Probing interfacial heat and mass transfer at the molecular scale

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1. Steady state evaporation of droplet using nonequilibrium MD
2. Thermal and electronic transport in functionalized graphene

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Outline

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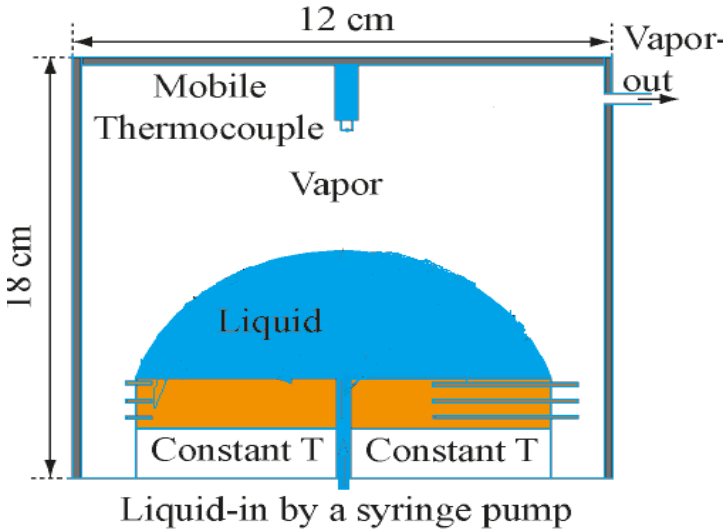
- **Introduction**
- **Two approaches to achieve steady state evaporation**
- **Results**

Introduction

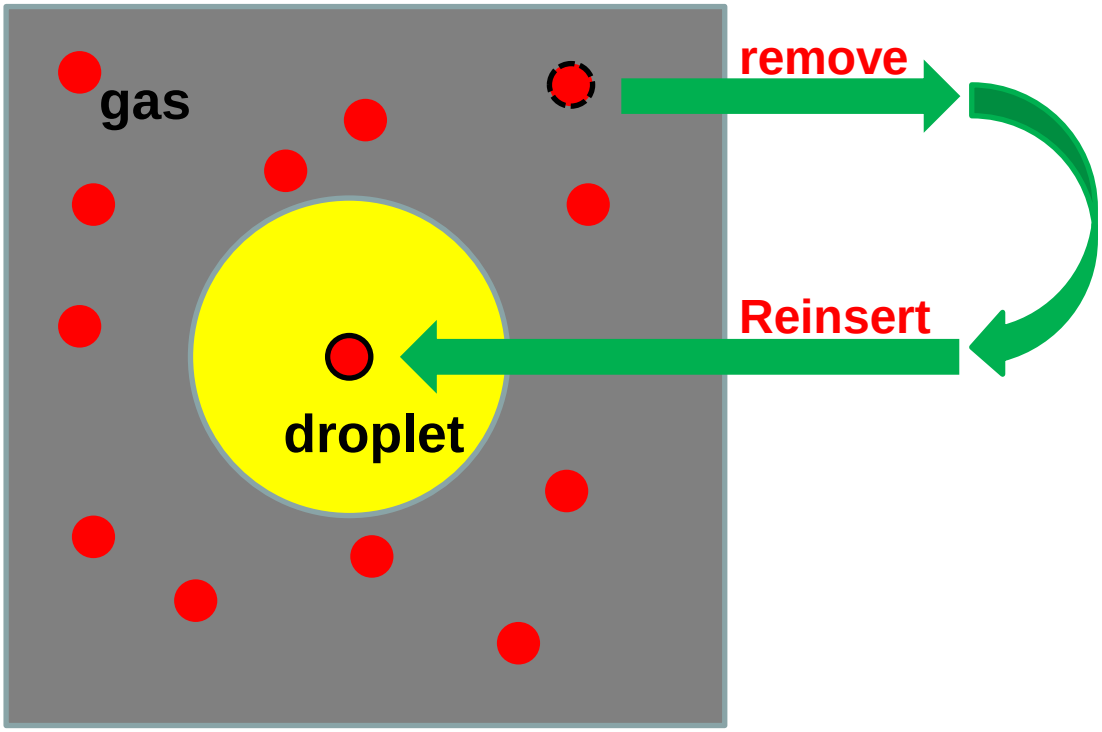
- **Investigate droplet evaporation under extreme conditions**
  - e.g. exteme temperature or pressure gradients, droplet shrinks very quickly , difficult to measure mass-transfer/heat-transfer. Bad statistics

- **Steady state evaporation**
  - constant radius c
  - constant mass flux



H.Ghasemi and C.A.Ward, J.Phys.Chem.C (2011),115,21311

Idea of Molecule Insertion



Two Kinds of Insertion Approaches

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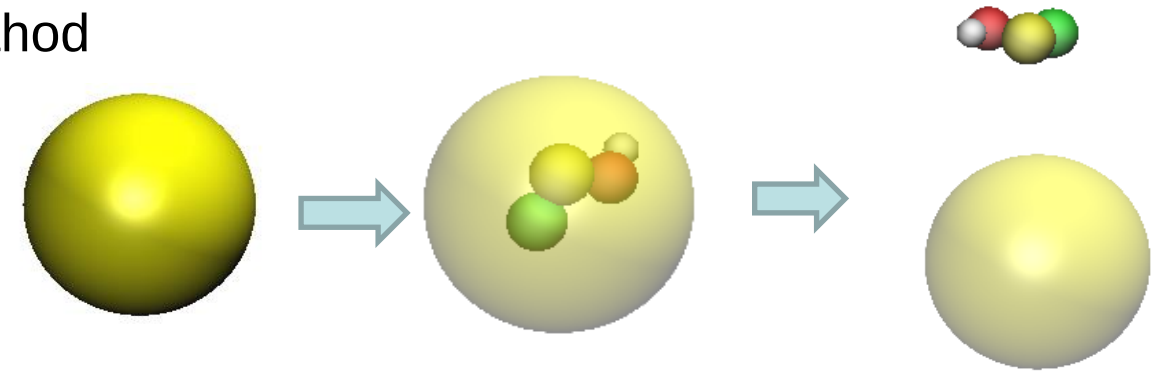
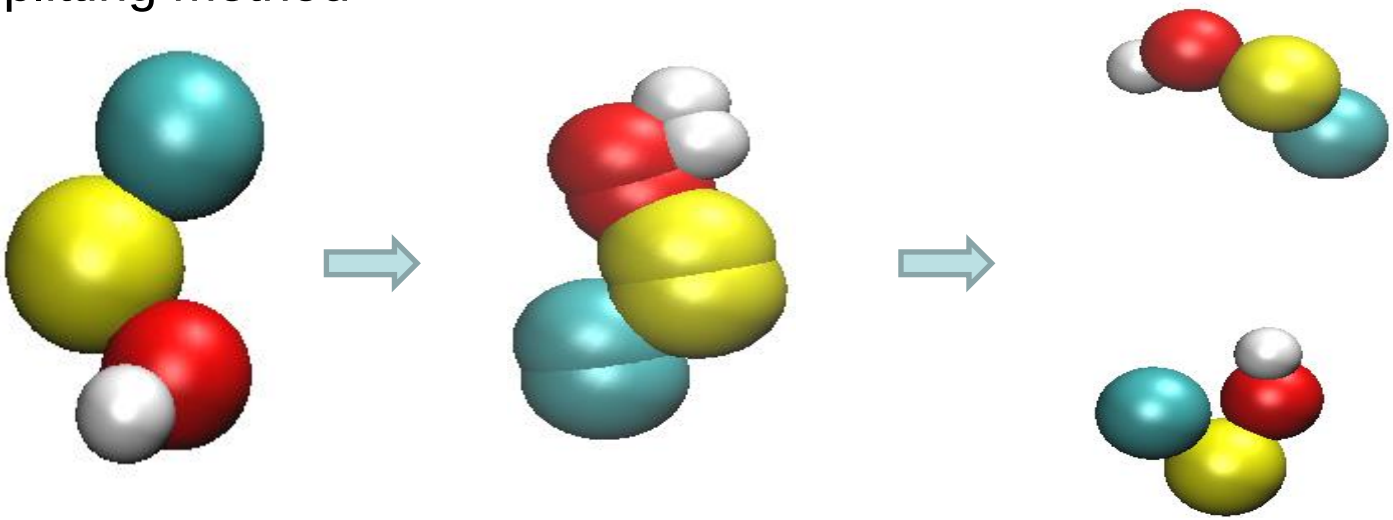
- Bubble method



- Splitting method



Bubble Method : preprocessing

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- **Simulations based on YASP, homemade MD code**
- **Modification** :

a: **Cluster analysis**

1. calculate the droplet size { evaporation rate; insertion frequency }

2. calculate the center of mass (COM) of the droplet

b: **Constraint method**

to fix the position of bubble :

harmonic potential: $\frac{1}{2}k(r-r_0)^2$

c: **Local thermostat**

Core area: spherical area around the COM (radius = 2 nm)

Shell area : the rest of the droplet and gas phase

Bubble Method : insertion process

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1. Select the farthest molecule (referring to COM)

2. Move the COM of the molecule to the center of the bubble

3. Switch on the Gaussian form potential for the nonbonded interactions between bubble and the inserted molecule

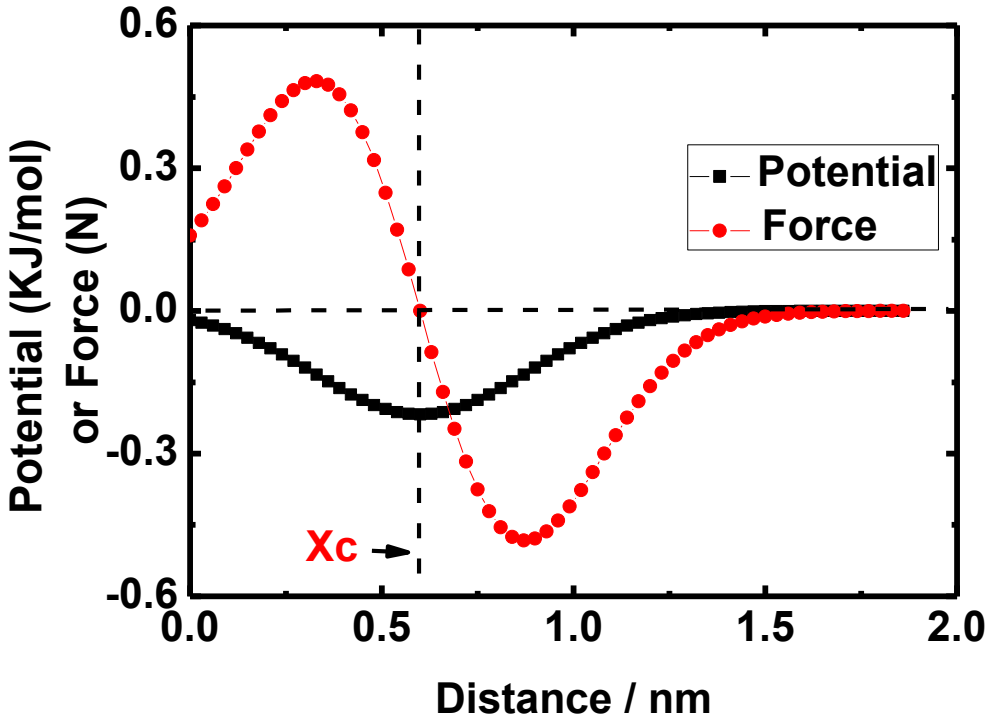
4. After a certain number of time steps, switch off the Gaussian form potential and turn on the normal LJ 12-6 potential

Bubble Method : soft potential

Gaussian function

$$y = y_0 + Ae^{\frac{-(x-x_c)^2}{2w^2}}$$

A : amplitude
X_c: center
W: width
Y_0: offset



Testing System

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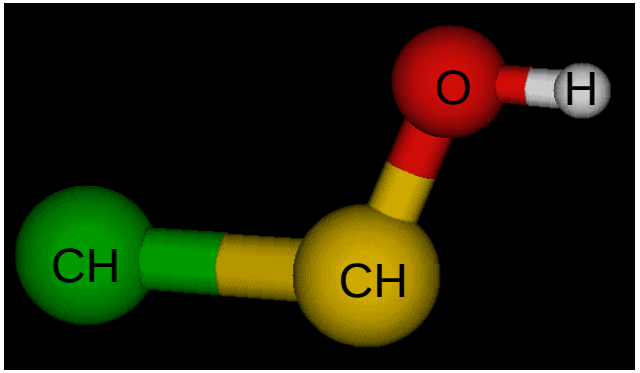
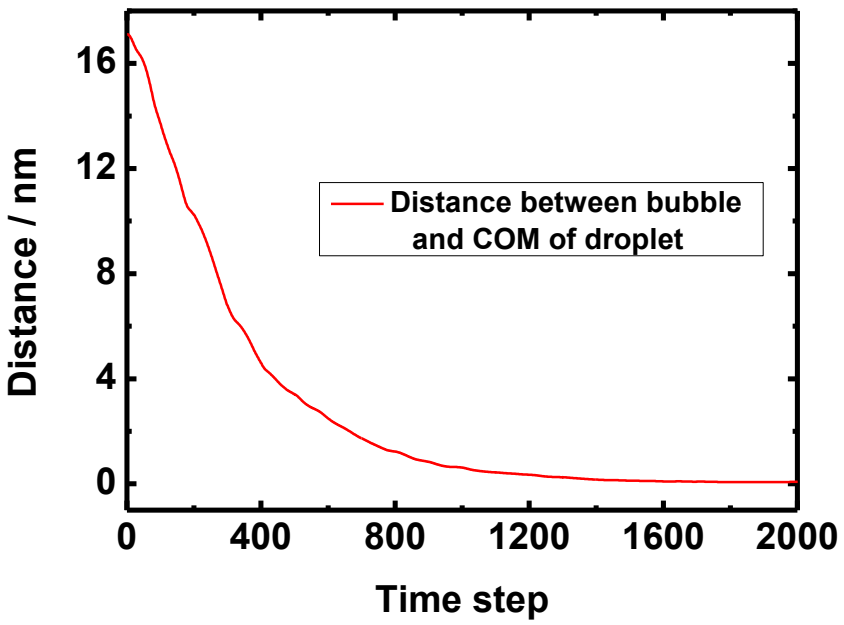
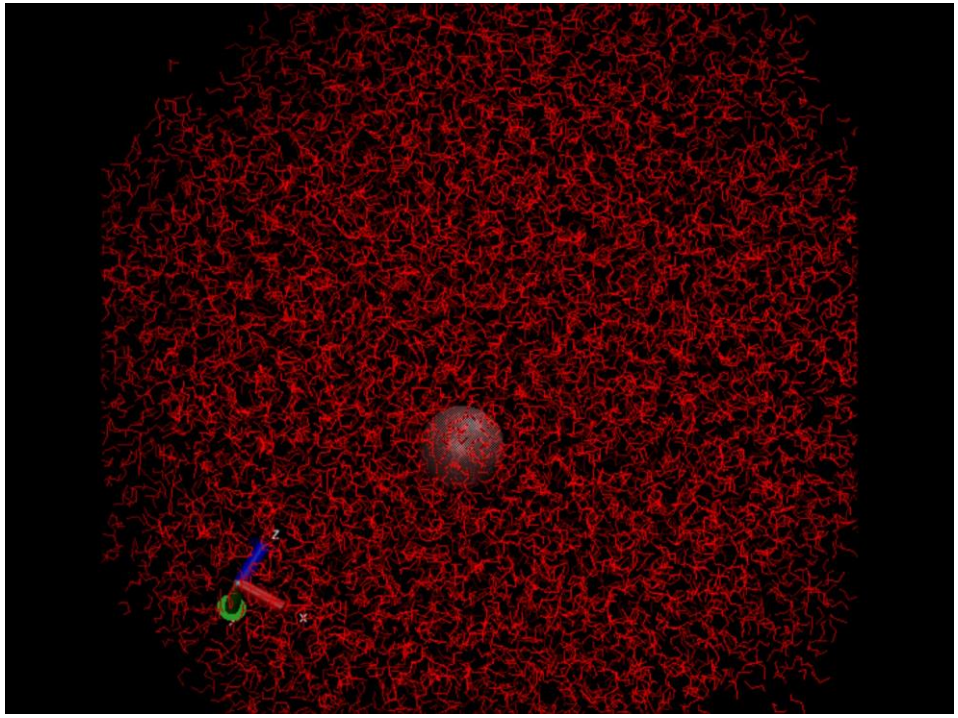
- **System: ethanol**
- **Size: 8192 molecules**
- **Temperature : 300 K**
- **Simulated in NVT ensemble**



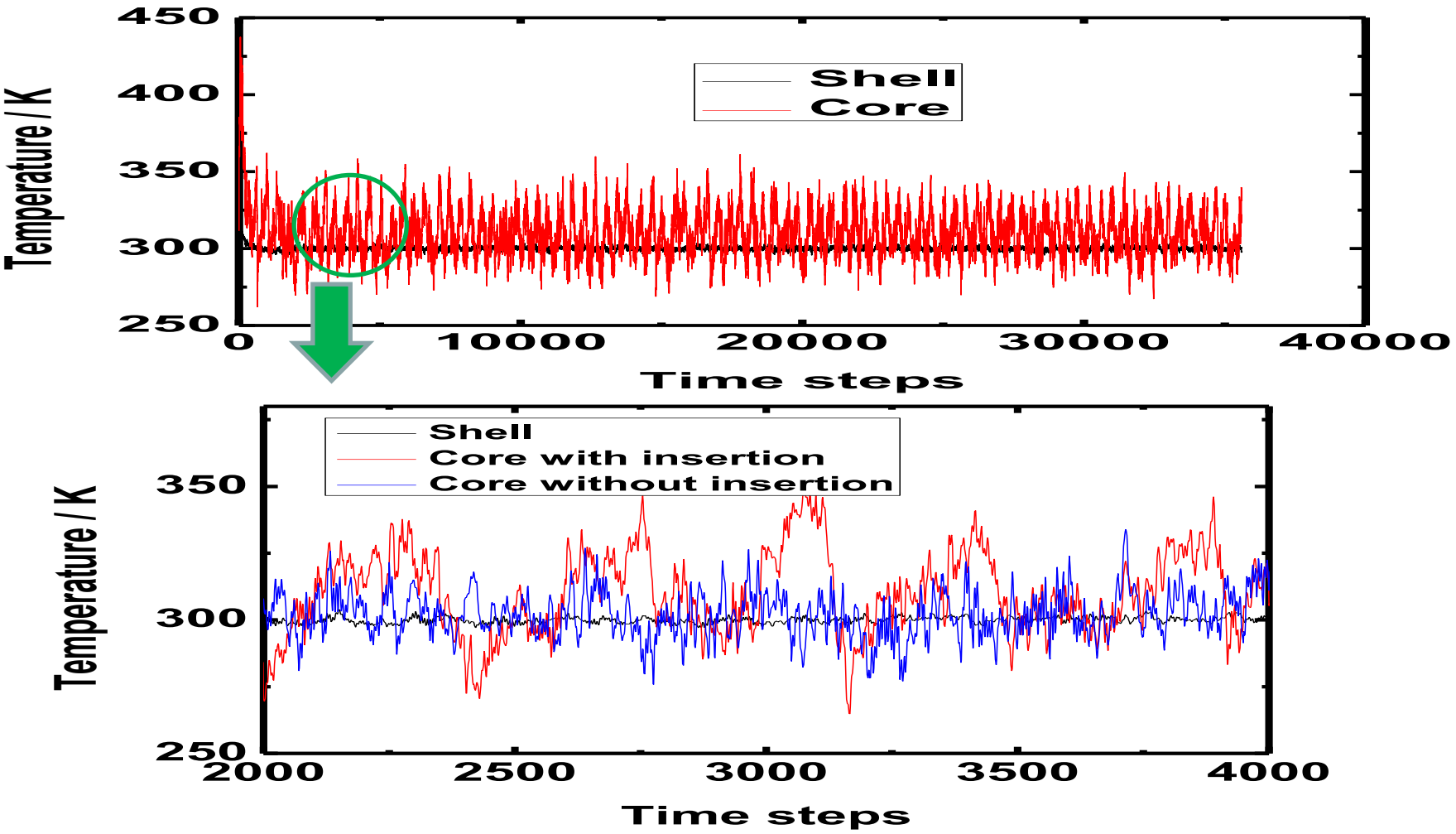
$$U_{ij}^{nonbond} = U_{ij}^{LJ} + U_{ij}^{C} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\varepsilon_0}\left[\frac{1}{r_{ij}} + \frac{r_{ij}}{r_c^2} - \frac{2}{r_c}\right]$$

Bubble Method : Insertion process

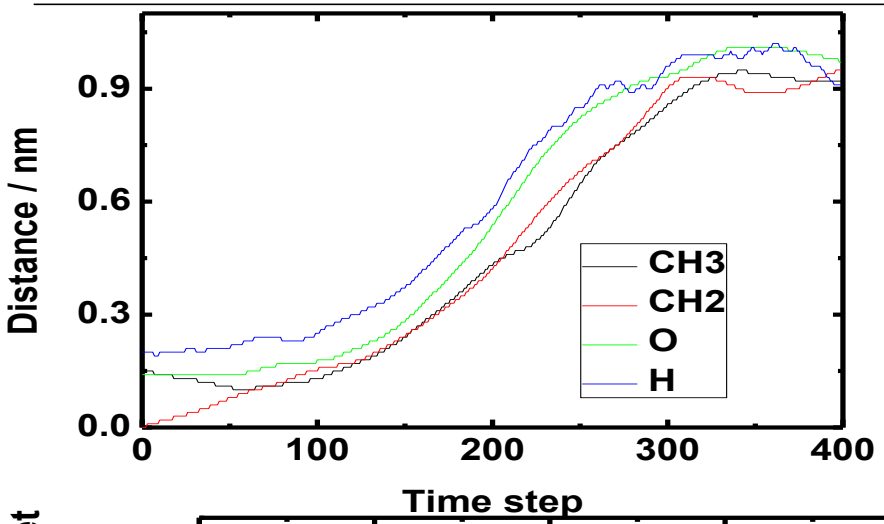


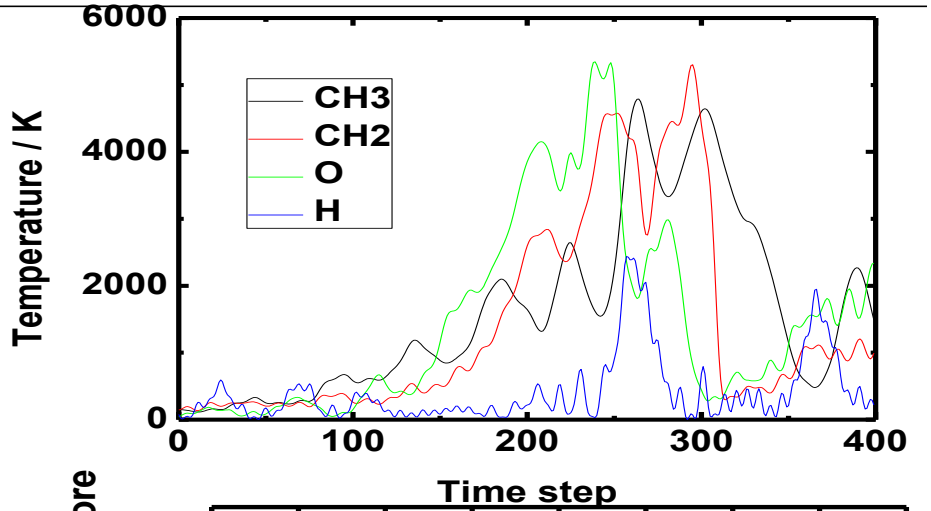


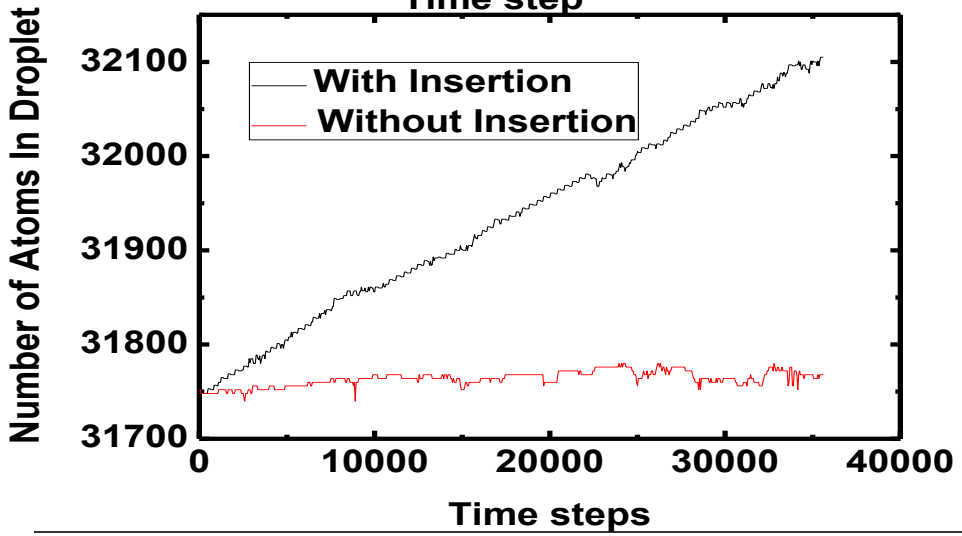
Bubble Method : Temperature

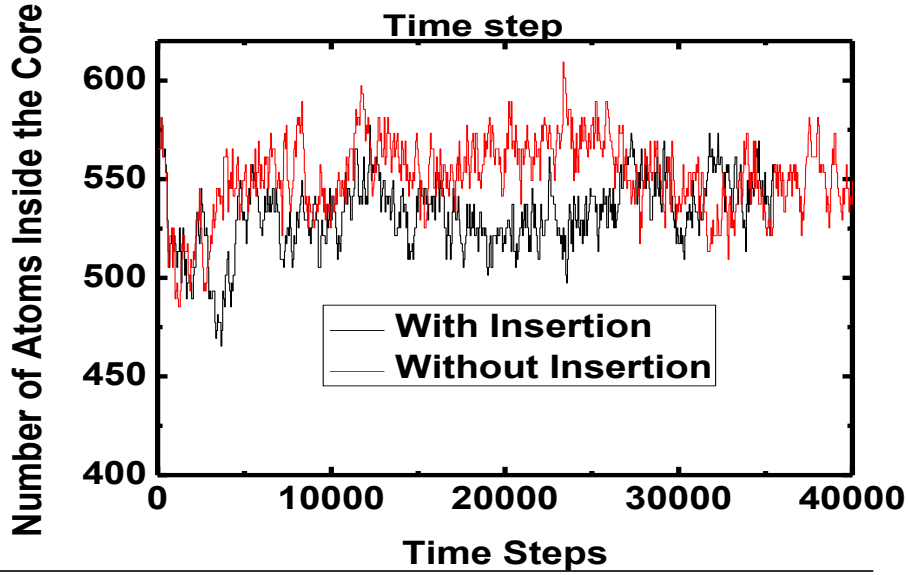


Bubble Method

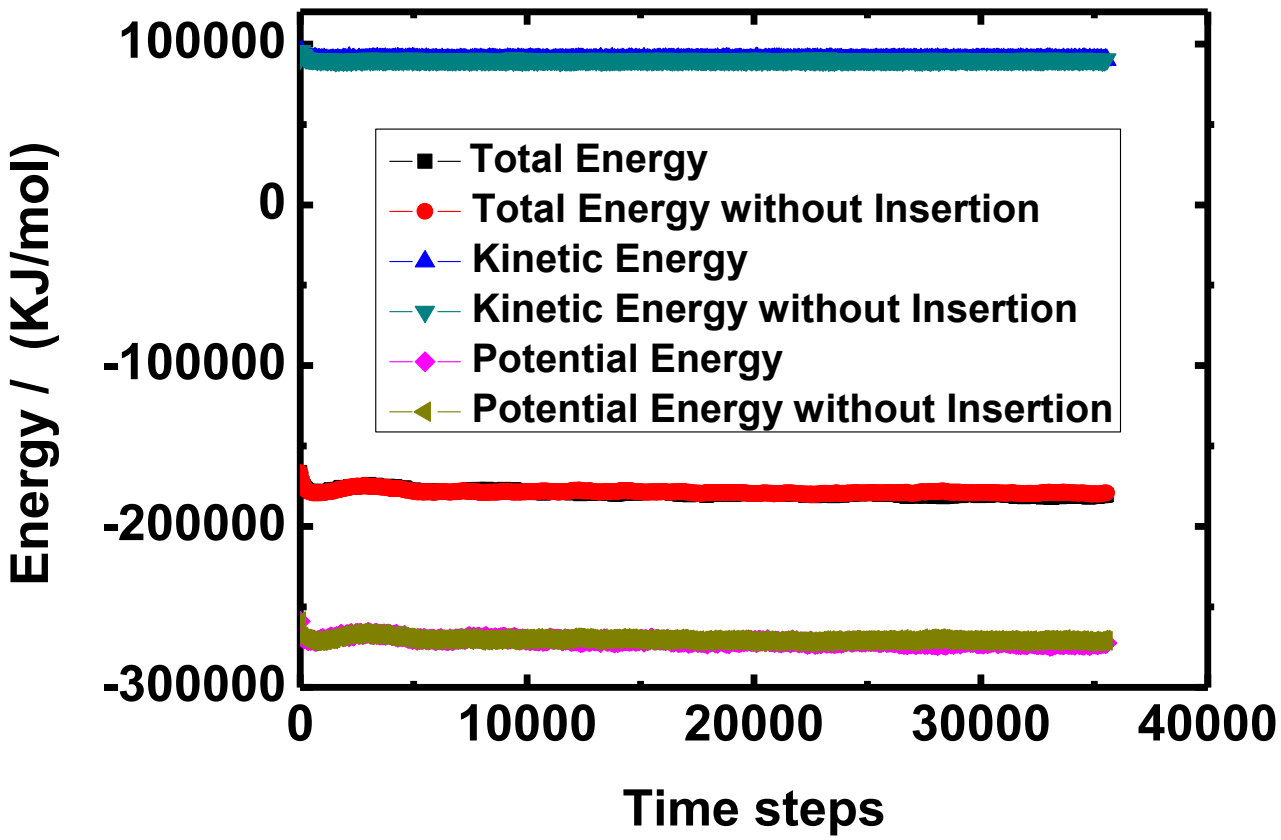








Bubble Method



Splitting Method

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Modification :

a: Cluster analysis

b: Local themostat

C: Insertion process

1. Select the farthest and nearest molecules

2. Copy the coordinates of the nearest molecule to the farthest molecule

3. Switch on the Gaussian form potential for the interactions between the two spiltting molecules

4. After one insertion period, turn on the normal LJ 12-6 potential for the nonbonded interactions between the two spiltting molecules

Splitting Method

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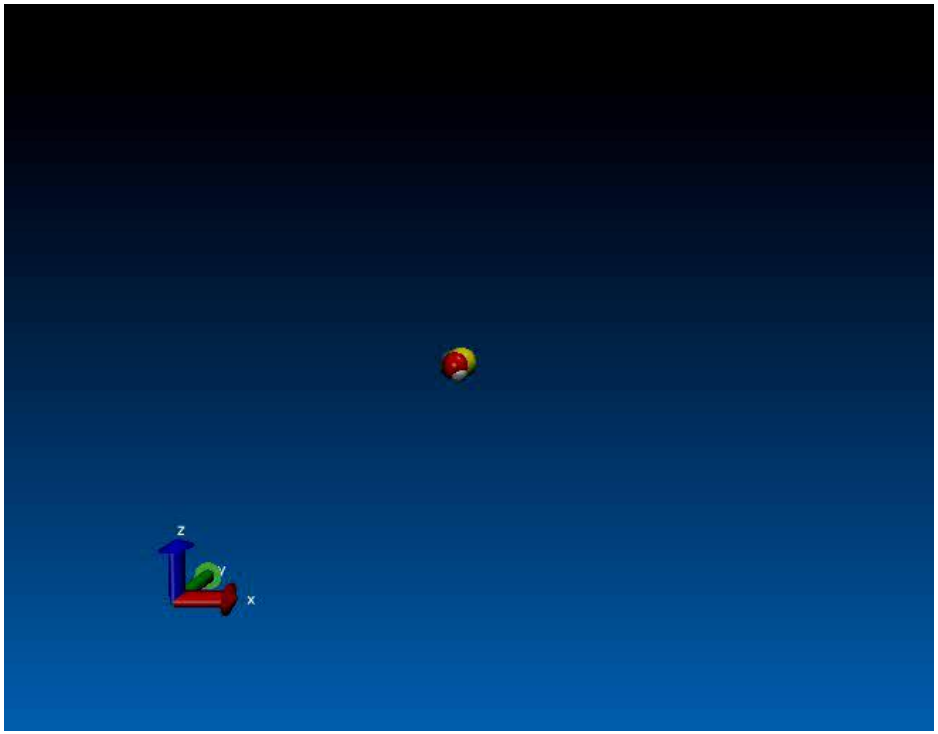
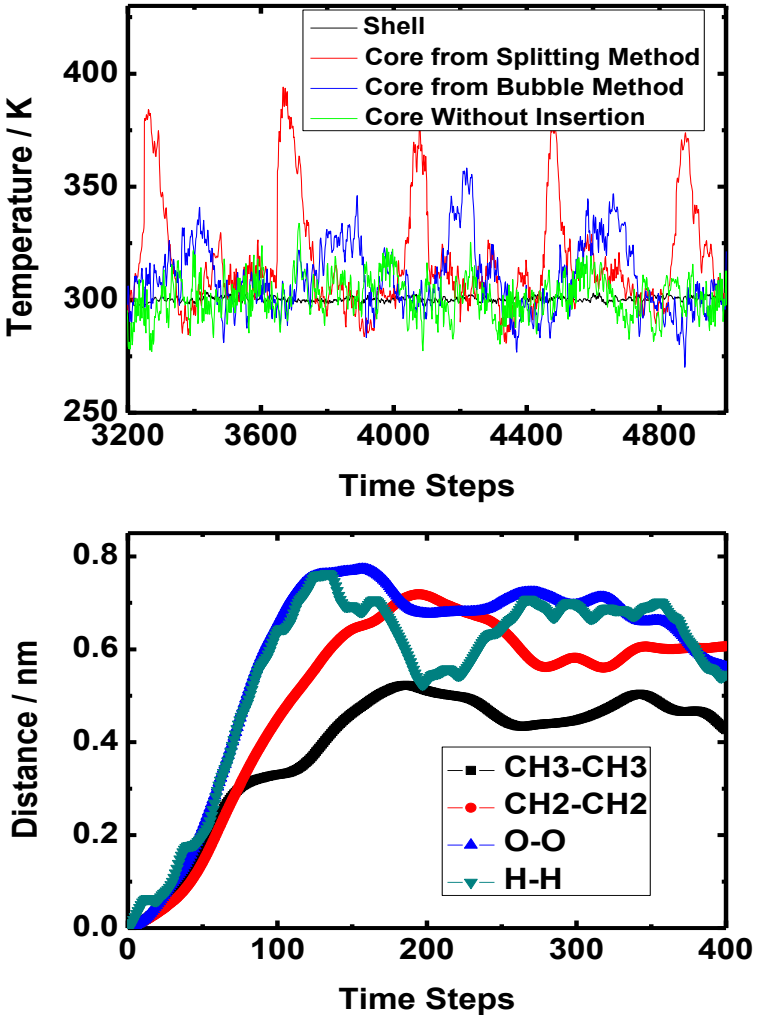
Splitting process





Splitting Method

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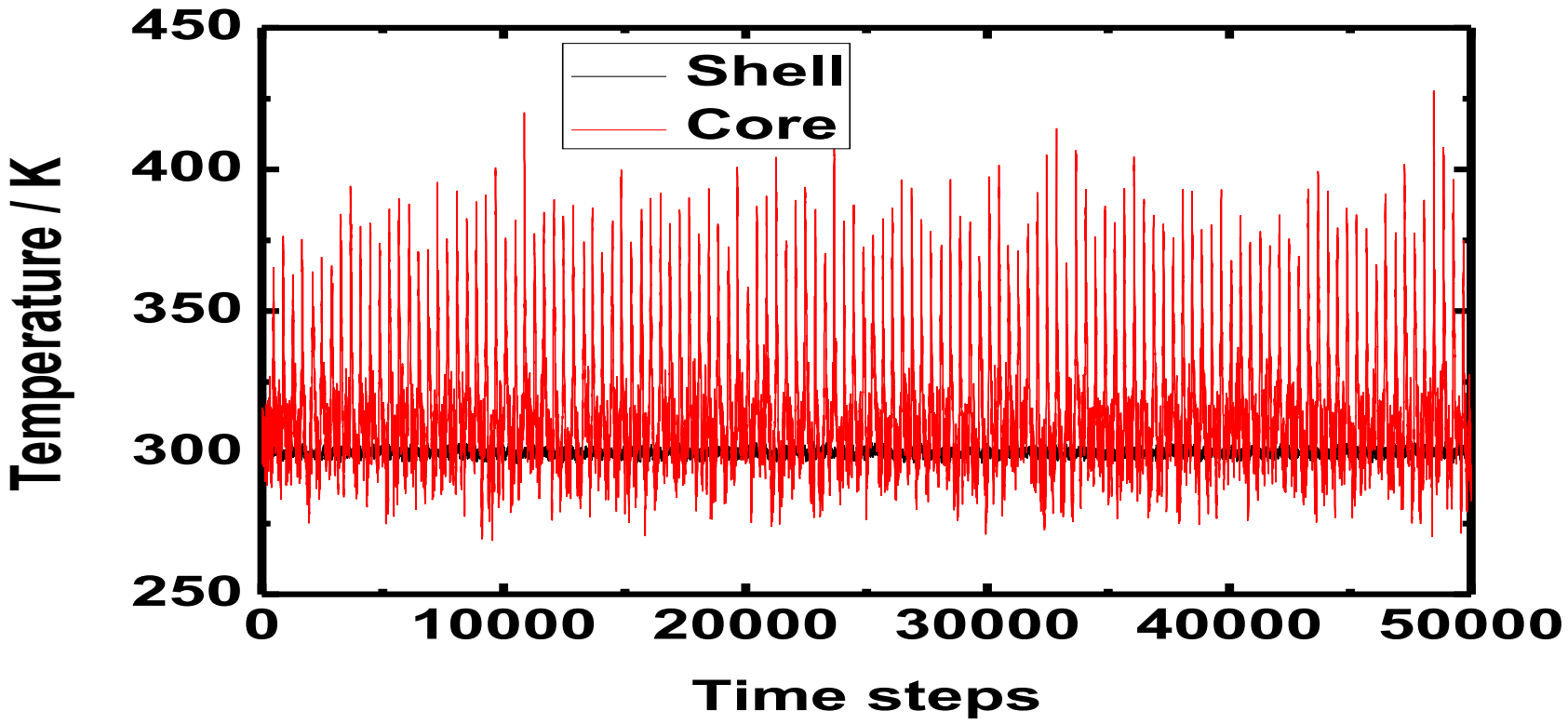
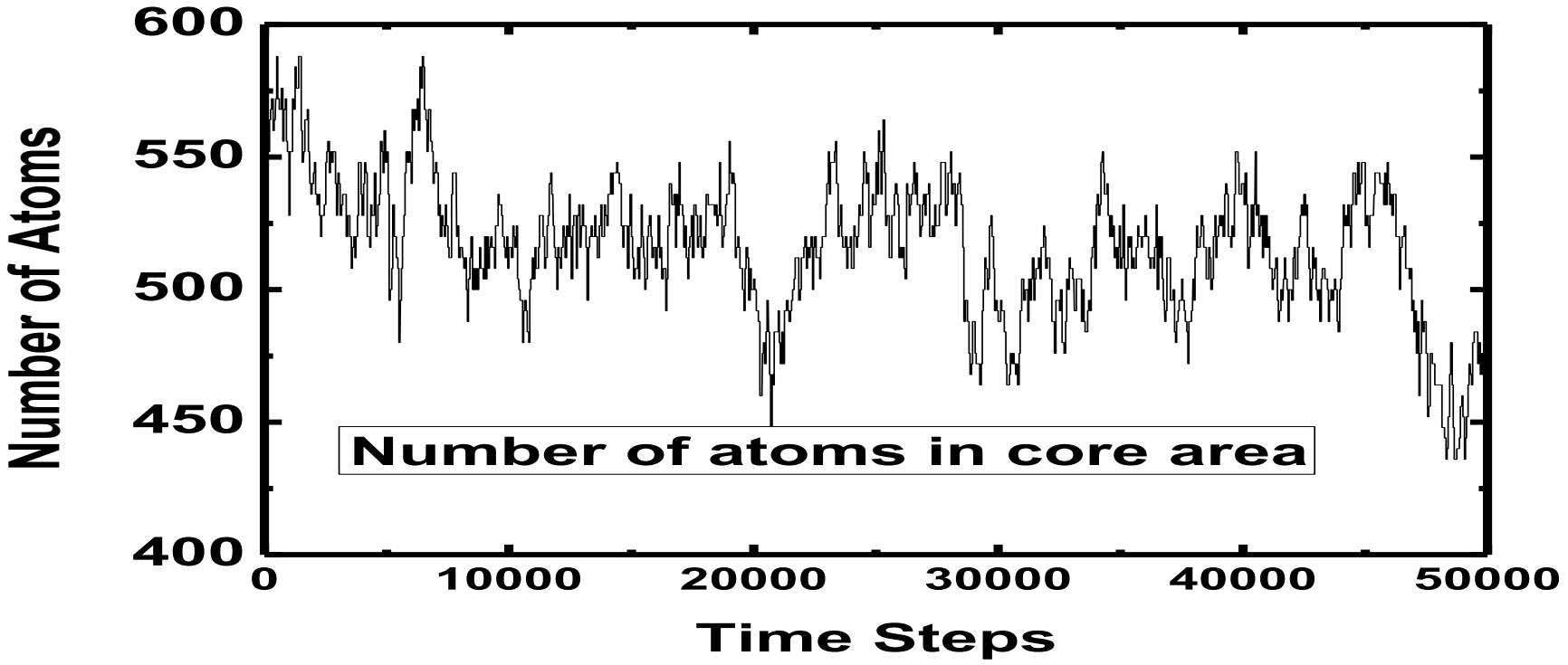
Longer run to test the stability



Splitting Method



Zhang, Leroy & Müller-Plathe,J. Chem. Phys. 139, 134701 (2013)

Conclusion

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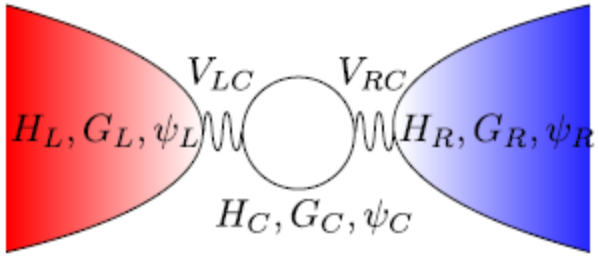
1. Both of the bubble and splitting methods work.

2. Compare these two methods, at lower insertion frequencies and for smaller molecules, both methods can be used, but at higher insertion frequencies and larger molecules, splitting method works better.

Phonon Green's function



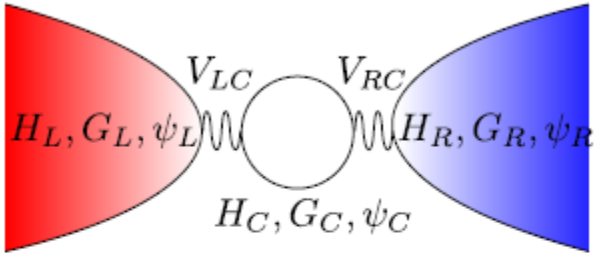
- Discrete Schrödinger equation $(E - \mathbf{H})\,|\psi\rangle = 0$
- The Hamiltonian and wavefunction can be divided

$$\begin{pmatrix} \mathbf{H}_L & \mathbf{V}_{LC} & 0 \\ \mathbf{V}_{CL} & \mathbf{H}_C & \mathbf{H}_{CR} \\ 0 & \mathbf{V}_{RC} & \mathbf{H}_R \end{pmatrix} \begin{pmatrix} |\psi_L\rangle \\ |\psi_C\rangle \\ |\psi_R\rangle \end{pmatrix} = E \begin{pmatrix} |\psi_L\rangle \\ |\psi_C\rangle \\ |\psi_R\rangle \end{pmatrix},$$

- The Green's function is defined as,

$$(E - \mathbf{H})\mathbf{G} = \mathbf{I},$$

Phonon Green's function



- The Green's function gives the response of a system to a perturbation $|v\rangle$,

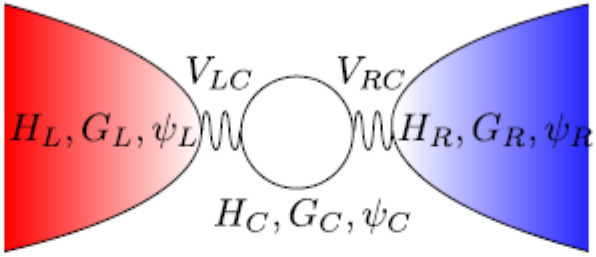
$$H\,|\psi\rangle = E\,|\psi\rangle + |v\rangle\,,$$

- The response writes

$$|\psi\rangle = -G\,|v\rangle\,,$$

- To obtain the response (phonon transmission), it's easier to calculate the Green's function than to solve the eigenvalue problem.

Phonon Green's function

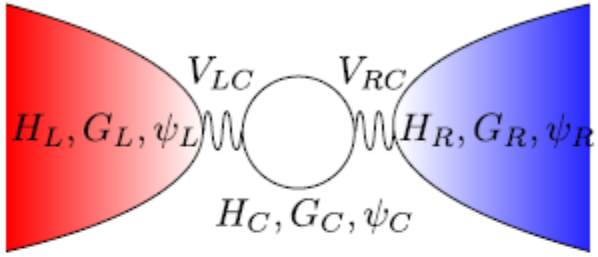


- The Green's function of the device writes,

$$\mathbf{G}_C = \left[\omega^2\mathbf{I} - \mathbf{H}_C - \mathbf{\Sigma}_L - \mathbf{\Sigma}_R\right]^{-1},$$

- $H_{3i+\alpha,3j+\beta} = \frac{1}{\sqrt{m_i m_j}}\Phi_{ij}^{\alpha\beta}$ is the force constant matrix of the phonon system. $\mathbf{\Sigma}_L = \mathbf{V}_{CL}\mathbf{g}_L\mathbf{V}_{CL}^{\dagger}$, $\mathbf{\Sigma}_R = \mathbf{V}_{CR}\mathbf{g}_R\mathbf{V}_{CR}^{\dagger}$ are the self-energies of the left and right leads,
- $\mathbf{g}_L$ and $\mathbf{g}_R$ refer to the surface Green's functions of the unperturbed left and the right leads

Phonon Green's function



- Phonon transmission $\Xi(\omega)$ writes,

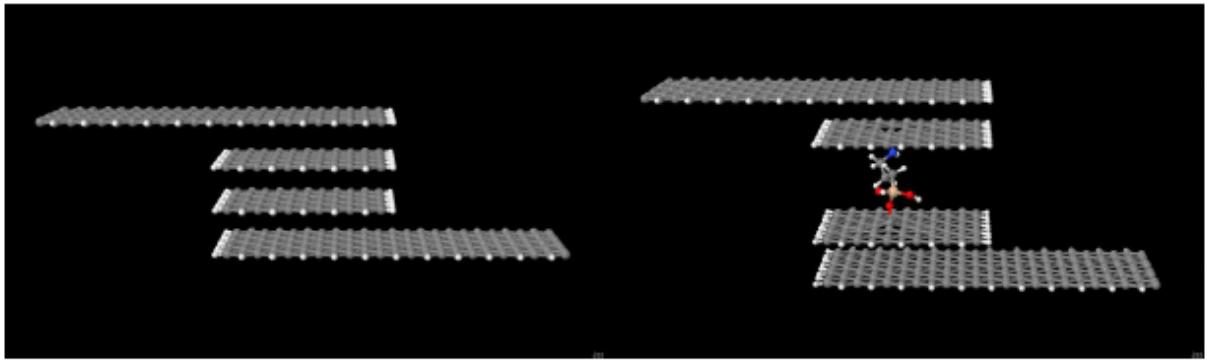
$$\Xi(\omega) = \mathrm{Tr}\left[\mathbf{\Gamma}_L \mathbf{G}_C \mathbf{\Gamma}_R \mathbf{G}_C^\dagger\right],$$

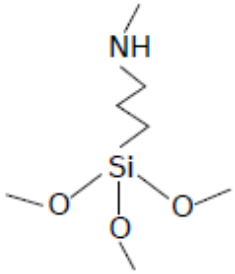
  where $\mathbf{\Gamma}_{L,R} = i[\mathbf{\Sigma}_{L,R} - \mathbf{\Sigma}_{L,R}^\dagger]$.
- Heat conductance reformulated from Landauer formula writes,

$$G_{\mathrm{ph}}(T_0) = \int_{BZ} \hbar\omega \left.\frac{\partial}{\partial T}\left(e^{\frac{\hbar\omega}{k_B T}} - 1\right)^{-1}\right|_{T_0} \Xi(\omega)\frac{\mathrm{d}\omega}{(2\pi)^3},$$

Model description

- Graphene - aminosilane “sandwich” heat spreader.
- DFT calculation with SIESTA
  geometry optimized with a generalized local-density approximations (LDA) within Ceperley-Alder version (CA), double-zeta polarized basis set, 0.01 eV/Å force tolerance and 250 Ry mesh cutoff.
- The Kohn-Sham Hamiltonians and overlap matrices from DFT calculations are used in the Green’s function to obtain the electron transmission $\mathcal{T}_{\mathrm{el}}$.

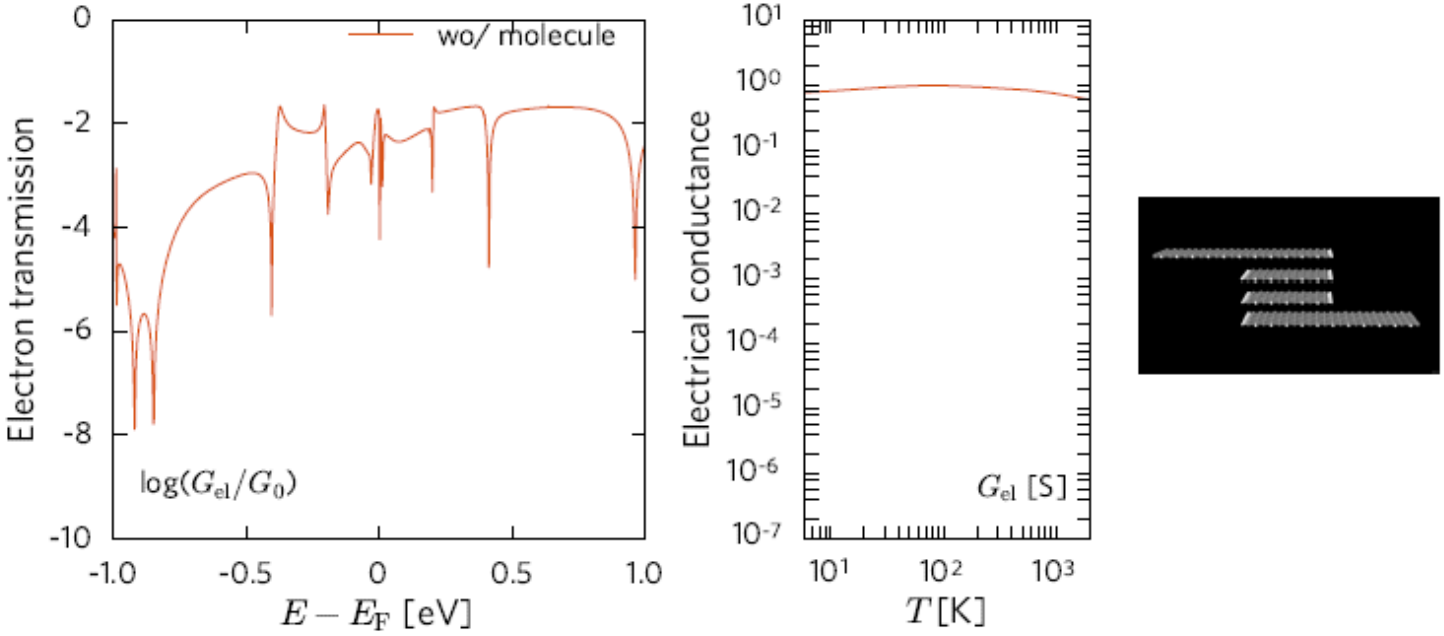




Soler *et al.*, J. Phys.: Cond. Matter 14, 2745 (2002).
Han *et al.*, Nature Communications 7, 11281 (2016)

Electron transport through the junction

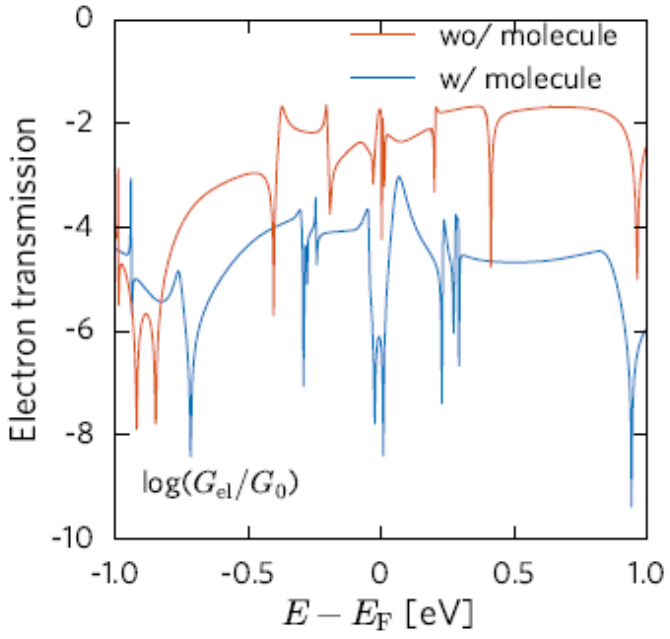
- Electron transmission through graphene layers and electrical conductance.

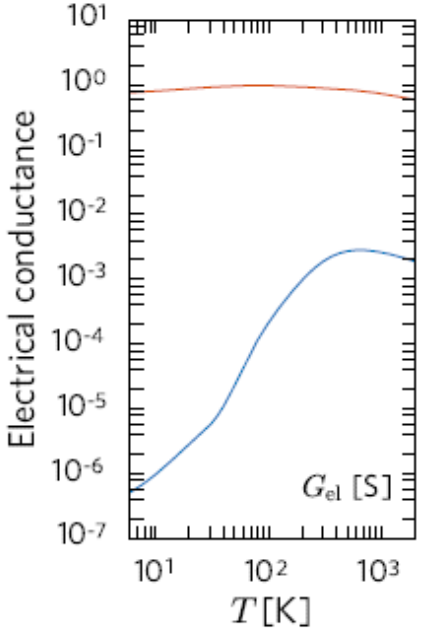


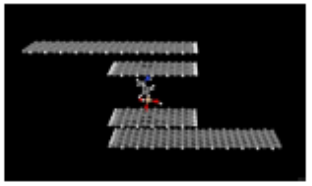
Han *et al.*, Nature Communications 7, 11281 (2016)

Electron transport through the junction

- The molecule electrically isolates the graphene contacts by interrupting the $\pi - \pi$ stacking of the phenyl rings.
- T_{el} rather symmetric at E_F, hence low thermopower is expected.



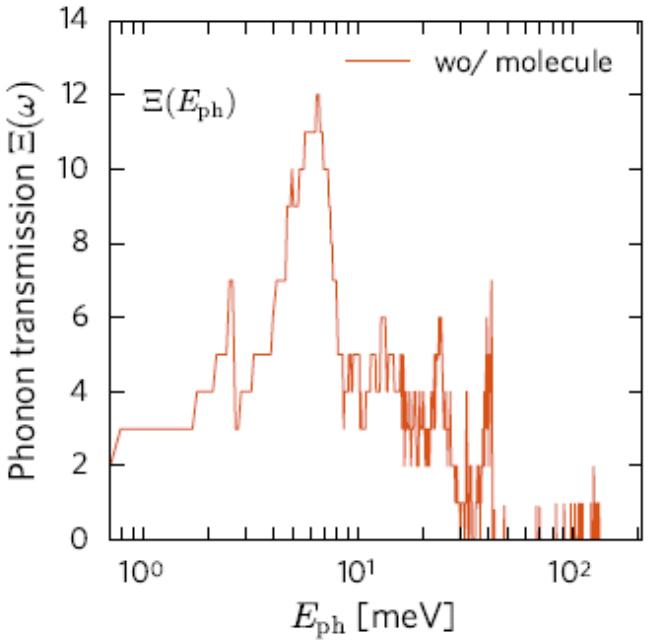


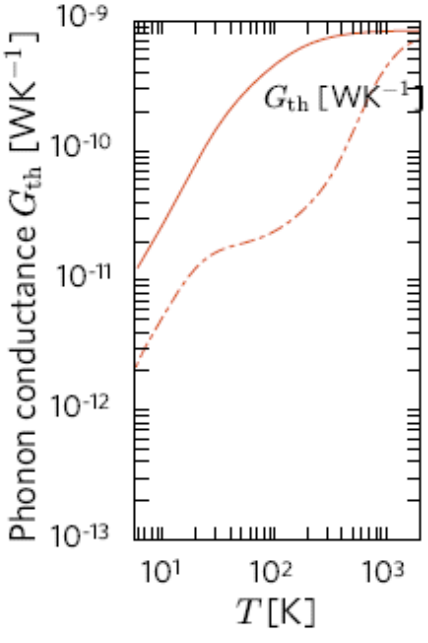


Han *et al.*, Nature Communications 7, 11281 (2016)

Phonon transport through the junction

- Phonon transmission through graphene layers and thermal conductance.
- $\Xi(\omega) = \mathcal{M}(\omega)$ number of phonon modes in the reservoir.

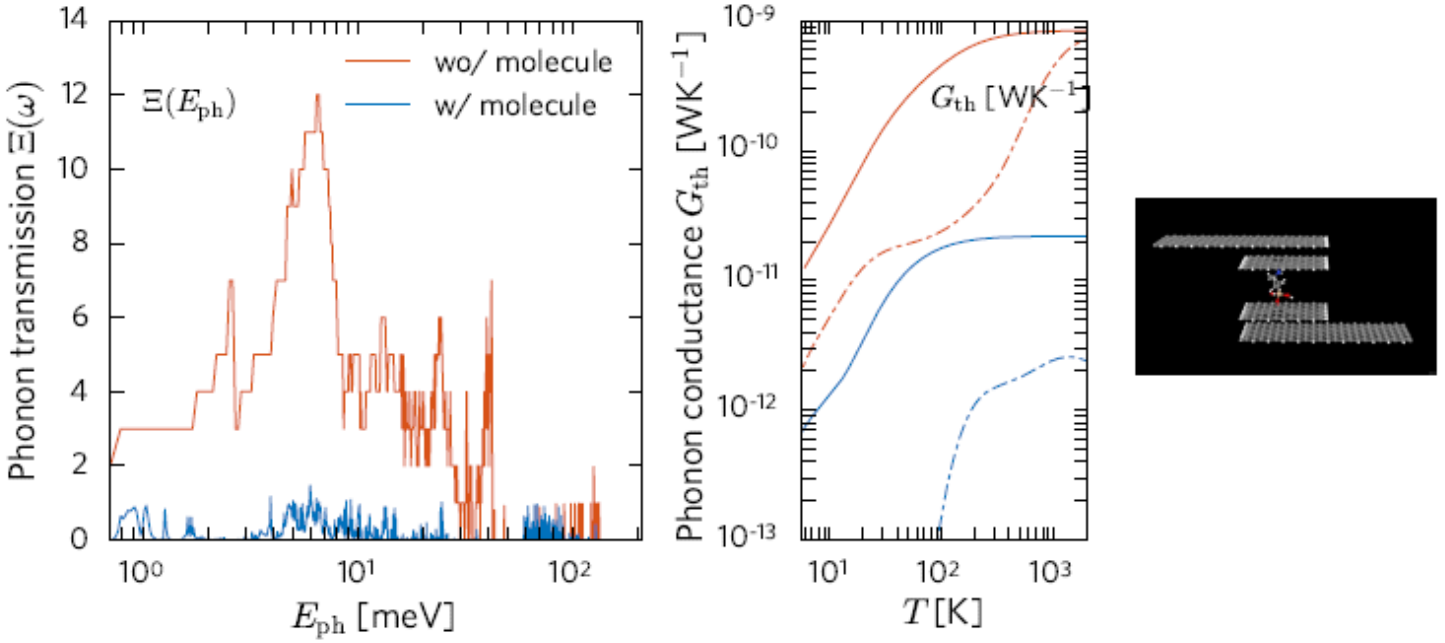




Han *et al.*, Nature Commun. 7, 11281 (2016), Adv. Func. Mater. 25, 4430 (2015)

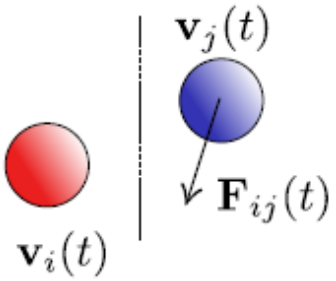
Phonon transport through the junction

- The molecule thermally isolates the graphene contacts, for a low number density(!) $\rho = 0.408\ \mathrm{nm}^{-2}$
- Electrons contribute $\approx 10\%$ to the total thermal conductance at room temperature.



Han *et al.*, Nature Commun. 7, 11281 (2016), Adv. Func. Mater. 25, 4430 (2015)

Heat flux and generalized phonon transmission



- The steady-state heat flux Q writes,

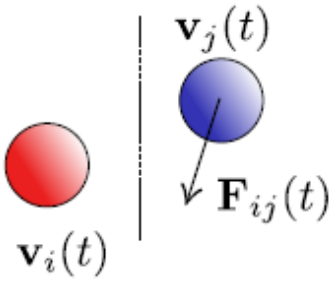
$$Q_{i\in L\to j\in R} = \frac{1}{2}\langle \mathbf{F}_{ij}(t)\cdot(\mathbf{v}_i(t)+\mathbf{v}_j(t))\rangle$$

- With fluctuation-dissipation theorem, decompose Q into the spectral domain $Q = \int q(\omega)\mathrm{d}\omega$,

$$q(\omega) = 2\,\mathrm{Re}\sum_{i\in L, j\in R}\int_{-\infty}^{\infty}\mathrm{d}\tau\langle \mathbf{F}_{ij}(\tau)\cdot\mathbf{v}_i(0)\rangle e^{i\omega\tau}$$

Volz, APL (2013). Han, PhD Thesis (2015). Xiong, Han, *et al.* PRL (2016)

Heat flux and generalized phonon transmission



- Generalized phonon transmission $\mathcal{T}(\omega)$ writes,

$$\mathcal{T}(\omega) = \frac{q(\omega)}{k_B \Delta T}$$

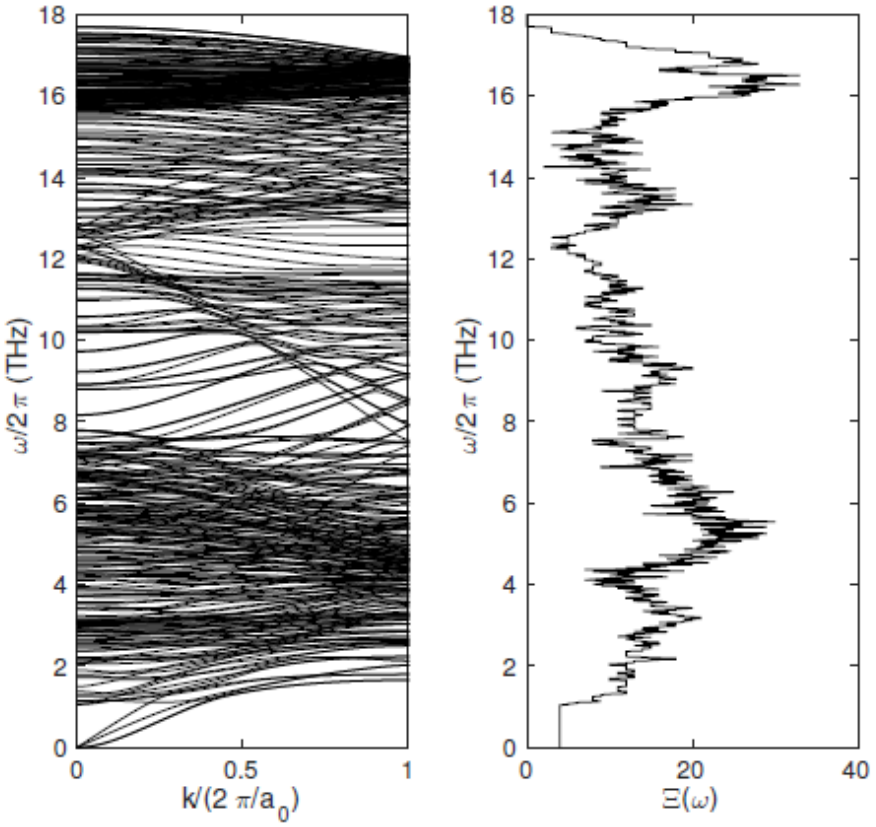
- relation with the number of modes $\mathcal{M}(\omega)$, phonon MFP $\Lambda(\omega)$ and system length L,

$$\mathcal{T}(\omega) = \frac{\mathcal{M}(\omega)}{1 + L/\Lambda(\omega)}$$

Volz, APL (2013). Han, PhD Thesis (2015). Xiong, Han, *et al.* PRL (2016)

Heat flux and generalized phonon transmission

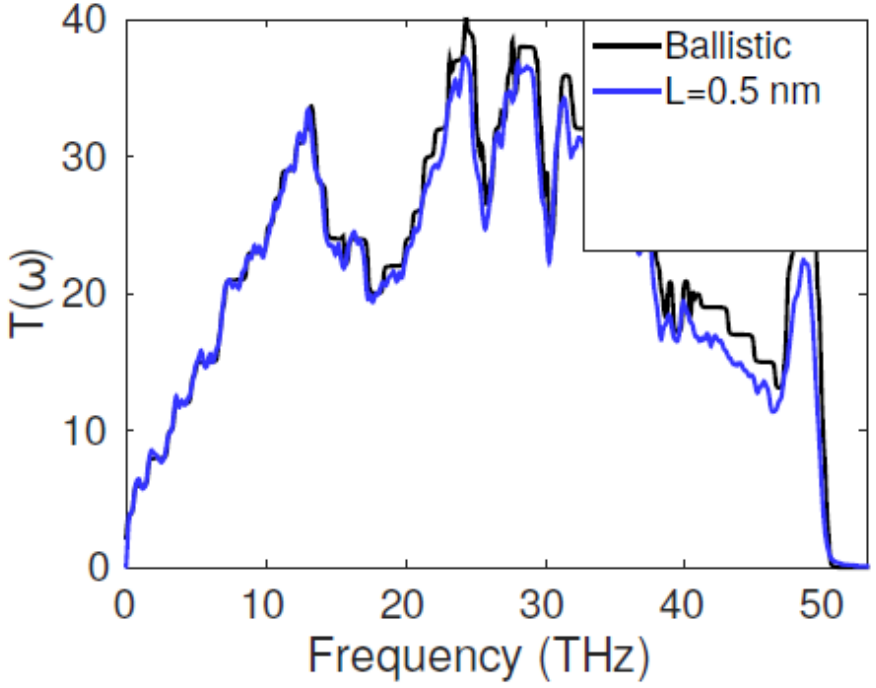
- Pristine silicon nanowire of cross-section 4.3×4.3 nm^2, ballistic transmission, $\mathcal{T}(\omega) = \mathcal{M}(\omega)$



Volz, APL (2013). Han, PhD Thesis (2015). Xiong, Han, *et al.* PRL (2016)

Heat flux and generalized phonon transmission

- Pristine (10,10) carbon nanotubes of diameter 1.6 nm with variable length, ballistic $\rightarrow$ diffusive transport
  $\mathcal{T}(\omega) = \mathcal{M}(\omega)/(1 + L/\Lambda(\omega))$



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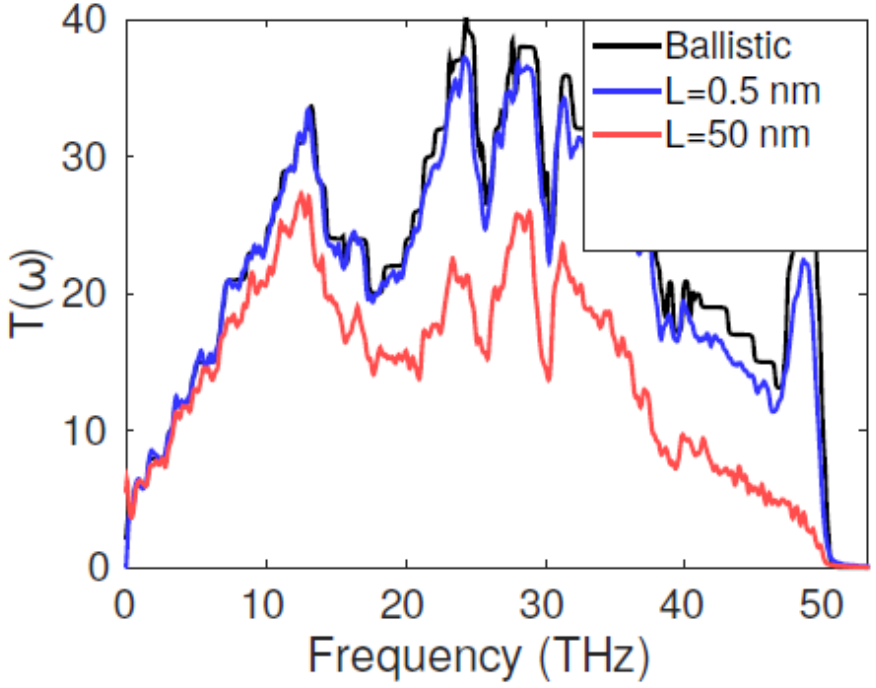

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Heat flux and generalized phonon transmission

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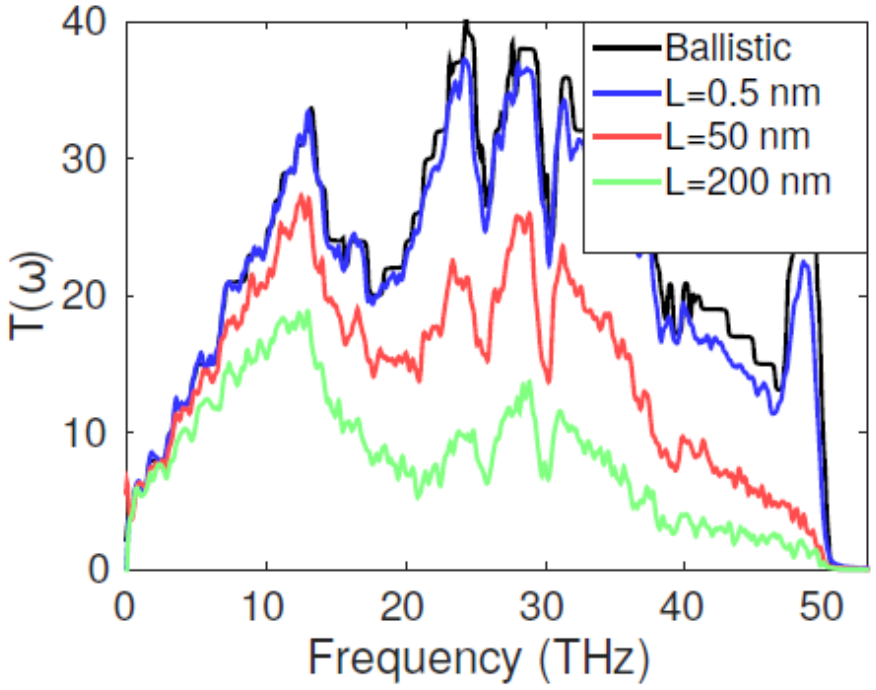

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