Heterogenous Nucleation in Hard Spheres Systems

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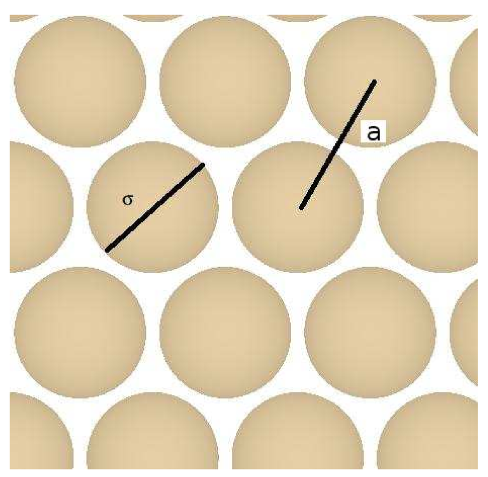
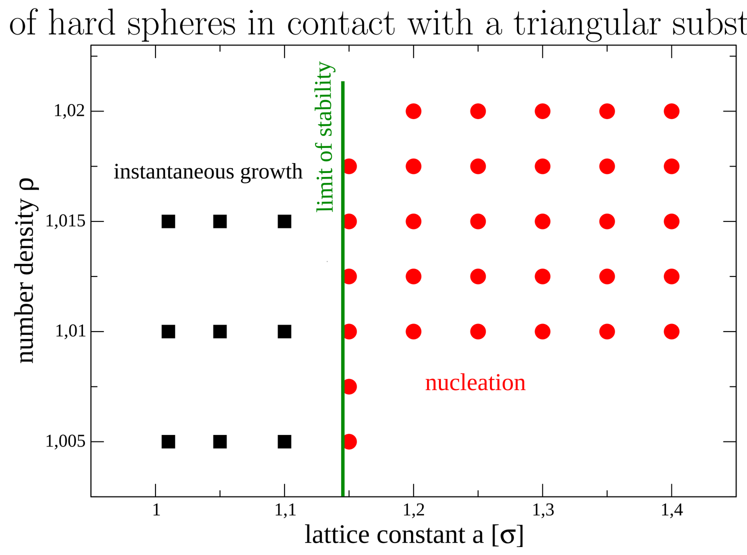
1 Setup

We studied a super- saturated fluid of hard spheres in contact with a triangular substrate.





- 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?
- Related work [1, 5, 3, 2]

2 How does one detect crystallites?

Observables for the Local Bond Ordering [4]:
In 3d: For all particles i with $n(i)$ neighbours, define

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

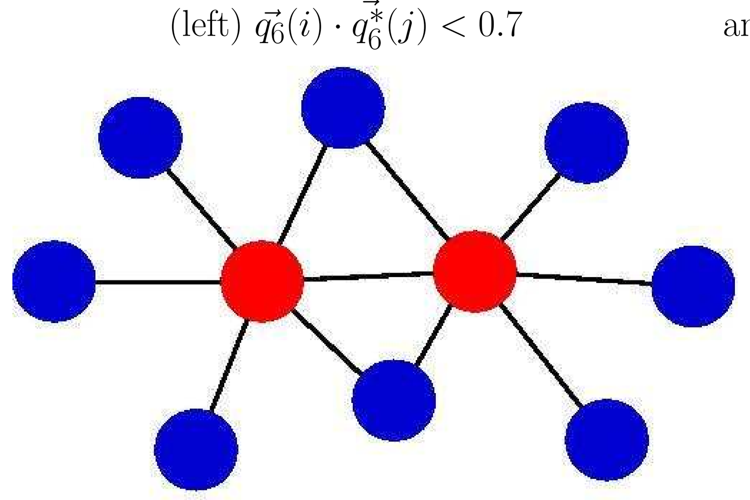
where $Y_{6m}\left(\vec{r}_{ij}\right)$ are the spherical harmonics (with l=6).
In 2d: For all particle i with $n(i)$ neighbours, define

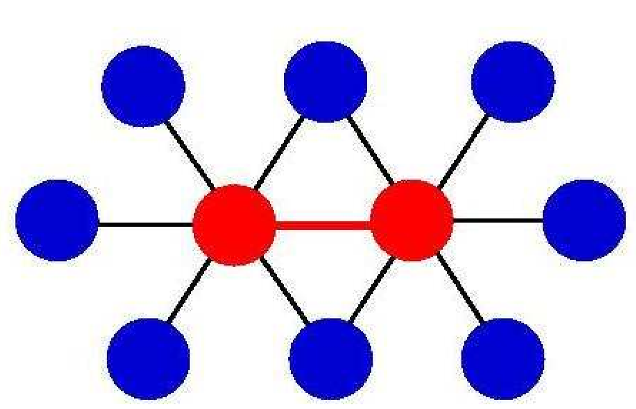
$$\bar{\psi}_6(i) := \frac{1}{n(i)} \sum_{j=1}^{n(i)} e^{i6\theta(r_{ij})} \quad ,$$

with $\theta(r_{ij})$ angle between vector $\vec{r}_{ij}$ and an arbitrary fixed axis in the plane.

Allow $r_{ij} < 1.4$ between particle i and its neighbour j.
Crystalline particles
colorcoded "green") if $n > 10$.
colorcoded "light brown" if $n > 5$.

(left) $\vec{q}_6(i) \cdot \vec{q}_6^{\,*}(j) < 0.7$ and (right) $\vec{q}_6(i) \cdot \vec{q}_6^{\,*}(j) > 0.7$





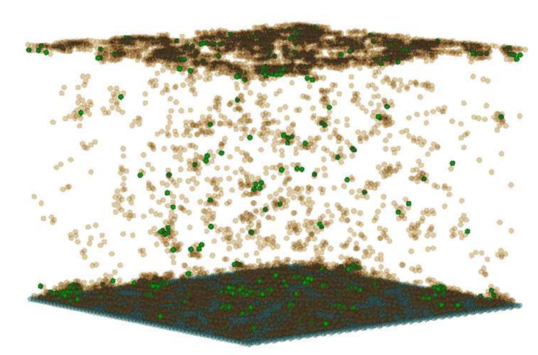
3 Simulation details

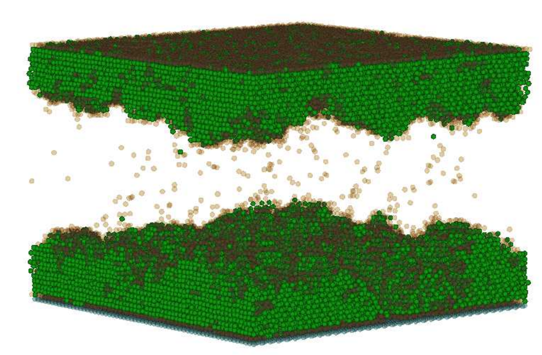
$N = 220200$ (216000 bulk + 4200 substrate) particles
$N\sigma^3/V = 1.005$ ($\eta = 0.526$) $- 1.02$ ($\eta = 0.534$)
Corresponding chemical potentials $-\Delta\mu \simeq 0.50 - 0.54\ k_BT$
D denotes the diffusion constant

4 Snapshots of the system $a < a_{sp}$

System made of 216000 + 4200 particles. a=1.1 and $\rho = 1.01$

(left) $t = 5 \cdot D$ and (right) $t = 100 \cdot D$

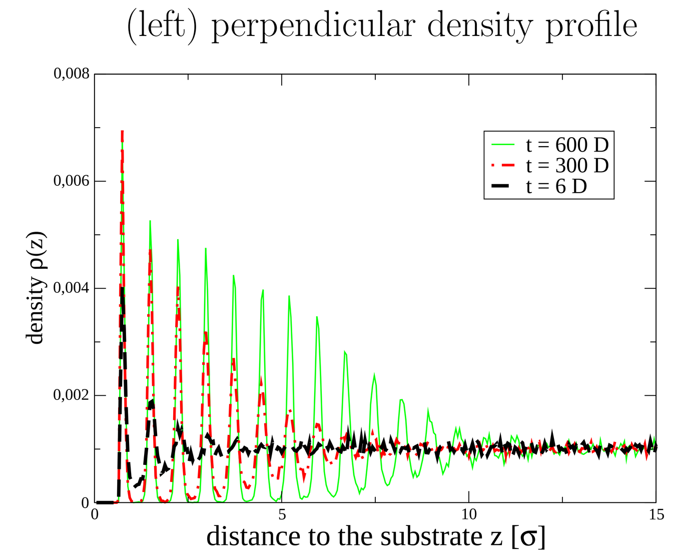


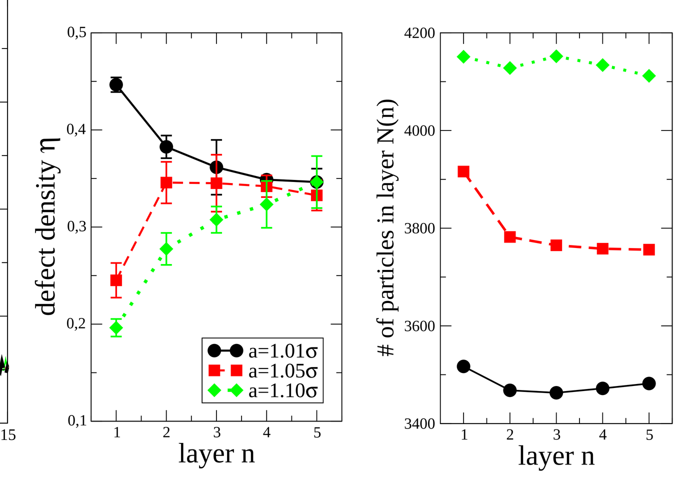


⇒ Complete layer growth onto the substrate

Analysis of the fully wetted substrate

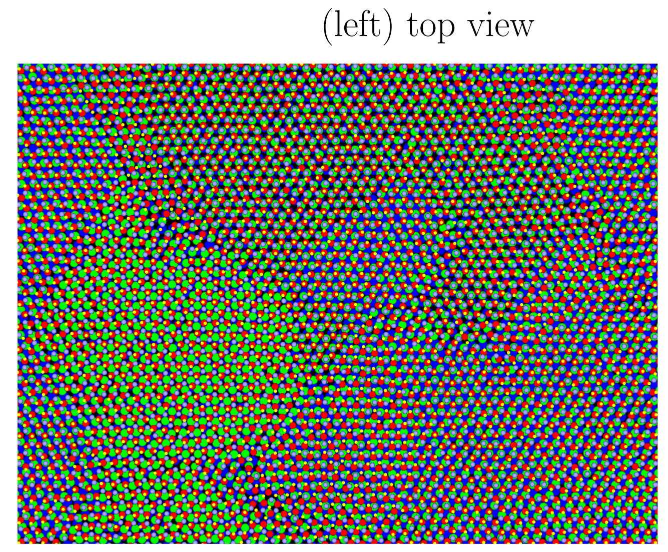
(left) perpendicular density profile (right) defect density η for the nth layer

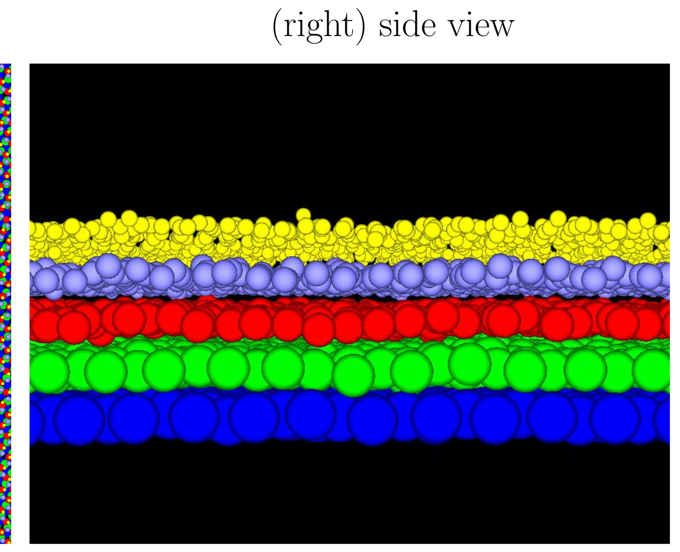




⇒ Induced defects are compensated in the first 3 layers

(left) top view (right) side view



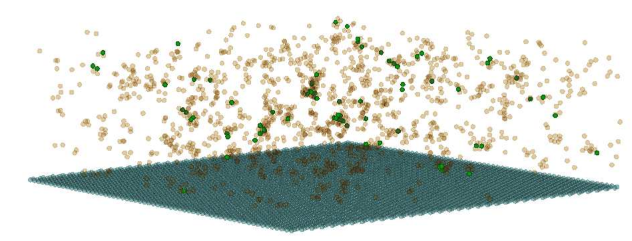


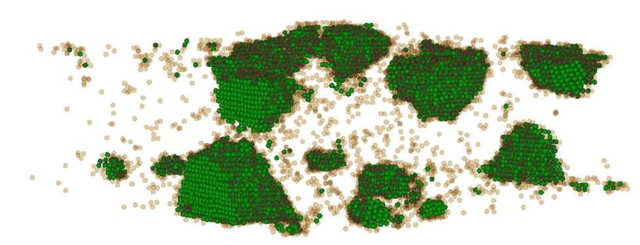
⇒ Crystal grows in random hexagonal closed packing (RHCP)

5 Snapshots of the system $a > a_{sp}$

System made of 216000 + 4200 particles. a=1.4 and $\rho = 1.01$

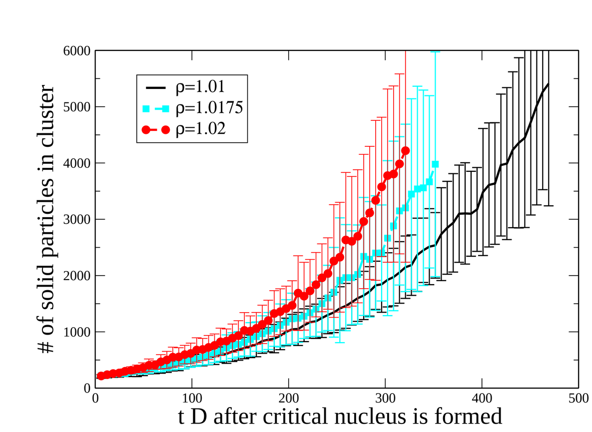
(left) $t = 20 \cdot D$ and (right) $t = 150 \cdot D$

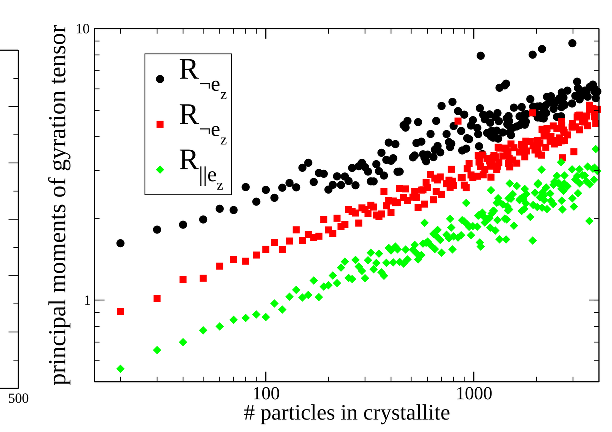




⇒ Droplet formation on the substrate

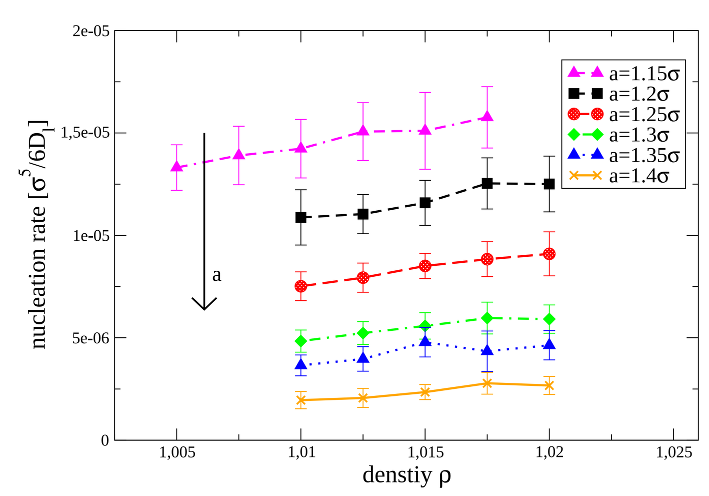
Time evolution of the largest cluster/droplet

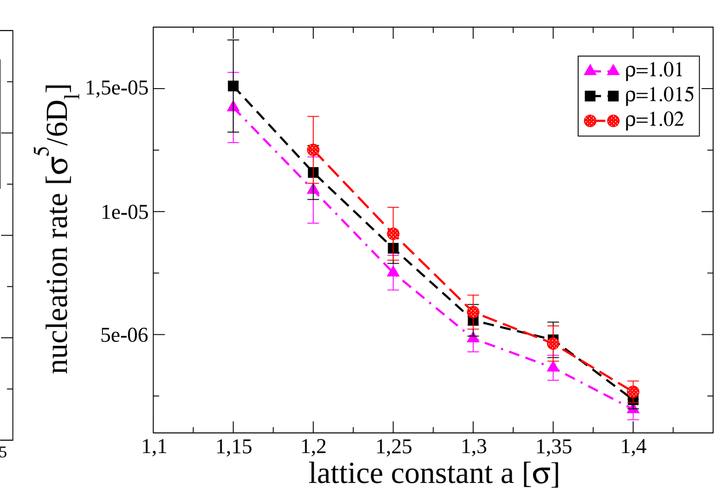




⇒ Analysis of the droplets shows non-spherical droplets even up to 4000 particles.

Effective nucelation rates due to the substrate





⇒ Decreasing nucleation rate with increasing mismatch to the substrate

References

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