Crystallization Onset of Aerosol Au Nanoparticles

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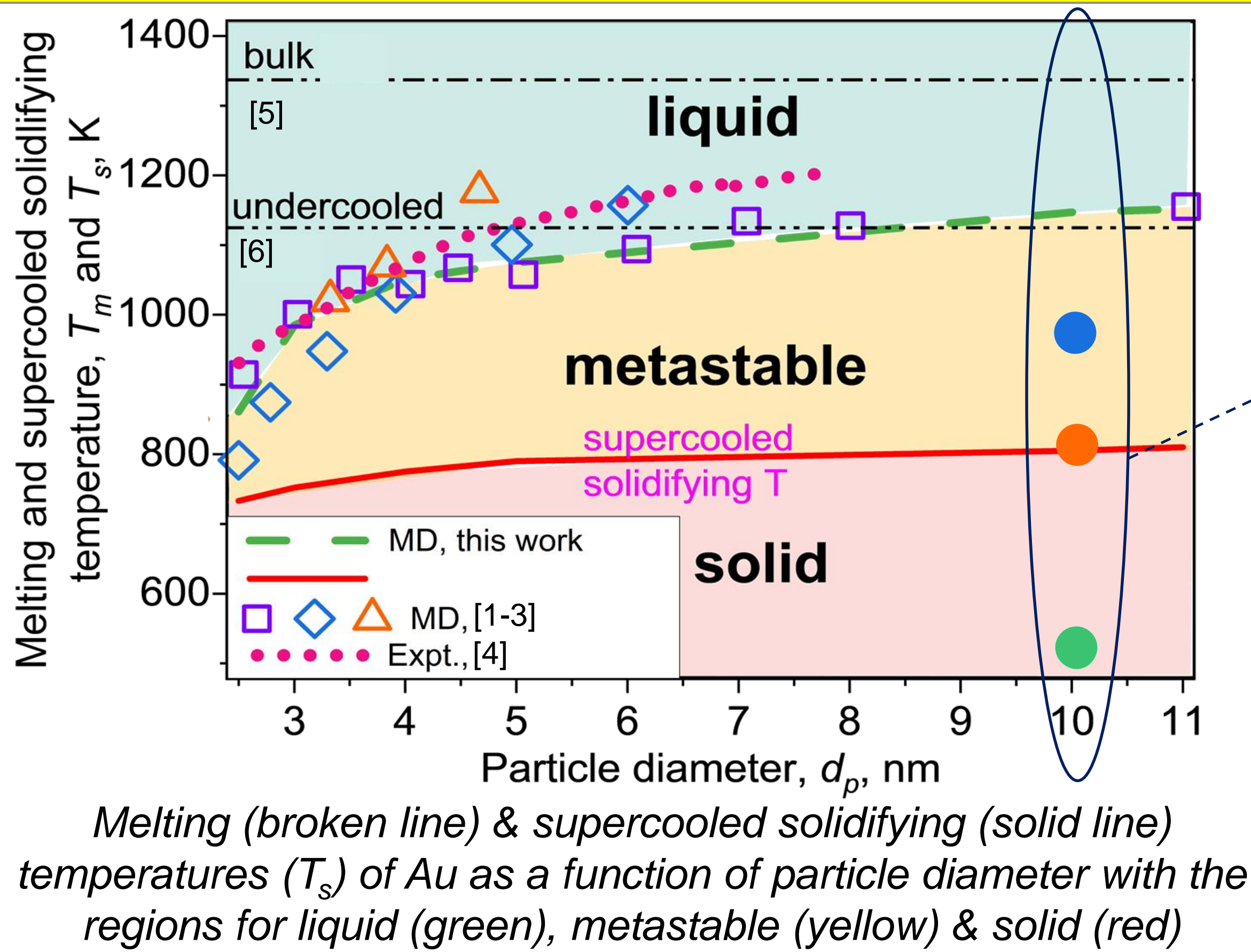**Swiss Federal Institute of Technology Zürich**
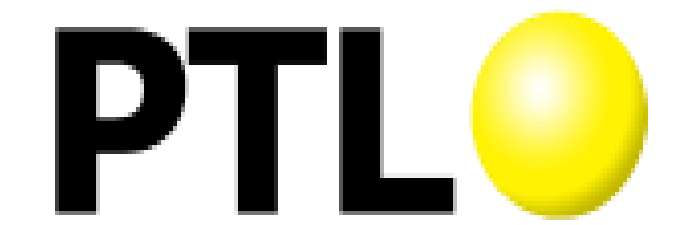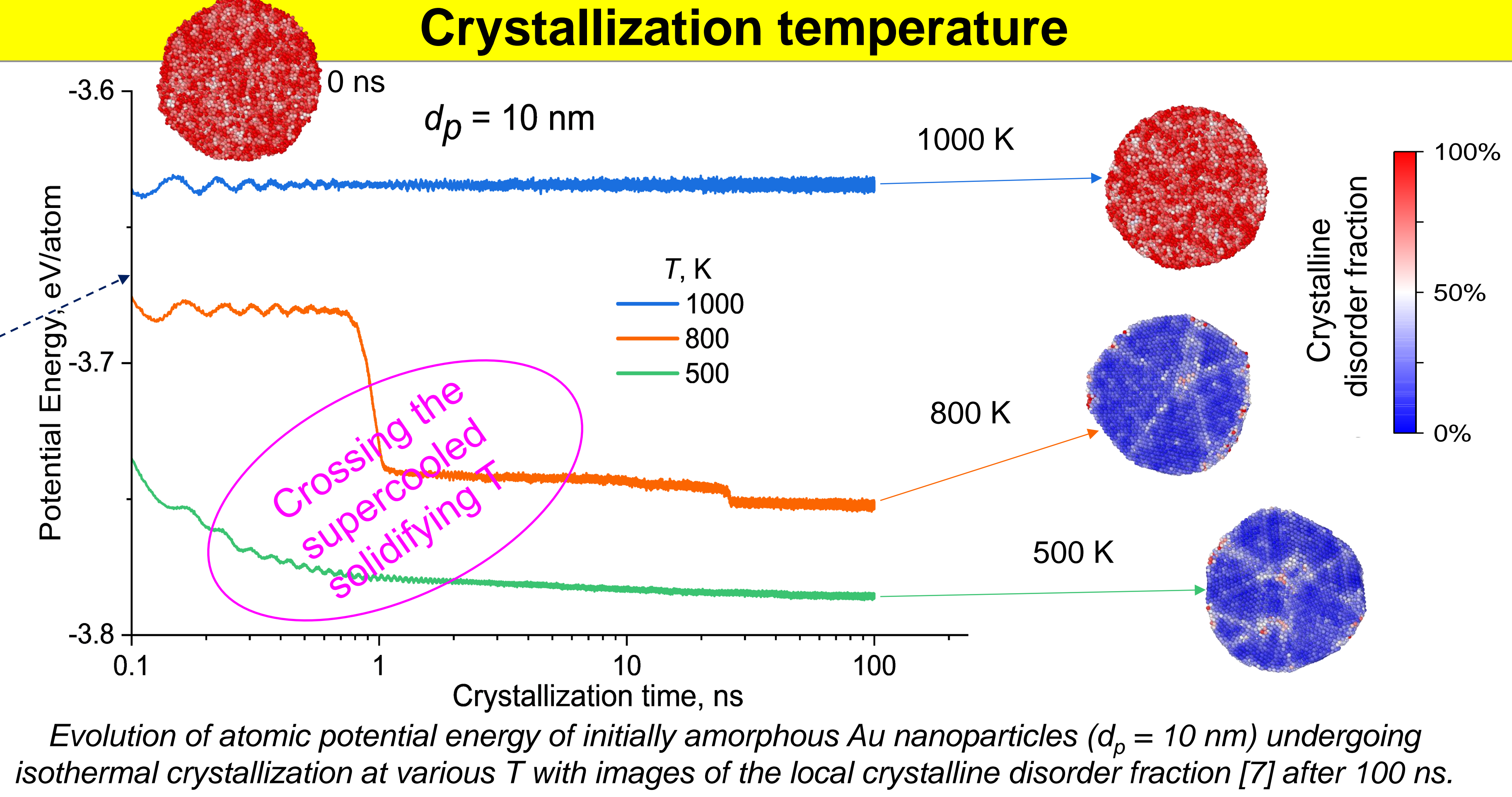
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Motivation

Gold nanoparticles have versatile applications in catalysis, gas sensing and medicine [1]. During aerosol synthesis, their crystallization sequence is elucidated by molecular dynamics. The onset of crystallization is revealed by tracking the largest cluster size and its retained atoms fraction (RAF) during crystallization.
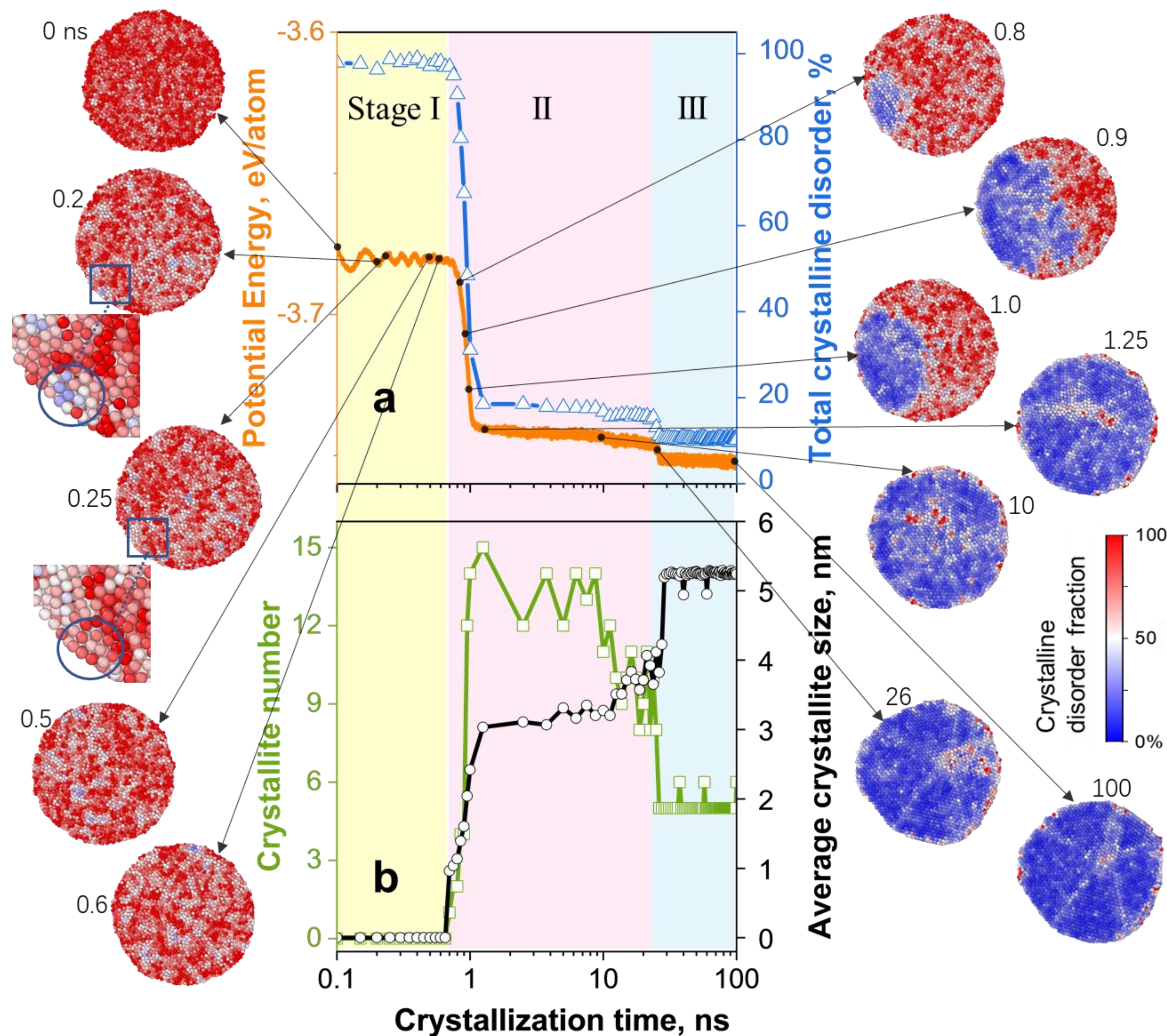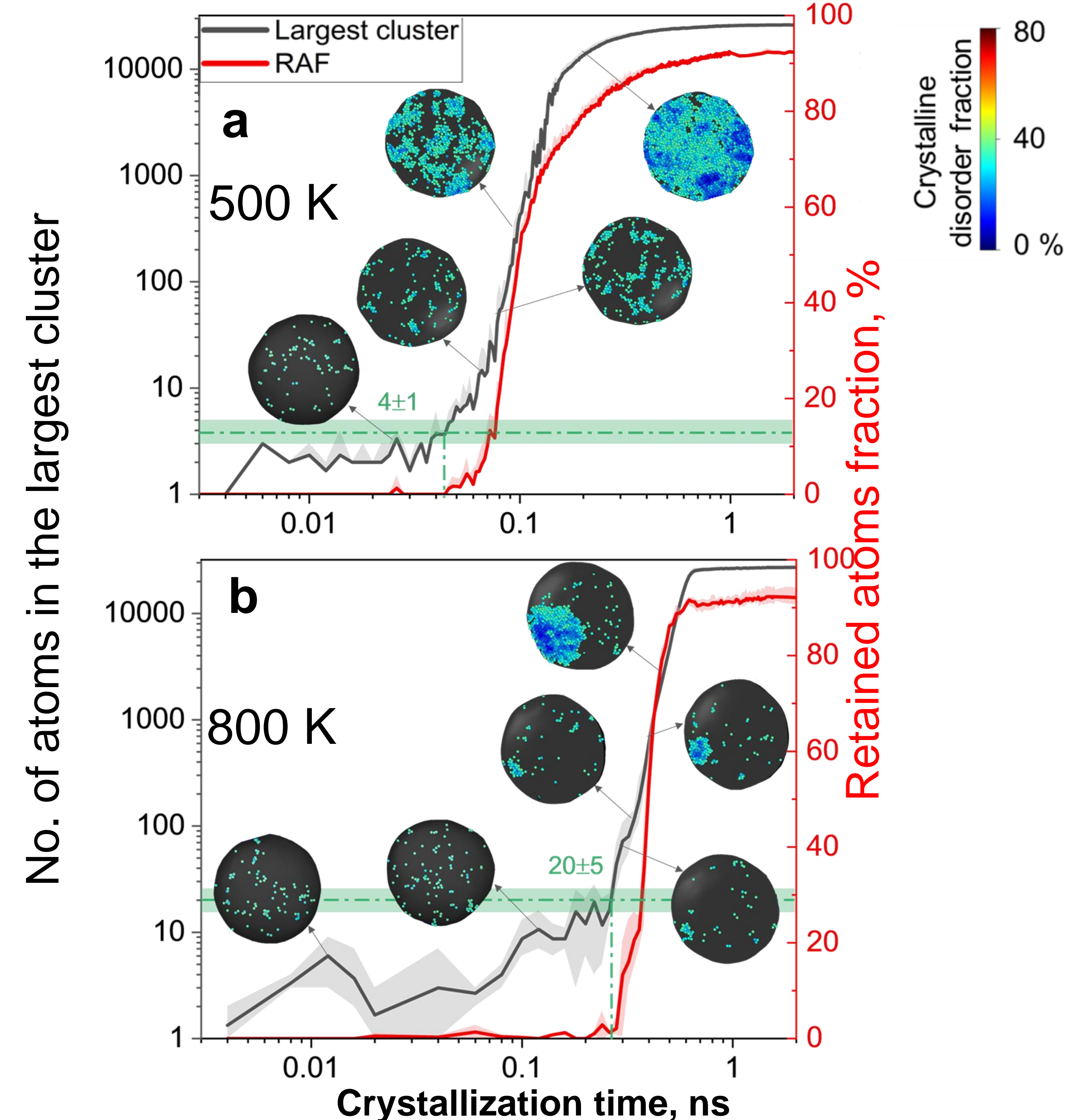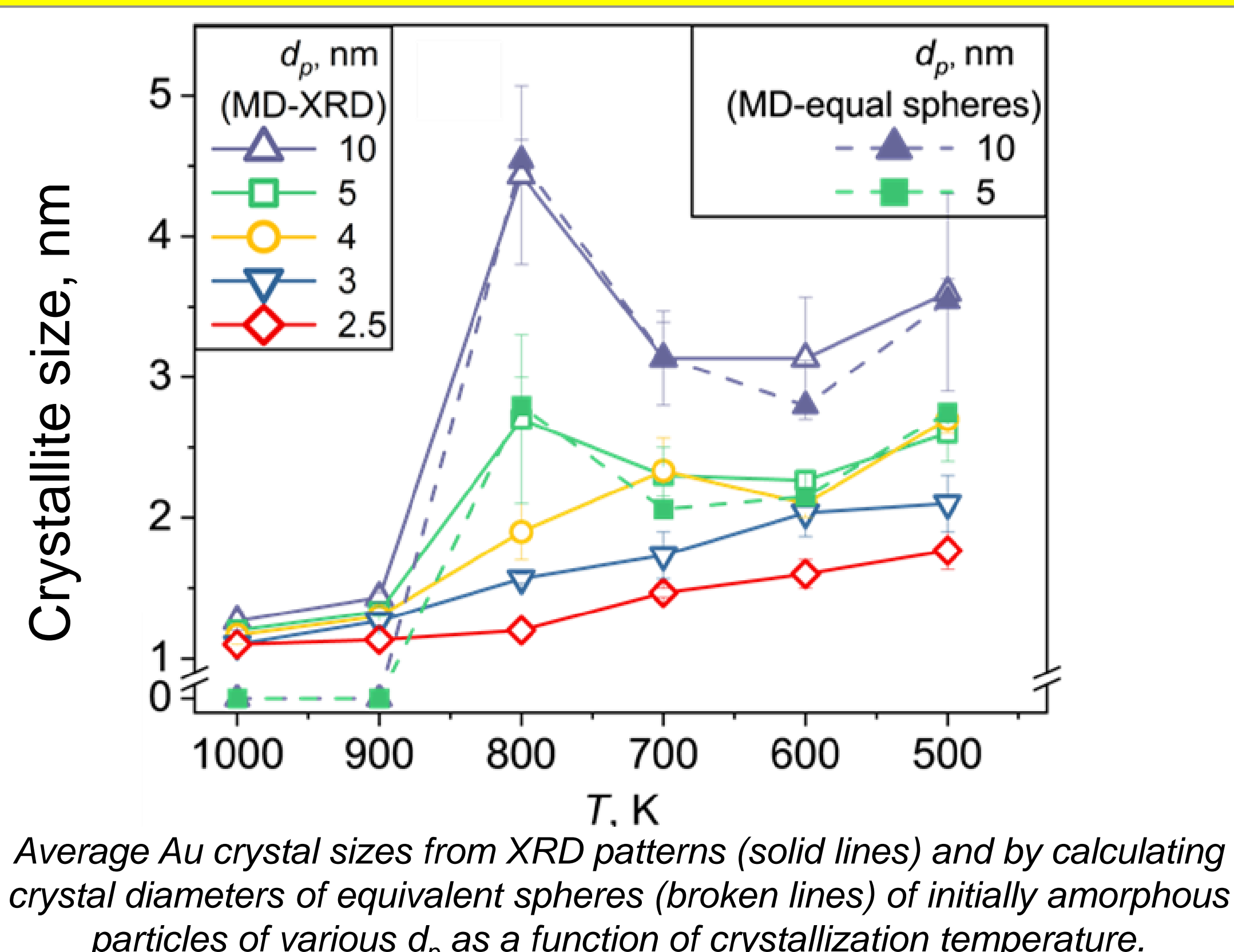
Method validation

Melting (broken line) & supercooled solidifying (solid line) temperatures (T_s) of Au as a function of particle diameter with the regions for liquid (green), metastable (yellow) & solid (red)

Crystallization temperature

Evolution of atomic potential energy of initially amorphous Au nanoparticles (d_p = 10 nm) undergoing isothermal crystallization at various T with images of the local crystalline disorder fraction [7] after 100 ns.

Sequence of Au crystallization

*Cross-section snapshots during crystallization of a 10 nm Au particle at 800 K for 100 ns. Evolution of (a) average atomic potential energy (orange line) and total crystalline disorder fraction (blue triangles) as well as its (b) number of crystallites (green squares) and average crystallite size (black circles). Crystallization proceeds in three stages: **(I) subcritical Au nuclei formation; (II) super-critical Au crystal formation and growth by accretion; (III) Au crystal domain formation.***

Crystallization nucleation pathways

*Number of atoms in the largest cluster (black lines, left axis) and its retained atoms fraction (RAF, red lines, right axis) of a 10 nm Au particle with 3D crystal projection colored by crystalline disorder fraction of each atom (for crystalline disorder fraction parameter smaller than 0.15). Crystallization takes place by **(A) "catastrophic" nucleation well below T_s** resulting in many small crystal domains (a, 500 K) and **(B) accretion nucleation near T_s** resulting in fewer nanocrystals and larger crystal domains (b, 800 K).*

Product crystallite size

Average Au crystal sizes from XRD patterns (solid lines) and by calculating crystal diameters of equivalent spheres (broken lines) of initially amorphous particles of various d_p as a function of crystallization temperature.

Conclusions

1. A metastable region is revealed as the MD are validated by the melting point dependence to particle diameter literature simulations and data.

2. Increasing temperature delays the crystallization that takes place with a metastable "jump"!

3. Three distinct stages are distinguished during isothermal crystallization.

4. Crystallization onset: (A) Catastrophic nucleation resulting in many small crystal domains well below T_s and (B) Accretion nucleation resulting in larger crystal domains near T_s.

5. The largest crystal size is obtained at temperatures near Ts.

References

[1] Goudeli, E., Pratsinis, S. E. (2016) *AIChE J.* **62,** 589.

[2] Nakaso, K., Shimada, M., Okuyama, K., Deppert, K. (2002) *J. Aerosol Sci.* **33**, 1061.

[3] Arcidiacono S., Bieri N.R., Poulikakos, D., Grigoropoulos, C. P. (2004) *Int. J. Multiph. Flow.* **30**, 979.

[4] Buffat, P., and Borel, J. P. (1976) *Phys. Rev. A.* **13**, 2287.

[5] Font, F., Myers, T. G. (2013) *J Nanopart Res.* **15**, 2086.

[6] Wilde G, Sebright JL, Perepezko, JH (2006) *Acta Mater.* **54**, 4759.

[7] Kawasaki, T., Onuki, A. (2011) *J. Chem. Phys.* **135**, 174109.