Growth kinetics of solid-liquid interfaces

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1. Introduction

Materials science makes extensive use of **coarse-grained** models for the dynamics and growth of **solid** and **melt** phases. In particular, so called **Phase-Field** models are used for the determination of macroscopic properties. This theory can be derived from a simplification of the **Dynamical Density Functional Theory** [1].

This effective approach implies that **few density modes** are sufficient for the description of the dynamics. We test this assumption on a simple **non-equilibrium** model for crystal growth, comparing **numerical simulations** and **3d DDFT calculations**.

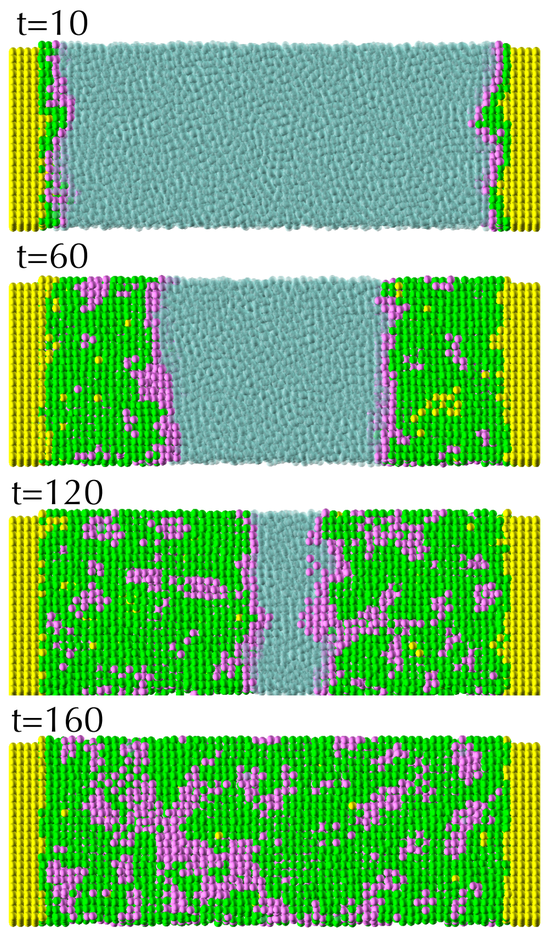


Fig.2. Crystalline growth: perfect, frozen fcc particles (yellow), free fcc particles (green), pre-structured particles (fuchsia) and liquid (turquoise), distinguished using the locally averaged bond order parameters. Pre-structured hcp patches are concentrated at the interfaces.

2. Langevin dynamics of LJ particles

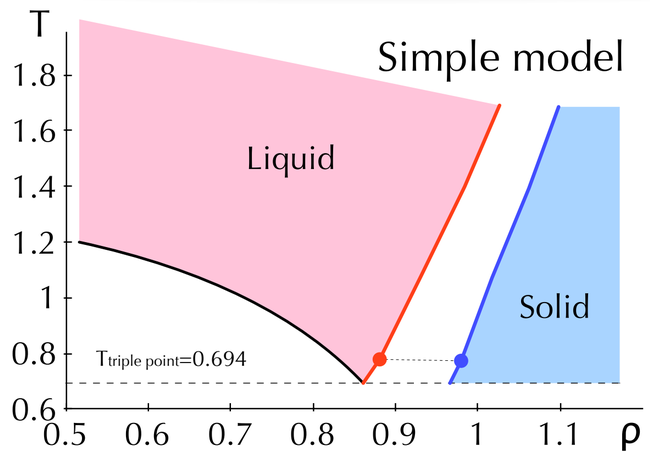


Fig.1 LJ phase diagram: melting line.

Planar growth of a crystal of **Lennard-Jones** particles.

- **Langevin dynamics** (for comparison with DDFT where Brownian motion is assumed)
- **NVT** ensemble.
- **Fixed structured perfect fcc walls** exposing the [100] orientation to the liquid.
- **Metastable** liquid such that $\rho_{liq}=\rho_{sol}=0.9732$.

3. Geometrical properties

Averaged local bond order parameters [2] distinguish liquid/solid phases (Fig.2). At the interface (Fig. 3) the particles jump from an **hcp** order to the **fcc** stacking.

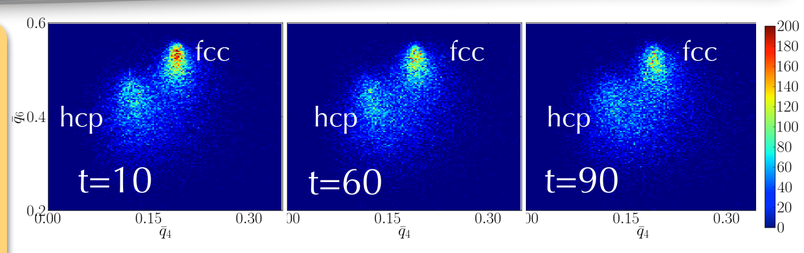


Fig.3. PDF of the averaged local bond order parameters $\bar{q}_4$ and $\bar{q}_6$ at different times during the growth (see fig.2 for comparison) for particles in the vicinity of the interface.

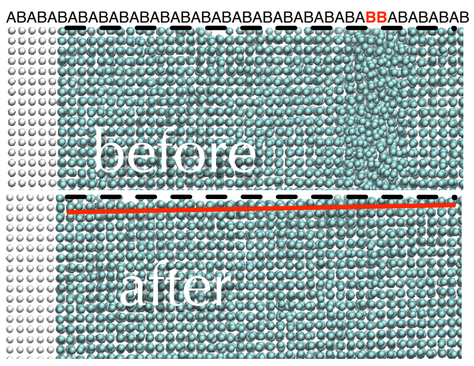


Fig.4. Formation of a dislocation.

After full growth, the ABAB fcc stacking in [100] implies a **defect** when the walls facets are not compatible. The defect is a **dislocation** of all the crystalline planes.

4. Modes and interface width

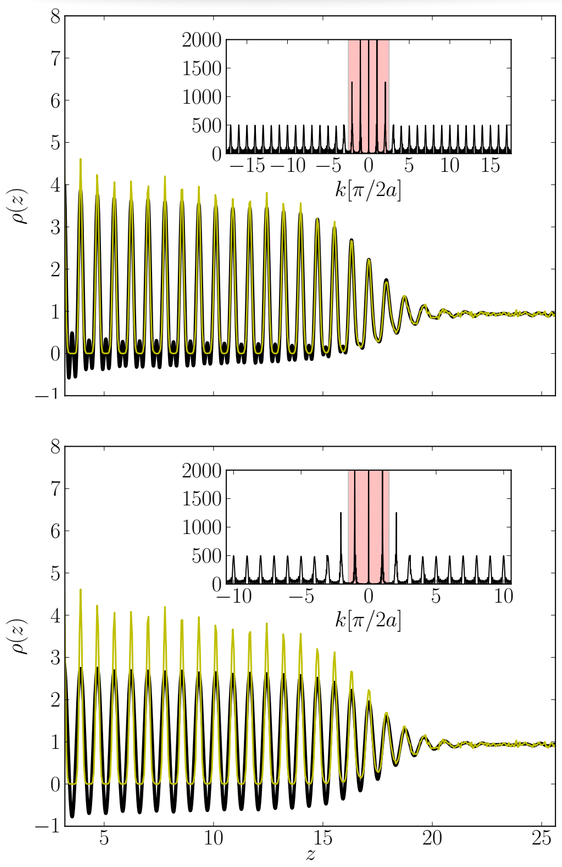


Fig.5. Laterally averaged density profile (yellow) and its reconstruction using low order modes (**black**) during growth.

A few modes are needed to determine the laterally averaged density profile, correctly matching the position of the interface (fig. 5).

Interface **widths** can be computed from both the density and the q6 profiles. The scaling $w \sim t^{\alpha}$ is different for the two approaches and deviates from the KPZ growth model .

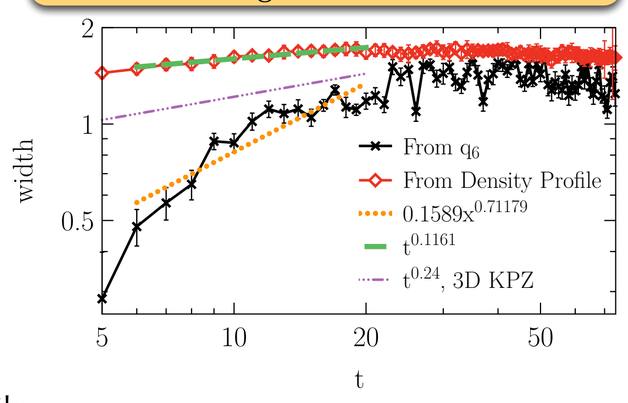


Fig.6. Interface widths computed from the BOP profile and the density profile compared with KPZ predictions.

5. DDFT

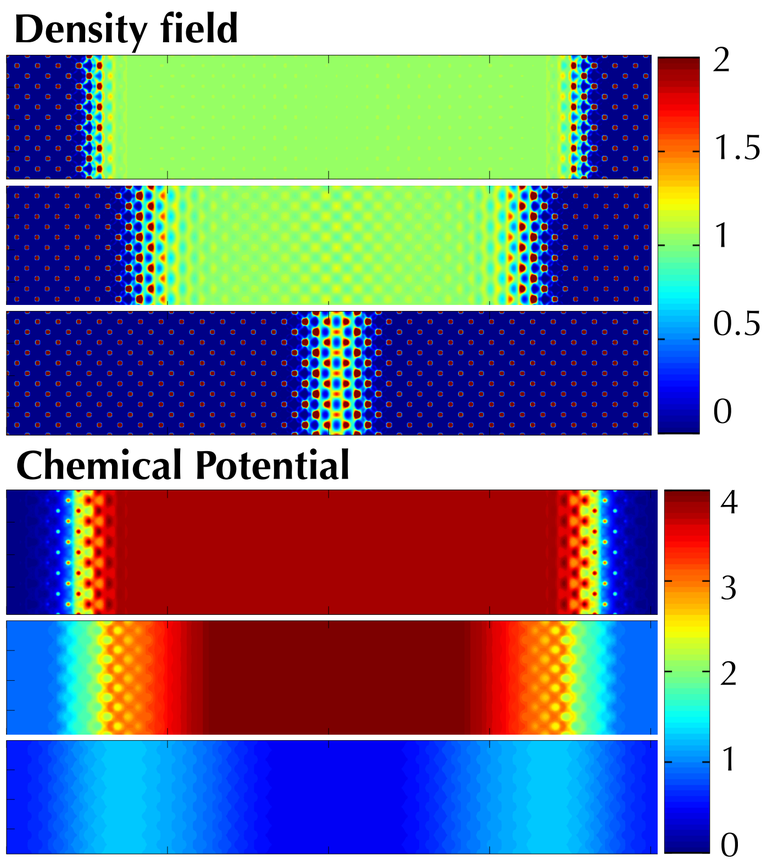
Deterministic evolution of the **density field** according to a diffusion-like equation

$$\frac{\partial \rho(\vec{r},t)}{\partial t} = \nabla\left[\rho(\vec{r},t)\nabla\left(\frac{\delta F}{\delta \rho} + V^{ext}(\vec{r})\right)\right]$$

where the chemical potential is chosen according to the **Ramakrishnan-Youssouf** approximation

$$\frac{\delta F}{\delta \rho} = \beta^{-1}(\ln\rho - \Delta\rho * c^{(2)}_{ref} + \mu_{ref})$$

with $c^{(2)}_{ref}$ being the **direct correlation function**, derived via mean field approximation from the pair potential of choice.



Real-space, discrete-time evolution provides the 3d density field and reproduces the crystal growth.

We have then access to related quantities such as the **free energy**, the **chemical potential** or the **grand potential**.

We will therefore extend previous **equilibrium** work [4] providing a full comparison of the interface properties between the **atomistic** and the **coarse-grained** model.

References

[1] H. Emmerich et al. Advances in Physics 61, 665 (2012).
[2] W. Lechner and C. Dellago, J. Chem. Phys. 129, 114707 (2008).
[3] E. Marinari et al., J. Phys. A, 33, 8181 (2000).
[4] M. Oettel et al, Physical Review E 86, 021404 (2012).