Crystallization Close to the Glass Transition: Dynamic heterogeneities do not precede crystallization

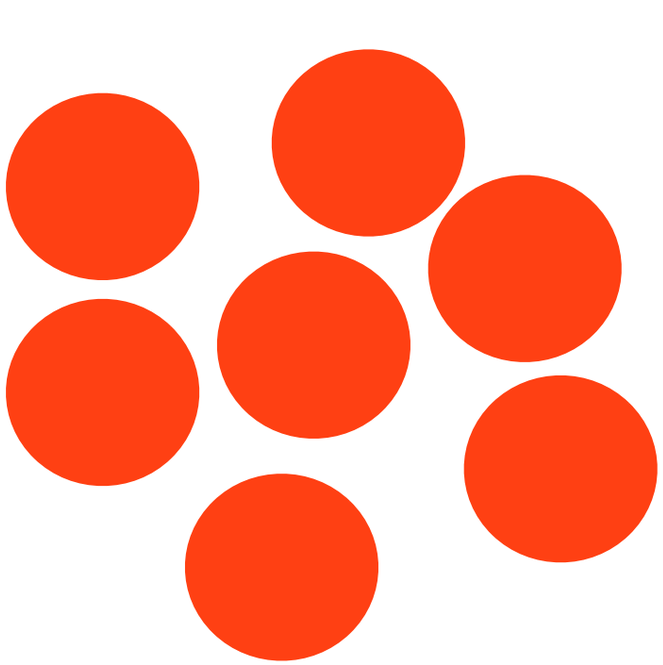
Sven Dorosz

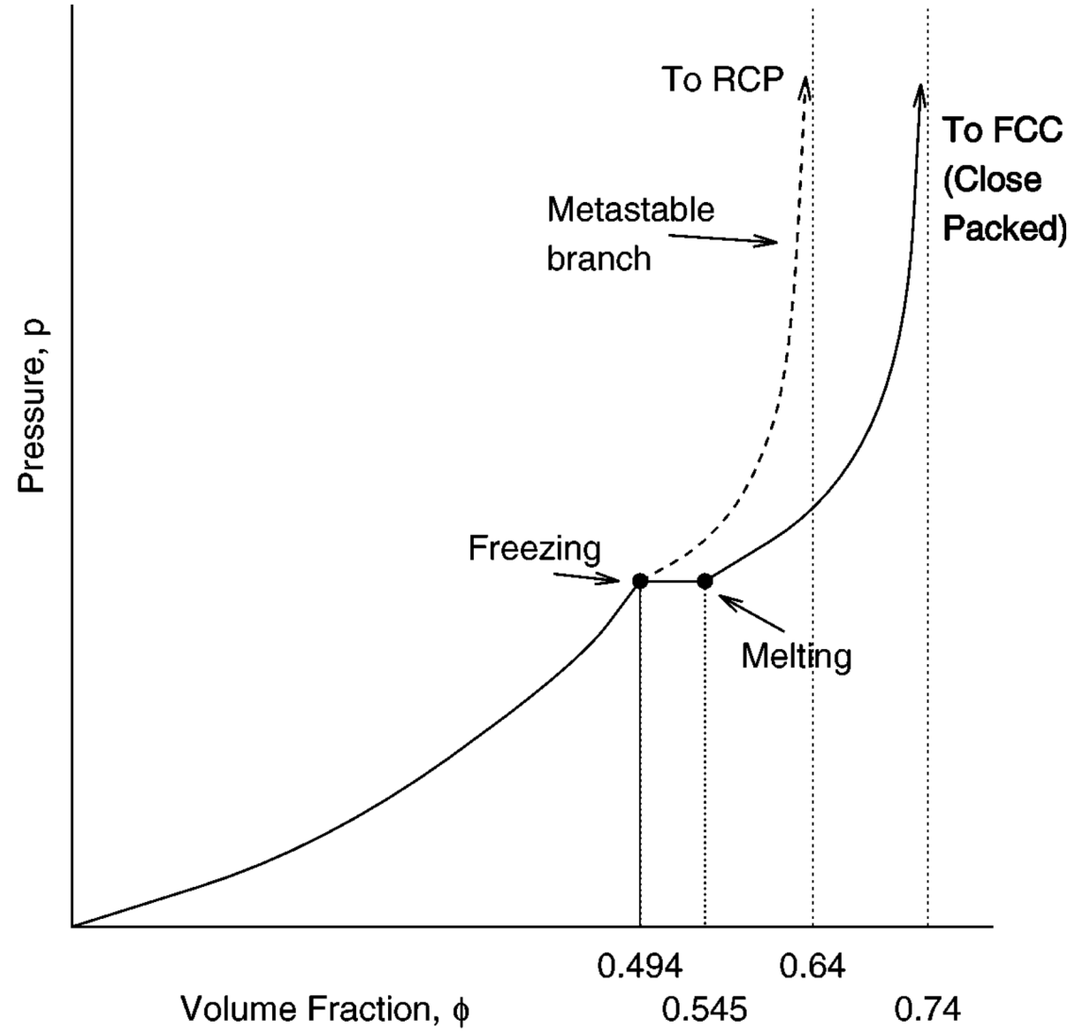
(in collaboration with Tanja Schillling)

Theory of Soft Condensed Matter,

University of Luxembourg, Luxembourg

Mono disperse systems of hard sheres present a liquid to solid phase transition





Rintoul, Md. and Torquato, S., 1996, PRL 77, 20, 4198-4201.

Even at moderate overcompressions the early stages of the cluster formation are still studied and different mechanisms are discussed.

T. Schilling, H.J. Schöpe, M. Oettel, G. Opletal, I. Snook, Phys. Rev. Lett. **105**, 025701 (2010)

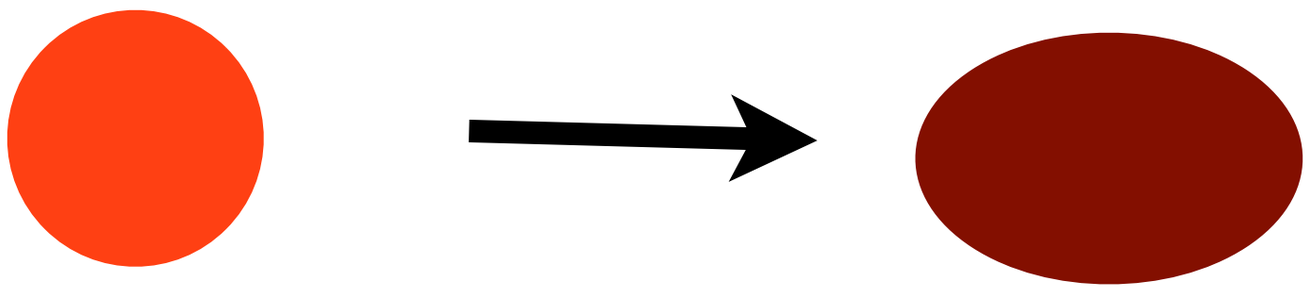
J. Russo and H. Tanaka, *Scientific Reports* **2**, 505 (2012)

What happens if we overcompress the system even further?

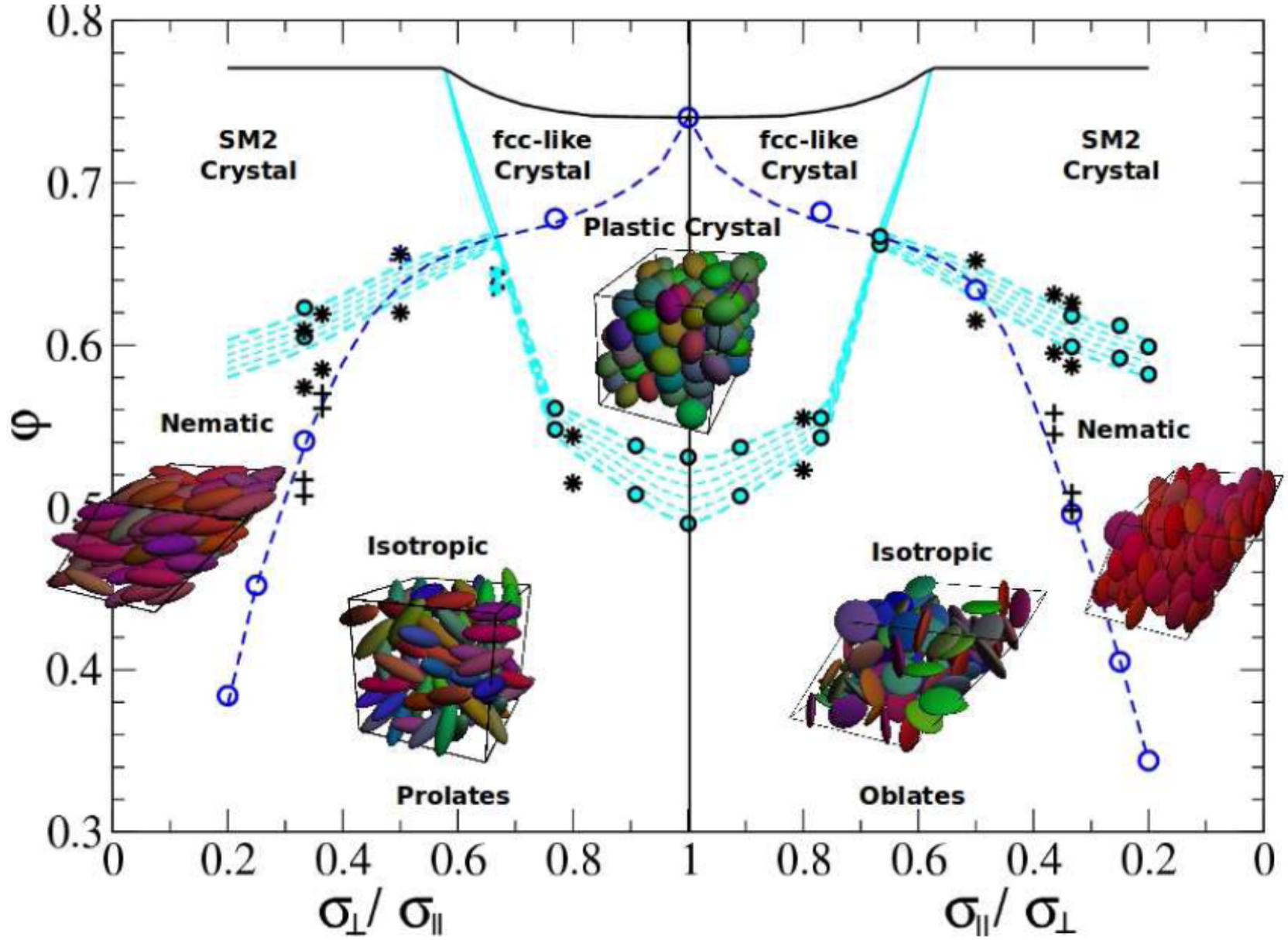
Will there be modified pathway to the final equilibrium ground state (fcc lattice) because of the slowing down of the dynamics and caging effects?

E. Zaccarelli, C. Valeriani, E. Sanz, W. C. K. Poon, M. E. Cates and P. N. Pusey, Phys. Rev. Lett., 2009, 103, 135704
C. Valeriani, E. Sanz, E. Zaccarelli, W. C. K. Poon, M. E. Cates and P. N. Pusey, JPCM, 2011, 23, 194117.
E. Sanz, C. Valeriani, E. Zaccarelli, W. C. K. Poon, P. N. Pusey and M. E. Cates, Phys. Rev. Lett., 2011, 4.

I will choose a system of
monodisperse hard ellipsoids
instead of monodisperse hard spheres.



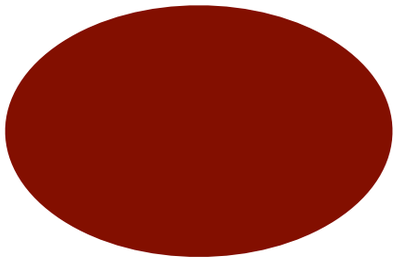
Monodisperse Hard Ellipsoids



Gerardo Odriozola, J. Chem. Phys. **136**, 134505 (2012)

NPT ensemble

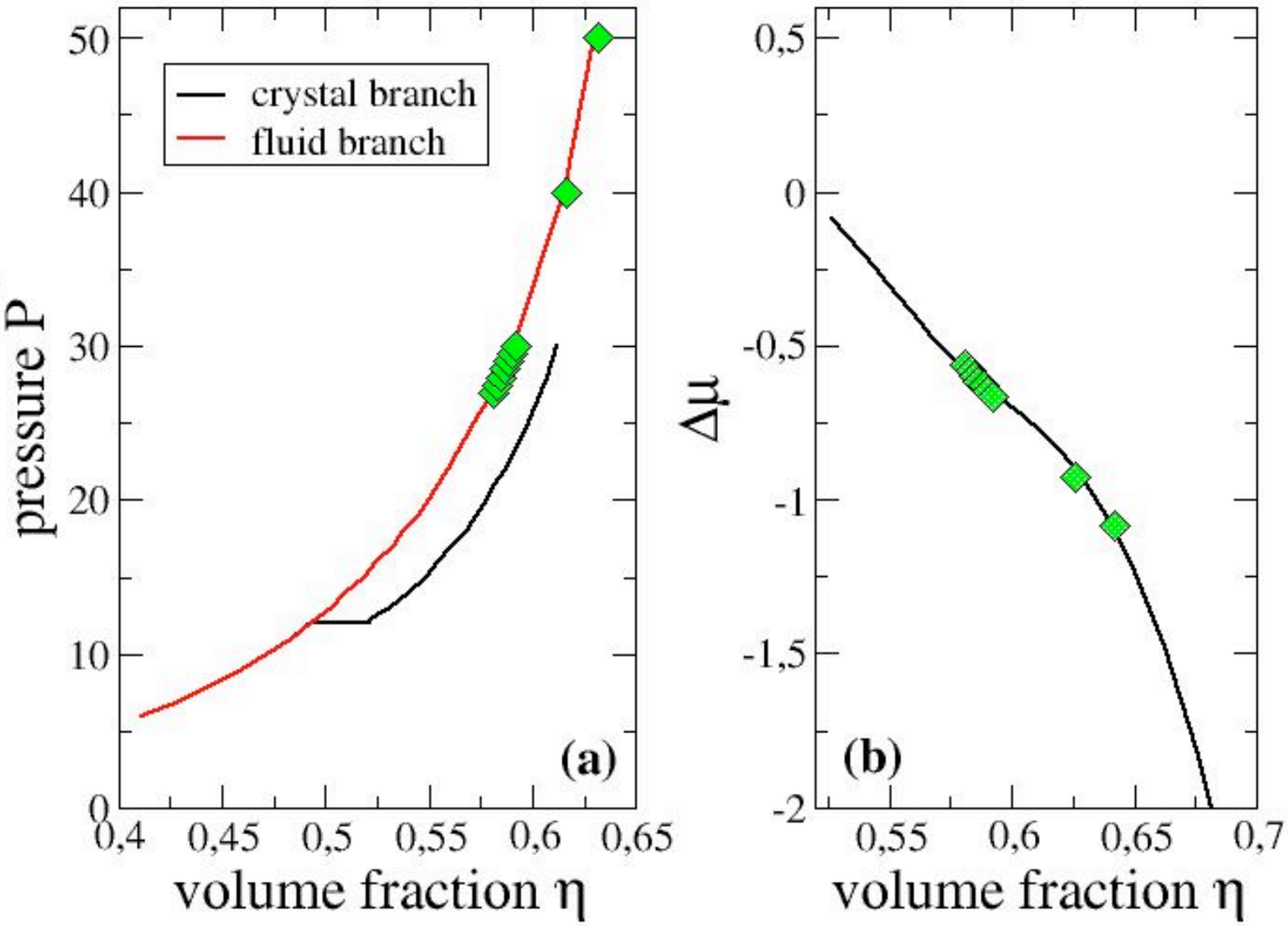
$$a/b = 1.25,$$



$$P_{coex} = 14.34$$

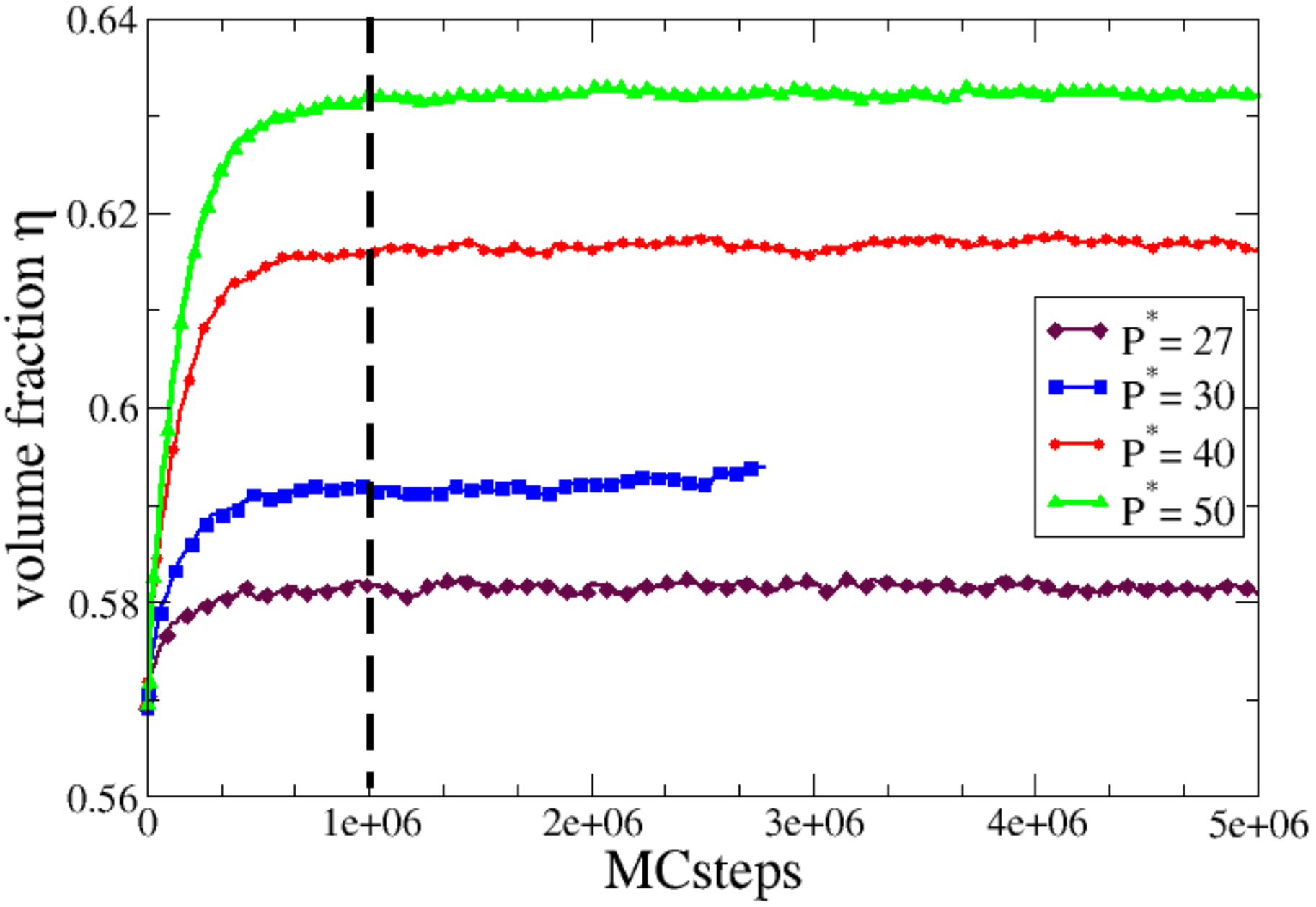
$$\eta_f^{coex} = 0.515$$

$$\eta_c^{coex} = 0.544$$



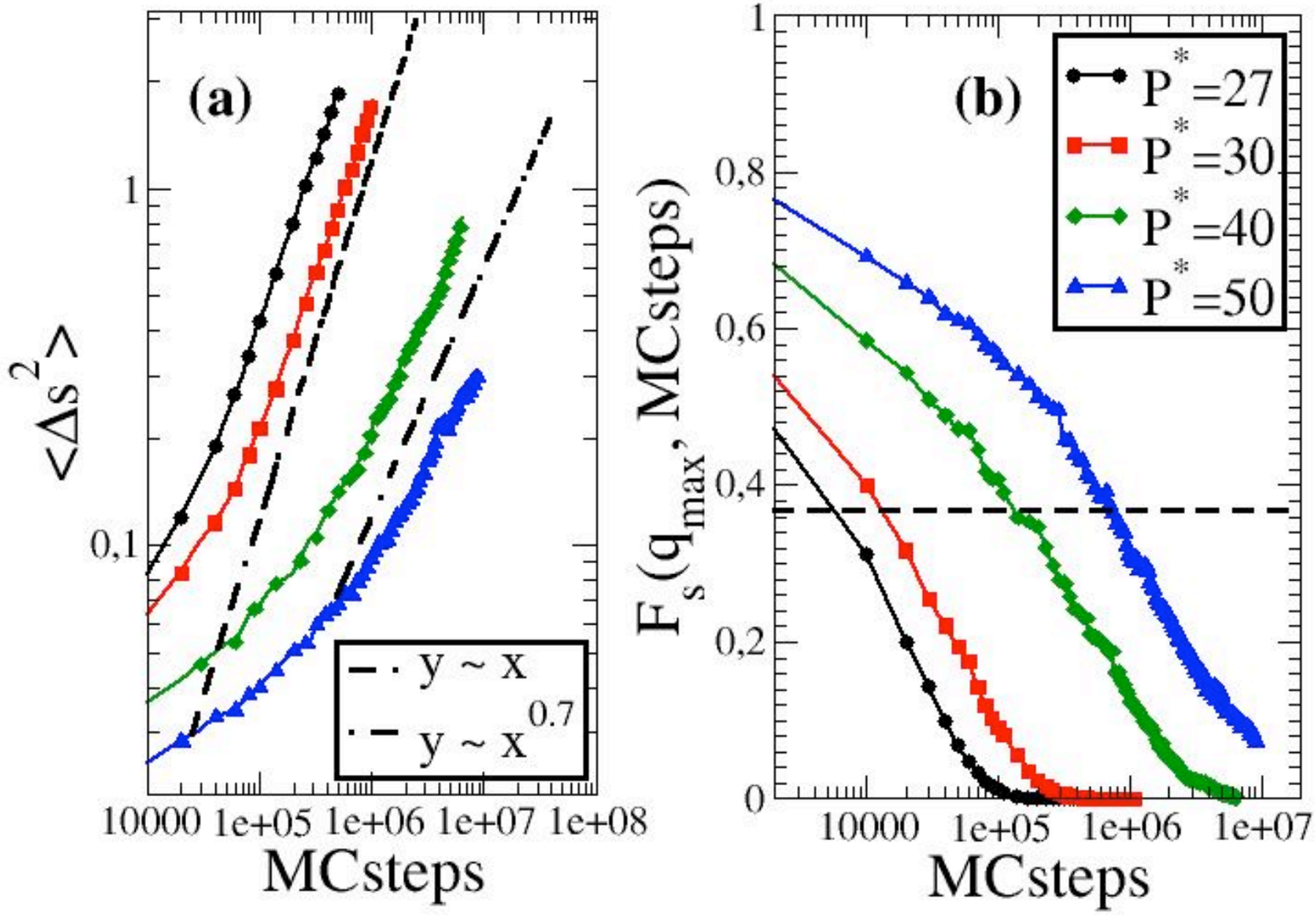
D. Frenkel, B. M. Mulder and J. P. Mctague, Molecular Crystals and Liquid Crystals, 1985, 123, 119–128.

Preparation process



Dynamical Properties

$$\langle \Delta s^2(t) \rangle = \langle (\vec{r}_i(t) - \vec{r}_i(0))^2 \rangle \qquad F_s(q,t) = \left\langle \frac{1}{N} \sum_i^N \exp[i\vec{q}(\vec{r}_i(t) - \vec{r}_i(0))] \right\rangle$$



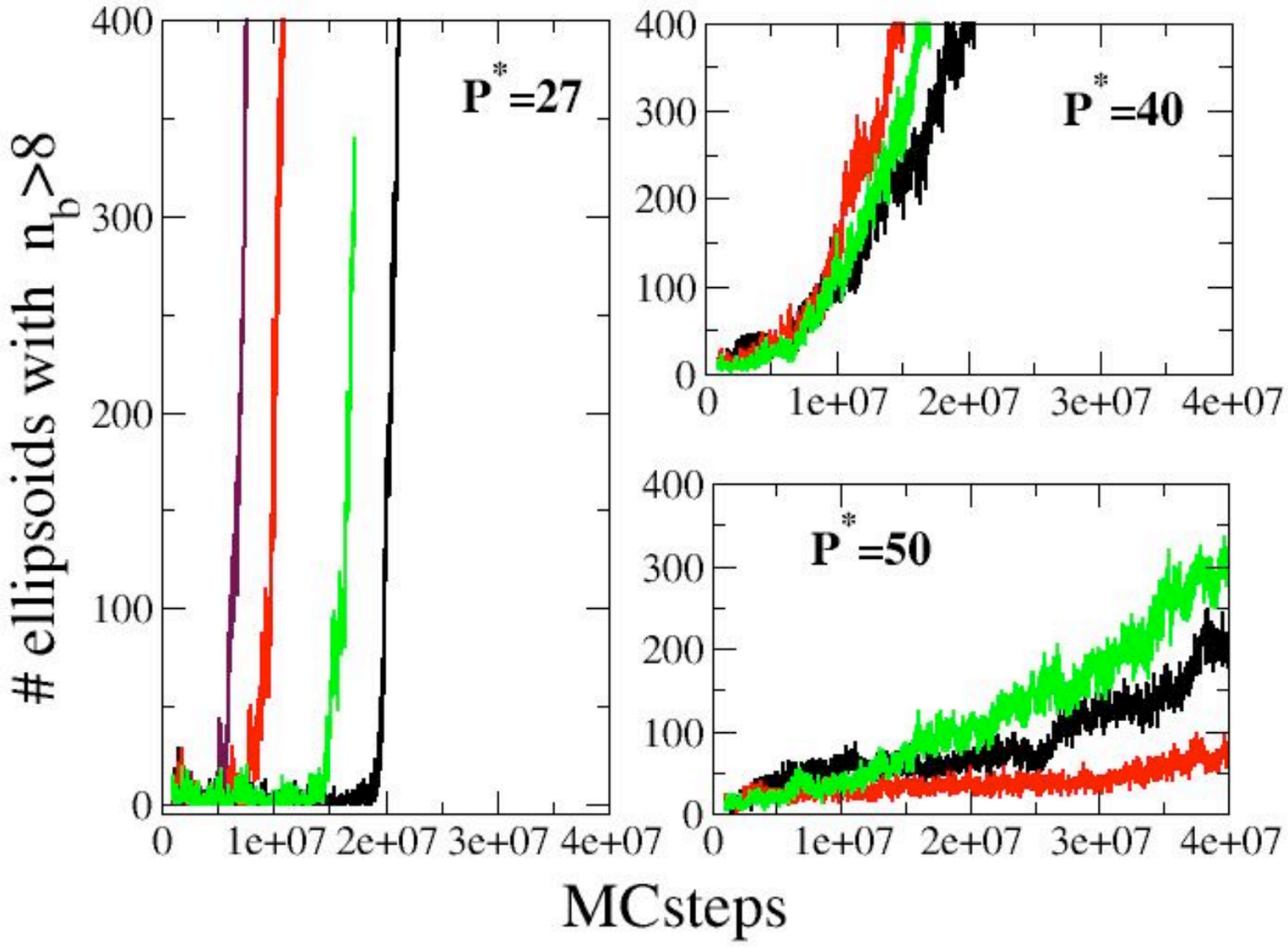
subdiffusive regime slow relaxation

previous work on the glass like dyanmics in P. Pfleiderer *et al* 2008 *EPL* **84** 16003

Crystallization process

$$\bar{q}_{lm}(i) := \frac{1}{n(i)} \sum_{j=1}^{n(i)} Y_{lm}\left(\vec{r}_{ij}\right)$$

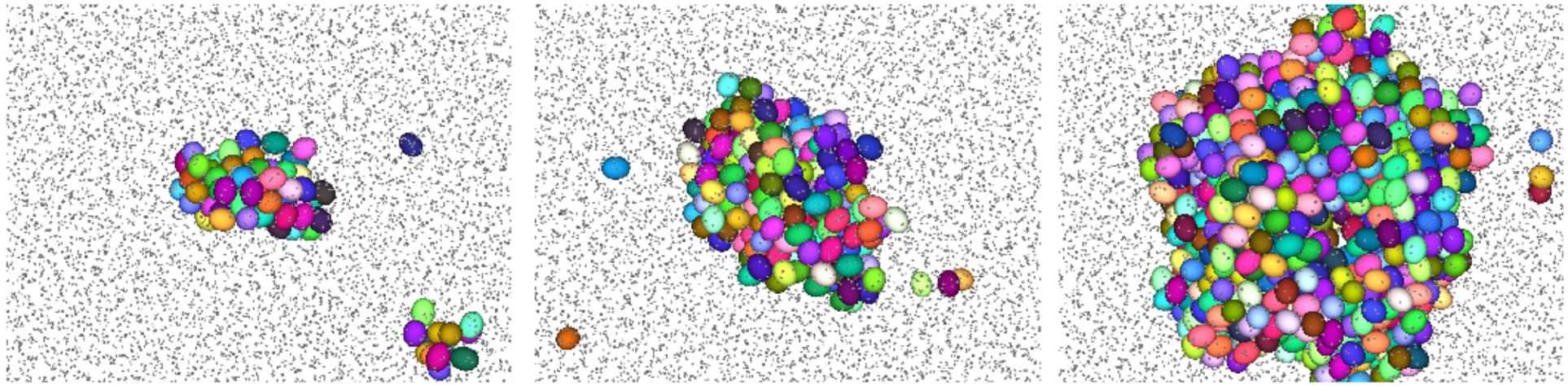
$$\vec{q_6}(i) \cdot \vec{q_6}^{*}(j) > 0.7$$



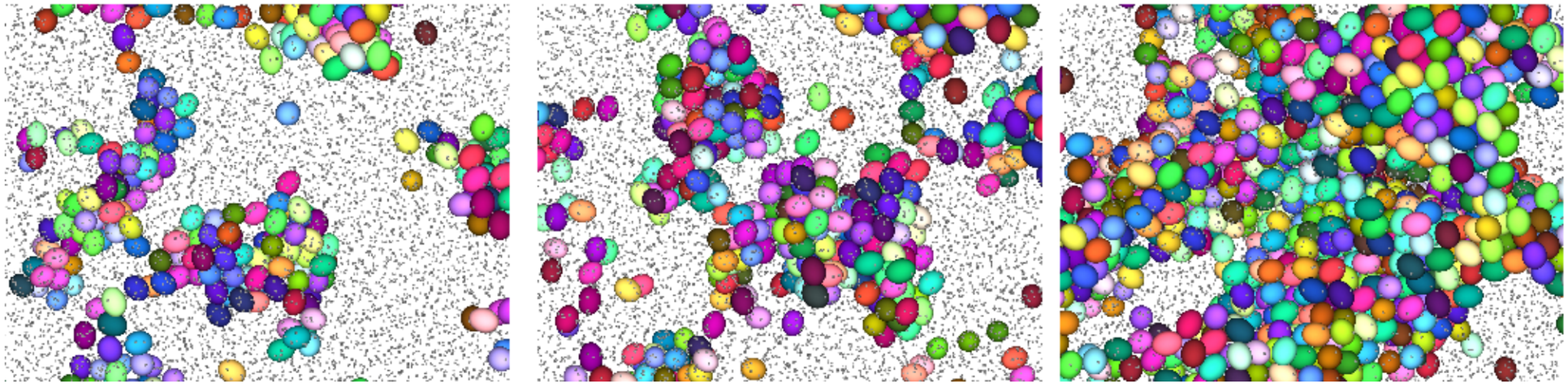
long induction time vs. immediate growth

Snapshots of the system

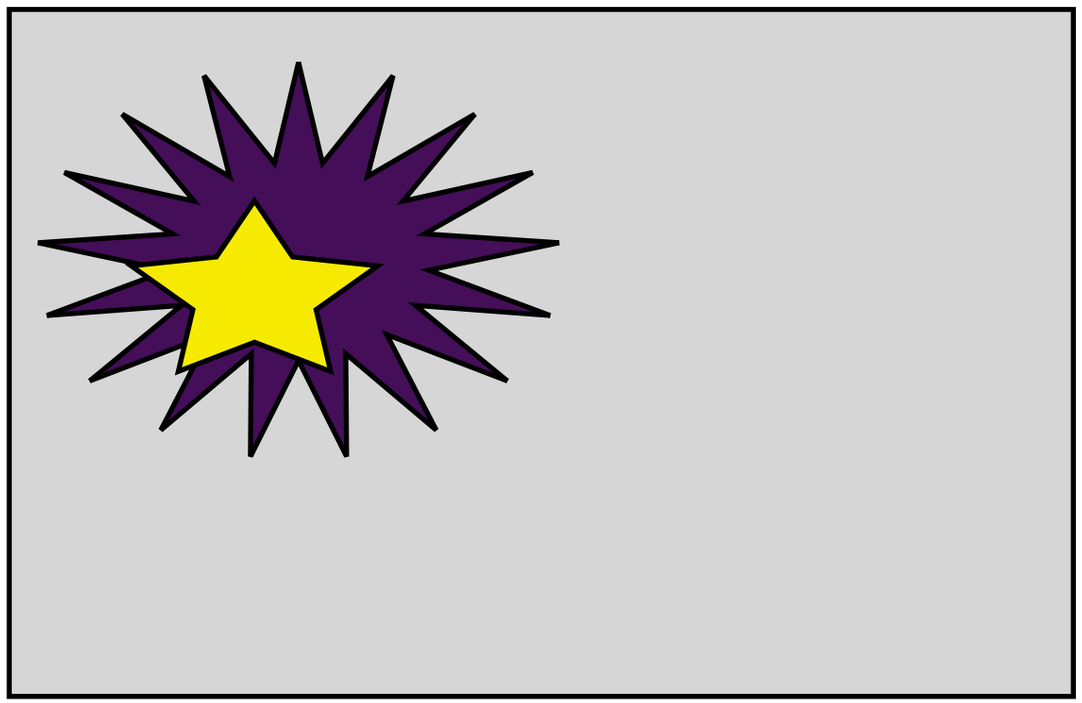
P*=27



P*=40



Structural and dynamical preconditions for crystallization

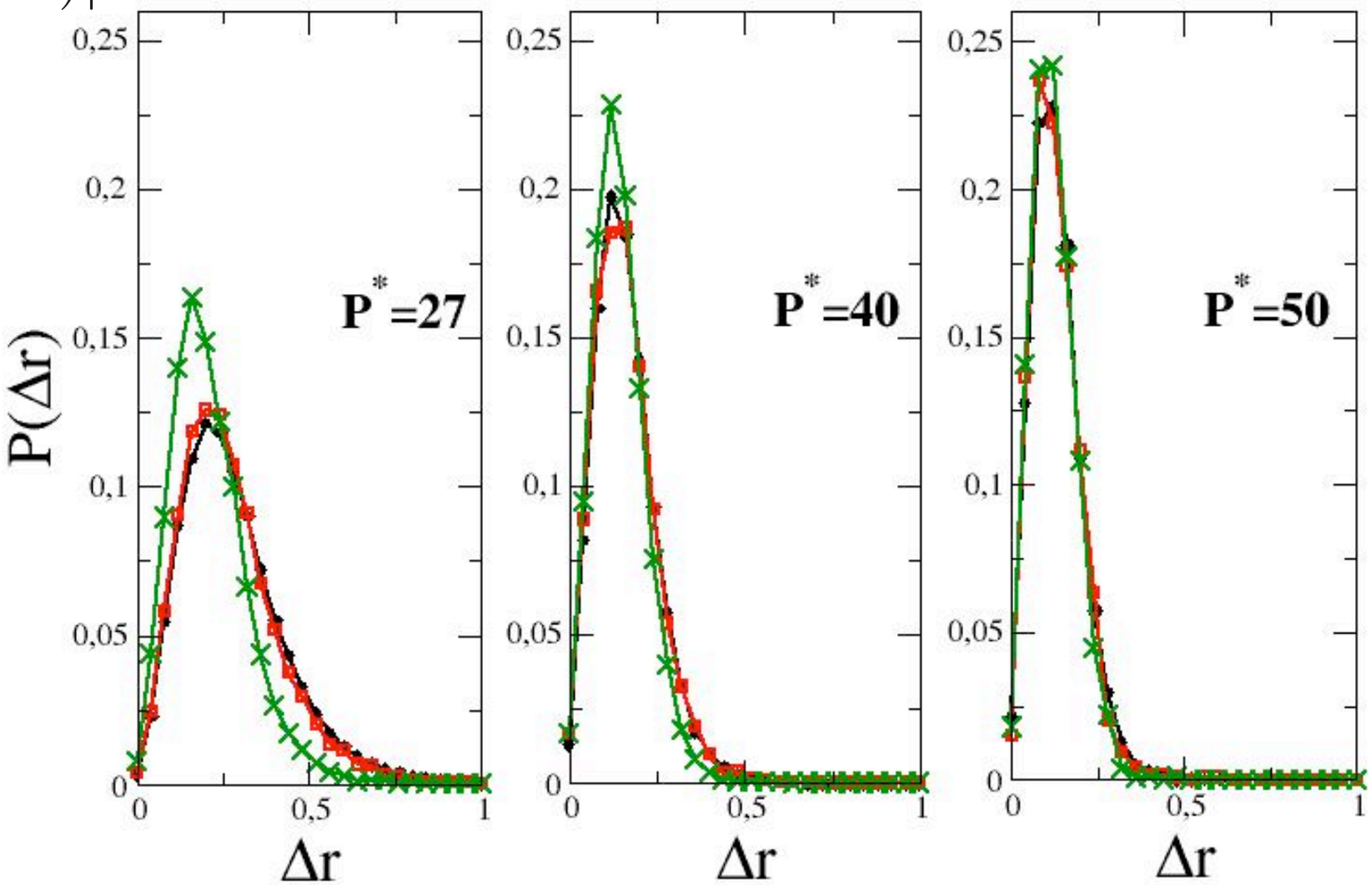


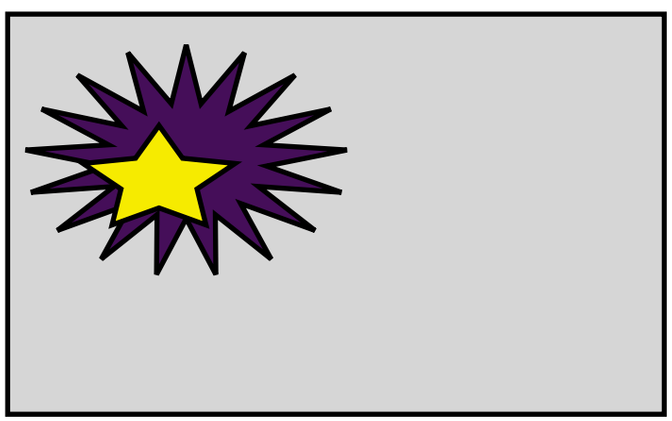
Short time mobility
Voronoi volume
Orientational correlations
Structure

Short time mobility

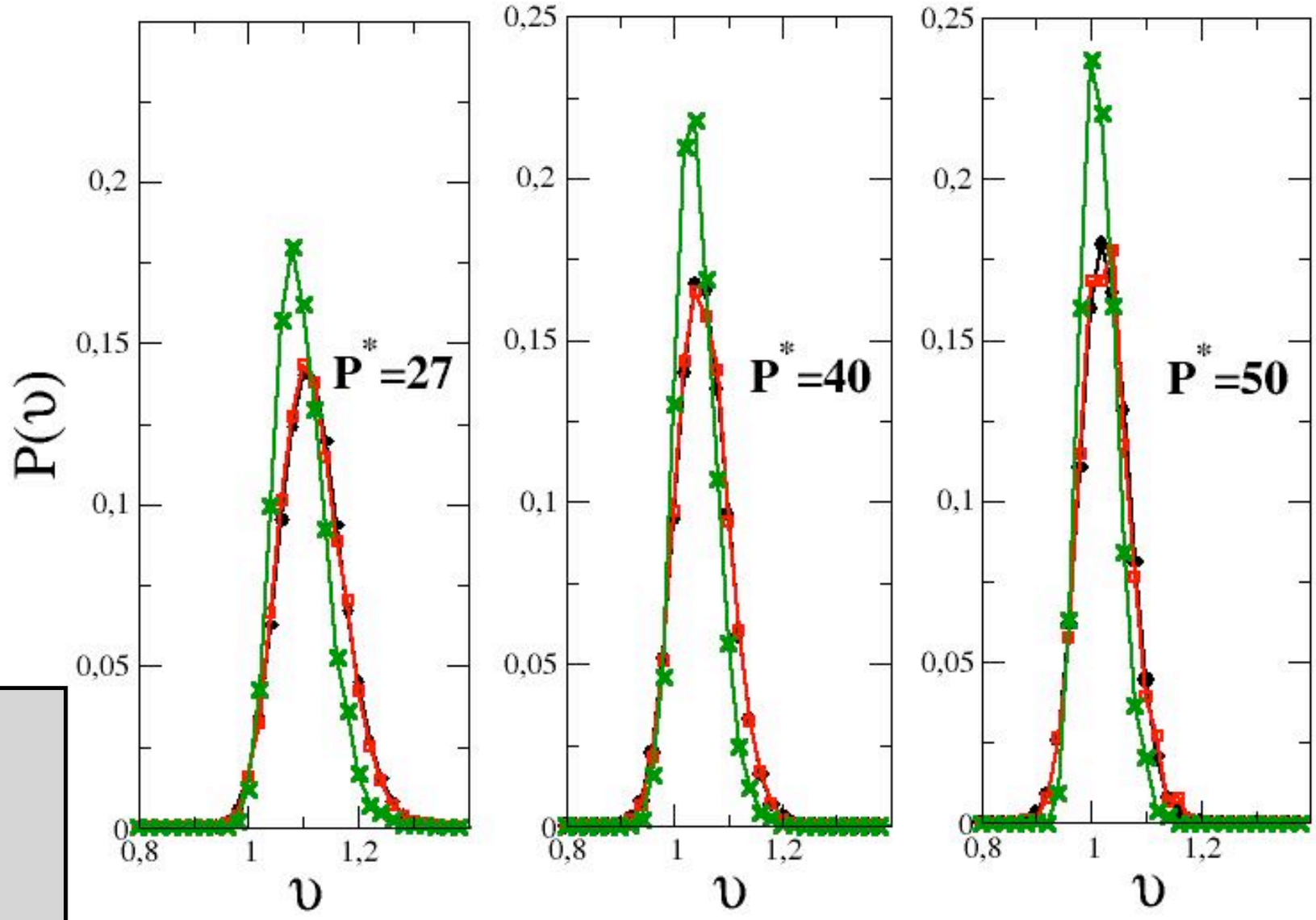
$$\Delta r_i(t) = |\vec{r}_i(t) - \vec{r}_i(t - \Delta t)|$$

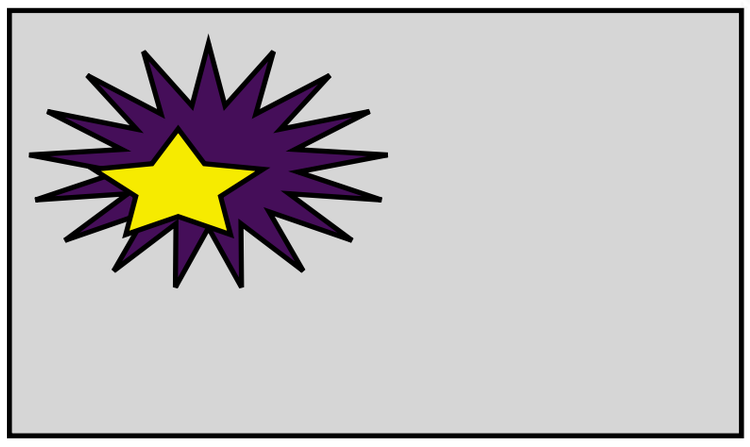
$\Delta t = 5 \cdot 10^5$ MC steps





Voronoi volume

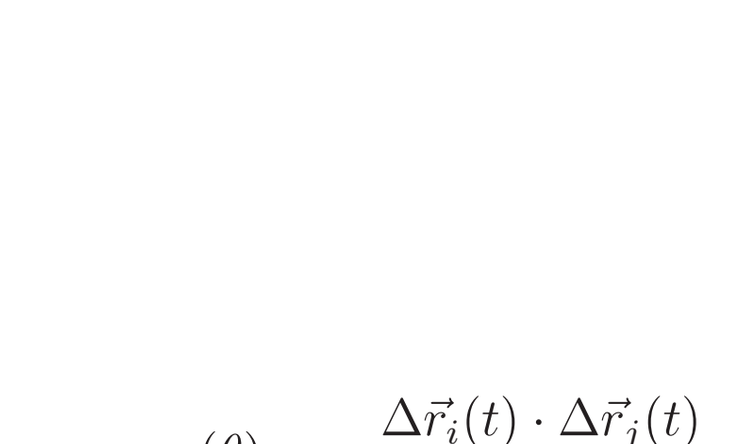


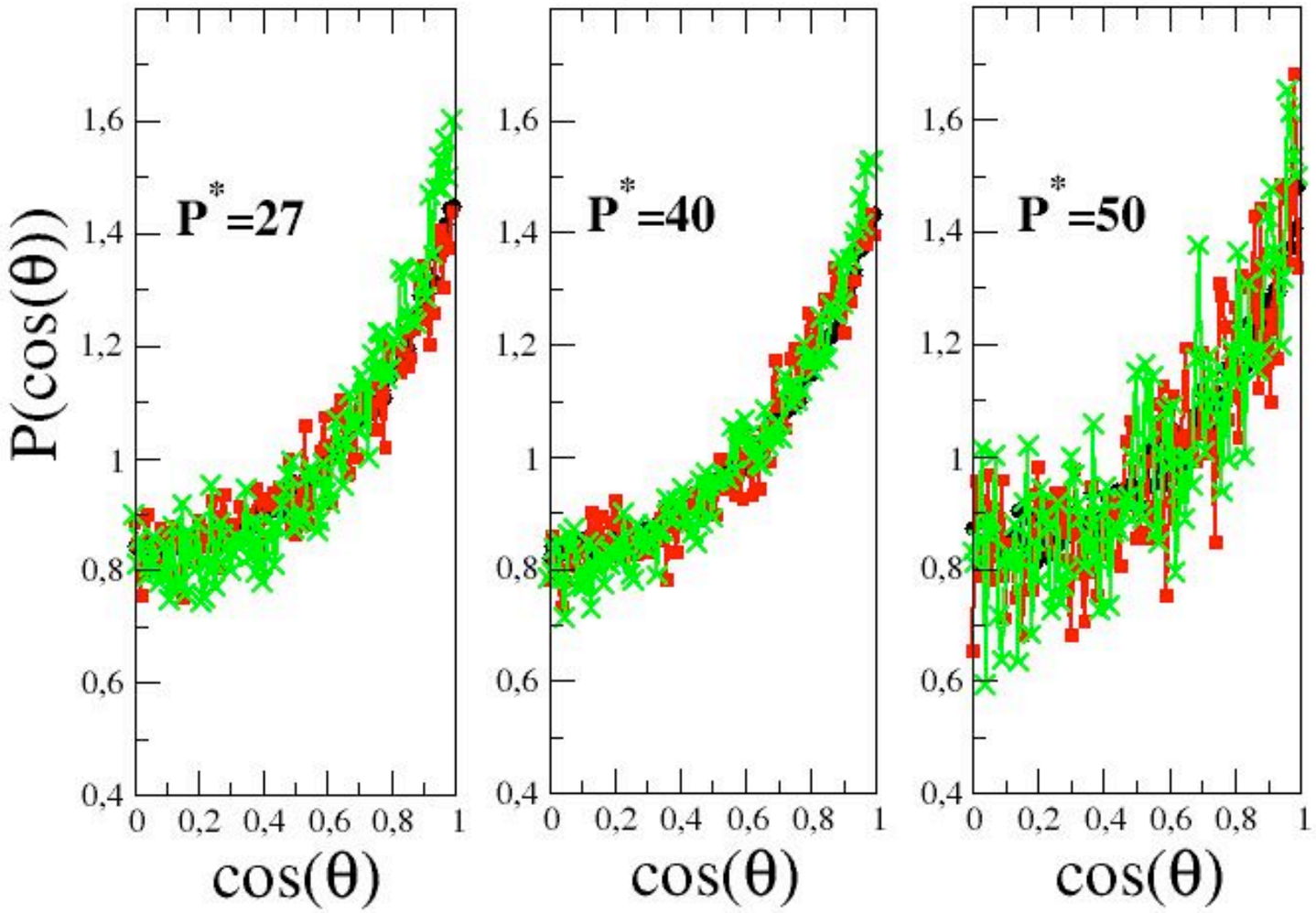


C.H.Roycroft, Chaos, 2009, 19, 041111

Orientational correlations

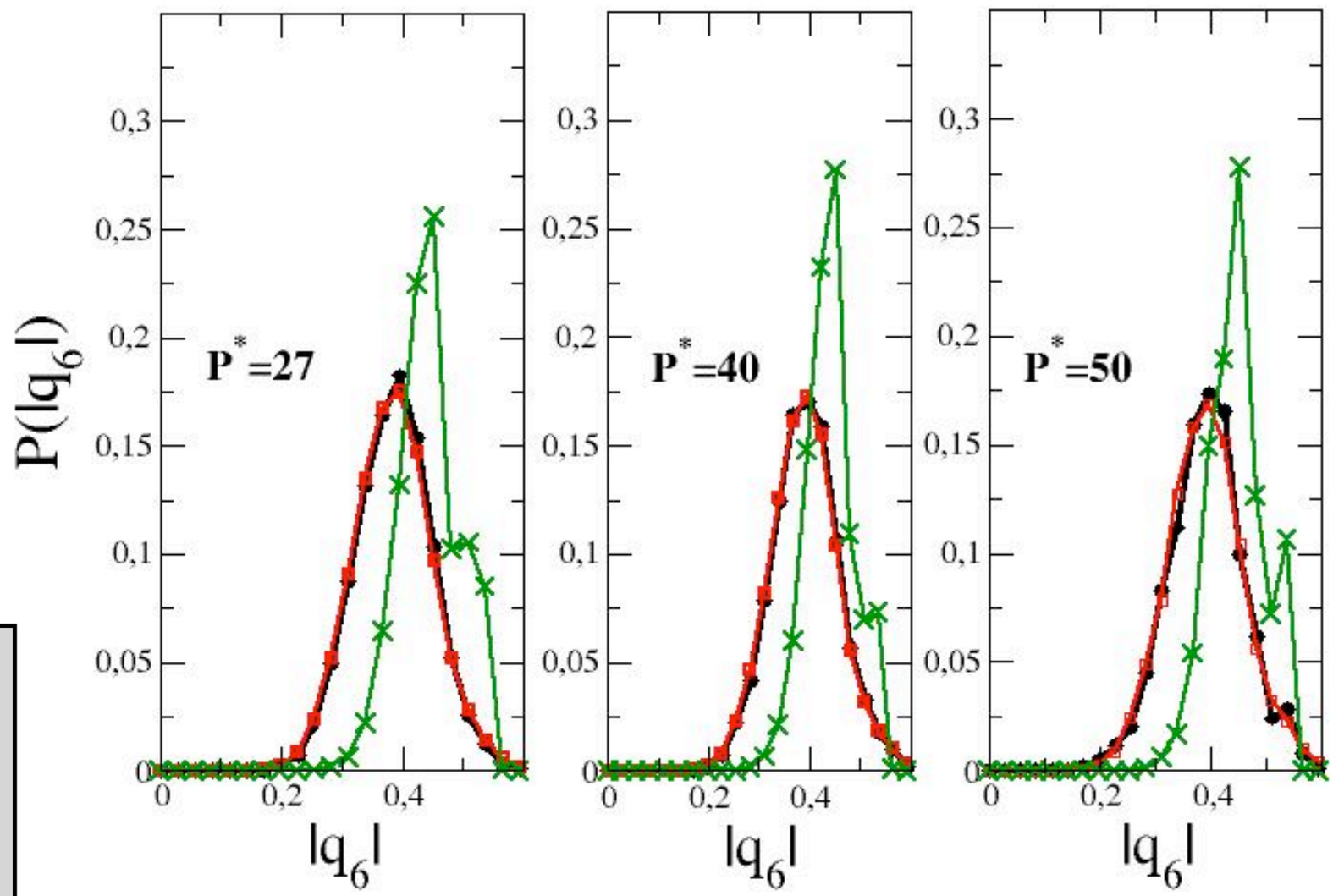
$$\cos(\theta) := \frac{\Delta\vec{r}_i(t) \cdot \Delta\vec{r}_j(t)}{|\Delta\vec{r}_i(t)| \cdot |\Delta\vec{r}_j(t)|},$$

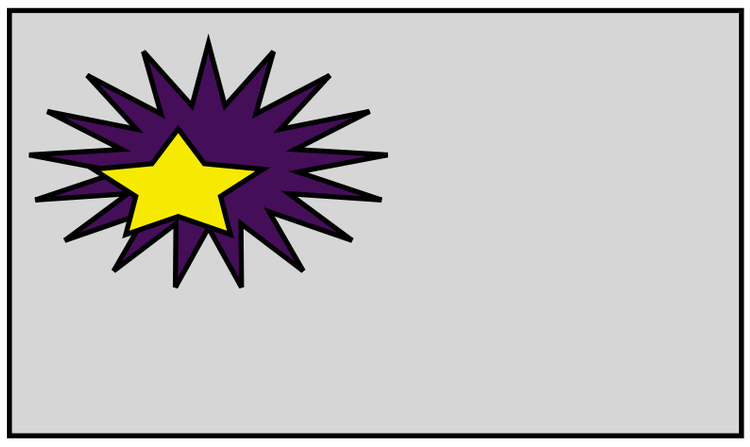




Structure

$$\bar{q}_{lm}(i) := \frac{1}{n(i)} \sum_{j=1}^{n(i)} Y_{lm}\left(\vec{r}_{ij}\right)$$





Conclusion

- crystallizing particles were studied backwards in time for their structural as well as dynamical properties
- no modification because of to the emerging glassy dynamics were found.
- the two mechanisms are acting on independent time scales.
- transition described by spinodal decomposition

Acknowledgements

- Tanja Schilling and Kurt Binder
- Financial supported by the National Research Fund, Luxembourg co-funded under the Marie Curie Actions of the European Commission (FP7-COFUND) and under the project FRPTECD.
- Computer simulations presented in this paper were carried out using the HPC facility of the University of Luxembourg.

Fonds National de la Recherche Luxembourg