A computational framework for studying normal mode dynamics

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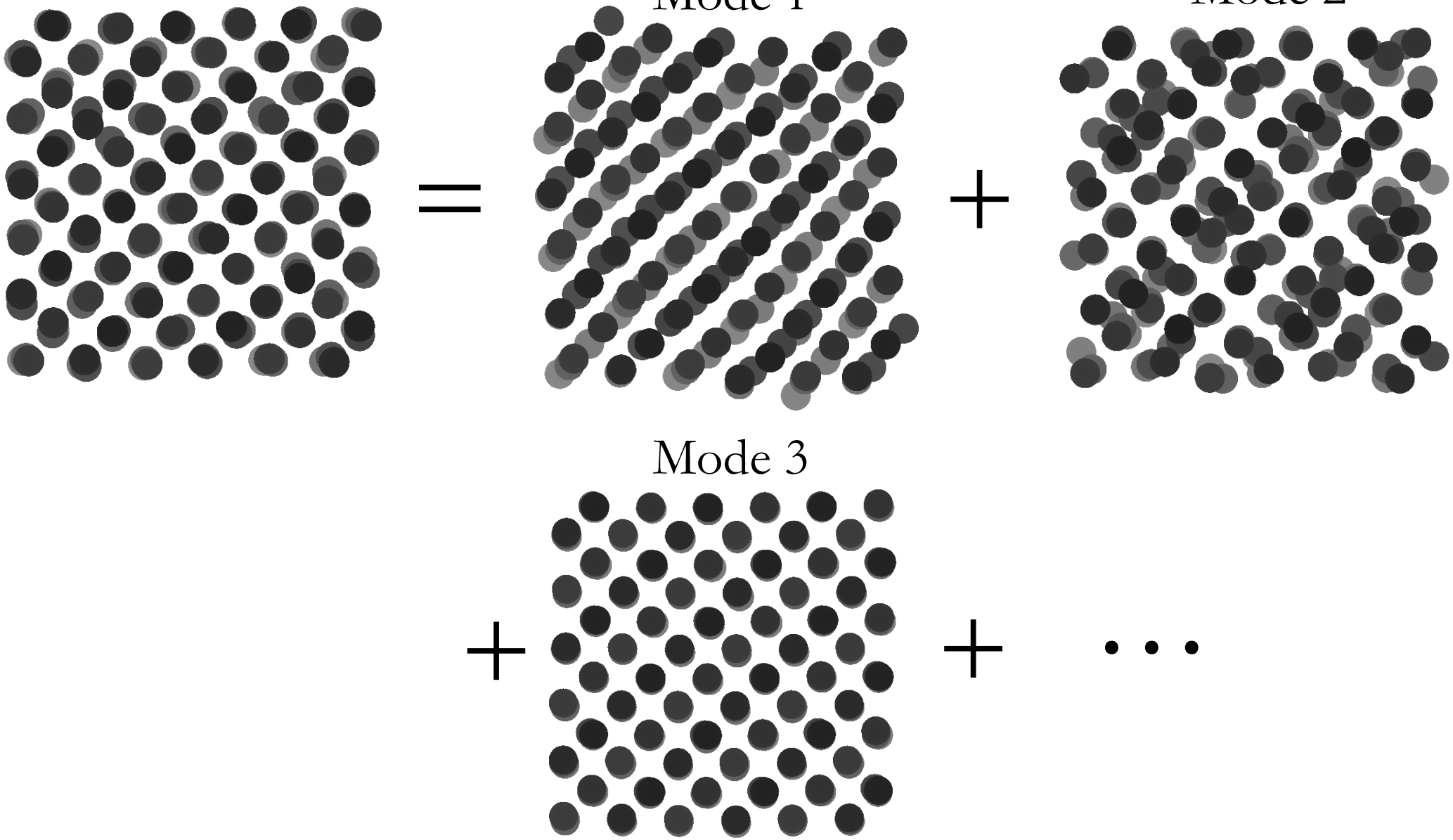
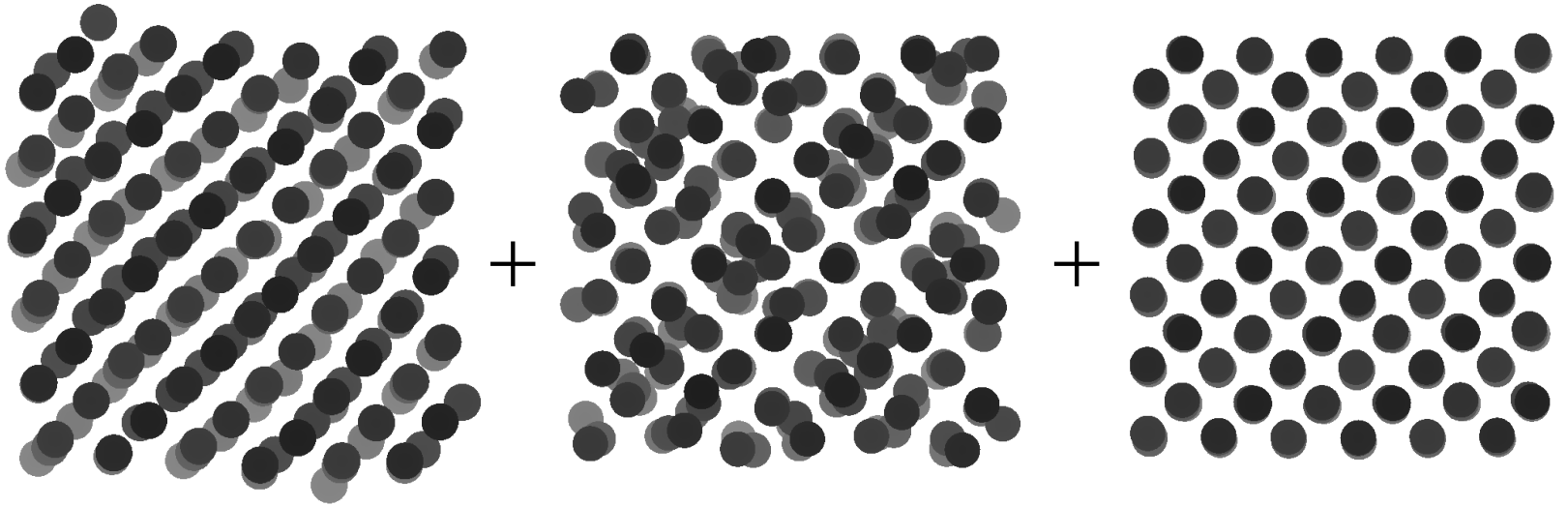
Modes & phonons

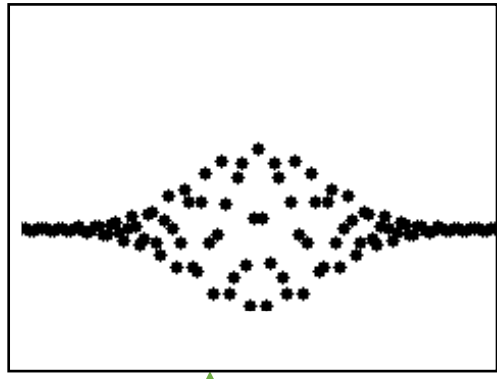


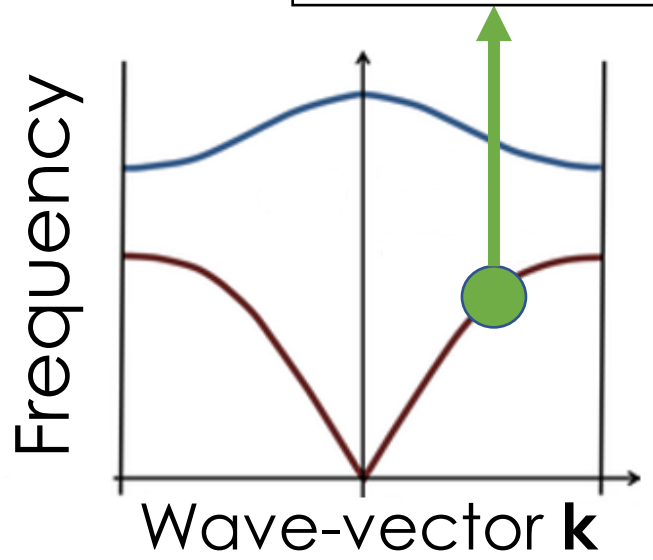
Modes & phonons: how does heat flow?

Mode 1 + Mode 2 + Mode 3 + ⋯ =

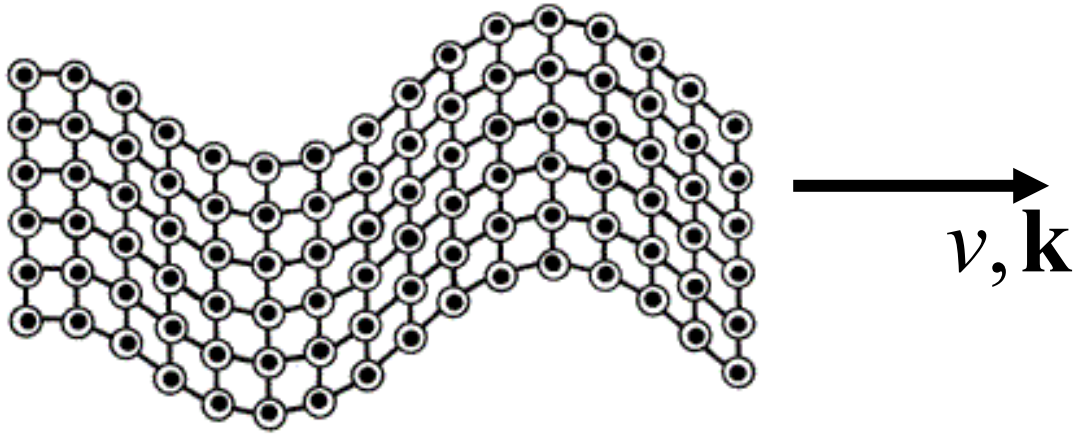


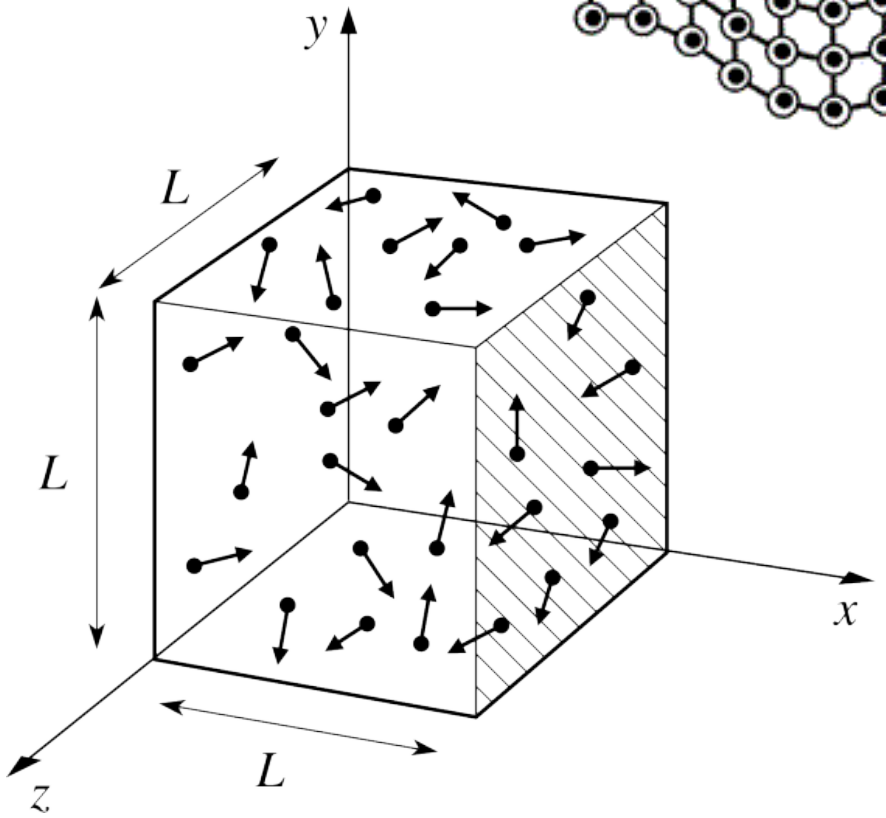
Phonon wave-packet





Traditional picture of heat transfer.



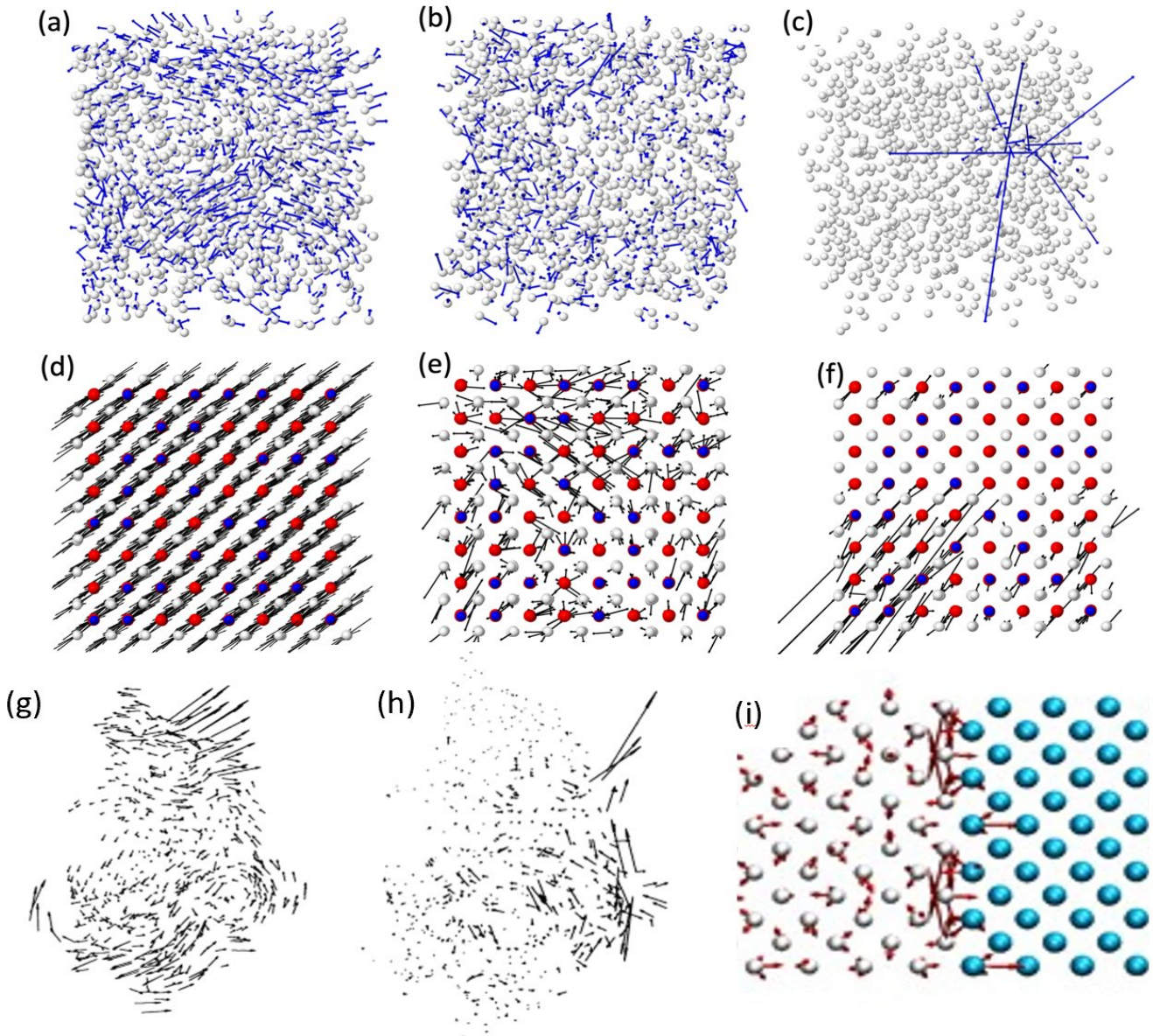


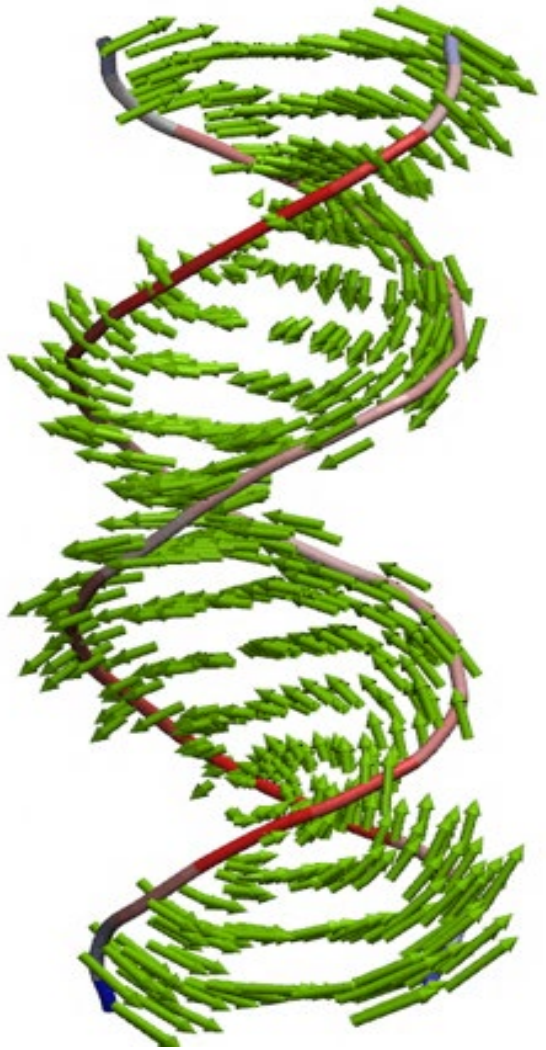
"Phonon gas model"

$$\kappa = \frac{1}{V}\sum_{\mathbf{k}} c_{\mathbf{k}} v_{\mathbf{k}} \Lambda_{\mathbf{k}}$$

Traditional theory can't describe these.

Arrows are eigenvectors centered on atoms.





Mode-space equations of motion

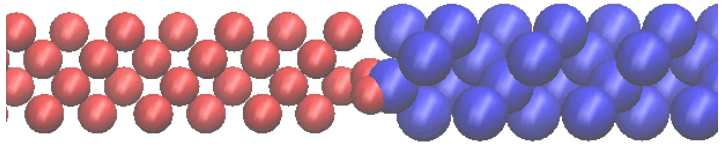
Real-space	Mode-space
Hamiltonian	
$H = \frac{1}{2}\sum_{i,\alpha} m_i \left(v_i^\alpha\right)^2 + \frac{1}{2!}\sum_{\substack{ij \\ \alpha\beta}} \Phi_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta + \frac{1}{3!}\sum_{\substack{ijk \\ \alpha\beta\gamma}} \Psi_{ijk}^{\alpha\beta\gamma} u_i^\alpha u_j^\beta u_k^\gamma + \cdots$	$H = \frac{1}{2}\sum_n \dot{X}_n^2 + \frac{1}{2!}\sum_n \omega_n^2 X_n^2 + \frac{1}{3!}\sum_{nml} K_{nml} X_n X_m X_l + \cdots$
Force	
$F_i^\alpha = -\frac{\partial H}{\partial u_i^\alpha} = -\sum_{j,\beta} \Phi_{ij}^{\alpha\beta} u_j^\beta - \frac{1}{2}\sum_{jk,\beta\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_j^\beta u_k^\gamma - \cdots$	$F_n = -\frac{\partial H}{\partial X_n} = -\omega_n^2 X_n - \frac{1}{2}\sum_{nml} K_{nml} X_m X_l - \cdots$
Power transfer	
$\dot{Q}_{ij} = \mathbf{F}_{ij} \bullet \mathbf{v}_i - \mathbf{F}_{ji} \bullet \mathbf{v}_j$	$\dot{Q}_{nm} = F_{nm}\dot{X}_n - F_{mn}\dot{X}_m$

$$K_{nml} = \sum_{ijk}\sum_{\alpha\beta\gamma} \frac{\Psi_{ijk}^{\alpha\beta\gamma} e_{ni}^\alpha e_{mj}^\beta e_{lk}^\gamma}{\sqrt{m_i m_j m_k}}$$

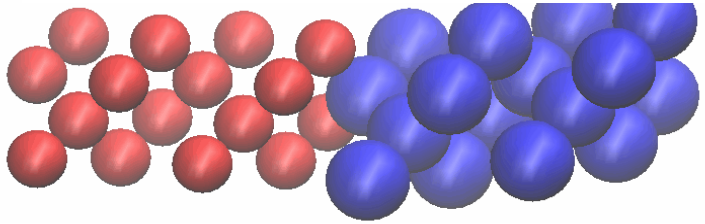
Mode coupling constants

Strongly interacting modes

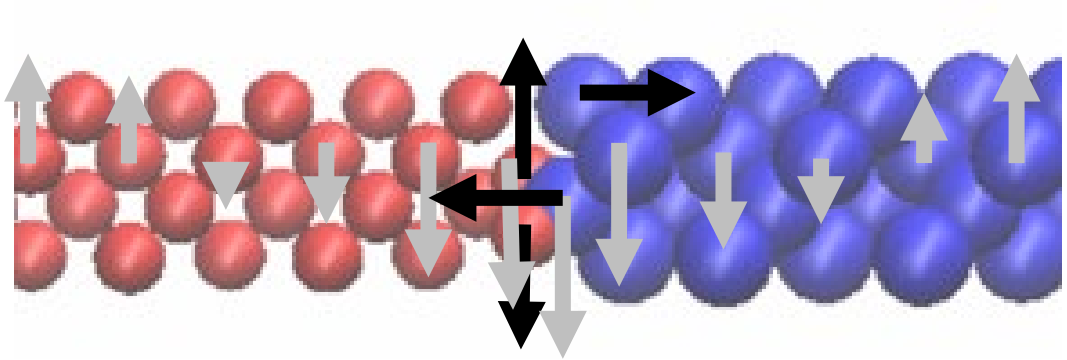
Interface mode



Extended mode

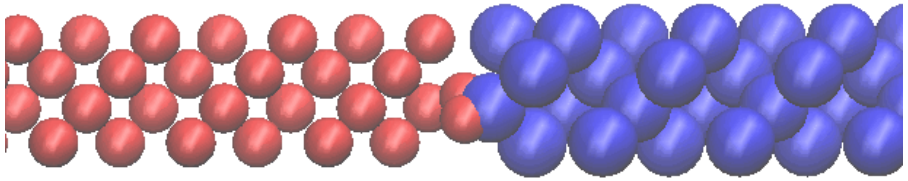


Eigenvector overlap

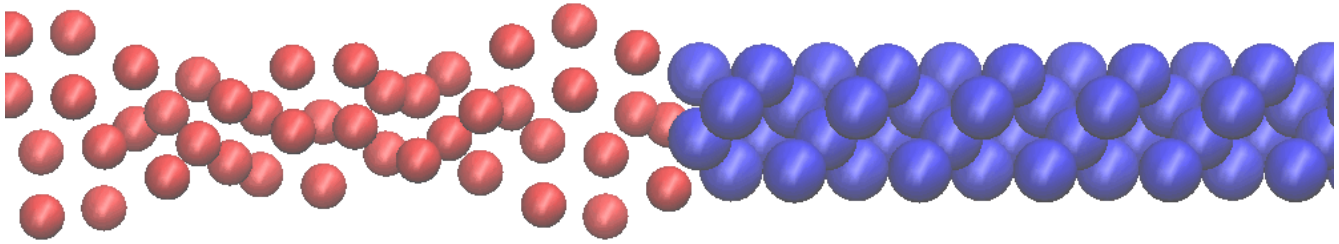


Strongly interacting modes

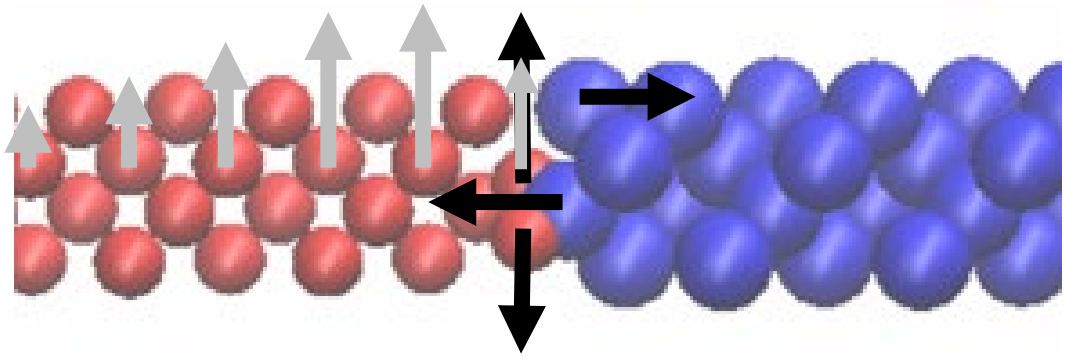
Interface mode



Optical mode

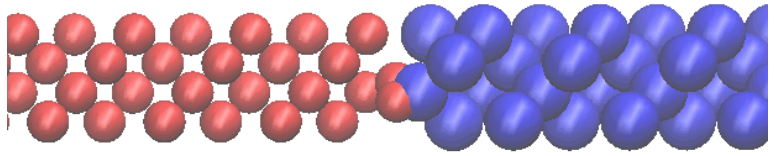


Eigenvector overlap

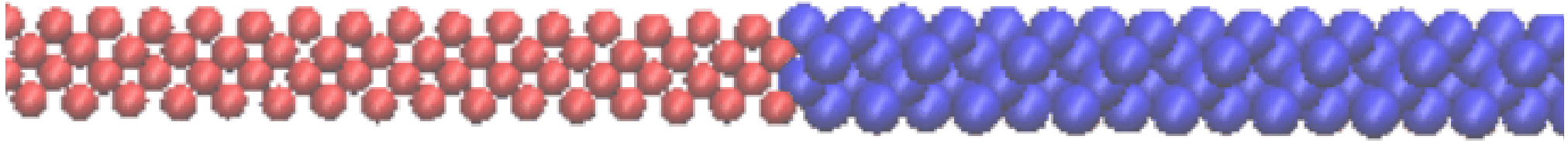


Weakly interacting modes

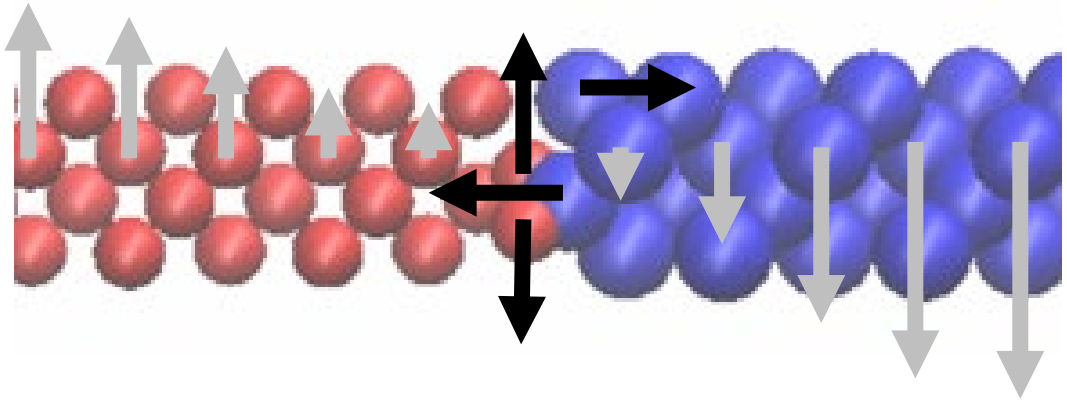
Interface mode



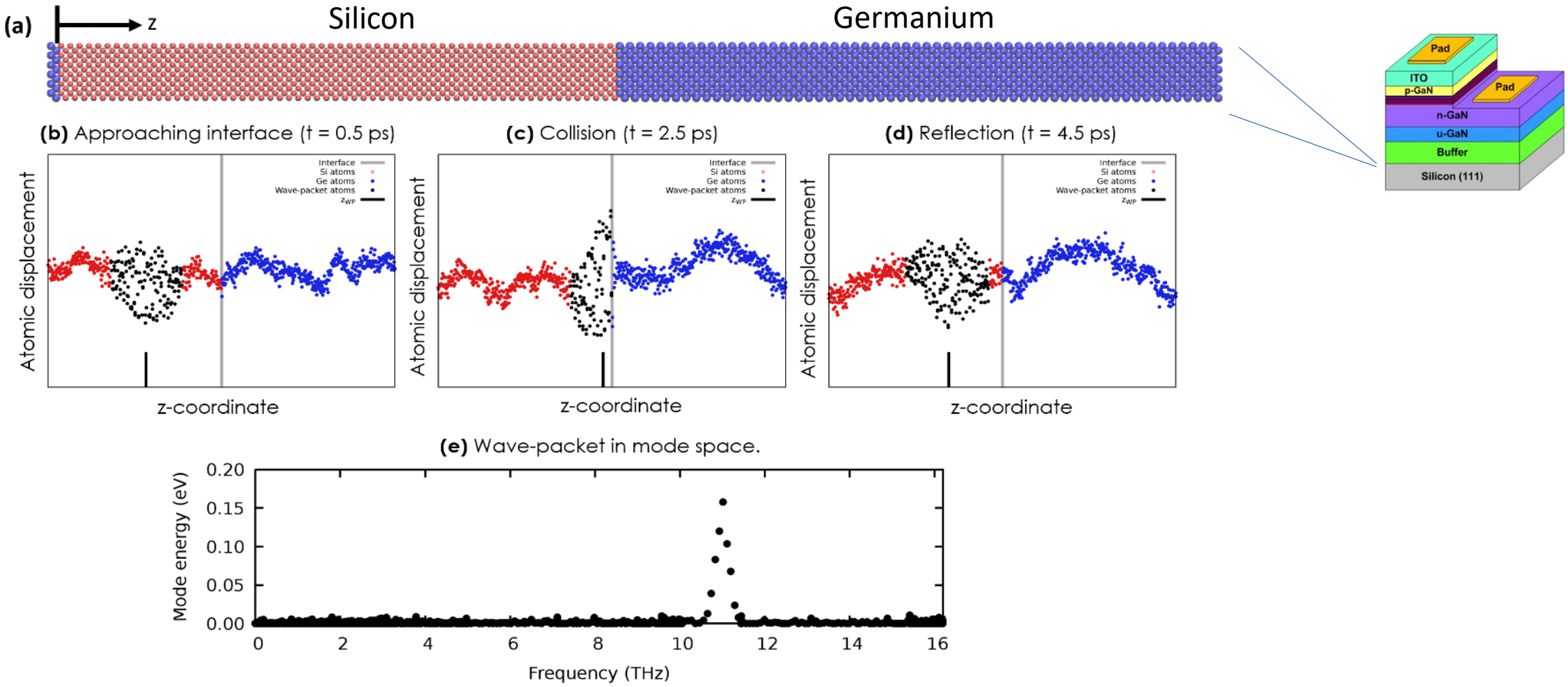
Extended mode



No eigenvector overlap



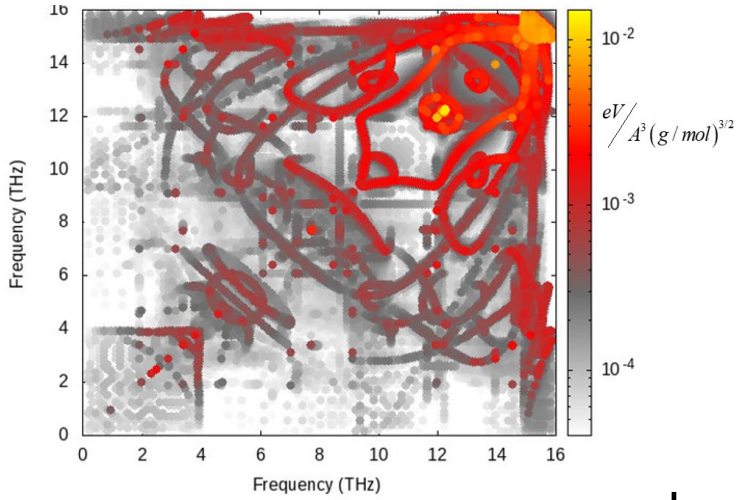
Studying real-time vibrational energy transfer

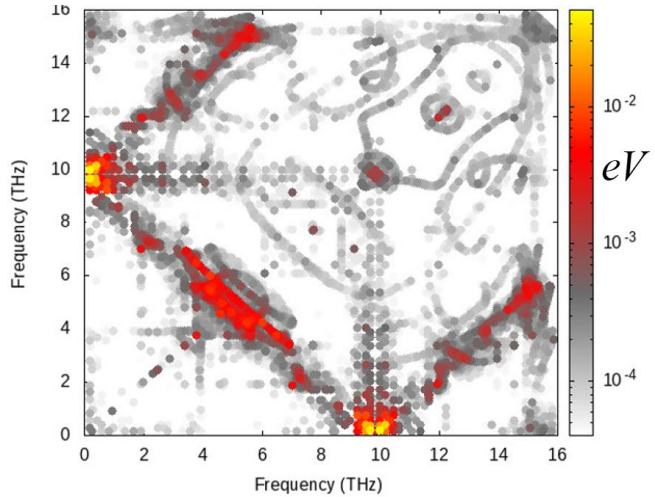


Studying real-time vibrational energy transfer

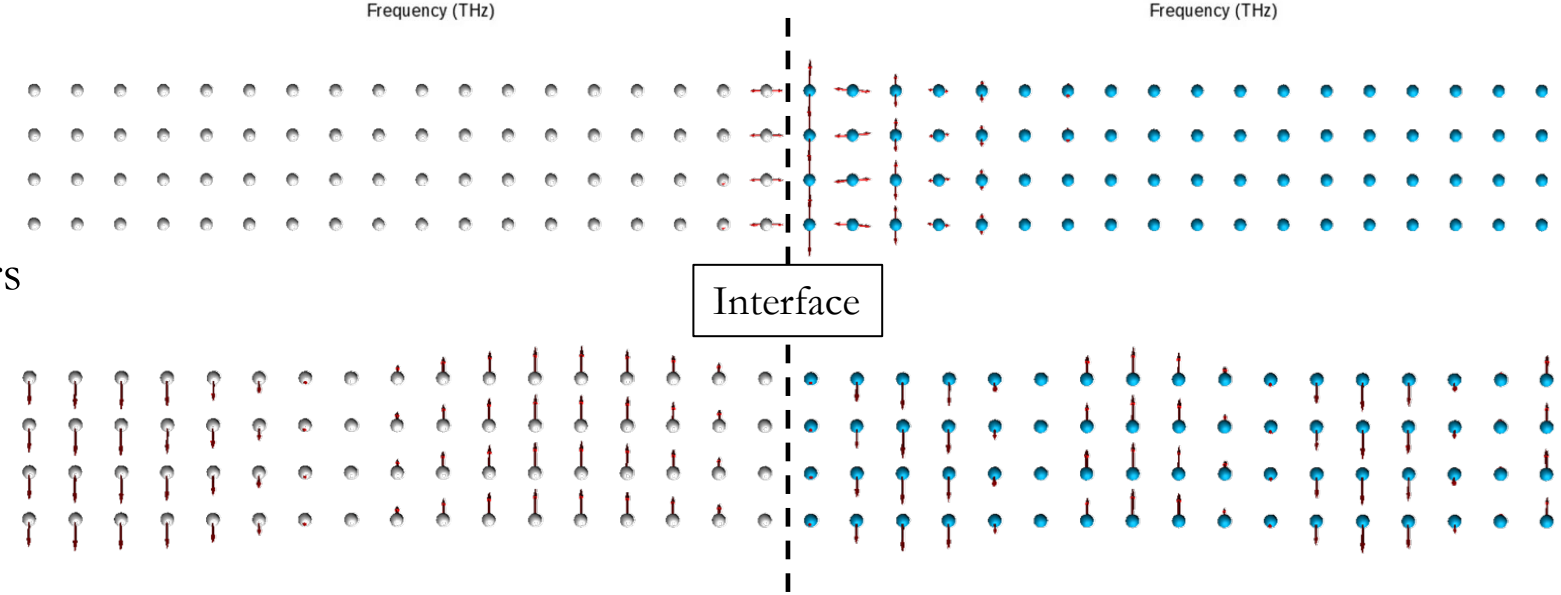
Coupling constants $K_{nml} = \sum_{ijk}\sum_{\alpha\beta\gamma} \frac{\Psi_{ijk}^{\alpha\beta\gamma} e_{ni}^{\alpha} e_{mj}^{\beta} e_{lk}^{\gamma}}{\sqrt{m_i m_j m_k}}$

Energy transfers $Q_{nml} = F_{nml}\dot{X}_n$





Inelastic scattering occurs with these:



Interface modes

Fully extended modes

Heat flux in mode coordinates

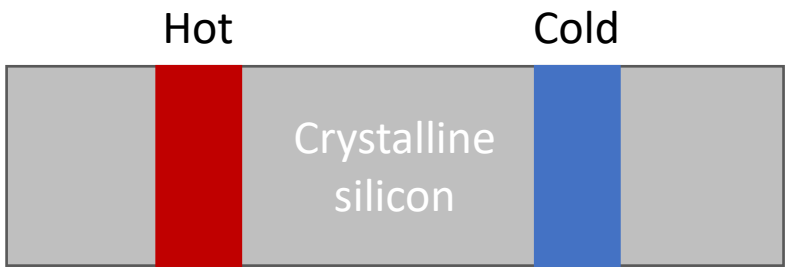
Hardy's heat flux in Cartesian coordinates

$$\mathbf{Q} = \frac{1}{V}\sum_i \left[E_i \cdot \mathbf{v}_i + \sum_j \left(-\nabla_{\mathbf{r}_i} \Phi_j \cdot \mathbf{v}_i \right) \cdot \mathbf{r}_{ij} \right]$$

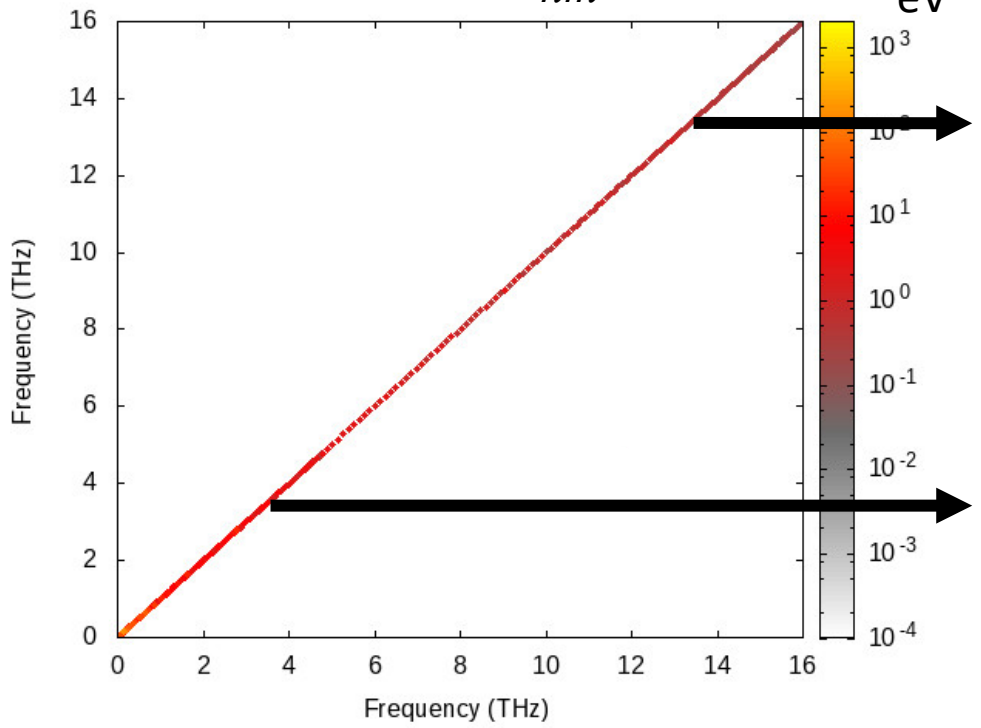
R. Hardy, *Phys. Rev.* 132, 168 (**1963**).

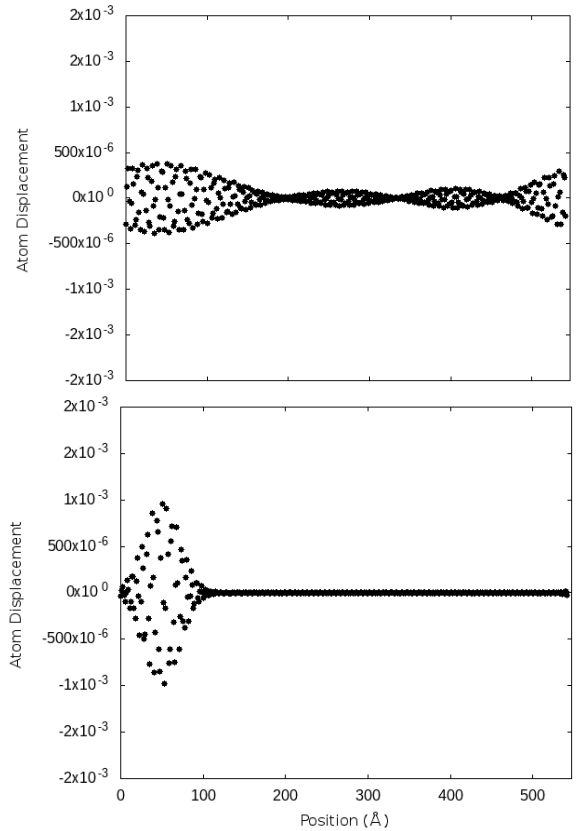
$$Q^x = \sum_{nm} K^x_{nm} X_n \dot{X}_m$$

$$K^x_{nm} = \frac{1}{2}\sum_{\substack{ij \\ \alpha\beta}} \frac{R^{x0}_{ij}}{\sqrt{m_i m_j}} \Phi^{\alpha\beta}_{ij} e^{\beta}_{ni} e^{\alpha}_{mj}$$

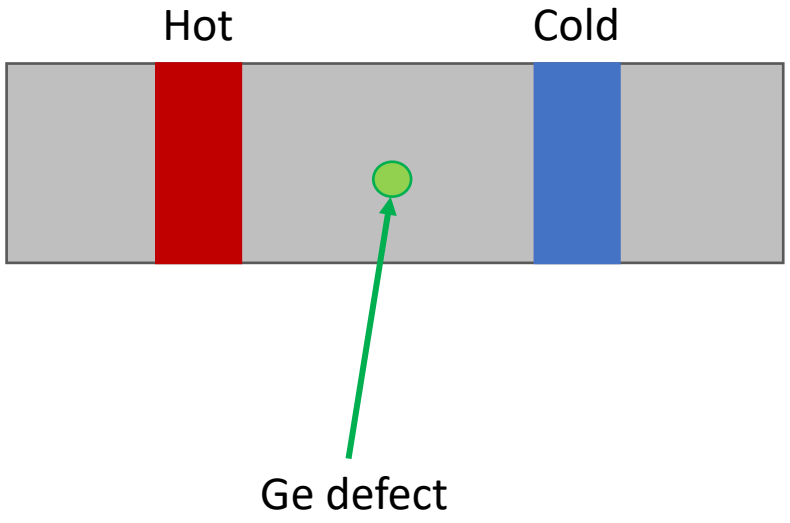


Heat flux Q_{nm}



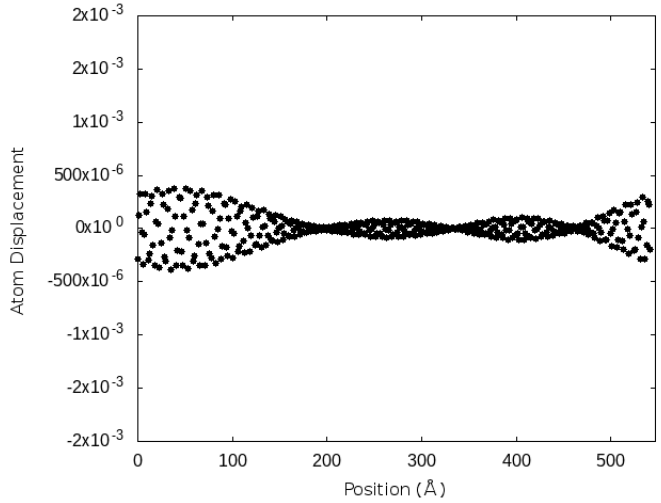


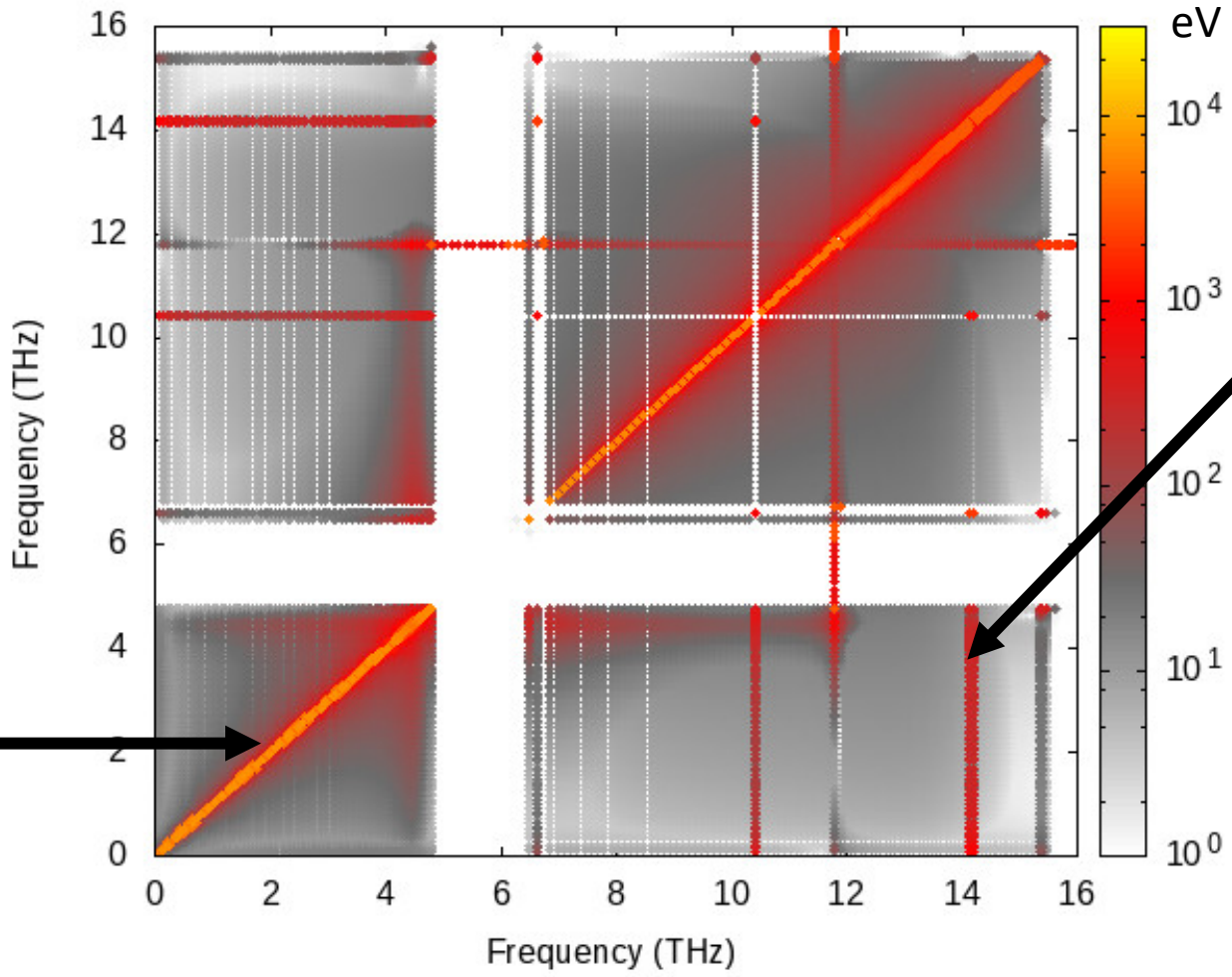
Breaking crystal symmetry with defects



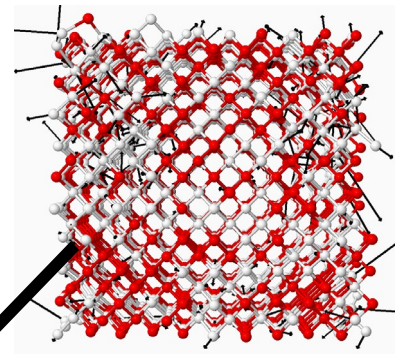
$$Q^x = \sum_{nm} K^x_{nm} X_n \dot{X}_m$$

Diagonal composed of “wave-packets”





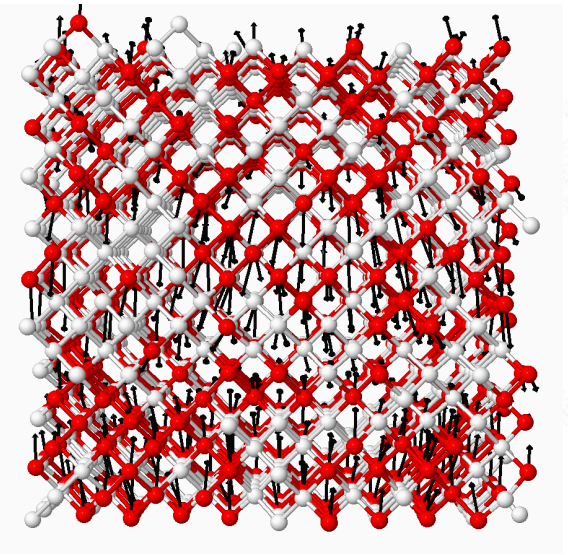
Localized modes

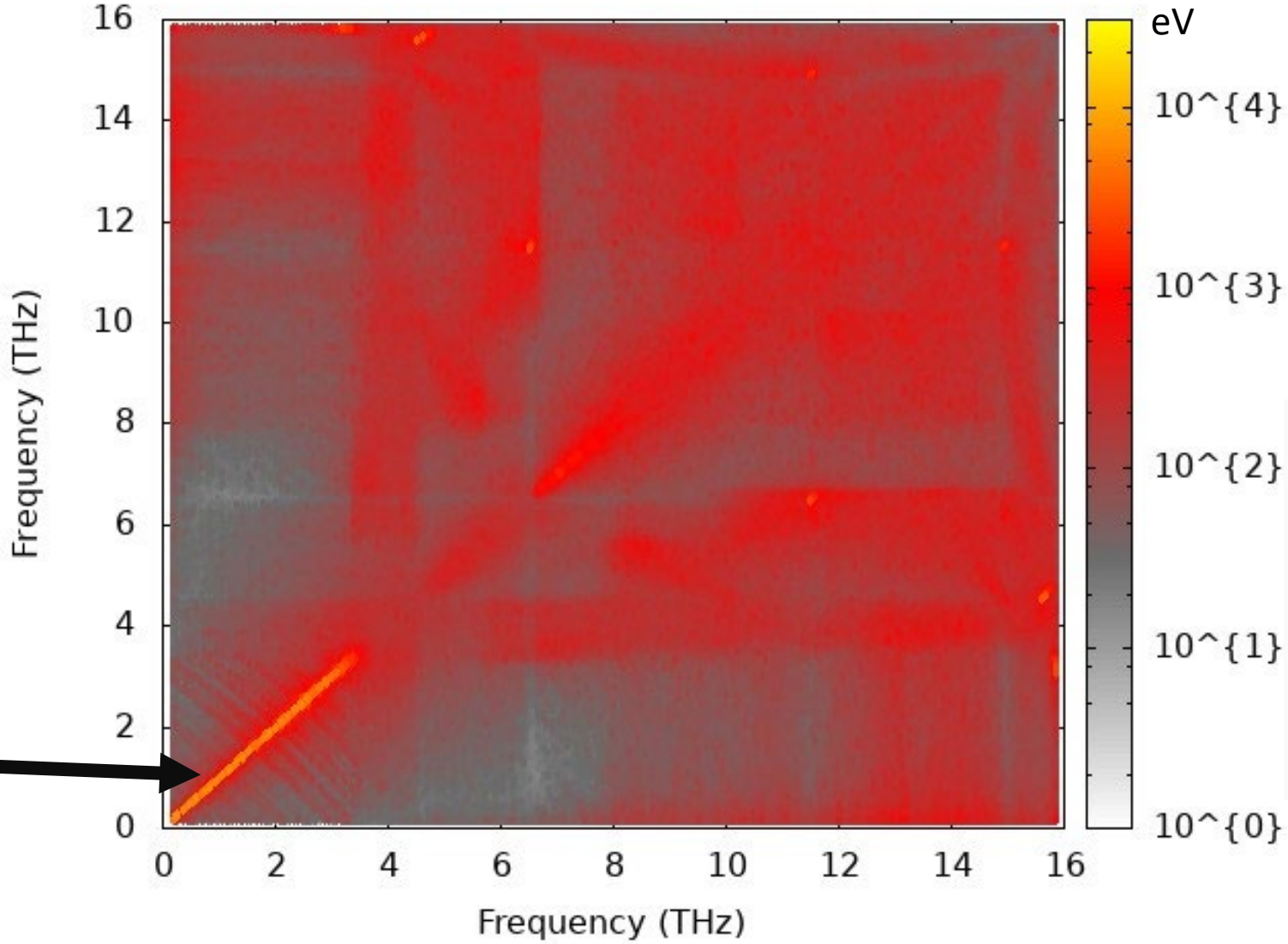


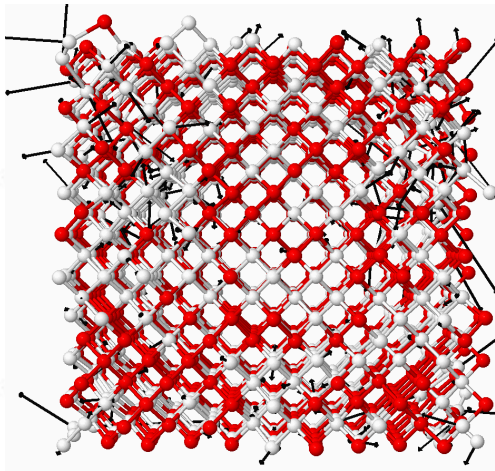
How does heat flow in alloys?

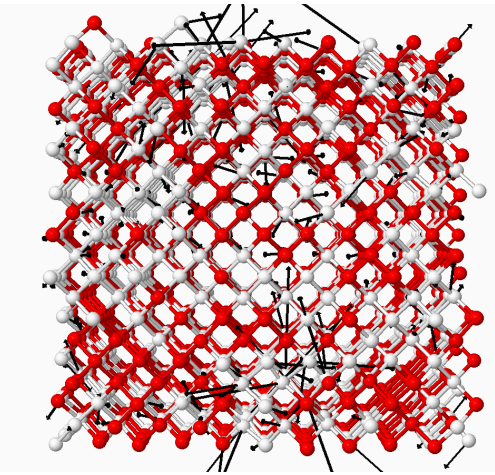
$$Q^x = \sum K^x_{nm} X_n \dot{X}_m$$

Everything else is localized or diffuse





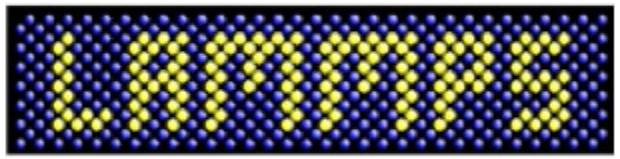




Diagonal is still significant.
Phonon gas model is somewhat valid!

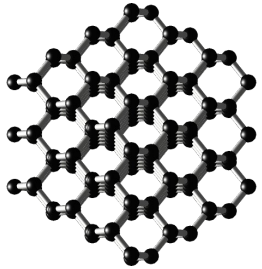
ModeCode extracts modes for any system

https://github.com/rohskopf/modecode



pair style

Structure
LAMMPS data files

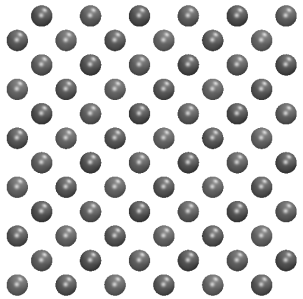


$$\frac{\partial^2 E}{\partial r_i \partial r_j}$$

- Finite difference
- Autodiff

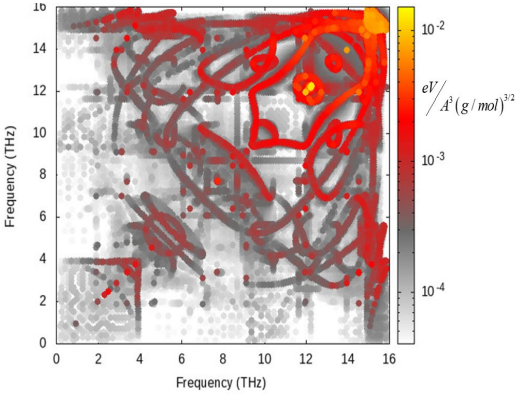
Diagonalize Hessian

Get the modes



Mode interactions

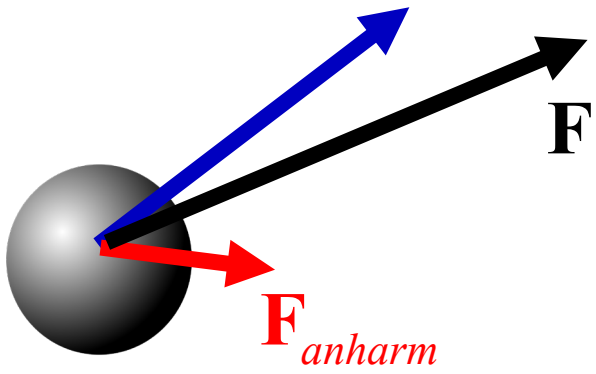
$$K_{nml} = \sum_{ijk} \sum_{\alpha\beta\gamma} \frac{\Psi_{ijk}^{\alpha\beta\gamma} e_{ni}^{\alpha} e_{mj}^{\beta} e_{lk}^{\gamma}}{\sqrt{m_i m_j m_k}}$$



Mode heat flow

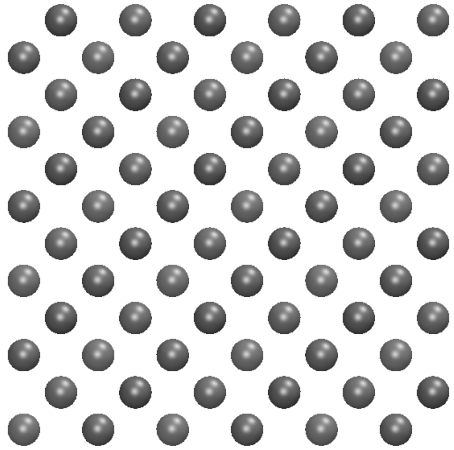
$$Q^x = \sum_{nm} K_{nm}^x X_n \dot{X}_m$$

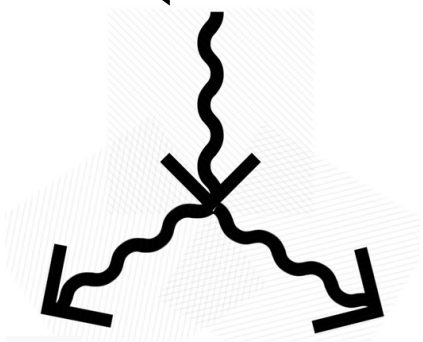
The “phonon potential”



$$\mathbf{F} = \mathbf{F}_{harm} + \mathbf{F}_{anharm}$$

$$E = \frac{1}{2}\sum_{ij} K_{ij} u_i u_j + E_{anharmonic}$$





$$E_{anharmonic} =$$

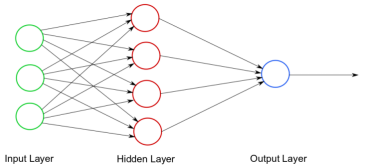
Morse

$$E = \lambda_1 \left[1 - \exp\left(-\lambda_2 \left(r - \lambda_3\right)\right)\right]^2$$

Linear Regression

$$E = \beta_0 + \sum_k \beta_k B_k$$

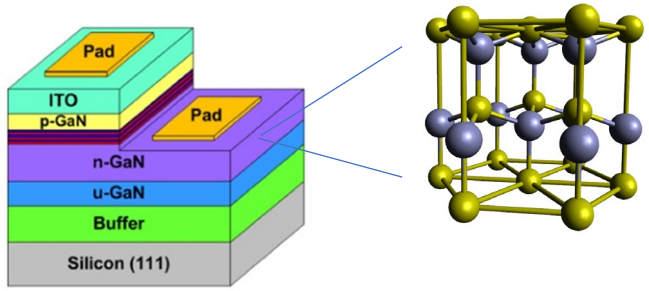
Neural Networks



Rohskopf, Andrew, et al. "Fast & accurate interatomic potentials for describing thermal vibrations." *Computational Materials Science* 184 (2020): 109884.

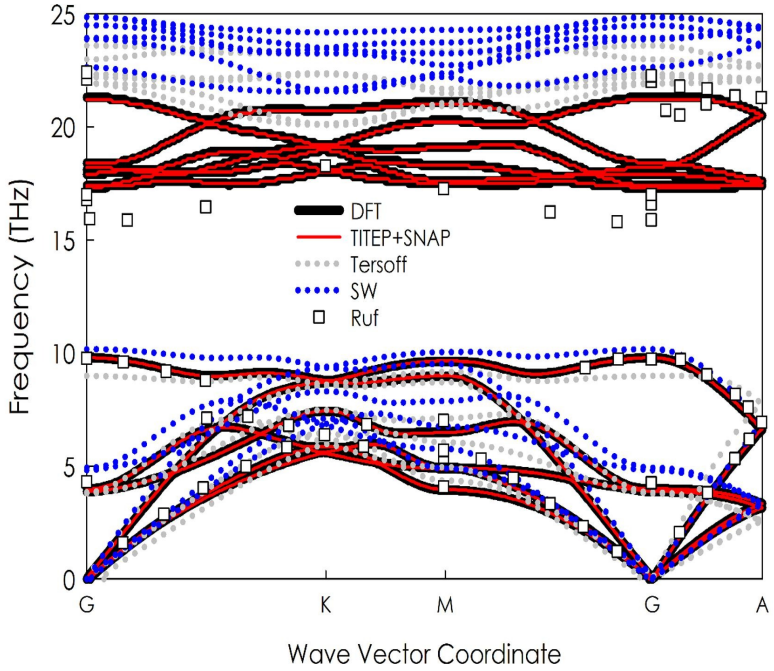
Rohskopf, Andrew, et al. "Empirical interatomic potentials optimized for phonon properties." *NPJ Computational Materials* 3.1 (2017): 1-7.

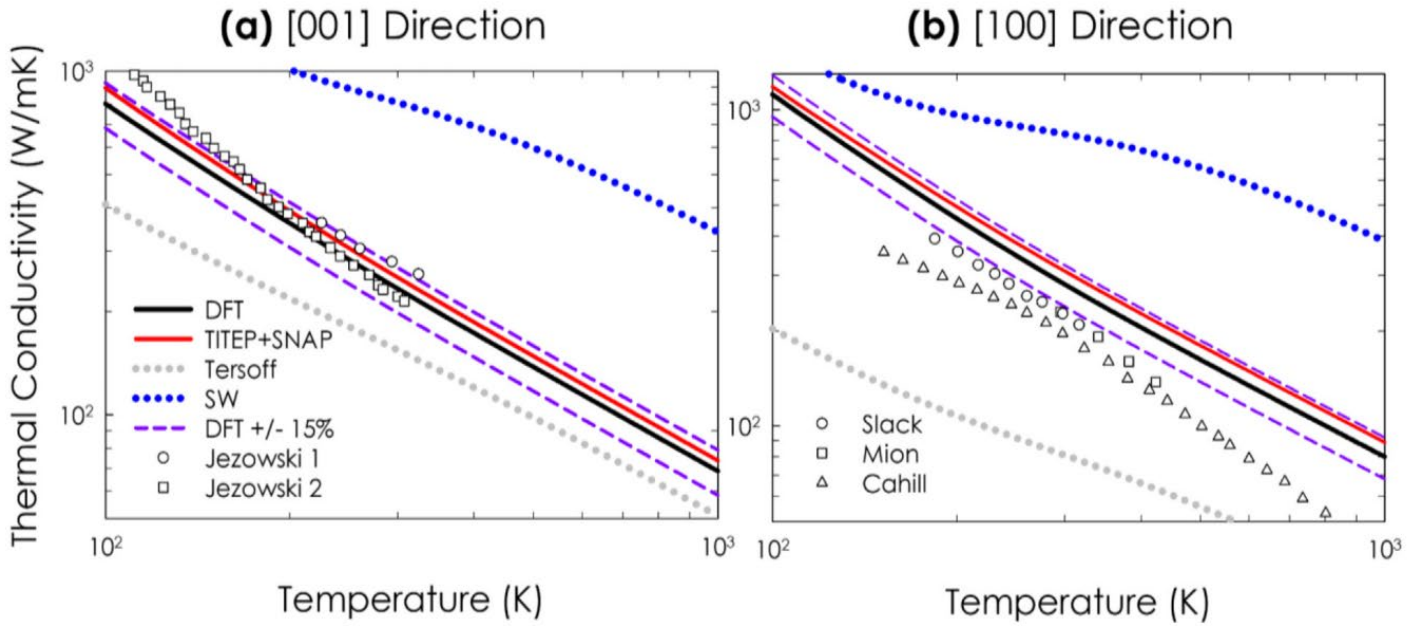
Accurate heat transfer simulations



Gallium nitride

$$E = \frac{1}{2}\sum_{ij} K_{ij} u_i u_j + E_{SNAP}$$





Rohskopf, Andrew, et al. "Fast & accurate interatomic potentials for describing thermal vibrations." *Computational Materials Science* 184 (2020): 109884.

Backup Slides

Mode coordinates

$$X_n = \sum_{i,\alpha} \sqrt{m_i} u_i^\alpha e_{ni}^\alpha$$

$$\dot{X}_n = \sum_{i,\alpha} \sqrt{m_i} v_i^\alpha e_{ni}^\alpha$$