

Glassy Dynamics and spinodal decomposition

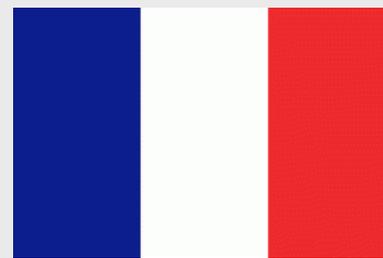
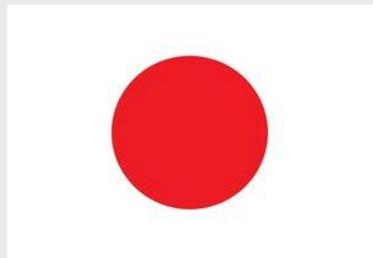
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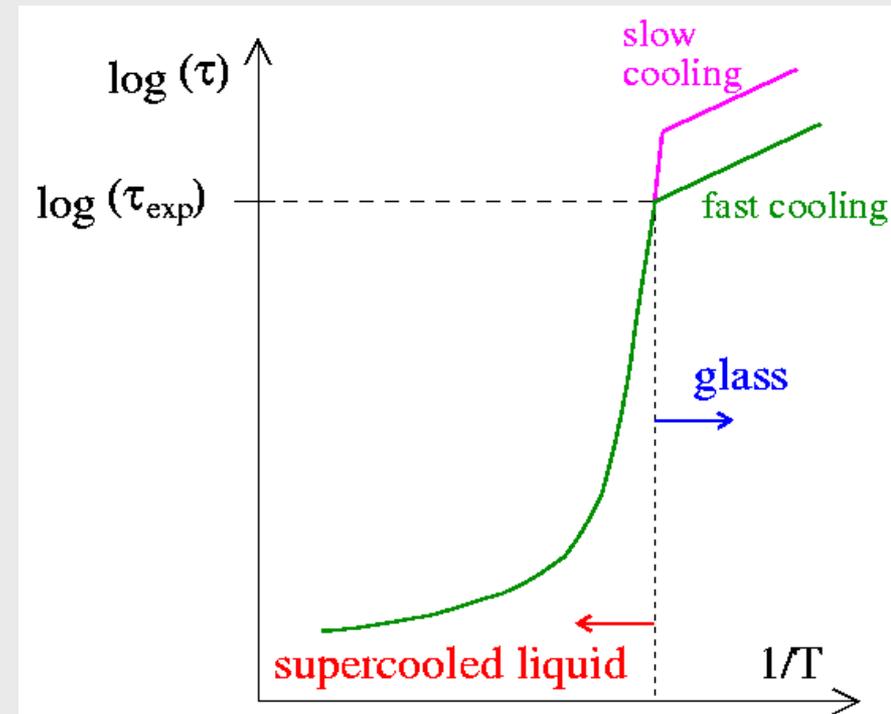


YITP, Kyoto
August 11-14, 2015

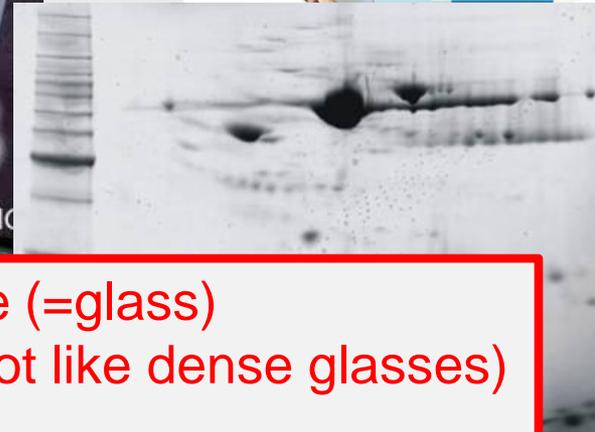
The glass transition

- If in an experiment (or simulation) one wants to investigate the properties of a system at a given T , one first has to bring the system to this temperature (by coupling it to a heat bath)
- If one wants to **study the equilibrium dynamics** one will have to **allow the system to equilibrate** and *usually* this takes a time that is comparable with the **relaxation time τ of the system**
- Due to the strong increase of τ with decreasing T **there will exist a temp. T at which the system falls out of equilibrium** (because we don't have enough patience) and forms a glass
 \Rightarrow the system undergoes a glass transition

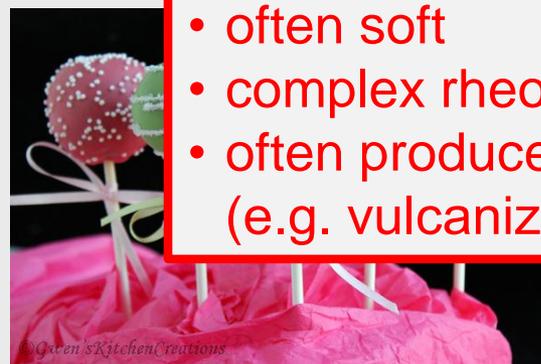
N.B.: The temperature of this glass transition and the properties of the glass depend on the experiment



On gels (as seen by Google)

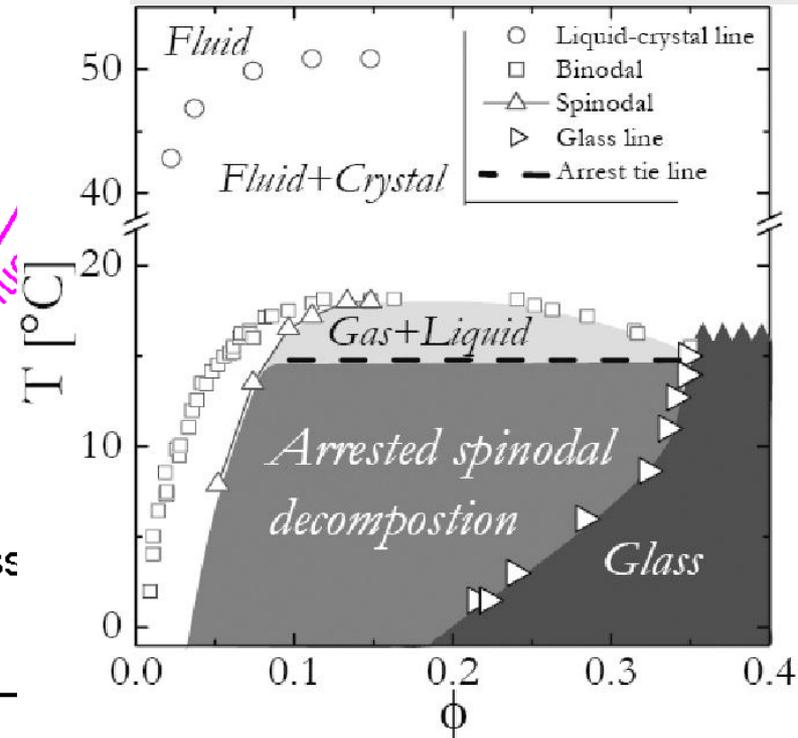
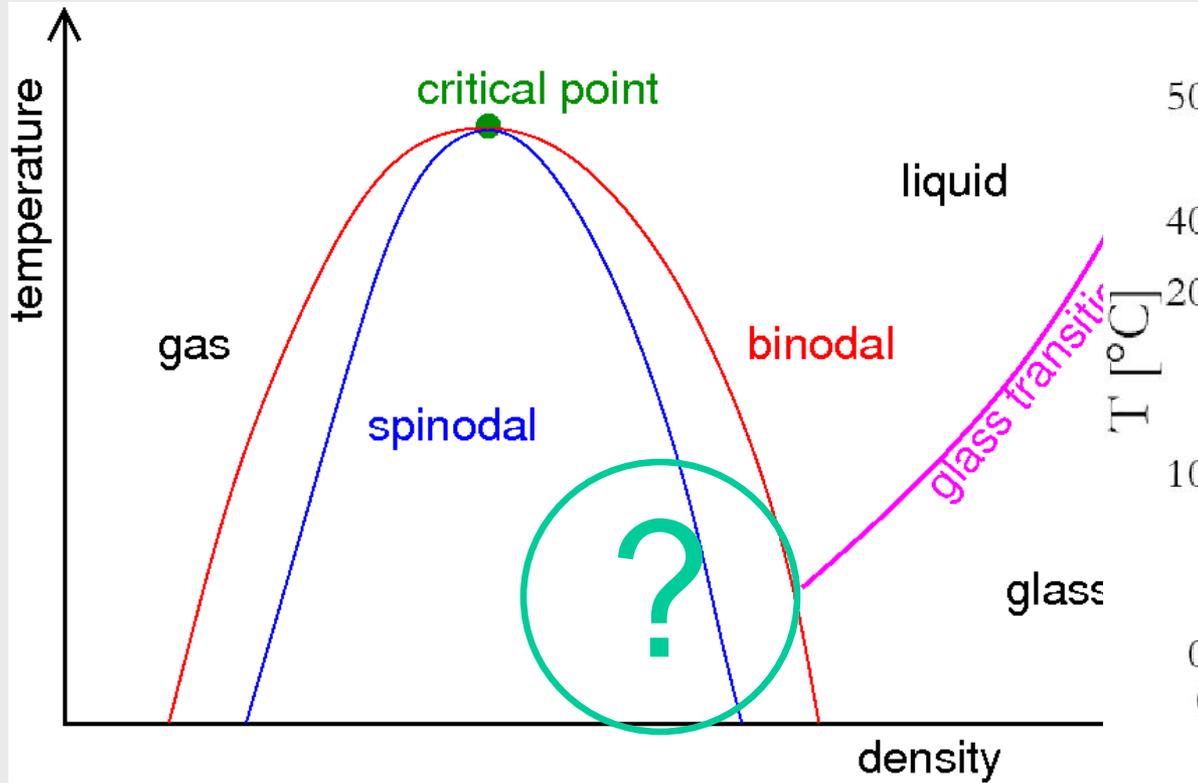


- disordered structure (=glass)
- structure is *open* (not like dense glasses)
- often soft
- complex rheological properties
- often produces via a chemical reaction (e.g. vulcanization) or...



Producing gels via spinodal decomposition

Phase diagram of a liquid



- What happens with the spinodal decomposition at low T's?
- What happens when the glass-transition line meets the binodal?

Experiments:

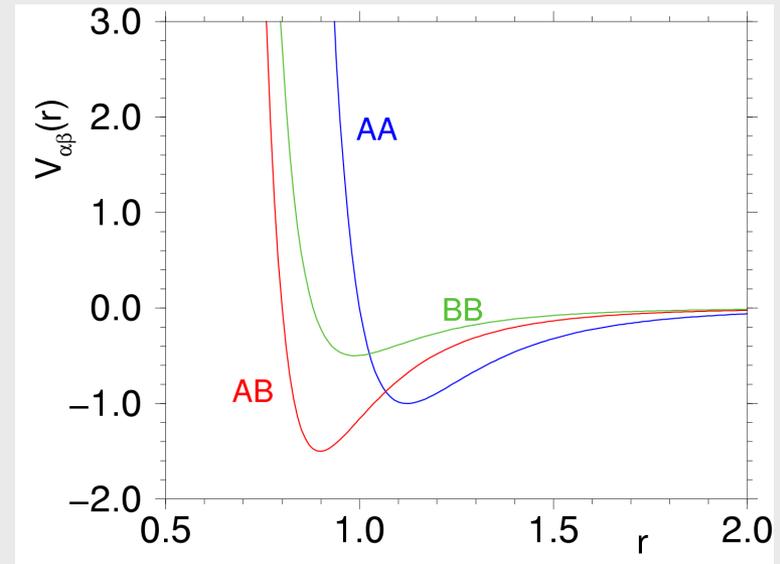
- Cardinaux et al. PRL 2007
- Lu et al. Nature (2008)

Our Glass-former (=Sample)

- Binary mixture of Lennard-Jones particles (model for $\text{Ni}_{80}\text{P}_{20}$, a metallic glass-former)

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

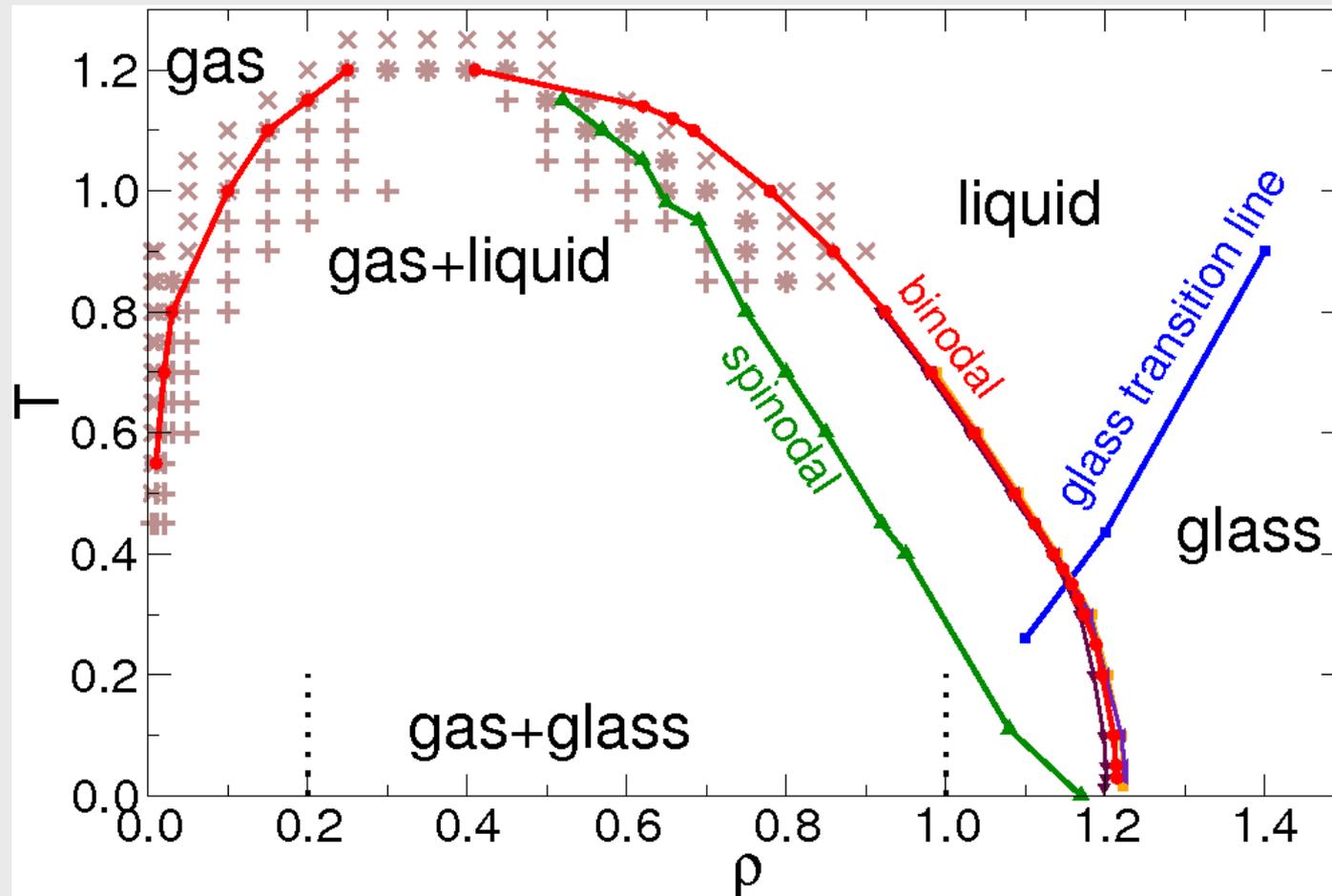
Parameters: $\epsilon_{AA} = 1.0$ $\epsilon_{AB} = 1.5$ $\epsilon_{BB} = 0.5$
 $\sigma_{AA} = 1.0$ $\sigma_{AB} = 0.8$ $\sigma_{BB} = 0.88$



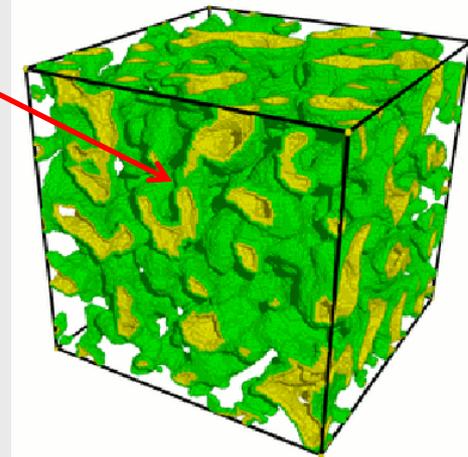
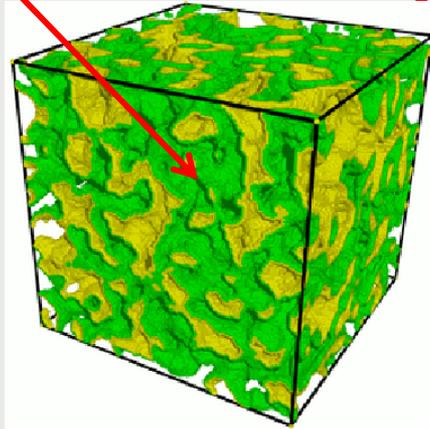
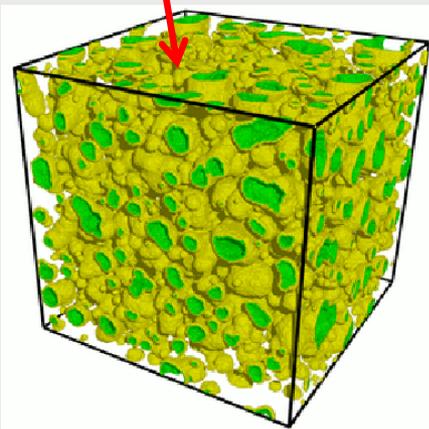
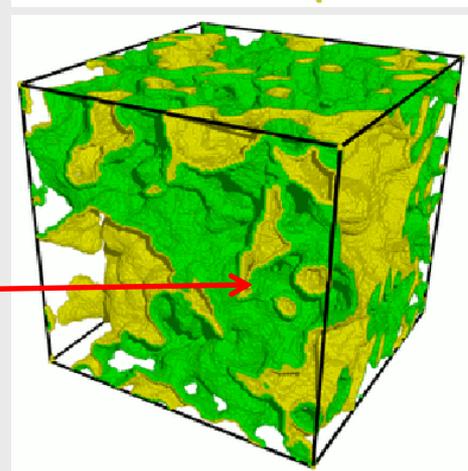
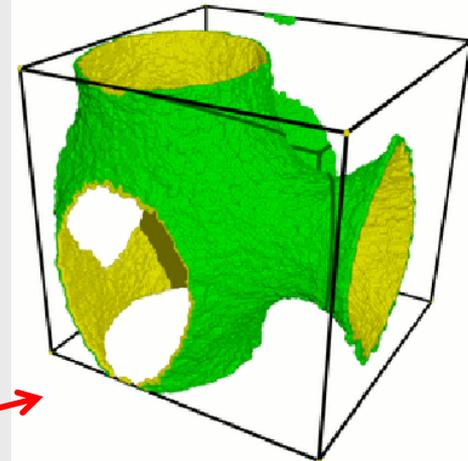
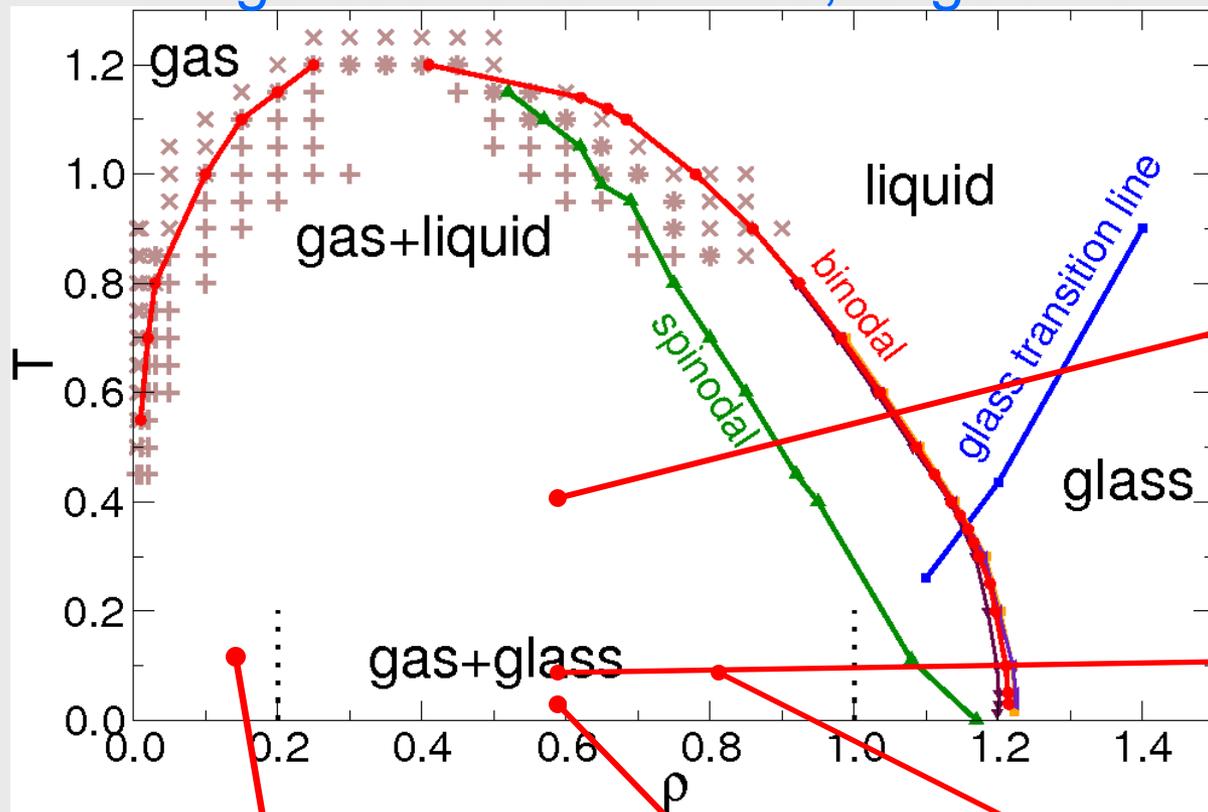
- System size: $N=8000, 49000, 300000, 10^6$

Phase diagram

- spinodal has been calculated by Sasty (PRL 2000)
- **binodal** is determined by $p=0$ simulations/quenches to low T 's
- **glass transition line** = Vogel-Fulcher line (Berthier et al. PRE 2010)

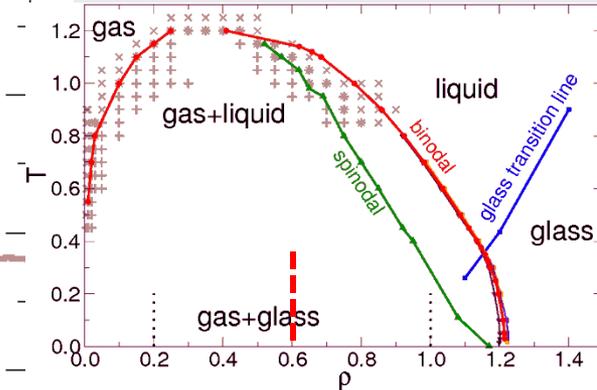
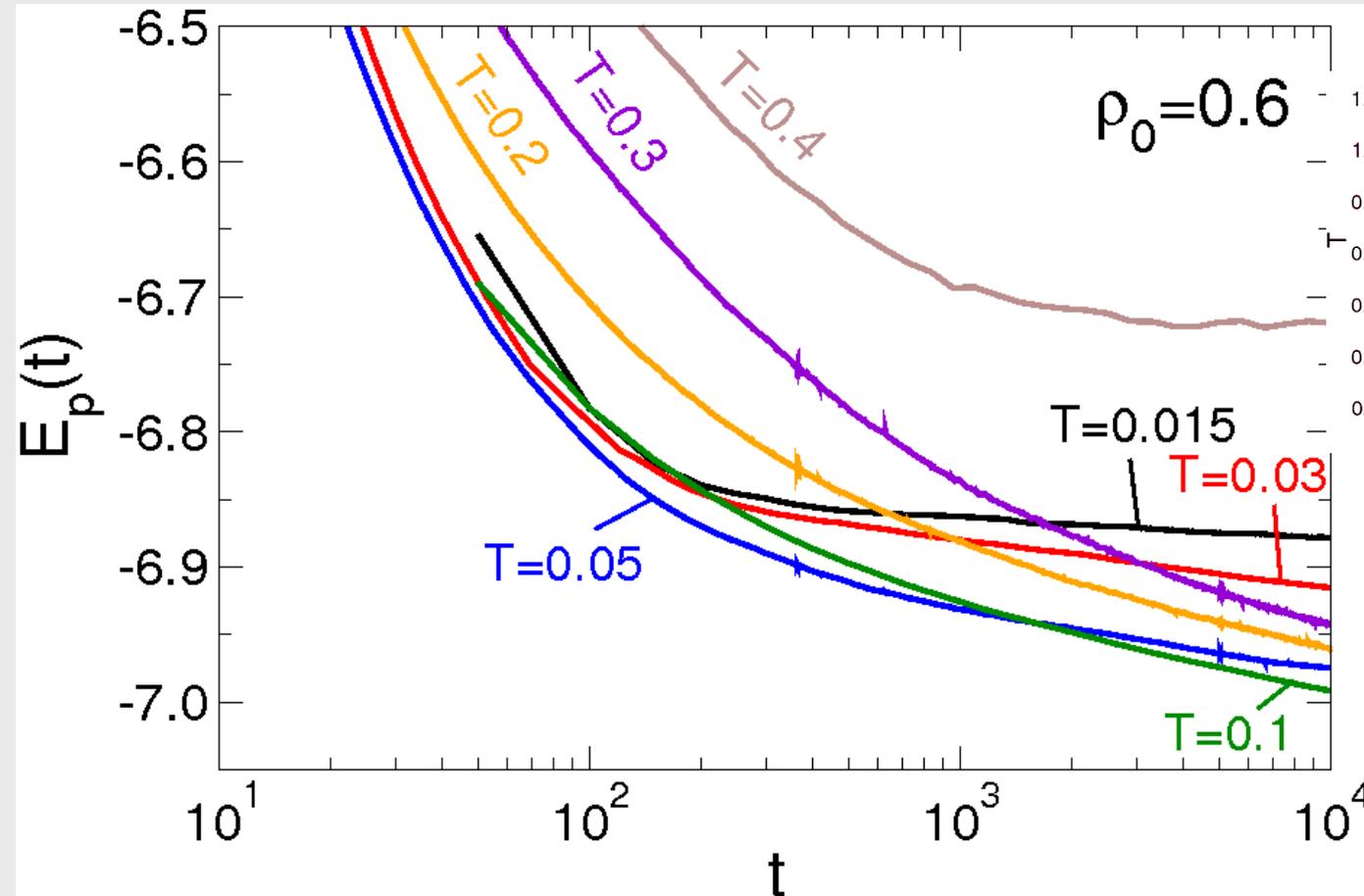


Configuration after a fixed, large time



Energy of the system

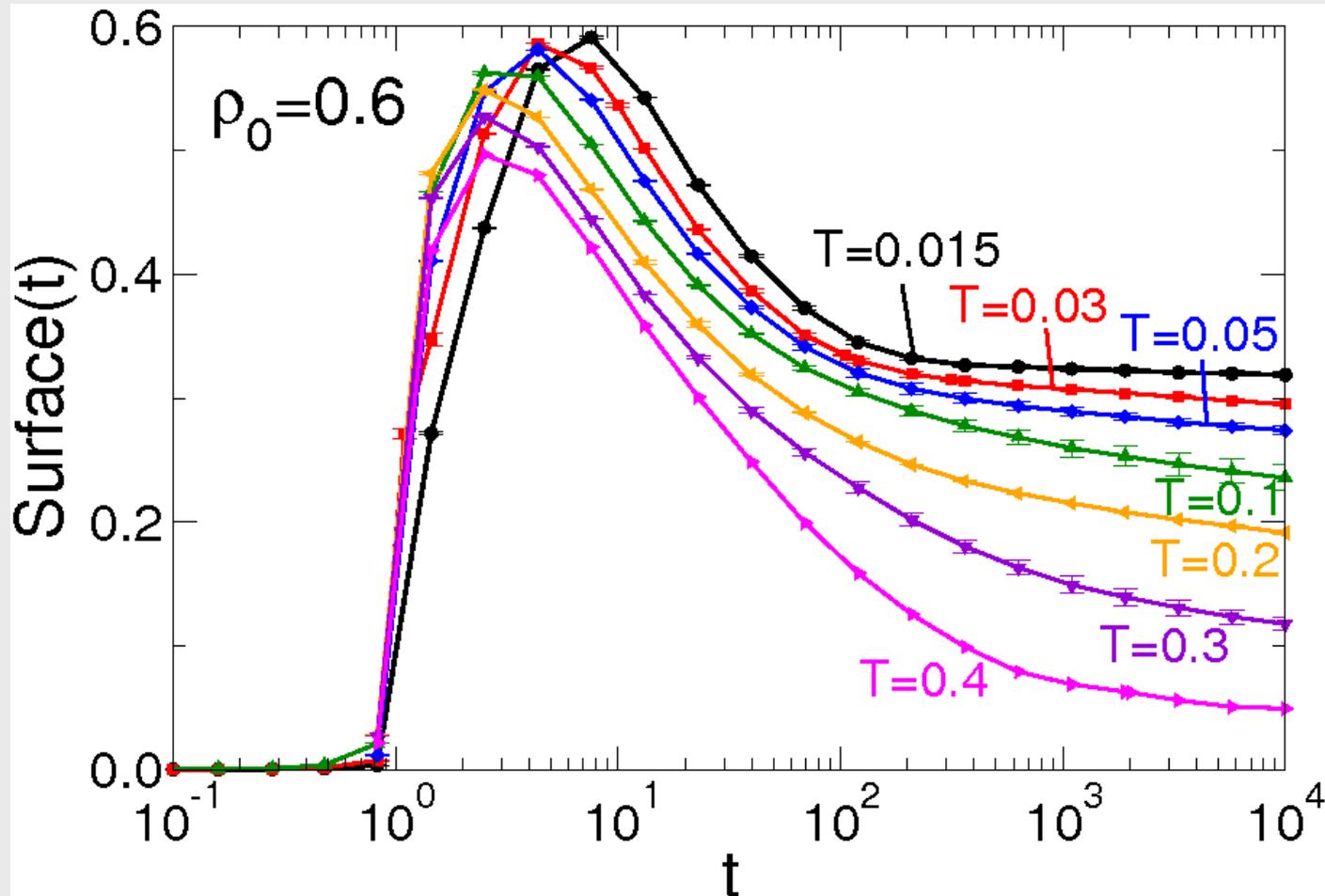
Look at potential energy as a function of time (after the quench)



- At intermediate temperatures E_p decreases with T
 - At low T , E_p increases with decreasing T
- ⇒ Competition between driving force and greediness

Total surface of the interface

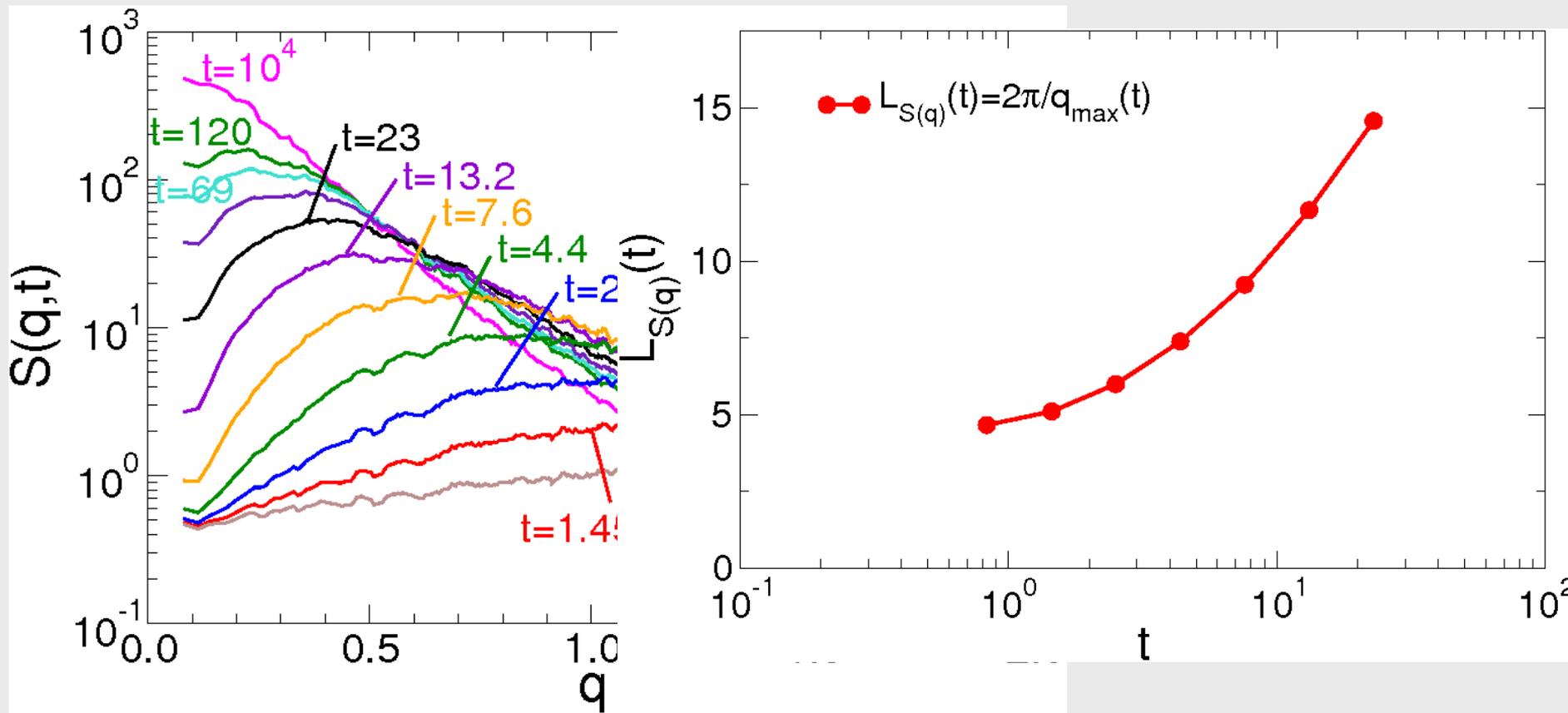
Look at surface of G-L interface as a function of time



- Non-monotonic t -dependence of $\text{Surface}(t)$
- At long times $\text{Surface}(t)$ increases with decreasing T (structure becomes more spongy)

Static structure factor

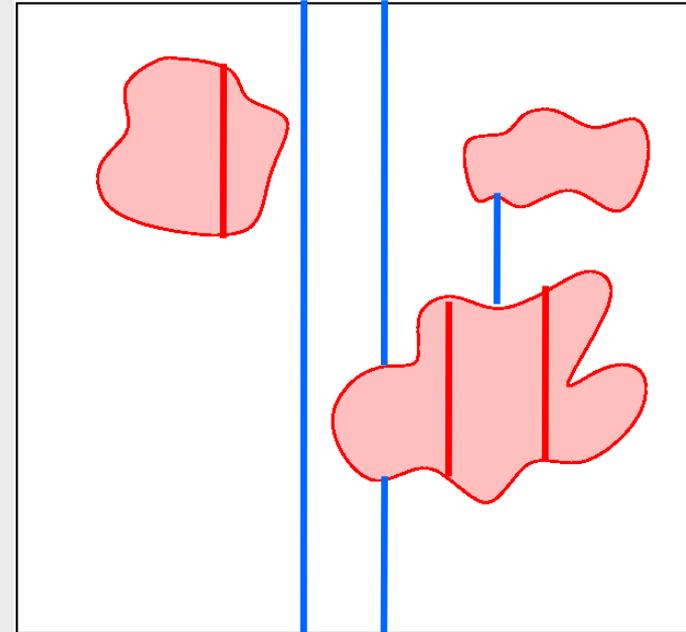
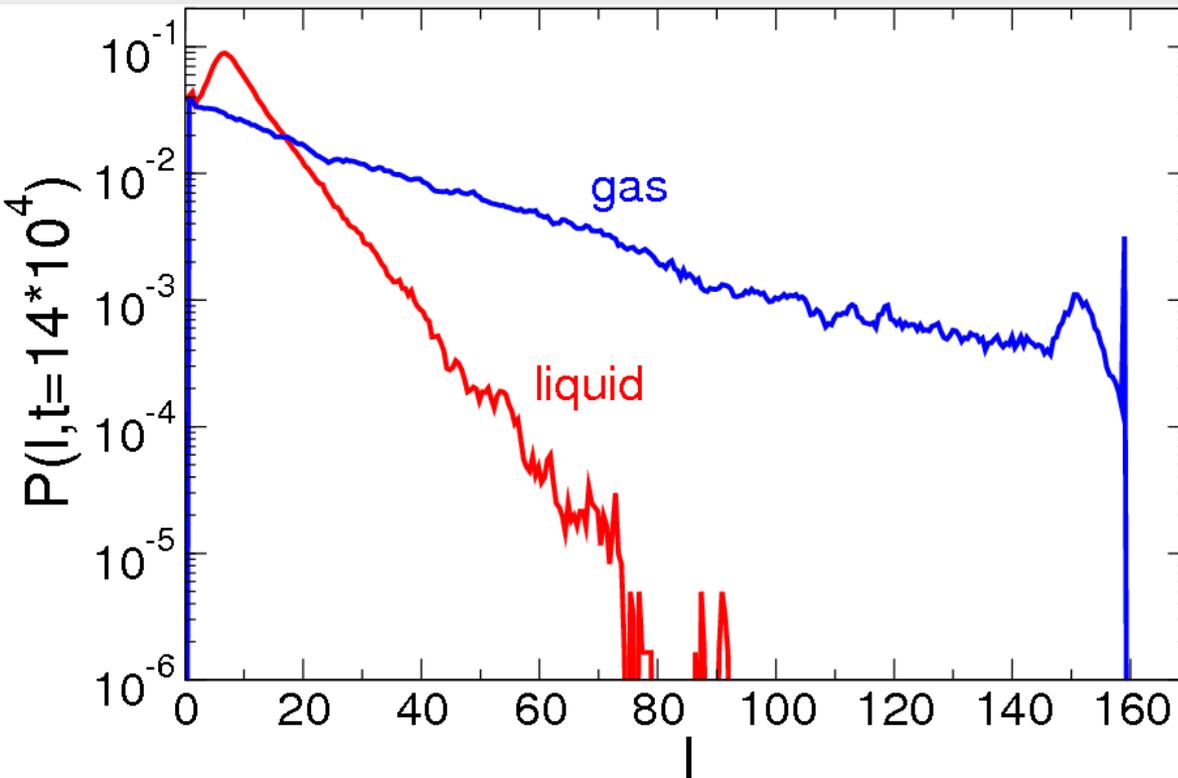
Experiments usually consider the first peak in the static *structure factor* to characterize the size of the domains



- Even for large systems ($N=300k$) it is hard to extract from $S(q,t)$ a length scale at long times

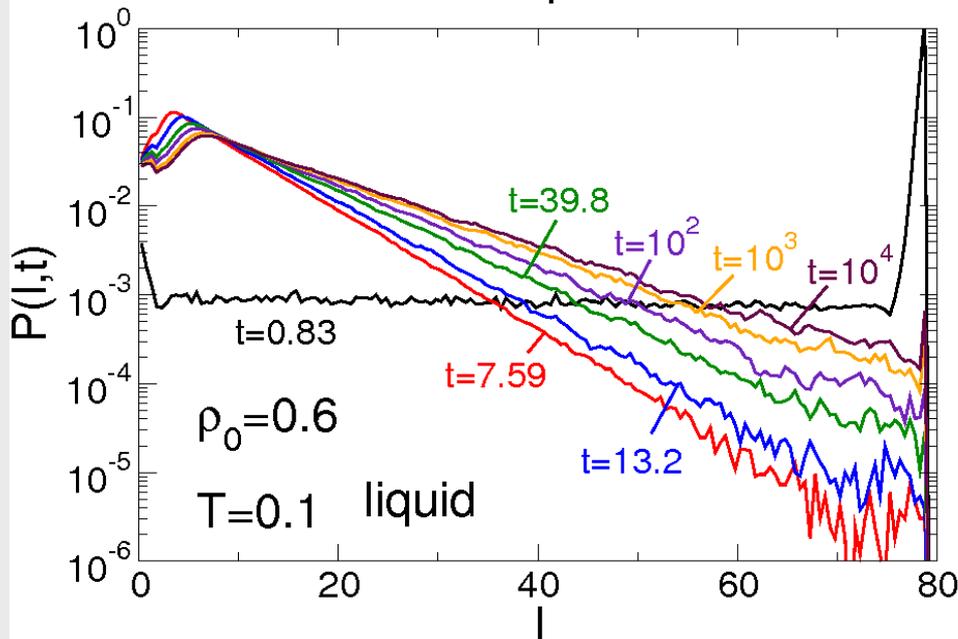
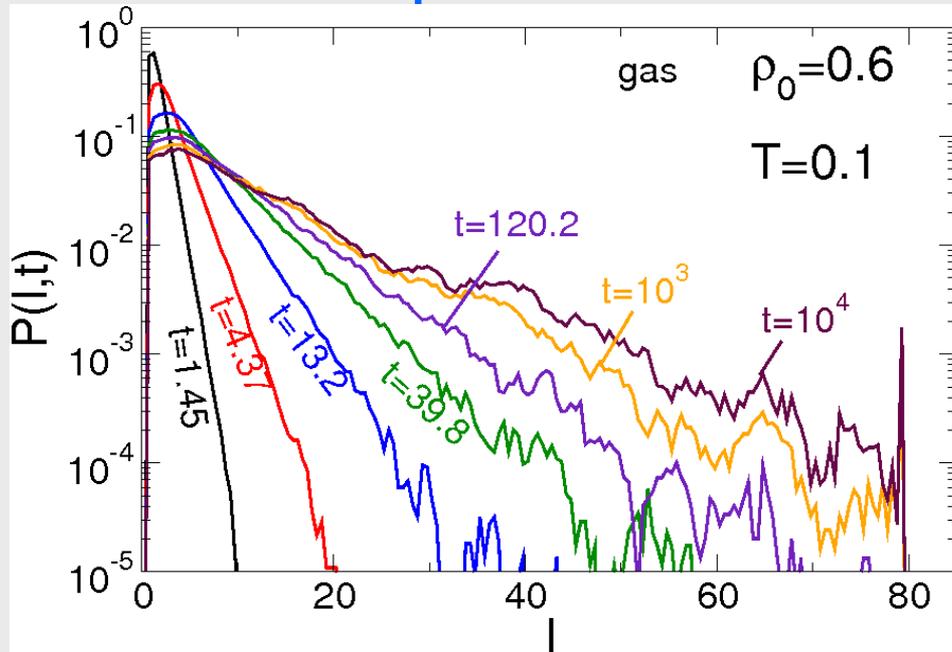
Chord length distribution

Define chords \Rightarrow chord length l
(for the liquid and the gas); P. Levitz



- Distribution $P(l, t)$
- $P(l, t)$ is at intermediate l given by an exponential
- Peak at large l is finite size effect
- Use first moment of $P(l, t)$ to define a length scale L

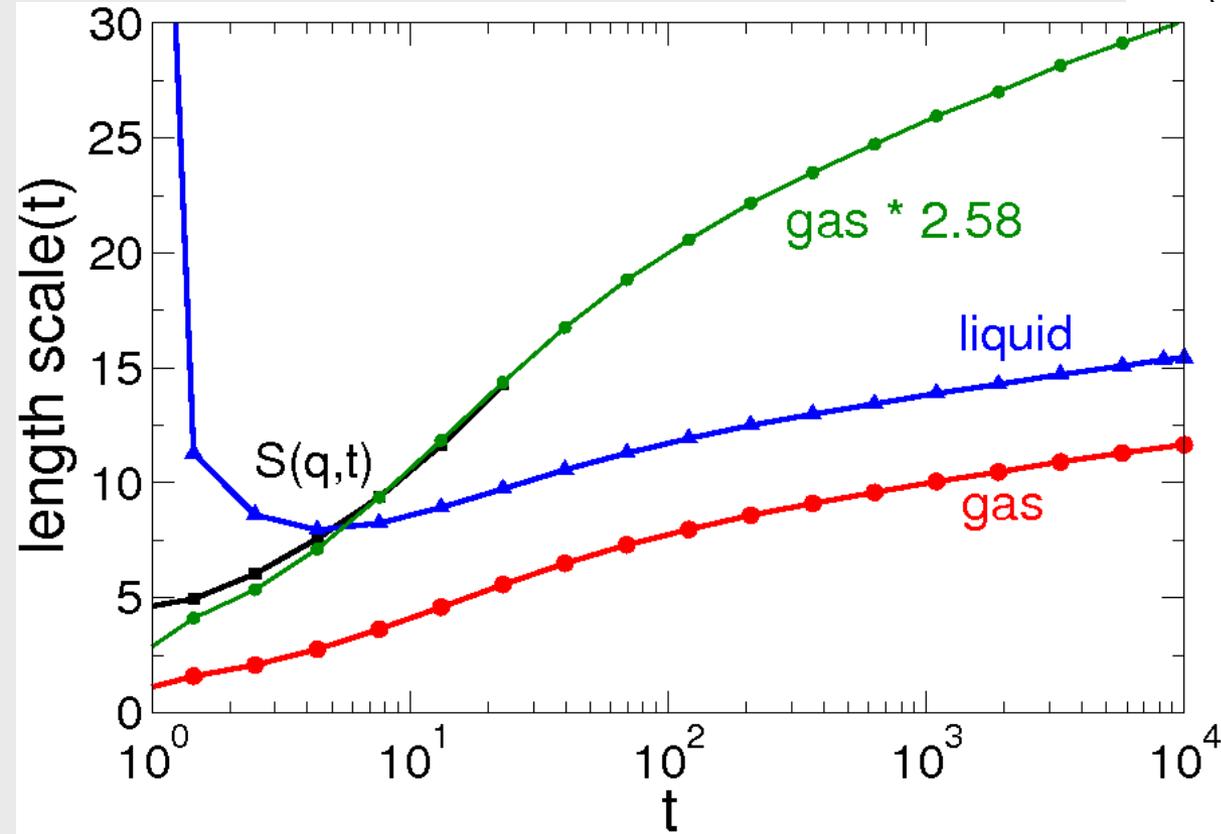
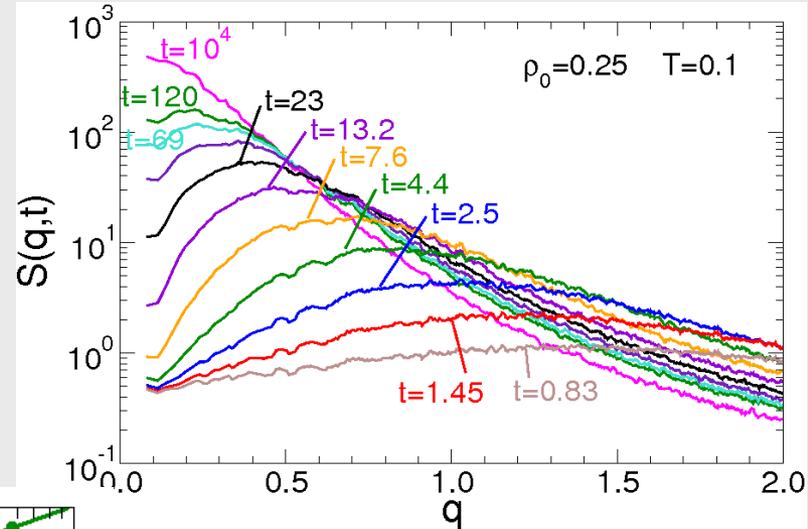
Time dependence of chord length distribution



- For all t the shape of $P(l,t)$ is the same
 \Rightarrow definition of length scale $L(t)$ via integral of $P(l,t)$ is reasonable
- Peak at large l is finite size effect, but is under control

Chord length distribution

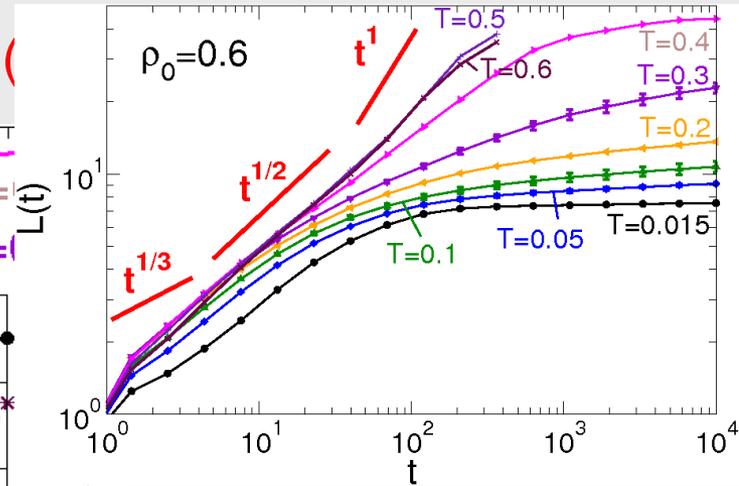
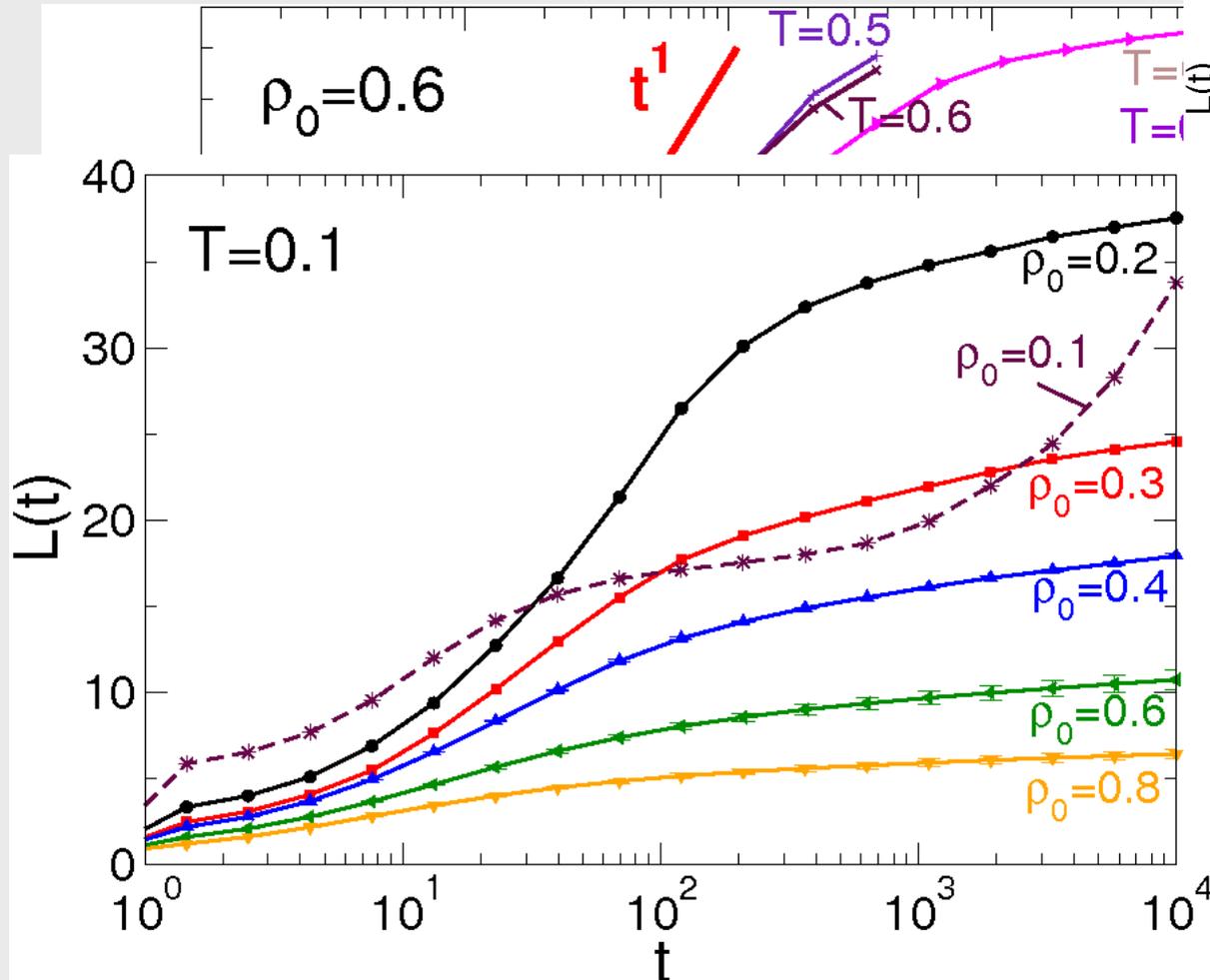
Compare $L(t)$ with length obtained from $S(q,t)$: $2\pi/q_{\max}$



- The two definitions give the same result
- Liquid and gas chord length show the same time dependence

Growth of length scale

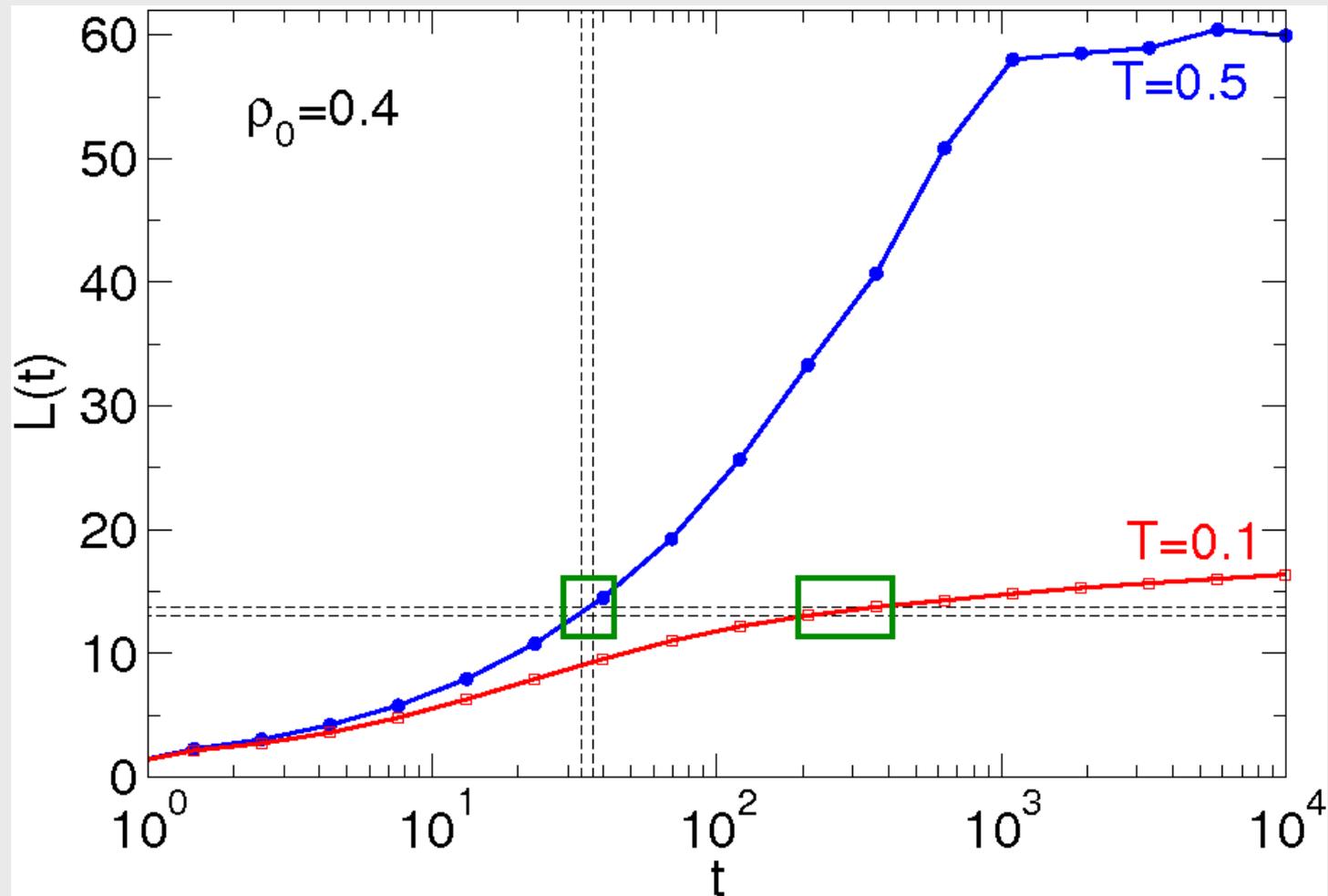
- Spinodal decomposition: growth of length depends on model (type of order parameter), dynamics, theory,...
- Usually $L(t) \propto t^\theta$ with $\theta=1/3$ (Kawasaki), $1/2$ (Cahn-Hilliard)



- ~~Not clear whether~~ power-laws give a good description of growth.
- At low T 's we rather see logarithmic growth; relation to visco-elastic effects?

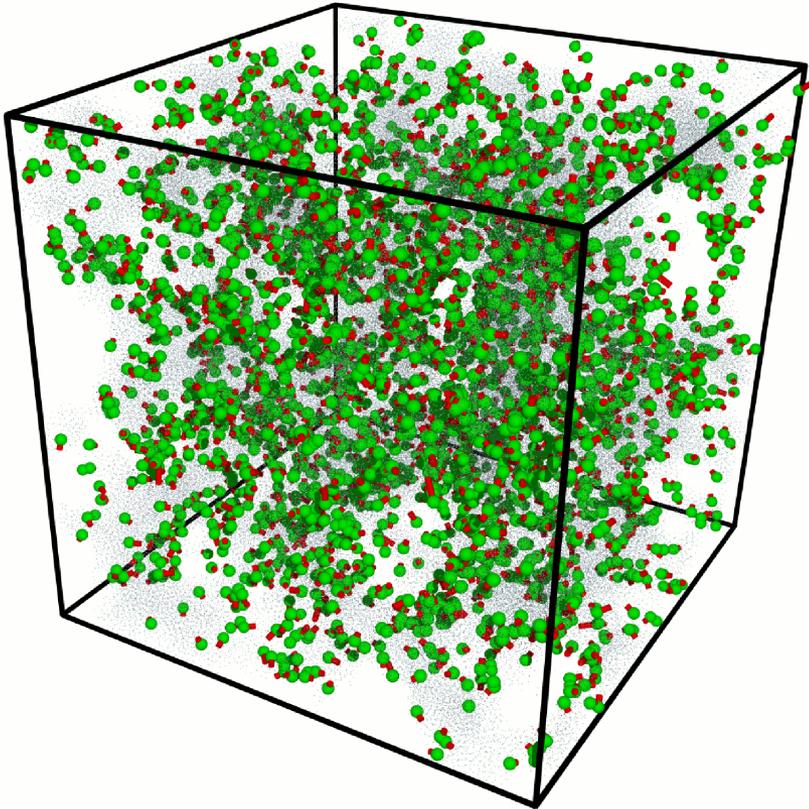
Relaxation mechanism

- How do the particles move during the spinodal decomposition?
⇒ Look at a *growth of fixed length scale*: $L \rightarrow L + \delta$



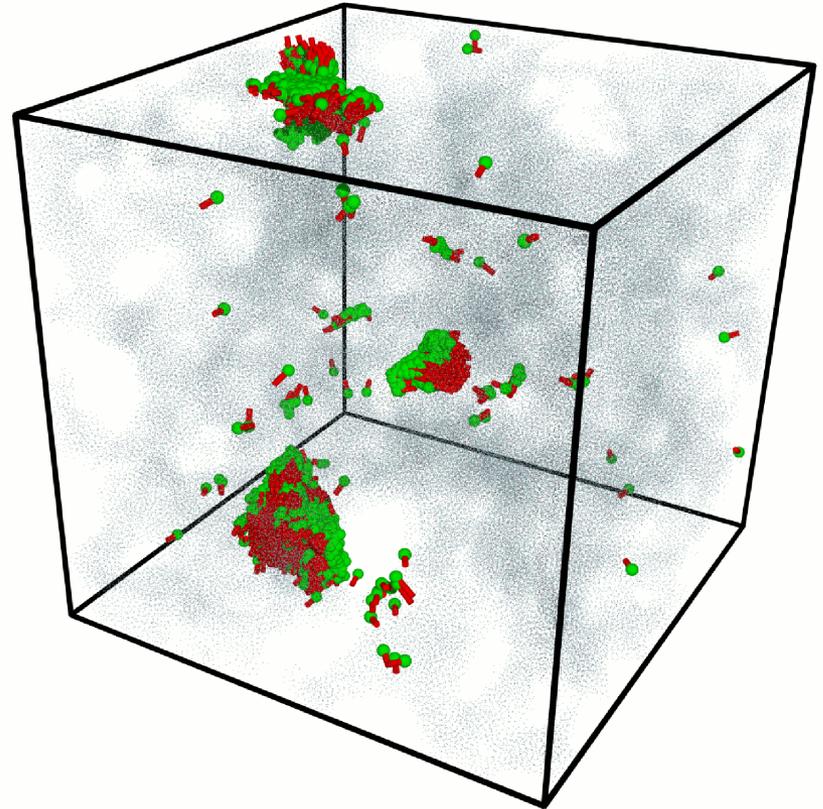
Relaxation mechanism 2

Displacement field of the fastest 3% of particles



$T=0.5$; $\rho_0 = 0.4$

Relaxation is quite homogeneous

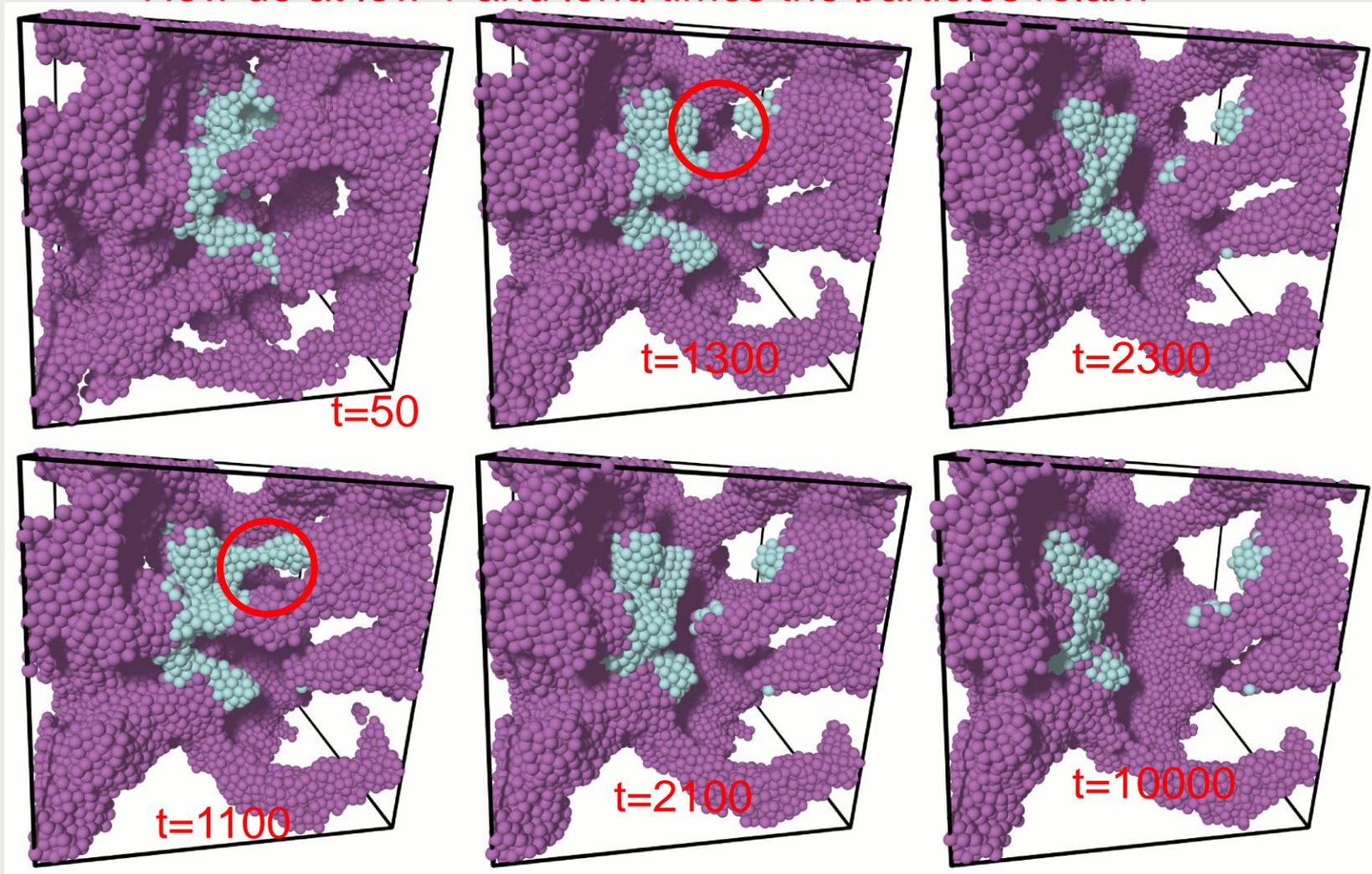


$T=0.1$; $\rho_0 = 0.4$

Relaxation is very heterogeneous

Relaxation mechanism 3

How do at low T and long times the particles relax?



- Arms are stretched and broken like in a very viscous fluid
- Relaxation of surface extremely slow \Rightarrow surface tension is no longer relevant

Summary

- Simulations of liquid-gas **spinodal decomposition of a simple glass former**
- For simulations static structure factor is not very helpful to characterize length scales \Rightarrow use **chord length distribution**
- At low T's the **time dependence of domain growth is very complex and not described by usual spinodal decomposition theories; need to include visco-elastic effects**
- At low T's the **relaxation events are very localized in space and time**
 \Rightarrow driving force for relaxation is the stored stress in the sample

Reference:

V. Testard, L. Berthier, and W. Kob, Phys. Rev. Lett. **106**, 125702 (2011);

VT, LB, and WK, J. Chem. Phys. **140**, 164502 (2014).