Simon K. Schnyder

Anomalous Transport in Heterogenous Media

Acknowledgements

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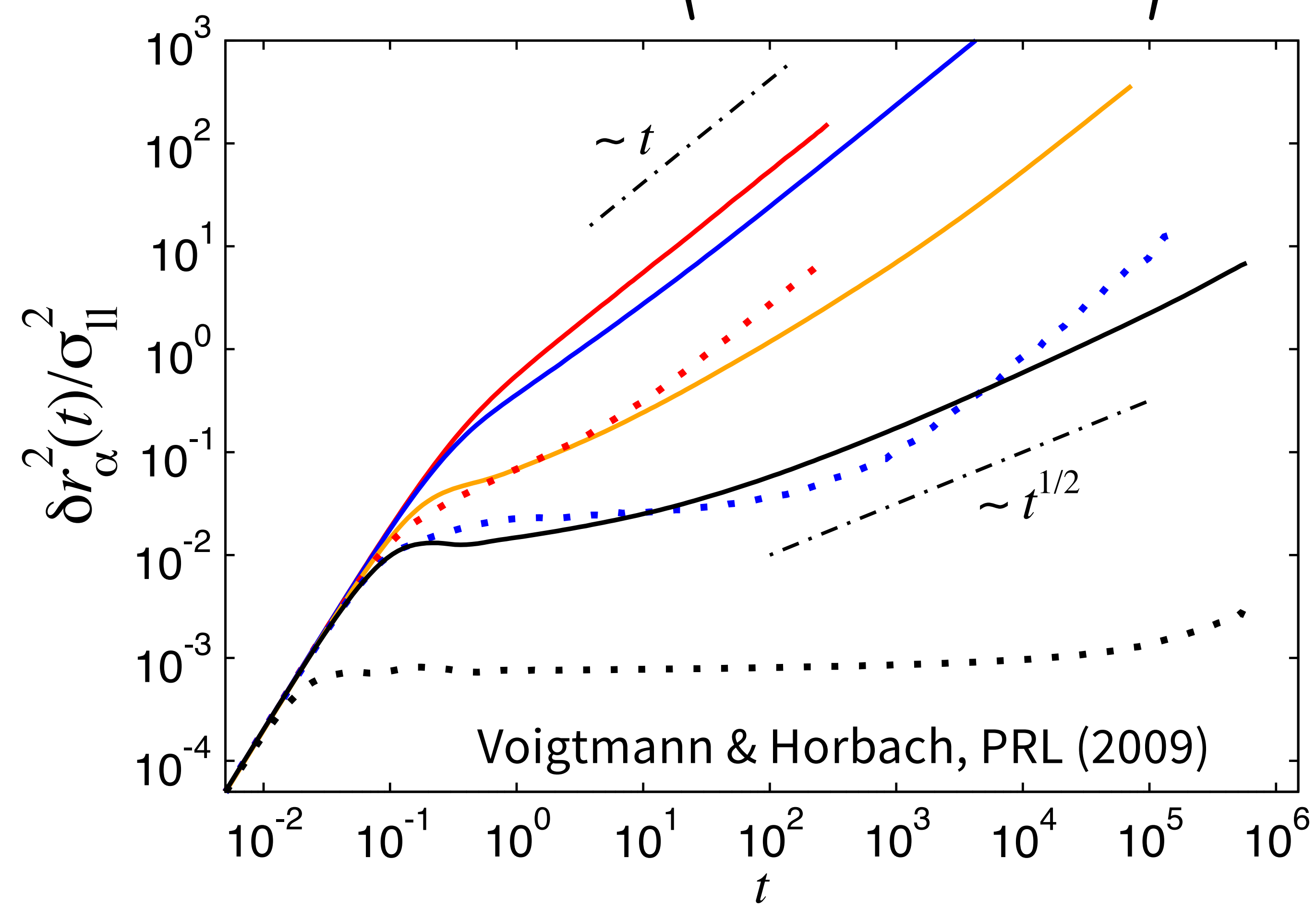
Part I

Rounding of the localisation transition and breakdown of universality

Heterogeneous or porous media

$$\delta r^2(t) := \left\langle \left(r(t) - r(0)\right)^2 \right\rangle$$

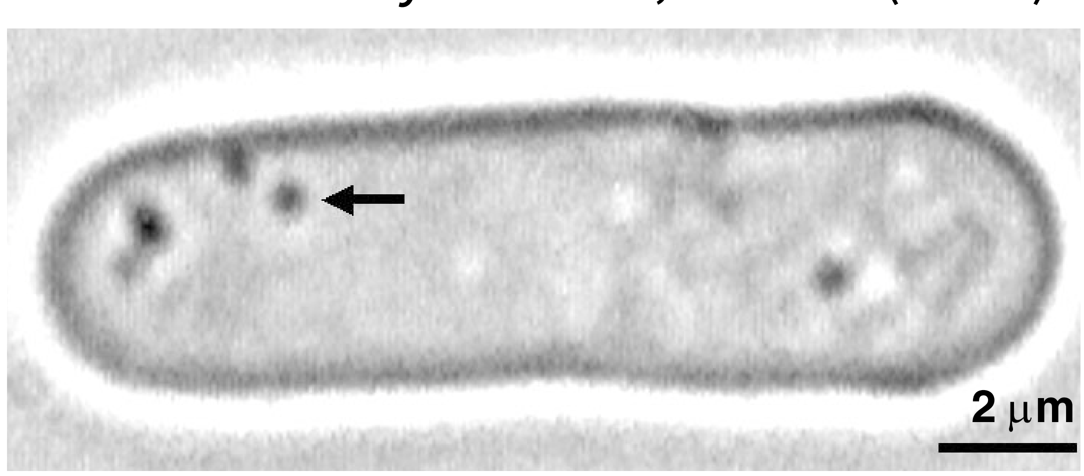


Defining features:

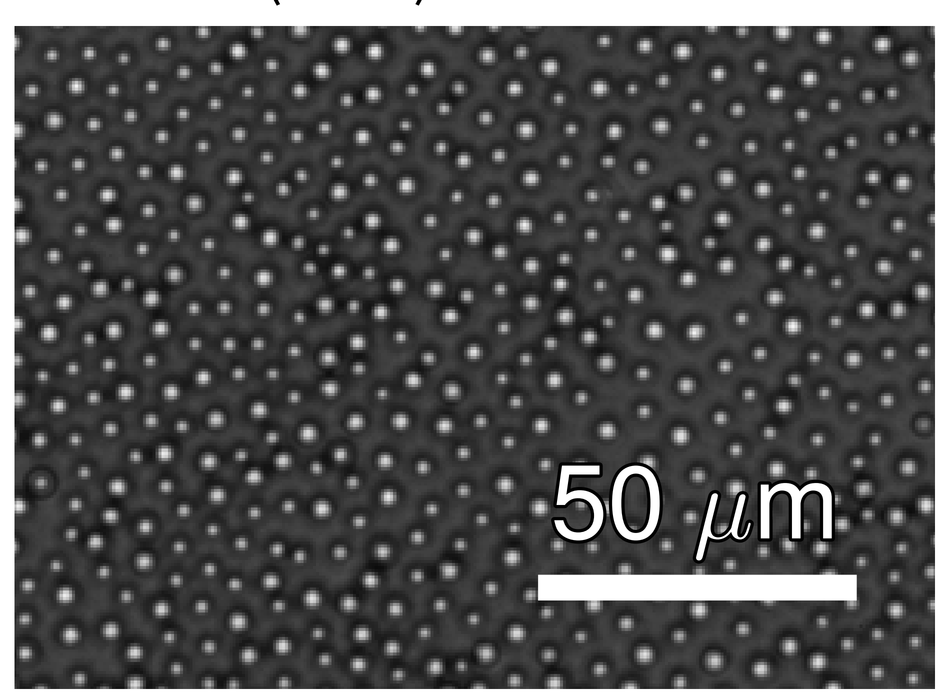
- At least two components
- Separation of time scales

Mass transport is anomalous

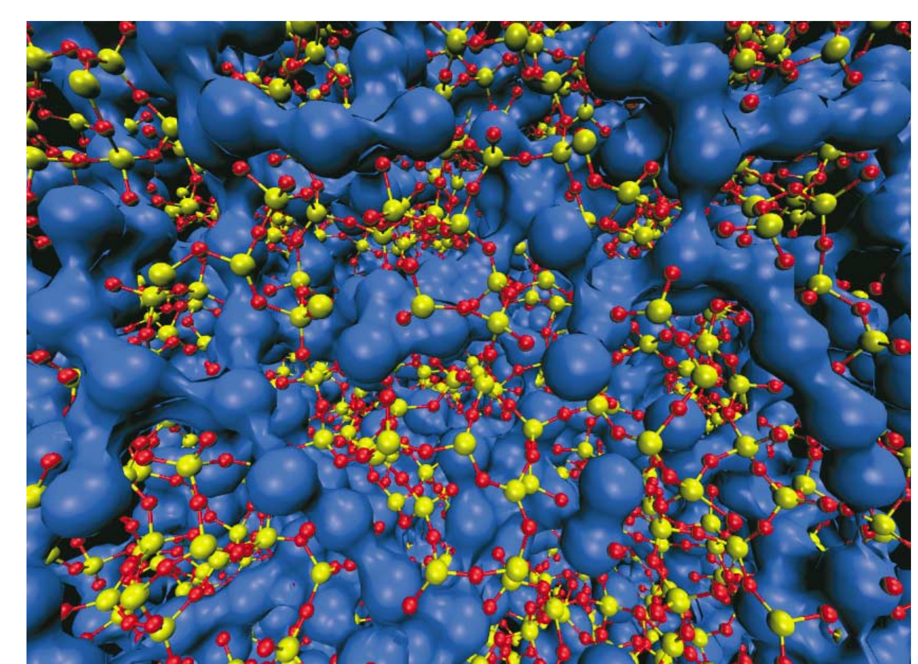
Fission yeast,
I. Tolić-Nørrelykke et al, PRL 93 (2004)



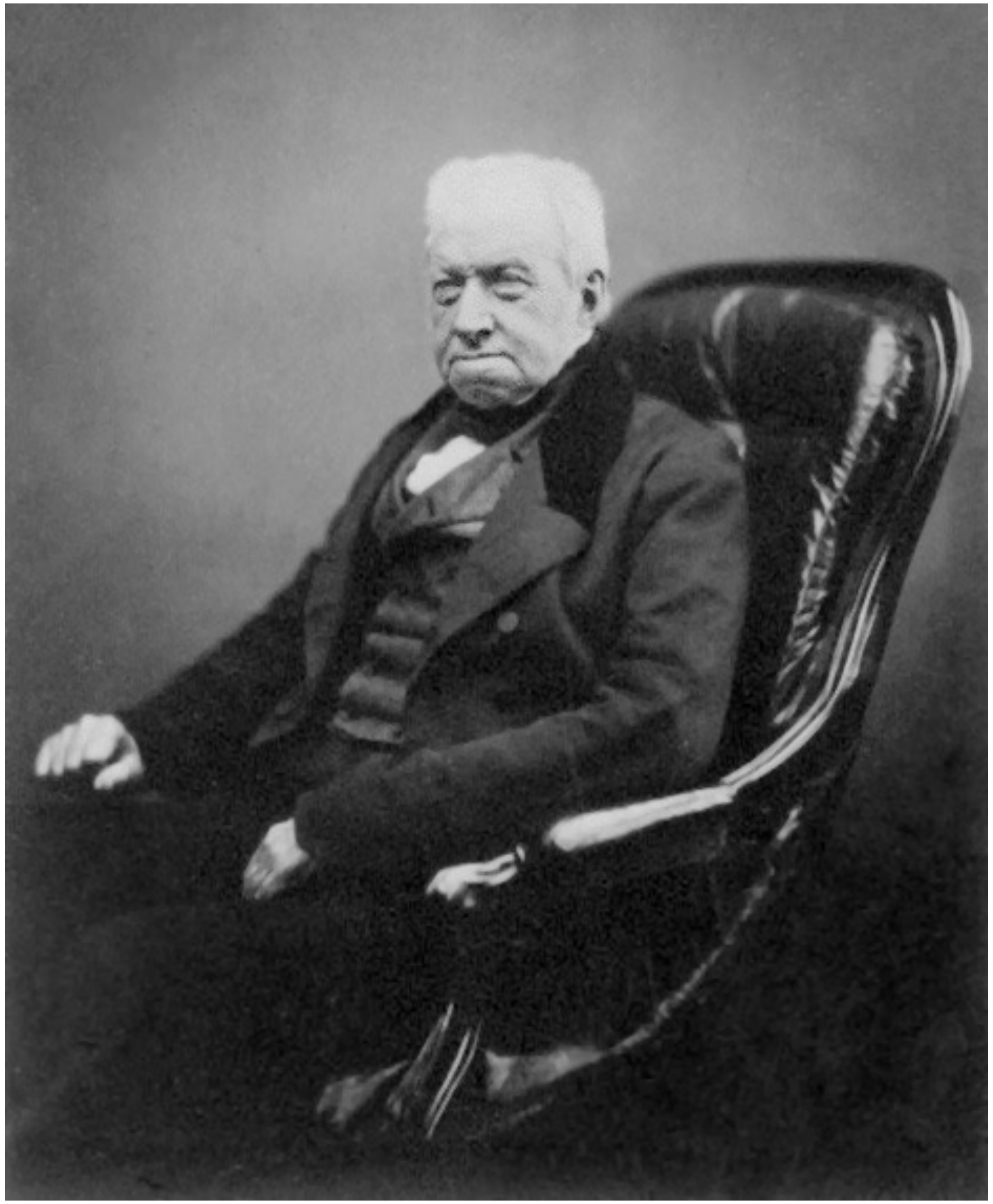
Colloidal model experiment,
T. Skinner, S.K. Schnyder et al, PRL 111 (2013)



Ion-conducting glassformer,
A. Meyer et al, PRL 93 (2004)

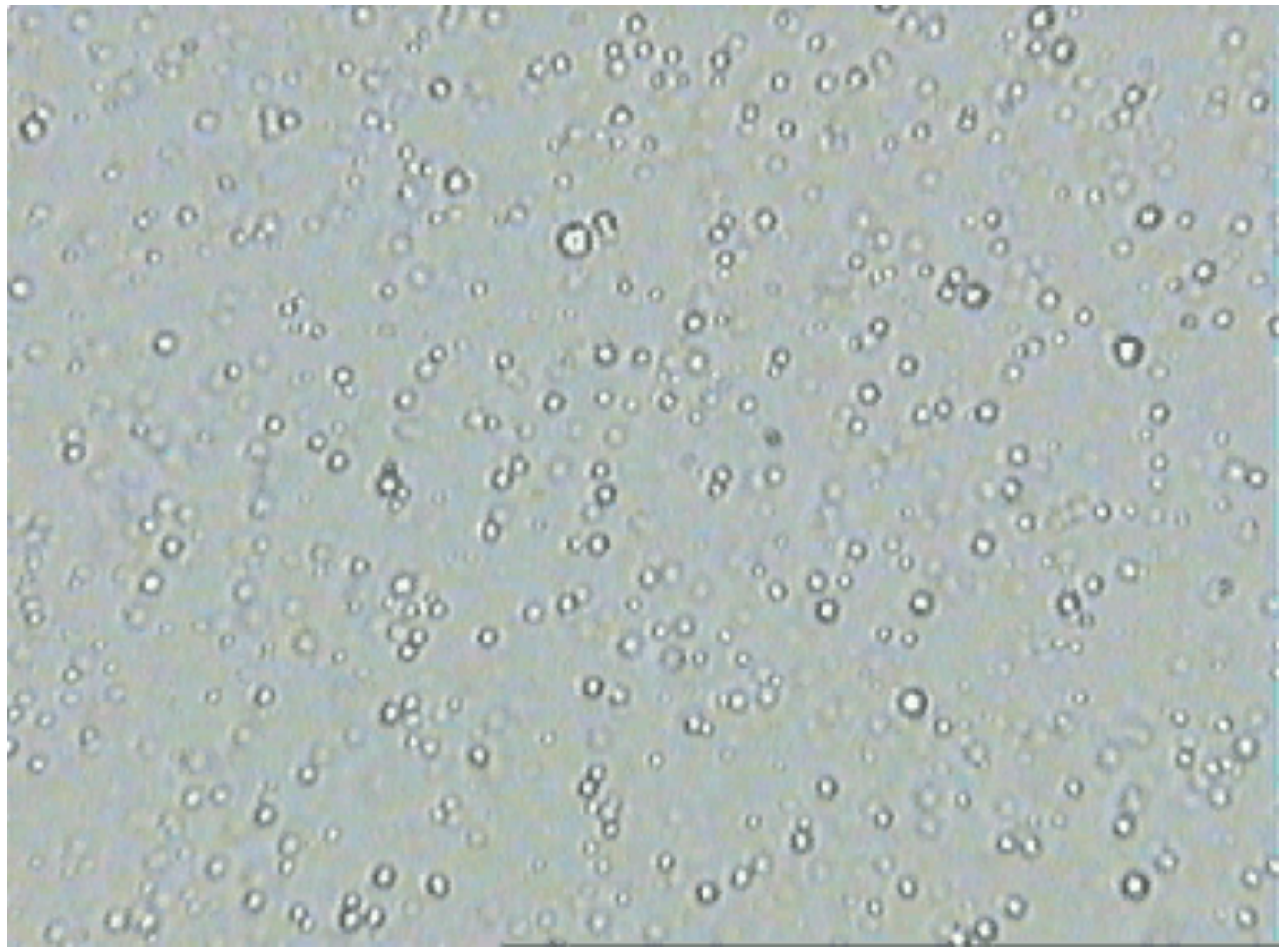


Brownian motion



1827 Robert Brown examines particles stemming from pollen in water and sees erratic motion

Fat globules in milk



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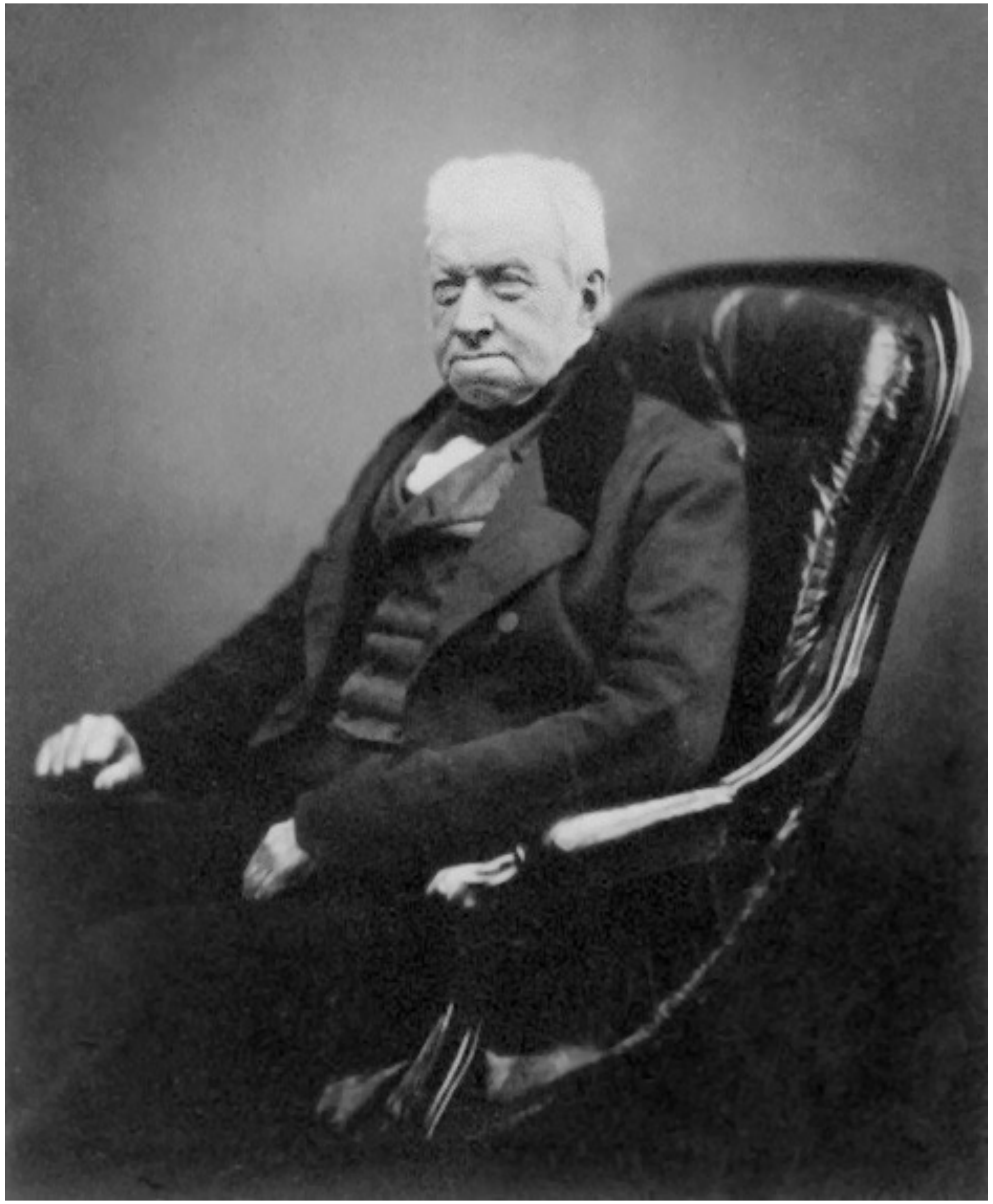
Brownian motion



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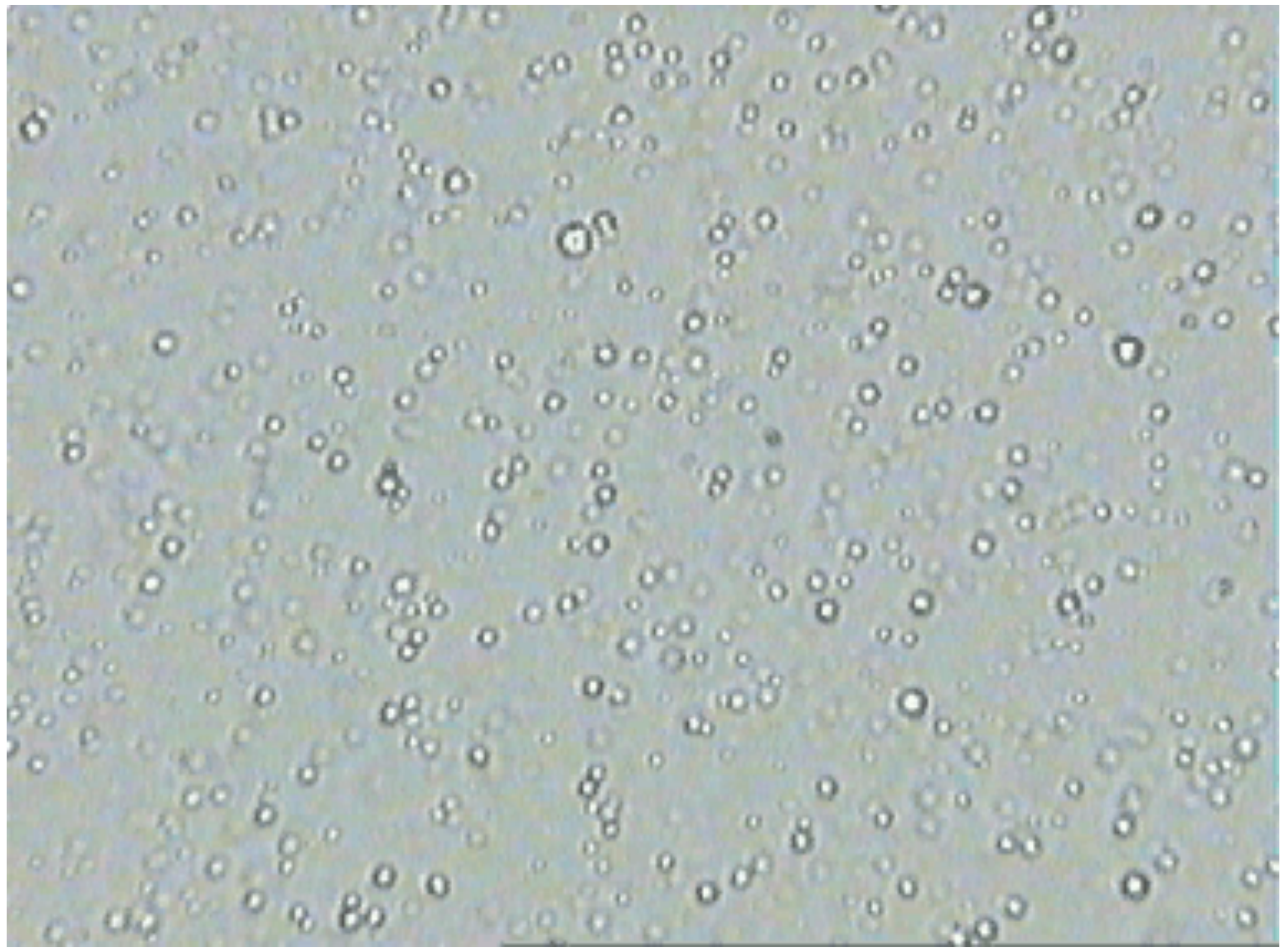
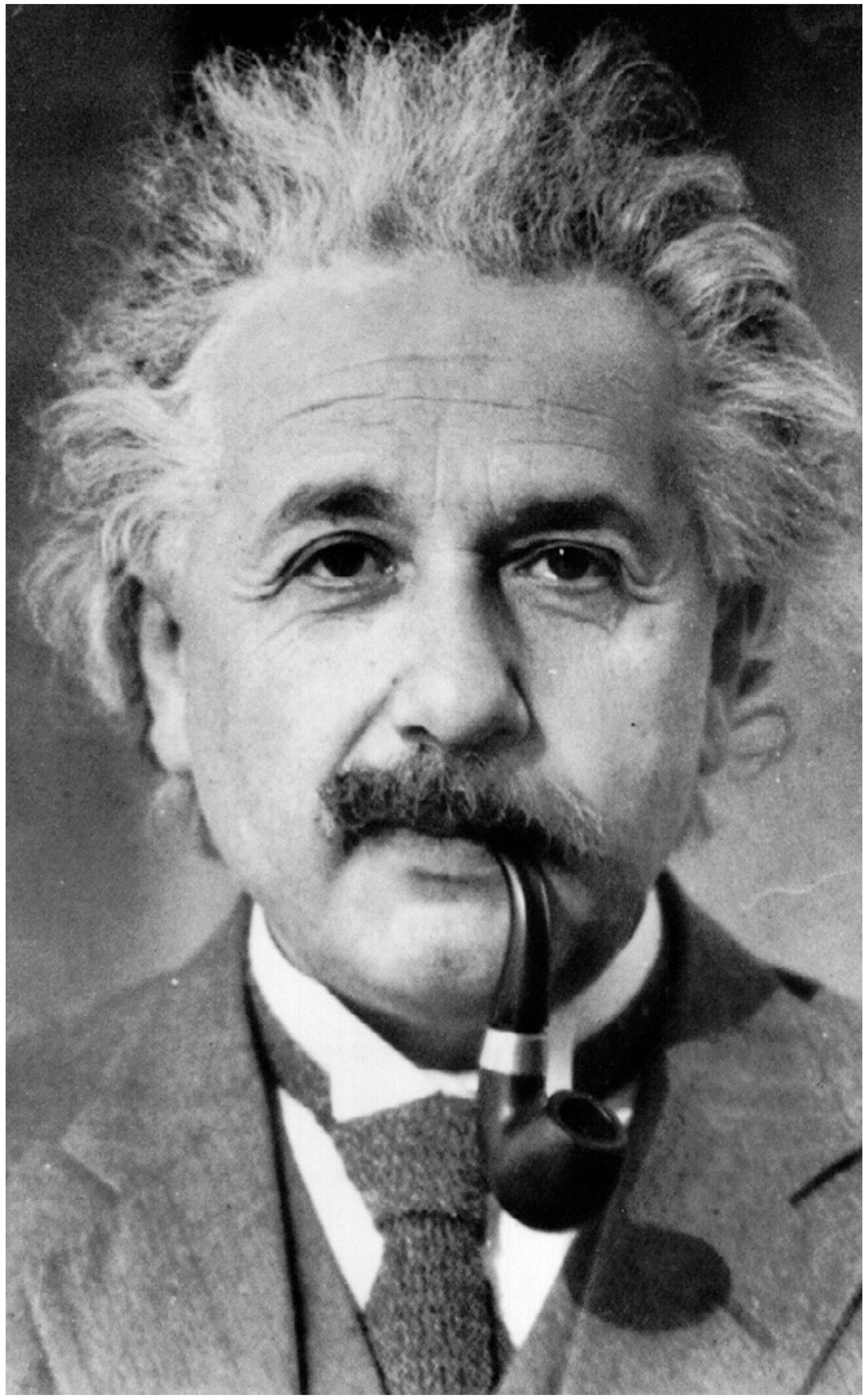


microscopy-uk.org.uk/amateurs/avi.html

Diffusion



1905 Albert Einstein gives explanation for Brownian motion:

Thermal motion of the fluid

$\Longrightarrow$ Frequent and disordered collisions of the fluid molecules with the particles

$\Longrightarrow$ Trajectory made of **independent** increments

$$\vec{r}(t) = \sum_{\tau_i < t} \Delta\vec{r}(\tau_i)$$

$\Longrightarrow$ ***Generic result:*** Trajectory diffusive with Diffusion coefficient *D*.

$$\langle r(t) \rangle = 0$$

$$\delta r^2(t) := \left\langle (r(t) - r(0))^2 \right\rangle = 2dDt$$

Mean-squared displacement grows *linearly*

Diffusion on fractals

E.g. Random walker on the Sierpinski gasket

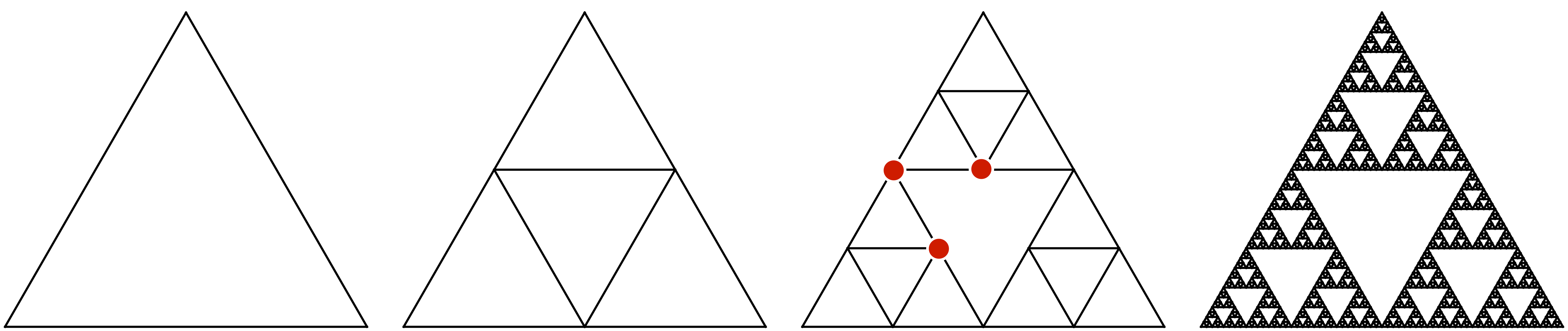
Self-similar geometry

All sites are not equivalent

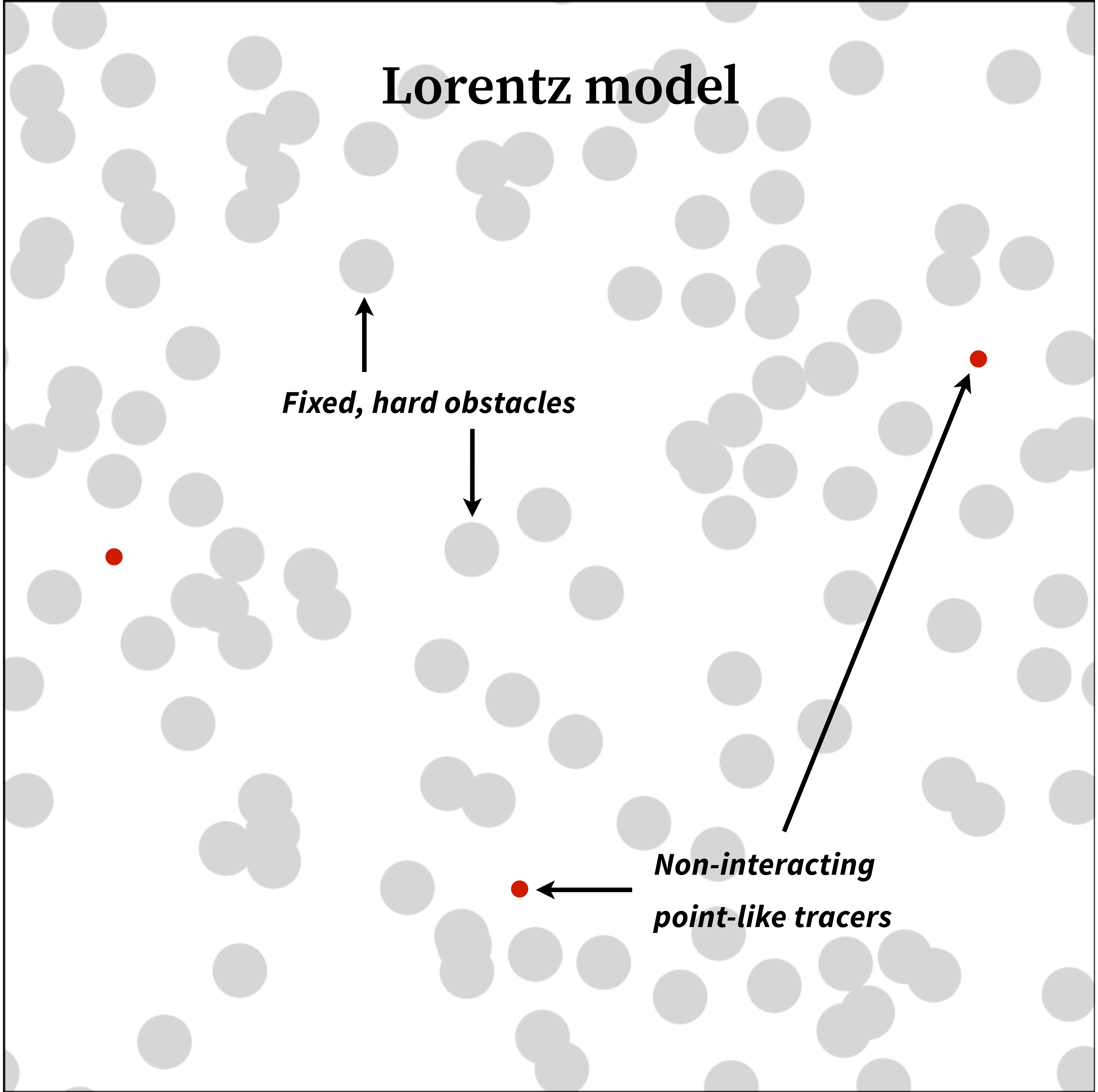
Persistent correlations on all lengthscales

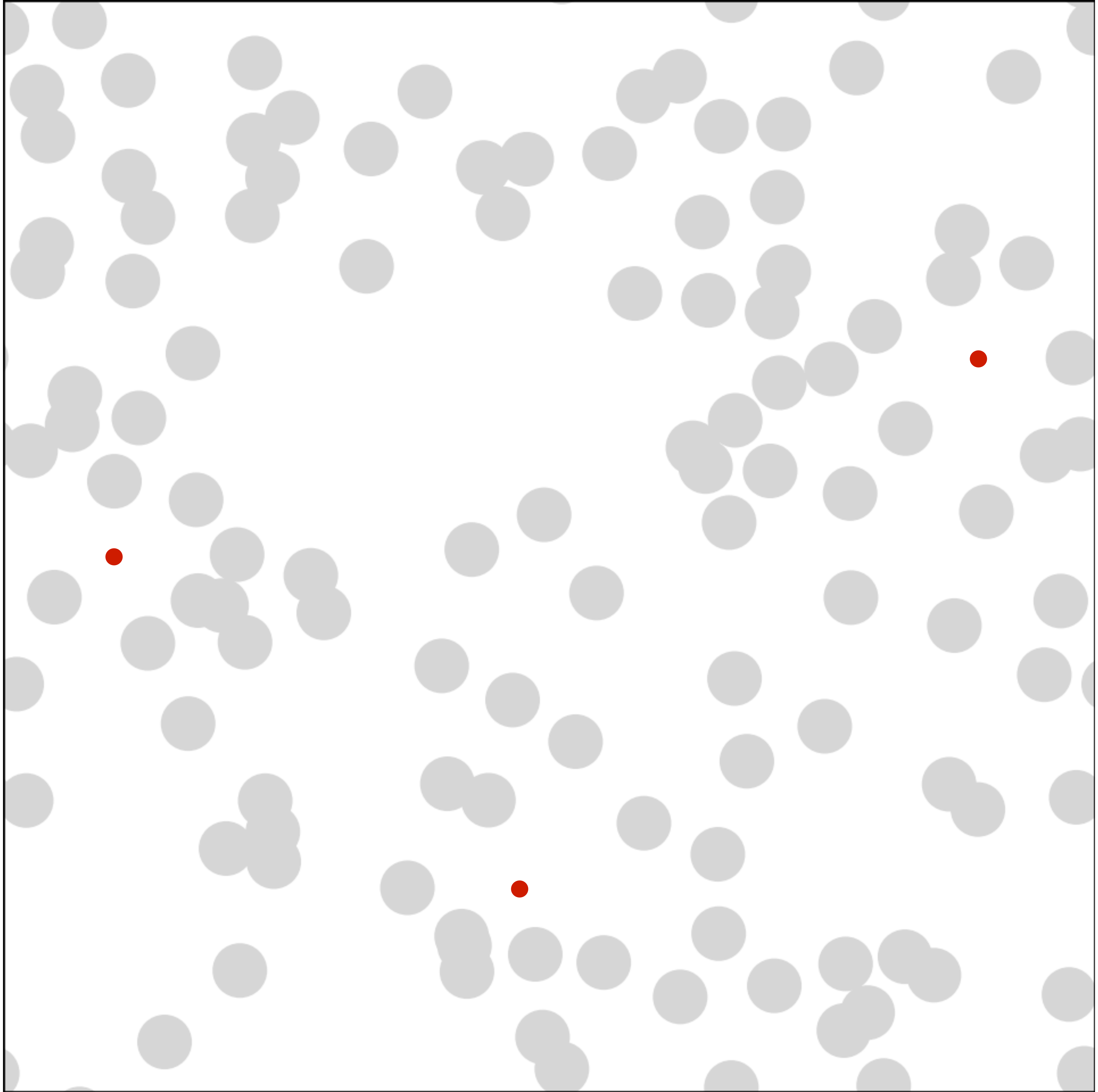
$\Rightarrow$ Increments Δr not independent anymore

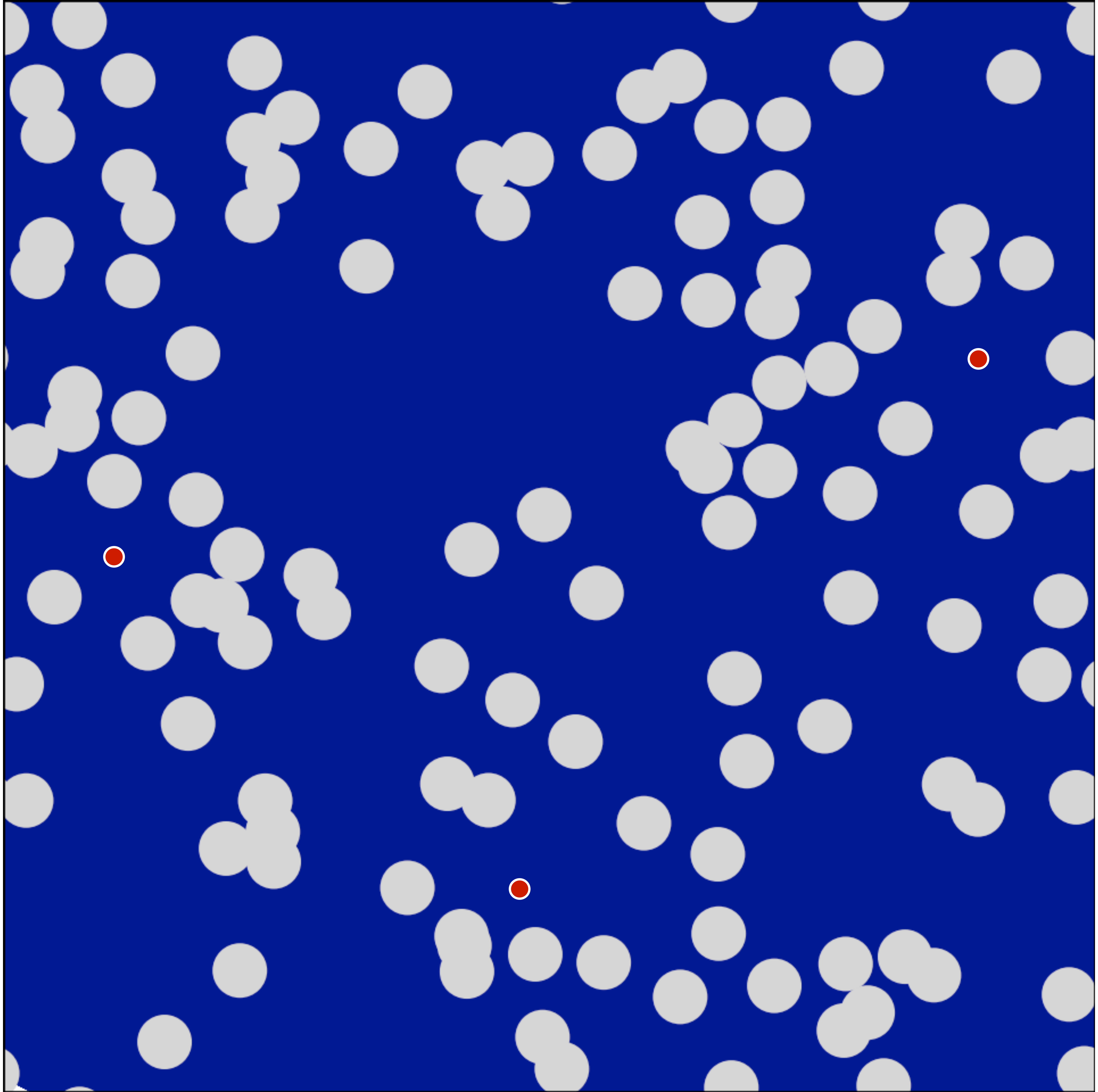
$\Rightarrow$ Anomalous diffusion $\delta r^2(t) \sim t^{2/z}$, with $z = \log 5/\log 2 \approx 2.3$

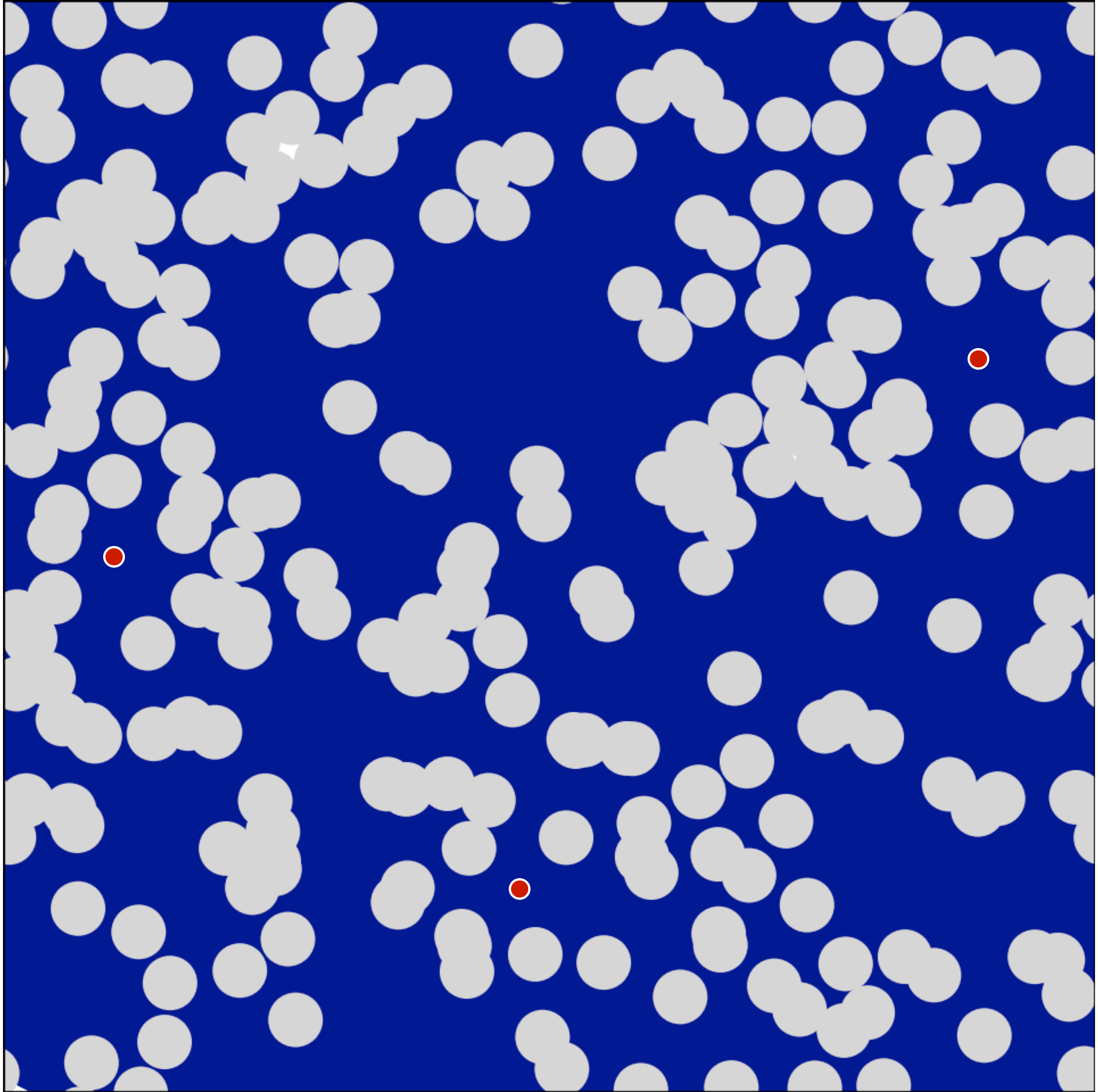


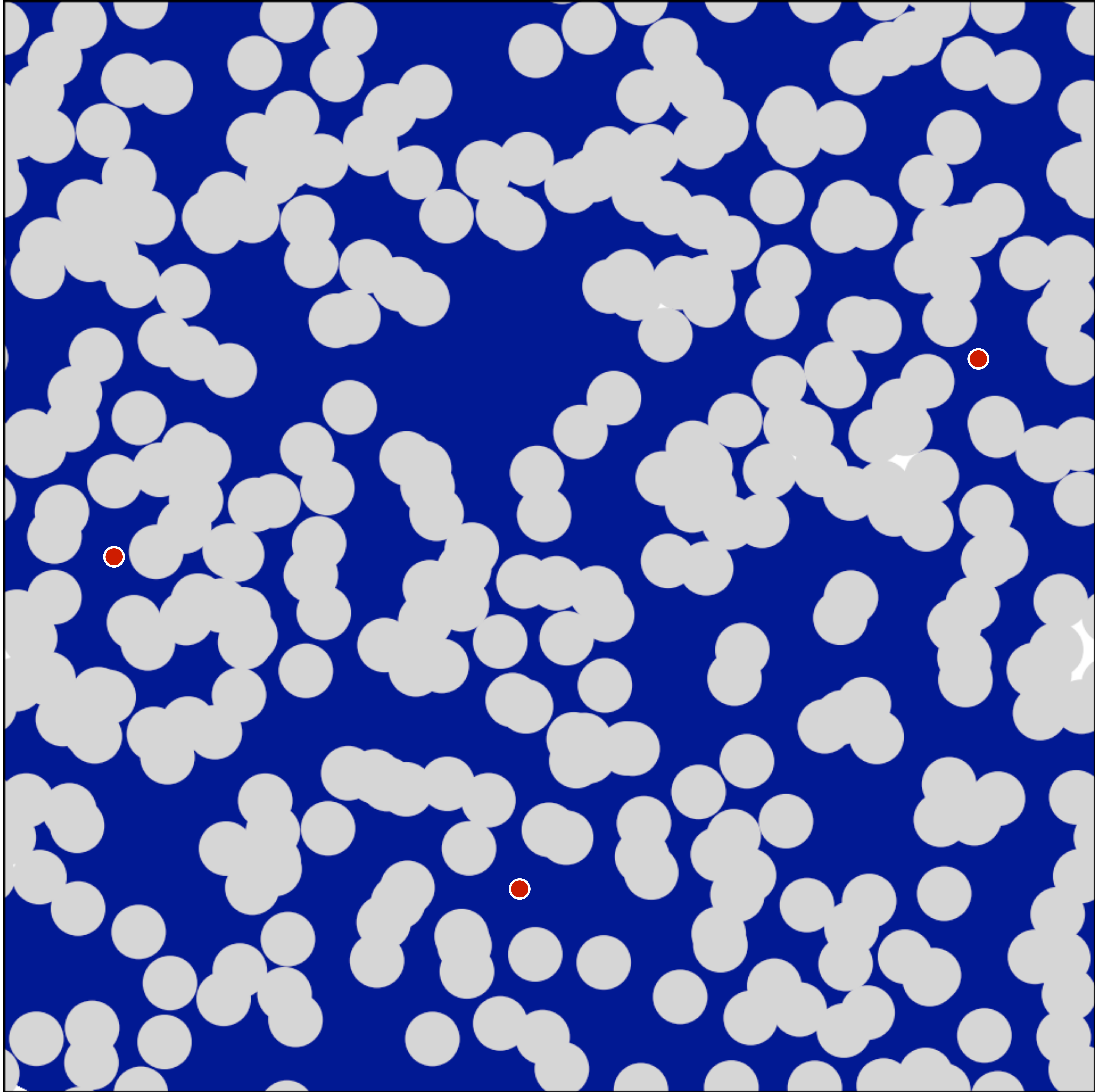
Lorentz model

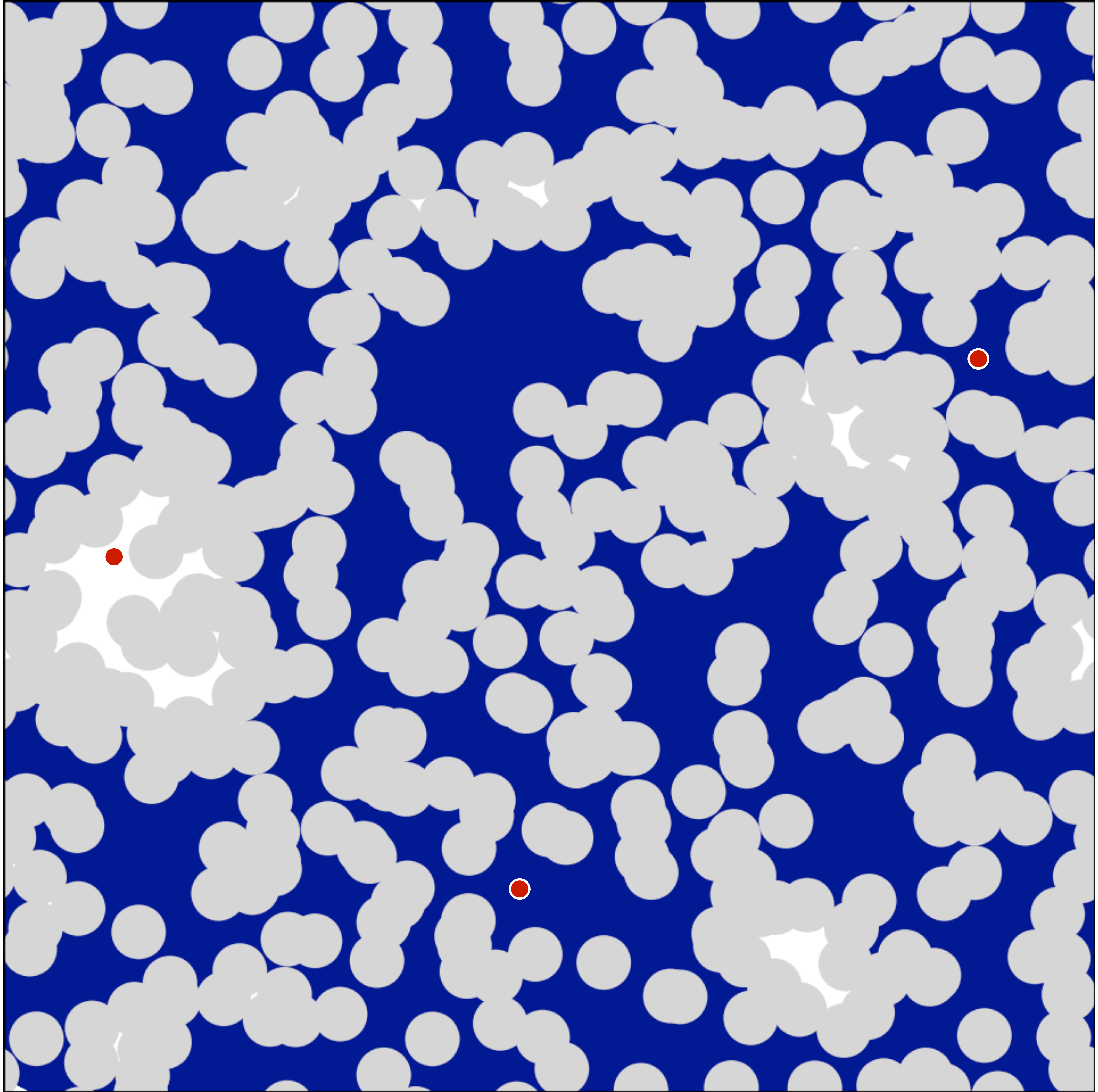


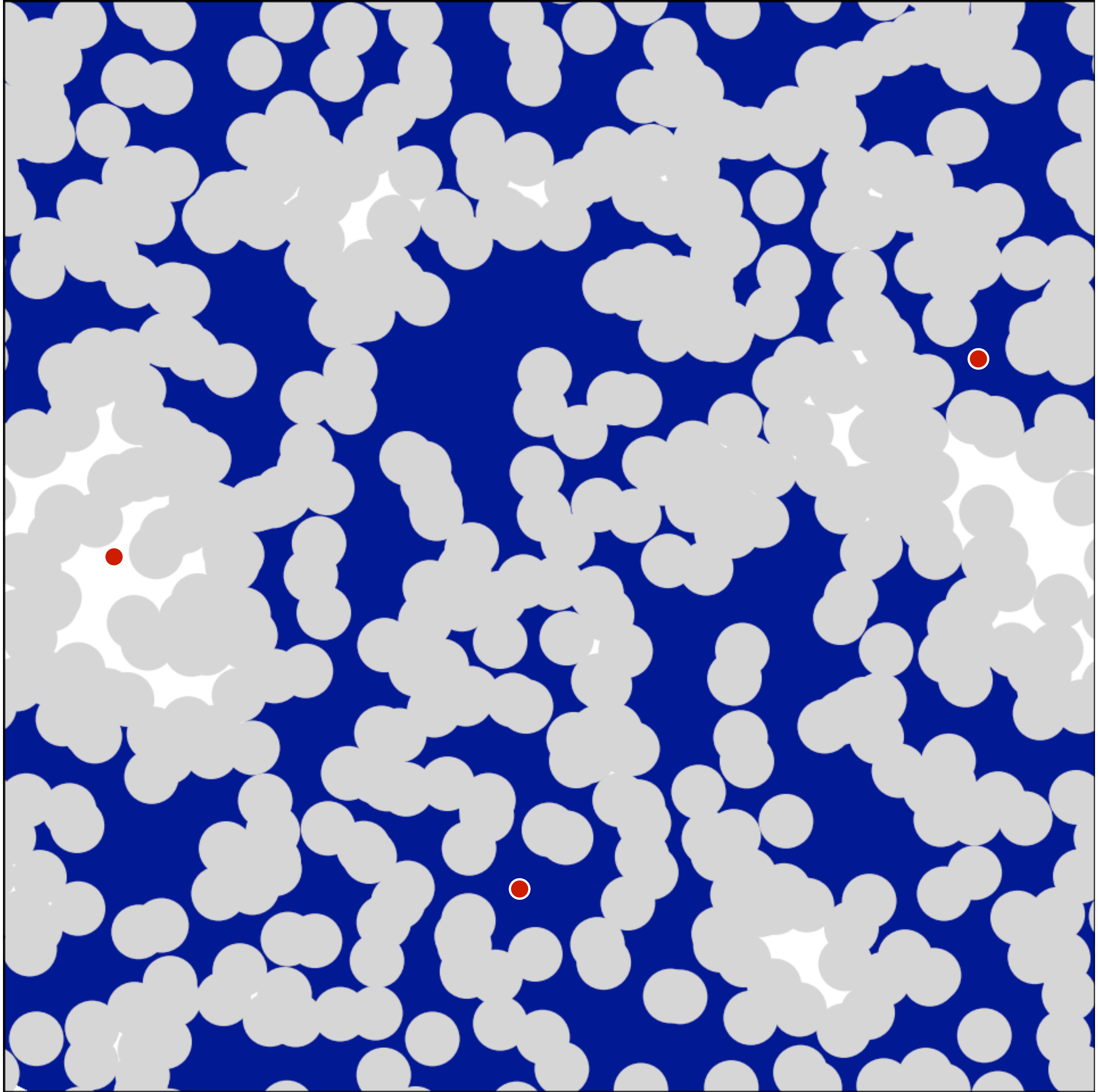


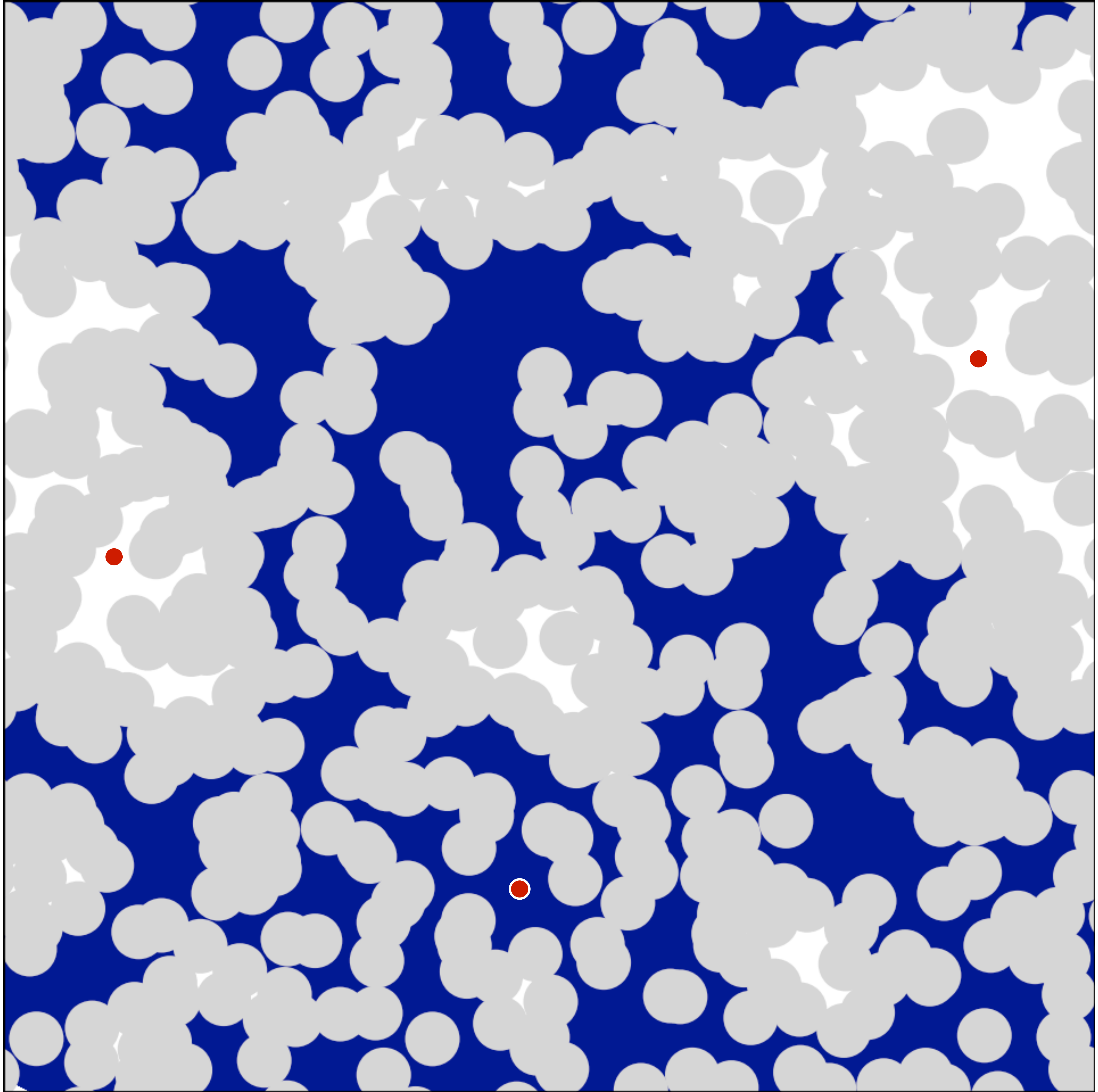


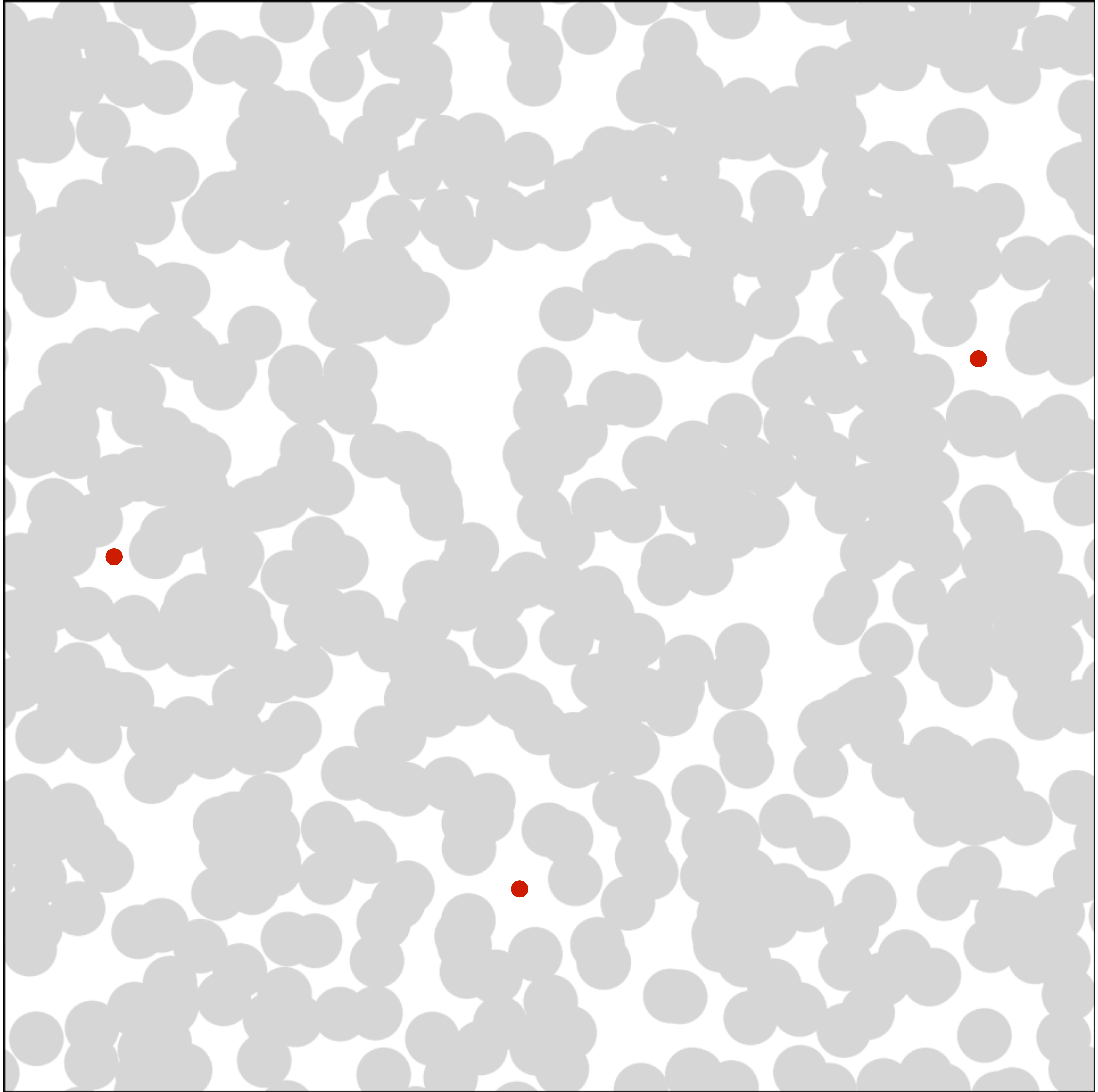


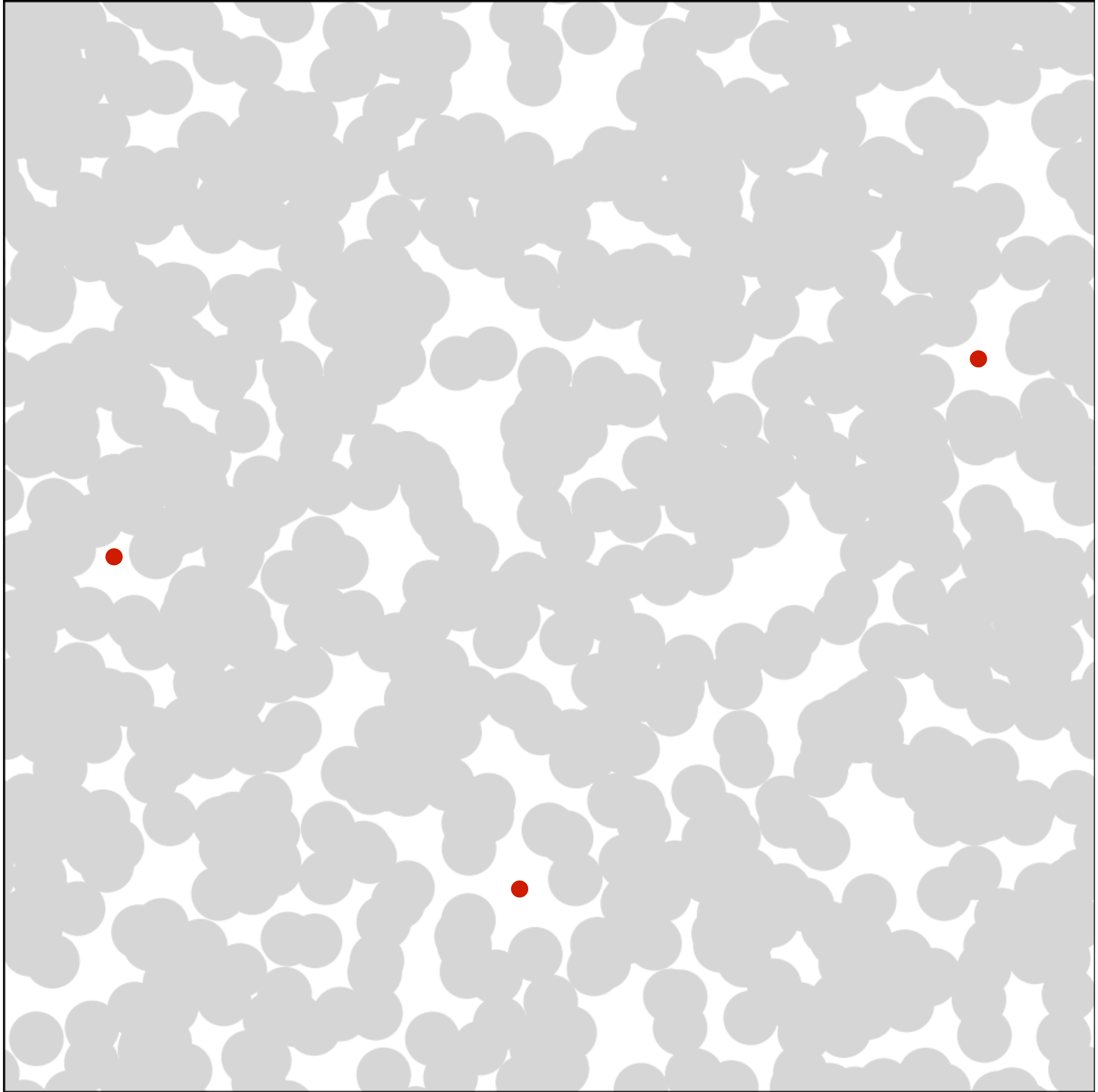


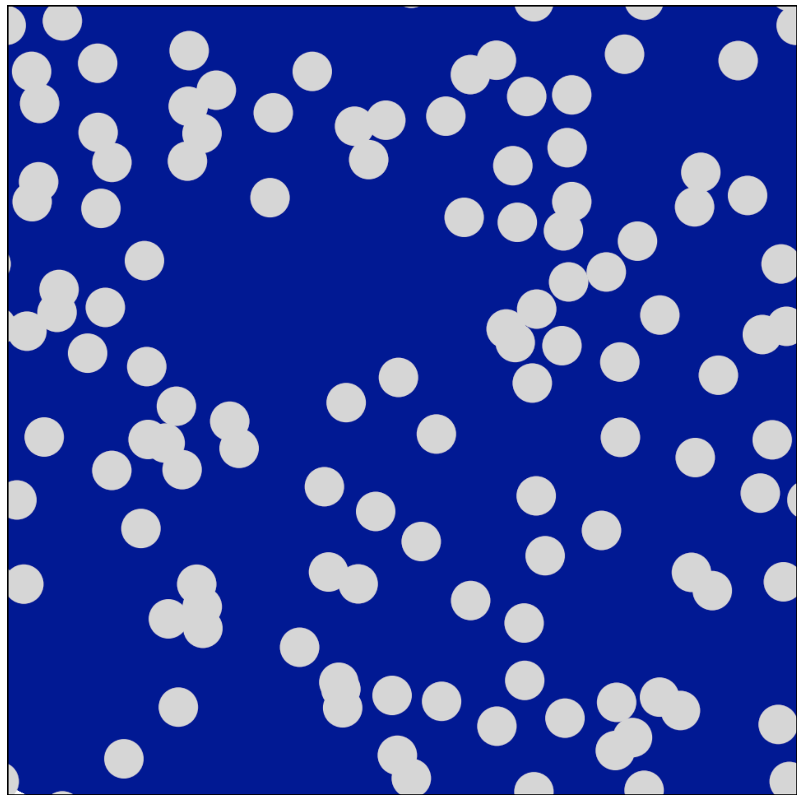
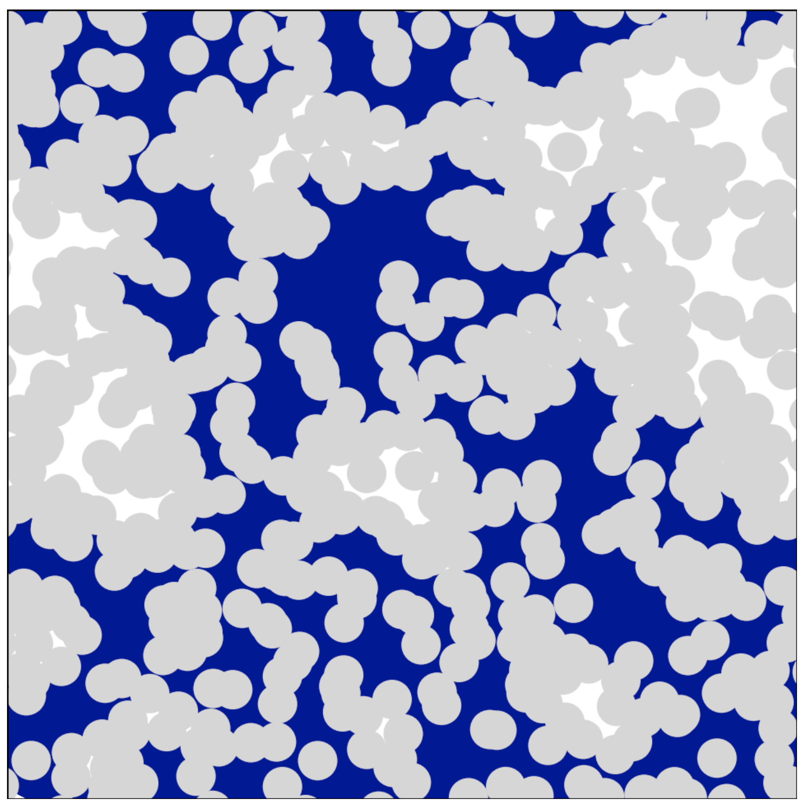
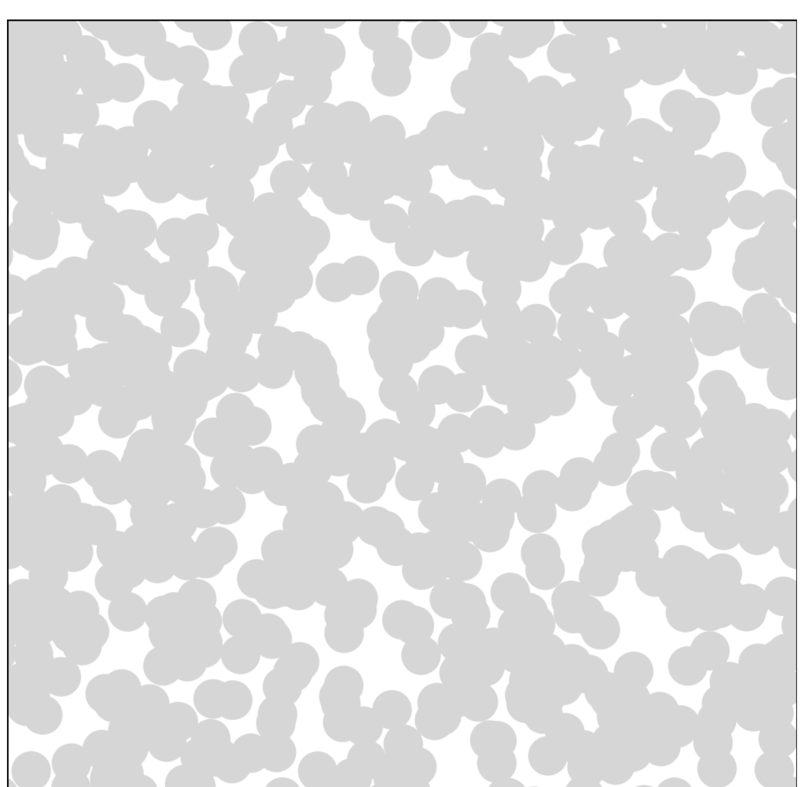




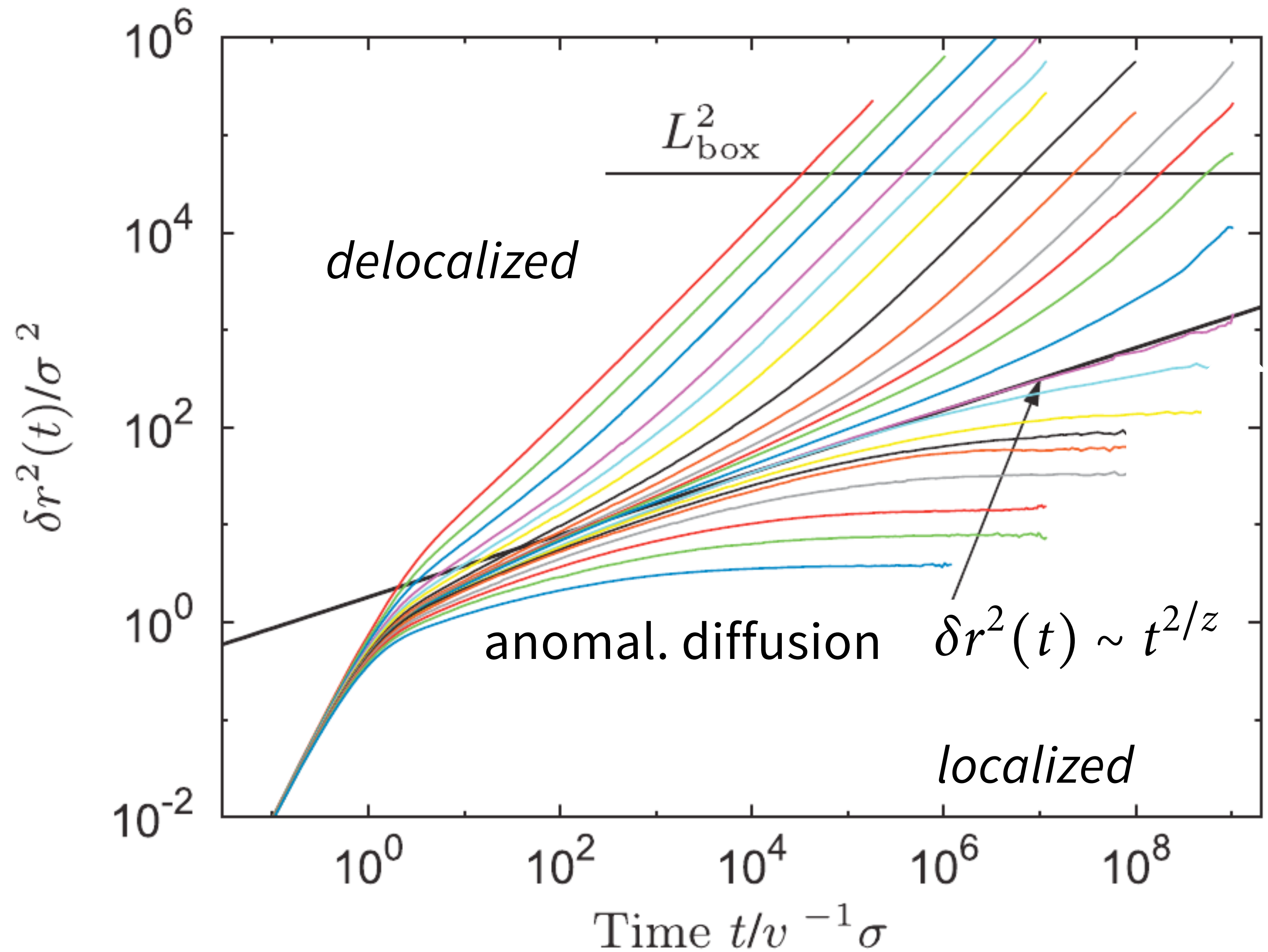






Lorentz model



Höfling *et al*, PRL (2006)

- Localization transition of the tracer at percolation point of the void space
- Dynamical Critical Phenomenon
- Anomalous diffusion due to fractal structure of the system at the percolation point

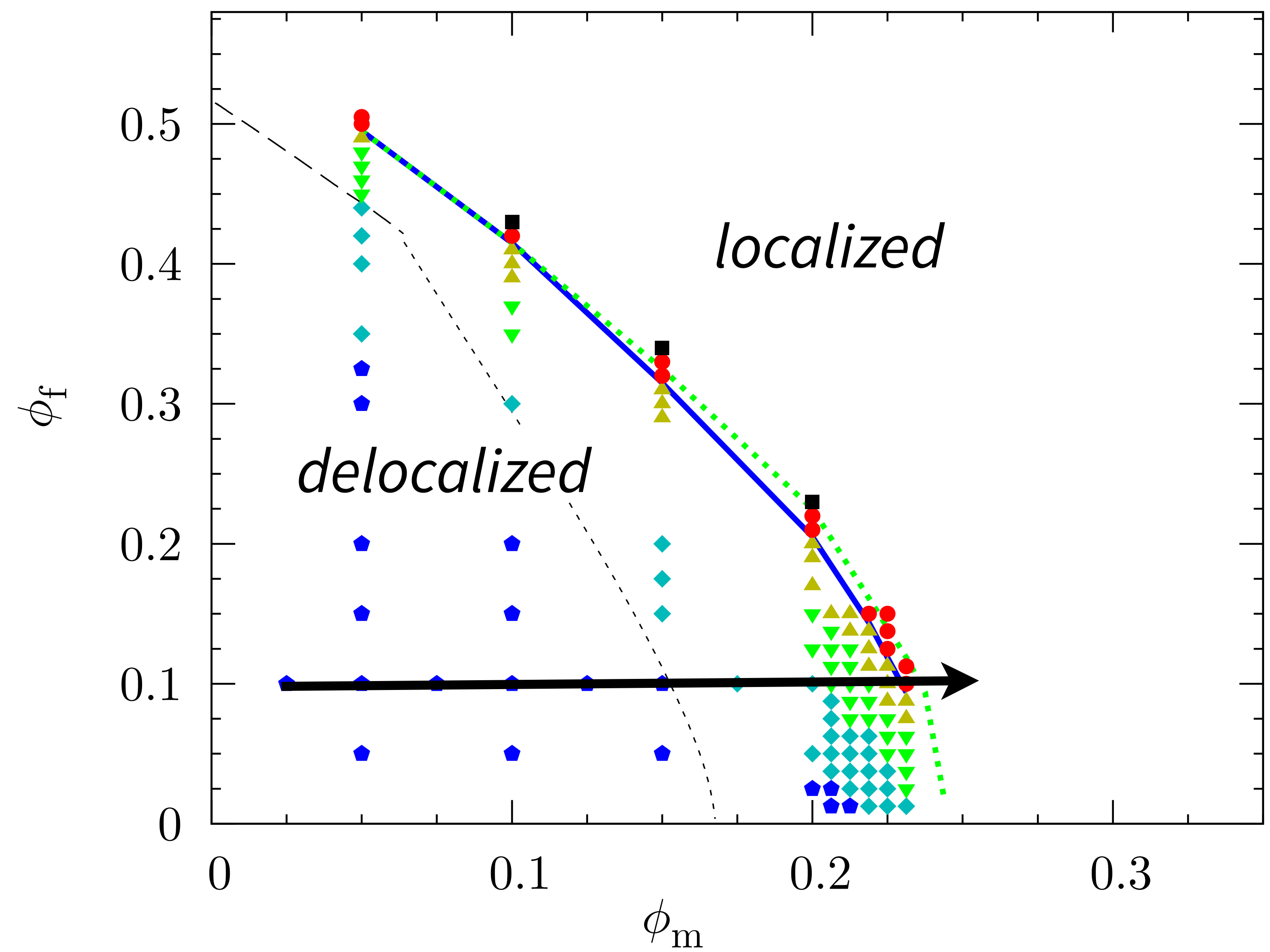
Quenched-annealed systems

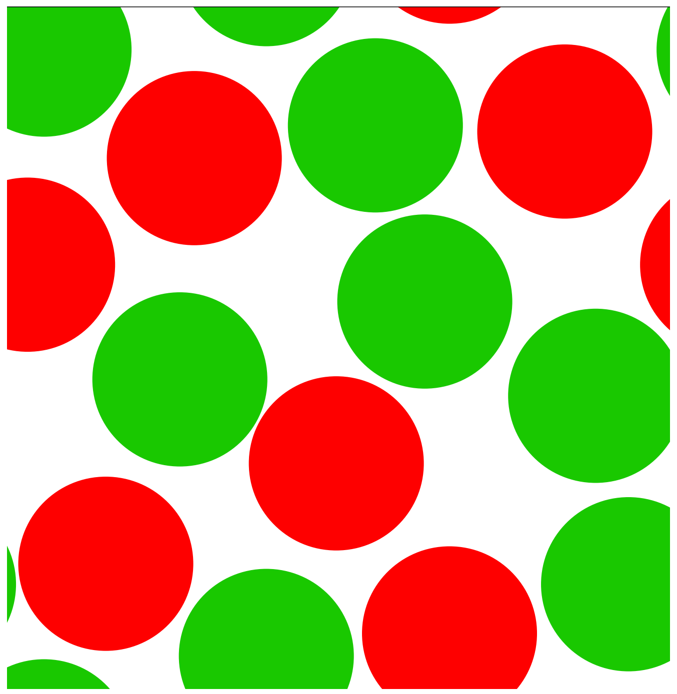
Kurzidim et al, PRE (2010)

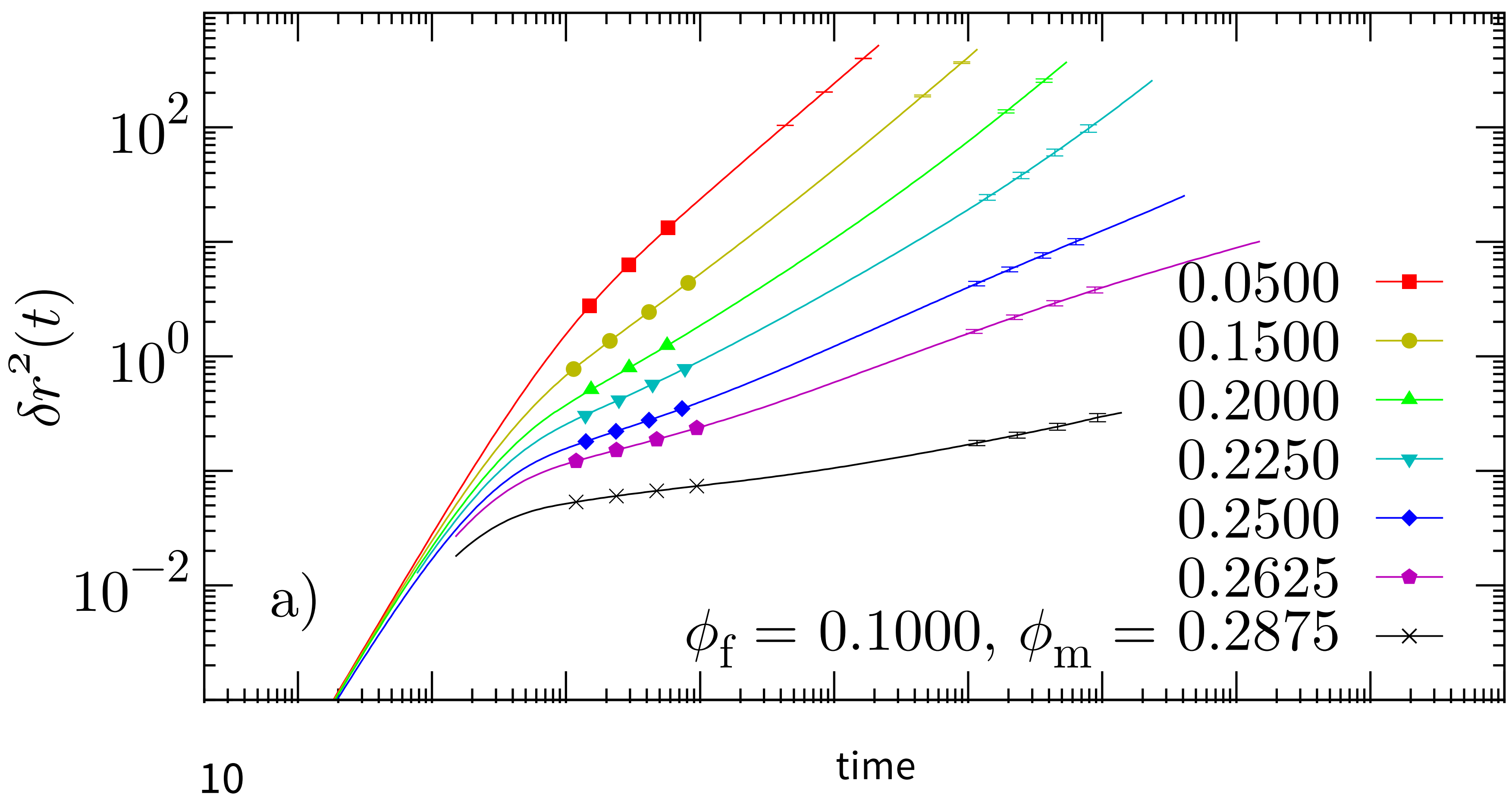
Correlated hard-sphere obstacles, interacting mobile particles

Localization transition with subdiffusion with *modified* exponent 0.5

Transition shifted to *smaller* matrix densities







Soft quenched-annealed systems

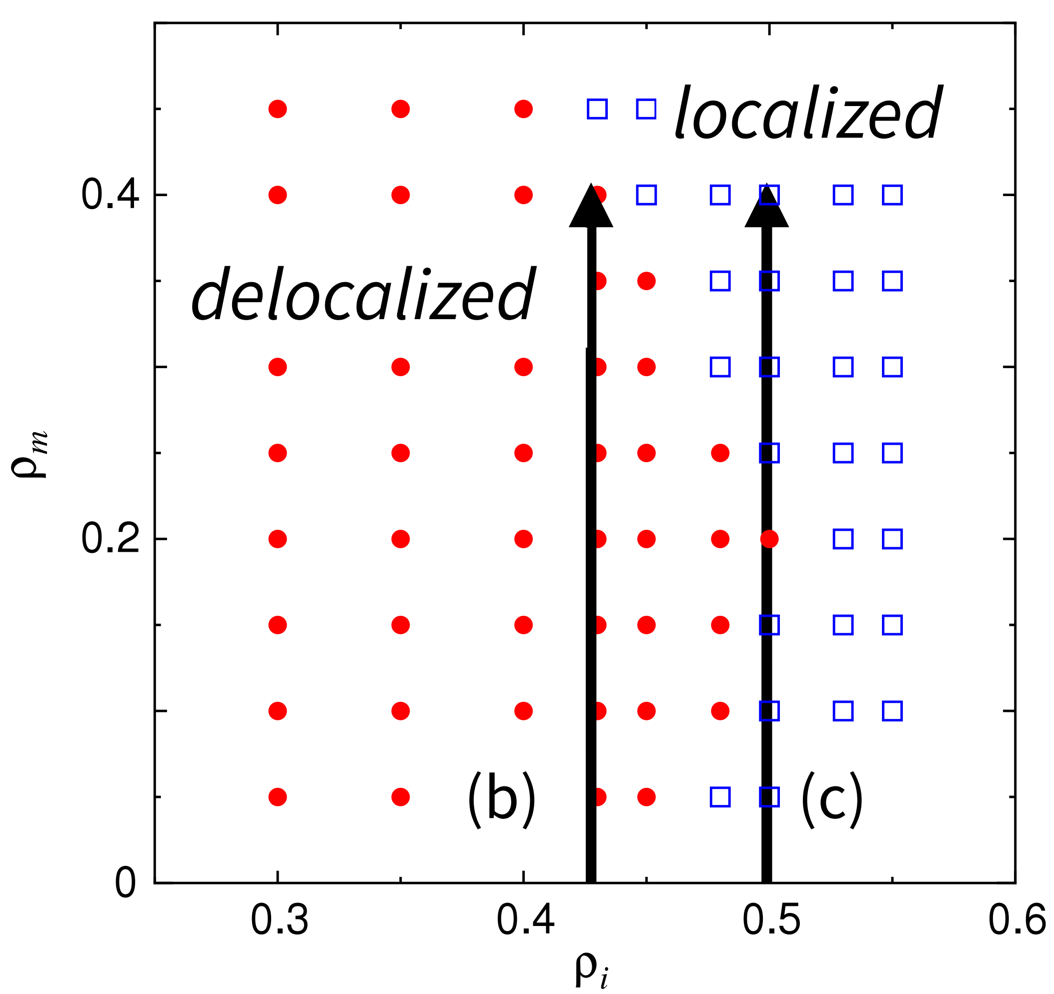
K. Kim et al, J. Phys. Condens. Matter 23 (2011)

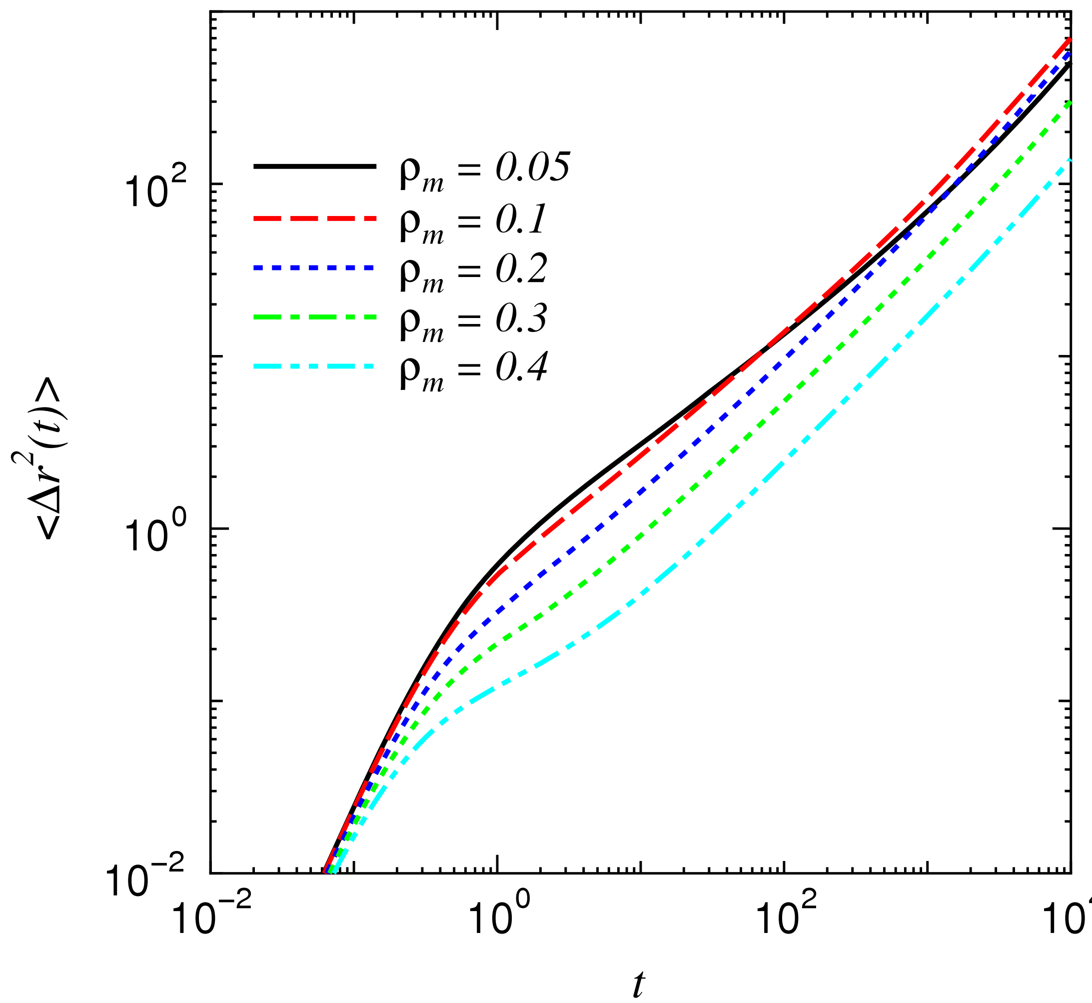
Soft particles now!

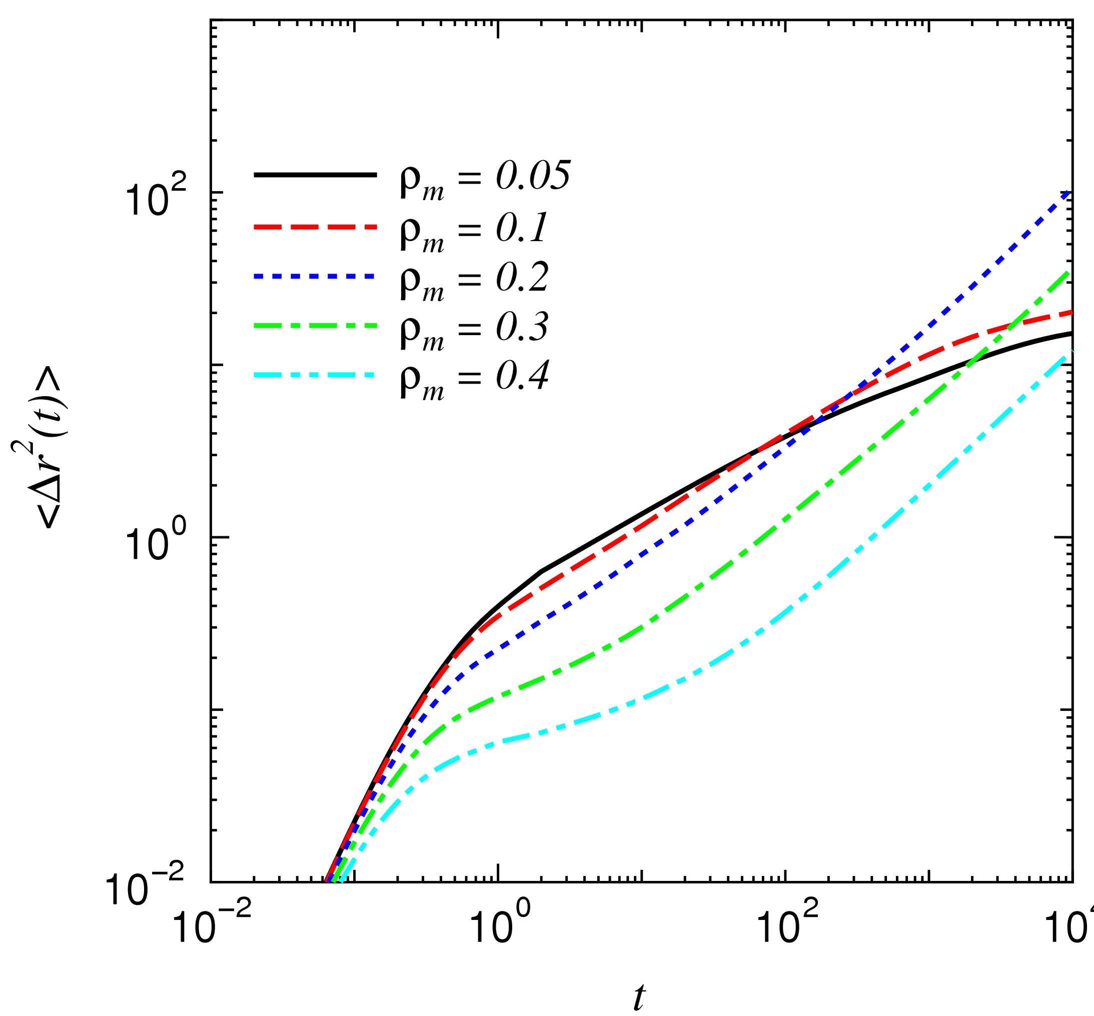
MCT prediction: *Reentrance* transition upon increase of the fluid number density

In simulations: *only* found if fluid changes matrix during equilibration

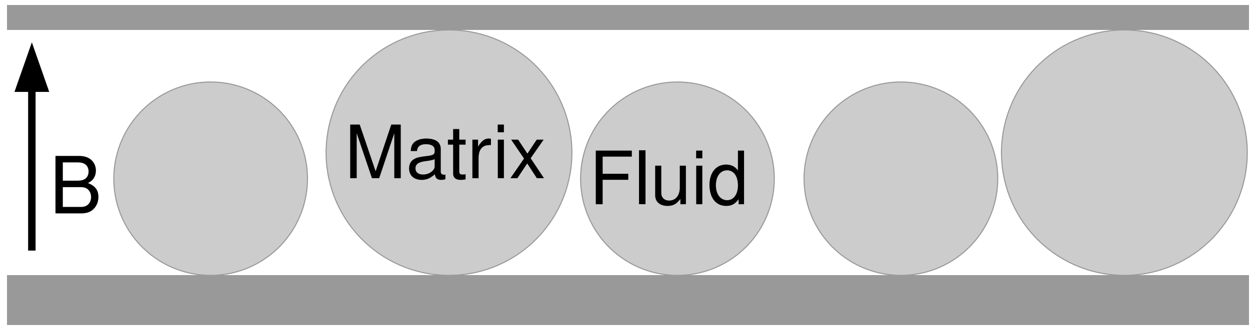
$\Longrightarrow$ Modification of matrix structure leads to **reentrance** transition

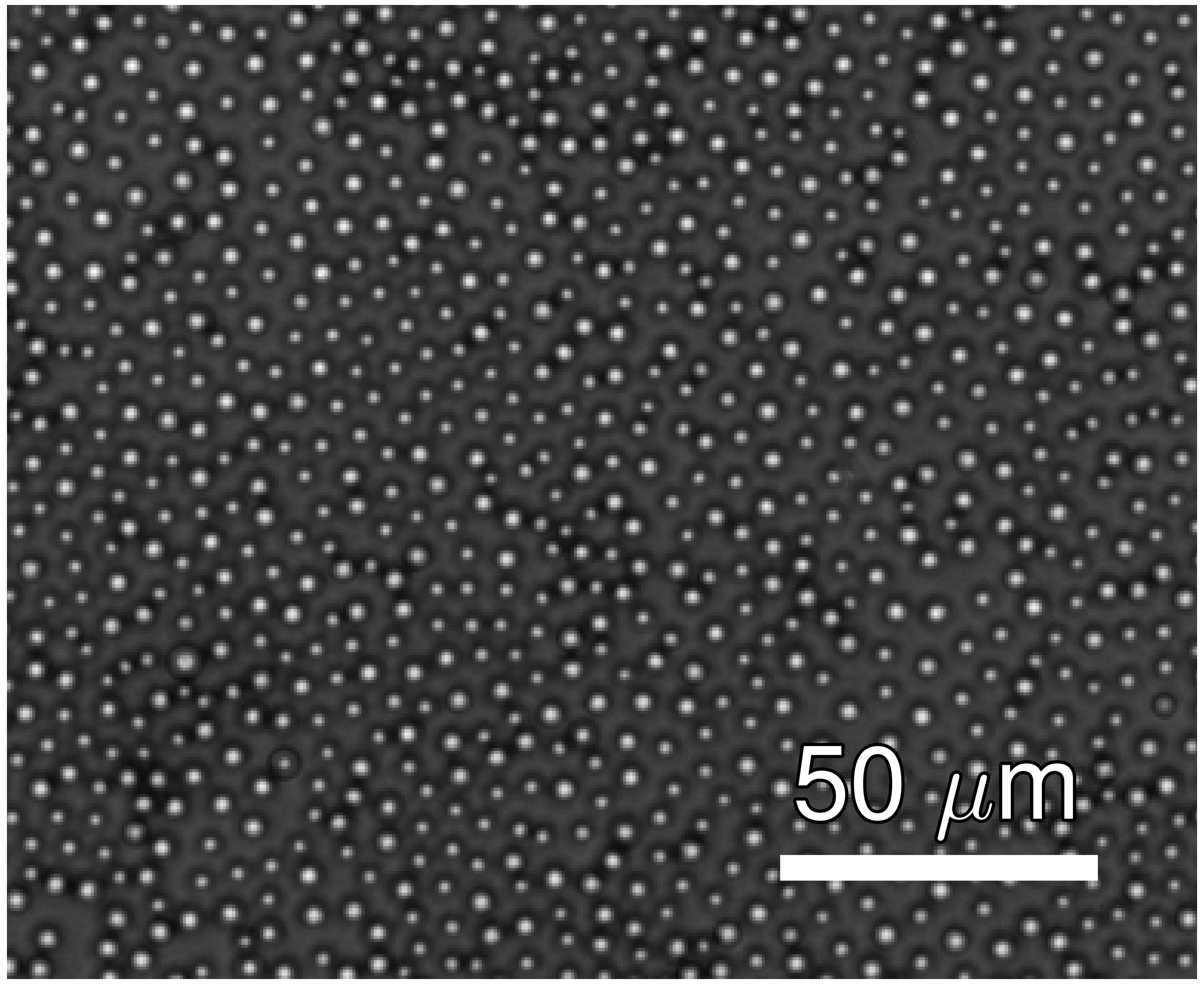


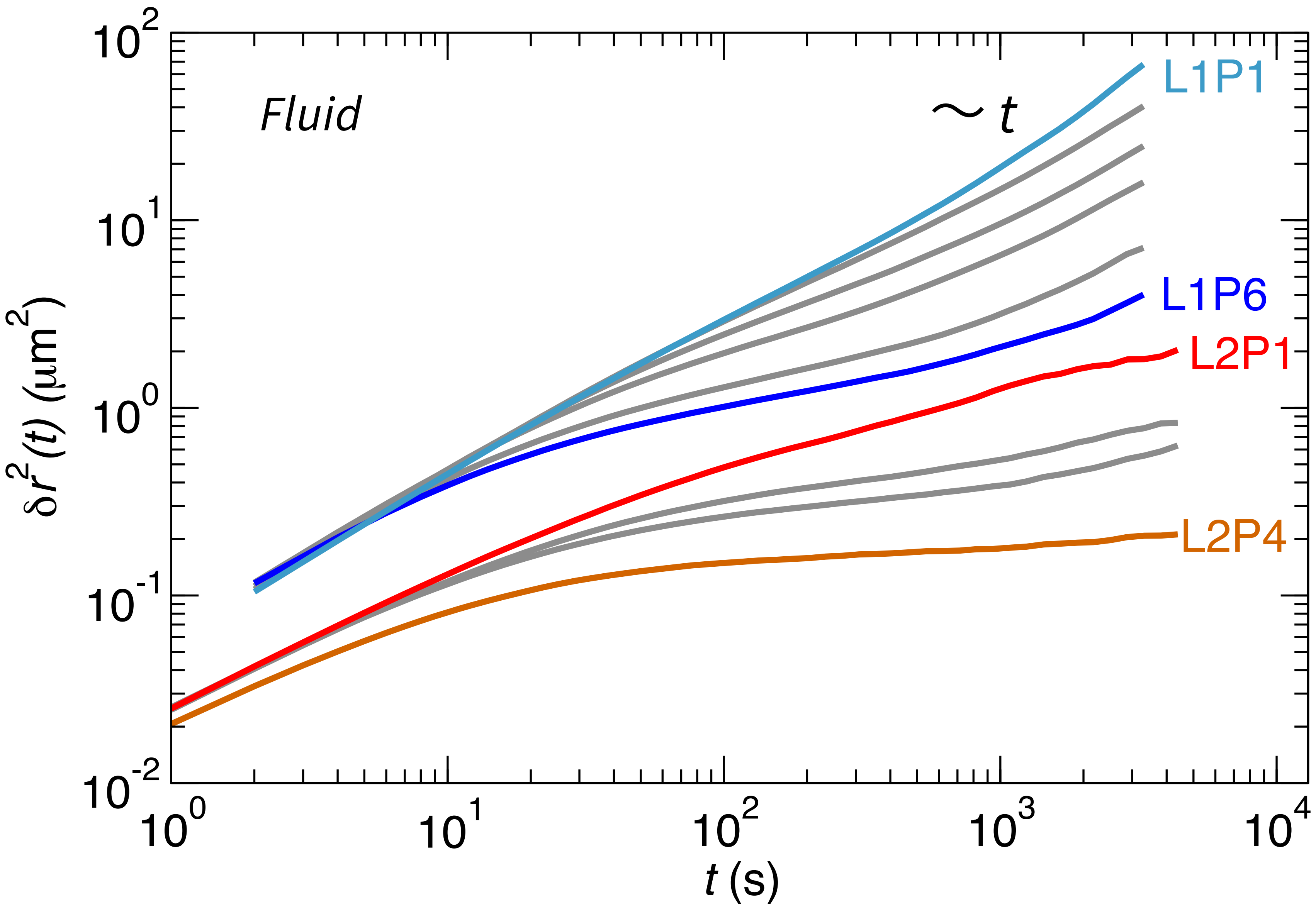




Superparamagnetic colloids confined between glass plates

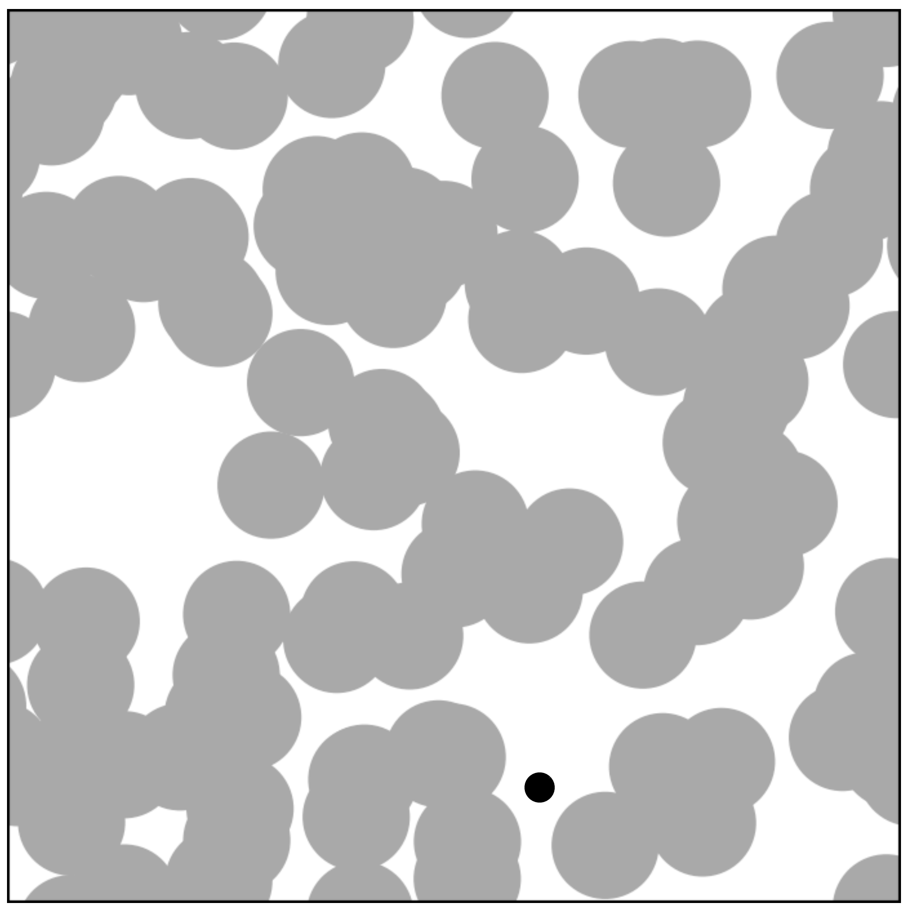






T. Skinner, S.K. Schnyder *et al*, PRL 111 (2013)

Investigate connection between Lorentz model and heterogeneous media



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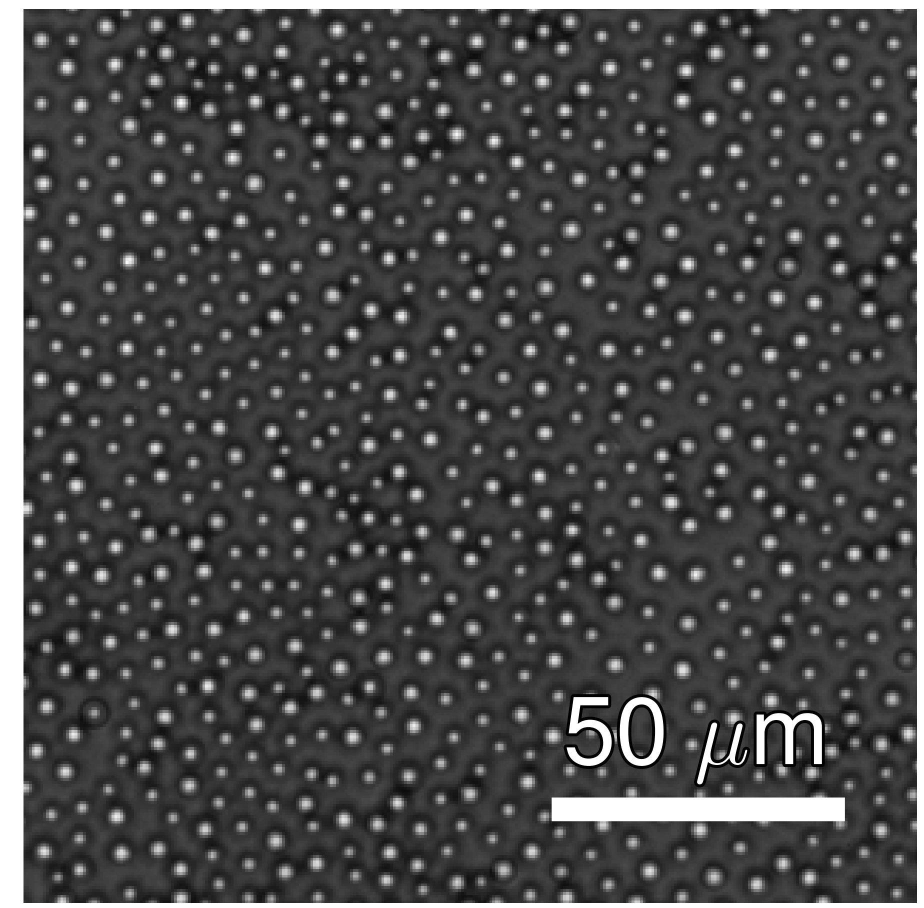


Colloidal model experiment,

T. Skinner et al, PRL 111 (2013)

- **Hard interactions with obstacles**
- **Non-interacting mobile component**

- **Soft interactions**
- **Interacting mobile component**

Soft-disk Lorentz model

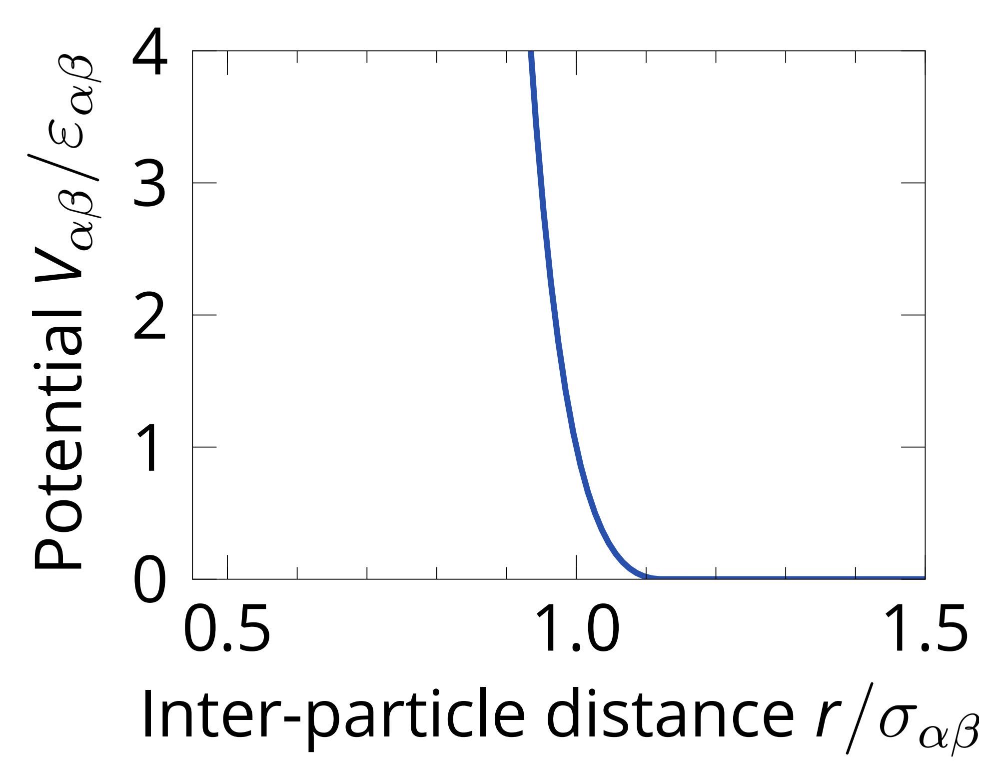
Soft-disk system (2D)

Molecular dynamics simulation

Interaction potential: repulsive part of LJ

$$V_{\alpha\beta} = 4\varepsilon_{\alpha\beta}\left(\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right) + \varepsilon_{\alpha\beta}$$

$\alpha, \beta \in M, F$ (Matrix, Fluid)



Finite barriers ➔ Energy scale now important:

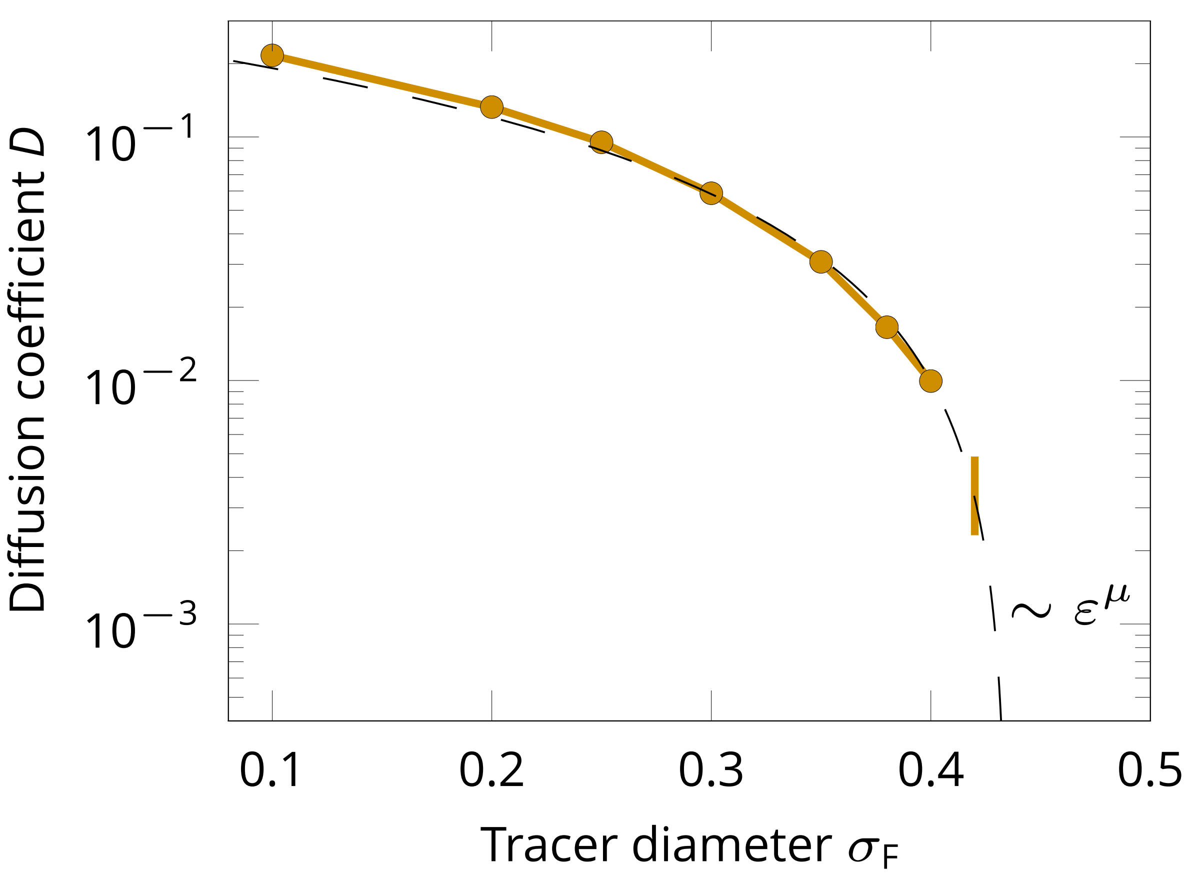
Mapping to hard disks $\sigma_{hd}(\sigma_F, E)$

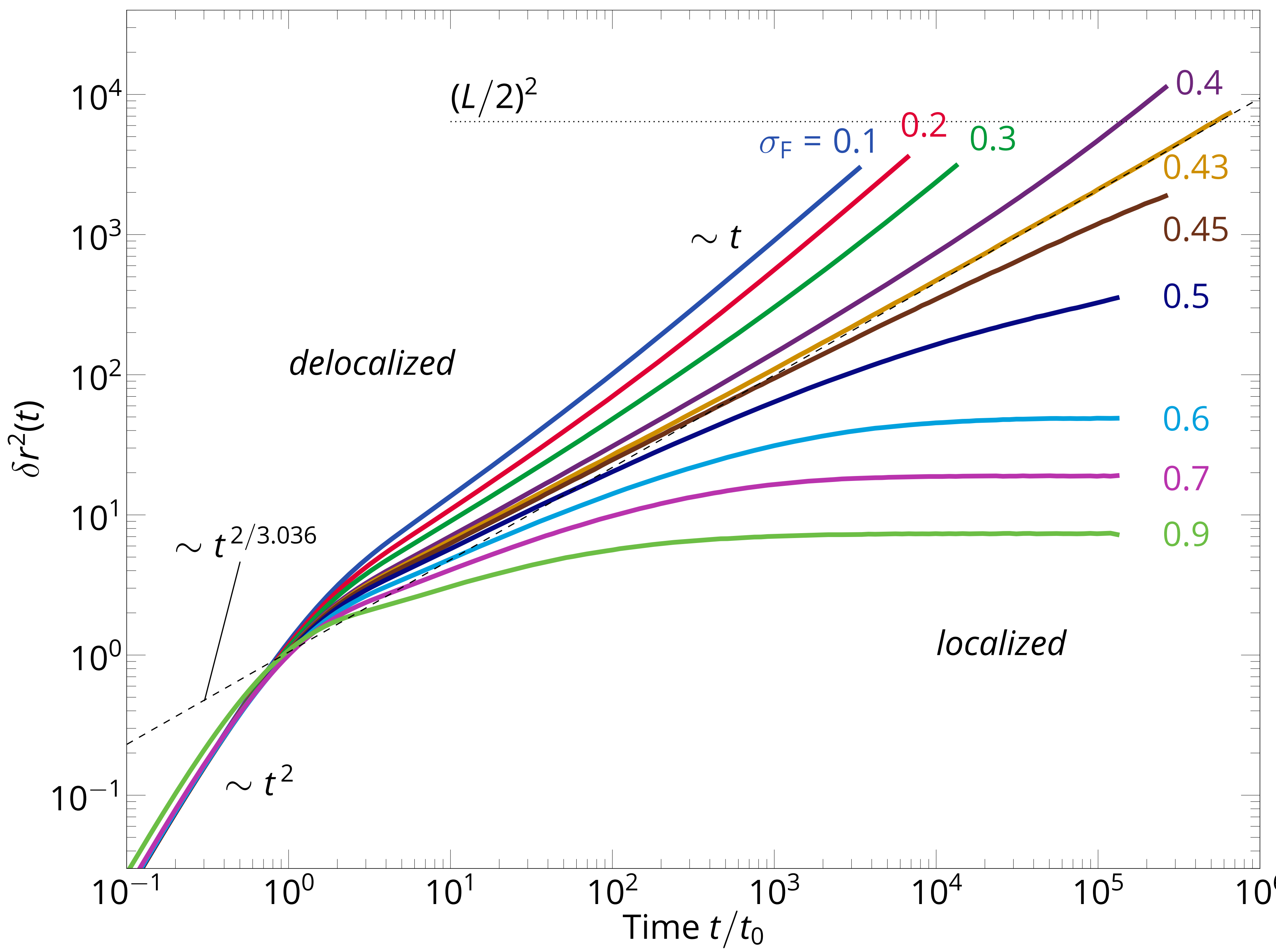
Soft-disk Lorentz model

Soft potential: set particles to same energy

Localization-delocalization transition at $\sigma_F \approx 0.43$

Anomalous exponent $2/z$ as in Lorentz model





S.K. Schnyder *et al*, Soft Matter 11 (2015)

Introduce
energy distribution

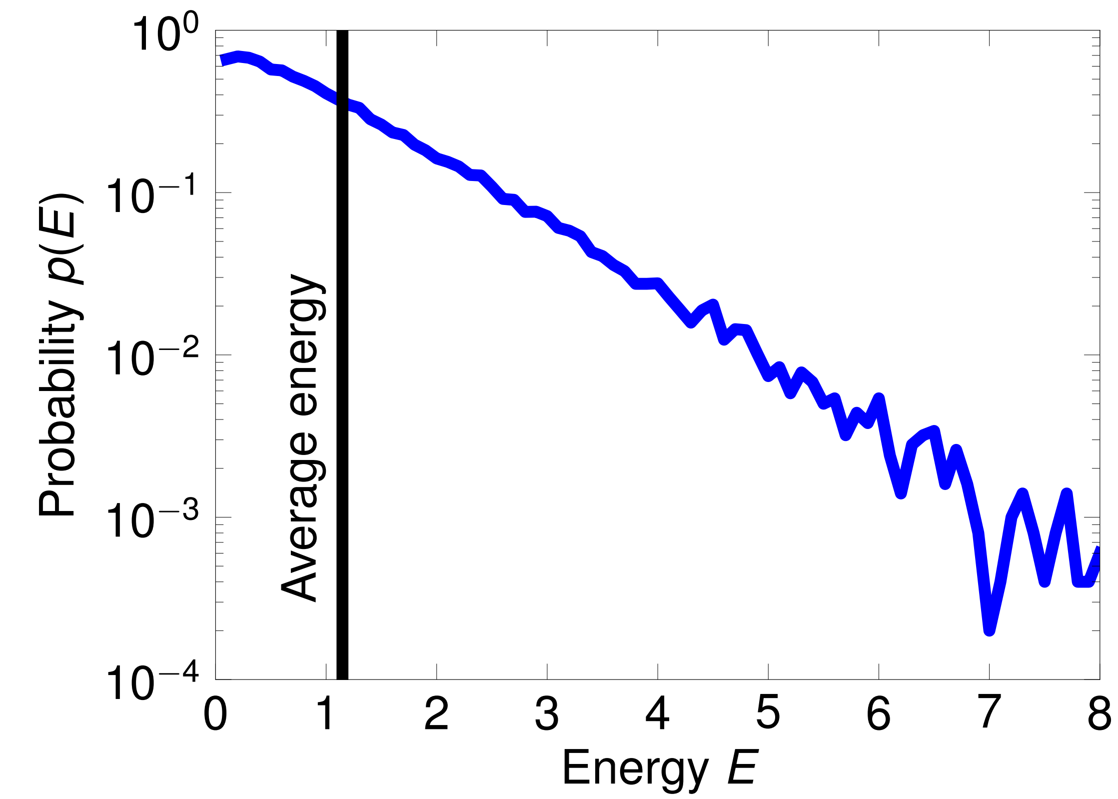
Confined ideal gas

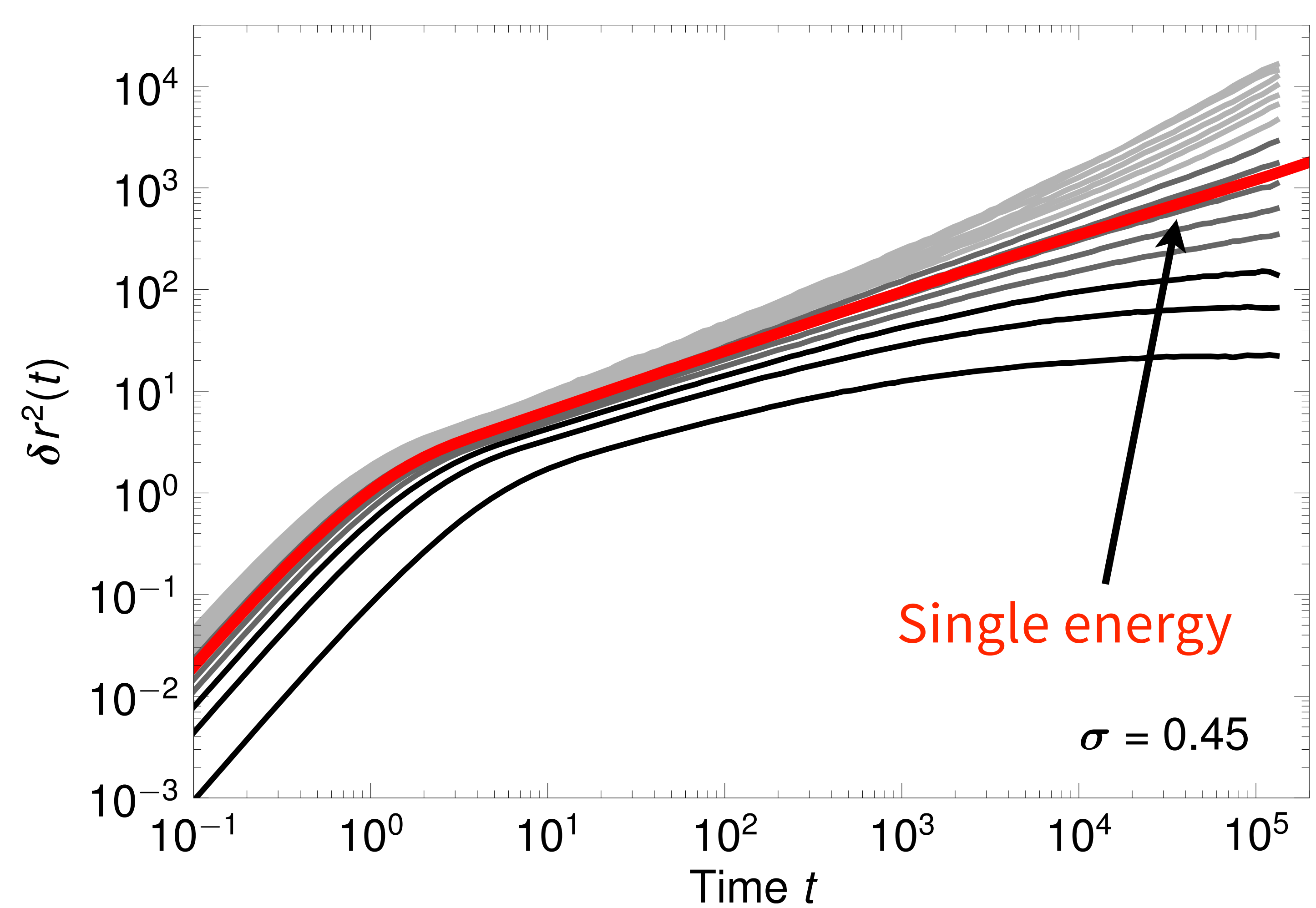
Single energy → Maxwell-Boltzmann distribution

Obstacles form *finite* barriers

$\Rightarrow$ Averaging of the dynamics

Does not occur in hard-disk systems





Diffusive at high energies

Anomalous at intermediate energies

Localized at low energies

Confined ideal gas

Single energy → Maxwell-Boltzmann distribution

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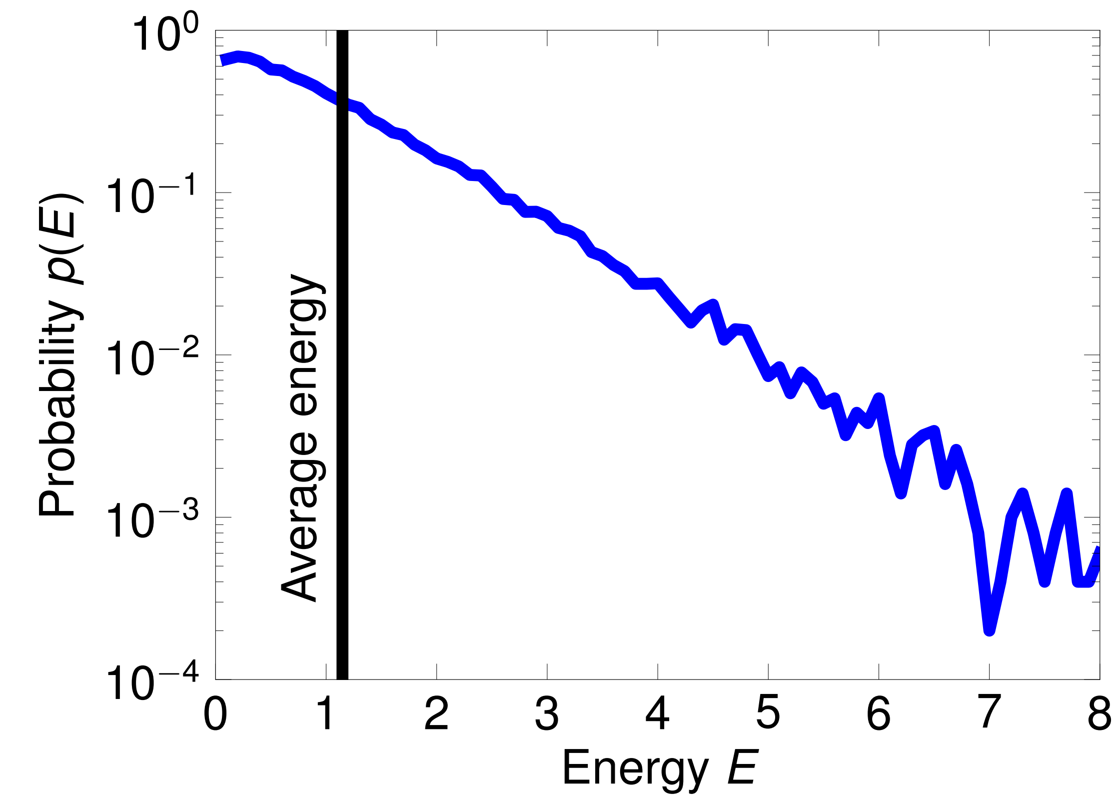
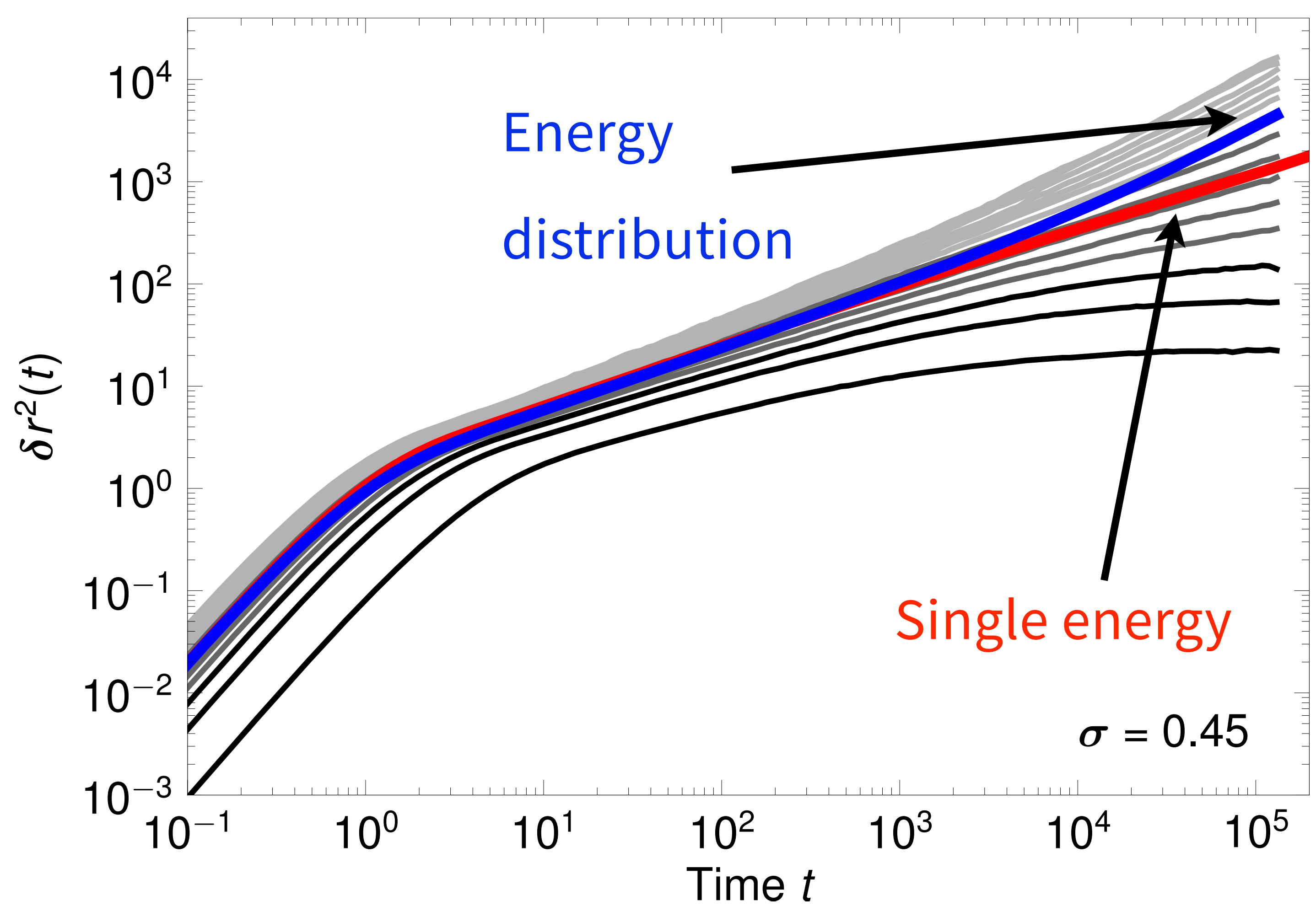




Diffusive at high energies

Anomalous at intermediate energies

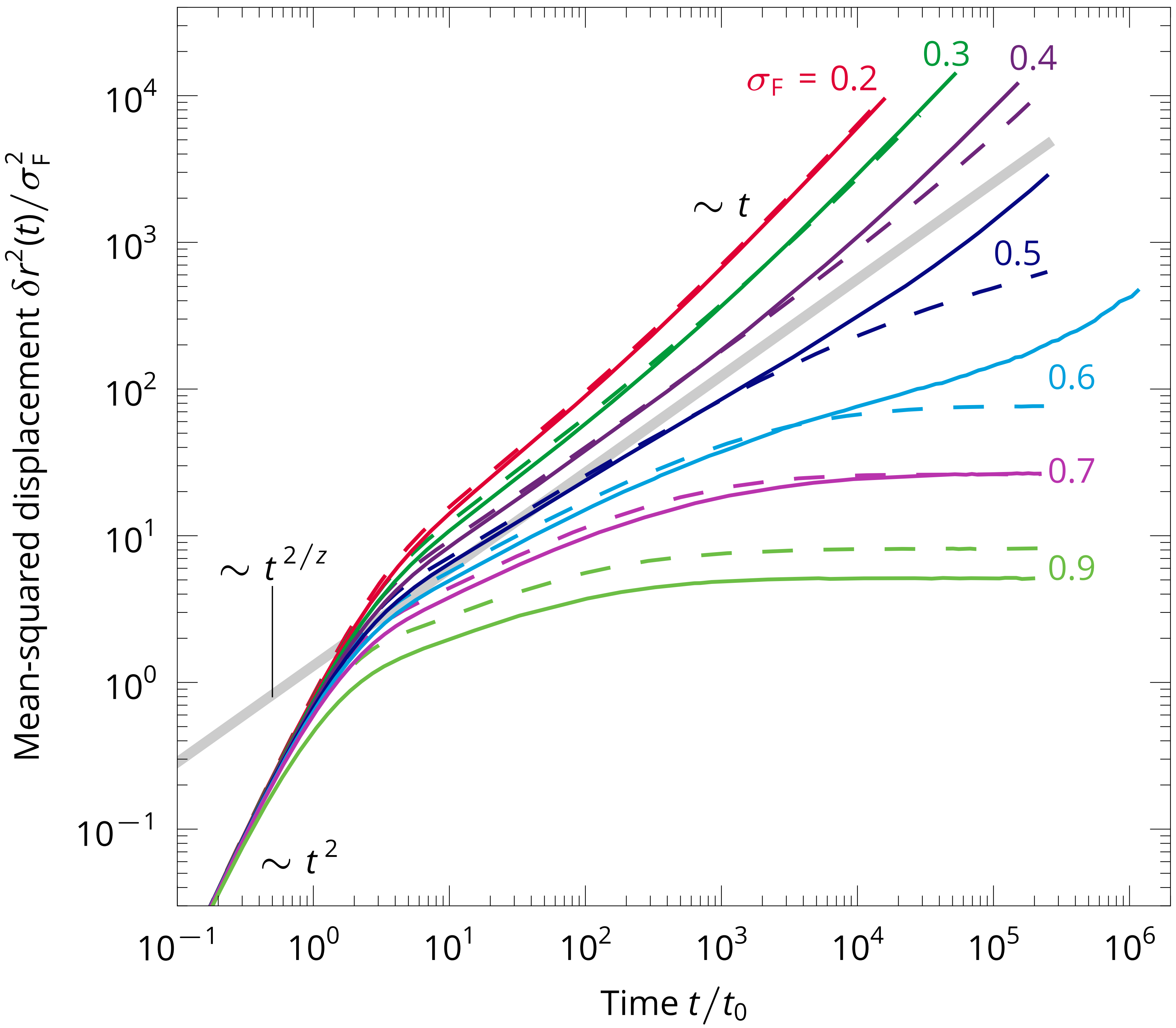
Localized at low energies

Confined ideal gas

Averaging of the dynamics

$\Longrightarrow$ Localization transition rounded

$\Longrightarrow$ No anomalous exponent *2/z*, effective exponents instead



T. Skinner, S.K. Schnyder *et al,* PRL 111 (2013)

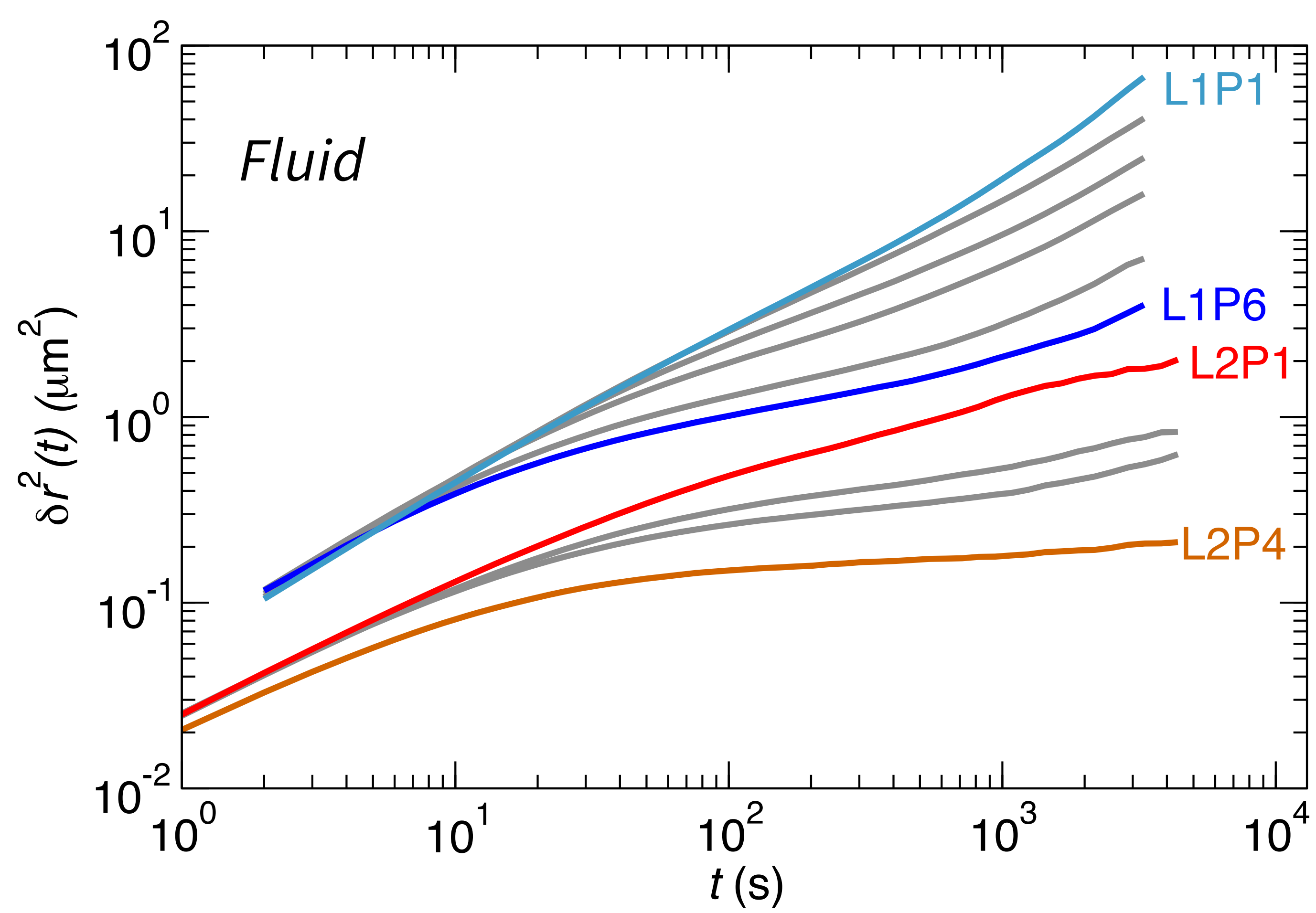
Confined ideal gas

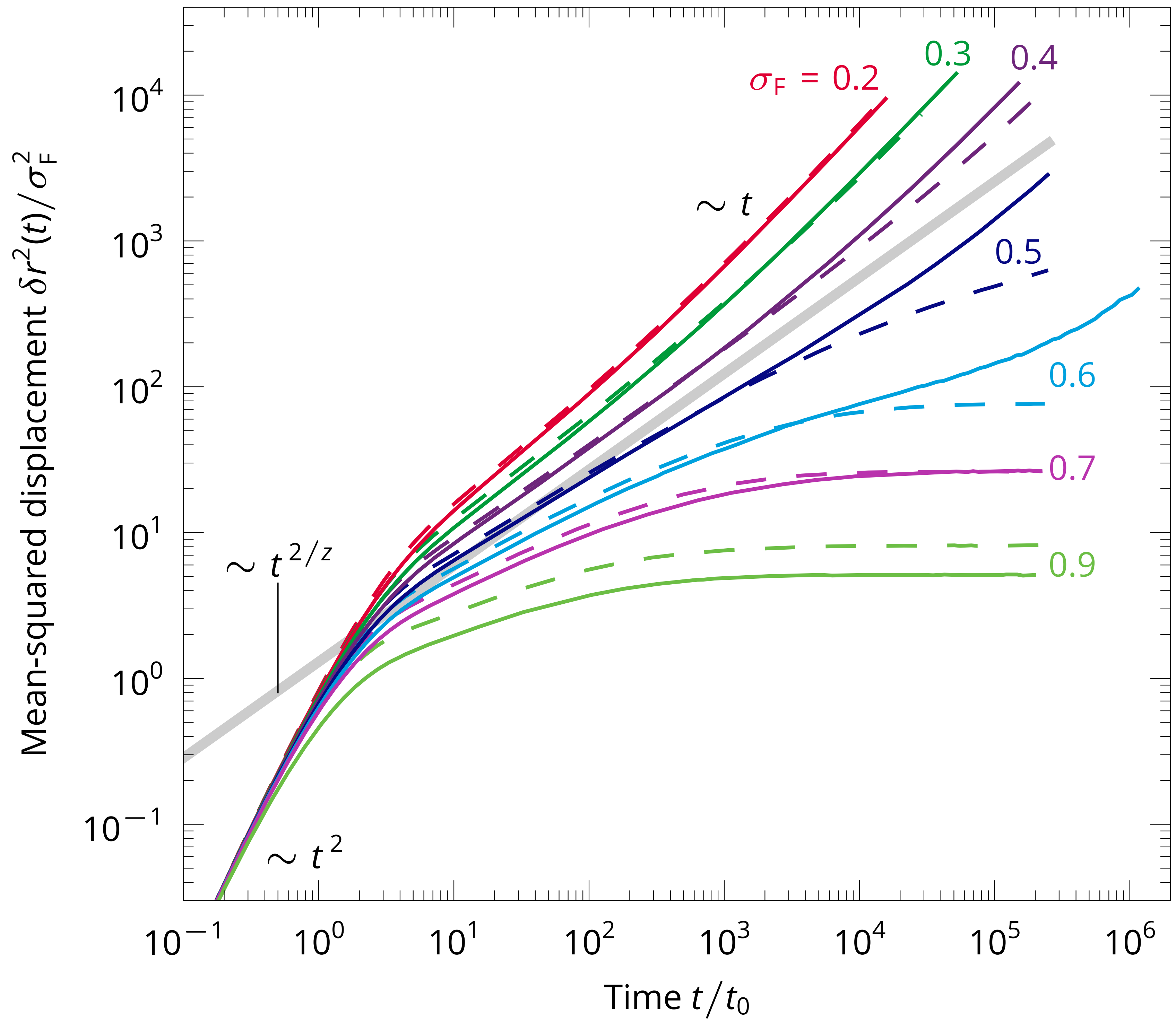
Averaging of the dynamics

⇒ Localization transition rounded

⇒ No anomalous exponent *2/z*, effective exponents instead

This holds for the experiments, too!





T. Skinner, S.K. Schnyder *et al*, PRL 111 (2013)

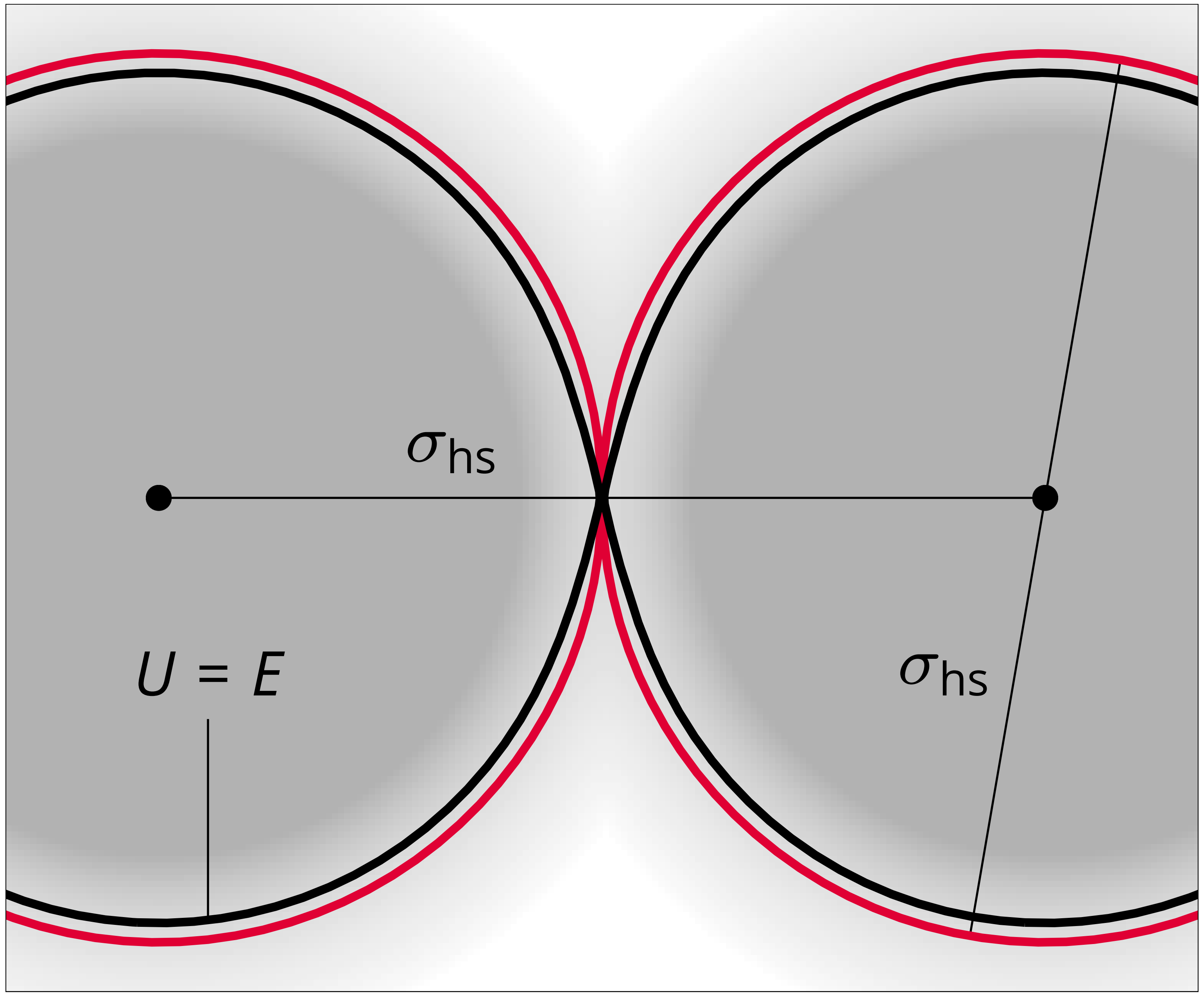
Hard-disk mapping

Mapping of energy E and interaction diameter σ_F onto a single effective interaction diameter σ_{hs}:

Mapping must conserve **topology:**

- *open* channels stay *open*
- *closed* channels stay *closed*

$\Longrightarrow$ need to exactly map situation where channel is **about to close**



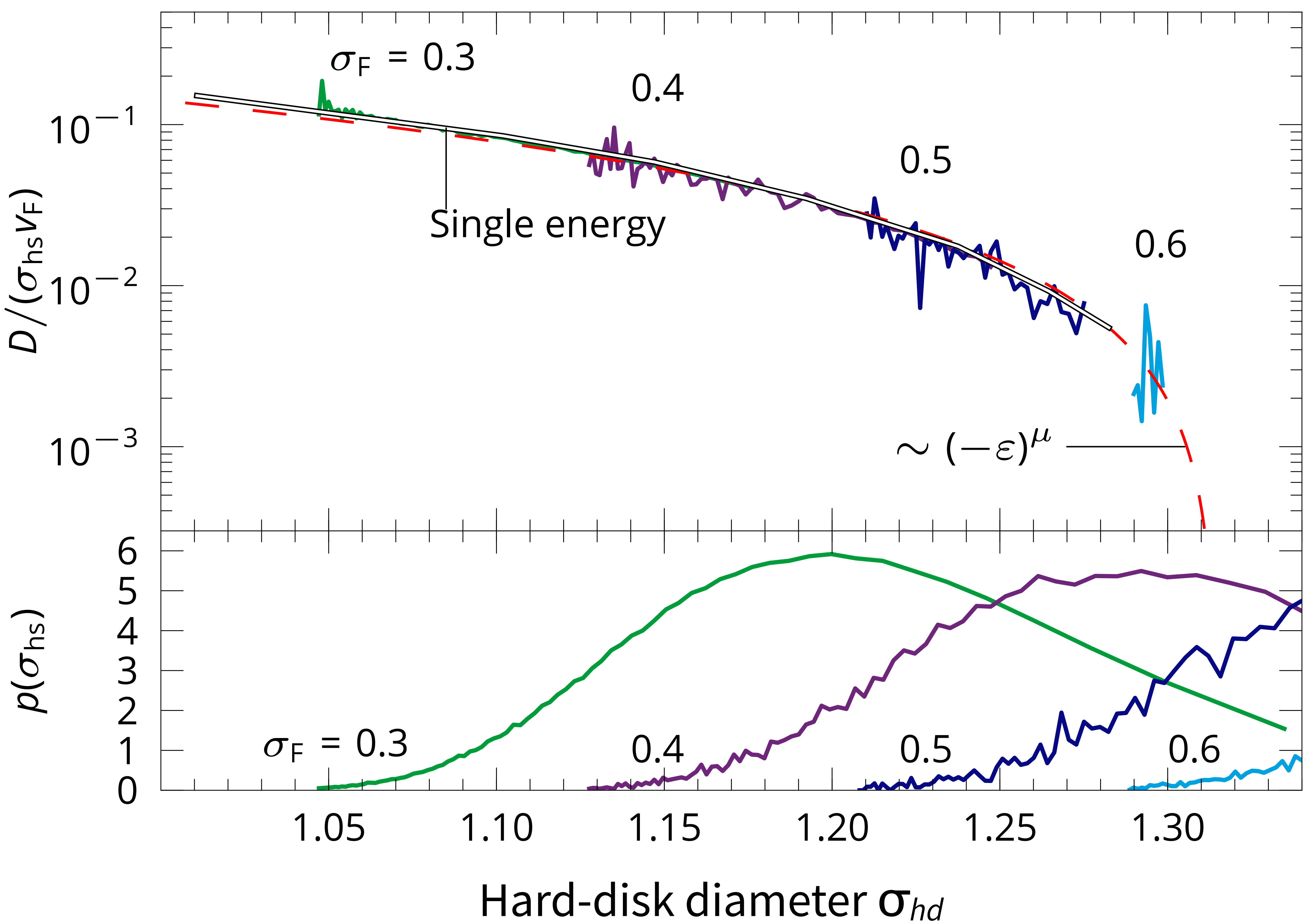
$$E \stackrel{!}{=} 8\varepsilon_{\mathrm{MF}}\left(\left(\frac{2\sigma_{\mathrm{MF}}}{\sigma_{\mathrm{hs}}}\right)^{12} - \left(\frac{2\sigma_{\mathrm{MF}}}{\sigma_{\mathrm{hs}}}\right)^{6}\right) + 2\varepsilon_{\mathrm{MF}}$$

$$\Rightarrow \sigma_{\mathrm{hs}} = 2\left(\frac{1}{2} + \sqrt{\frac{E}{8\varepsilon_{\mathrm{MF}}}}\right)^{-1/6} \sigma_{\mathrm{MF}}.$$

Hard-disk mapping

Energy E of a particle → Hard-disk diameter $\sigma_{hd}(\sigma_F, E)$

Energy distribution $p(E)$ → Hard-disk diameter distribution $p(\sigma_{hd})$

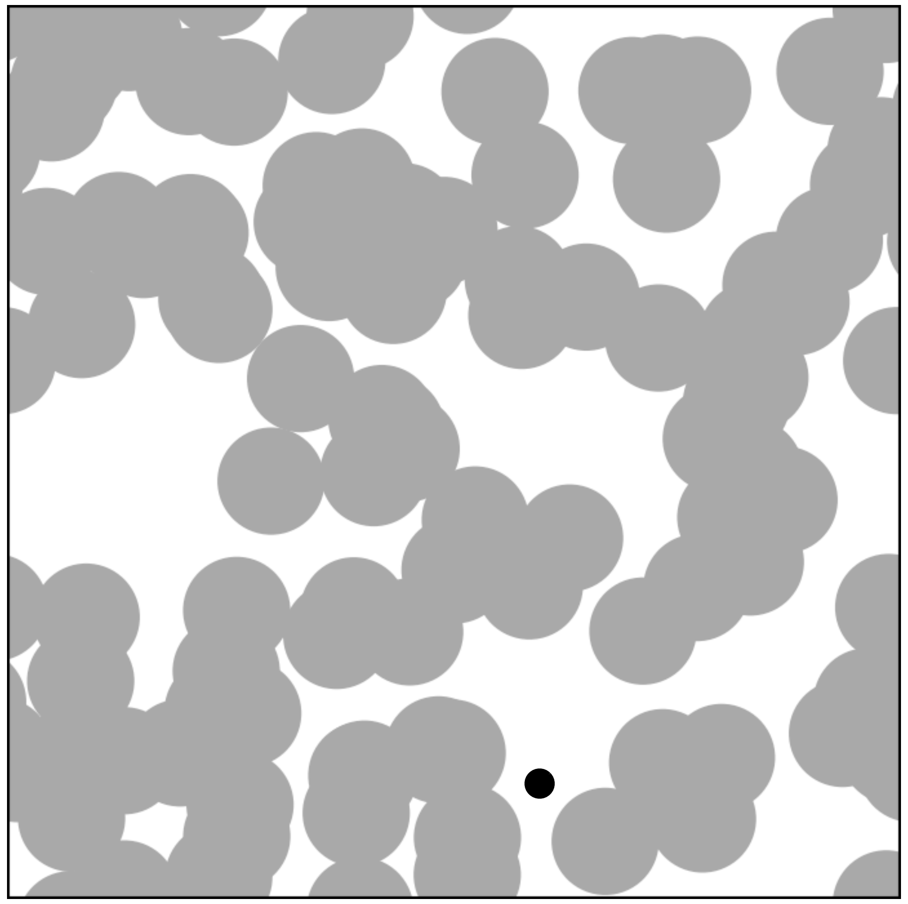


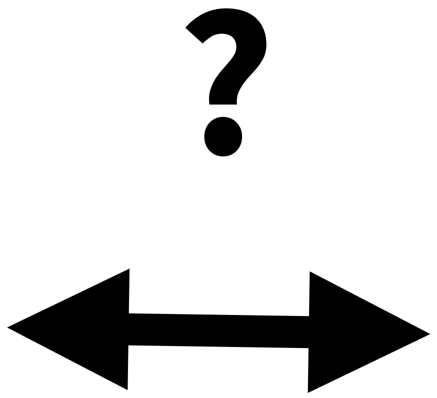
Energy-resolved dynamics matches the Lorentz model

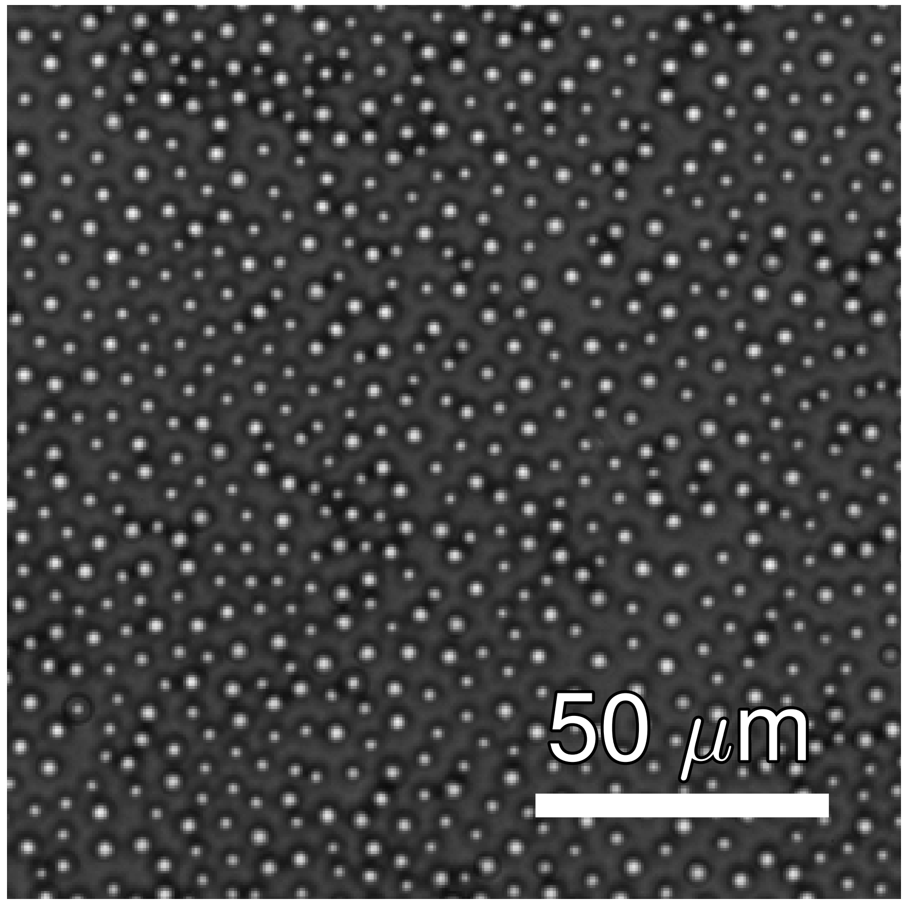
⟹ Confined ideal gas = energy average over Lorentz model

S.K. Schnyder *et al*, Soft Matter 11 (2015)

Investigate connection between Lorentz model and heterogeneous media







- Hard interactions with obstacles
- Non-interacting mobile component

- Soft interactions ✓
- Interacting mobile component

Introduce interactions between mobile particles

Interacting mobile particles

Now 2 control parameters:

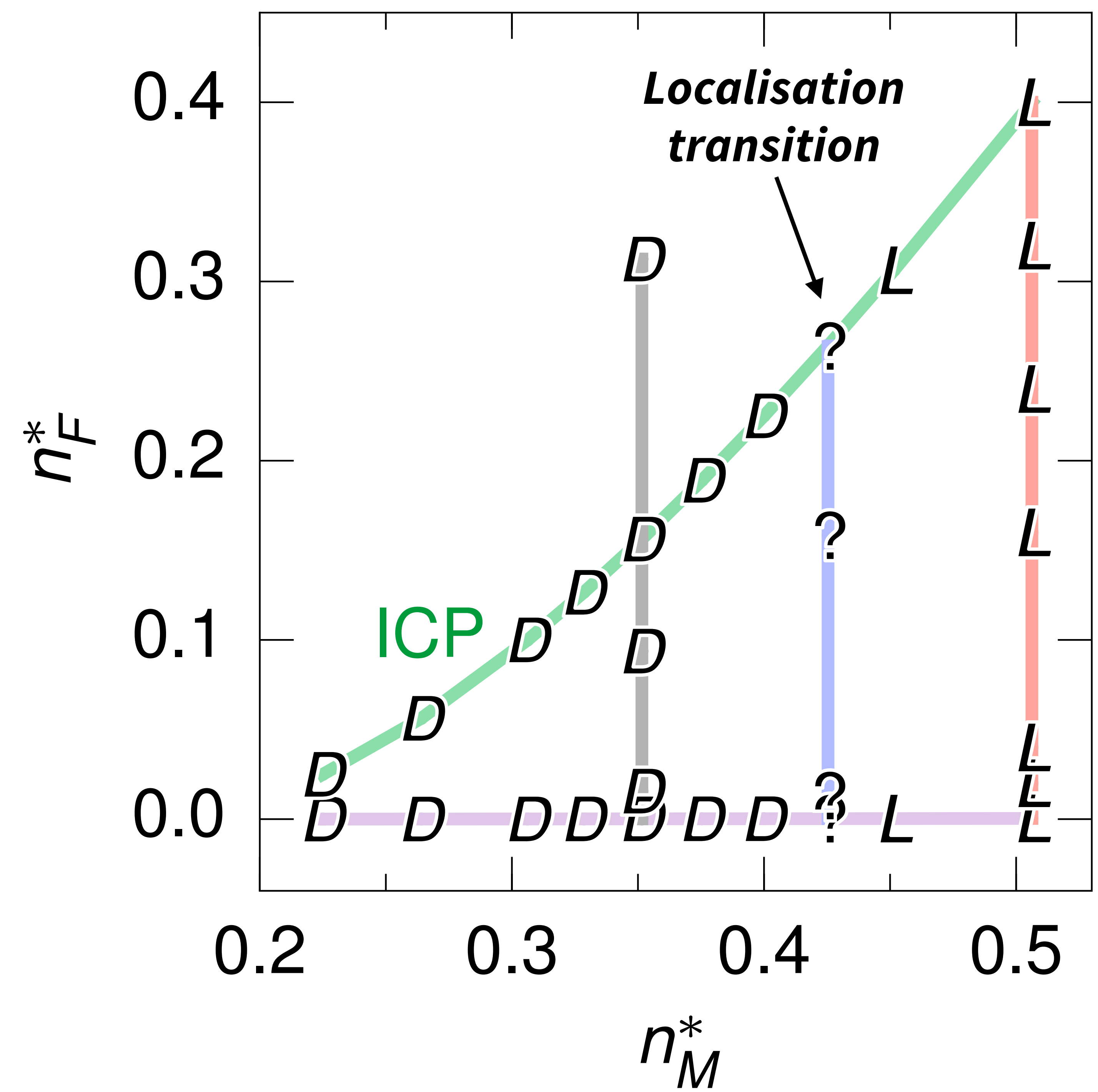
- Particle diameter σ_F
- Number density $n_F = N/L^2$

⇒ **Reduced number densities:**

- $n_M^* = n_M\,(\sigma_M + \sigma_F)^2/4$
- $n_F^* = n_F\,\sigma_F^2$

Study influence of interactions systematically by increasing n_F from 0.

Study localization transition at large n_F by crossing it.



SK Schnyder & J Horbach, PRL 120(7), 78001 (2018)

Speeding-up of the dynamics

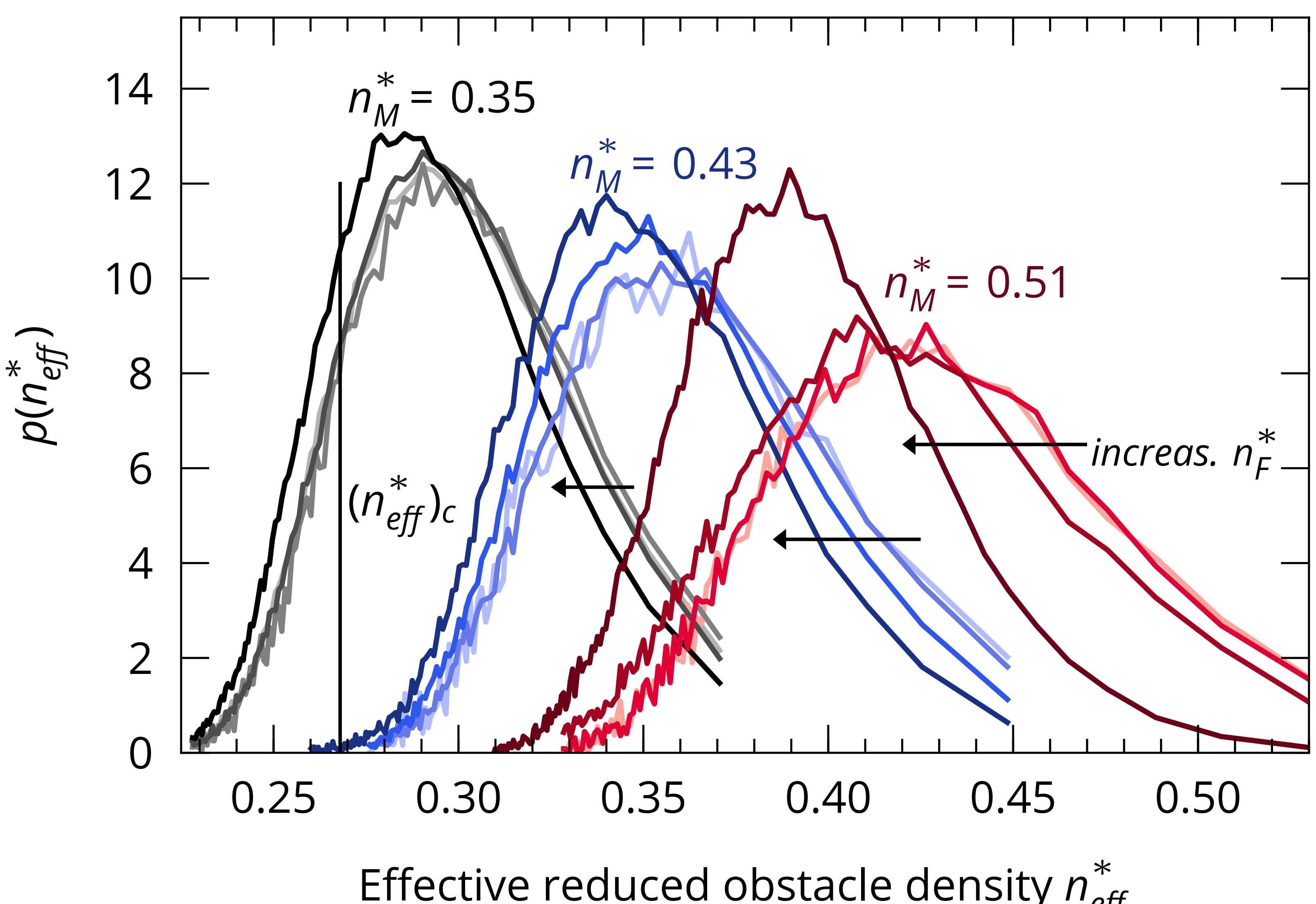
Dynamics in delocalized system

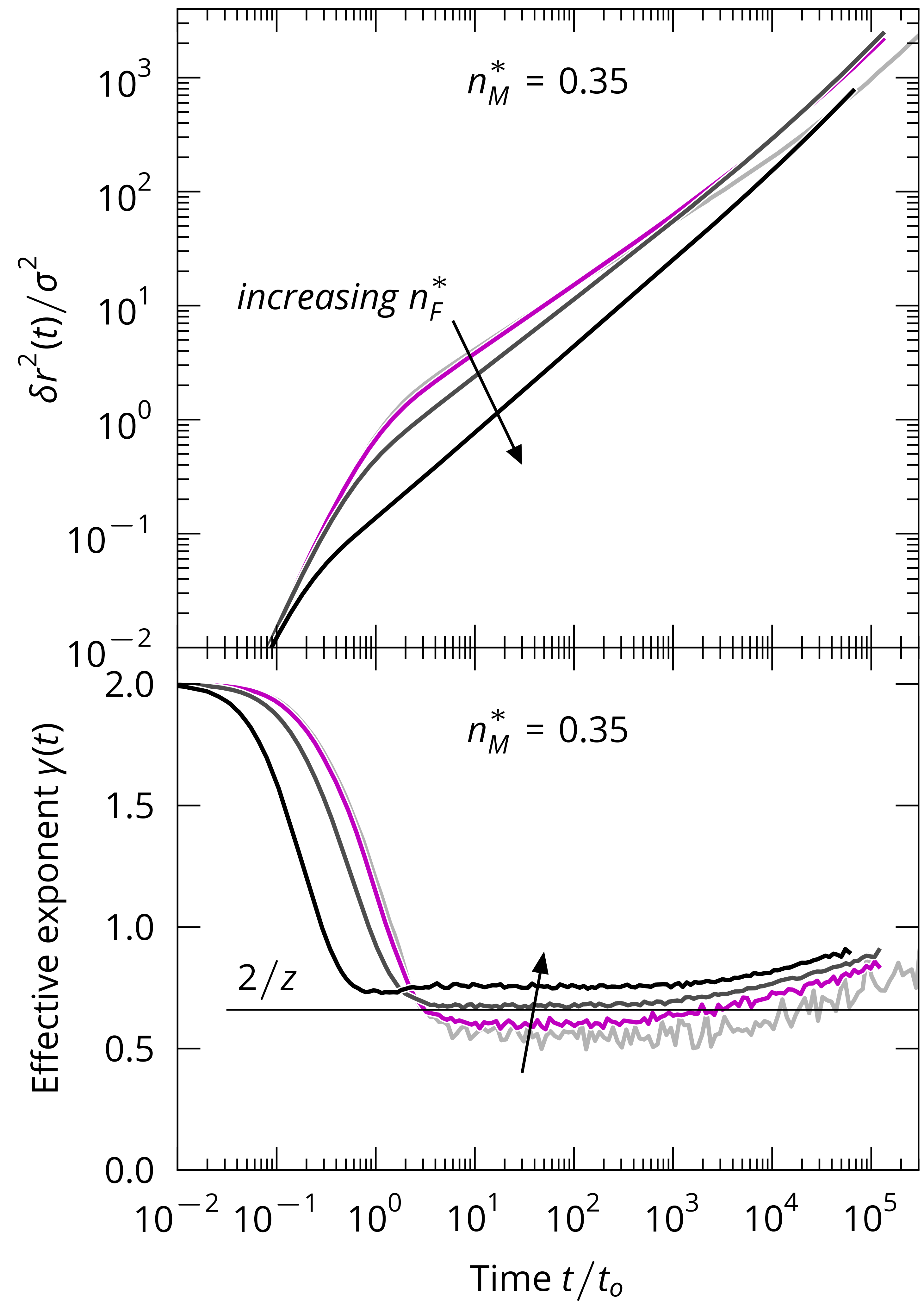
Increase number density of mobile particles

$\Rightarrow$ Frequent exchange of energy

$\Rightarrow$ Faster dynamics at long times

$\Rightarrow$ **Effective exponent becomes tuneable**



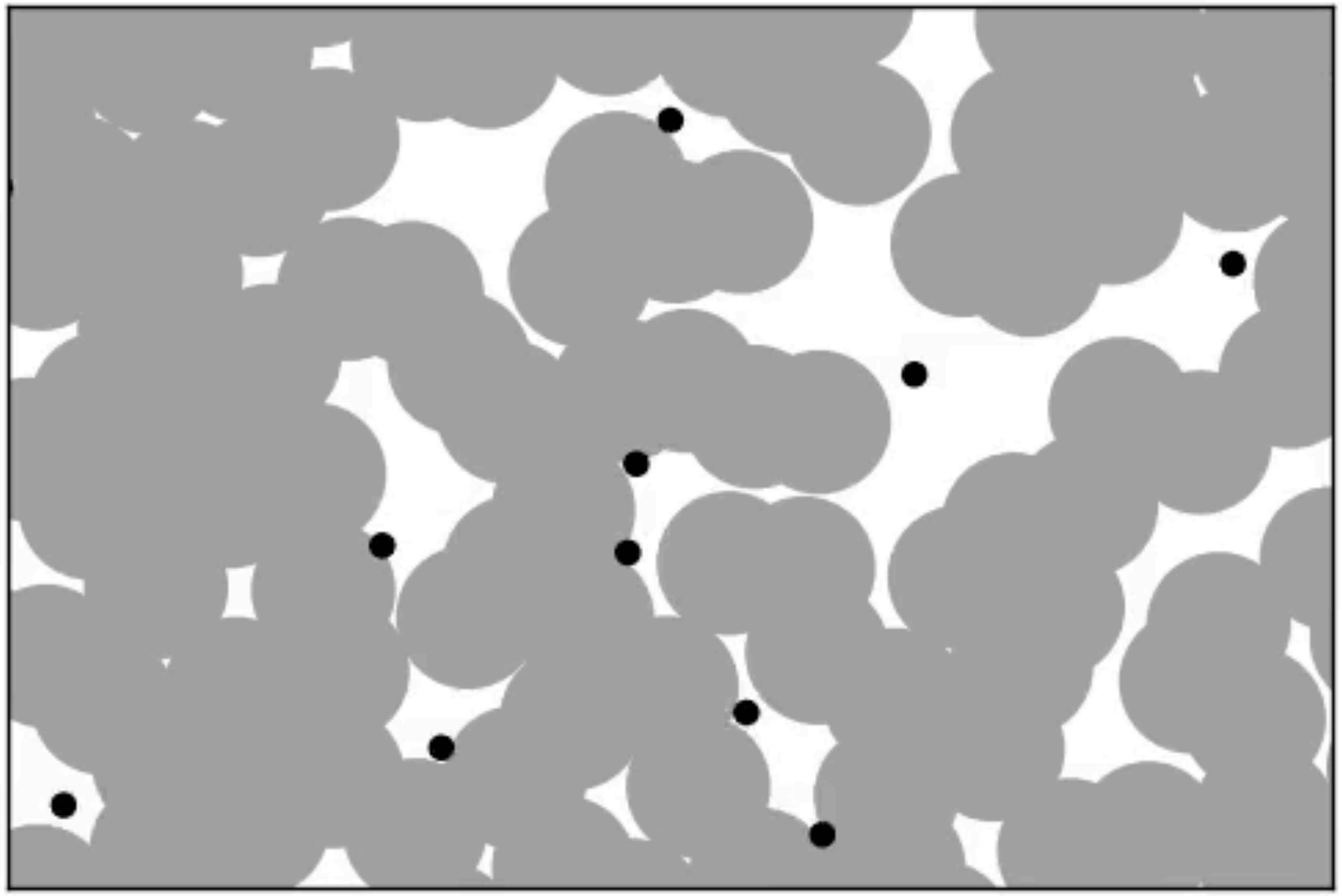


Cooperative dynamics

Finite potential barrier heights

⇒ Particles can kick each other out of pores in the matrix

⇒ **Dynamics become fundamentally different from the hard-disk case**



Cooperative dynamics

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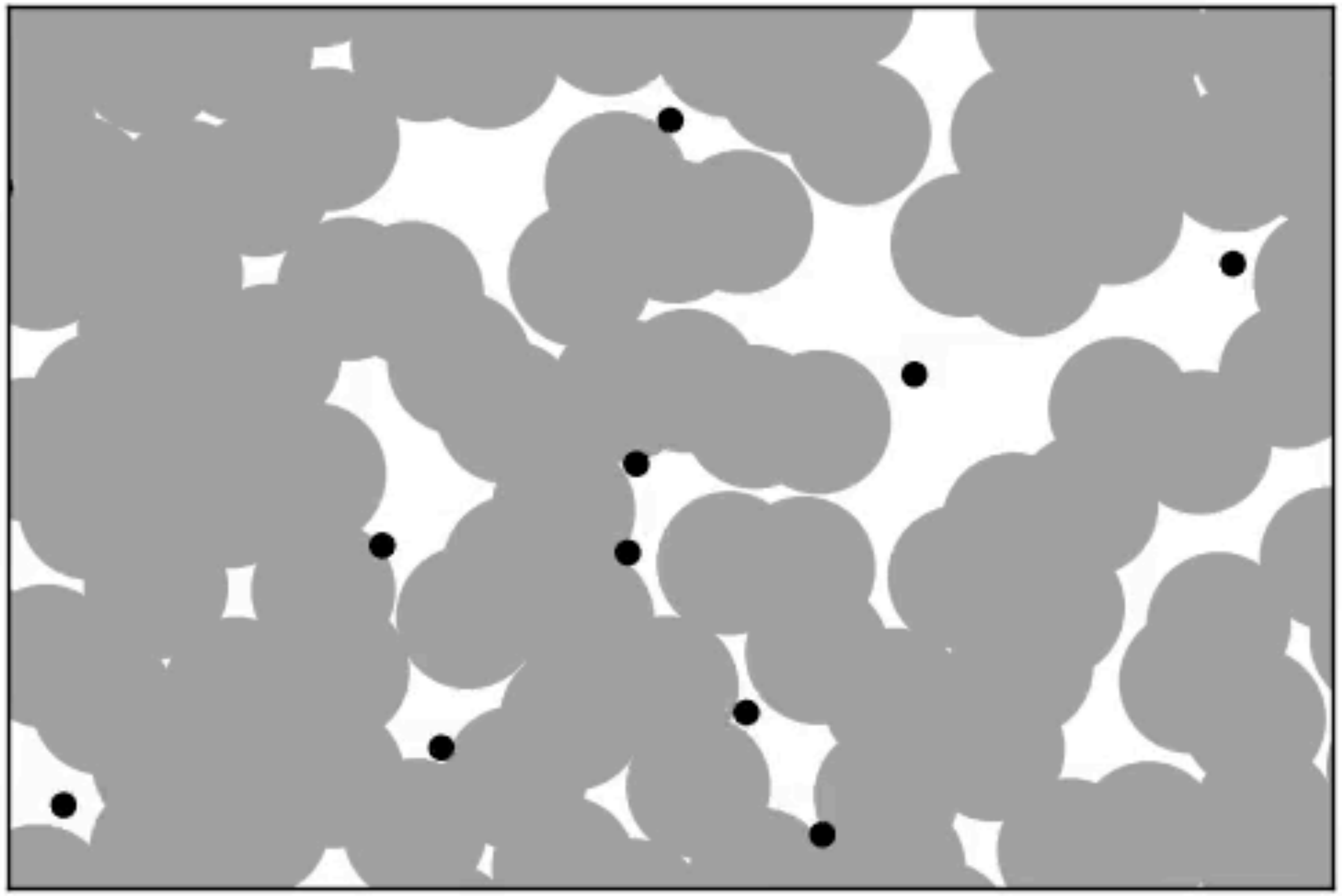


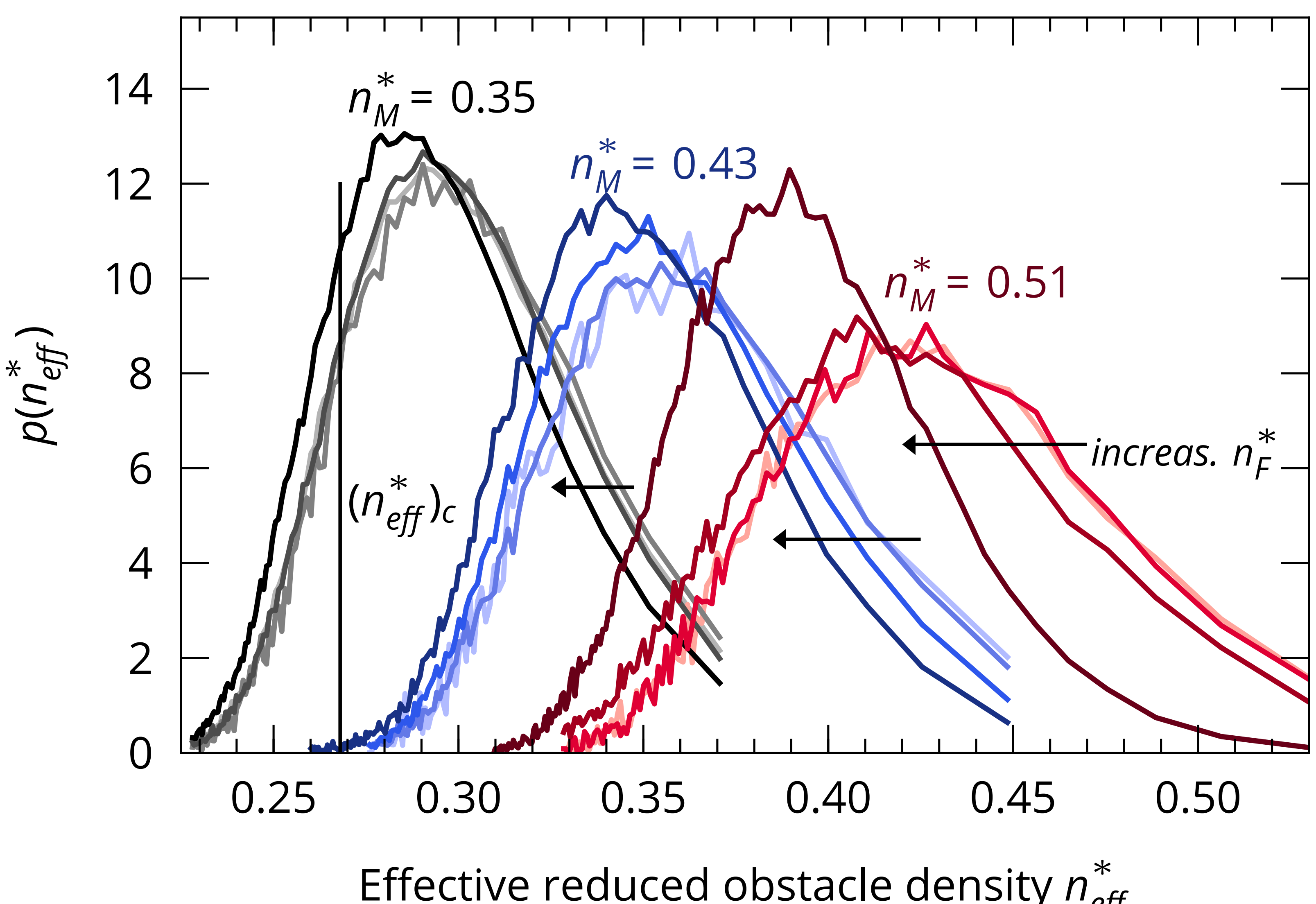
Reentrance transition

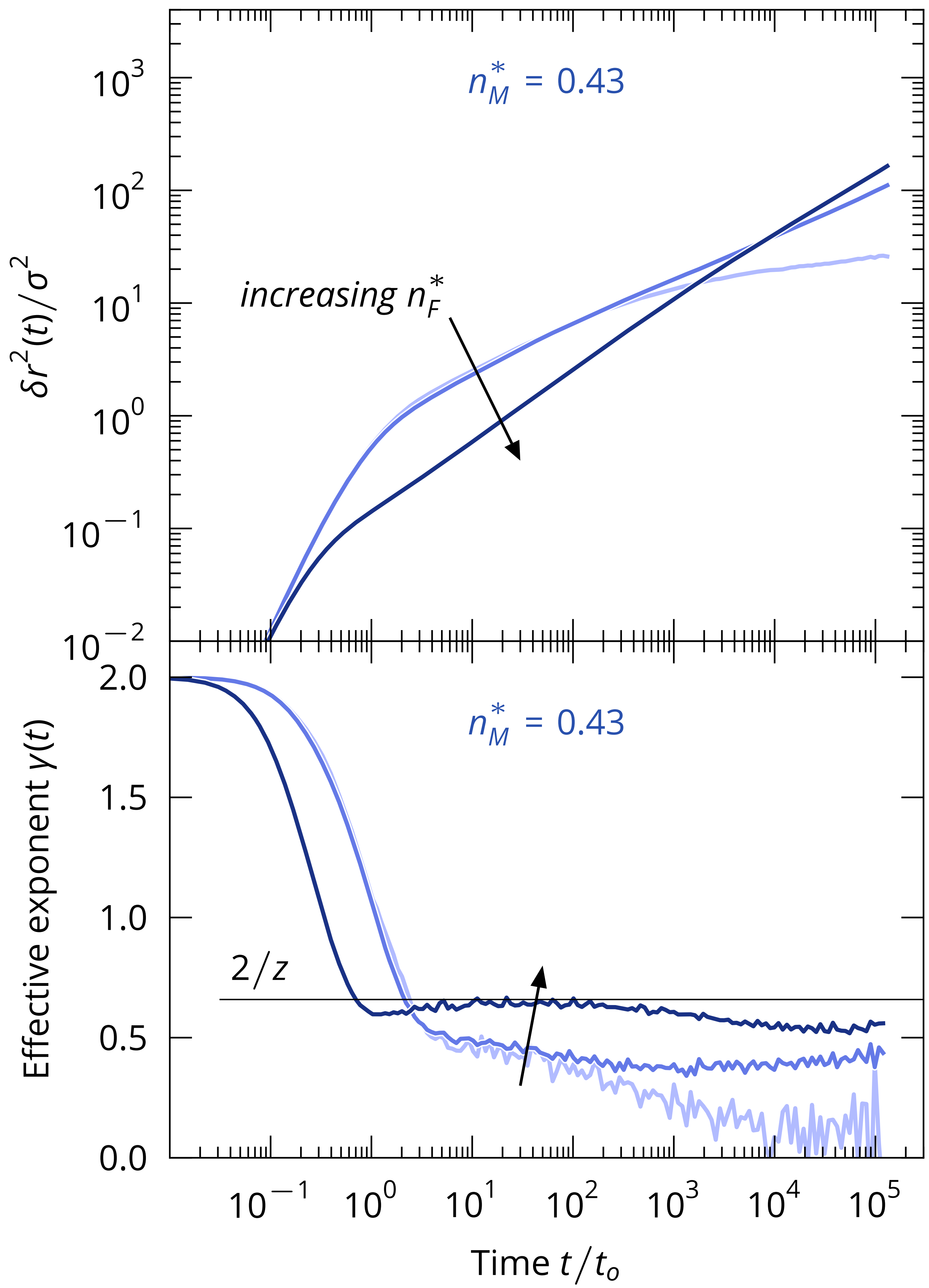
Dynamics close to localization transition

Delocalization of a previously localized system

$\Rightarrow$ **Reentrance transition**

Impossible for hard-disk systems with fixed obstacles

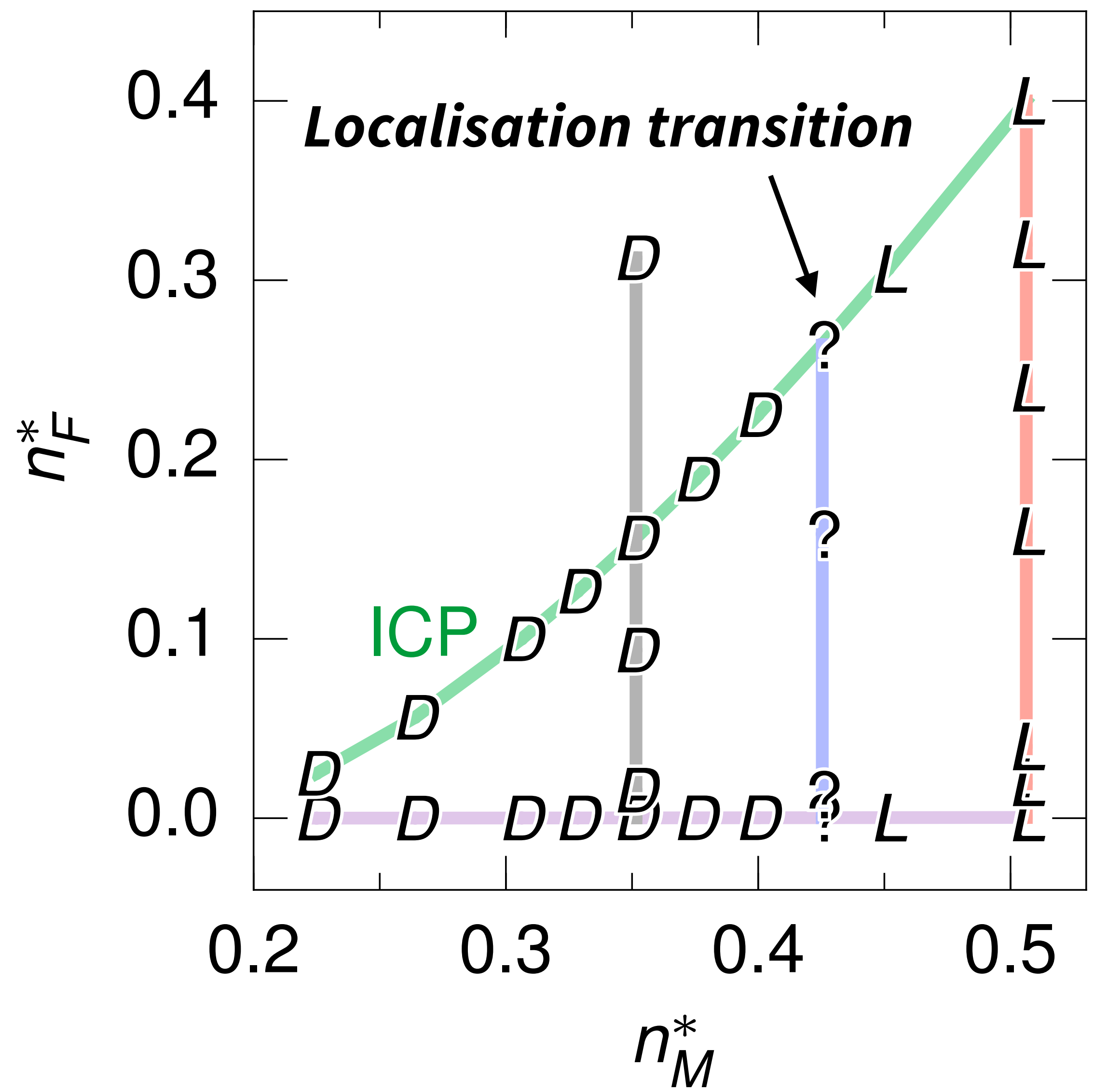


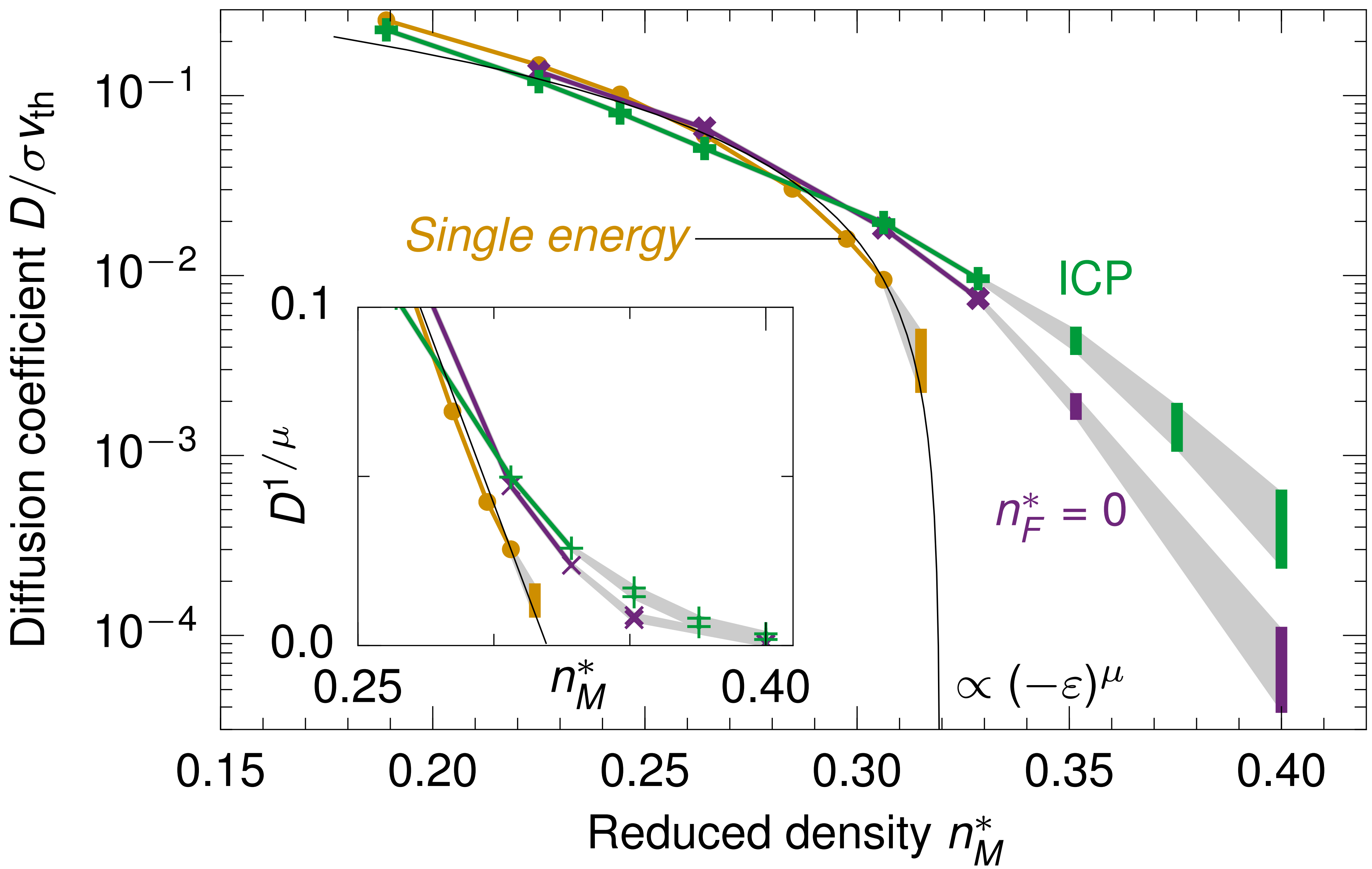


Crossing the localization transition

Dense system with $n_F = 0.625$

Effective **rounded** localization transition near $n_F^* \approx 0.43$





Conclusion I

Soft potential systems are fundamentally different from hard potential systems:

- **The localization transition is rounded** by the distribution of energies and the soft potential
- **Cooperation frees particles from pores**
- **Only effective exponents,** not related to the Lorentz model exponents

$\Rightarrow$ **Breakdown of universality**

Part II

Active non-linear micro-rheology in a glass-forming mixture

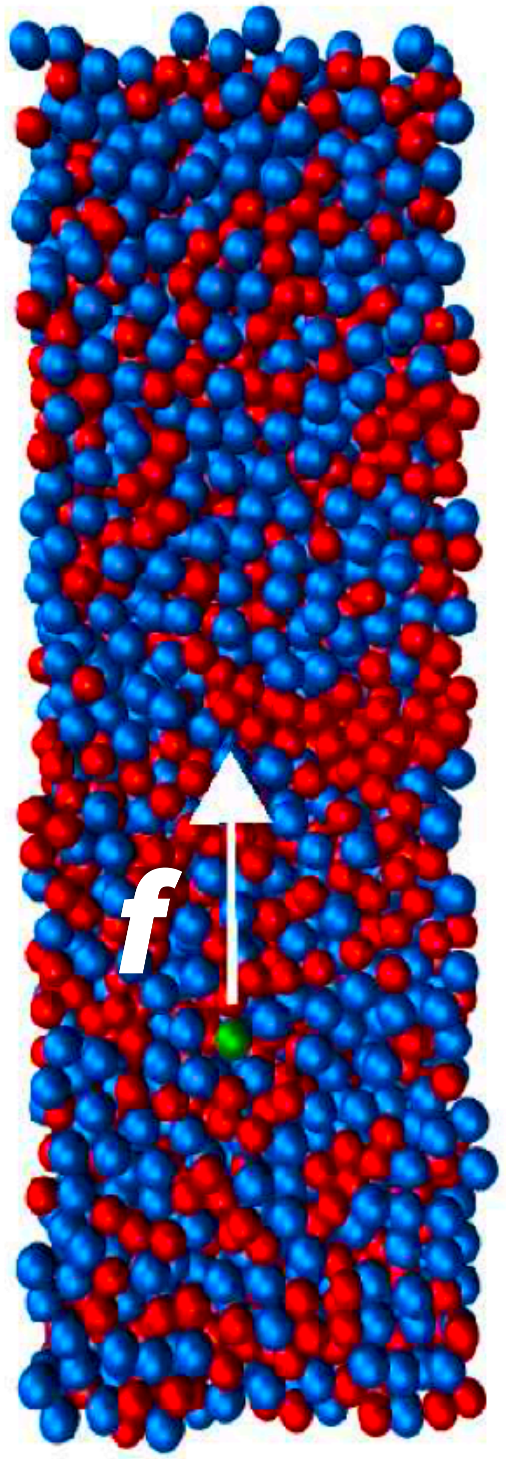
Intro

Active micro-rheology (AMR) can be seen as a tool to probe the mechanical response of bio- and soft matter systems on a local scale

- Pull a tracer particle through a colloidal system with a constant external force *f*.
- In the steady state, the tracer has a constant velocity v and one can define a friction coefficient ξ via ξ = f/v.

Linear response

- At small enough forces, ξ is independent of f
- In glass-forming systems, the linear response regime shrinks to a window of very small forces and vanishes at the glass transition
- We show in the following that the non-linear response in AMR is linked with anomalous diffusion dynamics.



Horbach, J., Siboni, N. H., & Schnyder, S. K., EPJ Special Topics 226(14), 3113–3128 (2017)
Winter, D., & Horbach, J., J. Chem. Phys 138(12), 12A512 (2013)
Winter, D., Horbach, J., Virnau, P., & Binder, K. PRL 108(2), 1–5 (2012)

Simulation setup

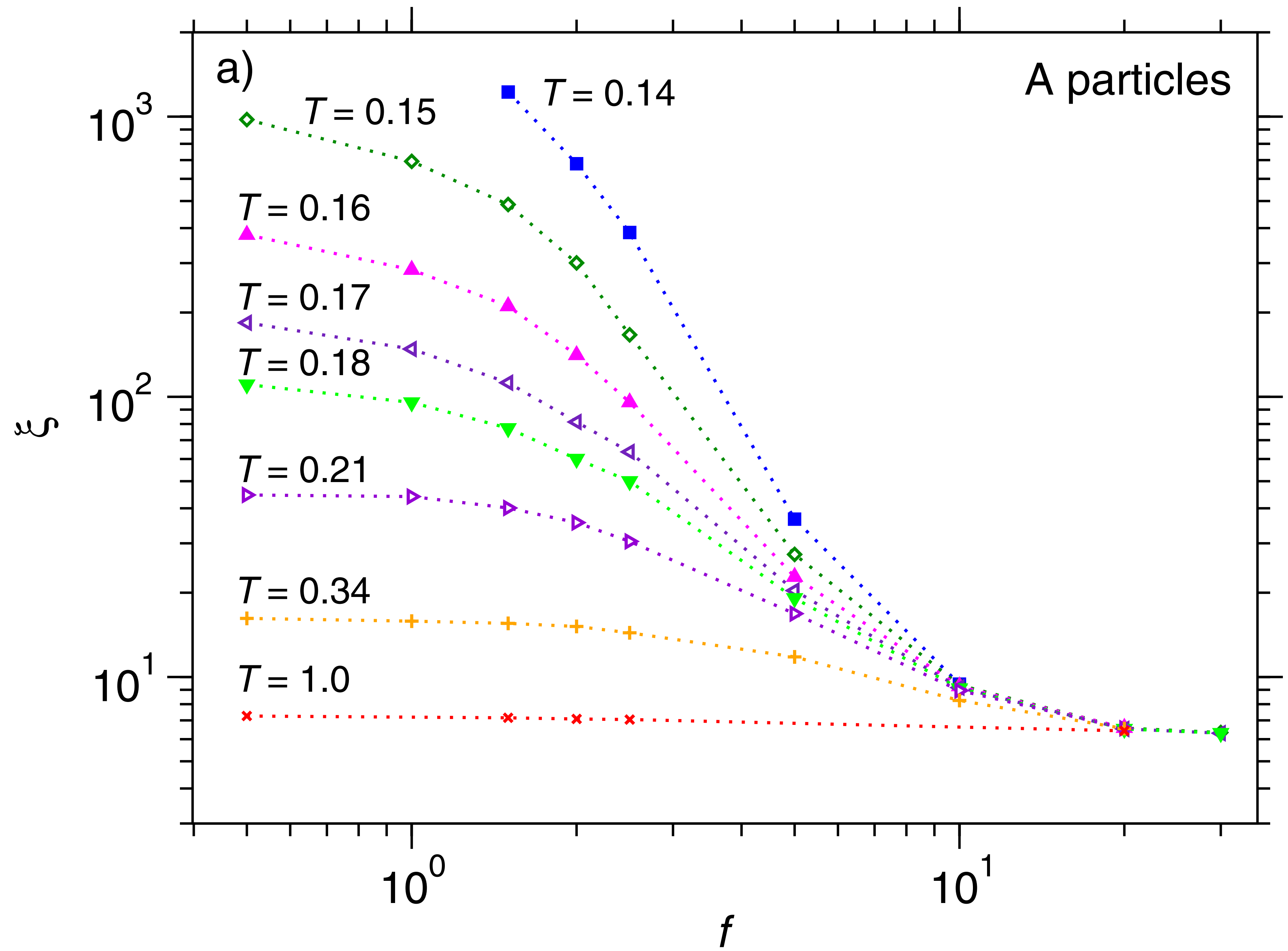
- Molecular dynamics simulations of a 3D glass-forming binary AB Yukawa mixture
- Equimolar mixture at number density $n = 0.675/d^3$ (with d the diameter of A particles)
- Reduced critical mode coupling temperature is at $T = 0.14$
- Initial configurations for the AMR runs:
  Fully equilibrated configurations for $1.0 \leq T \leq 0.14$, and glassy state at $T = 0.1$

AMR runs:

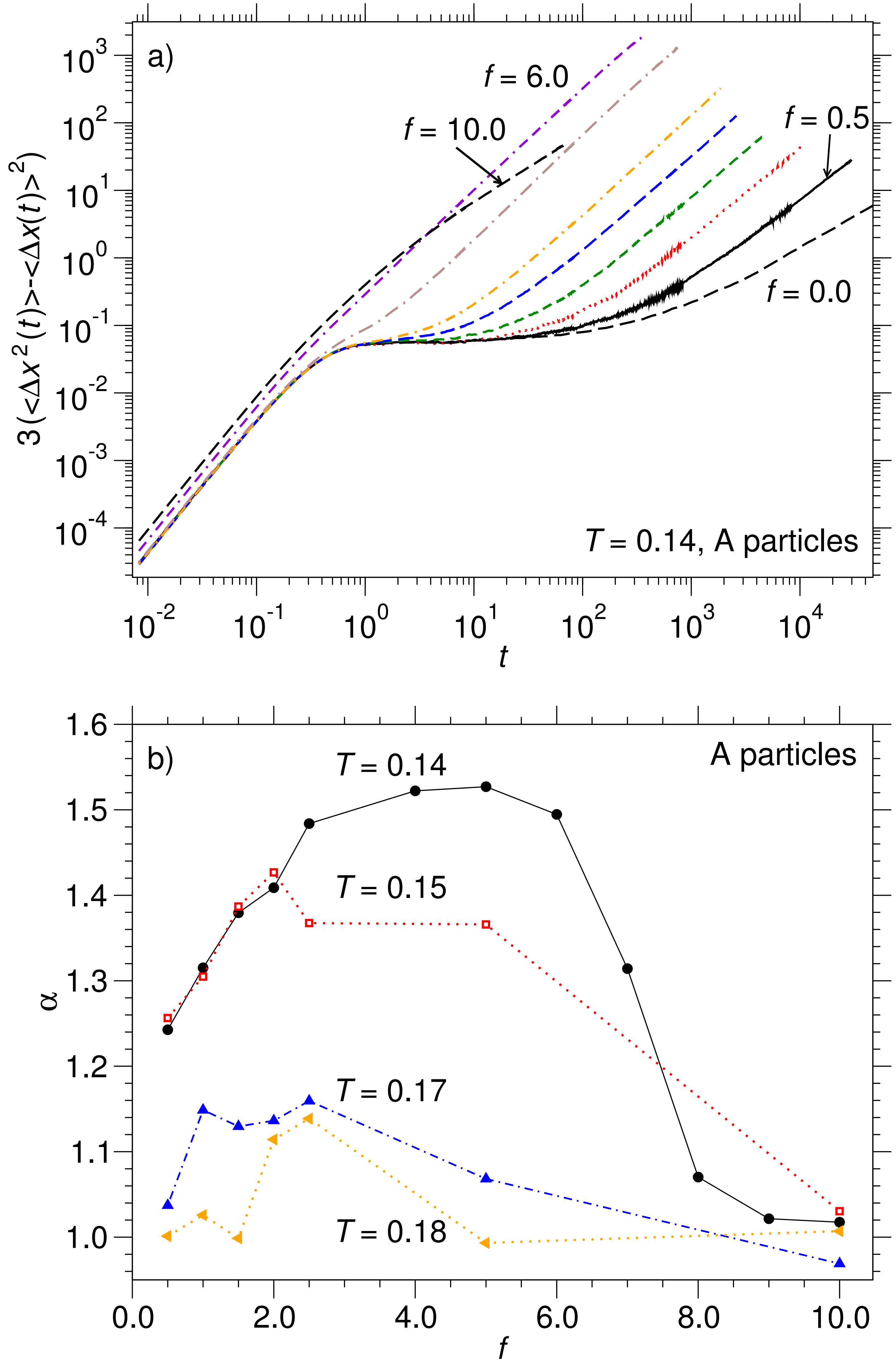
- Single particles are pulled with constant external force $F = (f, 0, 0)$ in x-direction, assuming periodic boundary conditions in all 3 spatial directions
- Dissipative particle dynamics (DPD) thermostat to keep T constant
- About 1000 independent trajectories of pulled particles at each force and temperature

Non-linear response in AMR

- Linear response regime exists at large temperatures
- Approaching the glass transition in glass-forming systems, the linear response regime first shrinks to a window of very small forces and then disappears at the glass transition.
- Non-linear response: **strong decrease of the friction coefficient as function of the force f** (analogous to shear-thinning in macro-rheology)



Drift-corrected MSD and effective exponent



Infer **anomalous transport** from the drift-corrected MSD in x-direction (i.e. in force direction)

$$\langle \Delta x^2(t) \rangle - \langle \Delta x(t) \rangle^2 =$$
$$\langle [x(t) - x(0)]^2 \rangle - \langle [x(t) - x(0)] \rangle^2$$

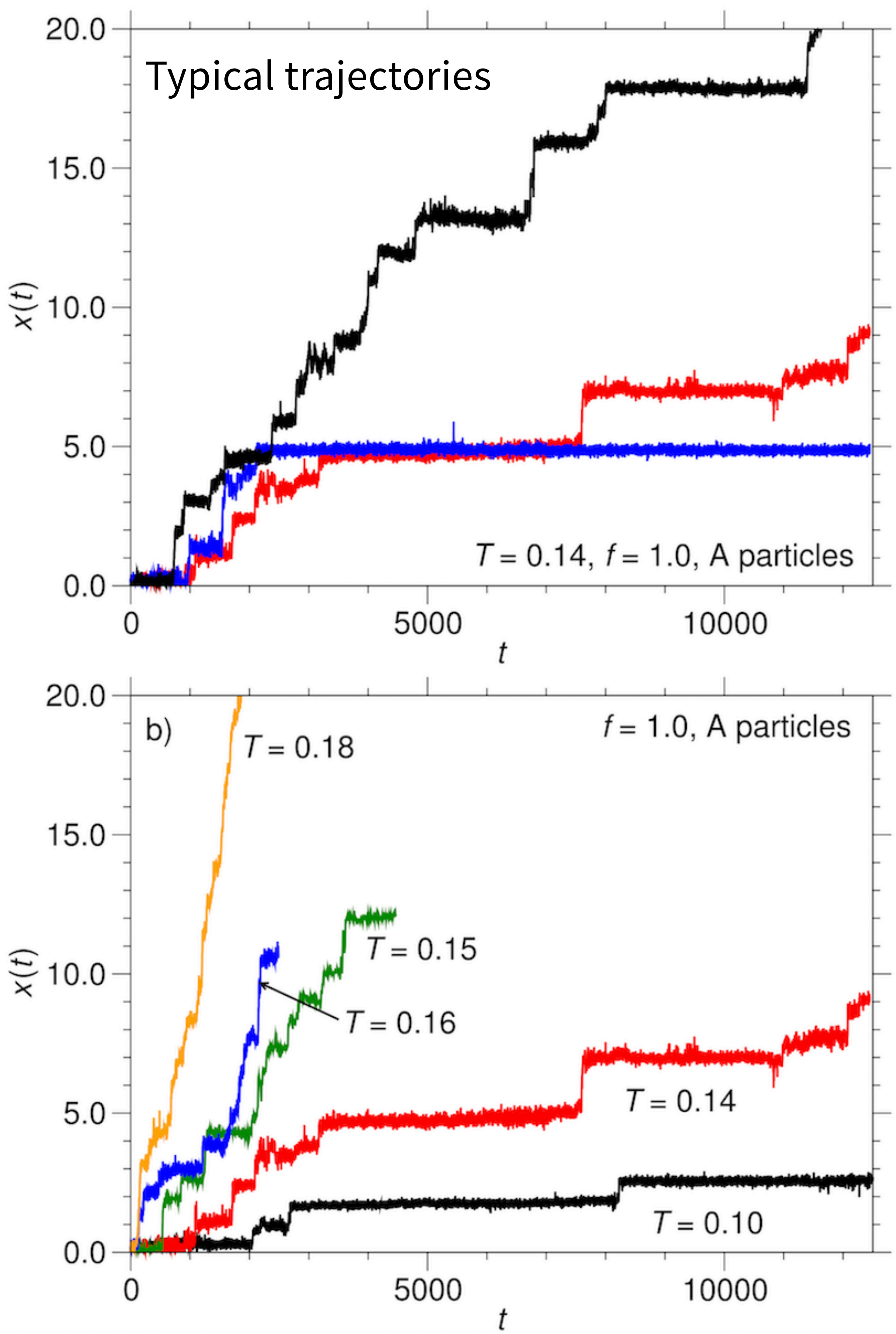
- At intermediate f, MSD is superlinear at long times
- At high f, α decreases to 1.0 for f > 6
- At higher temperatures, α is significantly lower

⇒ Superdiffusion occurs where host fluid is quasi-frozen on the time scale of the tracer particle.

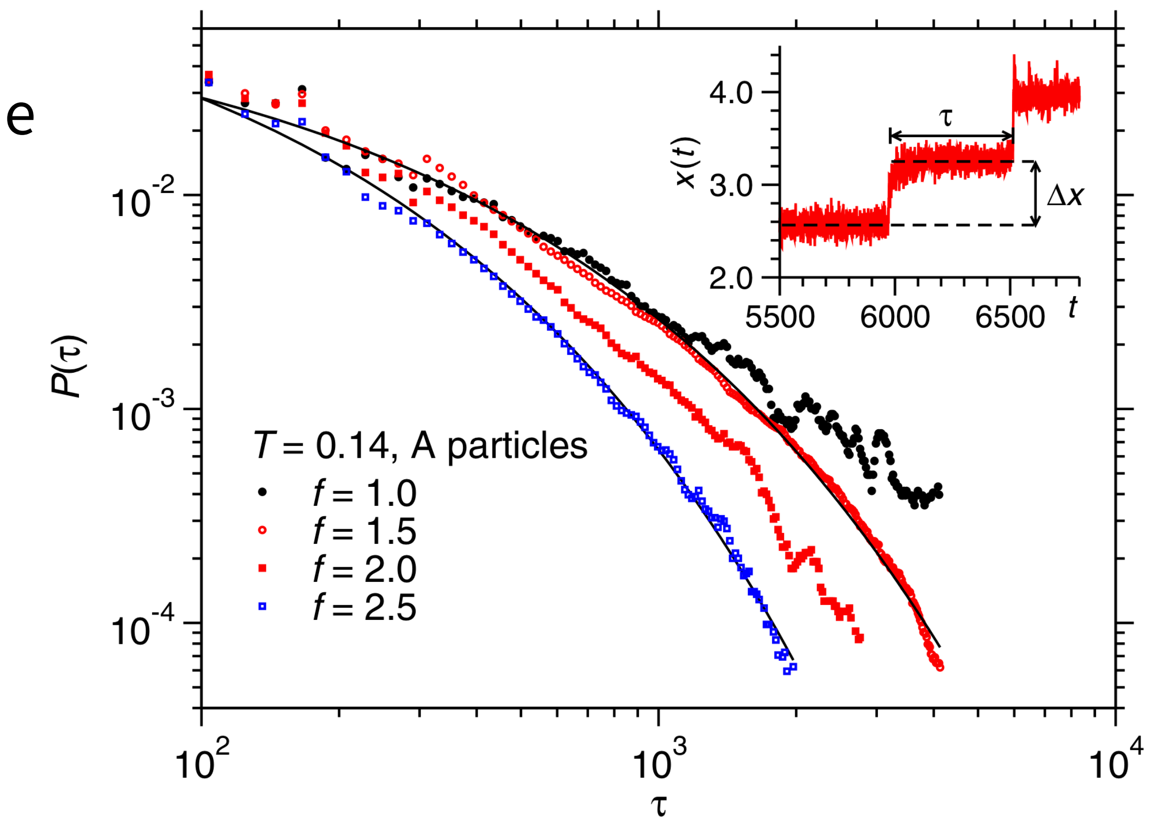
⇒ **Superdiffusion is directly related to the time scale separation between the motion of the pulled tracer particle and that of the surrounding host fluid.**

But on time scales of host particle diffusion, one would expect a crossover to normal diffusion also for the tracer particle.

Cage hopping



Residence time distribution



The time scale separation between the motion of the pulled tracer particle and the quasi-frozen host liquid is associated with cage hopping of the tracer

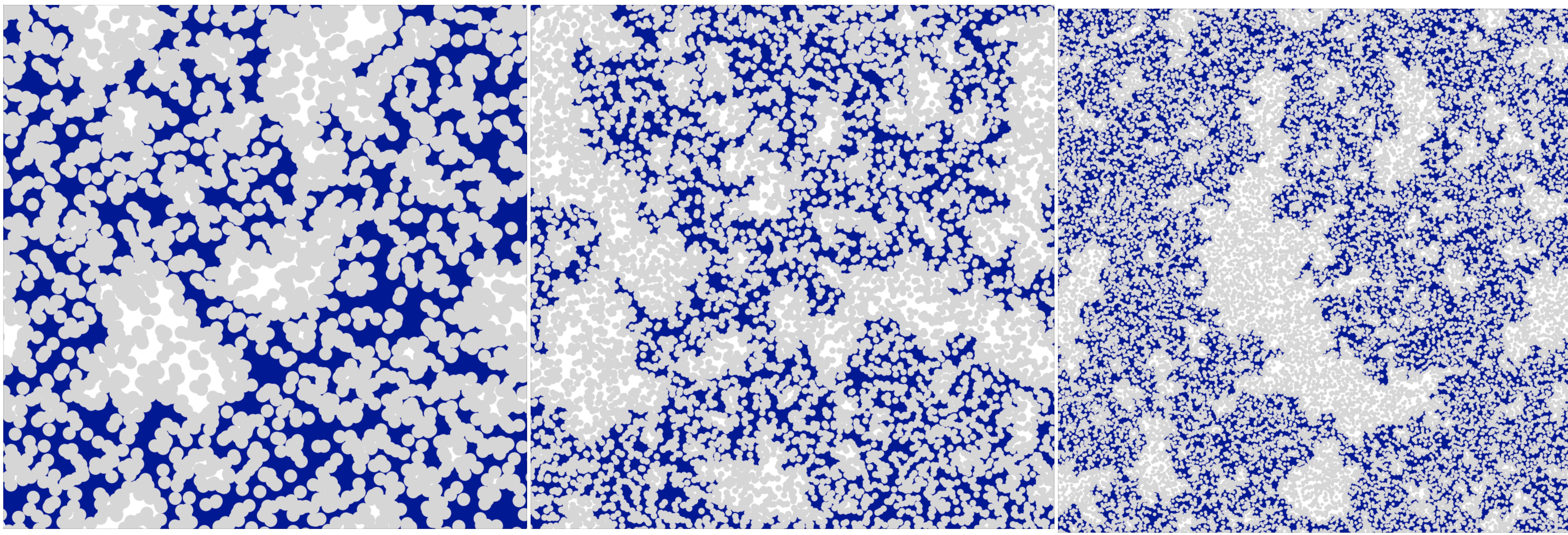
- At high temperatures, trajectories are relatively smooth
- At low temperatures, tracers reside in one cage and then hop to the next cage
- Residence time τ in the cages is heterogeneous at low T
- Waiting time distributions show broad tails
- Reminiscent of random force field models by Bouchaud et al

J.P. Bouchaud et al, Ann. Phys. 201, 285 (1990)
and Phys. Rep. 195, 127 (1990)

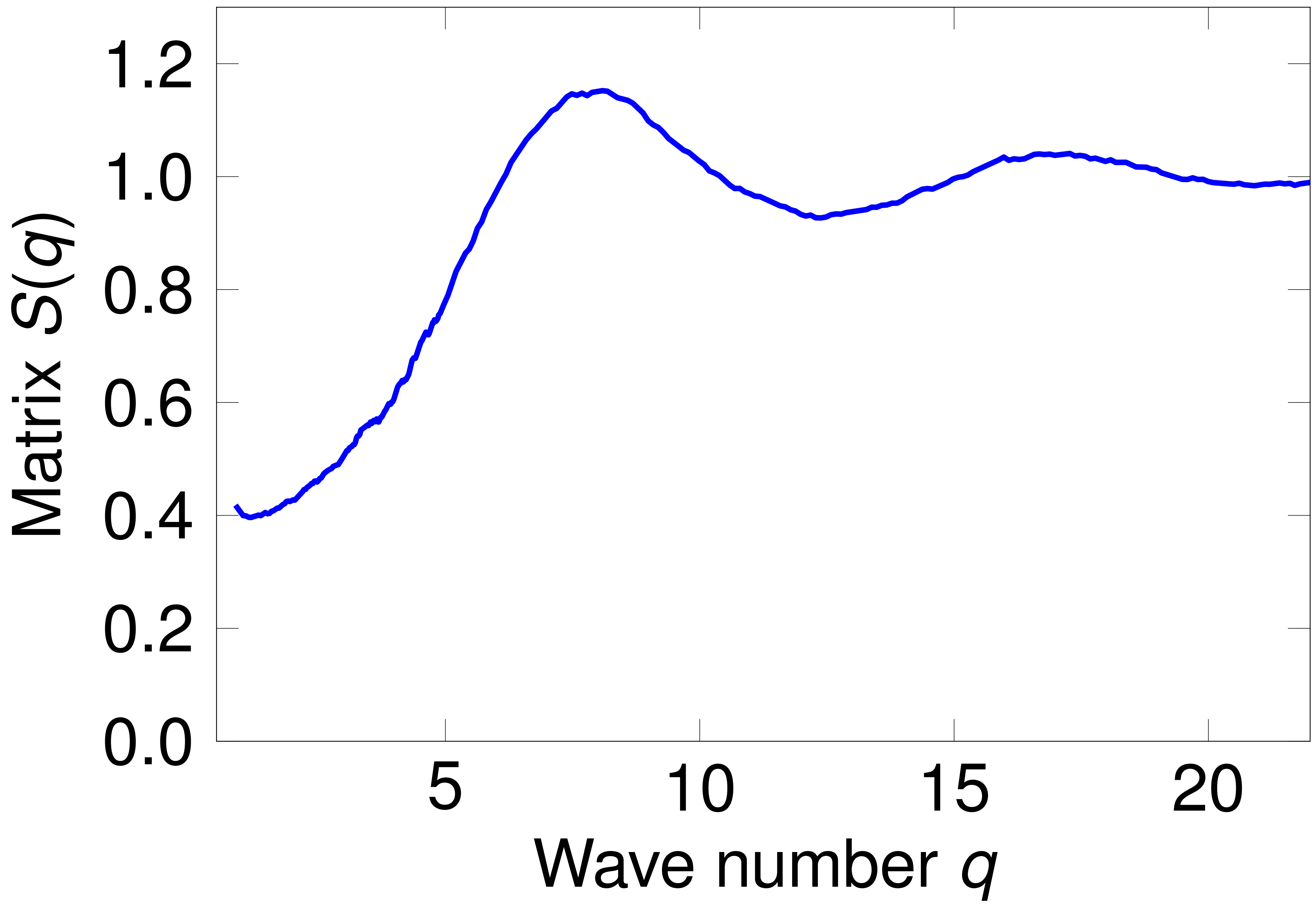
Conclusion II

- **The non-linear response in AMR is linked with anomalous diffusion dynamics.**
- **Superdiffusion of the pulled tracer** is directly related to the **time scale separation** between the motion of the pulled tracer particle and that of the host fluid.
- Still, on time scales where the host particles exhibit diffusive motion, one expects a **crossover to normal diffusion** also for the tracer particle.

Self-similarity

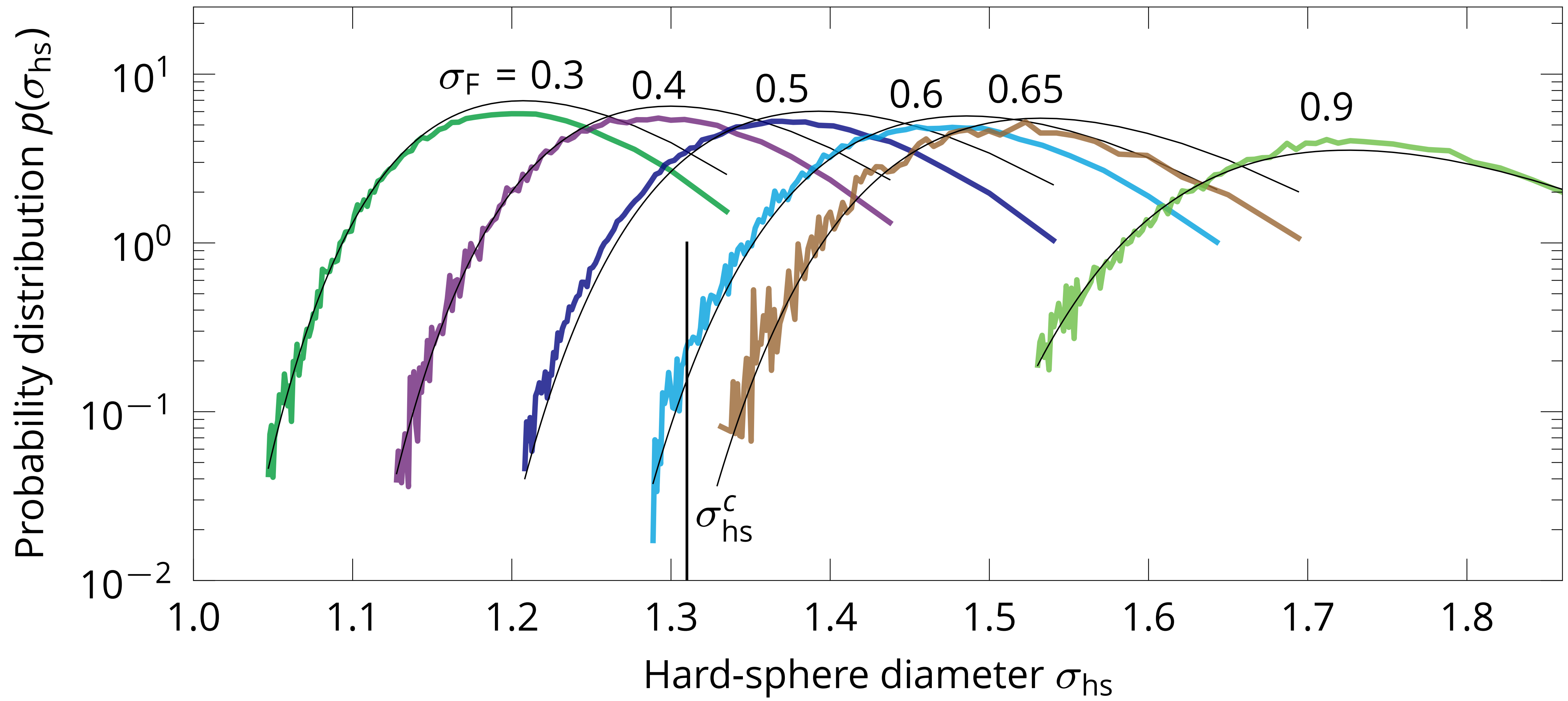


Structure of the Matrix



Weakly correlated matrix obtained by equilibration at low temperature and subsequent fixing.

Fraction of particles in the percolating system



Fraction of particles in the percolating system:

$$p_{perc} = \int_0^{\sigma_{hs}} p(\sigma_{hs}) d\sigma_{hs}$$

Exponential approximation $p(E) \sim \exp(-\beta E)$

$\Longrightarrow$ $p_{perc} > 0$

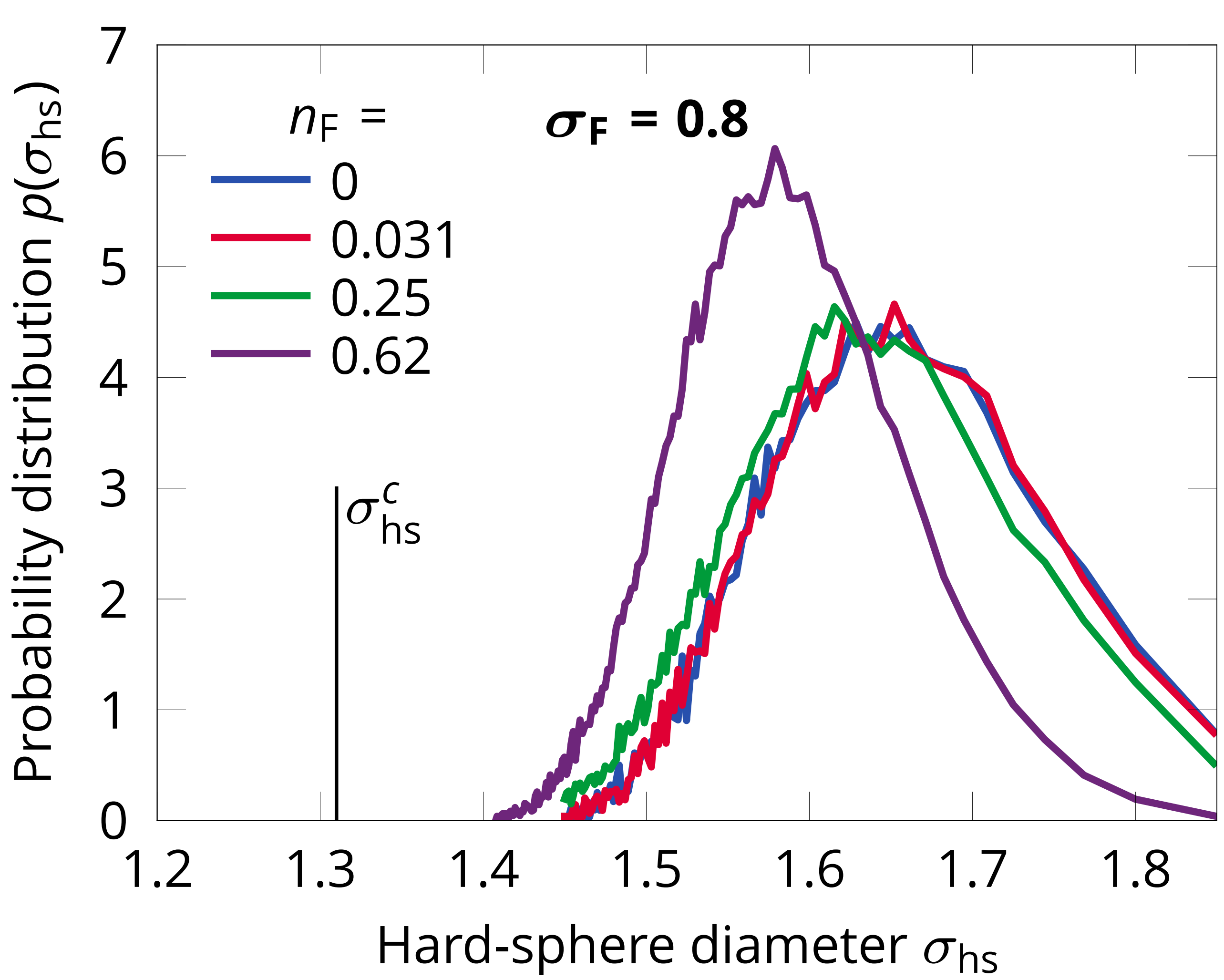
$\Longrightarrow$ *No true localization transition possible*

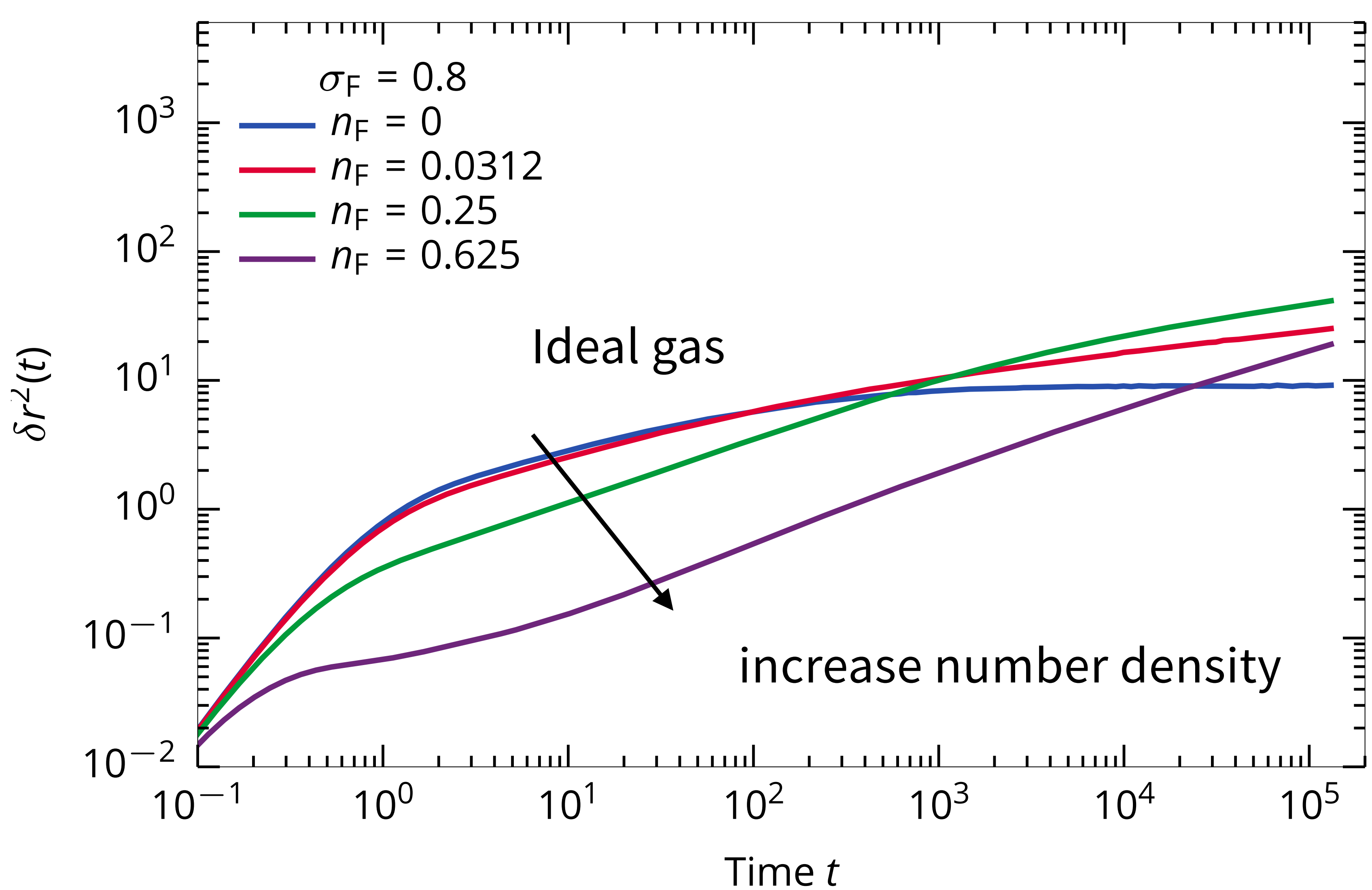
Interacting mobile particles

Localized systems:

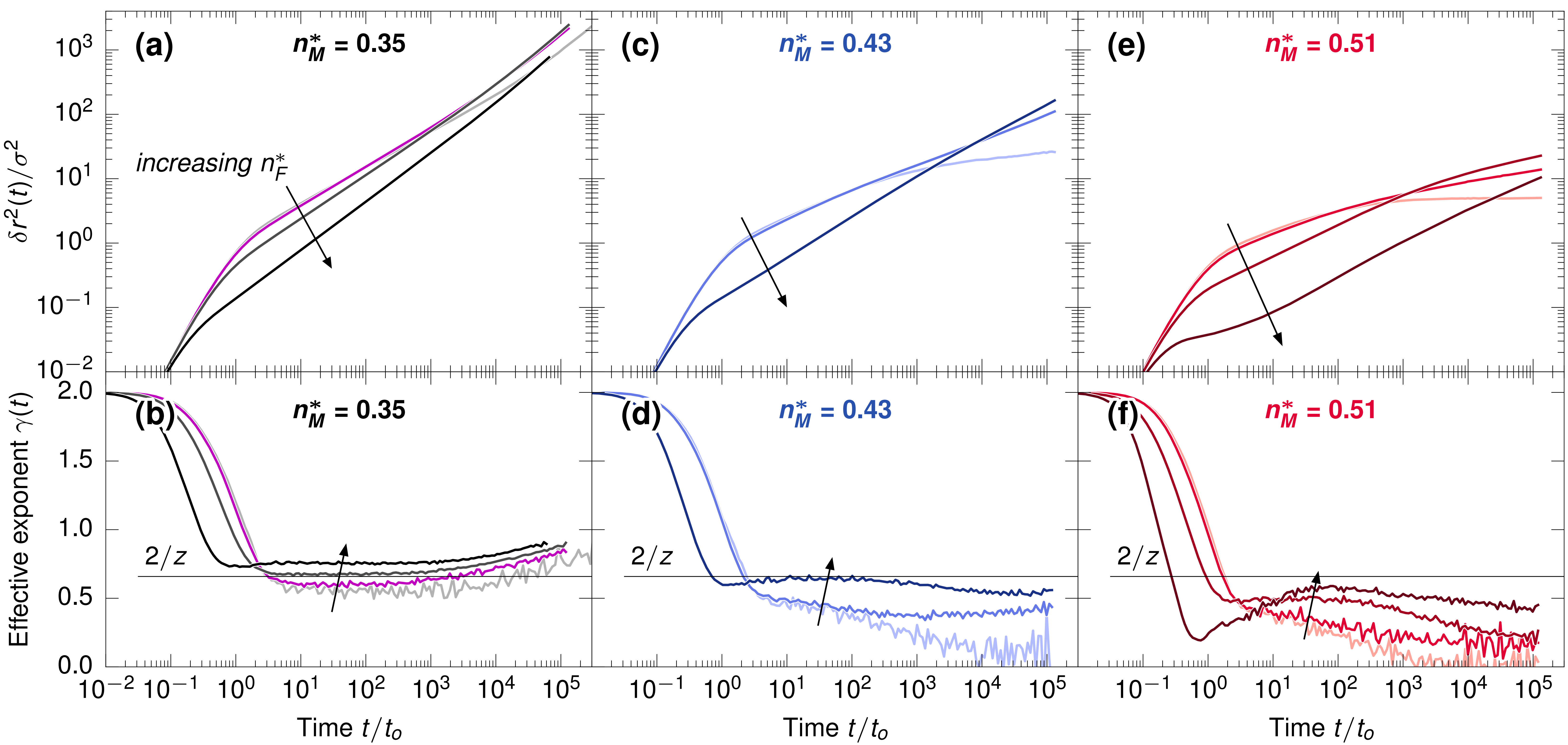
Increase number density of the fluid

$\Longrightarrow$ Localization length increases

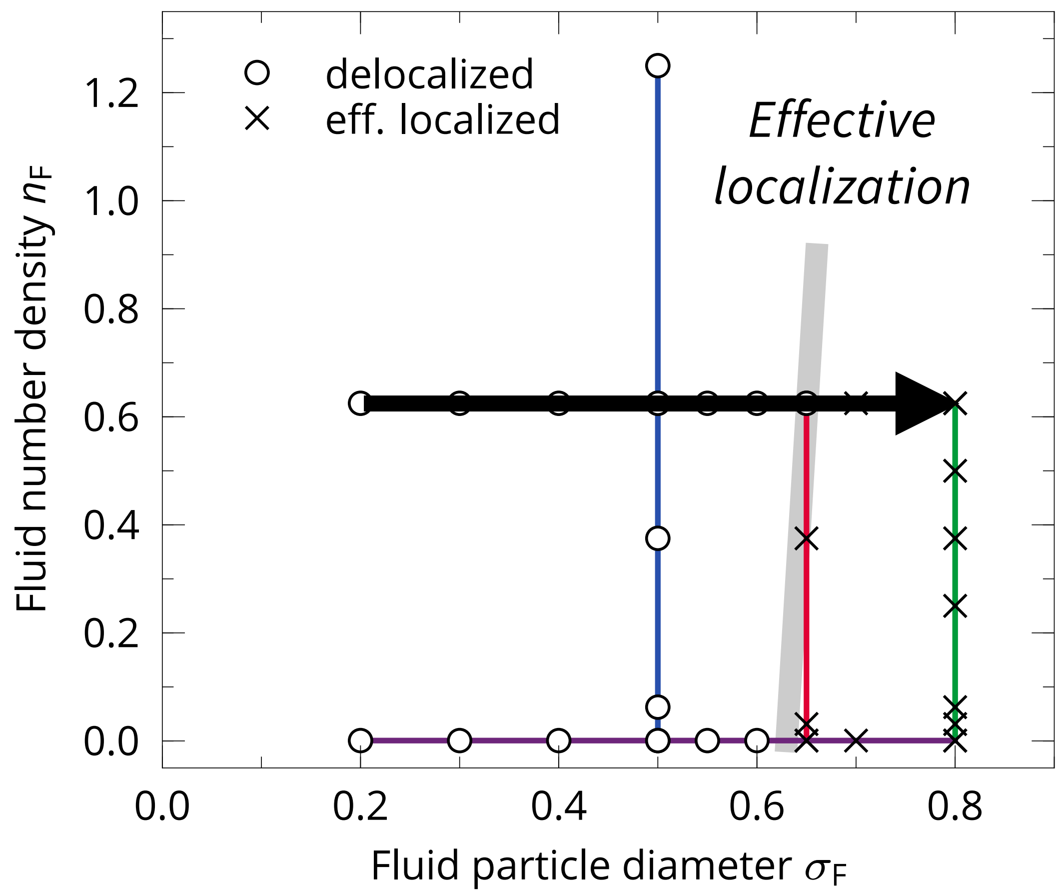


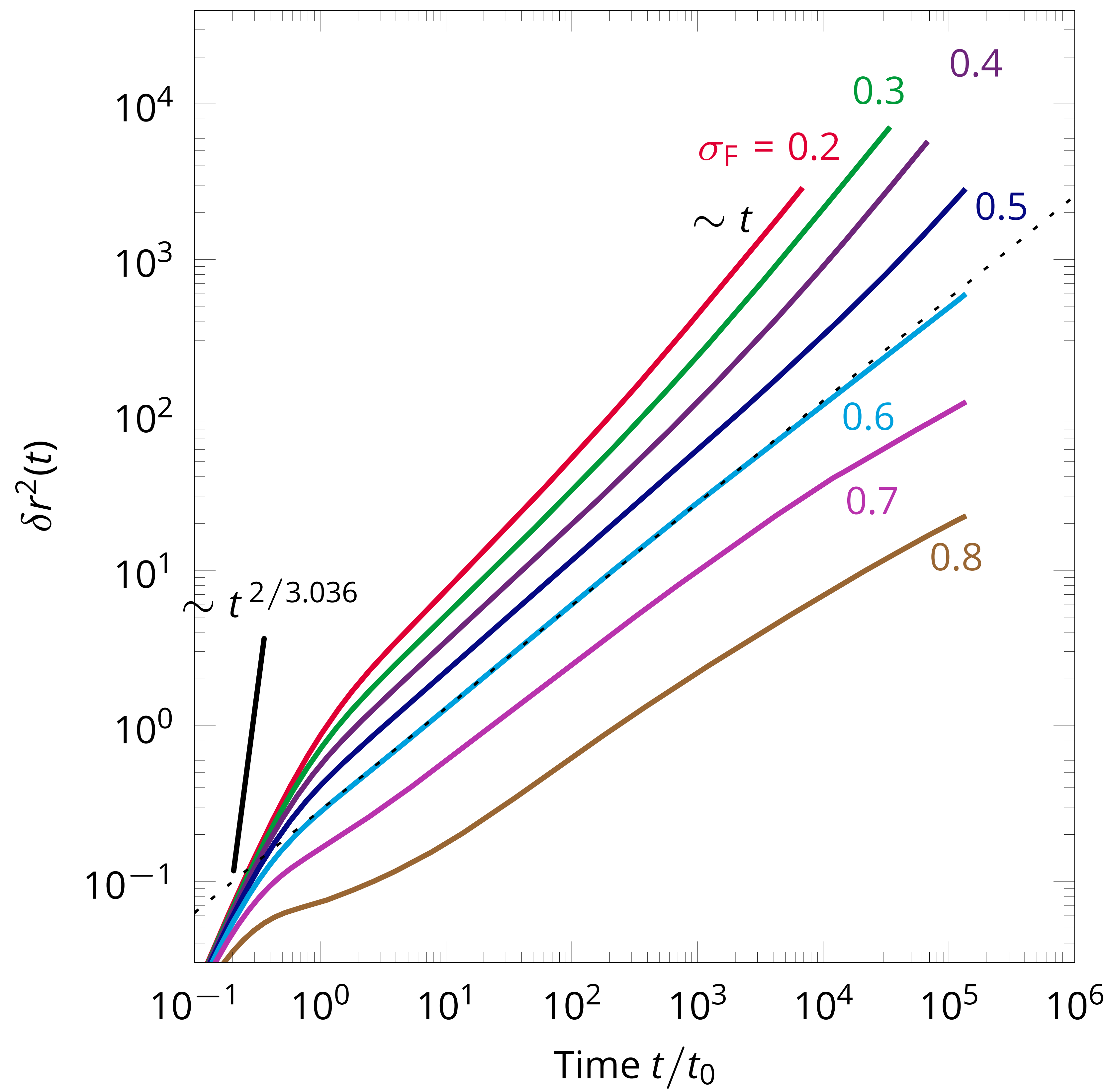


Tuning subdiffusion



Crossing the localization transition





Dense system with $n_F = 0.625$

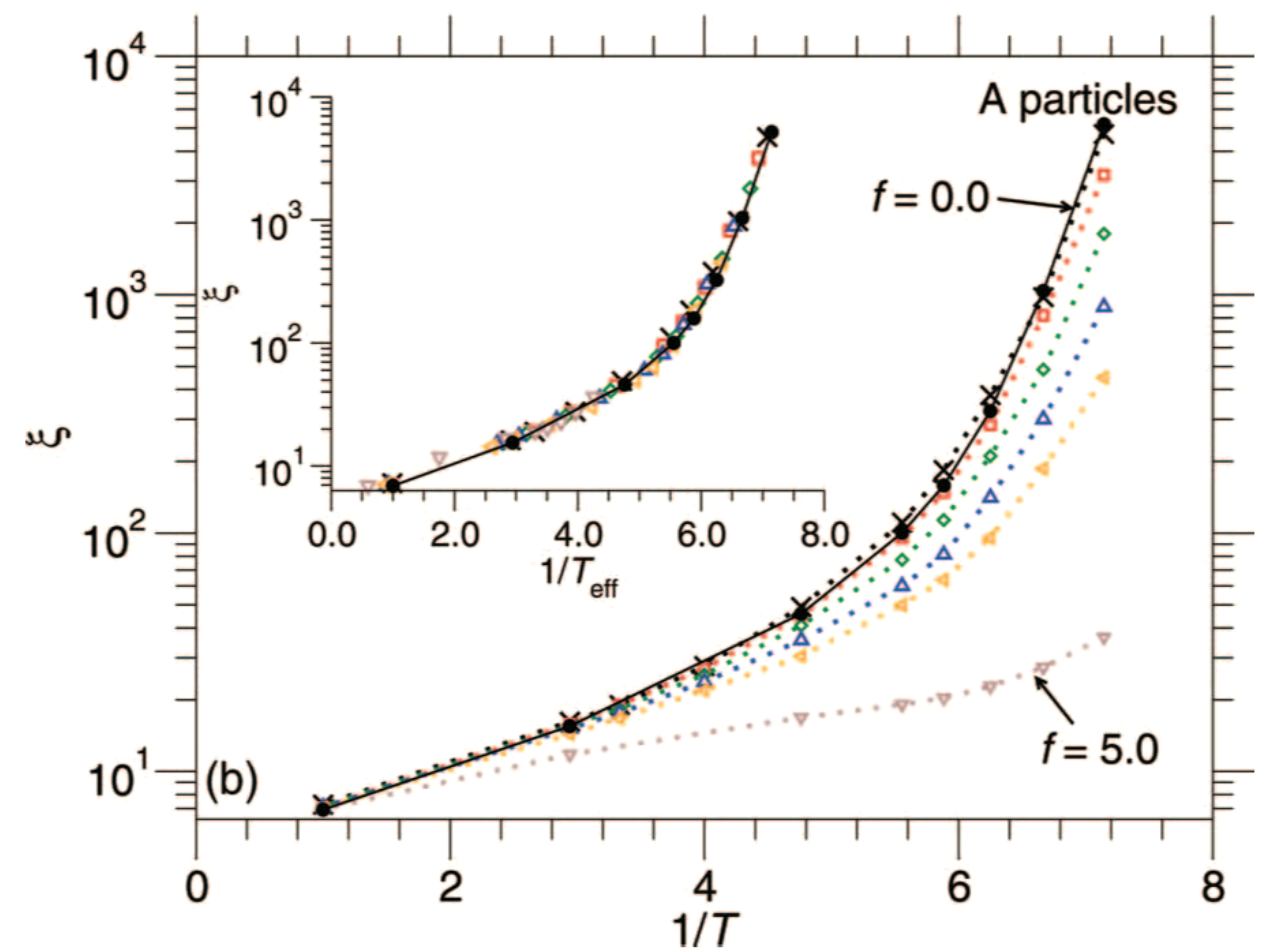
Effective localization transition near $\sigma_F \approx 0.6$

Critical exponent of the Lorentz model recovered due to homogenization of dynamics

Dynamics of the pulled particle normal to force

Data collapse onto master curve with an effective temperature $T^{eff} = T + Cf^2$ (with constant C)

A similar f^2 dependence of the effective temperature is predicted in a mean-field theory for Brownian particles in the presence of a strong external force by Santamaria-Holek and Perez-Madrid



I. Santamaria-Holek, A. Perez-Madrid, J. Phys. Chem. B 115, 9439 (2011)
and J. Chem. Phys. 145, 134905 (2016)