SAND2023-07937C

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Atomistic mechanisms of silicon nitride crystallization elucidated by molecular dynamics

Tesia D. Janicki[1], Carlos Chacon[1], Edwin Chiu[1], Jason Gibson[2], Scott Grutzik[1], Khalid Hattar[1,3], Richard Hennig[2], Calvin Parkin[1], Jennie Podlevsky[1], Aashique Rezwan[1], Chris Bishop[1], J. Matthew D. Lane[1]

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17 August 2023

ACS FALL 2023 HARNESSING THE POWER OF DATA

SAND2023-07937C

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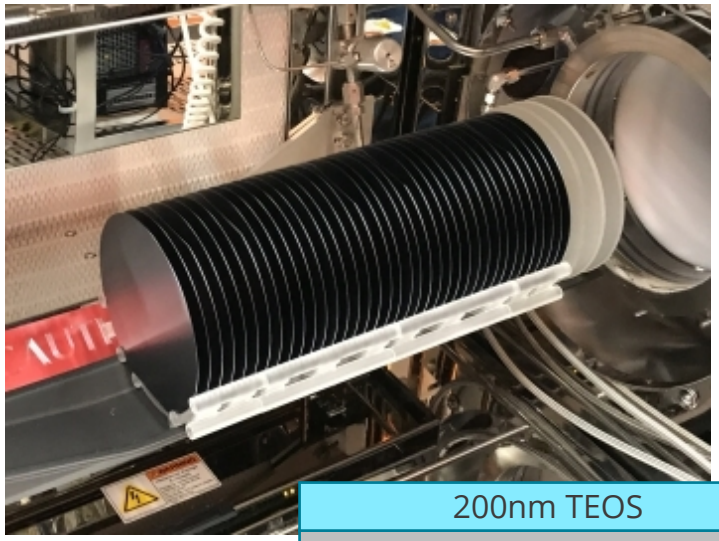
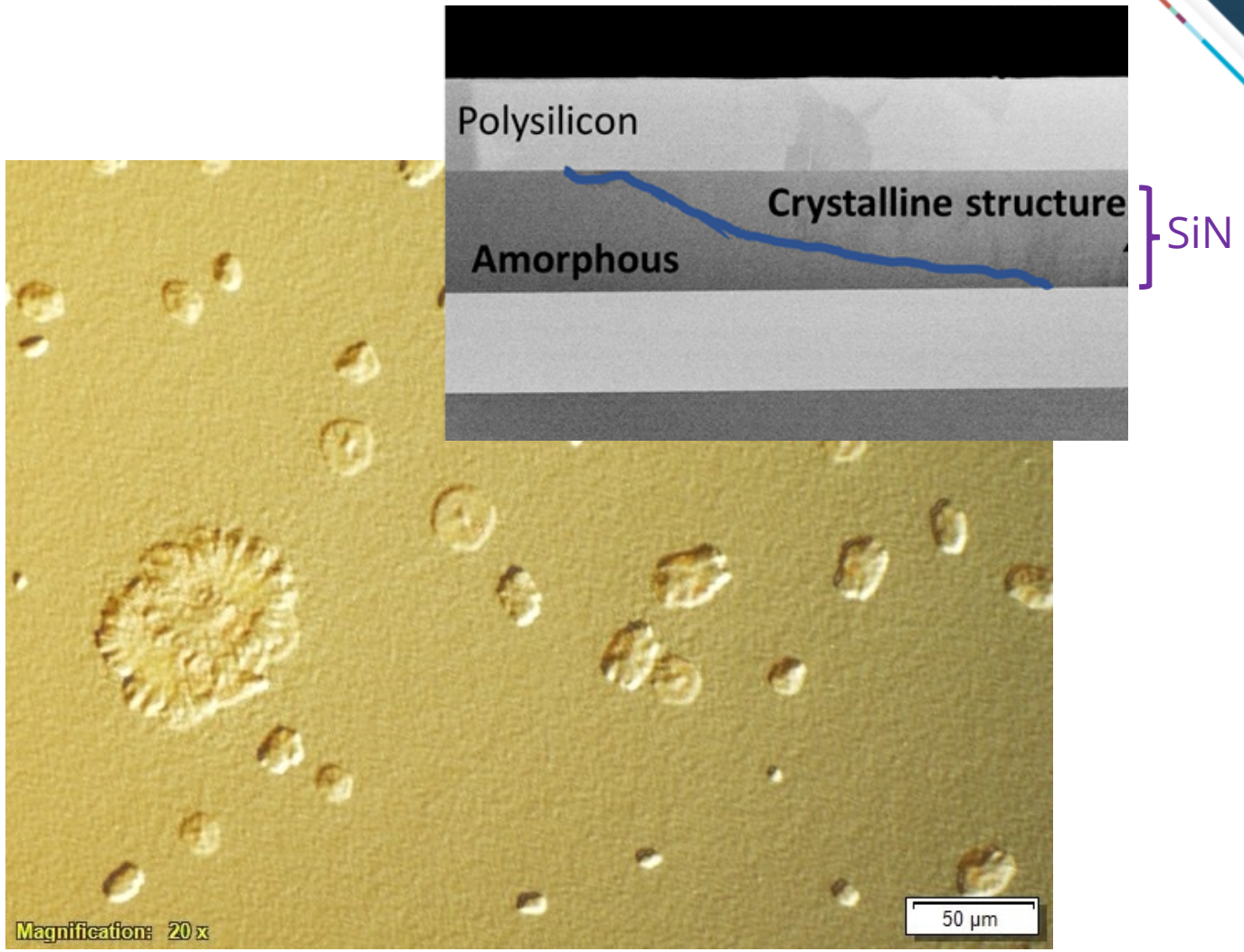
Silicon nitride crystallization in microelectronics fabrication



200nm TEOS
600nm doped poly Si
800nm LSN
630nm thermal oxide
Si

Anneal at
T > 1300K



Spurious crystallization of Si_3N_4 from the amorphous silicon nitride impacts microelectronics manufacturing.

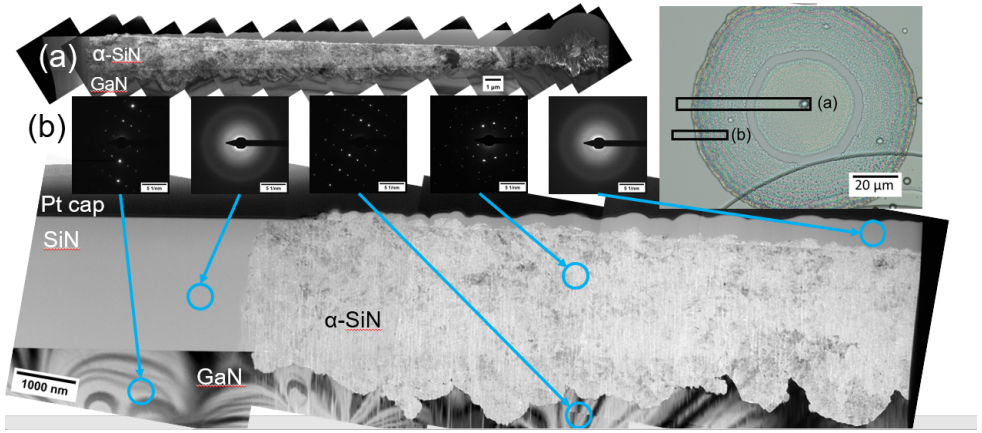
C. Bishop, et al. Experimental characterization and modification of Silicon Nitride crystallization reaction kinetics for microelectronics applications. *EMC June 2023*

Interdisciplinary approach: Experiment and multiscale models

Experiments

Materials synthesis with defect control

Time-resolved TEM imaging with *in situ* nanoindentation, laser heating, impurity mapping and diffraction

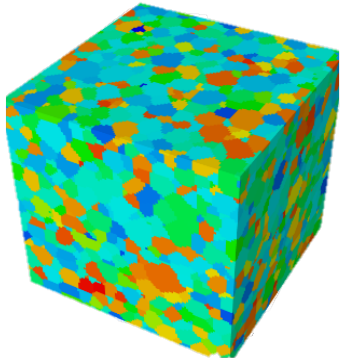


Mesoscale/Continuum modeling

Crystal plasticity

Local stress fields & microstructure

Thermomechanical modeling



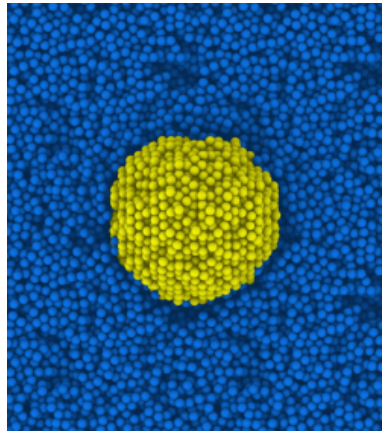
Atomistic modeling

Molecular dynamics using **LAMMPS**

SiN nucleation and growth

temperature, stress & imperfections

Quantum accurate potentials



Goals for atomistic modeling:

1. Model crystallization with empirical potentials.
2. Show these models retain kinetic properties which extrapolate to experimental conditions.
3. Extract qualitative and quantitative properties of crystallization mechanism.

Goals for atomistic modeling

1. Model crystallization with empirical potentials.

Using 3 models: Marian-Gastreich-Gale (MG2)
Tersoff
Vashishta

2. Show these models retain kinetic properties which extrapolate to experimental conditions.

Arrhenius fitting of 1D crystallization rates

3. Extract qualitative and quantitative properties of the crystallization mechanism.

How does crystallization proceed on an atomistic level?
Qualitative comparison with experiment
Quantitative input for mesoscale models

Empirical interatomic potentials

MG2

2-body potential

C. M. Marian, M. Gastreich and J. D. Gale. *Phys. Rev. B.* **62** (2000) 3117-3124

Tersoff

3-body potential

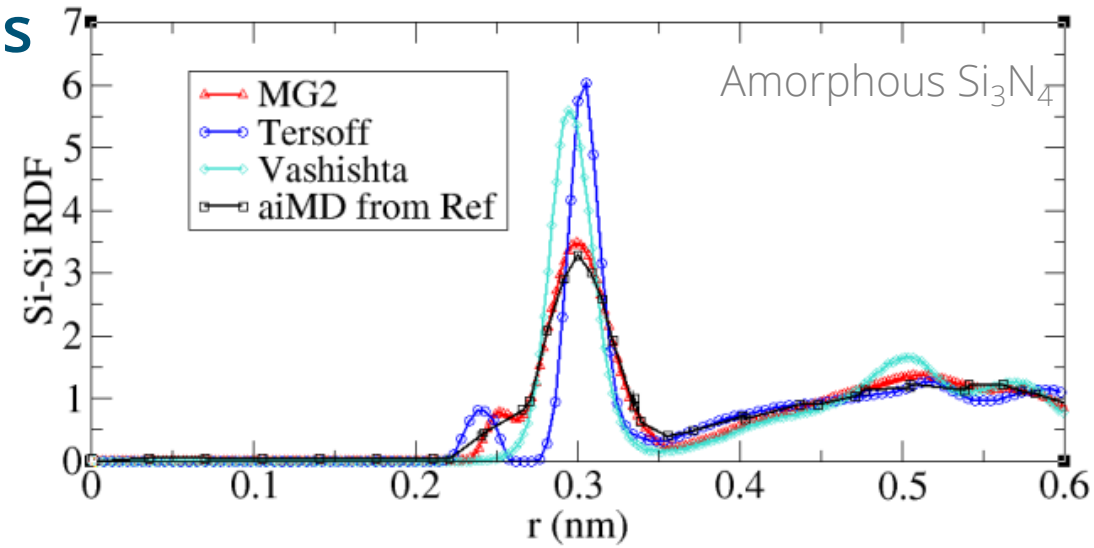
Parameterization by A. Dasmahapatra and P. Kroll. *Comput. Mater. Sci.* **148** (2018) 165-175

Vashishta

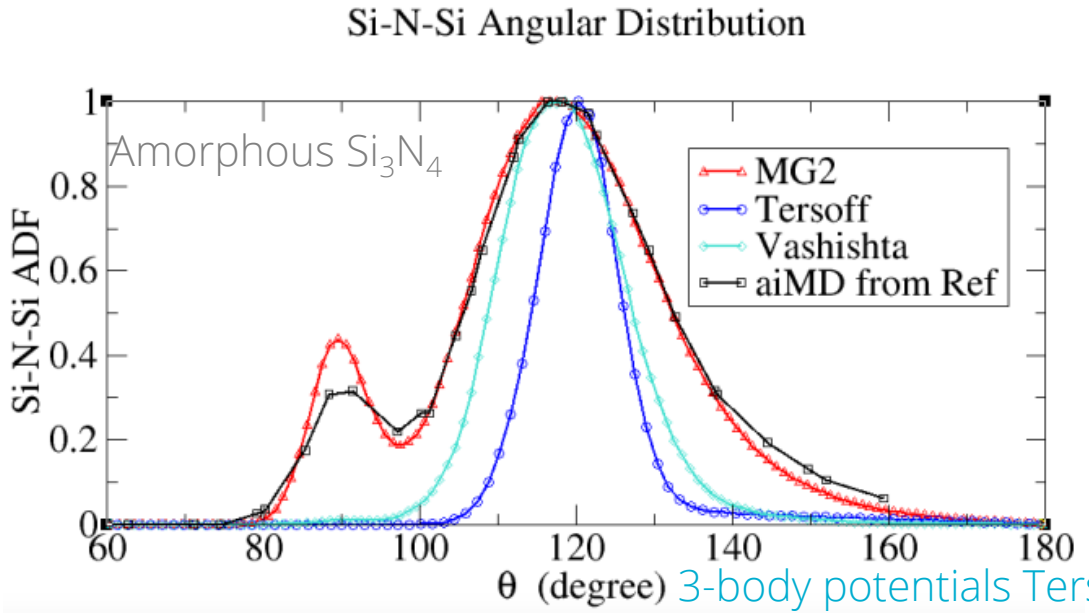
3-body potential + electrostatics

P. Vashishta, R. K. Kalia, A. Nakano, W. Li and I. Ebbsjö. in *Amorphous Insulators and Semiconductors,* edited by M. F. Thorpe and M. I. Mitkova (Kluwer Academic, Netherlands 1997) 151-213

aiMD from L. E, Hintzsche et al. *Phys. Rev. B.* **86** (2012) 235204



MG2 & Tersoff reproduce short-range Si-Si feature found in aiMD structure.



3-body potentials Tersoff & Vashishta retain more rigid bond angle.

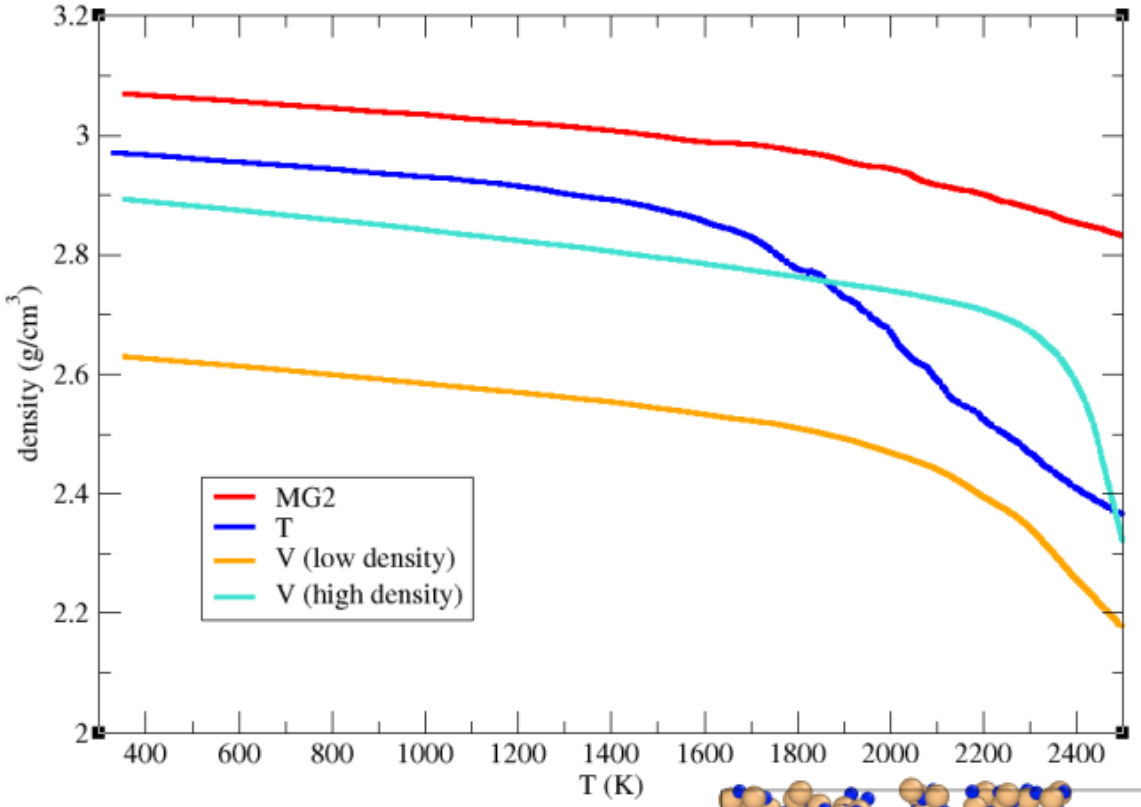
Structure generation and LAMMPS implementation

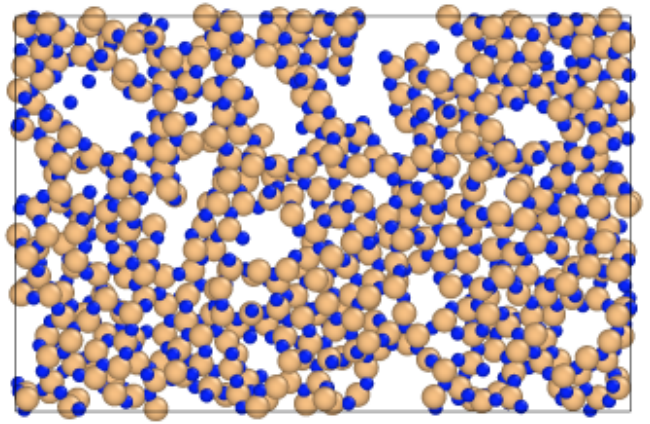
Seed generation

- α-Si_3N_4 unit cell is replicated for:
  - ~2.8nm length in growth direction
  - ~5nm x 5nm lateral contact
- Seed is thermalized to run temperature using Nose-Hoover thermostat and anisotropic barostat

Amorphous generation

- Melt-quench amorphous generation of 14,112-atom simulation cell (~5 nm)^3
- Box dimensions orthogonal to growth direction are fixed to match thermalized seed size
- Growth direction dimension permitted to fluctuate in volume according to Nose-Hoover barostat





1nm slice of V (low density) showing void presence

Structure generation and LAMMPS implementation

Seed generation

- α-Si_3N_4 unit cell is replicated for:
  ~2.8nm length in growth direction
  ~5nm x 5nm lateral contact
- Seed is thermalized to run temperature using Nose-Hoover thermostat and anisotropic barostat

Amorphous generation

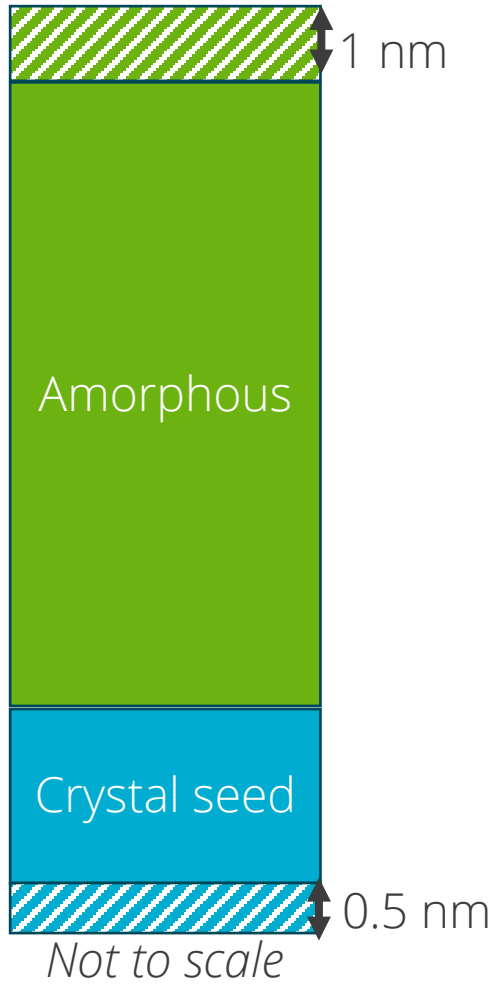
- Melt-quench amorphous generation of 14,112-atom simulation cell $(\sim 5\,nm)^3$
- Box dimensions orthogonal to growth direction are fixed to match thermalized seed size
- Growth direction dimension permitted to fluctuate in volume according to Nose-Hoover barostat

Seeded crystallization construction

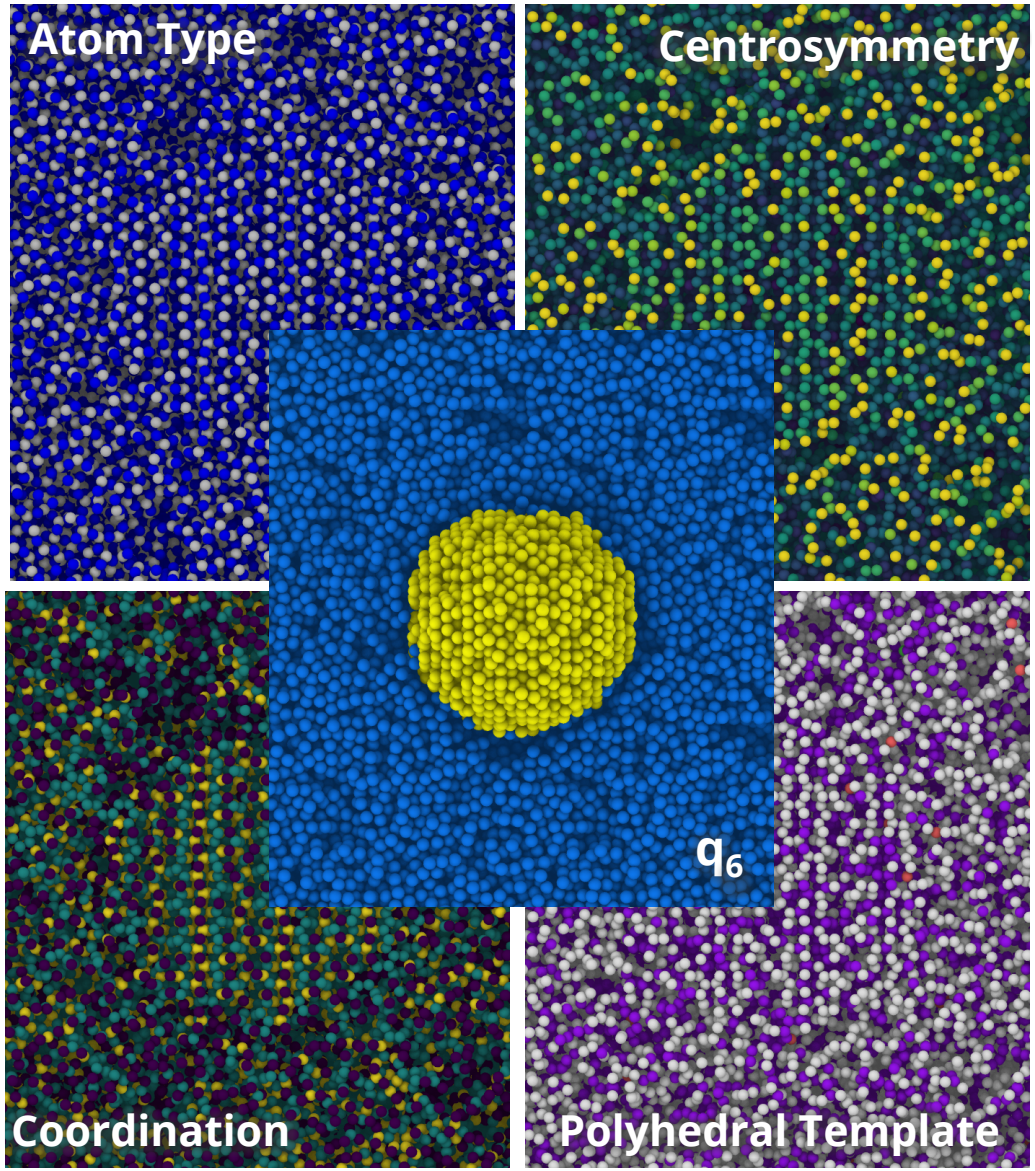
- Amorphous layer is replicated for at least 15nm total length in growth direction
- Pressure controlled by anisotropic Nose-Hoover barostat

"Dynamic" regions fixed to run temperature

Low-temperature regions fixed to 300K to inhibit growth from periodic interface



Quantifying local order via Steinhardt order parameter



The Steinhardt order parameter, $q_l(i)$, is a rotationally invariant order parameter which computes local coordination symmetry.

$$q_l(i) = \left(\frac{4\pi}{2l+1}\Sigma_{m=-l,l}\left|\overline{q_{lm}(i)}\right|^2\right)^{\frac{1}{2}}$$

$$\overline{q_{lm}(i)} = \frac{1}{N(i)+1}\left[q_{lm}(i) + \Sigma_{j=1,N(i)}q_{lm}(j)\right]$$

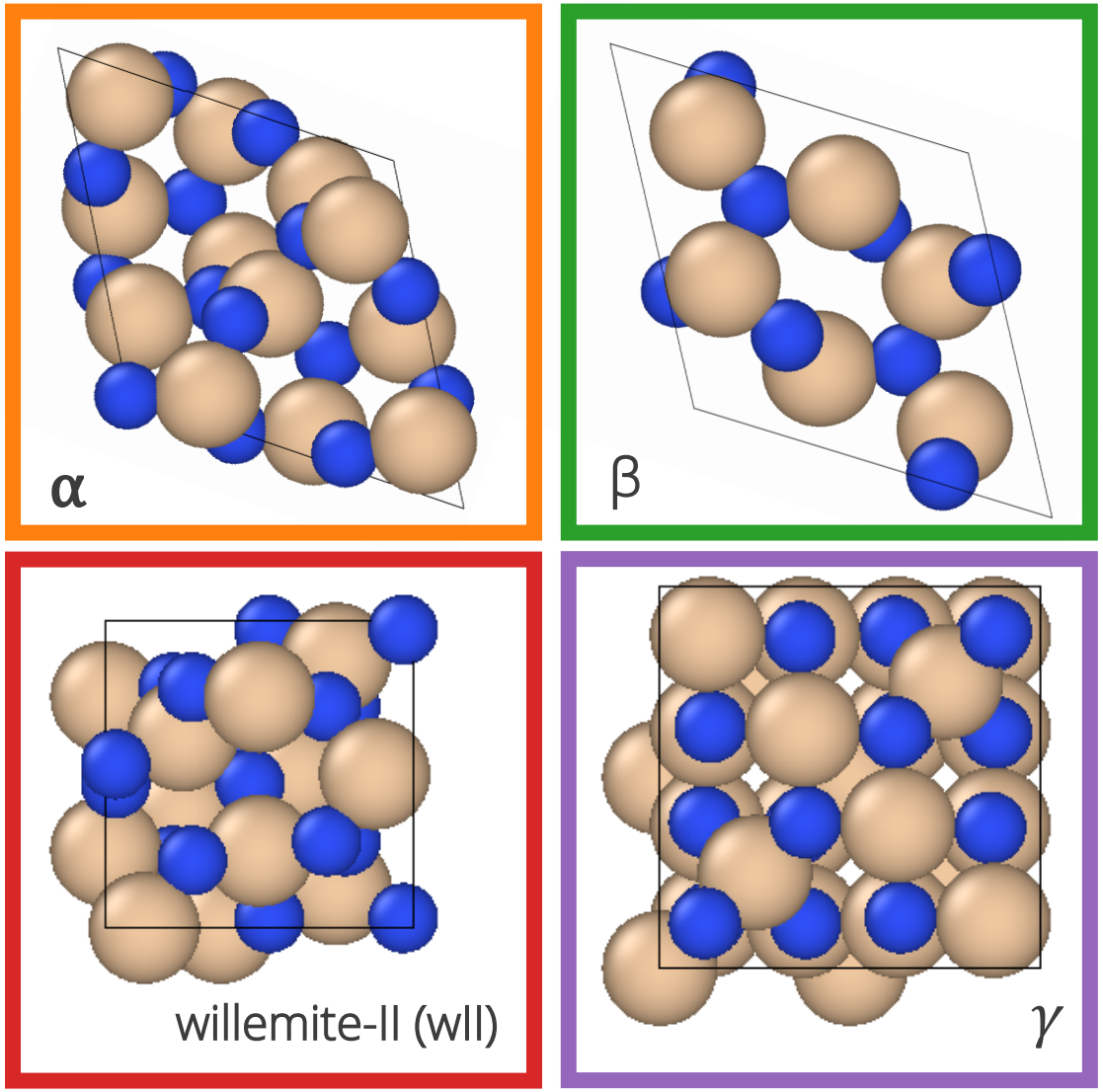
$$q_{lm}(i) = \frac{1}{N(i)}\Sigma_{j=1,N(i)}Y_{lm}(\theta_{ij},\phi_{ij})$$

Y_{lm} : Spherical harmonic of with angular quantum number l

$N(i)$: Number of nearest neighbors on atom i

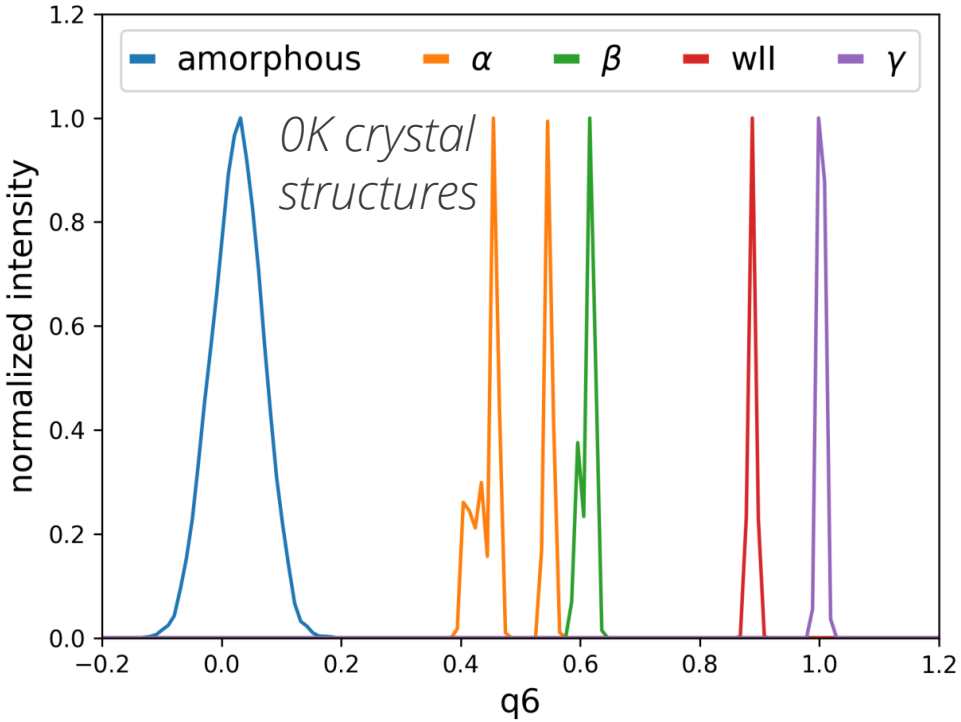
P. J. Steinhardt et al. Phys. Rev. B: Condens. Matter Mater. Phys. 1983, 28, 784–805.

Quantifying local order via Steinhardt order parameter



The Steinhardt order parameter, $q_l(i)$, is a rotationally invariant order parameter which computes local coordination symmetry.

For $l = 6$, applied to N-N local order **distinguishes not only between amorphous and α-Si_3N_4 but also among other known polymorphs.**



PLUMED toolkit used for q6 analysis

The PLUMED consortium. *Promoting transparency and reproducibility in enhanced molecular simulations*, Nat. Methods 16, 670 (2019)

A first look: Bulk seeded crystal growth

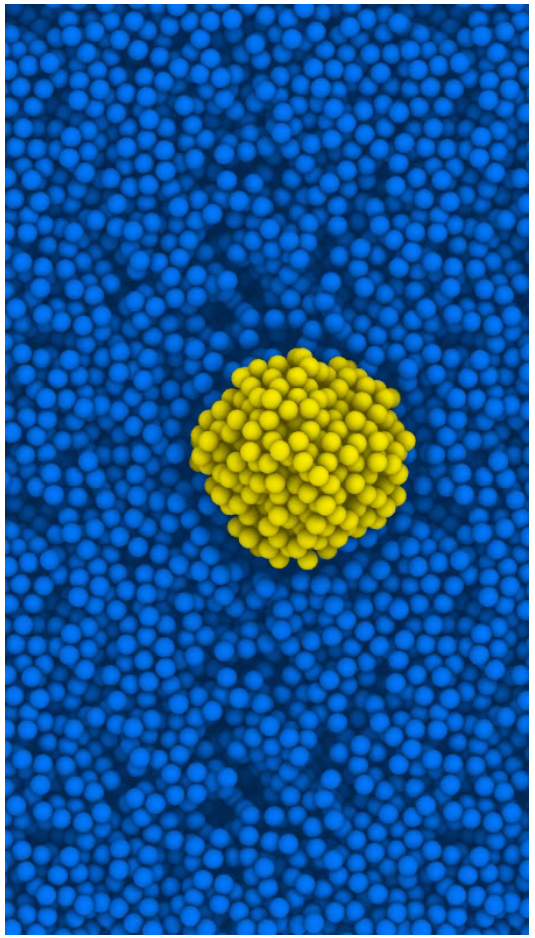
Spherical seed implanted in amorphous Si_3N_4 at varied temperatures and potentials

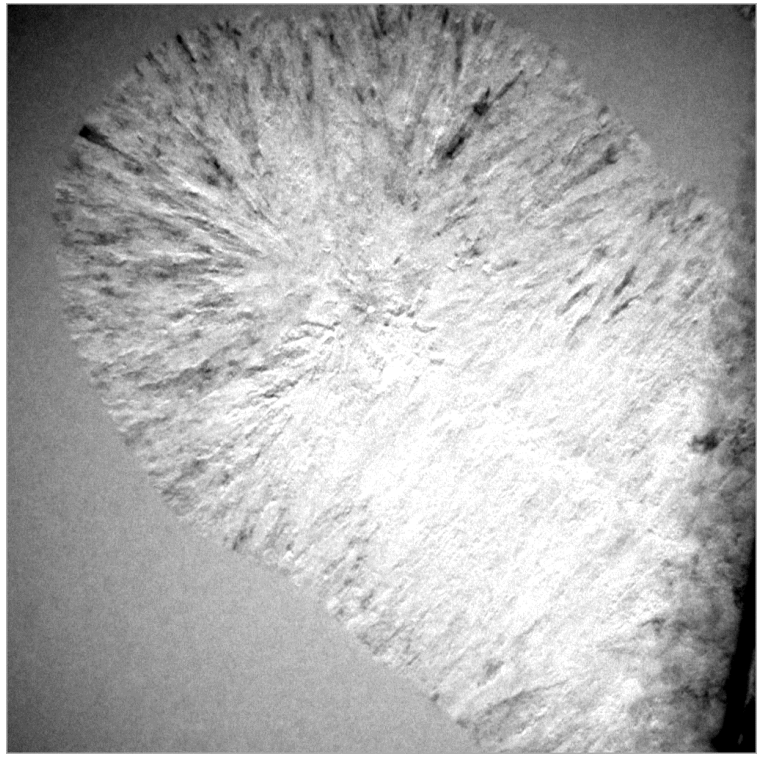
Results shown for Vashishta potential at elevated temperature, 2400K.

Only nitrogen shown.
Colored by Steinhardt q6

α-Si_3N_4 crystal

amorphous





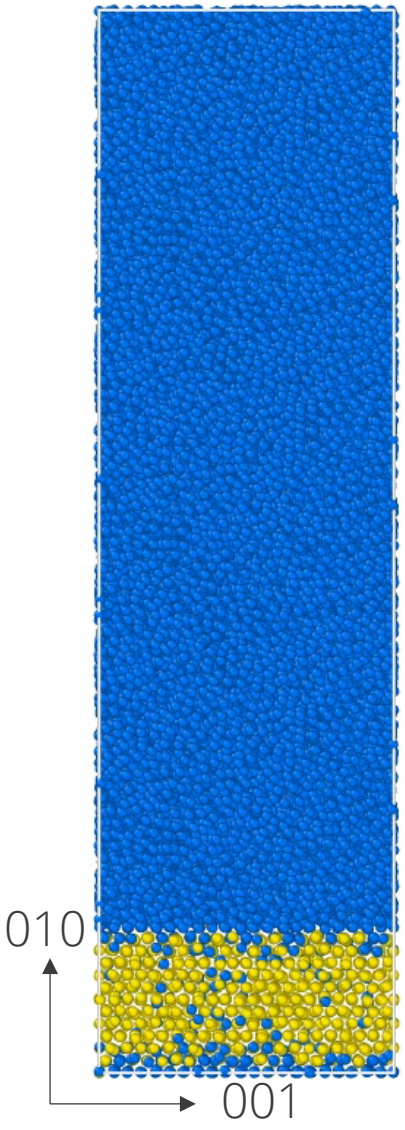
C. Parkin in-situ TEM

Key conclusions:

- Evidence of anisotropy in crystal growth. Similar growth behavior is observed by experiment.

Planar crystal growth analysis

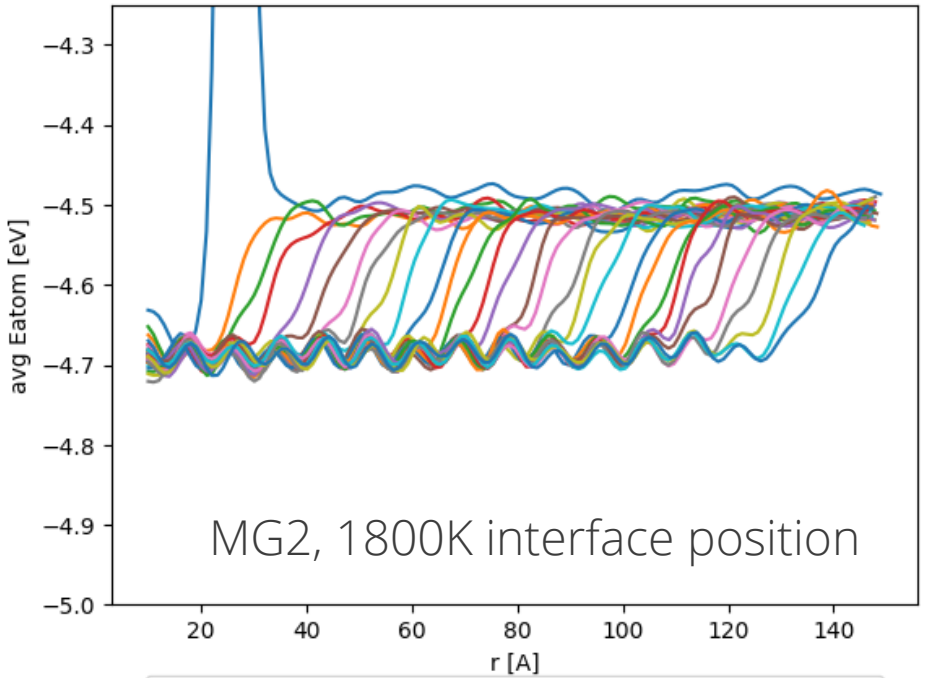
MG2, 1800K



N-only
Colored by q_6

α-Si_3N_4 crystal

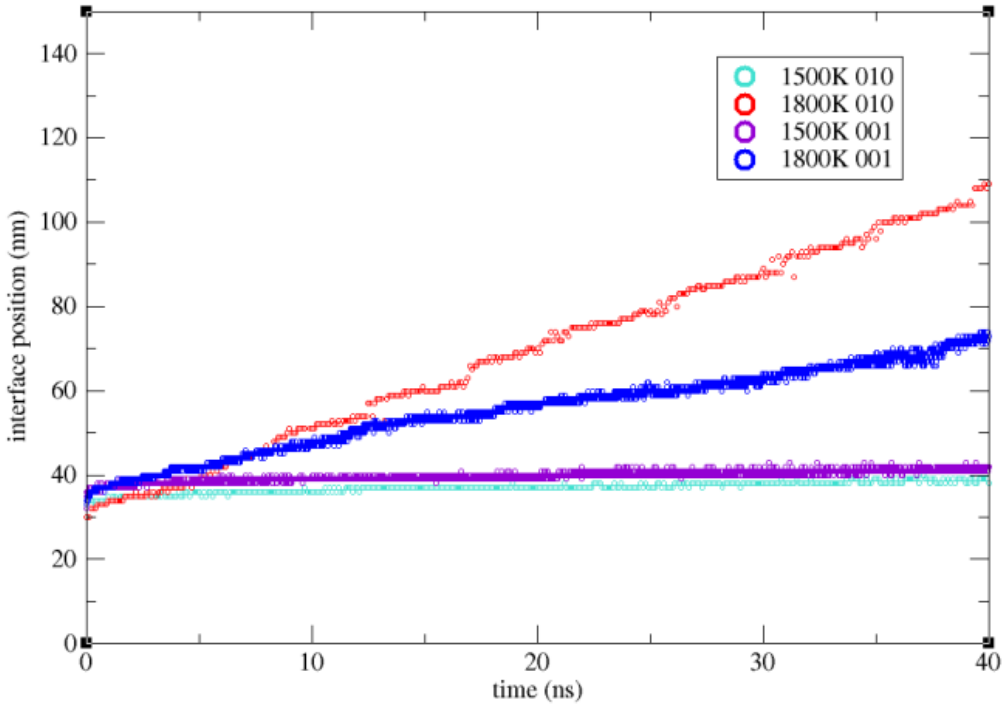
amorphous



Interface position identified by spatial binning of average potential energy values along the direction of growth.

Growth rates in 001 and 010 α-Si_3N_4 extracted for each potential.

MG2, growth progression



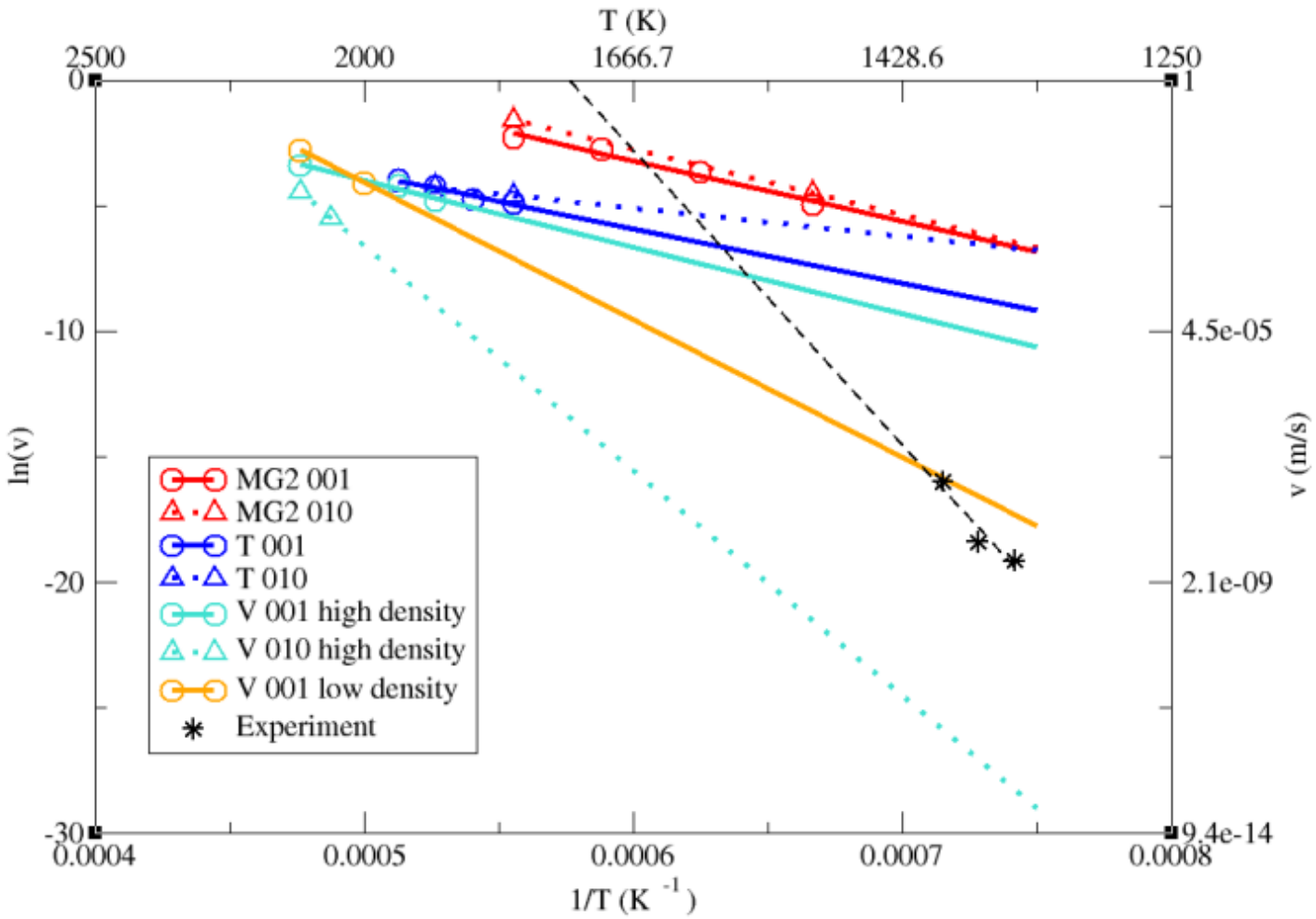
Key conclusions:

- Growth rate anisotropy is enhanced at higher temperatures

Planar crystal growth analysis

Simulation temperatures vary between potentials to account for characteristic glass transition.

Arrhenius fits of linear velocity show extrapolation to experiment at much lower temperatures.



Key conclusions:

- Both density and orientation impact growth rate
- Our potentials span a range of Arrhenius fits to lower temperature growth rates.

Multiscale & collaborative efforts

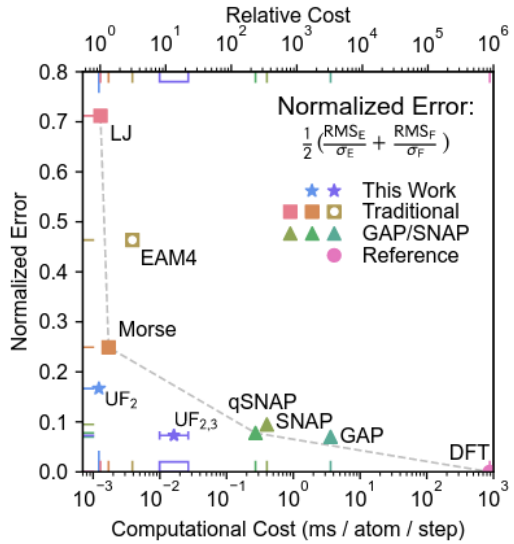
Integration with mesoscale models

- Bridging the time- and length-scale gap with experiment
- Computed properties from atomistic simulations become input parameters for phase-field models

A. Rezwan CNT demonstration

Ultra-fast (UF) interpretable machine-learning potentials

- Machine learning potentials show promise to obtain accuracy on par with 1st principle simulation at the computational cost of classical force field methods.

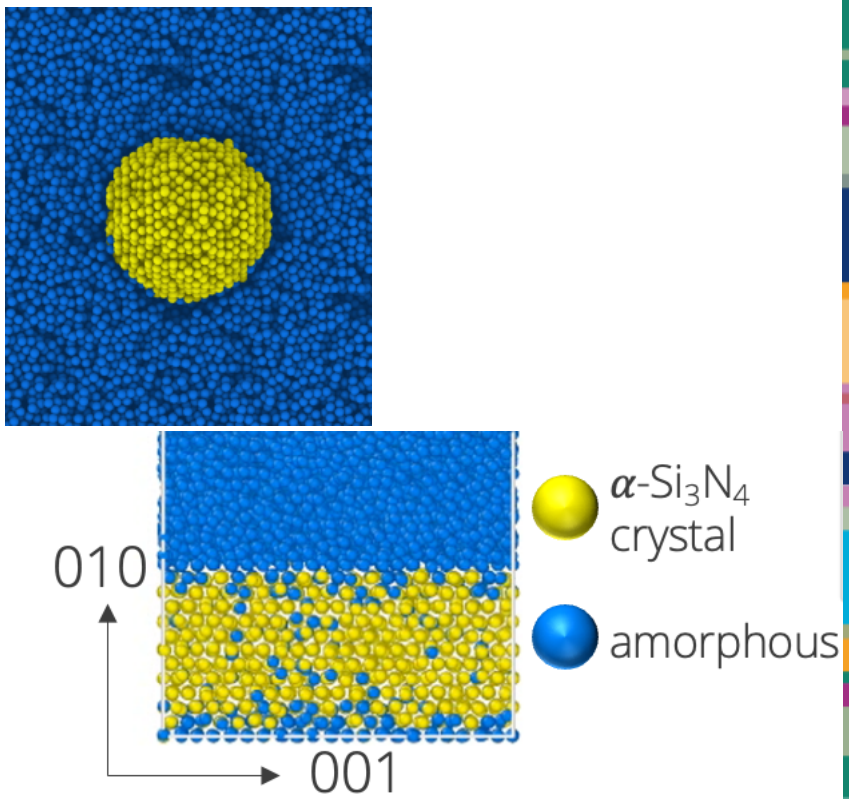


- Ongoing parameterization iterations

Xie, Rupp, Hennig, https://arxiv.org/abs/2110.00624 (2021).

Atomistic mechanisms of silicon nitride crystallization

1. Model crystallization with empirical potentials.



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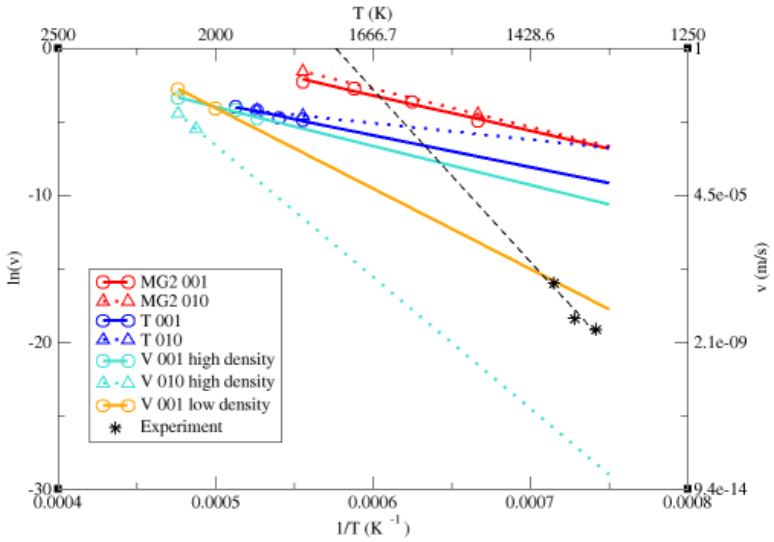
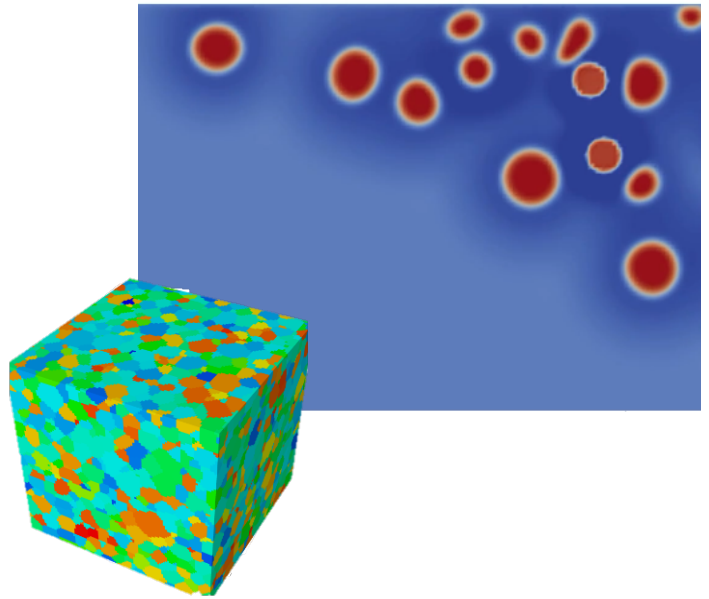


3. Extract qualitative and quantitative properties of crystallization mechanism.



Empirical interatomic potentials

MG2

$$E_{N-Si} = D_e\left\{\exp\left[-2a\left(r_{ij}-r_0\right)\right]-2\exp\left[-a\left(r_{ij}-r_0\right)\right]\right\}$$

$$E_{Si-Si} = \frac{A_{Si}}{r_{ij}}\exp\left[-\frac{r_{ij}}{\rho_{Si}}\right]$$

$$E_{N-N} = \frac{A_N}{r_{ij}}\exp\left[-\frac{r_{ij}}{\rho_N}\right]-\frac{C_6}{r_{ij}^6}\left(1-\exp\left[-b_6 r_{ij}\right]\Sigma_{k=0}^{6}\left[\frac{\left(b_6 r_{ij}\right)^k}{k!}\right]\right)$$

Additional tapering polynomial function used near cutoff

Vashishta

$$E = E_{2B} + E_{3B}$$

$$E_{2B} = \frac{H_{ij}}{r_{ij}^{\eta_{ij}}}+\frac{Z_i Z_j}{r_{ij}}\exp\left[-\frac{r_{ij}}{r_{1s}}\right]-\frac{P_{ij}}{r_{ij}^4}\exp\left[-\frac{r_{ij}}{r_{4s}}\right]$$

$$E_{3B} = B_{jik}\exp\left[\frac{1}{r_{ij}-r_{c3}}-\frac{1}{r_{ik}-r_{c3}}\right]\left(\cos\theta_{jik}-\cos\theta_{jik}^0\right)^2, \qquad r_{ij}, r_{ik} < r_{c3}$$

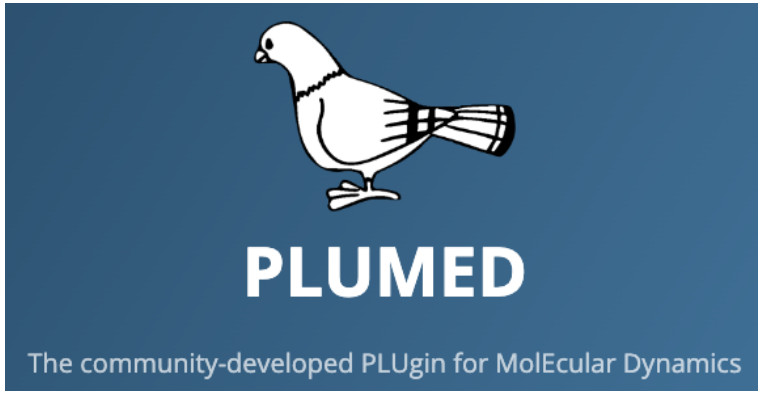
Tersoff

$$E = f_c(r_{ij})\left\{A_{ij}\exp\left(-\lambda_{ij}r_{ij}\right)+B_{ij}\exp\left[-\mu_{ij}r_{ij}\right]b_{ij}\right\}$$

$$b_{ij} = \chi_{ij}\left(1+\Sigma_{k\neq i,j}\left[f_c(r_{ik})\omega_{ik}\beta_i\left\{1+\frac{c_i^2}{d_i^2}-\frac{c_i^2}{d_i^2+\left(h_i-\cos\theta_{ikj}\right)^2}\right\}\right]\right)^{\frac{1}{2n_i}}$$

$$f_c(r_{ij}) = \begin{cases} 1 & , r_{ij} < R_{ij} \\ \frac{1}{2}+\frac{1}{2}\cos\left(\frac{\pi(r_{ij}-R_{ij})}{S_{ij}-R_{ij}}\right) & , R_{ij} < r_{ij} < S_{ij} \\ 0 & , r_{ij} > S_{ij} \end{cases}$$

Leveraging PLUMED2 for LAMMPS post-processing



What is PLUMED?

https://www.plumed.org/

PLUMED is an open-source, community-developed library that provides a wide range of different methods, which include:

- enhanced-sampling algorithms
- free-energy methods
- tools to analyze the vast amounts of data produced by molecular dynamics (MD) simulations.

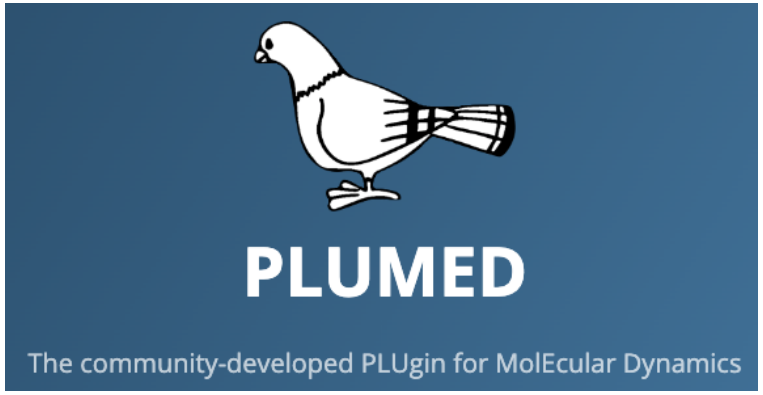
These techniques can be used in combination with a large toolbox of collective variables that describe complex processes in physics, chemistry, material science, and biology.

Collective variables include…

- Angles
- Bond directions
- Coordination number
- Density
- Distances
- Lattice similarity
- J coupling (e.g. FCC, simple cubic)
- Radius of gyration
- Reference structure RMSD
- SAXS intensity
- Steinhardt parameters (Q3, Q4, Q6)
- Torsions

The PLUMED consortium. *Promoting transparency and reproducibility in enhanced molecular simulations*, Nat. Methods 16, 670 (2019)

Leveraging PLUMED2 for LAMMPS post-processing



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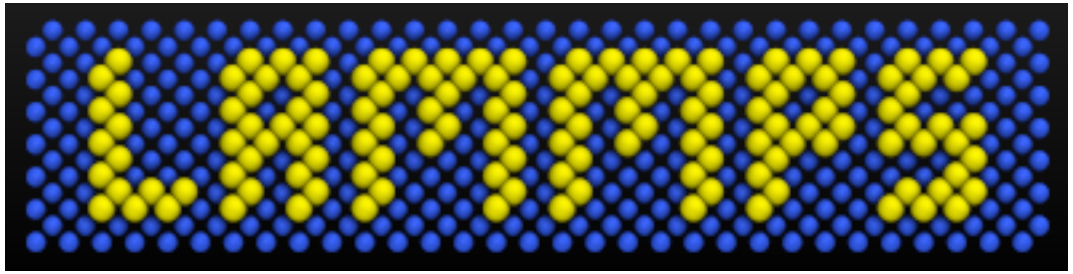

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lammps_postprocess.in:

```
fix 1 all plumed plumedfile plmd.proc
rerun myoutput.dump every 1 dump x y z
```

plmd.proc:

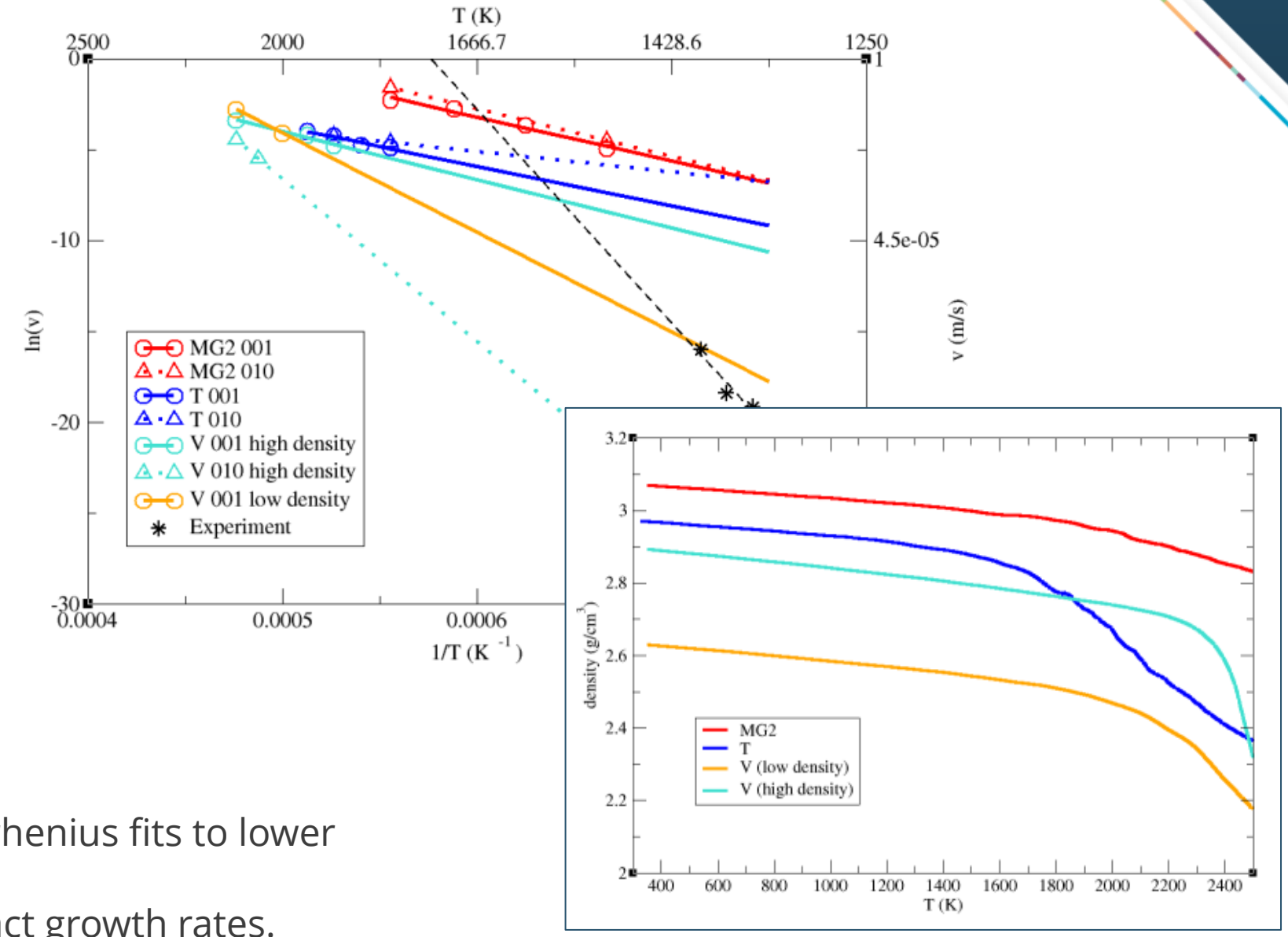
```
q6: Q6 SPECIES=<pID range> R_0=<cutoff>
lq6: LOCAL_Q6 SPECIES=q6 R_0=<cutoff>

DUMPMULTICOLVAR DATA=lq6 FILE=q6out.xyz
```

The PLUMED consortium. *Promoting transparency and reproducibility in enhanced molecular simulations*, Nat. Methods 16, 670 (2019)

Planar crystal growth analysis

Simulation temperatures vary between potentials to account for characteristic glass transition.

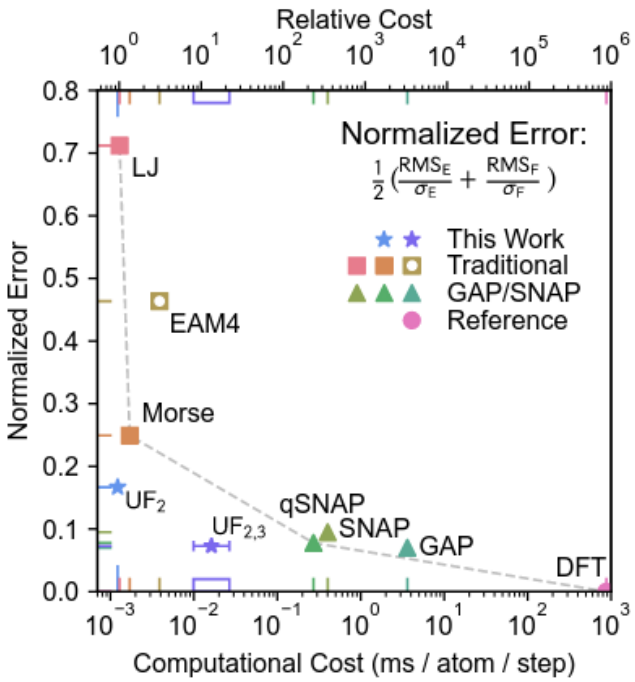
Arrhenius fits of linear velocity show extrapolation to experiment at much lower temperatures.



Key conclusions:

- Our potentials span a range of Arrhenius fits to lower temperature growth rates.
- Both density and orientation impact growth rates.

Ultra-Fast Interpretable Machine-Learning Potentials



Machine learning potentials show promise to obtain accuracy on par with 1st principle simulation at the computational cost of classical force field methods

The UF potential uses **cubic B-spline** functions in a linear basis expansion in pair distances r_{ij}.

Local support:

- Each cubic B-spline spans, at most, four knot intervals
- For any input, exactly four basis functions are non-zero
- Evaluation cost does not scale with the total number of basis functions.

Differentiability:

- 1st derivative is smooth (forces)
- 2nd derivative is continuous (phonons and elastic constants)

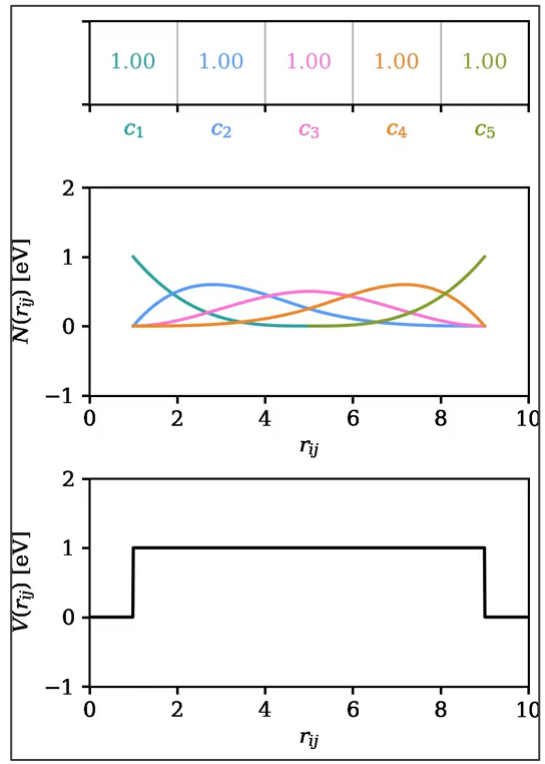
Representation of many-body potentials by 2-body and 3-body basis functions optimizes speed and memory efficiency in use of the potentials.

$$E = \sum_{i=1}^{N_s} \sum_{j=1}^{\infty} V_2(r_{ij})$$

$$V_2(r_{ij}) = \sum_{n=-2}^{K-1} c_n N_{n,3}(r)$$

Interpretable

- Learns coefficients of cubic B-spline to represent energy land scape from 1st principal data



Xie, Rupp, Hennig, https://arxiv.org/abs/2110.00624 (2021).