The Phonon Quasiparticle Approach for Anharmonic Properties of Solids

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Acknowledgements

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XSEDE
Extreme Science and Engineering Discovery Environment

This talk is based on these papers:

[1] D.-B. Zhang *et al.*, PRL **112**, 058501 (2014).

[2] T. Sun *et al.*, PRB **89**, 094109 (2014).

[3] Y. Lu *et al.*, PRL **118**, 145702 (2017).

[4] D.-B. Zhang *et al.*, PRB **96**, 100302(R) (2017).

[5] Z. Zhang *et al.*, Comput. Phys. Commun. **243**, 110 (2019).

[6] Z. Zhang *et al.*, PRB **103**, 104108 (2021).

[7] Z. Zhang *et al.*, PRB **103**, 144103 (2021).

[8] Z. Zhang *et al.*, PRB **104**, 184101 (2021).

[9] Z. Zhang *et al.*, PRB **106**, 054103 (2022).

Outline

- Introduction: Role of Lattice Anharmonicity in Materials Computation And Geophysics
- Method: Phonon Quasiparticle Approach
- Application to Si (Diamond Structure)
- Application to $MgSiO_3$ Pv/PPv (Weakly Anharmonic)
- Application to $CaSiO_3$ Pv (Strongly Anharmonic)
- Application to bcc/hcp Be (Strongly Anharmonic Metal)
- Hands-on: phq code

Lattice Anharmonicity in Real Space

Harmonic

$$V(x_1,\ldots,x_N) = V(0,\ldots,0) + \frac{1}{2}\sum_{n,n'}\left(\frac{\partial^2 V}{\partial x_n \partial x_{n'}}\right)_{(x_1,\ldots,x_N)=0} x_n x_{n'}$$

$$+\frac{1}{6}\sum_{n,n',n''}\left(\frac{\partial^3 V}{\partial x_n \partial x_{n'} \partial x_{n''}}\right)_{(x_1,\ldots,x_N)=0} x_n x_{n'} x_{n''}$$

$$+\frac{1}{24}\sum_{n,n',n'',n'''}\left(\frac{\partial^4 V}{\partial x_n \partial x_{n'} \partial x_{n''} \partial x_{n'''}}\right)_{(x_1,\ldots,x_N)=0} x_n x_{n'} x_{n''} x_{n'''} \cdot + \ldots$$

Anharmonic

Role of Anharmonicity in Materials Computation

1. Free energy and thermodynamics including anharmonicity

-- Phase transition

-- Thermal expansivity

-- Heat capacity

-- Thermal elasticity

} High *T*

2. Lattice thermal conductivity

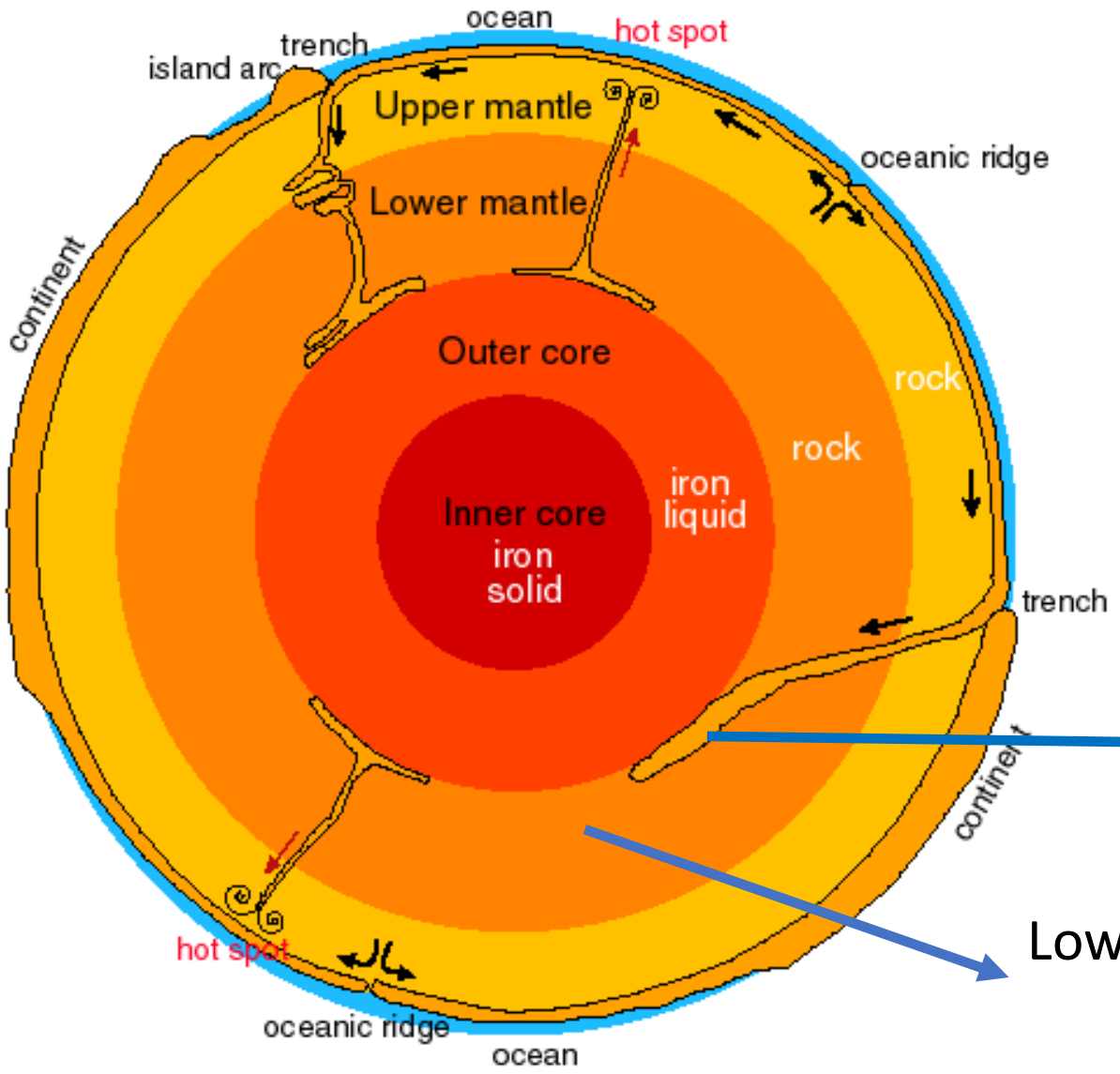
Role of Anharmonicity in Geophysics

- Thermodynamic properties are essential for geodynamic modeling (α, C_V, C_P, K_T, K_S)

- Accurate free energies are needed for determining phase boundary: seismic discontinuities

- Thermoelastic properties are needed for interpreting seismic tomography (c_{ij}, G, K_S, v_P, v_Φ, v_S)

- Thermal conductivity (κ) of the lower mantle (LM) minerals



Core-mantle boundary (CMB) ~ 2890 km depth

↓

Interface between molten metallic core and rocky mantle

↓

Mass transport is impeded

↓

Conduction: main mechanism of heat transport across the CMB

→ Subducted mid-ocean ridge basalt (MORB) accumulates above the CMB

Lower mantle: 55 vol% of the entire Earth

$23 < P < 135$ GPa, $2000 < T < 4000$ K

Ab initio methods to compute thermodynamic properties at high *T*

1. Perturbation theory + quasiharmonic approximation (QHA)

$$\left(\frac{\partial \omega}{\partial T}\right)_V = 0$$

2. *Ab initio* molecular dynamics + thermodynamic integration (TI)

Limited *N*

3. Phonon quasiparticle approach + phonon gas model

$$\tilde{\omega} = \tilde{\omega}\,(T), \quad N \to \infty$$

Ab initio methods to compute lattice thermal conductivity

1. Finite displacement method

- Explicitly express the higher-order interatomic force constants (IFCs).
- Higher-order IFCs are computationally heavy and may suffer from numerical errors and truncation issues.
- Considering only the 3rd-order IFCs may overestimate the κ.
- Fail for strongly anharmonic systems with imaginary phonon frequencies without the renormalization of IFCs.

2. Phonon quasiparticle approach + relaxation time approximation (RTA)

- Does not explicitly express the higher-order IFCs.
- Easy to compute.
- In principle, anharmonicity is included to all orders in perturbation theory.
- Renormalization of harmonic IFCs is included.

Method

Phonon quasiparticle approach + phonon gas model

phonon quasiparticle: $(\tilde{\omega}, \tau)$ $\Gamma = \frac{1}{2\tau}$

↓

Harmonic approximation: $\left(\frac{\partial \omega}{\partial T}\right)_V = 0$ $\tau \to \infty$

↓

Consider anharmonicity: $\tilde{\omega} = \tilde{\omega}(T)$ $\tau \sim$ps

↓

Phonon gas model: $\hbar\tilde{\omega}$

↓

Vibrational free energy: $F = U - TS_{vib}$

$$S_{vib} = k_B \sum [(n+1)\ln(n+1) - n\ln n] \qquad n = [\exp(\hbar\,\tilde{\omega}/k_B\,T) - 1]^{-1}$$

Method

Phonon quasiparticle approach

Mode-projected **V**elocity **A**utocorrelation **F**unction (**VAF**):

$$\langle V_{\mathbf{q}s}(0)V_{\mathbf{q}s}(t)\rangle = \lim_{\tau\to\infty}\frac{1}{\tau}\int_0^{\tau} V^*_{\mathbf{q}s}(t')V_{\mathbf{q}s}(t'+t)dt'$$

$$V_{\mathbf{q}s}(t) = \sum_{i=1}^{N}\sqrt{M_i}\mathbf{v}_i(t)e^{i\mathbf{q}\cdot\mathbf{R}_i}\cdot\hat{\mathbf{e}}^i_{\mathbf{q}s}$$

i: 1, 2, …, N supercell atoms

q: wave vector

s: 1, 2, …, 3n phonon branches

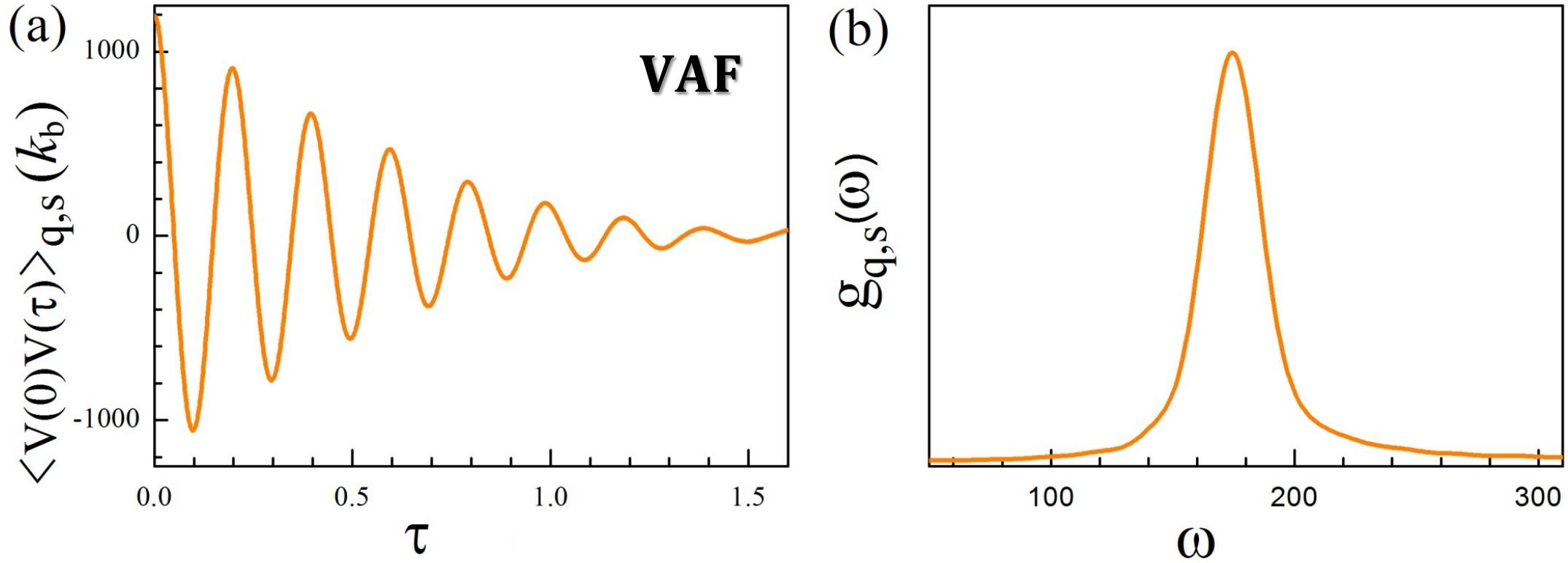
Ab initio molecular dynamics

Ab initio harmonic phonons

Method

Well-defined quasiparticle

$$\langle V_{\mathbf{q}s}(0)V_{\mathbf{q}s}(t)\rangle = A_{\mathbf{q}s}\cos(\tilde{\omega}_{\mathbf{q}s}t)e^{-\Gamma_{\mathbf{q}s}t} \qquad G_{\mathbf{q}s}(\omega) = \left|\int_0^\infty \langle V_{\mathbf{q}s}(0)V_{\mathbf{q}s}(t)\rangle e^{i\omega t}dt\right|^2$$



T. Sun *et al.*, PRB **82**, 224304 (2010); D.-B. Zhang *et al.*, PRL **112**, 058501 (2014).

Method

Well-defined quasiparticle

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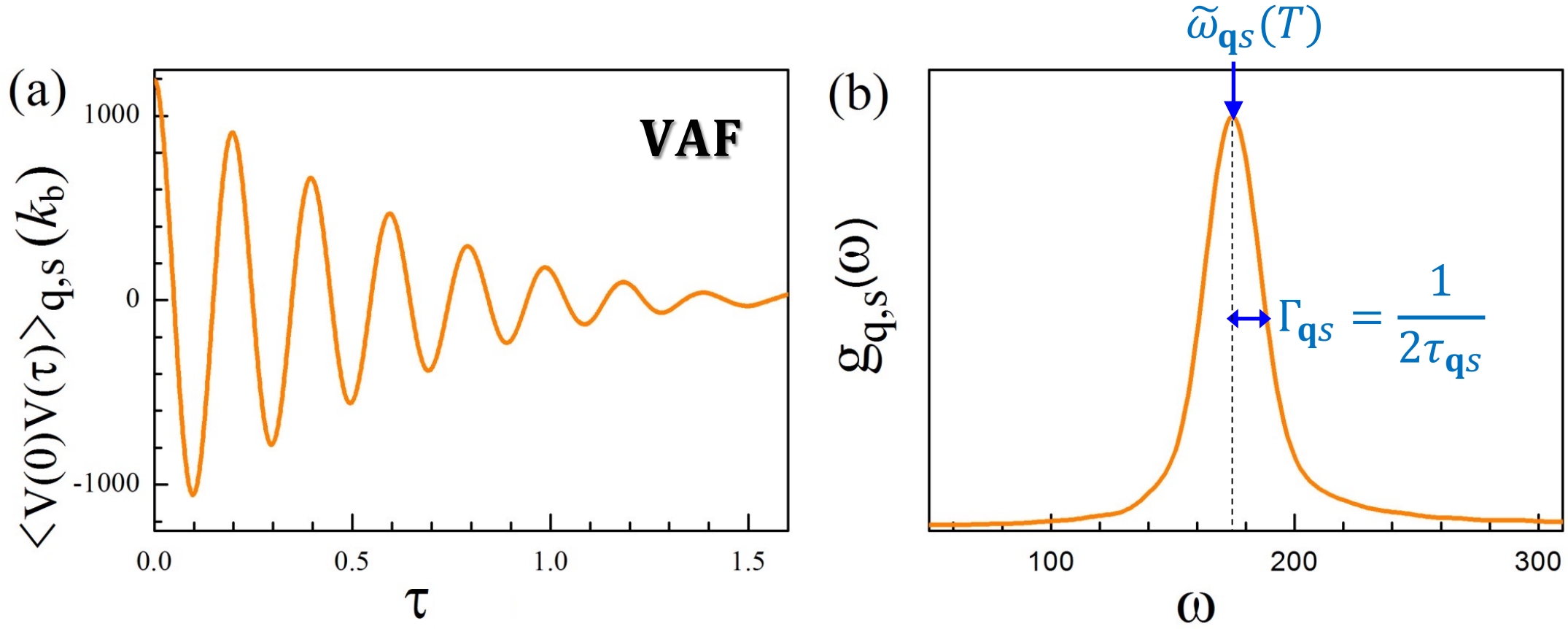


T. Sun *et al.*, PRB **82**, 224304 (2010); D.-B. Zhang *et al.*, PRL **112**, 058501 (2014).

$$\mathbf{VAF}(\tilde{\omega},\tau) = A_{\mathbf{q}s}\cos(\tilde{\omega}_{\mathbf{q}s}t)e^{-t/(2\tau_{\mathbf{q}s})}$$

Method

Effective harmonic dynamical matrix

$$[\hat{\mathbf{e}}_{\mathbf{q}}] = [\hat{\mathbf{e}}_{\mathbf{q}1}, \hat{\mathbf{e}}_{\mathbf{q}2}, \ldots, \hat{\mathbf{e}}_{\mathbf{q}3n}] \qquad \Omega_{\mathbf{q}} = \mathrm{diag}[\tilde{\omega}^2_{\mathbf{q}1}, \tilde{\omega}^2_{\mathbf{q}2}, \ldots, \tilde{\omega}^2_{\mathbf{q}3n}]$$

$$\tilde{D}(\mathbf{q}) = \hat{\mathbf{e}}_{\mathbf{q}} \Omega_{\mathbf{q}} \hat{\mathbf{e}}_{\mathbf{q}}{}^{\dagger}$$

$$\tilde{\Phi}(\mathbf{r}) = \sum_{\mathbf{q}} \tilde{D}(\mathbf{q})\, e^{i\mathbf{q}\cdot\mathbf{r}}$$

$$\tilde{D}(\mathbf{q}') = \sum_{\mathbf{r}} \tilde{\Phi}(\mathbf{r})\, e^{-i\mathbf{q}'\cdot\mathbf{r}}$$

T-dependent phonon dispersion, VDoS, phonon velocity $v_{\mathbf{q}s} = \frac{d\omega_{\mathbf{q}s}}{d\mathbf{q}}$

Method

Phonon gas model with *T*-dependent VDoS

$$S_{vib}(T) = k_B \sum_{\mathbf{q}s} [(n_{\mathbf{q}s} + 1)\ln(n_{\mathbf{q}s} + 1) - n_{\mathbf{q}s}\ln n_{\mathbf{q}s}]$$

$$n_{\mathbf{q}s} = \left[\exp(\hbar\tilde{\omega}_{\mathbf{q}s}(T)/k_B T) - 1\right]^{-1}$$

Method

Relaxation time approximation (RTA) of
linearized Boltzmann transport equation (LBTE)

$$\kappa = \frac{1}{3}\sum_{\mathbf{q}s} c_{\mathbf{q}s} v_{\mathbf{q}s} l_{\mathbf{q}s}$$

$$l_{\mathbf{q}s} = v_{\mathbf{q}s}\tau_{\mathbf{q}s}$$

$$\kappa = \frac{1}{3}\sum_{\mathbf{q}s} c_{\mathbf{q}s} v_{\mathbf{q}s}^2 \tau_{\mathbf{q}s}$$

Application to Si (Diamond Structure)

Si:

- Simple structure with a 2-atom primitive cell

- Anharmonicity is not strong

- Neutron scattering data is available

Si

Ab initio MD simulation details

PBE

4×4×4 supercells (128 atoms)

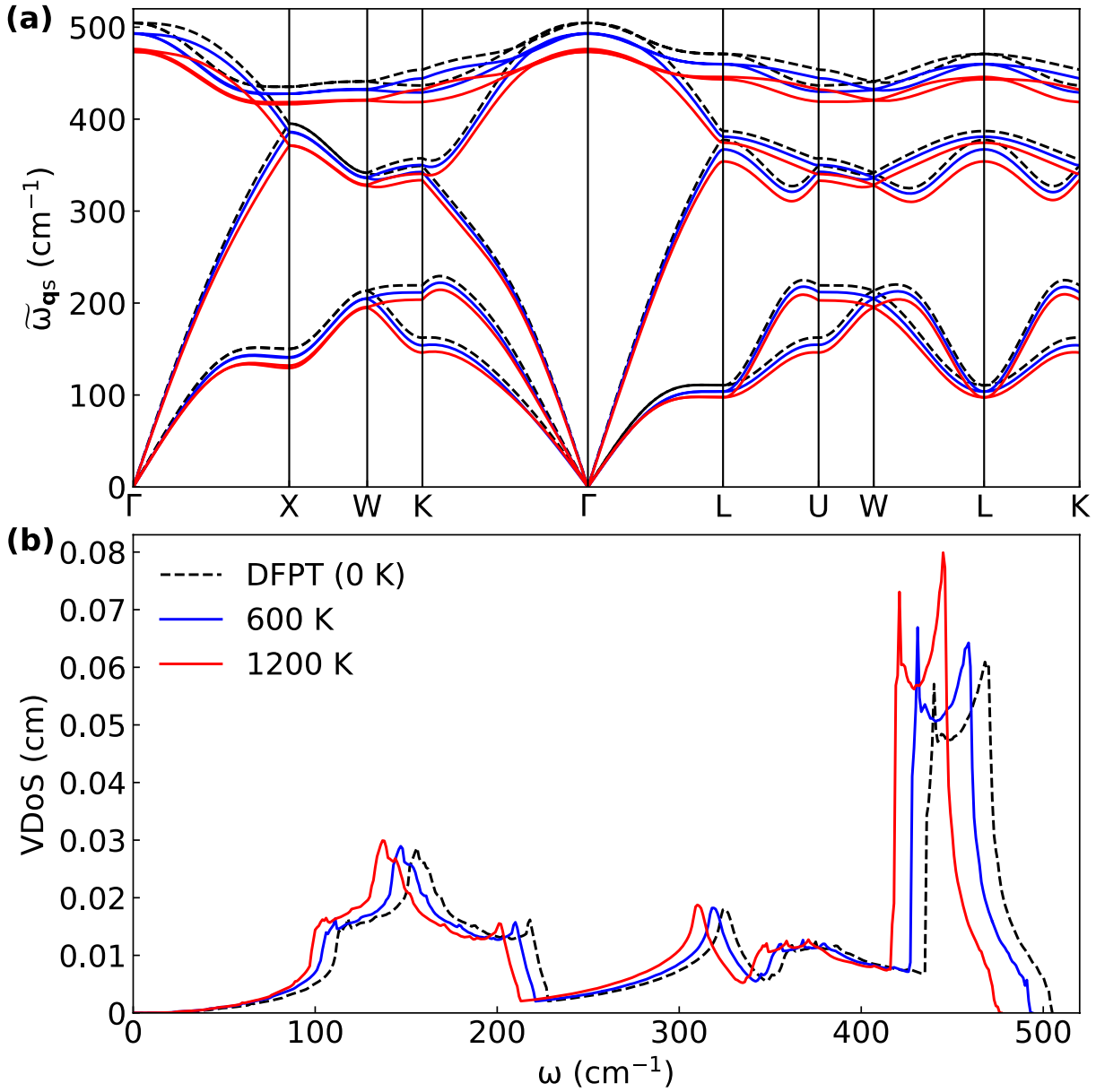
NVT ensemble

dt = 1 fs

Simulation time = 50 ps

Nosé dynamics

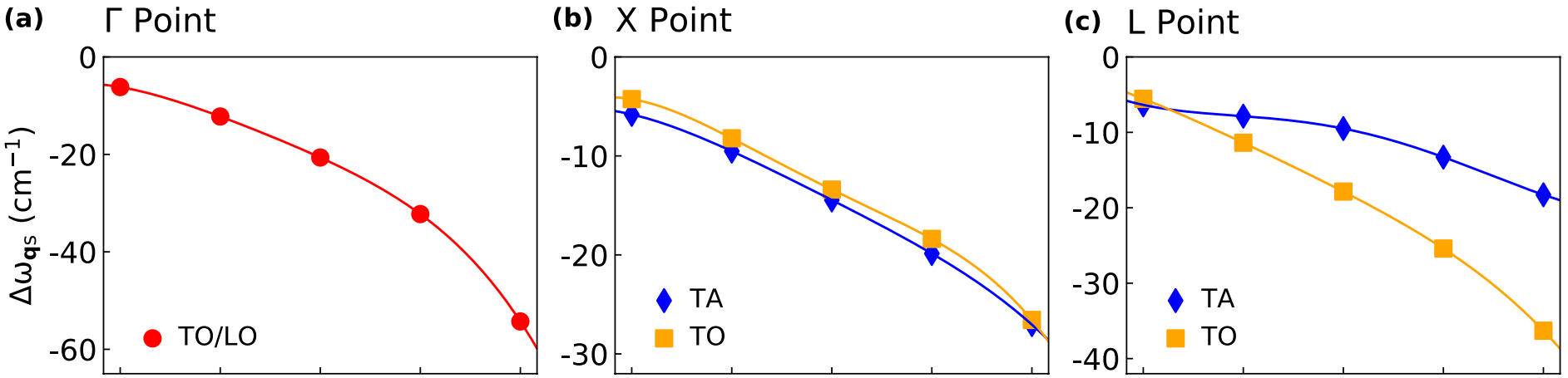
T-dependent phonon dispersions and vibrational density of states (VDoS)



20×20×20 **q**-mesh

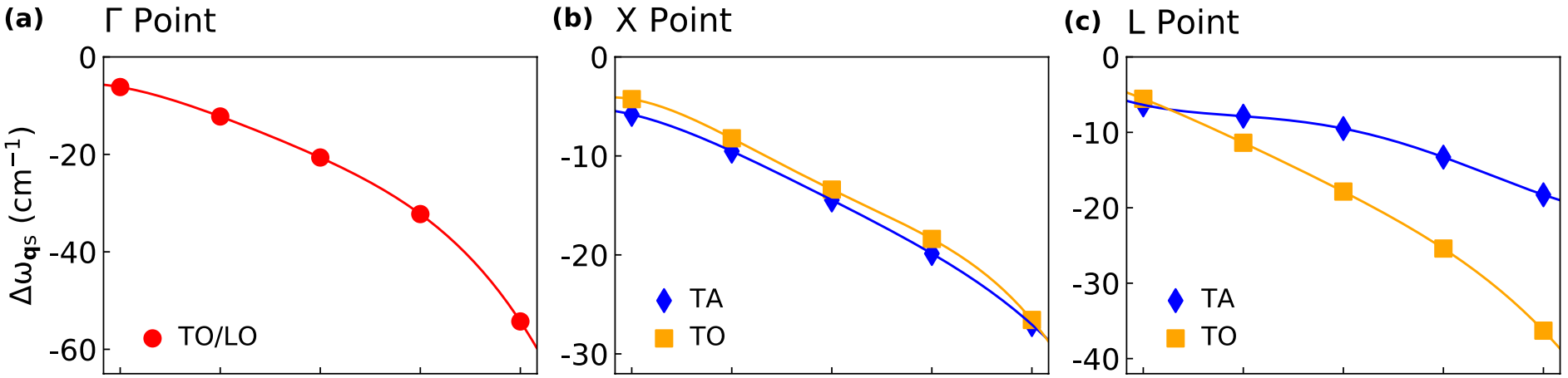
Frequency shifts

@ constant *V*



Frequency shifts

@ constant *V*



$$\widetilde{\omega}_{\mathbf{q}s}(T)|_{P=0} = \widetilde{\omega}_{\mathbf{q}s}(T)|_{V=V_{eq}} + \omega_{\mathbf{q}s}[\exp(-\gamma_{\mathbf{q}s}\bar{\alpha}T) - 1]$$

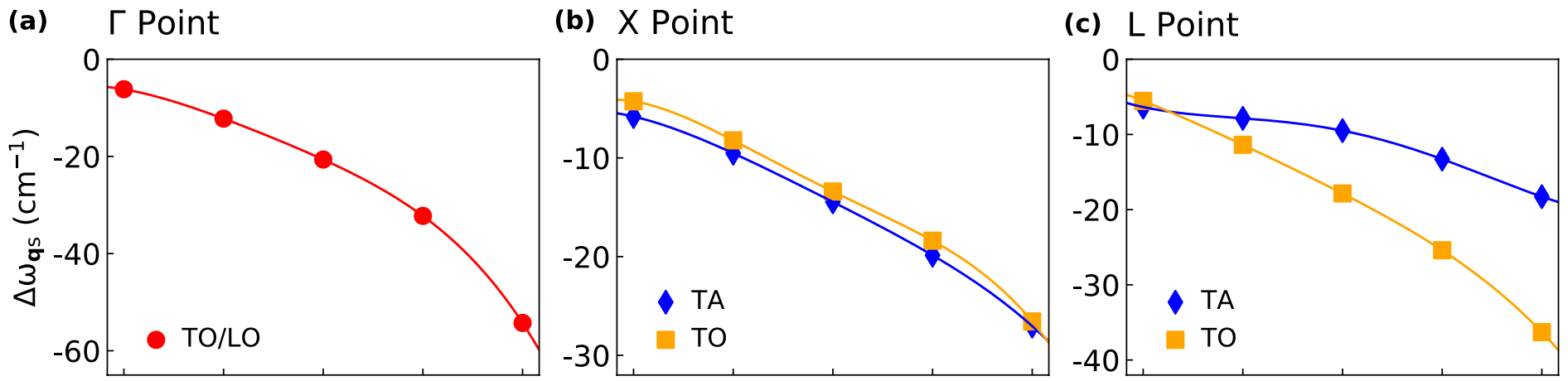
where,

$$\gamma_{\mathbf{q}s} = -\frac{d\ln\omega_{\mathbf{q}s}(0)}{d\ln V(0)}$$

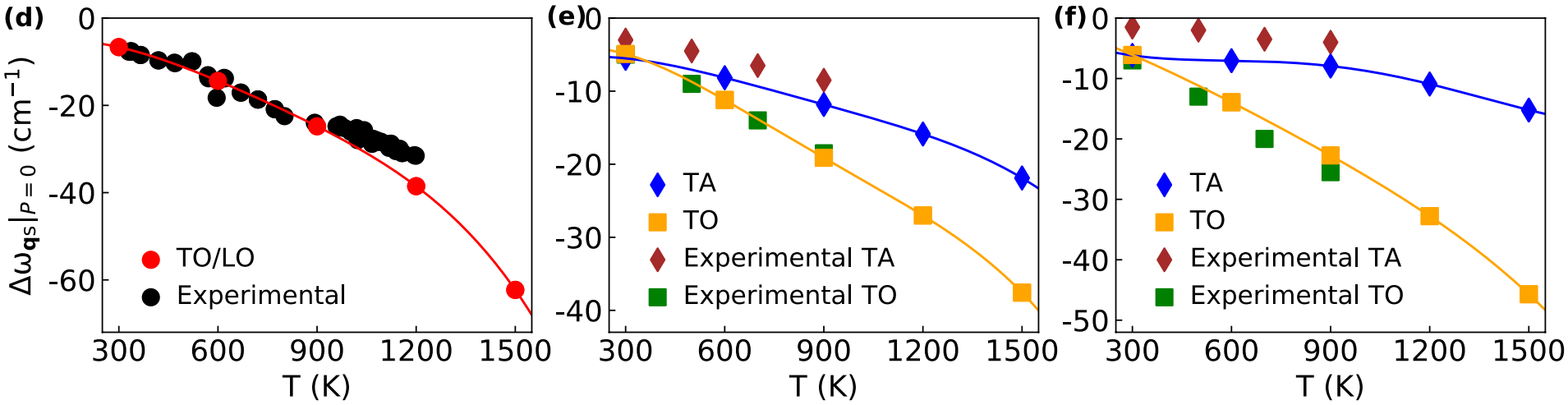
$$\bar{\alpha}(T) = \frac{1}{T}\ln\frac{V(T)}{V(0)}.$$

Frequency shifts

@ constant *V*



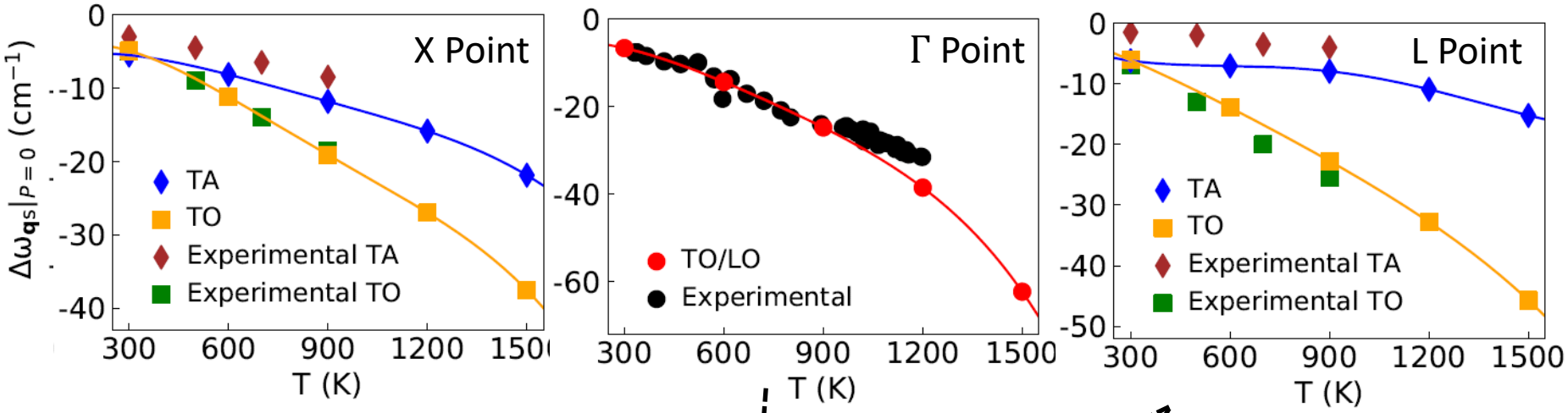
@ *P* = 0 GPa

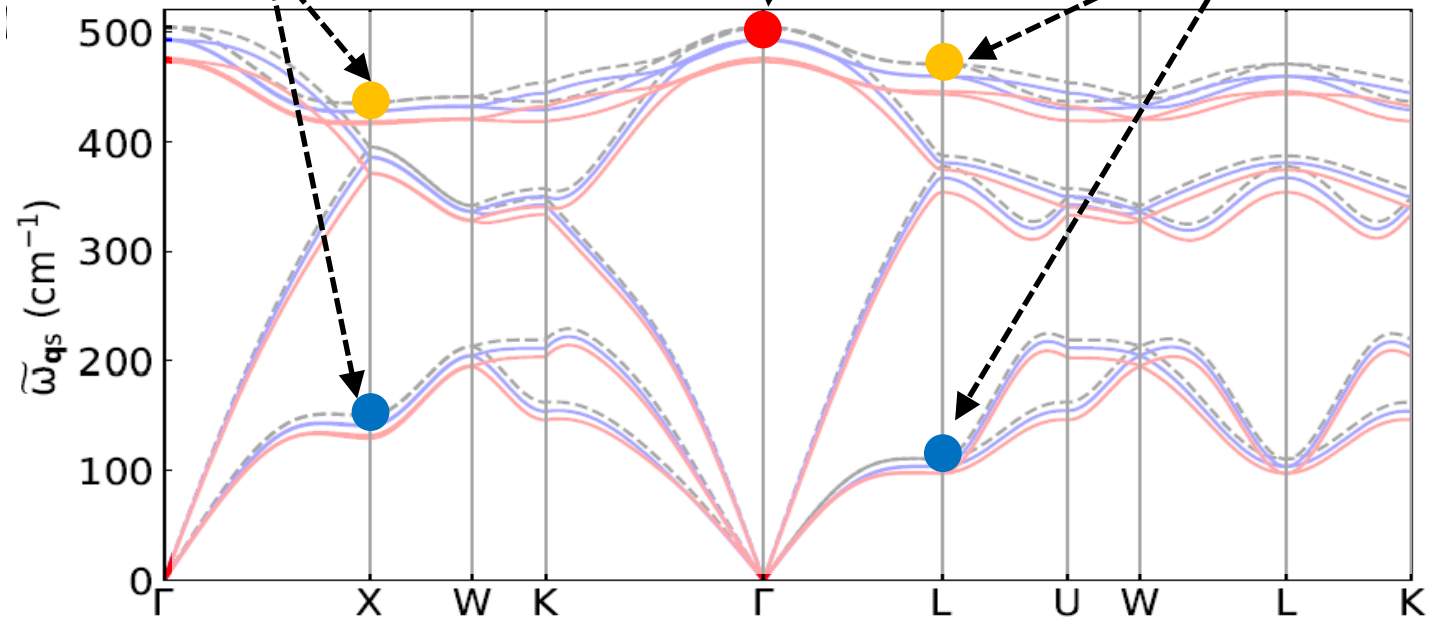


neutron scattering exp: PRB **28**, 1928 (1983). APL **41**, 1016 (1982).

Frequency shifts

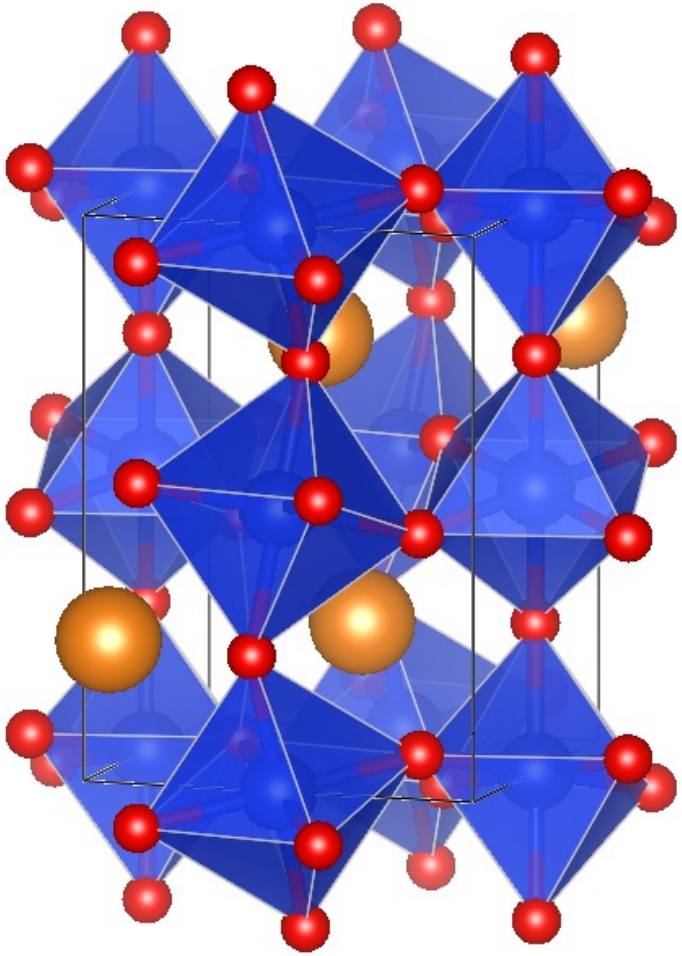
@ *P* = 0 GPa





neutron scattering exp: PRB **28**, 1928 (1983). APL **41**, 1016 (1982).

Application to $MgSiO_3$ Pv (weakly anharmonic)



$MgSiO_3$ Perovskite (MgPv):
most abundant phase of the LM (**75 vol%**)

Pbnm space group (20 atoms / primitive cell)

MgPv

Ab initio MD simulation details

LDA

2×2×2 supercells (160 atoms)

NVT ensemble

dt = 1 fs

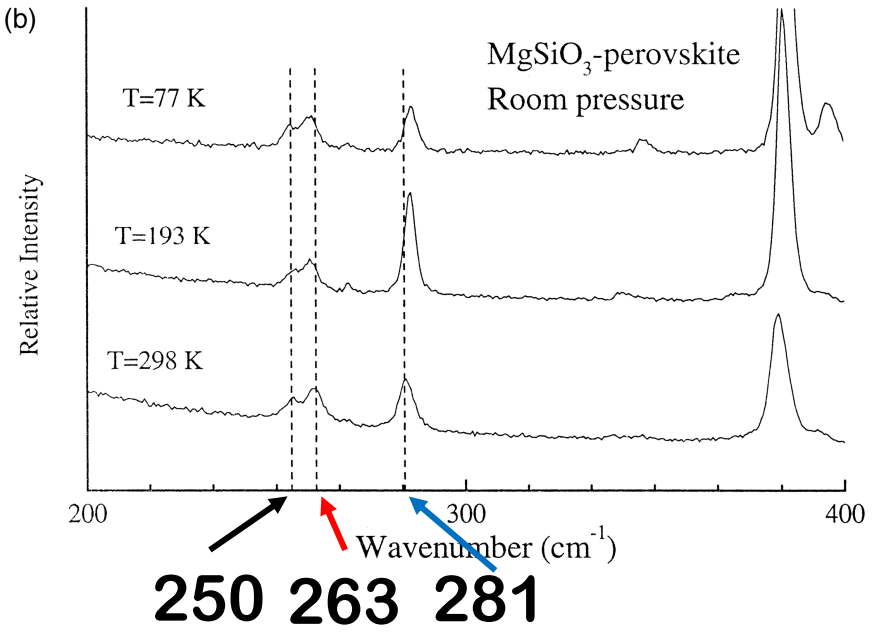
Simulation time = 60 ps

Nosé dynamics

MgPv

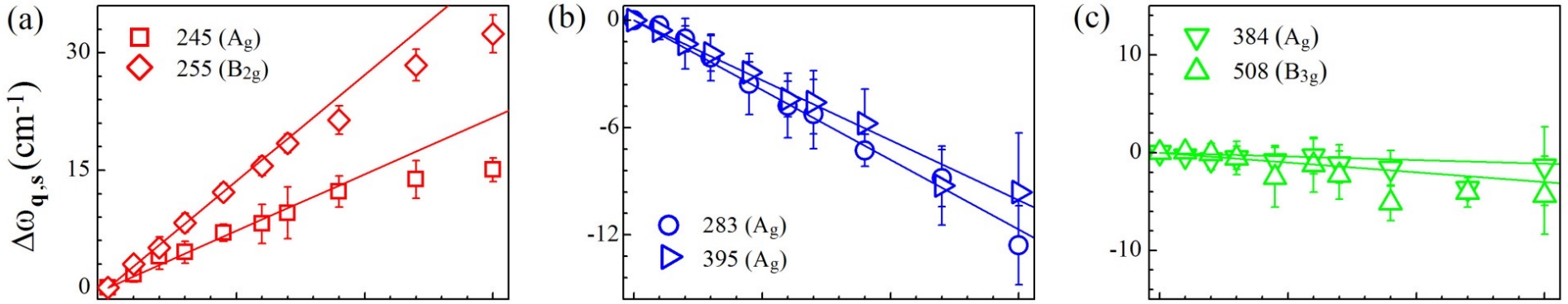
Experimental Results: Six Raman active modes with irregular thermal shifts under 700 K.

250 —
263 ↑
281 ↓
384 ↓
393 ↓
507 ↓
(cm^{-1})



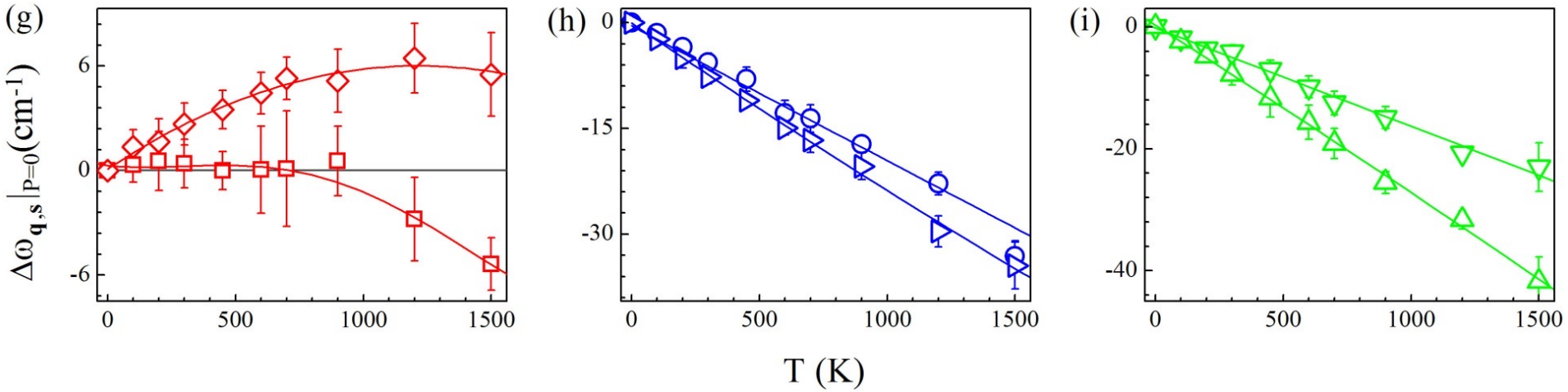
Durben and Wolf, American Mineralogist (1992).
Gillet et al, Physics of the Earth and Planetary Interiors (2000).
Lu et al, J. Geophys. Res. (1994).

@ constant *V*



$$\widetilde{\omega}_{\mathbf{q}s}(T)|_{P=0} = \widetilde{\omega}_{\mathbf{q}s}(T)|_{V=V_{eq}} + \omega_{\mathbf{q}s}[\exp(-\gamma_{\mathbf{q}s}\bar{\alpha}T) - 1]$$

@ *P* = 0 GPa



Zhang et al., PRL (2014)

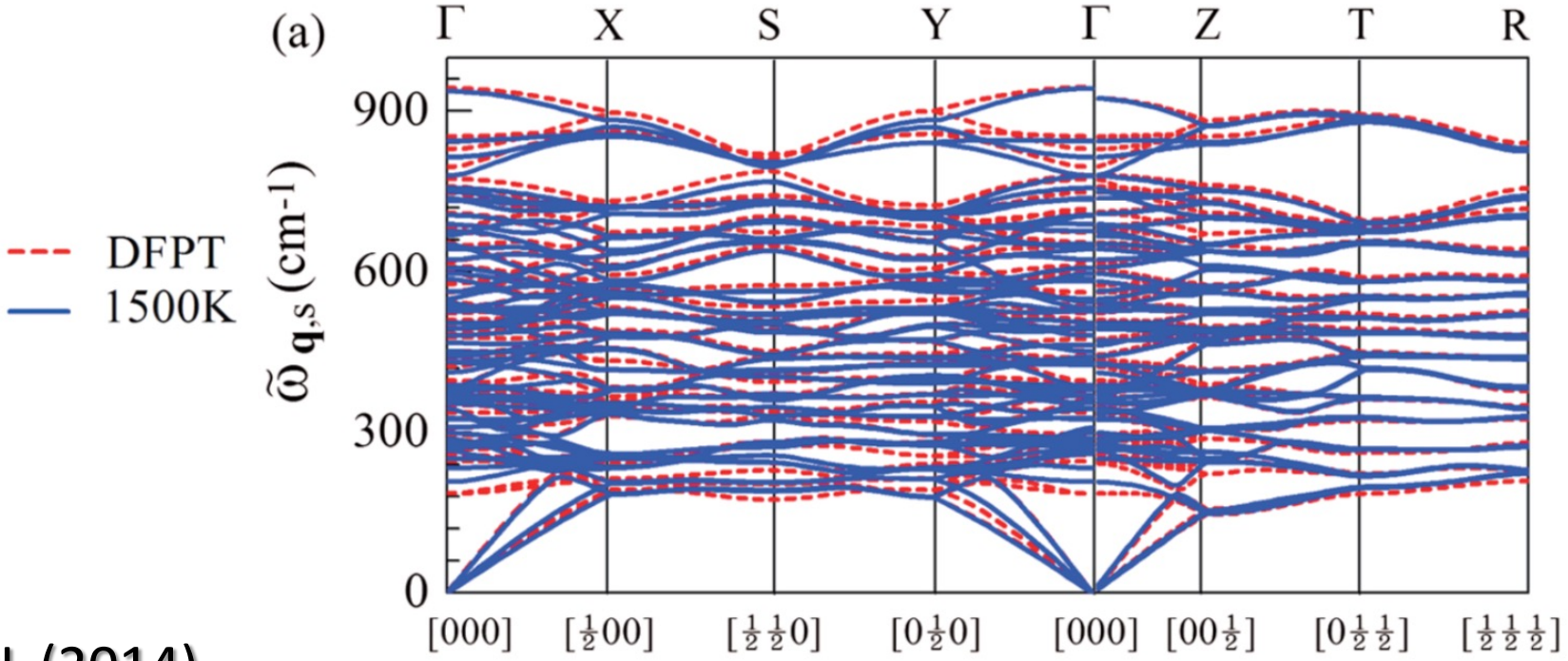
Fourier interpolation

$$\Omega_{\mathbf{q}} = \mathrm{diag}[\tilde{\omega}^2_{\mathbf{q}1}, \tilde{\omega}^2_{\mathbf{q}2}, \ldots, \tilde{\omega}^2_{\mathbf{q}3N}]$$

$$\tilde{D}(\mathbf{q}) = \hat{\mathbf{e}}_{\mathbf{q}} \Omega_{\mathbf{q}} \hat{\mathbf{e}}_{\mathbf{q}}{}^{\dagger}$$

$$\tilde{\Phi}(\mathbf{r}) = \sum_{\mathbf{r}} \tilde{D}(\mathbf{q}) \cdot e^{i\mathbf{q}\cdot\mathbf{r}}$$

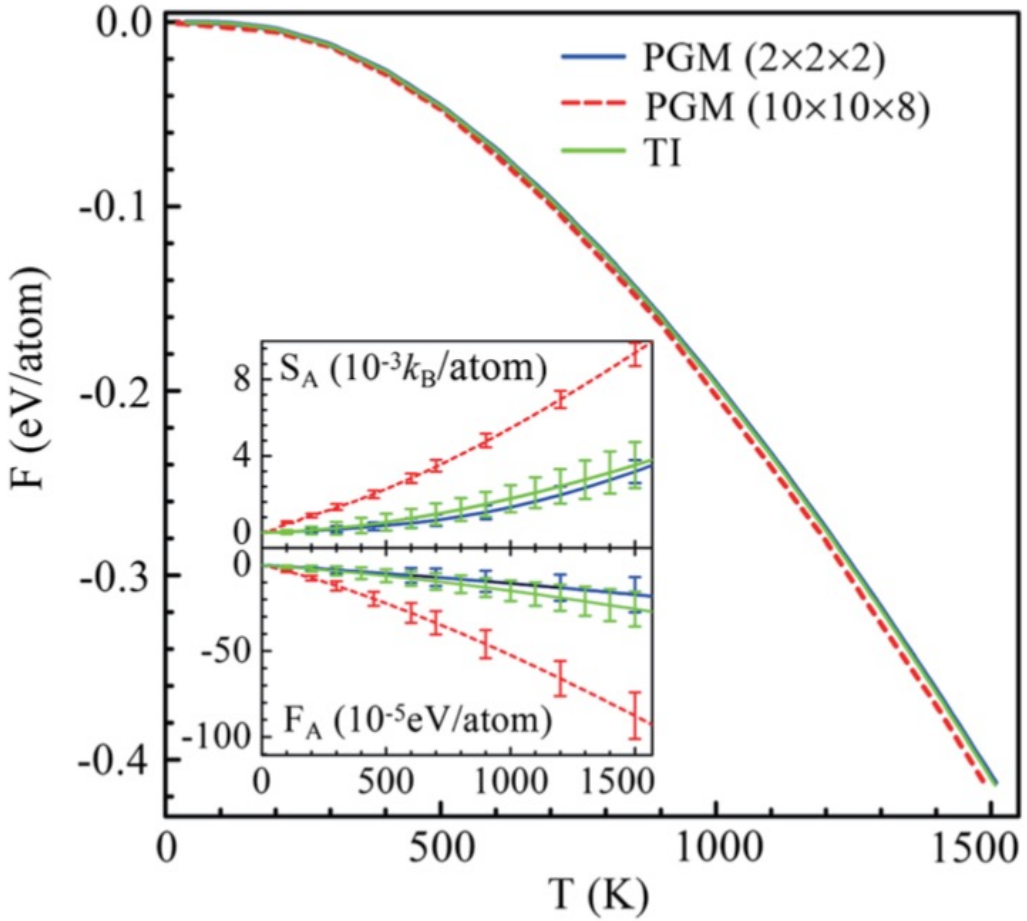
$$\tilde{D}(\mathbf{q}') = \sum_{\mathbf{r}} \tilde{\Phi}(\mathbf{r}) \cdot e^{-i\mathbf{q}'\cdot\mathbf{r}}$$



Zhang et al., PRL (2014)

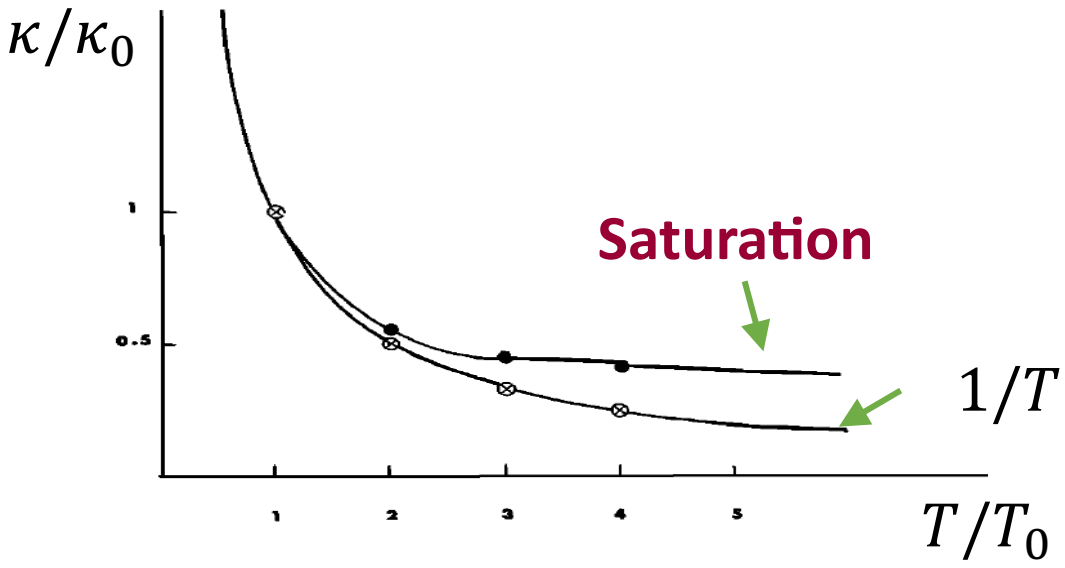
Fourier interpolation

$2 \times 2 \times 2 \rightarrow 10 \times 10 \times 8$ **q**-mesh
for accurate free energy evaluation

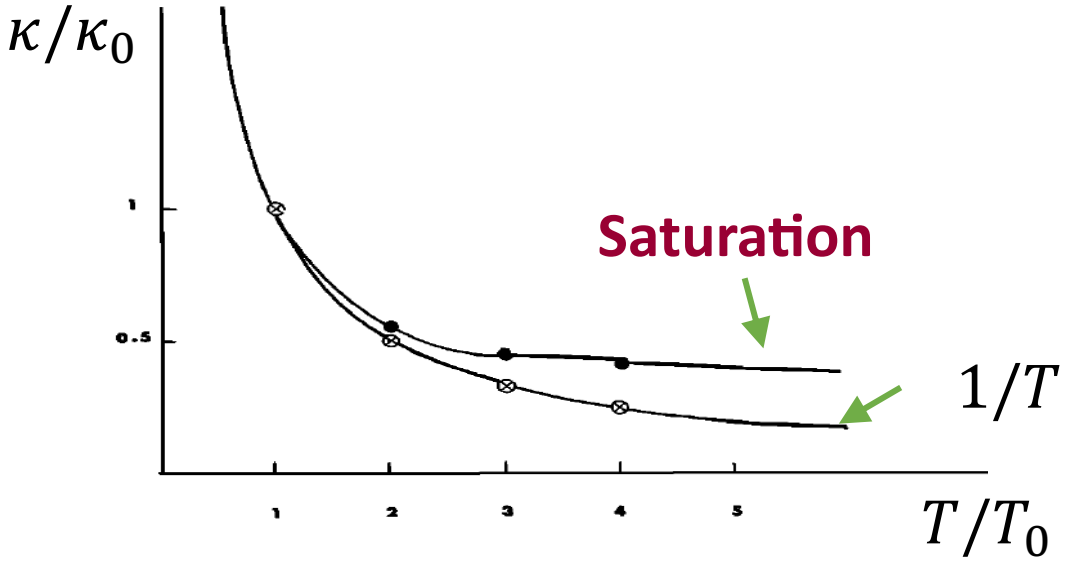


Zhang et al., PRL (2014)

Saturation of κ_{lat} at high T



Saturation of κ_{lat} at high T



Minimal Mean Free Path Theory

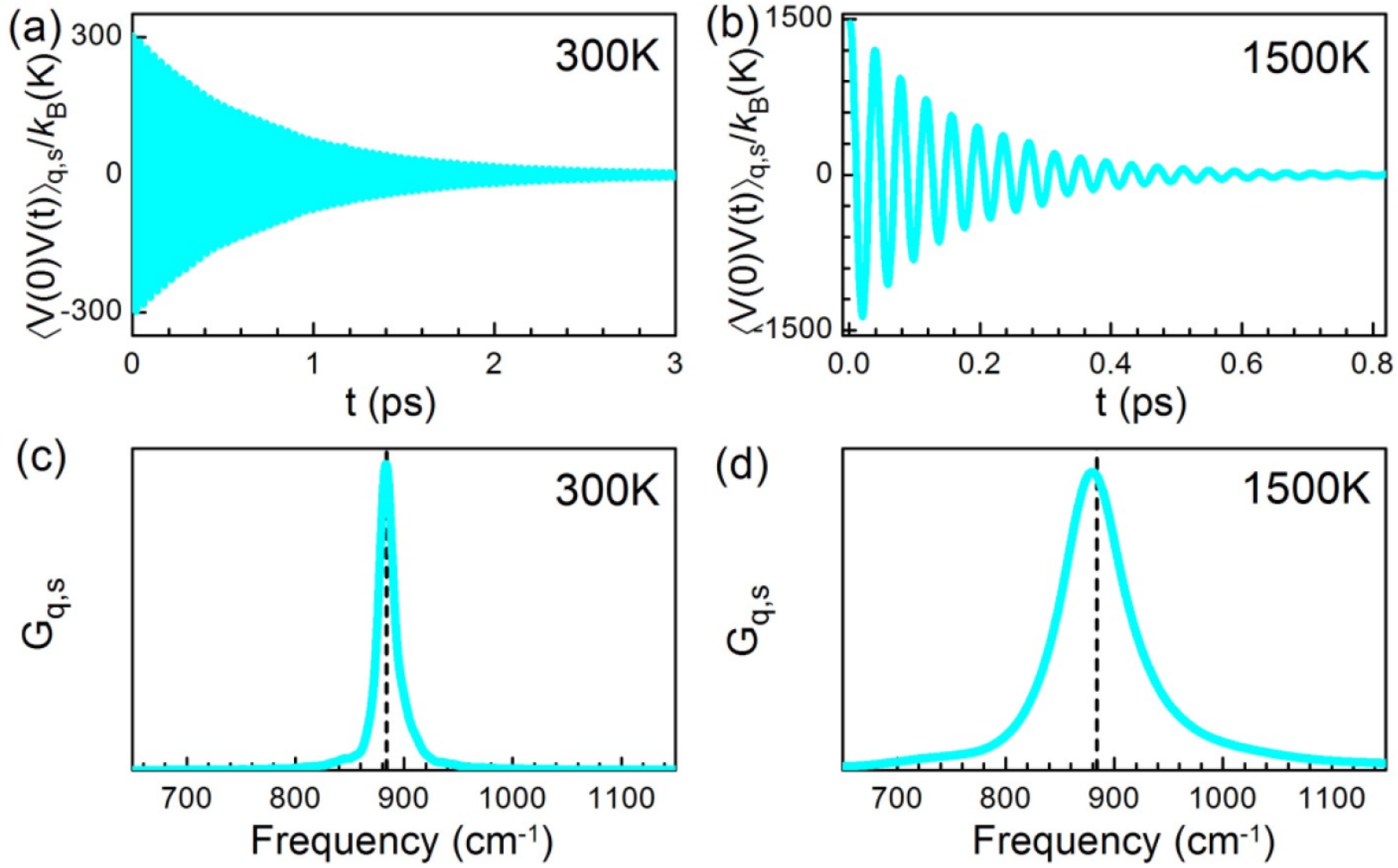
$$\kappa_{\text{lat}} = \frac{1}{3}\sum_{q,s} c_{q,s}\, v_{q,s}\, \ell_{q,s}$$

$\ell_{q,s}$ ≥ Lattice parameters

- Kittel, Phys. Rev. (1948).
- Ziman, Electrons and Phonons (New York 1960).
- Spitzer, J. Phys. Chem. Solids (1970).

q = (0, 0, 1/2)

MgPv



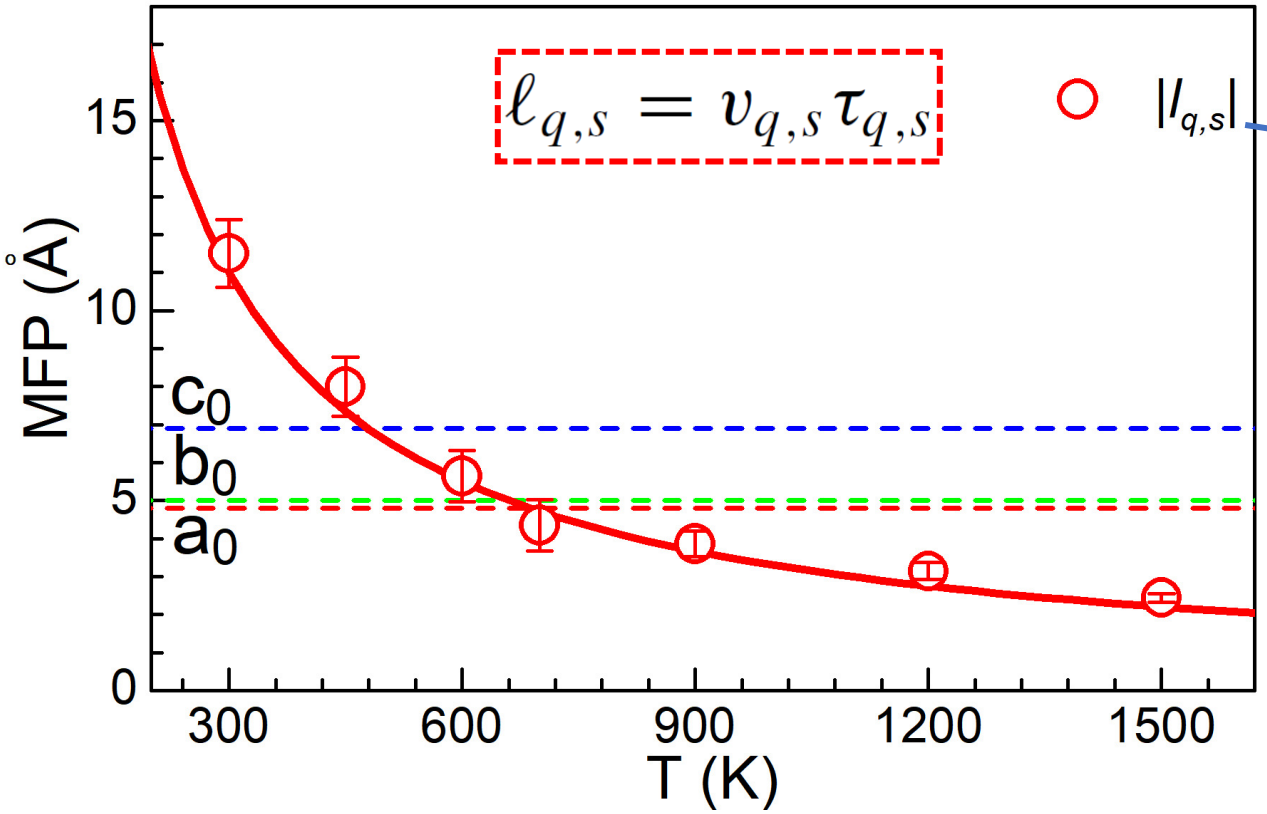
τ = 0.36 ps

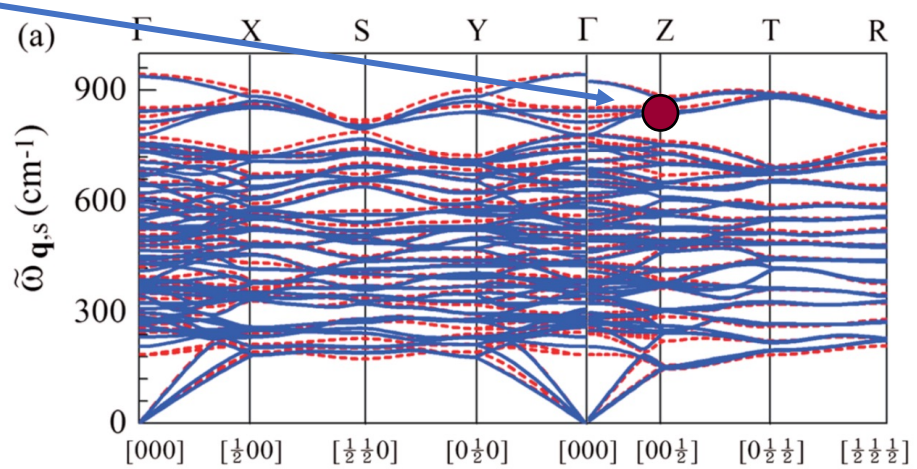
τ = 0.07 ps

Zhang et al., PRB (2017)

Breakdown of Minimal Mean Free Path Theory

MgPv

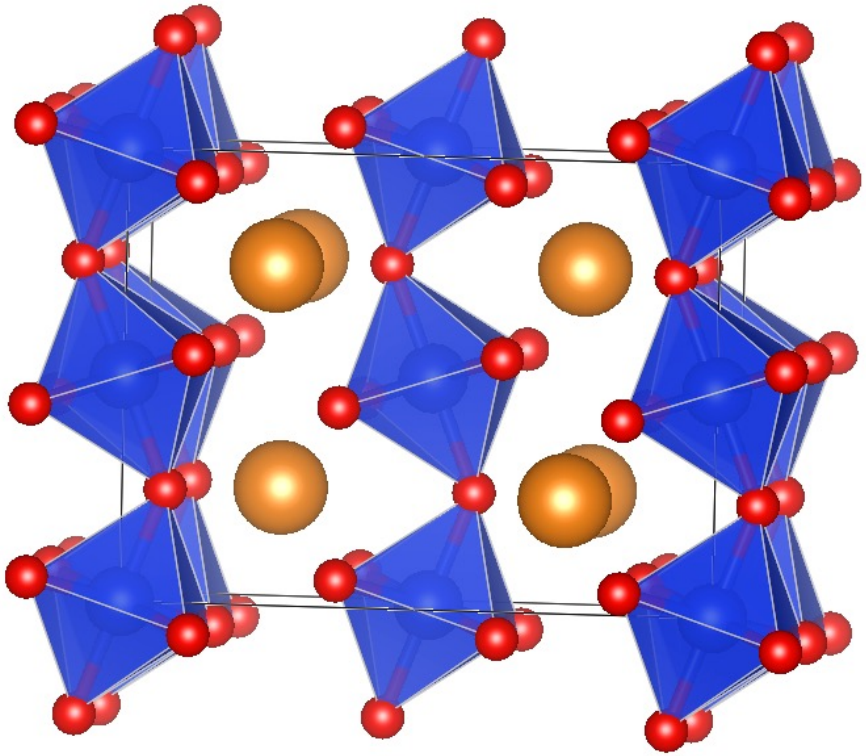




Lattice parameters of *Pbnm* crystal: **a_0 , b_0 , c_0**

Zhang et al., PRB (2017)

Application to $MgSiO_3$ PPv (weakly anharmonic)



$MgSiO_3$ Postperovskite (MgPPv)

MgPv → MgPPv above 125 GPa and 2500 K
MgPPv: most abundant phase in the lowermost mantle (D" region)

Cmcm space group (20 atoms / unit cell): layered structure
Monolinic 10-atom primitive cell

MgPPv

Ab initio MD simulation details

LDA

3×3×2 supercells (180 atoms)

NVT ensemble

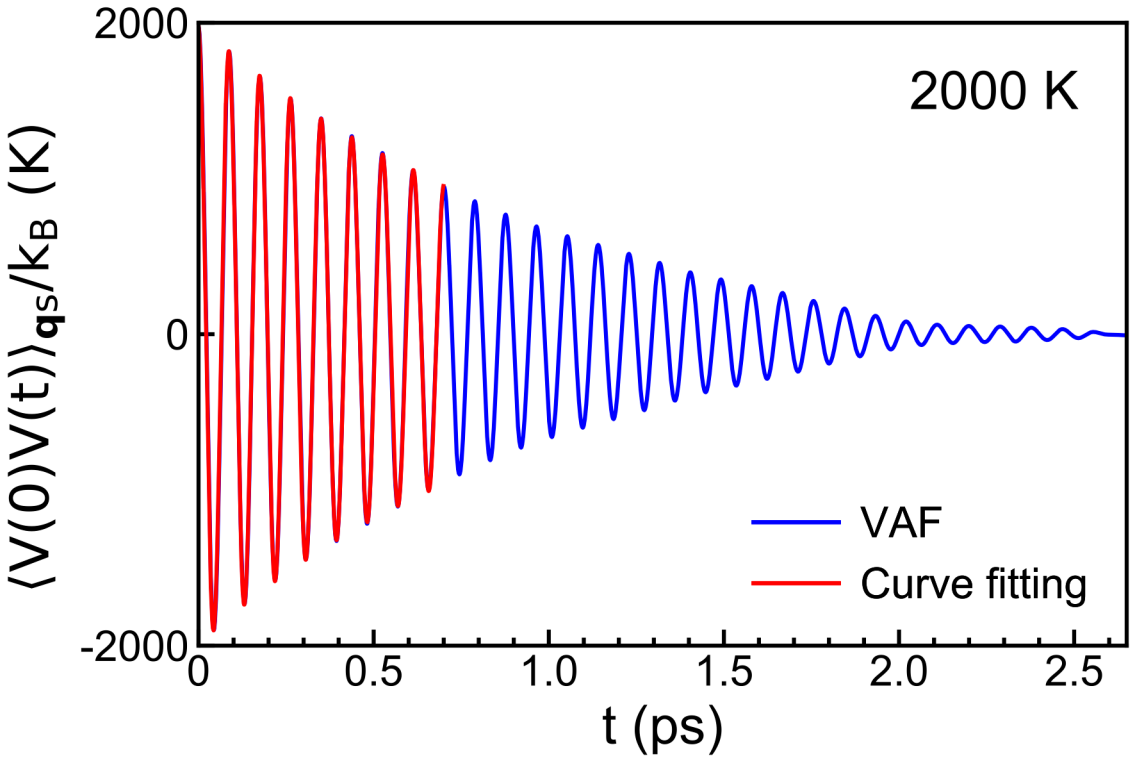
dt = 1 fs

Simulation time = 50 ps

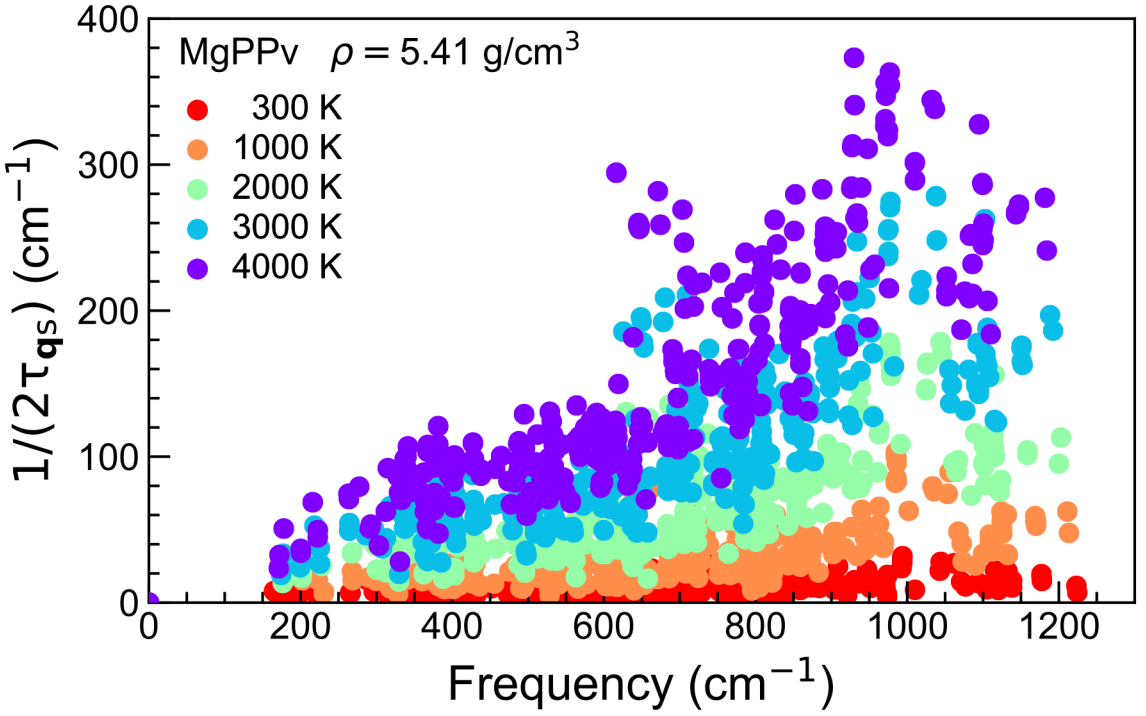
Nosé dynamics

MgPPv

$$\mathbf{VAF}(\tilde{\omega},\tau) = A_{\mathbf{q}s}\cos(\tilde{\omega}_{\mathbf{q}s}t)e^{-t/(2\tau_{\mathbf{q}s})}$$

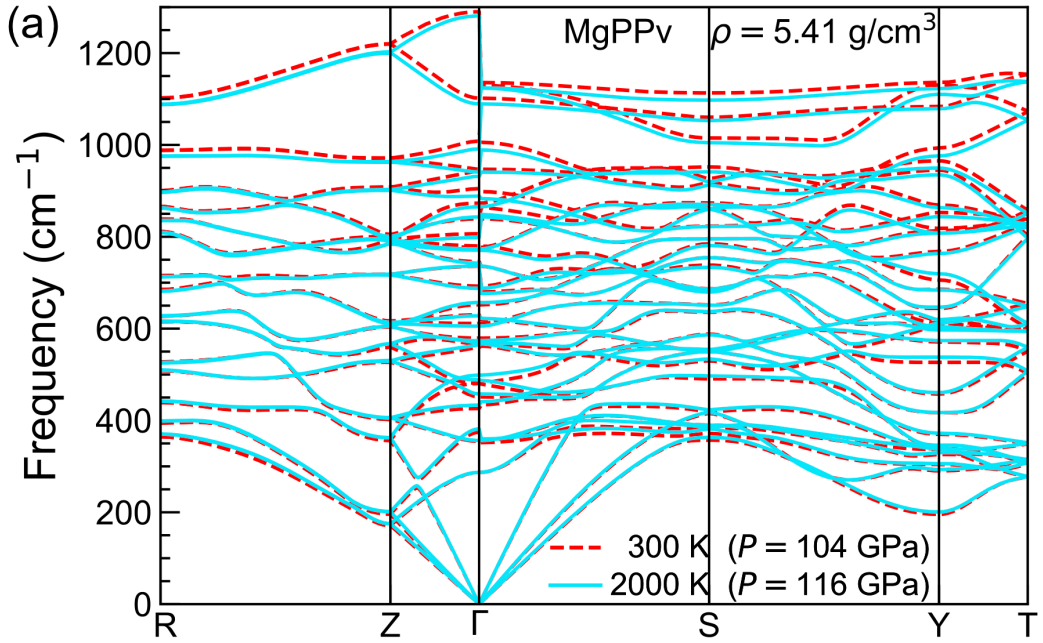


Collected phonon quasiparticles:

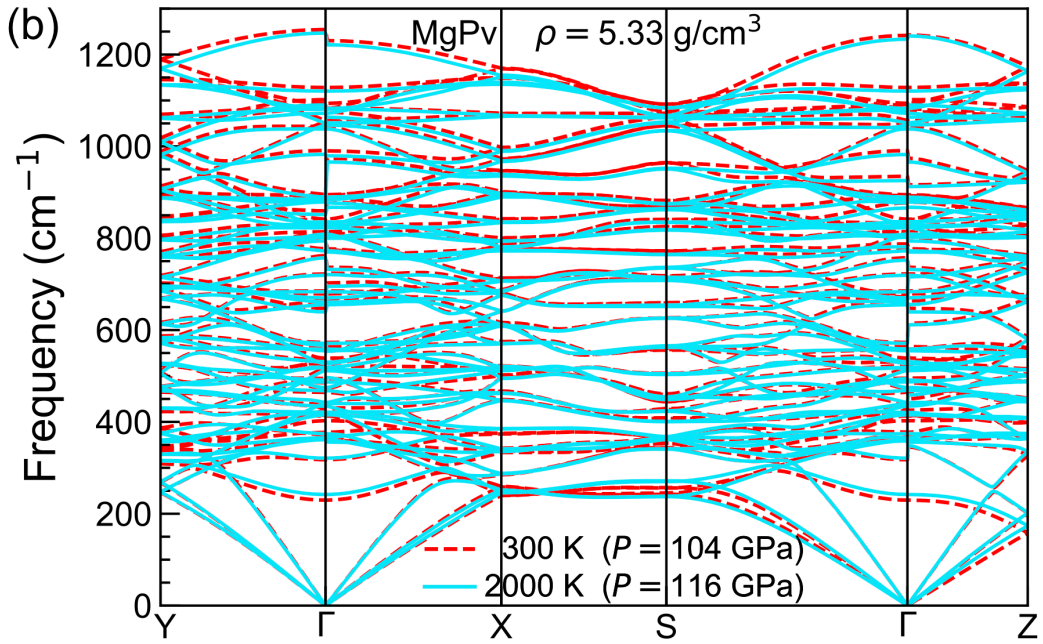


Zhang et al., PRB (2021)

MgPPv



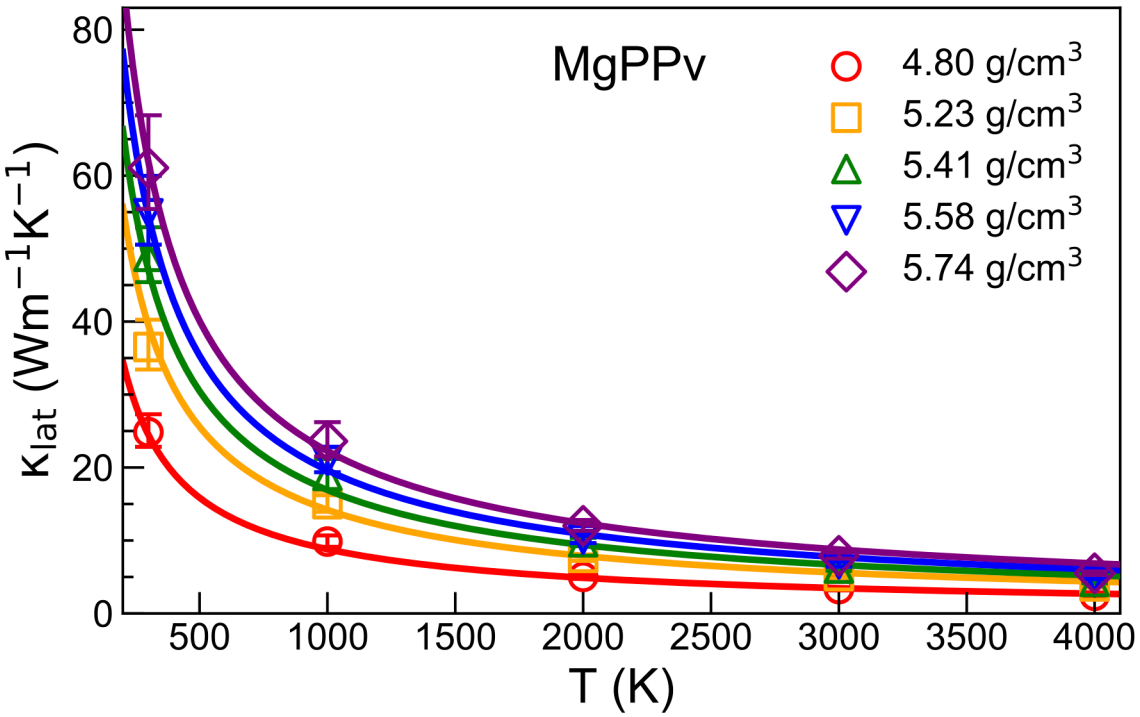
MgPv



Weakly anharmonic

Zhang et al., PRB (2021)

$$\kappa(V,T)$$



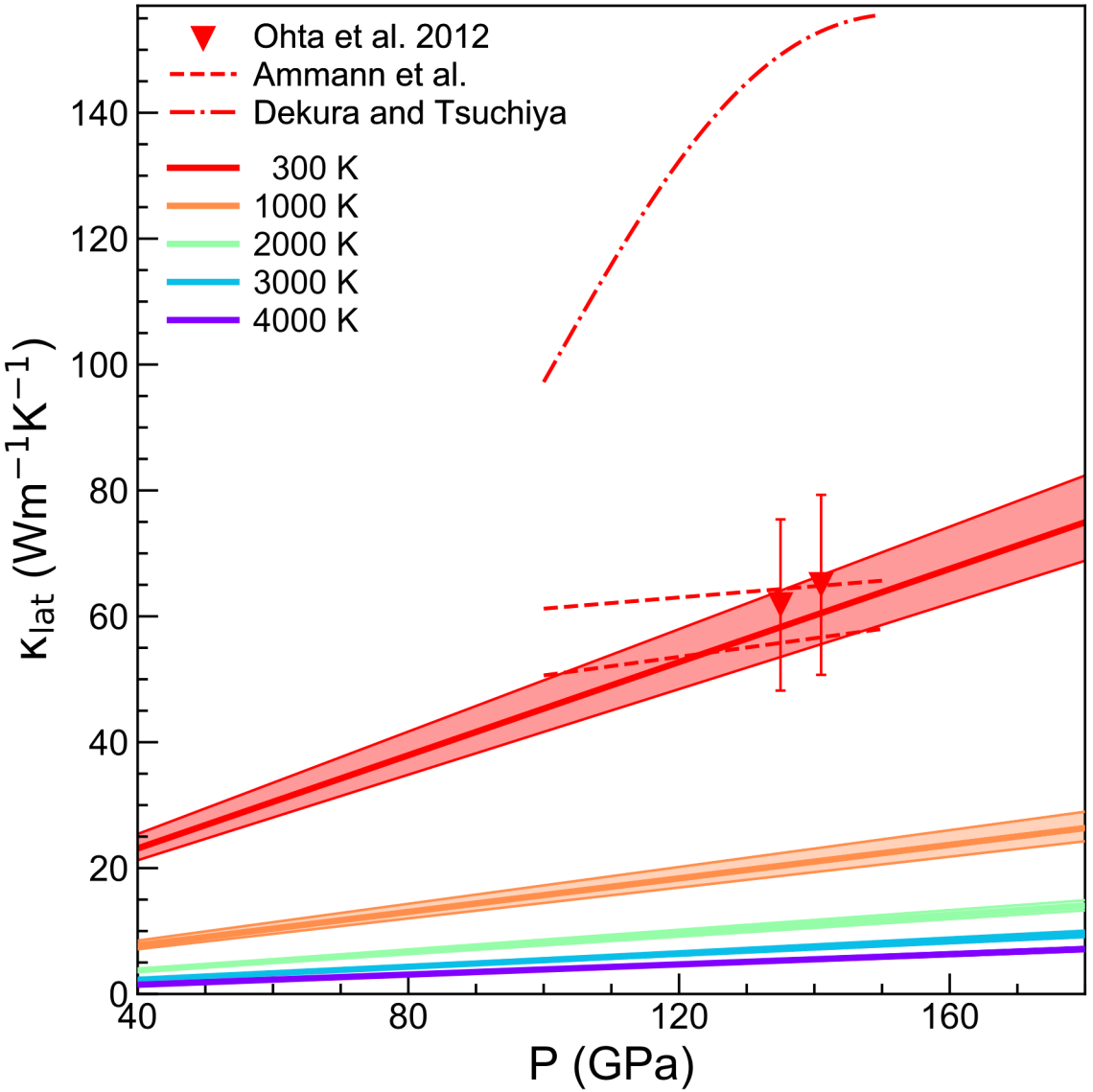
$$\kappa = \kappa_{ref} \left(\frac{T_{ref}}{T}\right)^{a} \left(\frac{V_{ref}}{V}\right)^{g}$$

$$g = b\ ln\left(\frac{V_{ref}}{V}\right) + c$$

Zhang et al., PRB (2021)

Using the quasiharmonic EoS:

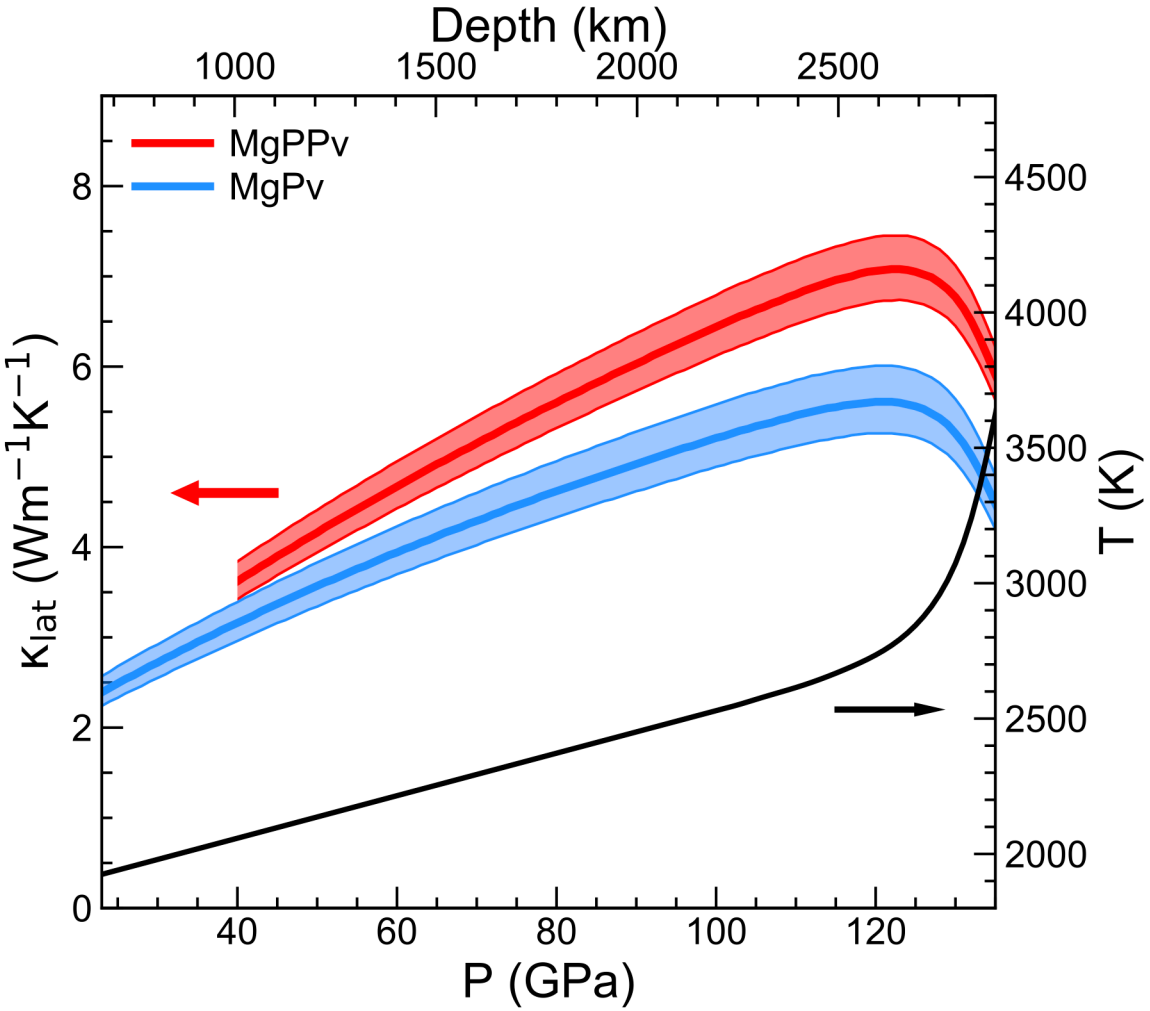
$$\kappa(V,T) \rightarrow \kappa(P,T)$$



Zhang et al., PRB (2021)

κ depends linearly on pressure

Modeling of κ_{MgPPv} and κ_{MgPv} along the geotherm



κ_{MgPPv} is ~25% larger

Zhang et al., PRB (2021)

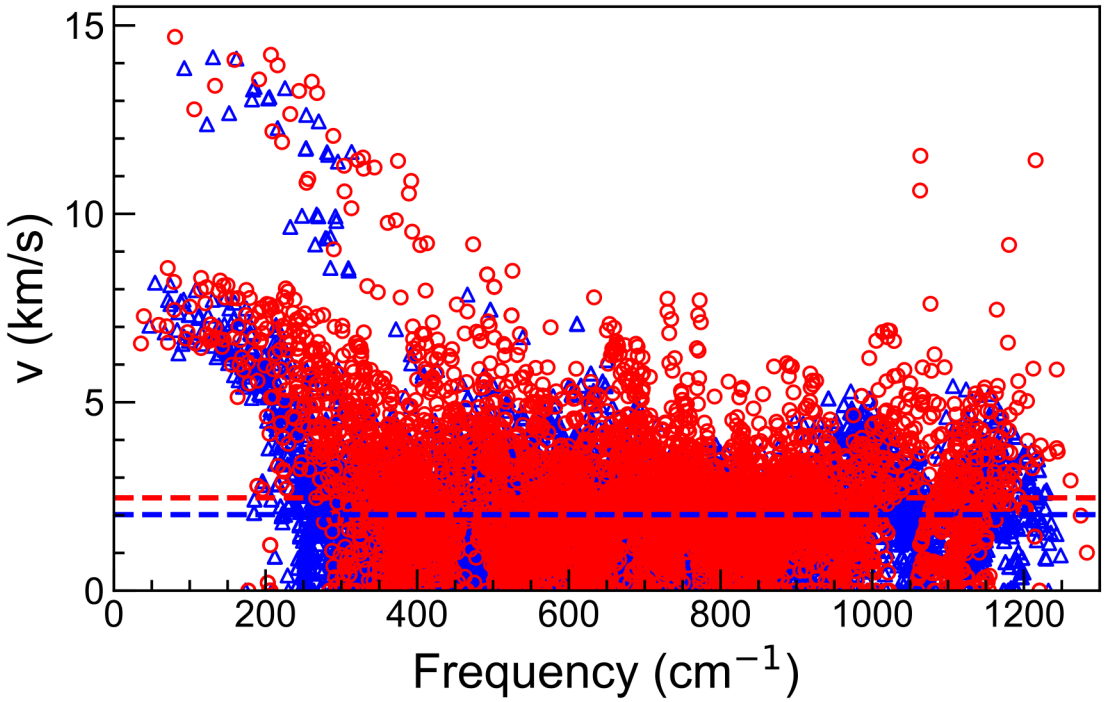
MgPPv's smaller primitive:
MgPPv (10 atoms), MgPv (20 atoms)

MgPPv's larger $\bar{v}$

MgPPv's higher proportion of acoustic branches:
MgPPv (3/30), MgPv (3/60)

MgPPv's larger κ

κ increase due to structural phase transition



Zhang et al., PRB (2021)

Free energy and thermodynamics calculations

The quasi-harmonic approximation (QHA) formula is no longer valid:

$$F(T) = E_0 + \frac{1}{2}\sum_{\mathbf{q}s} \hbar\omega_{\mathbf{q}s} + k_{\mathrm{B}}T \sum_{\mathbf{q}s} \ln\left(1 - e^{-\frac{\hbar\omega_{\mathbf{q}s}}{k_{\mathrm{B}}T}}\right)$$

Reason:

- The phonon quasiparticle frequencies are temperature-dependent

Phonon gas model

The formula for vibrational entropy is still valid:

$$S_{\mathrm{vib}}(T) = k_{\mathrm{B}} \sum_{\mathbf{q}s} \left[\left(n_{\mathbf{q}s} + 1 \right) \ln\left(n_{\mathbf{q}s} + 1 \right) - n_{\mathbf{q}s} \ln n_{\mathbf{q}s} \right]$$

$$n_{\mathbf{q}s} = \left[\exp(\hbar \tilde{\omega}_{\mathbf{q}s}(T) / k_{\mathrm{B}} T) - 1 \right]^{-1}$$

Helmholtz free energy (insulators):

$$F(T) = E_0 + \frac{1}{2} \sum_{\mathbf{q}s} \hbar \omega_{\mathbf{q}s} - \int_0^T S_{\mathrm{vib}}(T') dT'$$

E_0 is the static energy, $\omega_{\mathbf{q}s}$ are the harmonic frequencies.

$$S_{\mathrm{vib}}(T) = k_{\mathrm{B}} \sum_{\mathbf{q}s} \left[\left(n_{\mathbf{q}s} + 1\right) \ln\left(n_{\mathbf{q}s} + 1\right) - n_{\mathbf{q}s} \ln n_{\mathbf{q}s} \right]$$

$$n_{\mathbf{q}s} = \left[\exp(\hbar \tilde{\omega}_{\mathbf{q}s}(T) / k_{\mathrm{B}} T) - 1 \right]^{-1}$$

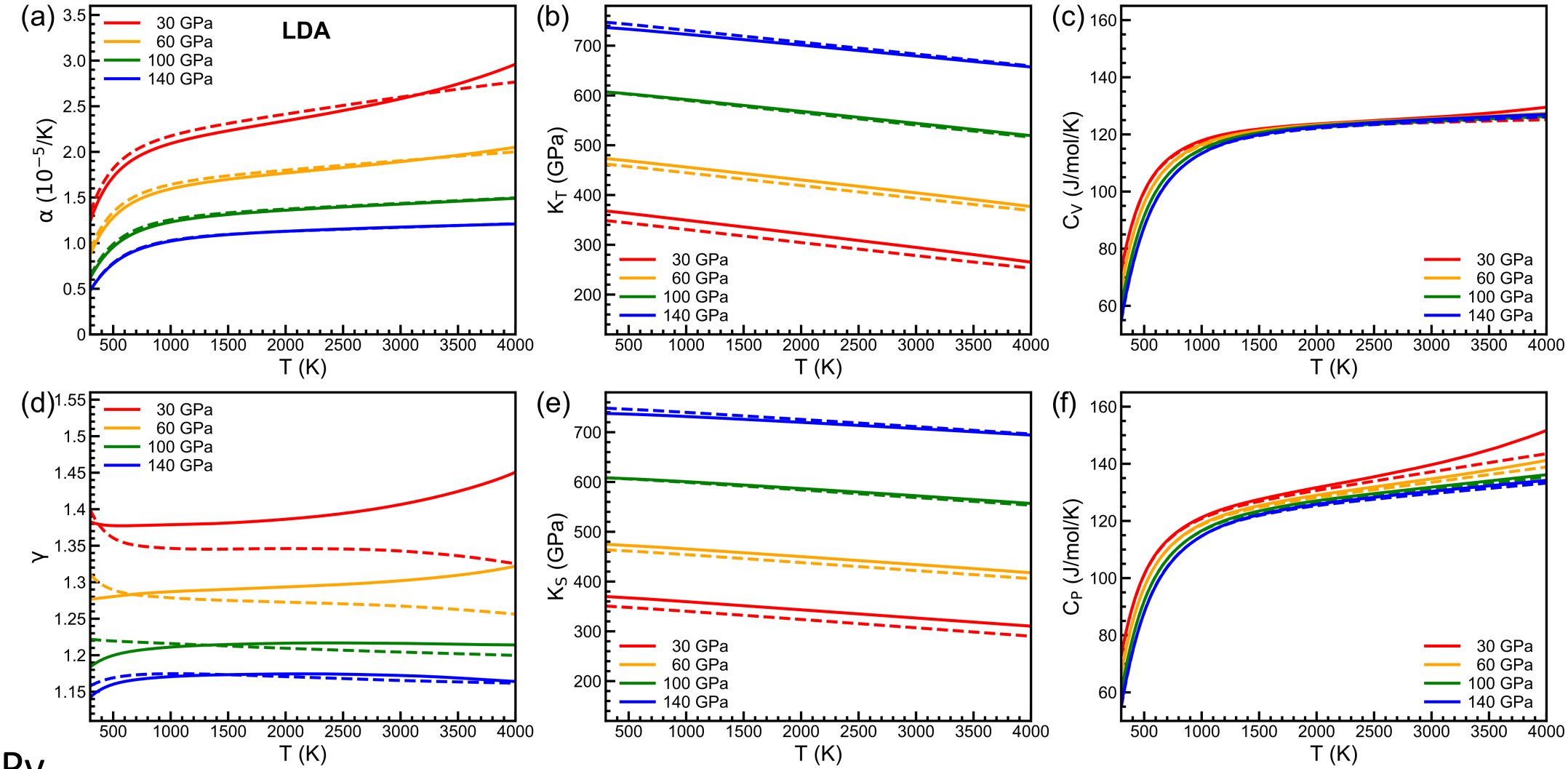
$$\tilde{\omega}_{\mathbf{q}s}(T) \rightarrow \omega_{\mathbf{q}s}$$

$$F(T) = E_0 + \frac{1}{2} \sum_{\mathbf{q}s} \hbar \omega_{\mathbf{q}s} - \int_0^T S_{\mathrm{vib}}(T') dT'$$

$$F(T) = E_0 + \frac{1}{2} \sum_{\mathbf{q}s} \hbar \omega_{\mathbf{q}s} + k_{\mathrm{B}} T \sum_{\mathbf{q}s} \ln\left(1 - e^{-\frac{\hbar \omega_{\mathbf{q}s}}{k_{\mathrm{B}} T}}\right)$$

Anharmonic thermodynamic properties

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad K_T = -V\left(\frac{\partial P}{\partial V}\right)_T \qquad C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$



Solid: Pv

Dashed: PPv

$$\gamma = \frac{V\alpha K_T}{C_V}$$

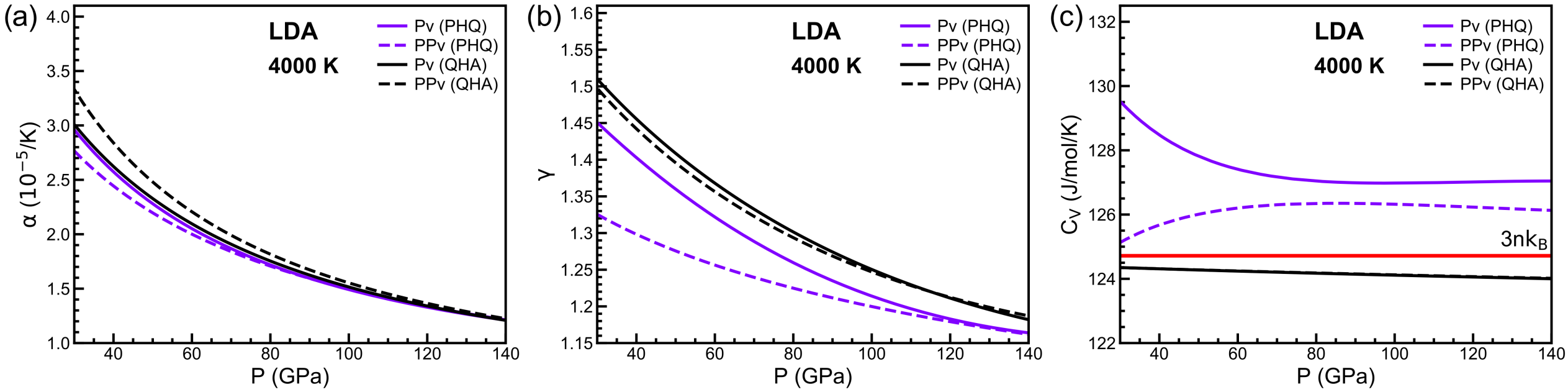
$$K_S = K_T(1 + \gamma\alpha T)$$

$$C_P = C_V(1 + \gamma\alpha T)$$

Z. Zhang *et al.*, PRB **106**, 054103 (2022).

PHQ and QHA comparison

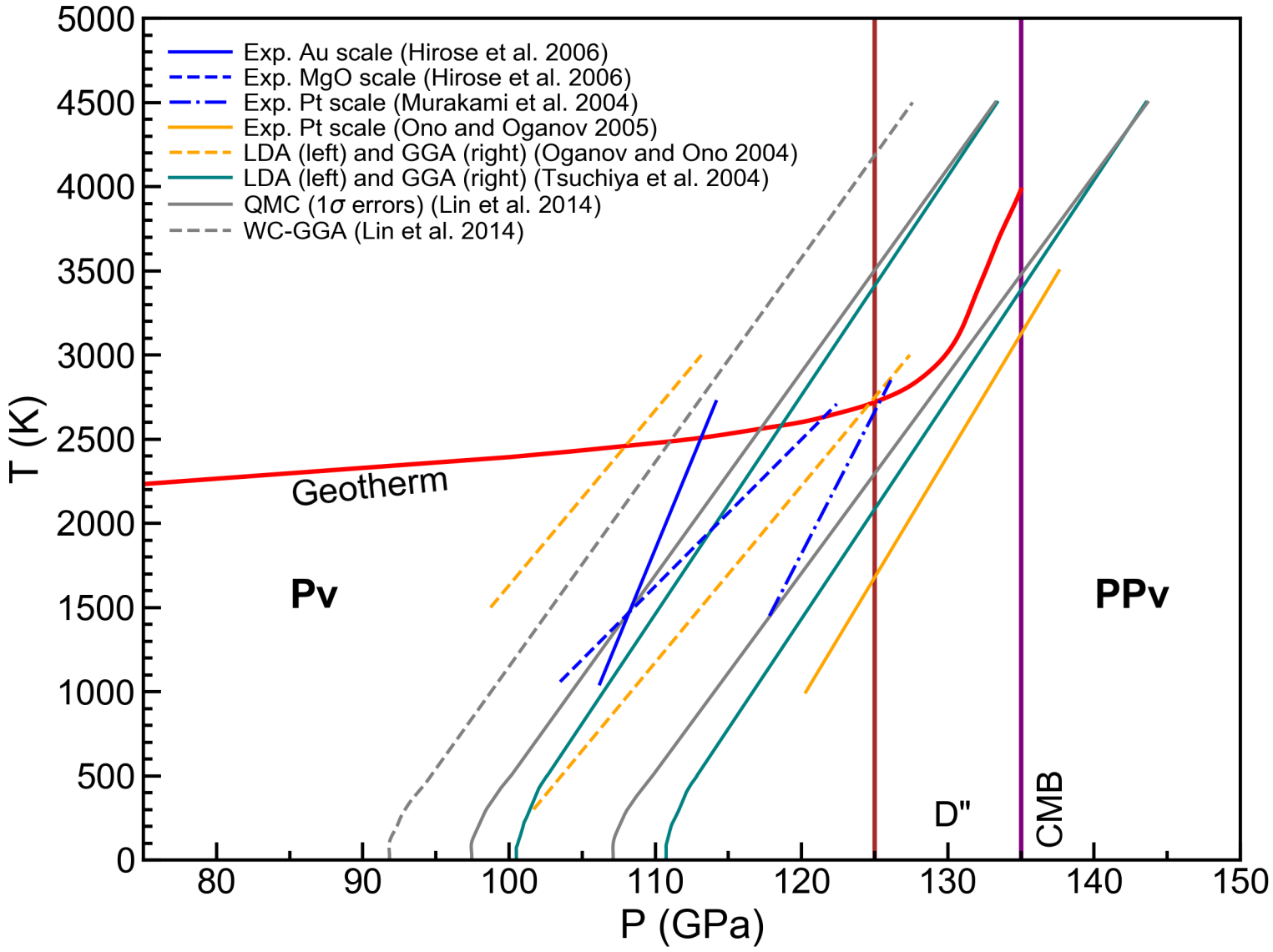
α γ C_V



Purple: PHQ
Black: QHA

Z. Zhang *et al.*, PRB **106**, 054103 (2022).

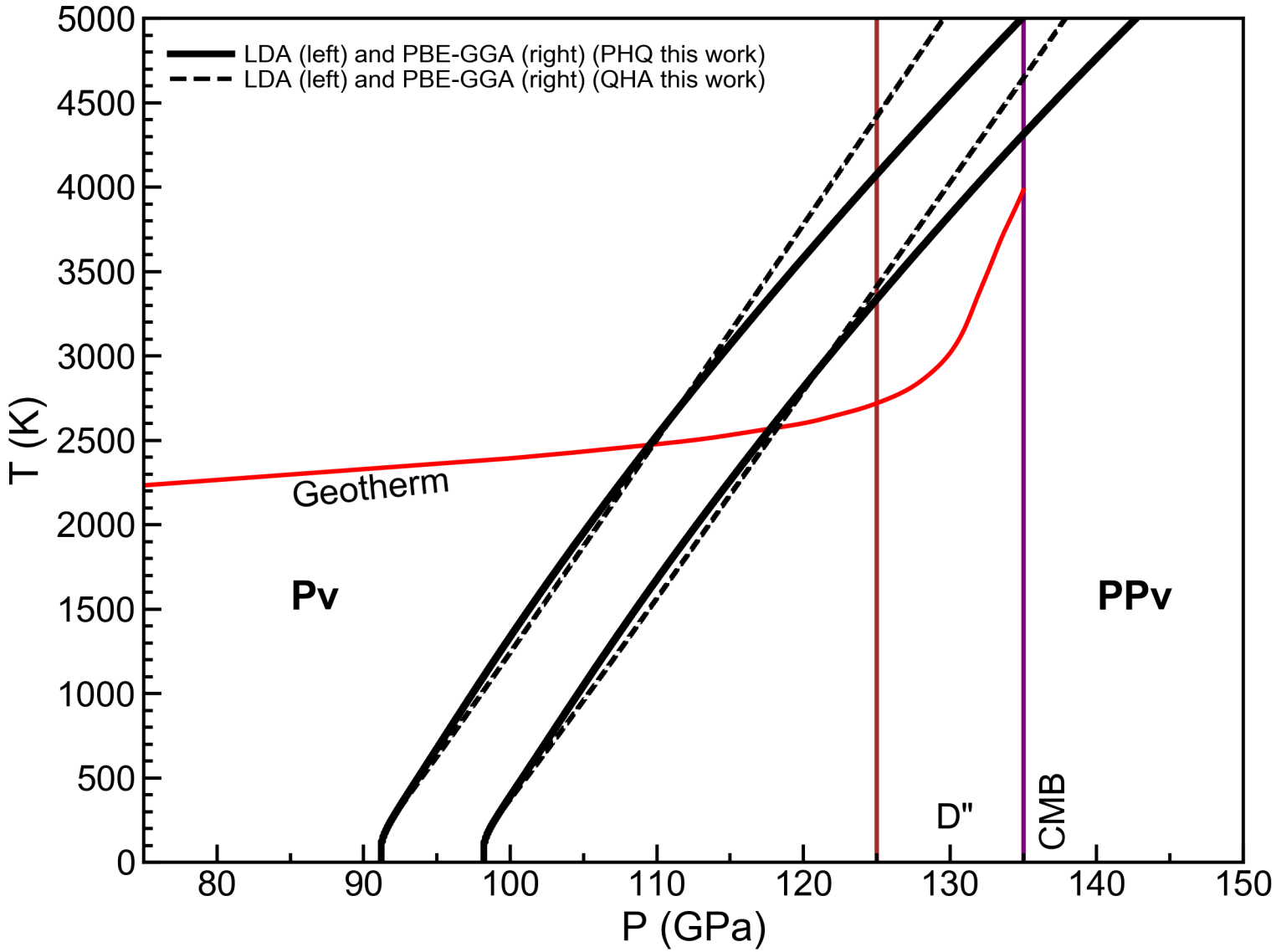
MgPv-PPv phase boundary



Z. Zhang *et al.*, PRB **106**, 054103 (2022).

MgPv-PPv phase boundary

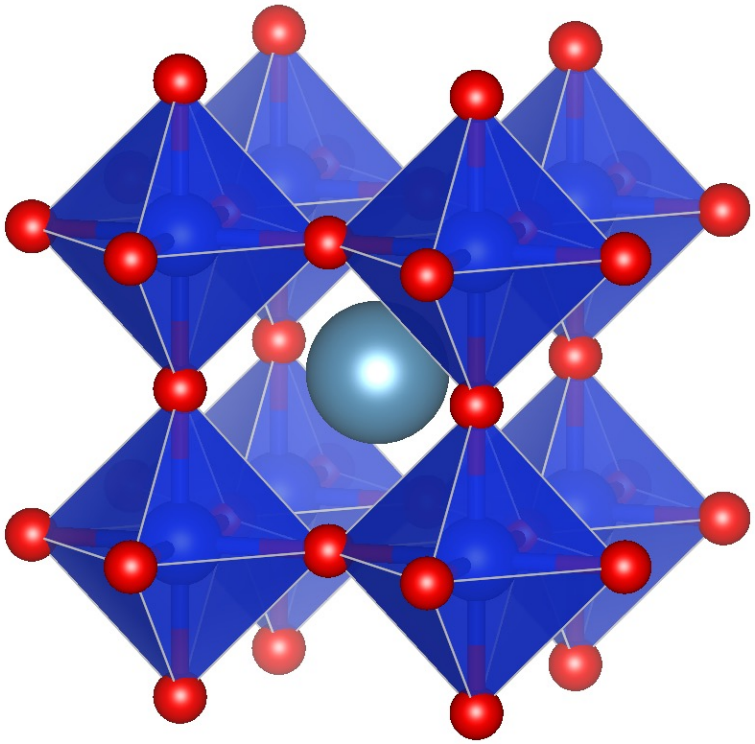
$G = F + PV$



Clapeyron slope (dP/dT) increases with T

Z. Zhang *et al.*, PRB **106**, 054103 (2022).

Application to $CaSiO_3$ Pv (strongly anharmonic)

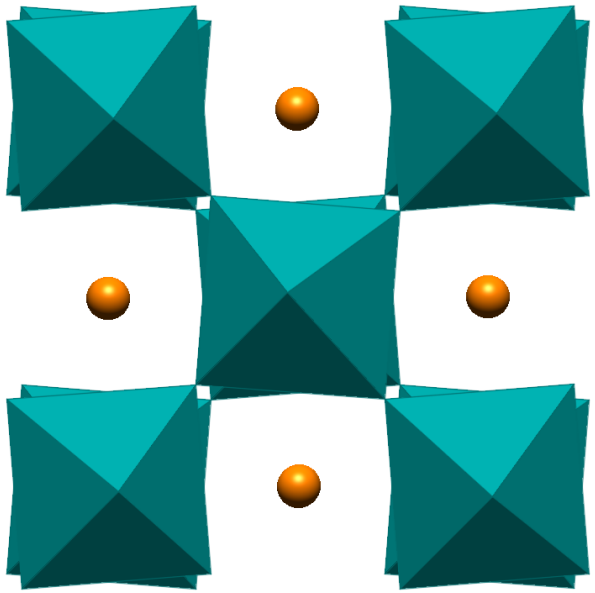


$CaSiO_3$ perovskite (CaPv):

Third most abundant mineral in the lower mantle: **~7 vol%**

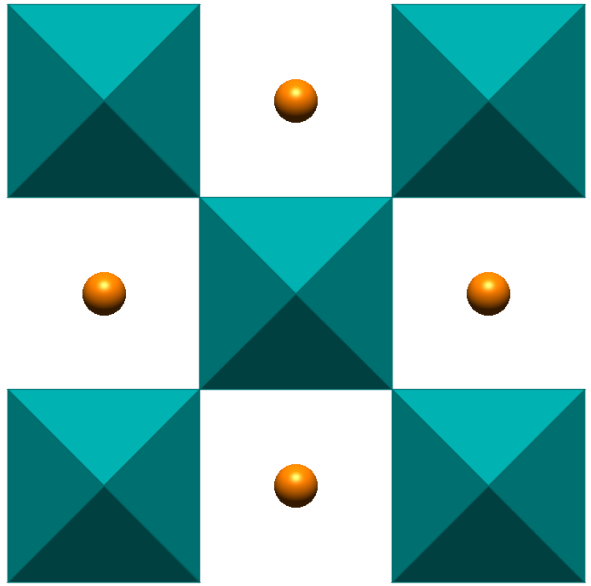
More abundant in subducted mid-ocean ridge basalt (MORB): $\geq$ **23 vol%**

Challenge for CaPv



Low *T*

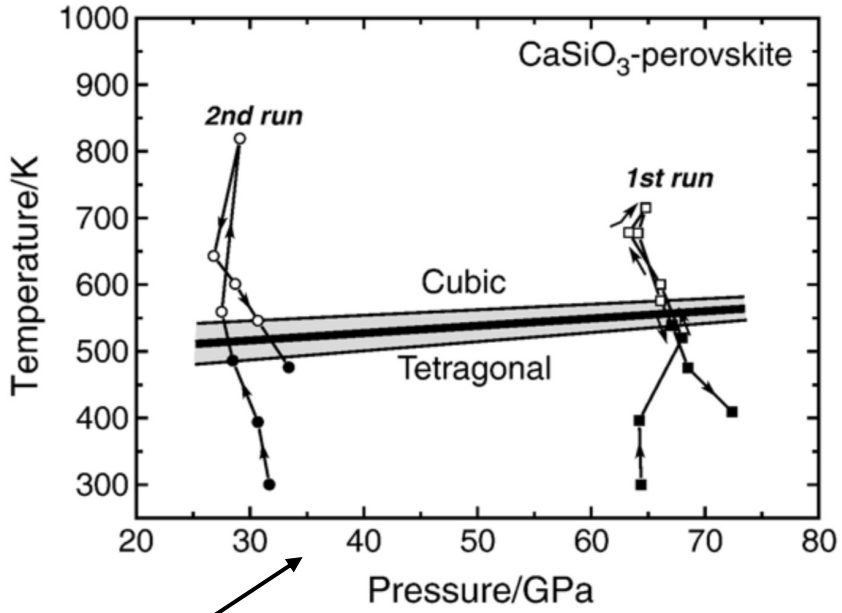
Tetragonal and orthorhombic



High *T*

Cubic

$T \geq 600$ K



- Komabayashi et al., Earth Planet. Sci. Lett. (2007).
- Ono et al., Am. Mineral. (2004).
- Kurashina et al., Phys. Earth Planet. Inter. (2004).

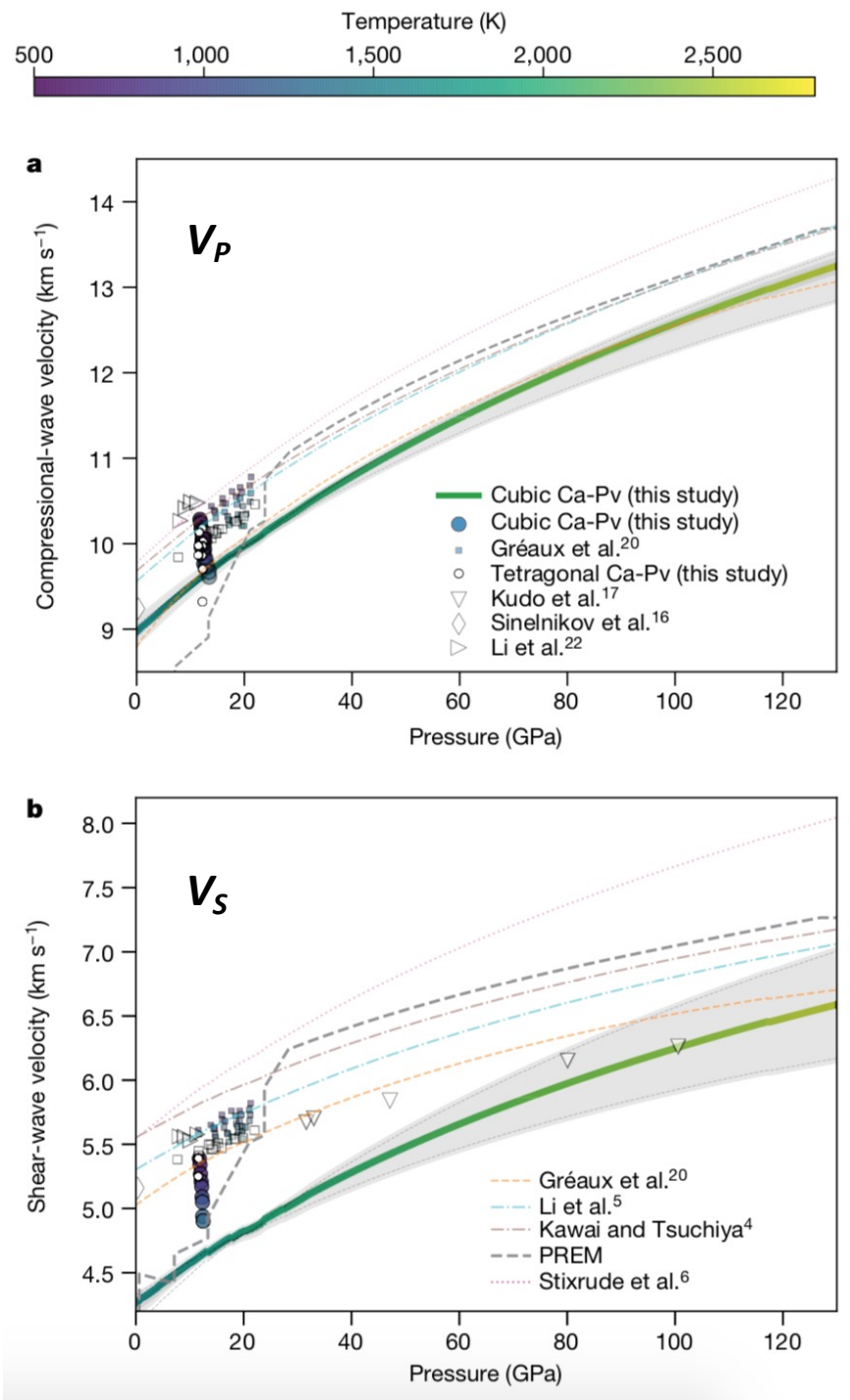
Challenge for CaPv

Thermal elasticity

Gréaux et al., Nature (2019). $P < 23$ GPa, $T < 1700$ K

Thomson et al., Nature (2019). $P < 16$ GPa, $T < 1500$ K

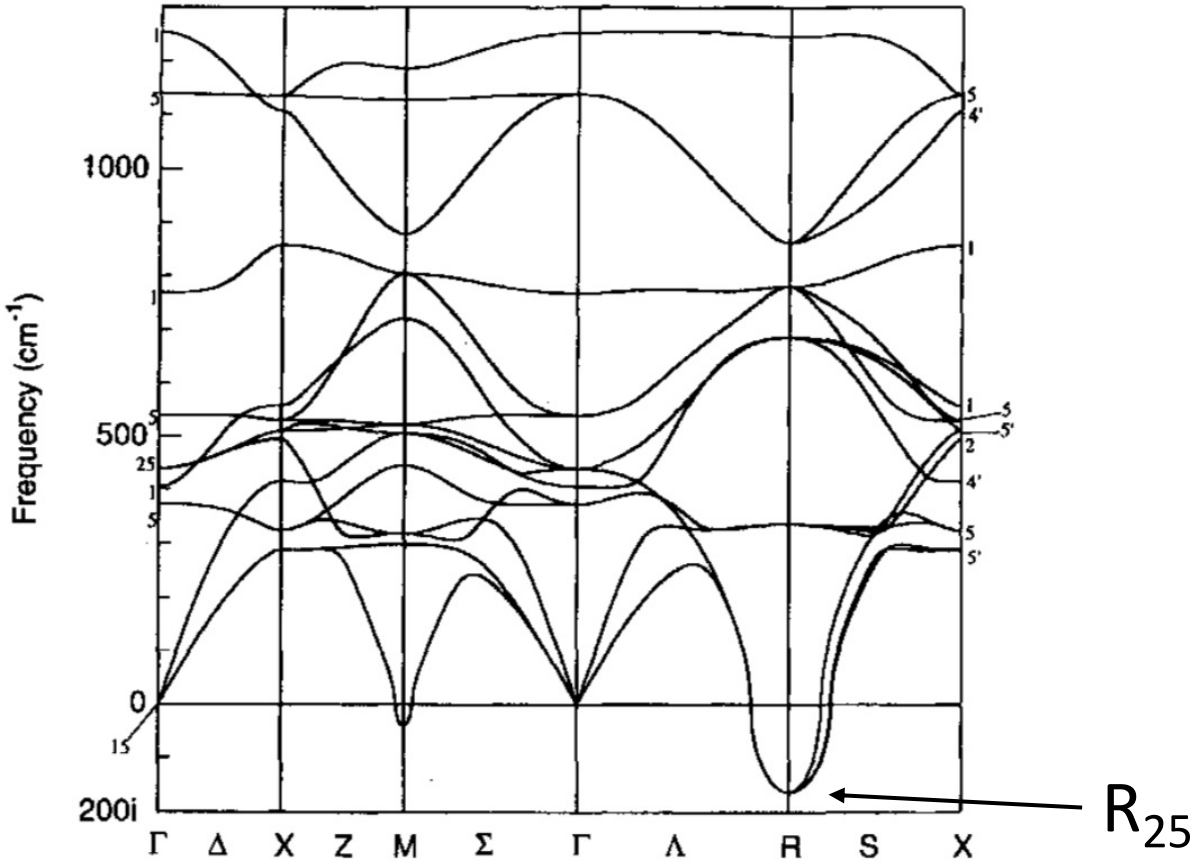
Measured shear moduli are substantially lower than theoretical predictions.



Challenge for CaPv

Cubic phase:

- Ground-state double-well potential
- *Ab initio* phonon dispersions have imaginary frequencies



Stixrude et al., Am. Mineral. (1996).

CaPv

Ab initio MD simulation details

LDA

NVT ensemble

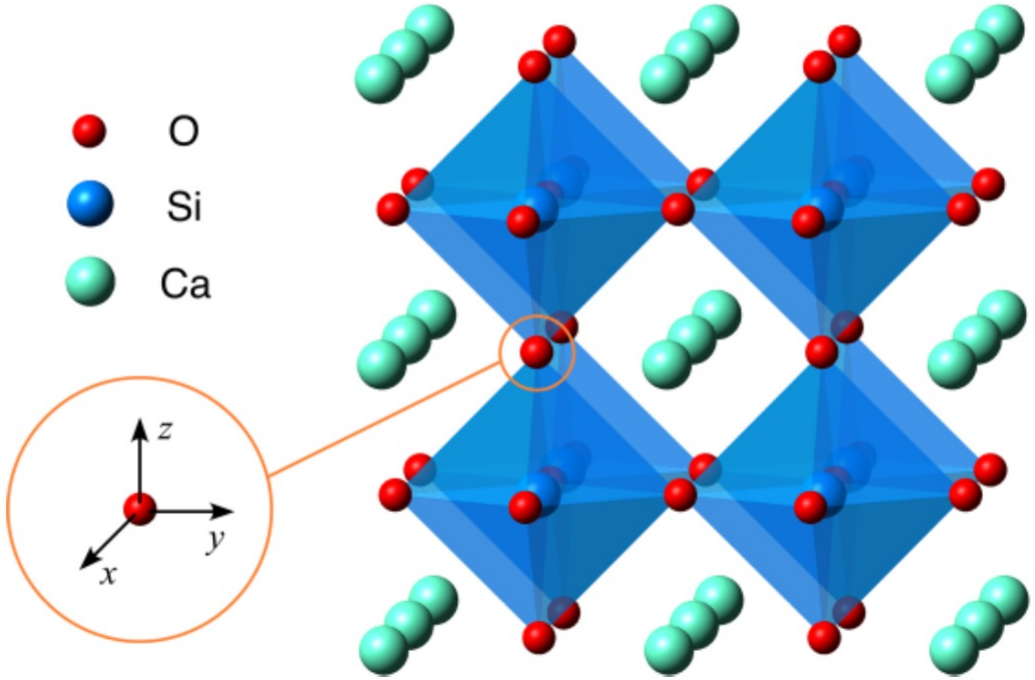
dt = 1 fs

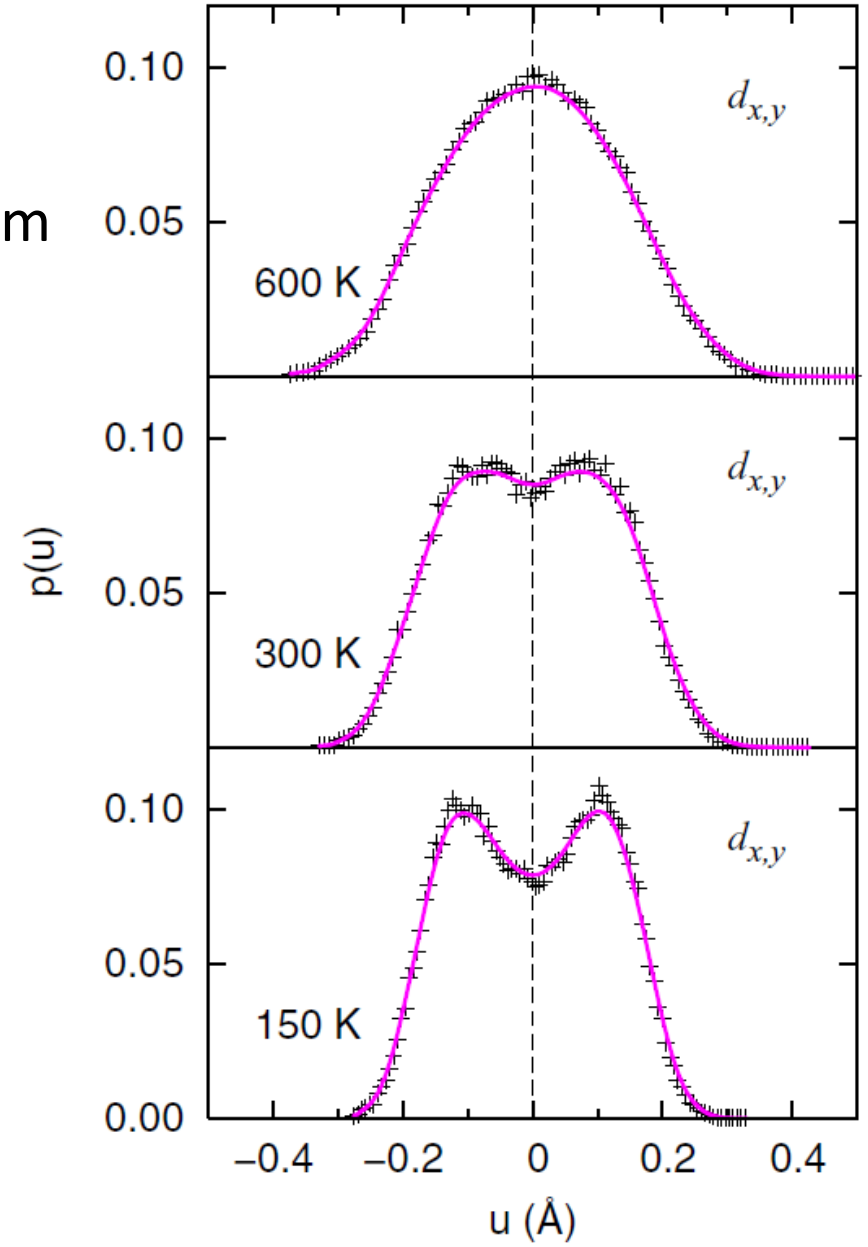
Simulation time = 60 ps

Nosé dynamics

Real space:

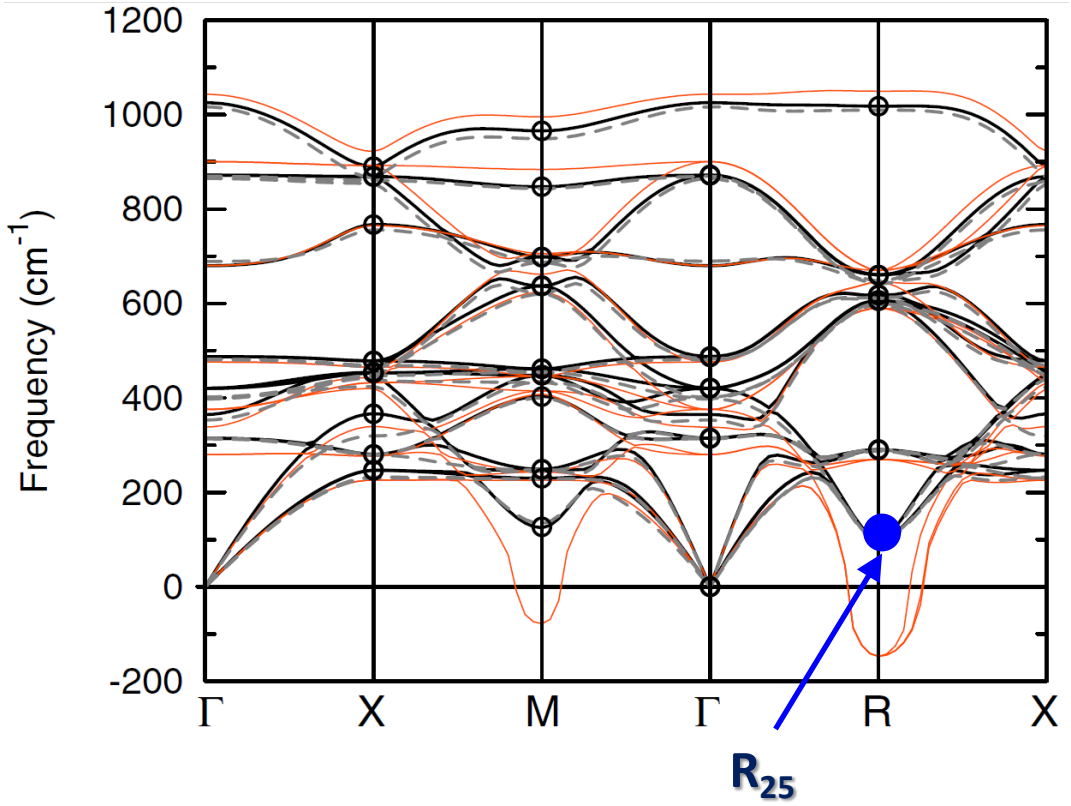
The distribution of atomic displacements of O atom of cubic **CaPv** from MD simulations

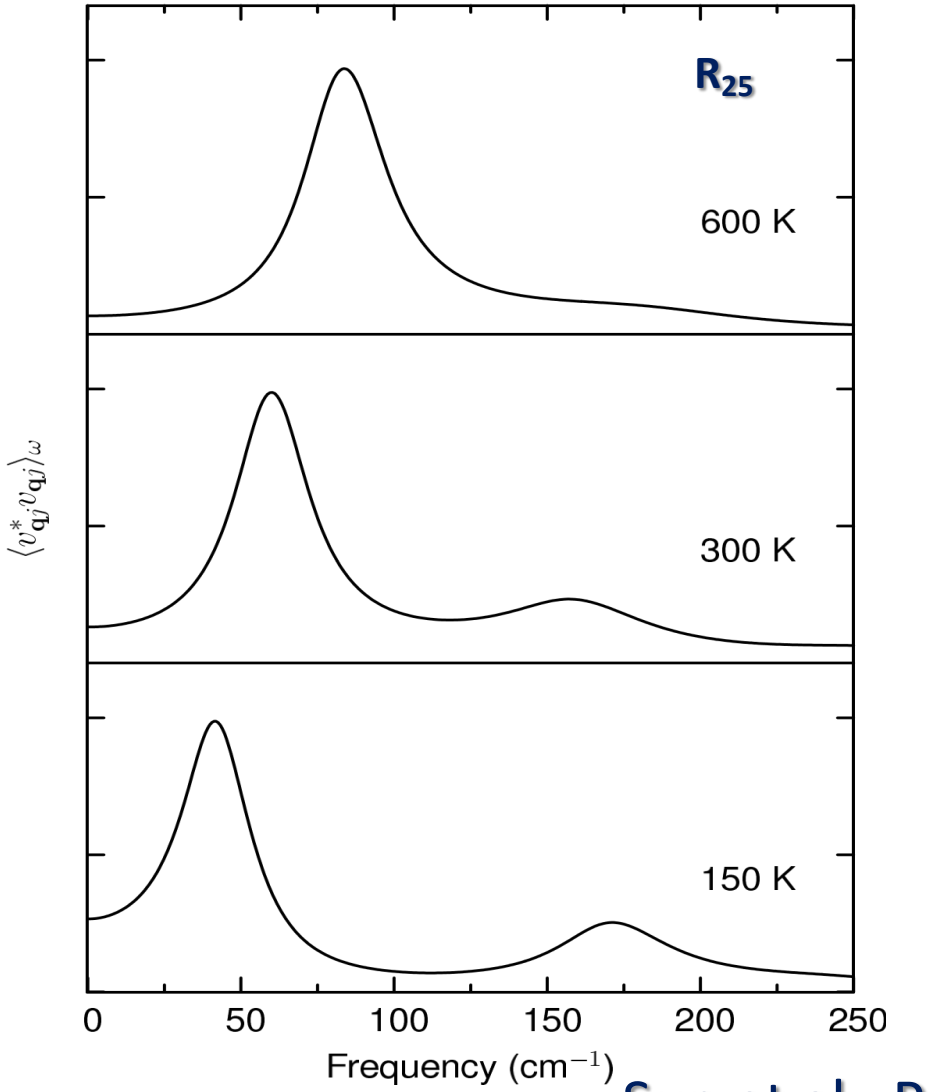




Sun et al., PRB (2014)

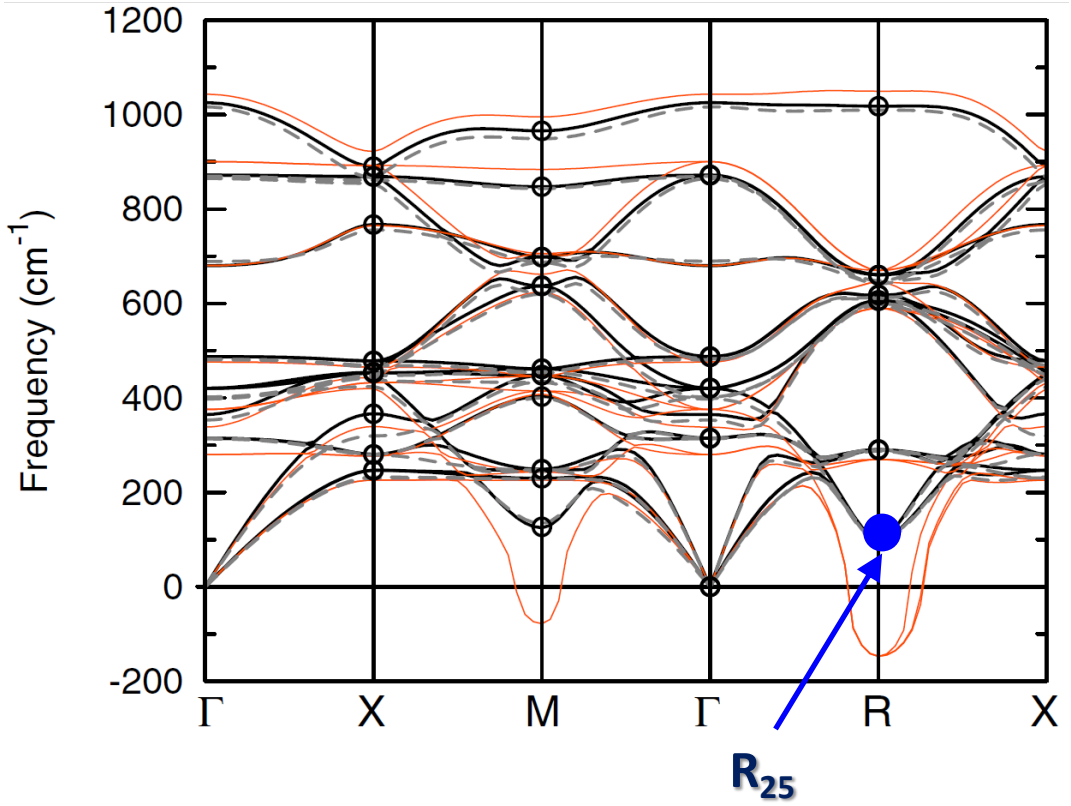
Phonon quasiparticle emerges at 600 K (at ~26 GPa) → CaPv is dynamically stable.

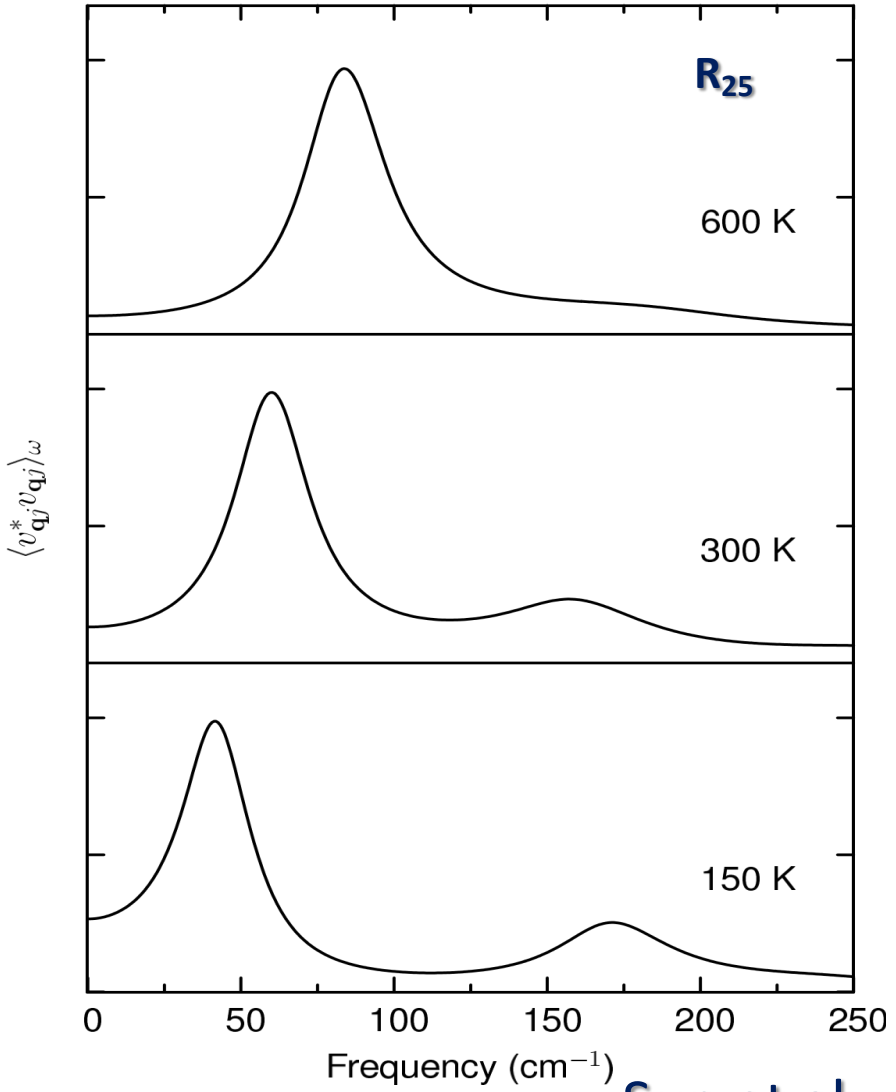




Sun et al., PRB (2014)

Phonon quasiparticle emerges at 600 K (at ~26 GPa) → CaPv is dynamically stable.

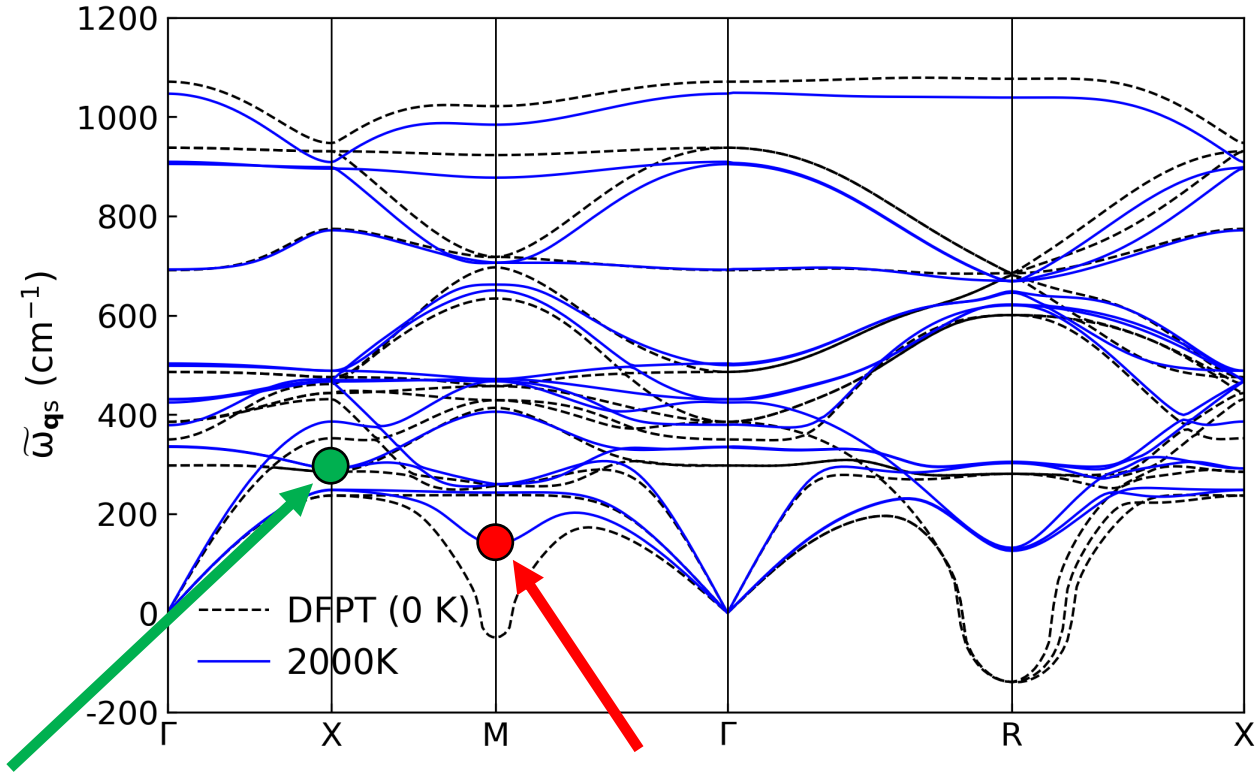


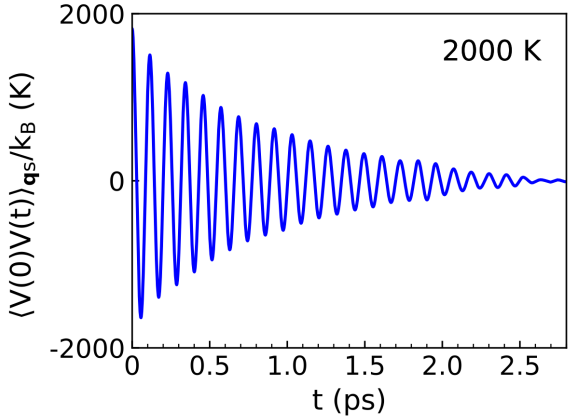


Good agreement with EXPs:

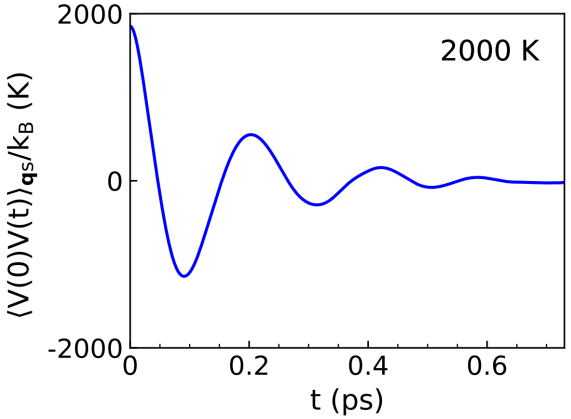
- Komabayashi et al., Earth Planet. Sci. Lett. (2007).
- Ono et al., Am. Mineral. (2004).
- Kurashina et al., Phys. Earth Planet. Inter. (2004).

Sun et al., PRB (2014)





Long-lived mode

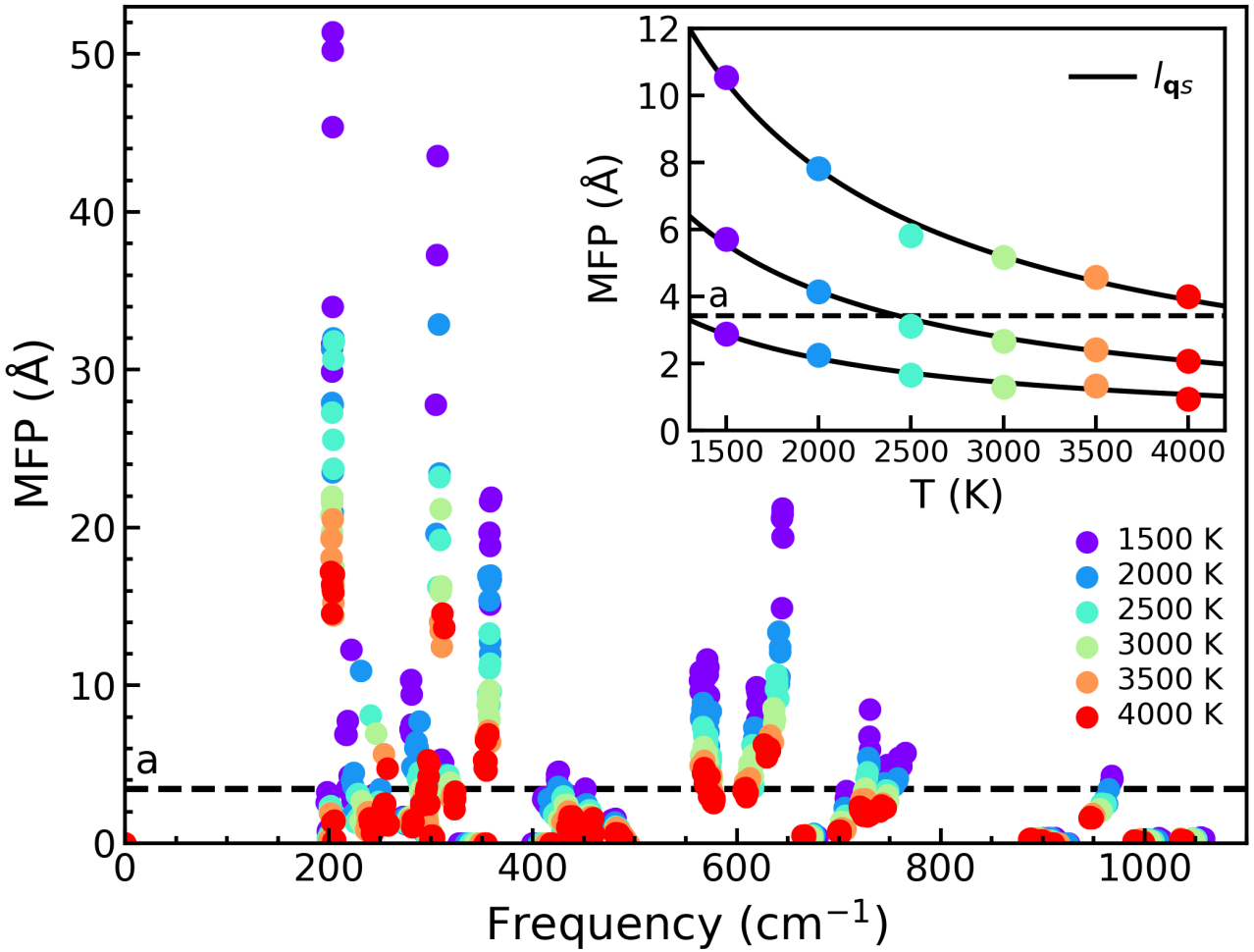


Short-lived soft mode

Quasiparticles remain well-defined at higher *T*

$$\langle V_{\mathbf{q}s}(0) \cdot V_{\mathbf{q}s}(t) \rangle = A_{\mathbf{q}s} \cos(\tilde{\omega}_{\mathbf{q}s} \boldsymbol{t}) e^{-t/(2\tau_{\mathbf{q}s})}$$

Subminimal mean free path

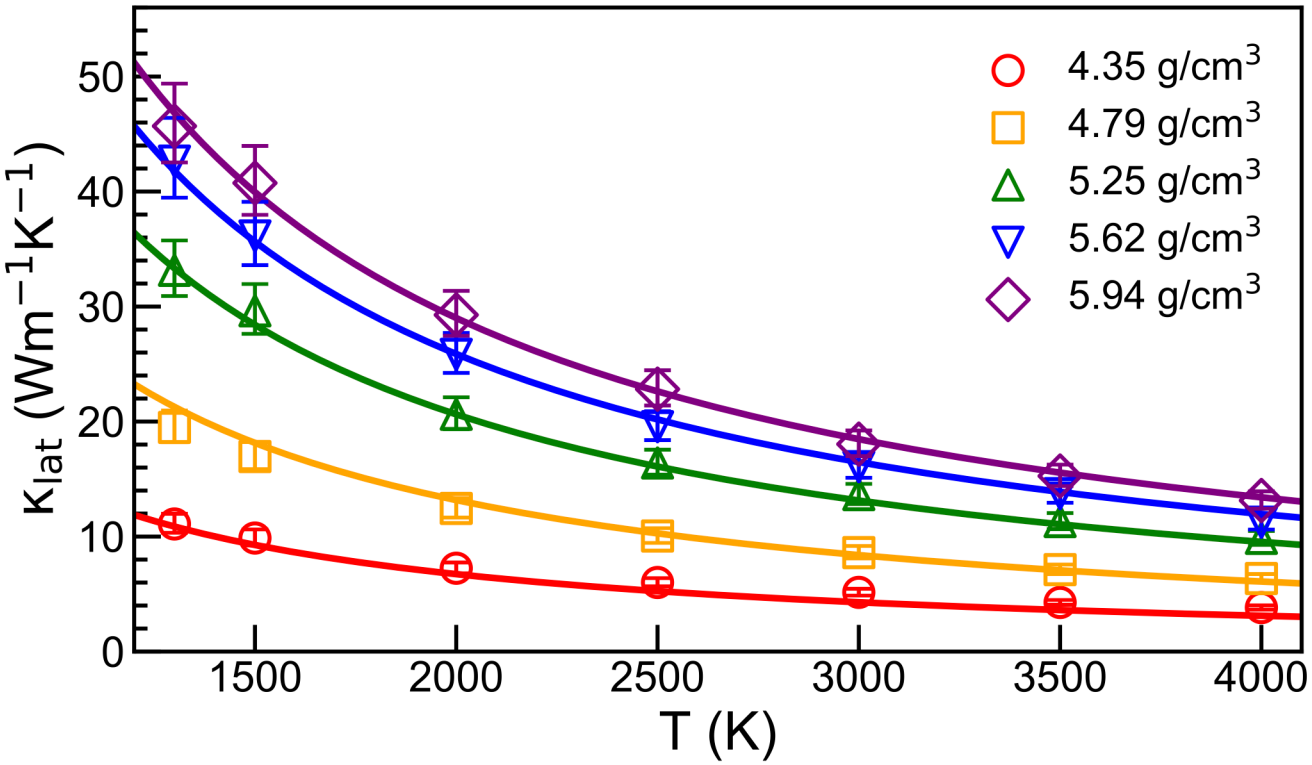


Zhang et al., PRB (2021)

Results

κ of CaPv

$\kappa(V,T)$



$$\kappa = \kappa_{ref}\left(\frac{T_{ref}}{T}\right)^{a}\left(\frac{V_{ref}}{V}\right)^{g}$$

$$g = b\ ln\left(\frac{V_{ref}}{V}\right) + c$$

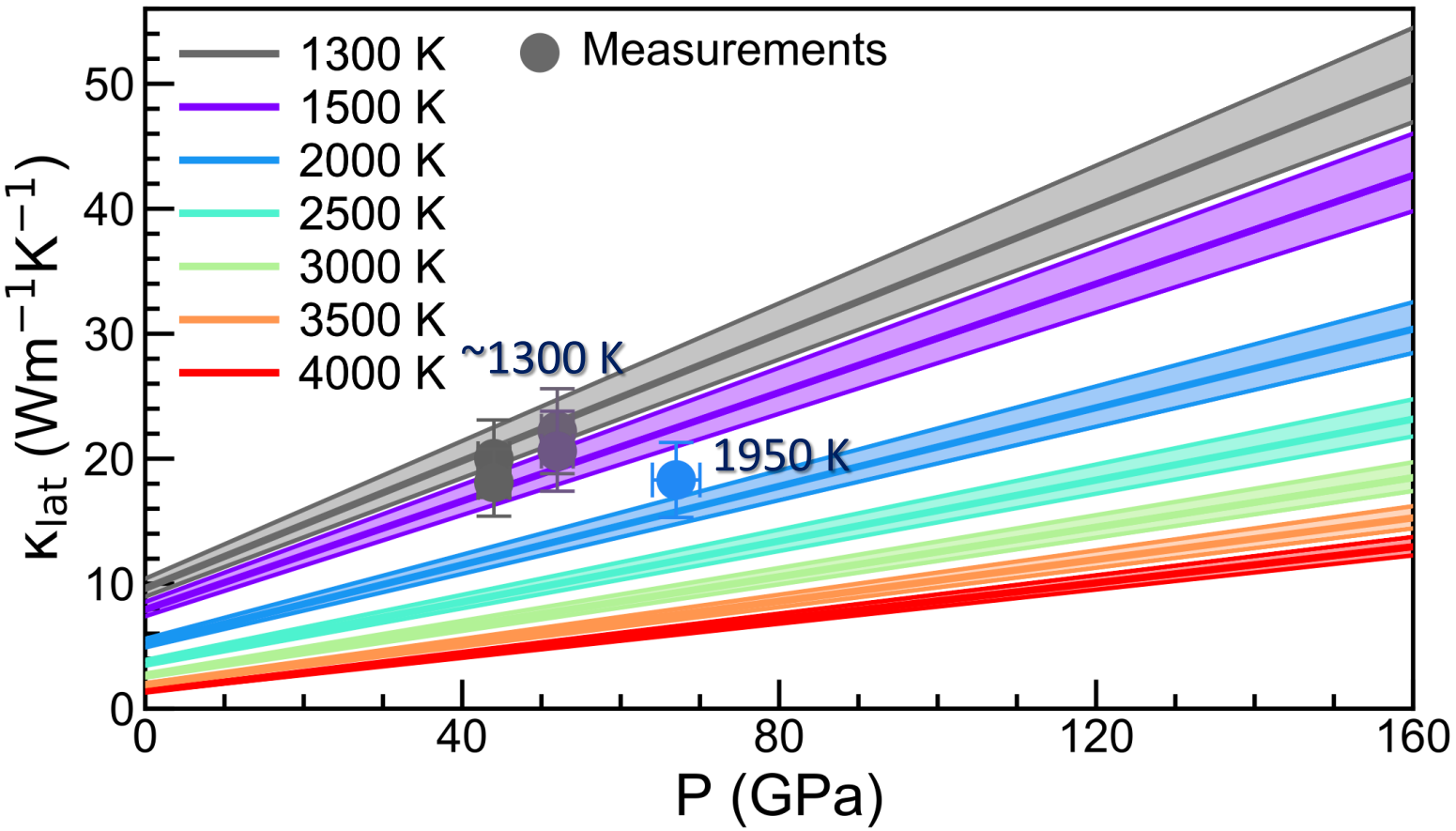
$$a = 1.11$$

Z. Zhang *et al.*, PRB **104**, 184101 (2021).

Results

κ of CaPv

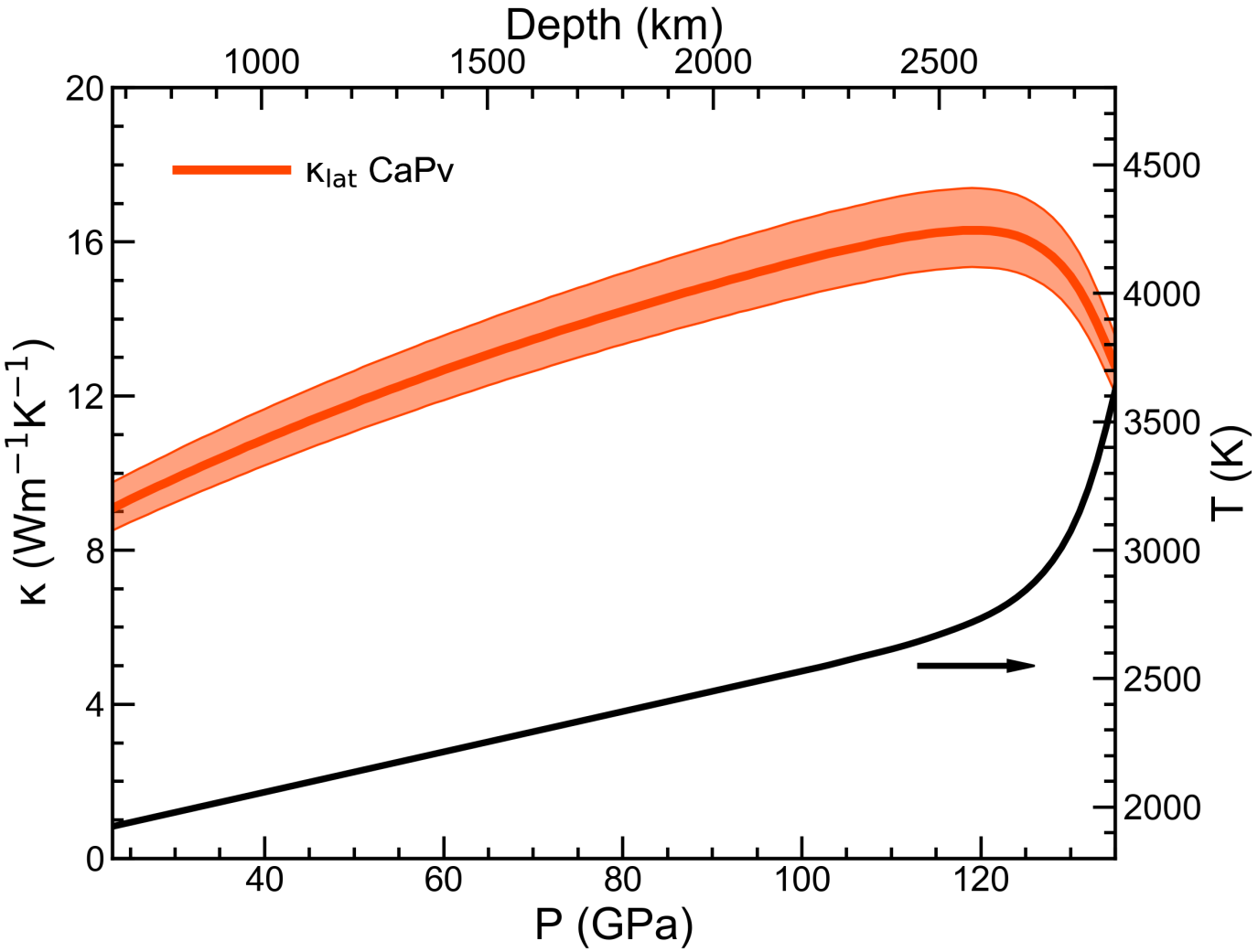
$$\kappa(P,T)$$



Z. Zhang *et al.*, PRB **104**, 184101 (2021).

Results

κ_{CaPv} along the geotherm



Geotherm:

Stacey et al., Physics of the Earth 4th edition (2008).

Z. Zhang *et al.*, PRB **104**, 184101 (2021).

Results

κ of the lower mantle

Pyrolite mantle:

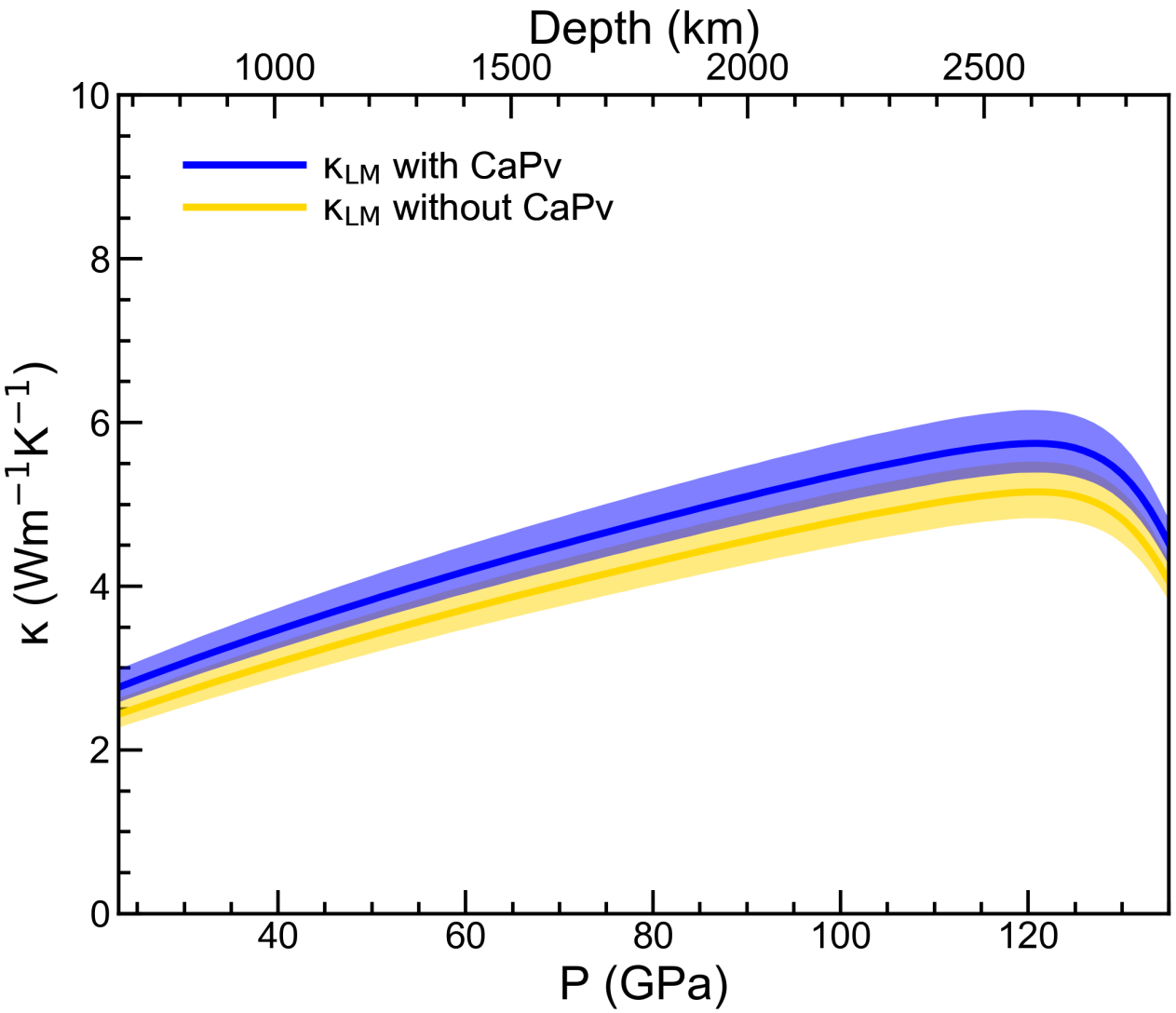
With CaPv:
7 vol% $CaSiO_3$ + 75 vol% $(Mg,Fe)SiO_3$ + 18 vol% $(Mg,Fe)O$

Without CaPv:
82 vol% $(Mg,Fe)SiO_3$ + 18 vol% $(Mg,Fe)O$

Voigt-Reuss-Hill averaging scheme

Results

Estimation of κ of the lower mantle



CaPv: 7 vol% abundance

Increases the κ_{LM} by ~11%

Z. Zhang *et al.*, PRB **104**, 184101 (2021).

Free energy and thermodynamics calculations

The quasi-harmonic approximation formula is no longer valid:

$$F = E_0 + \sum_{\mathbf{q}s} \frac{1}{2} \hbar\omega_{\mathbf{q}s} + k_B T \sum_{\mathbf{q}s} \ln\left(1 - e^{-\frac{\hbar\omega_{\mathbf{q}s}}{k_B T}}\right)$$

For two reasons:

- The phonon quasiparticle frequencies are intrinsically temperature-dependent

- The phonon quasiparticles of the cubic phase are not well-defined at low temperatures

Phonon gas model

The formula for vibrational entropy is still valid:

$$S_{vib}(T) = k_B \sum_{\mathbf{q}s} [(n_{\mathbf{q}s} + 1)\ln(n_{\mathbf{q}s} + 1) - n_{\mathbf{q}s}\ln n_{\mathbf{q}s}]$$

$$n_{\mathbf{q}s} = \left[\exp(\hbar\tilde{\omega}_{\mathbf{q}s}(T)/k_B T) - 1\right]^{-1}$$

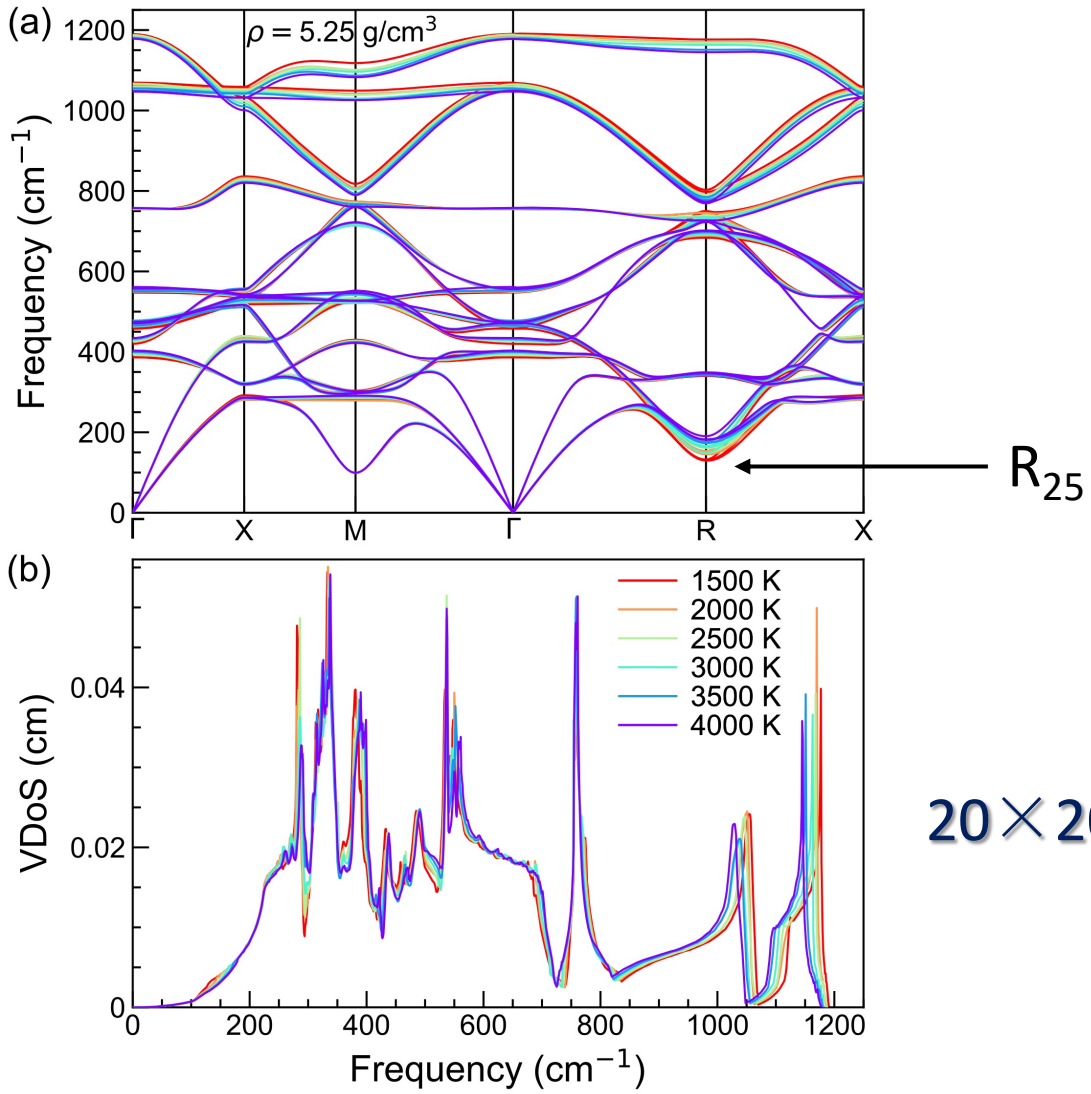
Helmholtz free energy:

$$F(V,T) = E(V,T_0) - T_0 S_{vib}(V,T_0) - \int_{T_0}^{T} S_{vib}(T')dT'$$

The reference temperature T_0 = 1500 K

$E(V,T_0)$ is the time-averaged internal energy obtained from the MD simulation at T_0.

Anharmonic phonon dispersions and vibrational density of states (VDoS)

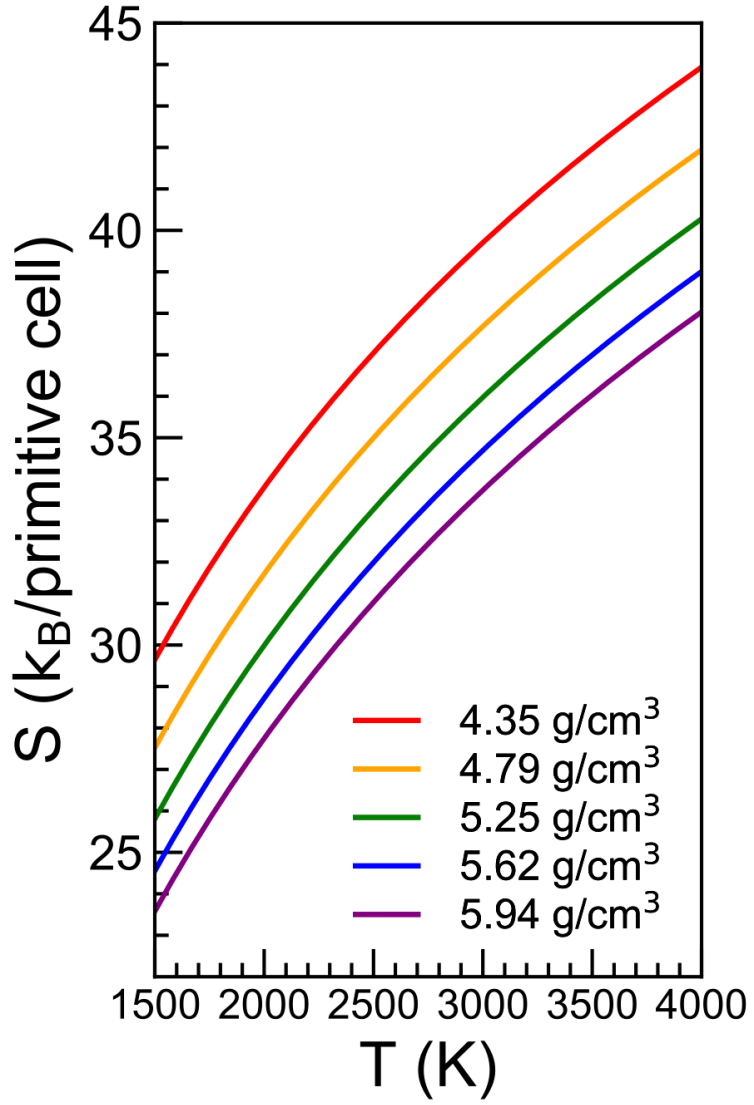


R_{25}

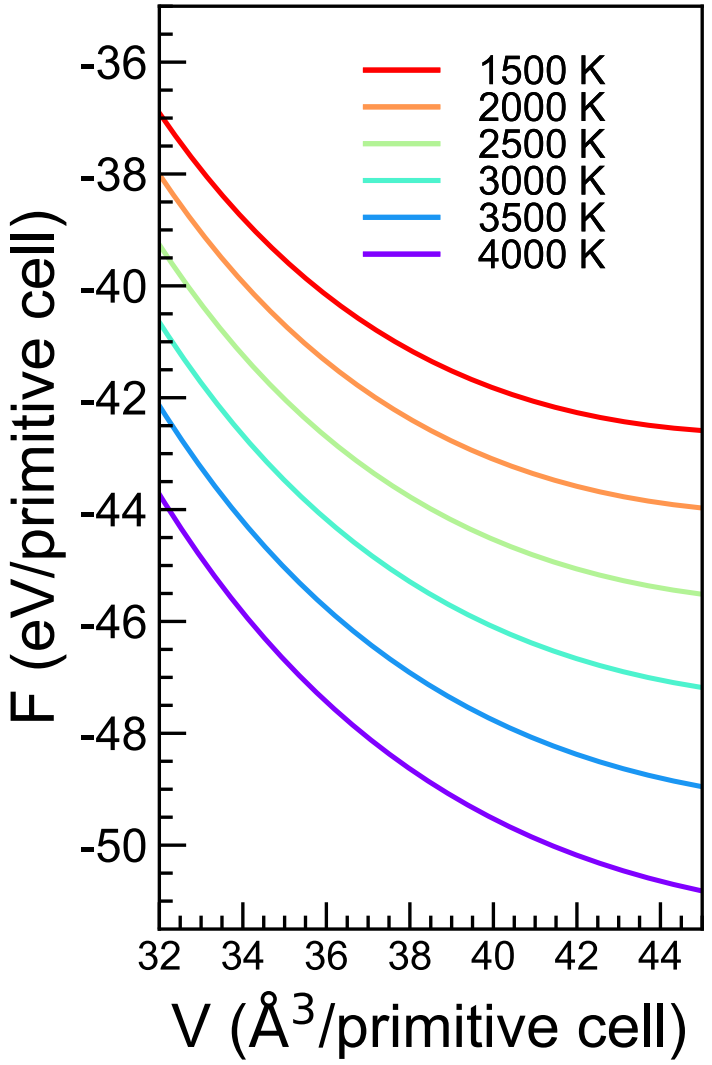
20×20×20 **q**-mesh

Zhang et al., PRB (2021)

Vibrational entropy:



Free energy:



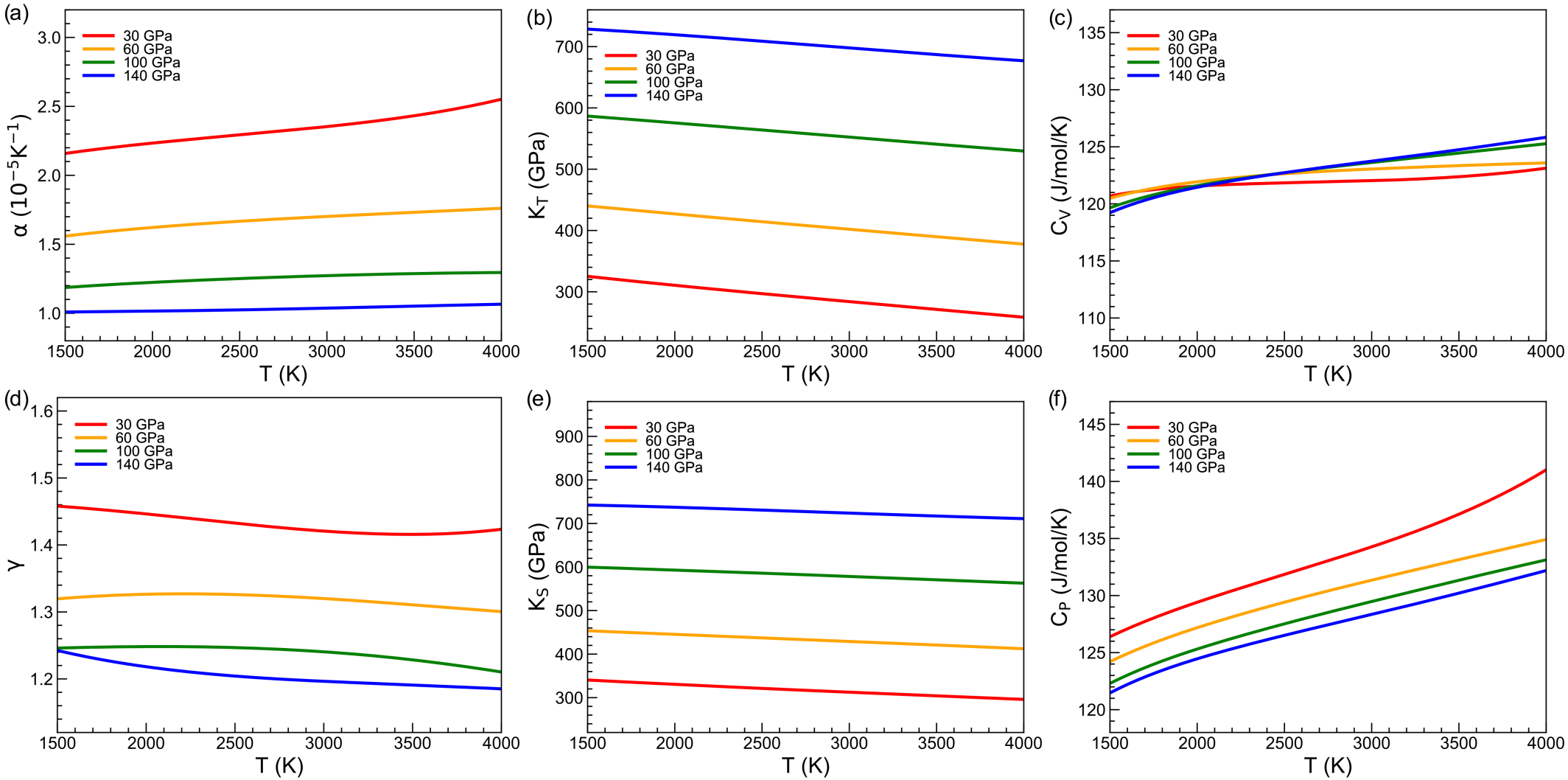
Pressure:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$

Z. Zhang *et al.*, PRB **103**, 104108 (2021).

Anharmonic thermodynamic properties

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad K_T = -V\left(\frac{\partial P}{\partial V}\right)_T \qquad C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

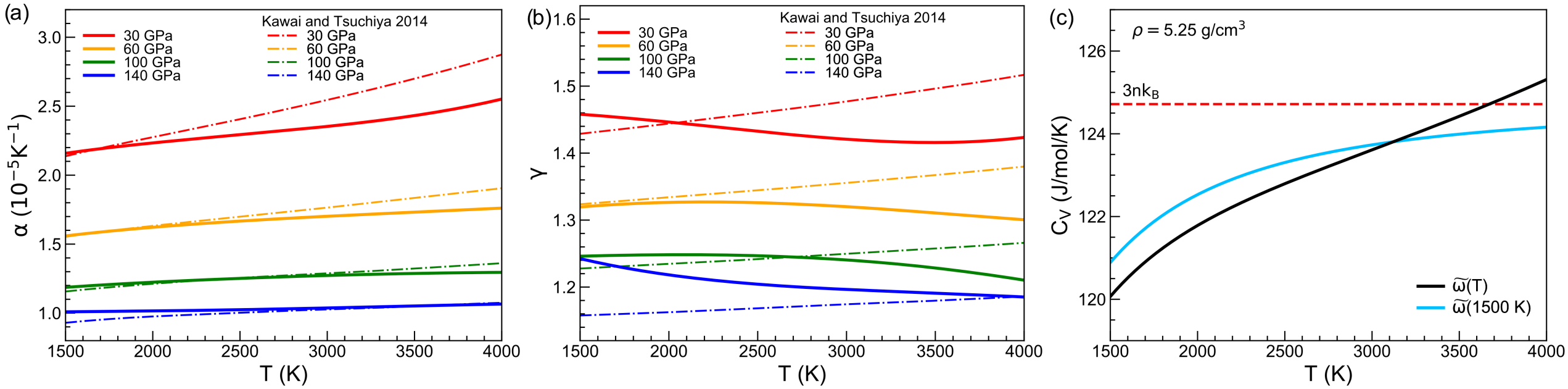


$$\gamma = \frac{V\alpha K_T}{C_V} \qquad K_S = K_T(1+\gamma\alpha T) \qquad C_P = C_V(1+\gamma\alpha T)$$

Z. Zhang *et al.*, PRB **103**, 104108 (2021).

Comparison

α γ C_V



Solid: PHQ

Dash-dotted: Mie-Grüneisen-Debye formulation

Z. Zhang *et al.*, PRB **103**, 104108 (2021).

Application to bcc/hcp Be (strongly anharmonic metal)

- Radiation windows: because of its low atomic number and very low absorption for X-rays.
- Lightweight structural components in high-speed aircraft, spacecraft, and satellites.
- Nuclear application: used to surround the fissile material.
- Neutron sources in laboratory devices.

Be

Ab initio MD simulation details

PBE

Mermin functional

4×4×4 supercells (128 atoms)

NVT ensemble

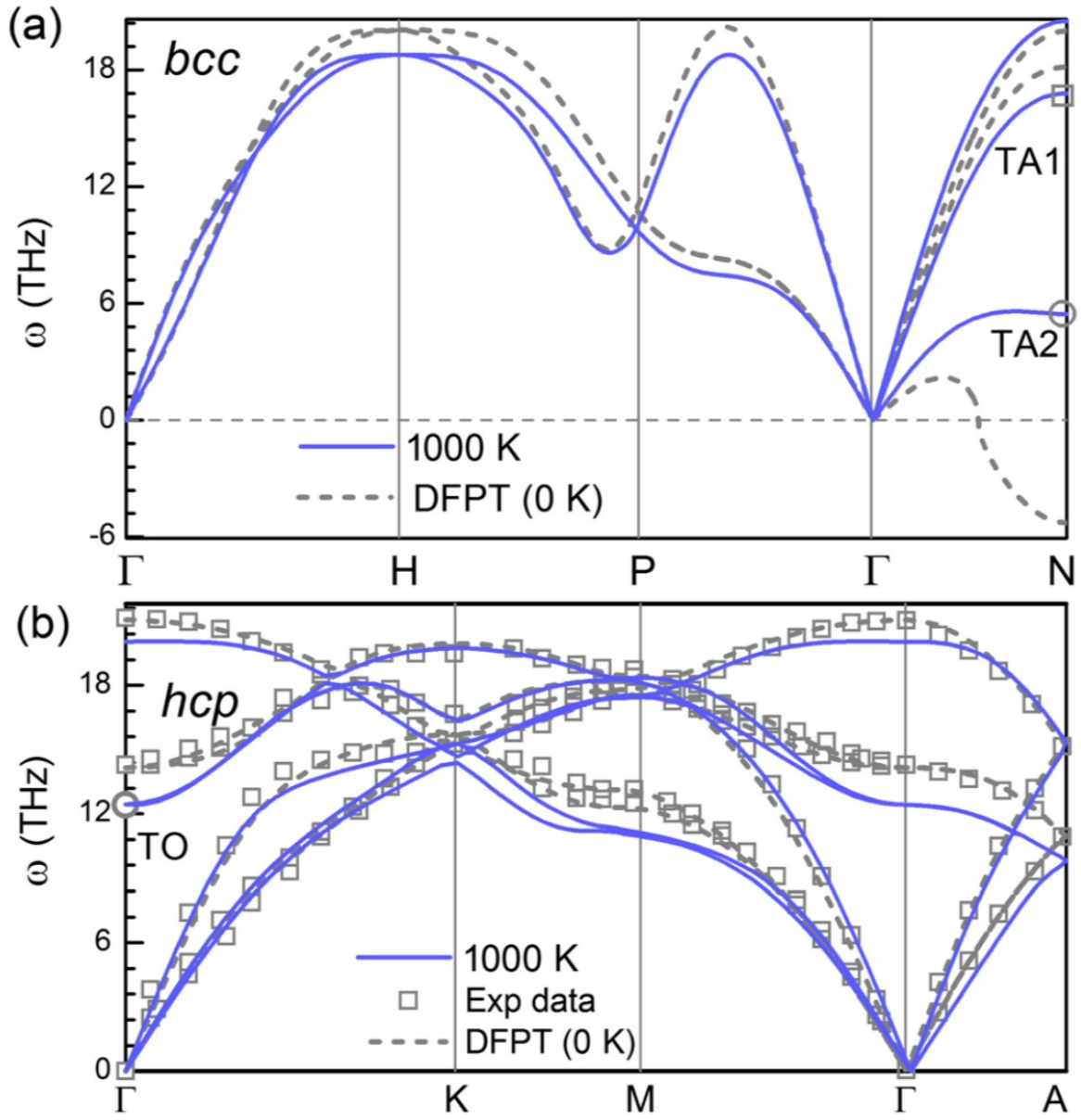
dt = 1 fs

Simulation time = 50 ps

Nosé dynamics

bcc Be

hcp Be



The bcc structural is unstable at low temperatures. Phonon quasiparticles of bcc Be are well-defined above 1000 K.

Lu et al., PRL (2017)

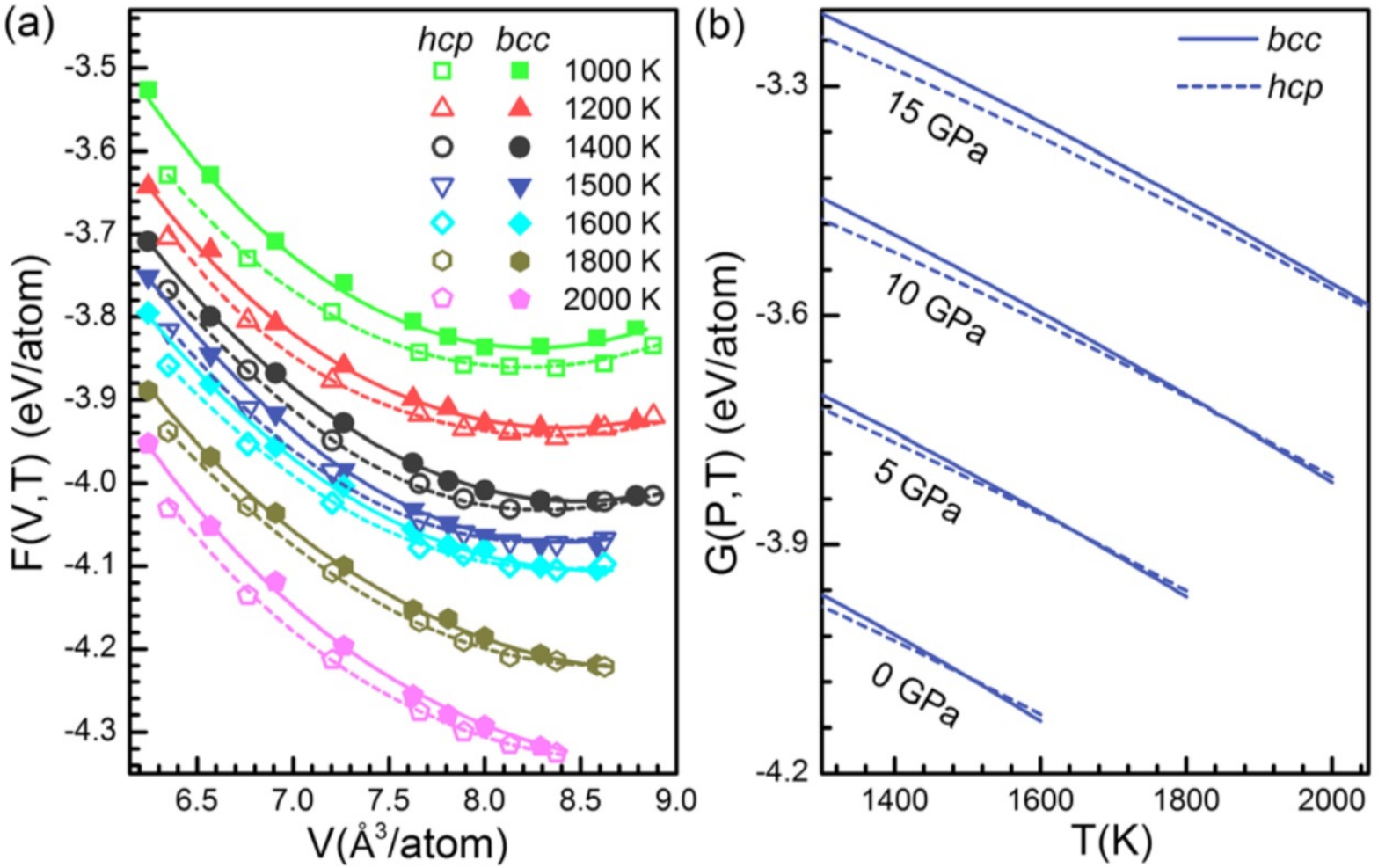
Helmholtz free energy:

$$F(V,T) = E(V,T_0) - T_0 S_{ele}(V,T_0) - T_0 S_{vib}(V,T_0) - \int_{T_0}^{T} S_{ele}(T')dT' - \int_{T_0}^{T} S_{vib}(T')dT'$$

The reference temperature T_0 = 1000 K
$E(V,T_0)$ is the time-averaged internal energy obtained from the MD simulation at T_0.

E and S_{ele} can be obtained from *ab initio* calculations software.
S_{vib} can be computed from the quasiparticle spectra.

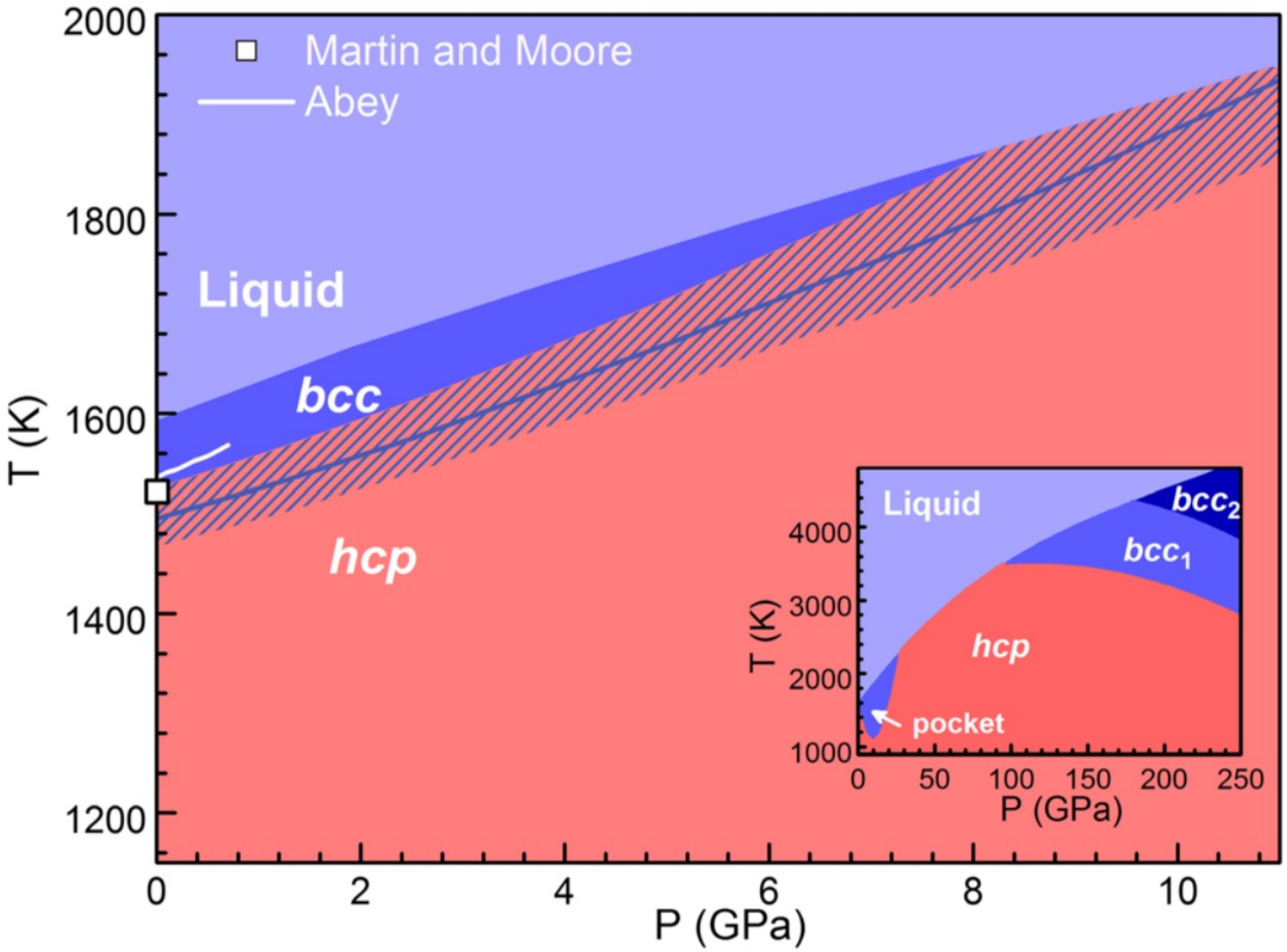
$F(V,T)$ $G(P,T) = F(V,T) + P(V,T)V$



20×20×20 **q**-mesh

Lu et al., PRL (2017)

Phase diagram of pre-melting bcc/hcp Be



Lu et al., PRL (2017)

Hands-on: phq code

https://github.com/MineralsCloud/phq

Zhang et al. Comput. Phys. Commun. (2019)

Method

Phonon quasiparticle approach

Mode-projected **V**elocity **A**utocorrelation **F**unction (**VAF**):

$$\langle V_{\mathbf{q}s}(0)V_{\mathbf{q}s}(t)\rangle = \lim_{\tau\to\infty}\frac{1}{\tau}\int_0^{\tau} V^*_{\mathbf{q}s}(t')V_{\mathbf{q}s}(t'+t)dt'$$

$$V_{\mathbf{q}s}(t) = \sum_{i=1}^{N}\sqrt{M_i}\mathbf{v}_i(t)e^{i\mathbf{q}\cdot\mathbf{R}_i}\cdot\hat{\mathbf{e}}^i_{\mathbf{q}s}$$

Ab initio molecular dynamics

Ab initio harmonic phonons

cubic diamond Si as an example

Ab initio MD:

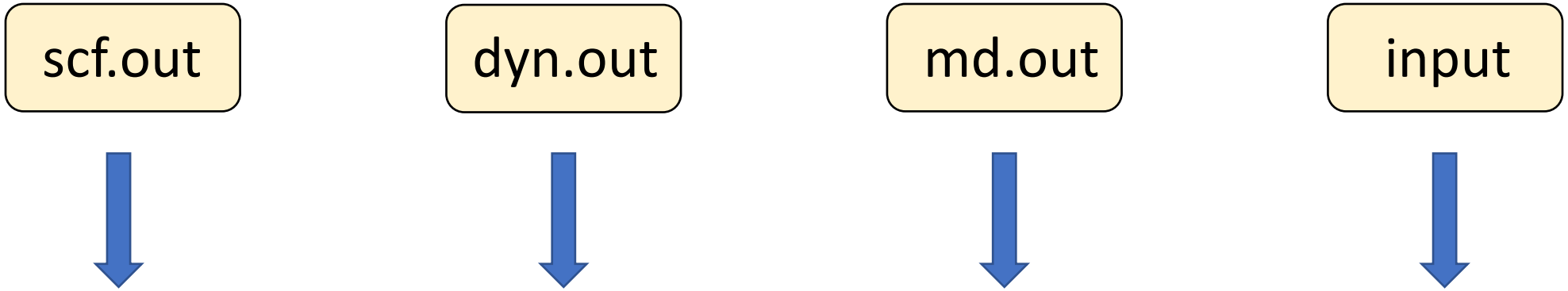
4×4×4 supercells (128 atoms)

Ab initio harmonic phonons:

4×4×4 **q**-mesh

The q-points sampling for the harmonic phonon calculations should be **commensurate** with the supercell size.

Input files



structure of the primitive cell

ab initio harmonic phonons

ab initio MD

settings for phq

Zhang et al. Comput. Phys. Commun. (2019)

scf.out

```
ntype  =  1
natom  =  2

mass
Si   28.0855

lattice_parameter  =  10.370817020

cell_parameters
    0.000000000    0.500000000    0.500000000
    0.500000000    0.000000000    0.500000000
    0.500000000    0.500000000    0.000000000

atomic_positions
Si    0.000000000    0.000000000    0.000000000
Si    0.250000000    0.250000000    0.250000000
```

Number of elements

Number of atoms

Element name followed by the mass

Lattice parameter in Bohr radius

Lattice vectors scaled by the lattice parameter

Atomic positions in crystal coordinates

dyn.out

```
Dynamical matrix file

  1    2  0 10.3708170  0.0000000  0.0000000  0.0000000  0.0000000  0.0000000
Basis vectors
      0.000000000    0.500000000    0.500000000
      0.500000000    0.000000000    0.500000000
      0.500000000    0.500000000    0.000000000
           1  'Si  '    25598.3672624059
    1    1      0.0000000000      0.0000000000      0.0000000000
    2    1      0.2500000000      0.2500000000      0.2500000000

     Dynamical  Matrix in cartesian axes

     q = (    0.000000000   0.000000000   0.000000000 )

    1    1
  0.27105449  0.00000000    0.00000000  0.00000000    0.00000009  0.00000000
  0.00000000  0.00000000    0.27105474  0.00000000    0.00000005  0.00000000
  0.00000009  0.00000000    0.00000005  0.00000000    0.27105465  0.00000000
    1    2
 -0.27078210  0.00000000   -0.00000004  0.00000000    0.00000000  0.00000000
 -0.00000003  0.00000000   -0.27078168  0.00000000    0.00000001  0.00000000
 -0.00000000  0.00000000    0.00000001  0.00000000   -0.27078187  0.00000000
    2    1
 -0.27078210  0.00000000   -0.00000003  0.00000000   -0.00000000  0.00000000
 -0.00000004  0.00000000   -0.27078168  0.00000000    0.00000001  0.00000000
  0.00000000  0.00000000    0.00000001  0.00000000   -0.27078187  0.00000000
    2    2
  0.27076057  0.00000000   -0.00000013  0.00000000    0.00000002  0.00000000
 -0.00000013  0.00000000    0.27076084  0.00000000    0.00000004  0.00000000
  0.00000002  0.00000000    0.00000004  0.00000000    0.27076071  0.00000000

     Dielectric Tensor:

         23.356590536997          -0.000010192749           0.000002086388
         -0.000010138151          23.356590677250           0.000014240984
          0.000002080351           0.000014287566          23.356594216403

     Effective Charges E-U: Z_{alpha}{s,beta}

     atom #    1
         -1.139812312715           0.000000103754          -0.000000410345
          0.000000394149          -1.139812558977          -0.000001034242
         -0.000000498373          -0.000001182086          -1.139812871792
     atom #    2
         -1.140677552970           0.000001193733           0.000000248824
          0.000001138321          -1.140677456367          -0.000001203593
          0.000000160442          -0.000000861857          -1.140678533945

     Effective Charges U-E: Z_{s,alpha}{beta}

     atom #    1
     -0.113982806114E+01      0.587992782082E-06     -0.166911820747E-06
      0.198030409404E-06     -0.113982227168E+01     -0.126084144858E-05
     -0.218511522654E-06     -0.109703644124E-05     -0.113982838261E+01
     atom #    2
     -0.114069392591E+01      0.941325949834E-06     -0.134977341103E-06
      0.938413025064E-06     -0.114068866787E+01     -0.115859147742E-05
     -0.656572640700E-07     -0.107594584664E-05     -0.114069435079E+01

     Diagonalizing the dynamical matrix

     q = (    0.000000000   0.000000000   0.000000000 )

*********************************************************************************
     freq (    1) =       0.230231 [THz] =       7.679670 [cm-1]
(  0.691018  0.000000  0.107566  0.000000 -0.103212  0.000000 )
(  0.691393  0.000000  0.107624  0.000000 -0.103268  0.000000 )
     freq (    2) =       0.230598 [THz] =       7.691912 [cm-1]
( -0.117487  0.000000  0.091697  0.000000 -0.691026  0.000000 )
( -0.117551  0.000000  0.091747  0.000000 -0.691401  0.000000 )
     freq (    3) =       0.230898 [THz] =       7.701920 [cm-1]
( -0.091760  0.000000  0.692640  0.000000  0.107512  0.000000 )
( -0.091810  0.000000  0.693016  0.000000  0.107571  0.000000 )
     freq (    4) =      15.133665 [THz] =     504.804713 [cm-1]
(  0.188638  0.000000  0.613826  0.000000 -0.296487  0.000000 )
( -0.188536  0.000000 -0.613493  0.000000  0.296326  0.000000 )
     freq (    5) =      15.133666 [THz] =     504.804762 [cm-1]
( -0.238099  0.000000  0.347584  0.000000  0.568125  0.000000 )
(  0.237970  0.000000 -0.347395  0.000000 -0.567816  0.000000 )
     freq (    6) =      15.133668 [THz] =     504.804811 [cm-1]
( -0.638745  0.000000  0.051713  0.000000 -0.299335  0.000000 )
(  0.638399  0.000000 -0.051685  0.000000  0.299172  0.000000 )
*********************************************************************************
 ...
```

dyn.out is simply a concatenation of all the output dynmat files by ph.x of Quantum ESPRESSO package.

$ cat dynmat* > dyn.out

md.out

```
total_step  =  10000

atomic_positions
Si      0.0000000000      0.0000000000      0.0000000000
Si      0.0625000000      0.0625000000      0.0625000000
Si      0.2500000000      0.0000000000      0.0000000000
Si      0.3125000000      0.0625000000      0.0625000000
Si      0.5000000000      0.0000000000      0.0000000000
Si      0.5625000000      0.0625000000      0.0625000000
Si      0.7500000000      0.0000000000      0.0000000000
Si      0.8125000000      0.0625000000      0.0625000000
Si      0.0000000000      0.2500000000      0.0000000000
Si      0.0625000000      0.3125000000      0.0625000000
Si      0.2500000000      0.2500000000      0.0000000000
Si      0.3125000000      0.3125000000      0.0625000000
Si      0.5000000000      0.2500000000      0.0000000000
Si      0.5625000000      0.3125000000      0.0625000000
 ...

md_step = 5000
atomic_md_positions
Si      0.9818033400      0.0143762200      0.9946054700
Si      0.0404658700      0.0934023800      0.0516911600
Si      0.2226678000      0.0006252700      0.0115934000
Si      0.2730537700      0.0664646000      0.0848089300
Si      0.4630747600      0.0178188900      0.0122942300
Si      0.5401123300      0.0498953600      0.0898588100
Si      0.7395603700      0.0033935100      0.0043052400
Si      0.7924060400      0.0673239000      0.0735076200
Si      0.9947108400      0.2859514400      0.9839587600
Si      0.0656859700      0.3279744000      0.0588671000
Si      0.2484133500      0.2476844600      0.0083361200
Si      0.3155499000      0.2918325400      0.0877569500
Si      0.5052480300      0.2315406000      0.0168115200
Si      0.5688188700      0.2985122700      0.0651846800

 ...
```

Total number of *ab initio* MD steps

Equilibrium atomic positions in crystal coordinates of the supercell

Step #

Atomic positions during the MD in crystal coordinates of the supercell

md.out

(a)

```
...
atomic_md_positions
Mg    0.011012016   0.019655128   0.077218163
Mg    0.175065423   0.174730483   0.092286993
Mg   -0.006628746  -0.012158547  -0.087891385
Mg   -0.167425371  -0.181918657  -0.082751697
Si   -0.002219084   0.160746545  -0.000420259
Si    0.173324080   0.003789656  -0.002351856
Si   -0.001711452   0.156018865   0.166685758
Si    0.172916863  -0.004894948   0.171334876
O     0.066899064   0.065512639  -0.020189318
O     0.237397581   0.100584987   0.013362569
O     0.107805148   0.237085282  -0.014012816
O     0.276499047   0.264195775   0.023048409
O     0.060545825   0.066580562   0.186499379
O     0.237425805   0.098108784   0.157168078
O     0.101975395   0.229736145   0.186048941
O     0.271668673   0.260684022   0.145131366
O     0.033189446   0.152985168   0.086405985
O     0.152673298   0.003449583   0.084545041
O    -0.038684585  -0.169063540  -0.082631003
O     0.193678933   0.004503128  -0.081978340
Mg    0.329400469   0.026607094   0.086048913
Mg    0.511185457   0.192406690   0.094622939
Mg    0.338549894  -0.007500880  -0.076490007
Mg    0.154239361  -0.190945762  -0.081472078
Si    0.333278727   0.171353846   0.008191164
Si    0.496563199  -0.009279888   0.002358487
...
```

1st primitive cell

2nd primitive cell

Correct

(b)

```
...
atomic_md_positions
Mg    0.011012016   0.019655128   0.077218163
Mg    0.175065423   0.174730483   0.092286993
Mg   -0.006628746  -0.012158547  -0.087891385
Mg   -0.167425371  -0.181918657  -0.082751697
Mg    0.329400469   0.026607094   0.086048913
Mg    0.511185457   0.192406690   0.094622939
...
Si   -0.002219084   0.160746545  -0.000420259
Si    0.173324080   0.003789656  -0.002351856
Si   -0.001711452   0.156018865   0.166685758
Si    0.172916863  -0.004894948   0.171334876
Si    0.333278727   0.171353846   0.008191164
Si    0.496563199  -0.009279888   0.002358487
...
O     0.066899064   0.065512639  -0.020189318
O     0.237397581   0.100584987   0.013362569
O     0.107805148   0.237085282  -0.014012816
O     0.276499047   0.264195775   0.023048409
O     0.060545825   0.066580562   0.186499379
O     0.237425805   0.098108784   0.157168078
O     0.101975395   0.229736145   0.186048941
O     0.271668673   0.260684022   0.145131366
O     0.033189446   0.152985168   0.086405985
O     0.152673298   0.003449583   0.084545041
...
```

All Mg atoms

All Si atoms

All O atoms

Wrong

input

```
dt                20.67055273
step_md_use       50000
correlation_time  1000
pole              1000
supercell         4 4 4
temperature       900
method            0
```

Time step for MD in Rydberg atomic unit,
1 a.u. = 4.8378 * 10^-17 s

Number of MD steps to use for the phq code

Correlation time in dt to calculate for the VAF

Parameter used in the maximum entropy method to filter high-frequency components. Usually a reasonable range (200 – 2000) can yield smooth spectrum.

Supercell size

Temperature of the MD

Quasiparticle properties obtained by which method to construct $\widetilde{D}$:

0: curve fitting (recommended)

$$\langle V_{\mathbf{q}s}(0) \cdot V_{\mathbf{q}s}(t) \rangle = A_{\mathbf{q}s} \cos(\widetilde{\omega}_{\mathbf{q}s} t) e^{-\Gamma_{\mathbf{q}s} t}$$

1: Fourier transform

$$G_{\mathbf{q}s}(\omega) = \left| \int_0^\infty \langle V_{\mathbf{q}s}(0) \cdot V_{\mathbf{q}s}(t) \rangle e^{i\omega t} dt \right|^2$$

2: maximum entropy method, also yields Lorentzian spectrum

Get phq

You can get phq from github

$ git clone https://github.com/MineralsCloud/phq

Compile phq

If you are using gfortran compiler on Linux machine

```
$ mv makefile_linux_gfortran makefile
$ make
```

If you are using ifort compiler on Linux machine

```
$ mv makefile_linux_ifort makefile
$ make
```

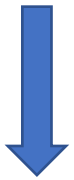
Run phq

phq is a serial Fortran code

$ ./phq < input

Output files

Renormalized frequencies



frequency.freq

Mode #	Harmonic ω	$\tilde{\omega}$ by curve fitting	$\tilde{\omega}$ by FT	$\tilde{\omega}$ by MEM
4	504.804735	484.491418	486.615909	484.609477
5	504.804768	483.889308	485.843363	484.776267
6	504.804835	485.847867	489.105830	485.610219
7	96.061524	88.830309	90.062307	89.149463
8	96.062358	89.105390	90.062307	89.232858
9	223.738687	216.332499	218.484486	216.577321
10	476.705195	457.364850	458.650638	457.255853
11	482.333789	464.307776	465.977662	465.011606
12	482.333922	463.673250	465.139461	463.427097
13	110.902625	101.037919	103.404871	101.158371
14	110.903325	101.621254	103.404871	101.658742
15	377.603067	361.358033	361.917049	361.684960
16	387.334900	378.419440	378.595254	379.114555
17	471.069229	454.091228	456.097851	452.418932
18	471.069529	450.608065	453.266532	451.168004
19	96.061524	88.830309	90.062307	89.149463
20	96.062358	89.105390	90.062307	89.232858
21	223.738687	216.332499	218.484486	216.577321
22	476.705195	457.364850	458.650638	457.255853
23	482.333789	464.307776	465.977662	465.011606
24	482.333922	463.673250	465.139461	463.427097
25	96.061157	88.829942	90.062307	89.066068
26	96.062591	88.920794	90.062307	89.149463
27	223.736686	216.249209	216.816665	216.410530
28	476.704694	458.551872	458.650638	457.923014
29	482.333755	463.538958	465.389306	465.011606
30	482.334056	464.615313	466.567507	465.678768

Output files

Effective harmonic dynamical matrices

- dynmatmd0
- dynmatmd1
- dynmatmd2
- •
- •
- •
- dynmatmd*nq*

```
Dynamical matrix file

  1    2  0 10.370817020  0.0000000  0.0000000  0.0000000  0.0000000  0.0000000
Basis vectors
     0.000000000     0.500000000     0.500000000
     0.500000000     0.000000000     0.500000000
     0.500000000     0.500000000     0.000000000
           1  'si  '    25598.3672624059
    1    1      0.0000000000      0.0000000000      0.0000000000
    2    1      0.2500000000      0.2500000000      0.2500000000

     Dynamical Matrix in cartesian axes

     q = (   0.000000000   0.000000000   0.000000000  )

   1    1
 0.25075481  0.00000000    0.00001014  0.00000000    0.00070269  0.00000000
 0.00001014  0.00000000    0.24954185  0.00000000   -0.00028793  0.00000000
 0.00070269  0.00000000   -0.00028793  0.00000000    0.24953501  0.00000000
   1    2
-0.25049367  0.00000000   -0.00001028  0.00000000   -0.00070218  0.00000000
-0.00001030  0.00000000   -0.24928041  0.00000000    0.00028791  0.00000000
-0.00070224  0.00000000    0.00028797  0.00000000   -0.24927361  0.00000000
   2    1
-0.25049367  0.00000000   -0.00001030  0.00000000   -0.00070224  0.00000000
-0.00001028  0.00000000   -0.24928041  0.00000000    0.00028797  0.00000000
-0.00070218  0.00000000    0.00028791  0.00000000   -0.24927361  0.00000000
   2    2
 0.25048339  0.00000000    0.00001023  0.00000000    0.00070183  0.00000000
 0.00001023  0.00000000    0.24927119  0.00000000   -0.00028783  0.00000000
 0.00070183  0.00000000   -0.00028783  0.00000000    0.24926381  0.00000000

     Dielectric Tensor:
```

$$\tilde{D}(\mathbf{q}) = \hat{\mathbf{e}}_{\mathbf{q}} \Omega_{\mathbf{q}} \hat{\mathbf{e}}_{\mathbf{q}}{}^{\dagger}$$

where, $\Omega_{\mathbf{q}} = \mathrm{diag}[\tilde{\omega}^2_{\mathbf{q}1}, \tilde{\omega}^2_{\mathbf{q}2}, \ldots, \tilde{\omega}^2_{\mathbf{q}3N}]$

Anharmonic phonon dispersion / VDoS from dynmatmd

q2r.in

```
&input
 zasr = 'simple' ,
 fildyn = 'dynmatmd' ,
 flfrc = 'fc'
/
```

$ q2r.x < q2r.in

$$\widetilde{\Phi}(\mathbf{r}) = \sum_{\mathbf{r}} \widetilde{D}(\mathbf{q})\, e^{i\mathbf{q}\cdot\mathbf{r}}$$

matdyn.in

```
&input
 asr = 'simple' ,
 flfrc = 'fc' ,
 flfrq = 'freq' ,
 q_in_band_form = .true. ,
 q_in_cryst_coord = .true.
/
10
 0      0      0      50
 0      0.5    0.5    50
 0.25   0.75   0.5    50
 0.375  0.75   0.375  50
 0      0      0      50
 0.5    0.5    0.5    50
 0.25   0.625  0.625  50
 0.25   0.75   0.5    50
 0.5    0.5    0.5    50
 0.375  0.75   0.375  1
```

$ matdyn.x < matdyn.in

$$\widetilde{D}(\mathbf{q}') = \sum_{\mathbf{r}} \widetilde{\Phi}(\mathbf{r})\, e^{-i\mathbf{q}'\cdot\mathbf{r}}$$

How to get anharmonic phonon dispersion

In the example/Si/postprocessing/dispersion folder:
q2r.in, dispersion.in, plotband.in

$ q2r.x < q2r.in > q2r.out
$ matdyn.x < dispersion.in > dispersion.out
$ plotband.x < plotband.in > plotband.out

Thank you!

XSEDE

Extreme Science and Engineering
Discovery Environment