Dynamical heterogeneity and structural relaxation in periodically deformed polymer glasses

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Movies, preprints @
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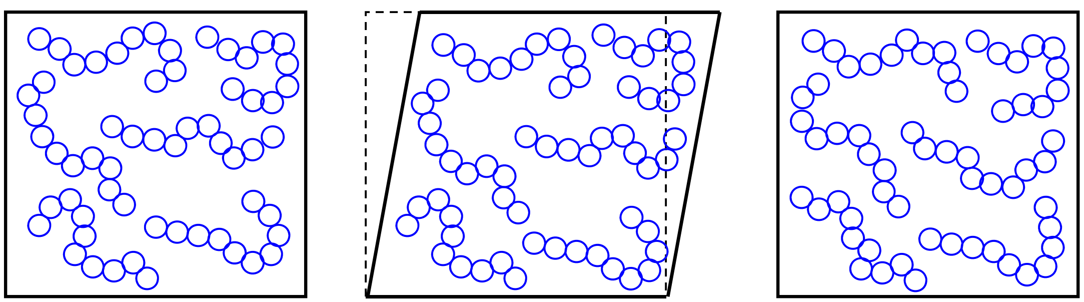
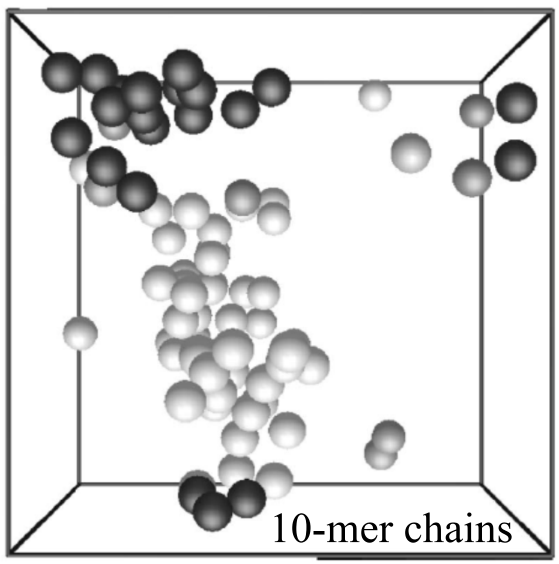


N. V. Priezjev, "Dynamical heterogeneity in periodically deformed polymer glasses", *Physical Review E* **89**, 012601 (2014).

N. V. Priezjev, "Heterogeneous relaxation dynamics in amorphous materials under cyclic loading", *Physical Review E* **87**, 052302 (2013).

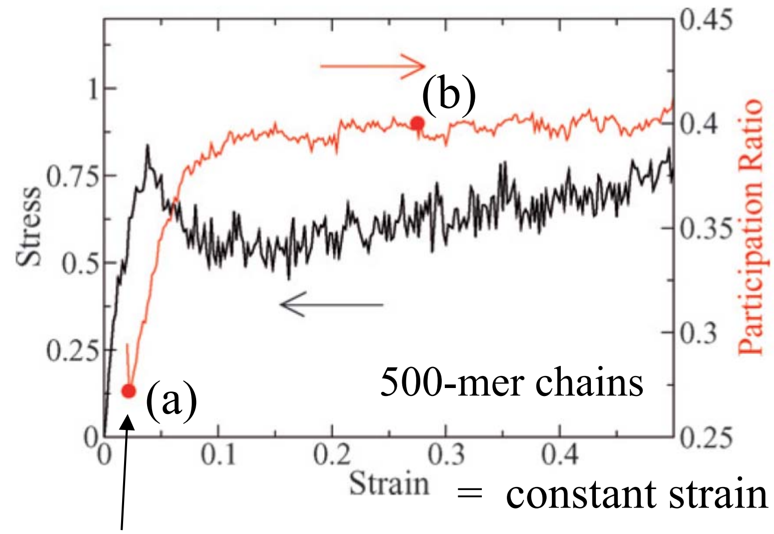
Dynamical heterogeneity in quiescent and deformed polymer glasses

Molecular dynamics simulations of a <u>quiescent</u> polymer glass near T_g



The most mobile monomers (top 5%) form transient clusters whose mean size increases upon cooling towards T_g

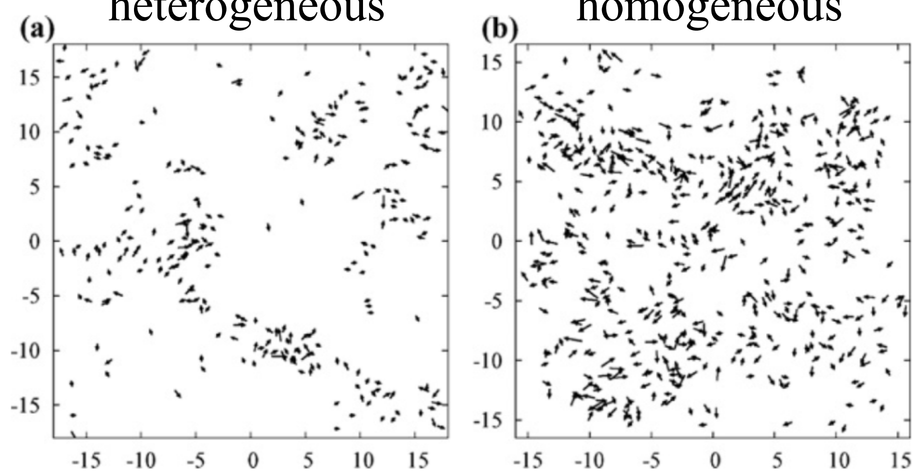
Gebremichael, Schroder, Starr, Glotzer, *J. Chem. Phys.* **64**, 051503 (2001).



= constant strain rate

heterogeneous

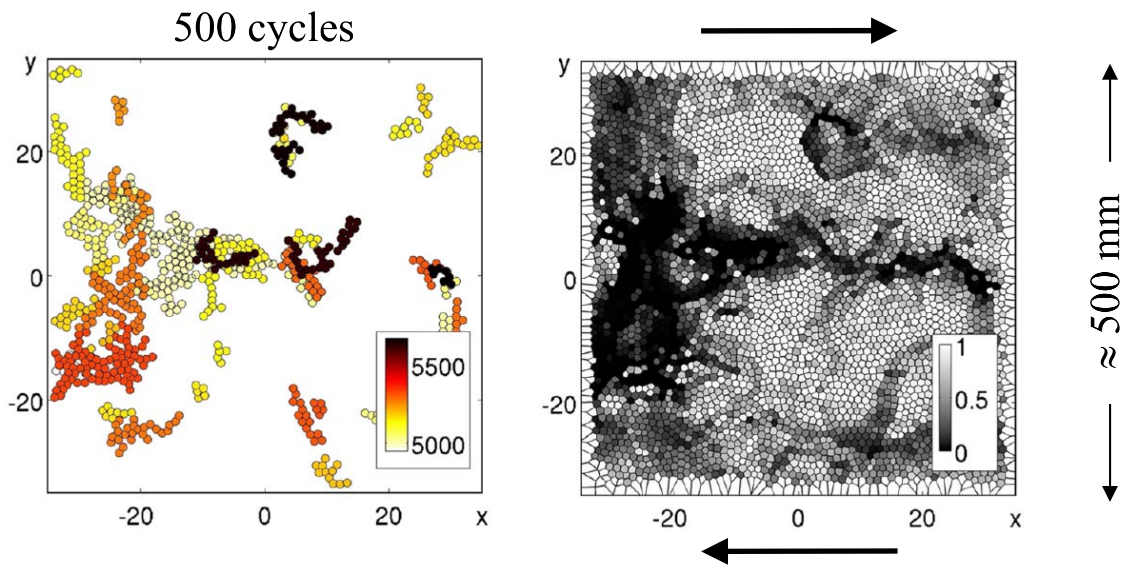
homogeneous



Riggleman, Lee, Ediger, and de Pablo, Soft Matter **6**, 287 (2010).

Dynamical heterogeneity in granular media and supercooled liquids

- Cyclic shear experiment on dense 2D granular media



Spatial location of successive clusters of cage jumps

Power-law distribution of clusters sizes

Candelier, Dauchot, and Biroli, *PRL* **102**, 088001 (2009).

- Fluidized bed experiment: Monolayer of bidisperse beads

Candelier, Dauchot, and Biroli, *EPL* **92**, 24003 (2010).

- 2D softly repulsing particle molecular dynamics simulation (supercooled liquids at γ=0)

Candelier, Widmer-Cooper, Kummerfeld, Dauchot, Biroli, Harrowell, Reichman, *PRL* (2010).

Present study:

- 3D polymer glasses under periodic strain?
- Monomer diffusion depends on the strain amplitude
- Structural relaxation and dynamical heterogeneities
- Particle hopping dynamics clusters of mobile particles
- Dynamical facilitation of mobile monomers

Details of molecular dynamics simulations and parameter values

Lennard-Jones potential: $V_{LJ}(r) = 4\varepsilon\left[\left(\frac{r}{\sigma}\right)^{-12} - \left(\frac{r}{\sigma}\right)^{-6}\right]$

FENE bead-spring model: $V_{FENE}(r) = \frac{1}{2}kr_o^2 \ln\left(1 - \frac{r^2}{r_o^2}\right)$

$k = 30\varepsilon\sigma^{-2}$ and $r_o = 1.5\sigma$

Kremer & Grest, *J. Chem. Phys.* **92**, 5057 (1990)

Monomer density: $\rho = 1.07\,\sigma^{-3}$, $N = 3120$

Temperature: $T = 0.1\ \varepsilon/k_B < T_g \approx 0.3\ \varepsilon/k_B$

Cubic box: $14.29\sigma \times 14.29\sigma \times 14.29\sigma$

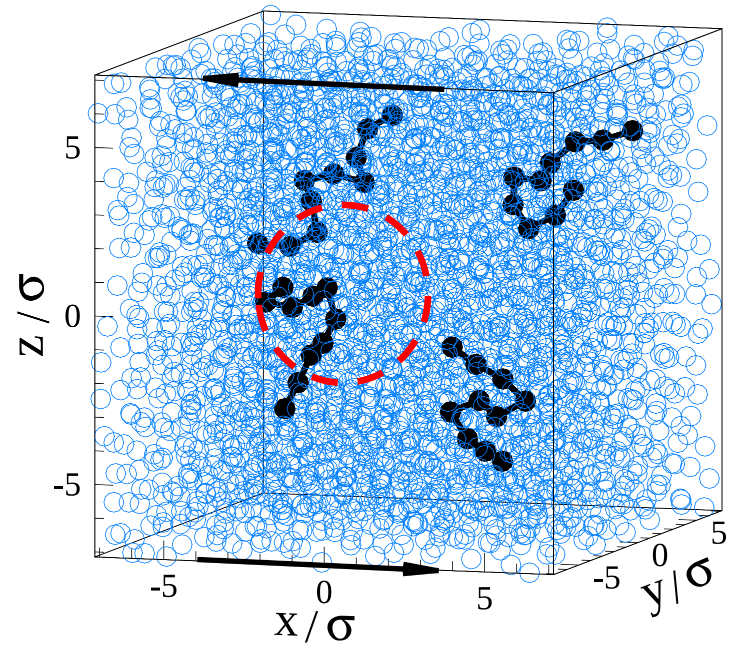
Lees-Edwards periodic boundary conditions

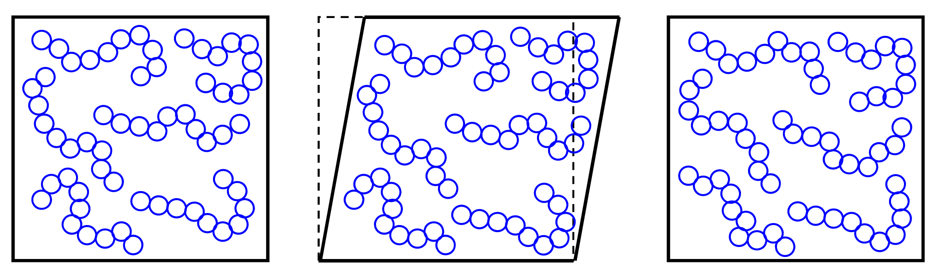
SLLOD equations of motion: $\Delta t_{MD} = 0.005\,\tau$

Oscillation period: $T = 2\pi/\omega = 125.66\,\tau$

Oscillatory shear strain: $\gamma(t) = \gamma_0 \sin(\omega t)$

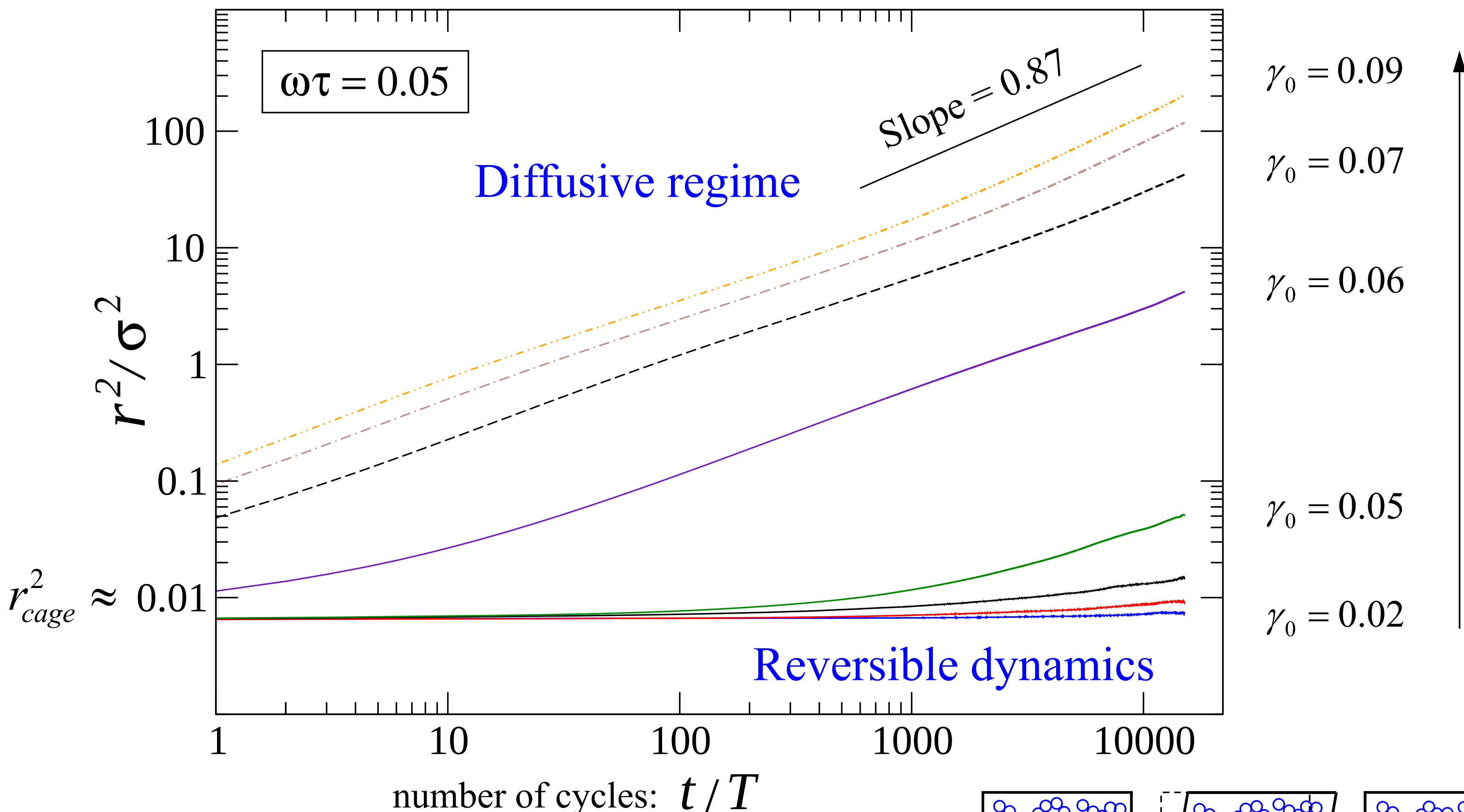
Strain amplitude: $\gamma_0 \leq 0.09$, $\omega = 0.05\tau^{-1}$



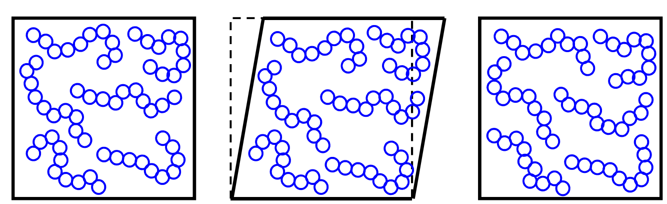


15,000 cycles ($\approx 3.8 \times 10^8$ MD steps)

Mean-square-displacement of monomers for different strain amplitudes γ_0



Oscillation period: $T = 2\pi/\omega = 125.66\,\tau$

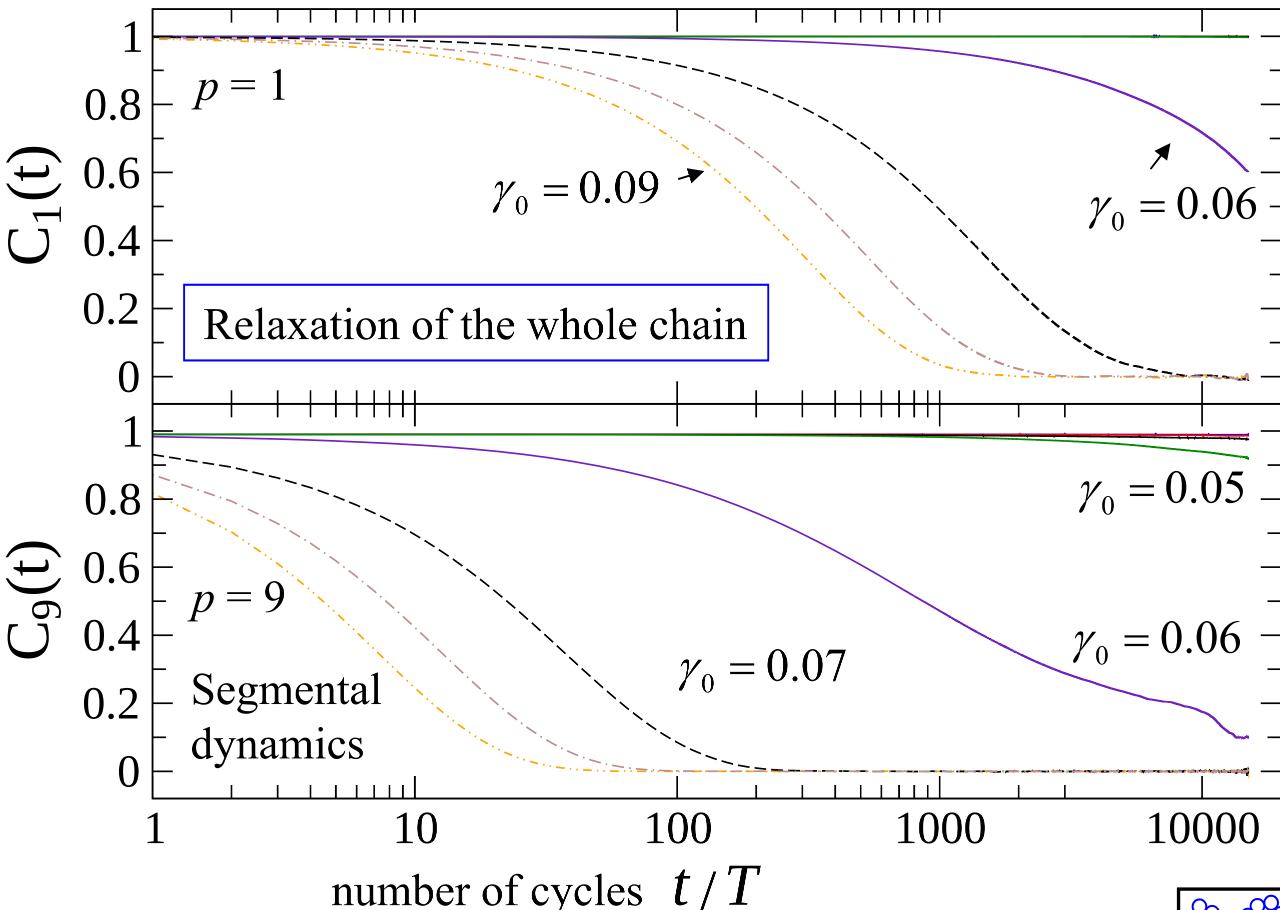


Time autocorrelation function of normal modes vs. strain amplitude γ_0

$$C_p(t) = \left\langle X_p(t) \cdot X_p(0) \right\rangle \qquad X_p(t) = \frac{1}{N}\sum_{i=1}^{N} r_i(t)\cos\frac{p\pi(i-1/2)}{N}$$

p = mode number

$N = 10$ chain length



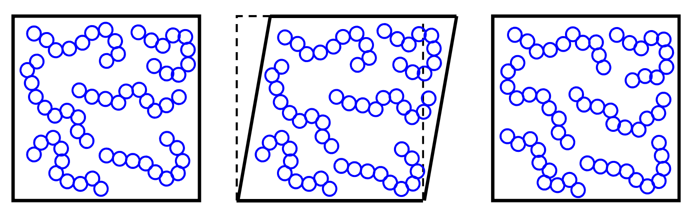
Reversible dynamics

$\gamma_0 \leq 0.05$

Chains are fully relaxed

$\gamma_0 \geq 0.07$

The relaxation dynamics of polymer chains undergoes a transition at the strain amplitude $\gamma_0 = 0.06$



Oscillation period: $T = 2\pi/\omega = 125.66\,\tau$

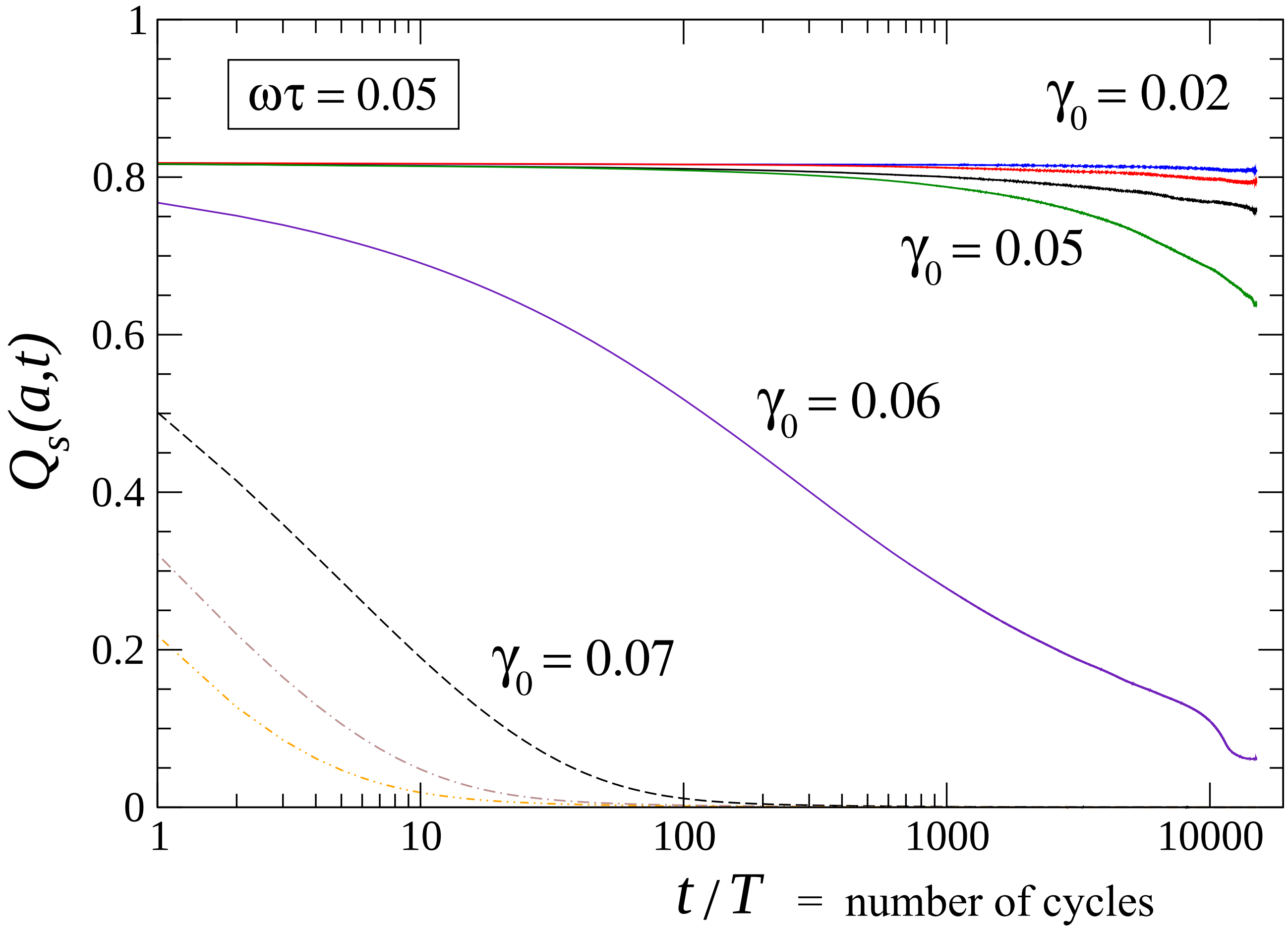
Self-overlap order parameter $Q_s(a,t)$ for different strain amplitudes γ_0

$$Q_s(a,t) = \frac{1}{N_m}\sum_{i=1}^{N_m}\exp\left(-\frac{\Delta r_i(t)^2}{2a^2}\right)$$

$a = 0.12\sigma$ = probed length scale (about the cage size)

N_m = total number of monomers in the system

$\Delta r_i(t)$ = the monomer displacement vector



$Q_s(a,t)$ describes structural relaxation of the material.

Measure of the spatial overlap between monomer positions.

Reversible dynamics:

$Q_s(t) \approx$ constant

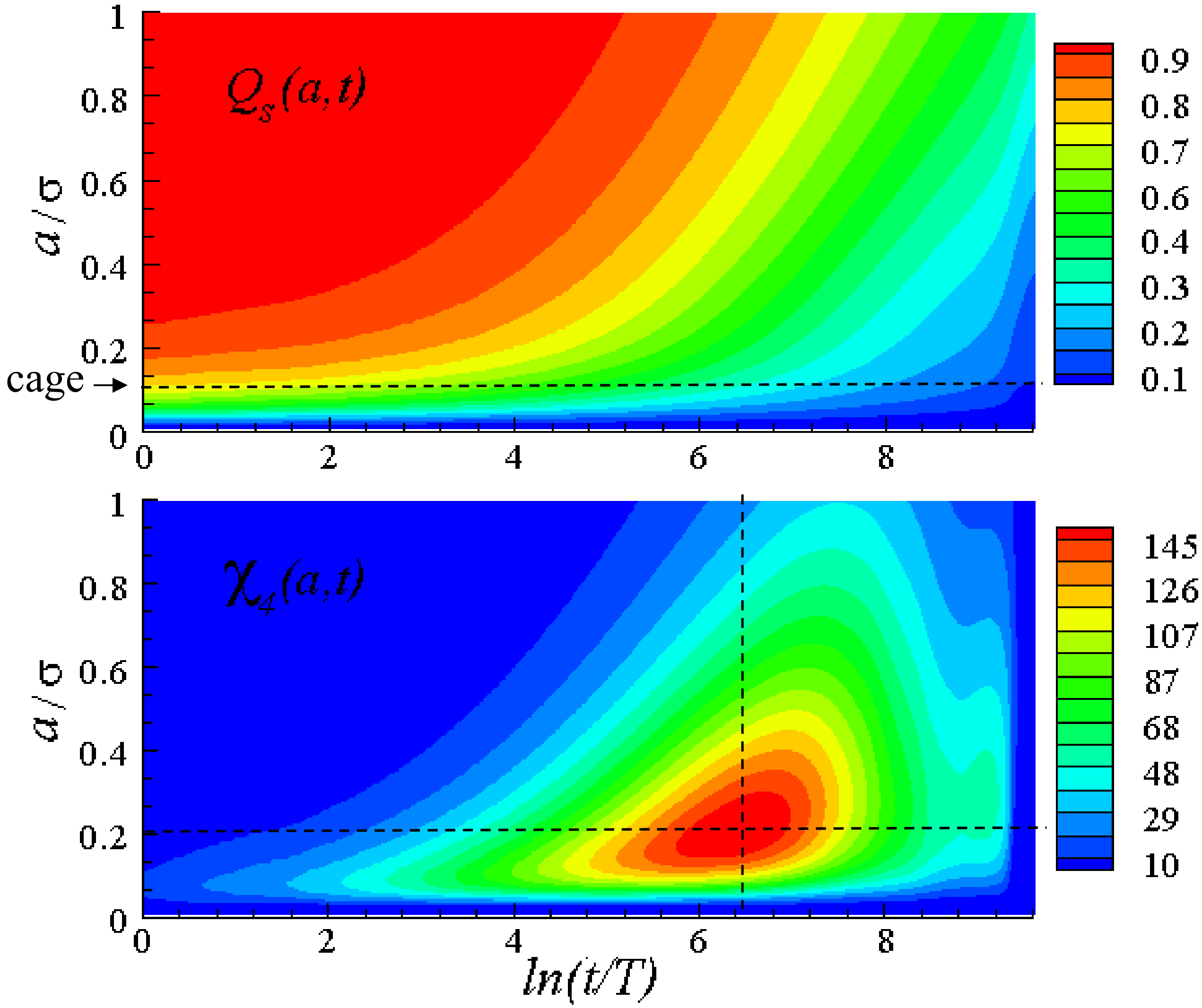
Diffusive regime:

$Q_s(t)$ vanishes at large t

Susceptibility

$X_4(a,t) = ?$

Contour plots of dynamical susceptibility $X_4(a,t)$ and $Q_s(a,t)$ for $\gamma_0 = 0.06$



Berthier & Biroli (2011)

$$Q_s(a,t) = \frac{1}{N_m}\sum_{i=1}^{N_m}\exp\left(-\frac{\Delta r_i(t)^2}{2a^2}\right)$$

Measure of the spatial overlap between monomer positions.

$$X_4(a,t) = N_m \cdot \left(\left\langle Q_s(a,t)^2\right\rangle - \left\langle Q_s(a,t)\right\rangle^2\right)$$

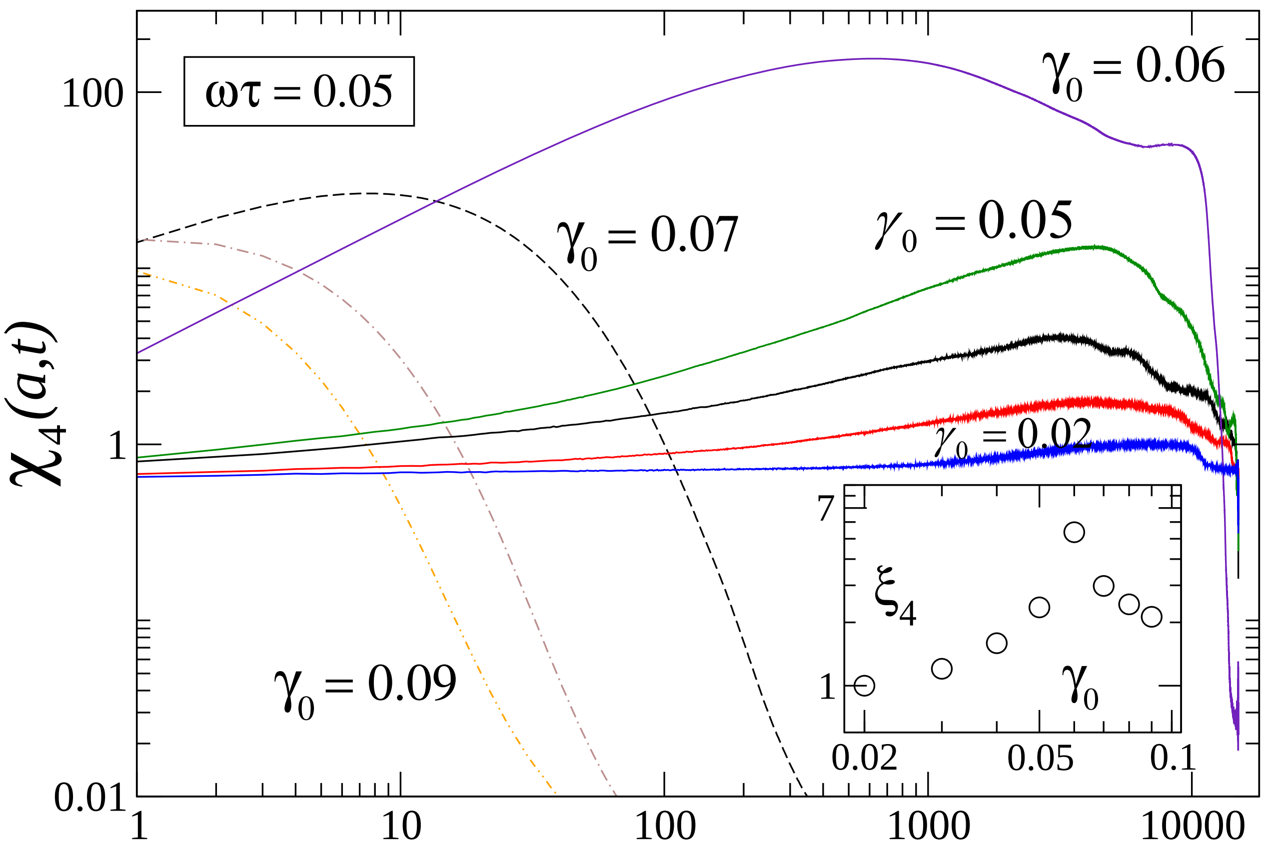
$X_4(a,t)$ is dynamical susceptibility, which is the variance of Q_s.

Maximum $X_4(a,t)$ indicates the largest number of monomers involved in correlated motion.

Dynamical susceptibility as a function of time for different strain amplitudes γ_0

$$X_4(a,t) = N_m \left(\left\langle Q_s(a,t)^2 \right\rangle - \left\langle Q_s(a,t) \right\rangle^2 \right)$$

probed length scale a = max in $X_4(a,t)$
N_m = total number of monomers



t/T = number of cycles

$$\xi_4 = \left[X_4^{\max}(a,t) \right]^{1/3}$$

$X_4(a,t)$ is dynamical susceptibility, which is the variance of Q_s.

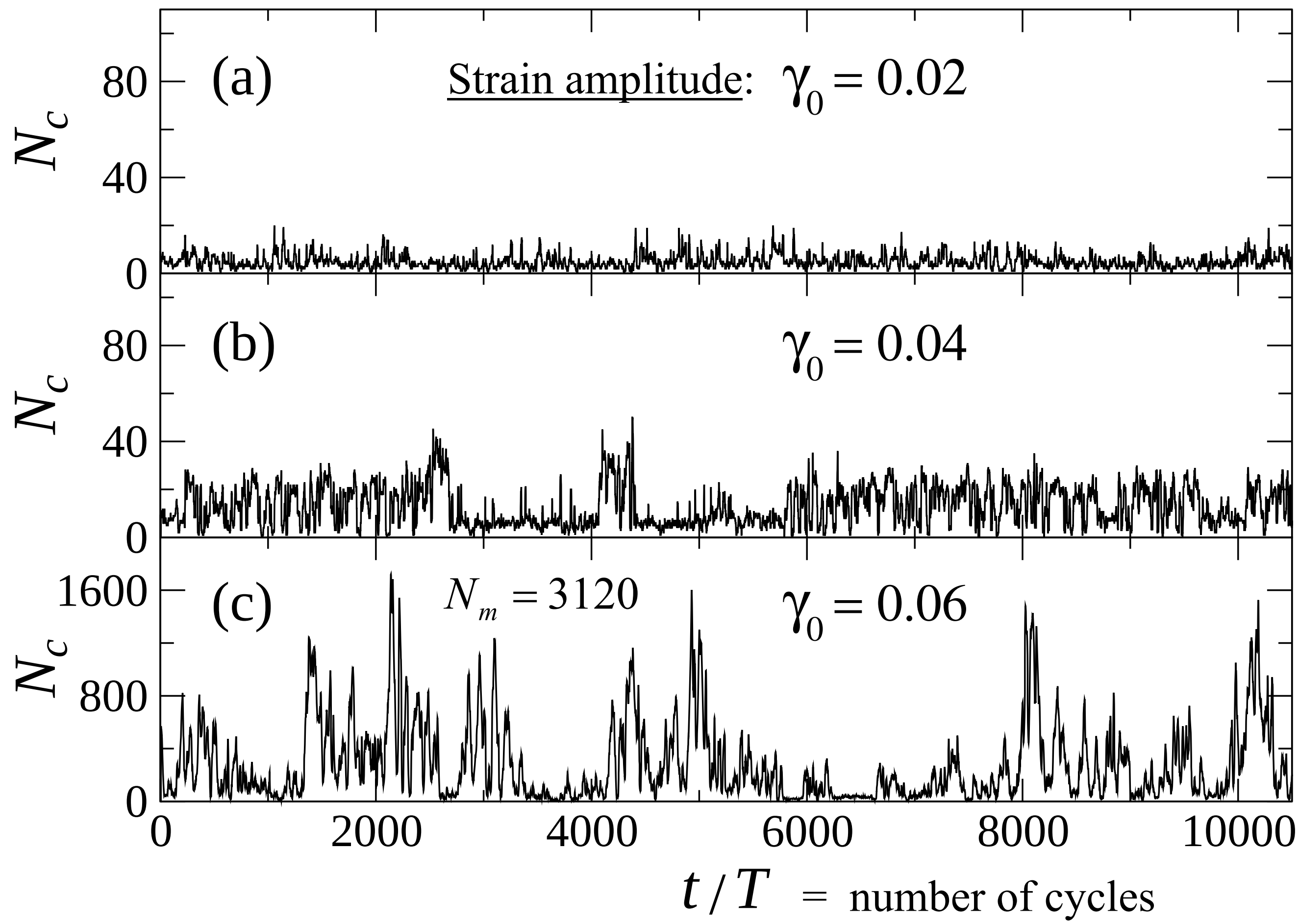
Maximum $X_4(a,t)$ indicates the largest spatial correlation between localized monomers.

Berthier & Biroli (2011)

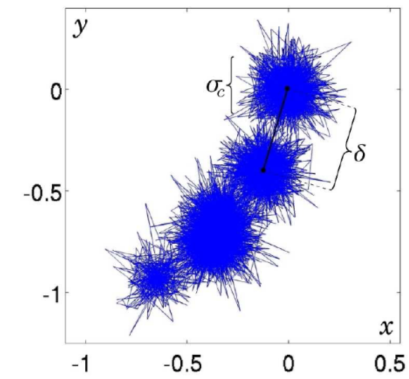
Transition at $\gamma_0 = 0.06$ maximum correlation length $\xi_4 = \left[X_4^{\max}(a,t) \right]^{1/3}$

(in contrast to steadily sheared supercooled liquids and glasses)
Mizuno & Yamamoto, *JCP* (2012), Tsamados, *EPJE* (2010)

Number of monomers undergoing cage jumps N_c as a function of time t/T



Numerical algorithm for detection of cage jumps:



Candelier, Dauchot, Biroli, *PRL* (2009).

Periodic deformation = intermittent bursts of large monomer displacements.

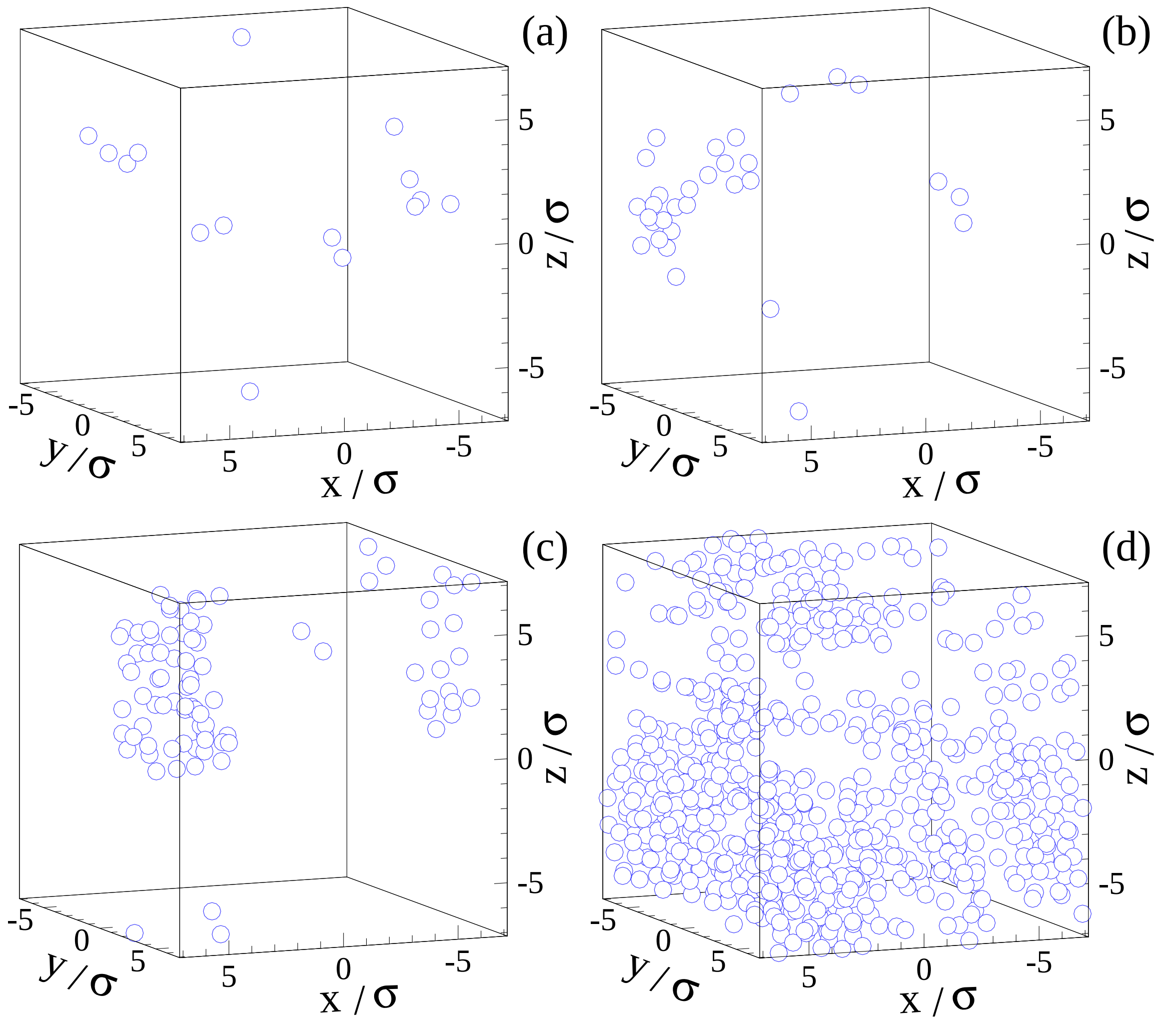
Power spectrum ~ frequency^{-2} = simple Brownian noise

Scale-invariant processes or Pink noise = "1/*f* noise"

Typical clusters of mobile monomers for different strain amplitudes γ_0

$\gamma_0 = 0.03$

Single particle reversible jumps:



Strain amplitude:

$\gamma_0 = 0.04$

$\gamma_0 = 0.05$

Compact clusters; Irreversible jumps:

$\gamma_0 = 0.06$

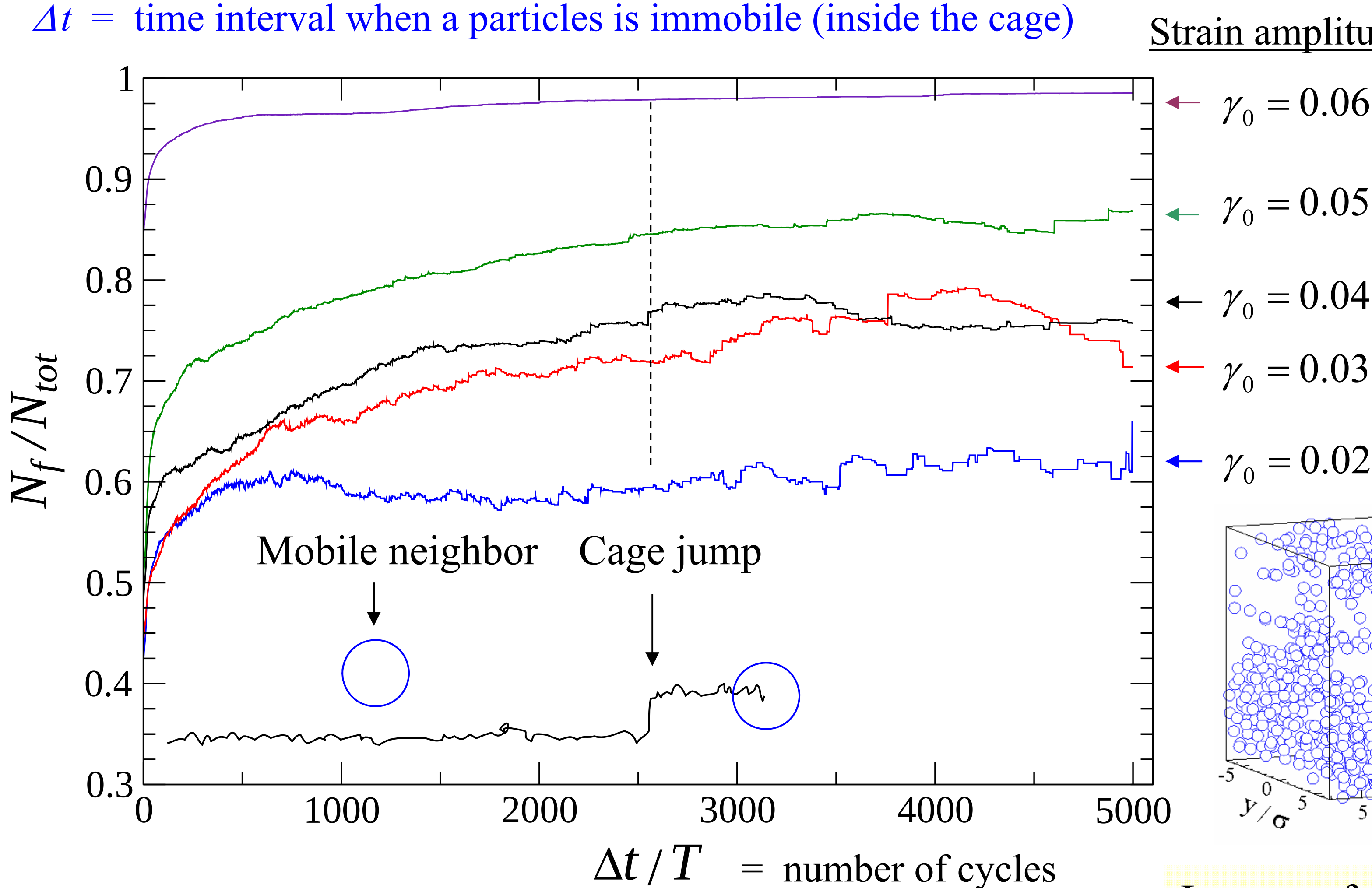
Cluster spans the whole system

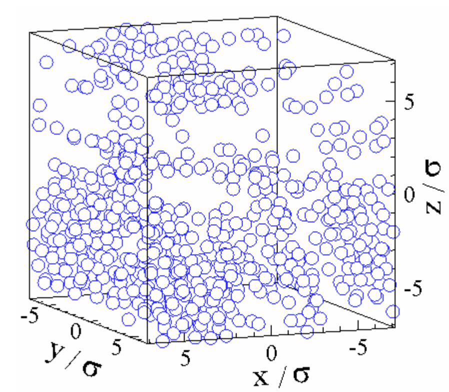
$\gamma_0 \geq 0.07$

The system is fully relaxed over about 100 cycles

Fraction of dynamically facilitated monomers increases with strain amplitude

Δt = time interval when a particles is immobile (inside the cage)



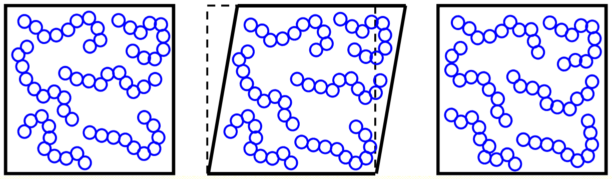


Large surface area = high probability to have mobile neighbors.

Oscillation period: $T = 2\pi / \omega = 125.66\,\tau$

Vogel and Glotzer, *Phys. Rev. Lett.* **92**, 255901 (2004).

Important conclusions:



- The coarse-grained bead-spring polymer glass at $T = 0.1\ \varepsilon/k_B < T_g$ under spatially homogeneous, time-periodic shear strain.

- At small strain amplitudes, the mean square displacement exhibits a broad sub-diffusive plateau and the system undergoes nearly reversible deformation over about 10^4 cycles.

- At the critical strain amplitude, the transition from slow to fast relaxation dynamics is associated with the largest number of dynamically correlated monomers as indicated by the peak value of the dynamical susceptibility. $\xi_4 = \left[X_4^{\max}(a,t)\right]^{1/3}$

- The detailed analysis of monomer hopping dynamics indicates that mobile monomers aggregate into clusters whose sizes increase at larger strain amplitudes. (This is in contrast to steadily sheared supercooled liquids and glasses).

- Fraction of dynamically facilitated mobile monomers increases at larger strain amplitudes.

N. V. Priezjev, "Dynamical heterogeneity in periodically deformed polymer glasses", *Physical Review E* **89**, 012601 (2014).