
# WEBINAR : Lattice Thermal Conductivity Calculation with MatSQ

Thu, June 4 @ 11AM, KST | Wed, June 3 @ 7PM, PST

# Contents


1. **Introduction**
   - Lattice Thermal Conductivity
   - Calculation Methods for Thermal Transport Calculations
     - Molecular Dynamics (MD)
     - Boltzmann Transport Equation (BTE)
     - Examples
   - Applications

2. **Tutorial**
   - Calculate Lattice Thermal Conductivity of Silicon via Materials Square (LAMMPS)
     - Non-equilibrium MD Simulation
     - Length dependent on Lattice Thermal Conductivity Calculations
   - Analyze Calculated Results
     - Theoretical Limit of Lattice Thermal Conductivity, Mode-independent Phonon Mean Free Path

3. **Q&A**

# Previous Webinar on Materials Square

**WEBINAR : Introduction to Materials Square**

Wed, March 18 @ 6PM PST | Thu, March 19 @ 10AM KST

**WEBINAR : Phonon Calculation**

Wed, April 7 @ 11PM PST | Thu, April 8 @ 3PM KST

**WEBINAR : Calphad with Materials Square**

Fri, May 8 @ 1 AM PST | Fri, May 8 @ 5 PM KST

# Introduction

## Molecular Dynamics (MD)

### I. Theory

- Numerically solves Newton's equations of motion at the atomic or molecular level
- Time integrates the equations of motion numerically : "*Time*" is treated as "*discontinuous*"
- Force calculation
  - The system is regarded as pairwise additive interactions
  - Explicit calculation : Perform $N^2$ times (*inefficient*) → Reduce calculation time by using cutoff radius, *Verlet list*[1], *Cell list*[2] scheme
  - Lennard-Jones system (Force calculation)
    - $\boldsymbol{f_\alpha(r) = -\frac{\partial U(r)}{\partial \alpha} = -\left(\frac{\alpha}{r}\right)\left(\frac{\partial U(r)}{\partial r}\right)}$
    - $\boldsymbol{f_\alpha^{LJ}(r) = \frac{48\alpha}{r^2}\left(\frac{1}{r^{12}} - 0.5\frac{1}{r^6}\right)}$

[1] *Phys. Rev.* ***136***, *A405 (1942)*

[2] *Mol. Sim.* ***14***, *137 (1995)*

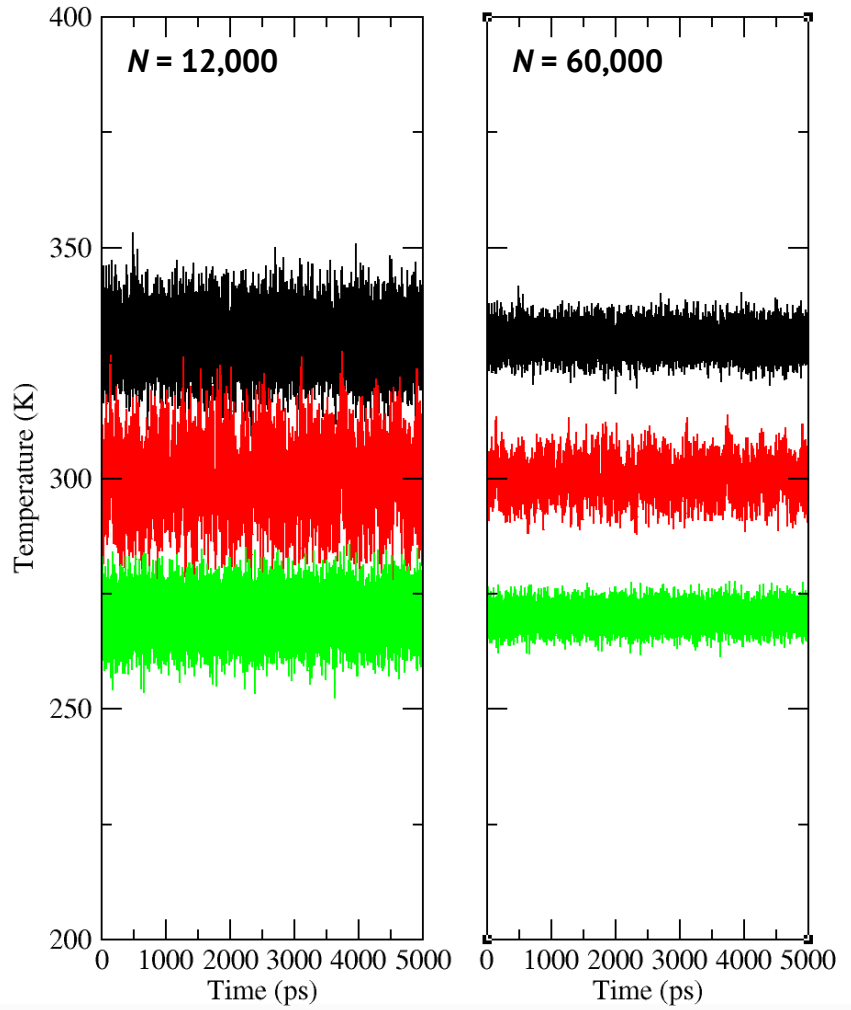
# Introduction

## Molecular Dynamics (MD)

### I. Theory

- Definition of temperature on the classical mechanics
  - The average kinetic energy, $\langle \frac{1}{2} m v_i^2 \rangle = \frac{1}{2} k_B T$
  - *N* particles with DOF, $N_f = 3N - 3$
  - $T(t) = \sum_{i=1}^{N} \frac{m_i v_i^2(t)}{k_B N_f}$

✓ **NB.** Therefore, enough number of atoms are required in system in order to define temperature accurately.



# Introduction

## Molecular Dynamics (MD)

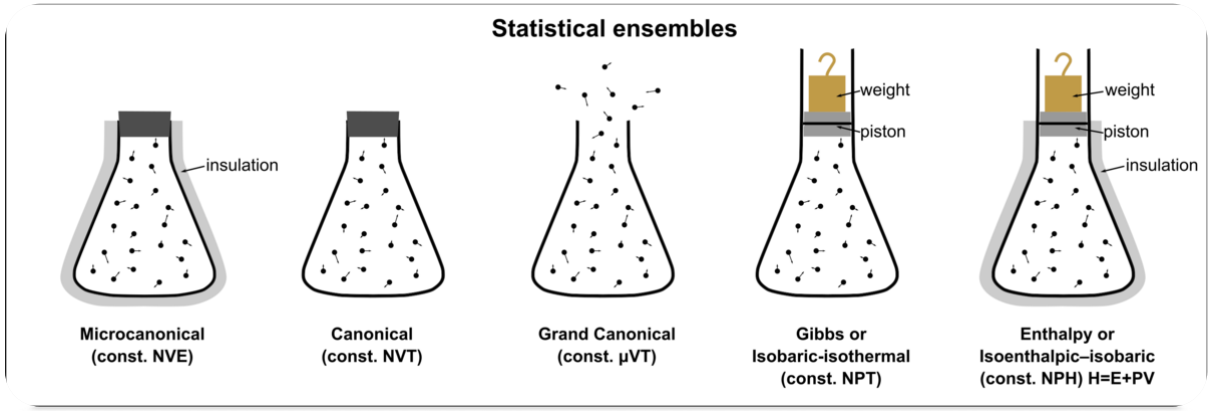
### II. Verlet integration algorithm

- Numerical method for integrating Newton's equations of motion
  - Let atomic position $x$, $x = vt$, $x_{i+1}$ , $x_{i+1} = x_i + v_i\Delta t$, $x_{i+2}$ , $x_{i+2} = x_{i+1} + v_{i+1}\Delta t$
  - However, it is “time-consuming”
  - The position of the next time point can be calculated only by the “current position”, the “past position”, and the “acceleration”, $x_{i+2} = x_{i+1} + v_i\Delta t + a_i\Delta t^2 = 2x_{i+1} - x_i + a_i\Delta t^2$
  - Disadvantages : Verlet integration does not explicitly calculate the velocities of an atom
  - $v_i(t + \Delta t) = v_i(t) + \frac{f_i(t+\Delta t)+f_i(t)}{2m}\Delta t$
  - Initial position : Verlet → New force and velocity : velocity-Verlet

# Introduction

## Molecular Dynamics (MD)

### III. Ensembles




- NVE, NVT, NPT …
- Assumptions
  - All the forces calculated in the classical MD are related to the potential energy
  - The total energy of the system is conversed (Kinetic + Potential energy)

I. NVE ensemble

- Fixed (constant) ***N*** and ***V*** in a unitcell, “Microcanonical ensemble”.
- The ensemble average quantity = The time average quantity obtained from MD simulation

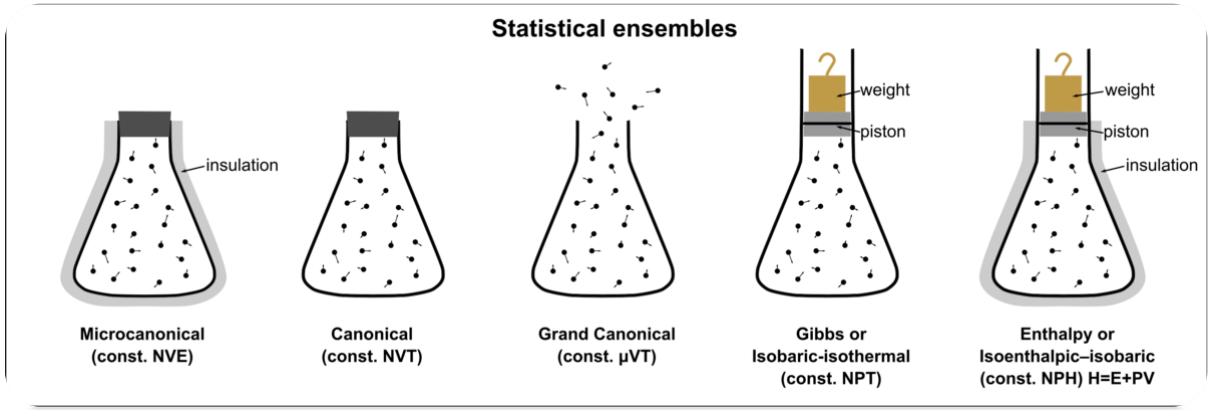
# Introduction

## Molecular Dynamics (MD)

### III. Ensembles

II. NVT ensemble

- Fixed (constant) ***N*** and ***T*** in a unitcell (Isothermal), “Canonical ensemble”
- Thermostat : Gaussian, Andersen, Berendsen and Nosé-Hoover thermostat
- What is good thermostat ? Velocity distribution is satisfied with Maxwell-Boltzmann distribution

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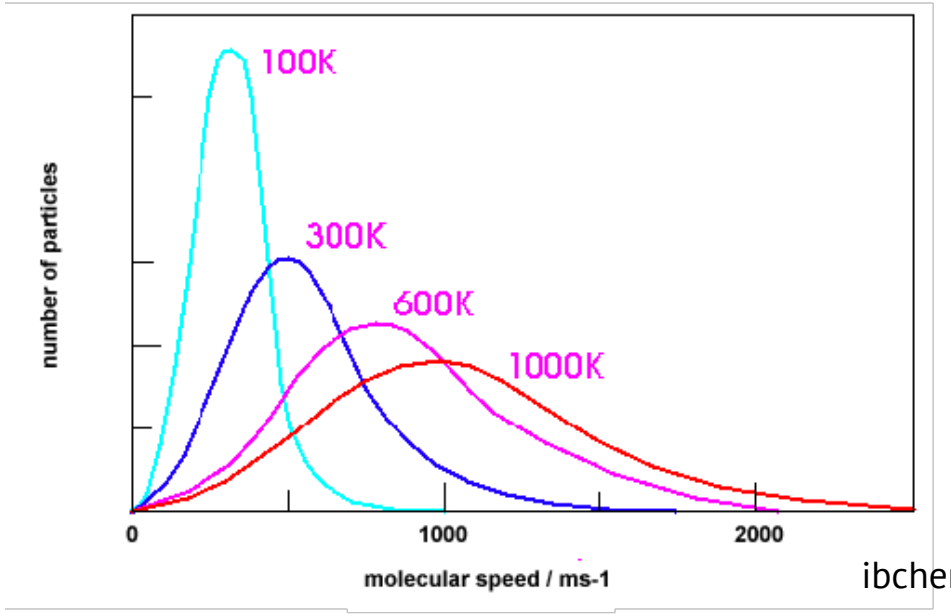



ibchem.com

# Introduction

## Molecular Dynamics (MD)

### III. Ensembles

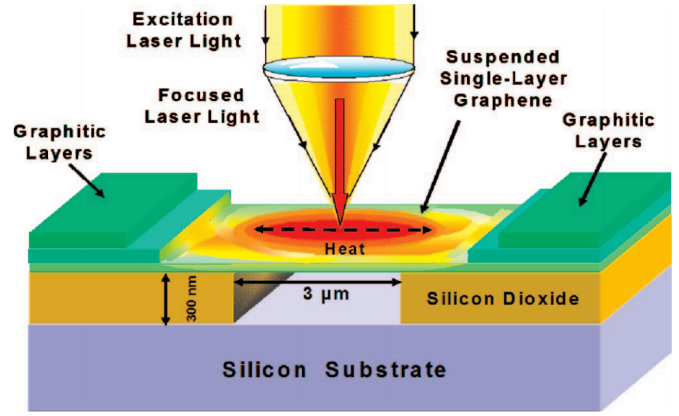
| Thermostat | Description |
|---|---|
| Velocity-rescaling | $v'_{i,\alpha} = \sqrt{T/T(t)}v_{i,\alpha}$ |
| Andersen | Stochastic collision of atoms in heat bath<br>(include velocity-rescaling) |
| Berendsen | Weak coupling between system and heat bath |
| Nosé-Hoover | Extended-Lagrangian approach<br>(artificial coordinates and velocities) |

# Introduction

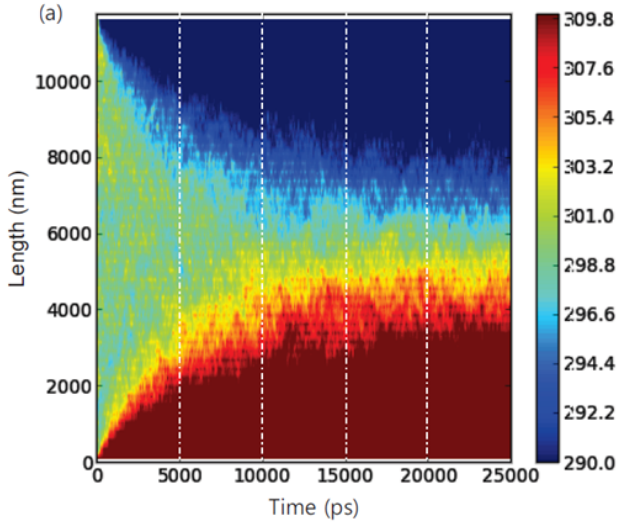
## Lattice Thermal Conductivity Calculation (MD)

### I. NEMD (Direct method)

- Called "*Direct method*"
- Based on Fourier's law, $J = \frac{\kappa}{L\nabla T}$
- Calculate heat flux ($J$) at thermal steady state
  - Heat flux : thermal energy transferred through unit area per unit time
  - Cumulative energy, $E_{cum}(t) = \frac{E_c(t) - E_h(t)}{2}$, $J = \frac{(E_{cum}/dt)}{A}$
- Crystalline, non-crystalline materials, thermal rectifier, defect ...




Nano Lett. **8**, 3, 902 (2008)



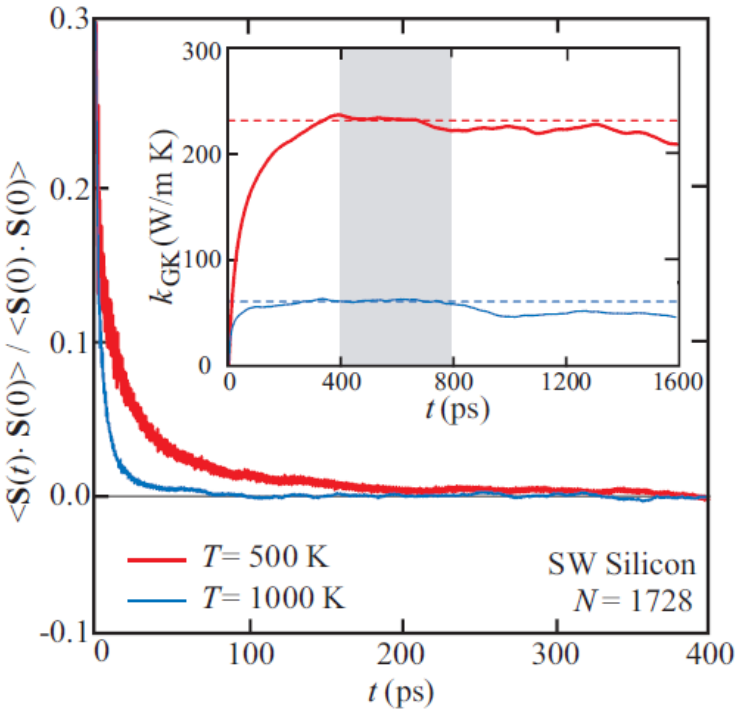

J. Appl. Phys. **114**, 053506 (2013)

# Introduction

## Lattice Thermal Conductivity Calculation (MD)

### II. EMD (Green-Kubo method)

- Based on *Green-Kubo* formula
- Calculate lattice $\kappa$ tensors from the *heat current auto-correlation function* at finite temperature **T**,
- $\kappa_{ii} = \frac{V}{K_B T^2} \int_0^\infty < J_i(t) J_i(0) > dt$
- All directions of lattice $\kappa$ can be obtained by one-shot calculation




*Phys. Rev. B* **81**, 214305 (2010)

# Introduction

## Lattice Thermal Conductivity Calculation (BTE)

Find the phonon distribution function at  out of equilibrium*

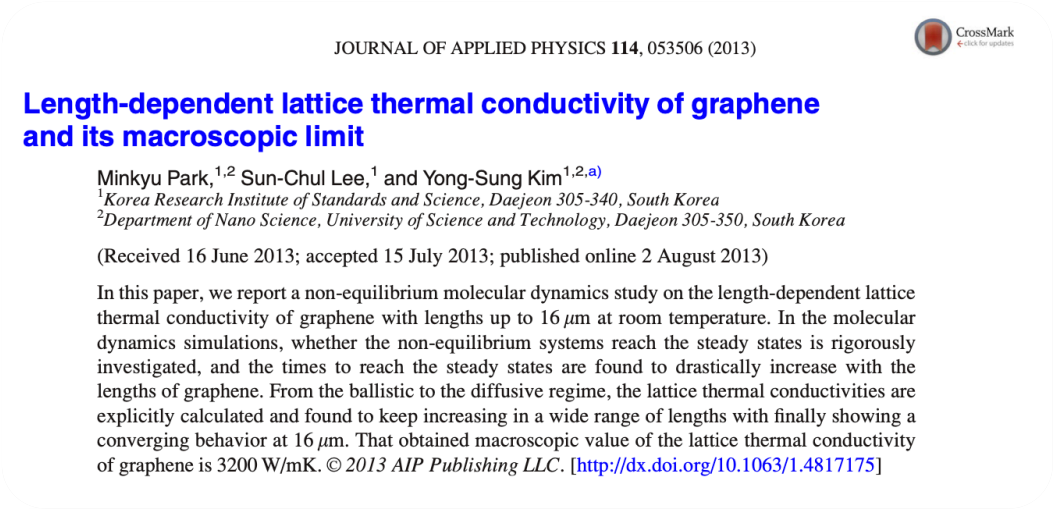
( out of equilibrium ? Temperature gradient, applied bias ... )

- $\kappa = \frac{1}{3}\sum_{\alpha} C_{\alpha} v^2{}_{\alpha} \tau_{\alpha} = \frac{1}{3}\sum_{\alpha} C_{\alpha} v_{\alpha} l_{\alpha}$
- Total heat capacity C, group velocity *v*, relaxation time $\tau$, mean free path of phonon $l$, excitations $\alpha$

  ($\alpha$ : electrical carriers, lattice waves, electromagnetic waves ...)
- Practically,
  - Harmonic properties : Calculated from 2nd order IFC
  - Anharmonic properties : Calculated from 3rd order IFC

# Introduction

## Example (NEMD) : Lattice Thermal Conductivity of Graphene



JOURNAL OF APPLIED PHYSICS **114**, 053506 (2013)

**Length-dependent lattice thermal conductivity of graphene and its macroscopic limit**

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[2]*Department of Nano Science, University of Science and Technology, Daejeon 305-350, South Korea*

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In this paper, we report a non-equilibrium molecular dynamics study on the length-dependent lattice thermal conductivity of graphene with lengths up to 16 $\mu$m at room temperature. In the molecular dynamics simulations, whether the non-equilibrium systems reach the steady states is rigorously investigated, and the times to reach the steady states are found to drastically increase with the lengths of graphene. From the ballistic to the diffusive regime, the lattice thermal conductivities are explicitly calculated and found to keep increasing in a wide range of lengths with finally showing a converging behavior at 16 $\mu$m. That obtained macroscopic value of the lattice thermal conductivity of graphene is 3200 W/mK. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4817175]

Summary

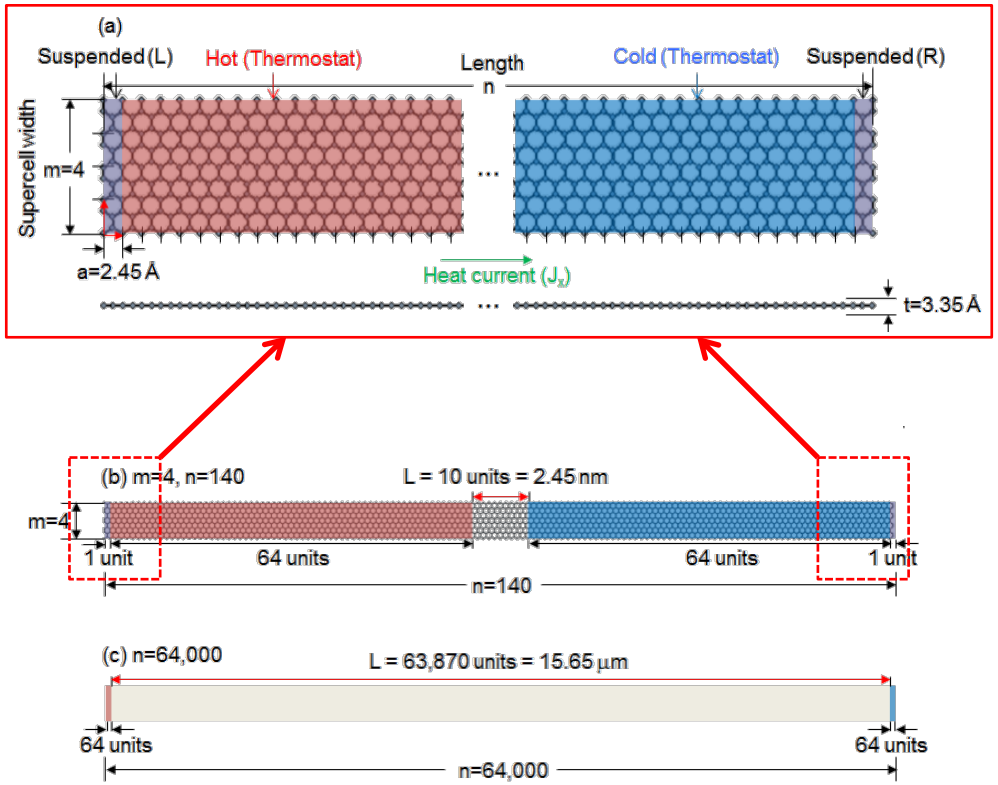
- Length-dependent lattice thermal conductivity of graphene
- NEMD (LAMMPS classical MD code)
- Explicitly calculate from ballistic to diffusive regime
- Macroscopic lattice thermal conductivity of graphene :

  3,200 W/m-K (16 µm) at RT

J. Appl. Phys. **114**, 053506 (2013)

# Introduction

## Example (NEMD) : Lattice Thermal Conductivity of Graphene

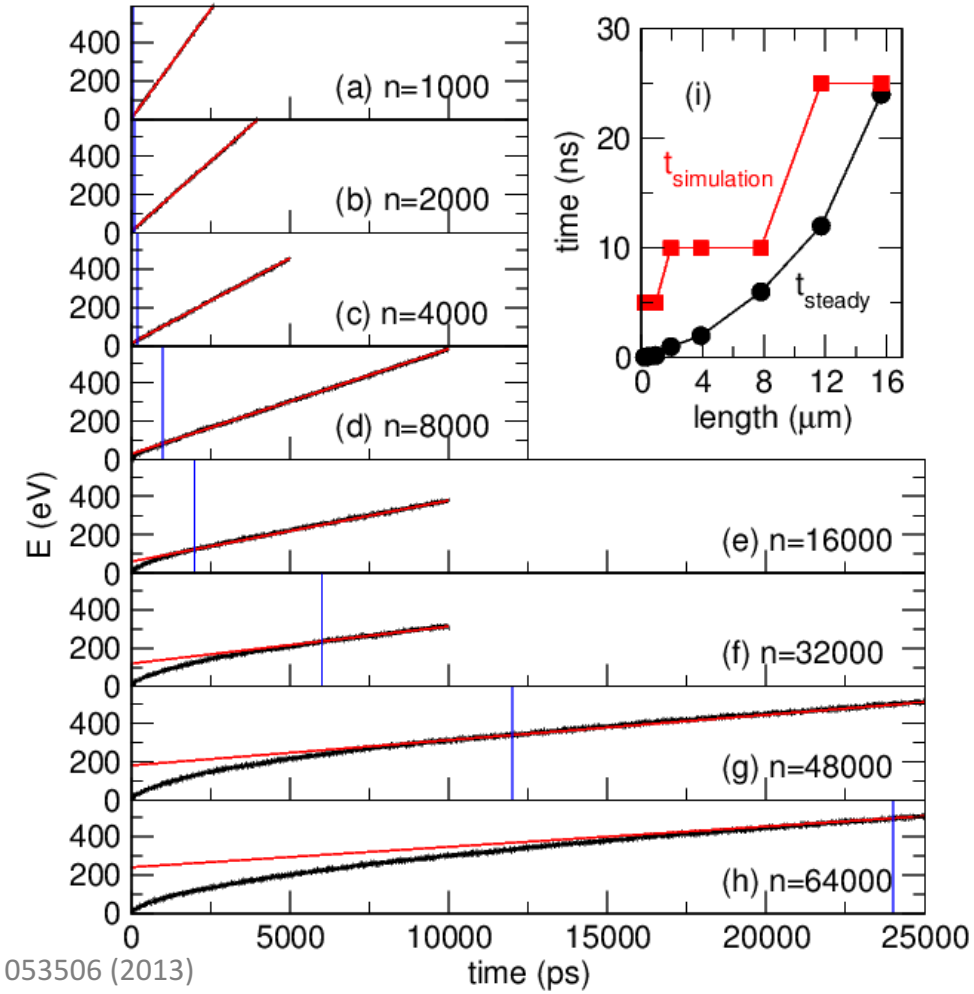



- $T_{HOT}$=330K, $T_{COLD}$=270K (Nosé-Hoover thermostat)
- *W* : 4, 40 unit cells (~ 17 nm)
- *L* : ~ 64,000 unit cells (~15.65 μm)
- Thickness : 3.35 Å
- Number of atoms : ~ 2,560,000
- Optimized Tersoff FF with LAMMPS
- MD time-step : 0.5 fs

J. Appl. Phys. **114**, 053506 (2013)

# Introduction

## Example (NEMD) : Lattice Thermal Conductivity of Graphene




J. Appl. Phys. **114**, 053506 (2013)

**Extract energy**

- $E(t) = \frac{[E_h(t) - Ec(t)]}{2}$
- **Constant heat flux,** $J = \frac{dE/dt}{Wh}$

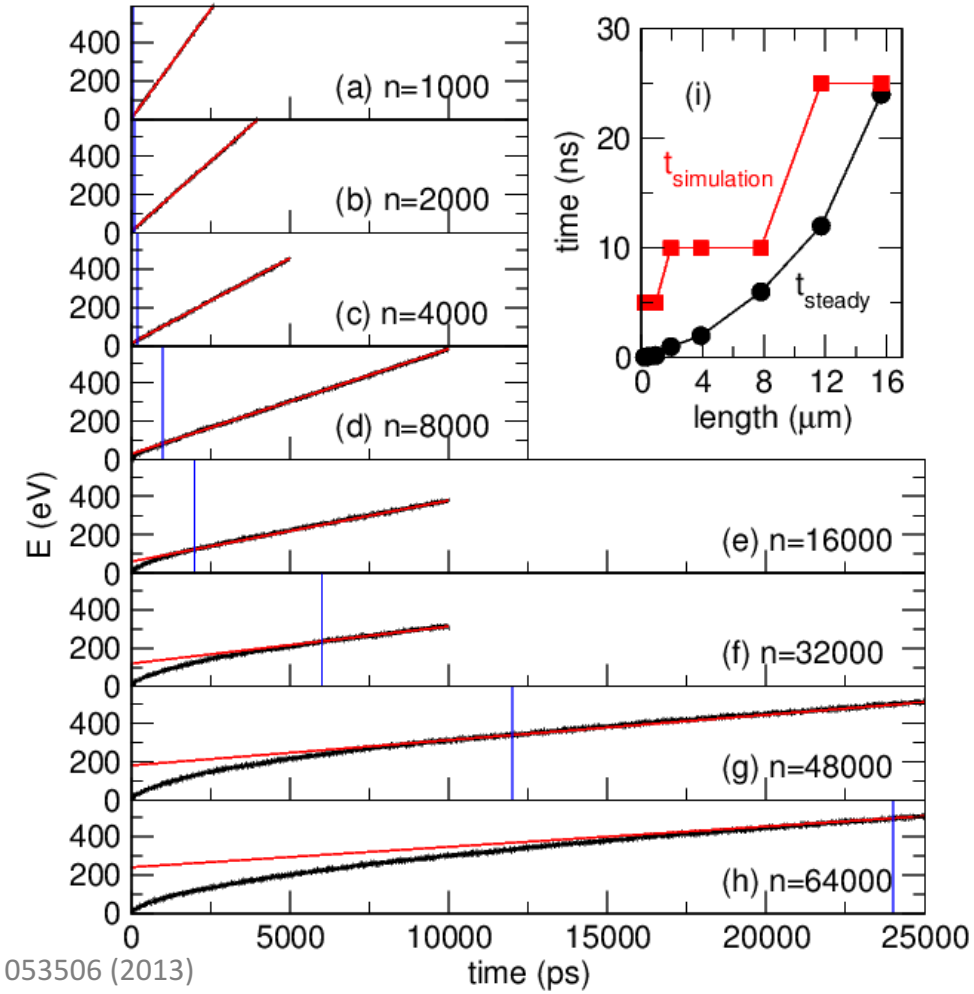
**Cross-section area**

- **Time to reach steady state** : Rapidly increases as a function of the length of graphene

- (i) : Simulation time (■) ,
  time to reach steady state (●)
  ALWAYS, $t_{simulation} > t_{steady}$

# Introduction

## Example (NEMD) : Lattice Thermal Conductivity of Graphene

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Incorporate energy

- $E(t) = \frac{[E_h(t) - Ec(t)]}{2}$
- **Constant heat flux,** $J = \frac{dE/dt}{Wh}$

Cross-section area

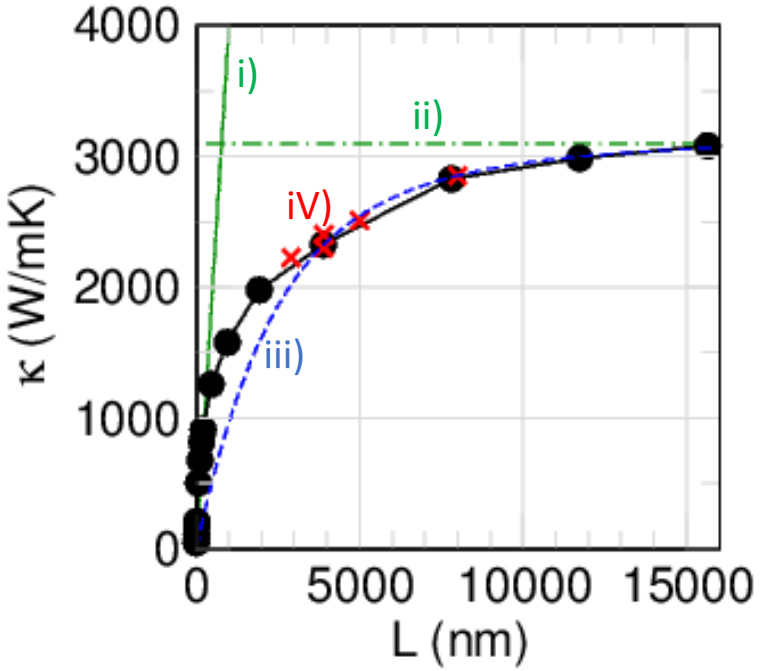
- **Time to reach steady state** : Rapidly increases as a function of the length of graphene

- (i) : Simulation time (■) ,
  time to reach steady state (●)
  ALWAYS, $t_{simulation} > t_{steady}$

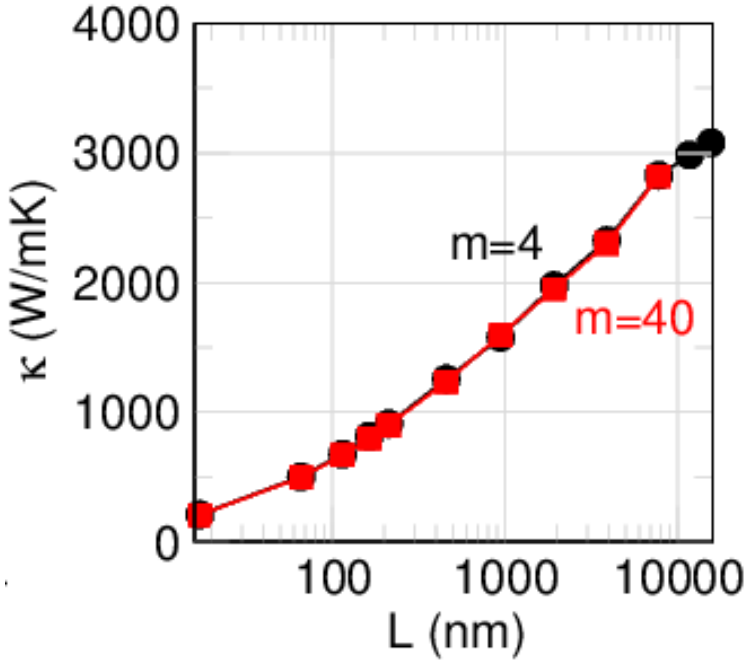
# Introduction

## Example (NEMD) : Lattice Thermal Conductivity of Graphene

- Lattice $\kappa$ of graphene as a function of ***L***




- Comparison lattice $\kappa$ of graphene with ***W*** = 4 and 40




J. Appl. Phys. **114**, 053506 (2013)

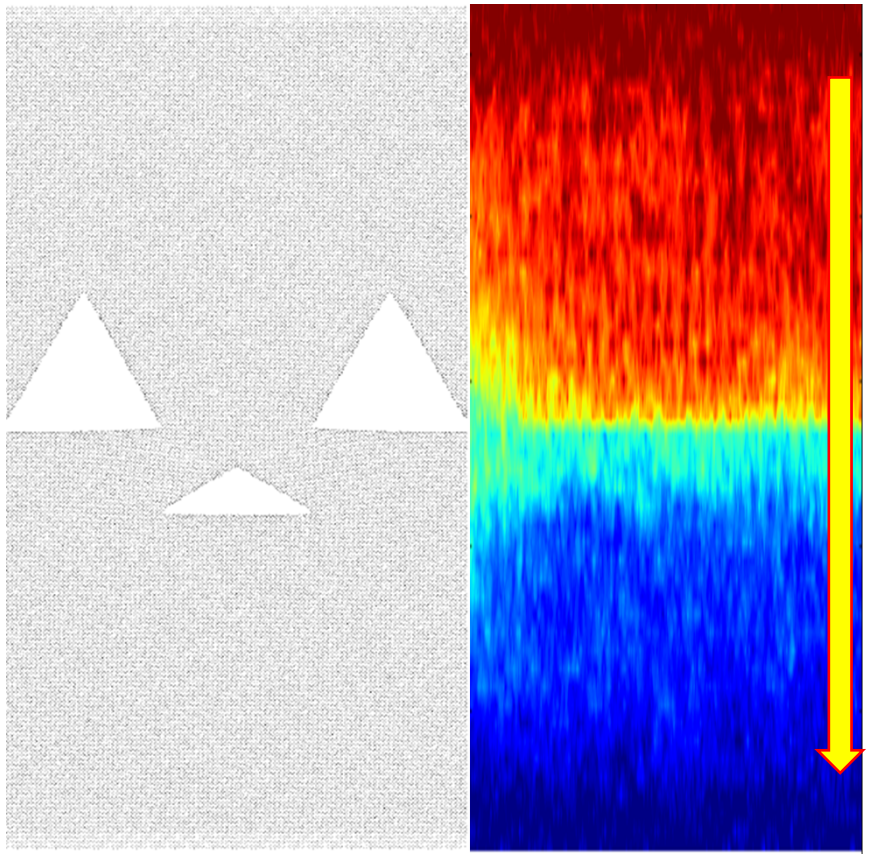
# Introduction

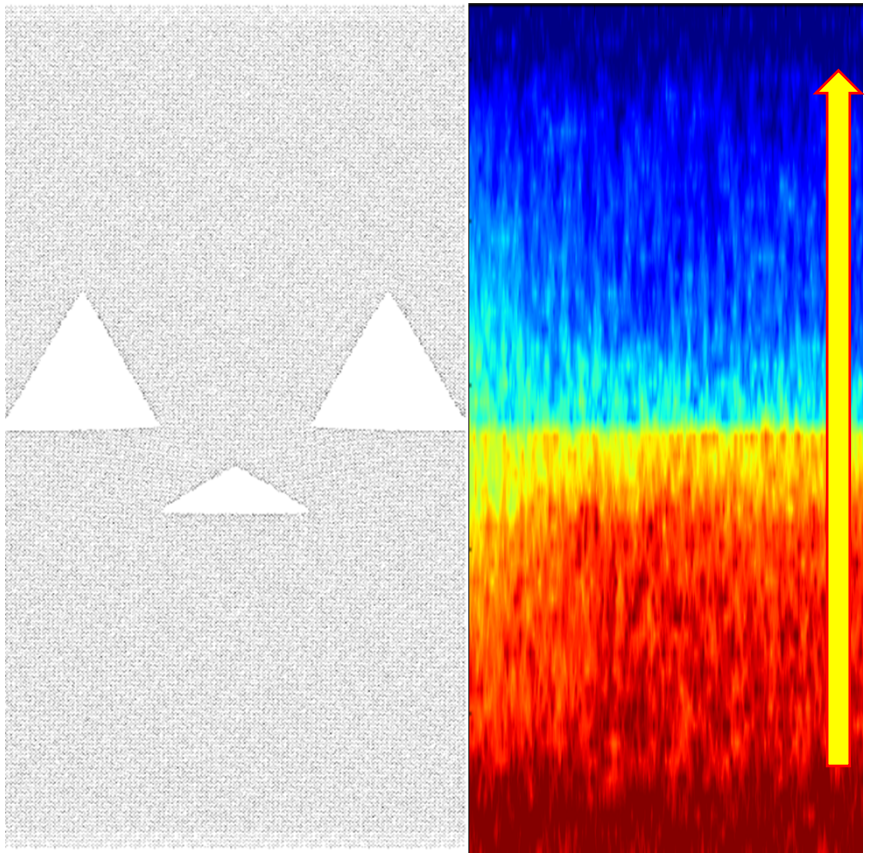
## MD vs. BTE

| Method | | Advantages | Disadvantages |
|---|---|---|---|
| MD | NEMD<br>(Direct method) | * Fast<br>* Calculate various type of structures : Defect, Thermal rectifier, non-crystalline structure ...<br>* Large scale calculation | * Finite-size effect<br>* Need appropriate FF<br>* Relatively low accuracy |
| | EMD<br>(Green-Kubo method) | * Fast<br>* Get thermal conductivity tensor at once<br>* Large scale calculation | * Auto-correlation function converging problem<br>* Need appropriate FF<br>* Relatively low accuracy |
| BTE | | * Accurate and diversity<br>* Easy to handle various thermal properties<br>* (Relatively) Easy to implement scattering mechanism | * High computational cost<br>* Limited size ( ~ few thousand atoms)<br>* Only finite temperature could be handled. |

# Applications

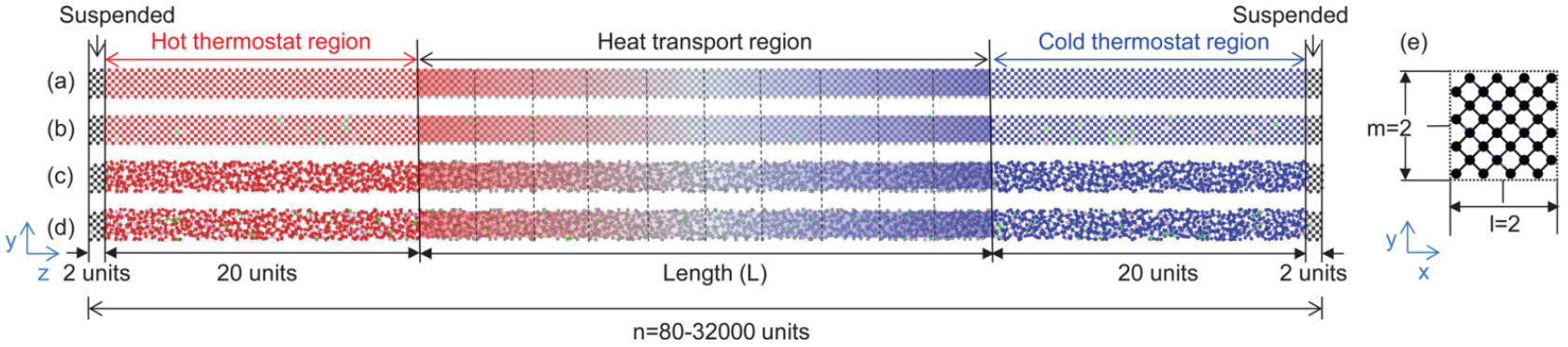
## Applications # 1 (Thermal Rectifier)

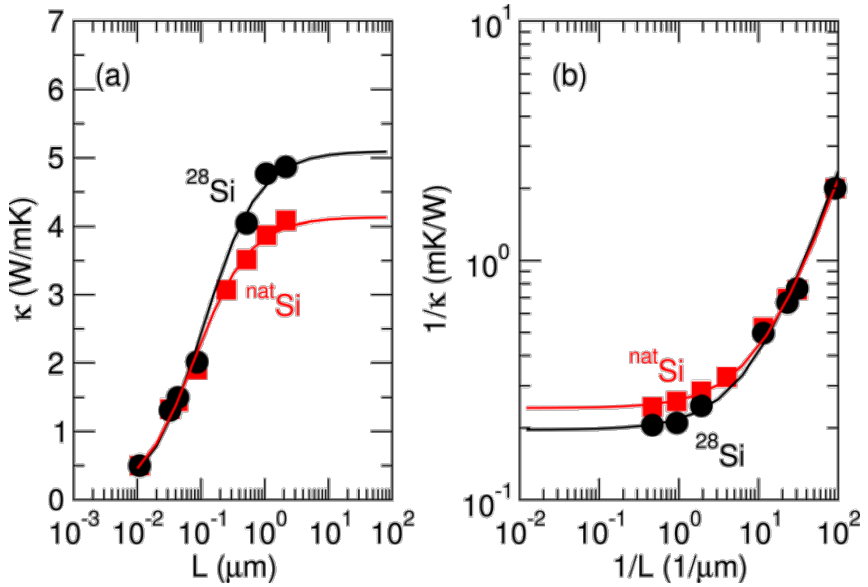




# Applications

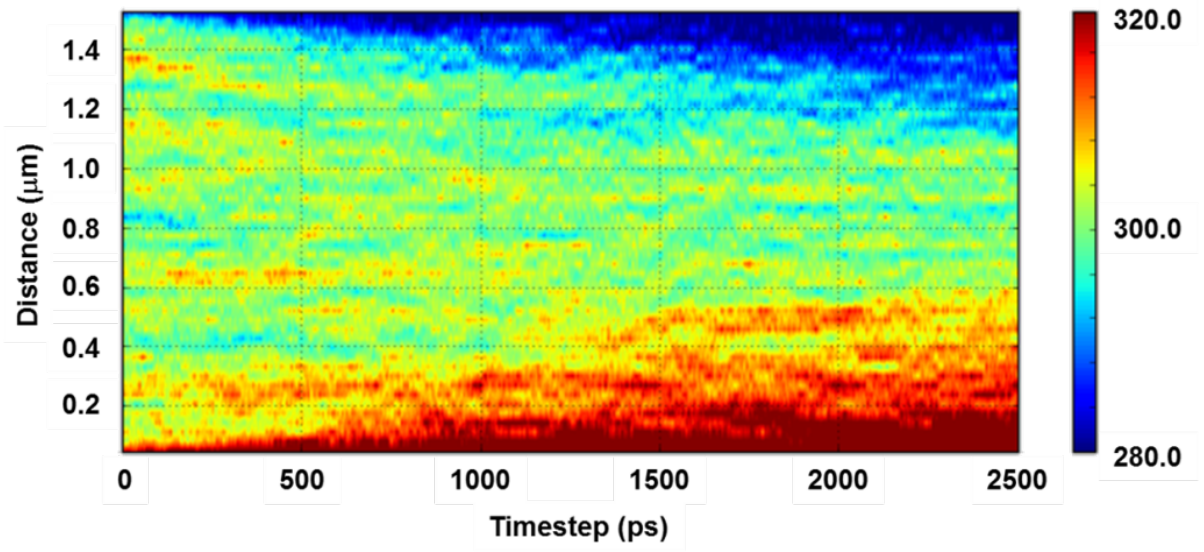
## Applications # 2 (Amorphous Structure and Its Isotope)



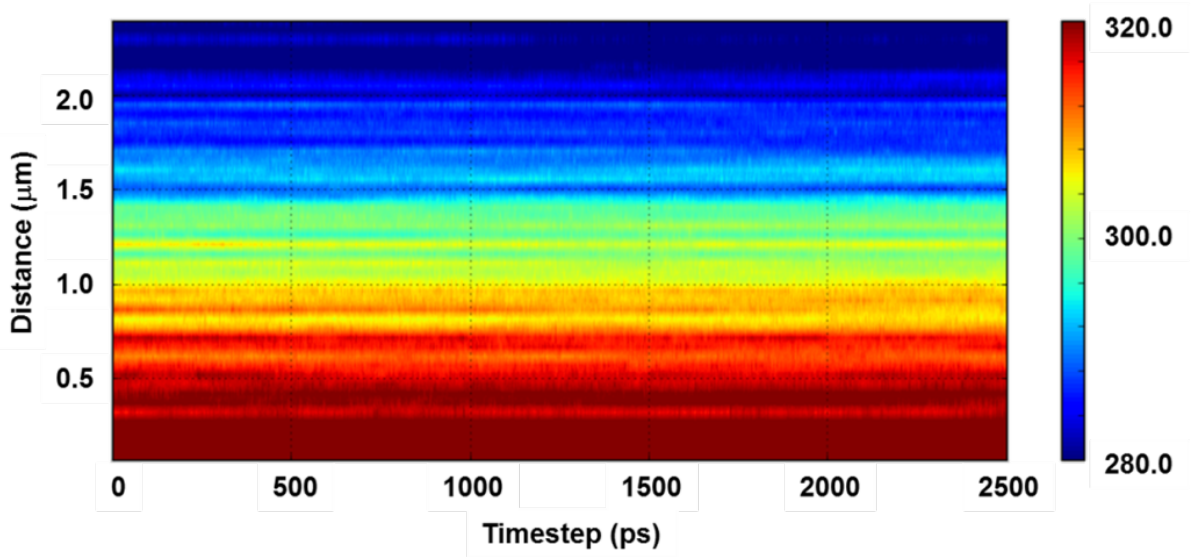



# Applications

## Applications # 3 (Estimations, Higher / Lower $K$)




Expect higher κ



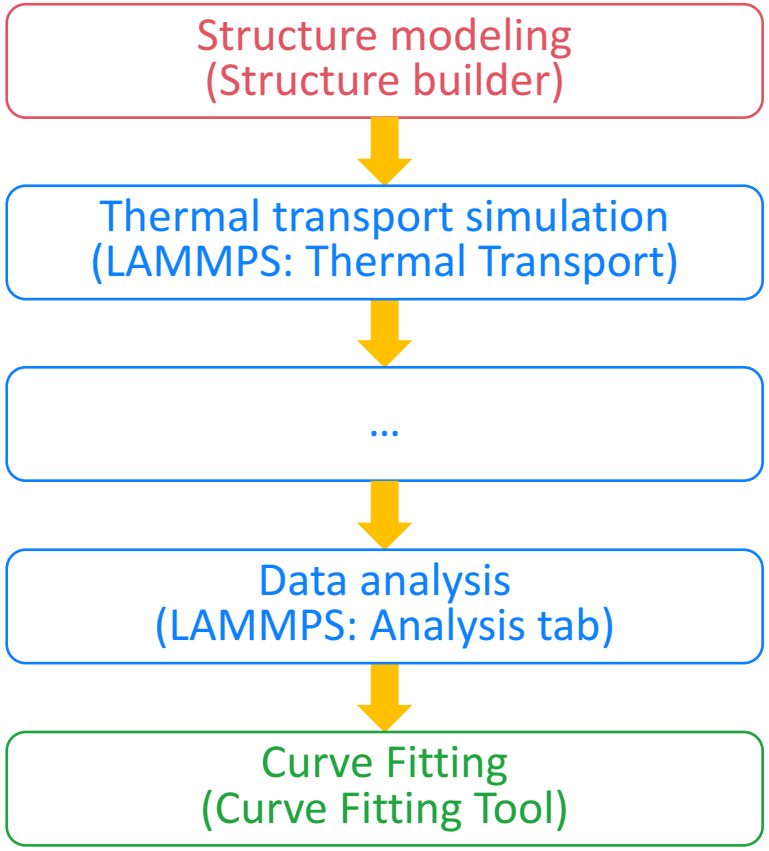

Expect lower κ

# Tutorial Session

# Notice

- Before starting the tutorial, please open your web-browser and enter ‘matsq.com’.
- Materials Square is optimized for Google Chrome, Safari browser. Internet Explorer is not recommended.
- It is good to view the screen and the Materials Square side by side.

# Calculate Lattice Thermal Conductivity




**Modeling (Silicon conventional cell)**

1. Add silicon conventional cell at the 'PRESET'.

**Non-equilibrium Molecular Dynamics Simulation**

1. Add LAMMPS module and click 'Thermal Conductivity' menu.
2. Connect that to the 'Structure Builder' module
3. Set the input script
    1) Transport direction
    2) The size of the supercell
    3) Temperature
    4) Simulation time
    5) Simulation timestep
4. Enter the job name and start job.

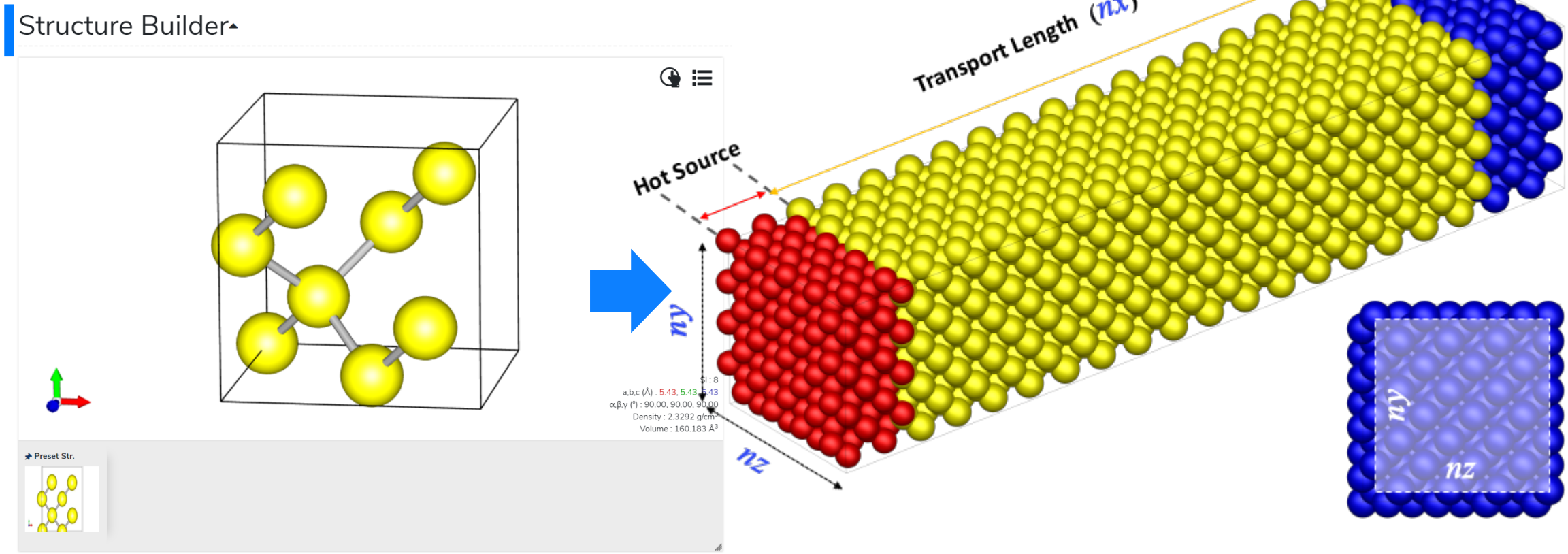
**Length dependent on Lattice Thermal Conductivity**

**Calculations**

1. Repeat Step 2~5 for different lattice
2. Check the result on the 'Analysis' tab

# Modeling

- Modeling conventional cell.



# Input setting

LAMMPS

Cascade

Equation of States

Thermal Conductivity

Custom

1. Transport direction
2. The size of the supercell
3. Temperature
4. Simulation time
5. Simulation timestep

Transport direction : x y z

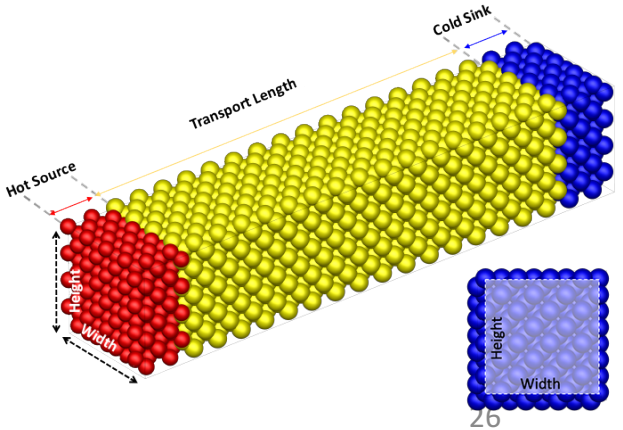
Supercell : 100 2 2

4544 atoms

Temperature (K) : 300

Time (ps) : 500

Timestep (fs) : 0.5



# Notice

- Now your thermal transport simulation was started.
- The calculation will be finished around 10 minutes.
- The tutorial will resume after the job finished.

# Analysis

## LAMMPS (Thermal Conductivity)

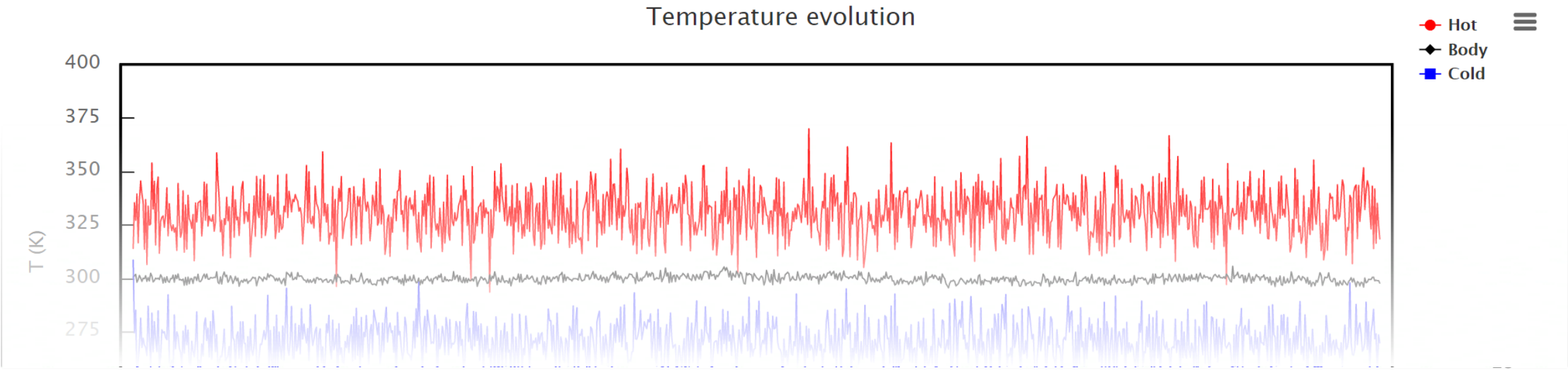
This job has been finished normally (id : 32422)

Simulation | Analysis

**Thermal Conductivity (W/m-K) :** 84.301

**Length (Å) :** 2943.548

**Cross section (Å$^2$) :** 117.979



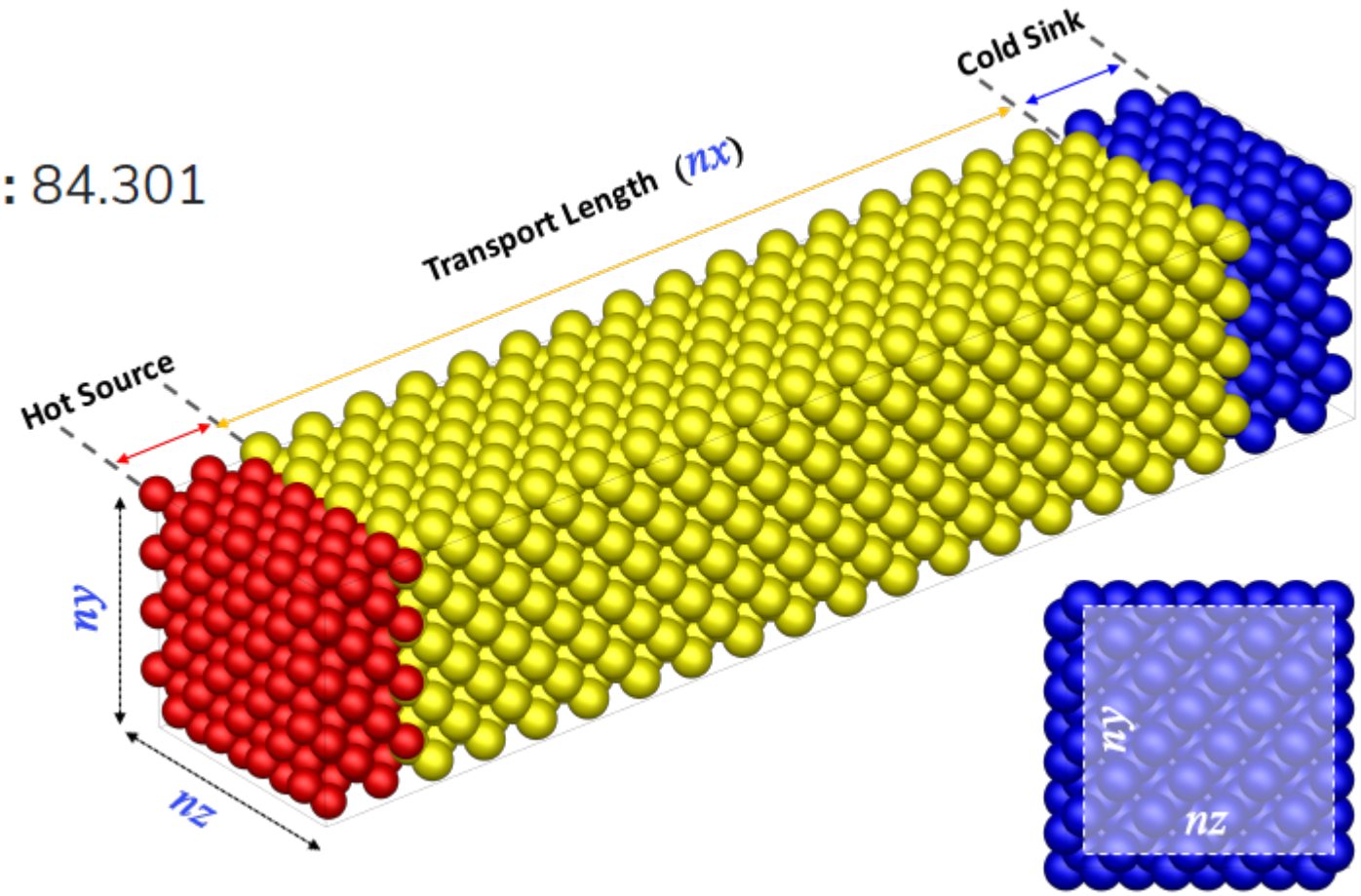
# Analysis

- Results

**Thermal Conductivity (W/m-K) :** 84.301

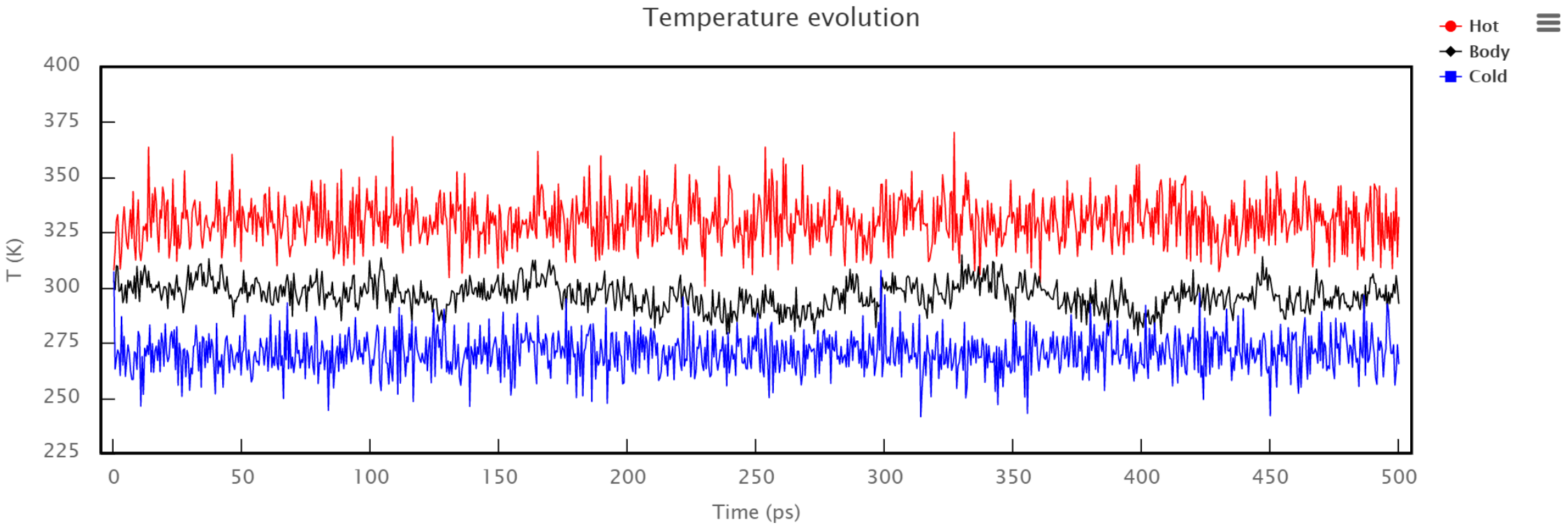
**Length (Å) :** 2943.548

**Cross section (Å$^2$) :** 117.979



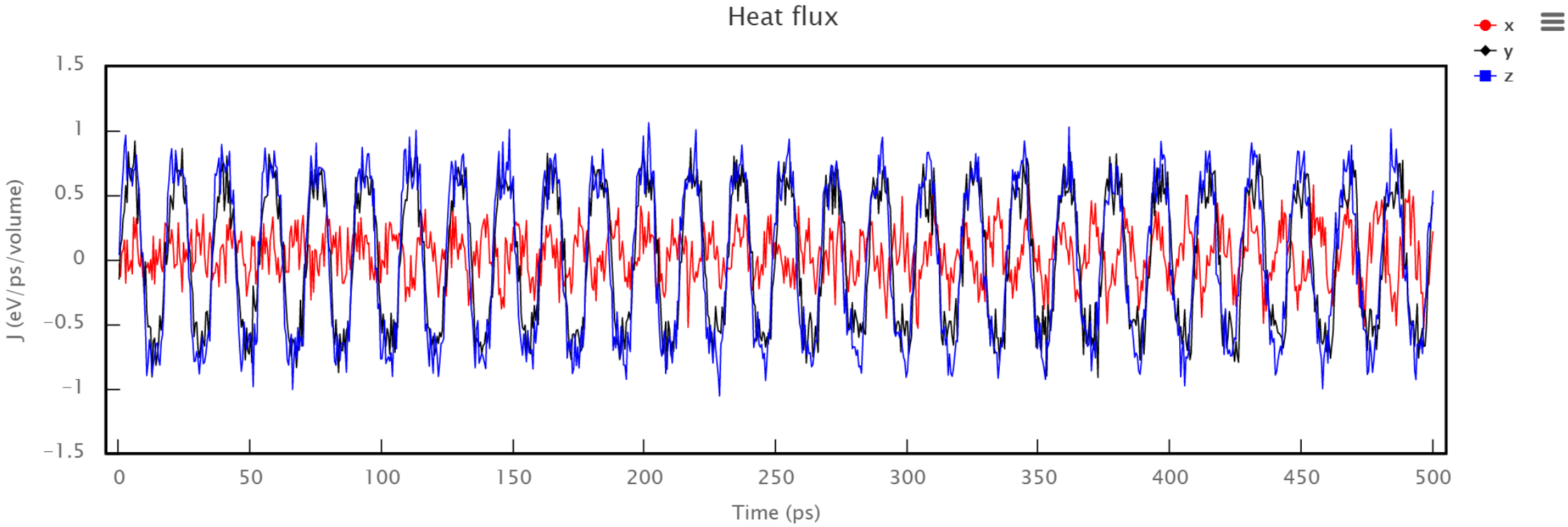
# Analysis

- Temperature evolution



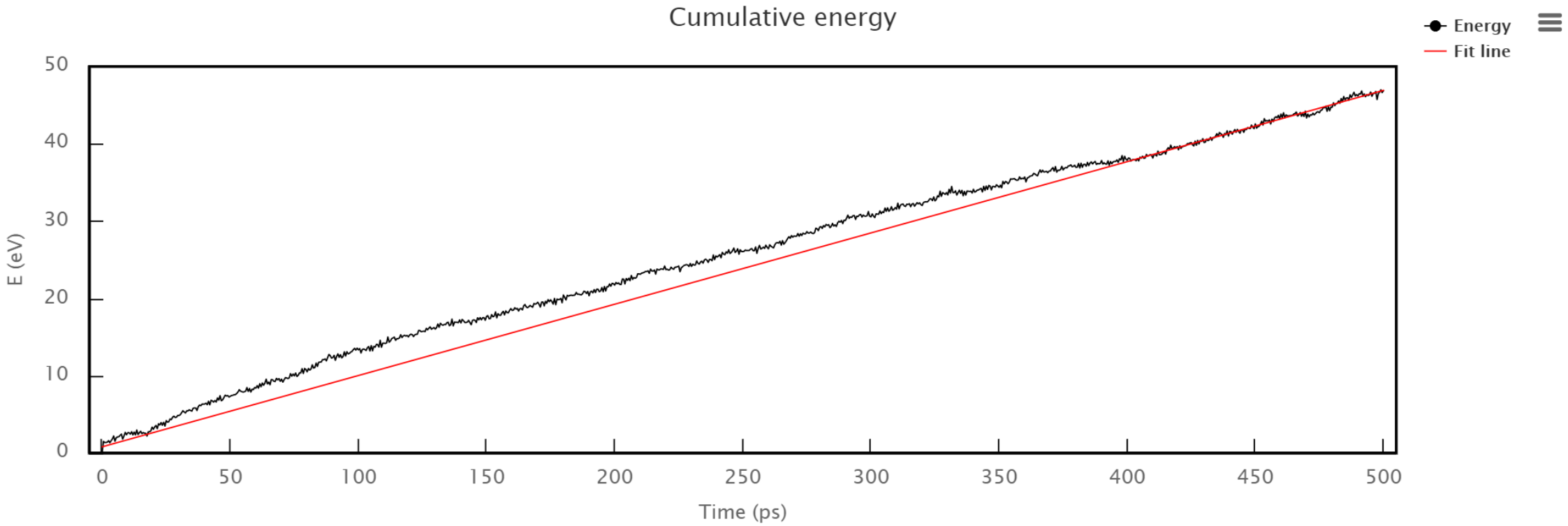
# Analysis

- Heat flux



# Analysis

- Cumulative energy



# Curve Fitting Tool

## Curve Fitting Tools

Type of Fitting: Custom

# Coeffs.: 2

Equation: a*x/(b+x)

Data

| | A | B |
|---|---|---|
| 1 | 49.9643 | 22.67 |
| 2 | 77.1188 | 35.68 |
| 3 | 131.4278 | 55.46 |
| 4 | 294.3548 | 84.30 |
| 5 | 565.8998 | 139.80 |
| 6 | | |

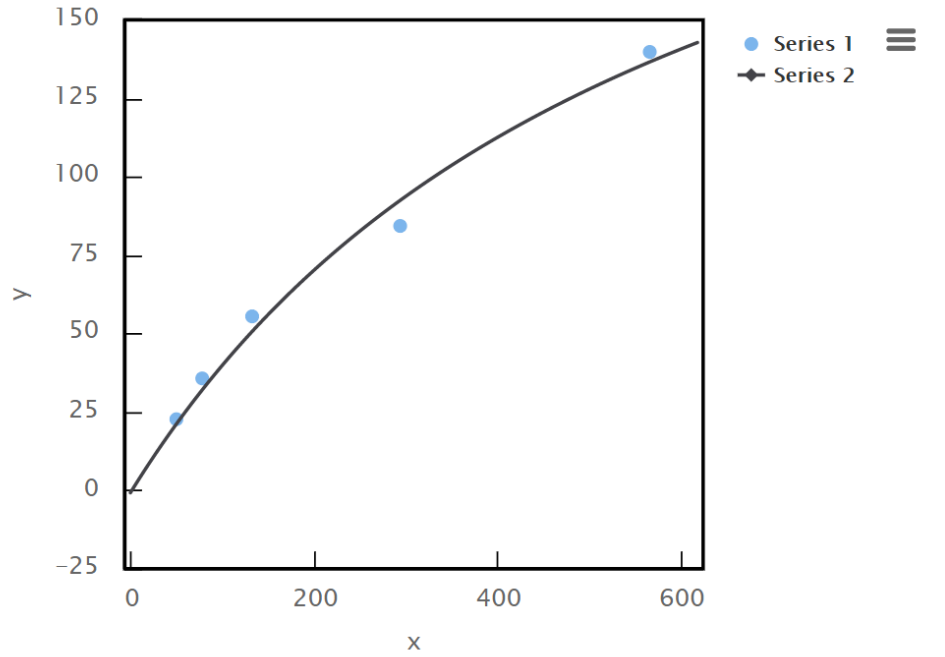
Fit

Result

y = a*x/(b+x)
a = 280.62329, b = 595.48508,

Graph

Hold :

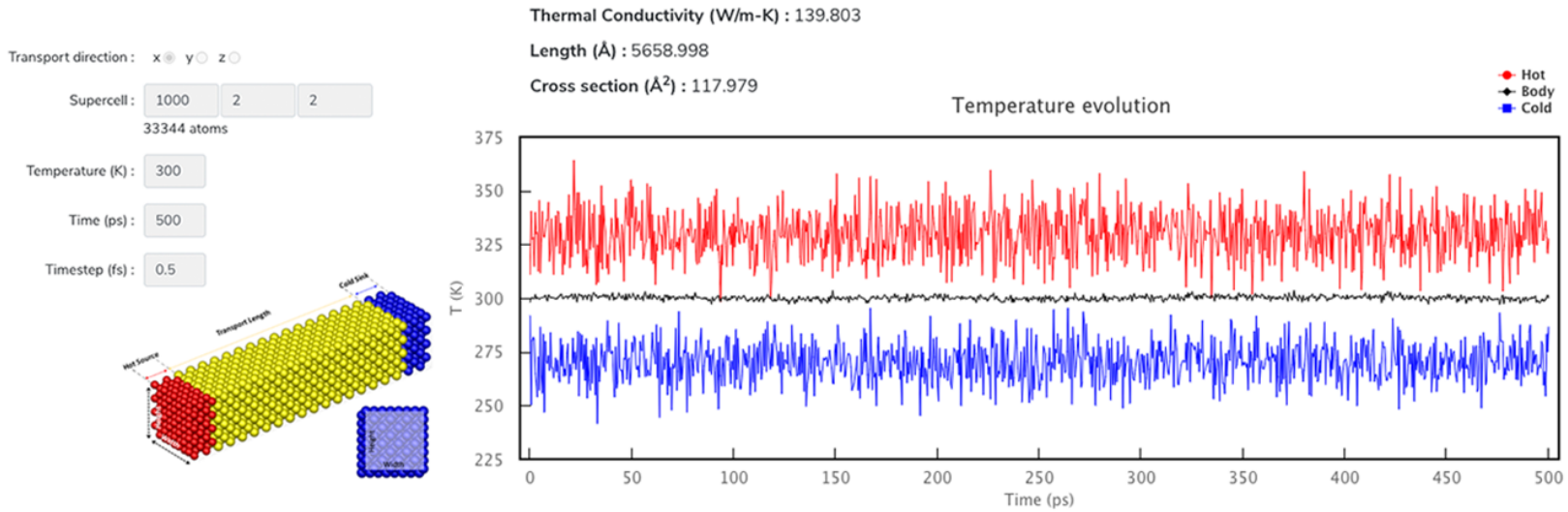


# Si bulk lattice thermal conductivity

TABLE IV. Comparison of the calculated diffusive thermal conductivities of crystalline and amorphous $^{28}$Si and $^{nat}$Si in the NEMD and BTE approaches. The experimental values and the system lengths ($L$) in the calculations are also listed. The $\kappa$ and $\kappa_0$ are in unit of W/m K, and the $L$ is in $\mu$m. The numbers in parentheses are the thermal conductivity enhancement factors by the isotope enrichment.

| | NEMD | | BTE | | Expt. |
|---|---|---|---|---|---|
| System | $\kappa$ | $L$ | $\kappa_0$ | $L$ | $\kappa_0$ |
| Cryst. $^{28}$Si | 205 | 17 | 256 (+28%) | $\infty$ | 237[6,7] (+58%), 160[8,9] (+7%) |
| Cryst. $^{nat}$Si | 156 | 17 | 199 | $\infty$ | 150[6–9,38] |
| Amorph. $^{28}$Si | 4.9 | 2 | 5.1 (+24%) | $\infty$ | 1.2–6.0[43–47] |
| Amorph. $^{nat}$Si | 4.1 | 2 | 4.1 | $\infty$ | … |

# The 2nd Follow Me Contest

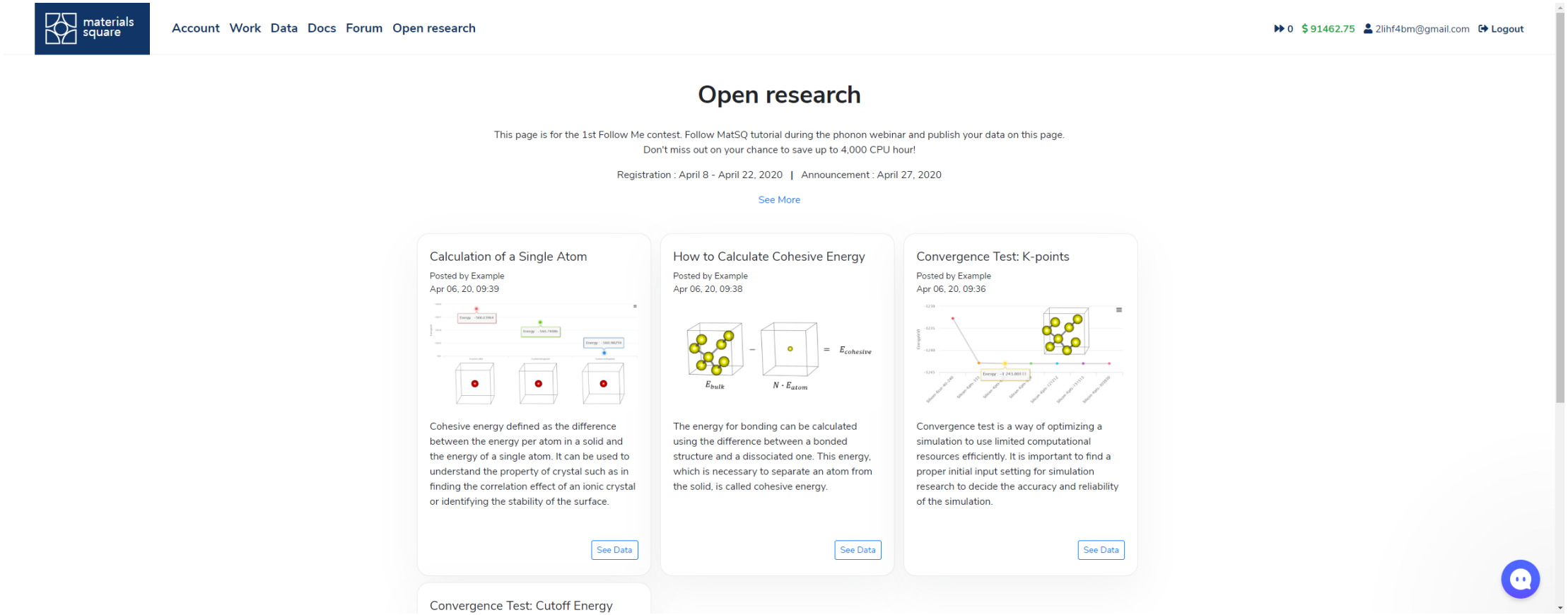

**1st Prize**

**$500**

**2nd – $200**

**3rd – $100**

# Open Research

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