Separation and fractionation of order and disorder in highly polydisperse systems

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Objective

We study a polydisperse soft-sphere model for colloids and liquids by means of microcanonical Monte Carlo simulations in the high polydispersity region

Overview

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1. Introduction
2. Model and Particle Interaction
3. Simulation Algorithms

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4. Results

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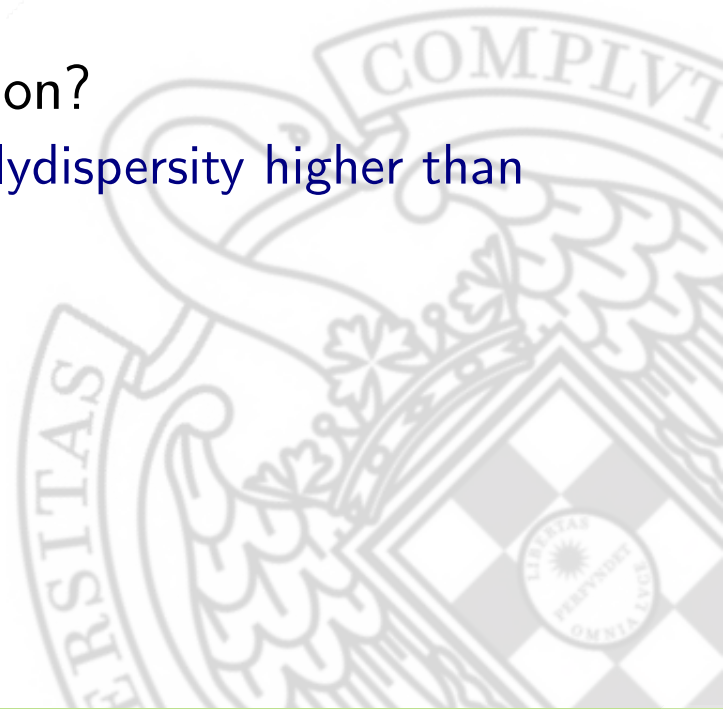
   In experiments, crystallization of samples of polydispersity higher than 12% is not found



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   $\Rightarrow$The so-called *terminal polydispersity scenario* states that above $\delta_t \sim 0.12$ crystal phase becomes thermodynamically unstable

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   - Density functional analysis$\Rightarrow$ amorphous
   - The moment free-energy approach$\Rightarrow$ *fractionation*
   - Recent numerical simulations found that there is a first-order fluid-solid transition at any polydispersity [Fernández et al., Phys. Rev. Lett. 98,085702 (2007)], though solid phase is complex

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   δ_t is purely a kinetic phenomenon

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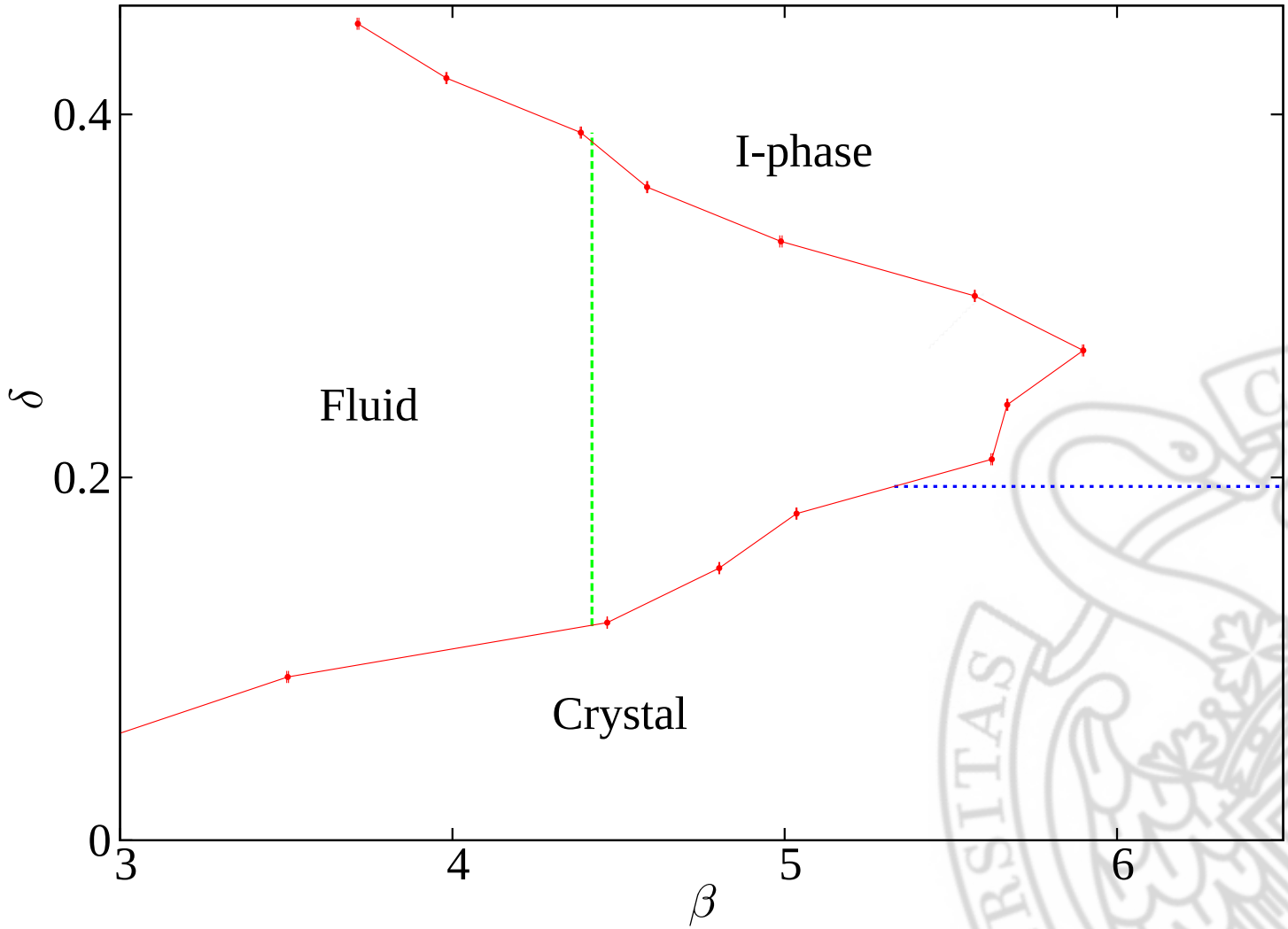
- Length units σ_0 ($\sigma_0 \sim 1\mu m$: colloids, $\sigma_0 \sim 10$Å: glass-forming liquids)
- Relevant thermodynamic parameter $\Gamma = \rho T^{-1/4}$ ($\rho = 1/\sigma_0^3$)

Phase Diagram [Fernández et al., Phys. Rev. Lett. **98**,085702 (2007)]



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- Total energy ($\boldsymbol{R} = \{\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N\}$)

$$\mathcal{E}(\boldsymbol{R}, \boldsymbol{P}) = \sum_{i=1}^{N} \frac{p_i^2}{2} + N\, u(\boldsymbol{R}), \qquad e = \mathcal{E}(\boldsymbol{R}, \boldsymbol{P})/N$$

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- Microcanonically, the entropy density

$$\begin{aligned} e^{Ns(e,N)} &= \int_{-\infty}^{\infty} \prod_{i=1}^{N} \mathrm{d}p_i \sum_{\{\boldsymbol{r}_i\}} \delta\left(Ne - \mathcal{E}(\boldsymbol{R}, \boldsymbol{P})\right) \\ &= \frac{(2\pi N)^{N/2}}{N\Gamma(N/2)} \sum_{\{\boldsymbol{r}_i\}} (e-u)^{\frac{N}{2}-1} \theta(e-u) \end{aligned}$$

Microcanonical MC

- Microcanonical average at fixed e [R. Lustig, J. Chem. Phys. **109**, 8816(1998)]

$$\langle O \rangle_e = \frac{\sum_{\{\boldsymbol{r}_i\}} O(e, \{\boldsymbol{r}_i\})(e-u)^{\frac{N}{2}-1}\theta(e-u)}{\sum_{\{\boldsymbol{r}_i\}} (e-u)^{\frac{N}{2}-1}\theta(e-u)}$$

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- Inverse temperature [V. Martin-Mayor, Phys. Rev. Lett. **98**, 137207(2007)]

$$\beta(e) = \frac{s(e,N)}{\mathrm{d}e} = \left\langle \frac{N-2}{2N(e-u)} \right\rangle_e$$

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- The canonical probability density for e is $\exp\{N[s(e,N) - \beta e]\}$

$$\log P_\beta^{(L)}(e_2) - \log P_\beta^{(L)}(e_1) = N \int_{e_1}^{e_2} \mathrm{d}e\, (\beta(e) - \beta)$$

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- In the thermodynamically stable region $\left(\frac{\mathrm{d}\beta(e)}{\mathrm{d}e}\right) < 0$, and a single root $\beta(e) = \beta$

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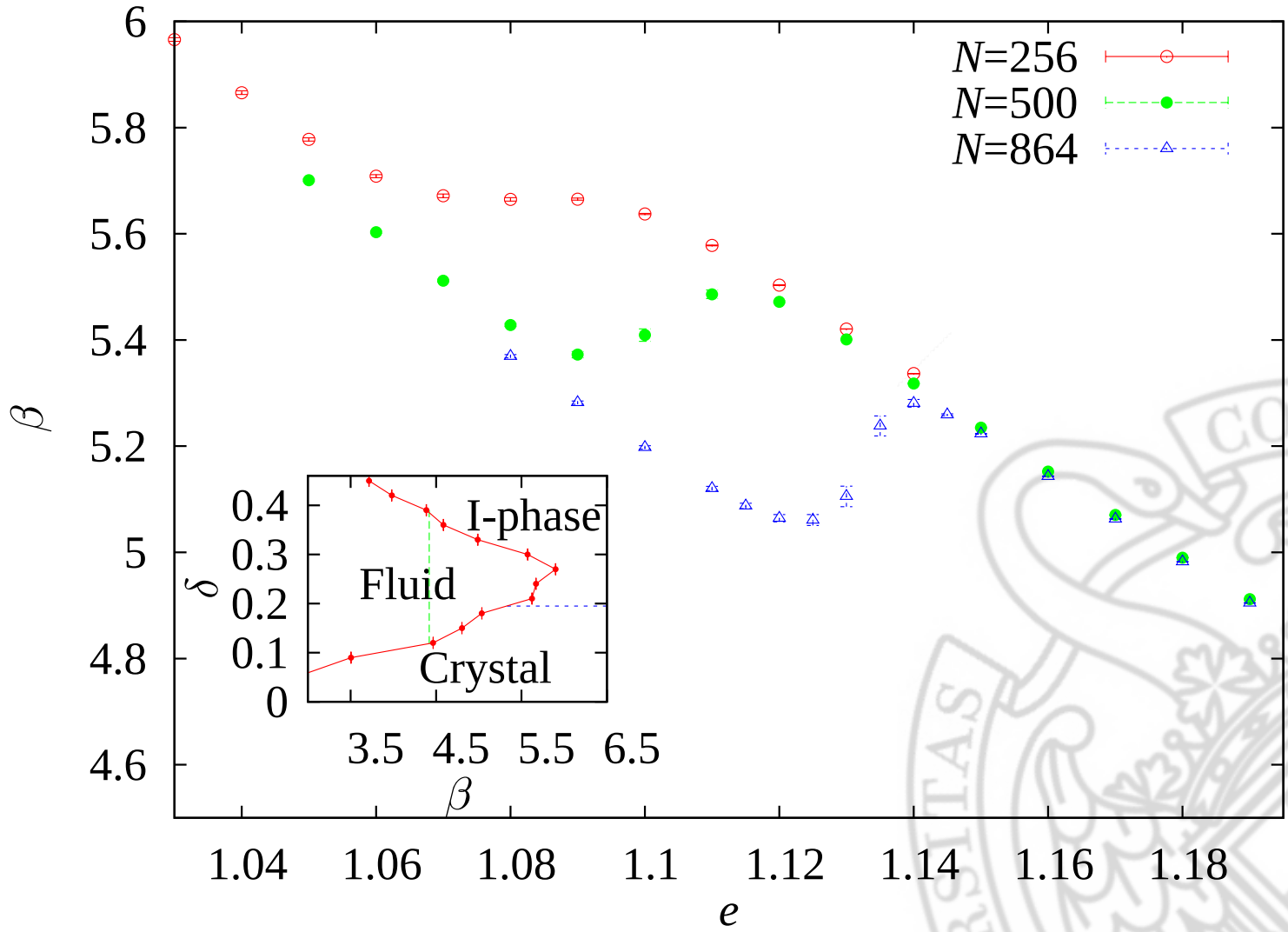

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$$P^{(L)}_{\beta_{\mathrm{c}}^{N}}(e_N^{\mathrm{L}}(\beta_{\mathrm{c}}^{N})) = P^{(L)}_{\beta_{\mathrm{c}}^{N}}(e_N^{\mathrm{S}}(\beta_{\mathrm{c}}^{N})) \Rightarrow 0 = \int_{e_N^{\mathrm{S}}(\beta_{\mathrm{c}}^{N})}^{e_N^{\mathrm{L}}(\beta_{\mathrm{c}}^{N})} \mathrm{d}e \left(\beta(e) - \beta_{\mathrm{c}}^{N}\right)$$

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- The surface tension

$$\Sigma^{L} = \frac{N}{2L^{2}} \int_{e^{*}(\beta_{\mathrm{c}}^{N})}^{e_{N}^{\mathrm{L}}(\beta_{\mathrm{c}}^{N})} \mathrm{d}e \left(\beta(e) - \beta_{\mathrm{c}}^{N}\right)$$

Maxwell construction $\Rightarrow$

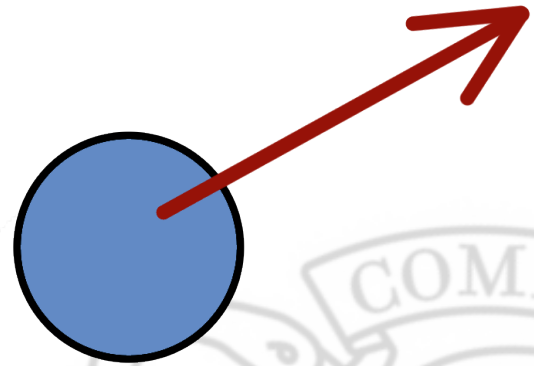
- Critical temperature

$$\beta_c^N = \beta_c^\infty + a_1/N \Rightarrow \beta_c^\infty = 4.624(2) \Rightarrow \Gamma_c^\infty = 1.4664(15)$$

Independently, $\Gamma_g = 1.455(5)$ Transition is *below* the glass transition, dynamically difficult!!

Particle moves

1. Single particle moves



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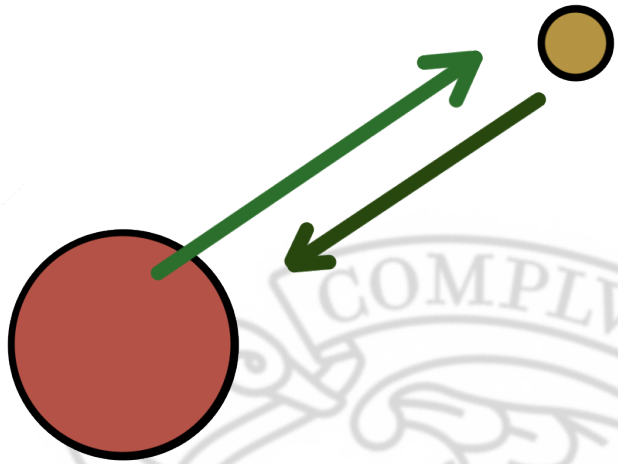

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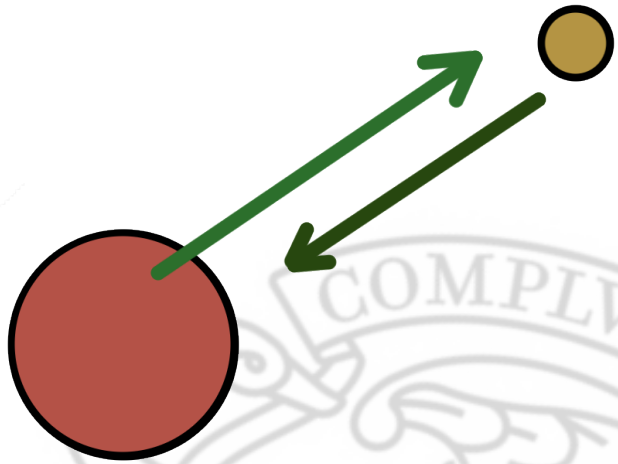

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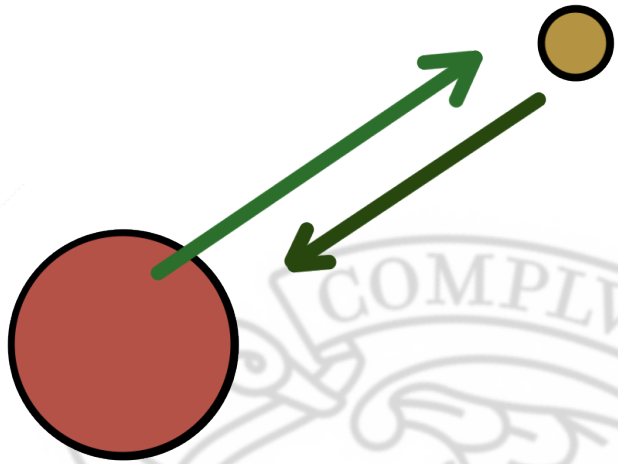

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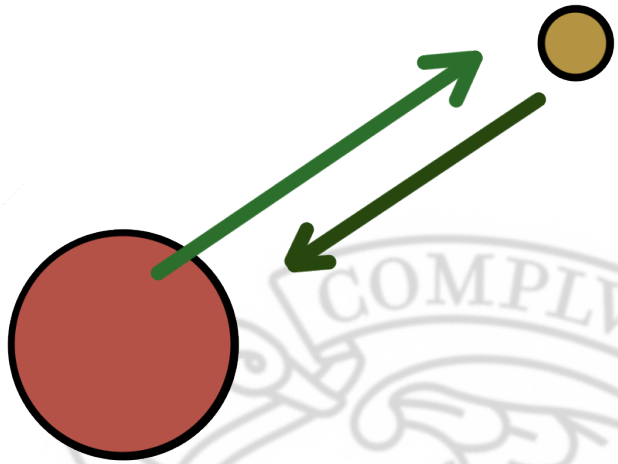

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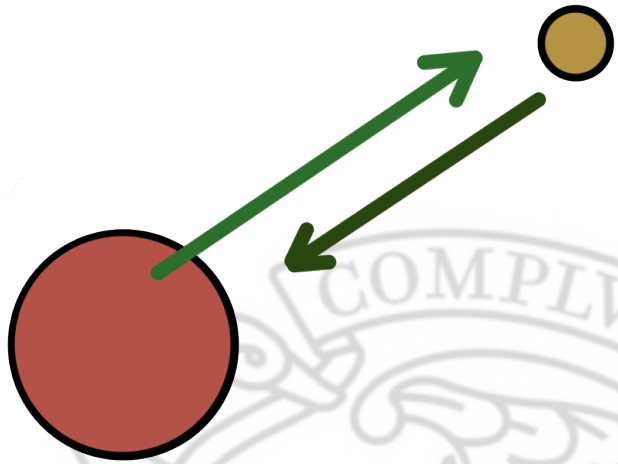

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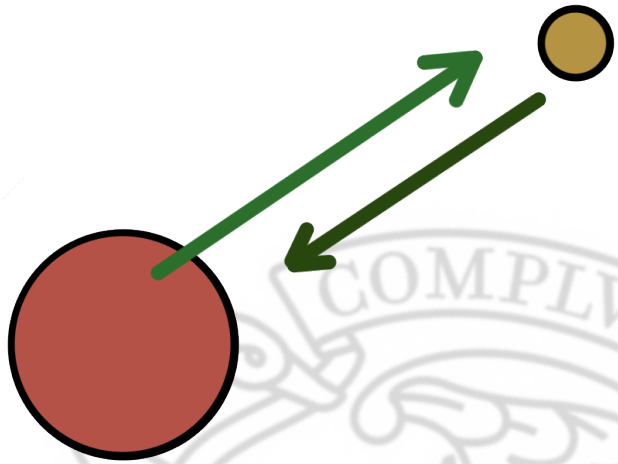

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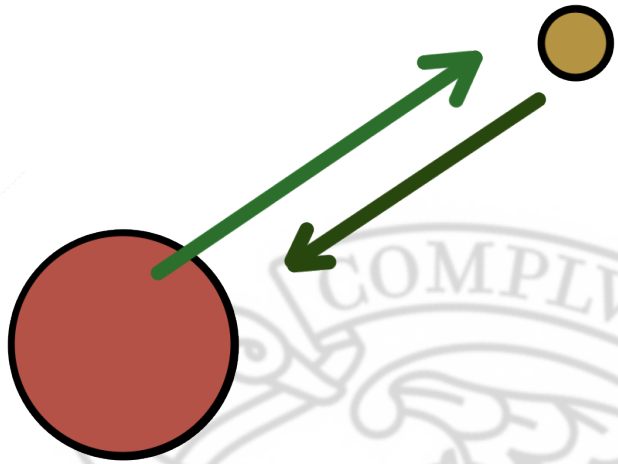
     - Interchange only similar size particles $\Rightarrow$ increase the acceptance
     - Preferred not too similar interchanges $\Rightarrow$ accelerate the dynamics



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- Once in a while, we interchange the particle configurations of two neighbouring energies with probability

$$A\left(\{e_1, \boldsymbol{r}_1\}, \{e_2, \boldsymbol{r}_2\} \rightarrow \{e_1, \boldsymbol{r}_2\}, \{e_2, \boldsymbol{r}_1\}\right) =$$
$$\min\left[1, \left[\frac{(e_1 - u(\boldsymbol{r}_2))(e_2 - u(\boldsymbol{r}_1))}{(e_1 - u(\boldsymbol{r}_2))(e_2 - u(\boldsymbol{r}_2))}\right]^{\frac{N}{2}-1} \theta\left(e_1 - u(\boldsymbol{r}_2)\right)\theta\left(e_2 - u(\boldsymbol{r}_1)\right)\right]$$

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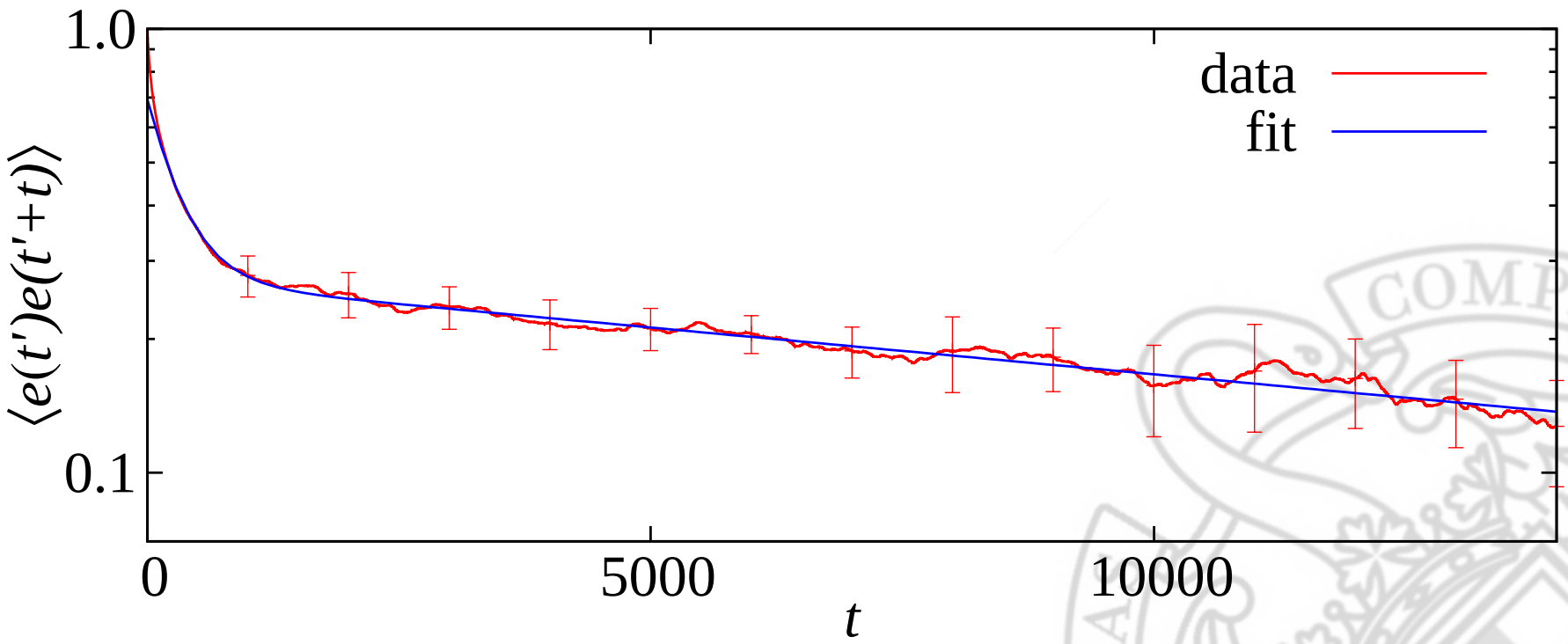
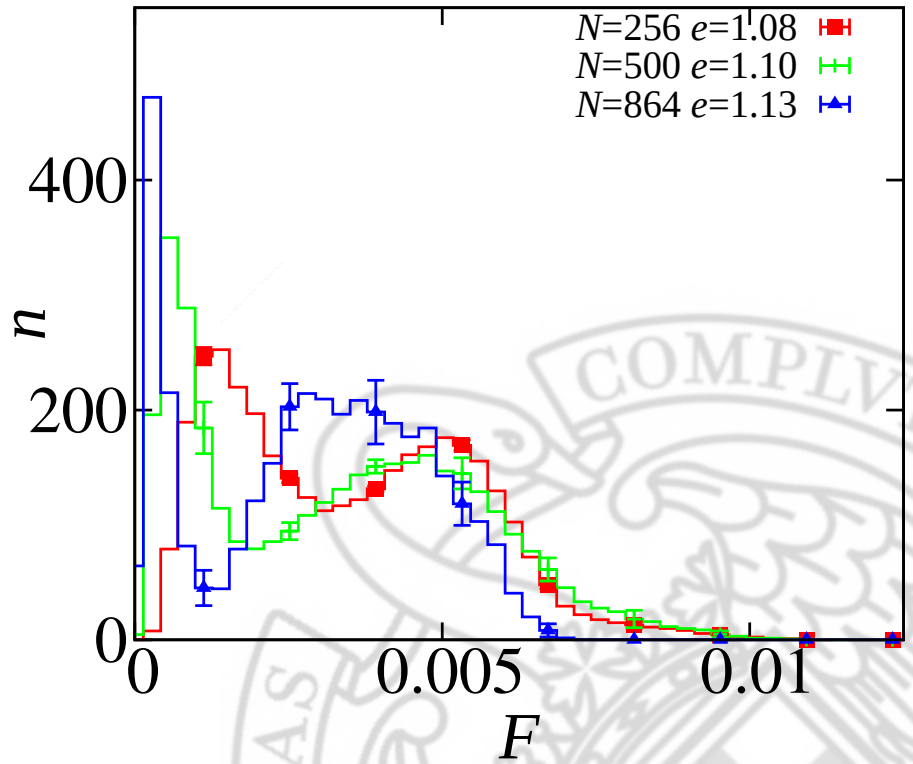


Density fluctuations of length L

$\mathcal{F} \equiv [\mathcal{S}(2\pi/L, 0, 0) + \text{ permutations}]/3$

where

$$\mathcal{S}(\boldsymbol{q}) = \left| \sum_i e^{i\boldsymbol{q}\cdot\boldsymbol{r}_i}/N \right|$$



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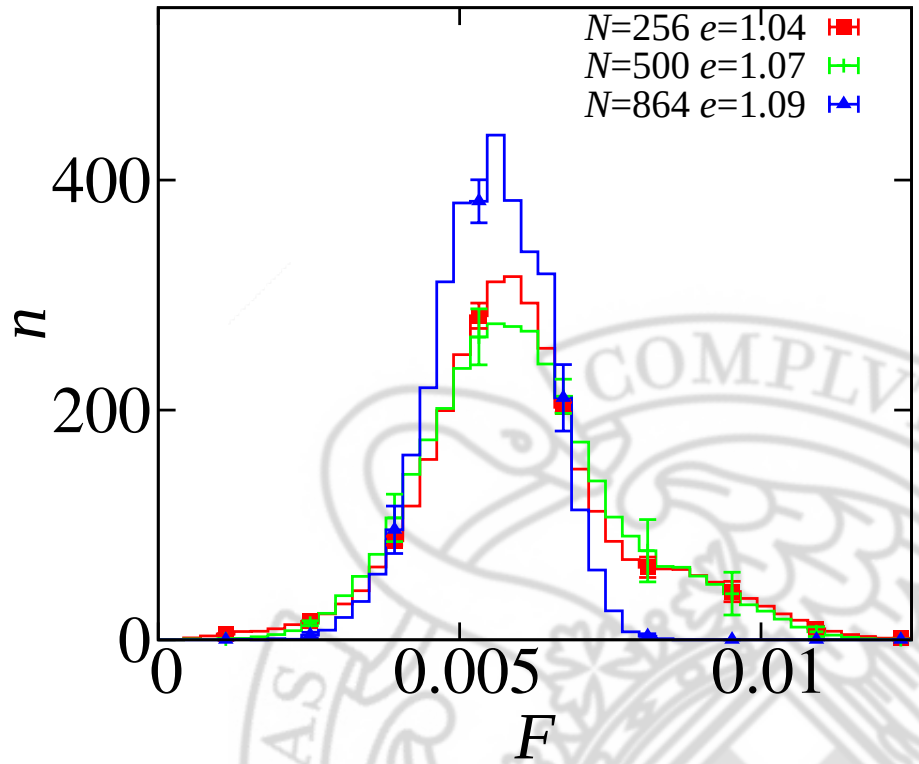
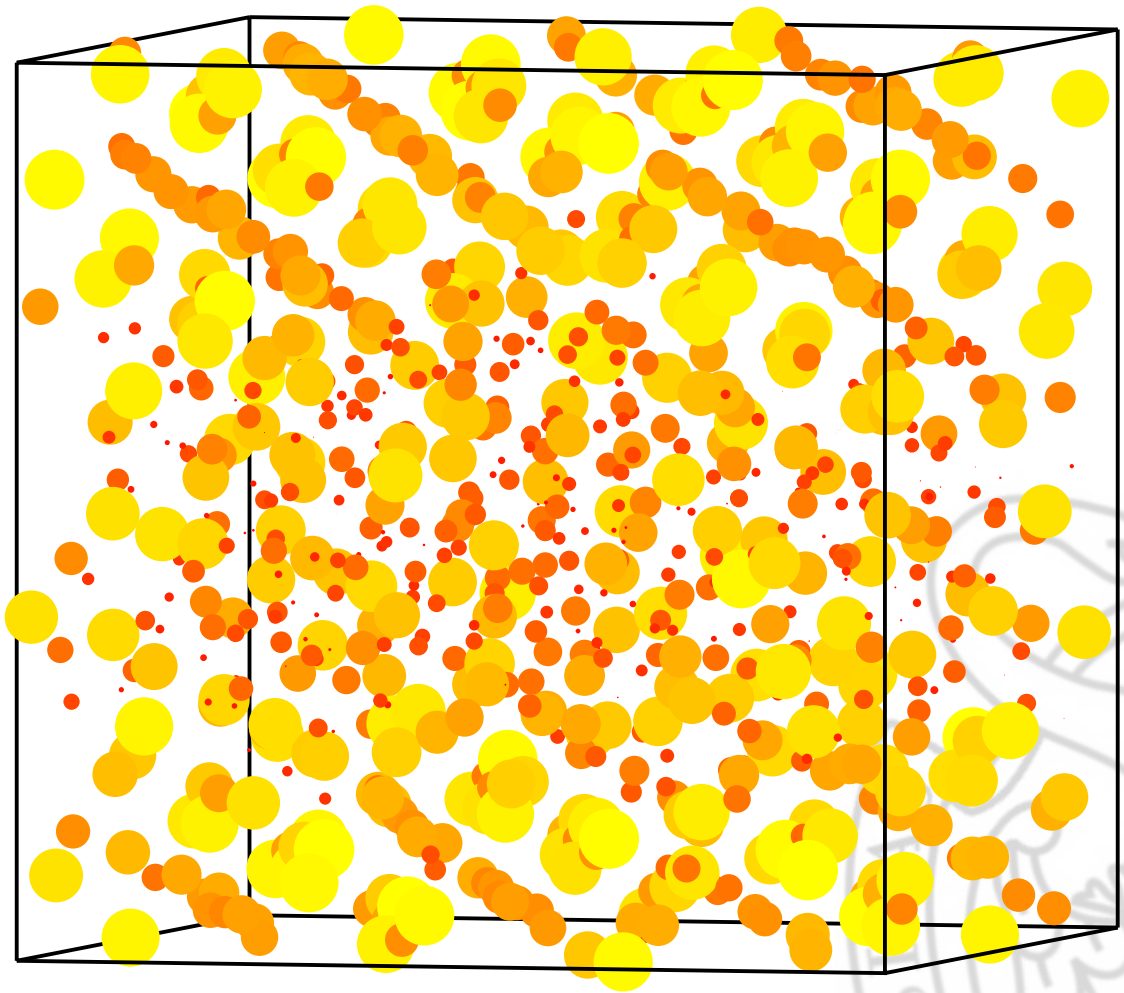


Crystallization and fractionation



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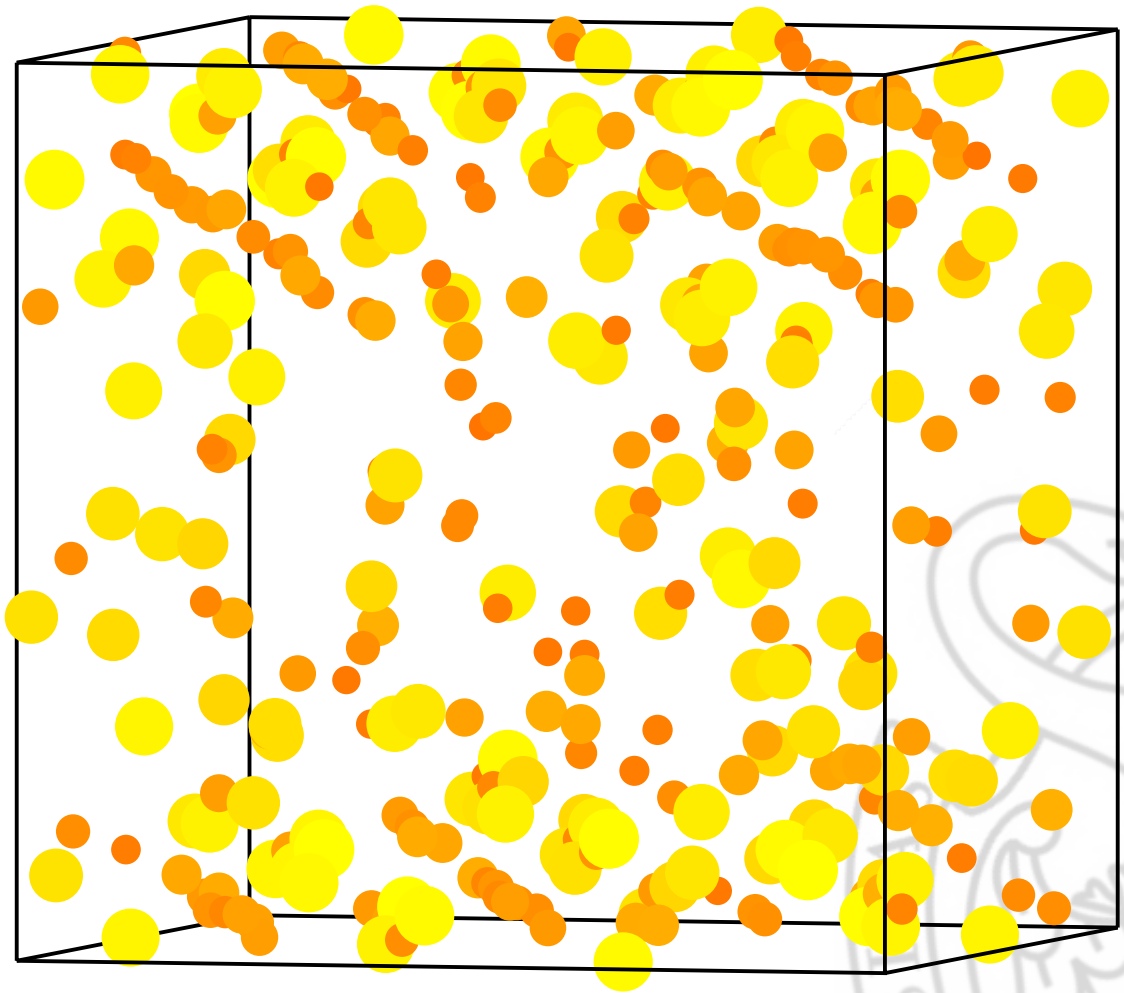

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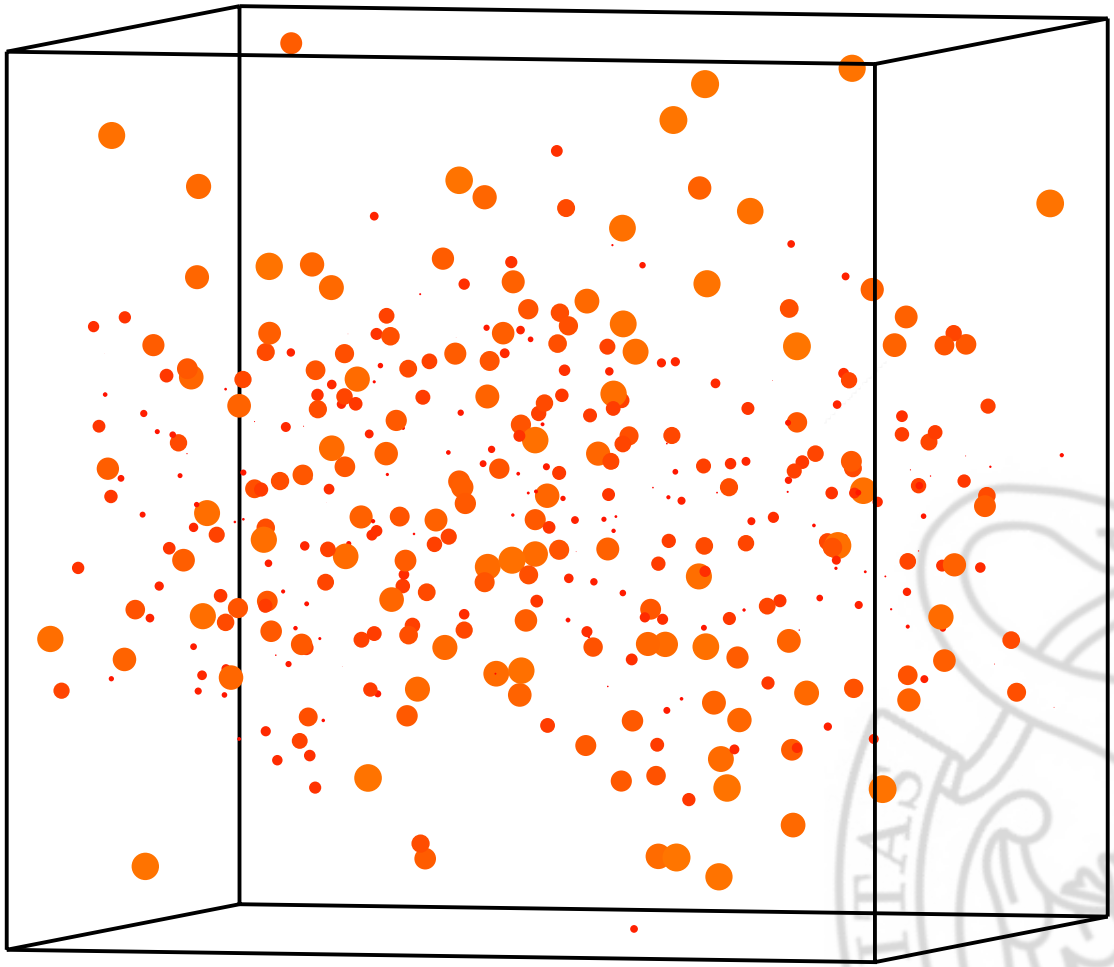
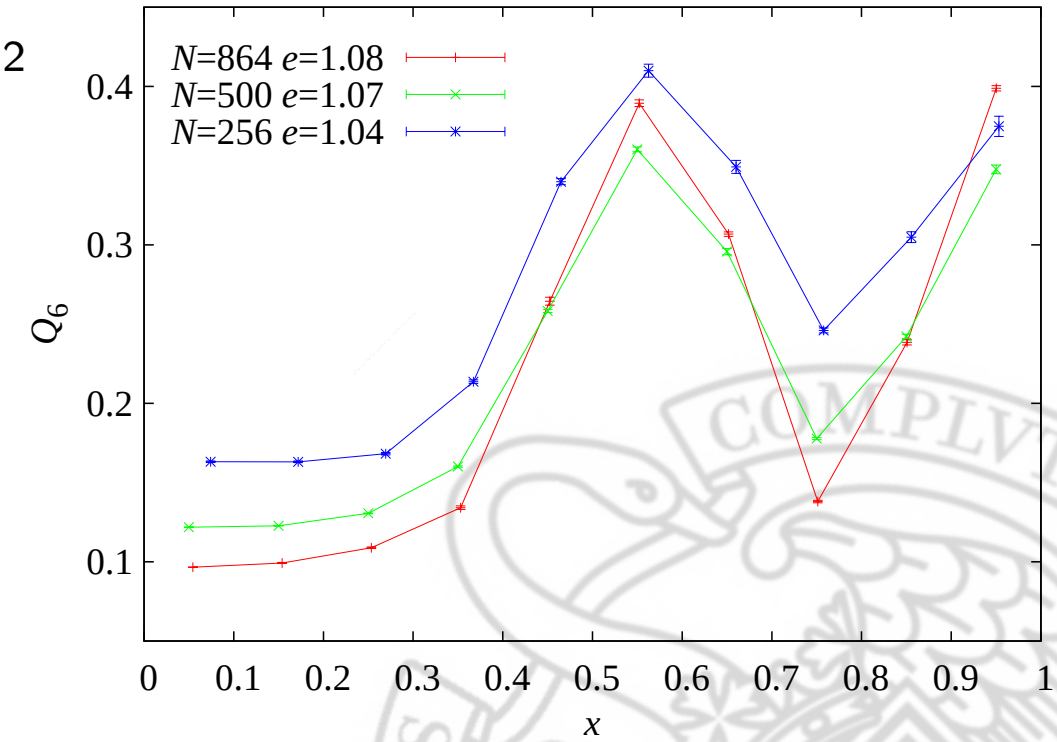


Crystal ordering

$$Q_l(x) \equiv \left(\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |Q_{lm}(x)|^2 \right)^{1/2}$$

$$Q_{lm}(x) \equiv \frac{\sum_{\sigma_i \in \mathcal{I}(x)} q_{lm}(i)}{\sum_{\sigma_i \in \mathcal{I}(x)} N_b(i)}$$

$$q_{lm}(i) \equiv \sum_{j=1}^{N_b(i)} Y_{lm}(\hat{r}_{ij})$$



[P. R. ten Wolde *et al.*, J. Chem. Phys. **104**, 9932(1996)]

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- Such phase-separation is preceded by the dynamic glass transition.
- Small and big particles arrange themselves in the two phases according to a complex pattern not predicted by any *fractionation* scenario.