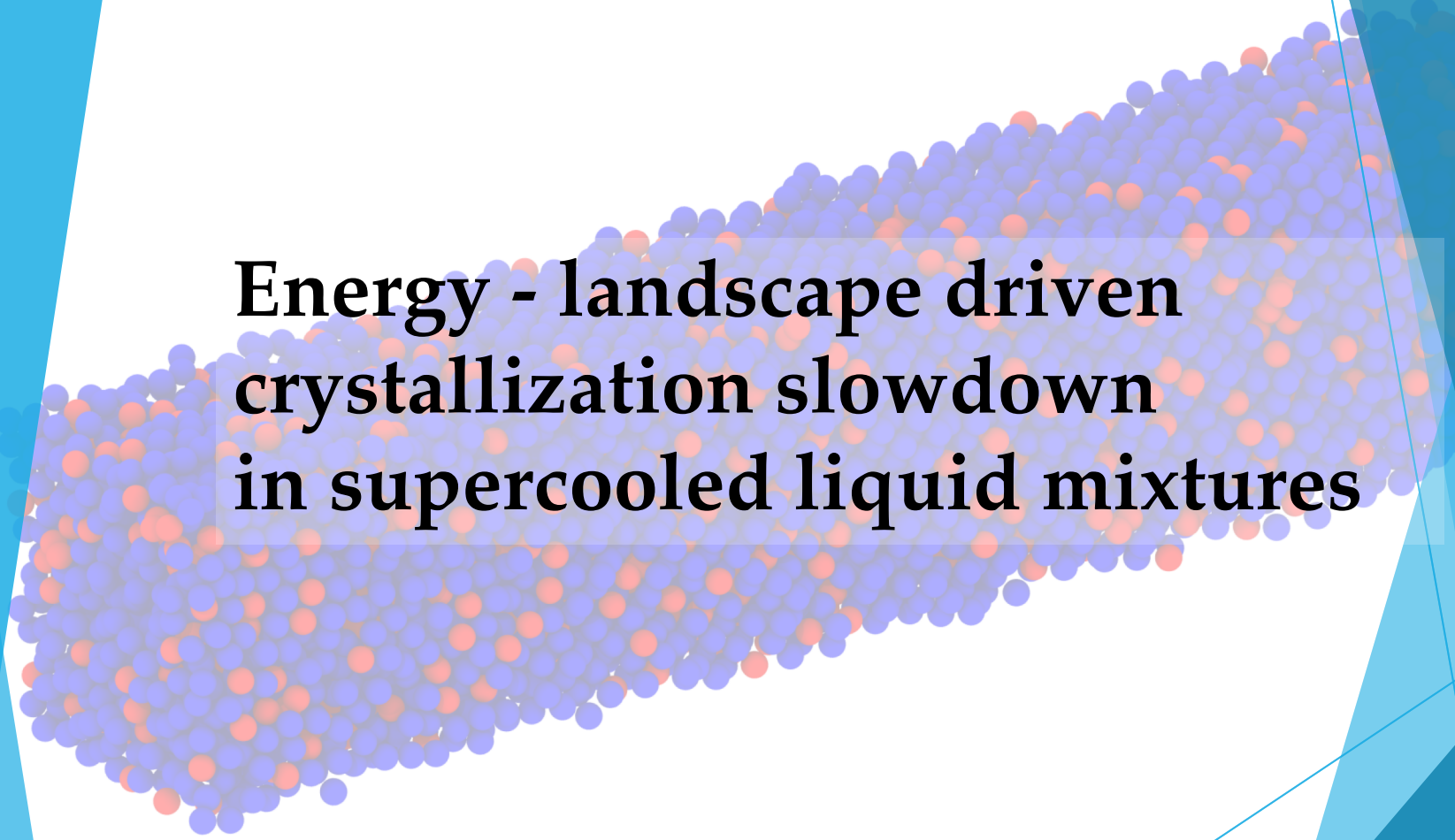
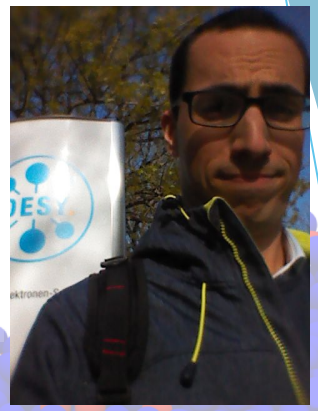
Francesco Mambretti



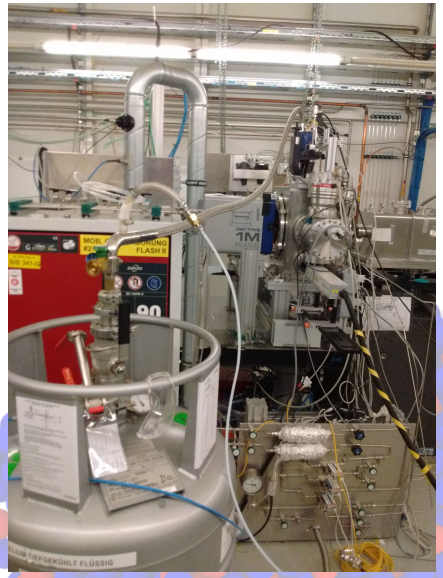
# Energy - landscape driven crystallization slowdown in supercooled liquid mixtures

End first-year of the PhD students in Physics: Workshop 2018
Dipartimento di Fisica, Università degli Studi di Milano – October 10th 2018

# 2015 - 2018: three experimental campaigns on supercooled Argon – Krypton liquid mixtures @ PETRAIII synchrotron source c/o DESY

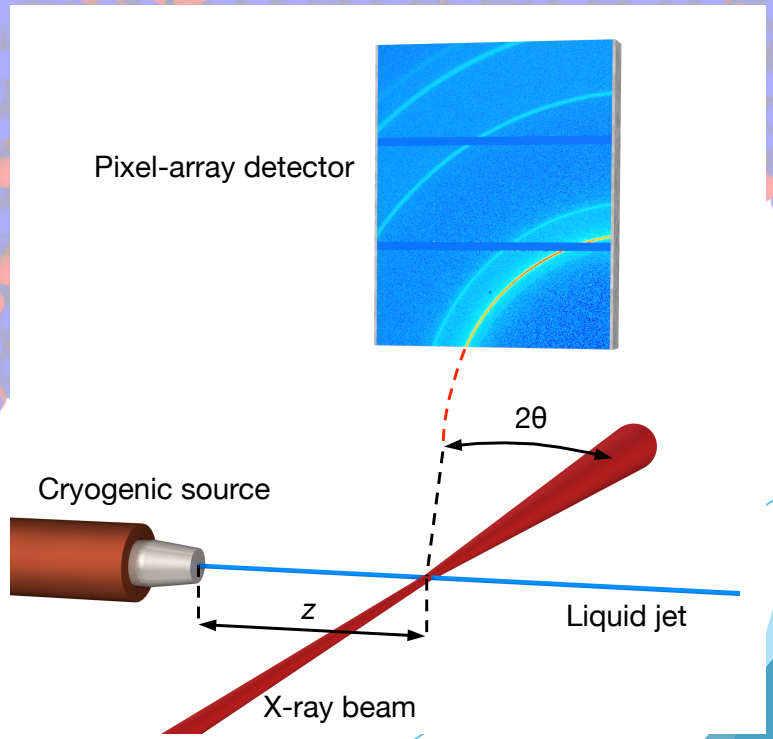






- Liquid microjets technique[1]
- Evaporative cooling

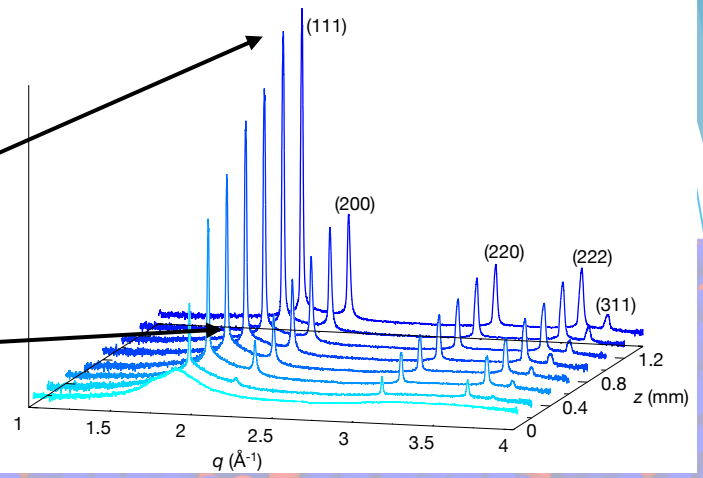
- Distance from nozzle: time evolution ($t=z/v$, $v$ of the jet constant)
- X-rays diffraction on the supercooled filament

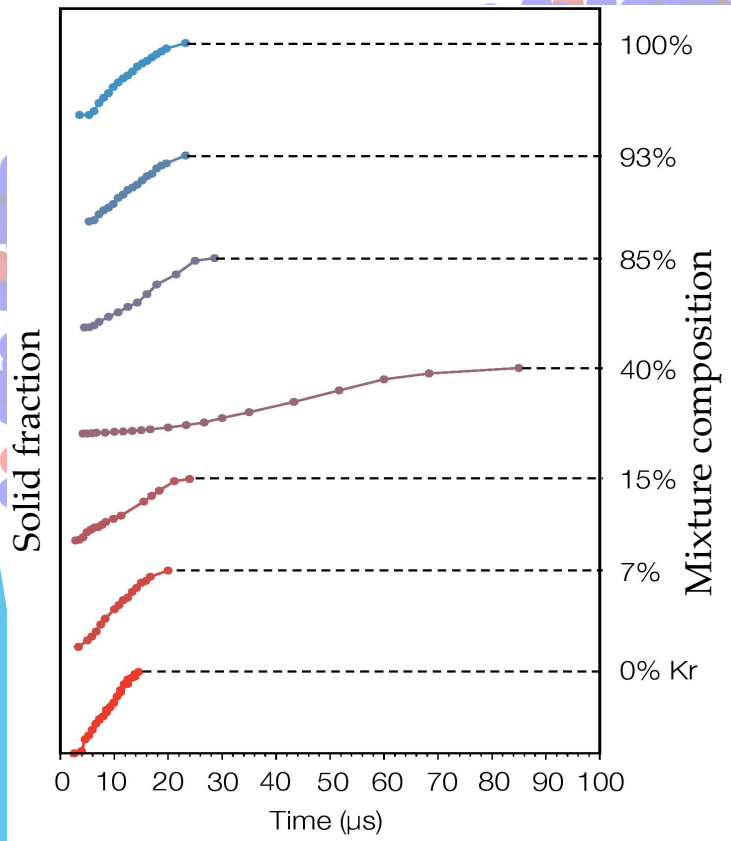



1. Grisenti *et al.*, Adv. Phys. X (2018)

- Crystal growth rate extracted from the area below Bragg peaks in the **static structure factor**

FCC crystal peaks




- Crystallization slowdown!

- Slowdown for Ar-rich and Kr-rich systems both

- Crystallization of supercooled liquids: from climate science to amorphous solids

- Crystallization delay observed in various simulated systems (binary metallic alloys[1], Kob-Andersen[2] model…) + link with **glass transition**

- **Why the slowdown?**

atomic size

crystal deposition rate

**Geometric frustration? Diffusion?**

$$u = f a \nu \left(1 - e^{-\Delta G / k_B T}\right)$$

fraction of active sites

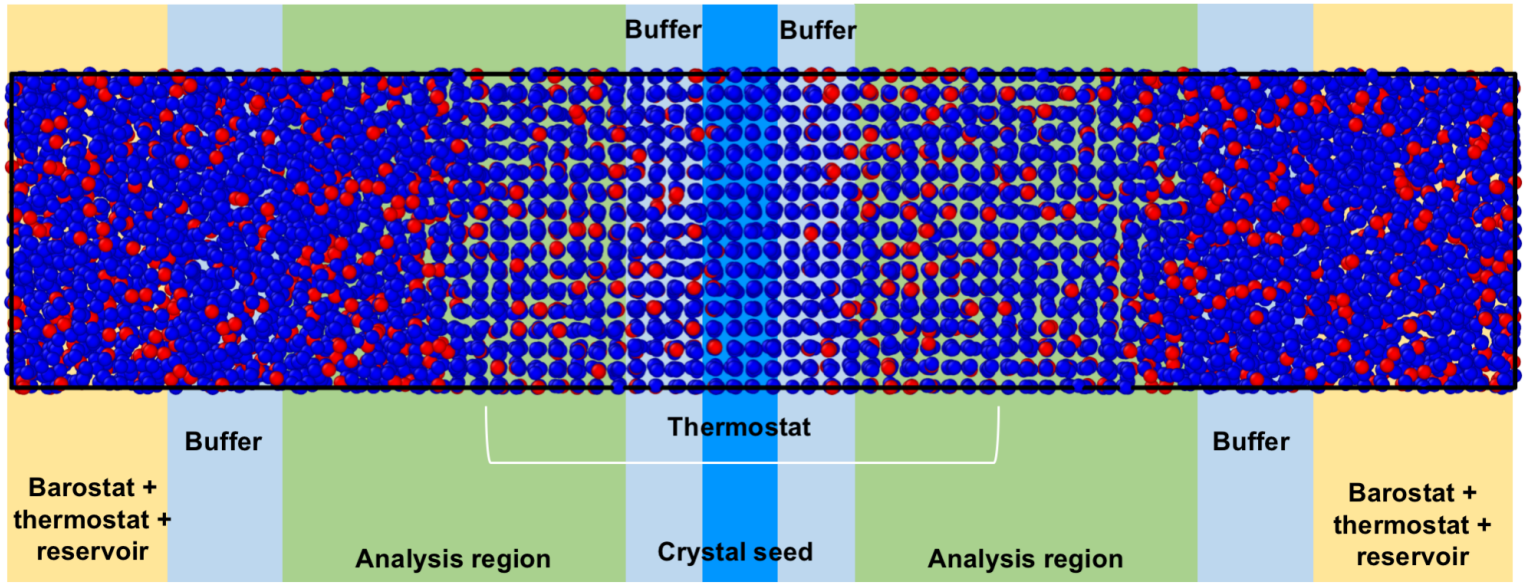
- Frenkel-Wilson equation for crystal growth rate

- Does this model lack the dependence on mixing ratio in $\nu$?



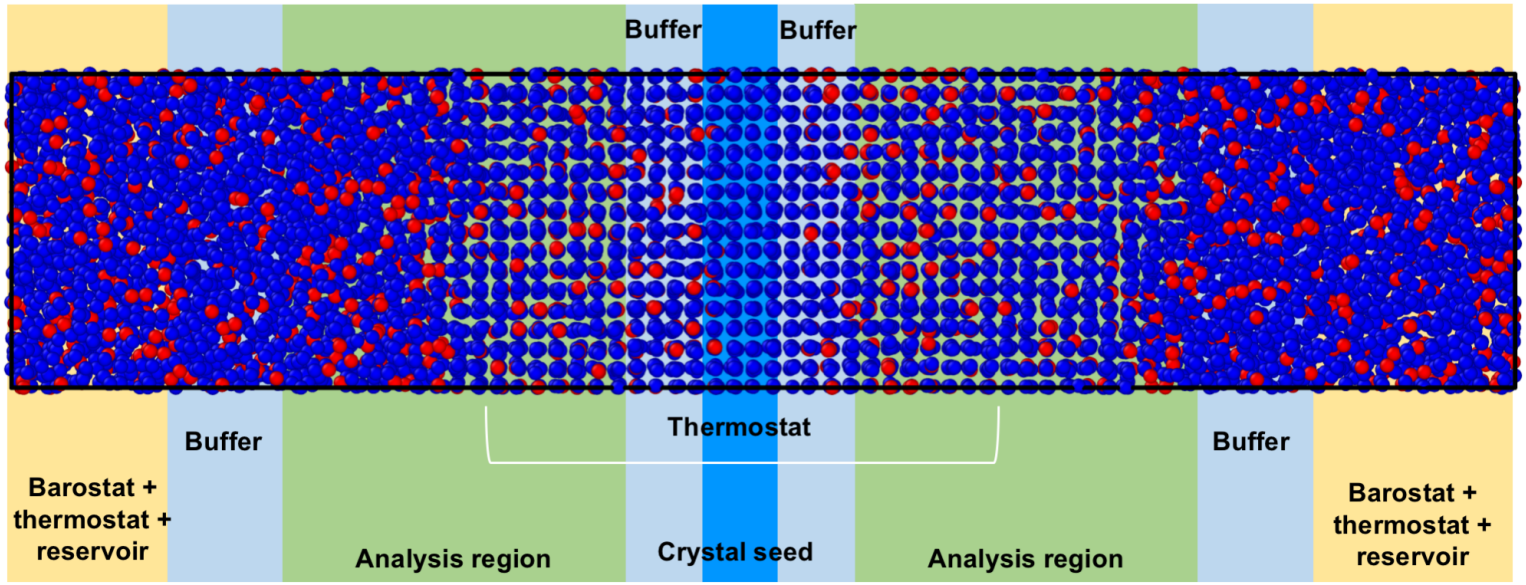
1. Tang *et al.*, Nature Mat. (2013)
2. Pedersen *et al.*, Phys. Rev. Lett. (2018)

- Simulation method: Molecular Dynamics
  LAMMPS package (www.lammps.sandia.gov)




- Elongated box, (100) and (111) directions, from 9000 up to 21000 atoms, 3D PBC
- Realistic central crystal seed

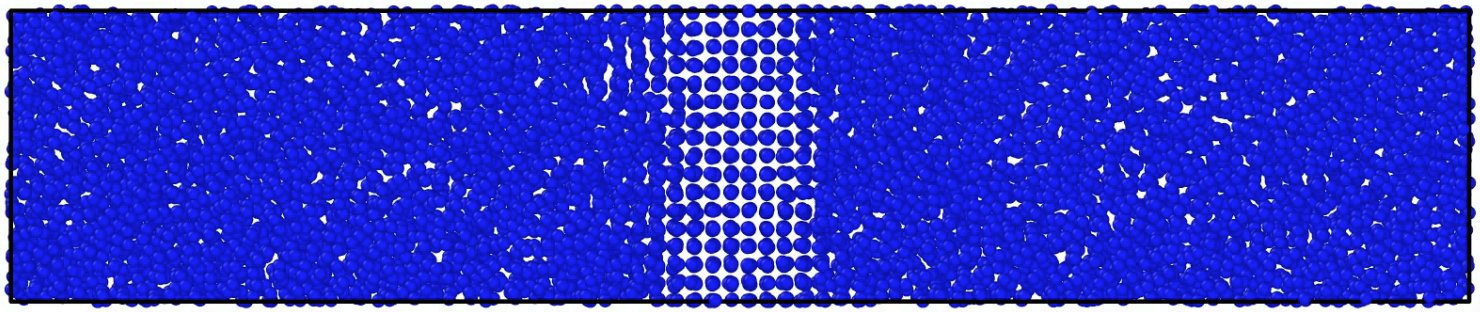
- Uniform crystallization process → constant pressure and chemical potential [1,2,3]



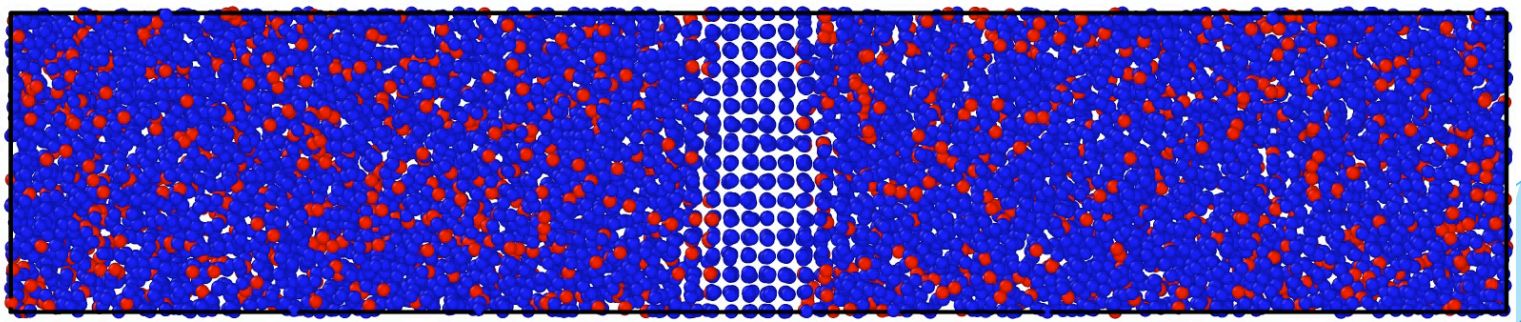

- barostat corrections only in external regions and along crystallization axis
- adaptive Bussi-Parrinello thermostat[4]

1. Perego *et al.*, J. of Chem. Phys. (2015)
2. Radu *et al.*, Phys. Rev. Lett. (2017)
3. Tang *et al.*, Nature Mat. (2013)
4. Bussi *et al.*, J. of Chem. Phys. (2007)

100% Argon



15% Krypton - 85% Argon

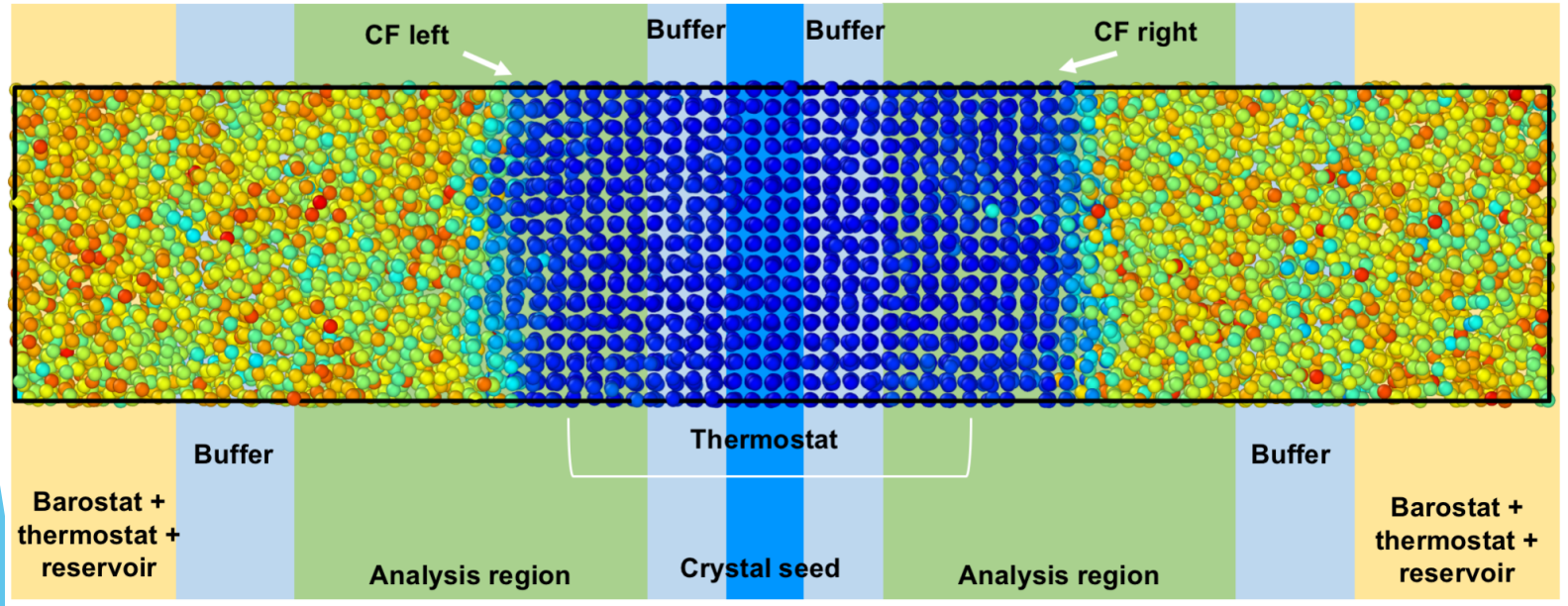


- Structural order parameter[1,2]

liquid solid

$S(i)$ -0.4 1.0

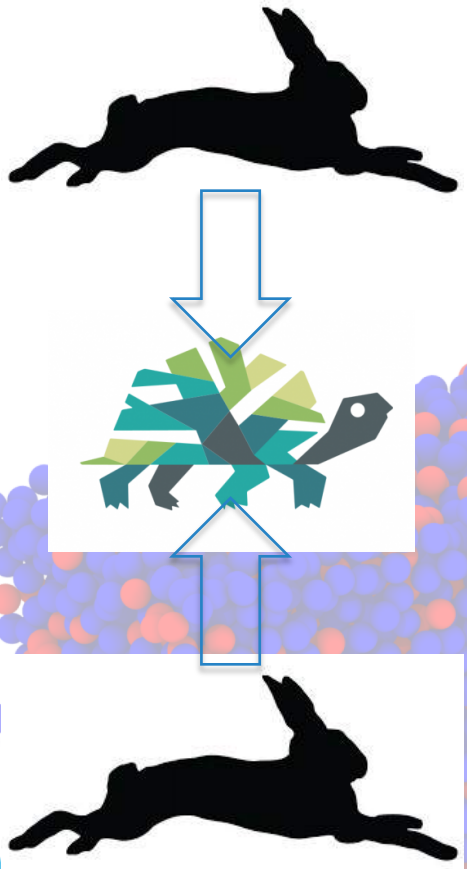
- Find the **crystal front** position

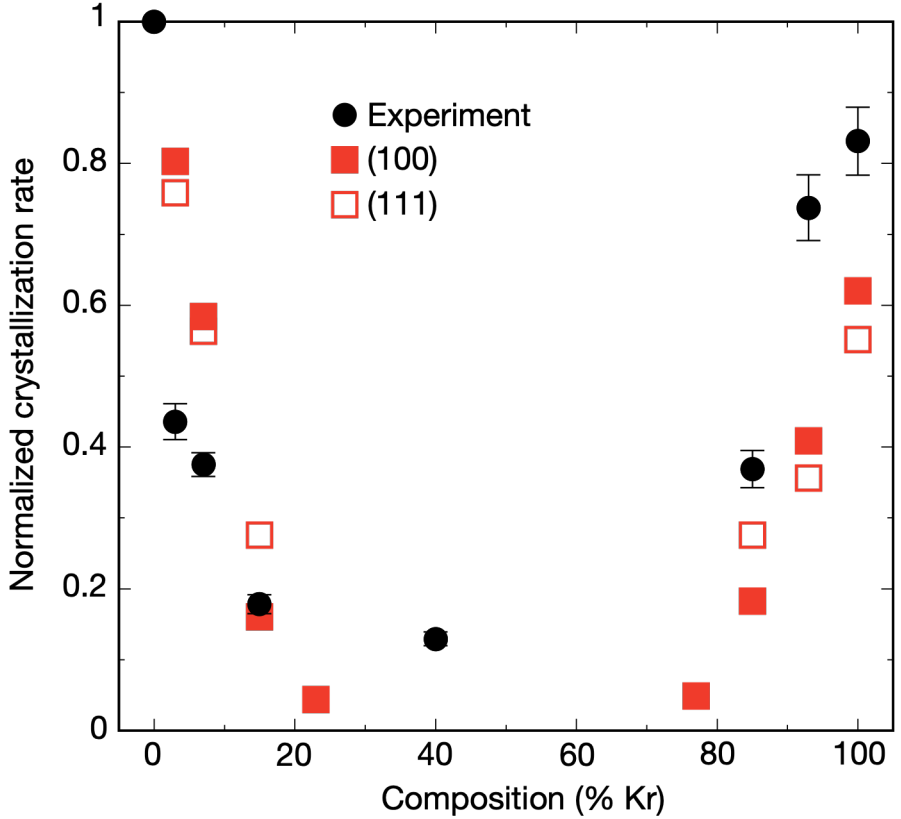



- velocity of the crystal front

**crystal growth rate!**

1. Steinhardt *et al.*, Phys. Rev. B (1985)
2. Lechner *et al.*, J. of Chem. Phys. (2008)

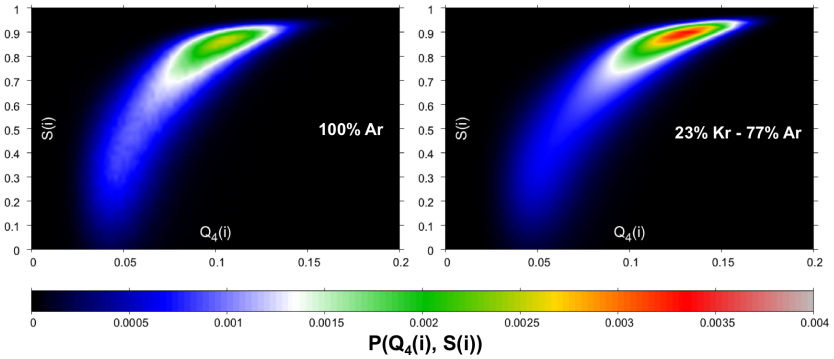





- Good agreement with experimental data: MD simulations capture relevant details!

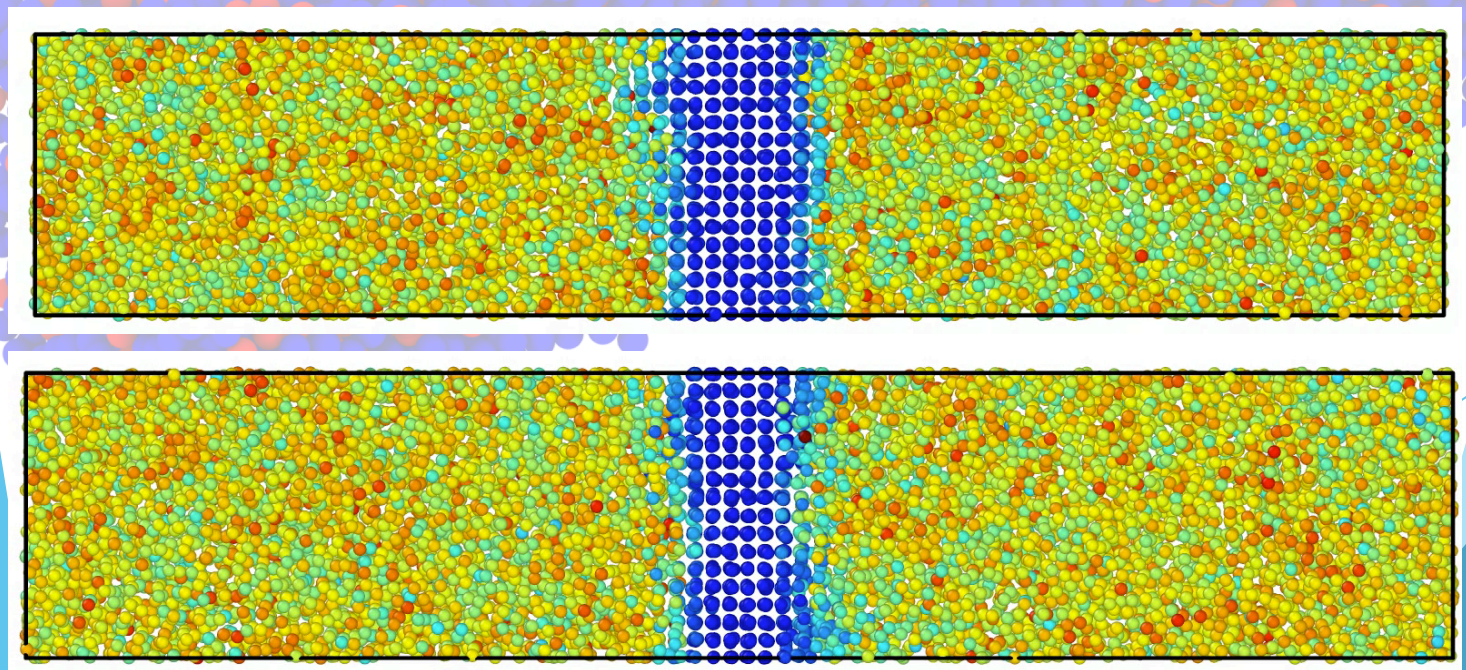
Slowdown on both sides → No temperature effect!

- No icosahedra or peculiar locally favoured structures (typical reason addressed for slowdown)
- What happens at the **crystal/liquid interface**?




- Appreciable differences: crystal/liquid interface is more variegated for mixtures

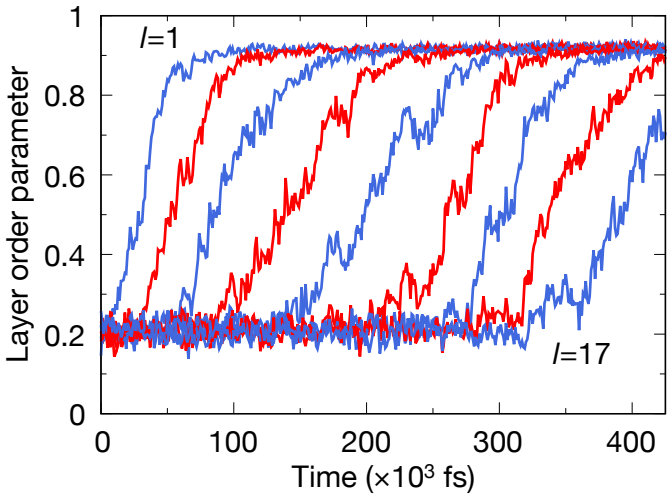




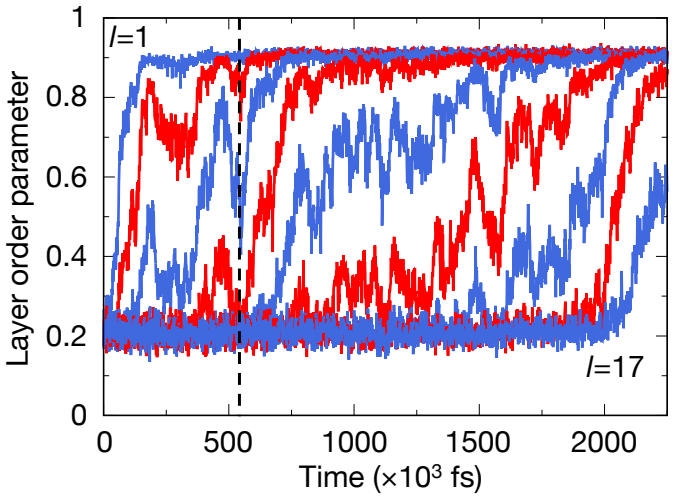
- Define the layer average of S(i), $\langle S \rangle_l$
- Time evolution of $\langle S \rangle_l$ for a pure system and a mixture



100% Ar



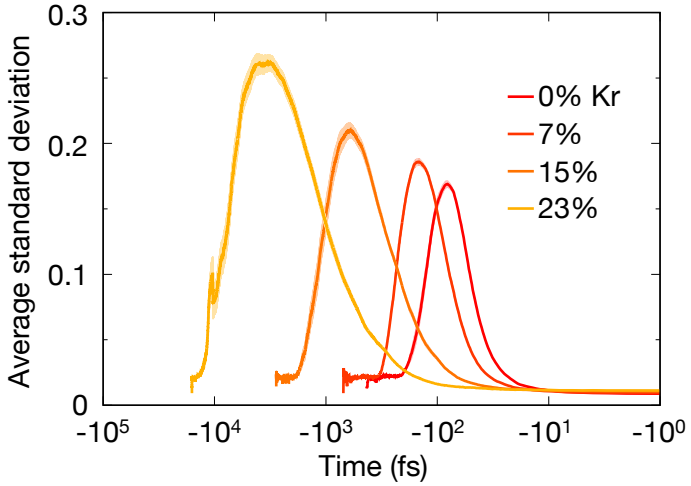

15% Kr – 85% Ar



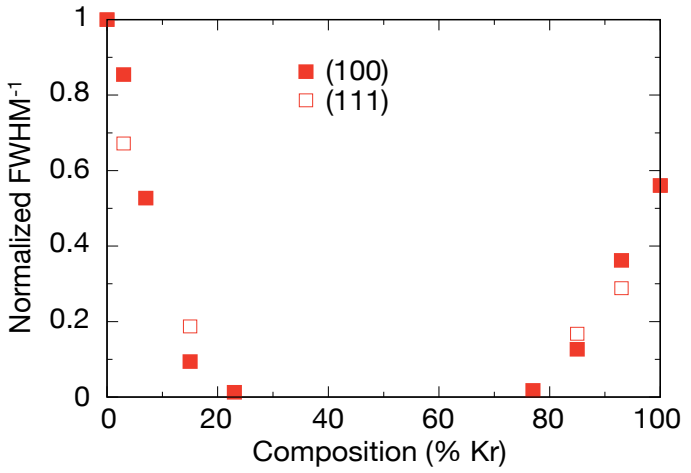

- Intrinsical slope of the $\langle S \rangle_l$ (t) curves is almost identical
- $\langle S \rangle_l$ drops (different timescales!)
- Regression towards a more disordered state is more frequent in binary systems

- **Microscopic explanation of the crystallization slowdown**

- Statistical analysis of $\langle S \rangle_l$ (t) → Standard deviation of $\langle S \rangle_l$ (t)




- Note the x-log scale
- Negative time: result of a time-shift to allow statistical analysis
- Height + width: extent of the fluctuations

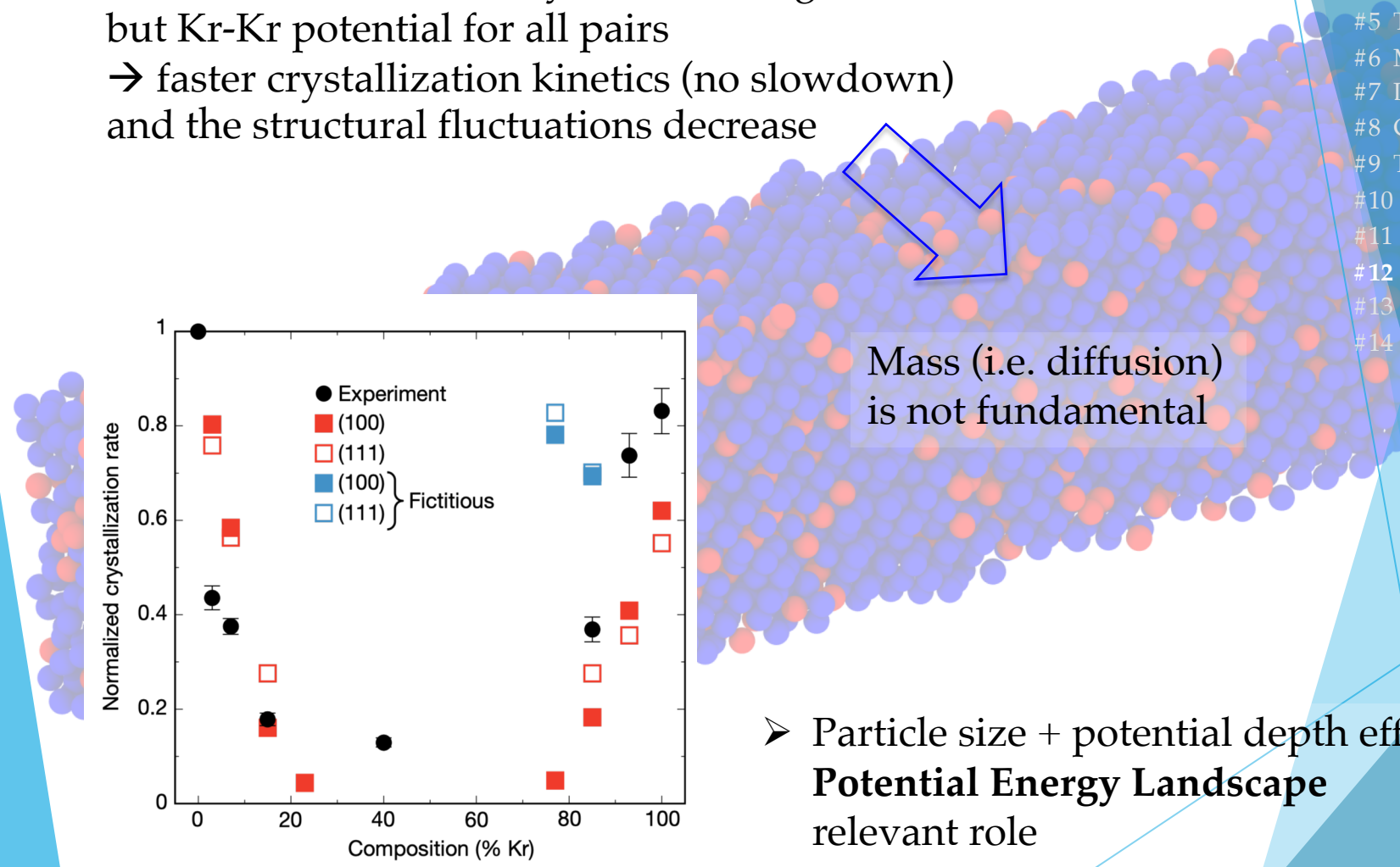



- Striking similarity between $FWHM^{-1}$ and crystal growth rate as a function of the composition
- Structural fluctuations between the liquid and crystal states → a fundamental feature of the mechanism of crystal growth

- Is the dominant effect a **kinetic** or a **potential** contribution?

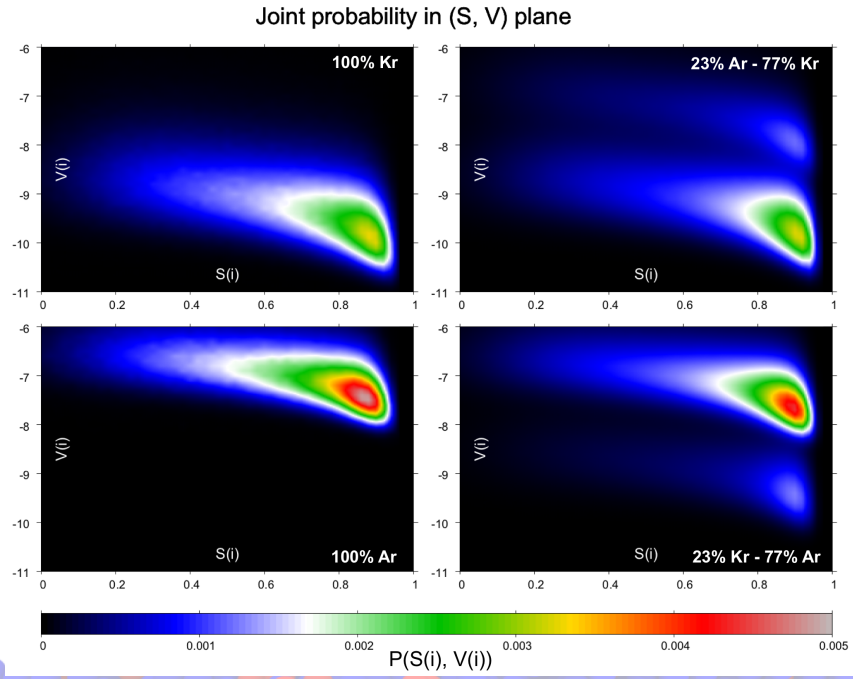
- Simulation of fictitious systems: distinguished masses, but Kr-Kr potential for all pairs
  → faster crystallization kinetics (no slowdown) and the structural fluctuations decrease






Mass (i.e. diffusion) is not fundamental

- Particle size + potential depth effect **Potential Energy Landscape** relevant role



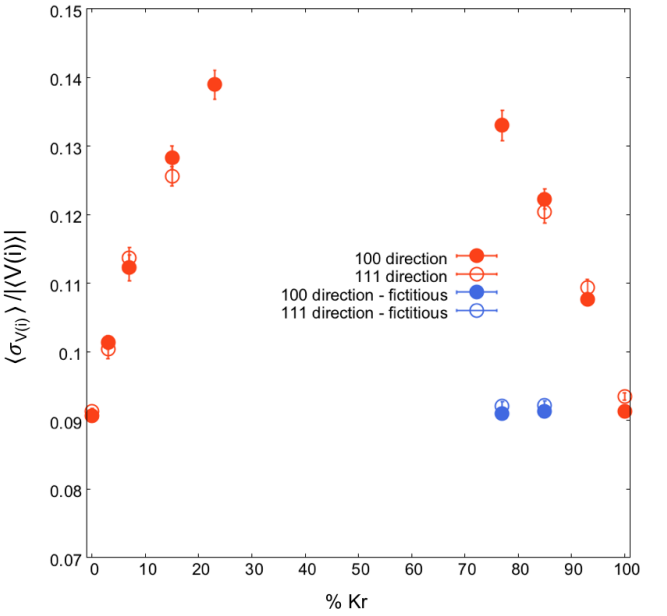



- Deep modifications induced in the PEL by the mixed interactions

$$V(i) = \sum_{j(\neq i)} V_{\alpha(i)\beta(j)}(|\mathbf{r}_i - \mathbf{r}_j|)$$

- Measure of the average relative fluctuations of the potential energy at the interface for the *i*-th particle

- Direct link between the crystal growth rate and the modification of the PEL exploration



# Our work:

- ✓ First experiment ever on x-ray diffraction of liquid/solid filaments → real sample & ideal model for binary LJ mixtures
- ✓ Simulated & experimental crystal growth rates
  → substantial agreement
- ✓ Fictitious systems (mass/size effects)
- ✓ Detection of $\langle S \rangle_l$ (t) structural fluctuations
  → slowdown microscopic origin!
- ✓ Potential energy landscape key role[1]



# What's next?

- ➢ How to effectively include these concepts into a more sophisticated theory of crystal growth, extending present models?
- ➢ Energy minimization at the interface[2]
- ➢ Free energy enhanced sampling methods
- ➢ Nucleation study
- ➢ More powerful experimental technique (XCCA)

European XFEL

1. Schottelius, Mambretti *et al.*, under review in Nat. Mat. (2018)
2. Sun *et al.*, Nat. Mat. (2018)

- Need for HPC resources: MARCONI & GALILEO supercomputing facilities (CINECA)

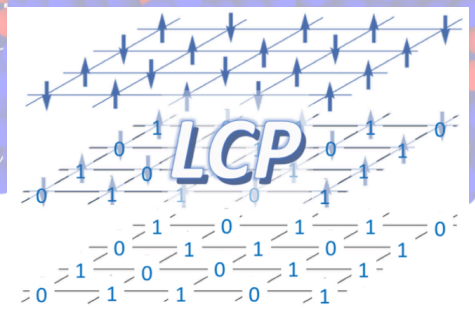
- *CINECA LISA 2016:*
  PUMAS project

- *ISCRA C 2017:*
  GLEMD project

- *ISCRA B 2018:*
  MEMETICO project

RegioneLombardia

CINECA

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# Thanks for your time!