Thermal conductivity of Au systems: from bulk to nanoassembled films

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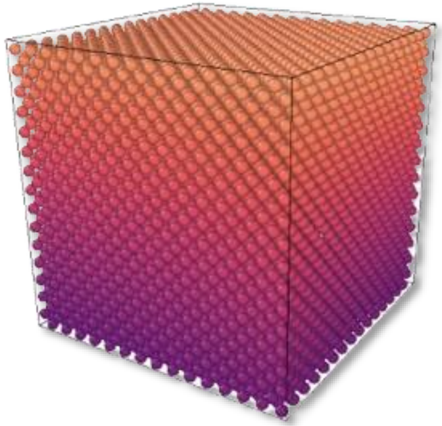
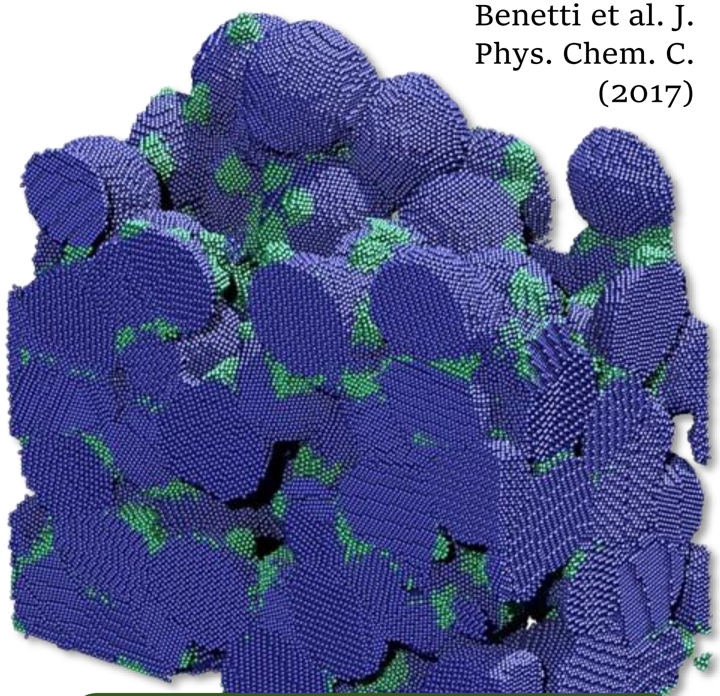
UNIVERSITÀ DEGLI STUDI DI MILANO
FACOLTÀ DI SCIENZE E TECNOLOGIE

Study on phononic thermal transport in different Au-systems

Impact of porosity-driven defects

From bulk



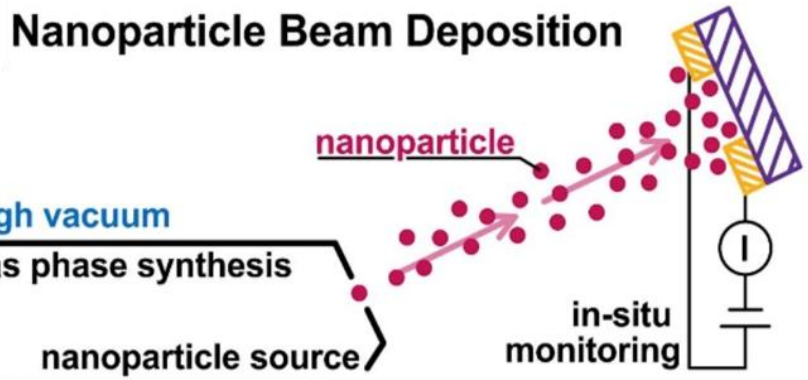


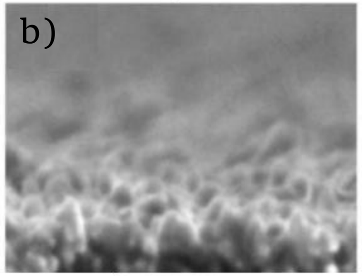
Benetti et al. J. Phys. Chem. C. (2017)

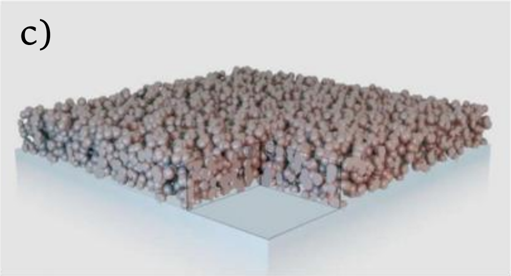
To nanostructured assemblies

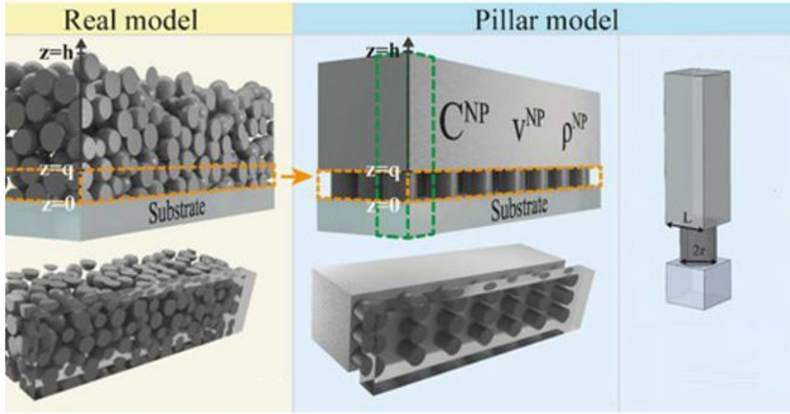
Motivation

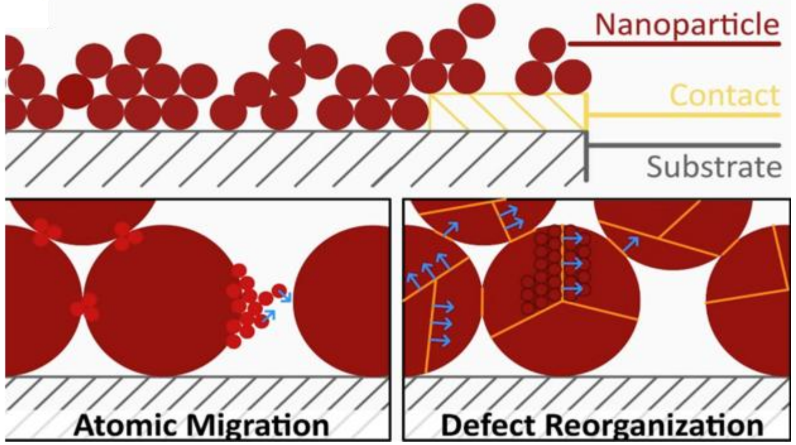
(a)-(b)-(e)-(f) from A. Vahl et al. J. Phys. D: Appl. Phys. (2024)
(c)-(d) from G. Benetti et al Nanomaterials (2021)

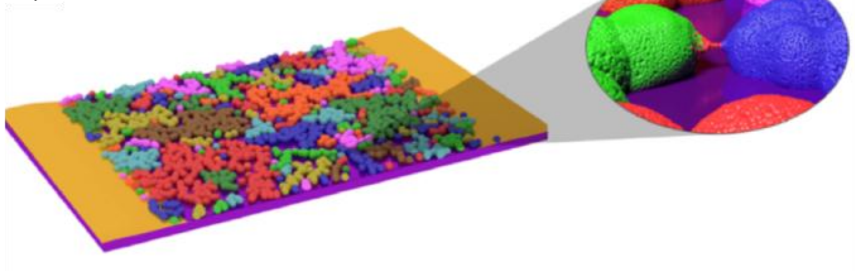
a)


b)


c)


d)


e)


f)


Applications:

- Gas membrane
- Sensors
- Hydrogen batteries
- Resistor
- Neuromorphic circuits

Systems Investigated

Aim: Study thermal conductivity in nanostructured materials

Approach: Start from simpler systems with controlled porosity and coordination number

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Aim: Study thermal conductivity in nanostructured materials

Approach: Start from simpler systems with controlled porosity and coordination number

$$\text{Porosity} = \frac{V_{void}}{V_{tot}} = \frac{N_{del}}{N_{tot}}$$

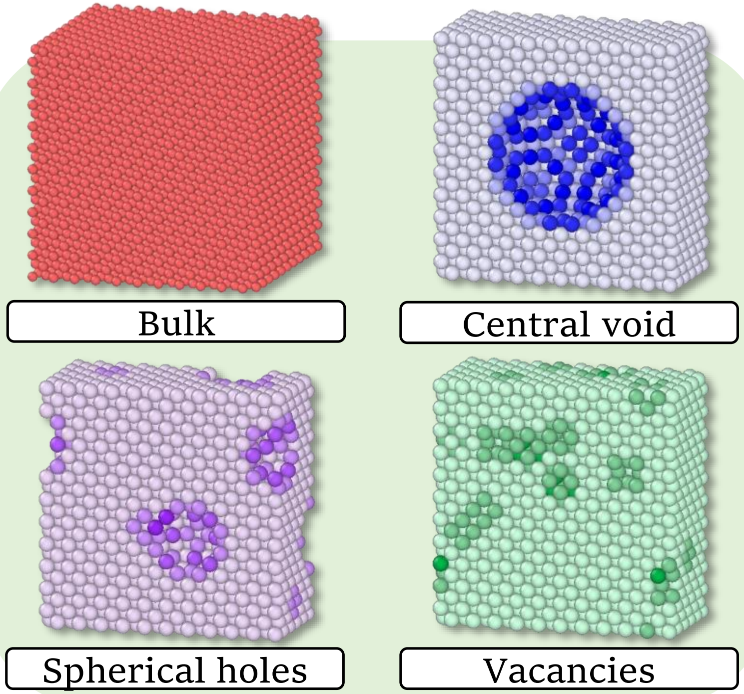
Coordination Number (CN): number of nearest neighbours around an atom.

$$\mathrm{CN}_i = \sum_{j \neq i} \begin{cases} 1, & r_{ij} < r_c \\ 0, & r_{ij} \geq r_c \end{cases}$$

Systems Investigated

Aim: Study thermal conductivity in nanostructured materials

Approach: Start from simpler systems with controlled porosity and coordination number



$$\text{Porosity} = \frac{V_{void}}{Vtot} = \frac{N_{del}}{N_{tot}}$$

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Systems Investigated

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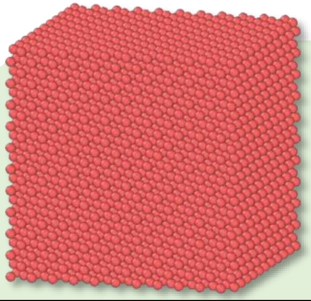
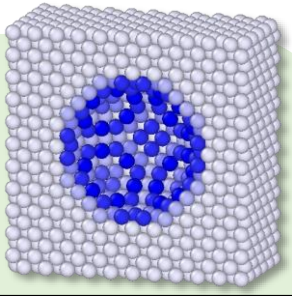
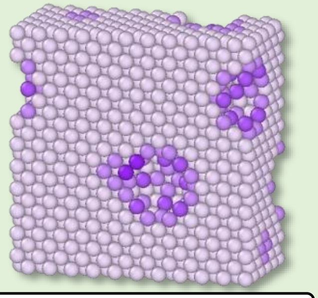
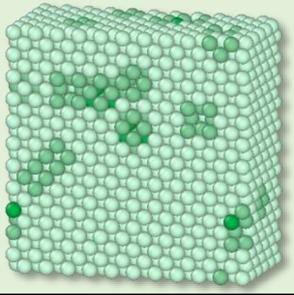

Bulk


Central void

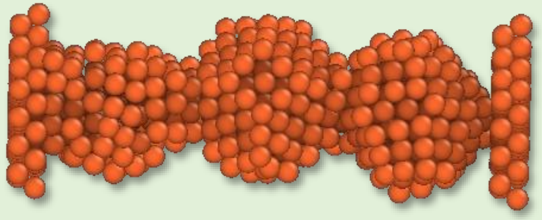

Spherical holes


Vacancies

$$\text{Porosity} = \frac{V_{void}}{V_{tot}} = \frac{N_{del}}{N_{tot}}$$

Coordination Number (CN): number of nearest neighbours around an atom.

More complex architectures:

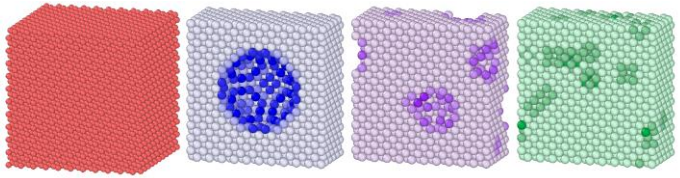

Nanopillar assemblies


Nanofilms

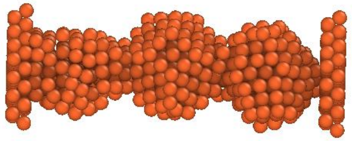
Developed Workflow

Building the systems using ASE

Construction of the initial bulk-like atomic structures:



Assembly of nanopillars:



Structural characterisation of the systems:

$$\mathrm{aCN} = \frac{\sum CN_i}{N} \qquad \mathrm{Porosity} = \frac{V_{void}}{V_{tot}}$$

EMD simulations in LAMMPS

NVT — Thermalization phase

NVE — Equilibrium phase

NVE — Production phase

Production of the output files:
- thermodynamic data
- $\mathbf{J} = \frac{1}{V}\left[\sum_{i=1}^{N} e_i \mathbf{v}_i - \sum_{i=1}^{N} \mathbf{S}_i \mathbf{v}_i\right]$

Then we verify that the system is in equilibrium.

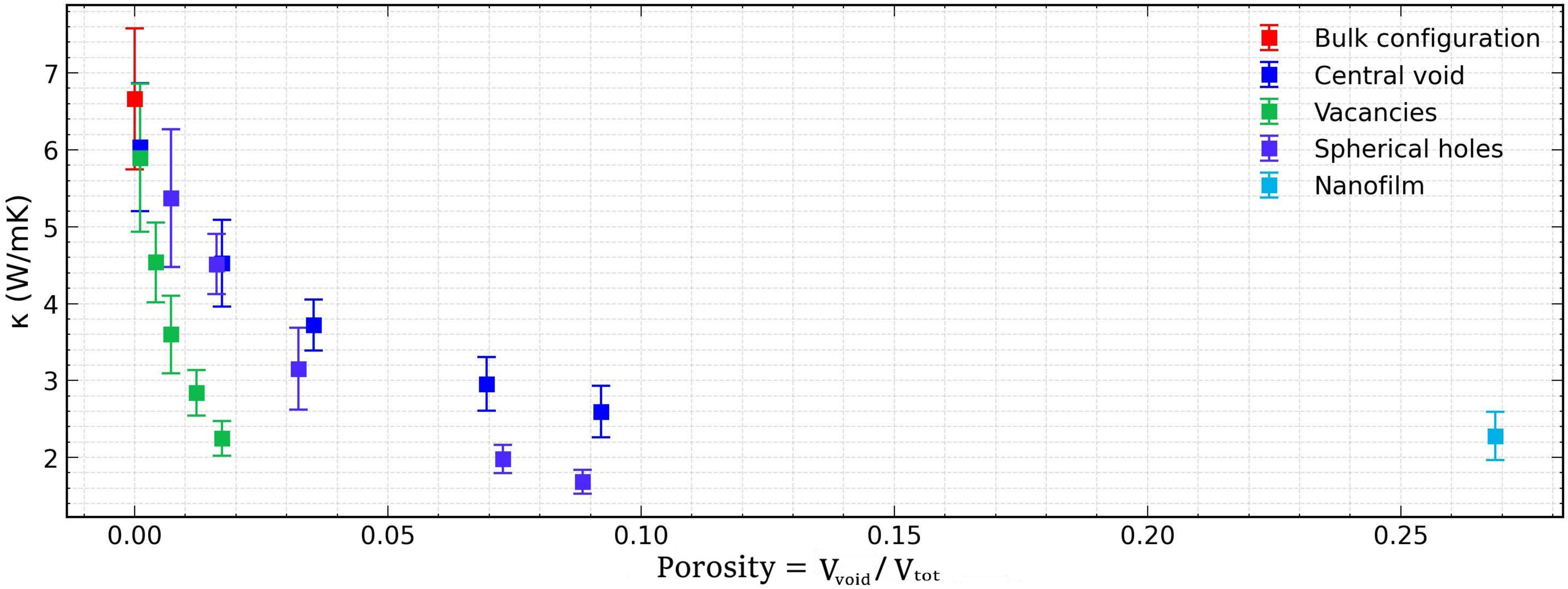
Post-Processing in Python

Green-Kubo method

$$\kappa_u = \frac{V}{k_B T^2} \int_0^{\infty} \langle J_u(0) J_u(t) \rangle \, \mathrm{d}t$$

- ❑ Computing HFACF
- ❑ Determination of the cut-off time τ_c
- ❑ Integration of the HFACF up to τ_c
- ❑ Production of comparable results

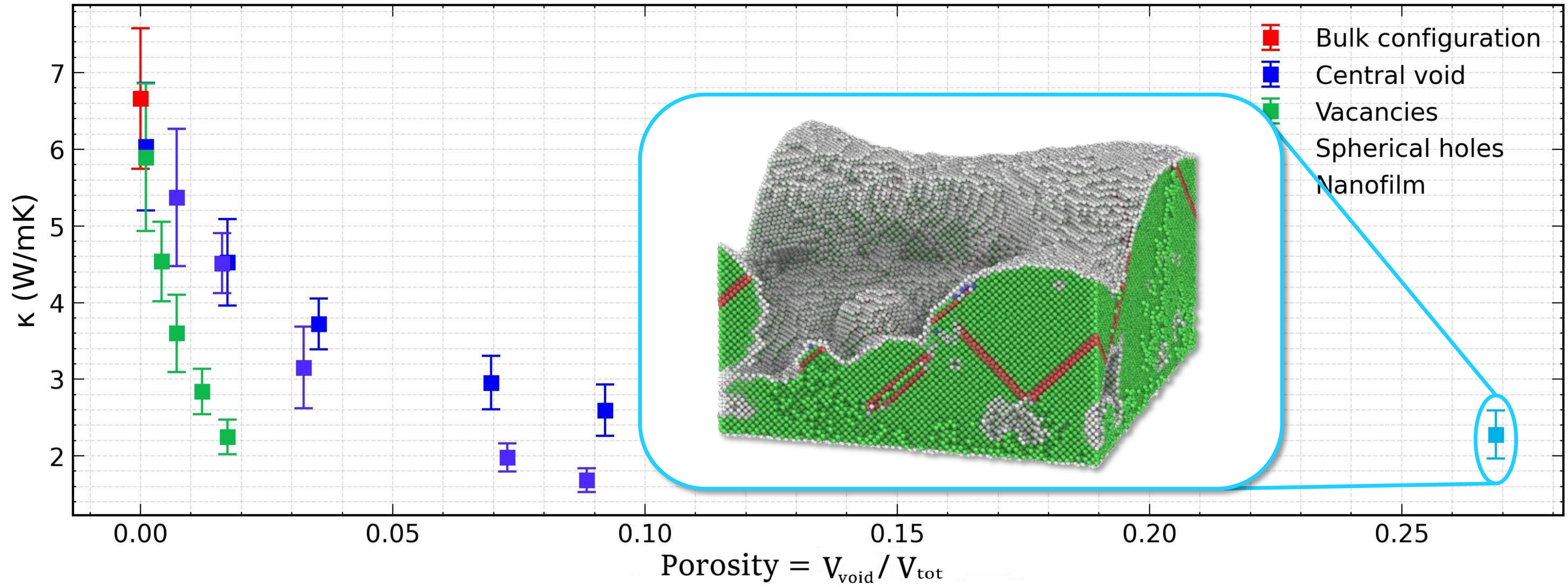
Results: Thermal Conductivity vs Porosity



Increase in porosity

Decrease in conductivity

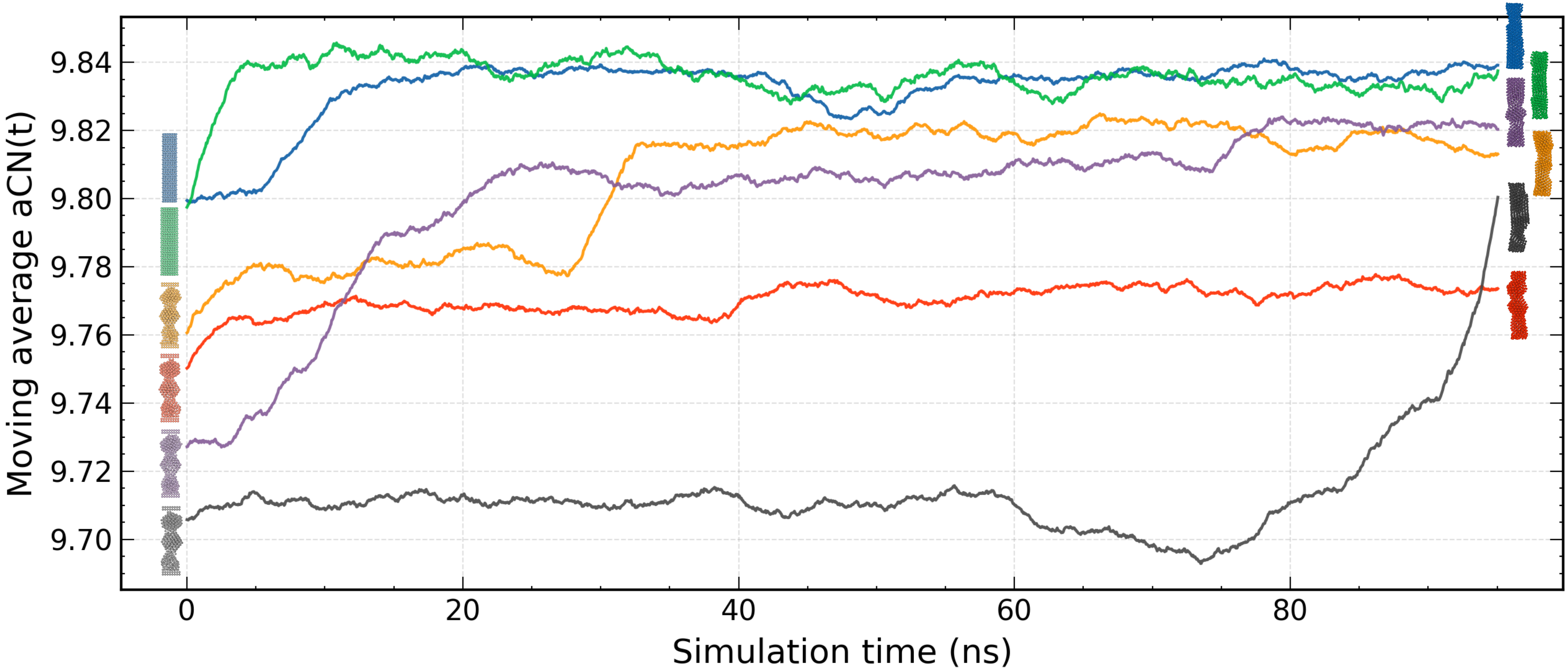
Results: Thermal Conductivity vs Porosity



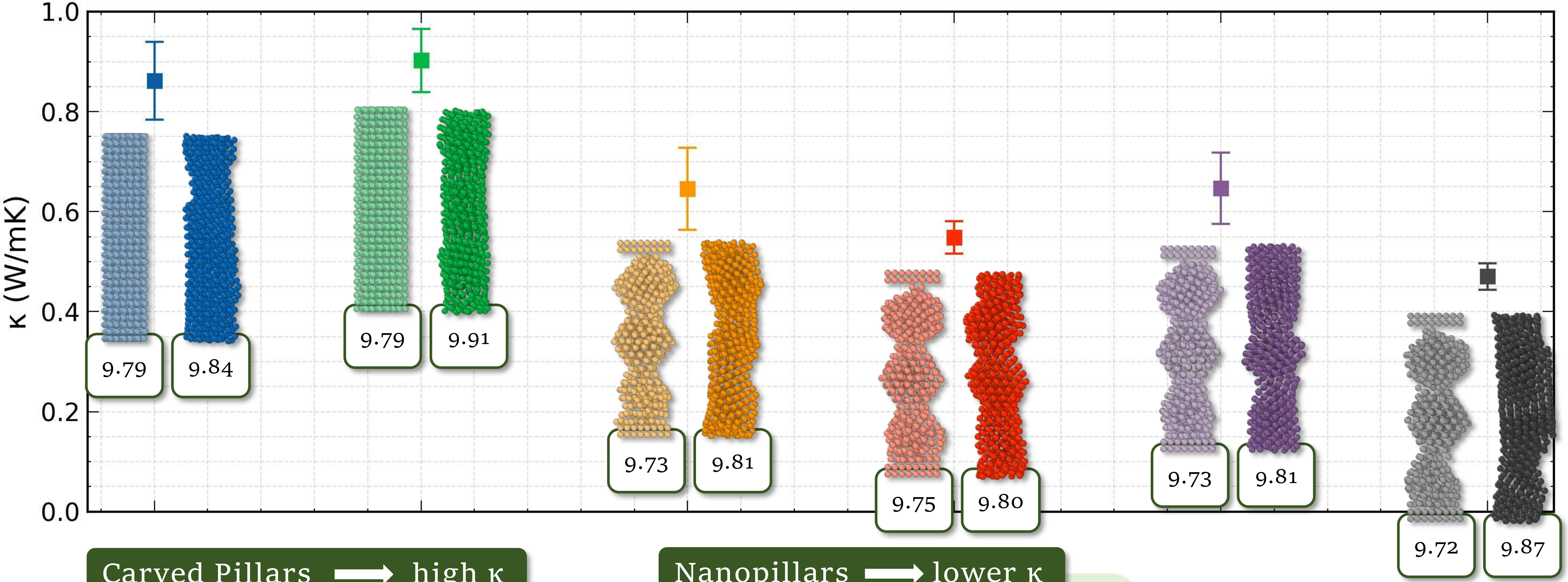
Increase in porosity

Decrease in conductivity

Nanopillars



Nanopillars



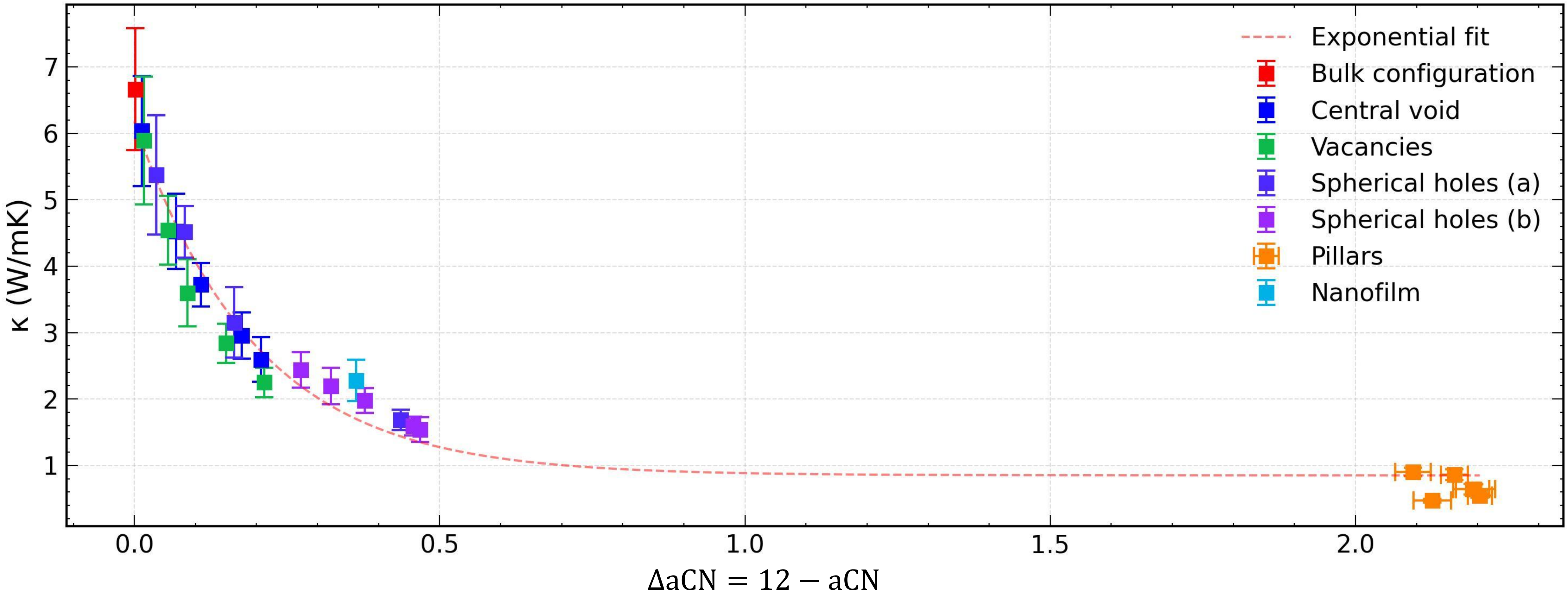
Carved Pillars ⟶ high κ

- Preserve crystalline order
- Continuous cross-section

Nanopillars ⟶ lower κ

- Initially under-coordinated
- Irregular cross-section

Results: Thermal Conductivity vs aCN



Fit: $\kappa_{FA} = a\, e^{-b\,(\Delta aCN)} + c$ $\quad a = 5.329,\ b = 5.055,\ c = 0.850$

Discussion & Conclusions

Phononic thermal transport

Impact of porosity-driven defects

Developed Workflow:

Building various systems → EMD simulations → Geometrical descriptors & thermal conductivity

Results

- Increase in porosity
- Decrease in thermal conductivity

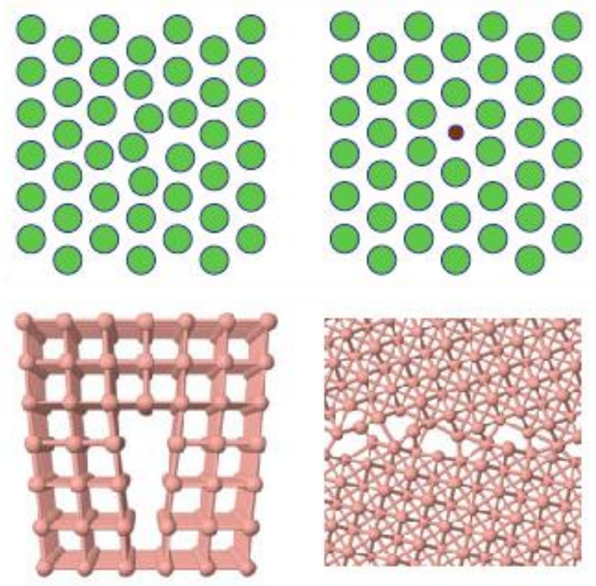
But

- = Porosity
- ≠ Thermal conductivity

- Decrease in aCN
- Decrease in thermal conductivity

From bulk to nanoassemblies CN governs Au phononic heat conduction

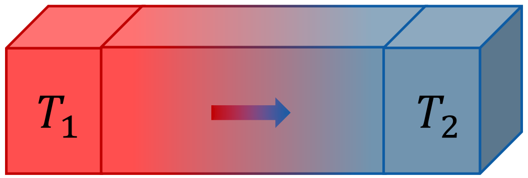
Future Developments



Explore the effects of other defects

A more robust determination of the Green–Kubo integration cut-off

Comparison with Non-Equilibrium Molecular Dynamics (NEMD) methods



Combine EMD/NEMD with ML-potentials

Thank you for your attention

Antonio Sacco

Setting up the simulations

NVT — Thermalization phase

NVE — Equilibrium phase

NVE — Production phase

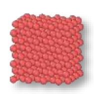
Producing output files

MD simulations in LAMMPS:

$$\boxed{F = m\,\ddot{x}}$$

- Second-order algorithm
- Timestep: 1 fs
- EAM potential

EMD Simulations in LAMMPS



Setting up the simulations

NVT — Thermalization phase

NVE — Equilibrium phase

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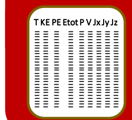
Producing output files



- NVT (Nosé–Hoover) ⇨ T = 300 K
- Simulation time 1 ns (= 10^6 steps)

- NVE ⇨ Total energy conserved
- Simulation time 1 ns (= 10^6 steps)

- NVE ⇨ Total energy conserved
- Simulation time 100 ns (= 10^8 steps)

EMD Simulations in LAMMPS

Setting up the simulations

NVT — Thermalization phase

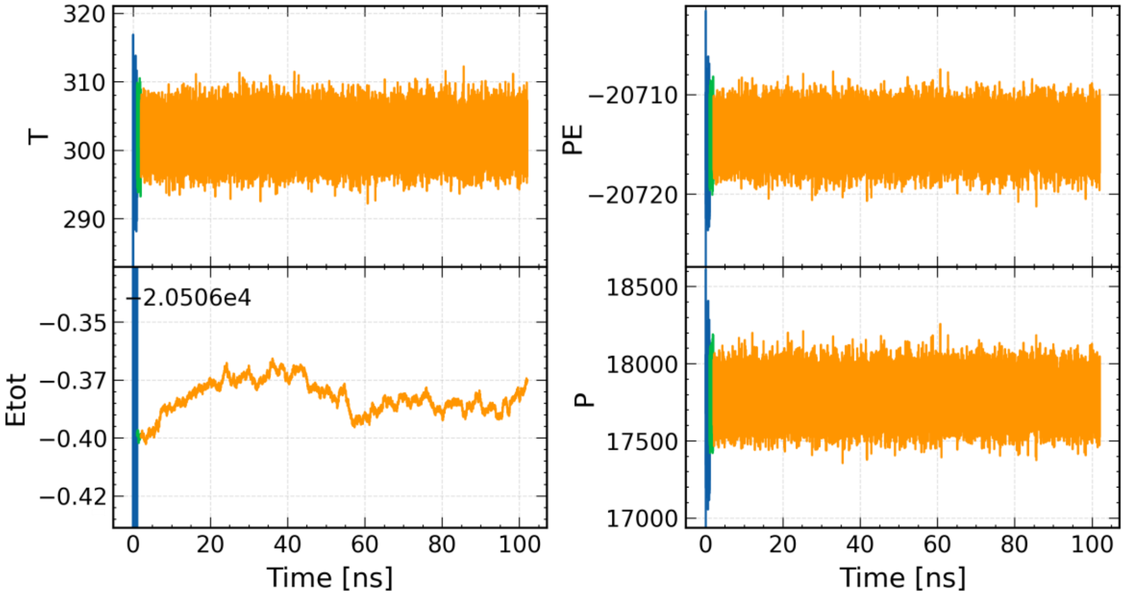
NVE — Equilibrium phase

NVE — Production phase

Producing output files

Checking equilibrium

- Plot T, PE, Etot, P over time:



- Linear regression ➡ *total drift*
- Ensure *total drift* < *StdDev*

Post–Processing in Python

- Computing and fitting HFACF
- Determination of the cut-off time τ_c using the First Avalanche method
- Integration of the HFACF up to τ_c
- Production of comparable results

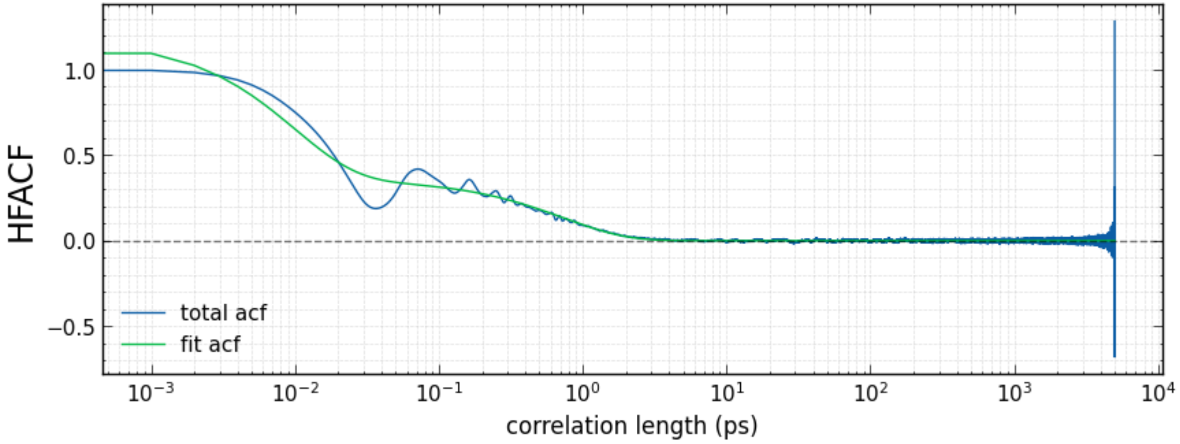
Heat flux $\mathbf{J} = \frac{1}{V}\left[\sum_{i=1}^{N} e_i \mathbf{v}_i - \sum_{i=1}^{N} \mathbf{S}_i \mathbf{v}_i\right]$

Green-Kubo method:

$$\kappa_u = \frac{V}{k_B T^2} \int_0^\infty \langle J_u(0) J_u(t)\rangle \, \mathrm{d}t$$

$$\text{HFACF} = \frac{\langle J_u(0) \cdot J_u(t)\rangle}{\langle J_u(0) \cdot J_u(0)\rangle}$$

window = 10 ns



Post–Processing in Python

- Computing and fitting HFACF
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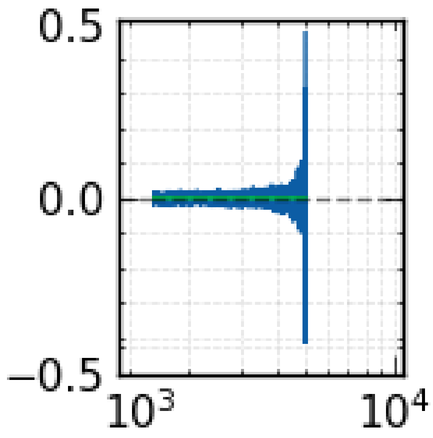
HFACF is noisy at long times

Reliable up to a cut-off time τ_c



Determination of τ_c via:

First Avalanche (FA) method, identifies τ_c where the cumulative HFACF increases due to <u>noise</u>.

- Computing and fitting HFACF
- Determination of the cut-off time τ_c using the First Avalanche method
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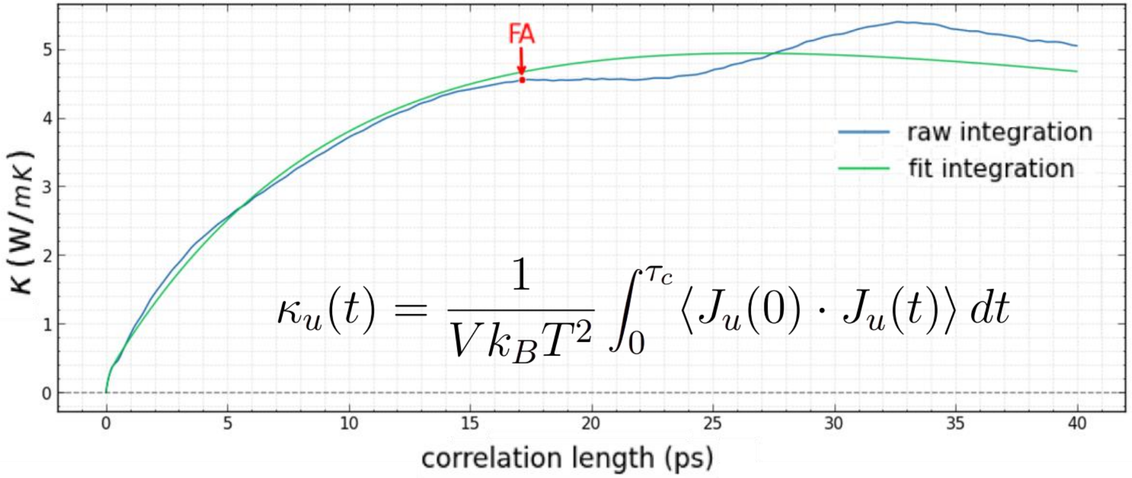
Thermal conductivity (direct):



$$\kappa_u(t) = \frac{1}{V k_B T^2} \int_0^{\tau_c} \langle J_u(0) \cdot J_u(t) \rangle \, dt$$

Thermal conductivity (fit-based):

$$\kappa_F = \frac{A_{\text{corr}}(0)}{k_B T^2 V} (A_1 \tau_1 + A_2 \tau_2 + Y_0 \tau_c)$$

Formula by Chen et al. Jctn (2013)

Post–Processing in Python

- Computing and fitting HFACF
- Determination of the cut-off time τ_c using the First Avalanche method
- Integration of the HFACF up to τ_c
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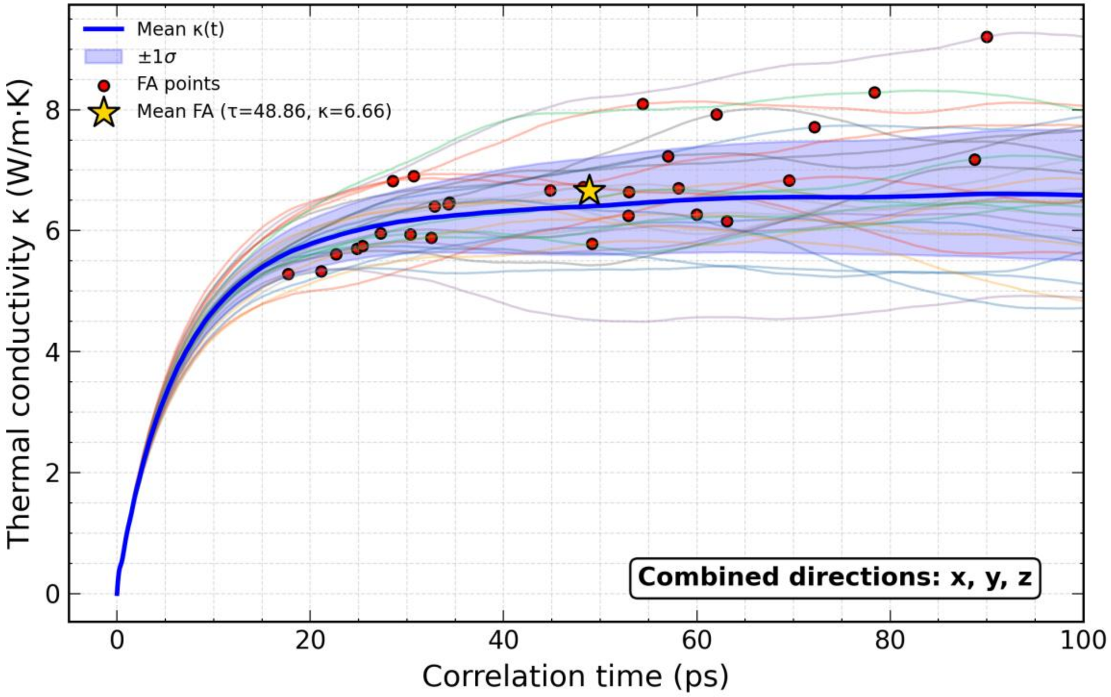
Isotropic system → Average $\kappa_x, \kappa_y, \kappa_z$

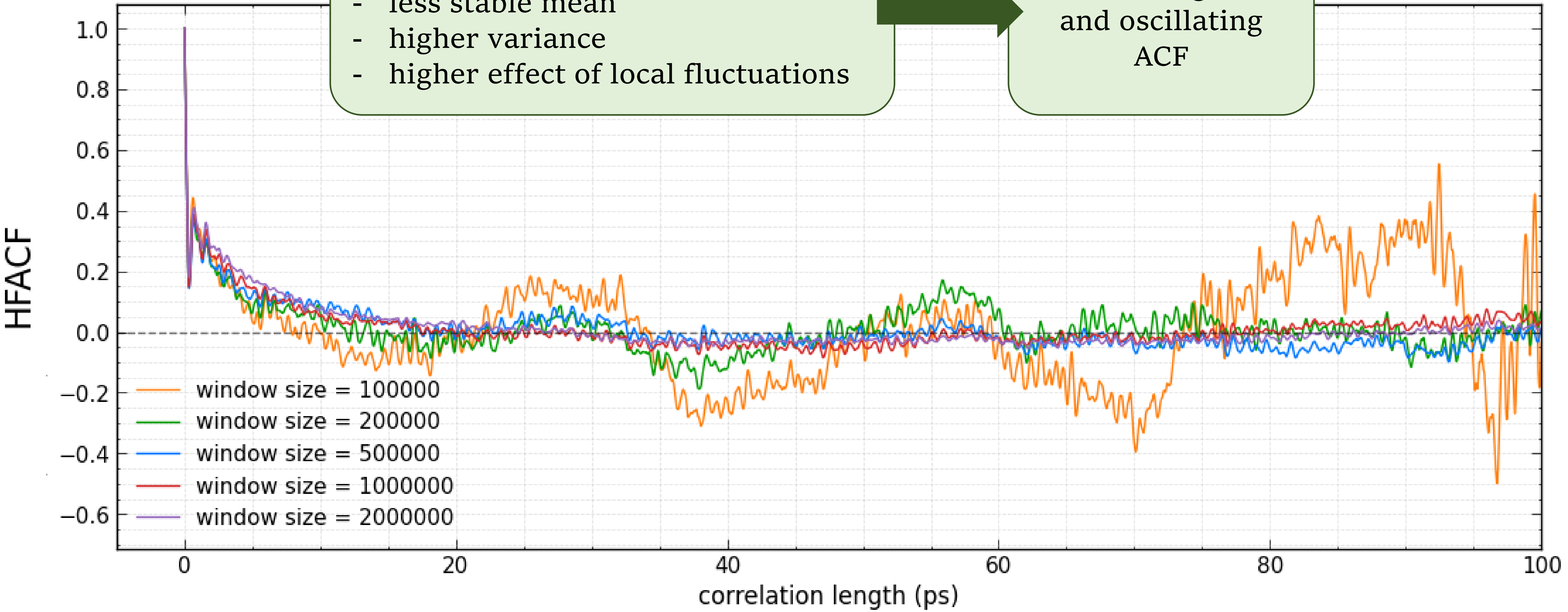
Anisotropic system → $\kappa_x, \kappa_y, \kappa_z$ separately



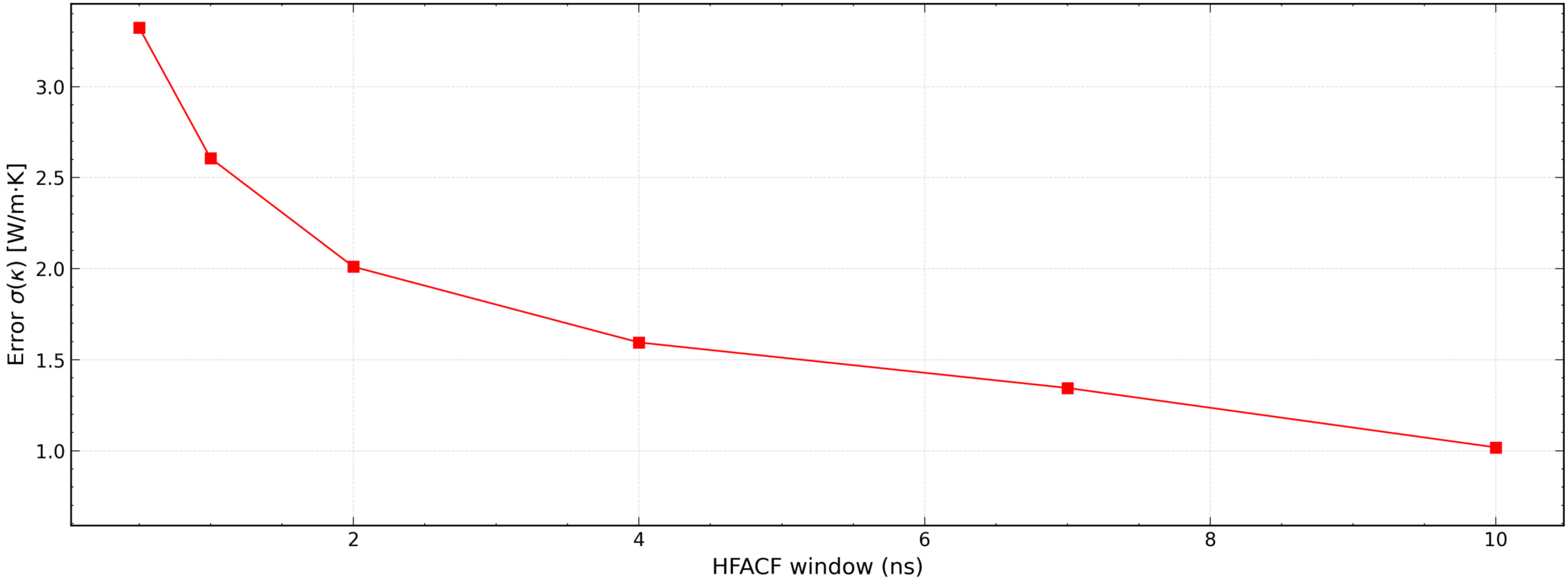
Window-size

Small window:
- less stable mean
- higher variance
- higher effect of local fluctuations

More irregular and oscillating ACF



Window-size

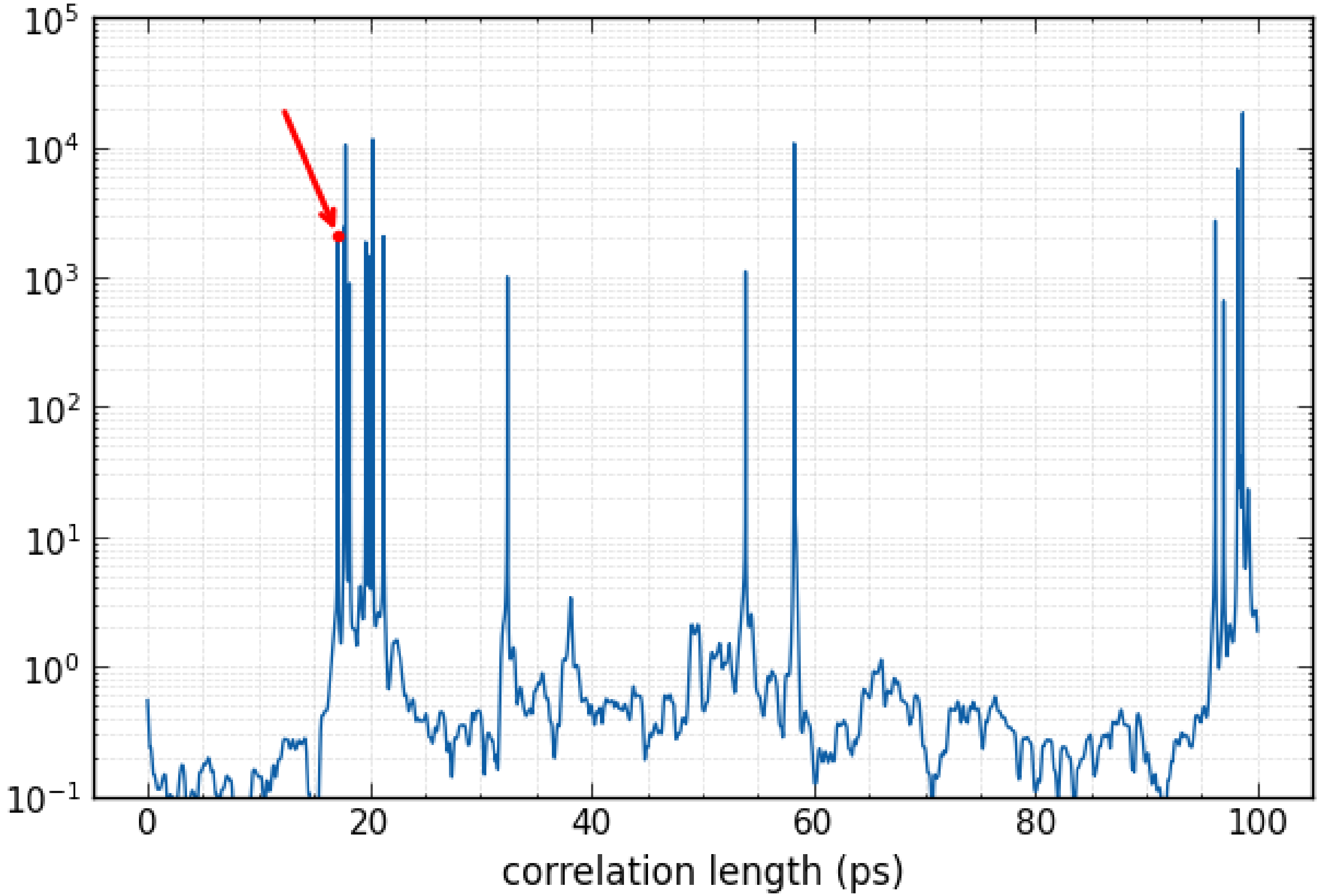


Larger windows → Smaller error σ(κ)

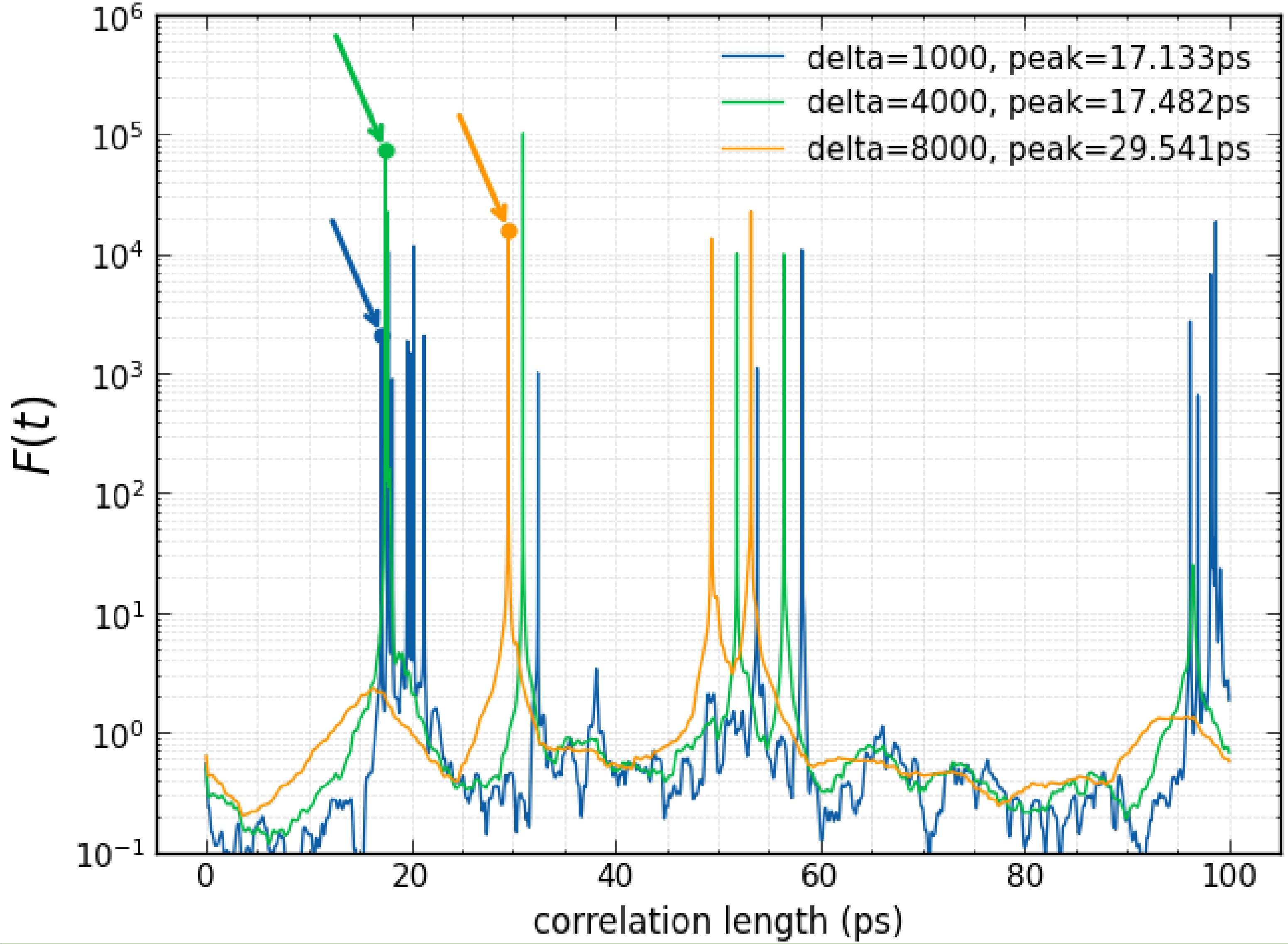
Relative Fluctuation Function

$$F_\delta(t) = \frac{\sigma_\delta(\mathrm{HFACF}(t))}{\langle \mathrm{HFACF(t)} \rangle_\delta}$$

δ = 1000 steps – moving window

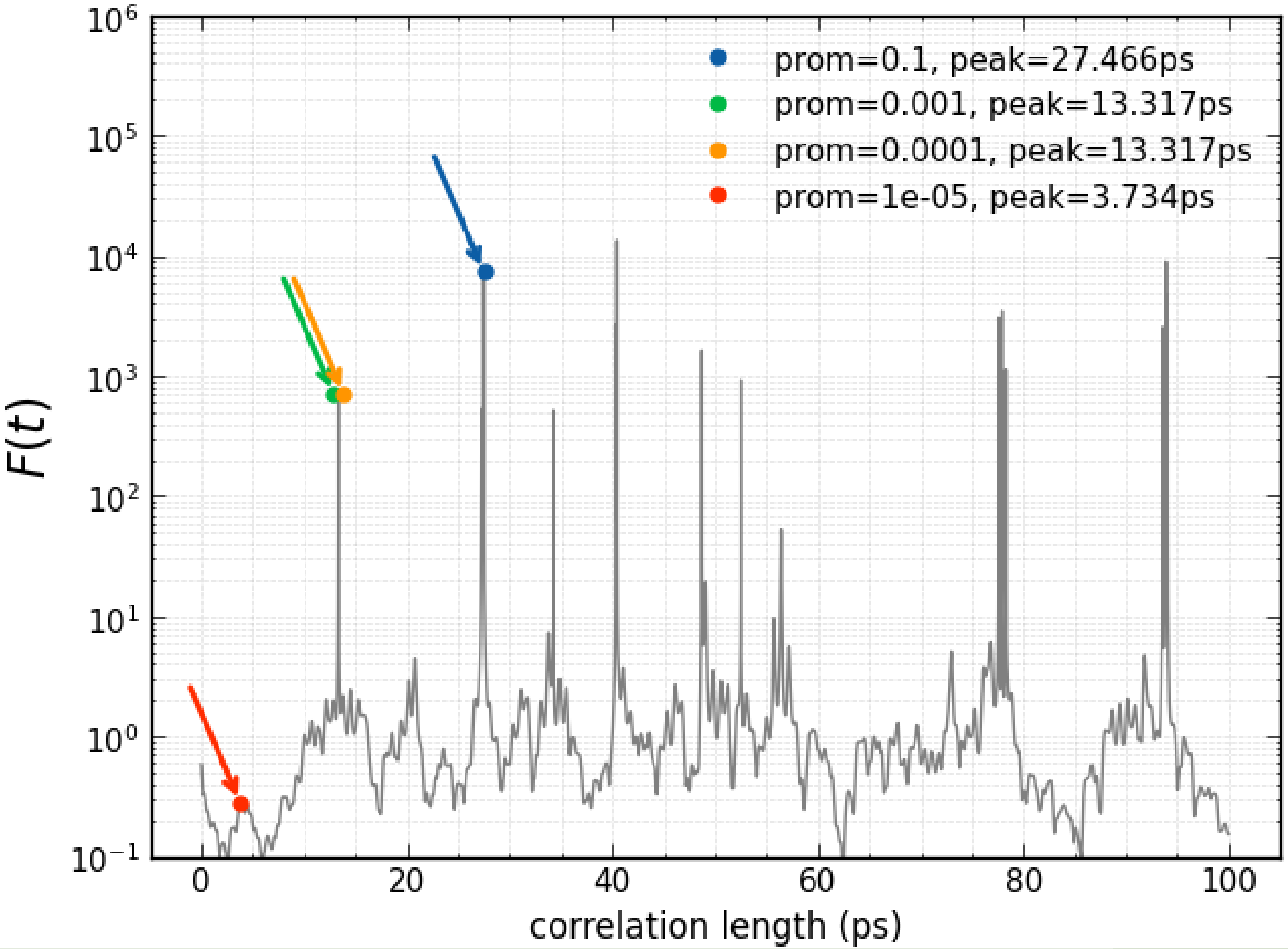


Influence of the δ parameter

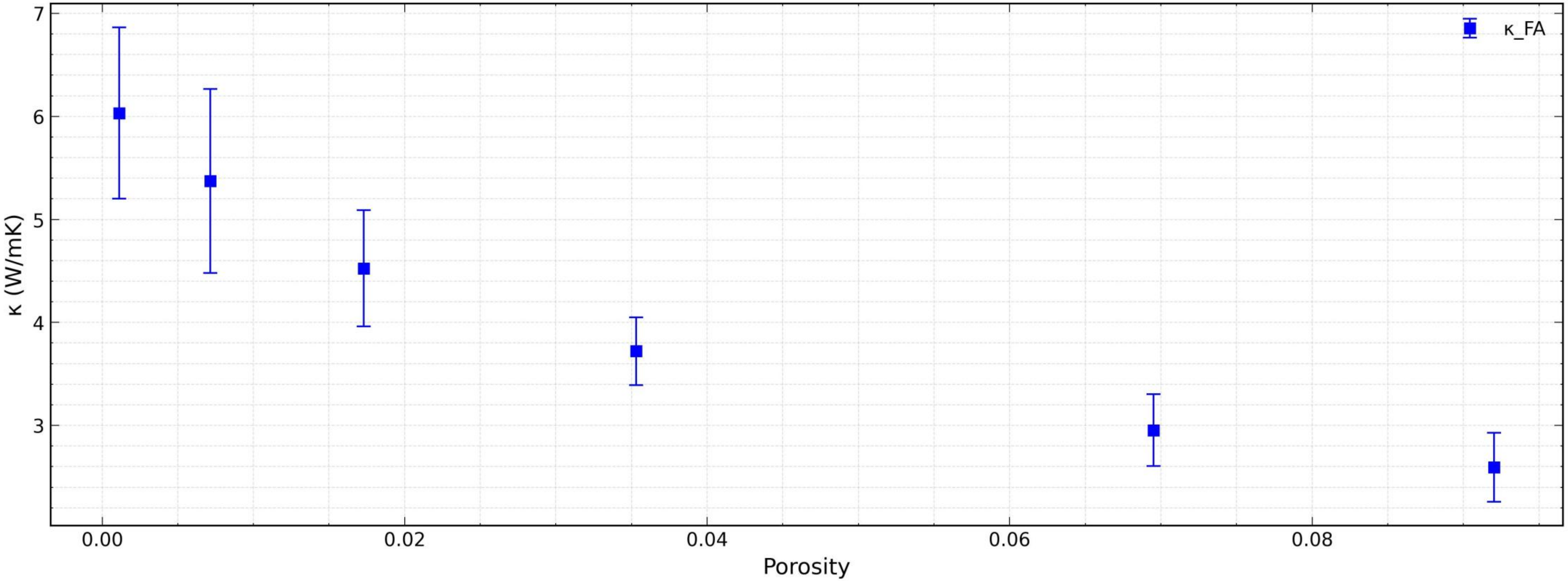


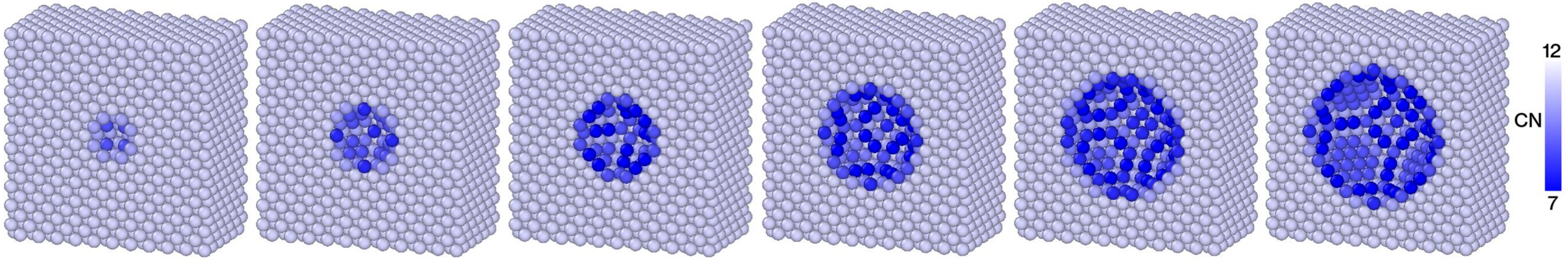
Prominence

- Def: height of a peak relative to surrounding valleys
- Significance vs local noise
- Purpose: select only peaks that stand out
- `find_peaks(F, prominence=0.0007)`

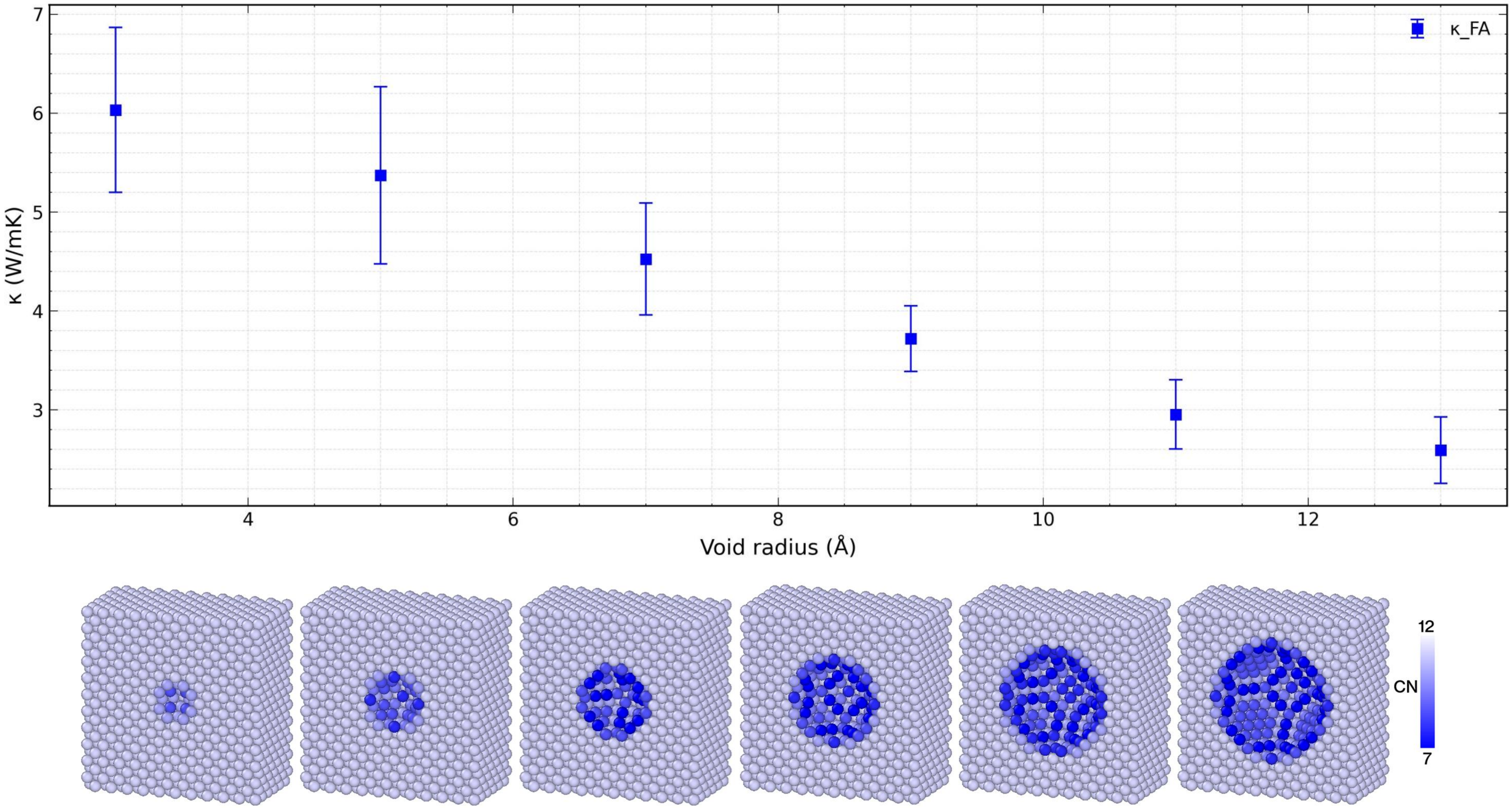


Voids

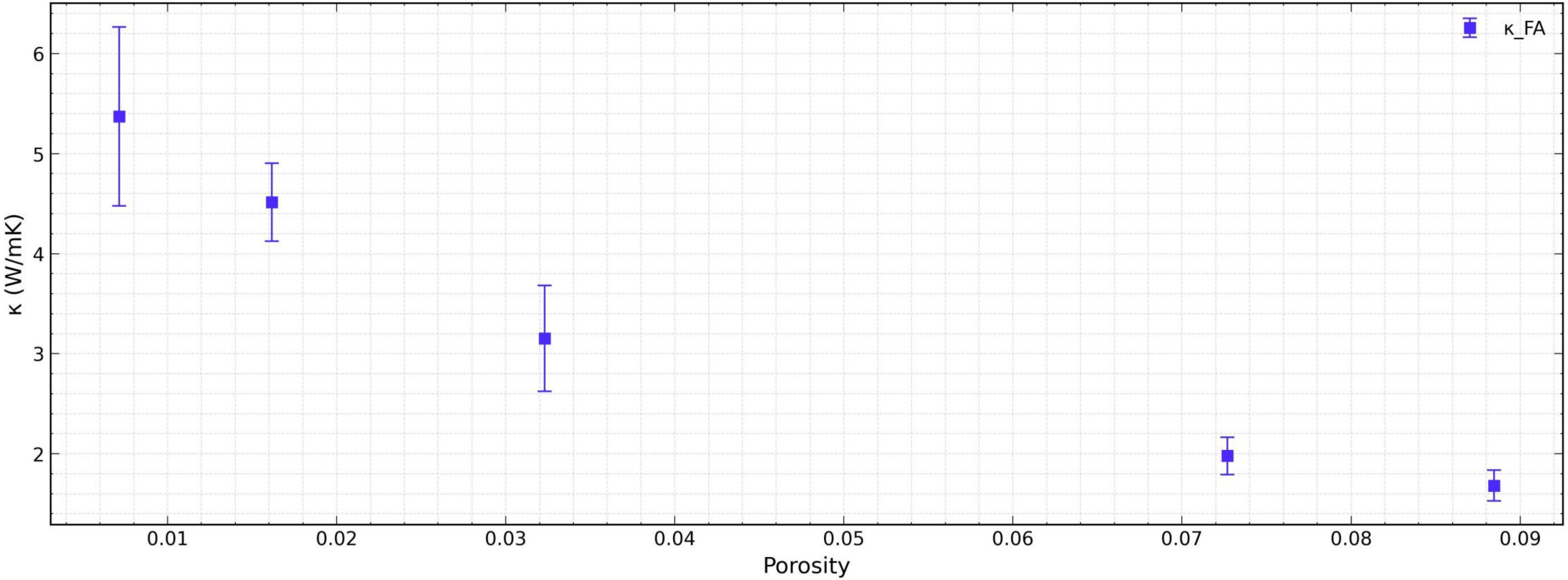


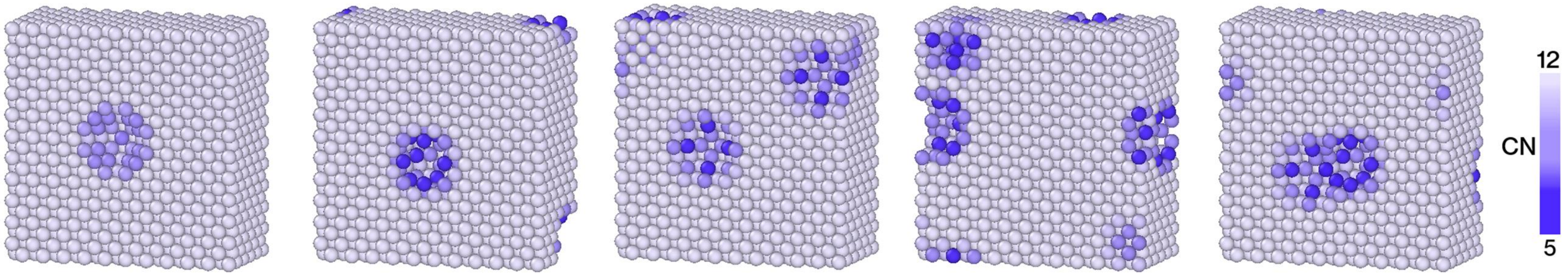


Voids vs radius

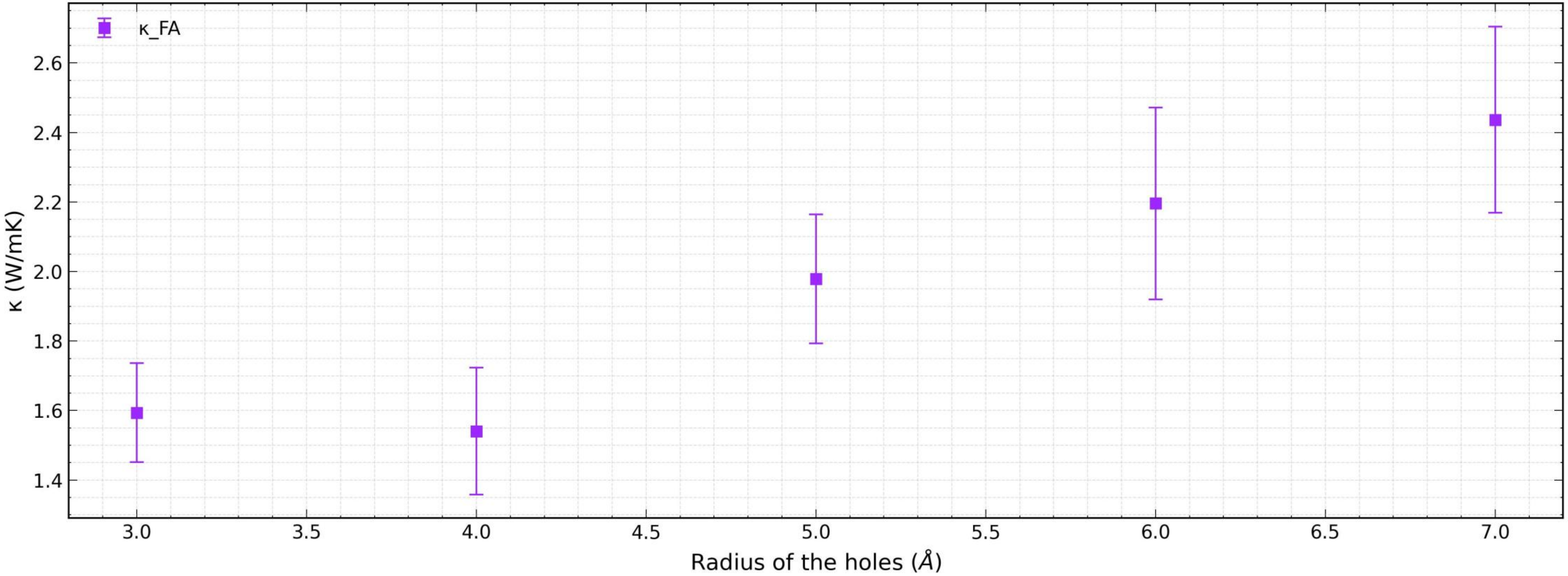


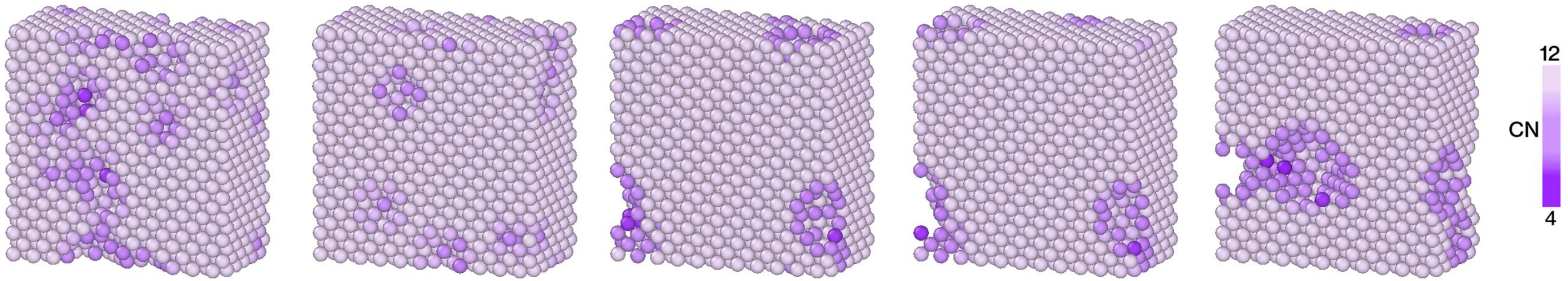
Holes fixed radius



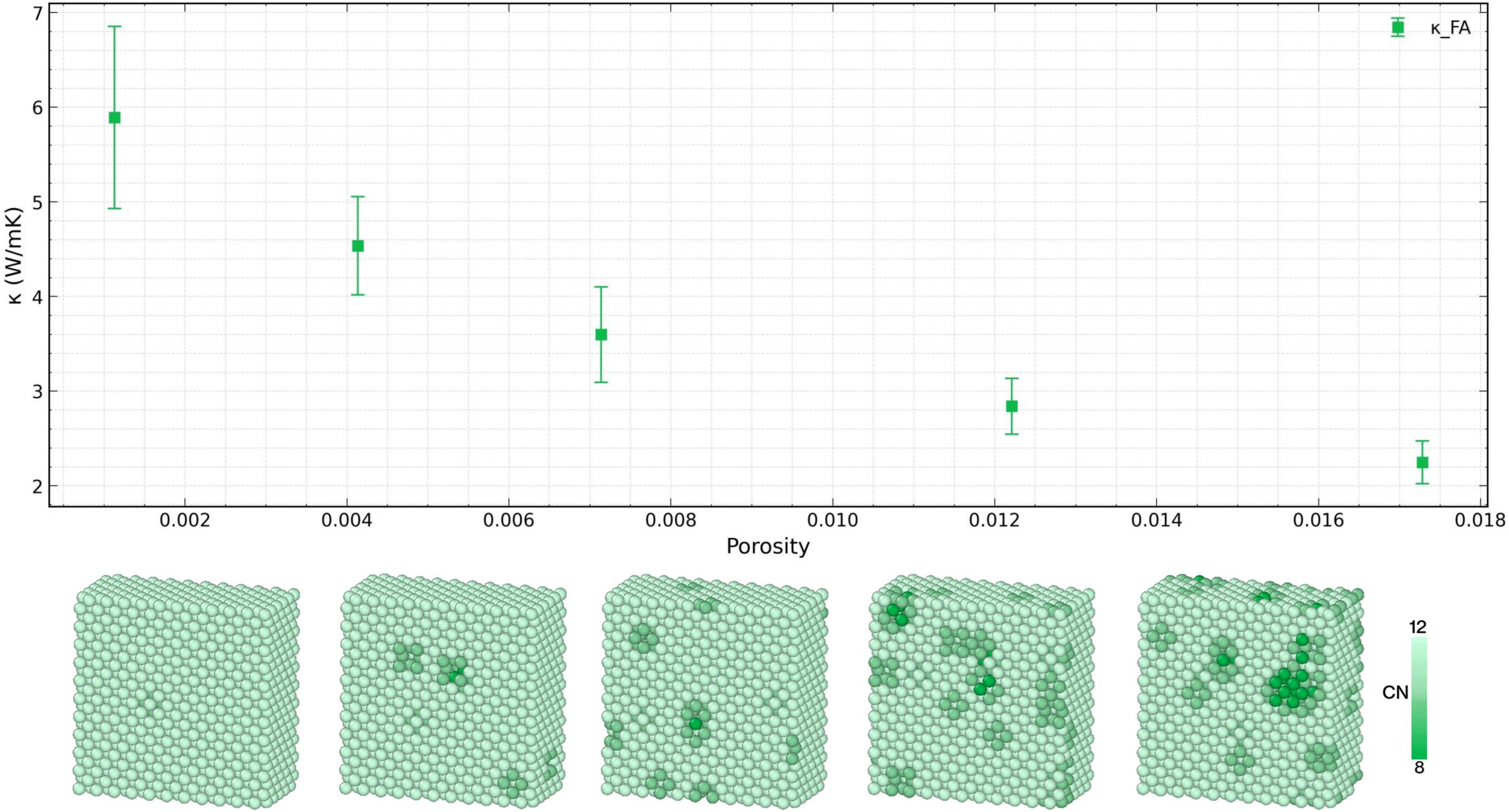


Holes fixed porosity





Vacancies



κ_FA
κ (W/mK)
7
6
5
4
3
2
0.002
0.004
0.006
0.008
0.010
0.012
0.014
0.016
0.018
Porosity
12
CN
8

Green-Kubo Formalism

Macroscopic transport coefficients

κ_u

fluctuation–dissipation theorem

time integrals of microscopic current ACFs

$$\frac{V}{k_B T^2} \int_0^\infty \langle J_u(0) J_u(t) \rangle \, \mathrm{d}t$$

Validity Conditions

- Linear response
- Thermodynamic equilibrium
- Homogeneity and isotropy (for simplicity)
- Time stationarity (no drifts)
- ACFs convergence

GK still valid in heterogeneous or anisotropic systems.

*

Green-Kubo Formalism

Macroscopic transport coefficients

κ_u

fluctuation–dissipation theorem

time integrals of microscopic current ACFs

$$\frac{V}{k_B T^2} \int_0^\infty \langle J_u(0) J_u(t) \rangle \, \mathrm{d}t$$

*

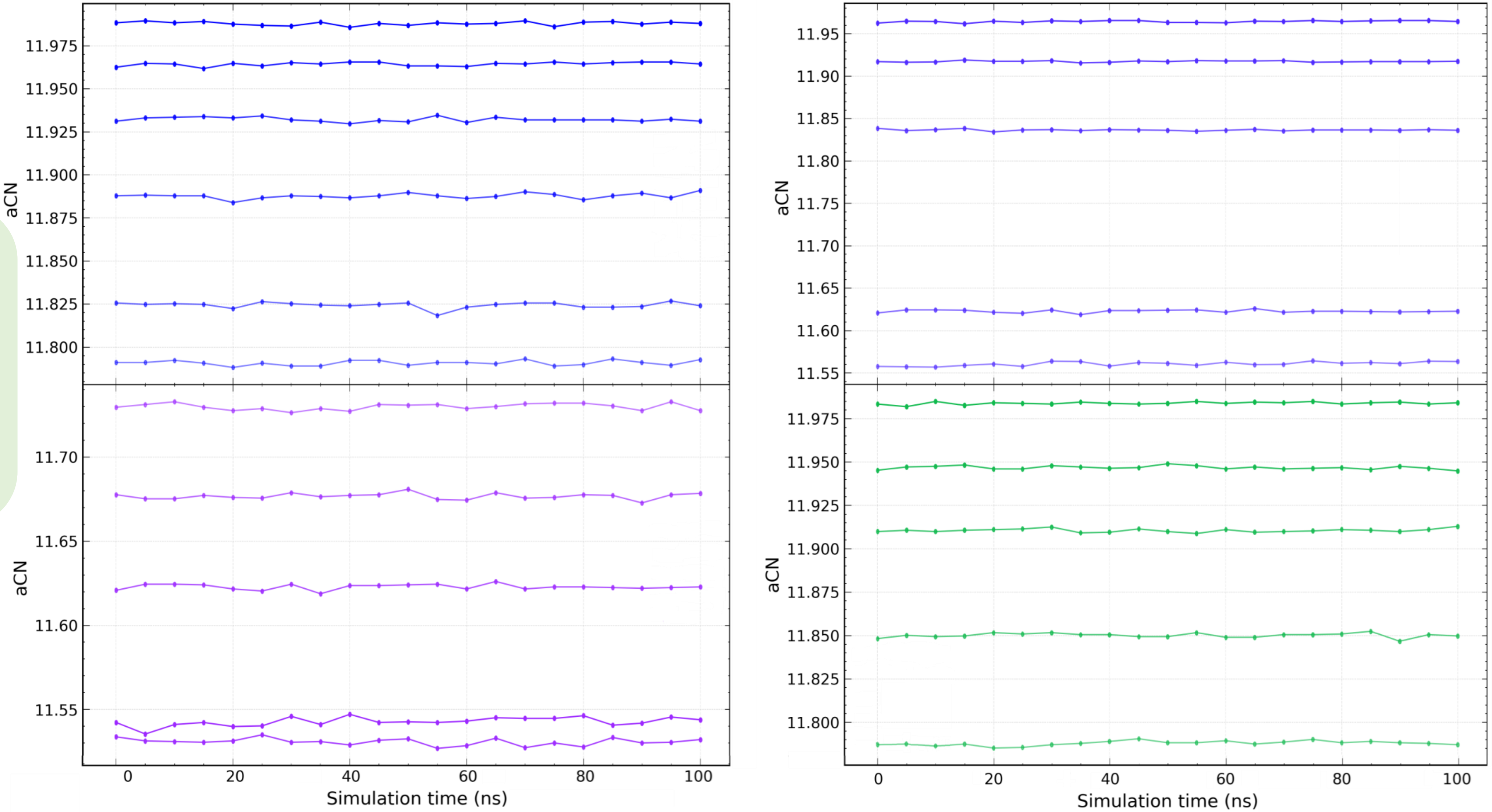
Can be safely applied to nanoscale and disordered systems:

- Does not rely on well-defined phonon wave vectors
- Does not require periodicity
- Does not require phonon mode definition

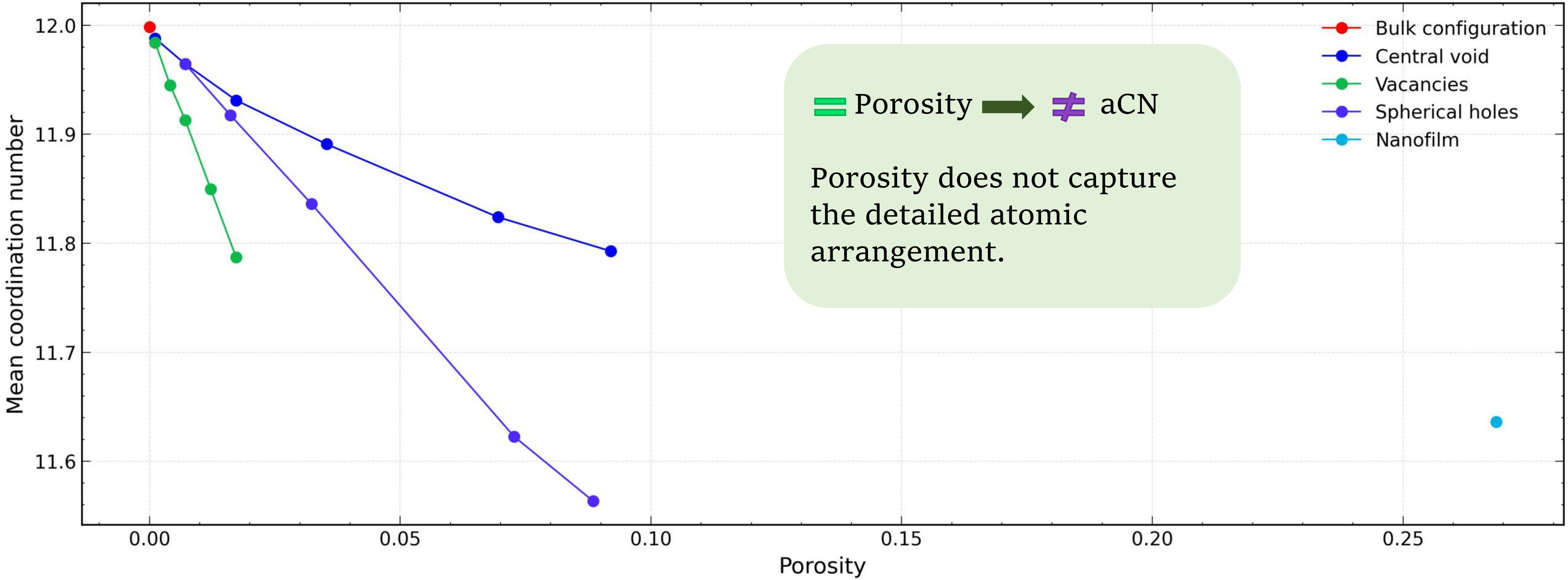
aCN(t)

aCN(t) = *cost.*

Stable configurations



CN vs Porosity



= Porosity → ≠ aCN

Porosity does not capture the detailed atomic arrangement.

Materials with identical porosity may differ in: pore connectivity, surface roughness, local bonding environment, degree of atomic coordination.