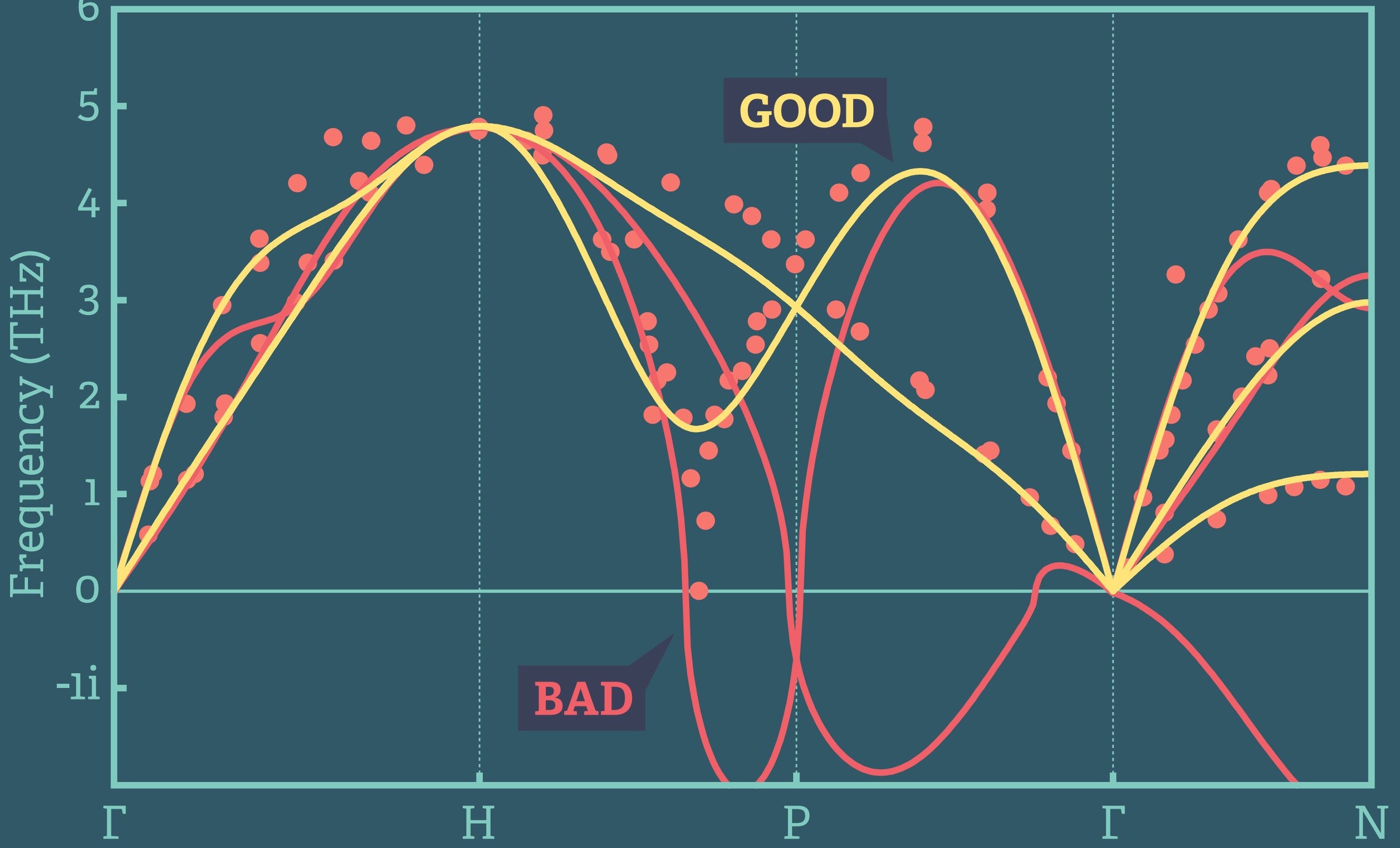
Finite temperature lattice dynamics, but faster!

Really quick background:

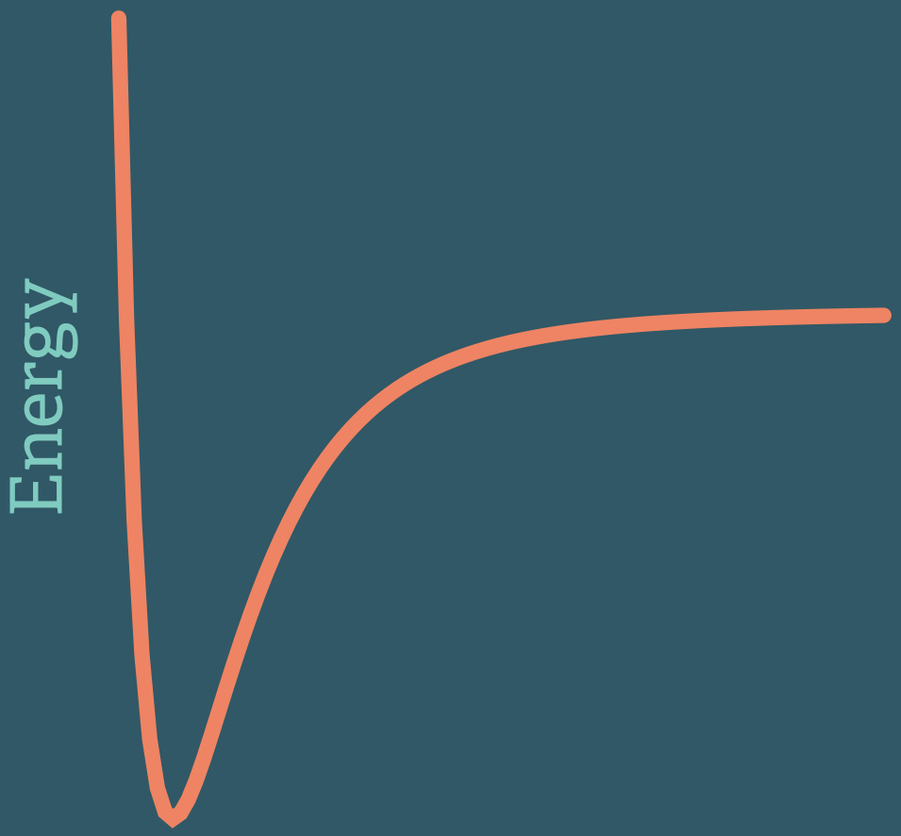


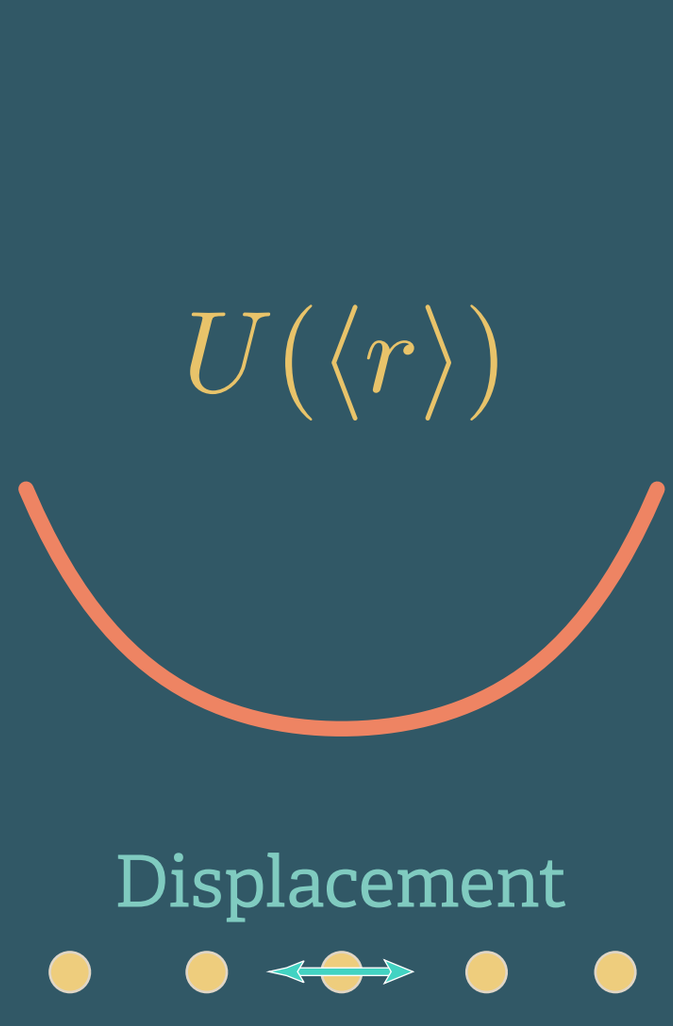
Effective potential depends depends on state

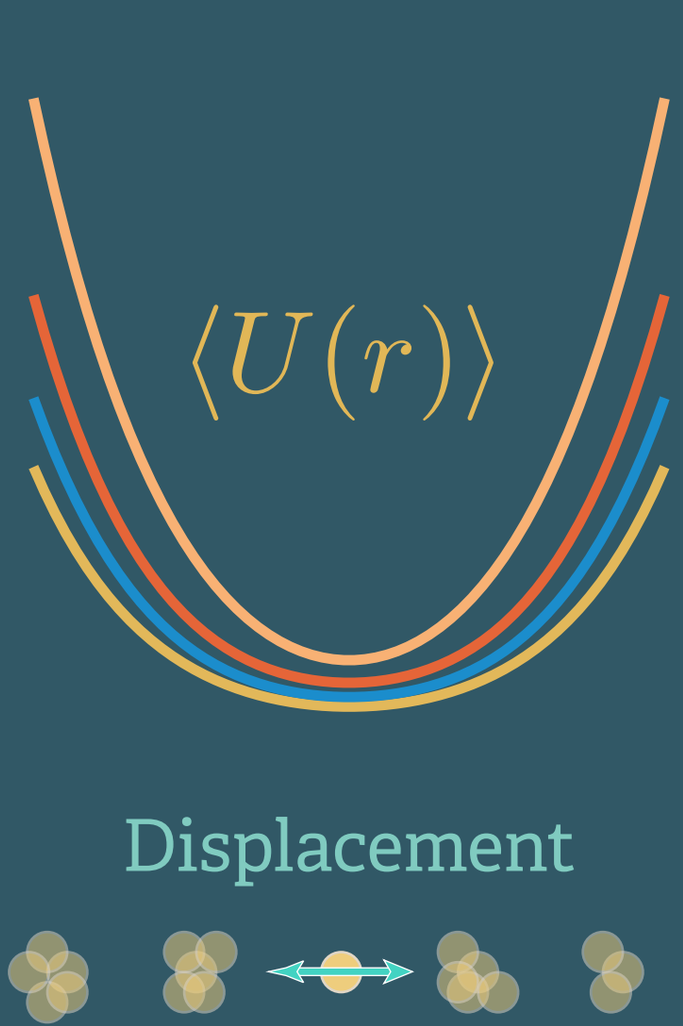
Pair potential (Lennard-Jones)

Potential at zero K

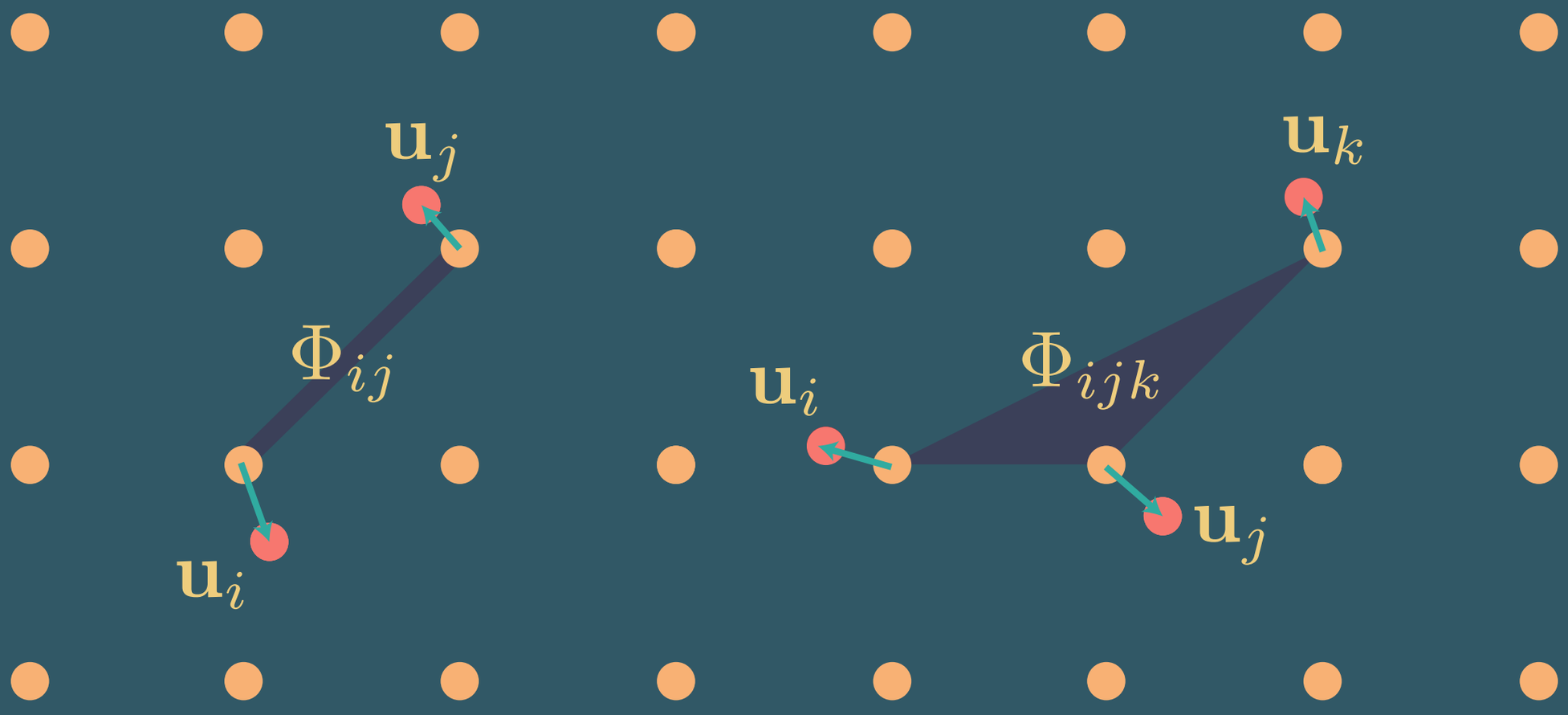
Potential at finite T







Fit lattice dynamical Hamiltonian to force-displacement data



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

Minimize the difference in forces

$$\min_{\Phi} \Delta F = \frac{1}{N_j N_a} \sum_j \sum_i \left| \mathbf{f}_{ji}^r - \mathbf{f}_{ij}^m \right|^2$$

$\mathbf{f}^{\mathbf{r}} =$ forces from DFT

$$\mathbf{f}_i^m = \sum_{j\beta} \Phi_{ij}^{\alpha\beta} u_j^\beta + \frac{1}{2} \sum_{jk\beta\gamma} \Phi_{ijk}^{\alpha\beta\gamma} u_j^\beta u_k^\gamma + \dots$$

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

O. Hellman, I.A. Abrikosov, and S.I. Simak, Phys. Rev. B 84, 180301 (2011)
O. Hellman, P. Steneteg, I.A. Abrikosov, and S.I. Simak, Phys. Rev. B 87, 104111 (2013)

Convenient model Hamiltonian

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

Phonons

Free energy

Elastic constants

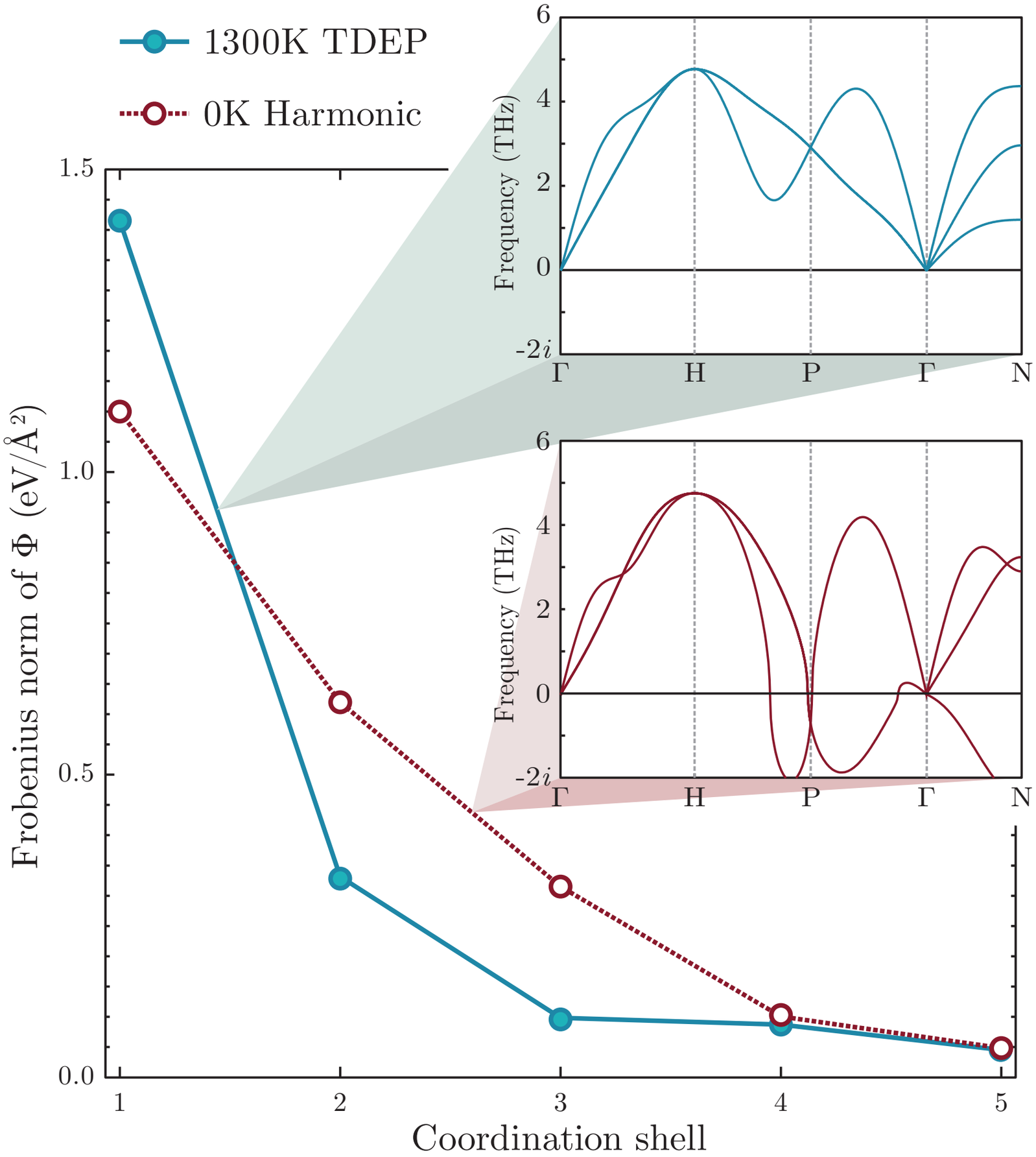
Lattice thermal conductivity

Phonon spectral function / S(q,E)

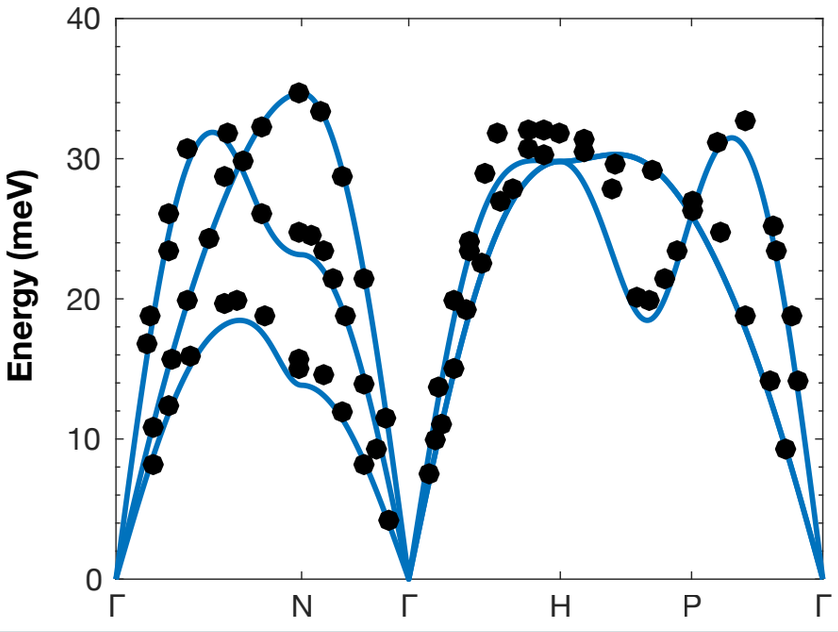
Unfolded bandstructures

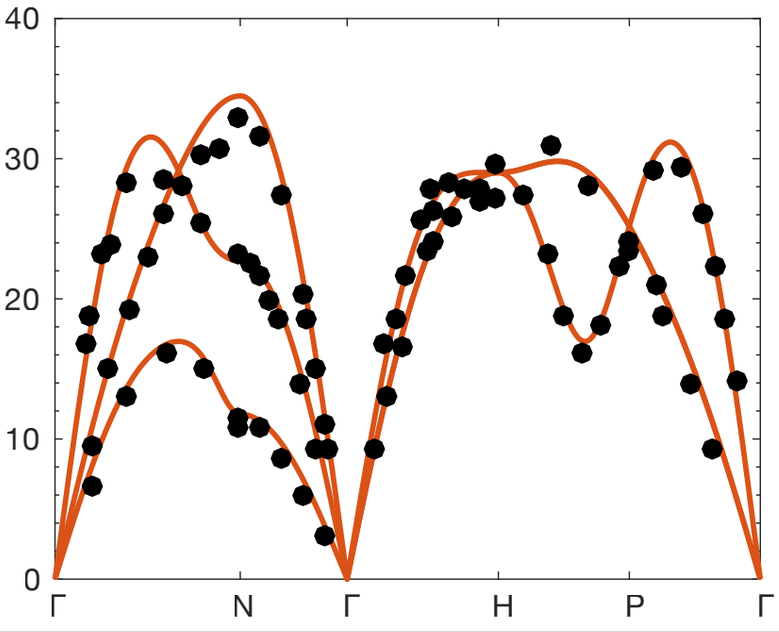
...

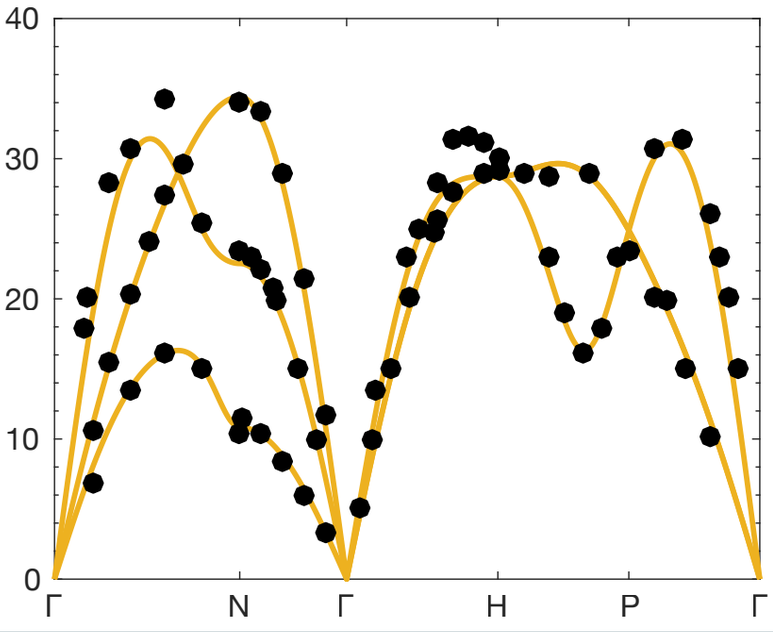
bcc Zr


1300K TDEP
0K Harmonic
Frobenius norm of Φ (eV/Å²)
Coordination shell
Frequency (THz)
Γ
H
P
Γ
N

bcc Fe







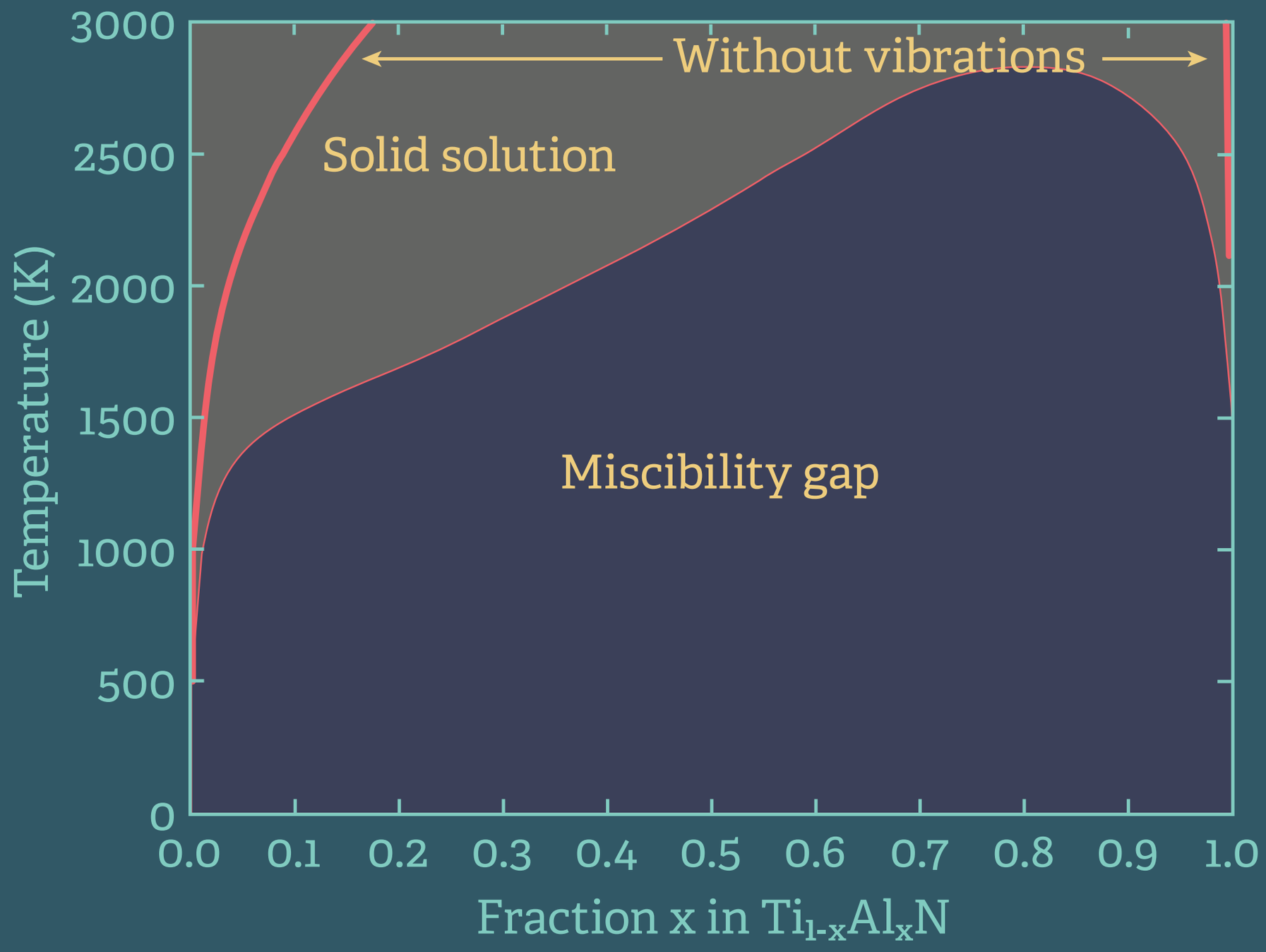
773K < Tc

1043K

1173K > Tc

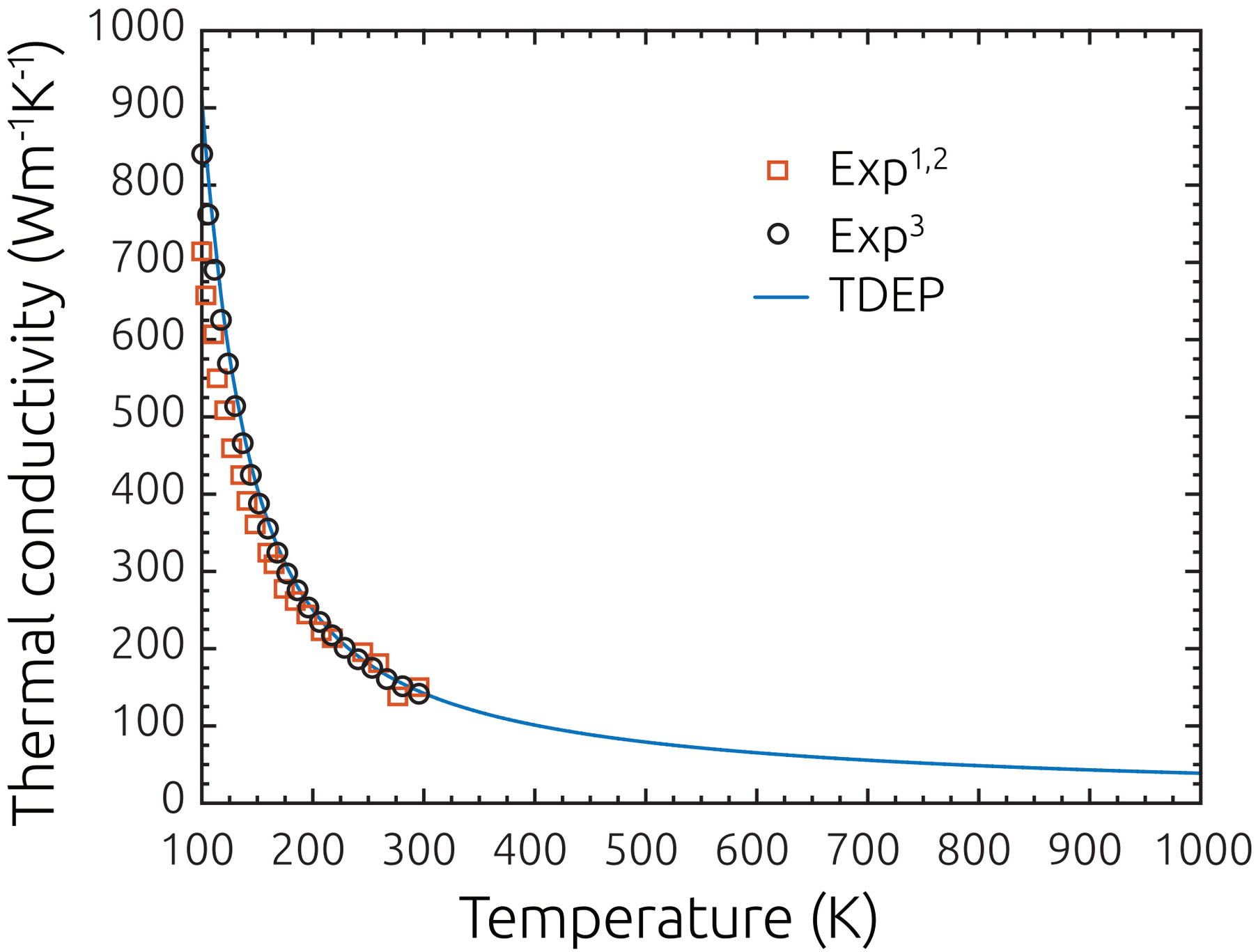
Captures magnon-phonon coupling and anharmonicity simultaneously.

$Ti_{1-x}Al_xN$

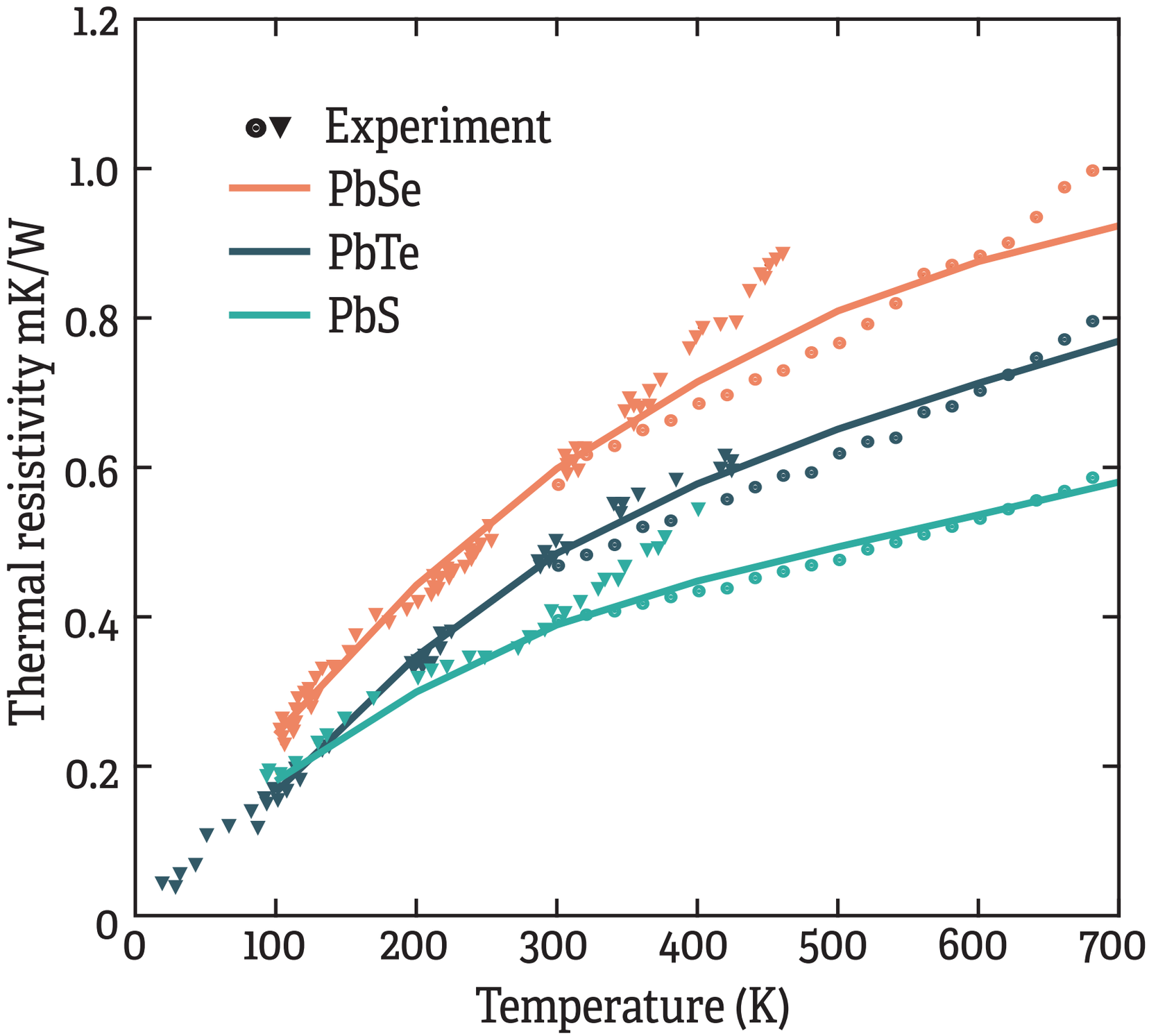


Vibrational free energies including anharmoncicity and substitutional disorder

Thermal conductivity (Si)

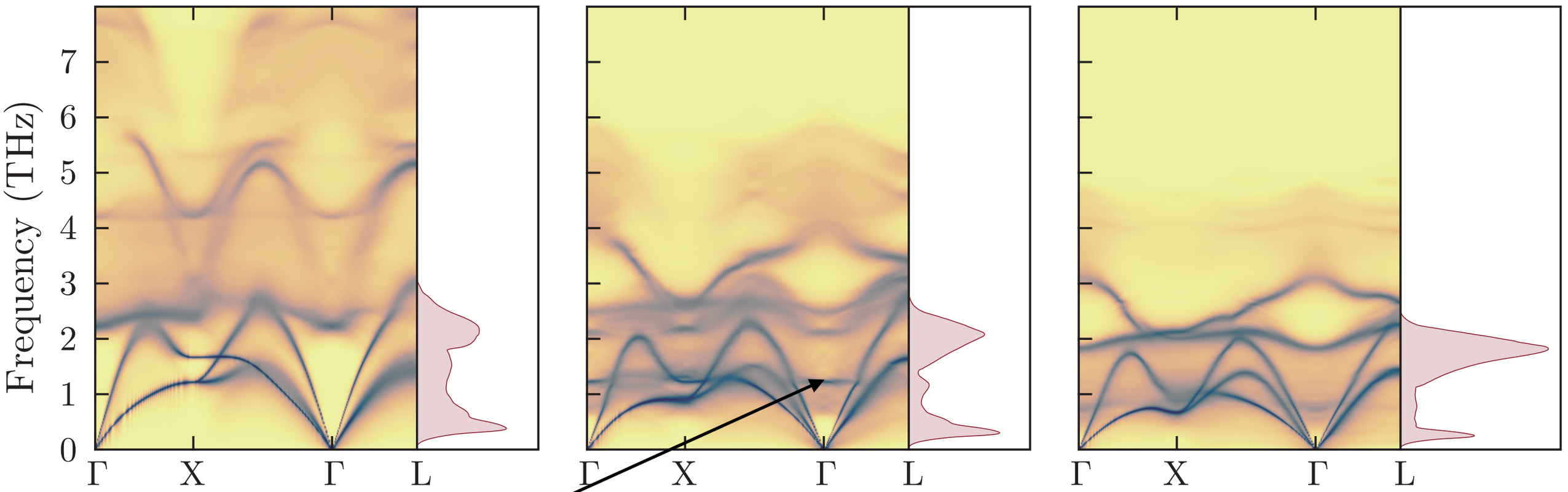


Nonlinear thermal resistivity



Phonon spectral function

PbS PbSe PbTe



Strange flat mode!

Shulumba, N., Physical Review B, 95(1), 14302. 2017

Linearized problem:

"simple" function of displacements → $Ax = B$ ← Forces

Force constants

How to choose displacements?

Path-integral MD (best, slow)

Born-Oppenheimer MD (kinda slow, ok at high T)

Stochastic (wrong, but faster!)

TDEP

Finite difference

Count

Relative error

10^{0}

10^{-1}

10^{-2}

10^{-2}

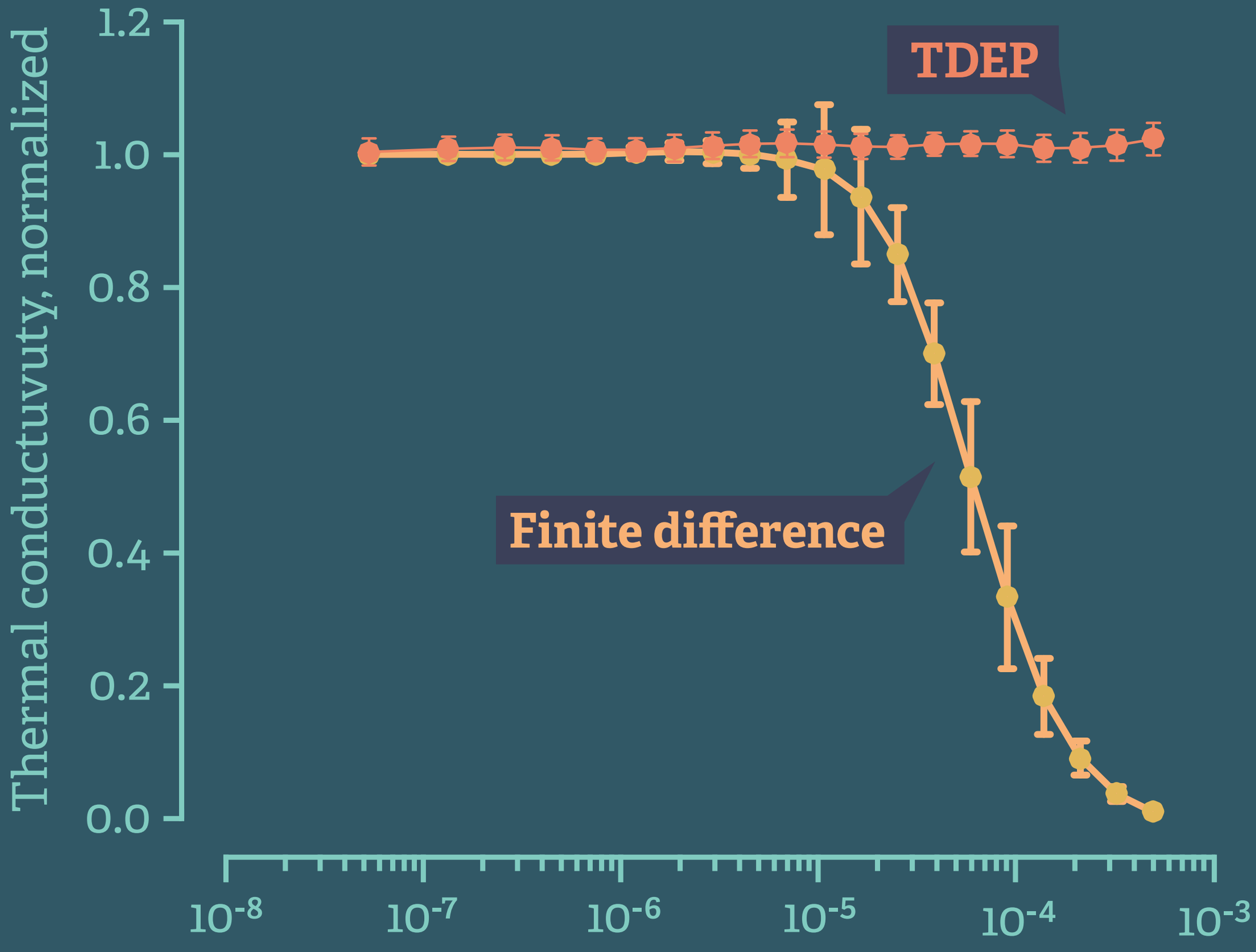
10^{-1}

10^{0}

10^{1}

Magnitude of force (eV/Å)

Thermal conductivity vs precision



Max Power way

Choose displacements from a canonical ensemble (at the harmonic level)

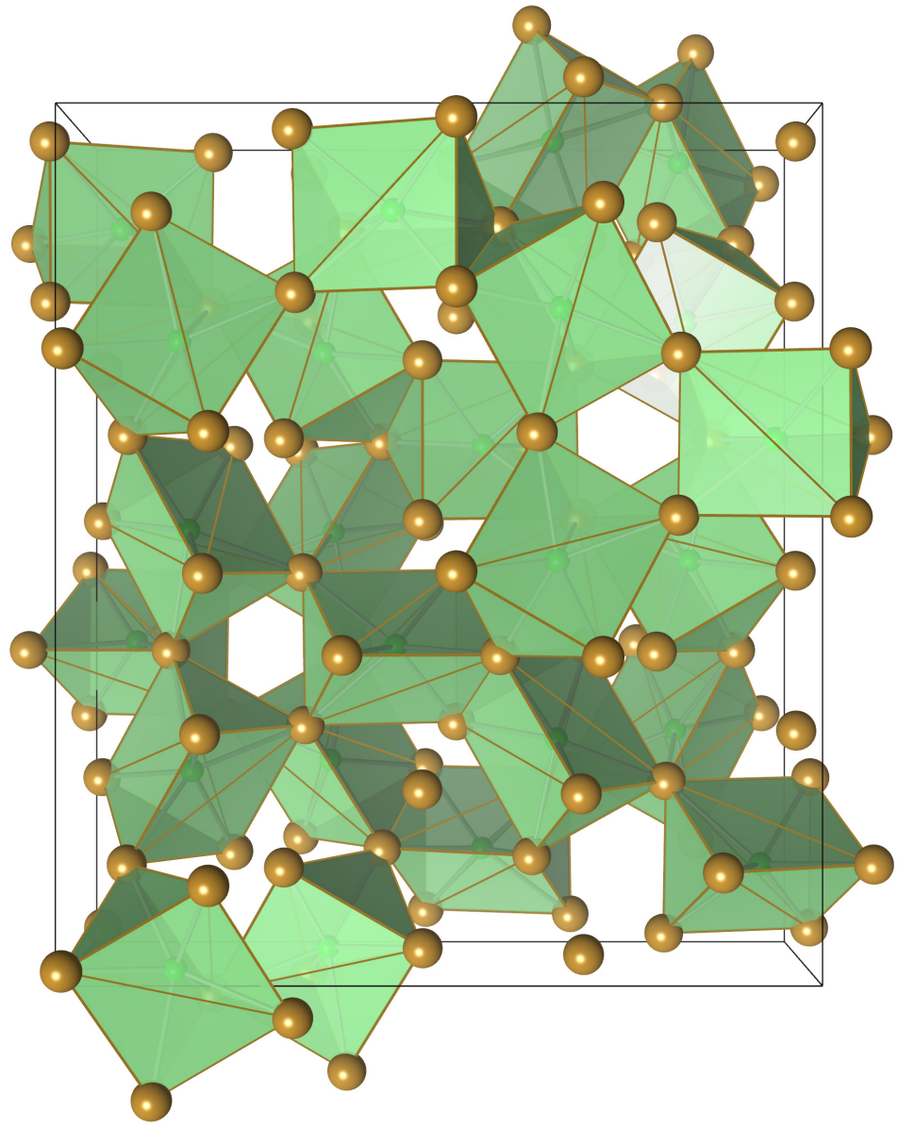
$$u_i = \sum_s \epsilon_{is} \langle A_{is} \rangle \sqrt{-2 \ln \xi_1} \sin 2\pi \xi_2$$

$$\langle A_{is} \rangle = \sqrt{\frac{\hbar(2n_s + 1)}{2m_i \omega_s}} \approx \frac{1}{\omega_s} \sqrt{\frac{k_B T}{m_i}}$$

Choose between quantum and classical occupation

Fast stochastic sampling

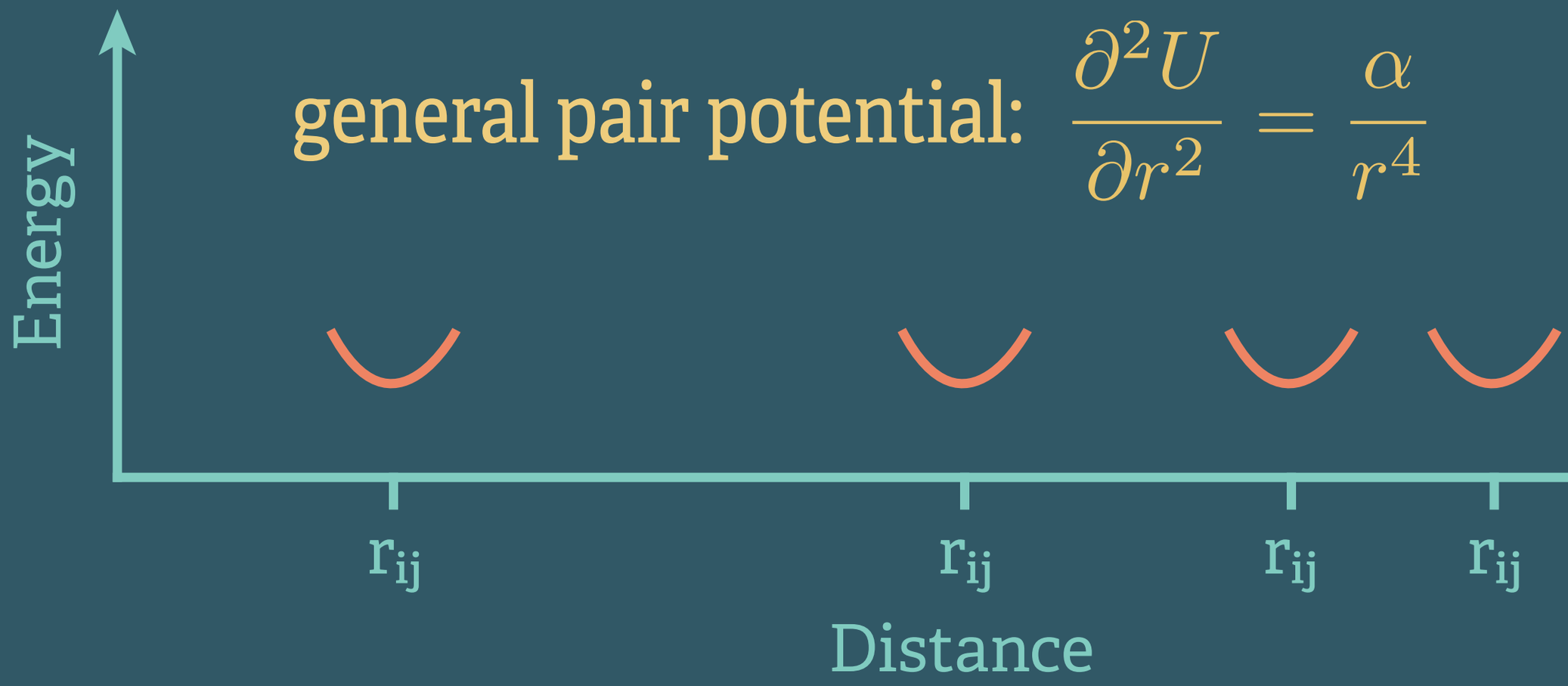
phonons > displacements > forces > new phonons



for complicated structures getting the initial seed is more expensive than the finite temperature phonons.

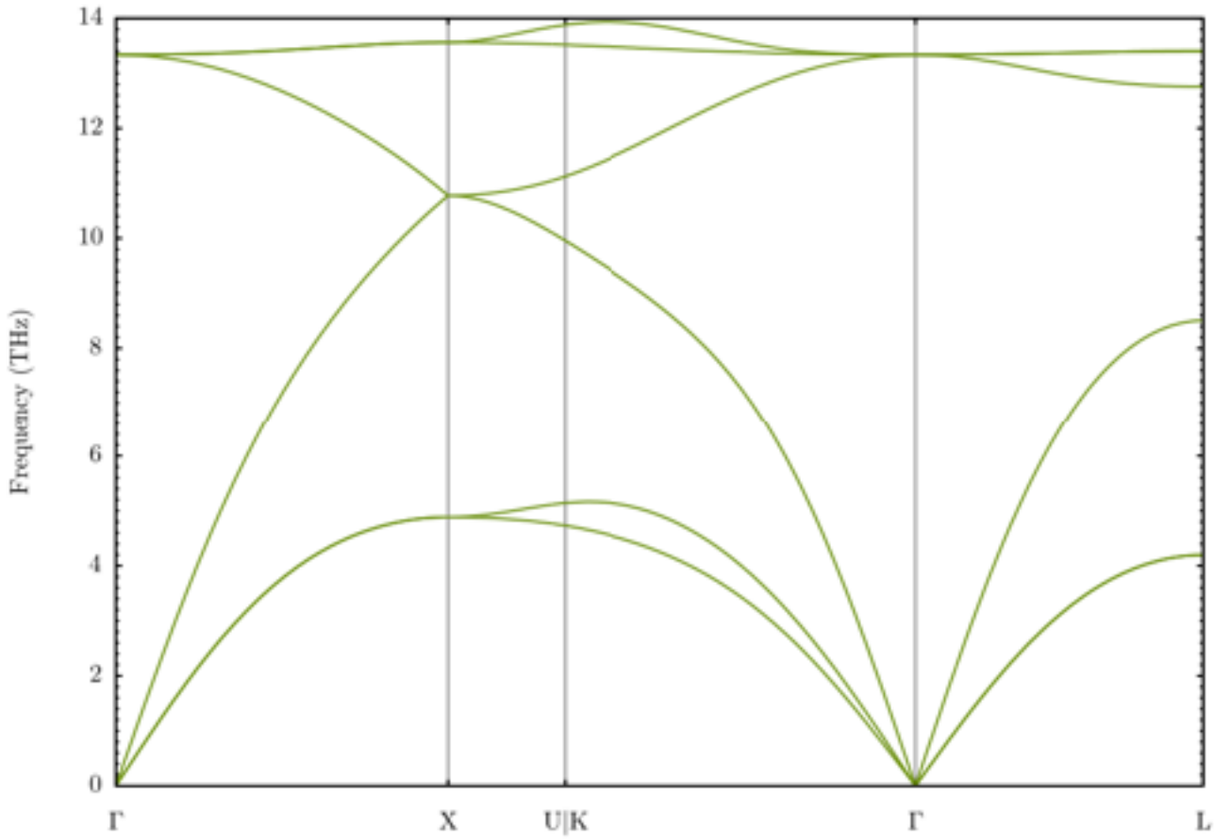
How do you guess phonons?

general pair potential: $\frac{\partial^2 U}{\partial r^2} = \frac{\alpha}{r^4}$

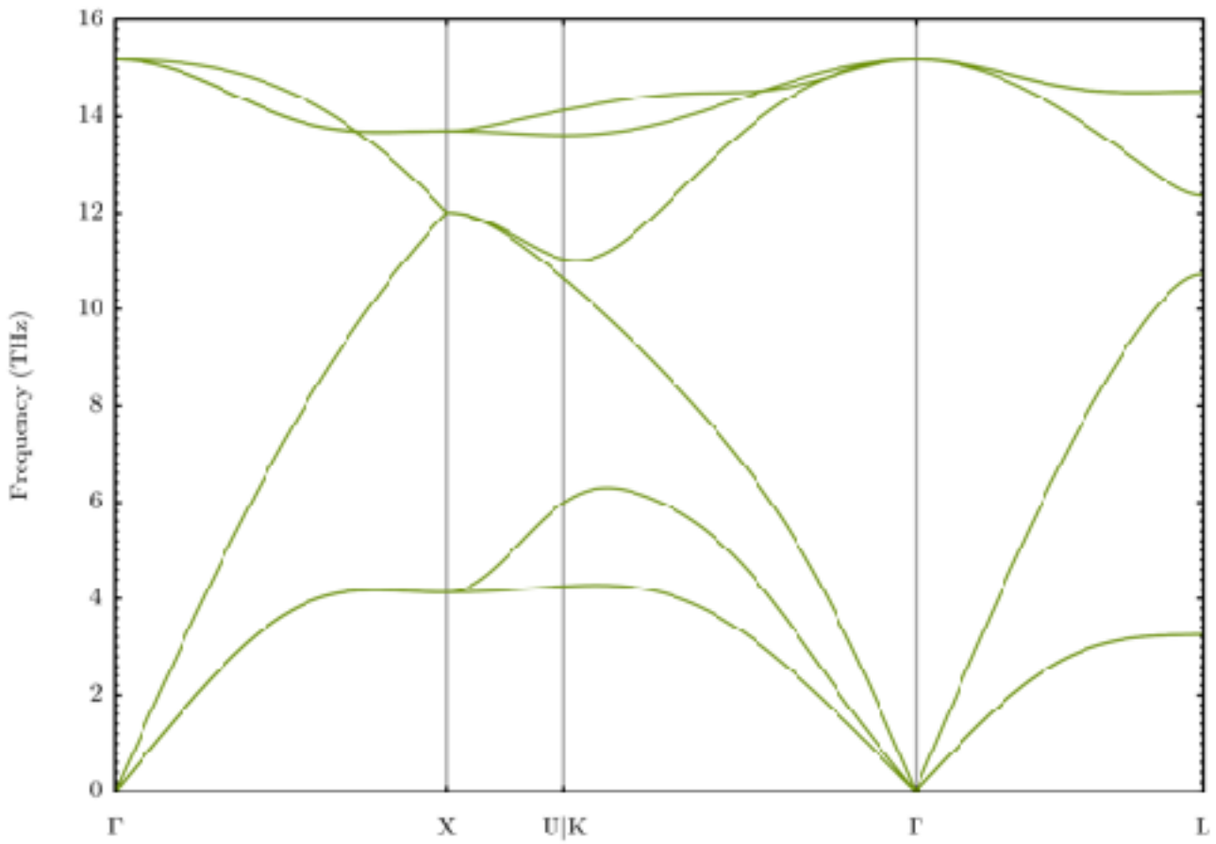


Trivially turned into forceconstants and phonons, depends on a single parameter that is matched to a Debye temperature/maximum frequency

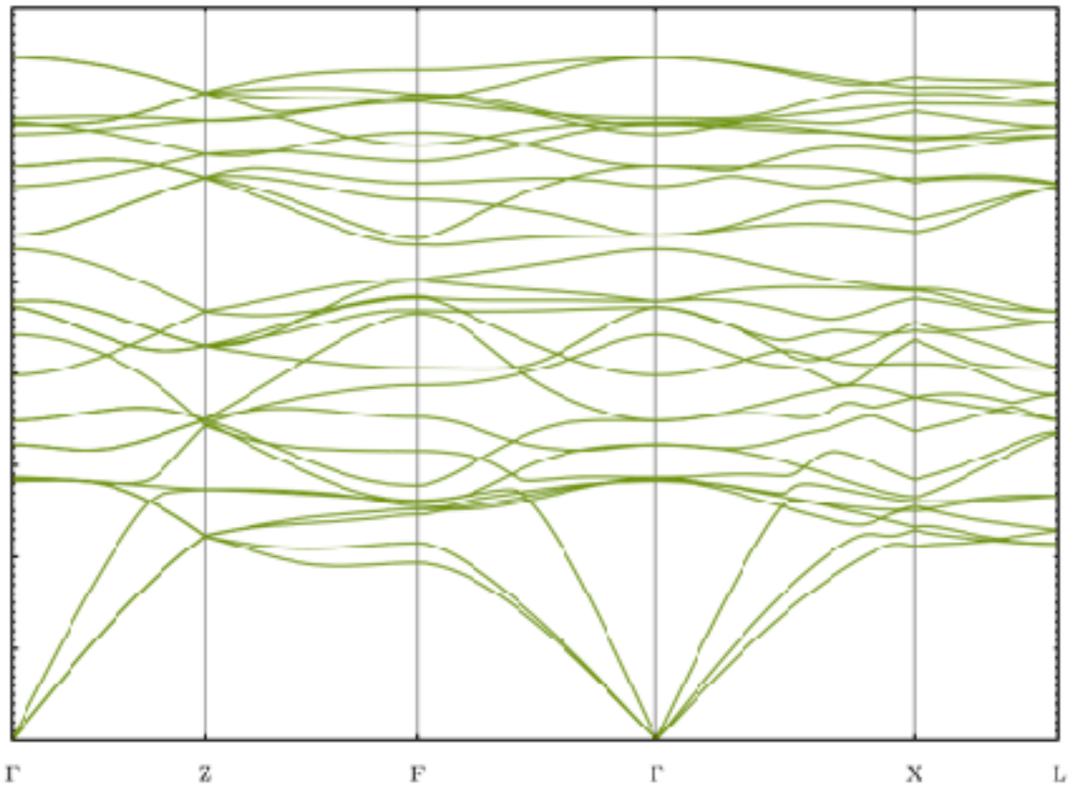
Fake seed phonons



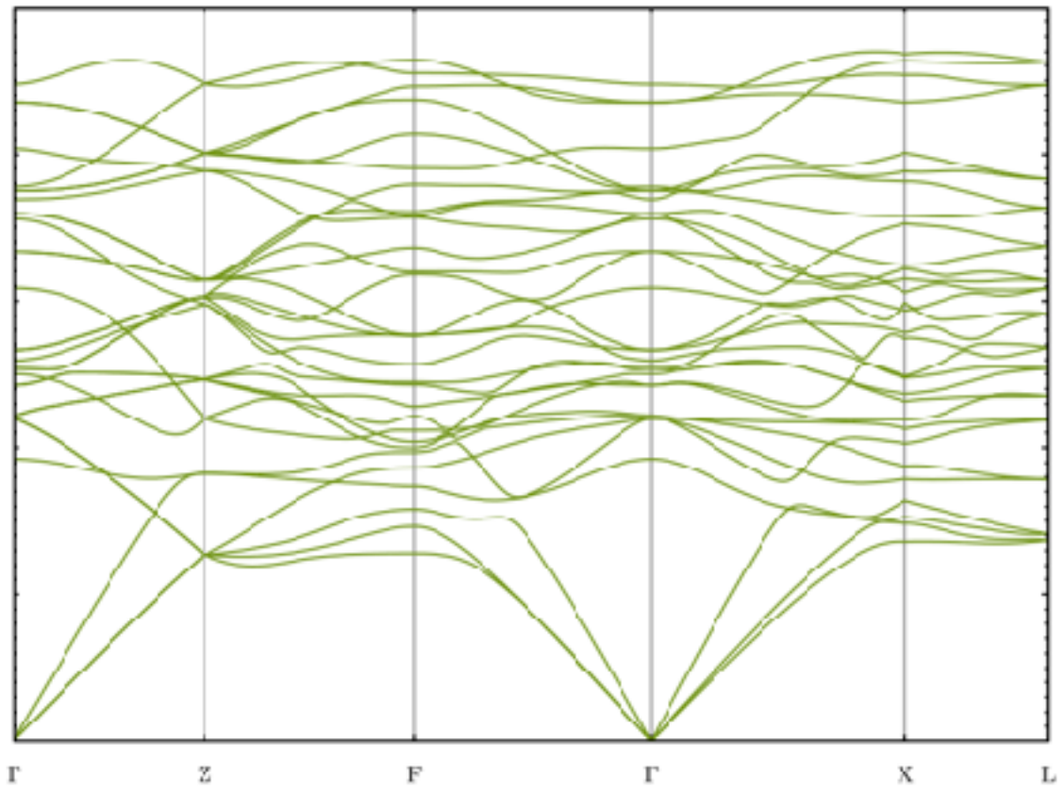
Real phonons



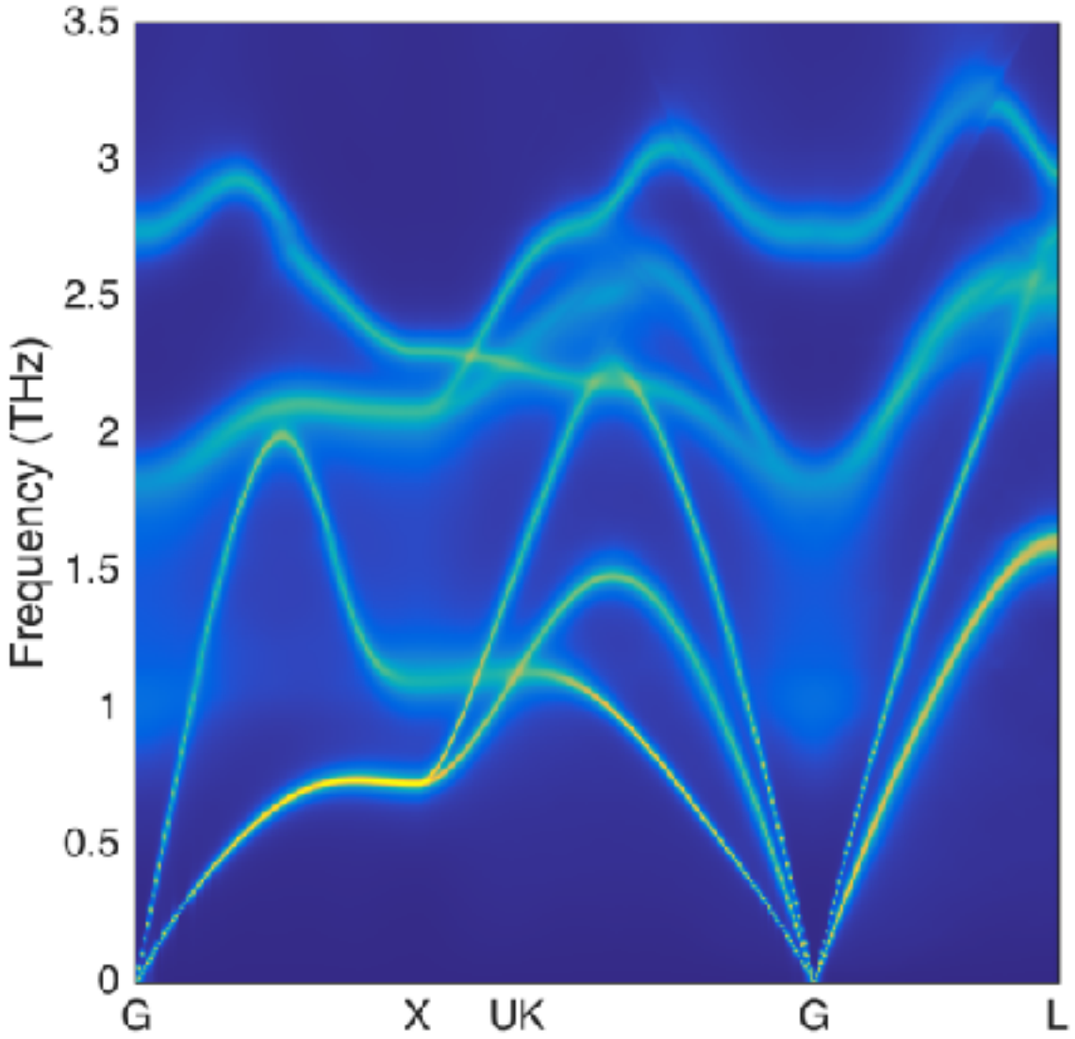
Fake seed phonons

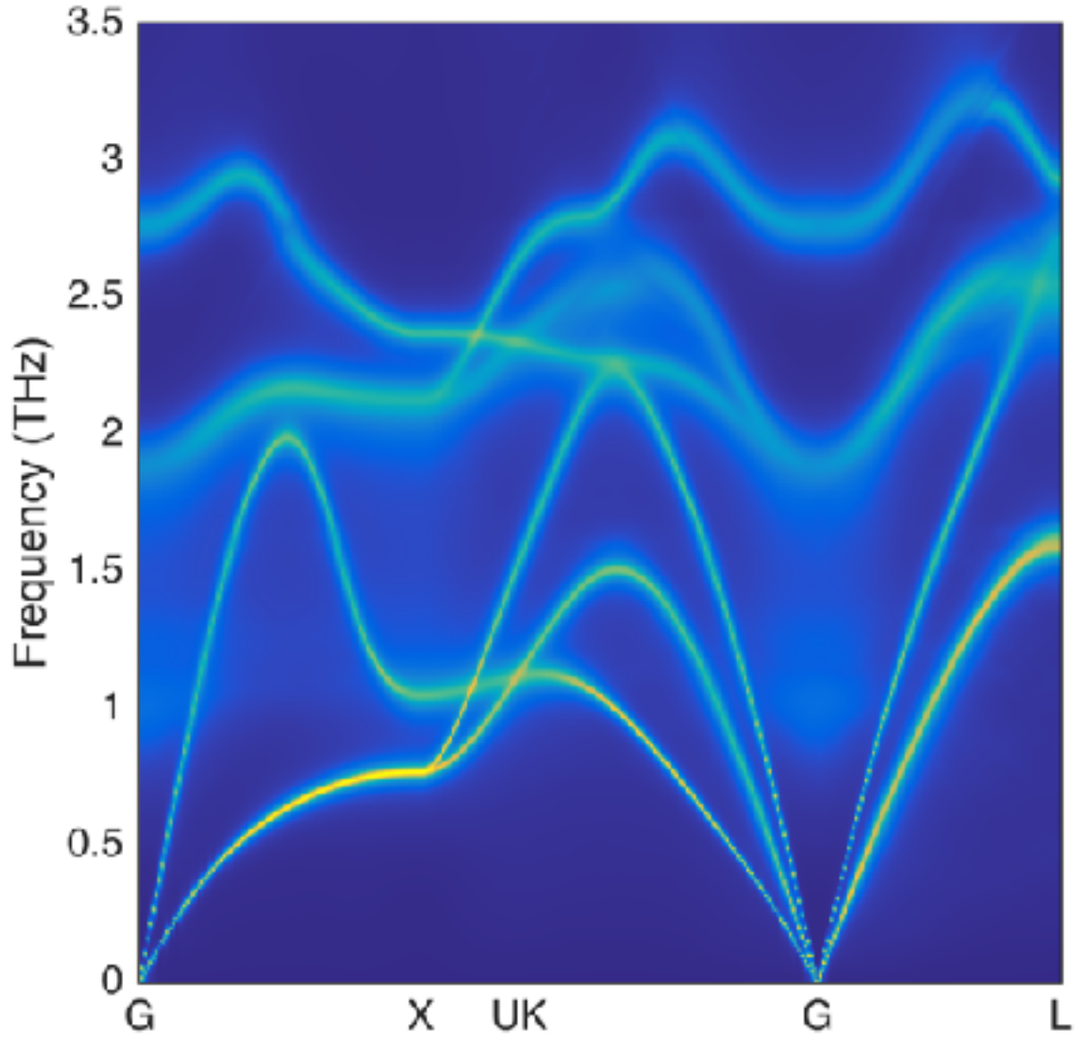


Real phonons



Gives more or less the same as MD





~30000 MD steps

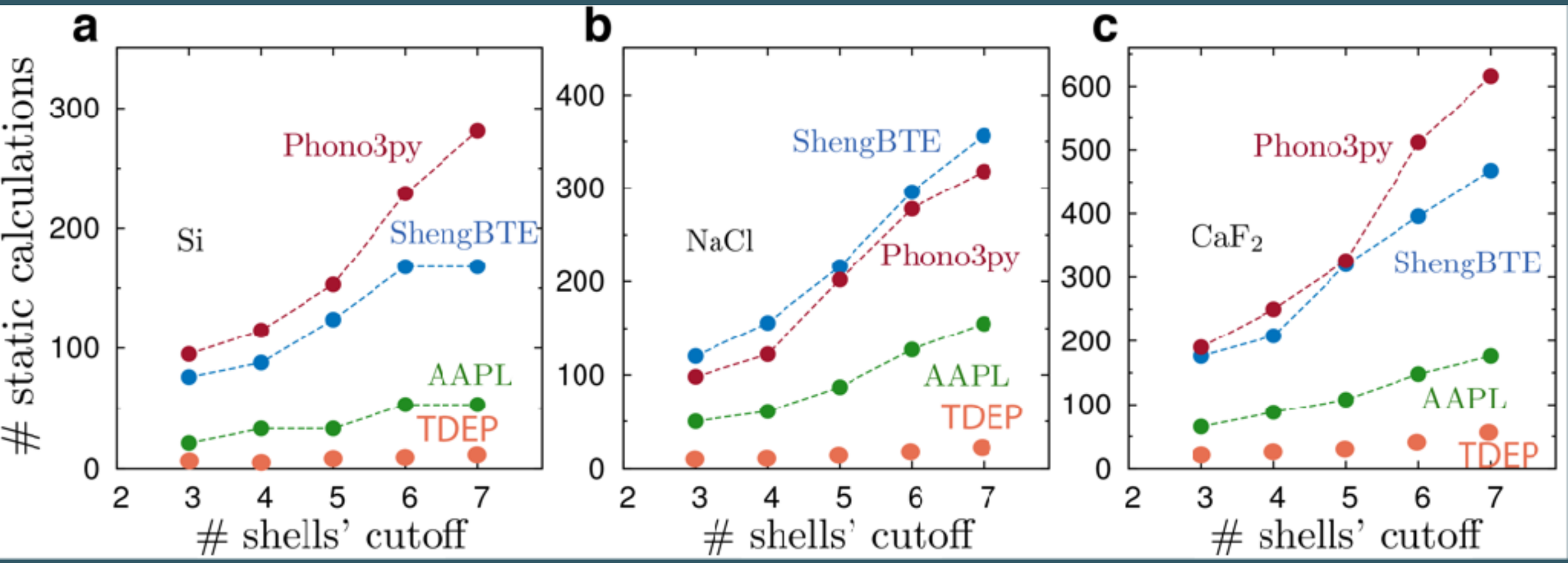
five supercell calculations

Scales in a quite nice way

	# atoms/cell	# independent IFCs
Si	2	31+74+12
GaAs	4	100+28
$BaTiO_3$	5	49+54
Sapphire	10	236 + 300
Tetrahedrite	29	153 + 86
Fe_7C_3	80	2028

3N equations per supercell calculation

Quite a bit faster than the competition



It’s in Abinit, sort of

Input:

ionmov 24

Max frequency/Debye temperature

Temperature

Which orders to calculate (2nd, 3rd, 4th)

Copied the normal MD routine

Instead of MD, draw configurations:

$$u_i = \sum_s \epsilon_{is} \langle A_{is} \rangle \sqrt{-2 \ln \xi_1} \sin 2\pi\xi_2 \qquad \langle A_{is} \rangle = \sqrt{\frac{\hbar(2n_s+1)}{2m_i\omega_s}} \approx \frac{1}{\omega_s}\sqrt{\frac{k_B T}{m_i}}$$

Calculate the forceconstants on-the-fly, every timestep

Update frequencies/eigenvectors after some interval

(Reweight via the density matrix)

Works fine, but some ?

Electrostatics

Better anaddb output

Stopping criteria?

Other?