Simulating Thermal Conductivity

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- Molecular Dynamics
  - Background
  - What is required
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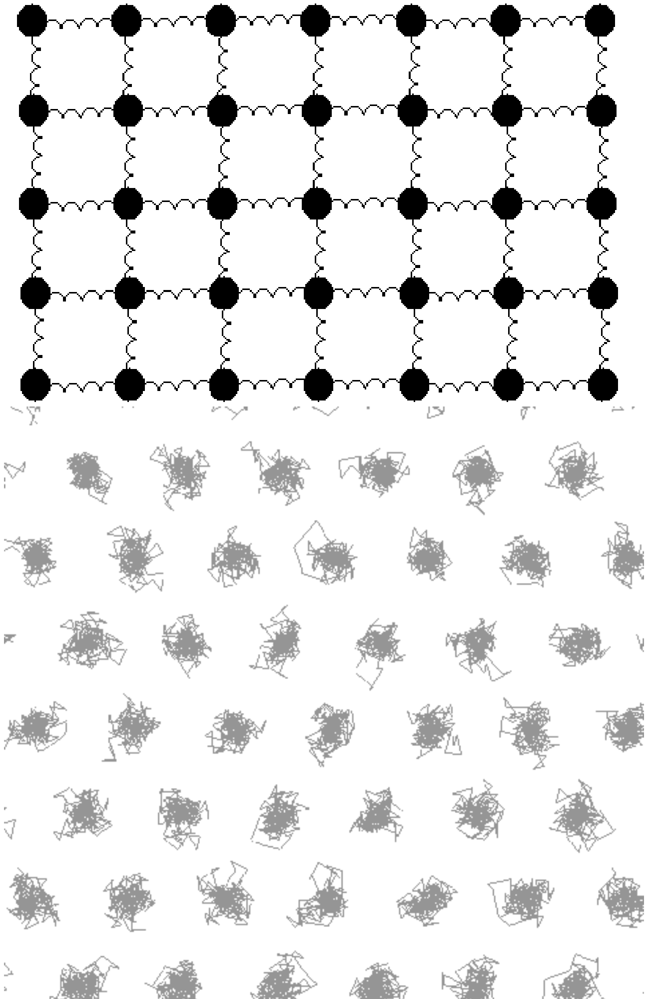


Microscopic view

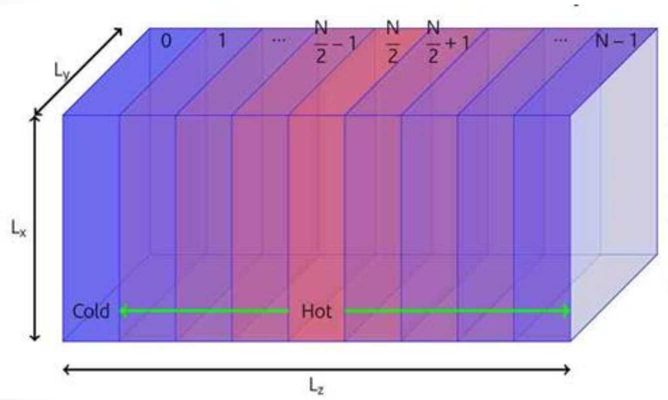
- Heat is transferred by conduction when adjacent atoms or molecules collide.
- Conduction is greater in solids because the close proximity of atoms helps them to transfer energy between them by vibration.
- Hence, KEY: simulating molecular vibrations

A collective vibration of atoms in the crystal forms a wave of allowed *wavelength* and *amplitude*.

Just as light expresses wave motion that is considered as composed of particles called photons, we can think of the normal modes of vibration in a solid as being particle-like. **Quantum of lattice vibration is called the *phonon***.

Microscopic view: κ_{Latt}

Thermoelectric Figure of Merit



Seebeck coefficient

Electrical conductivity

$$ZT = \frac{S^2\sigma T}{\kappa_{Elec} + \kappa_{Latt}}$$

Electronic + lattice thermal conductivity

Figure of merit

The contribution of a phonon mode to the thermal conductivity, κ_{Latt}, equals

(i) how much energy can be stored in it [modal heat capacity]

multiplied by

(ii) how fast it propagates through the material [group velocity]

multiplied by

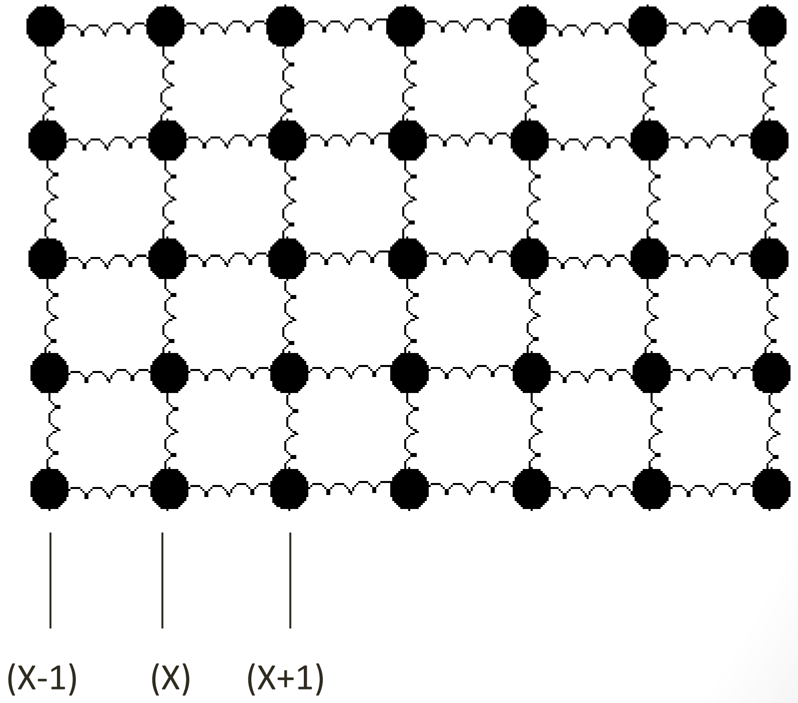
(iii) how long it lives before being scattered [lifetime].

Uniform Solid

In a uniform solid material comprised of atoms arranged in a regular lattice the interactions between them mean that they cannot vibrate independently.

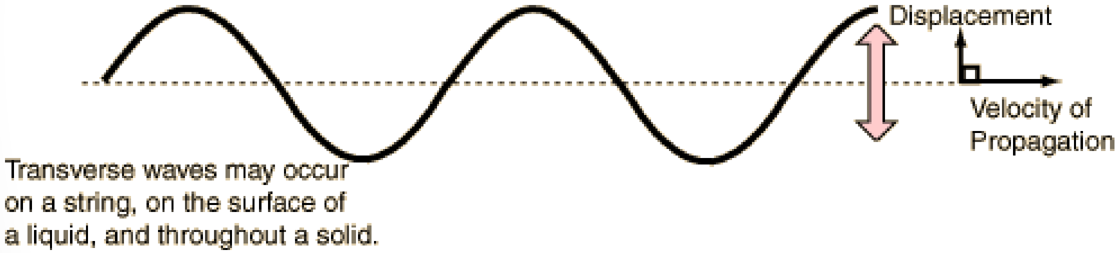
These vibrations take the form of collective modes which propagate through the material.

There will be 3N modes, where N is the number of atoms in the unit cell.

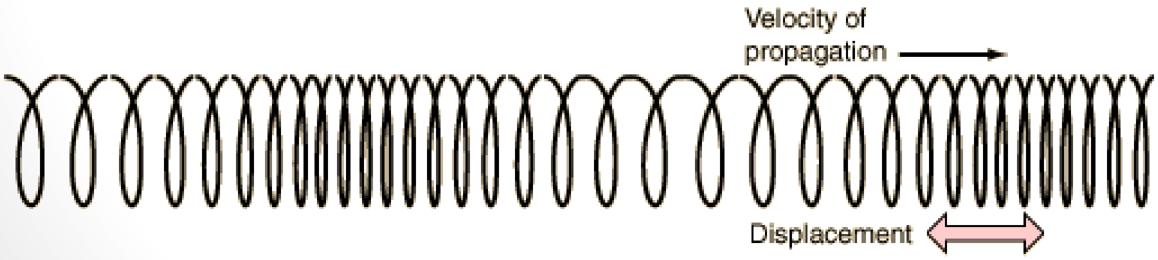


One Atom per unit cell

- 3 Vibrational Models
- Acoustic / Travelling Waves



Transverse wave x2

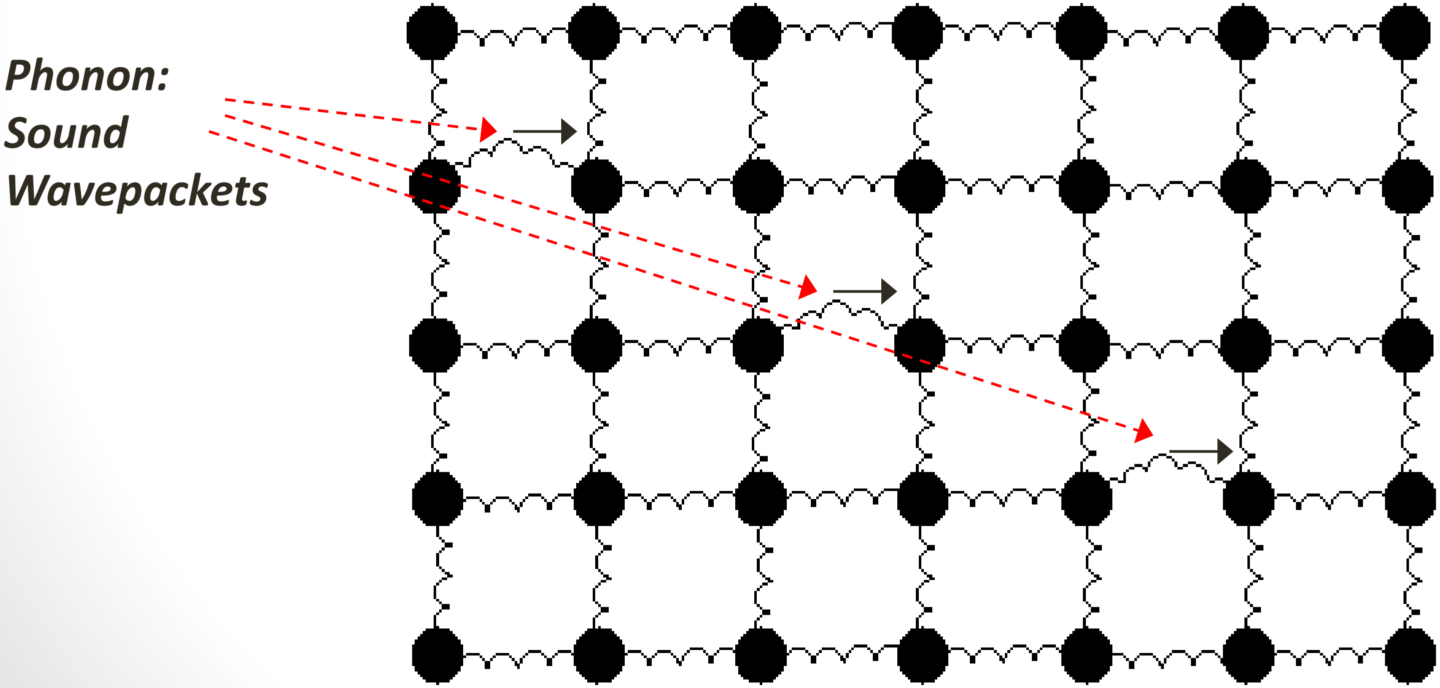


Longitudinal wave

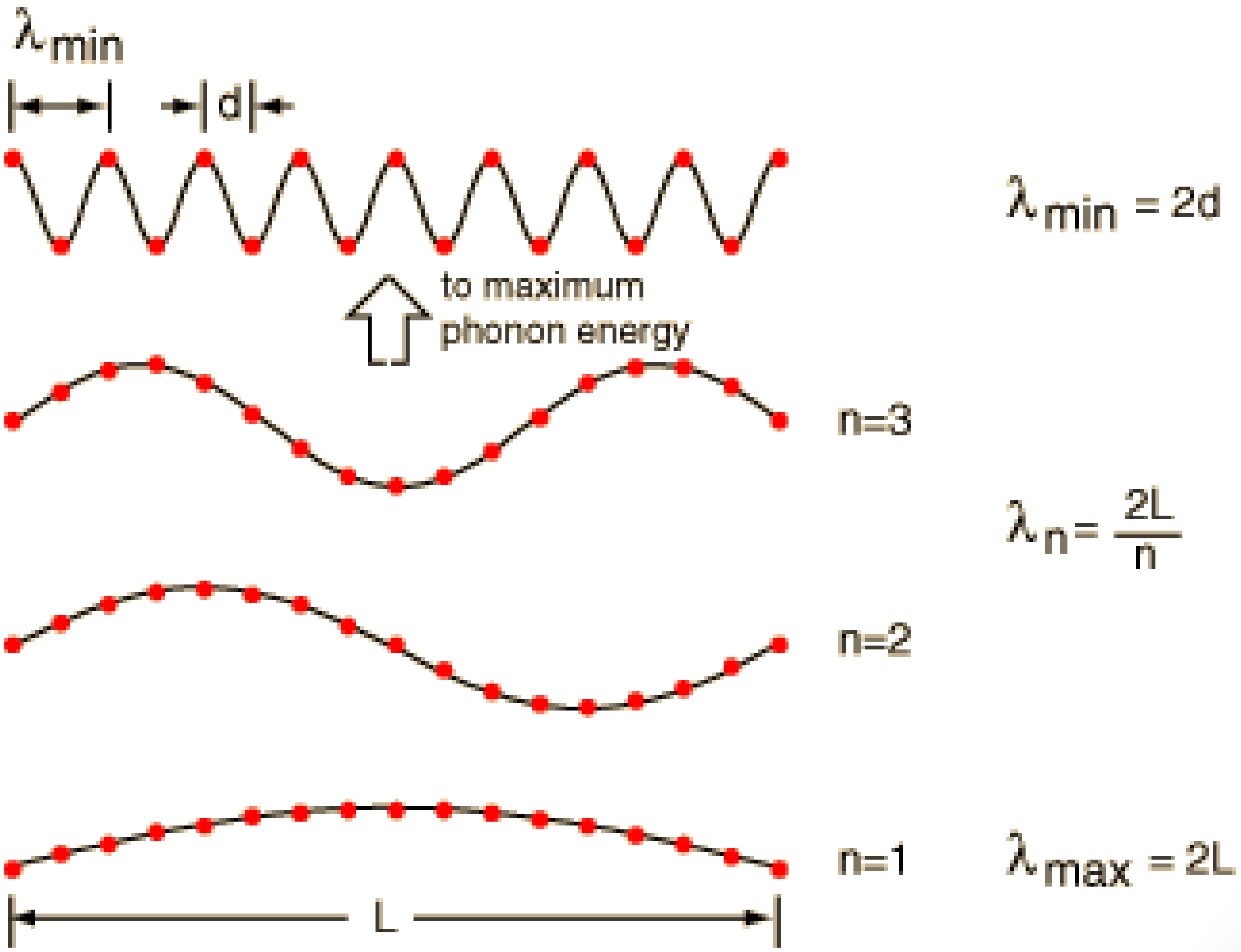
Acoustic Wave

Propagating lattice vibrations can be considered to be sound waves, and their propagation speed is the speed of sound in the material.

And may be different in different directions



Solid is a periodic array of atoms and there are constraints on both the minimum and maximum wavelength associated with a vibrational mode.

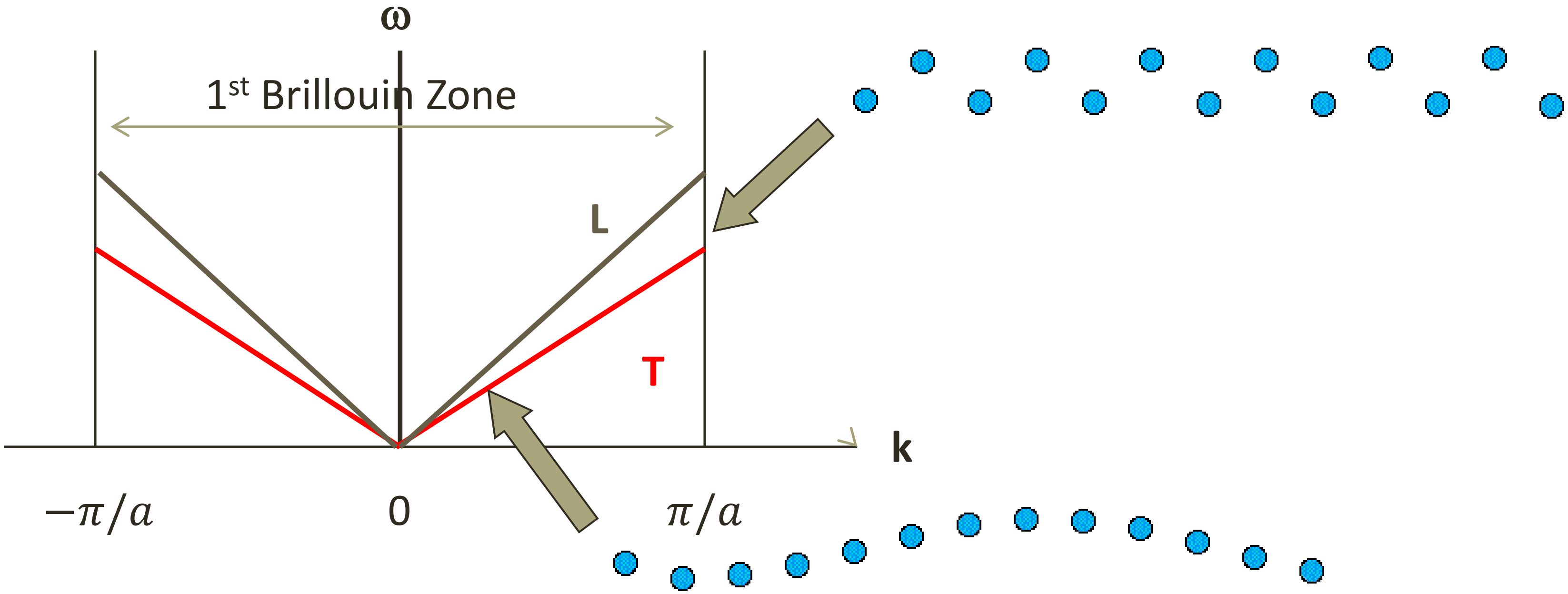


Wave Vectors, **k**

- It is usually convenient to consider phonon wave vectors **k** which have the smallest magnitude (|**k**|) in their "family". The set of all such wave vectors defines the *first Brillouin zone*.
- Additional Brillouin zones may be defined as copies of the first zone, shifted by some reciprocal lattice vector.

Wave Vectors, **k**

- One atom per unit cell

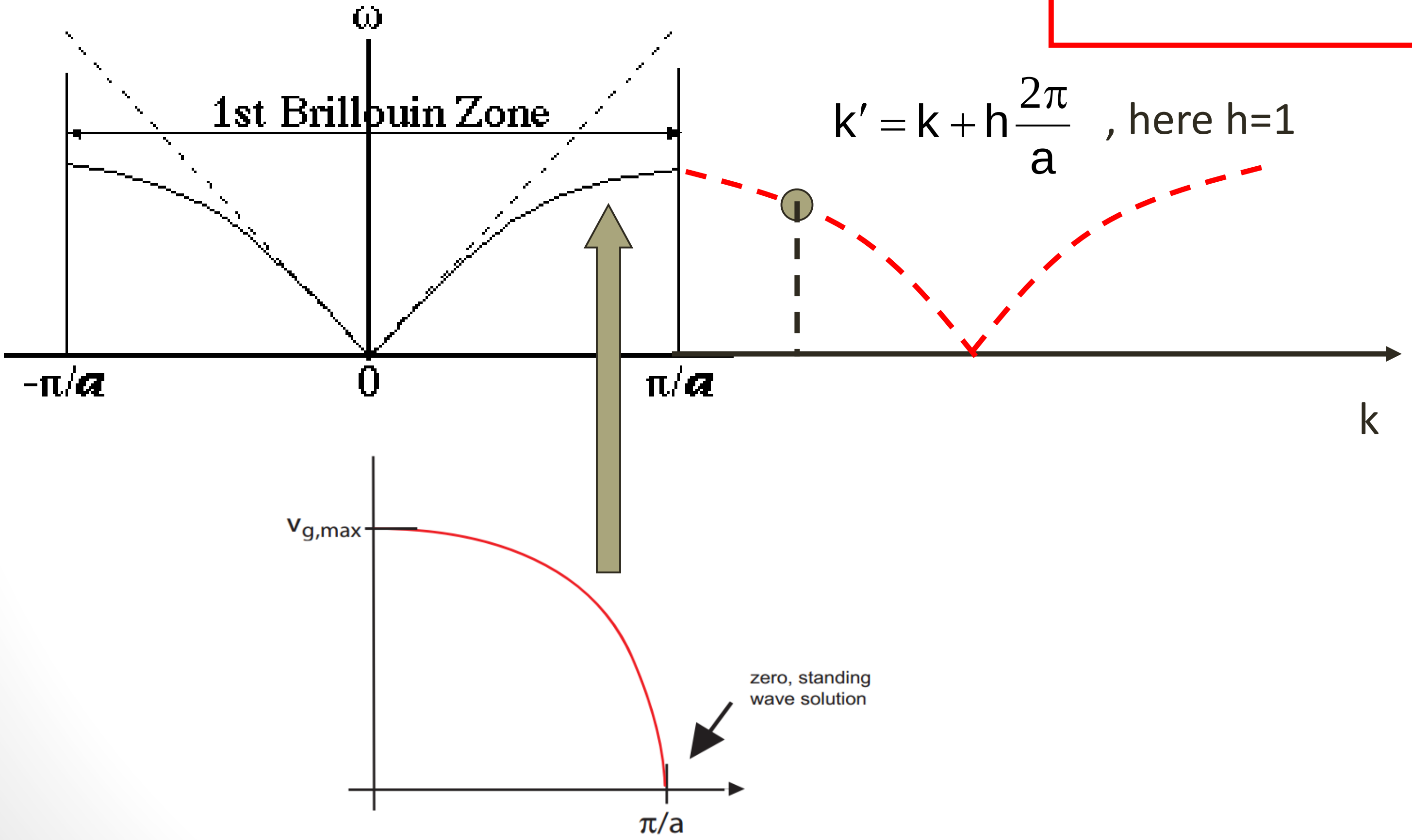


- Slope is speed of sound
- Longitudinal waves travel faster than transverse (slope of LA bigger than slope of TA)

Wave Vectors, **k**

- One atom per unit cell

Region $-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$ is called first Brillouin zone



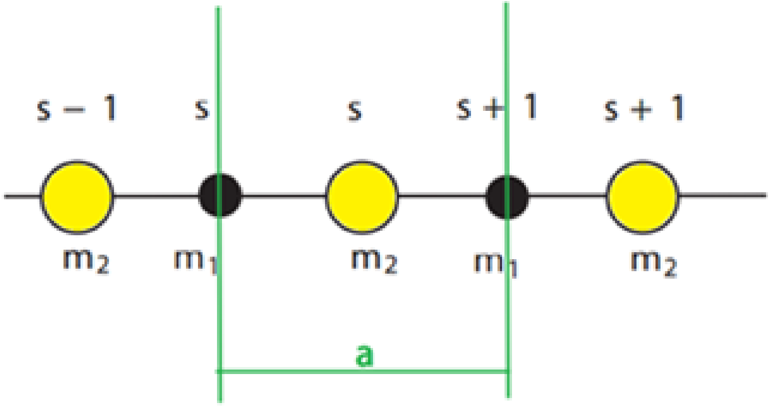
$k' = k + h\frac{2\pi}{a}$, here h=1

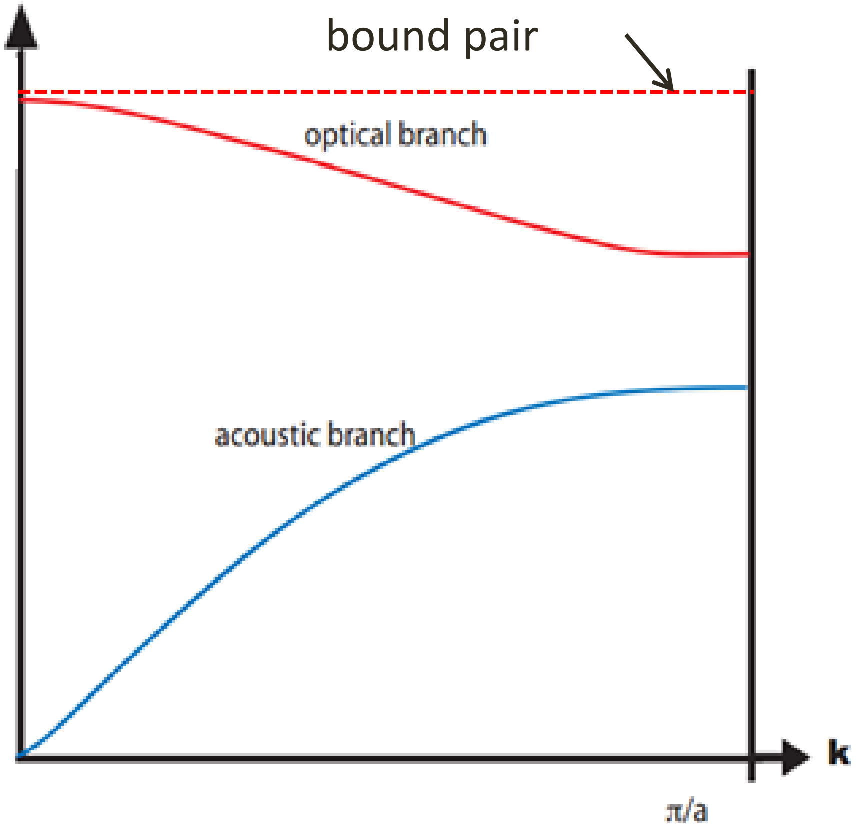
N Atoms per cell

- Acoustic phonons occur when wave numbers are small (i.e. long wavelengths) and correspond to sound transmission in crystals. Acoustic phonons vary depending on whether they are longitudinal or transverse
- "Optical phonons," which arise in crystals that have more than one atom in the unit cell. They are called "optical" because in ionic crystals are often excited by light (e.g. by infrared radiation in NaCl).

N Atoms per cell

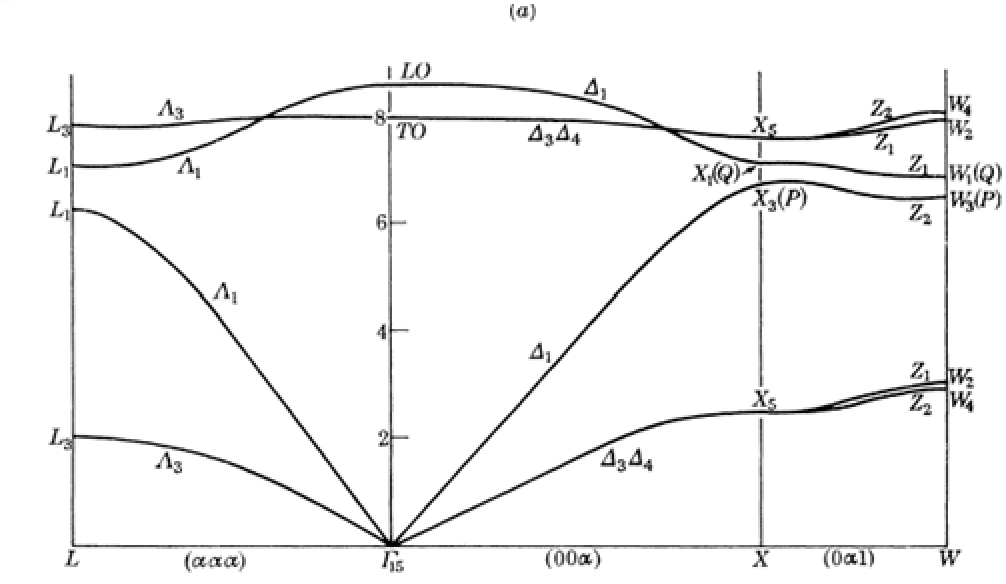
- 3N vibrational branches,
  - 3 Acoustic (1LA + 2TA)
  - 3N-3 Optic (N-1 Longitudinal Optic (LO) + 2N-2 Transverse Optic (TO))



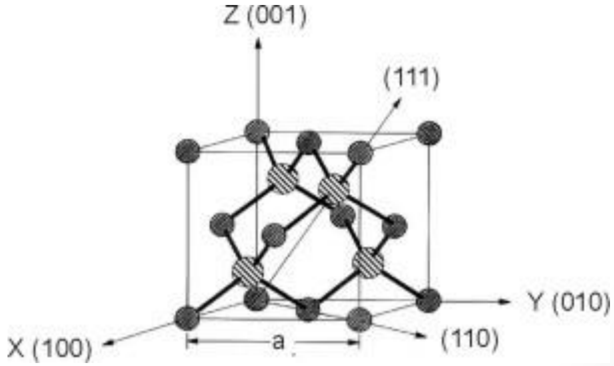

bound pair

N Atoms per cell

- 3N vibrational branches,
  - 3 Acoustic (1LA + 2TA)
  - 3N-3 Optic (N-1 Longitudinal Optic (LO) + 2N-2 Transverse Optic (TO))
  - Different behaviour in different directions



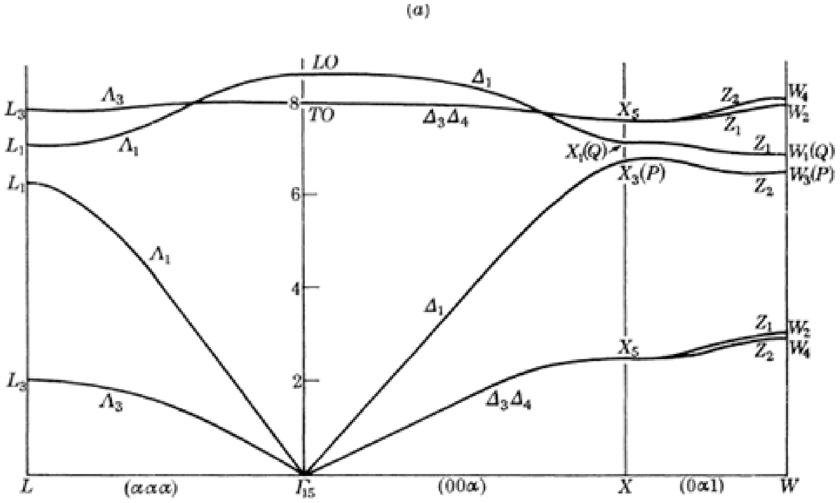
Calculated phonon dispersion relation of GaAs (zincblende structure)



Adapted from:
H. Montgomery, " The symmetry of lattice vibrations in zincblende and diamond structures", Proc. Roy. Soc. A. 309, 521-549 (1969)

Summary

- To get a good description of the vibrational frequencies in a solid we need to be able to calculate the frequency at different wave vectors, **k**.
- The calculation of this dependence called Lattice Dynamics
- In general, the challenge for simulation is to represent this diversity.



What is lattice dynamics…?

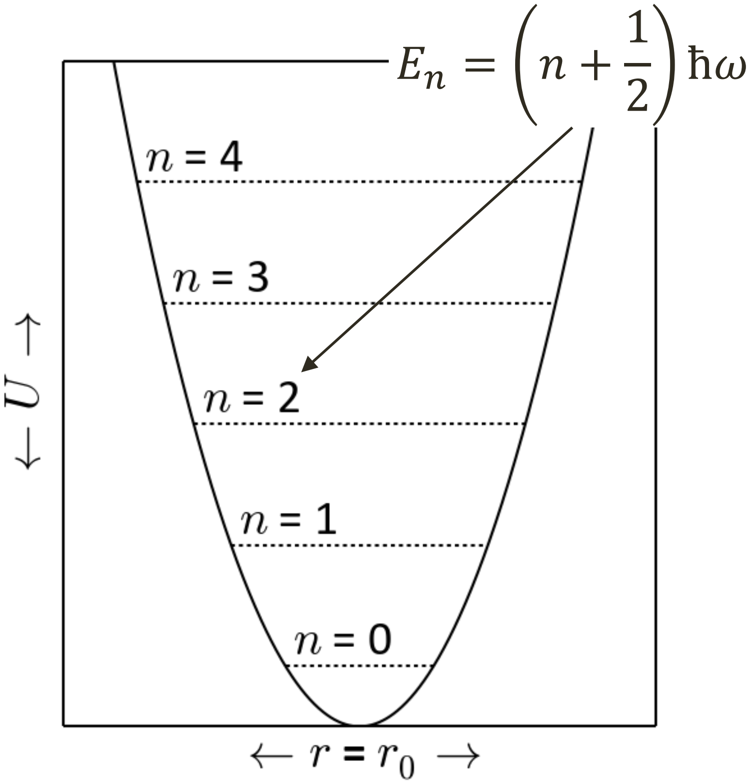
- *A theoretical framework for modelling the phonons in periodic solids*

… and what can we do with it?

- Get an atomistic view of thermal motion in crystals - e.g. displacement ellipsoids in X-ray structures
- Simulate vibrational spectra - e.g. IR, Raman, THz…
- Study thermodynamics - contributions to free energy and entropy
- Model structure and properties at finite temperature - thermal expansion, bulk moduli, *etc.*
- Understand certain types of phase transitions
- Calculate transport properties (e.g. thermal conductivity)

The harmonic approximation

- The simplest quantum-mechanical model for vibrations - but it works



$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

$$\boldsymbol{F} = -\mu\omega^2(\boldsymbol{r} - \boldsymbol{r}_0)$$

$$U = \frac{1}{2}\mu\omega^2|\boldsymbol{r} - \boldsymbol{r}_0|^2$$

Models a crystal with 3*N* atoms in the unit cell as *3N* independent oscillators

Phonons modelled as waves with an associated reciprocal-space wavevector ***k*** (3*N* modes/***k***-point)

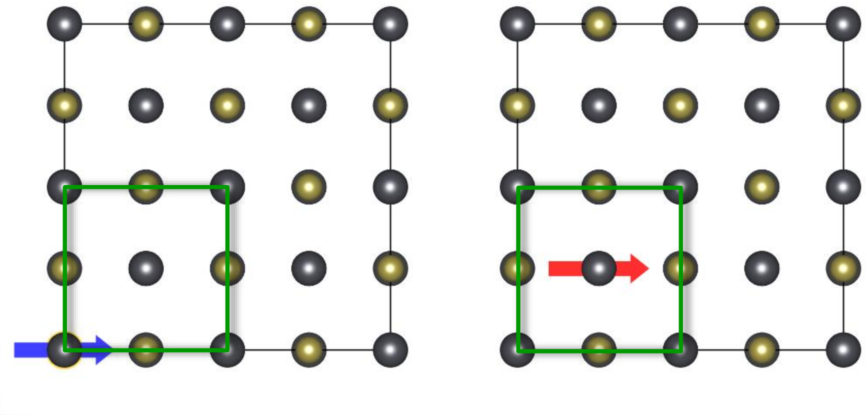
Can calculate using standard electronic structure codes:
e.g. *VASP, Wien2k, Abinit, Pwscf*
NOTE: convention – use **q** for phonons and **k** for electrons

The finite-displacement method

- The key thing we need to calculate are the force-constant matrices

$$\Phi_{\alpha\beta}(il, jl') = -\frac{\partial F_{\alpha}(il)}{\partial r_{\beta}(jl')}$$

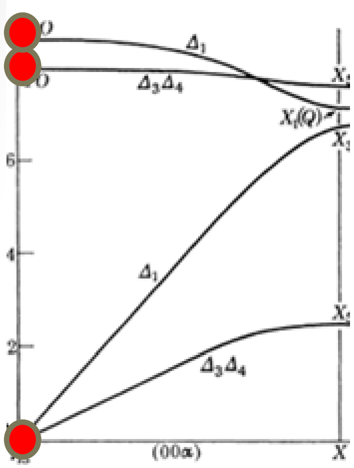
- The most straightforward way to do this is by physically moving atoms a small distance from their equilibrium position, and computing the forces



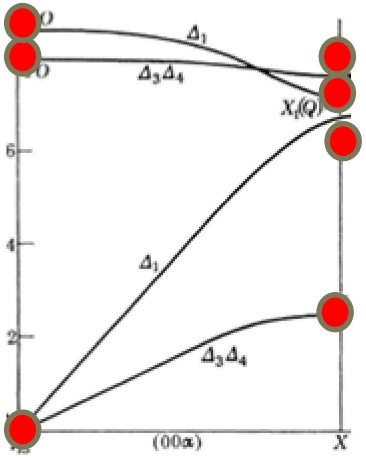
In principle, need to displace every atom forward and backward along x, y and z, but this can be reduced by symmetry

Phonopy: phonon code (http://phonopy.sf.net)

Supercells



Single unit cell

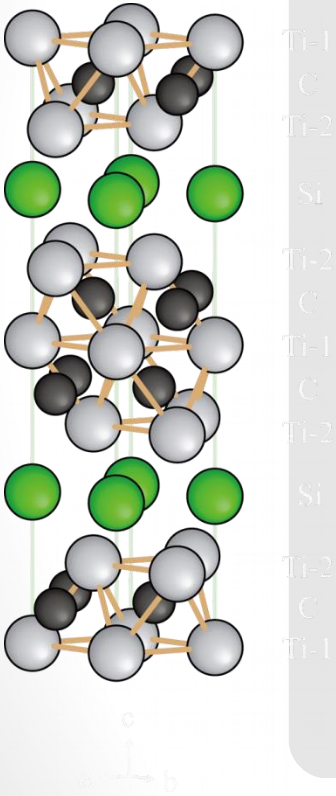


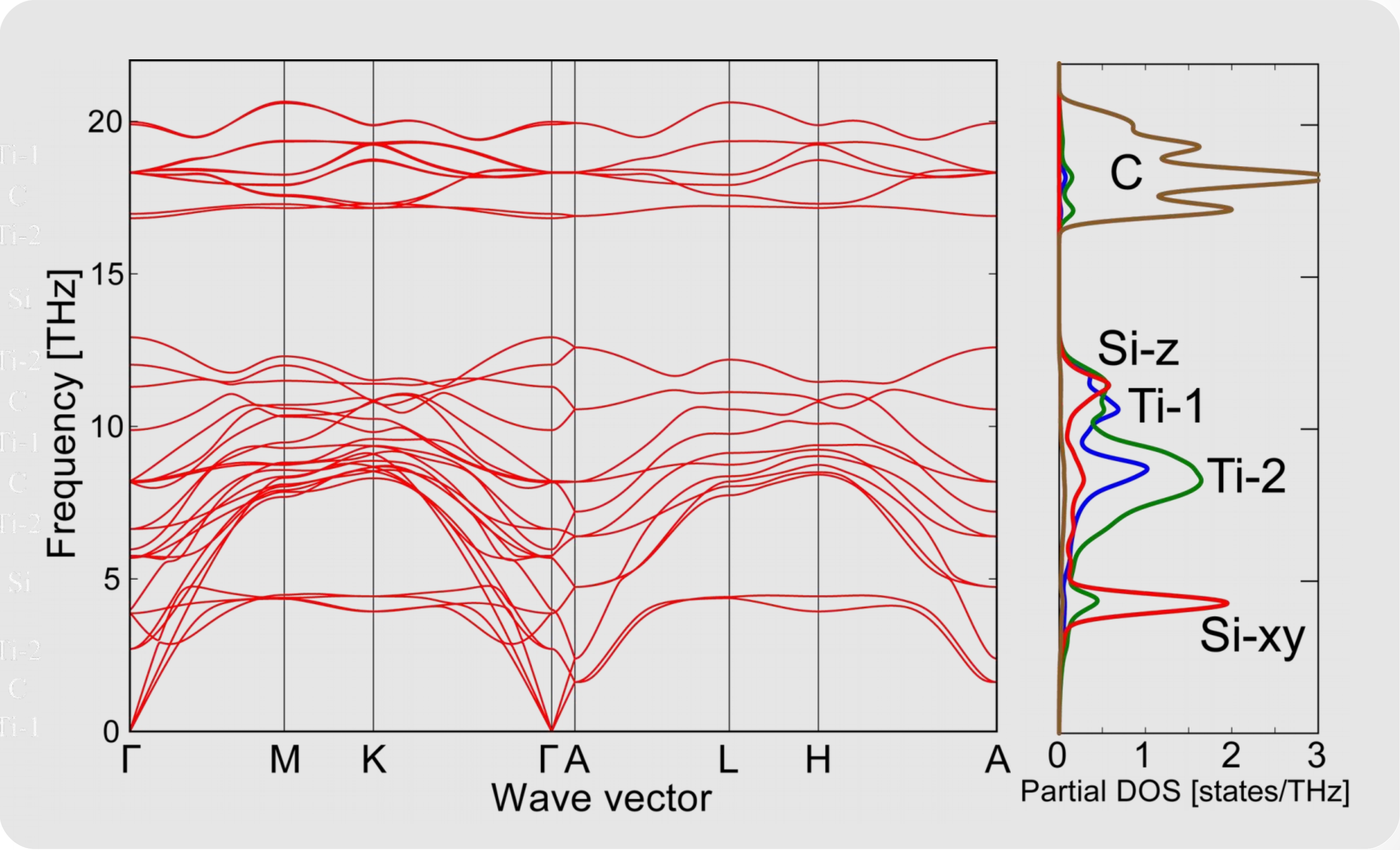
Doubled unit cell

Red: Calculated frequencies

- To be sure of reproducing the dispersion curves need to consider larger supercells (e.g. 4 times the unit cell size would give 4 sets of points).

Phonon band structure of Ti_3SiC_2

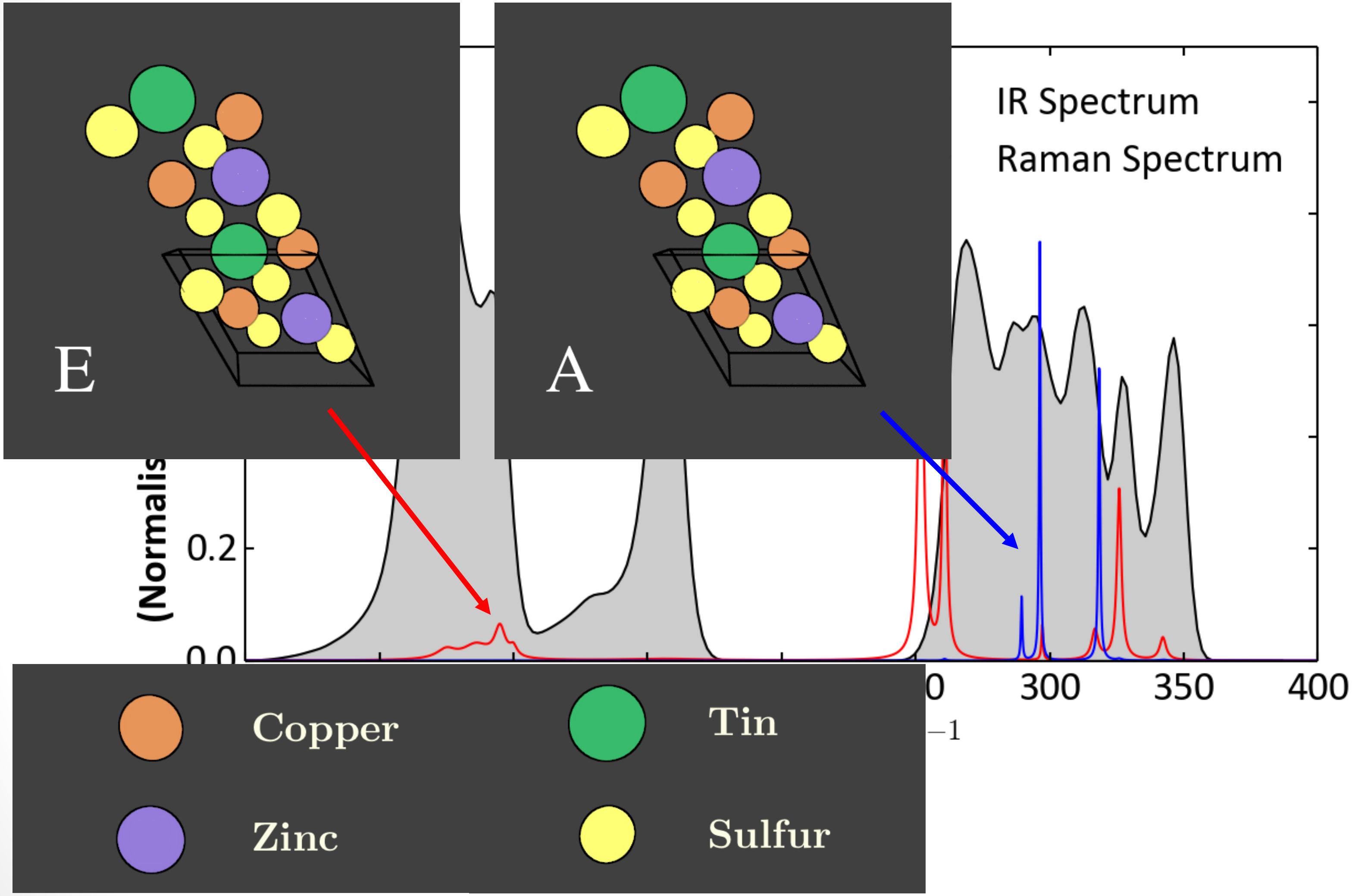




Togo *et al*., Phys. Rev. B **81**, 174301 (2010)

Localized bands at ~5 THz

Modelling vibrational spectra: Cu_2ZnSnS_4



J Skelton

Calculating κ_{Latt}

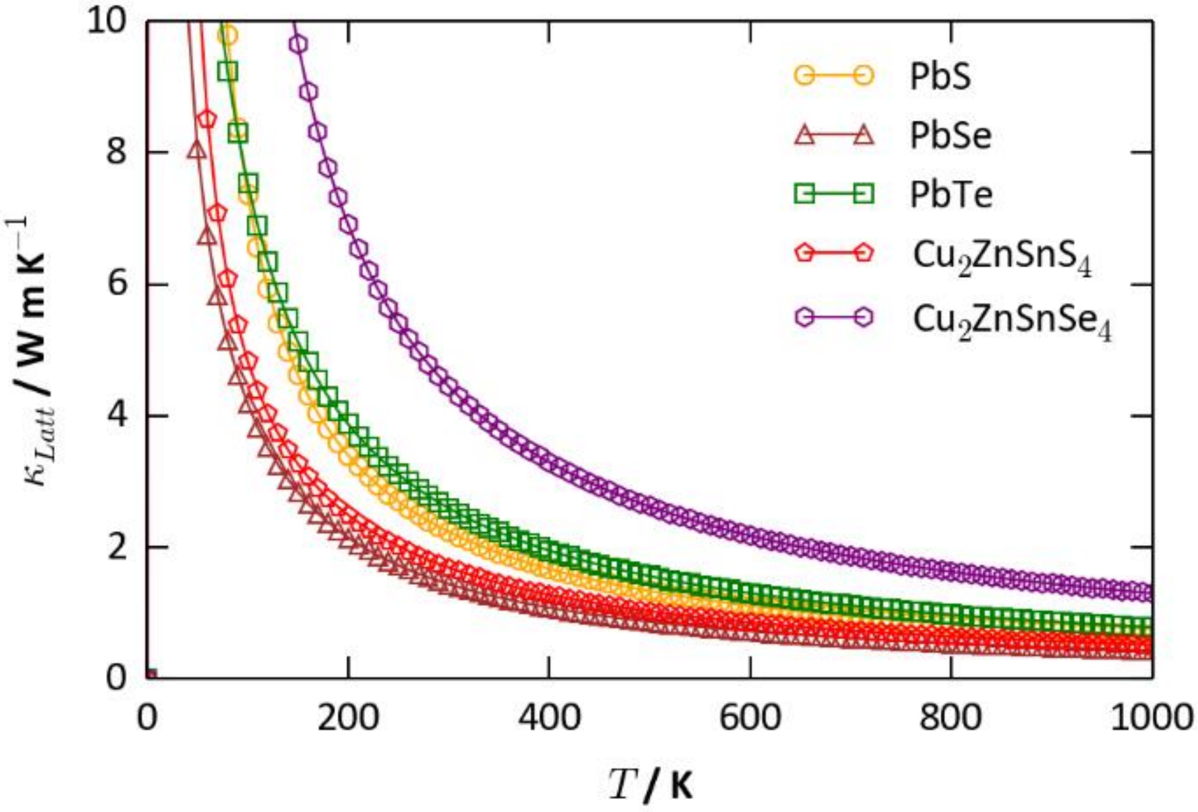
- Finite κ_{Latt} arises from phonon-phonon interactions, and to model these we need to evaluate the third order force constants:

$$\Phi_{\alpha\beta\gamma}(il, jl', kl'') = -\frac{\partial F_{\alpha}(il)}{\partial r_{\beta}(jl')\partial r_{\gamma}(kl'')}$$

- Similar computational requirements to a harmonic calculation, but need to run force calculations on many more displaced structures

	System	# Atoms (SC)	# Disp 2nd	# Disp 3rd (2x2x2 SC)
☺	PbTe	2 (16)	2	62
😐	Cu_2ZnSnS_4	8 (64)	14	5,390
☹	*c*$MAPbI_3$	12 (96)	72	41,544

Quaternary semiconductors as thermoelectrics?



J. M. Skelton *et al.*, *APL Materials* **3**, 041102 (**2015**)

“Practical” Theory

Force-constant matrix: $\Phi_{\alpha\beta}(il, jl') = \dfrac{\partial^2 E}{\partial r_\alpha(l)\partial r_\beta(l')} = -\dfrac{\partial F_\alpha(il)}{\partial r_\beta(jl')}$

From finite differences: $\Phi_{\alpha\beta}(il, jl') \approx -\dfrac{F_\alpha(il)}{\Delta r_\beta(jl')}$

Sum over atom j in adjacent unit cells l' -> supercell expansion to improve accuracy

Dynamical matrix: $D_{\alpha\beta}(i, j, \mathbf{q}) = \dfrac{1}{\sqrt{m_i m_j}} \sum_{l'} \Phi_{\alpha\beta}(i0, jl') \exp[i\mathbf{q}.(\boldsymbol{r}(jl') - \boldsymbol{r}(i0))]$

After diagonalisation: $e(\mathbf{q}).\Omega(\mathbf{q}) = D(\mathbf{q}).e(\mathbf{q})$

- The force constant matrices $\Phi_{\alpha\beta}(il, jl')$ can be calculated by `phonopy` from finite-displacement calculations, or directly from some codes using e.g. internal DFPT or finite-differences

[Hopefully digestible] theory

- Start from the top, and work backwards...:

$$\boldsymbol{\kappa}_L\,(T) = \frac{1}{NV_0}\sum_{\lambda} C_{V,\lambda}(T)\boldsymbol{v}_{\lambda} \otimes \boldsymbol{v}_{\lambda}\tau_{\lambda}(T)$$ [Single-Mode Relaxation Time Model]

$\boldsymbol{\kappa}_L\,(T)$:= lattice thermal conductivity

$C_{V,\lambda}(T)$:= modal (const. V) heat capacity

$\boldsymbol{v}_{\lambda}$:= mode group velocity

$\tau_{\lambda}(T)$:= mode lifetime

λ := phonon mode (w/ associated ω_{λ} and $\mathbf{q}_{\lambda}$)

$\otimes$:= tensor product

[Hopefully digestible] theory

- The modal heat capacity $C_{V,\lambda}$ and group velocity $\boldsymbol{v}_\lambda$ are harmonic quantities:

$$\boldsymbol{\kappa}_L\ (T) = \frac{1}{NV_0}\sum_\lambda C_{V,\lambda}(T)\boldsymbol{v}_\lambda \otimes \boldsymbol{v}_\lambda \tau_\lambda(T)$$

$$C_{V,\lambda} = k_B\left(\frac{\hbar\omega_\lambda}{k_BT}\right)^2 \frac{\exp(\hbar\omega_\lambda/k_BT)}{[\exp(\hbar\omega_\lambda/k_BT)-1]^2}$$

$$n_\lambda(T) = \frac{1}{\exp(\hbar\omega_\lambda/k_BT)-1}$$

$$\boldsymbol{v}_\lambda = \frac{\partial\omega_\lambda}{\partial\mathbf{q}}$$

ω_λ := phonon frequency

$n_\lambda(T)$:= phonon occupation number

[Hopefully digestible] theory

- The mode lifetimes, $\tau_{\mathbf{q}\lambda}(T)$, come from the phonon linewidths, which are the imaginary parts of the self energies in MBPT

$$\tau_\lambda(T) = \frac{1}{2\Gamma_\lambda(\omega_\lambda, T)}$$

Self-energy expression is defined for all ω, not just ω_λ, but ω_λ does enter into $\phi_{-\lambda\lambda'\lambda''}$

$$\Gamma_\lambda(\omega, T) = \frac{18\pi}{\hbar^2} \sum_{\lambda'\lambda''} \left|\phi_{-\lambda\lambda'\lambda''}\right|^2$$

Phonon occupation numbers

$$\times \left\{ \left(n_{\lambda'}(T) + n_{\lambda''}(T) + 1\right)\delta\left(\omega - \omega_{\lambda'} - \omega_{\lambda''}\right) \right.$$

Conservation of energy

$$\left. + \left(n_{\lambda'}(T) - n_{\lambda''}(T)\right)\left[\delta\left(\omega + \omega_{\lambda'} - \omega_{\lambda''}\right) - \delta\left(\omega - \omega_{\lambda'} + \omega_{\lambda''}\right)\right] \right\}$$

$\phi_{-\lambda\lambda'\lambda''}$:= three-phonon interaction strength

[Hopefully digestible] theory

- Finally, the three-phonon interactions can be obtained from the third-order interatomic force-constant matrices (IFCs), $\phi_{\alpha\beta\gamma}(0j, l'j', l''j'')$

$$\phi_{\lambda\lambda'\lambda''} = \frac{1}{\sqrt{N}}\frac{1}{3!}\sum_{jj'j''}\sum_{\alpha\beta\gamma} W_{\alpha}(j,\lambda)W_{\beta}(j',\lambda')W_{\gamma}(j'',\lambda'')$$

Phonon eigenvectors

Sum over atoms

Sum over Cartesian coordinates

$$\times \sqrt{\frac{\hbar}{2m_j\omega_\lambda}}\sqrt{\frac{\hbar}{2m_{j'}\omega_{\lambda'}}}\sqrt{\frac{\hbar}{2m_{j''}\omega_{\lambda''}}}$$

Atomic positions

$$\times \sum_{l'l''}\phi_{\alpha\beta\gamma}(0j, l'j', l''j'')e^{i\mathbf{q}'[\mathbf{r}(l'j')-\mathbf{r}(0j)]}e^{i\mathbf{q}''[\mathbf{r}(l''j'')-\mathbf{r}(0j)]}$$

$$\times e^{i(\mathbf{q}+\mathbf{q}'+\mathbf{q}'').\mathbf{r}(0j)}\Delta(\mathbf{q}+\mathbf{q}'+\mathbf{q}'')$$

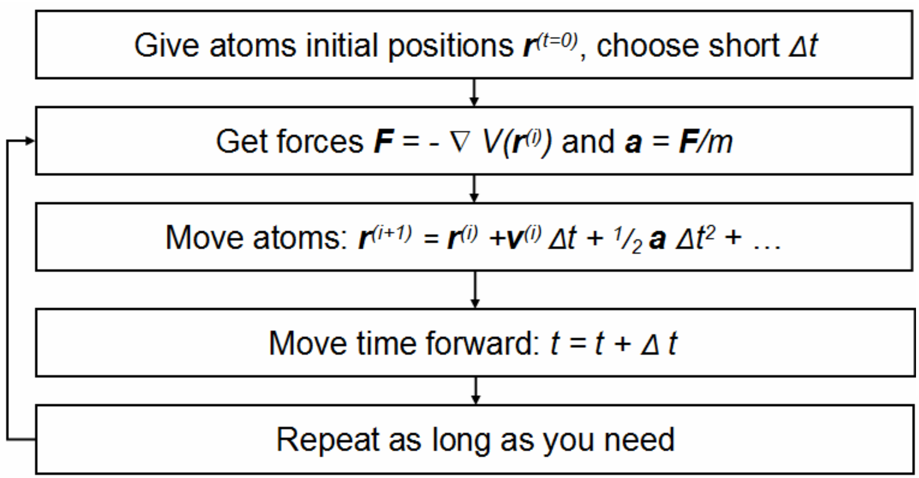
1 if the sum is a reciprocal lattice vector, 0 otherwise; imposes conservation of momentum

Lattice Dynamics: Summary

- Strength is that it is generally based on the quantised harmonic oscillator, and the vibrational frequencies can be calculated directly from the dynamical matrix.
- Strength is that can be used to calculate a wide range of properties, and investigate phase stability, spectroscopy.
- Strength is that can easily be used in conjunction with DFT codes.
- Weakness is that it misses intrinsic anharmonicity (although work is ongoing to include these terms, e.g. self consistent phonon theory: x^4…) and dynamical matrix (3N x 3N) (N=number of atoms in cell) can become to be too large for routine computation.
- An approach which includes intrinsic anharmonicity and can be readily applied to large systems is via Molecular Dynamics..

Modelling Methods – Molecular Dynamics

- Acceleration calculated from particle interactions
- Atom positions updated based on current velocities and calculated accelerations
- Repeat in a series of discrete “timesteps” (Δt) to dynamically evolve the system
- Using the LAMMPS code



Give atoms initial positions $\boldsymbol{r}^{(t=0)}$, choose short Δt

Get forces $\boldsymbol{F} = -\nabla V(\boldsymbol{r}^{(i)})$ and $\boldsymbol{a} = \boldsymbol{F}/m$

Move atoms: $\boldsymbol{r}^{(i+1)} = \boldsymbol{r}^{(i)} + \boldsymbol{v}^{(i)}\Delta t + {}^{1}\!/_{2}\,\boldsymbol{a}\,\Delta t^2 + \ldots$

Move time forward: $t = t + \Delta t$

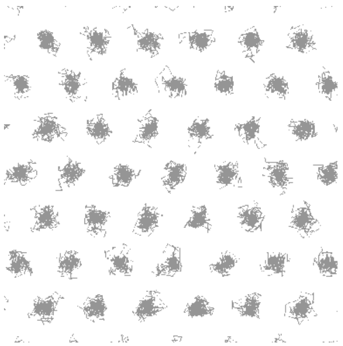
Repeat as long as you need

S.J. Plimpton, *JOURNAL OF COMPUTATIONAL PHYSICS*, 117, 1, 1, 1995. http://lammps.sandia.gov

Modelling Methods – Molecular Dynamics

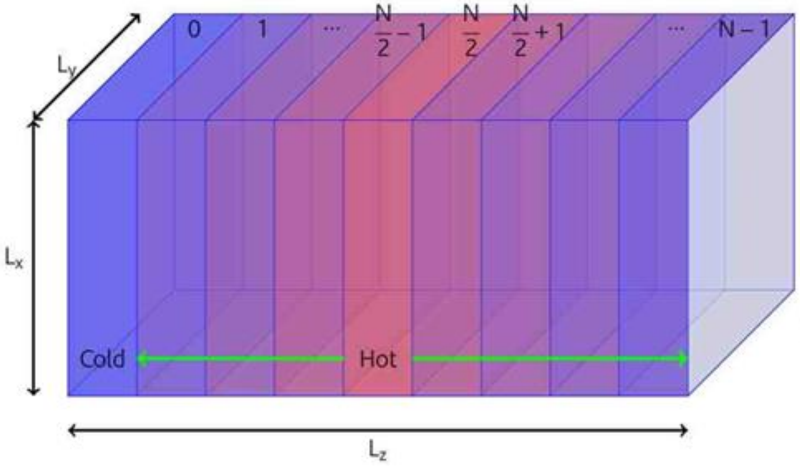
Ab Initio MD feasible, but generally use force field approaches

- **Green Kubo**



- Considers Crystal is in equilibrium
- Calculates heat flux
- Slow to converge
- 3 D approach

- **Non-Equilibrium MD**



- 1 D approach,
- gives higher values than GK

[1] A. Torres-Sánchez, J. M. Vanegas, and M. Arroyo, Phys. Rev. Lett., 114, p. 258102, Jun 2015, doi: 10.1103/PhysRevLett.114.258102.

[2] U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee, and L. G. Pedersen, The Journal of Chemical Physics, 103(19), p. 8577, 1995, doi: http://dx.doi.org/10.1063/1.470117.

[3] R. Zwanzig, Annual Review of Physical Chemistry, 16(1), p. 67, 1965, doi: 10.1146/annurev.pc.16.100165.000435.

[4] F. Müller-Plathe, The Journal of Chemical Physics, 106(14), p. 6082, 1997, doi: http://dx.doi.org/10.1063/1.473271.

[5] D. Bedrov and G. D. Smith, The Journal of Chemical Physics, 113(18), p. 8080, 2000, doi: http://dx.doi.org/10.1063/1.1312309.

[6] T. W. Sirk, S. Moore, and E. F. Brown, The Journal of Chemical Physics, 138(6), p. , 2013, doi: http://dx.doi.org/10.1063/1.4789961.

[7] B.-Y. Cao, The Journal of Chemical Physics, 129(7):074106, 2008, doi: http://dx.doi.org/10.1063/1.2969762.

Green-Kubo Method

- A dynamical method of calculating thermal conductivity from a system in **EQUILIBRIUM**.
  - Avoids problems involved with imposing temperature gradients
  - Includes all anharmonicity explicitly (rather than to some low level approximation as found in lattice dynamics)
- Calculate the heat-flux of the system every few timesteps during a long simulation (5-20 ns)
- Autocorrelate the heat-flux in each dimension
- Integrate the autocorrelations and multiply by constants to get the thermal conductivity
  - Gives the thermal conductivity in each dimension from a **SINGLE** calculation

M.S. Green , J. Chem. Phys., 1954, **22**, 398.

The Heat-Flux

$$\boldsymbol{J} = \left[\sum_i e_i \boldsymbol{v}_i - \sum_i \boldsymbol{S}_i \boldsymbol{v}_i\right]$$

$$\boldsymbol{J} = \left[\sum_i e_i \boldsymbol{v}_i - \sum_{i<j} (\boldsymbol{f}_{ij} \cdot \boldsymbol{v}_j)\boldsymbol{r}_{ij}\right]$$

$$\boldsymbol{J} = \left[\sum_i e_i \boldsymbol{v}_i - \frac{1}{2}\sum_{i<j} \left(\boldsymbol{f}_{ij} \cdot (\boldsymbol{v}_i + \boldsymbol{v}_j)\right)\boldsymbol{r}_{ij}\right]$$

J = Heat flux
e_i = per-atom energy
v_i = per-atom velocity
S_i = per-atom stress
f_{ij} = force between atom i and j
r_{ij} = distance between atom i and j

M.S. Green , J. Chem. Phys., 1954, **22**, 398.

The Heat-Flux

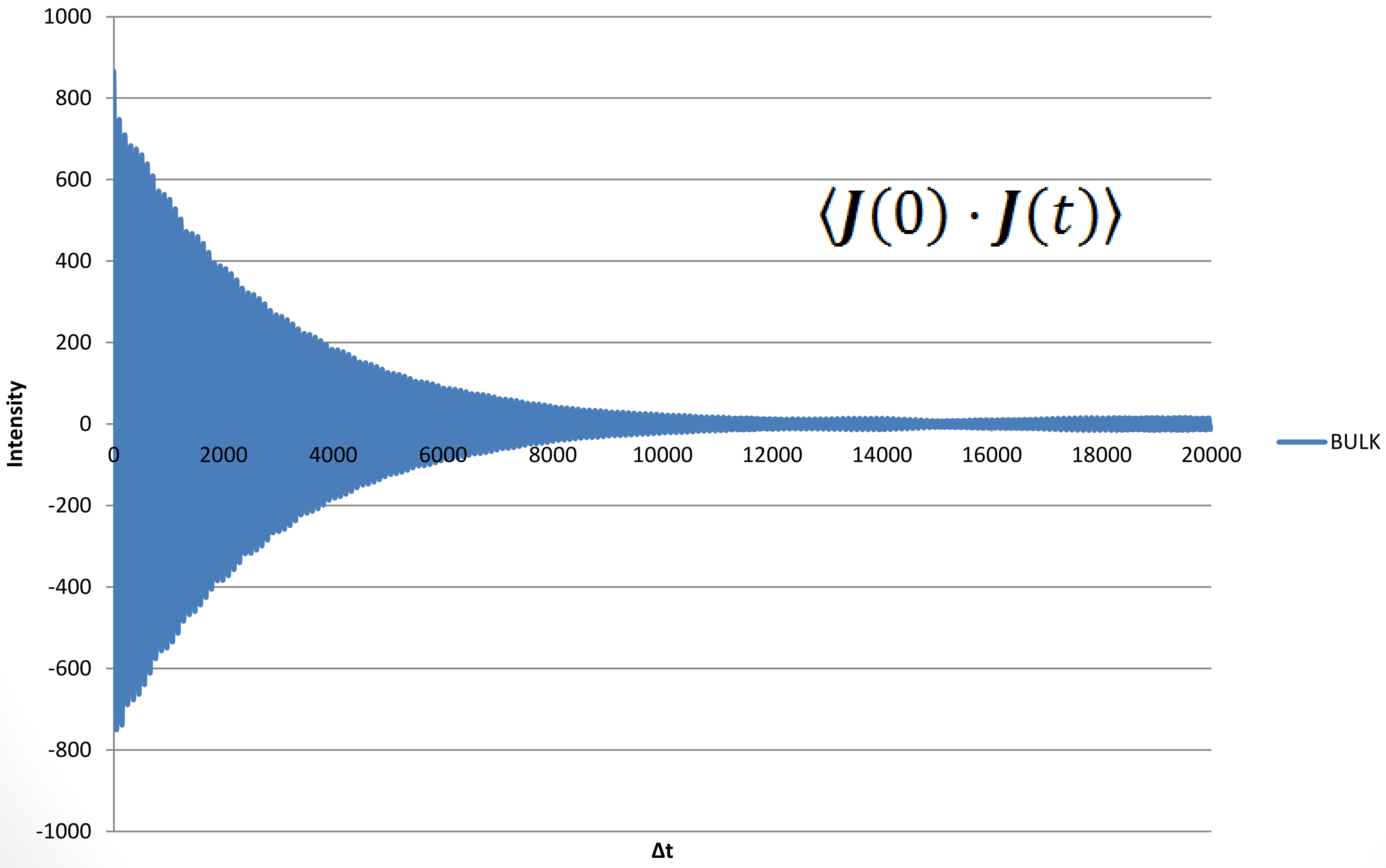
$$\boldsymbol{J} = \left[\sum_{i} e_i \boldsymbol{v}_i - \frac{1}{2}\sum_{i<j}\left(\boldsymbol{f}_{ij}\cdot\left(\boldsymbol{v}_i + \boldsymbol{v}_j\right)\right)\boldsymbol{r}_{ij}\right]$$

J = Heat flux
e_i = per-atom energy
v_i = per-atom velocity
S_i = per-atom stress
f_{ij} = force between atom i and j
r_{ij} = distance between atom i and j

- We have access to these quantities from the MD simulation time integration!
- Often easiest to output the heat-flux during the simulation and post-process the data
  - Avoids having to keep every heat-flux sample in memory
  - Heat-flux data from a restarted simulation can simply be appended
  - Decision of integral length can be delayed
  - Different autocorrelation integration methods can be tried

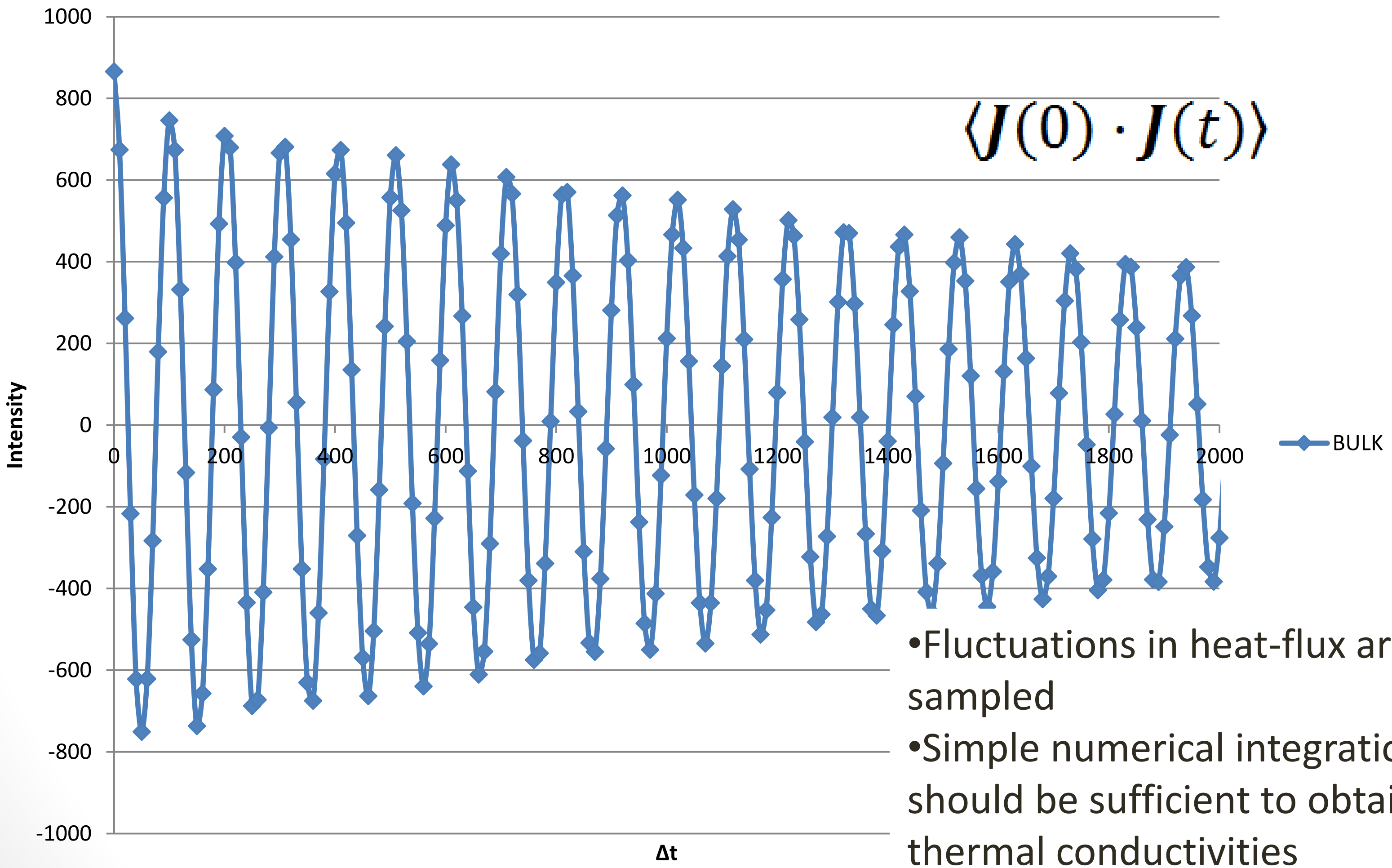
M.S. Green , J. Chem. Phys., 1954, **22**, 398.

Autocorrelation



$$\langle \boldsymbol{J}(0) \cdot \boldsymbol{J}(t) \rangle$$

Autocorrelation (fine detail)



$$\langle \boldsymbol{J}(0) \cdot \boldsymbol{J}(t) \rangle$$

- Fluctuations in heat-flux are well sampled
- Simple numerical integration should be sufficient to obtain good thermal conductivities
  - i.e. Trapezoidal rule

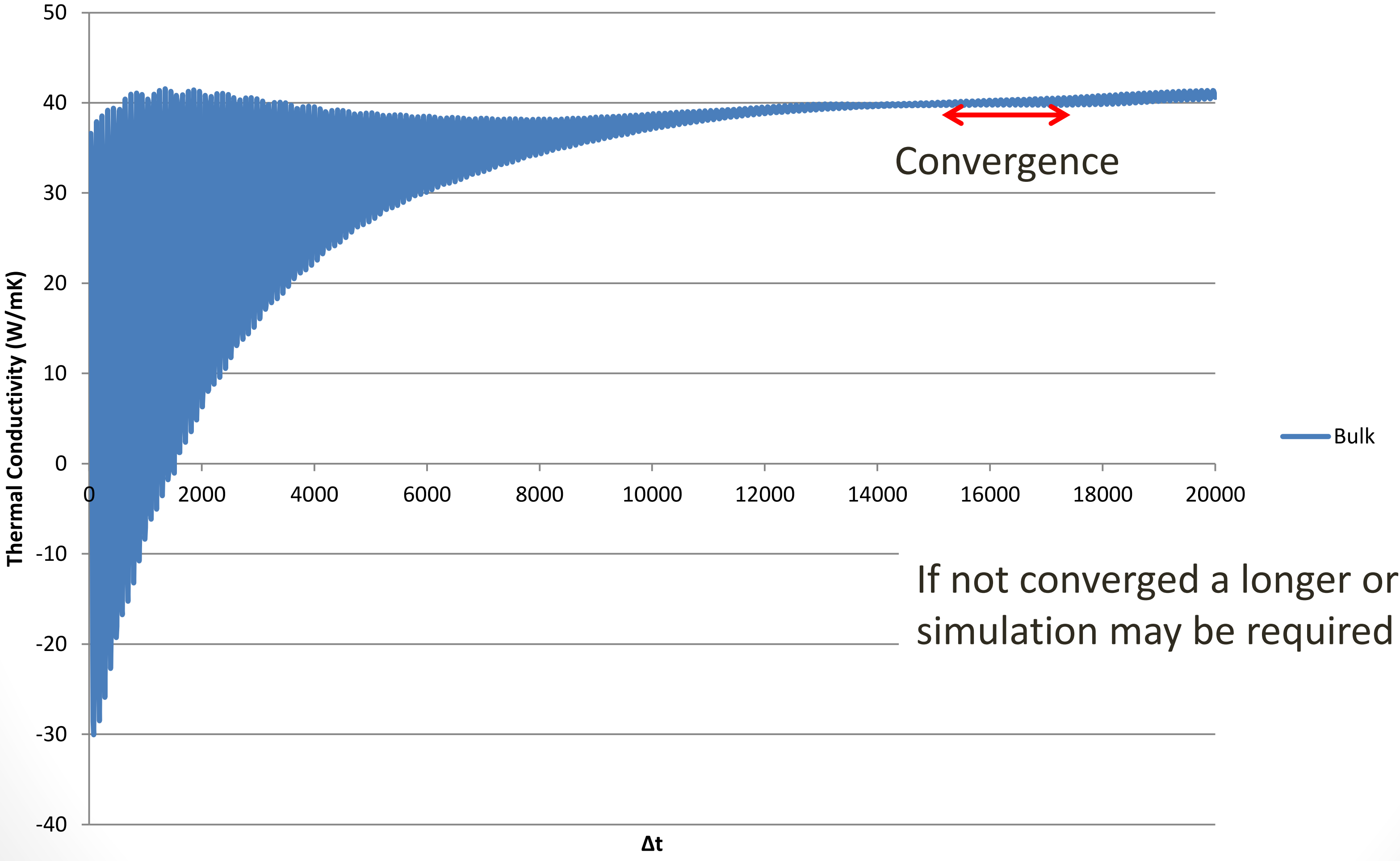
Thermal Conductivity

- Integrate the autocorrelation and multiply by constants
- How far?
  - Until converged
  - Difficult to specify
- Can obtain thermal conductivity as a function of autocorrelation length
  - Useful for finding point of convergence

$$\boldsymbol{\kappa} = \frac{s\Delta t}{V k_B T^2} \int_0^\infty \langle \boldsymbol{J}(0) \cdot \boldsymbol{J}(t) \rangle \Delta t$$

s = sampling interval
Δt = simulation timestep
V = system volume
k_B = Boltzmann's constant
T = system temperature
J = Heat flux

Thermal Conductivity as a Function of Integral Length



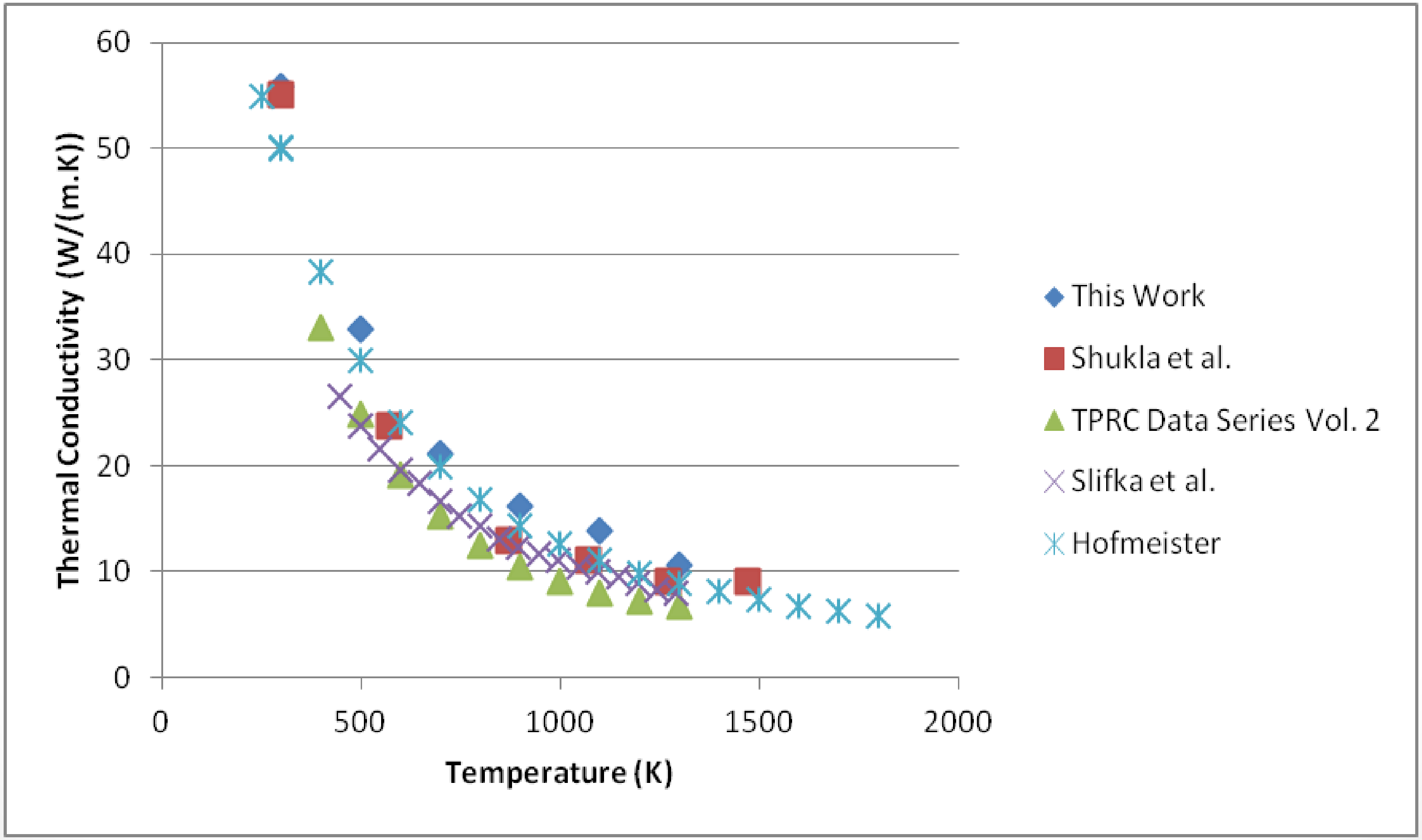
If not converged a longer or larger simulation may be required!

DP Sellan *et al*, Phys. Rev. B, 81, 2010, 214305.

S Yeandel

Examples

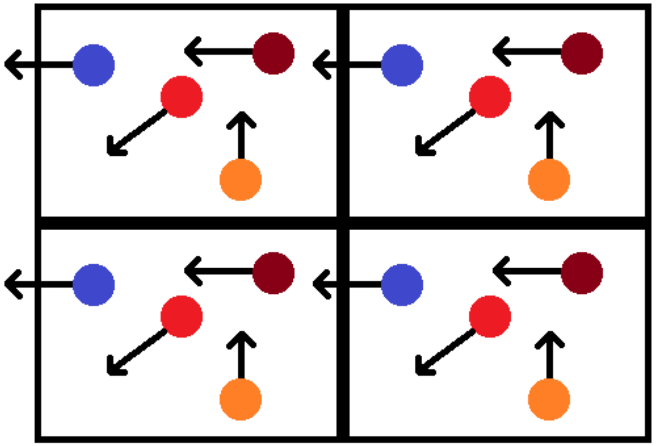
- MgO as a function of temperature

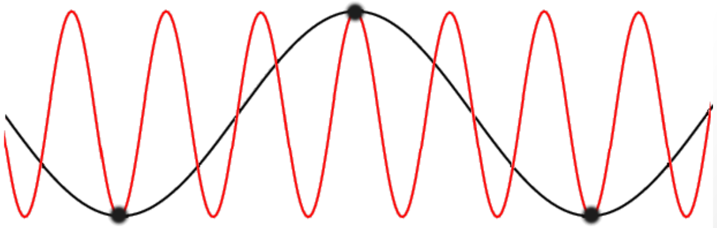


S Yeandel

Molecular Dynamics Summary

- Strength is that treats anharmonicity and can deal with very large simulation cells.
- Weakness is that it does not explicitly consider **k** space.
- Different sized simulation cells allow different wavelength phonons
  - Larger cells allow more longer wavelength phonons to exist
  - However, phonons of shorter wavelength may be forbidden if not commensurate with simulation cell length
- Sampling frequency is important
  - Choose the sampling interval carefully!
    - Too frequent - SLOW
    - Too infrequent – INACCURATE
  - Must capture the highest frequency phonon involved in scattering
  - Every ~10 fs usually suffices





Summary

- To obtain reliable results you need to be aware of the phonon dispersion, i.e. it is virtually impossible to calculate the complete dispersion curve in every direction – so is you supercell or choice of **k** (or **q**) vectors appropriate?
- If you favour using DFT, then lattice dynamics is currently the best established approach, but for most researchers limits the number of atoms to less than 100 atoms (at present), particularly if calculating phonon-phonon interactions.
- If interested in complex microstructures, i.e. understanding the influence of say, nanostructuring and additives, then molecular dynamics using force field methods is best placed. Although need to check force field against expt (and/or DFT).

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- Codes
- Lattice Dynamics
  - VASP: https://www.vasp.at/
  - Phonopy: http://phonopy.sourceforge.net/
- Molecular Dynamics
  - LAMMPS: http://lammps.sandia.gov/
  - DL_POLY: http://www.ccp5.ac.uk/