Facoltà di Fisica, scuola di dottorato
A.A. 2014-2015

Università di Pisa

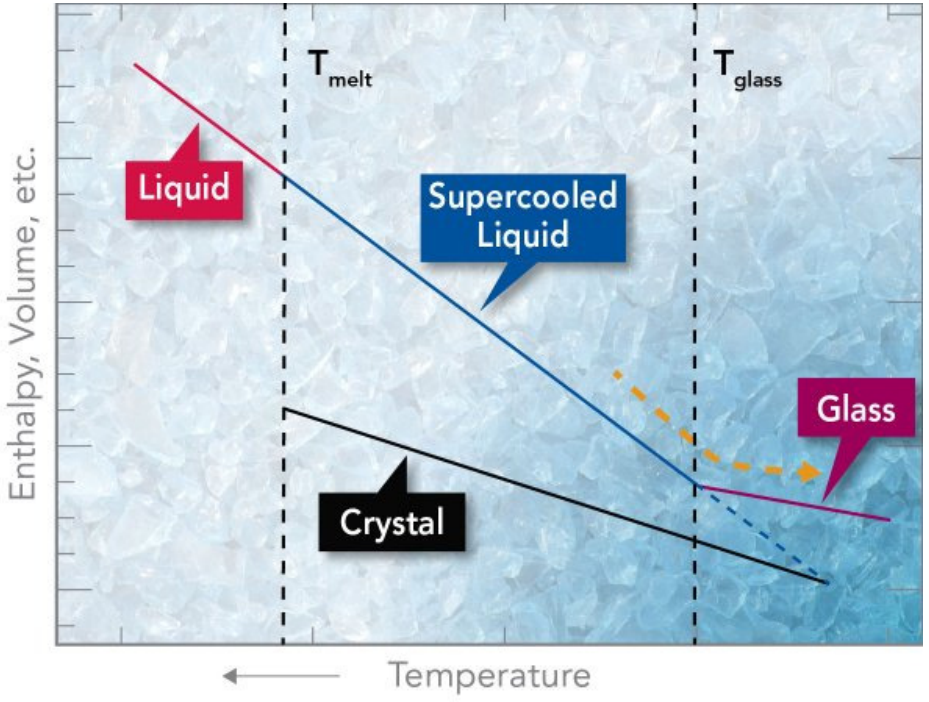
Confinement effect on the dynamics of polymeric liquids above the glass transition

Candidate
Andrea Giuntoli

Supervisor
Prof. Dino Leporini

Summary

1. Glass transition
2. Simulation of supercooled liquids
   - Polymer model
   - MD algorithms
   - Dynamical properties
3. Confinement
   - Thin films preparation
   - Confinement effects
4. Conclusion and future goals



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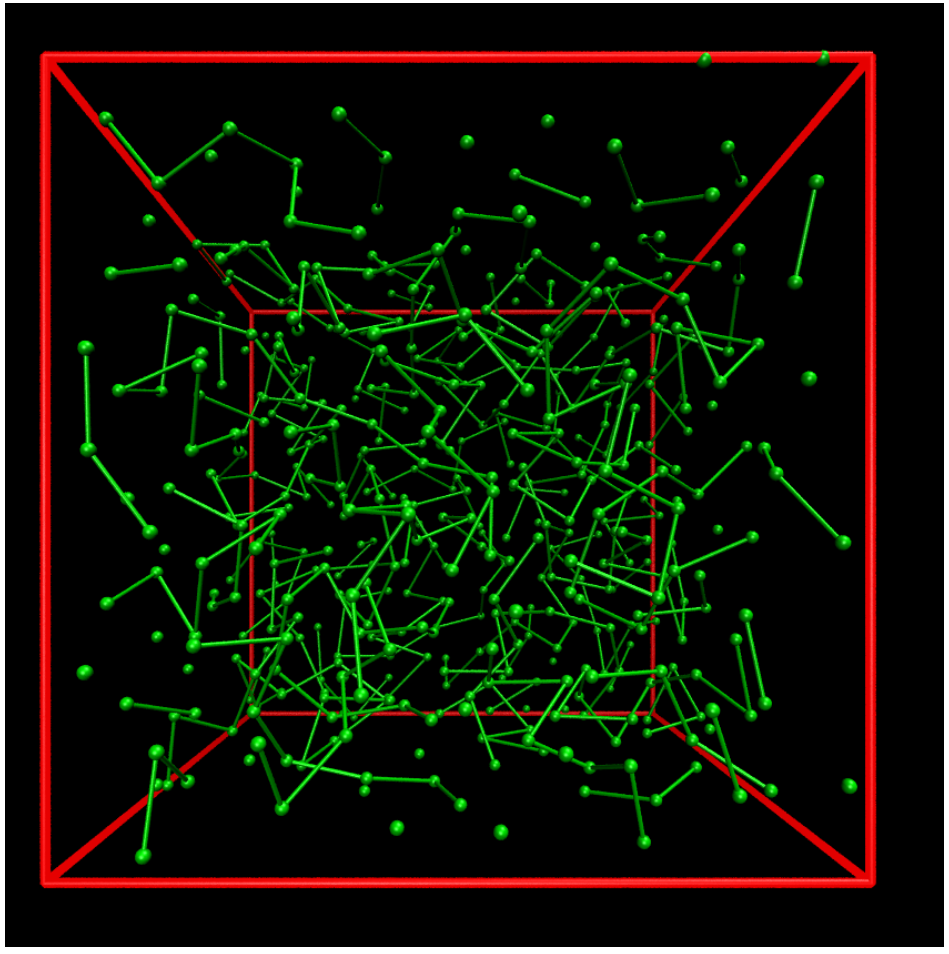

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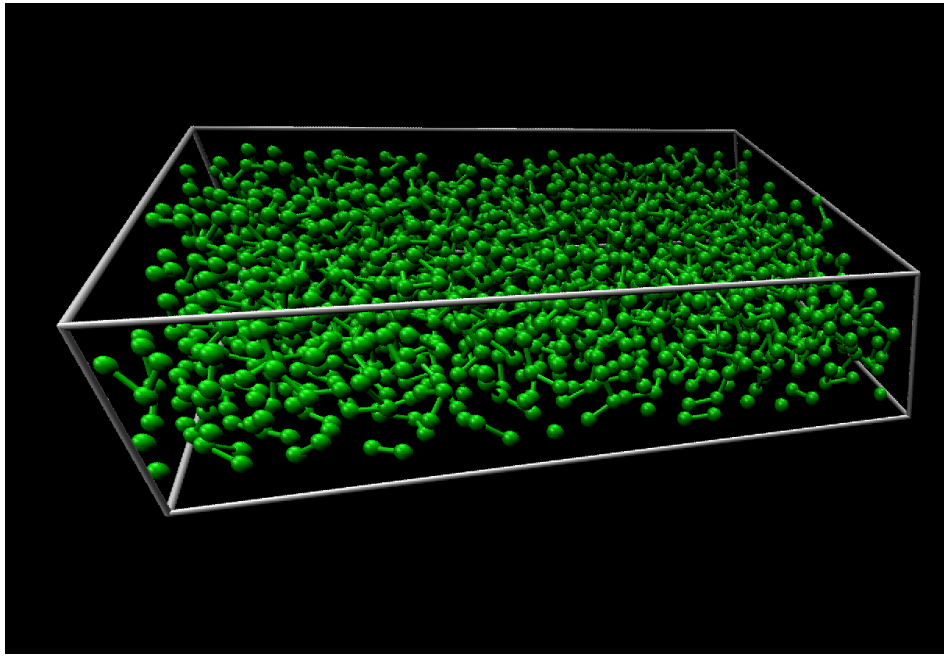

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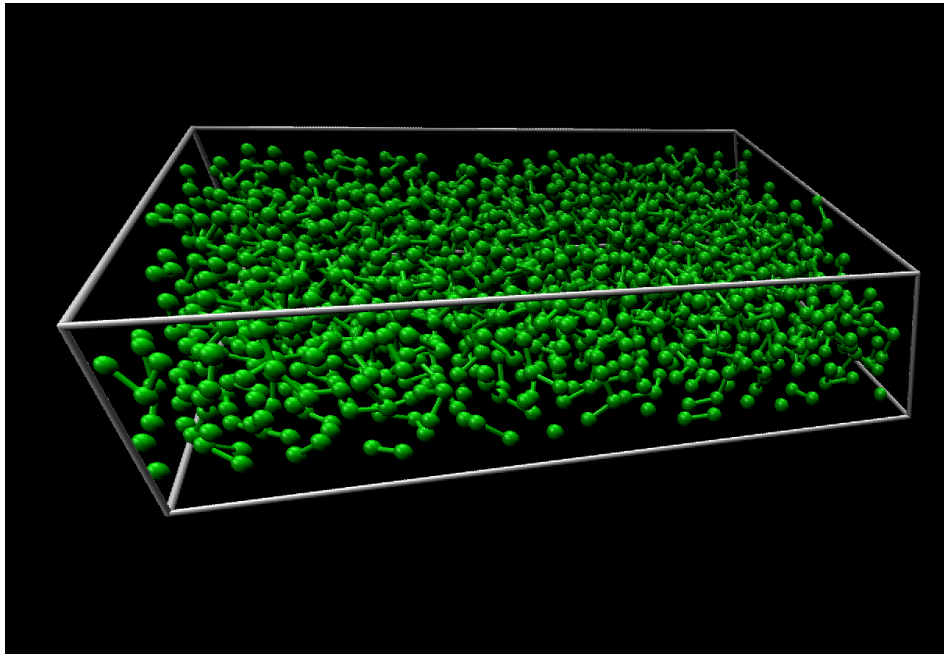


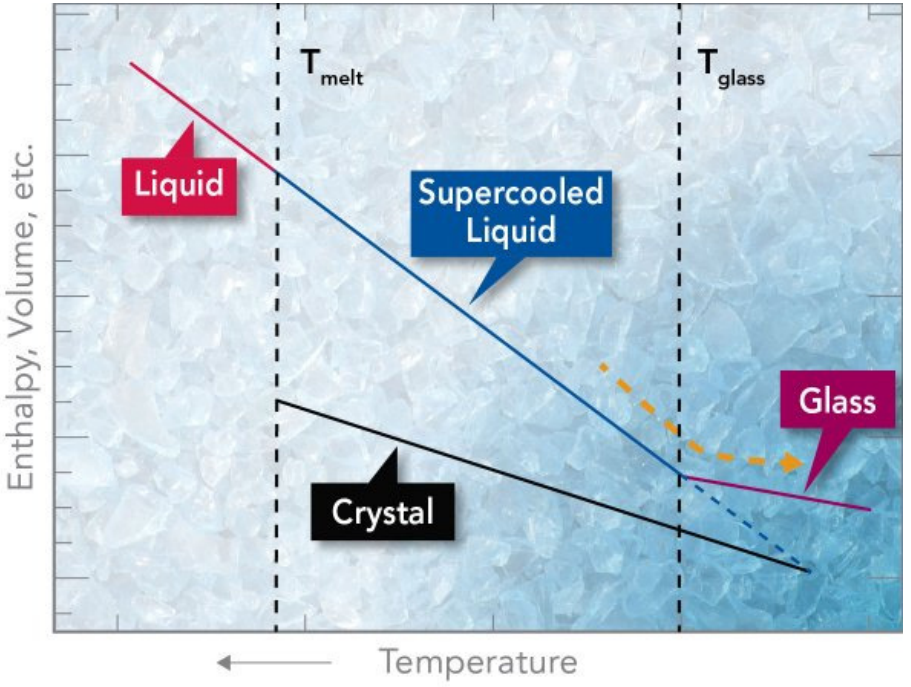
Supercooled liquids
cooling below the melting point

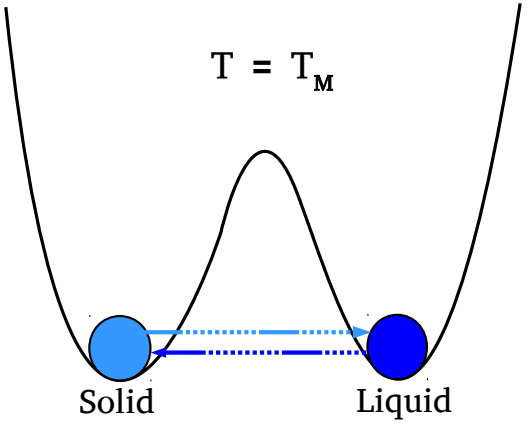
Supercooled liquid: metastable state below the melting temperature T_{melt}

Slowing down of the dynamics

Structural relaxation time longer then experimental time-scales

$\tau_\alpha > 100s \rightarrow$ a glass is formed





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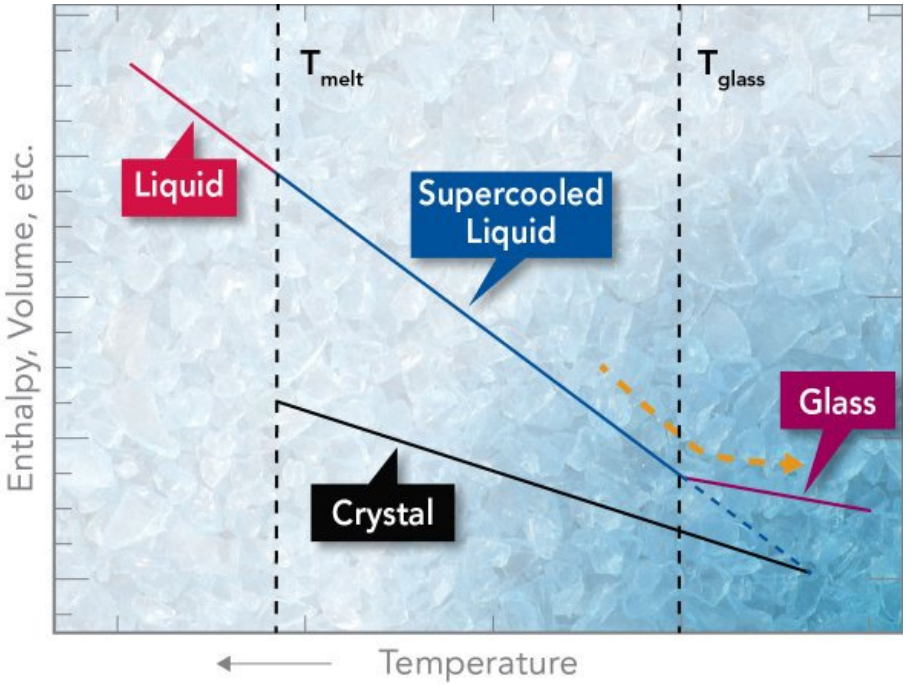

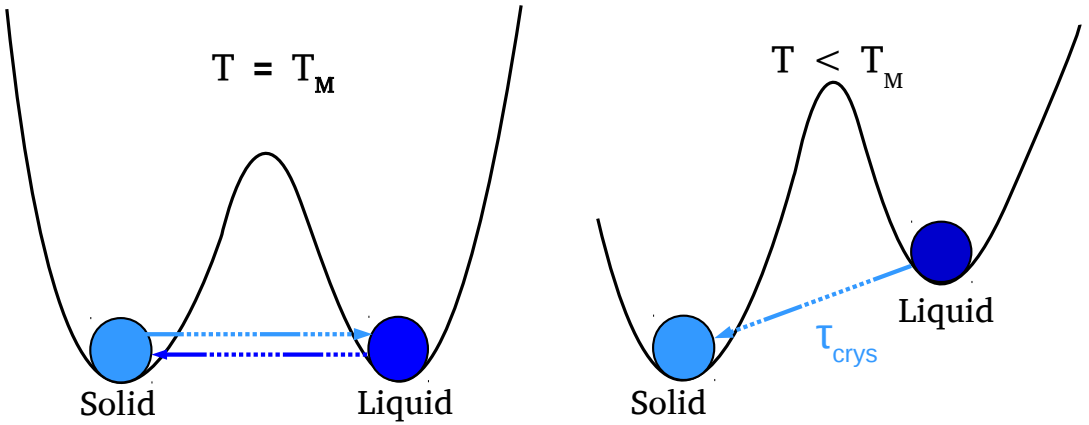

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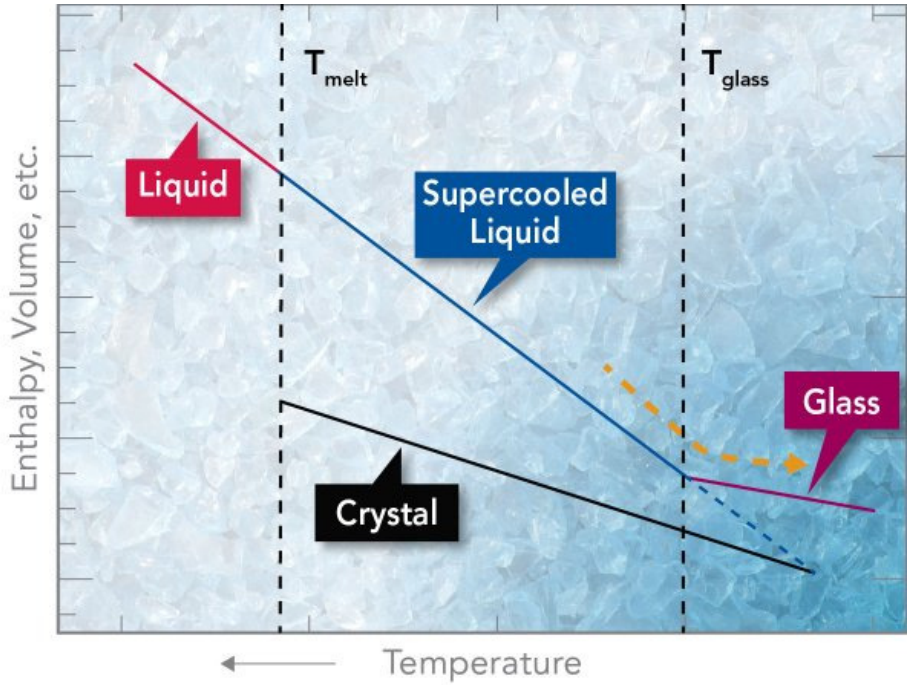

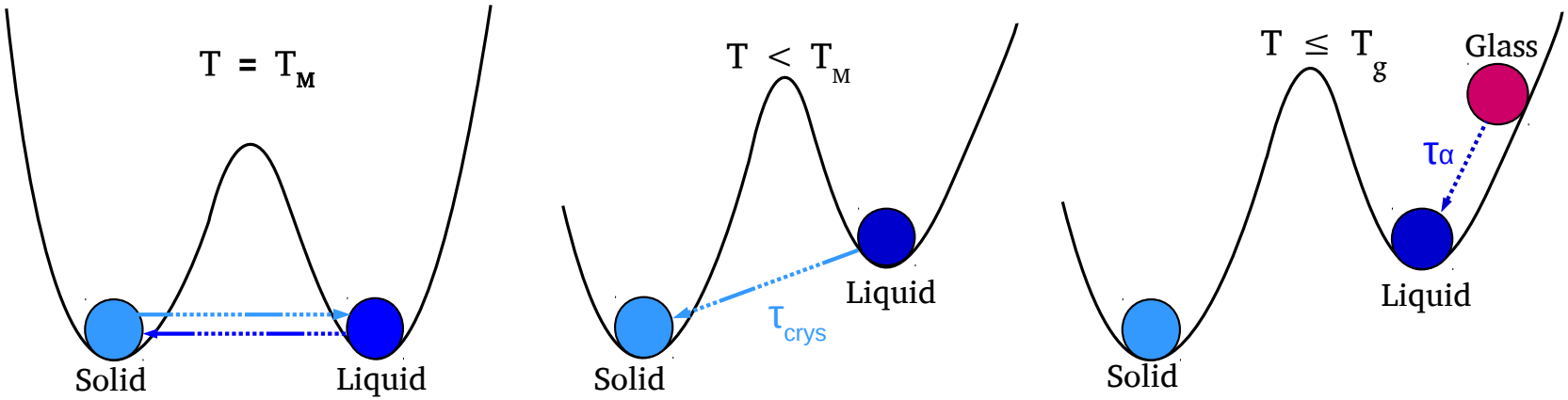

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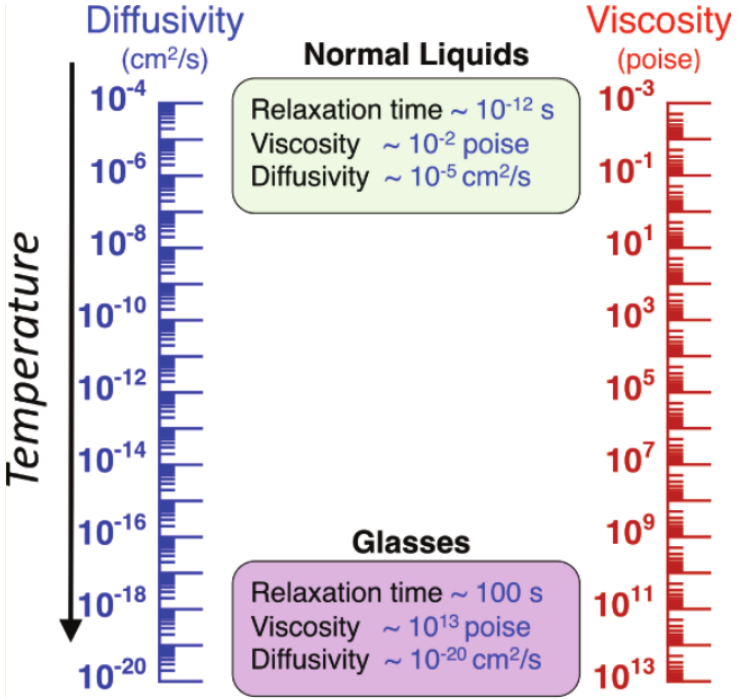
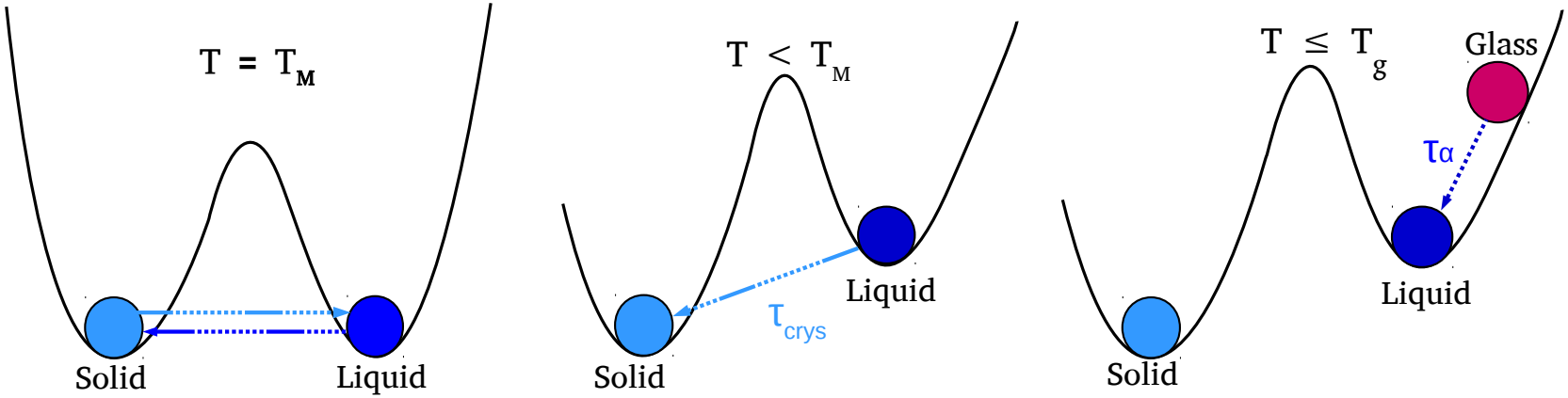


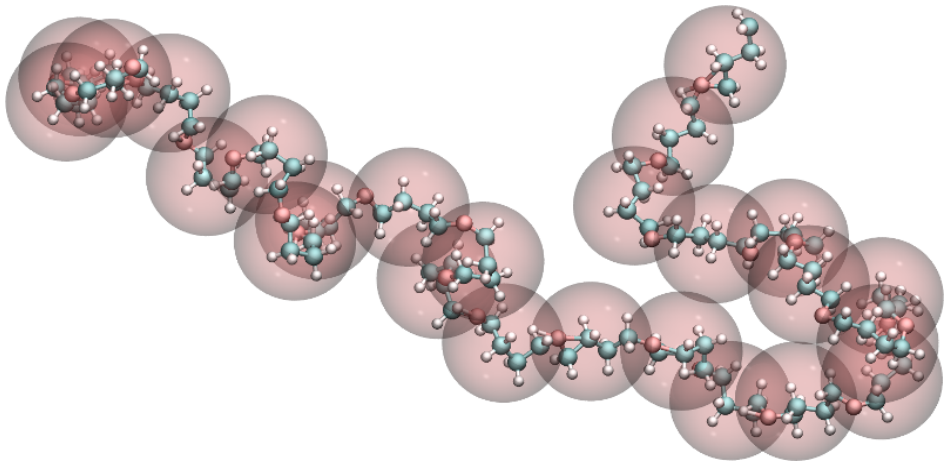


Molecular Dynamics

Model resolution and classical MD algorithms

Polymers: good glass formers

No internal structure: universal properties of the liquid



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- Interaction potentials
- Temperature, pressure, density

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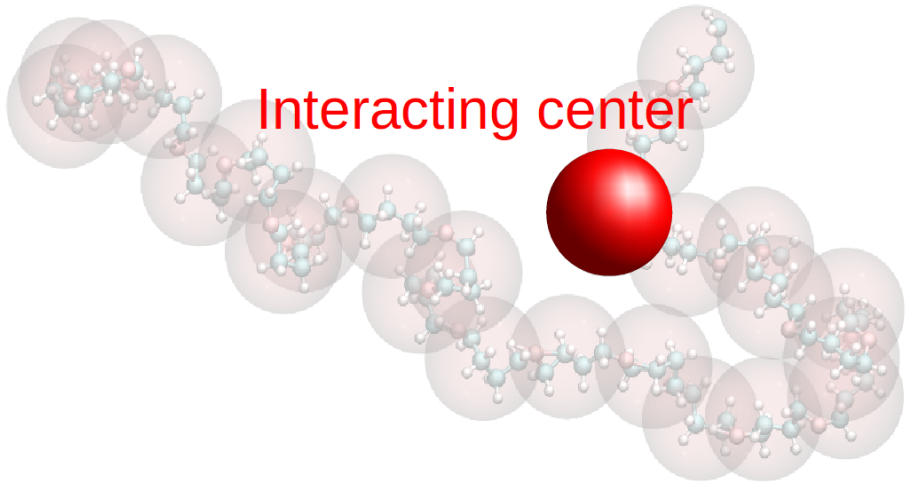

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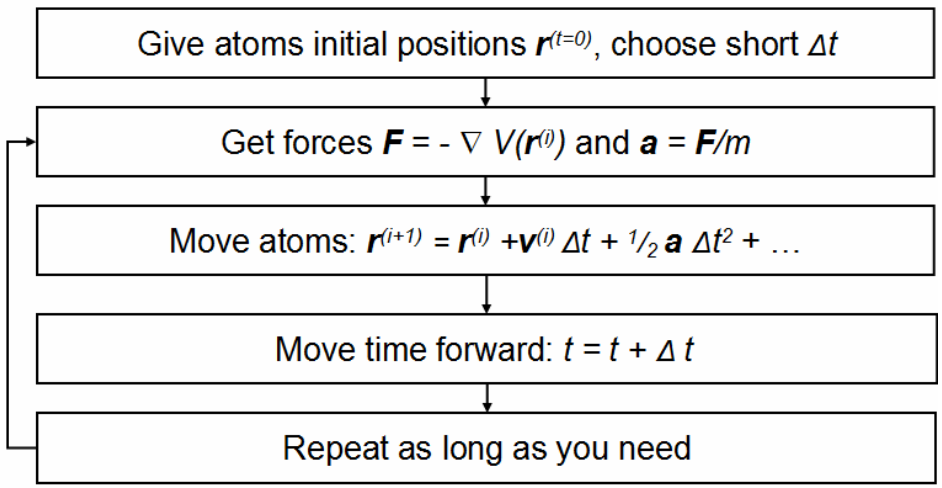

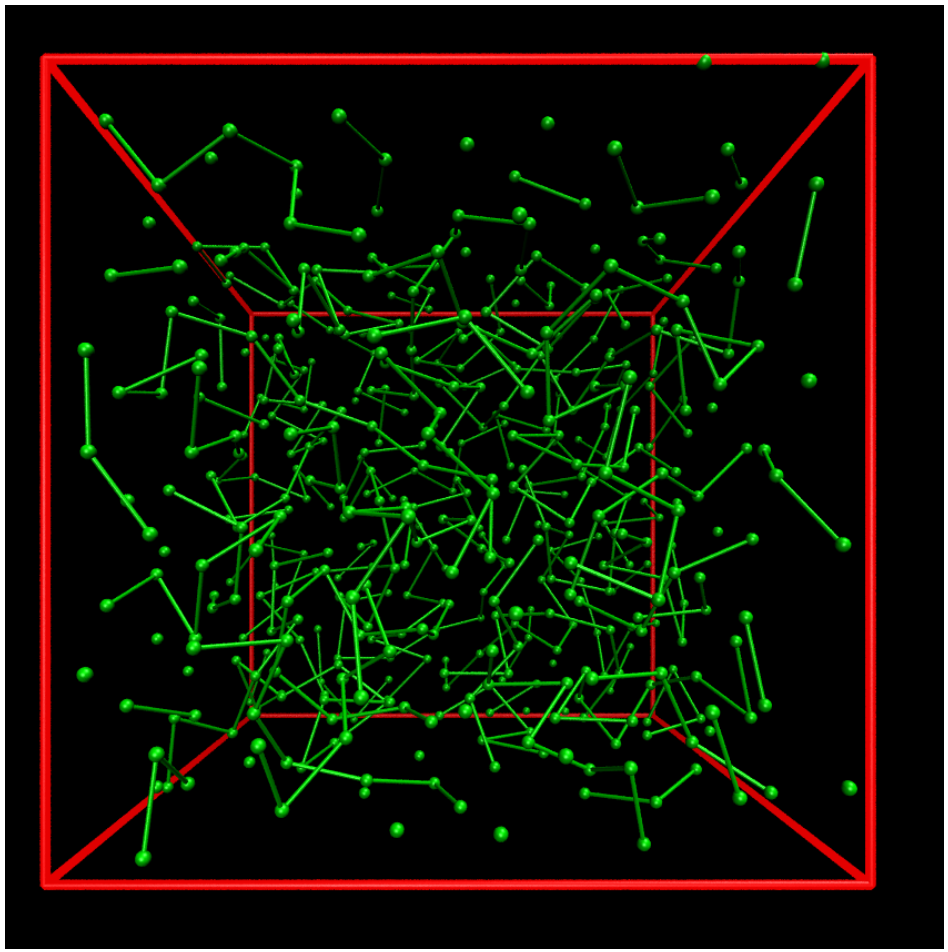

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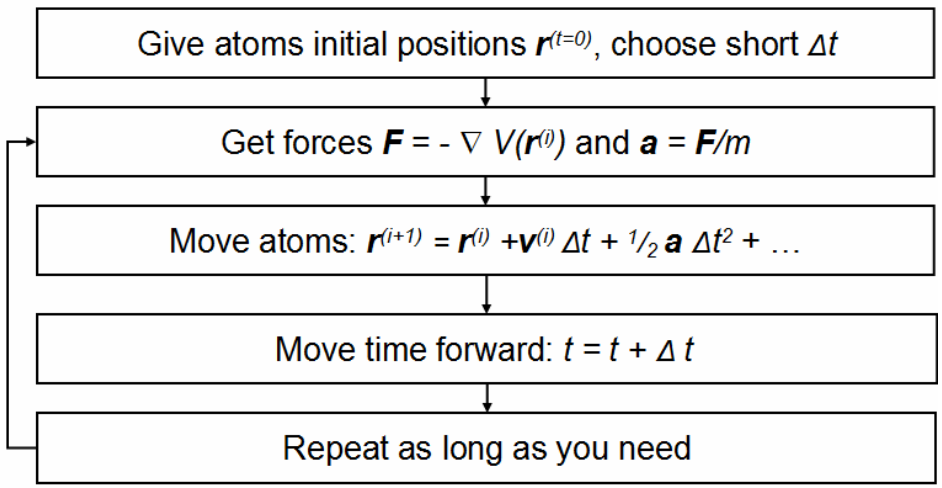

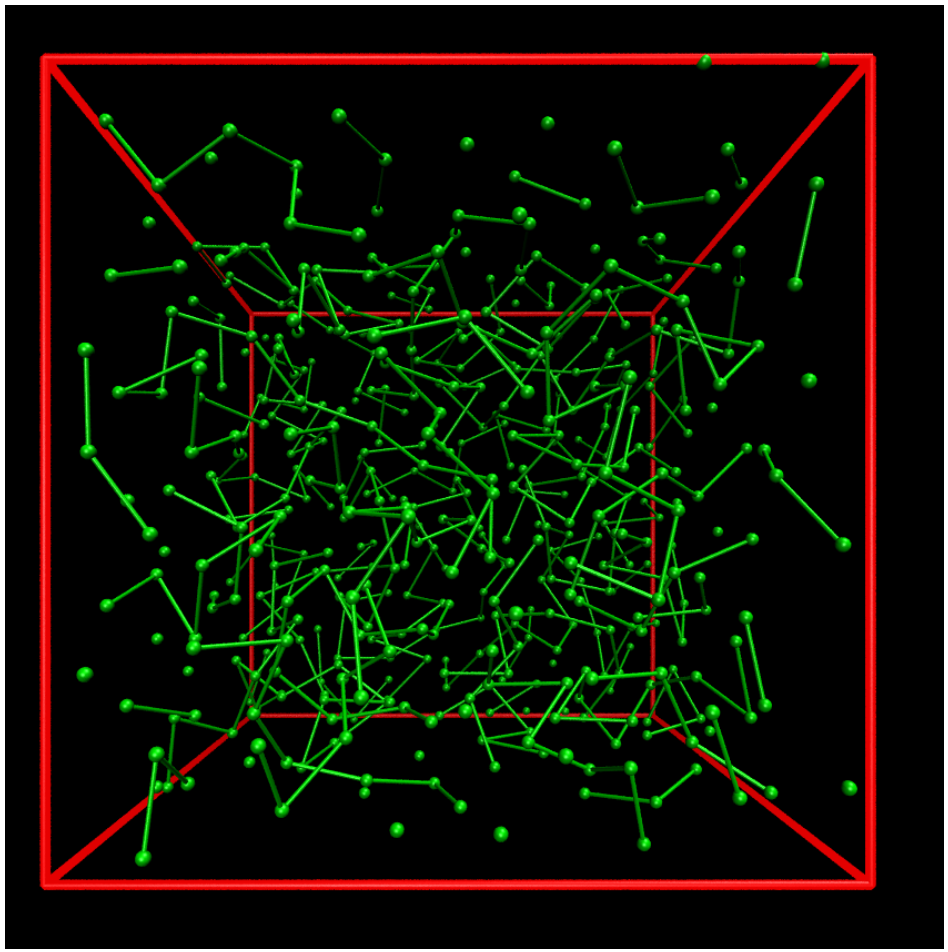

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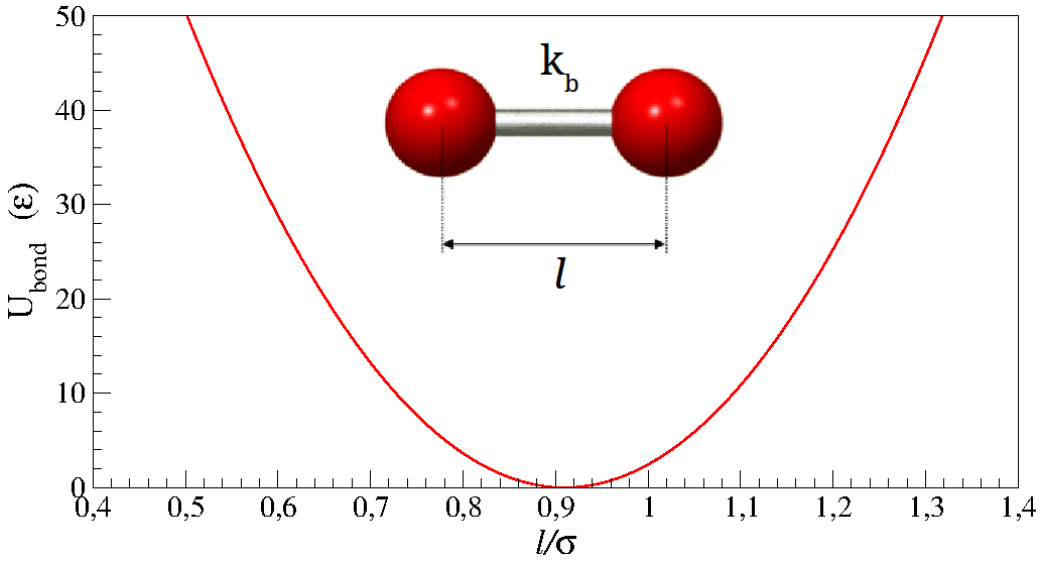
Molecular Dynamics

Model interactions

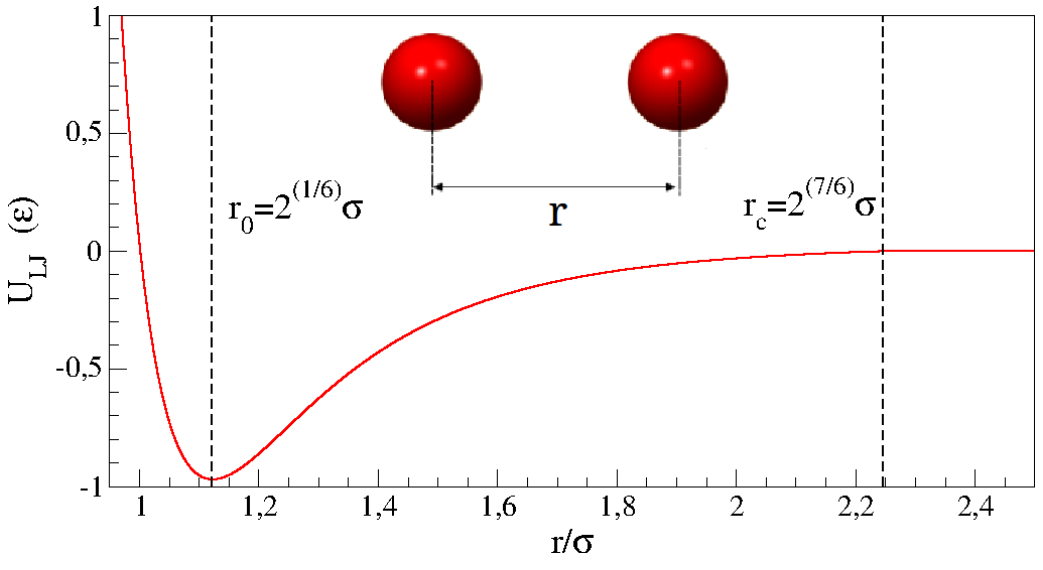
Harmonic bond interaction

$$U_{bond}(l) = k_b (l - l_b)^2$$



Lennard-Jones interaction between non-bonded monomers

$$U_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] - C$$



Molecular Dynamics

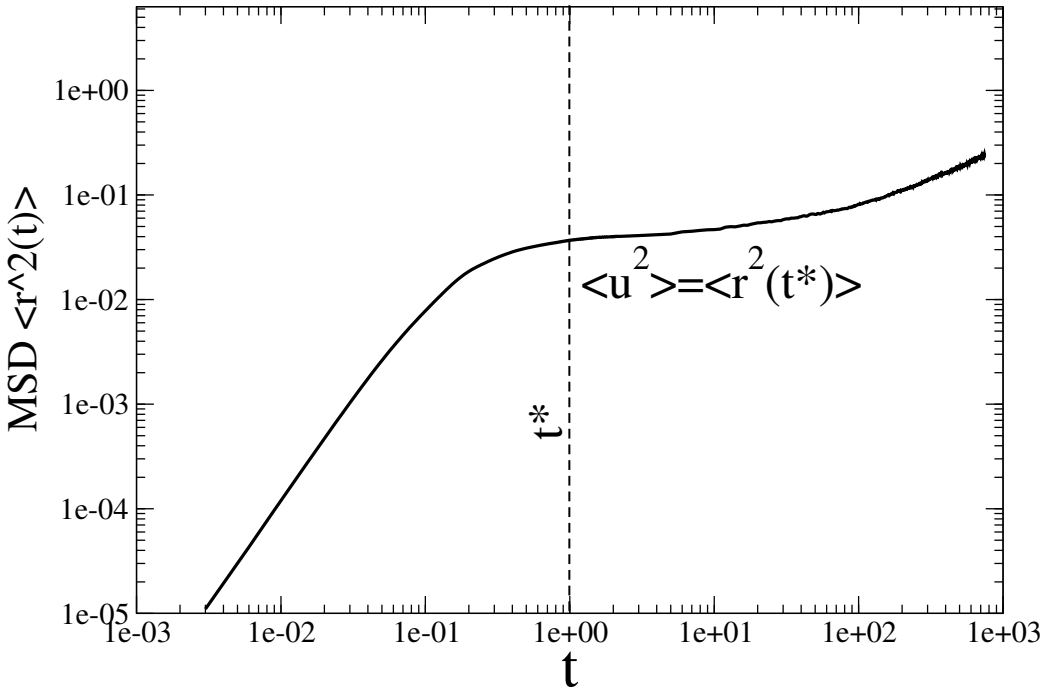
Reduced units

$$U_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + C \qquad r \leq r_c$$

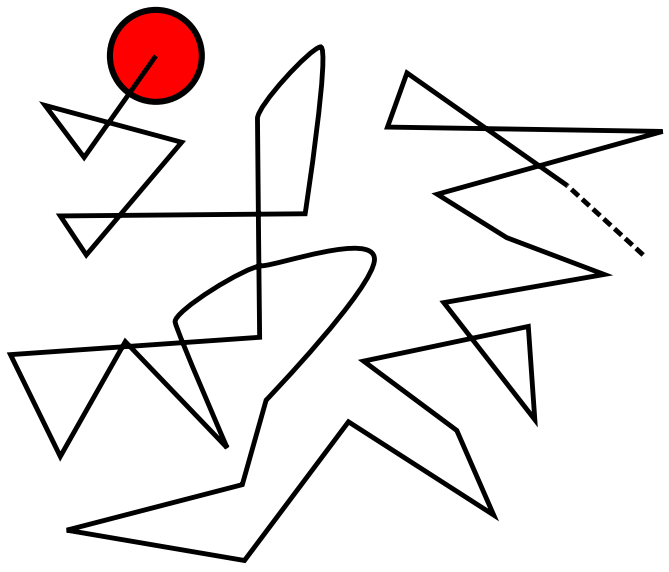
Physical quantity	Unit	Value for Ar
length	σ	$3.4 \cdot 10^{-10}\, m$
energy	ε	$1.65 \cdot 10^{-21}\, J$
mass	m	$6.69 \cdot 10^{-26}\, Kg$
time	$\left(\sigma^2 m/\varepsilon\right)^{1/2}$	$2.17 \cdot 10^{-12}\, s$
velocity	(ε/m)	$1.57 \cdot 10^{2}\, m/s$
force	ε/σ	$4.85 \cdot 10^{-12}\, N$
pressure	ε/σ^3	$4.20 \cdot 10^{7}\, N/m^2$
temperature	ε/k_B	$120\, K$

Markers of the dynamics

cage rattling



Diffusion



Mean Squared Displacement:

$$\langle r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^{i=N} (r_i(t) - r_i(0))^2$$

$\langle u^2 \rangle$

amplitude of the rattling motion

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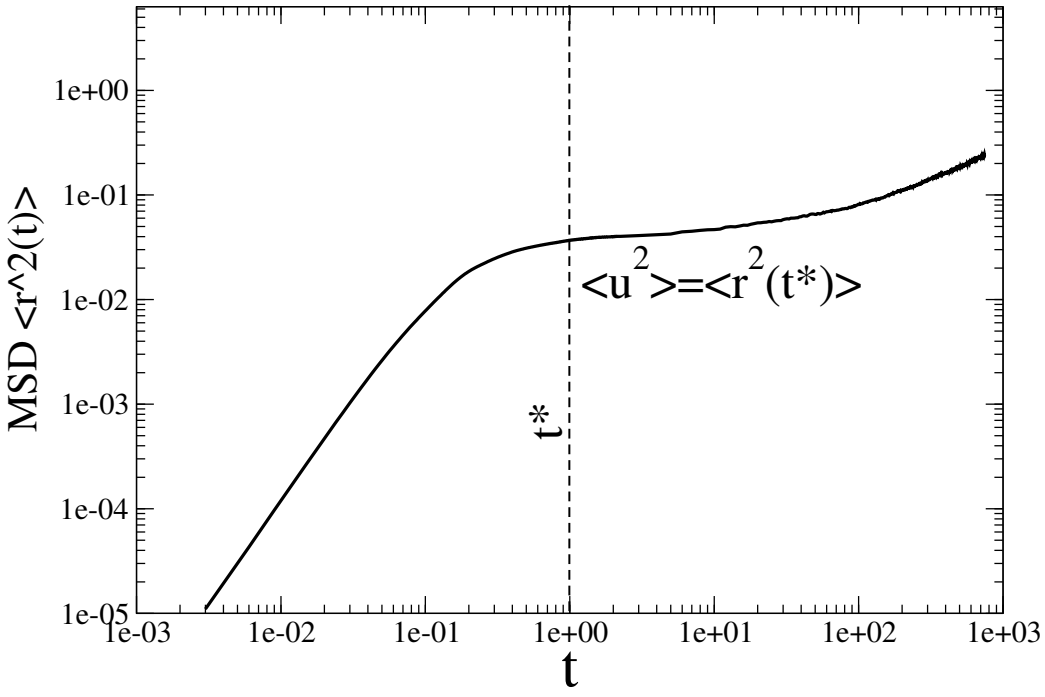

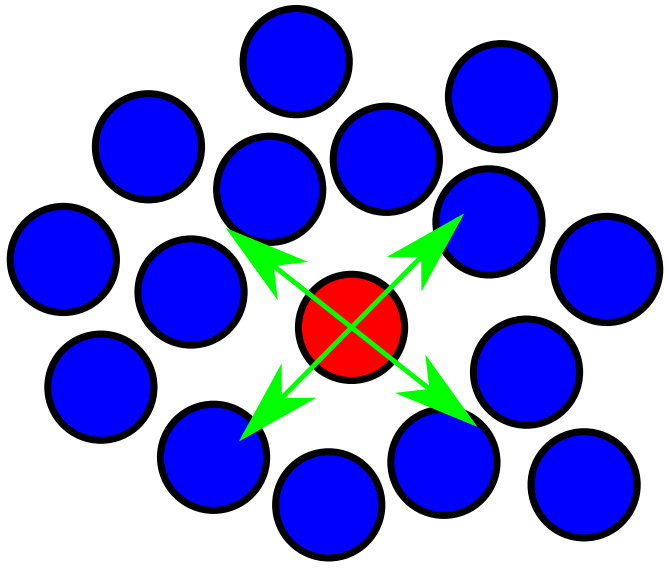

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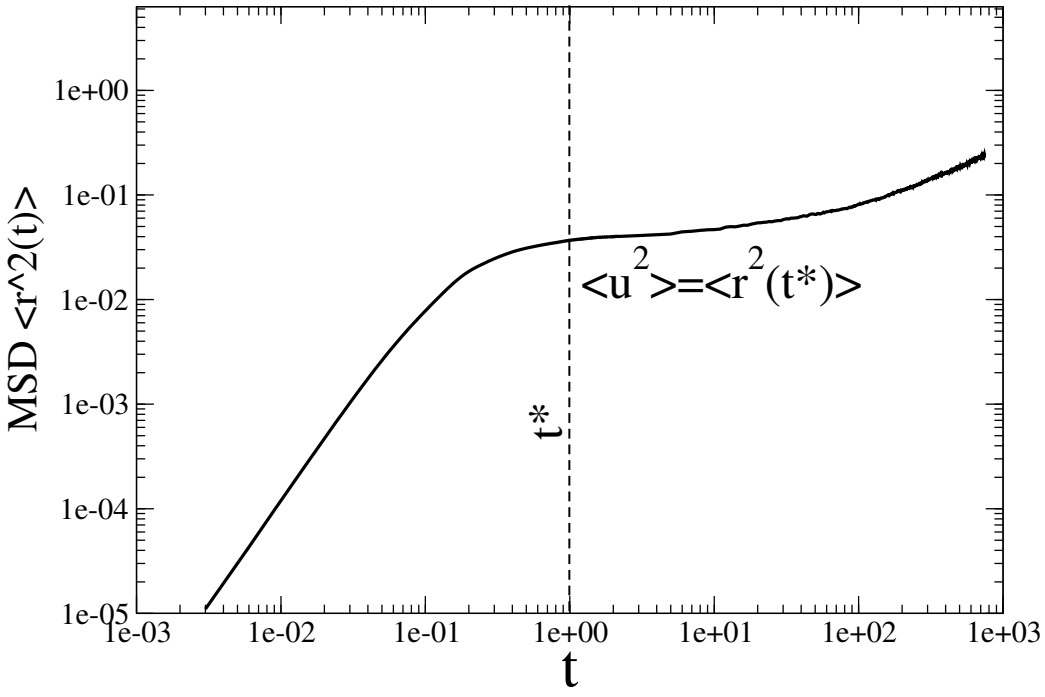

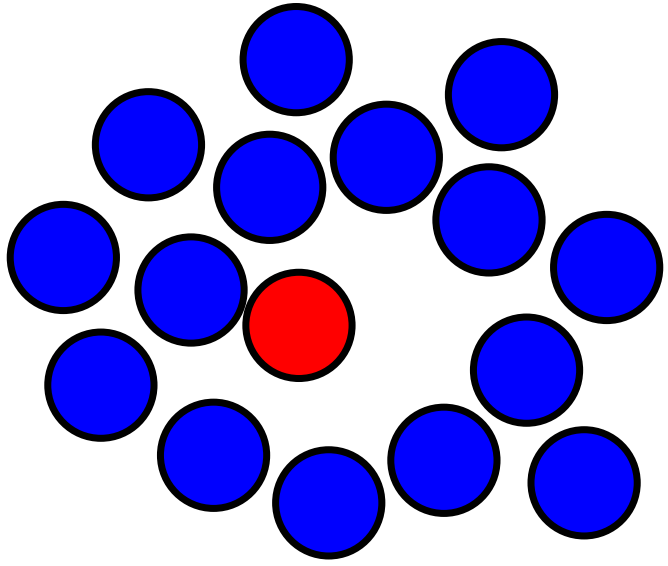

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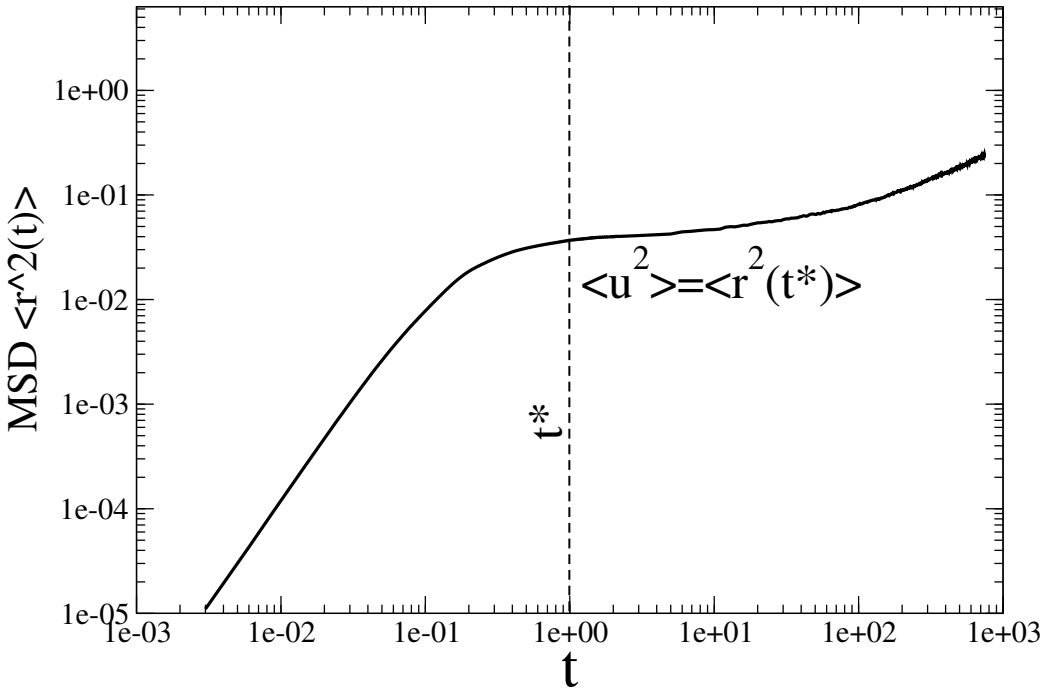

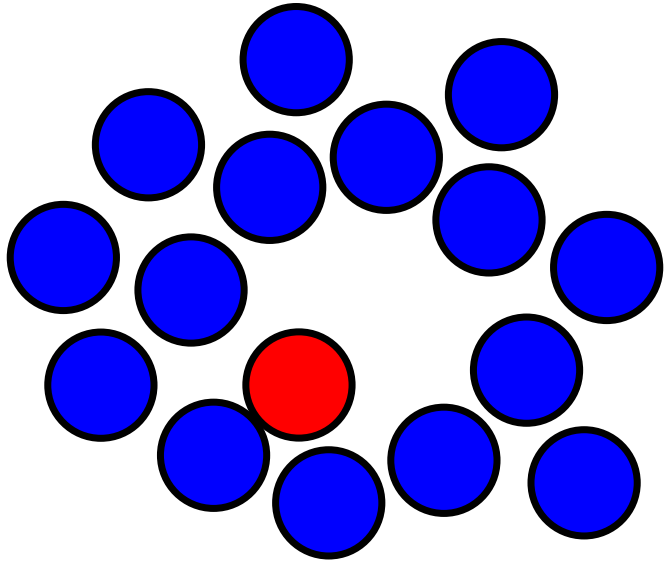

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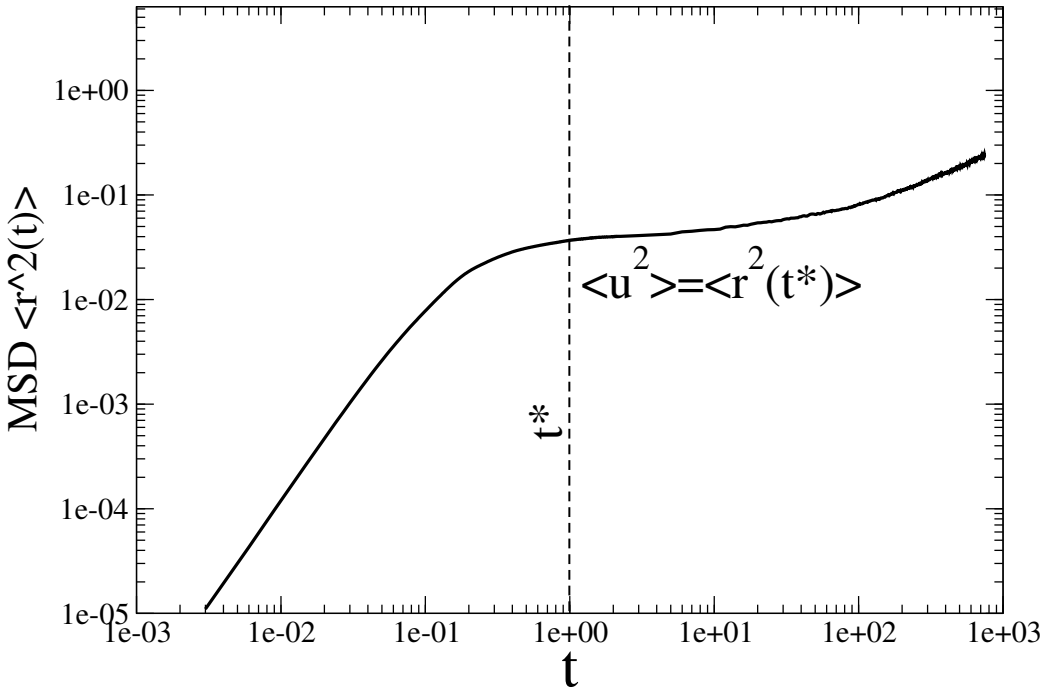

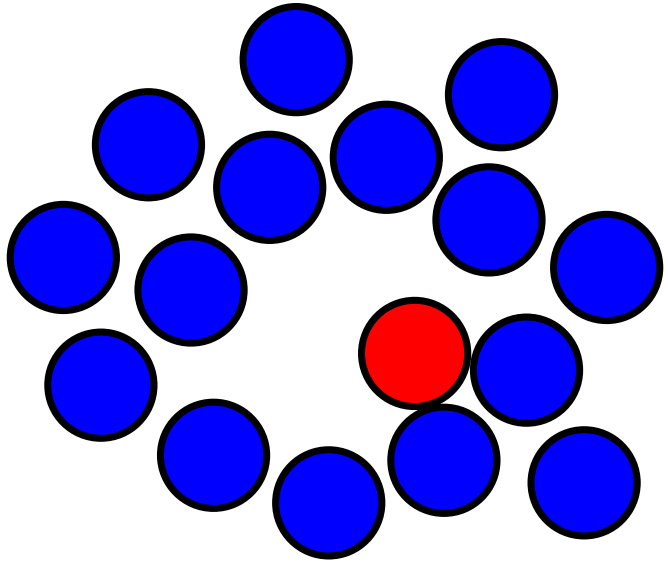

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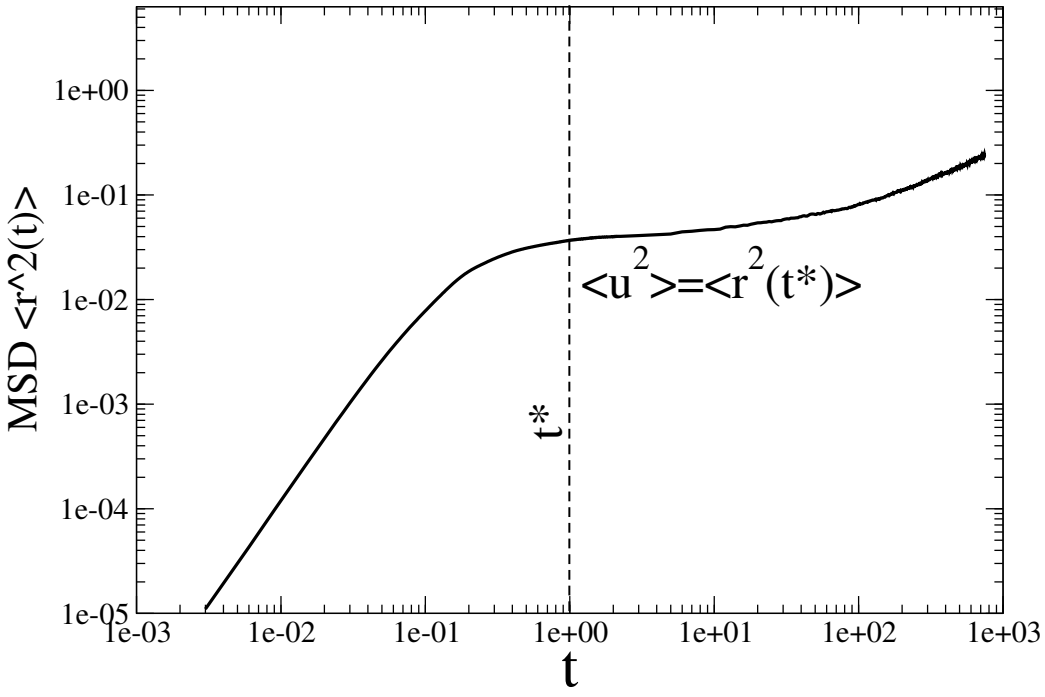

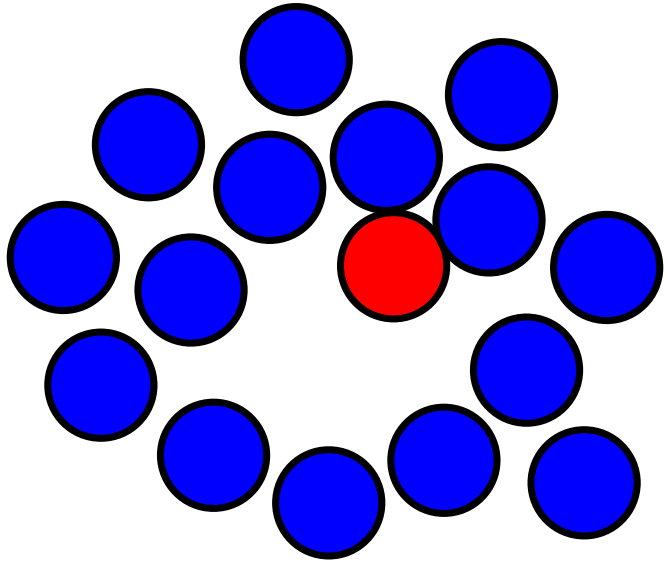

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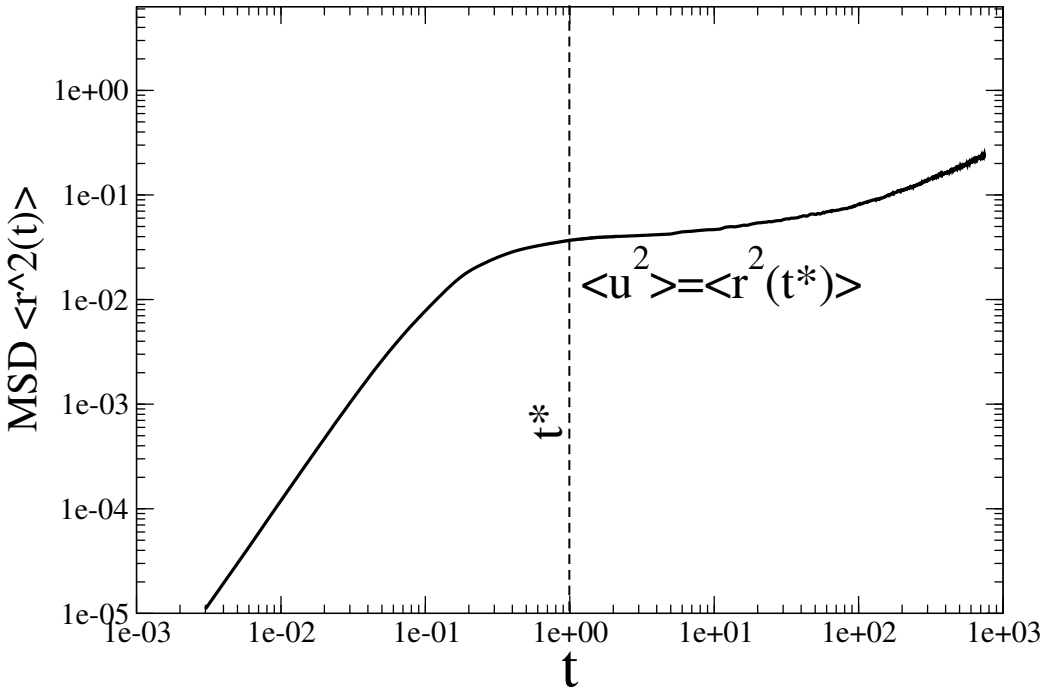

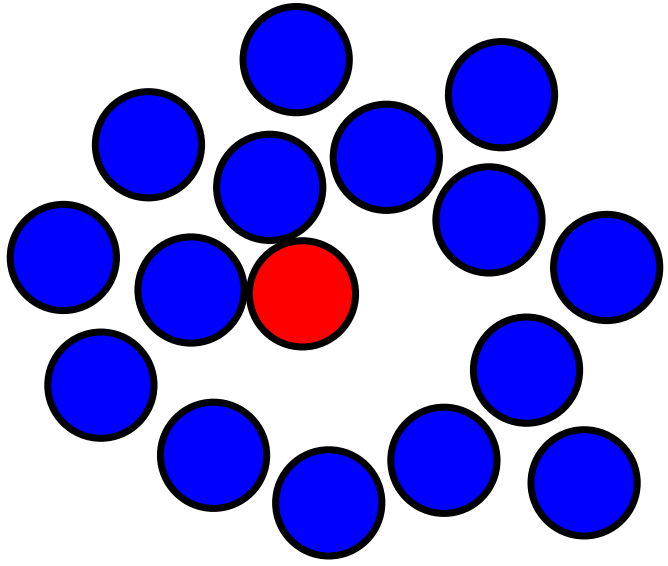

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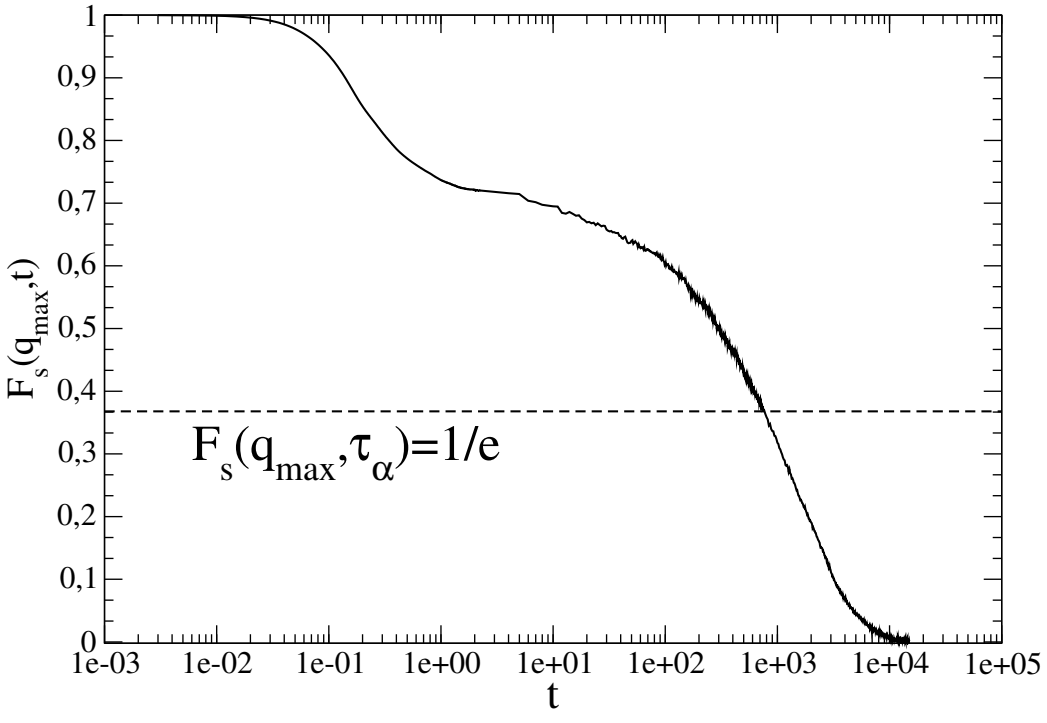
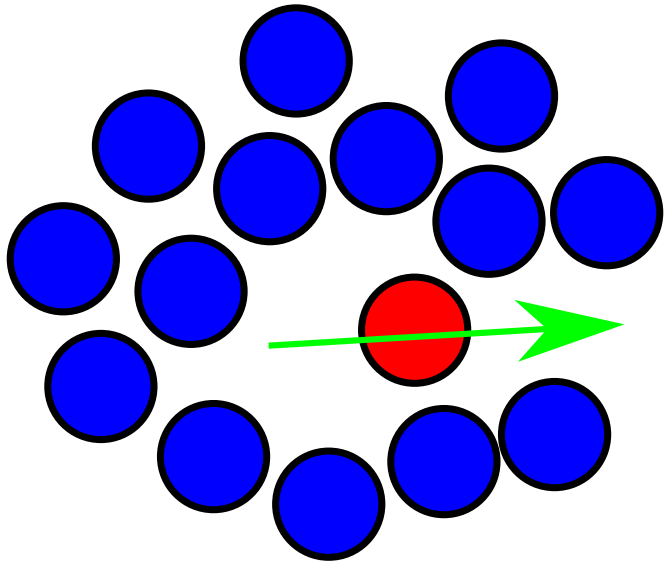
Markers of the dynamics

structural relaxation





Intermediate Scattering Function

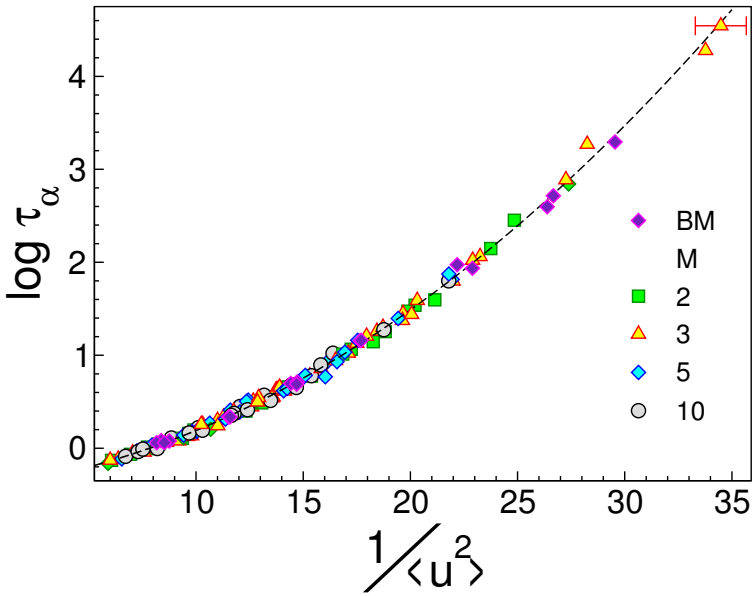
$$F_s(q,t) = \frac{1}{N}\sum_{i=1}^{i=N} e^{i\mathbf{q}\cdot(\mathbf{r}_i(t)-\mathbf{r}_i(0))}$$

τ_α

structural relaxation time

A universal master curve

From MD simulations...



... to experiments

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Larini et. al. *Nat. Phys.* (2008)
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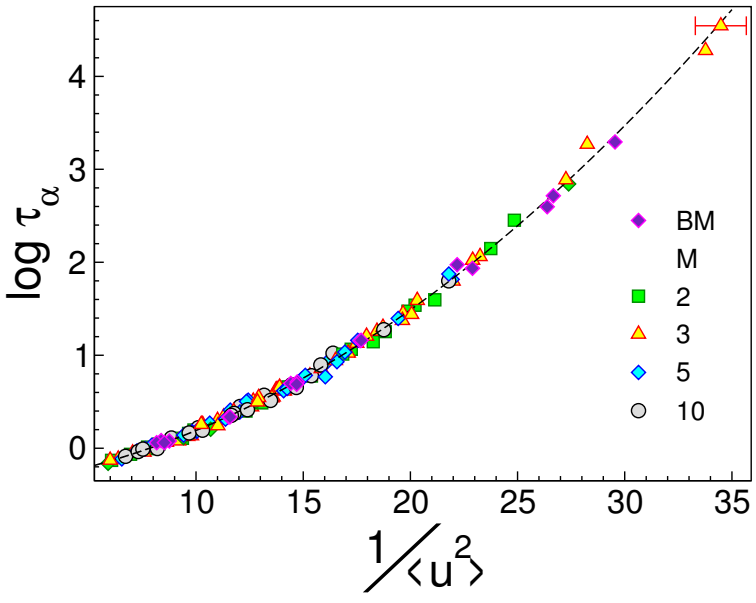

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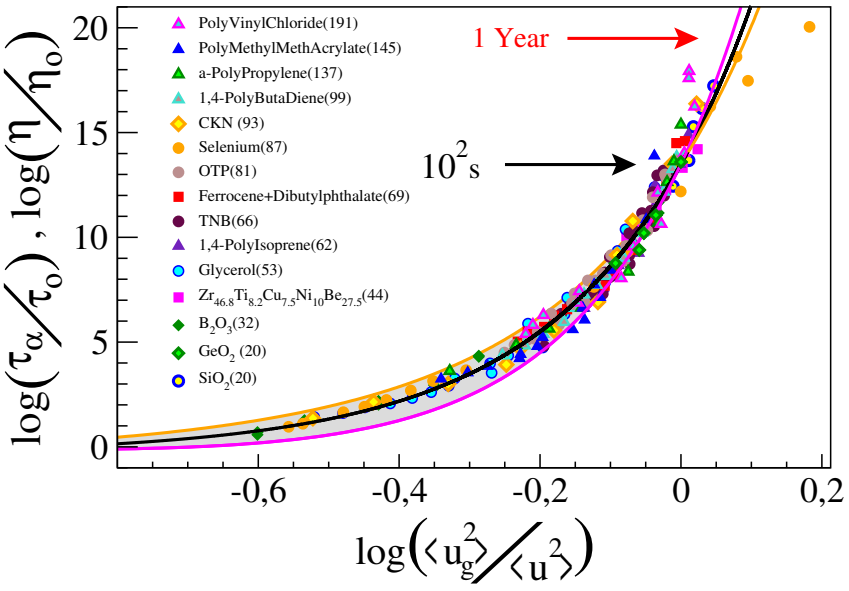

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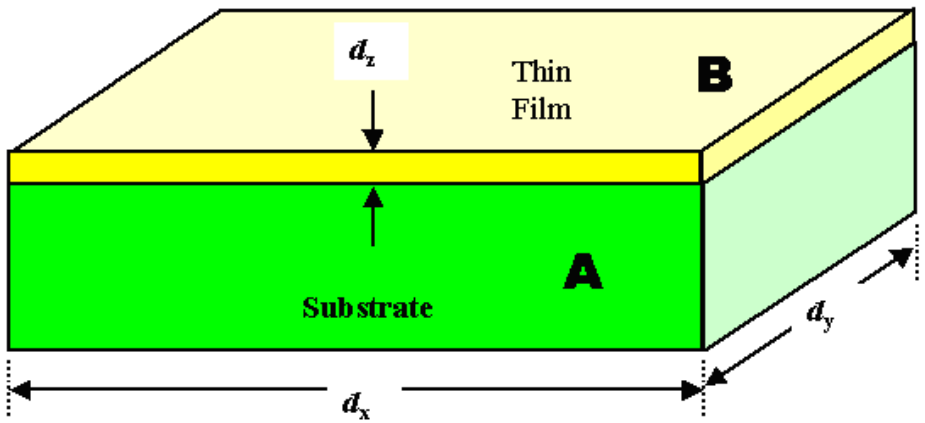
Thin films

Simulation of the substrate

Confinement: new length scales and border effects $\rightarrow$ new physics to explore!

Thin films ($1 \sim 10\,nm$): many experimental results $\rightarrow$ time to simulate!



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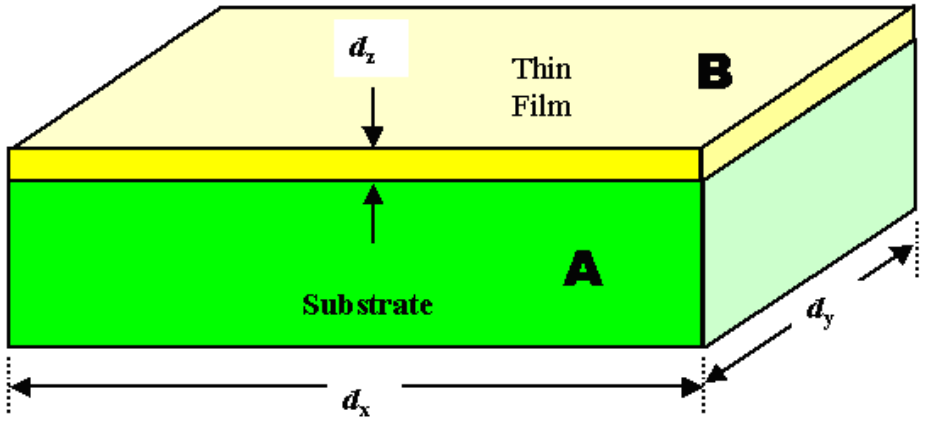

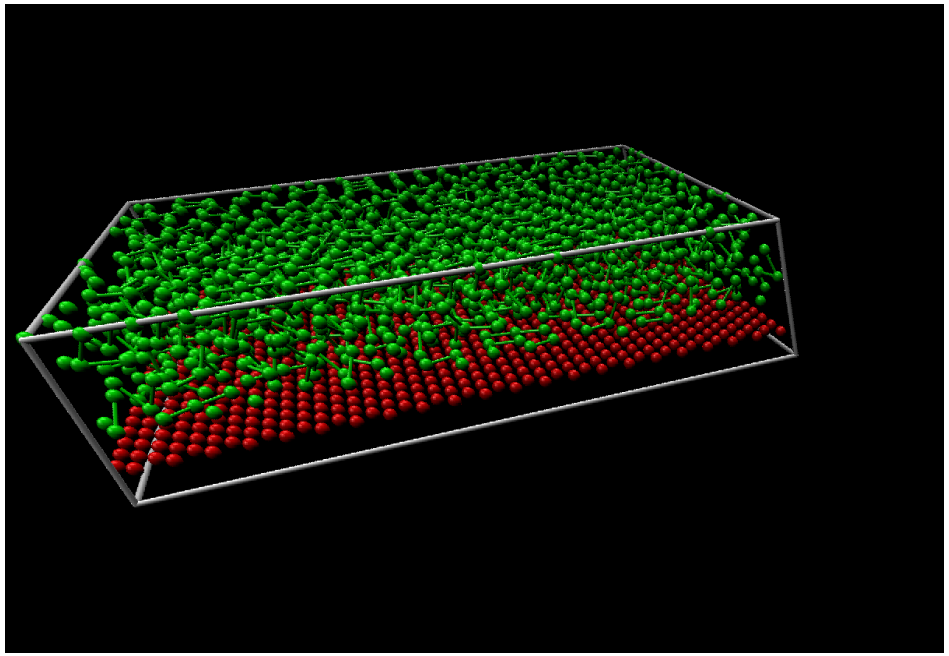

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2. film-substrate interactions
   - Rough substrate
   - Smooth substrate

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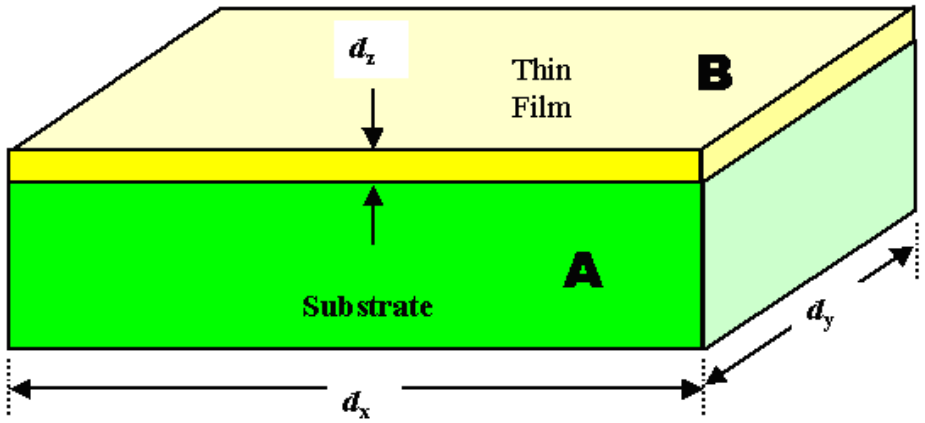

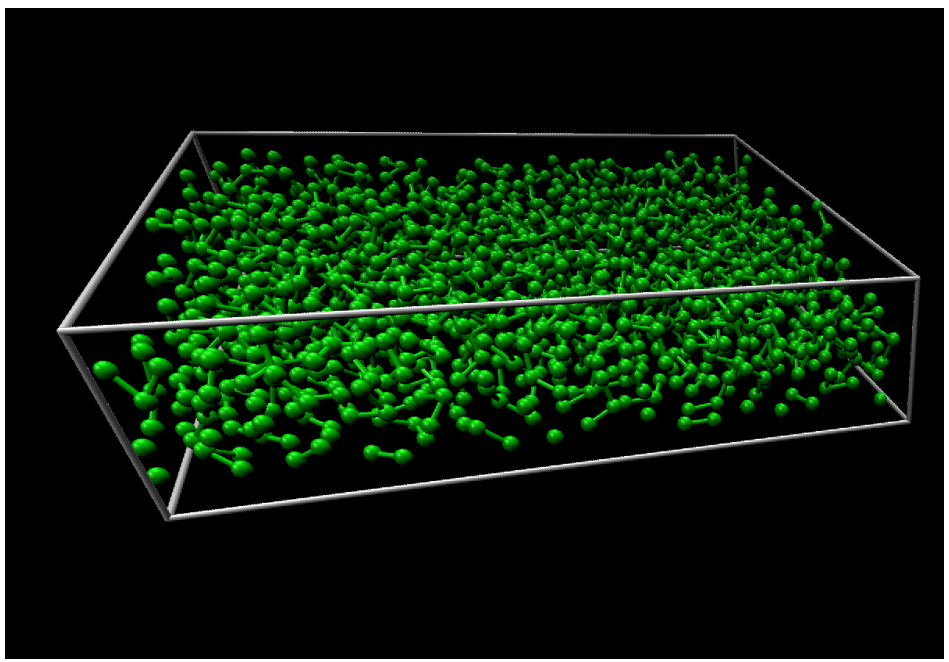

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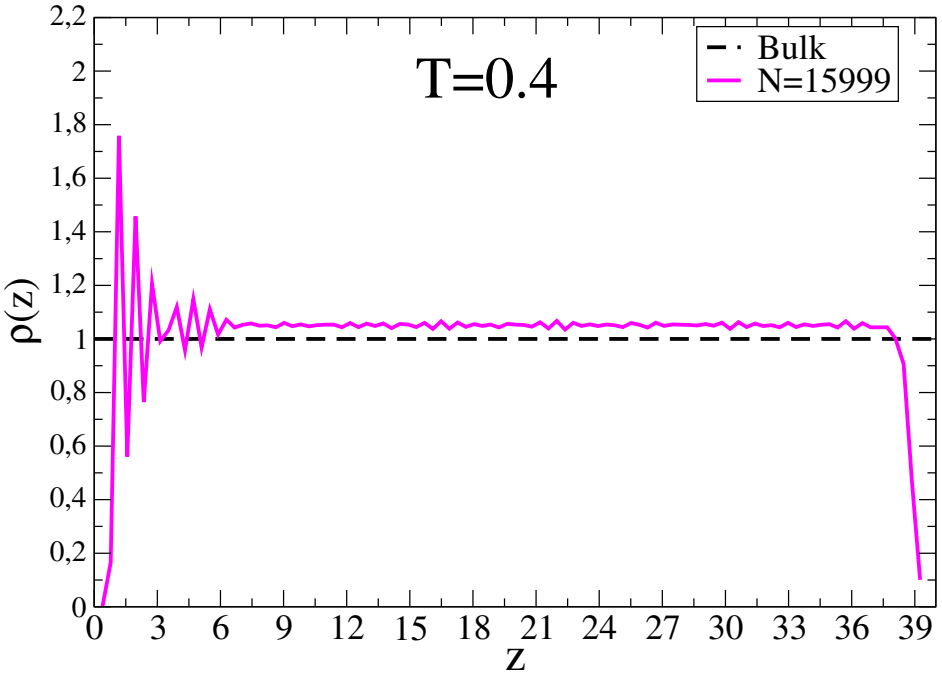
Thin films
density structure

Simulation of films of different thickness

$P_z = 0$ due to mechanical equilibrium

Films with less atoms N are thinner and thinner and thinner...



Non-homogeneous density structure: wall and free surface enhanced dynamics

1. Layered structure near the wall
2. Bulk-like region in the middle
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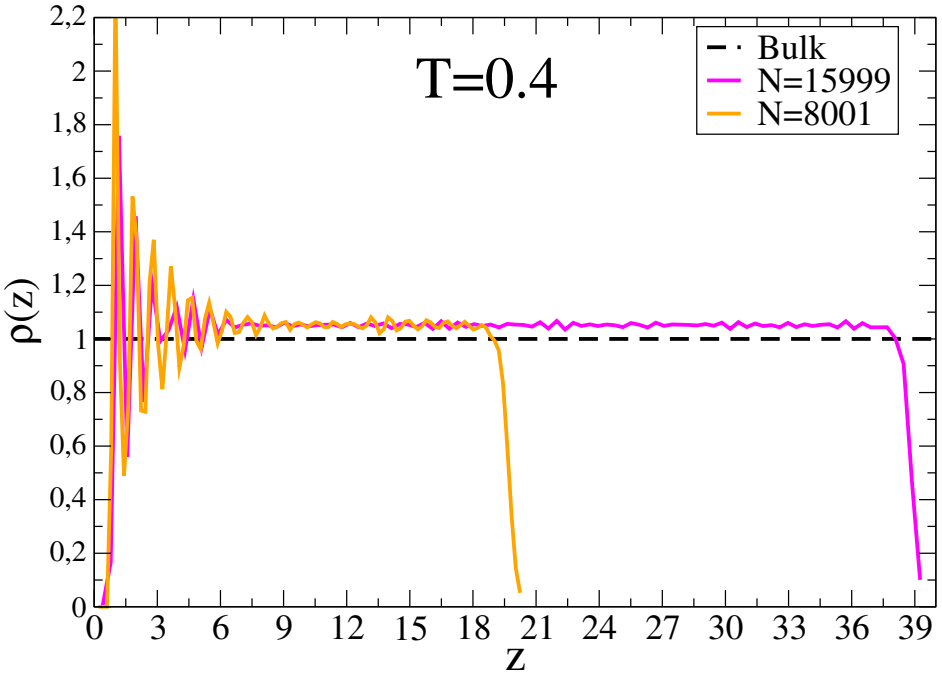

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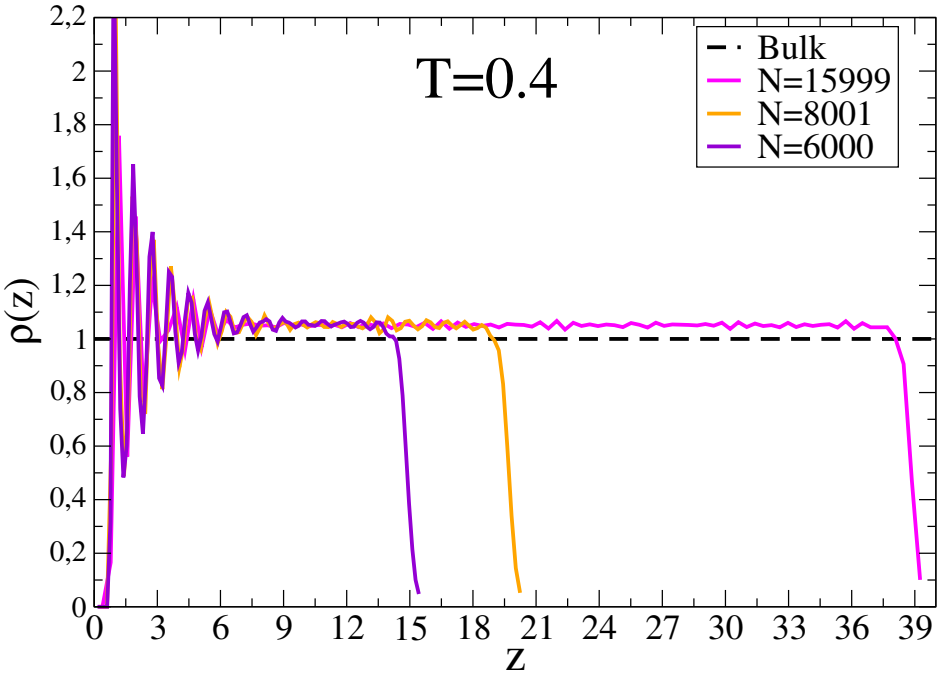

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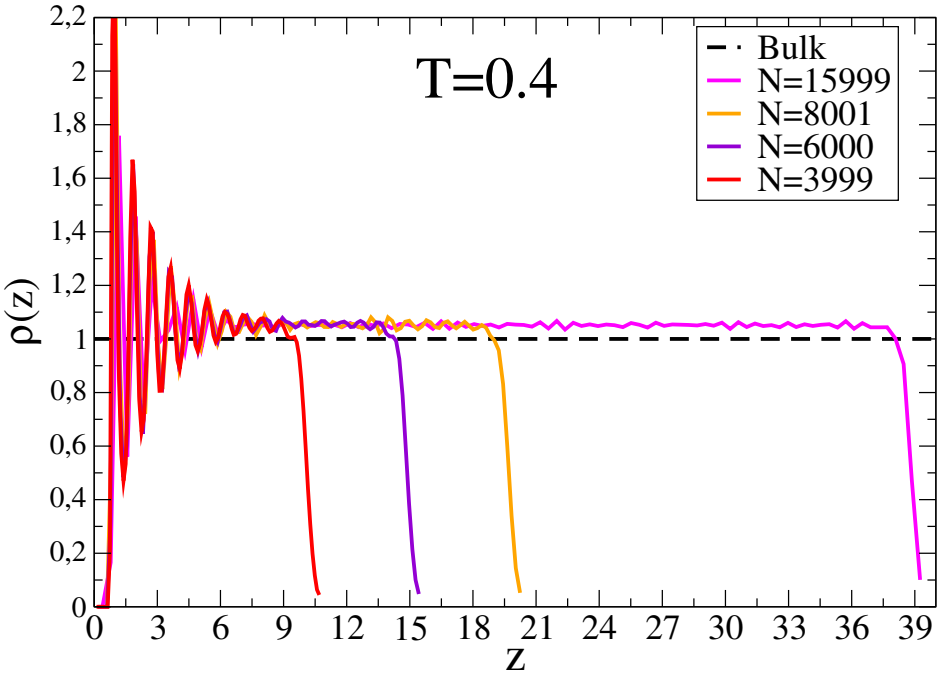

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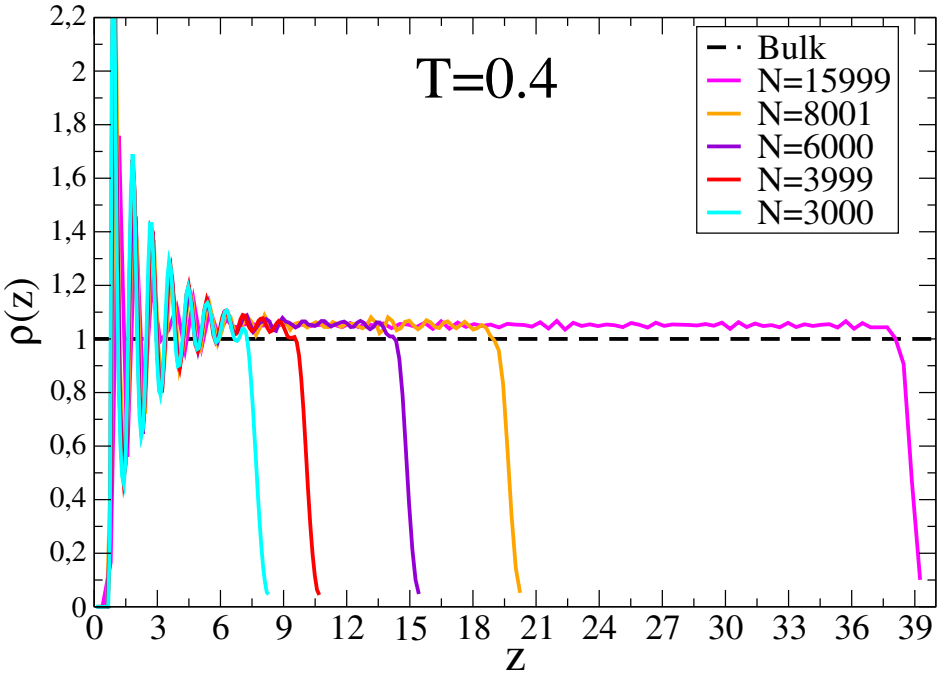

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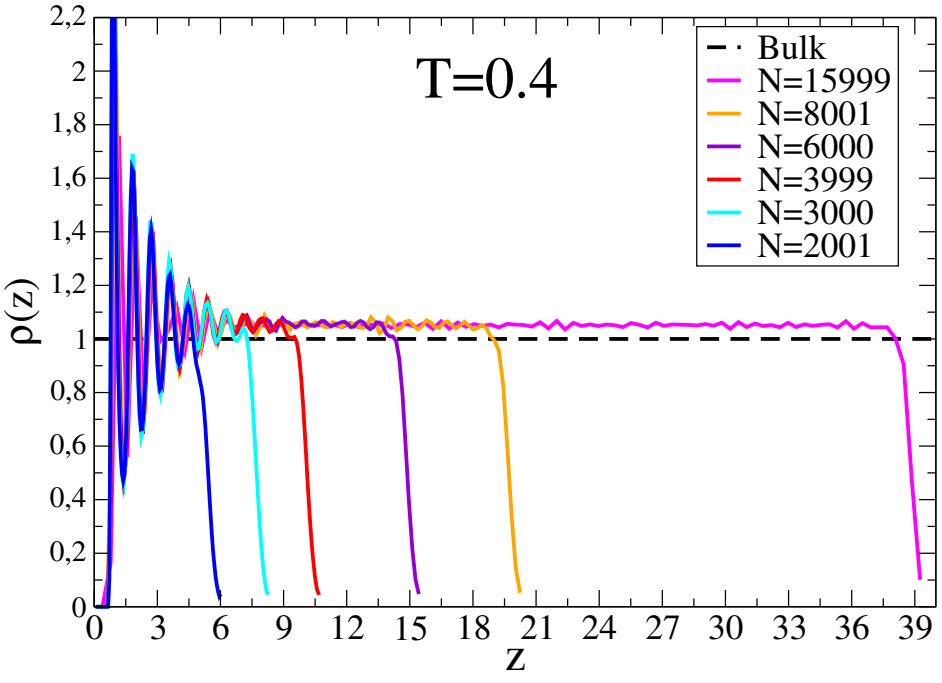

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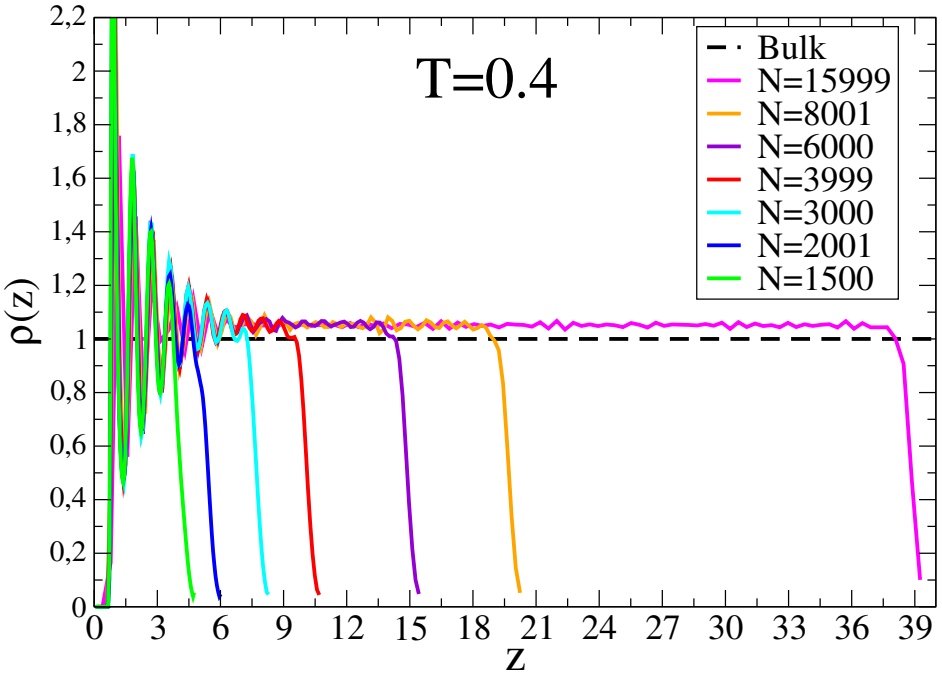

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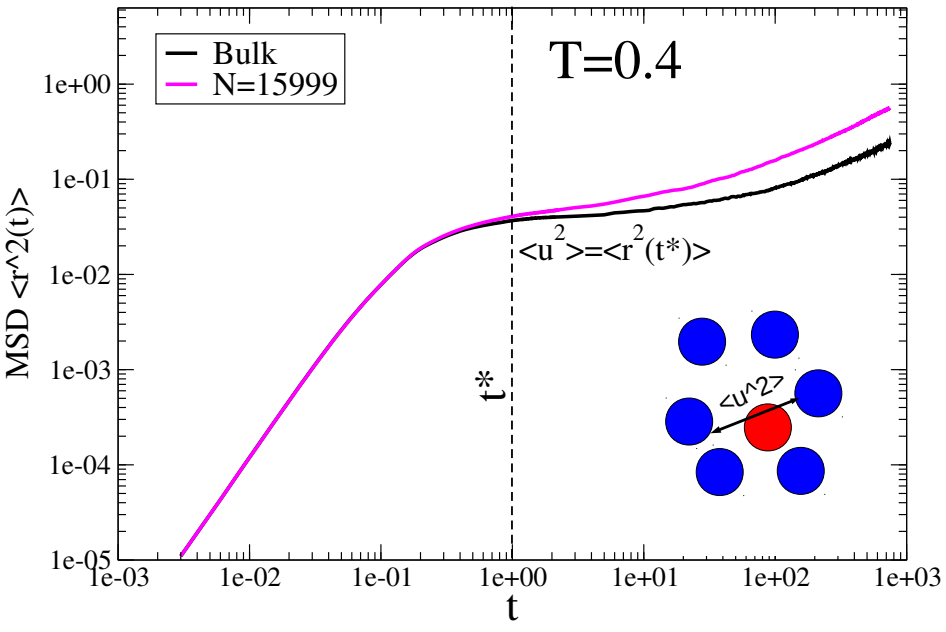
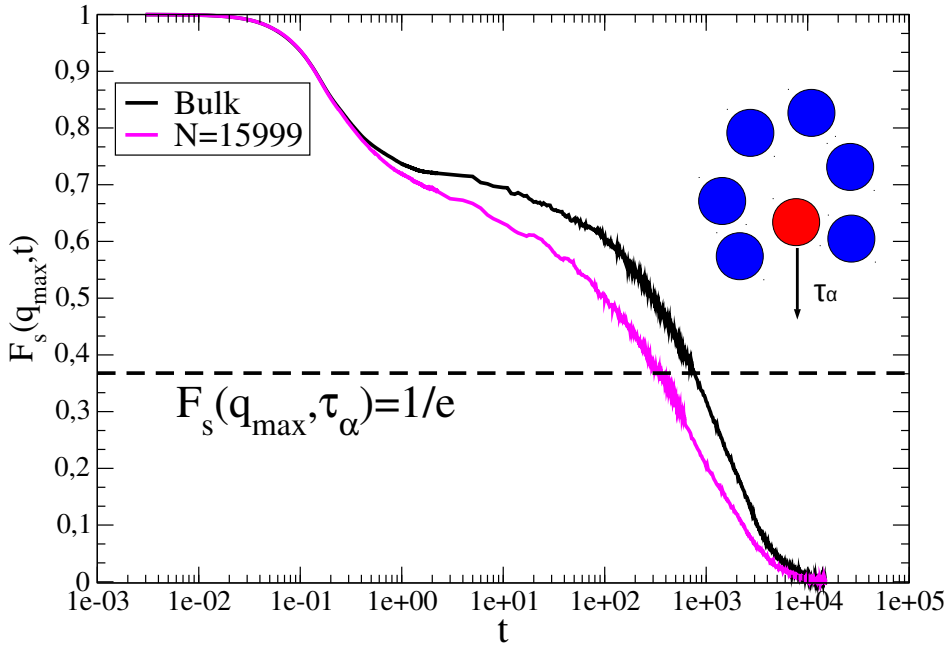
Film dynamics
MSD and ISF





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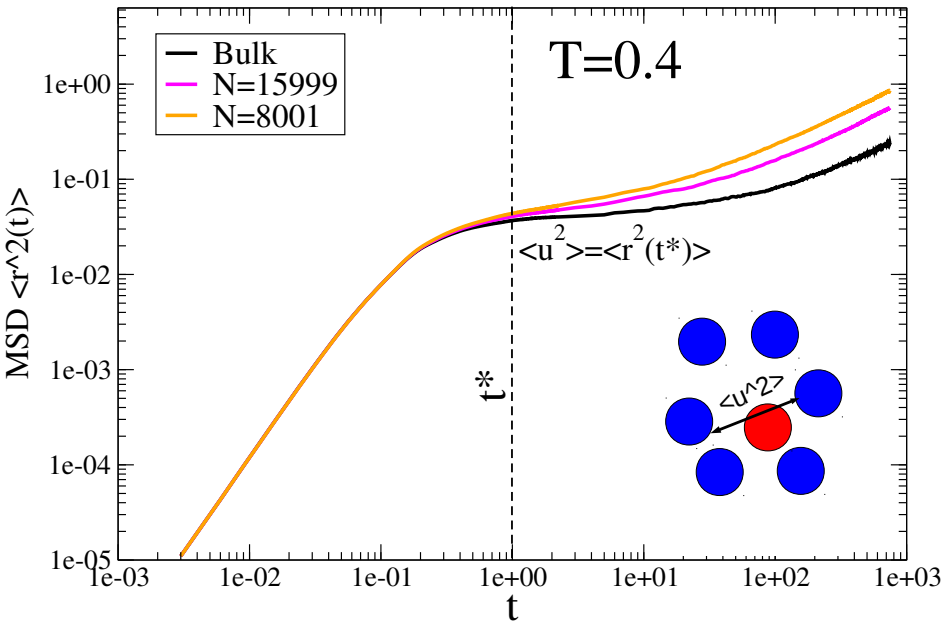

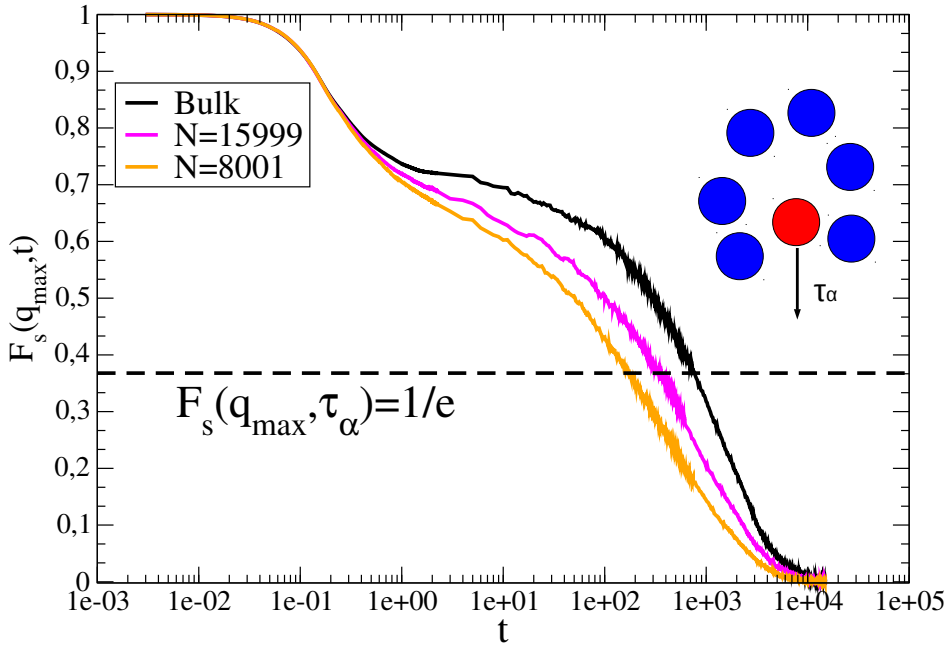

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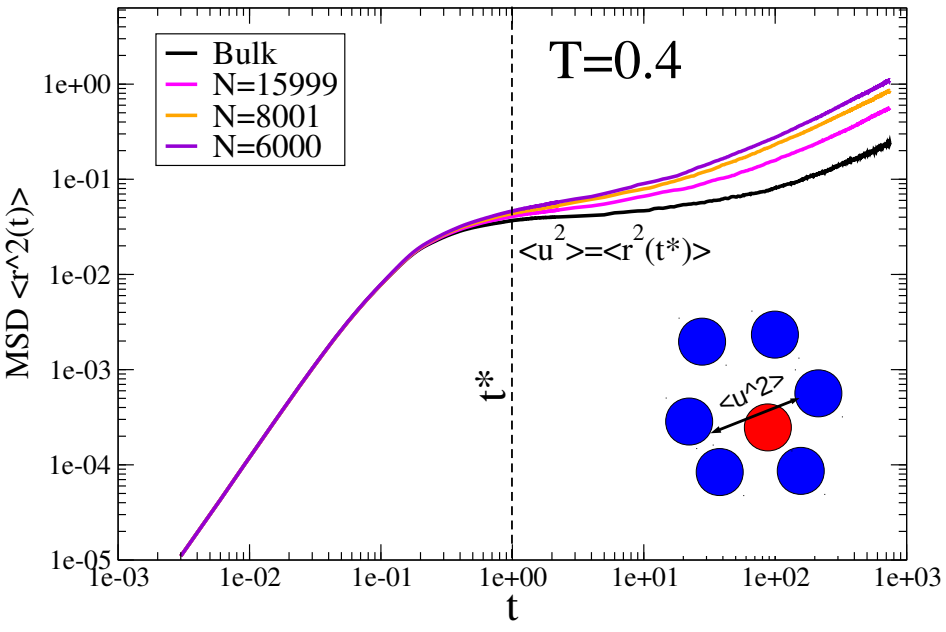

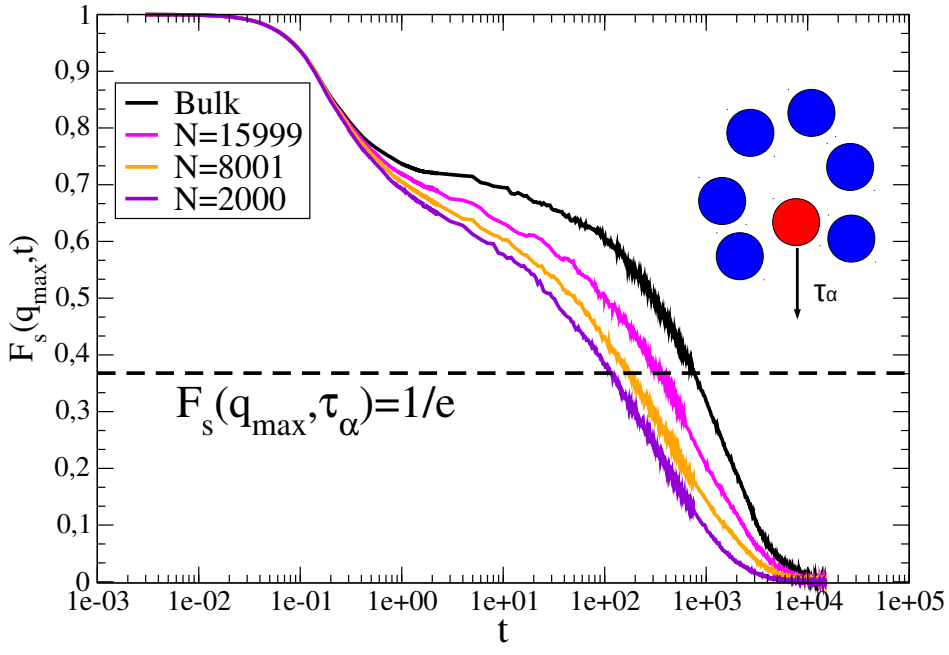

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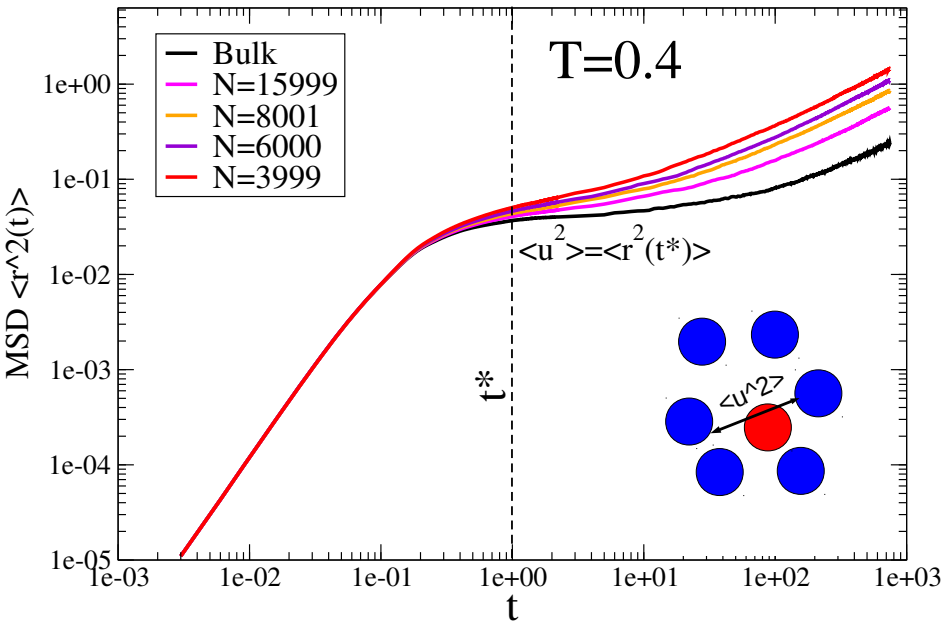

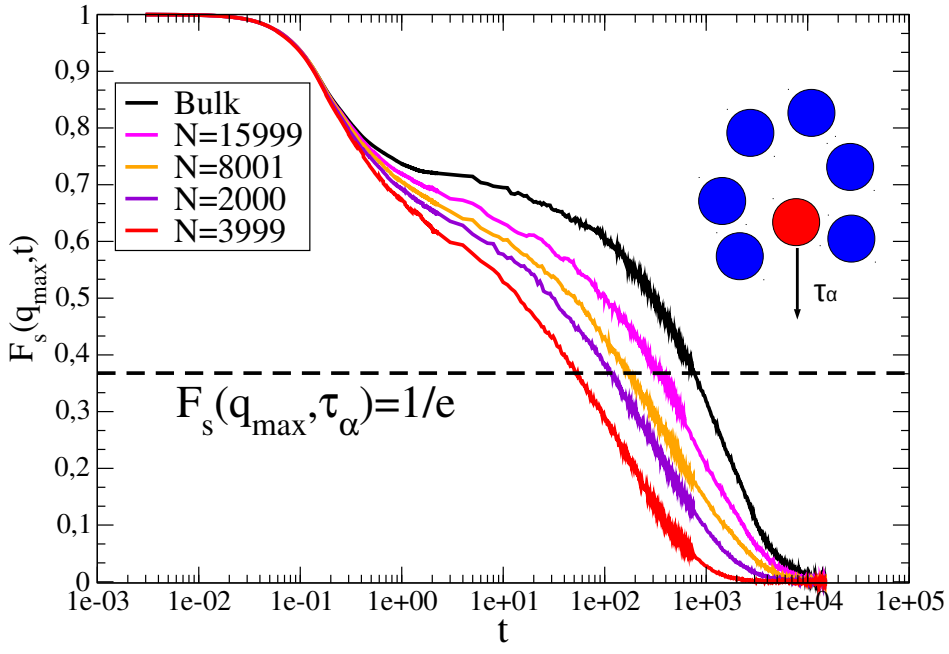

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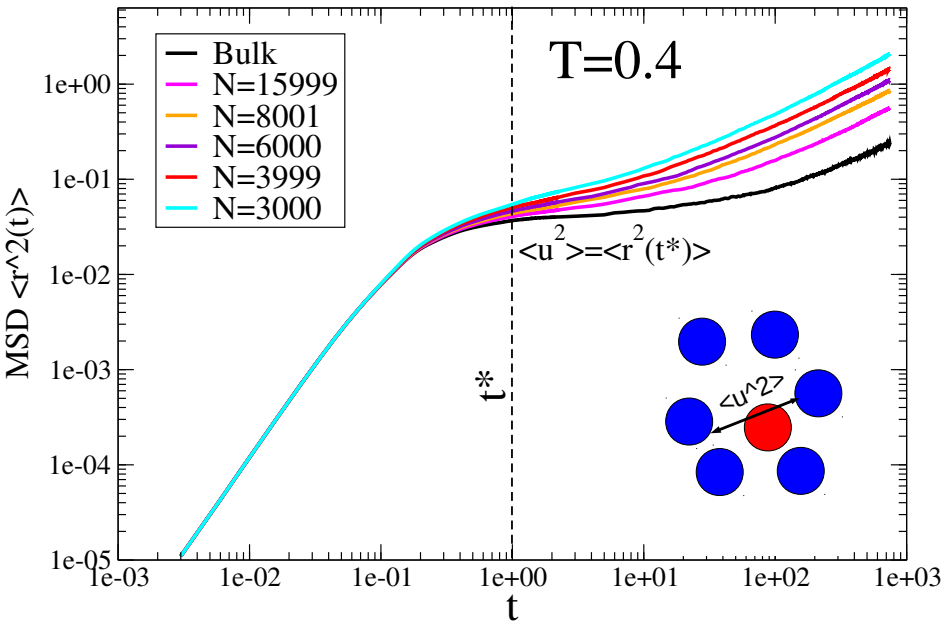

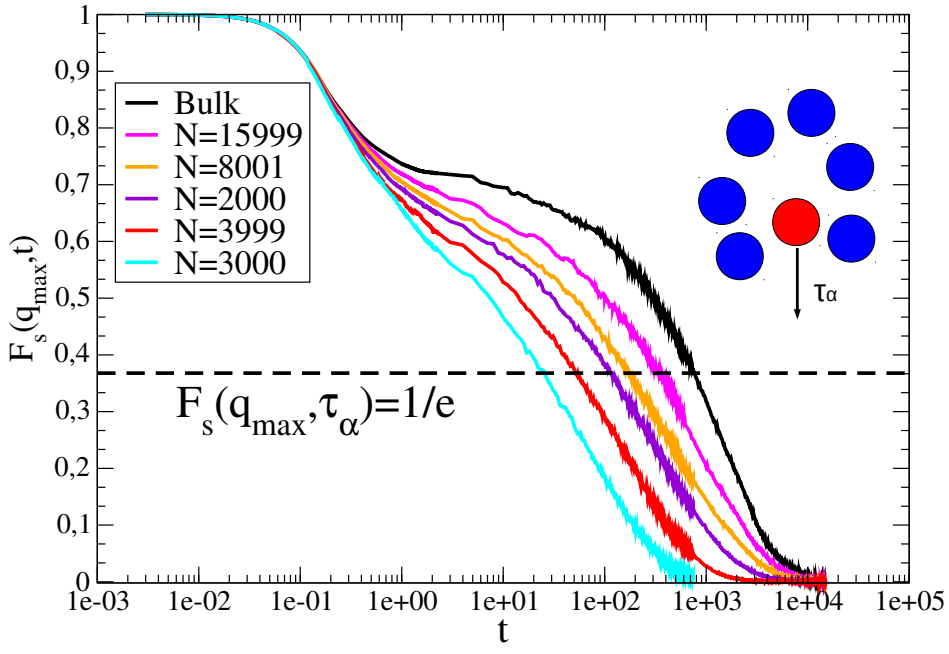

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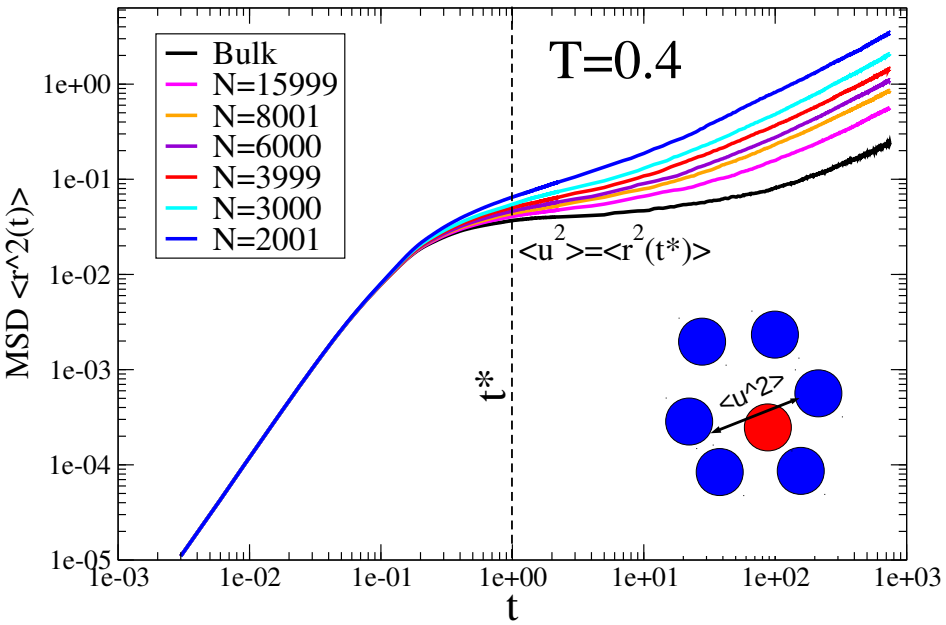

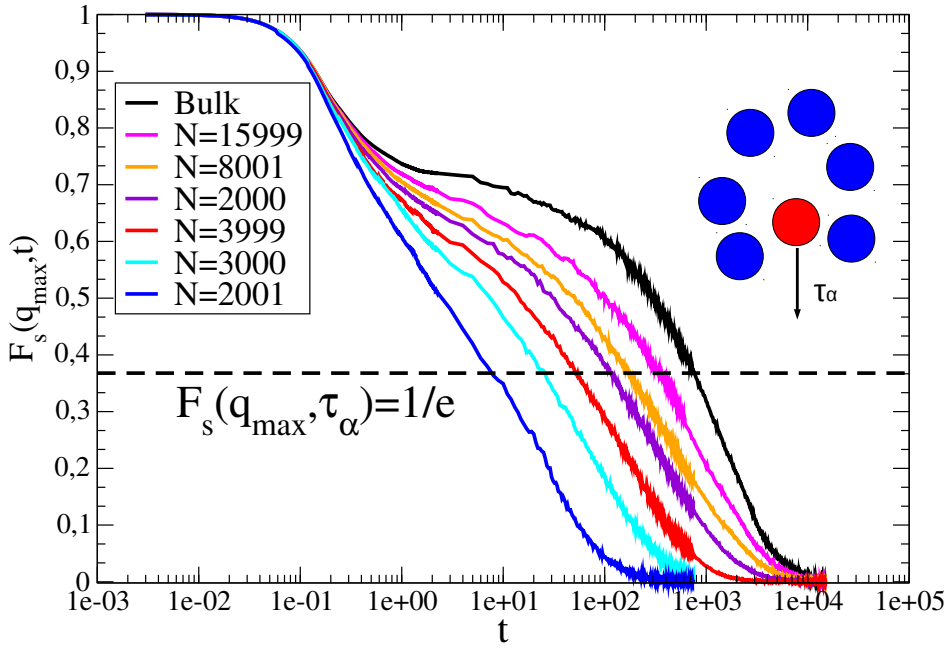

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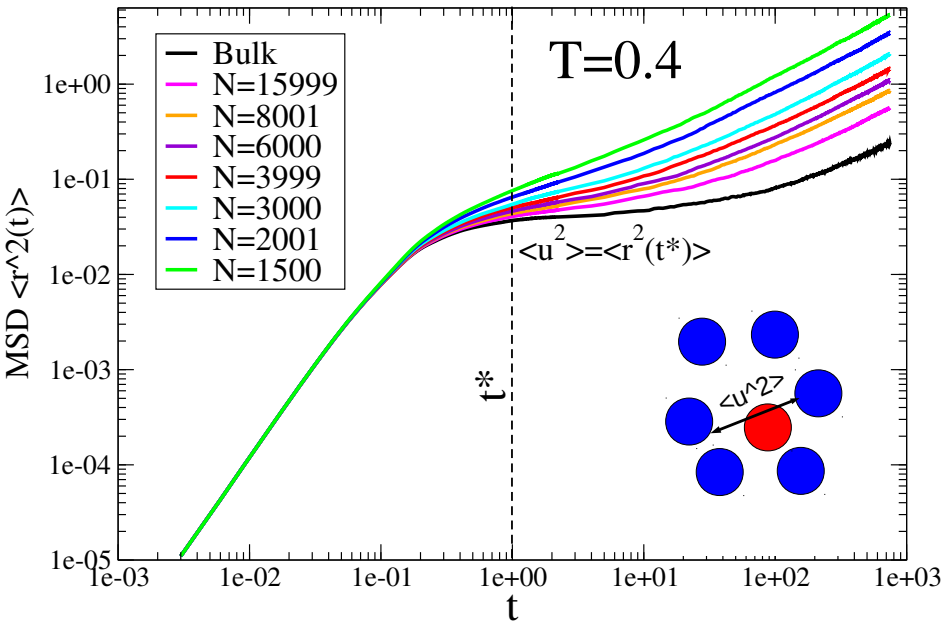

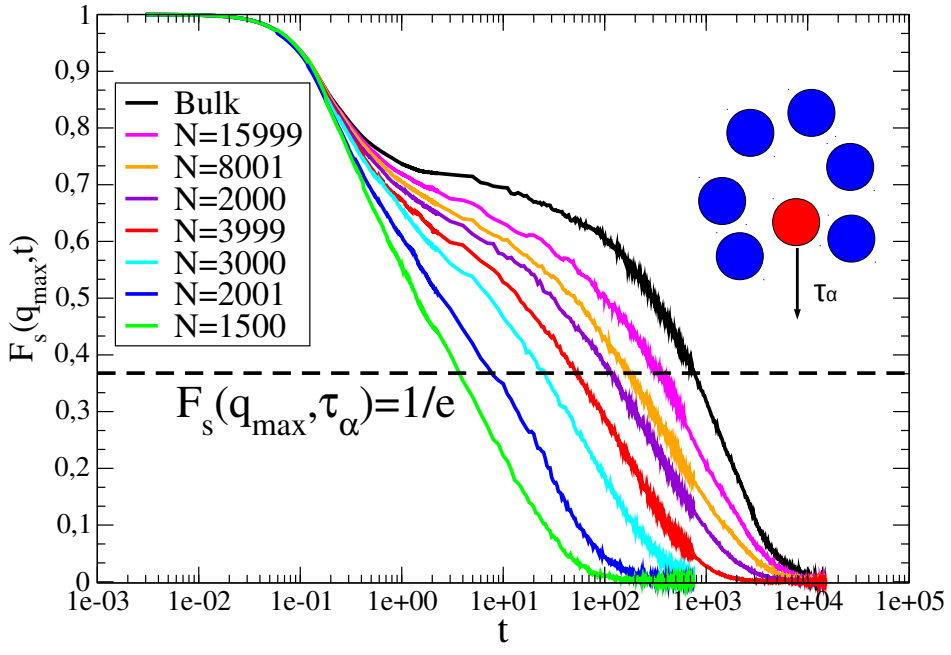

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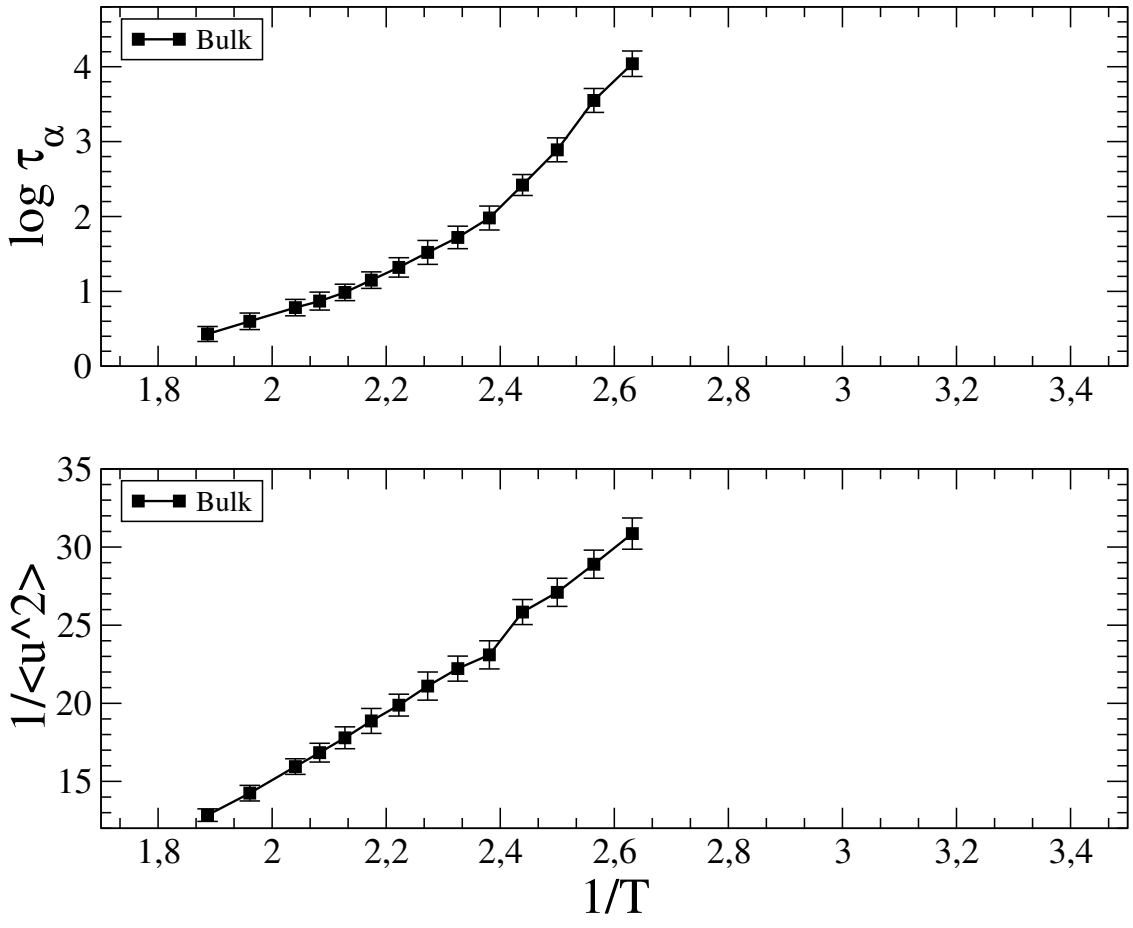
Arrhenius plots
changing the temperature

Temperature decrease $\rightarrow$ the system slows down

Arrhenius plots show the increase of the time scales

Due to confinement, each curve is shifted

$\langle u^2 \rangle$ is more sensitive than τ_α to film thickness



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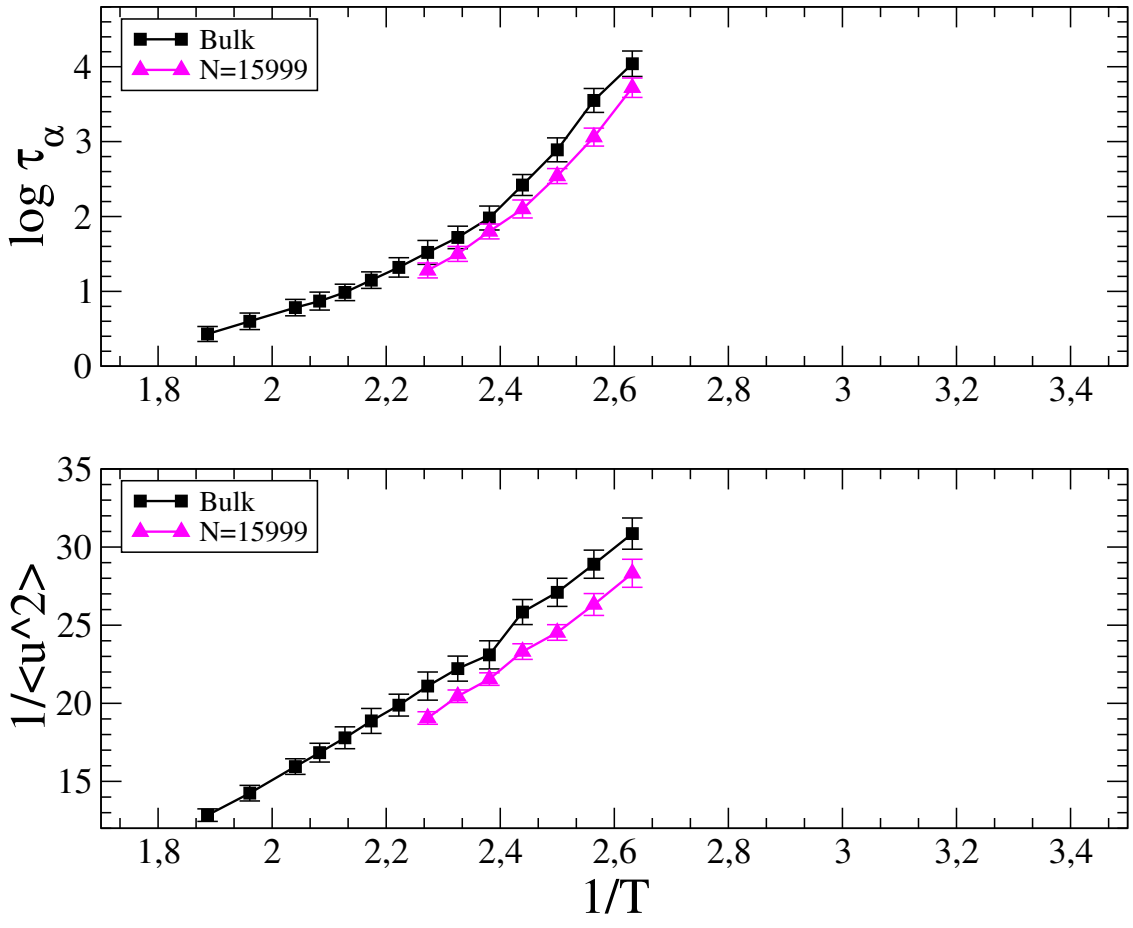

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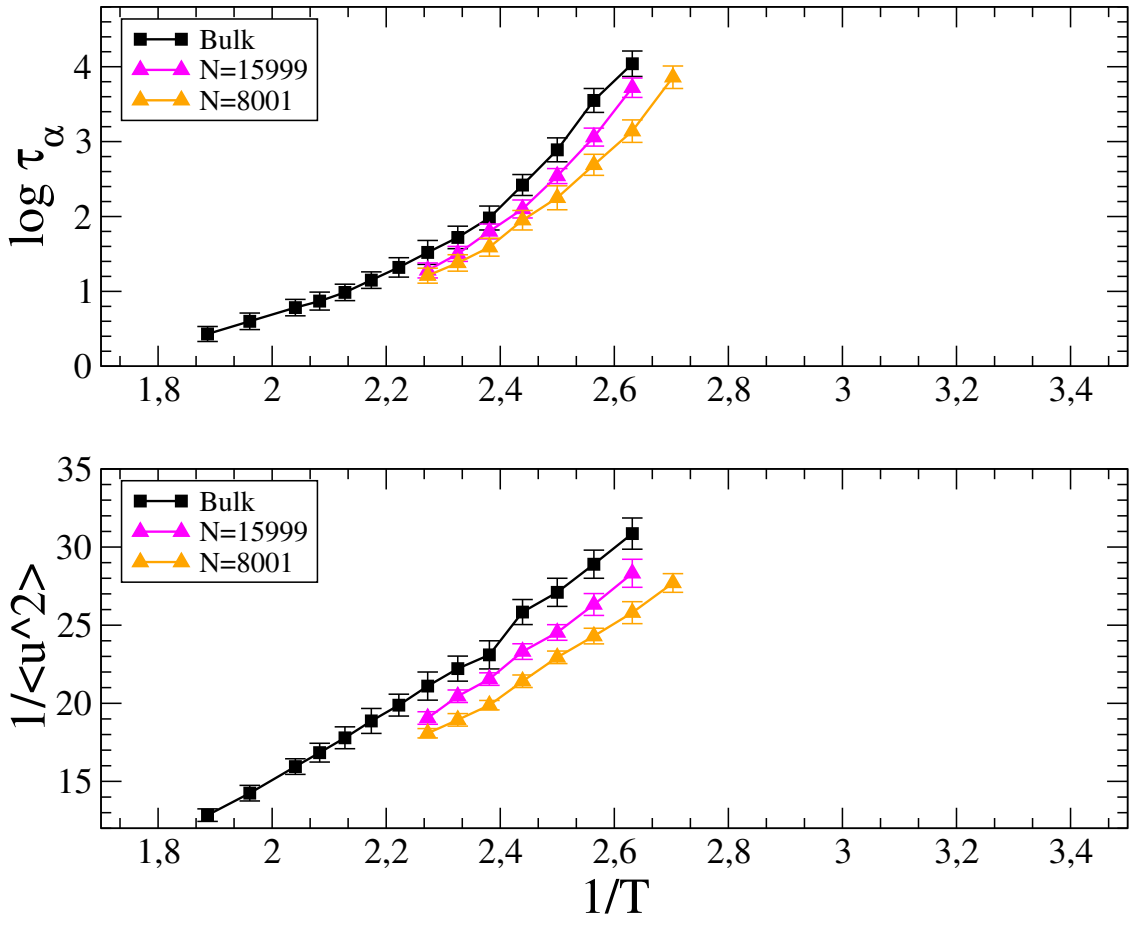

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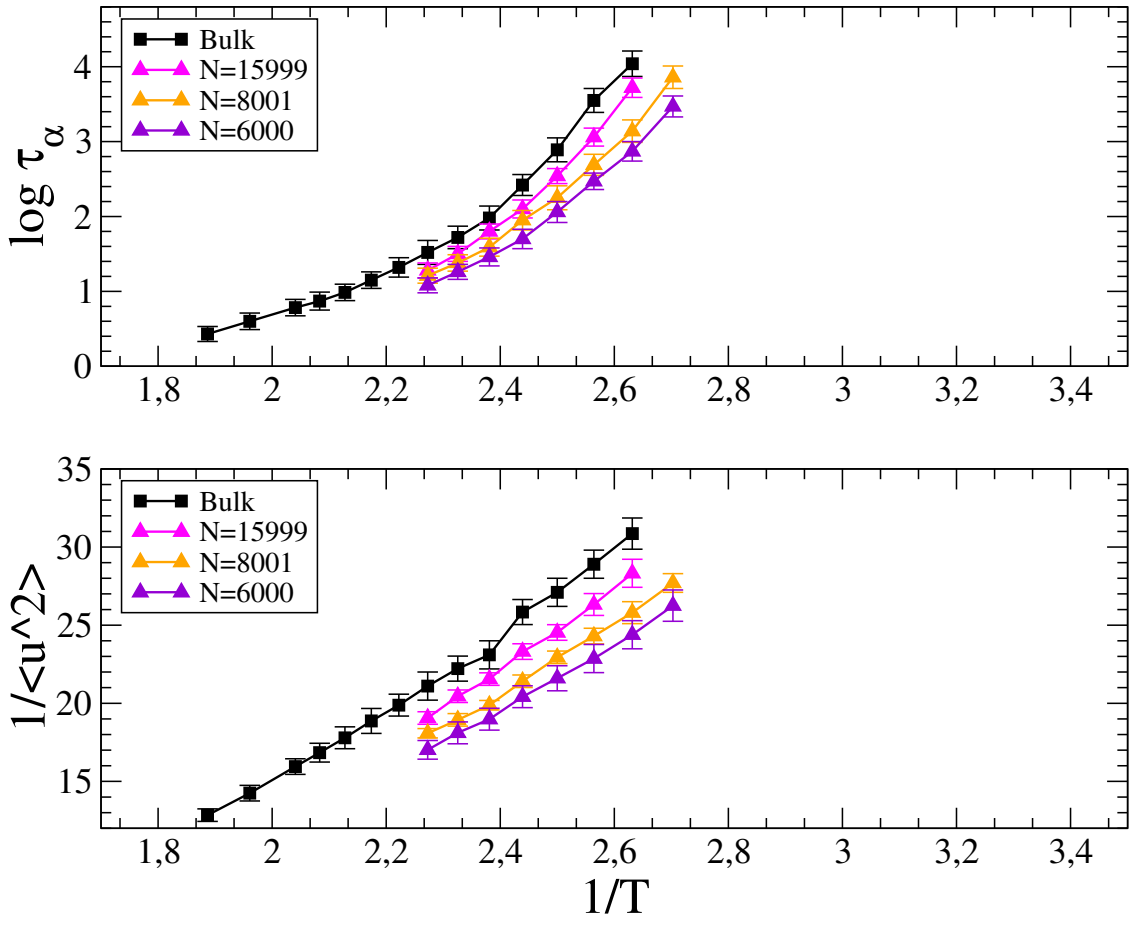

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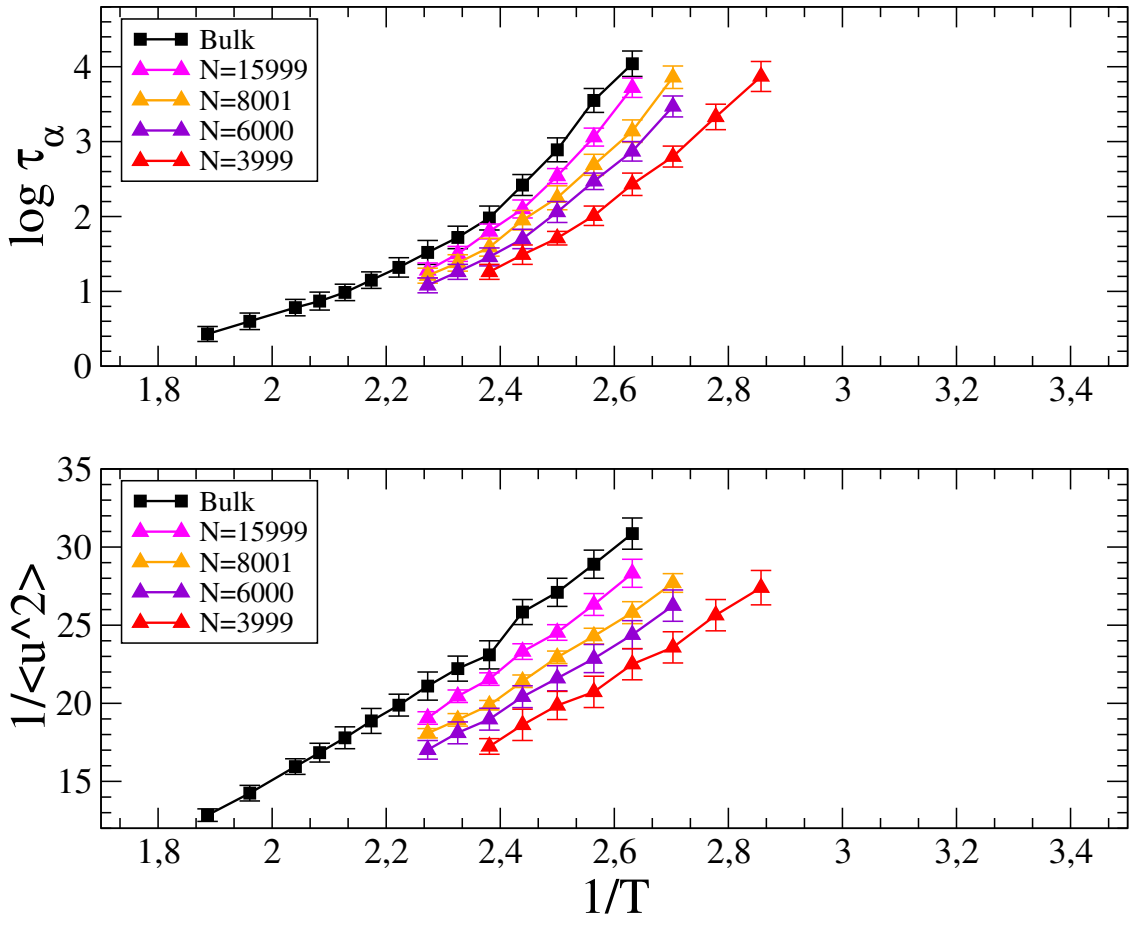

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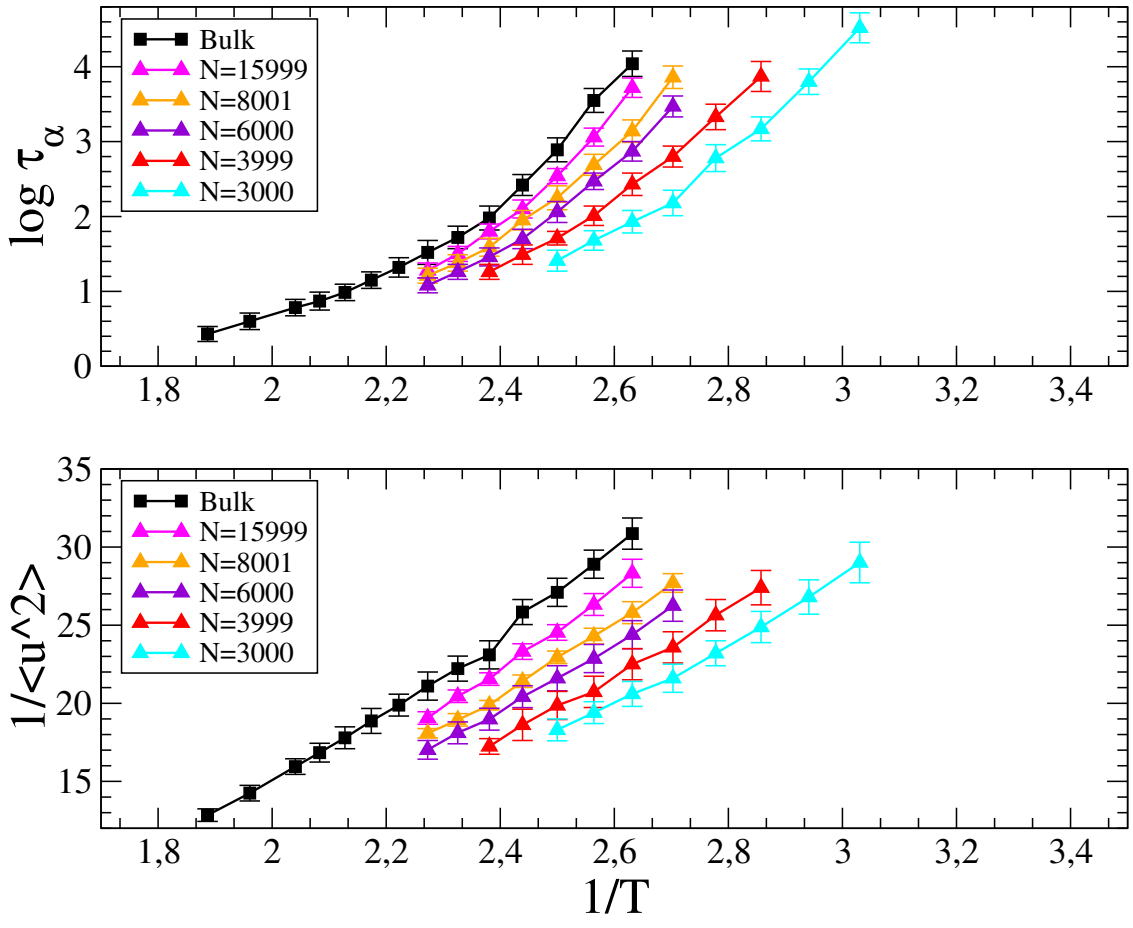

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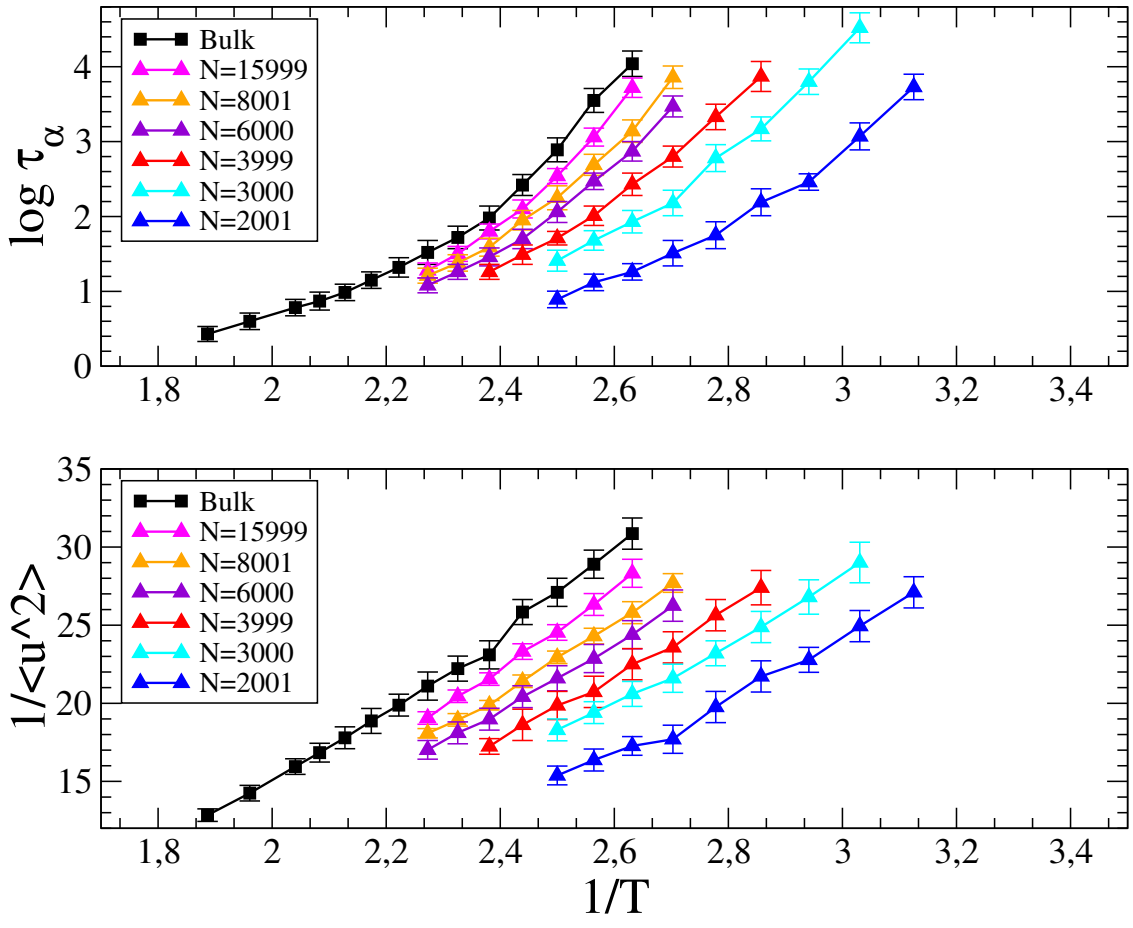

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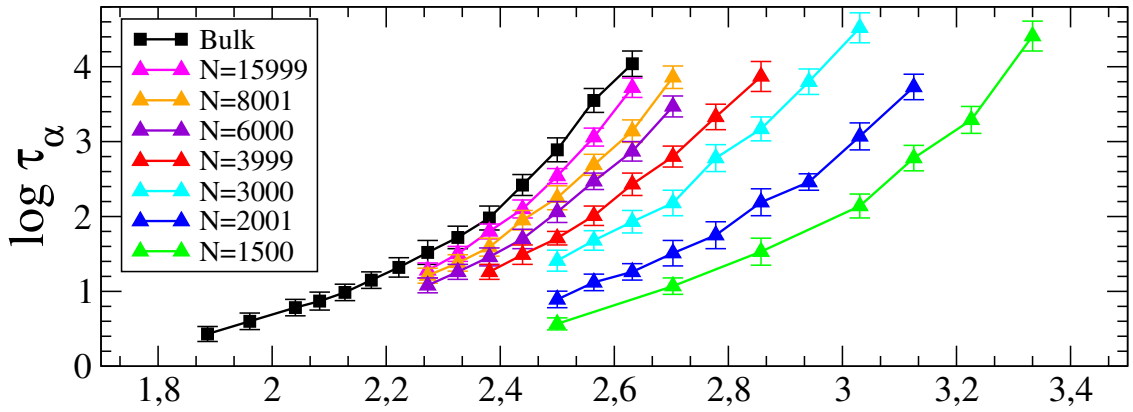

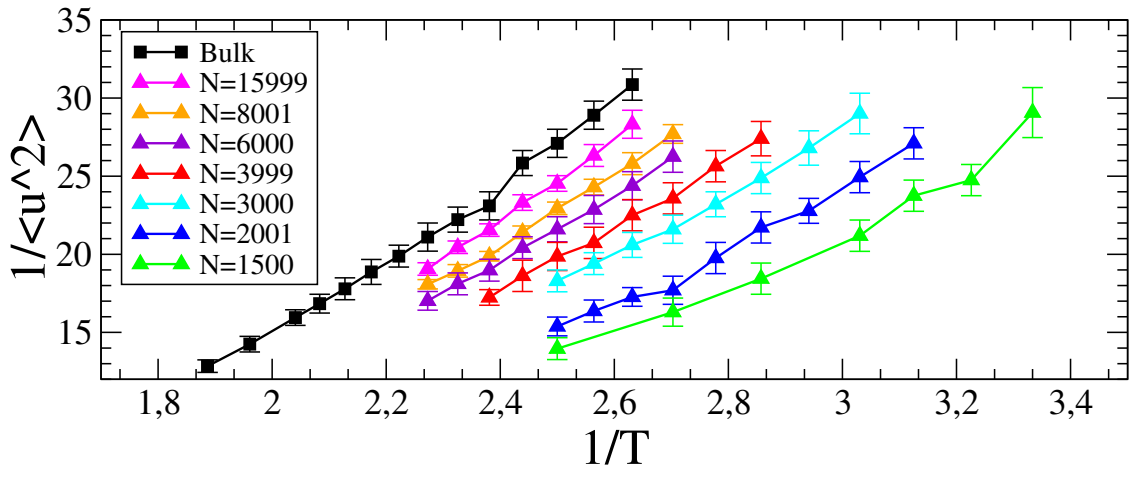

Confinement effect on the scaling

scaling shift

Back to the scaling

Scaling slightly modified, with a drift from the bulk

Upward drift $\rightarrow \langle u^2 \rangle$ related to spatial scales bigger than the cage

The drift starts earlier for thinner films

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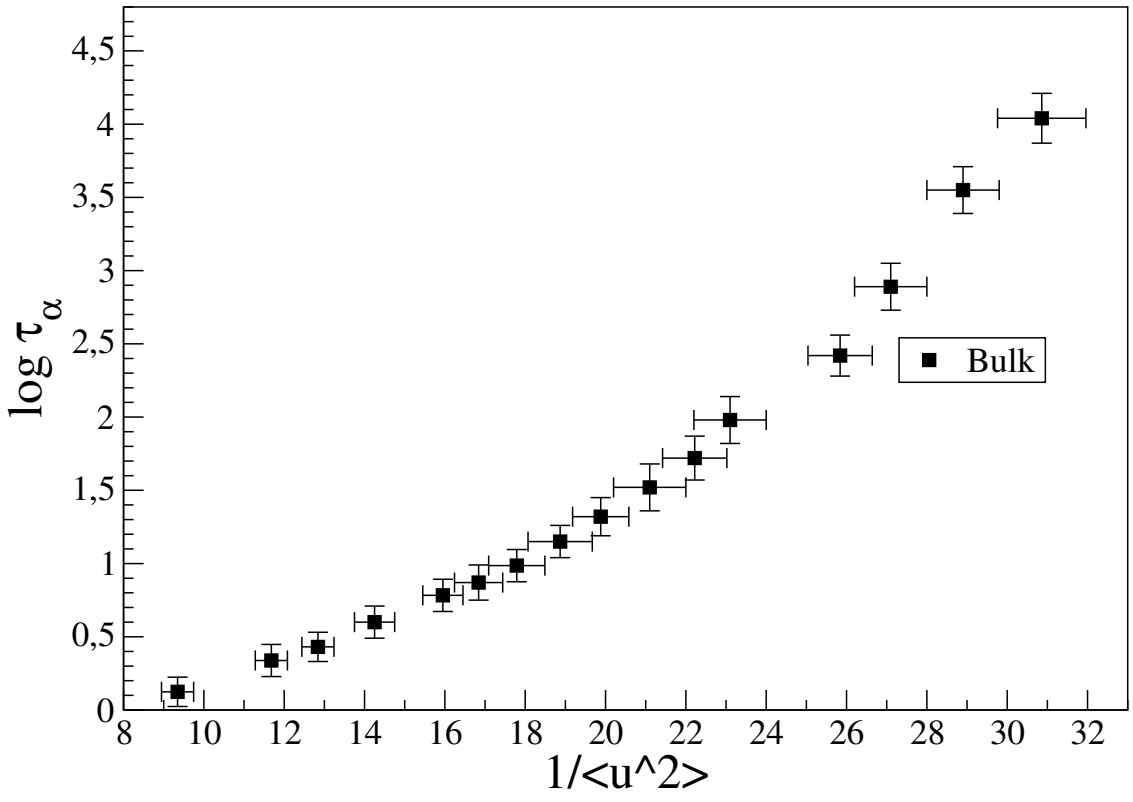

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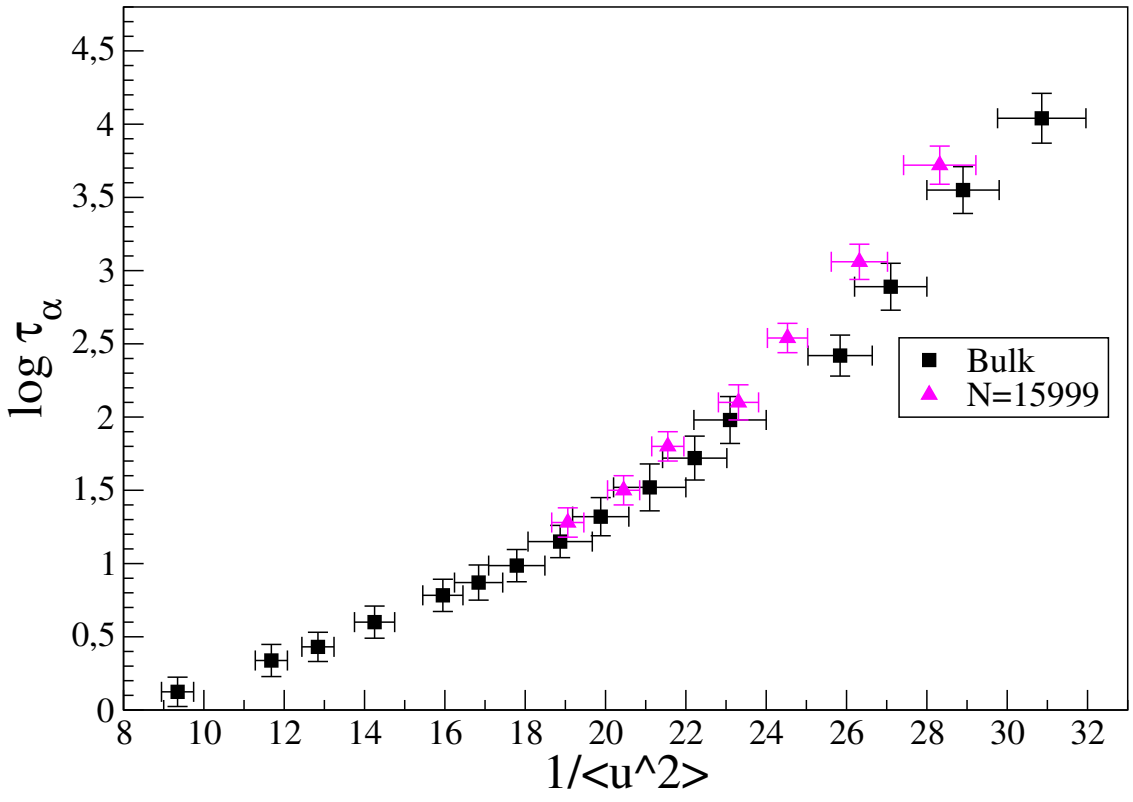

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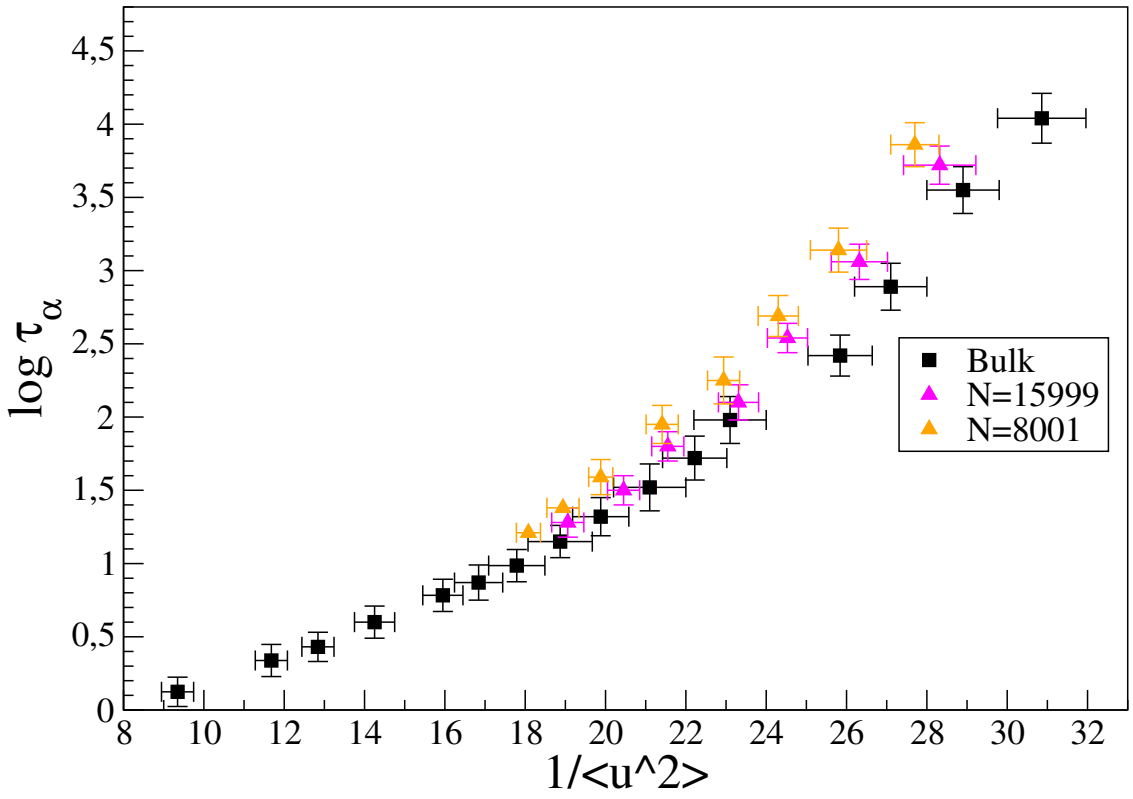

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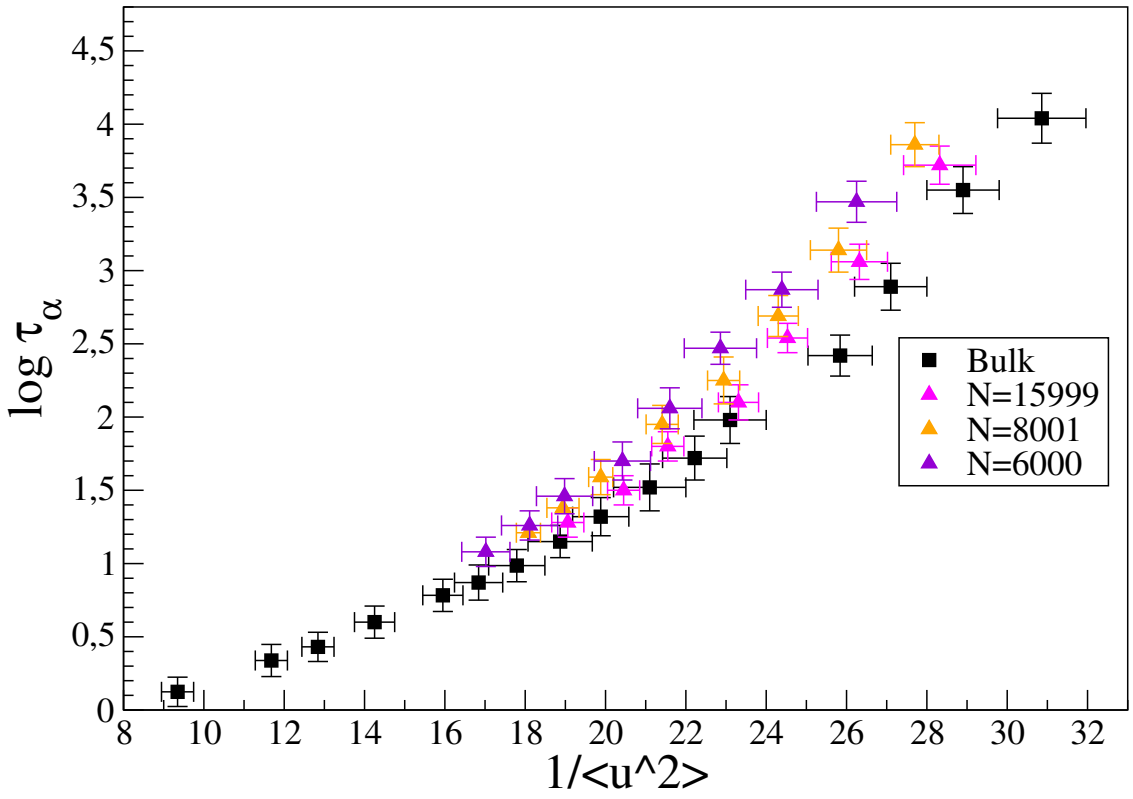

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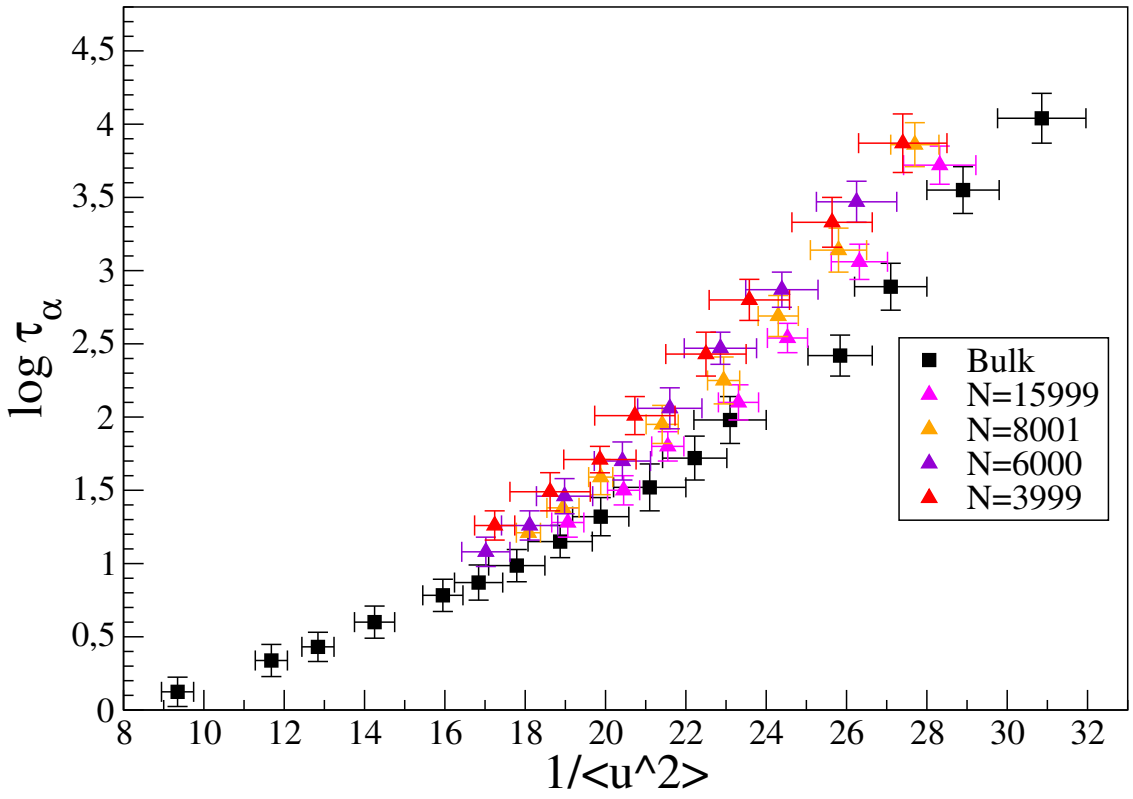

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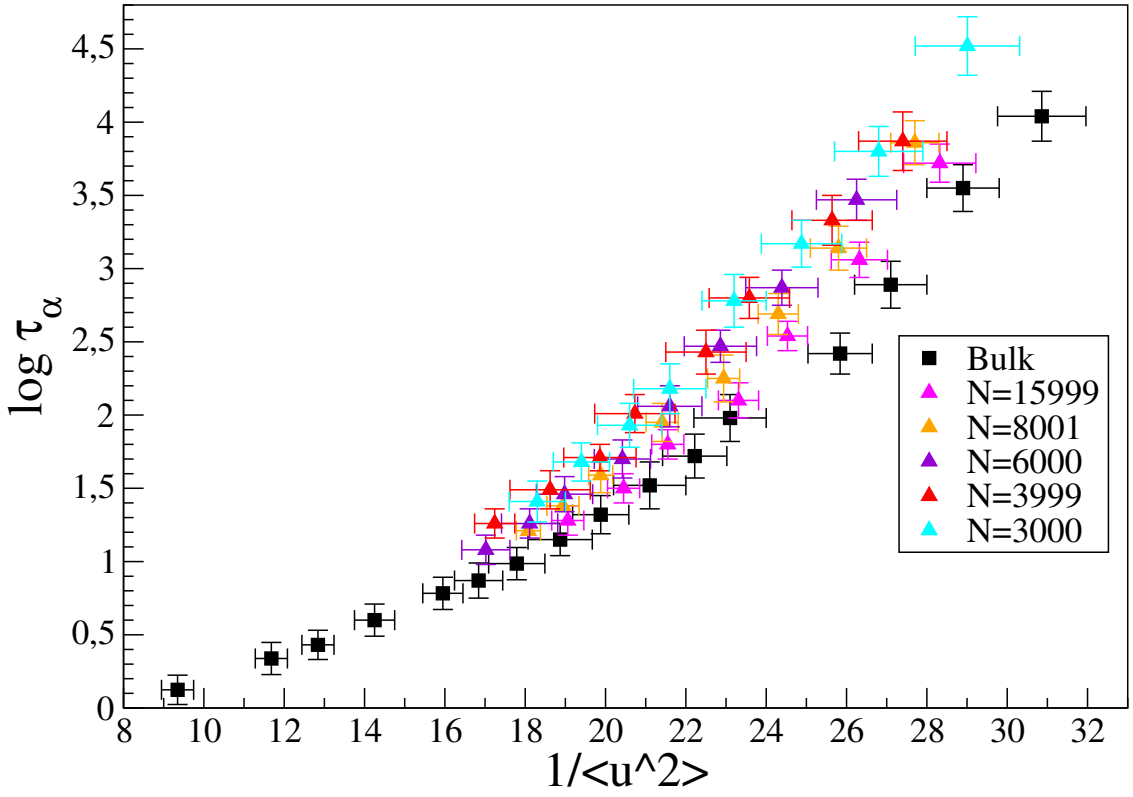

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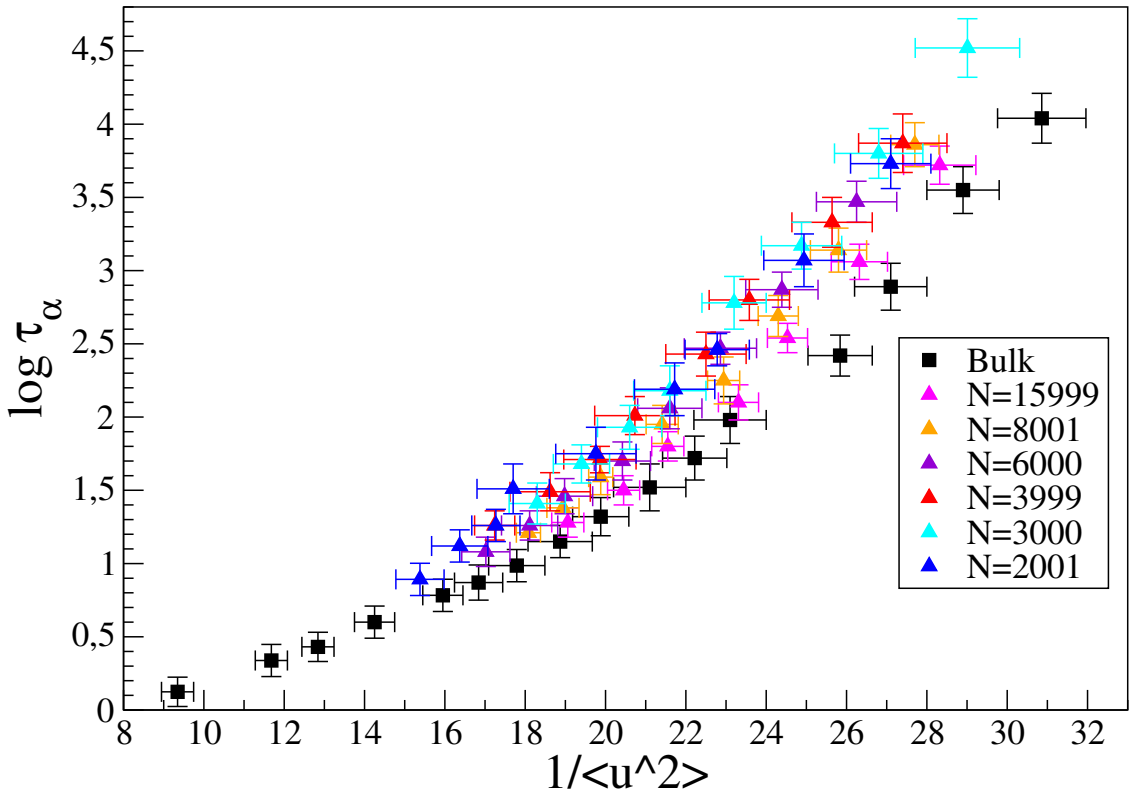

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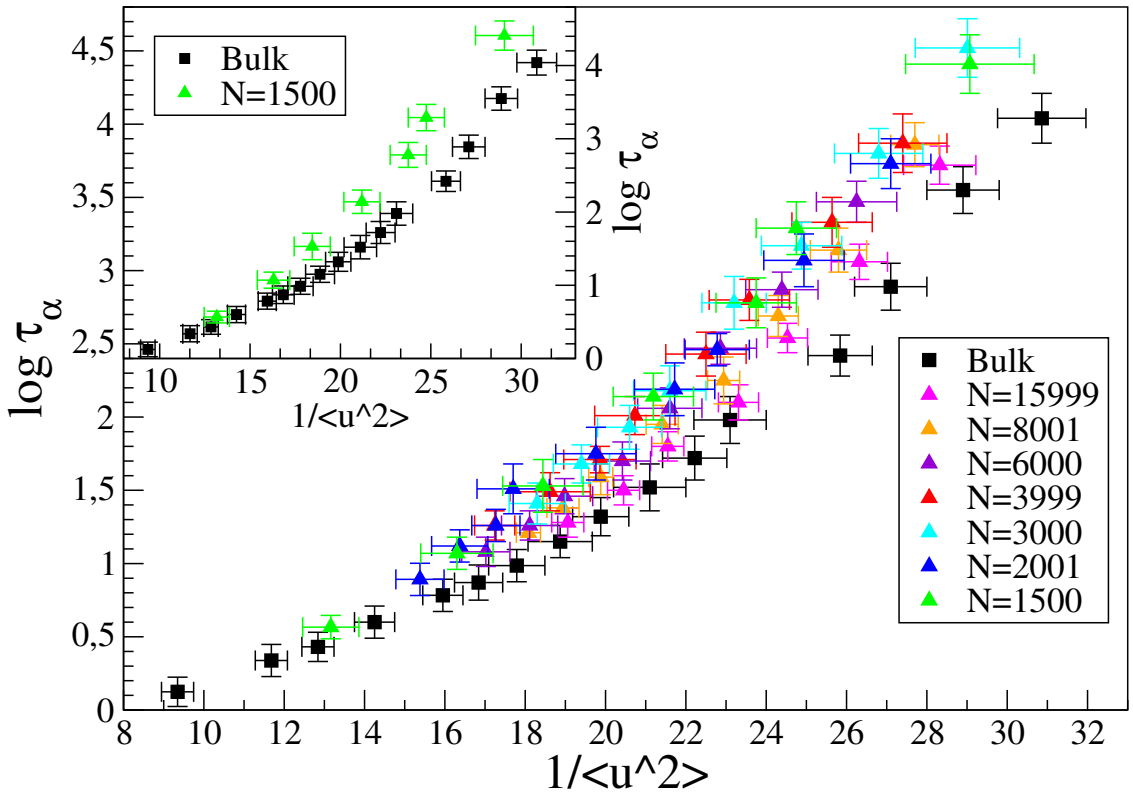

Conclusions and future goals

Main results

- New code to simulate confined liquids and films
- Small thickness effect on the universal scaling
- non-locality of fast dynamics ($1ps$)

What now

- Elastic scaling: confinement effects
- 2D simulations and interface contributions

Additional completed work

- Spontaneous crystallization of polymer melts
- Elastic properties under deformations

Thanks for your attention, any question is welcomed!

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quadratic term: $a^2 \rightarrow P(a^2)$ with gaussian distribution

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Lennard-Jones interaction between monomers and supporting smooth wall

$$U_{LJ}(r) = \varepsilon \left[\left(\frac{\sigma}{r} \right)^9 - \left(\frac{\sigma}{r} \right)^3 \right] - C$$

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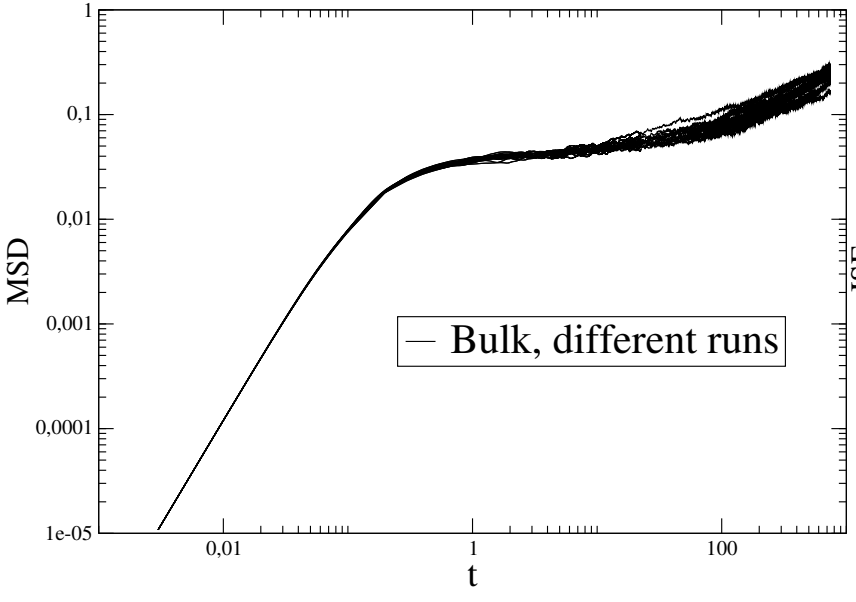
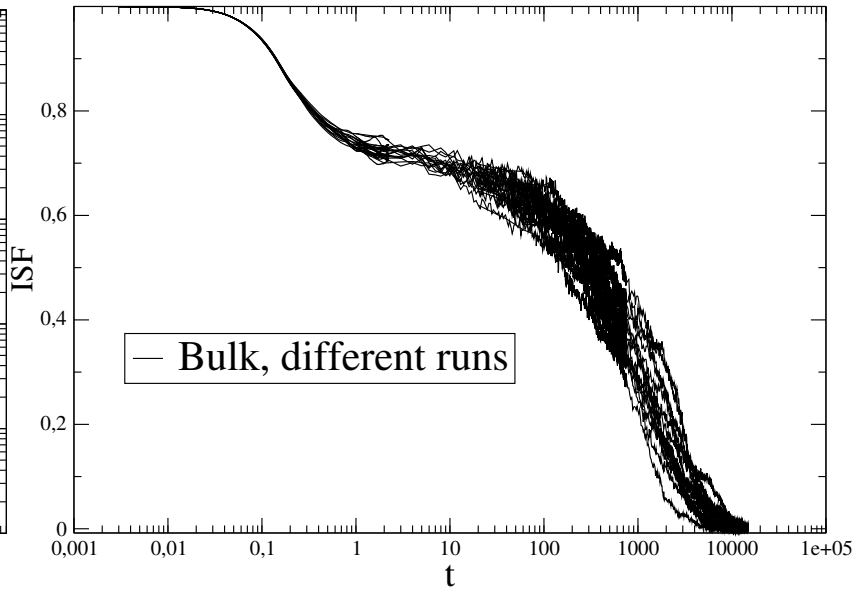
Simulation error on measures

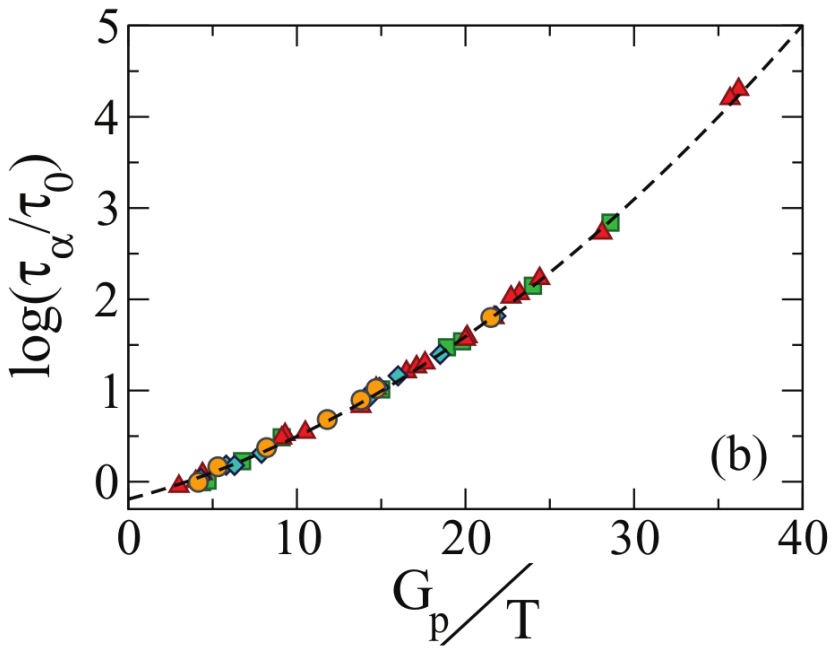
The error on the measures is given by the statistical variance obtained averaging over many simulation runs





Elastic scaling

A scaling is also found with the Elastic modulus G_p measure from the stress tensor decorrelation



Still to study in films