Nucleation and Crystallization of the Metastable Hard Sphere Fluid - Master Colloquium

Wilkin Wöhler,
Albert-Ludwigs-Universität Freiburg

May 13, 2021

Content

- Introduction
  - Metastable hard sphere fluid
  - Memory effects in non-stationary processes
  - Nucleation rate discrepancy
- Simulation scheme and testing
- Cluster growth rate
- Nucleation rate
  - Definition
  - Estimation
  - Comparison
- Memory kernel shape analysis

The Hard Sphere Fluid

- Simplest model of a fluid

$$V(r_{ij}) = \begin{cases} \infty & r_{ij} \leq \sigma \\ 0 & r_{ij} > \sigma \end{cases}$$

- Experimentally and theoretically studied
- Liquid-Solid phase transition
  - $\eta_{RCP} \approx 64\%$, $\eta_{HCP} \approx 74\%$
  - Entropy increase

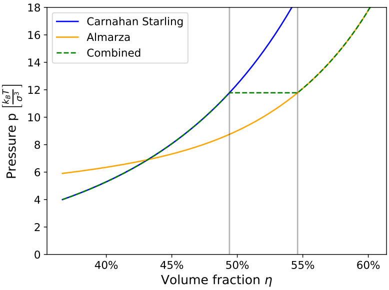


Fig.: Carnahan-Starling[1], Almarza[2] and equilibrium equation of state

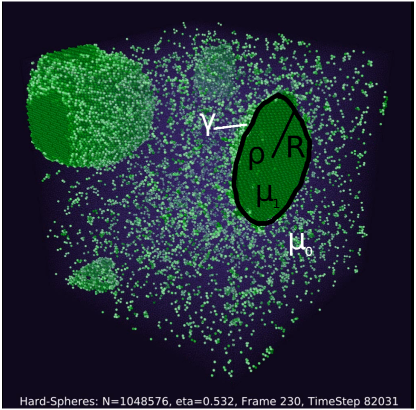
Nucleation and Crystallization - Phase Transitions

- Technological and scientific importance
- Commonly described by classical nucleation theory

- Other Approaches
  - Modifying the free energy landscape
  - Markovian reaction coordinates
  - Memory effects

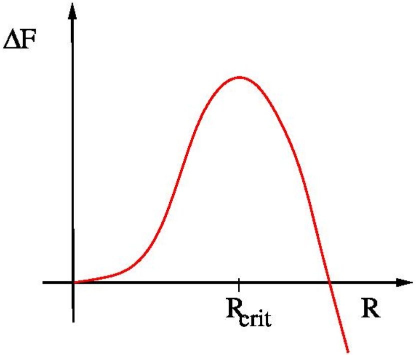
Classical Nucleation Theory (CNT)

- Spherical clusters
- Coarse grained observable R
- $\Delta F = 4\pi R\gamma_{fs} - \frac{4\pi}{3}R^3\rho\,\Delta|\mu|$
- Markovian fluctuations
- Nucleation rate $\kappa \propto \exp\left(-\frac{\Delta F}{k_B T}\right)$



Classical Nucleation Theory (CNT)

- Spherical clusters
- Coarse grained observable R
- $\Delta F = 4\pi R \gamma_{fs} - \frac{4\pi}{3} R^3 \rho \Delta|\mu|$
- Markovian fluctuations
- Nucleation rate $\kappa \propto \exp\left(-\frac{\Delta F}{k_B T}\right)$



Nucleation and Crystallization - Phase Transitions

- Technological and scientific importance
- Commonly described by classical nucleation theory
  $\rightarrow$ qualitatively correct
  $\rightarrow$ quantitatively not accurate

- Other Approaches
  - Modifying the free energy landscape
  - Markovian reaction coordinates
  - Including memory effects

Memory Effects Nucleation Processes

Earlier work in the group:

- Memory effects observed in Lennard-Jones nucleation, Anja[3]
- Non-stationary generalized Langevin equation, Hugues[4]

$$\frac{dA_t}{dt} = \omega(t)A_t + \int_0^t K(\tau, t)A_\tau d\tau + \eta_{0,t}$$

- Non-Markovian kernel in the Lennard-Jones nucleation, Philipp P.[5]

This work:

- Memory kernel of hard sphere nucleation process

Nucleation Rate Discrepancy

- Steeper decrease in simulations
- Possible differences:
  1. Hydrodynamics
  2. Sedimentation
  3. Polydispersity
  4. Measurement geometry
  5. ...

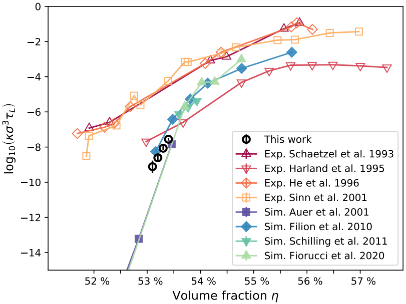


Fig.: Experimental and theoretical nucleation rates [6–13]

Simulation Scheme and Testing

Event driven molecular dynamics (EDMD)

- Discontinuous potential
- Resolve dynamics
- Based on analytical-
  - ballistic trajectory
  - collision time
  - collision outcome

- Validated dynamics by diffusion
- Cell system
  $\Rightarrow \mathcal{O}(N)$ calculation effort

Simulation Scheme and Testing

Event driven molecular dynamics (EDMD)

- Discontinuous potential
- Resolve dynamics
- Based on analytical-
  - ballistic trajectory
  - collision time
  - collision outcome
- Validated dynamics by diffusion
- Cell system
  $\Rightarrow \mathcal{O}(N)$ calculation effort

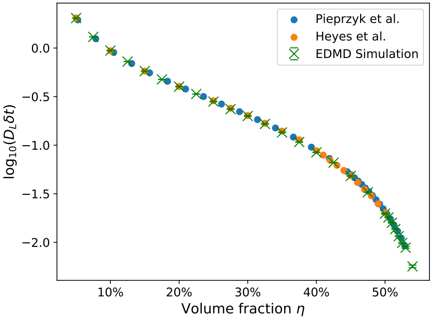


Fig.: Logarithmic plot of long time diffusion constant [14, 15]

Simulation Scheme and Testing

Event driven molecular dynamics (EDMD)

- Discontinuous potential
- Resolve dynamics
- Based on analytical-
  - ballistic trajectory
  - collision time
  - collision outcome
- Validated dynamics by diffusion
- Cell system
  $\Rightarrow \mathcal{O}(N)$ calculation effort

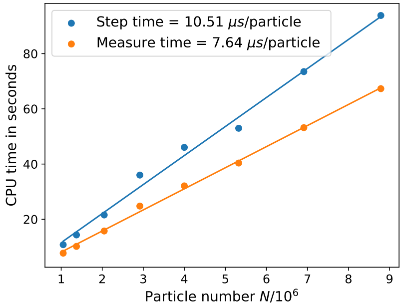


Fig.: CPU time per simulation step

Choice of Data Production Parameters

- $\mathcal{O}(N)$ calculation effort

$$\Rightarrow \frac{\delta T_{\text{CPU}}}{\delta t_{\text{Sim.}}} \propto N \propto V$$

- Without initial induction time

$$\Rightarrow \langle \tau_{\text{Nucleation}} \rangle \propto \frac{1}{V}$$

- Time to nucleation

$$\Rightarrow \langle T_{\text{CPU}} \rangle \propto \frac{\delta T_{\text{CPU}}}{\delta t_{\text{Sim.}}} \cdot \langle \tau_{\text{Nucleation}} \rangle \propto \text{const.}$$

$\Rightarrow$ Large system sizes possible

Cluster Growth - Constant Attachment Rate

- Constant attachment rate $\Rightarrow R \propto t$
- Spherical growth $\Rightarrow V \propto R^3 \propto t^3 \quad \Rightarrow N(t) = c^3(t - t_0)^3$

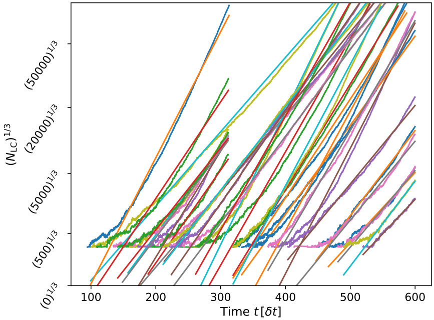


Fig.: Third root of the number of particles in the largest cluster

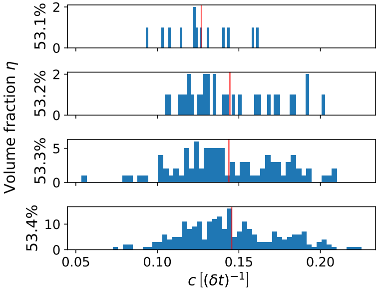


Fig.: Comparison of growth rates in the constant attachment regime.

Nucleation Time Distribution

Assume simulation geometry and $\kappa(t) = \text{const.}$

- N subvolumes of size V_{box}
- $n(t)$ nucleated boxes

$$\langle \Delta n \rangle = (N - n(t))\, V_{\text{box}} \kappa \, \Delta t$$

- In the continuous limit of $N \to \infty$ with $V_{\text{box}} \kappa = k$

$$\Leftrightarrow x_s = \frac{n(t)}{N} = 1 - \exp\left(-t\, k\right)$$
$$\Leftrightarrow \dot{x}_s = k \exp\left(-t\, k\right)$$

$\Rightarrow$ Exponentially distributed nucleation times

Nucleation Rate Estimator I - Maximum Log-Likelihood Estimator

- Probability Density Function of censored exponential distribution

$$p(t) = \begin{cases} k \exp(-t\,k) & t < T \\ \exp(-T\,k) & t \geq T \end{cases}$$

- Likelihood of measurement

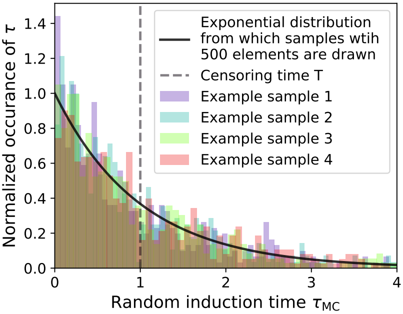
$$\mathcal{L}(k) = \binom{N}{m}\, k^n \, \exp\left(-k \sum_{i=1}^{n} t_i\right) \, \exp\left(-T\,k\right)^m$$

- Necessary condition of maximum likelihood

$$\hat{k}^{-1} = \frac{1}{n}\left(\sum_{i=1}^{n} t_i + mT\right)$$

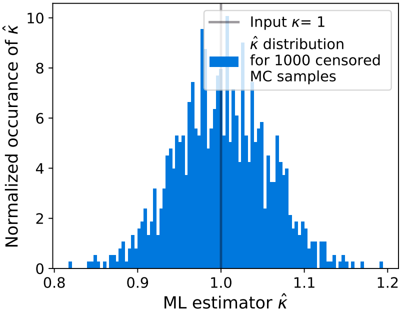
Nucleation Rate Estimator II - Monte Carlo Uncertainty

1. Exponentially distributed random samples with $k = \hat{k}$
2. Censoring at T
3. Calculate $\hat{k}_{MC}$
4. $\sigma_{\hat{k}}$ estimated by $\sigma_{\hat{k}_{MC}}$



Nucleation Rate Estimator II - Monte Carlo Uncertainty

1. Exponentially distributed random samples with $k = \hat{k}$
2. Censoring at T
3. Calculate $\hat{k}_{MC}$
4. $\sigma_{\hat{k}}$ estimated by $\sigma_{\hat{k}_{MC}}$



Nucleation Rate Comparison

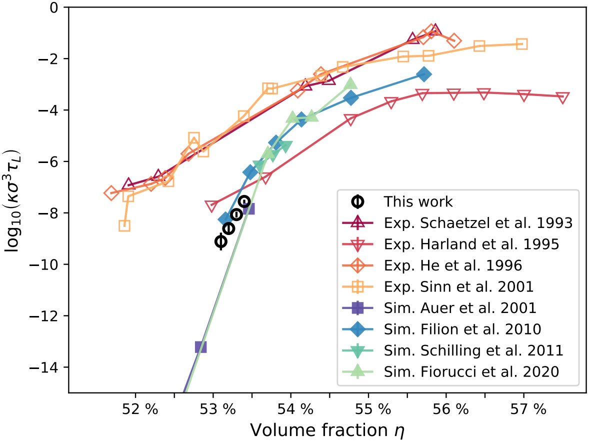


Fig.: Experimental and theoretical nucleation rates from the literature[6–13]

Simulations and experiments:

- Different rates
- Different slopes

Comparison to Real World Experiments

Simulation	Experiment
Microscopic disjunct subvolumes	Macroscopic volume
$\tau_{cryst.} \ll \tau_{nuc.}$	$\tau_{cryst.} \not\ll \tau_{nuc.}$
$x_s \approx \frac{n(t)}{m} = 1 - \exp(-\kappa t)$	$x_s(t) = t^4 \frac{\kappa c^3}{4\rho_{\text{melt}}},\ x_s \ll 1$

- κ and c are measured
- Assume $x_s(t^*) \stackrel{!}{=} 1/8 \quad \Rightarrow t^* = \sqrt[4]{\frac{\rho_{\text{melt}}}{2\kappa c^3}}$

Modified Nucleation Rate Comparison

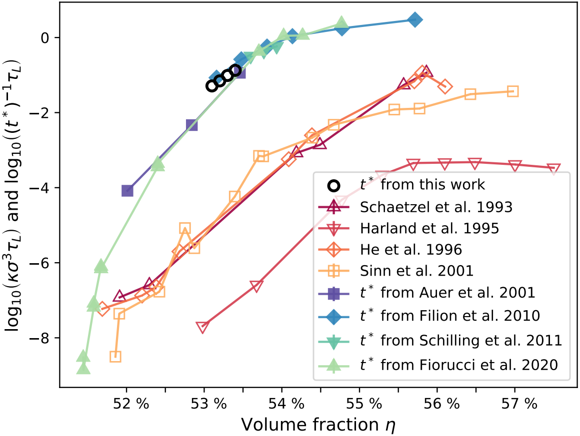


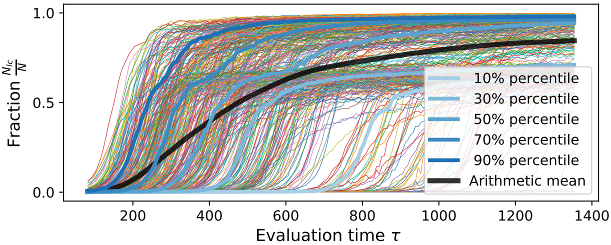
Fig.: Experimental nucleation rates[6–10] alongside with $(t^*)^{-1}$ calculated from simulation studies[11–13]

Simulations and experiments:

- Different rates
- Similar slopes

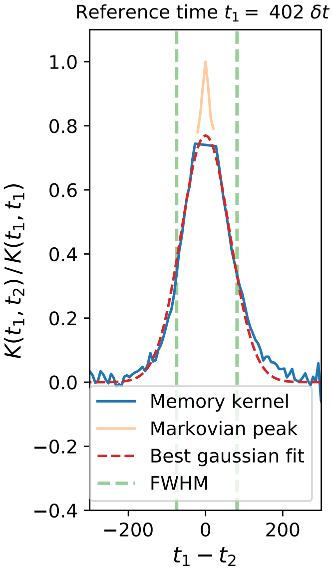
Memory Kernel I - Largest Cluster Trajectories

Last but not least,



- N = 16384 particles
- $\eta = 54.0\%$
- $\tau_{ind.} \approx 400\delta t$
- $\tau_{cry.} \approx 150\delta t$

Memory Kernel II -Shape Analysis

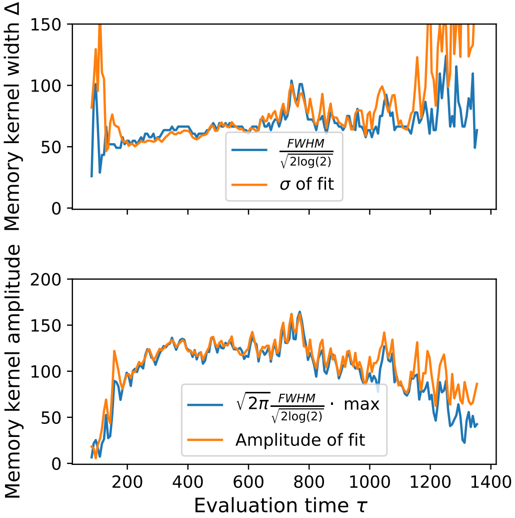


Shape analysis:

- Exclude Markovian contribution
- FWHM of crest as first estimate
- Best Gaussian fit as second estimate

Memory Kernel II -Shape Analysis

- Constant width $\sim \tau_{cry}$.
- Variable amplitude

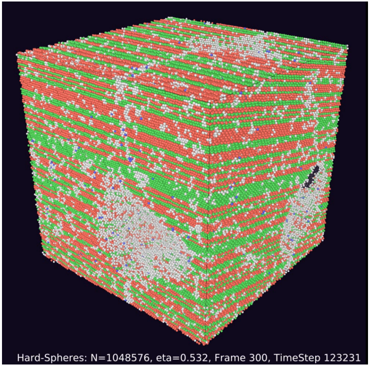


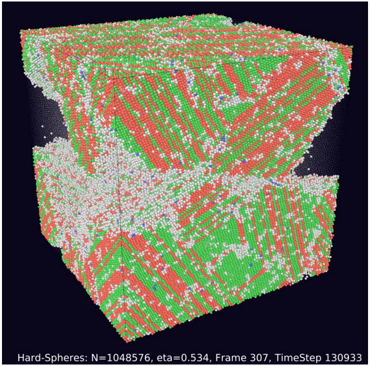
$\Rightarrow$ Possibly only memory depending on the arbitrary transition width is observed.

Conclusion - Summary

- Constant attachment rate
- Estimate of nucleation rate density + statistical uncertainty
  $\Rightarrow$ Confirming the difference
- System geometries in simulation and experiment
  $\Rightarrow$ Possible accordance
- Memory kernel shape analysis
  $\Rightarrow$ Future research in other observables

Thank you for your attention





Bibliography I

N. F. Carnahan and K. E. Starling, “Equation of state for nonattracting rigid spheres”, The Journal of Chemical Physics **51**, 635–636 (1969).

N. G. Almarza, “A cluster algorithm for Monte Carlo simulation at constant pressure”, Journal of Chemical Physics **130**, 184106 (2009).

A. Kuhnhold et al., “Derivation of an exact, nonequilibrium framework for nucleation: Nucleation is a priori neither diffusive nor Markovian”, Physical Review E **100**, 52140 (2019).

H. Meyer, “Generalized Langevin Equations and memory effects in non-equilibrium statistical physics”, Dissertation (Université du Luxembourg, Albert-Ludwigs-Universität Freiburg, 2020).

P. Pelagejcev, “Simulation study of non-Markovian effects in crystal nucleation”, Master Thesis (Albert-Ludwigs-Universität Freiburg, 2019).

J. L. Harland and W. van Megen, “Crystallization kinetics of suspensions of hard colloidal spheres”, Physical Review E **55**, 3054–3067 (1997).

Bibliography II

Y. He et al., “Dynamics of crystallization in hard-sphere suspensions”, Physical Review E **54**, 5286–5297 (1996).

K. Schätzel and B. J. Ackerson, “Density fluctuations during crystallization of colloids”, Physical Review E **48**, 3766–3777 (1993).

C. Sinn, A. Heymann, A. Stipp, and T. Palberg, “Solidification kinetics of hard-sphere colloidal suspensions”, Trends in Colloid and Interface Science XV. Progress in Colloid and Polymer Science **118**, 266–275 (2001).

S. Auer and D. Frenkel, “Prediction of absolute crystal-nucleation rate in hard-sphere colloids”, Nature **409**, 1020–1023 (2001).

L. Filion, M. Hermes, R. Ni, and M. Dijkstra, “Crystal nucleation of hard spheres using molecular dynamics, umbrella sampling, and forward flux sampling: A comparison of simulation techniques”, Journal of Chemical Physics **133**, 244115 (2010).

Bibliography III

G. Fiorucci, G. M. Coli, J. T. Padding, and M. Dijkstra, "The effect of hydrodynamics on the crystal nucleation of nearly hard spheres", Journal of Chemical Physics **152**, 064903 (2020).

T. Schilling, S. Dorosz, H. J. Schöpe, and G. Opletal, "Crystallization in suspensions of hard spheres: A Monte Carlo and molecular dynamics simulation study", Journal of Physics Condensed Matter **23**, 194120 (2011).

S. Pieprzyk et al., "Thermodynamic and dynamical properties of the hard sphere system revisited by molecular dynamics simulation", Physical Chemistry Chemical Physics **21**, 6886–6899 (2019).

D. M. Heyes, M. J. Cass, J. G. Powles, and W. A. Evans, "Self-diffusion coefficient of the hard-sphere fluid: System size dependence and empirical correlations", Journal of Physical Chemistry B **111**, 1455–1464 (2007).