Heterogenous Nucleation in Hard Spheres Systems

Sven Dorosz and Tanja Schilling

University of Luxembourg,
Softmatter Theory Group

May, 2012

Table of contents

Motivation Event Driven Molecular Dynamics

Time Driven MD simulation vs. Event Driven MD simulation

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

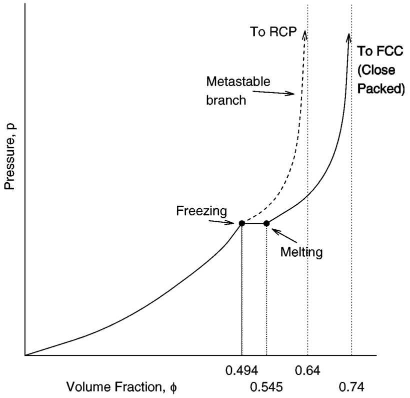
$\Rightarrow$ free flight between collisions

NVE ensemble.

$\tau = \frac{\sigma^2}{D}$ sets the timescale

B. J. Alder and T. E. Wainwright, J. Chem. Phys., 27, 1208 (1957).

Phasediagram for Hard Spheres



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

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).

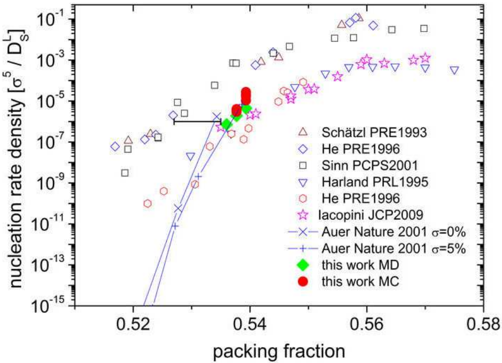
P. J. Steinhardt, D. R. Nelson, and M. Ronchetti. Phys. Rev. B, 28(2) (1983)

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"), $n_b > 5$.

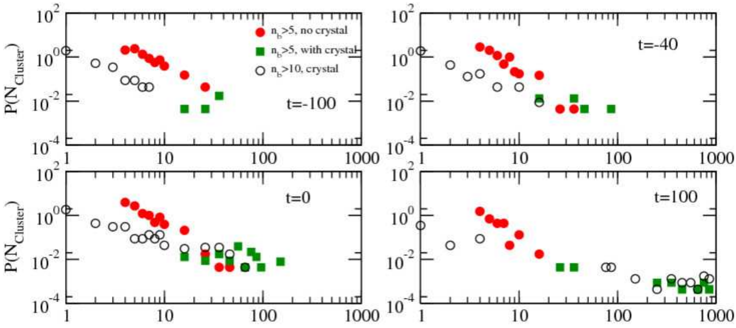
Nucleation rates



⇒ MD and MC simulations produce rates match the experimental results

T. Schilling, S. Dorosz et al. JPCM, 23, 19, 194120 (2011).

Precursor nucleation



⇒ Effective two step process. Precursor mediated nucleation

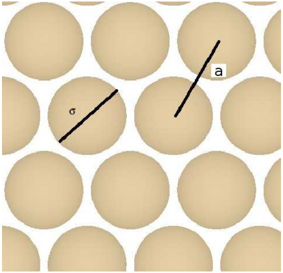
T. Schilling, S. Dorosz et al. JPCM, 23, 19, 194120 (2011).

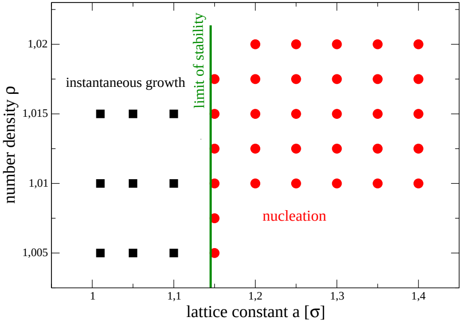
Motivation

- 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.

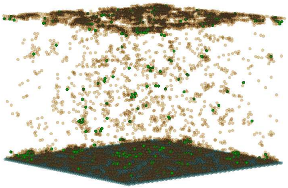




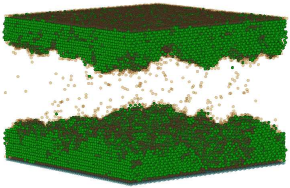
$N = 220200$ (216000 bulk + 4200 substrate) particles
$N/V = 1.005$ ($\eta = 0.526$) $- 1.02$ ($\eta = 0.534$)
Corresponding chemical potentials $-\Delta\mu \simeq 0.50 - 0.54\ k_B T$

Immediate wetting

$a < a_{sp}$



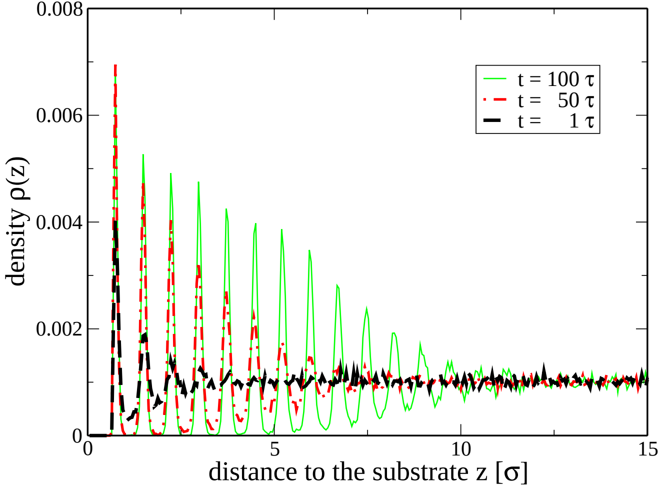
$t = 6\tau$



$t = 70\tau$

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

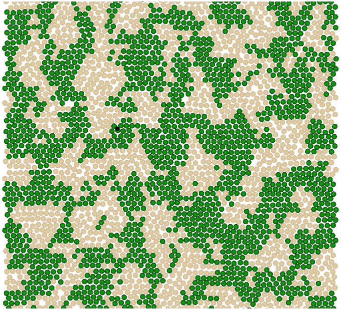
Vertical density profile



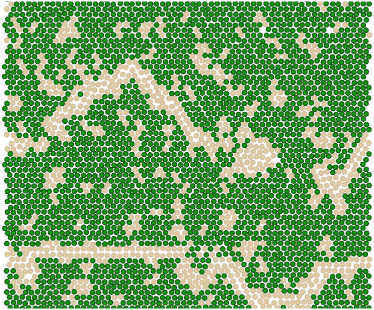
S.D. and T. Schilling, J. Chem. Phys. 136, 044702 (2012).

The first layer

at $t > 150\tau$



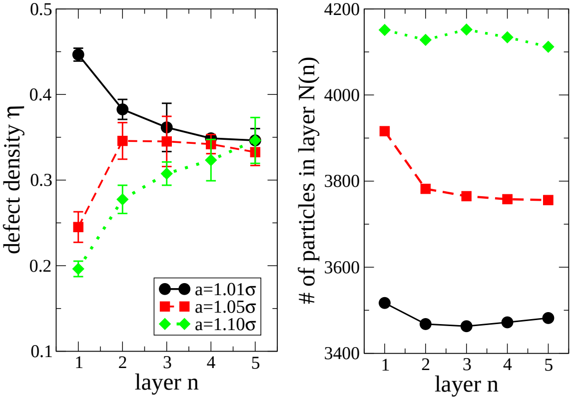
$a = 1.01\sigma$



$a = 1.1\sigma$

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

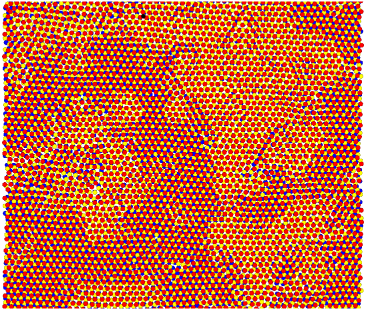
Defect density

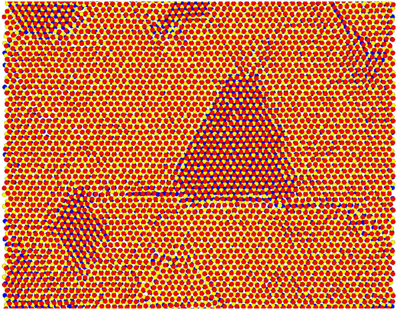


⇒ Induced defects are compensated in the first 3 layers

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

3 layer stacking

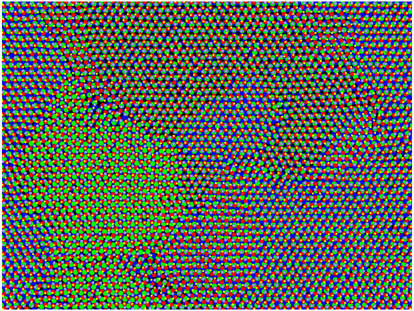


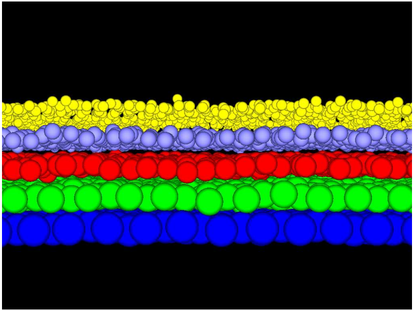


$\Rightarrow$ Domains of ABA and ABC structure

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

5 layer stacking





⇒ Crystal grows in random hexagonal closed packing (RHCP)

Distinguishing fcc/hcp and bcc

more detailed structure analysis with w_4 and w_6

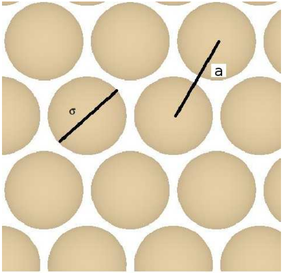
$$w_l = \frac{\sum_{m_1+m_2+m_3} \begin{pmatrix} l & l & l \\ m_1 & m_2 & m_3 \end{pmatrix} q_{lm_1} q_{lm_2} q_{lm3}}{\left(\sum_{l=-m}^{m} |q_{lm}|^2\right)^{3/2}}$$

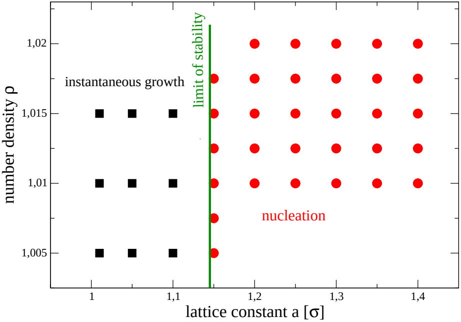
fcc	$-0.05 < w_6 < 0$	$w_4 < 0$
hcp	$-0.05 < w_6 < 0$	$w_4 > 0$
bcc	$0 < w_6 < 0.05$	$w_4 > 0$

$\Rightarrow$ 85% of the crystal has fcc resp. hcp structure

S. Jungblut and C. Dellago, 2011, J. Chem. Phys. 134, 104501.

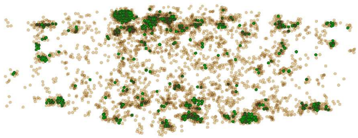
Setup of the system



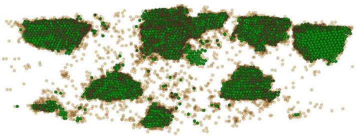


Nucleation at the wall

$a > a_{sp}$



$t = 6\tau$

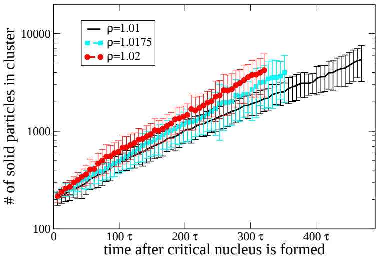


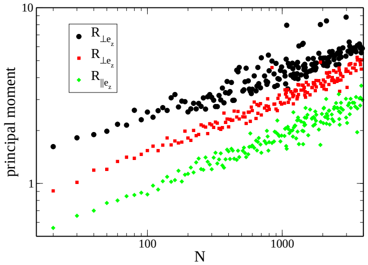
$t = 80\tau$

$\Rightarrow$ Droplet formation on the substrate

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

Droplet characterization

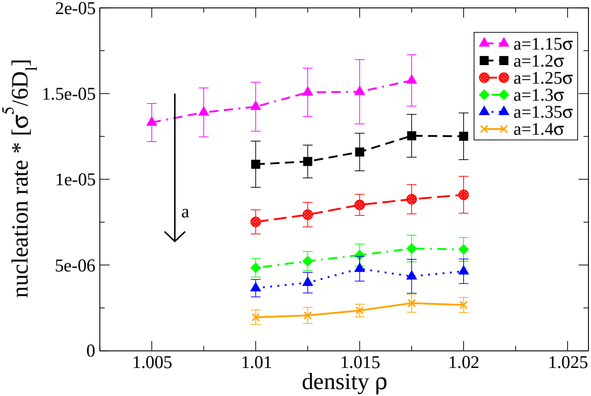




⇒ non-spherical droplets even up to 4000 particles.

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.

Conclusion

- precursor mediated nucleation in homogeneous hard spheres systems
- two regimes of crystallization :

  immediate full wetting of the surface

  heterogeneous nucleation at the substrate

Acknowledgements

- 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)