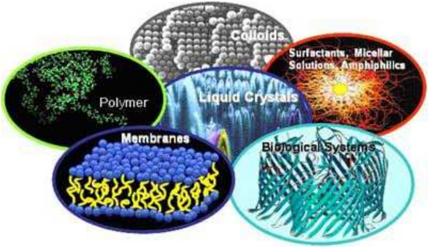
Nucleation in Hard Spheres Systems

Sven Dorosz

University of Luxembourg,
Group of Tanja Schilling - Softmatter Theory

February, 2012

Softmatter

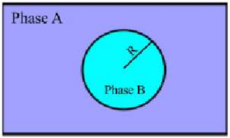


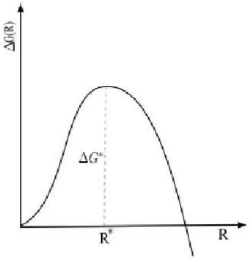
Liquids, colloids, polymers, foams, gels, granular materials, and a number of biological materials.

Illustration taken from SoftComp website

Table of contents

Classical Nucleation Theory





$$\Delta G = 4\pi\gamma R^2 + \frac{4\pi\Delta\mu\rho}{3}R^3$$

$$R^* = \frac{2\gamma}{\rho|\Delta\mu|}$$

$$\Delta G_{crit} = \frac{16\pi\gamma^3}{3(\rho|\Delta\mu|)^2}$$

$$I = \kappa \exp\left[-\frac{16\pi\gamma^3}{3k_B T(\rho|\Delta\mu|)^2}\right]$$

source Hamed Maleki, PhD Thesis, University of Mainz, 2011

Hard Spheres

$$V(r) = \begin{cases} \infty & \text{if } r < R \\ 0 & \text{if } r \geq R \end{cases}$$

collisions
are elastic ⇒ internal energy constant

$$F = -TS$$

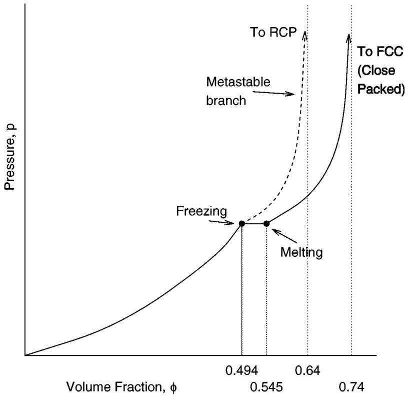
most simple model for a liquid

$$\eta = \frac{1}{6}\pi R^3 \rho$$

The equation of state is given by

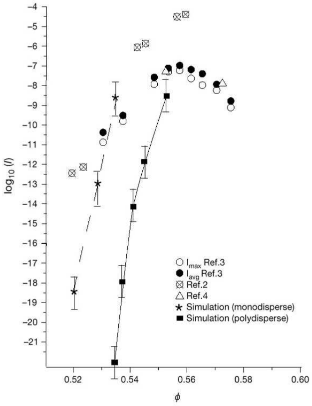
$$\frac{\beta P}{\rho} = \frac{(1+\eta+\eta^2)}{(1-\eta)^3}$$

Phasediagram for Hard Spheres



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

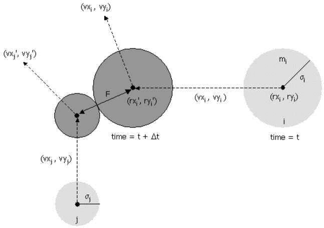
Comparison Experiment to Theory



Stefan Auer and Daan Frenkel, Nature 409, 1020-1023 (2001)

Motivation Event driven molecular dynamics

time driven MD simulation vs. event driven MD simulation



$V(r)$ discontinuous ⇒ free flight between collisions
NVE ensemble ⇒ T is trivial parameter ⇒ sets timescale

Alder, B. J., and Wainwright, T. E., 1957, J. chem. Phys., 27, 1208.

Algorithm Event driven molecular dynamics

Diagram

⇒ Neighboring boxes

Find the first collision for each particle

Insert into collision list - don't execute yet

Then execute earliest collision

Find next collision of the two particles ⇒ update the list

Then execute earliest collision ...

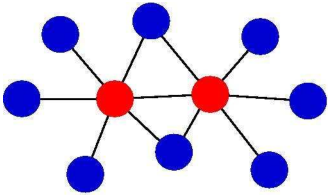
Algorithm by setup serial execution
scales with $N \log N$. N number of particles in system

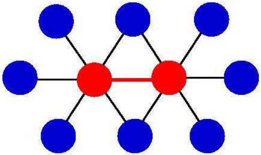
Local crystal symmetry

Hard spheres system. $\rho = 1.03$

Loading

Local crystal symmetry





Definition of the order parameter

Observables for the Local Bond Ordering:
In 3d:

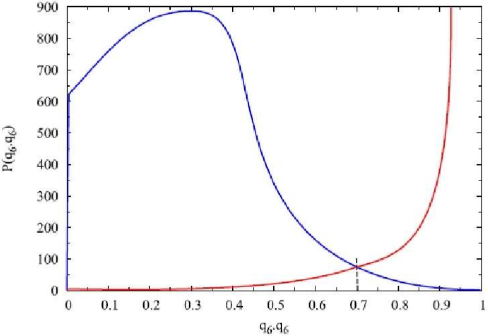
$$\bar{q}_{6m}(i) := \frac{1}{n(i)} \sum_{j=1}^{n(i)} Y_{6m}\left(\vec{r}_{ij}\right) \quad , r_{ij} < 1.4$$

where $Y_{6m}\left(\vec{r}_{ij}\right)$ *are the spherical harmonics (with l=6).*

P. J. Steinhardt, D. R. Nelson, and M. Ronchetti. Phys. Rev. B, 28(2), 1983

Distribution of the order parameter

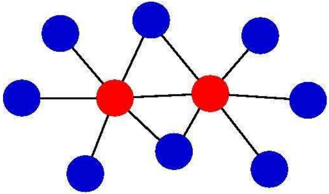
scalar product $\vec{q_6}(i) \cdot \vec{q_6}^*(i)$



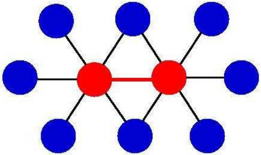
source Hamed Maleki, PhD Thesis, University of Mainz, 2011

Local crystal symmetry

scalar product $\vec{q_6}(i) \cdot \vec{q_6}^*(j)$ measures relative angle orientation



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



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

Detecting emerging crystallites

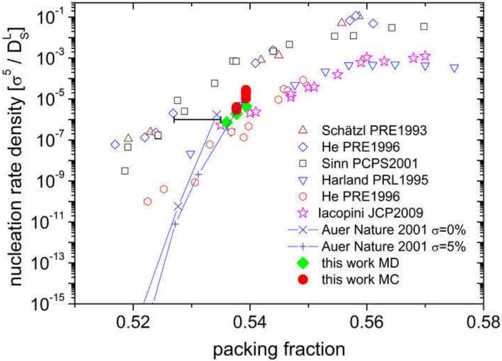
If particle i and n_b neighbouring particle j satisfy
$\vec{q_6}(i) \cdot \vec{q_6}^*(j) > 0.7$

Crystalline particles (colorcoded "green"), $n_b > 10$.
Low symmetry cluster (LSC)(colorcoded "light brown"), $n_b > 5$.

Motivation

- How do the theoretical nucleation rates compare to the experiment?
  (Brute force molecular dynamics simulation)
- What are the structural properties of the emerging nuclei?
- Can we identify characteristic preconditions near nucleation sites?
- What are the properties of the growing nuclei?

nucleation rates

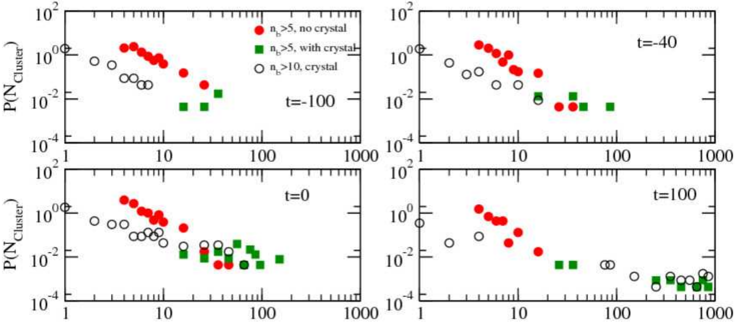


⇒ MD and MC simulations produce rates match the experimental results

⇒ SPRES as the first full non equilibrium rare event sampling method

Schilling T.; Dorosz S.; Schöpe H. J.; et al. JPCM, 23, 19, 194120, 2011

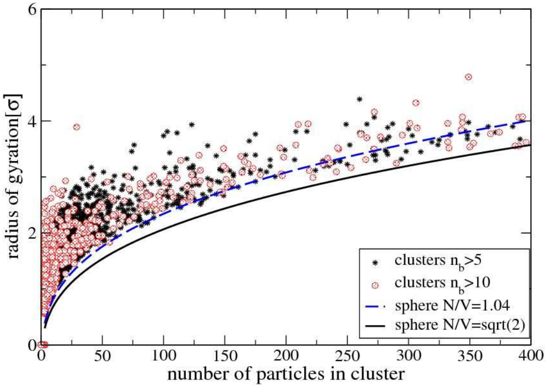
Precursor nucleation



⇒ Effective two step process. Precursor formation

Schilling T.; Dorosz S.; Schöpe H. J.; et al. JPCM, 23, 19, 194120, 2011

Radius of gyration

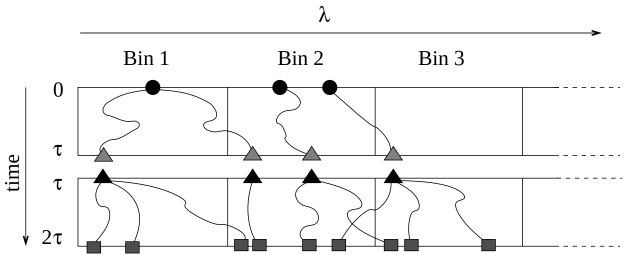


⇒ Small crystallites are far from being spherical

Schilling T.; Dorosz S.; Schöpe H. J.; et al. JPCM, 23, 19, 194120, 2011

SPRES

Going to lower densities ρ.



J.T. Berryman and T. Schilling. Sampling rare events in nonequilibrium and nonstationary systems.

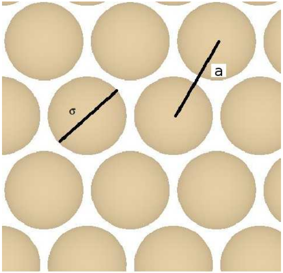
J Chem Phys, 133(24):244101, 2010.

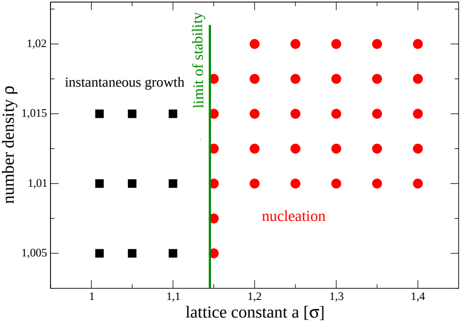
Motivation

- Will the substrate induce different nucleation pathways?
- Where does the nucleation happen?
- What are the consequences of the mismatch between substrate and equilibrium crystal lattice constant?
- What is the crystal structure of the nucleus?
- How does the substrate change the nucleation rate?

Setup of the system

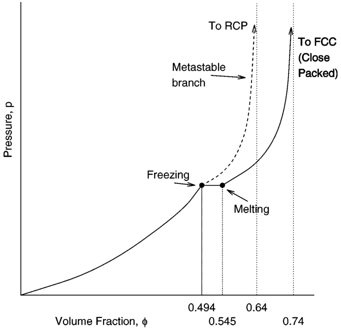
Super-saturated fluid of hard spheres in contact with a triangular substrate.





Parameters

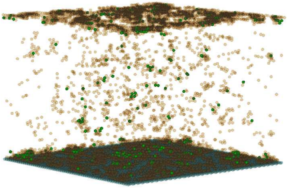
$N = 220200$ (216000 bulk + 4200 substrate) particles
$N/V = 1.005$ $(\eta = 0.526) - 1.02$ $(\eta = 0.534)$
Corresponding chemical potentials $-\Delta\mu \simeq 0.50 - 0.54\ k_B T$



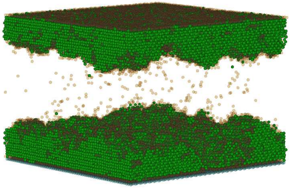
Rintoul, Md. and Torquato, S., 1996, PRL 77, 20, 4198-4201.

Immediate wetting

$a < a_{sp}$



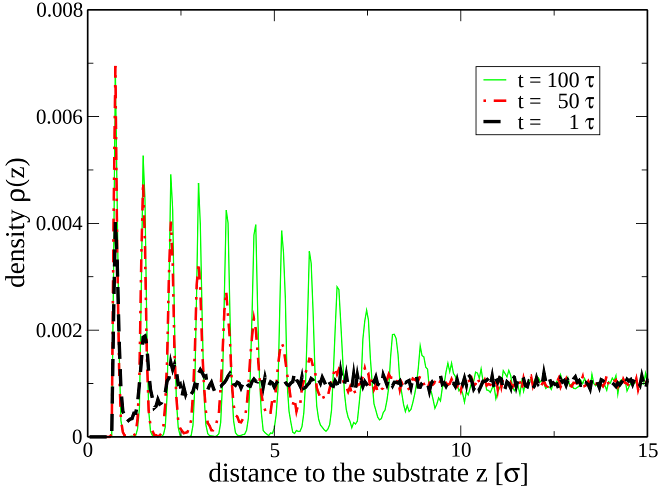
$t = 6D$



$t = 70D$

S.D. and T. Schilling, 2012, J. Chem. Phys. 136, 044702.

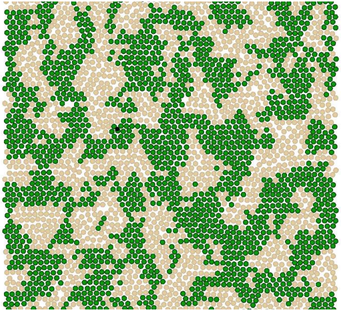
Vertical density profile



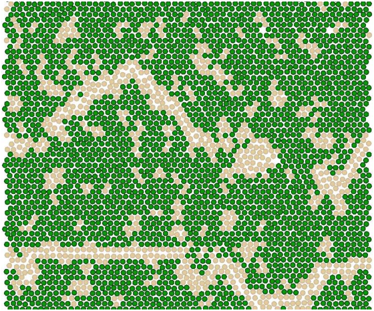
S.D. and T. Schilling, 2012, J. Chem. Phys. 136, 044702.

The first layer

at $t > 150D$



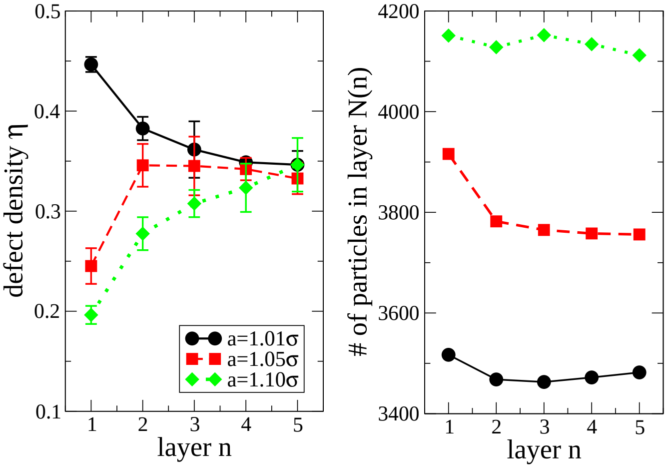
$a = 1.01\sigma$



$a = 1.1\sigma$

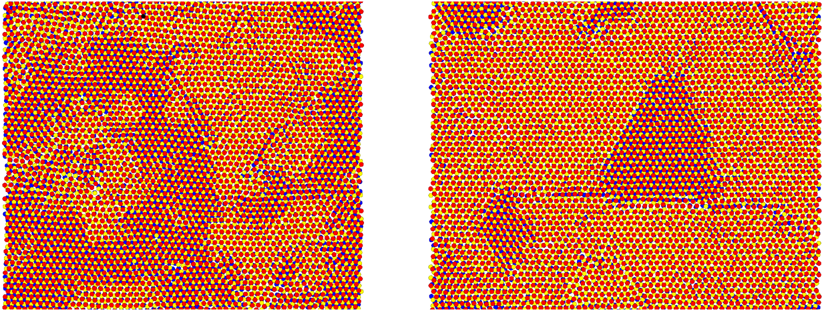
S.D. and T. Schilling, 2012, J. Chem. Phys. 136, 044702.

Defect density



⇒ Induced defects are compensated in the first 3 layers

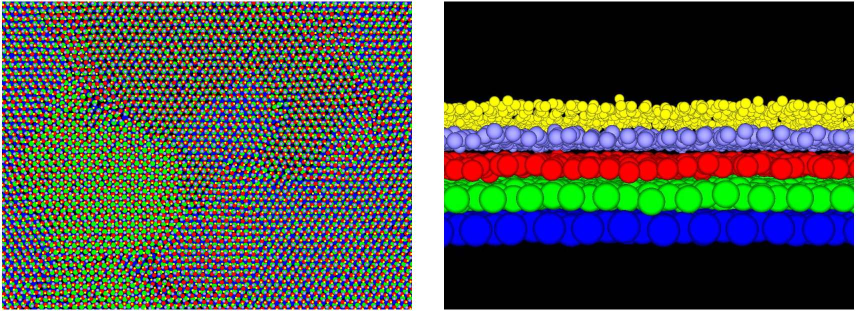
3 layer stacking



⇒ Domains of ABA and ABC structure

S.D. and T. Schilling, 2012, J. Chem. Phys. 136, 044702.

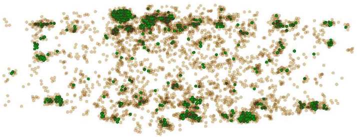
5 layer stacking



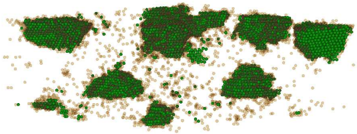
⇒ Crystal grows in random hexagonal closed packing (RHCP)

Nucleation at the wall

$a > a_{sp}$



$t = 6D$

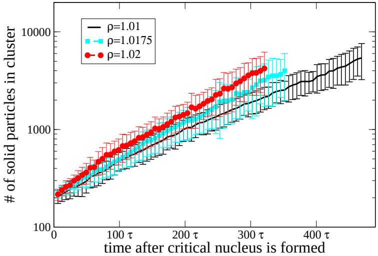


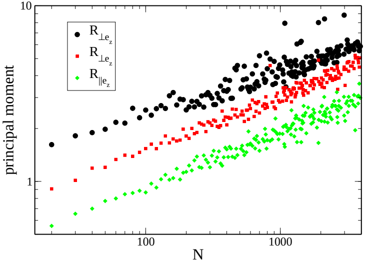
$t = 80D$

$\Rightarrow$ Droplet formation on the substrate

S.D. and T. Schilling, 2012, J. Chem. Phys. 136, 044702.

Droplet characterization

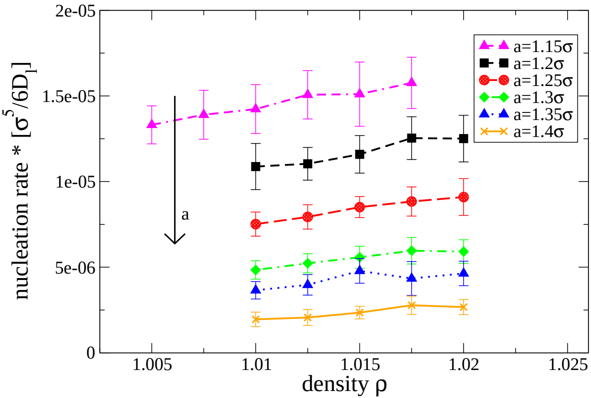




$\Rightarrow$ non-spherical droplets even up to 4000 particles.

S.D. and T. Schilling, 2012, J. Chem. Phys. 136, 044702.

Nucleation rates



⇒ Decreasing nucleation rate with increasing mismatch to the substrate

S.D. and T. Schilling, 2012, J. Chem. Phys. 136, 044702.

Acknowledgements

aides à la formation recherche

Fonds National de la Recherche Luxembourg

COFUNDED BY MARIE CURIE ACTIONS

- Tanja Schilling, University of Luxembourg
- Martin Öttel, Frederike Schmid, Hamed Maleki, Hajo Schöpe, and Kurt Binder, University of Mainz
- The present project is supported by the National Research Fund, Luxembourg and cofunded under the Marie Curie Actions of the European Commission (FP7-COFUND)

Softmatter Theory Group - UL

J. Berryman, M. Sinha, T. Schilling, M. Anwar, S. Dorosz.

M. Radu, M. Esposito, M. Mathew, Z. Heng, and G. Diana.

There is an open postdoc position.