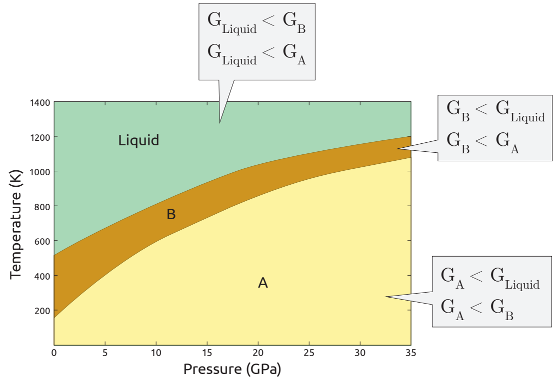
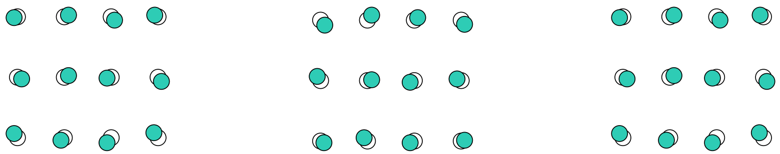
Phonons and anharmonicity



$$G(p,T) = U(p,T) - pV - TS(p,T)$$

Entropy is tricky

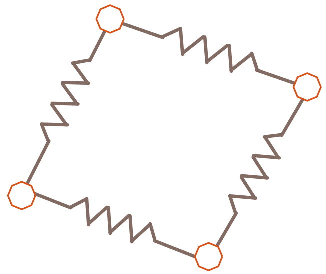
Atoms tend not to sit still



$$S = -k_B \sum_i p_i \ln p_i$$

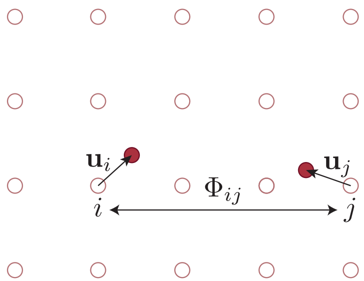
The number of states is far too large to enumerate, we need to approximate this

Electrons are too complicated



Electrons are reduced to springs that connect nuclei

Harmonic approximation



$$\Phi_{ij}^{\mu\nu} = \left.\frac{\partial^2 U}{\partial u_i^\mu \partial u_j^\nu}\right|_{u=0}$$

$$U(\{\mathbf{u}\}) = U_0 + \frac{1}{2}\sum_{ij}\sum_{\mu\nu}\Phi_{ij}^{\mu\nu} u_i^\mu u_j^\nu$$

Hamiltonian:

$$H = U_0 + \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2!}\sum_{ij\alpha\beta}\Phi_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta$$

Introduce the Fourier transformed force constant matrix, the dynamical matrix:

$$\mathbf{\Phi}_{\mu\nu}(\mathbf{q}) = \sum_l \frac{e^{i\mathbf{q}\cdot\mathbf{R}_l}}{\sqrt{M_\mu M_\nu}}\mathbf{\Phi}_{\mu\nu}(\mathbf{R}_l)$$

Get eigenvalues and eigenvectors of this matrix

$$\omega_{\mathbf{q}s}^2 \epsilon_{\mathbf{q}s} = \mathbf{\Phi}(\mathbf{q})\epsilon_{\mathbf{q}s}$$

Use eigenvalues and eigenvectors

$$\omega_{\mathbf{q}s}^2 \epsilon_{\mathbf{q}s} = \mathbf{\Phi}(\mathbf{q})\epsilon_{\mathbf{q}s}$$

Construct a transformation

$$u_i^\mu = \sum_{\mathbf{q}s}\sqrt{\frac{\hbar}{2Nm_i\omega_{\mathbf{q}s}}}\epsilon_{\mathbf{q}s}^{i\mu} e^{i\mathbf{q}\cdot\mathbf{R}_i}\left(a_{\mathbf{q}s} + a_{-\mathbf{q}s}^\dagger\right)$$

$$p_i^\mu = \sum_{\mathbf{q}s}\frac{1}{i}\sqrt{\frac{\hbar m_i\omega_{\mathbf{q}s}}{2N}}\epsilon_{\mathbf{q}s}^{i\mu} e^{i\mathbf{q}\cdot\mathbf{R}_i}\left(a_{\mathbf{q}s} - a_{-\mathbf{q}s}^\dagger\right)$$

New Hamiltonian:

$$H = \sum_{\mathbf{q}s}\hbar\omega_{\mathbf{q}s}\left(a_{\mathbf{q}s}^\dagger a_{\mathbf{q}s} + \frac{1}{2}\right)$$

A sum of uncoupled harmonic oscillators!

Each harmonic oscillator will have the partition function

$$Z_{\mathbf{q}s} = \sum_{n=0}^{\infty}\exp\left(-\frac{(n+\frac{1}{2})\hbar\omega_{\mathbf{q}s}}{k_B T}\right) = \frac{\exp\left(\frac{\hbar\omega_{\mathbf{q}s}}{2k_BT}\right)}{\exp\left(\frac{\hbar\omega_{\mathbf{q}s}}{k_BT}\right) - 1}$$

We will have the total partition function

$$Z = \prod_{\mathbf{q}s}\frac{\exp\left(\frac{\hbar\omega_{\mathbf{q}s}}{2k_BT}\right)}{\exp\left(\frac{\hbar\omega_{\mathbf{q}s}}{k_BT}\right) - 1}$$

And the (Helmholtz) free energy

$$F = -k_BT\ln Z = \sum_{s\mathbf{q}}\frac{\hbar\omega_{s\mathbf{q}}}{2} + k_BT\ln\left(1 - \exp\left(-\frac{\hbar\omega_{s\mathbf{q}}}{k_BT}\right)\right)$$
$$= \int g(\omega)\left[\frac{\hbar\omega}{2} + k_BT\ln\left(1 - \exp\left(-\frac{\hbar\omega}{k_BT}\right)\right)\right]\mathrm{d}\omega$$

Phonon DOS

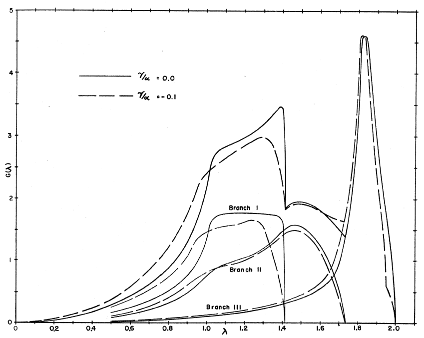


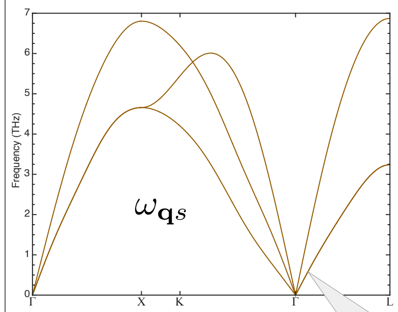
FIG. 1. The frequency spectrum of a face-centered cubic crystal lattice. The three branches extend from λ=0 to λ=√2, λ=√3, and λ=2, respectively.

$$g(\omega) = \frac{1}{(2\pi)^3} \sum_s \int \delta(\omega - \omega_{\mathbf{q}s}) d\mathbf{q}$$

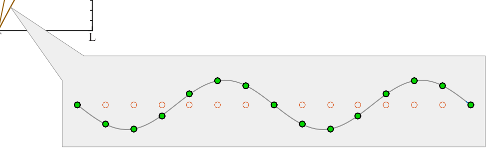
Entropy, free energy and so on are given analytically from the phonon DOS.

R.B. Leighton, Rev. Mod. Phys. 20, 165 (1948).

What does the oscillators represent

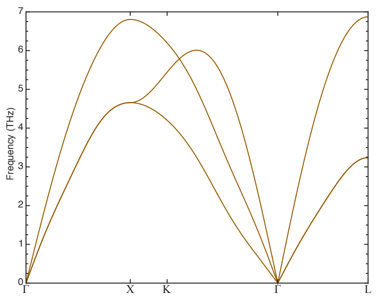


Displacement pattern for each oscillator is determined by the eigenvectors, and varies in time as $\sin(\omega_{\mathbf{q}s} t)$



The real and reciprocal representations are equivalent, with the atomic displacements described as a sum of plane waves.

What does the oscillators represent



Or equivalently, we can see the phonon dispersions as the allowed thermal excitations in a material, such that they define the inelastic neutron spectra.

For a specific change in momentum (q), it tells us what changes in neutron energies are allowed.

How to get force constants

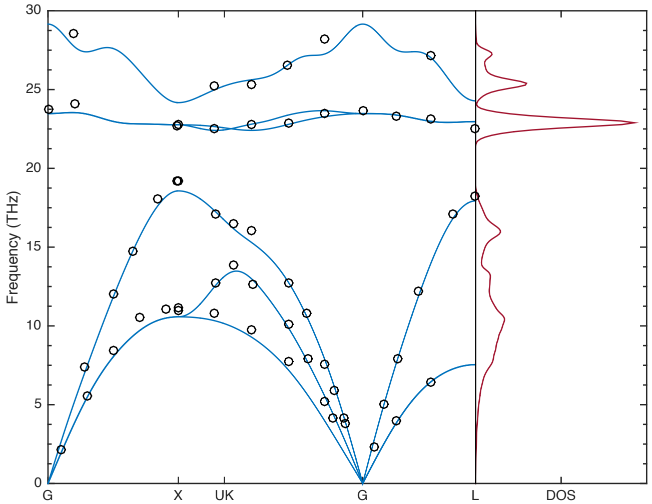
$$\mathbf{f}_i = -\sum_j \Phi_{ij} \mathbf{u}_j$$

You move atom j, measure the force on atom i

Repeat until you know all force constants.

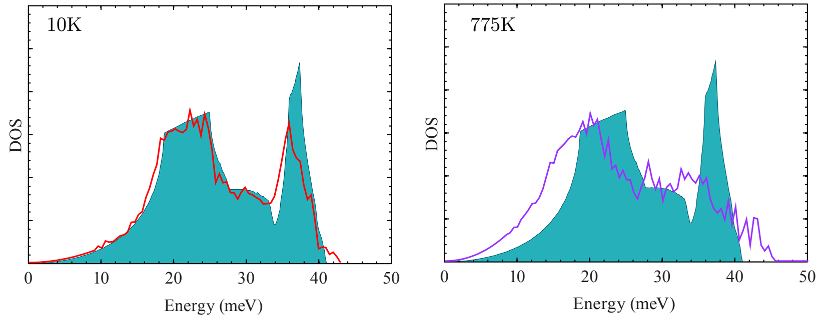
Analytically, with DFPT, or manually as numerical derivatives

3C SiC



J. Serrano, J. Strempfer, M. Cardona, M. Schwoerer-Böhning, H. Requardt, M. Lorenzen, B. Stojetz, P. Pavone, and W.J. Choyke, Appl. Phys. Lett. 80, 4360 (2002).

Aluminium phonon DOS Harmonic

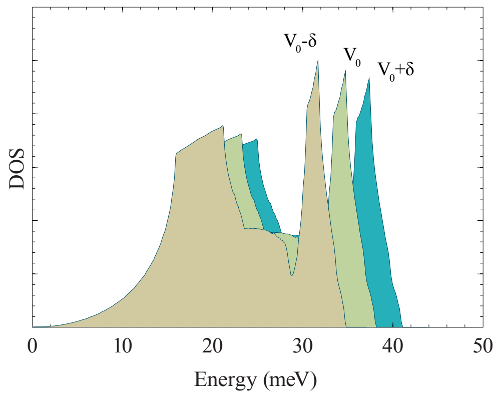


Significant disagreement at high temperature. something is missing!

M. Kresch, M. Lucas, O. Delaire, J. Lin, and B. Fultz, Phys. Rev. B 77, 024301 (2008).

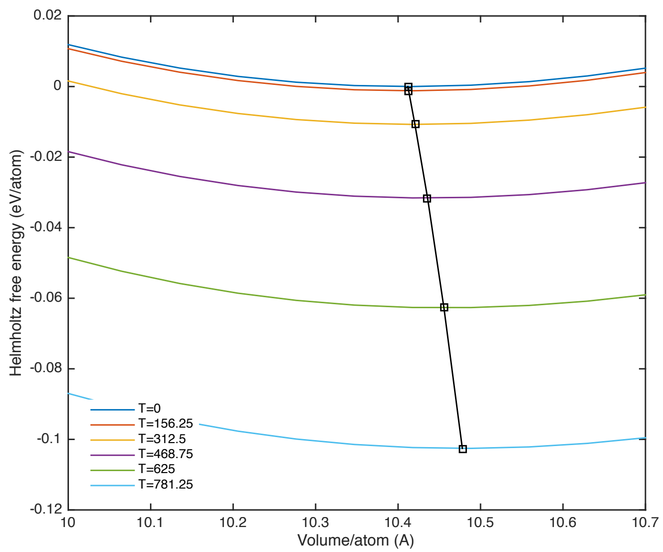
Quasiharmonic approximation

$$\omega_{\mathbf{q}s}(V,T) \approx \omega_{\mathbf{q}s}(V(T))$$

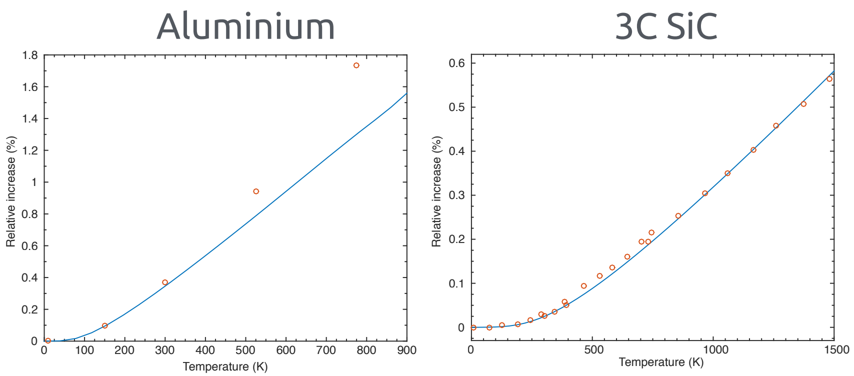


Use the harmonic approximation for different volumes, gives you F(V,T)

Free energy vs volume

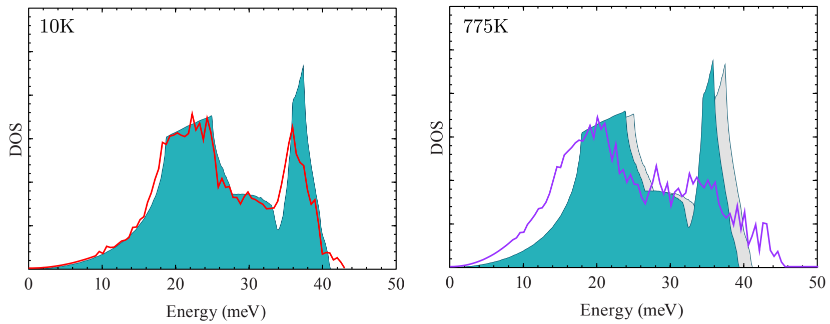


Volume vs temperature



Taylor, A., Jones, R.M. in Silicon Carbide - A High Temperature Semiconductor , Eds. O'Connor, J.R., Smiltens, J., Pergamon Press, Oxford, London, New York, Paris 1960, 147

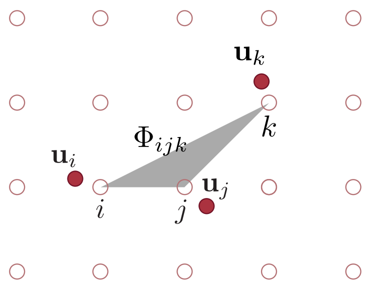
Aluminium phonon DOS Quasiharmonic



The experimental spectra has distinctly different features, there is no way the quasiharmonic approach could fix that.

Reconsider the independent oscillators

The harmonic approximation has perfect principle of superposition. That is not a good approximation



We have to consider interactions beyond pairs, three-body, four-body and so on.

Reconsider the independent oscillators

Add high order terms to the expansion of the potential energy surface

$$H = U_0 + \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2!}\sum_{ij\alpha\beta} \Phi_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta + \frac{1}{3!}\sum_{ijk\alpha\beta\gamma} \Phi_{ijk}^{\alpha\beta\gamma} u_i^\alpha u_j^\beta u_k^\gamma + \frac{1}{4!}\sum_{ijkl\alpha\beta\gamma\delta} \Phi_{ijkl}^{\alpha\beta\gamma\delta} u_i^\alpha u_j^\beta u_k^\gamma u_l^\delta + \dots$$

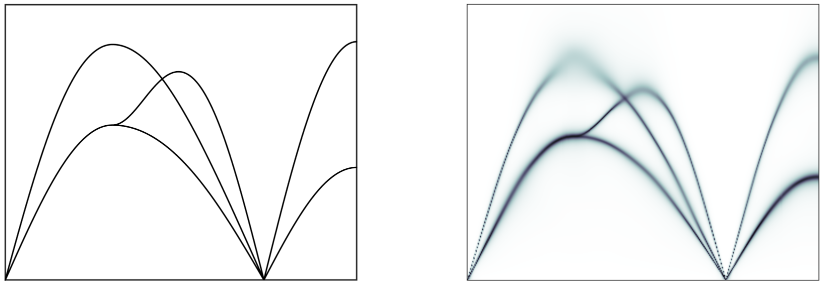
Complicates things a little

$$H = \sum_{\mathbf{q}s} \hbar\omega_{\mathbf{q}s}\left(a^\dagger_{\mathbf{q}s} a_{\mathbf{q}s} + \frac{1}{2}\right)$$

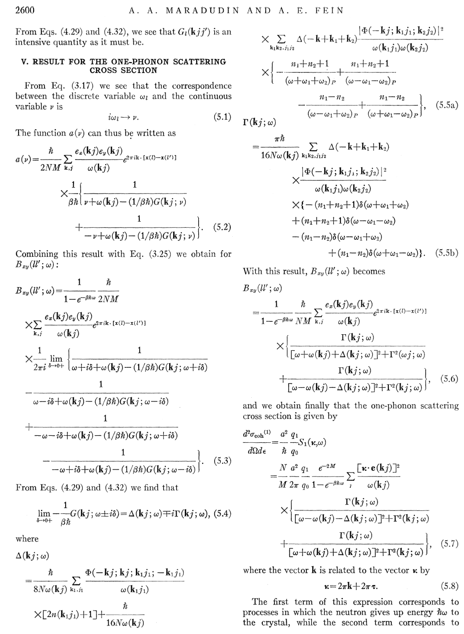
A plane wave ansatz no longer diagonalise the system

Non-interacting

Interacting



Different, but not too different. Perturbation theory!



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From Eqs. (4.29) and (4.32), we see that $G_l(\mathbf{k}jj')$ is an intensive quantity as it must be.

V. RESULT FOR THE ONE-PHONON SCATTERING CROSS SECTION

From Eq. (3.17) we see that the correspondence between the discrete variable ω_l and the continuous variable ν is

$$i\omega_l \to \nu. \quad (5.1)$$

The function $a(\nu)$ can thus be written as

$$a(\nu)=\frac{\hbar}{2NM}\sum_{\mathbf{k},j}\frac{e_x(\mathbf{k}j)e_y(\mathbf{k}j)}{\omega(\mathbf{k}j)}e^{2\pi i\mathbf{k}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}\times\frac{1}{\beta\hbar}\left\{\frac{1}{\nu+\omega(\mathbf{k}j)-(1/\beta\hbar)G(\mathbf{k}j;\nu)}+\frac{1}{-\nu+\omega(\mathbf{k}j)-(1/\beta\hbar)G(\mathbf{k}j;\nu)}\right\}. \quad (5.2)$$

Combining this result with Eq. (3.25) we obtain for $B_{xy}(ll';\omega)$:

$$B_{xy}(ll';\omega)=\frac{1}{1-e^{-\beta\hbar\omega}}\frac{\hbar}{2NM}\times\sum_{\mathbf{k},j}\frac{e_x(\mathbf{k}j)e_y(\mathbf{k}j)}{\omega(\mathbf{k}j)}e^{2\pi i\mathbf{k}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}\times\frac{1}{2\pi i}\lim_{\delta\to0+}\left\{\frac{1}{\omega+i\delta+\omega(\mathbf{k}j)-(1/\beta\hbar)G(\mathbf{k}j;\omega+i\delta)}-\frac{1}{\omega-i\delta+\omega(\mathbf{k}j)-(1/\beta\hbar)G(\mathbf{k}j;\omega-i\delta)}+\frac{1}{-\omega-i\delta+\omega(\mathbf{k}j)-(1/\beta\hbar)G(\mathbf{k}j;\omega+i\delta)}-\frac{1}{-\omega+i\delta+\omega(\mathbf{k}j)-(1/\beta\hbar)G(\mathbf{k}j;\omega-i\delta)}\right\}. \quad (5.3)$$

From Eqs. (4.29) and (4.32) we find that

$$\lim_{\delta\to0+}-\frac{1}{\beta\hbar}G(\mathbf{k}j;\omega\pm i\delta)=\Delta(\mathbf{k}j;\omega)\mp i\Gamma(\mathbf{k}j;\omega), \quad (5.4)$$

where

$$\Delta(\mathbf{k}j;\omega)=\frac{\hbar}{8N\omega(\mathbf{k}j)}\sum_{\mathbf{k}_1,j_1}\frac{\Phi(-\mathbf{k}j;\mathbf{k}j;\mathbf{k}_1j_1;-\mathbf{k}_1j_1)}{\omega(\mathbf{k}_1j_1)}\times[2n(\mathbf{k}_1j_1)+1]+\frac{\hbar}{16N\omega(\mathbf{k}j)}\times\sum_{\mathbf{k}_1\mathbf{k}_2,j_1j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\frac{|\Phi(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)|^2}{\omega(\mathbf{k}_1j_1)\omega(\mathbf{k}_2j_2)}\times\left\{-\frac{n_1+n_2+1}{(\omega+\omega_1+\omega_2)_P}+\frac{n_1+n_2+1}{(\omega-\omega_1-\omega_2)_P}-\frac{n_1-n_2}{(\omega-\omega_1+\omega_2)_P}+\frac{n_1-n_2}{(\omega+\omega_1-\omega_2)_P}\right\}, \quad (5.5a)$$

$$\Gamma(\mathbf{k}j;\omega)=\frac{\pi\hbar}{16N\omega(\mathbf{k}j)}\sum_{\mathbf{k}_1\mathbf{k}_2,j_1j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\times\frac{|\Phi(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)|^2}{\omega(\mathbf{k}_1j_1)\omega(\mathbf{k}_2j_2)}\times\{-(n_1+n_2+1)\delta(\omega+\omega_1+\omega_2)+(n_1+n_2+1)\delta(\omega-\omega_1-\omega_2)-(n_1-n_2)\delta(\omega-\omega_1+\omega_2)+(n_1-n_2)\delta(\omega+\omega_1-\omega_2)\}. \quad (5.5b)$$

With this result, $B_{xy}(ll';\omega)$ becomes

$$B_{xy}(ll';\omega)=\frac{1}{1-e^{-\beta\hbar\omega}}\frac{\hbar}{NM}\sum_{\mathbf{k},j}\frac{e_x(\mathbf{k}j)e_y(\mathbf{k}j)}{\omega(\mathbf{k}j)}e^{2\pi i\mathbf{k}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}\times\left\{\frac{\Gamma(\mathbf{k}j;\omega)}{[\omega+\omega(\mathbf{k}j)+\Delta(\mathbf{k}j;\omega)]^2+\Gamma^2(\omega j;\omega)}+\frac{\Gamma(\mathbf{k}j;\omega)}{[\omega-\omega(\mathbf{k}j)-\Delta(\mathbf{k}j;\omega)]^2+\Gamma^2(\mathbf{k}j;\omega)}\right\}, \quad (5.6)$$

and we obtain finally that the one-phonon scattering cross section is given by

$$\frac{d^2\sigma_{\mathrm{coh}}^{(1)}}{d\Omega d\epsilon}=\frac{a^2}{\hbar}\frac{q_1}{q_0}S_1(\kappa,\omega)=\frac{N}{M}\frac{a^2}{2\pi}\frac{q_1}{q_0}\frac{e^{-2M}}{1-e^{-\beta\hbar\omega}}\sum_j\frac{[\kappa\cdot\mathbf{e}(\mathbf{k}j)]^2}{\omega(\mathbf{k}j)}\times\left\{\frac{\Gamma(\mathbf{k}j;\omega)}{[\omega-\omega(\mathbf{k}j)-\Delta(\mathbf{k}j;\omega)]^2+\Gamma^2(\mathbf{k}j;\omega)}+\frac{\Gamma(\mathbf{k}j;\omega)}{[\omega+\omega(\mathbf{k}j)+\Delta(\mathbf{k}j;\omega)]^2+\Gamma^2(\mathbf{k}j;\omega)}\right\}, \quad (5.7)$$

where the vector $\mathbf{k}$ is related to the vector κ by

$$\kappa=2\pi\mathbf{k}+2\pi\tau. \quad (5.8)$$

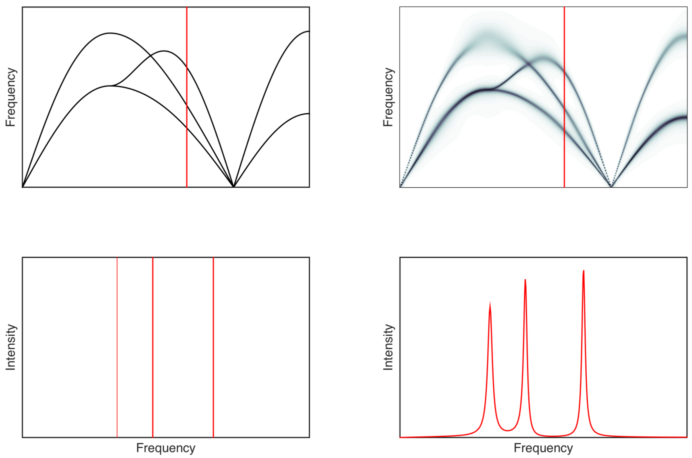
The first term of this expression corresponds to processes in which the neutron gives up energy $\hbar\omega$ to the crystal, while the second term corresponds to

The theory tends be a bit dense

A.A. Maradudin and A. Fein, Phys. Rev. 128, 2589 (1962).

Non-interacting

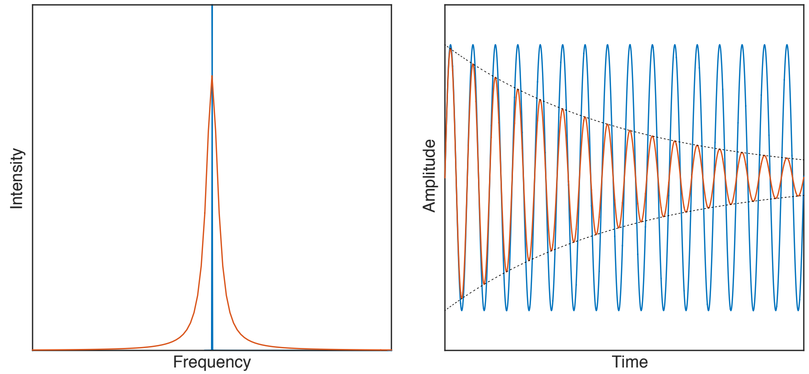
Interacting



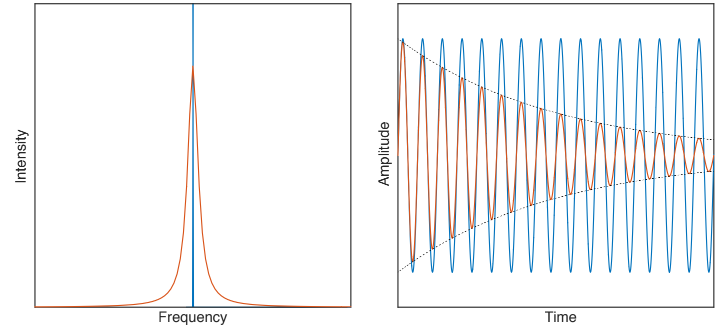
Dirac delta

Sort of Lorentzian

Fourier transform in time



A broadening in frequency domain is equivalent to a dampening in time, a finite lifetime.



A deltafunction means infinite lifetime

$$\mathcal{F}\left\{\delta(\omega-\omega_{\mathbf{q}s})\right\} = e^{i\omega_{\mathbf{q}s}t}$$

Lorentzian means finite lifetime

$$\mathcal{F}\left\{\frac{\sigma}{\pi}\frac{1}{(\omega-\omega_{qs})^2+\sigma^2}\right\} = e^{i\omega_{\mathbf{q}s}t}e^{-\sigma t}$$

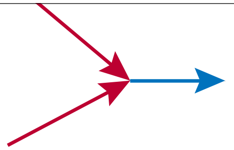
If we know the lifetime, we know the broadening

Consider three-phonon processes

$$\mathbf{q}_1+\mathbf{q}_2=\mathbf{q}_3 \qquad \mathbf{q}_1=\mathbf{q}_2+\mathbf{q}_3$$

$$\omega_1+\omega_2=\omega_3 \qquad \omega_1=\omega_2+\omega_3$$

The probability of these determine the rate of change of the occupation, i.e. the lifetime



Fermi golden rule

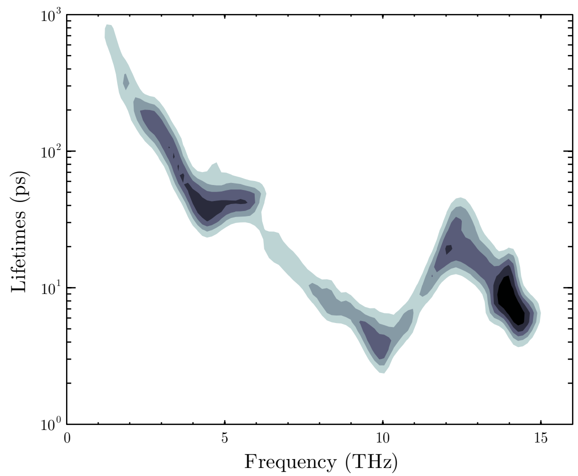
$$P_{\mathbf{q}s+\mathbf{q}'s'\rightarrow\mathbf{q}''s''} = \frac{2\pi}{\hbar}\left|\langle f|H^3|i\rangle\right|^2\delta(E_f-E_i) =$$
$$= \frac{\hbar^2\pi}{4N}n_{\mathbf{q}s}n_{\mathbf{q}'s'}(n_{\mathbf{q}''s''}+1)\left|\Psi^{\mathbf{q}\mathbf{q}'\mathbf{q}''}_{ss's''}\right|^2\delta(E_f-E_i)$$

The probability per unit time that two specific phonons recombine into a third

$$\Psi^{\mathbf{q}\mathbf{q}'\mathbf{q}''}_{ss's''} = \sum_{ijk}\sum_{\alpha\beta\gamma}\frac{\epsilon^{\mathbf{q}s}_{\alpha i}\epsilon^{\mathbf{q}'s'}_{\beta j}\epsilon^{\mathbf{q}''s''}_{\gamma k}}{\sqrt{m_i m_j m_j}\sqrt{\omega_{\mathbf{q}s}\omega_{\mathbf{q}'s'}\omega_{\mathbf{q}''s''}}}\Phi^{\alpha\beta\gamma}_{ijk}e^{i\mathbf{q}\cdot\mathbf{r}_i+i\mathbf{q}'\cdot\mathbf{r}_j+i\mathbf{q}''\cdot\mathbf{r}_k}$$

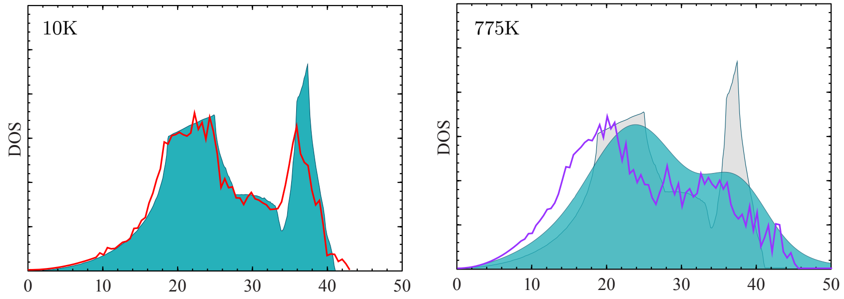
The probability depends on the strength of the three-body interactions

Add up all the probabilities for all possible processes gives you the lifetime per mode



$$\frac{1}{\tau_{\mathbf{q}s}} = \sum_{s's''}\frac{\hbar\pi}{16}\iint_{\mathrm{BZ}}\left|\Psi^{\mathbf{q}\mathbf{q}'\mathbf{q}''}_{ss's''}\right|^2\left[(n_{\mathbf{q}'s'}+n_{\mathbf{q}''s''}+1)\delta(\omega_{\mathbf{q}s}-\omega_{\mathbf{q}'s'}-\omega_{\mathbf{q}''s''})\right.$$
$$\left.+2(n_{\mathbf{q}'s'}-n_{\mathbf{q}''s''})\delta(\omega_{\mathbf{q}s}-\omega_{\mathbf{q}'s'}+\omega_{\mathbf{q}''s''})\right]d\mathbf{q}'d\mathbf{q}''$$

Aluminium phonon DOS Quasiharmonic+broadening



The shape is better, but the energies are not that great.

In general, not just broadening

The line shape is described by the one-neutron cross section:

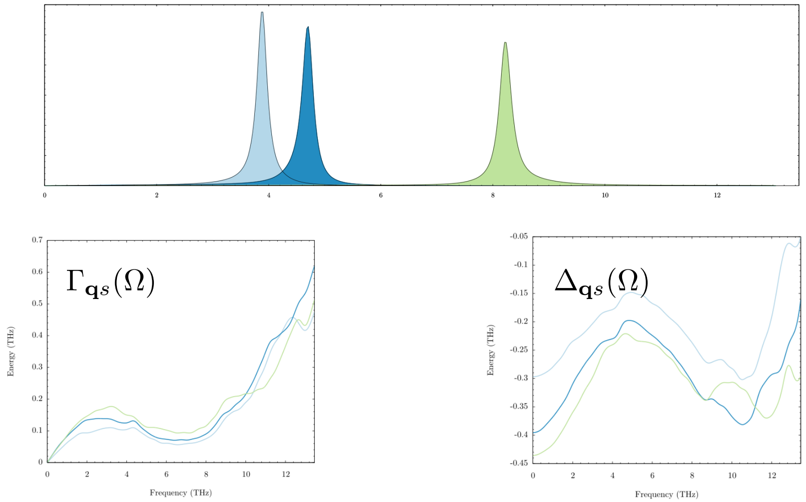
$$\sigma_{\mathbf{q}s}(\Omega) \propto \frac{2\omega_{\mathbf{q}s}\Gamma_{\mathbf{q}s}(\Omega)}{\left(\Omega^2 - \omega_{\mathbf{q}s}^2 - 2\omega_{\mathbf{q}s}\Delta_{\mathbf{q}s}(\Omega)\right)^2 + 4\omega_{\mathbf{q}s}^2\Gamma_{\mathbf{q}s}^2(\Omega)}$$

Determined by the real and imaginary parts of the self-energy:

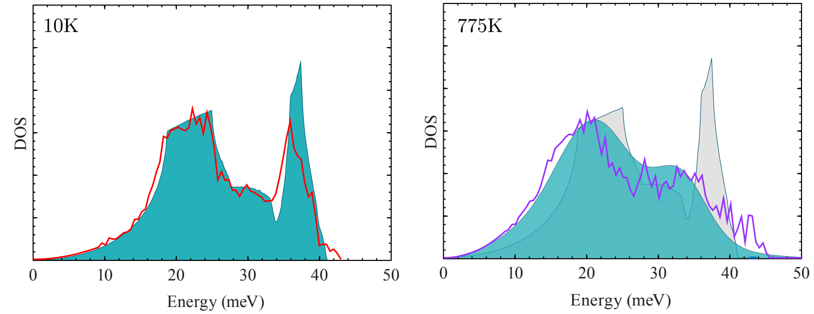
$$\Gamma_{\mathbf{q}s}(\Omega) = \sum_{s's''} \frac{\hbar\pi}{16} \frac{V}{(2\pi)^3} \iint_{\mathrm{BZ}} \left|\Psi_{ss's''}^{\mathbf{q}\mathbf{q}'\mathbf{q}''}\right|^2 \Delta_{\mathbf{q}\mathbf{q}'\mathbf{q}''} \times \left[(n_{\mathbf{q}'s'} + n_{\mathbf{q}''s''} + 1)\delta(\Omega - \omega_{\mathbf{q}'s'} - \omega_{\mathbf{q}''s''}) + 2(n_{\mathbf{q}'s'} - n_{\mathbf{q}''s''})\delta(\Omega - \omega_{\mathbf{q}'s'} + \omega_{\mathbf{q}''s''})\right] d\mathbf{q}' d\mathbf{q}''$$

$$\Delta(\mathbf{q}s,\Omega) = -\frac{18}{\hbar}\left\{\sum_{s's''}\sum_{\mathbf{q}'\mathbf{q}''}\left|\Phi_{ss's''}^{\mathbf{q}\mathbf{q}'\mathbf{q}''}\right|^2 \frac{n_{\mathbf{q}'s'} + n_{\mathbf{q}''s''} + 1}{\omega_{\mathbf{q}'s'} + \omega_{\mathbf{q}''s''} + \Omega} + \frac{n_{\mathbf{q}'s'} + n_{\mathbf{q}''s''} + 1}{\omega_{\mathbf{q}'s'} + \omega_{\mathbf{q}''s''} + \Omega} + \frac{n_{\mathbf{q}'s'} + n_{\mathbf{q}''s''} + 1}{\omega_{\mathbf{q}'s'} + \omega_{\mathbf{q}''s''} + \Omega} + \frac{n_{\mathbf{q}'s'} + n_{\mathbf{q}''s''} + 1}{\omega_{\mathbf{q}'s'} + \omega_{\mathbf{q}''s''} + \Omega}\right\} + \frac{12}{\hbar}\sum_{\mathbf{q}'s'}\Phi_{sss's'}^{\mathbf{q}\bar{\mathbf{q}}\mathbf{q}'\bar{\mathbf{q}}'}(2n_{\mathbf{q}'s'} + 1)$$

cross section/spectral function



Aluminium phonon DOS Quasiharmonic+lineshapes



Now it is starting to look ok
More or less within experimental error bars

Thermal conductivity

$$\kappa \propto C v^2 \tau$$

How fast it travels, how much heat it carries,
how long it lives

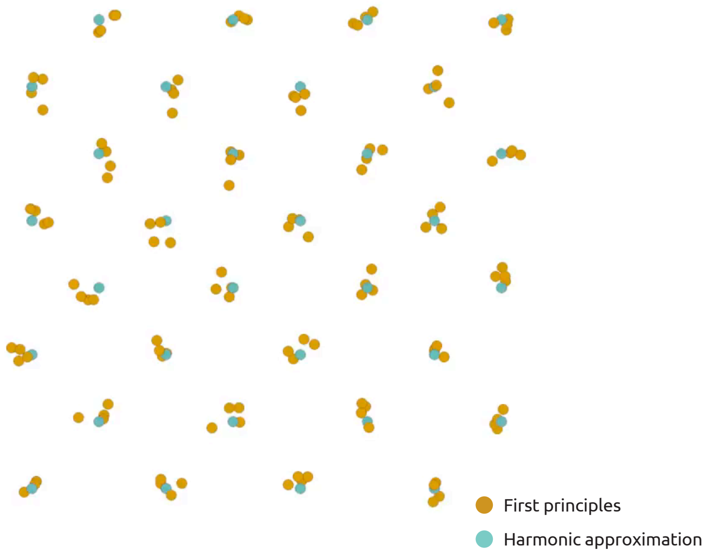
So, to summarize, we started with the potential energy.

$$U(\{\mathbf{R}\}) \approx \frac{1}{2!} \sum_{ij\alpha\beta} \Phi_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta + \frac{1}{3!} \sum_{ijk\alpha\beta\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_i^\alpha u_j^\beta u_k^\gamma + \dots$$

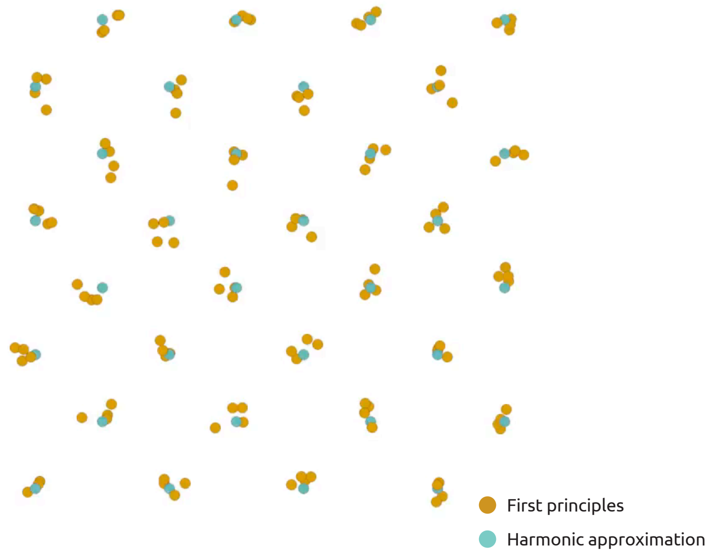
Solve harmonic parts analytically, the rest with perturbation theory.
We got Aluminium to look ok.

Does it always work?

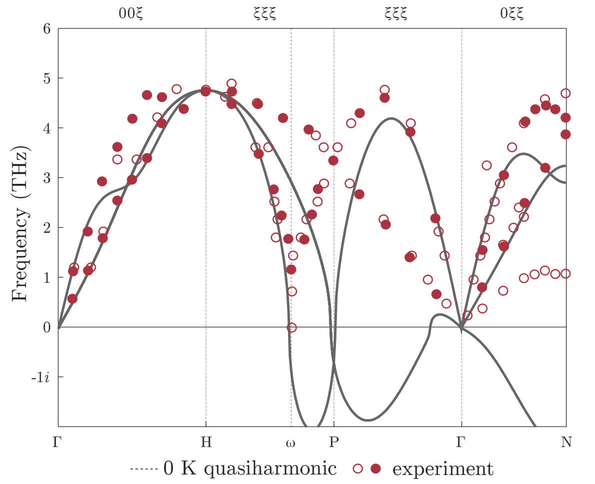
Sometimes it works



Sometimes not



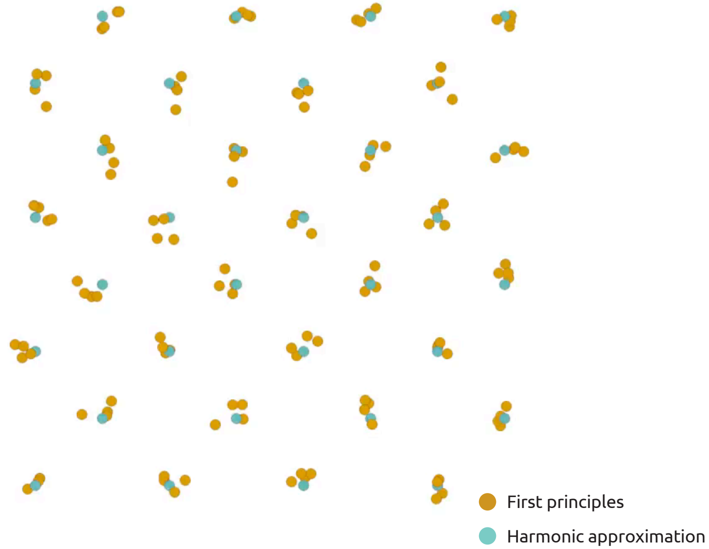
bcc Zr at 1300K



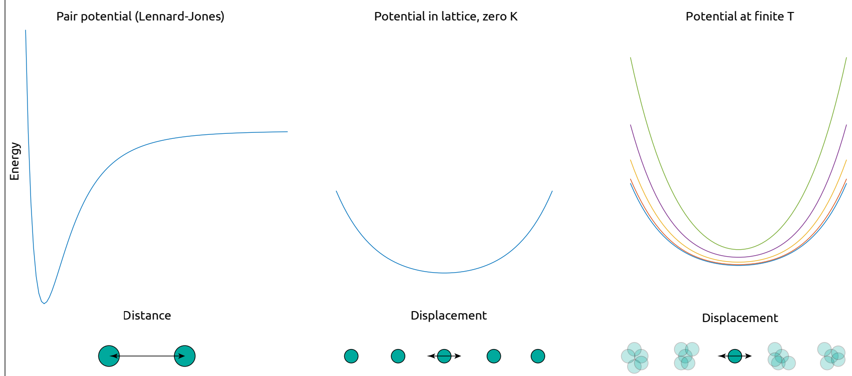
C. Stassis, Solid State Commun. 52, 9 (1984).

A. Heiming *et al.* Phys. Rev. B 43, 10948 (1991).

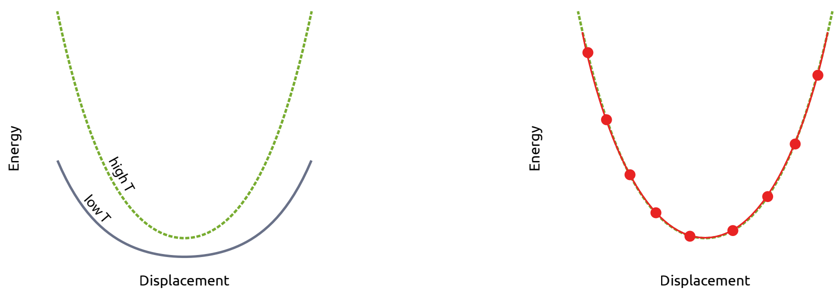
The ab initio MD looks ok



Effective potential depends depends on state

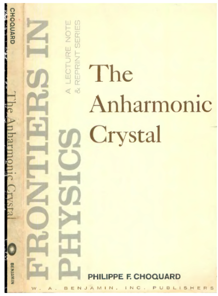


Taylor expanding from the solid line to the dashed is hard



Easier to sample the high-temperature potential energy landscape, and fit a model potential

Treating this analytically is tricky




THERMAL PROPERTIES 134

$$= (-)\,2\,\frac{KT}{\upsilon}\sum_{\underset{\sim}{q}\underset{\sim}{q}'} \Gamma^{+}_{\underset{\sim}{q}T\lambda} : C_{\underset{\sim}{q};\underset{\sim}{q}'} : \Gamma_{\underset{\sim}{q}'T\lambda} \qquad (4\text{-}49)$$

where $\Gamma^{+}_{\underset{\sim}{q}T\lambda}$ is the transposed matrix of $\Gamma_{\underset{\sim}{q}T\lambda}$. Here, one uses the property $D^{+}_{\underset{\sim}{q}} = D_{\underset{\sim}{q}}$. Next, with

$$\left(\frac{\partial L_{q}}{\partial T}\right)_{\upsilon} = \frac{1}{T}\,\Delta_{\underset{\sim}{q}\upsilon}\,L_{\underset{\sim}{q}} = K\,\Delta_{\underset{\sim}{q}\upsilon}\,\frac{1}{D_{\underset{\sim}{q}}}$$

$C_{\upsilon} - C_{\upsilon\lambda}$ becomes

$$\frac{1}{2}\sum_{\underset{\sim}{q}} \mathrm{Tr}\left(D_{\underset{\sim}{q}}\left(\frac{\partial D_{q}}{\partial \ln T}\right)_{\upsilon,\lambda}\right)\left(\frac{\partial L_{q}}{\partial T}\right)_{\upsilon}$$

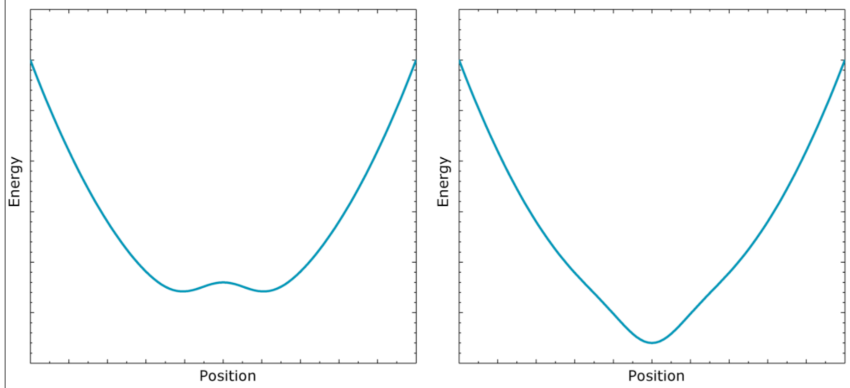
$$= \frac{1}{2}K\sum_{\underset{\sim}{q}} \mathrm{Tr}\, D_{\underset{\sim}{q}}\Delta_{\underset{\sim}{q}\upsilon\lambda}\Delta_{\underset{\sim}{q}\upsilon}\frac{1}{D_{\underset{\sim}{q}}} = \frac{1}{2}K\sum_{\underset{\sim}{q}} \mathrm{Tr}\,\Delta_{\underset{\sim}{q}\upsilon\lambda}\,\Delta_{\underset{\sim}{q}\upsilon}$$

$$= \frac{1}{2}K\sum_{\underset{\sim}{q}} \Delta^{+}_{\underset{\sim}{q}\upsilon\lambda} : \Delta_{\underset{\sim}{q}\upsilon} = \frac{1}{2}K\sum_{\underset{\sim}{q}'} \Delta^{+}_{\underset{\sim}{q}\upsilon\lambda} : C_{\underset{\sim}{q};\underset{\sim}{q}'} : \Delta_{\underset{\sim}{q}\upsilon\lambda} \qquad (4\text{-}50)$$

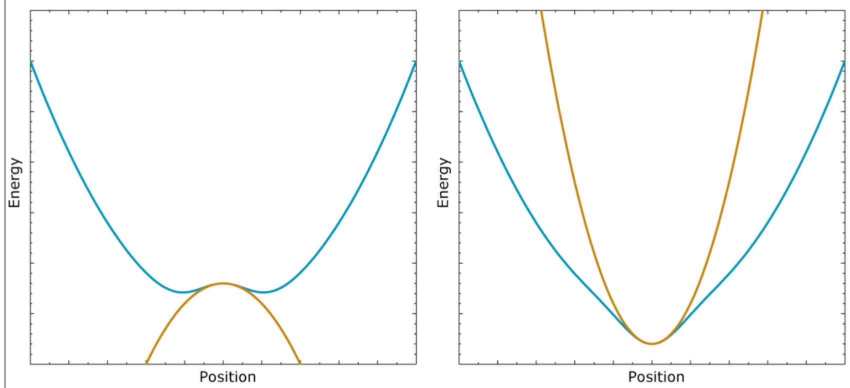
Lastly, $L_{\upsilon} - L_{\upsilon\lambda}$ reads

Even if one could implement it, it will contain approximations that are not necessary

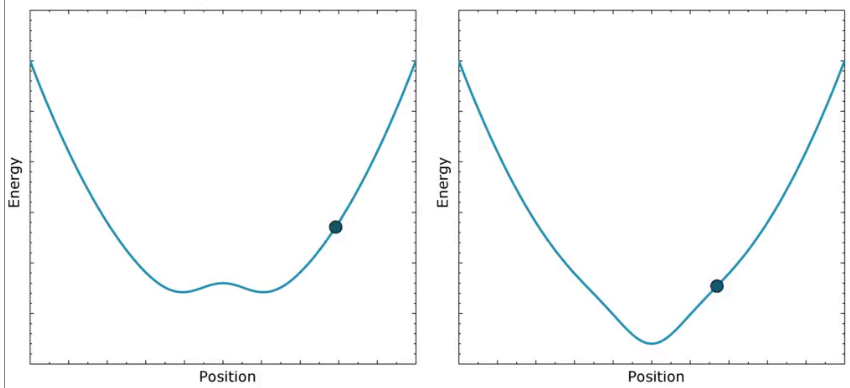
We want to compare the free energies of these two potentials



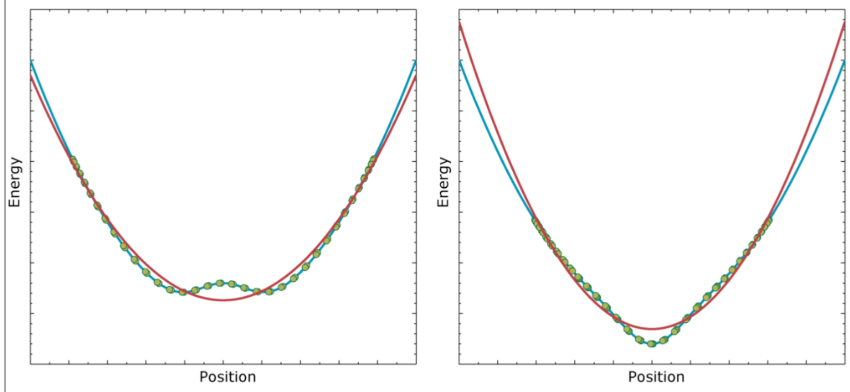
The harmonic approximation does not work well



Find the effective harmonic potential



Find the effective harmonic potential



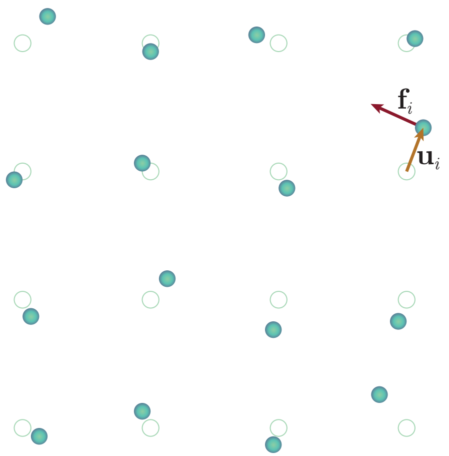
Same thing for a lattice:

Use Born-Oppenheimer molecular dynamics to provide statistics, fit an effective Hamiltonian:

$$H = U_0 + \sum_i \frac{m_i \mathbf{p}_i^2}{2} + \frac{1}{2!}\sum_{ij\alpha\beta} \Phi_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta + \frac{1}{3!}\sum_{ijk\alpha\beta\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_i^\alpha u_j^\beta u_k^\gamma + \ldots$$

I could use any form, but it is practical to use the same analytical form as before.

Born-Oppenheimer molecular dynamics



every time step is a set of forces and positions corresponding to a canonical ensemble

Express the forces in terms of the model Hamiltonian:

$$\underbrace{\begin{pmatrix} \mathbf{f}_1 \\ \mathbf{f}_2 \\ \vdots \\ \mathbf{f}_{N_a} \end{pmatrix}}_{\mathbf{F}_t^{\mathrm{H}}} = \underbrace{\begin{pmatrix} \Phi_{11} & \Phi_{12} & \cdots & \Phi_{1N_a} \\ \Phi_{21} & \Phi_{22} & \cdots & \Phi_{2N_a} \\ \vdots & \vdots & \ddots & \vdots \\ \Phi_{N_a 1} & \Phi_{N_a 2} & \cdots & \Phi_{N_a N_a} \end{pmatrix}}_{\Phi} \underbrace{\begin{pmatrix} \mathbf{u}_1 \\ \mathbf{u}_2 \\ \vdots \\ \mathbf{u}_{N_a} \end{pmatrix}}_{\mathbf{U}_t}$$

Minimize the difference in forces between model system and real system

$$\min_{\bar{\bar{\mathbf{\Phi}}}} \Delta \mathbf{F} = \frac{1}{N_t} \sum_{t=1}^{N_t} \left| \mathbf{F}_t^{\mathrm{MD}} - \mathbf{F}_t^{\mathrm{H}} \right|^2$$

Determined with a symmetry constrained least squares solution

Symmetry constrained least squares

$$\begin{pmatrix} f_x \\ f_y \\ f_z \end{pmatrix} = \begin{pmatrix} \phi_{xx} & \phi_{xy} & \phi_{xz} \\ \phi_{yx} & \phi_{yy} & \phi_{yz} \\ \phi_{zx} & \phi_{zy} & \phi_{zz} \end{pmatrix} \begin{pmatrix} u_x \\ u_y \\ u_z \end{pmatrix}$$

Original equation, 9 unknown

$$\begin{pmatrix} f_x \\ f_y \\ f_z \end{pmatrix} = \begin{pmatrix} \theta_1 & \theta_2 & 0 \\ \theta_2 & \theta_1 & 0 \\ 0 & 0 & \theta_2 \end{pmatrix} \begin{pmatrix} u_x \\ u_y \\ u_z \end{pmatrix}$$

$$\begin{pmatrix} f_x \\ f_y \\ f_z \end{pmatrix} = \begin{pmatrix} u_x\theta_1 + u_y\theta_2 \\ u_y\theta_1 + u_x\theta_2 \\ u_z\theta_2 \end{pmatrix}$$

$$\begin{pmatrix} f_x \\ f_y \\ f_z \end{pmatrix} = \begin{pmatrix} u_x & u_y \\ u_y & u_x \\ 0 & u_z \end{pmatrix} \begin{pmatrix} \theta_1 \\ \theta_2 \end{pmatrix}$$

Constrained equation, 2 unknown

About 10000 unknown variables

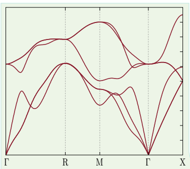
$$\underbrace{\begin{pmatrix} \mathbf{f}_1 \\ \mathbf{f}_2 \\ \vdots \\ \mathbf{f}_{N_a} \end{pmatrix}}_{\mathbf{F}_t^{\mathrm{H}}} = \underbrace{\begin{pmatrix} \Phi_{11} & \Phi_{12} & \cdots & \Phi_{1N_a} \\ \Phi_{21} & \Phi_{22} & \cdots & \Phi_{2N_a} \\ \vdots & \vdots & \ddots & \vdots \\ \Phi_{N_a1} & \Phi_{N_a2} & \cdots & \Phi_{N_aN_a} \end{pmatrix}}_{\Phi} \underbrace{\begin{pmatrix} \mathbf{u}_1 \\ \mathbf{u}_2 \\ \vdots \\ \mathbf{u}_{N_a} \end{pmatrix}}_{\mathbf{U}_t}$$

Symmetry constrained least squares

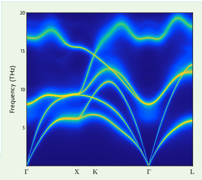
$$\mathbf{F} = C(\mathbf{U})\boldsymbol{\Theta}, \quad C(\mathbf{U})_{k\gamma} = \sum_{\delta} c^k_{\gamma\delta} u_\delta$$

About 10 unknown

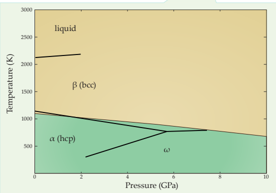
Phonon dispersions



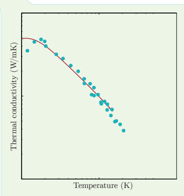
S(Q,E)



$$H = U_0 + \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2!}\sum_{ij\alpha\beta} \Phi_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta + \frac{1}{3!}\sum_{ijk\alpha\beta\gamma} \Phi_{ijk}^{\alpha\beta\gamma} u_i^\alpha u_j^\beta u_k^\gamma + \frac{1}{4!}\sum_{ijkl\alpha\beta\gamma\delta} \Phi_{ijkl}^{\alpha\beta\gamma\delta} u_i^\alpha u_j^\beta u_k^\gamma u_l^\delta + \ldots$$



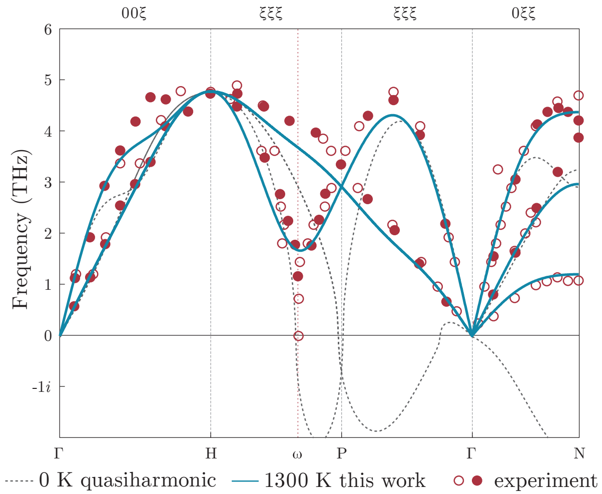
Free energy



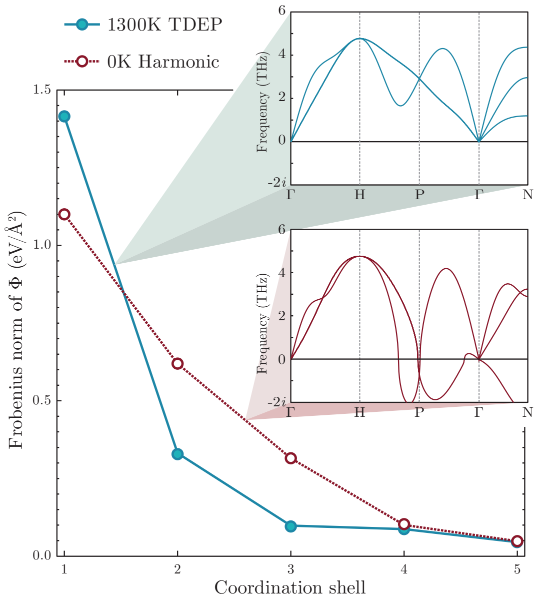
Thermal conductivity

Same as before, but temperature dependent!

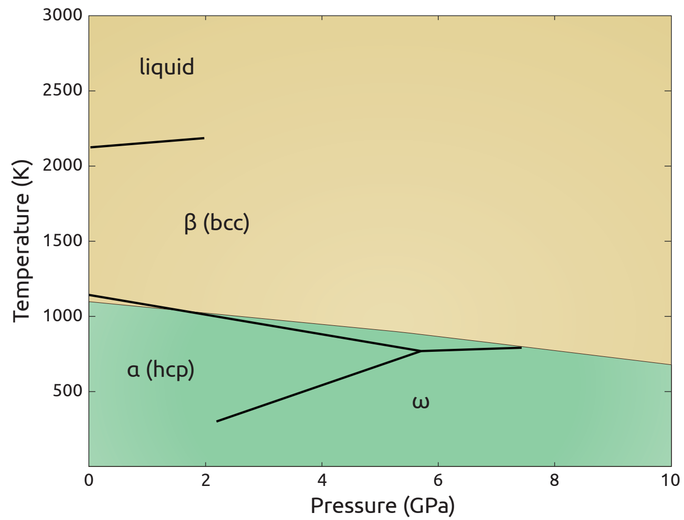
bcc Zr at 1300K



C. Stassis, Solid State Commun. 52, 9 (1984).
A. Heiming *et al.* Phys. Rev. B 43, 10948 (1991).

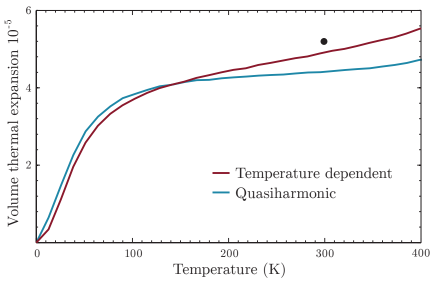


Zirconium

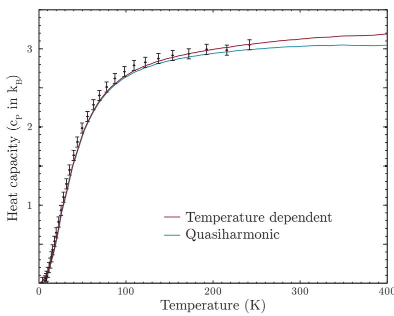


D. Young, Phase Diagrams of the Elements (University of California Press, Berkeley, 1991).

Zr is pathological.
More subtle cases, such as Bi_2Te_3

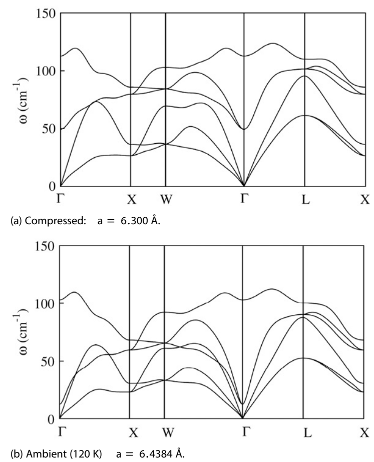


Coefficient of thermal expansion



Heat capacity

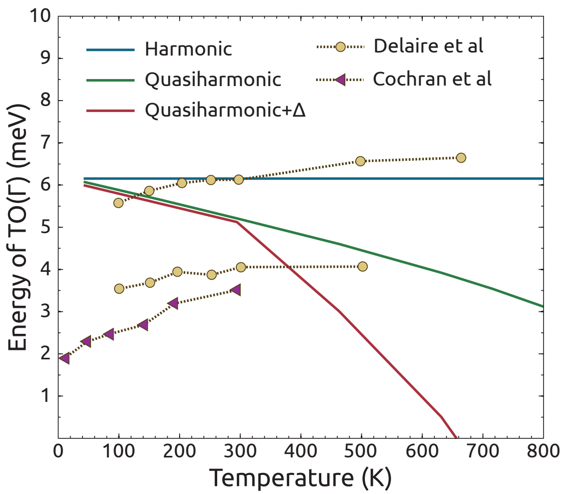
PbTe



Expanding the lattice decreases the thermal conductivity by factor 100

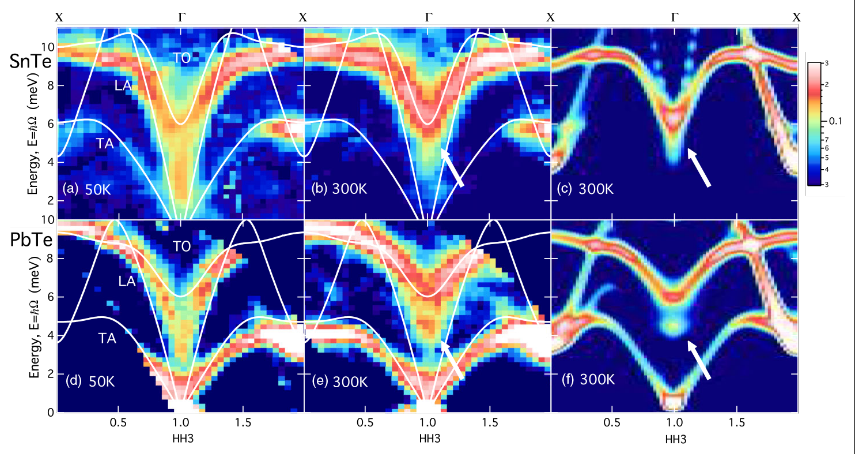
Extremely strong coupling between low optical modes and acoustic

PbTe



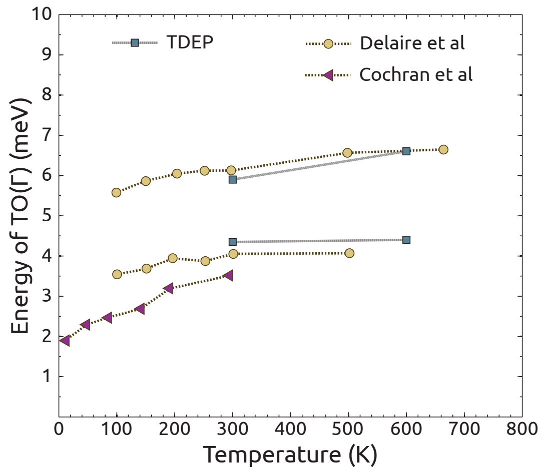
O. Delaire *et al.*, Nat. Mater. 10, 614 (2011).
W. Cochran *et al.*, Proc. R. Soc. A Math. Phys. Eng. Sci. 293, 433 (1966).

T-dependent S(Q,E)



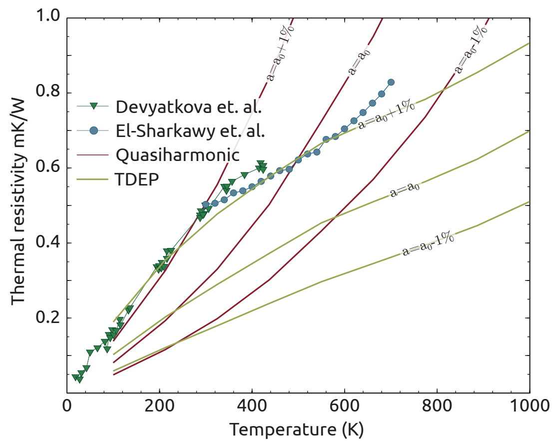
C.W. Li, O. Hellman, J. Ma, A. F. May, H.B. Cao, X. Chen, A. D. Christianson, G. Ehlers, D.J. Singh, B.C. Sales, and O. Delaire, Phys. Rev. Lett. 112, 175501 (2014).

PbTe



O. Delaire *et al.*, Nat. Mater. 10, 614 (2011).
W. Cochran *et al.*, Proc. R. Soc. A Math. Phys. Eng. Sci. 293, 433 (1966).
A.H. Romero, E.K.U. Gross, M.J. Verstraete, and O. Hellman, Phys. Rev. B 91, 214310 (2015).

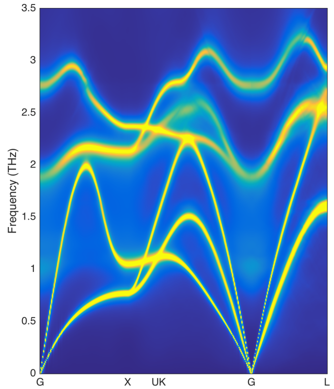
PbTe thermal resistivity



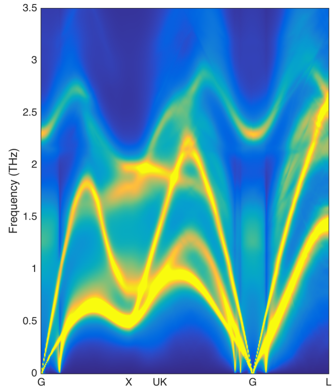
E.D. Devyatkova and I.A. Smirnov, Sov. Phys. Solid State, USSR 4, 2507 (1962).
A.A. El-Sharkawy *et al.*, Int. J. Thermophys. 4, 261 (1983).
A.H. Romero, E.K.U. Gross, M.J. Verstraete, and O. Hellman, Phys. Rev. B 91, 214310 (2015).

Ensemble matters

AIMD 600K



AIMD 100K



You can not use forceconstants from one ensemble and extrapolate to another in general

Max Power way

-isn't that just the wrong way? Yes, but faster!

Some people thing AIMD takes too long.

Obtaining force constants to all orders are reduced to a single matrix equation:

$$C\Theta = F$$

Matrix whose elements are a function of displacements $\times$ Irreducible force constants $=$ Forces from calculations

Max Power way

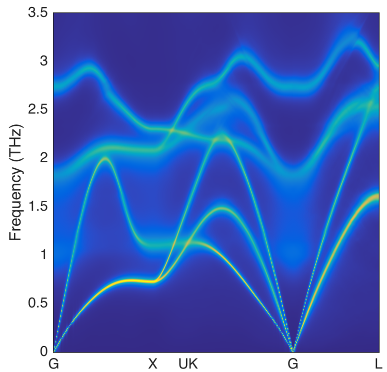
Choose displacements from a canonical ensemble (at the harmonic level) that minimize the condition number of matrix C

$$u_i = \sum_k \epsilon_{ik} c_{ik} e^{i\omega_k t+\delta_k} \qquad c_{ik} = \frac{1}{\omega_k}\sqrt{\frac{k_B T}{m_i}}\sqrt{2-\log\xi_1}$$

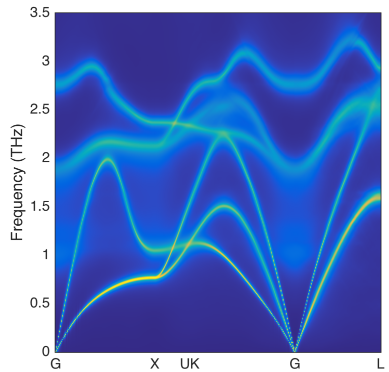
Monte Carlo solver to find the configurations in the given ensemble that give the most reliable solution

(could of course just use random displacements, but then I have no idea what ensemble I sample)

Gives more or less the same as MD

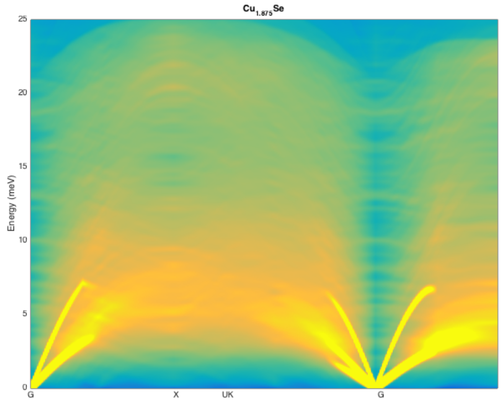


~30000 MD steps



five supercell calculations

What I am working on now



really really anharmonic systems

Nothing amuses more harmlessly than computation, and nothing is oftener applicable to real business or speculative inquiries.

A thousand stories which the ignorant tell, and believe, will die away at once, when the computist takes them in his gripe.

Cultivate in yourself a disposition to numerical inquiries: they will give entertainment in solitude by the practice, and reputation in public by the effect.

Samuel Johnson