Machine learning potentials for phase change materials for electronic memories

Marco Bernasconi

Department of Materials Science, University of Milano-Bicocca, Milano, Italy

Car-Parrinello Parrinello-Rahman Molecular Dynamics

EUROPHYSICS LETTERS 10 May 1994

Europhys. Lett., **26** (5), pp. 345-351 (1994)

Structural Phase Transformations via First-Principles Simulation.

P. FOCHER (*), G. L. CHIAROTTI (*), M. BERNASCONI (*)
E. TOSATTI (*)(**) and M. PARRINELLO (***)

(*) *International School for Advanced Studies (SISSA)*
Via Beirut 2, I-34014 Trieste, Italy
(**) *International Centre for Theoretical Physics (ICTP)*
P.O. Box 586, I-34014 Trieste, Italy
(***) *IBM Research Division, Zurich Research Laboratory*
CH-8803 Rüschlikon, Switzerland

(received 1 December 1993; accepted in final form 5 April 1994)

PACS. 71.20A – Developments in mathematical and computational techniques.
PACS. 05.70F – Phase transitions: general aspects.
PACS. 62.50 – High-pressure and shock-wave effects in solids.

Abstract. – We present a new simulation scheme for structural phase transitions via first-principles molecular dynamics. The method is obtained by combining the Car-Parrinello method for *ab initio* simulation with the Parrinello-Rahman method to account for variable cell shape. We demonstrate the validity of our approach by simulating the spontaneous transformation of silicon from diamond to simple hexagonal phase under high pressure.

MPI - Stuttgart

VOLUME 76, NUMBER 16 PHYSICAL REVIEW LETTERS 15 APRIL 1996

New High-Pressure Phase of Ice

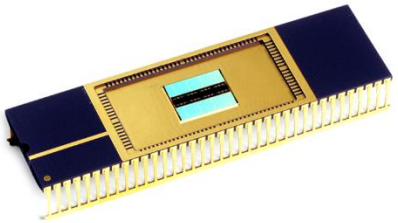
M. Benoit,[1,2] M. Bernasconi,[1] P. Focher,[3] and M. Parrinello[1]
[1]*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany*
[2]*Laboratoire de Science des Matériaux Vitreux, Université Montpellier II, 34095 Montpellier, France*
[3]*International School for Advanced Studies, Via Beirut 4, I-34014 Trieste, Italy*
(Received 7 November 1995)

Based on *ab initio* constant pressure molecular dynamics simulation, we predict a new phase transition in ice from ice X to a new phase (ice XI) at ~3 Mbar and room temperature. Ice XI preserves the symmetric hydrogen bond and is a wide gap insulator up to and beyond 7 Mbar. This new phase is stable up to 2000 K at 4 Mbar, where the system shows large protonic diffusion.

Phase Change Materials for Data Storage

Chalcogenides alloys: **$Ge_2Sb_2Te_5$ (GST225) , GeTe**

- Optical data storage: DVD and Blue-Ray DISC since ‘90

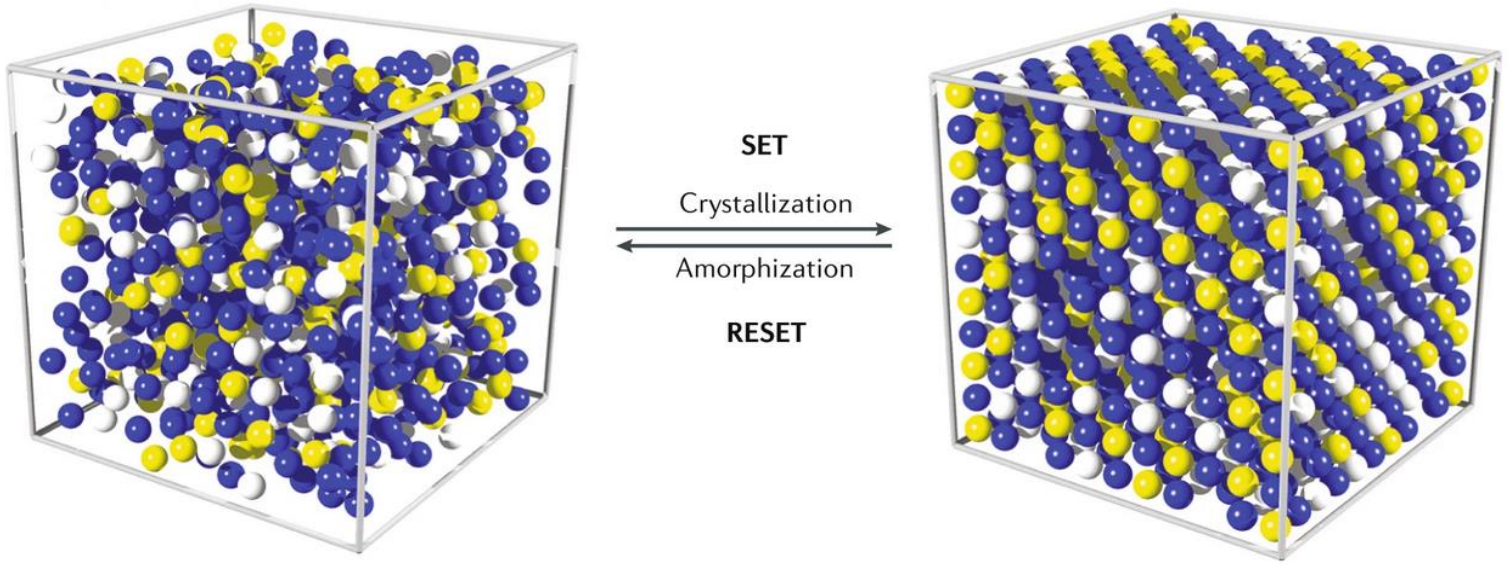


- Electronic non-volatile memory: Phase Change Memory

Phase Change Materials for Data Storage

- Fast (10-100 ns) and reversible change between amorphous and crystalline phase upon heating - laser irradiation or Joule effect

  - Amorphous - insulating "1"
  - Crystal - metallic "0"



Large difference in properties between the two phases

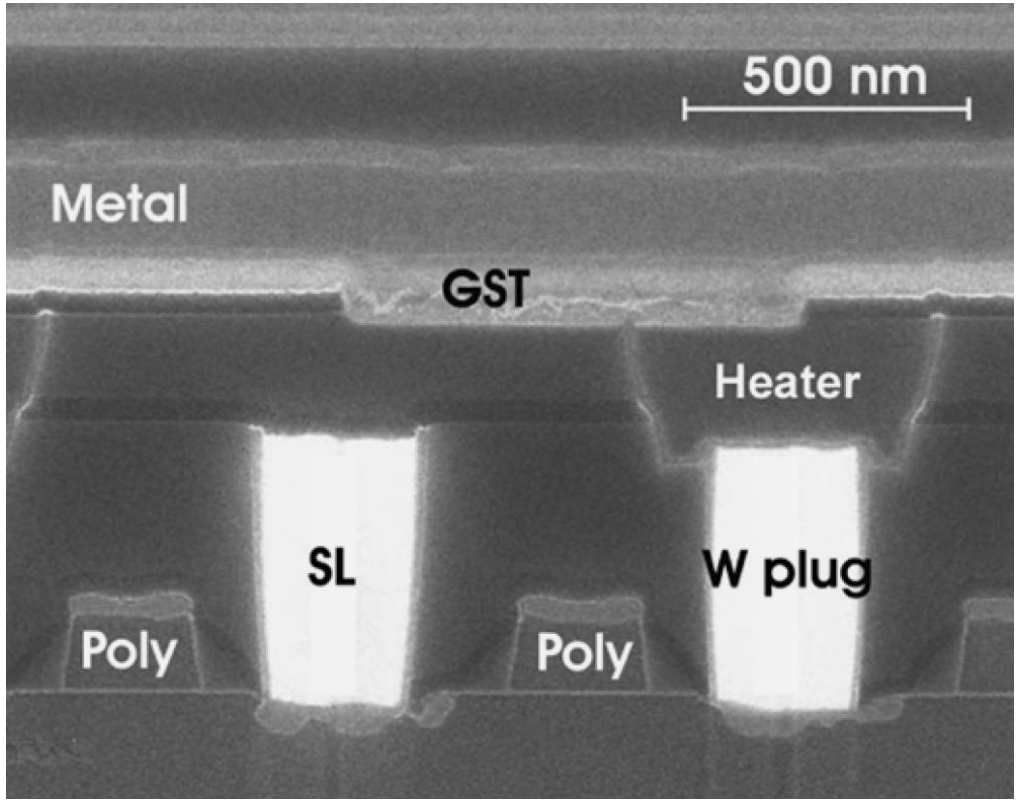
Zhang et al.
Nat. Rev. Mater. 4, 150 (2019)

Reflectivity change by 30 % → optical storage (DVD. Blue-ray discs)

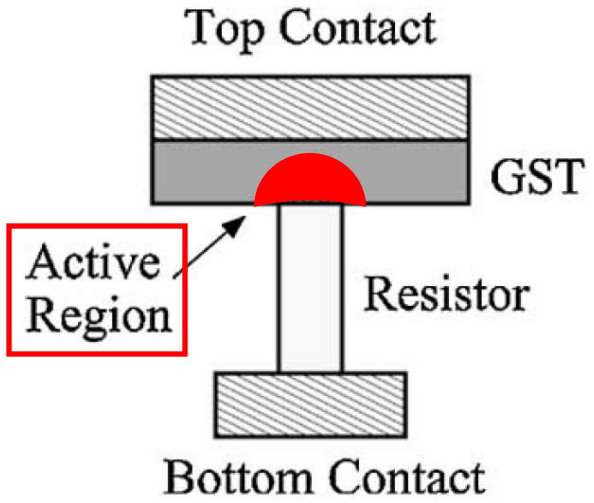
Resistivity change by 10^3 → PCM

Phase Change Memory (PCM) Cell

SEM cross section (STMicroelectronics 2010)



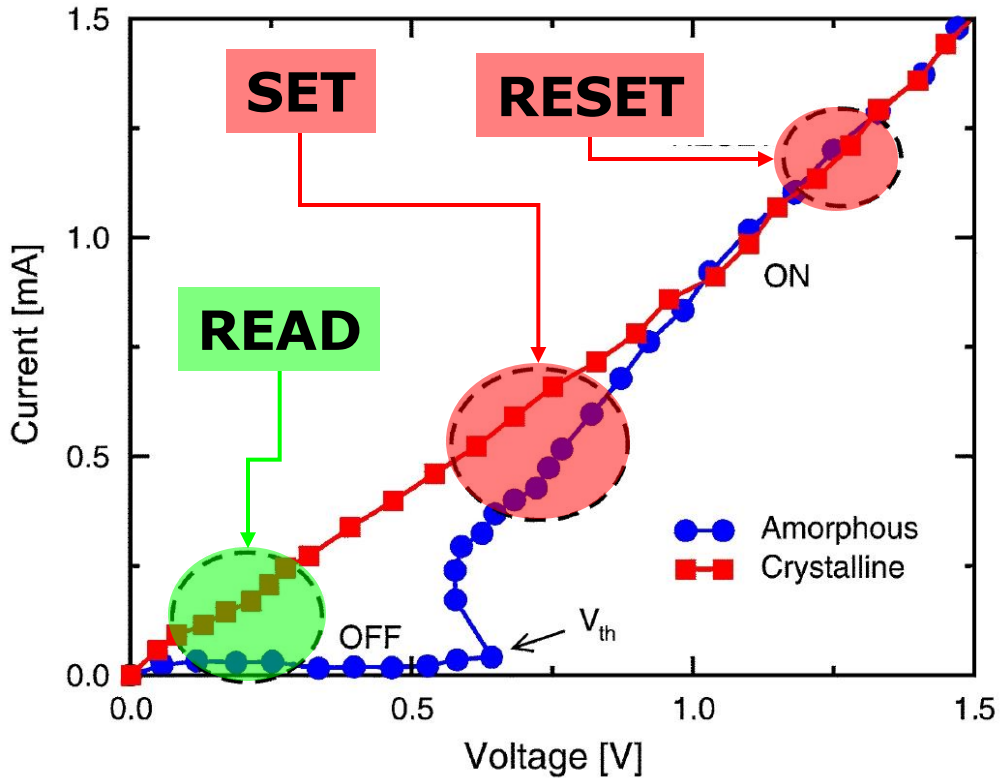
Schematic representation

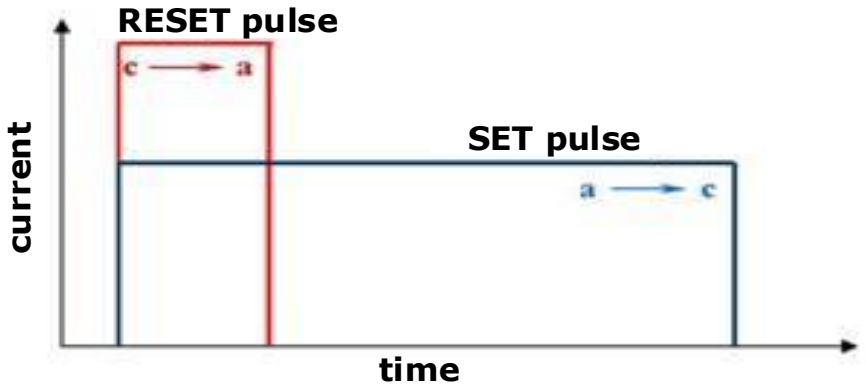


- Active region: a small dome within GST film undergoes the phase transition
- Phase–change by heating via Joule effect

I-V characteristic of PCM : threshold switching

- cell readout: performed at low bias ($V<V_{th}$)
- set/reset: bias higher than threshold ($V>V_{th}$)





- RESET:
  higher current & shorter pulse

  crystal → *amorphous*

- SET:
  lower current & longer pulse:

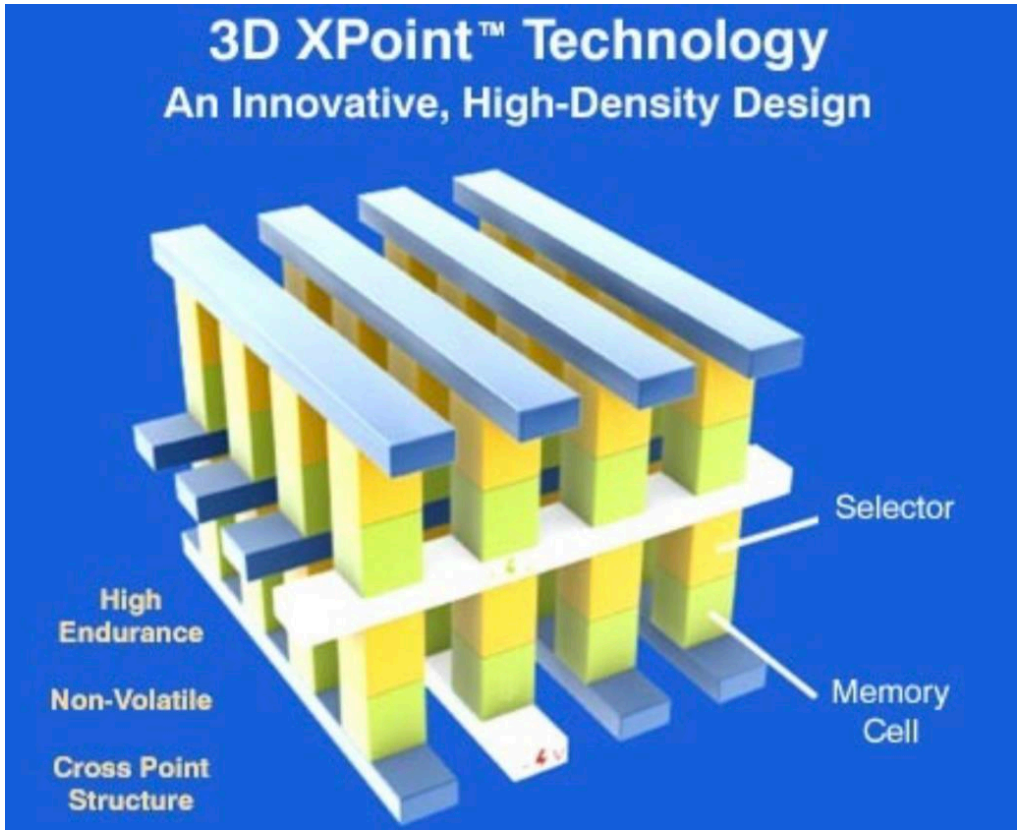
  amorphous → *crystal*

Concept first proposed by Ovshinsky in 1968

The past of PCM: 3D XPoint™ Technology

Since April 2017 Intel and Micron commercialized high-density PCM Memory Card

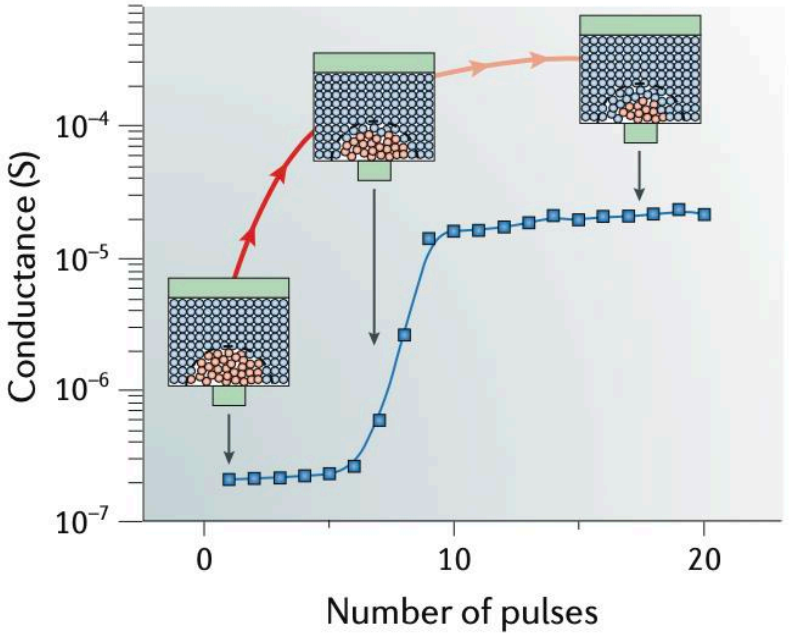
3D XPoint™ Technology - non-volatile electronic memories much faster than SSD

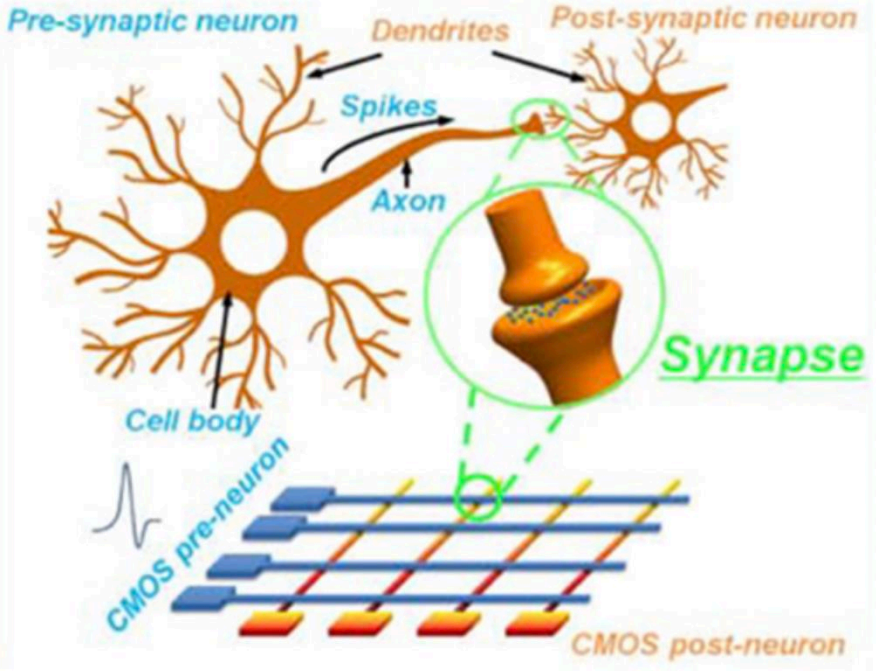


The future of PCM: neuromorphic computing

- Programming by current pulses - single pulse for set/reset in PCMs

- Several pulses to induce partial crystallization during set or variable size of amorphous dome during reset: intermediate discrete/analogic resistance states that depend on the history of current pulses → artificial synapses

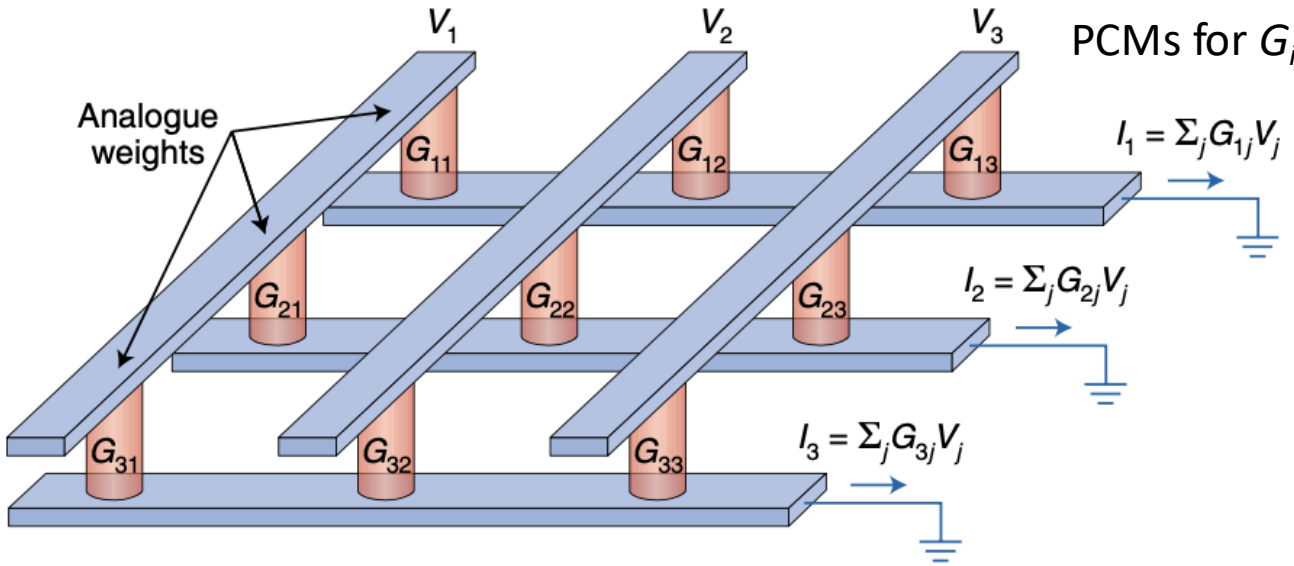




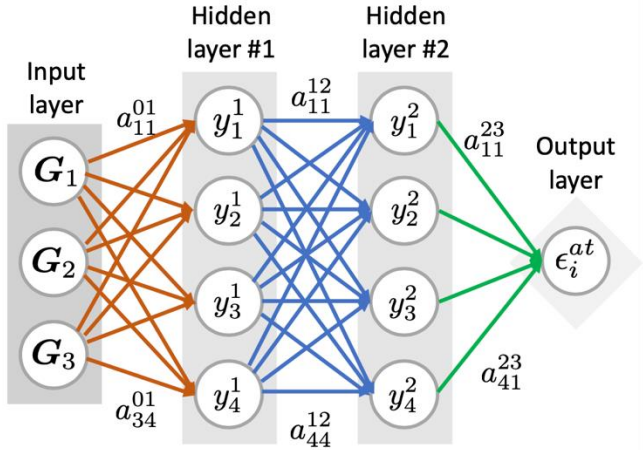
Zhang et al.,Nat. Rev. Mater. 4, 150 (2019)

Neuromorphic Computing

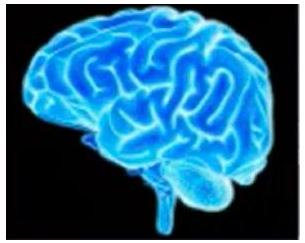
Matrix-vector multiplication for inference in artificial deep neural networks



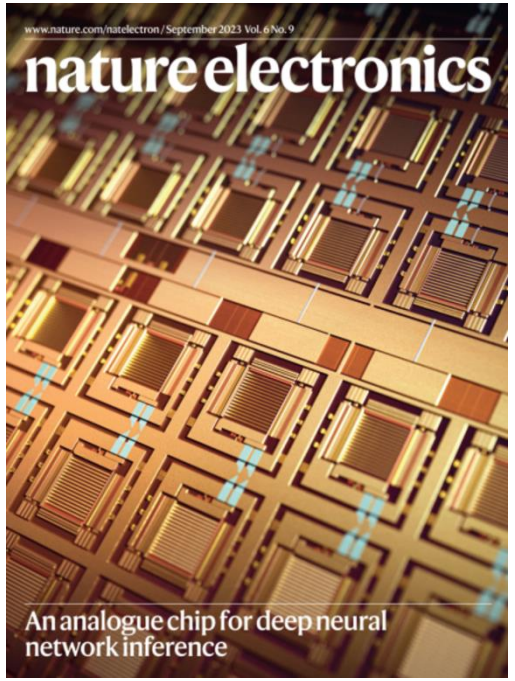
PCMs for G_{ij} synaptic weights



Ielmini and Wong, Nat. Electr. 1, 333 (2018)

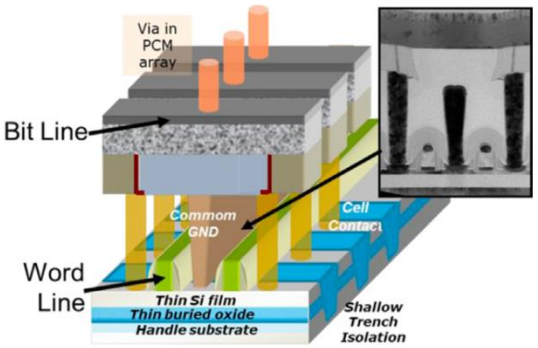


Sebastian et al. Nature Nanotechnology 15, 529 (2020);
Le Gallo et al. Nature Electronics 6, 680 (2023)



Embedded Phase Change Memory

- Embedded non-volatile memories in microcontrollers
- PCM cheaper than Flash at and below 28 nm node



Cappelletti et al, J. Phys. D 53, 193002 (2020)
Redaelli et al, Mat. Sci. Semic. Process. 137, 106184 (2022)

STMicroelectronics

18 nm MCU with embedded PCM announced in March 2024

Crystallization temperature (T_x) of flagship GST225 ~ 120 °C not suitable for applications in embedded memories (soldering compliance: few minutes at 260 °C)

Non-stoichiometric Ge-rich GeSbTe alloys are actually used, raise in T_x due to Ge segregation

Ab-initio modeling of phase change materials

Models (300 atoms) of amorphous $Ge_2Sb_2Te_5$ (GST225) generated by quenching from the melt (100 ps) in second generation CP molecular dynamics in 2007

Caravati, Bernasconi, Kühne, Krack, and Parrinello, Appl. Phys. Lett. 91, 171906 (2007)

- Structure of the amorphous phase
- Origin of resistivity and optical contrast amorphous vs crystal
- Origin of resistance drift with time (aging) in amorphous phase

DFT simulations limited to a few hundreds atoms for a few ns at most

Machine learning potentials to enlarge the scope of DFT methods

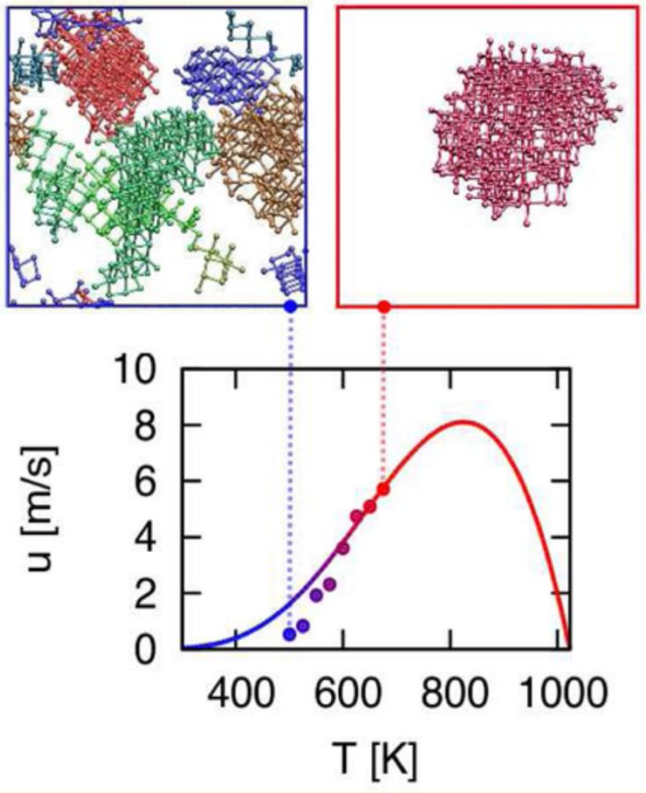
large scale simulations (million atoms for ns) with DFT accuracy

Neural Network interatomic potentials

NN potential for GeTe fitting the DFT energy of 36000 structures (60-100 atoms)

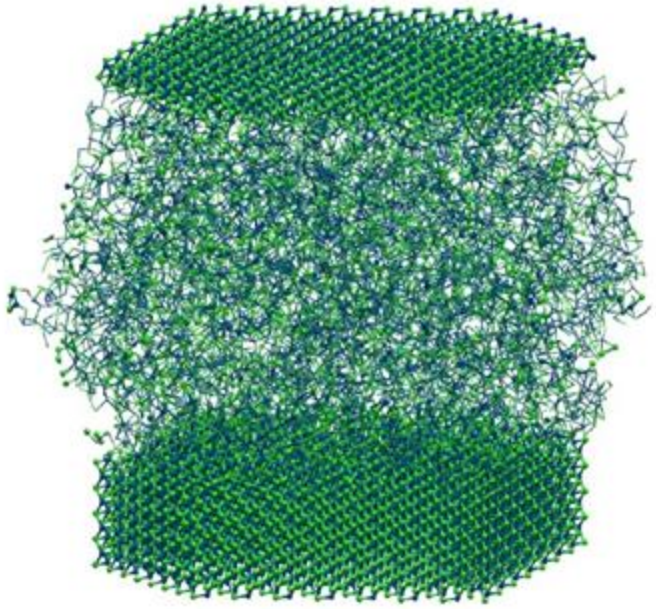
Sosso et al. *PRB* 85, 174103 (2012)

Code RuNNer (Behler, Parrinello PRL 2007)



Nucleation and crystal growth in bulk GeTe

Sosso et al, *JPCL* 4, 4241 (2013); *JPCC* 119, 6428 (2015)



Nanowire crystallization (16.000 atoms for 10 ns)

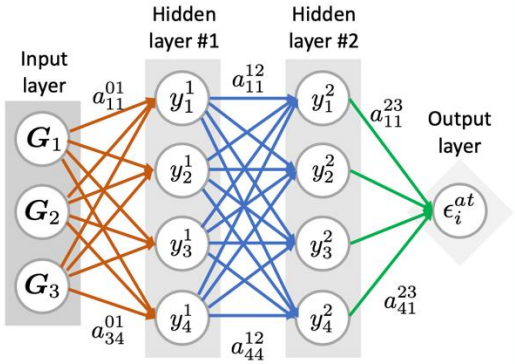
Gabardi *et al, J. Phys. Chem. C* 21, 23827 (2017)

Thermal transport

Sosso, Donadio, Behler, Bernasconi, PRB 86, 104301 (2012)

A machine learning potential for $Ge_2Sb_2Te_5$

Omar Abou El Kheir, Bonati, Parrinello, Bernasconi, npj Comp. Mater. 10, 33 (2024)



- DeePMD package, descriptors generated by a second neural network

  Han Wang et al., Comp. Phys. Comm., 228, 178 (2018)

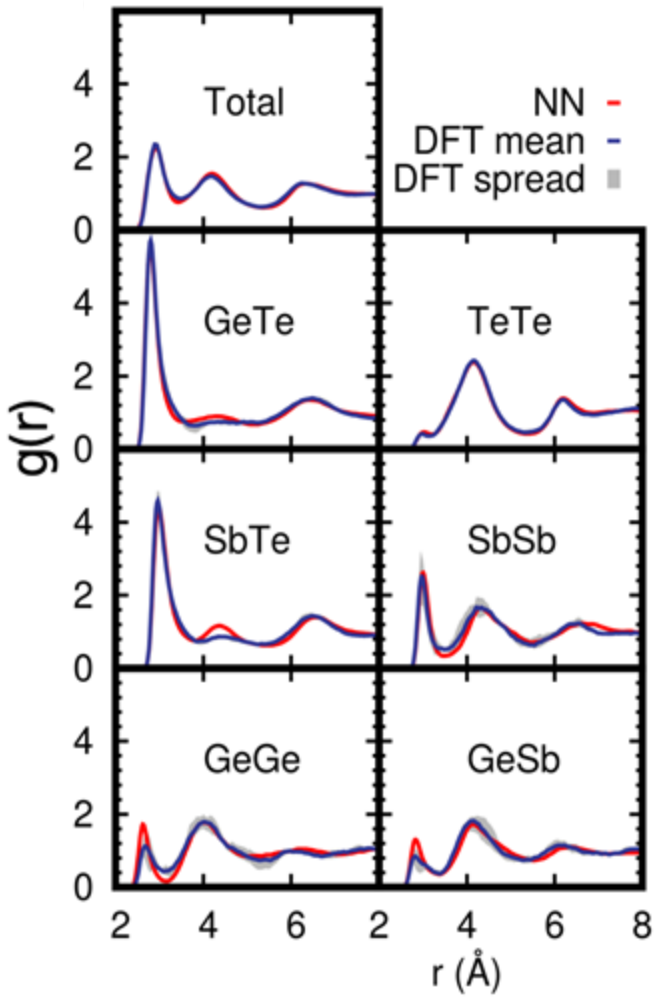
- Training over DFT energy and forces of 180.000 configurations (57-104 atoms cell); RMSE energy&forces 8 meV/atom & 160 meV/Å

- Configurations generated by ab-initio MD at different conditions (CP2k code)

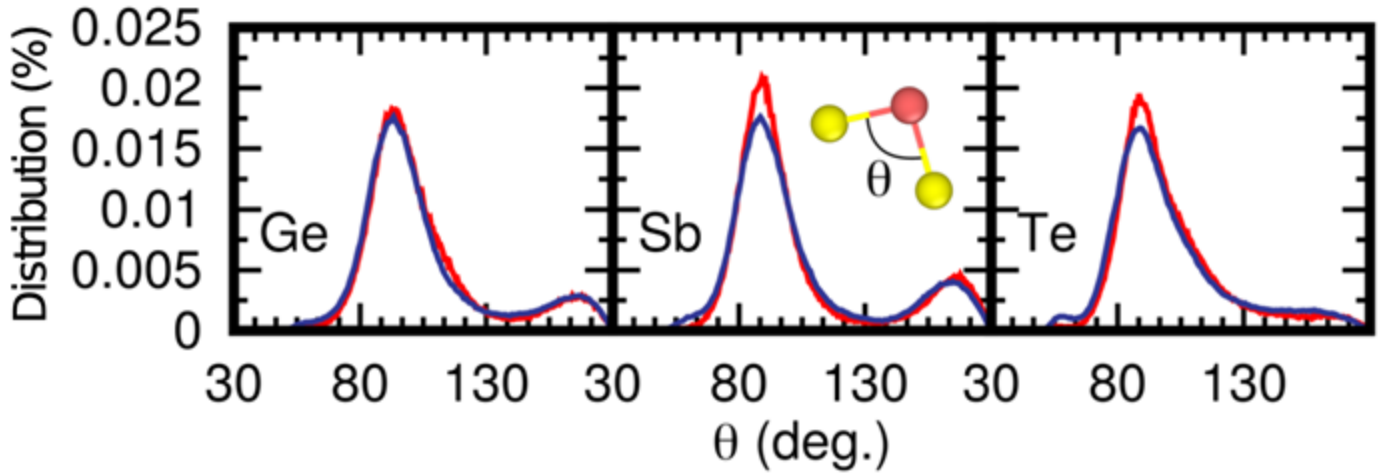
- Total energy computed with PBE functional, pseudopotentials, Gaussian-type-orbitals expansion of KS orbitals, BZ integration (CP2k code)

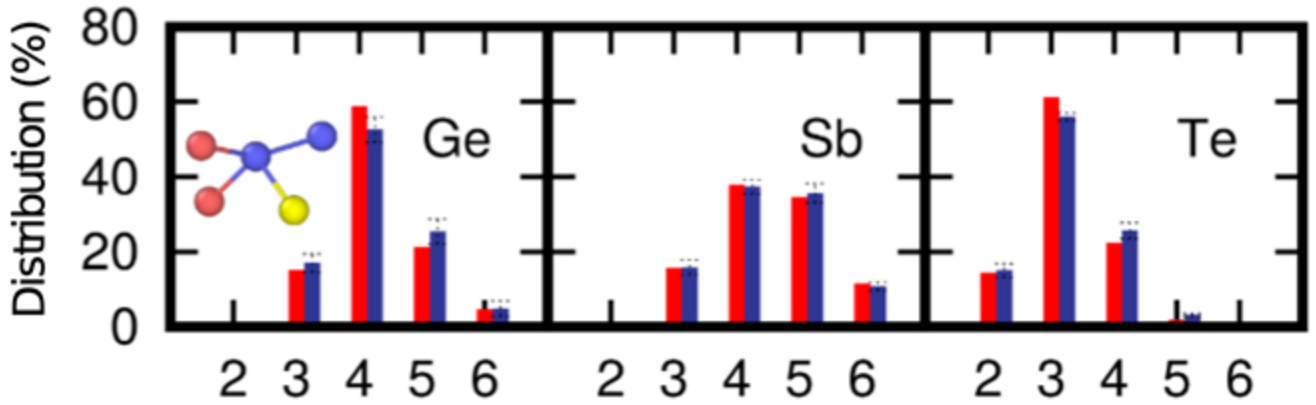
Validation of the NN potential: amorphous phase

NN model 1000 atoms vs 4 DFT models 216 atoms



Bond angle distribution functions



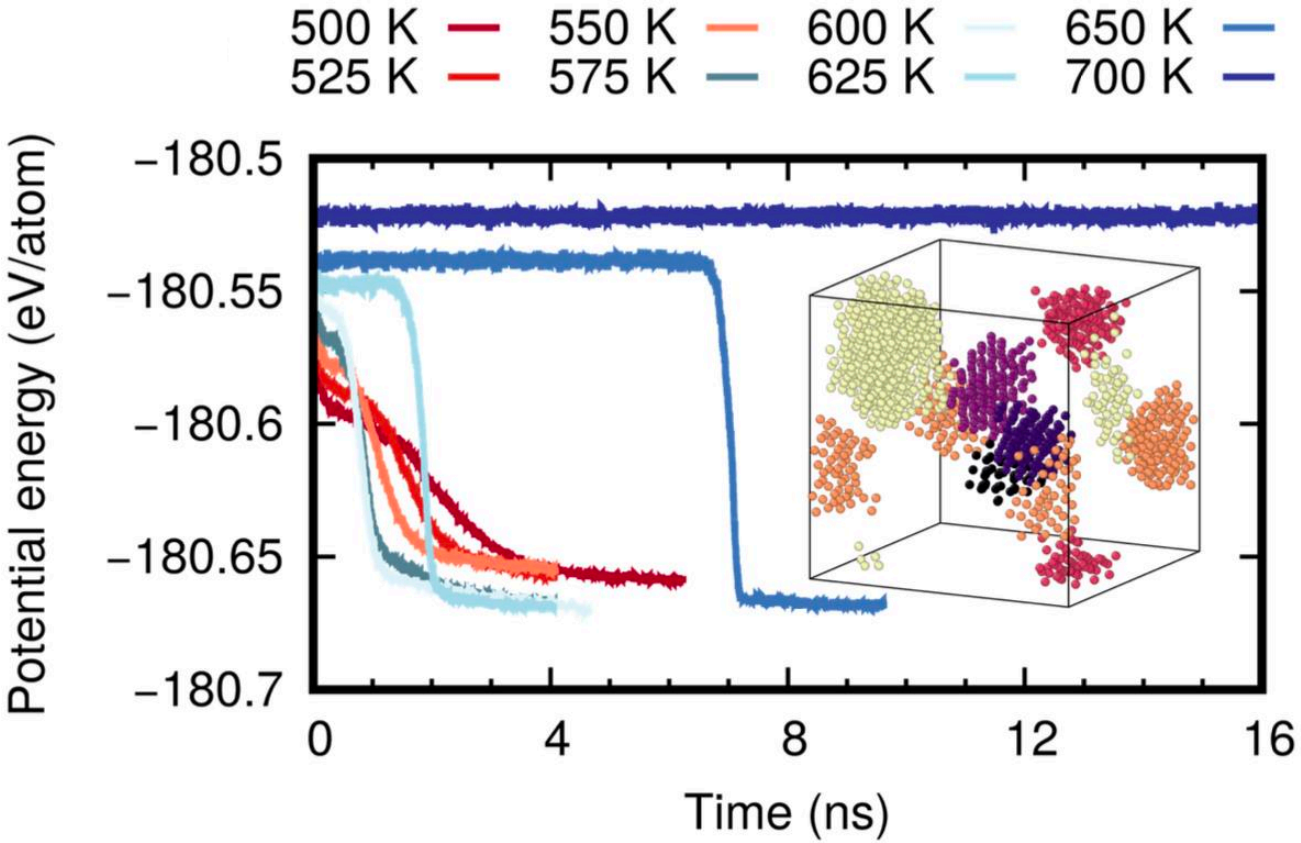


Coordination numbers

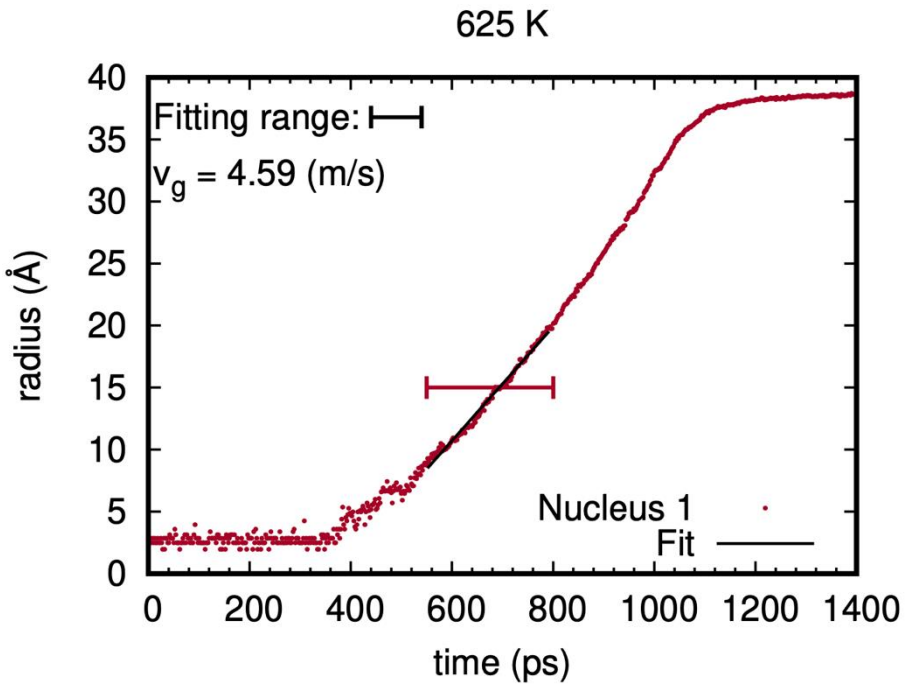
Abou El Kheir et al., npj Comput. Mat. 10, 33 (2024)

Homogeneous crystallization

Simulation of homogenous crystal nucleation and growth in supercooled liquid and overheated amorphous phases (8000 atoms)



$$v_g = \frac{dR}{dt} \qquad R = \sqrt[3]{\frac{3V_{cryst}}{4\pi}}$$

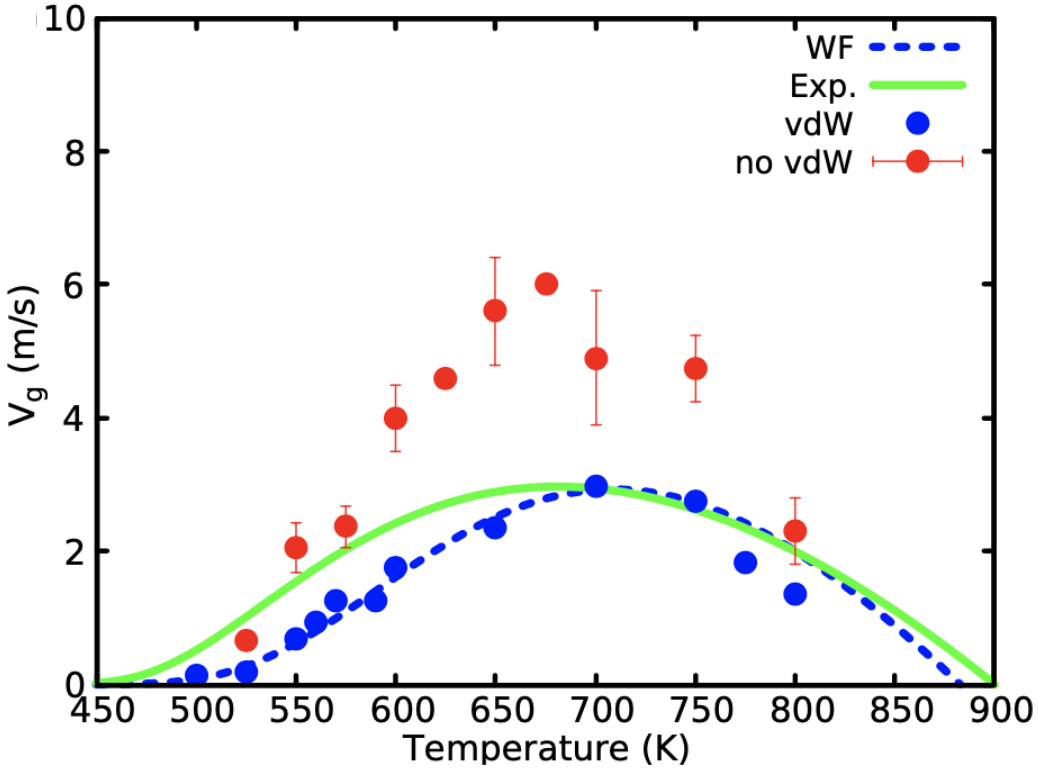


Radius of a crystalline nucleus vs time

Abou El Kheir et al., npj Comput. Mat. 10, 33 (2024)

Homogeneous crystallization

- NN potential was benchmarked on crystal growth velocity (v_g) as a function of temperature
- NN+vdW (Grimme D2) data is in good agreement with experimental results from ultrafast DSC measurements

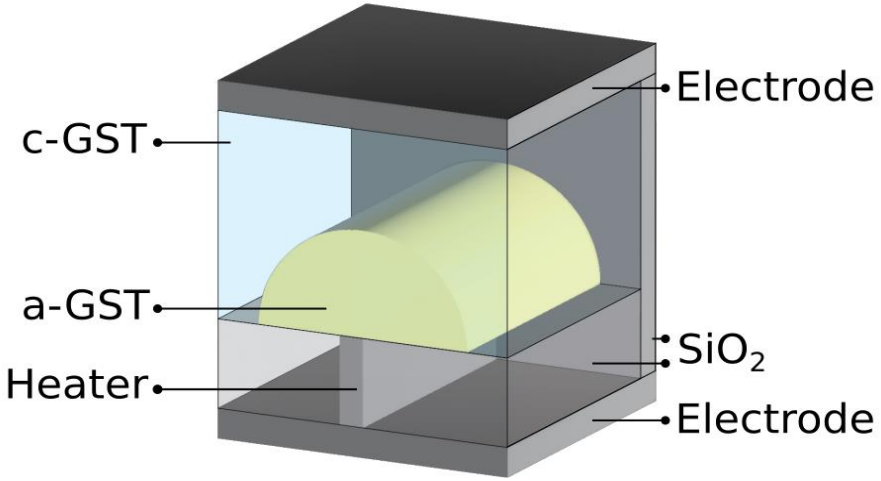


Exp: Orava et al., Nat. Mater. (2012)

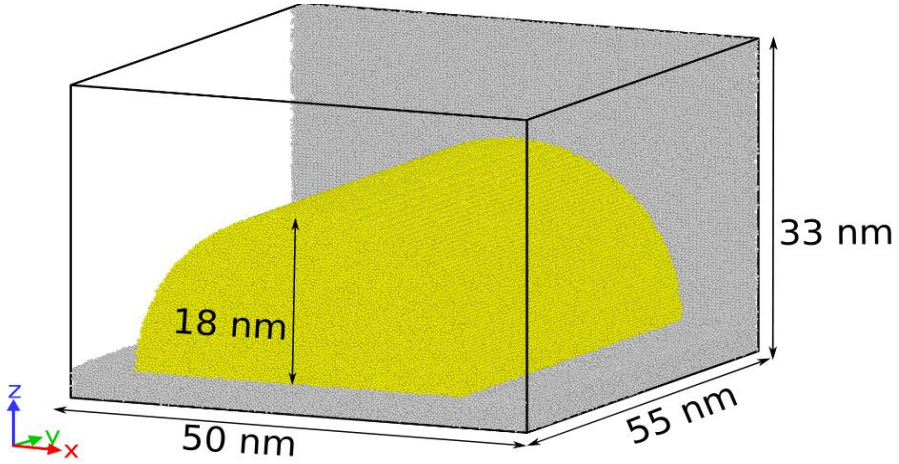
Acharya, Abou El Kheir, Marcorini, Bernasconi, *Nanoscale* 17, 13828-13841 (2025)

Device-scale simulation

Wall architecture



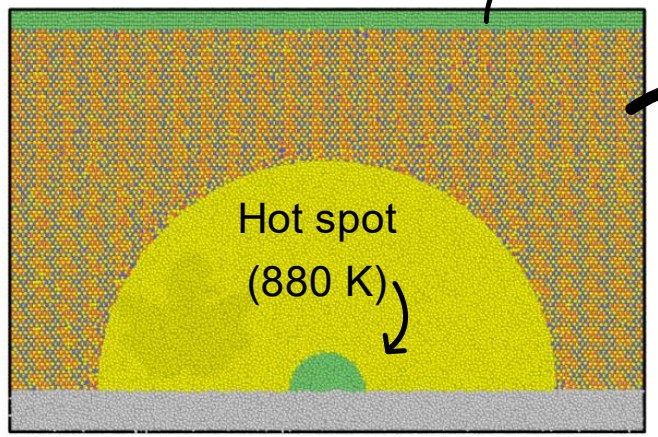
Three million atom model



Active region
(Amorphous phase)

Dielectric barrier
(Frozen a-GST225)

Thermostat set at 300 K

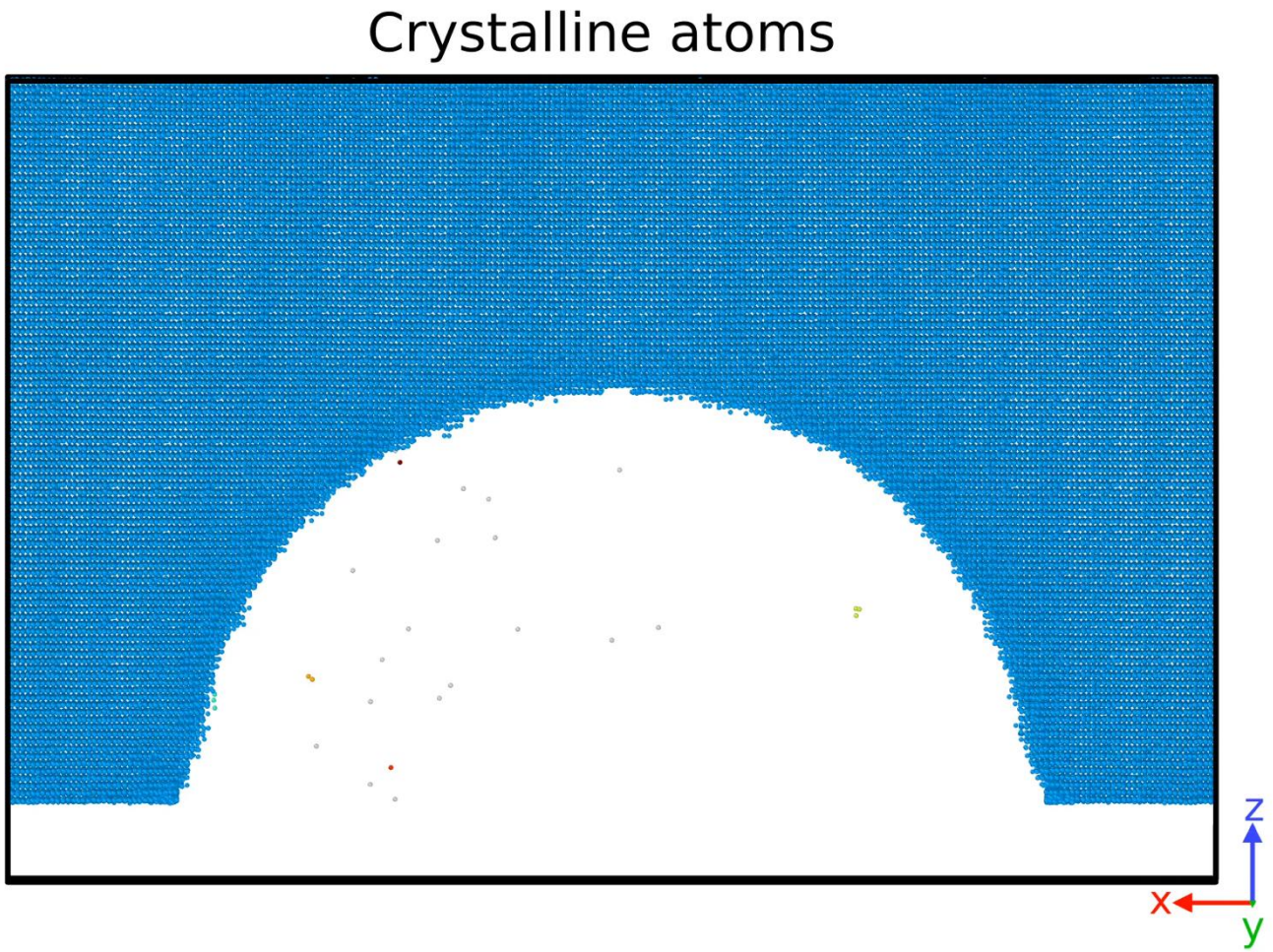


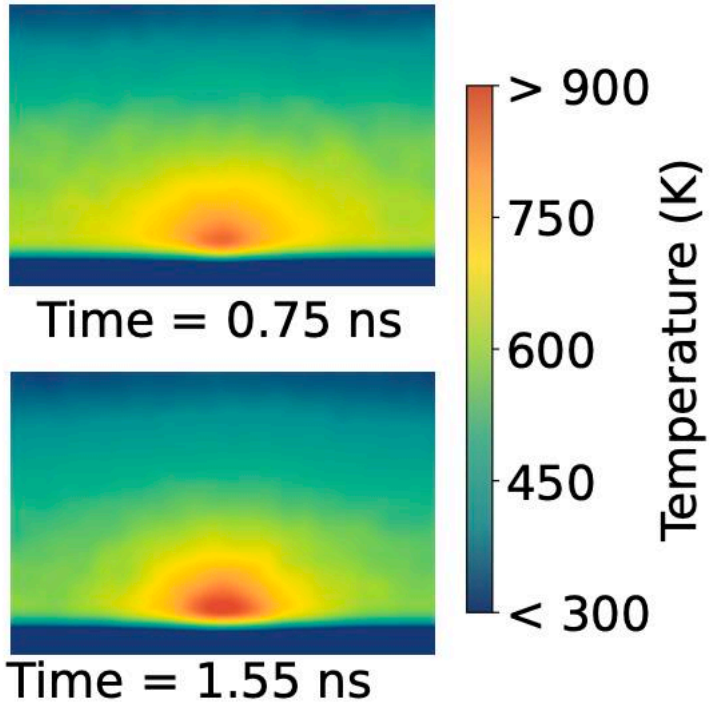
Ge Sb Te
(Crystalline matrix – cubic phase)

O Abou El Kheir, M Bernasconi, Adv. Elect. Mater. 11, e2500110 (2025)

Device-scale simulation

2.8 million atoms - 1.5 ns

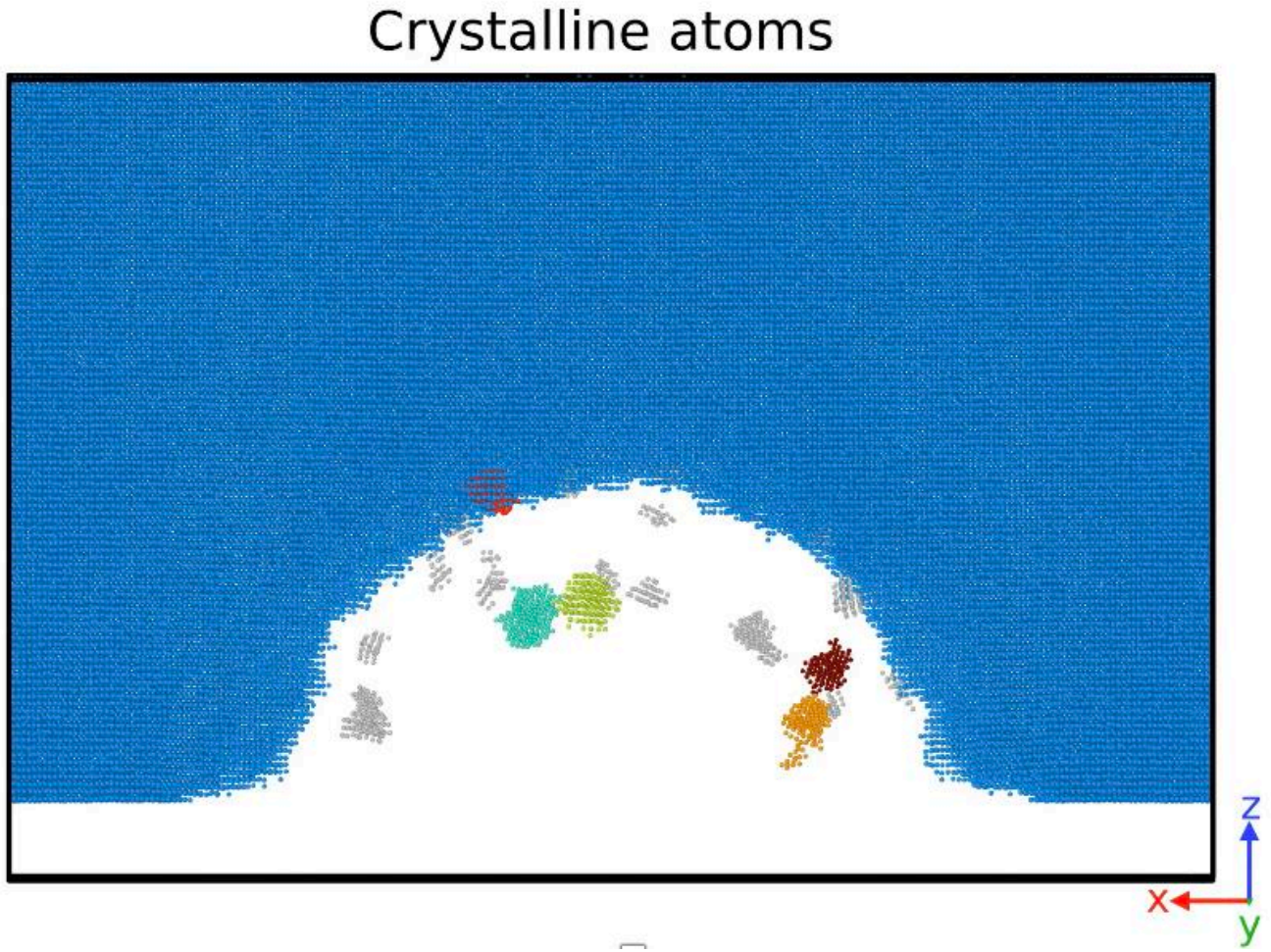


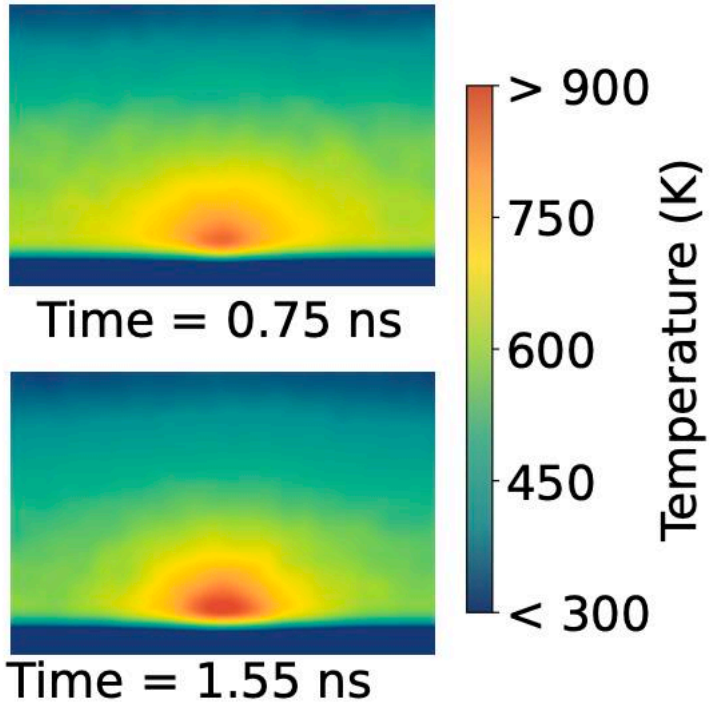


87 % of recrystallized atoms from crystal growth at interface

Device-scale simulation

2.8 million atoms - 1.5 ns

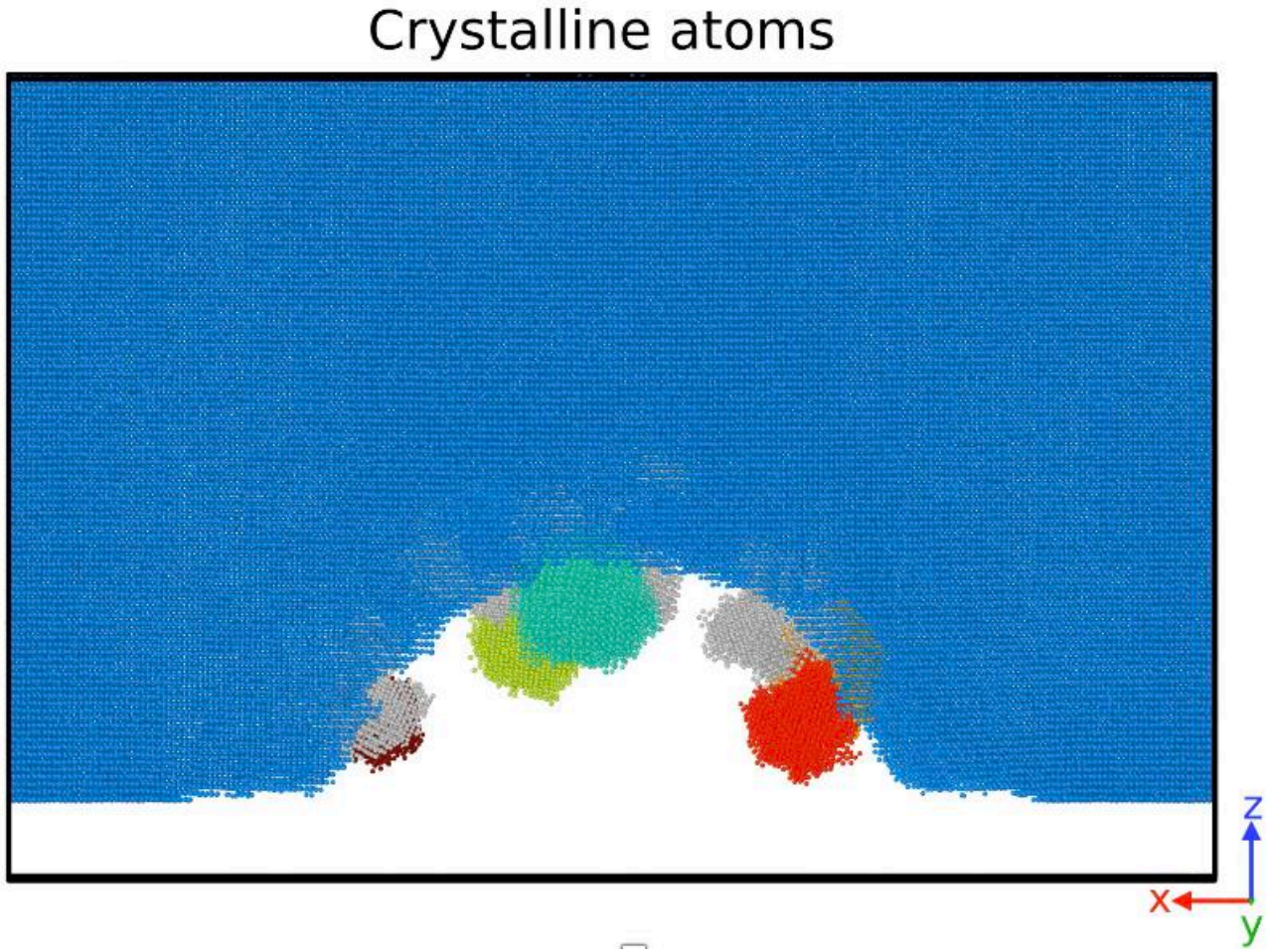


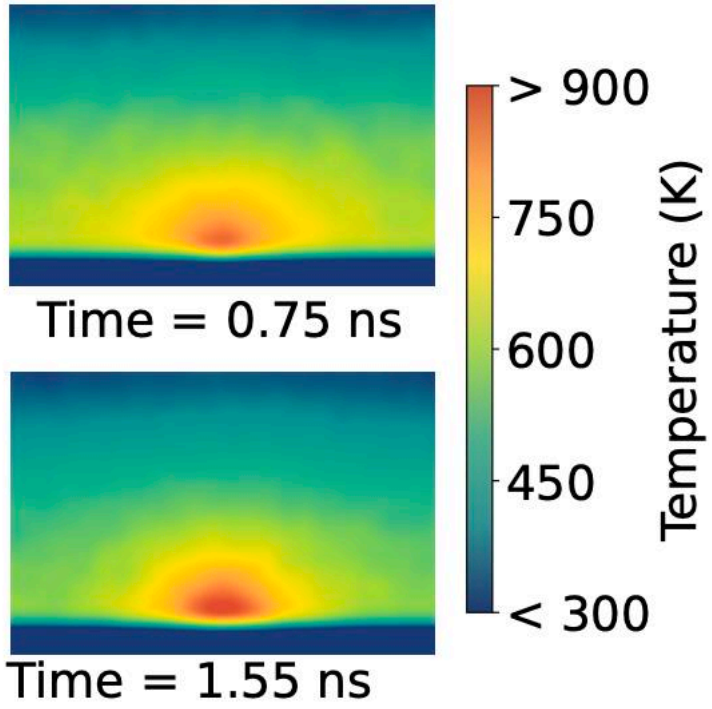


87 % of recrystallized atoms from crystal growth at interface

Device-scale simulation

2.8 million atoms - 1.5 ns

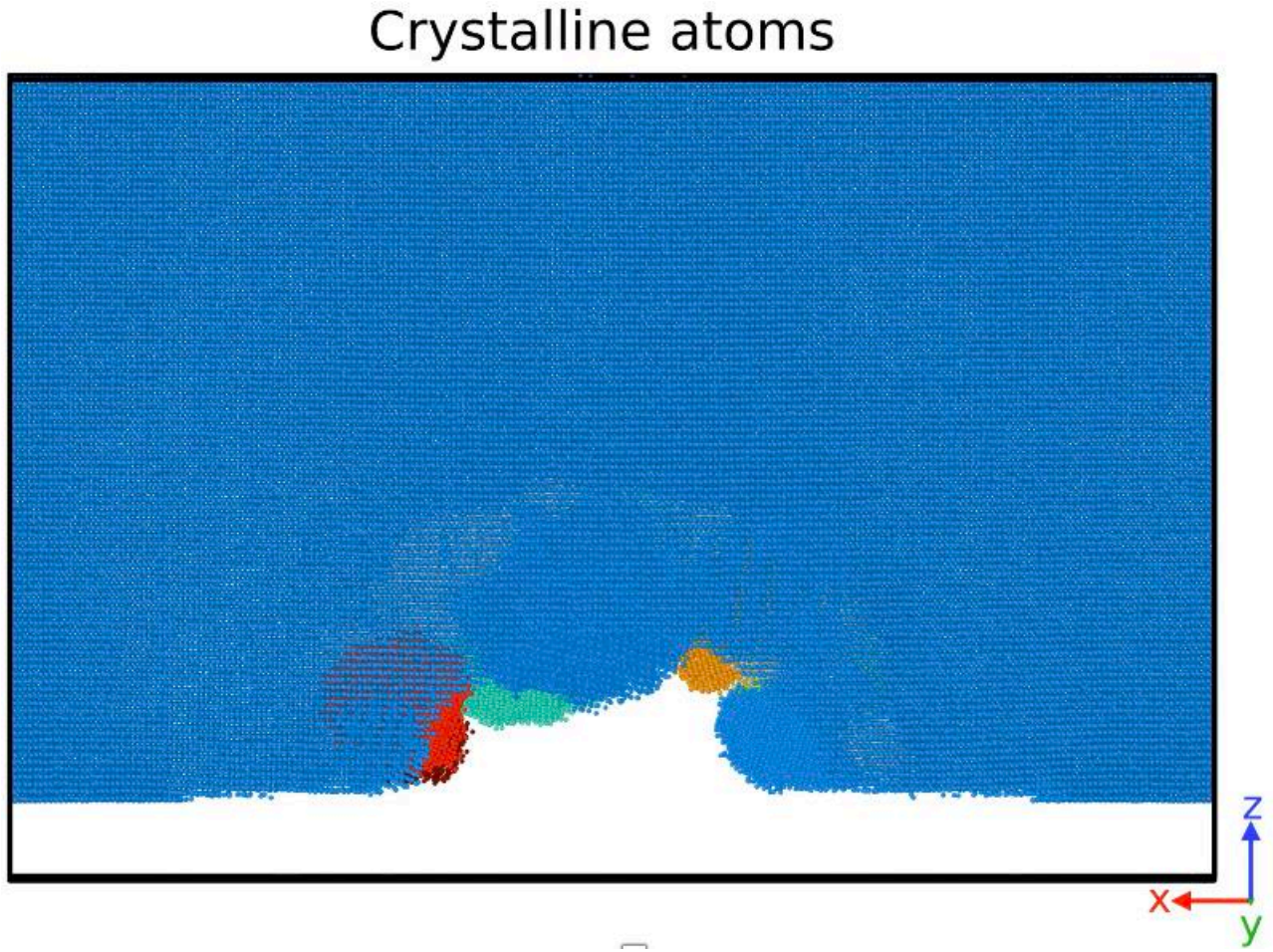


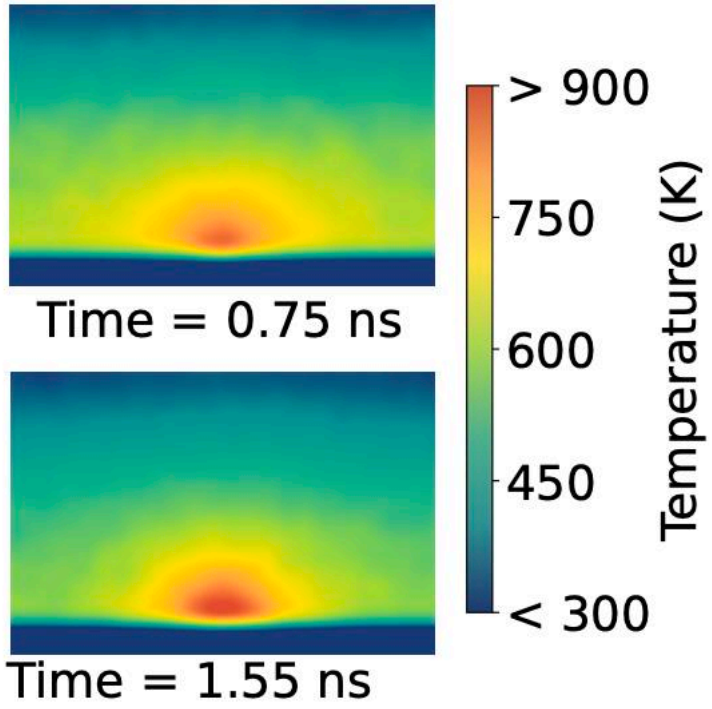


87 % of recrystallized atoms from crystal growth at interface

Device-scale simulation

2.8 million atoms - 1.5 ns

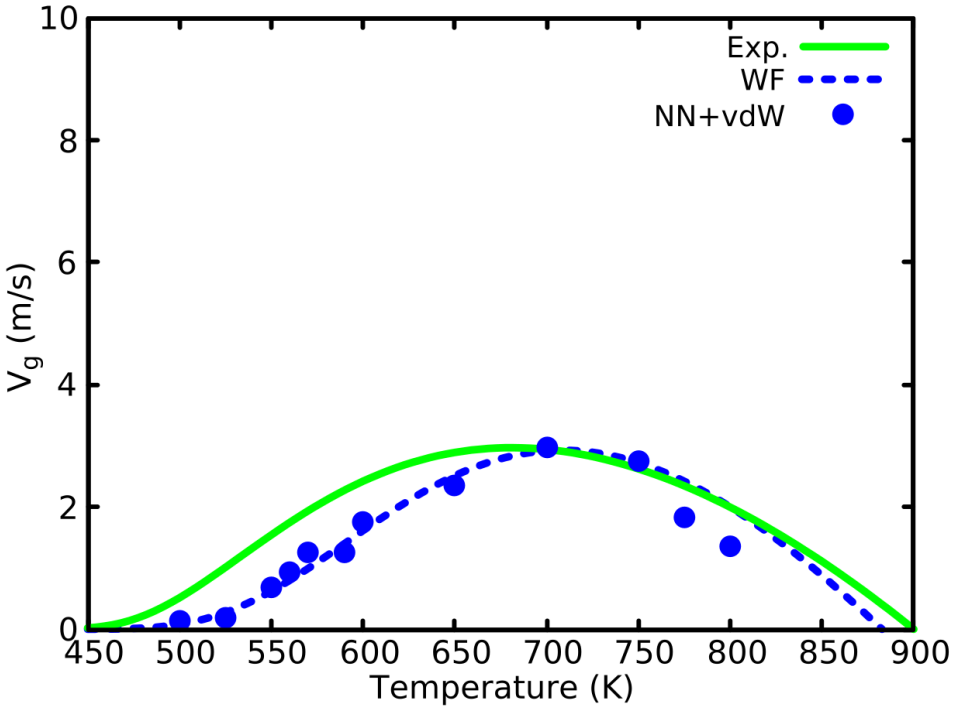




87 % of recrystallized atoms from crystal growth at interface

Homogeneous crystallization

- NN potential was benchmarked on crystal growth velocity (v_g) as a function of temperature
- NN+vdW data is in good agreement with experimental results from ultrafast DSC measurements
- Crystal growth velocities well described by phenomenological Wilson-Frenkel formula



Acharya, Abou El Kheir, Marcorini, Bernasconi, *Nanoscale* 17, 13828-13841 (2025)

Classical Nucleation Theory

Crystal growth velocity $u \propto D(1 - e^{-\frac{\Delta\mu}{k_B T}})$ Wilson-Frenkel

$\Delta\mu$ = free energy difference liquid & cryst

driving force for crystallization

D = diffusion coefficient

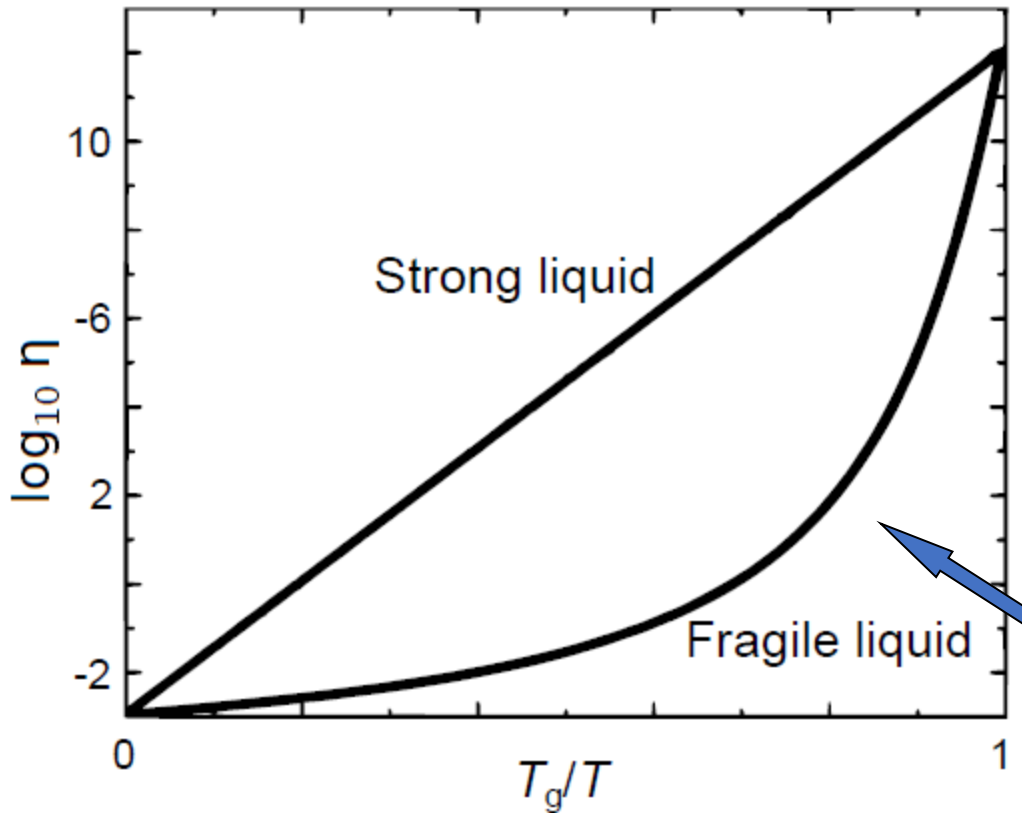
Nucleation rate $I_{ss} \propto D \exp(-G_c/(k_B T))$

Free energy critical nucleus $G_c = 16\pi\sigma^3/(3\Delta\mu^2)$

Fast crystallization due to fragility of the liquid

Angell, Science 267, 1924 (1995)

viscosity η



fragility index

Silica m =15

PVC m=195

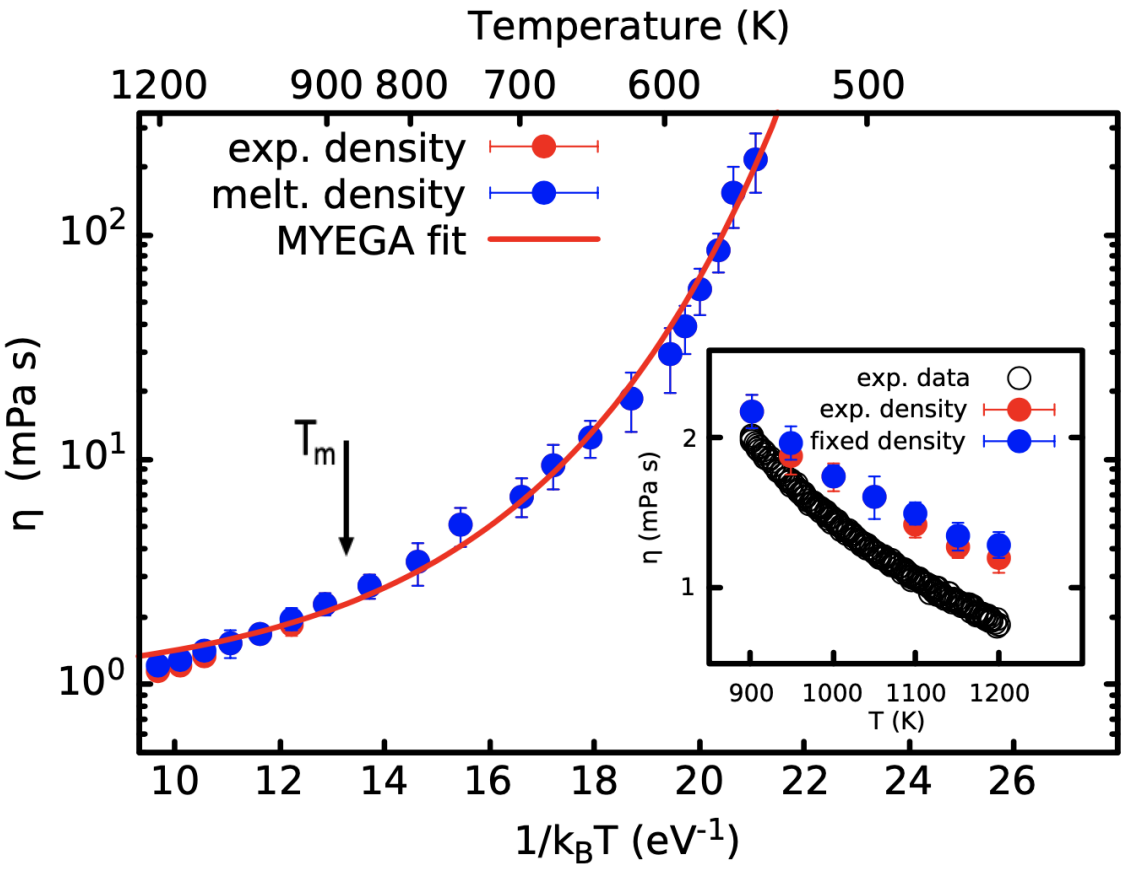
$$m = d(log_{10}\eta)/d(T_g/T)\ |_{T=T_g}$$

$$\eta \sim e^{\frac{1}{A(T-T_k)}}$$

Non-Arrhenius shape

Viscosity

4000-atom simulations



exp. $T > T_m$ (900 K): Schumacher et al. Sci. Rep. 2016

Green-Kubo $\eta = \frac{V}{k_B T} \int_0^\infty \langle \sigma_{xy}(t)\sigma_{xy}(0)\rangle dt$

↓ stress tensor

MYEGA fitting

fragility index m = 94 ; T_g = 392 K

very close to DSC data (Orava et al Nat. Mat. 2012)

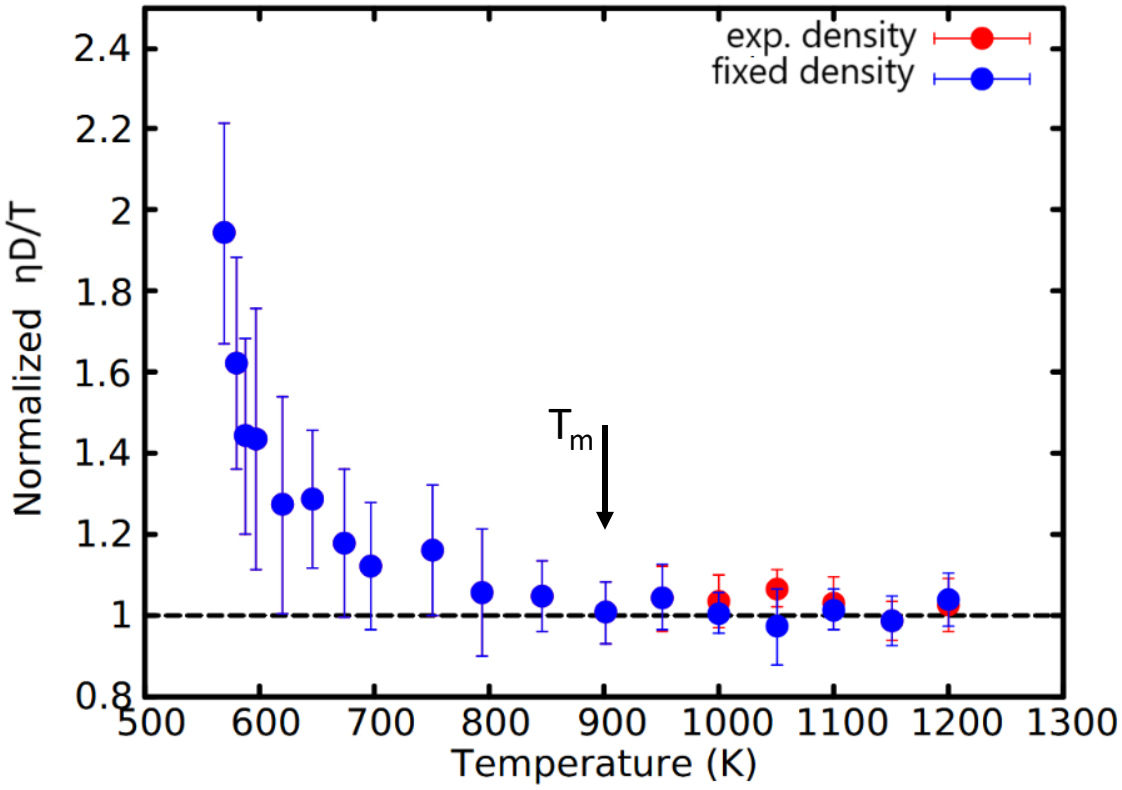
m = 90 ; T_g = 383 K

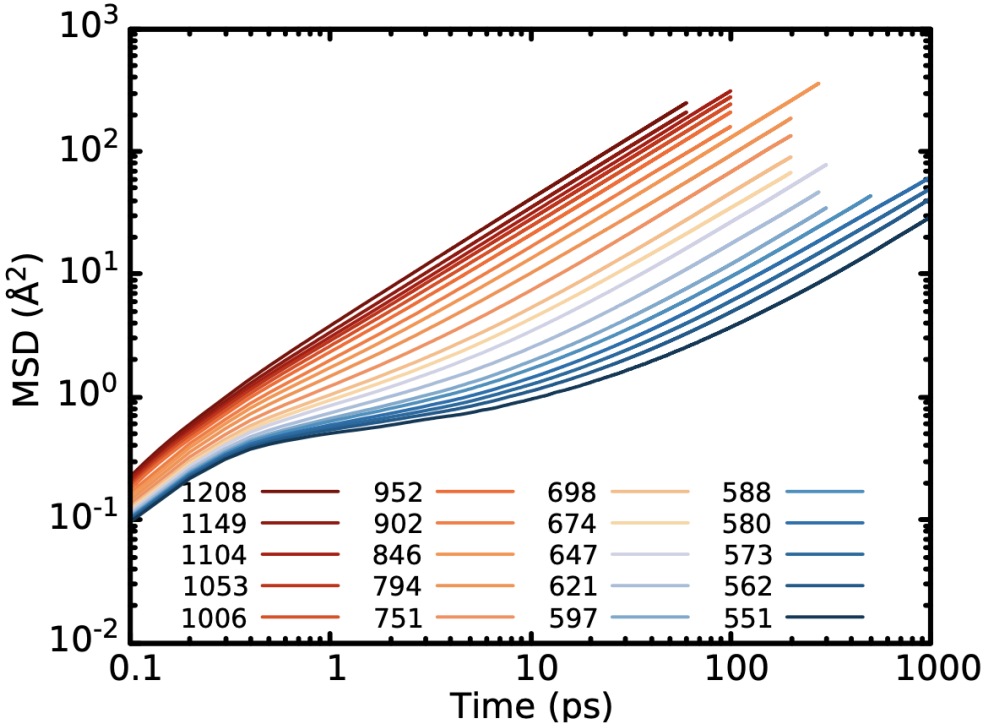
Marcorini, et al. arXiv.2506.13668

Breakdown of Stokes-Einstein Relation

$$D \not\propto \frac{T}{\eta}$$

Breakdown of SER at about 700 K in simulations
Breakdown of SER further boosts crystallization



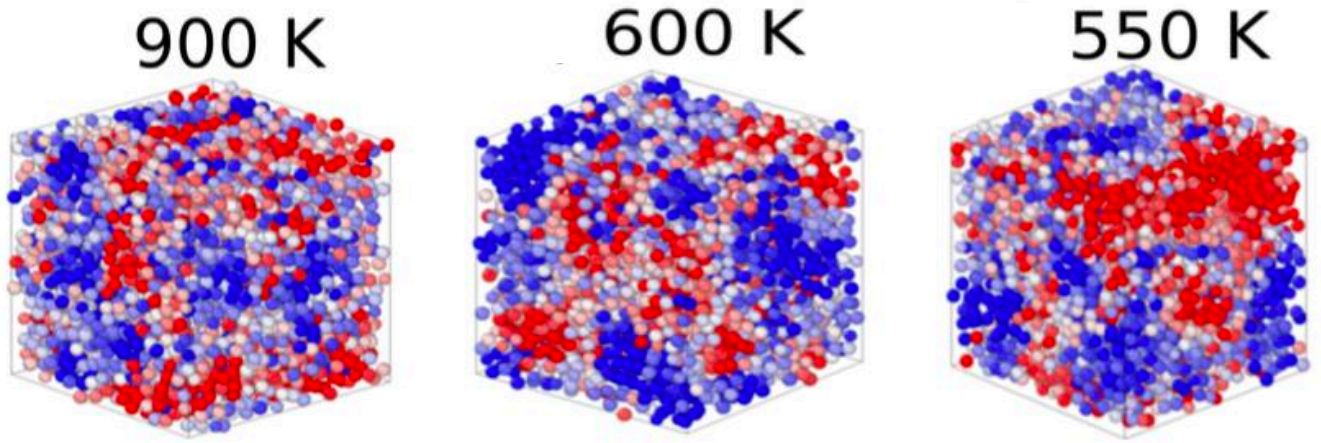


Marcorini, et al. arXiv.2506.13668, under review at JCP for Michele's Festschrift

Dynamical Heterogeneity in GST

spatially separated regions of atoms moving fast or slow lead to breakdown of Stokes-Einstein relation

$$\frac{1}{<\eta>} \neq < \frac{1}{\eta} >$$



red: most mobile MM regions

blu: most immobile MI regions

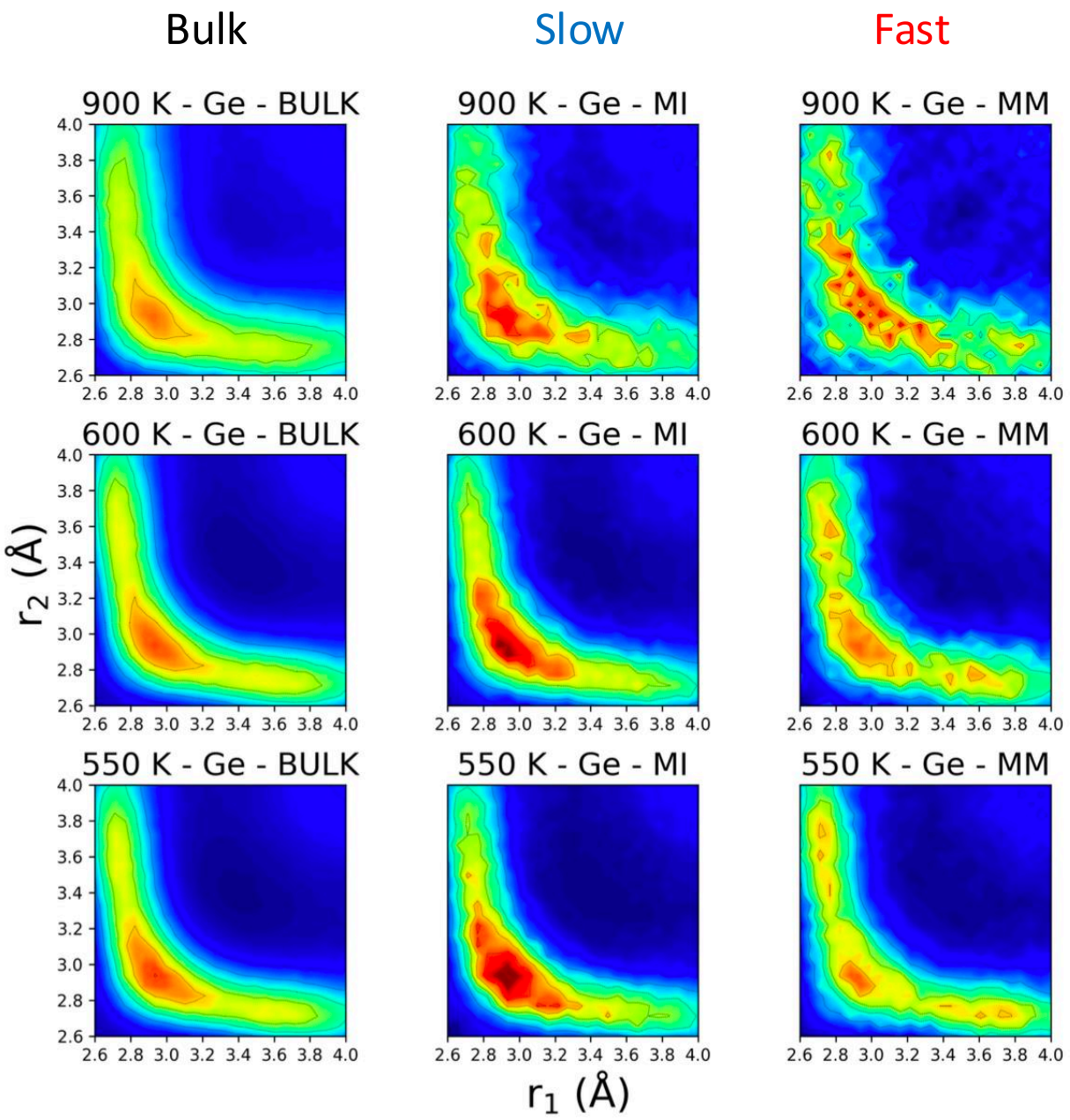
Iso-configurational analysis of dynamical propensity

(Widmer-Cooper and Harrowell, PRL 96, 185701 (2006))

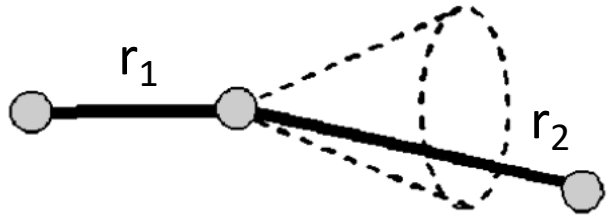
In GeTe: MM due to high content of Ge-Ge bonds

Sosso, et al., J. Phys. Chem. B 118, 13621 (2014)

Dynamical Heterogeneities in GST



Angular Limited Two-body Correlation Function (ALTBC) for Ge atoms



Presence of an axial atom just outside the first coordination shell enhances Ge mobility in MM regions; enhanced Peierls distortion reduces mobility in MI regions

Marcorini, et al. arXiv.2506.13668

Acknowlegments

Generation of NN GST225: Omar Abou El Kheir (UNIMIB)
Luigi Bonati and Michele Parrinello (IIT, Genova)

NN simulation of GST225: Omar Abou El Kheir, Simone Marcorini, Rocco Pomodoro

Italian Research Center on HPC, Big Data and Quantum Computing

Finanziato dall'Unione europea NextGenerationEU

Ministero dell'Università e della Ricerca

Italiadomani
PIANO NAZIONALE DI RIPRESA E RESILIENZA

Thank you for your attention

Thank you Michele!

Happy 80th birthday!