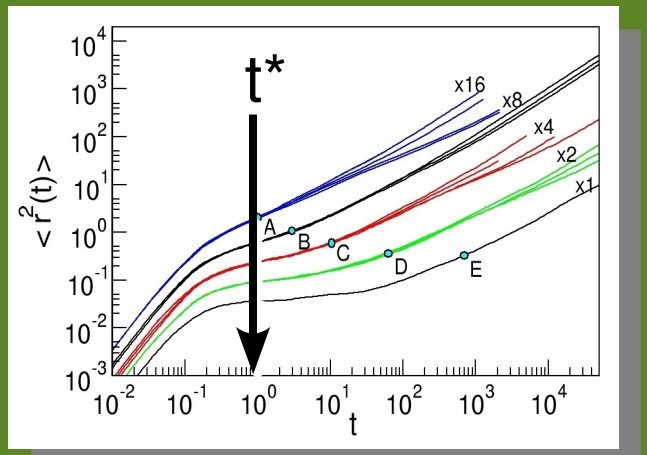
$$\alpha_2(t) = \frac{3}{5}\frac{\langle r^4(t)\rangle}{\langle r^2(t)\rangle^2} - 1$$

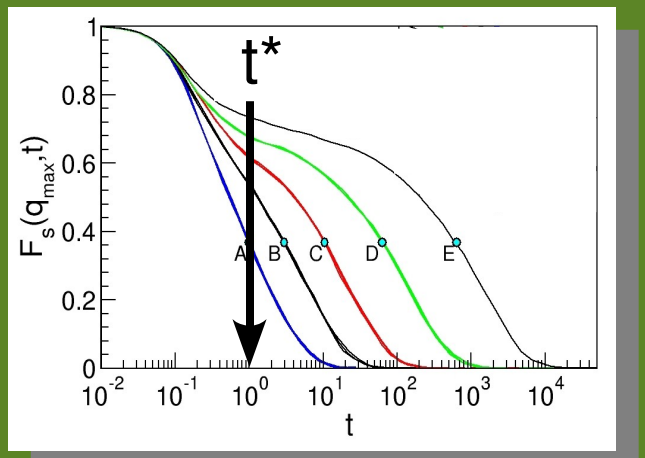


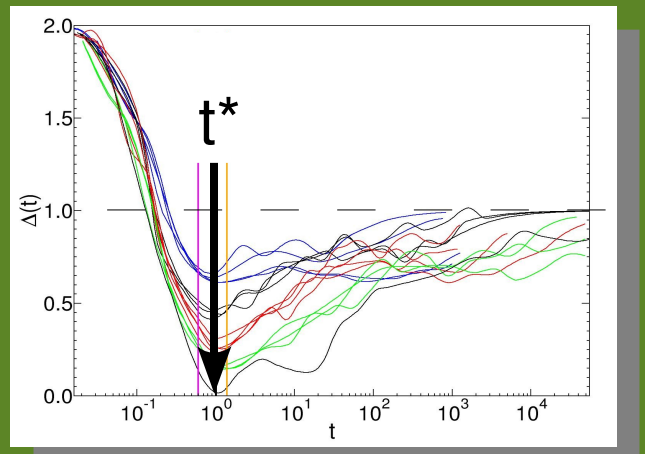
No differences with experimental conventional definitions

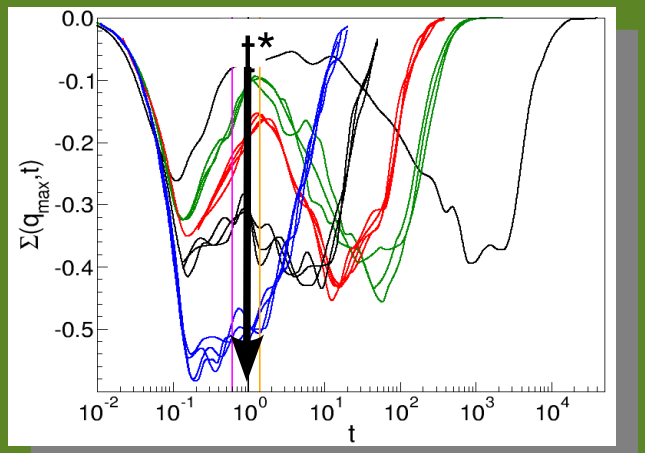
$$\langle u^2_{MSD} \rangle = \langle \Delta r^2 (t = t^*) \rangle$$

$$\langle u^2_{ISF} \rangle = -\frac{3}{q^2_{max}} \ln \left[F_s(q_{max}, t^*) \right]$$

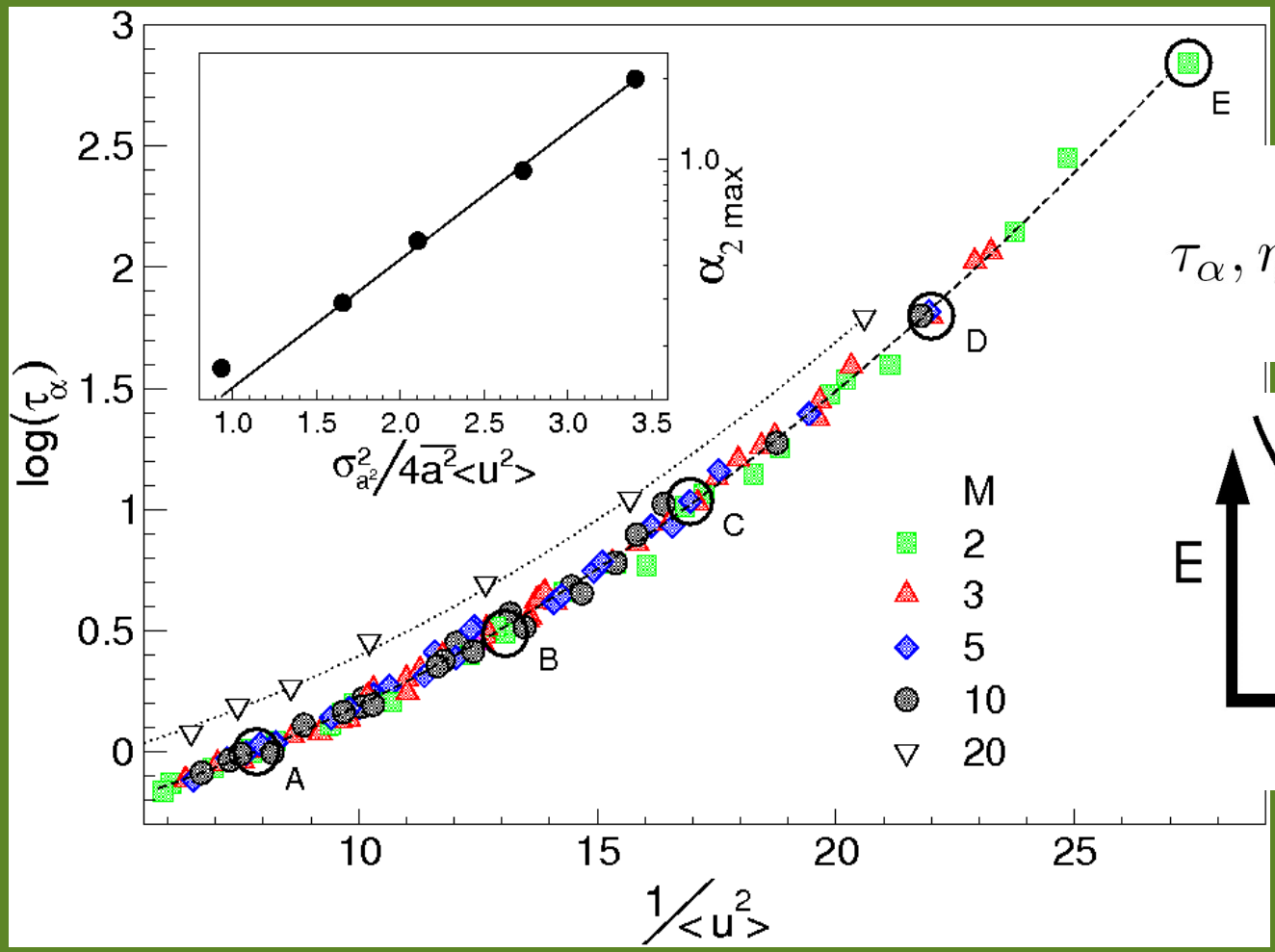




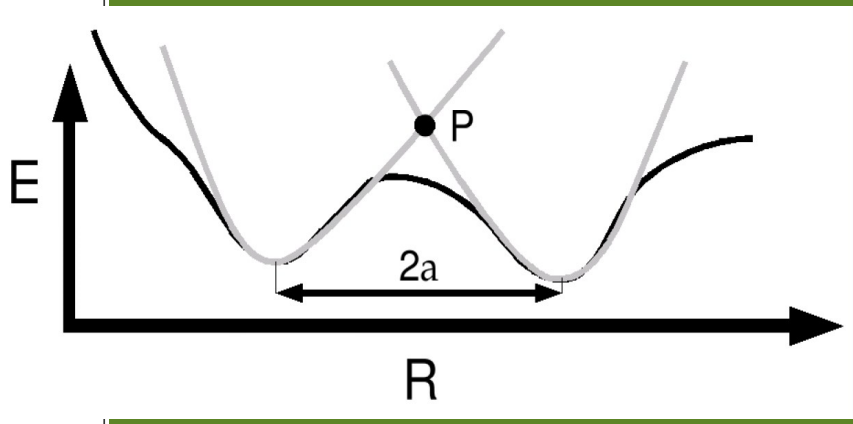




“Universal” scaling curve (poly+BM)



$$\tau_\alpha, \eta \propto \exp\left(\frac{a^2}{2\langle u^2\rangle} + \frac{\sigma^2_{a^2}}{8\langle u^2\rangle^2}\right)$$



Quartic term due to the spread of the distance between the EL minima (heterogeneous dynamics)

No evidence of dynamic divergencies (Dyre et al., 2008)

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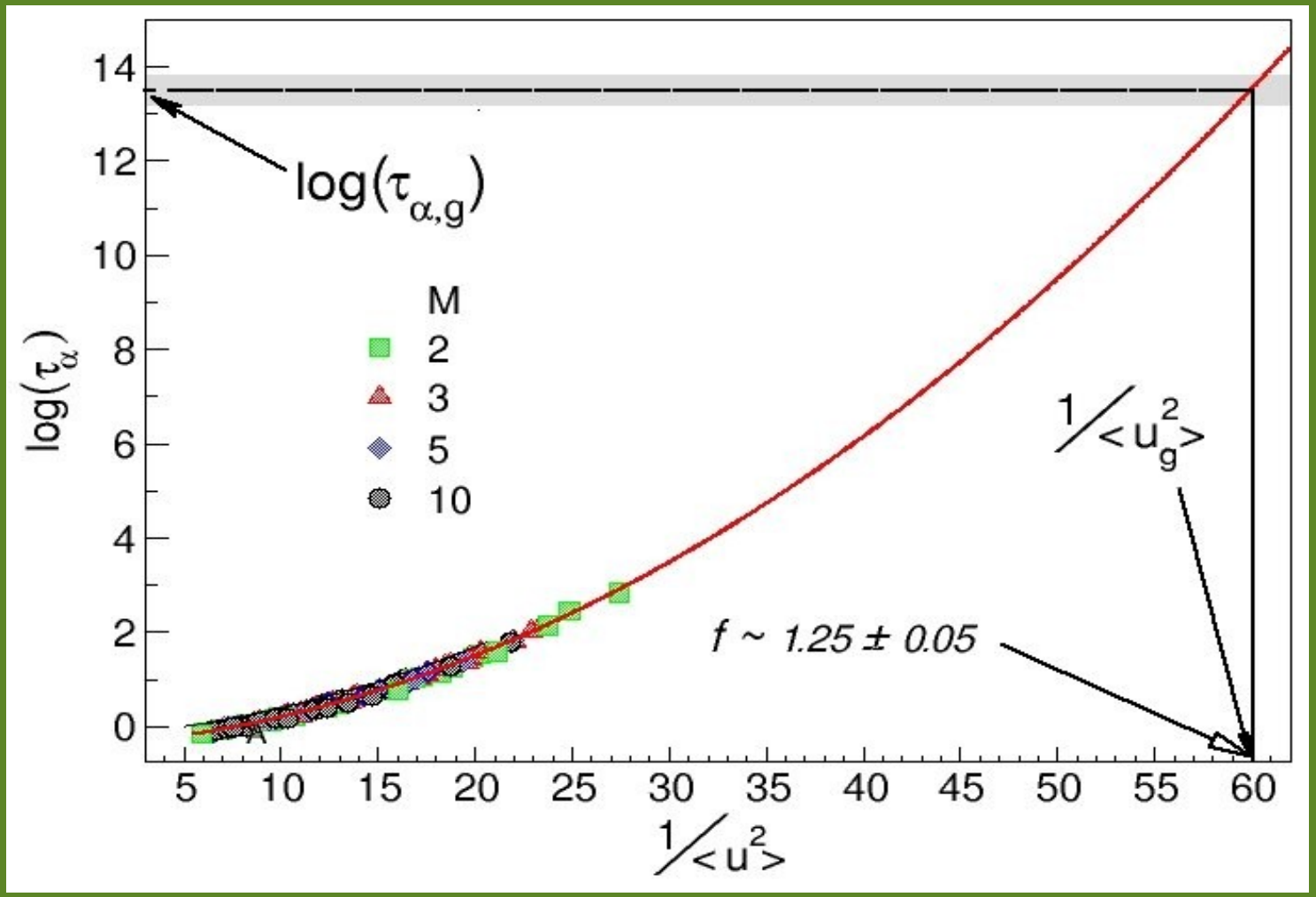
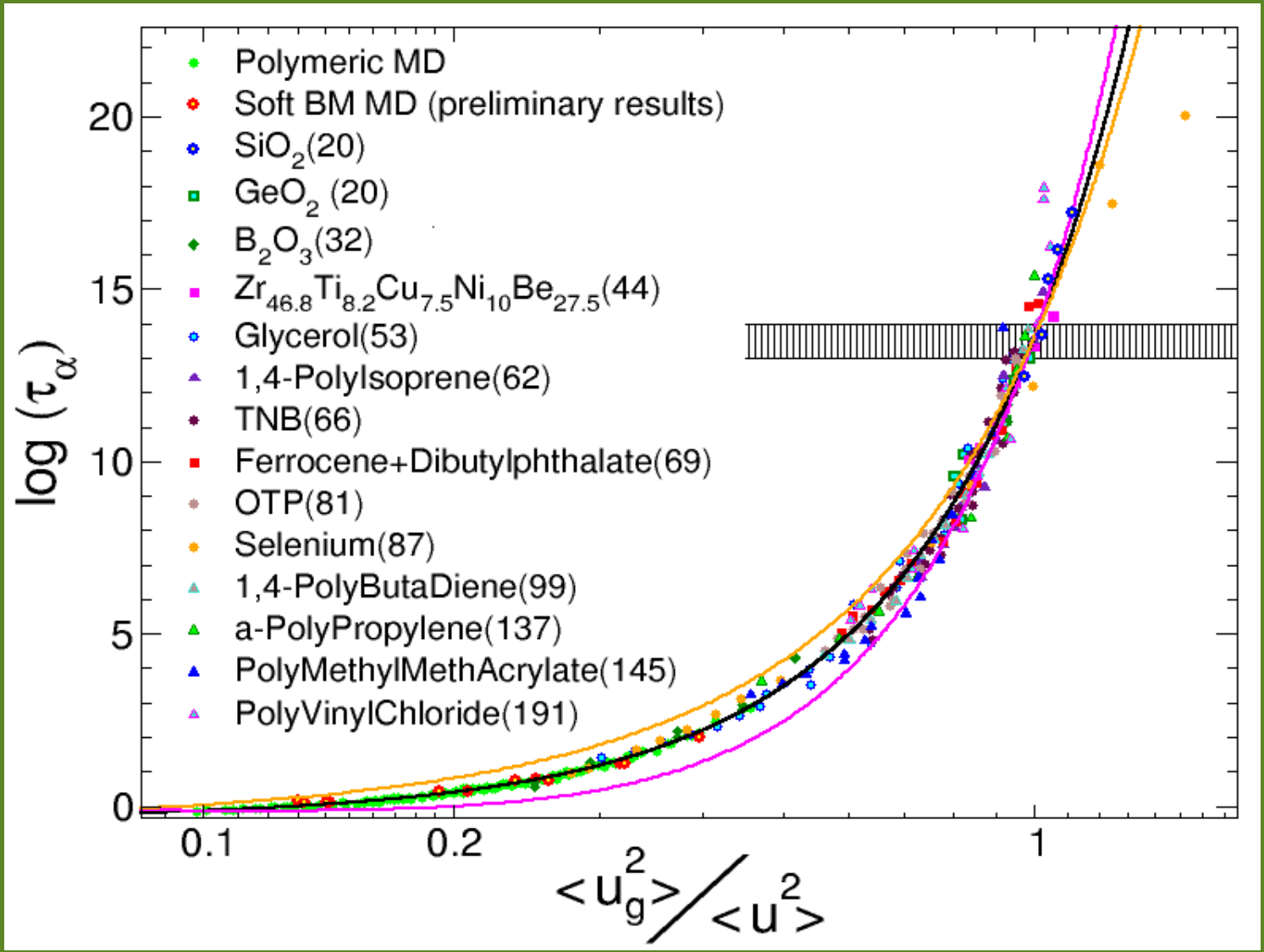
Locating the Glass Transition of the MD models



$\langle u_g^2 \rangle$ consistent with both the Lindemann ratio f and free-volume ideas

1 MD time unit: ≈ 1-10 ps

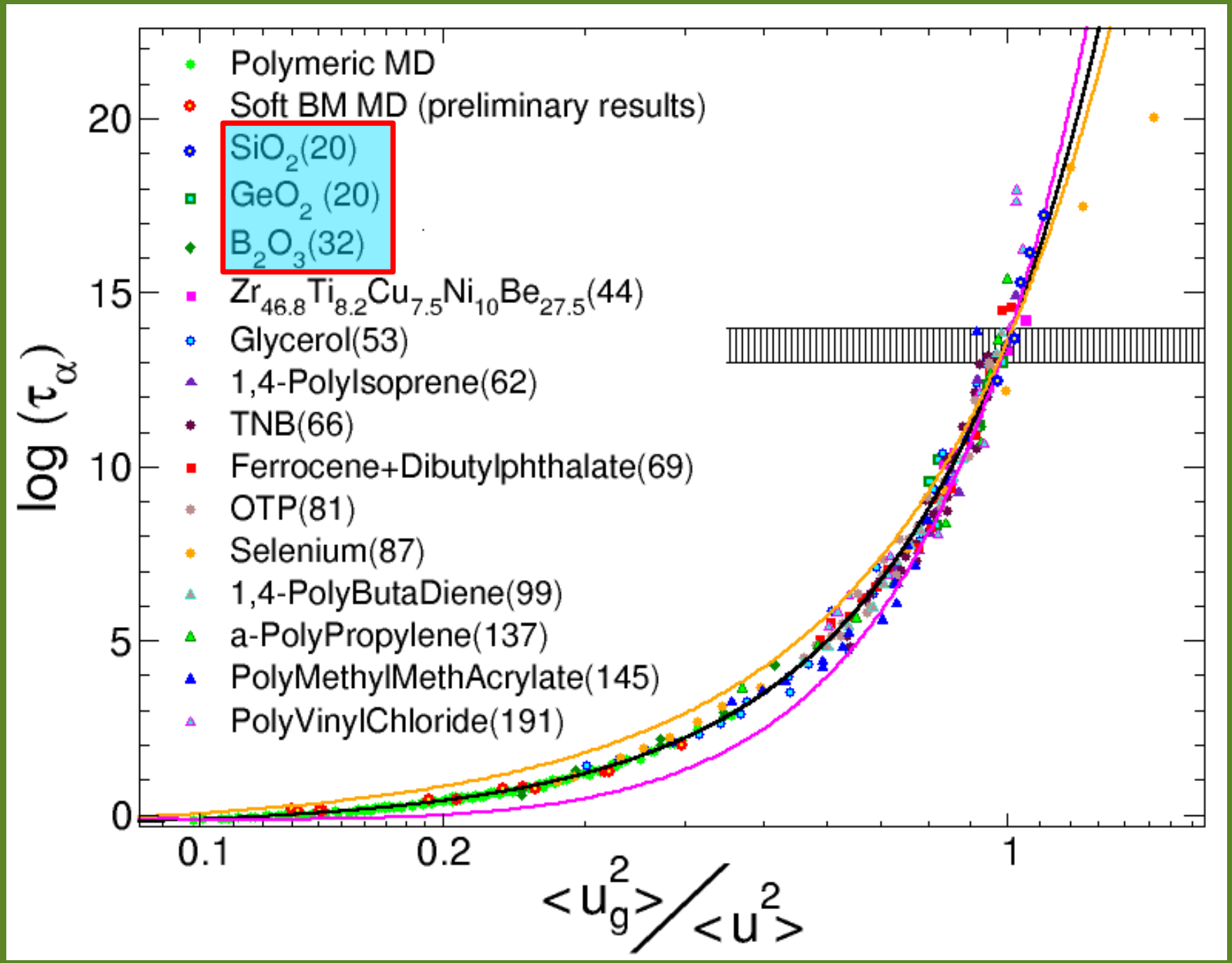
Rescaled universal curve



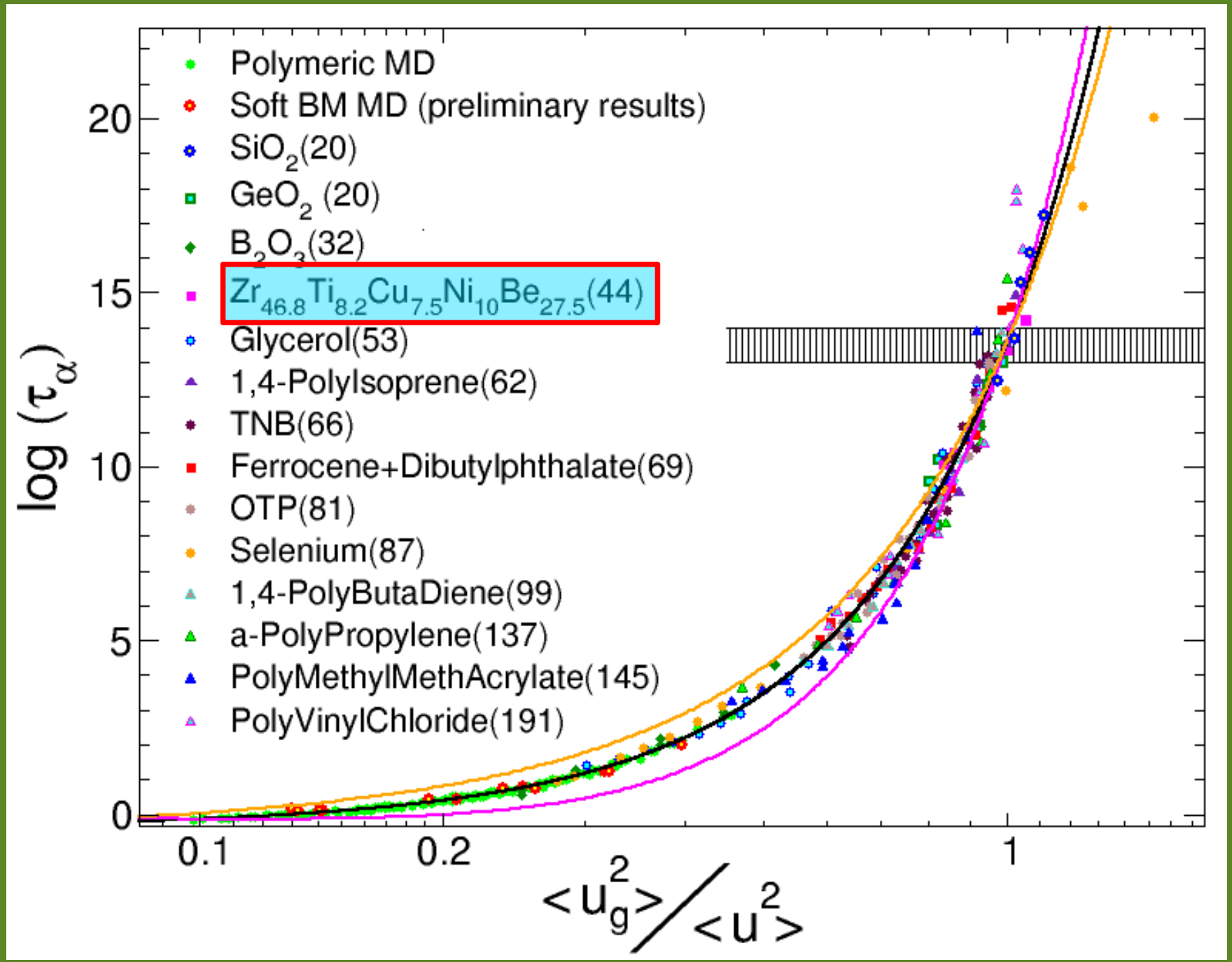
The reduced MD master curve is suited for comparison with experimental data.

Agreement over about eighteen decades of relaxation times.

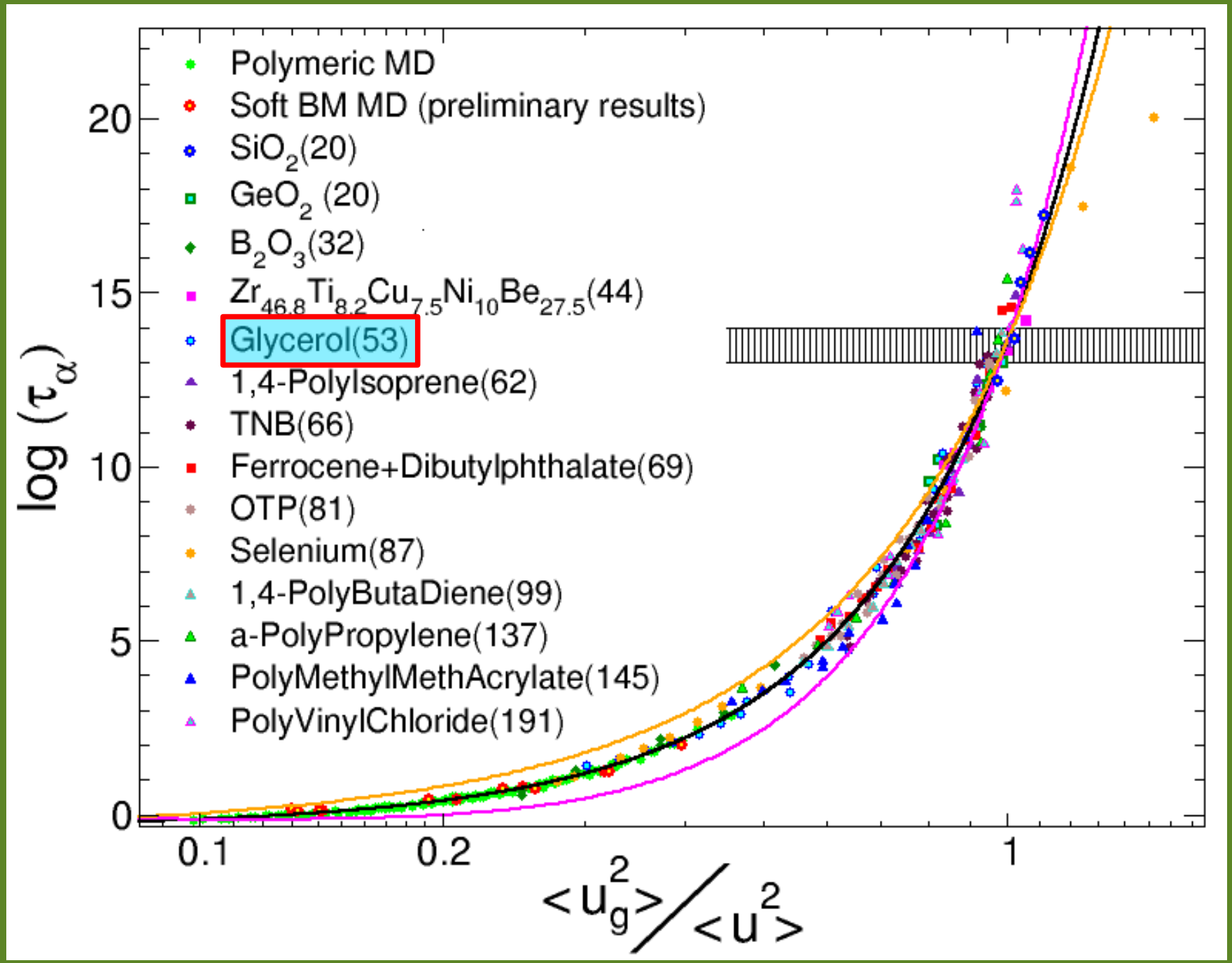
Rescaled universal curve



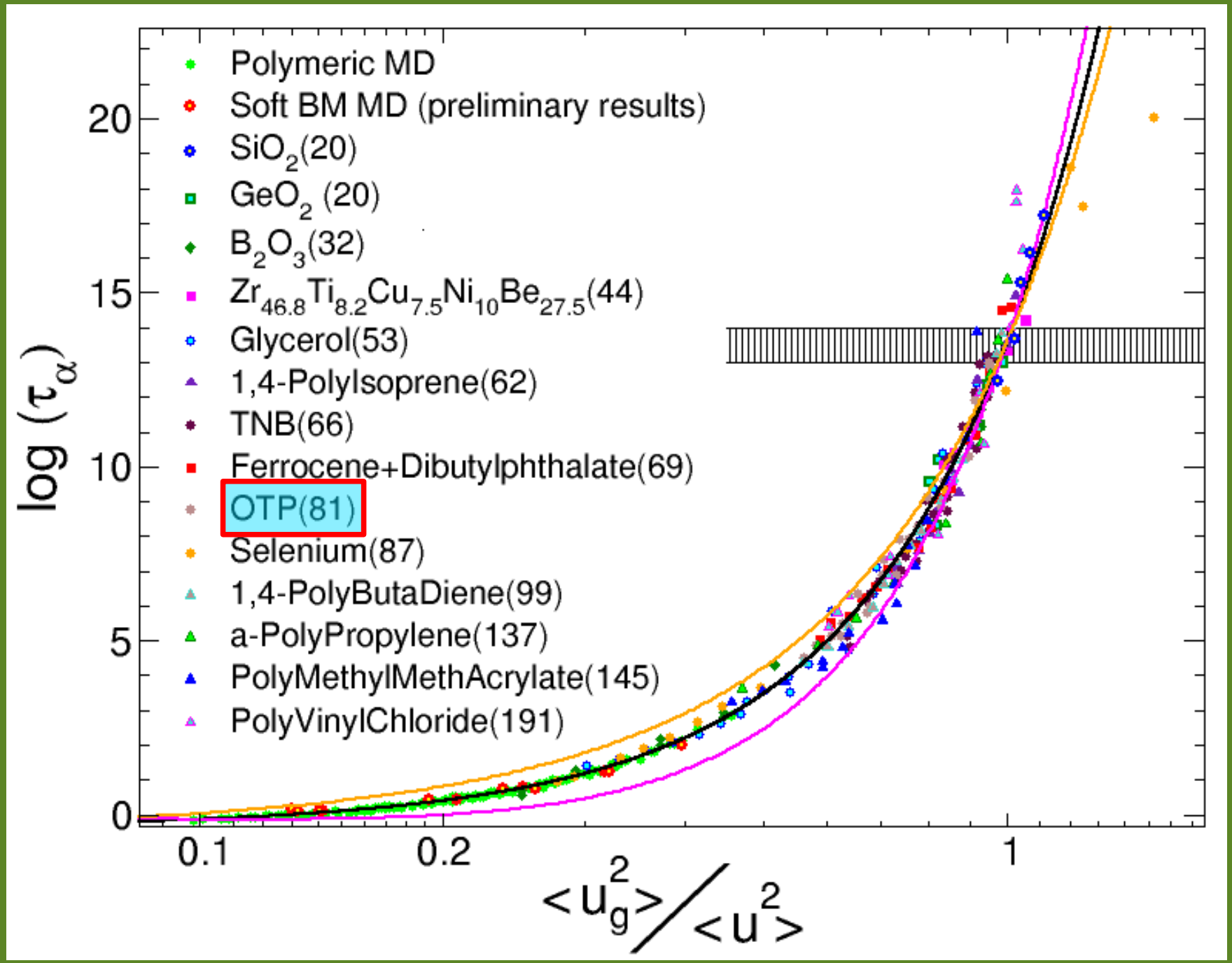
Rescaled universal curve



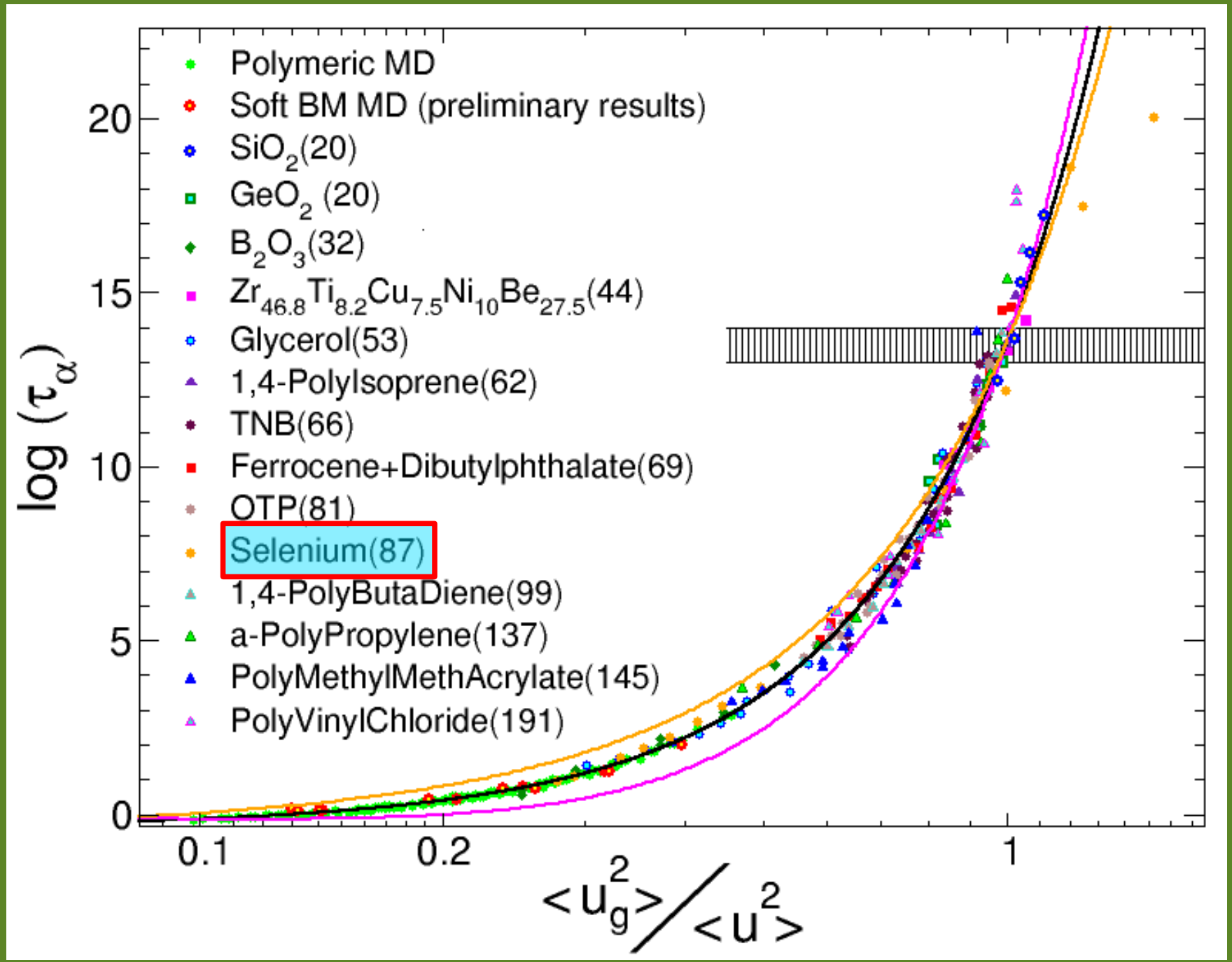
Rescaled universal curve



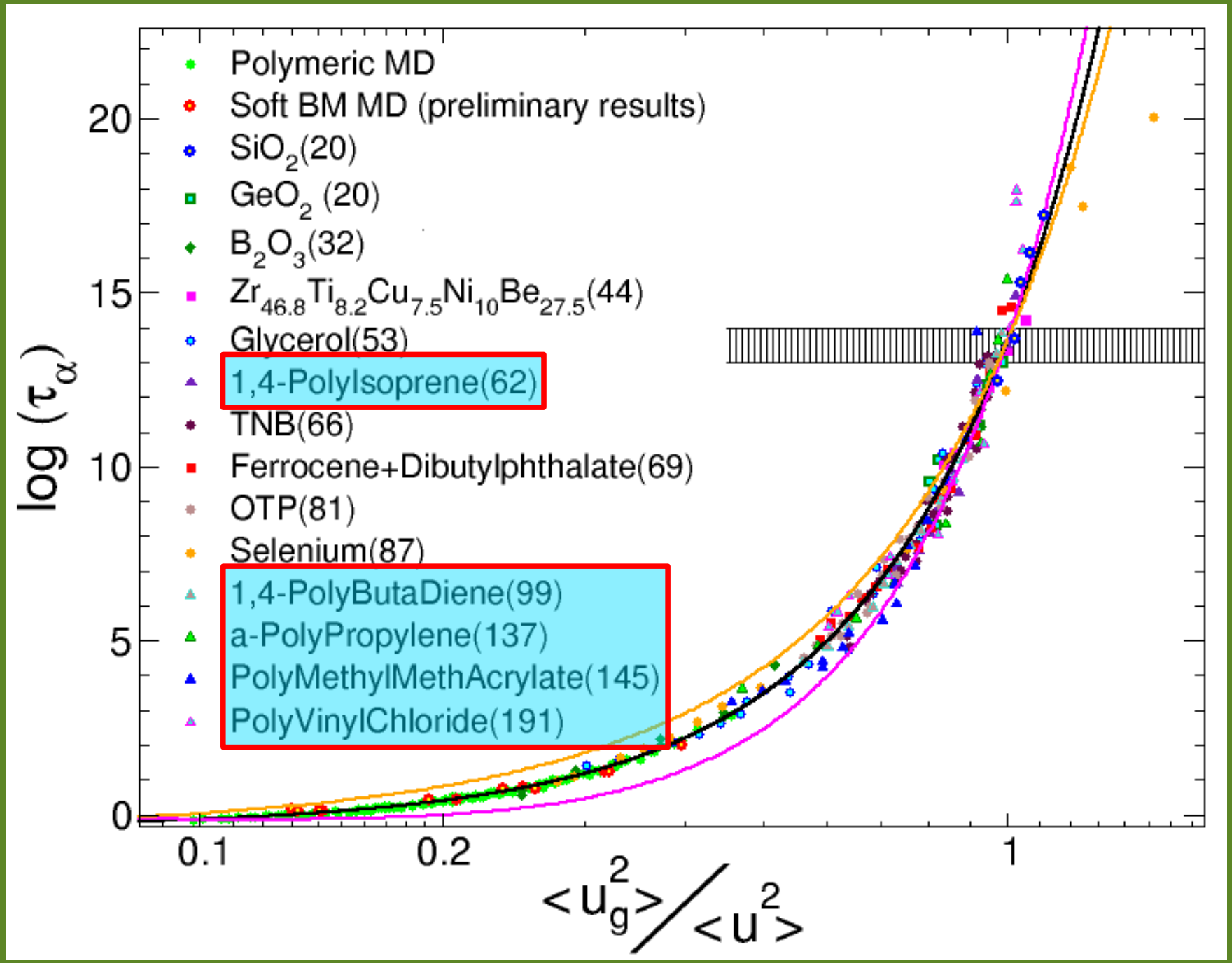
Rescaled universal curve



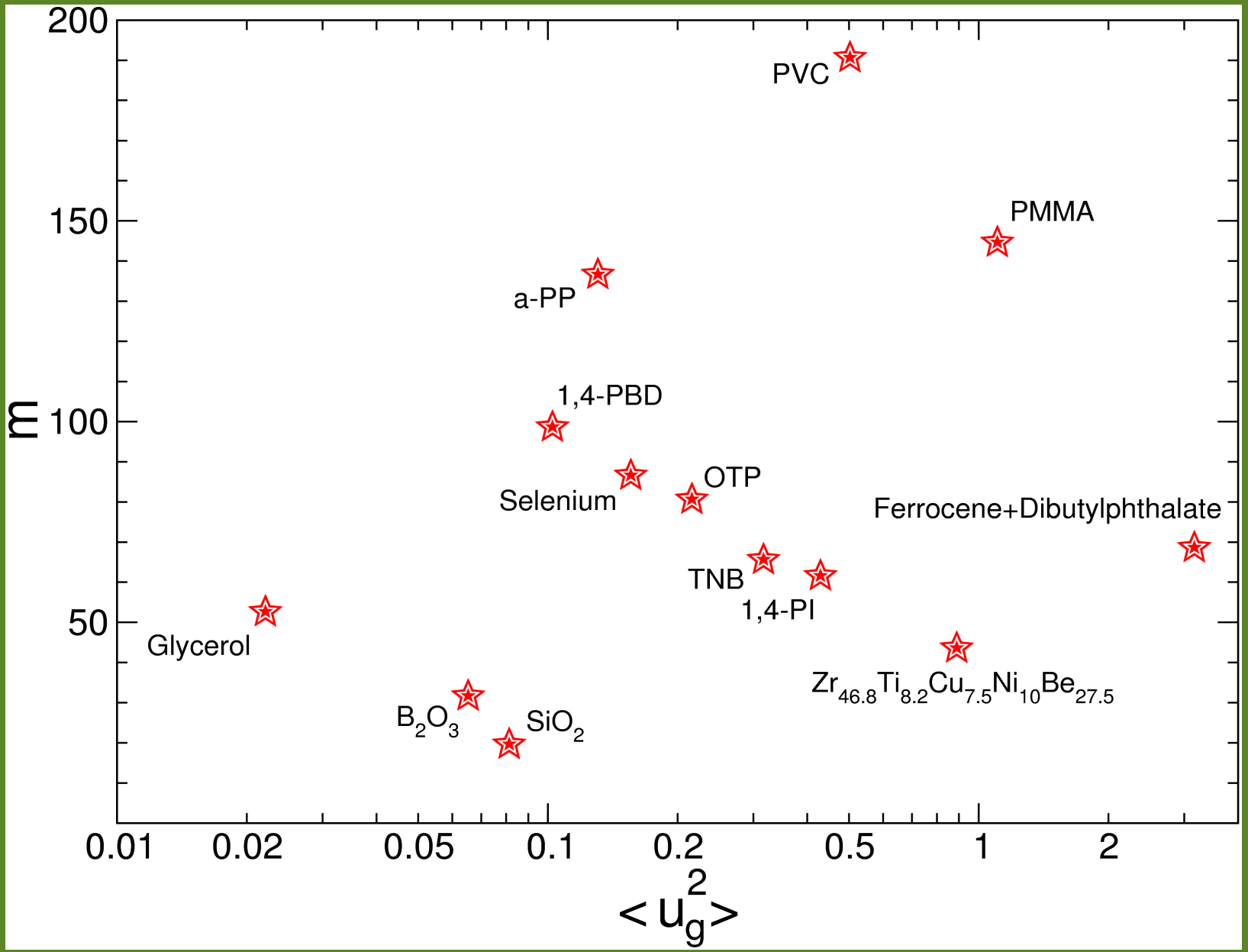
Rescaled universal curve



Rescaled universal curve



No correlation between fragility and $\langle u_g^2 \rangle$



Outline

- Background
- Numerical Simulations
- Comparison with experiments
- Conclusions

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