Hands-on Tutorial on Phonon calculations

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> Adams DJ
  donat.adams@geo.unibe.ch

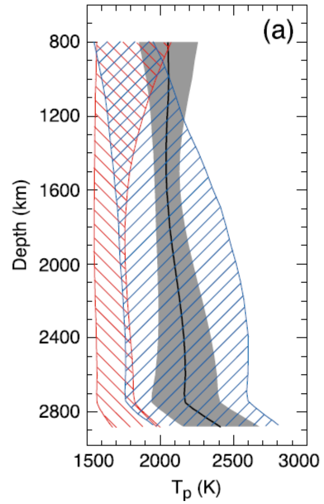
> Overview
  - Introduction: How include thermal effects in theory?
  - Phonons, harmonic approximation: Theory
    - Harmonic oscillator
    - Thermodynamics (Quasi Harmonic Approximation, QHA)
    - Contributions from long wavelength phonons
  - Structure of the Earth's mantle: Applicaionts QHA
  - Extension of Quasiharmonic approximation: Decoupleed anharmonic Mode approximation (DAMA)
  - Conclusions and outlook

Introduction:
How include thermal effects in theory?

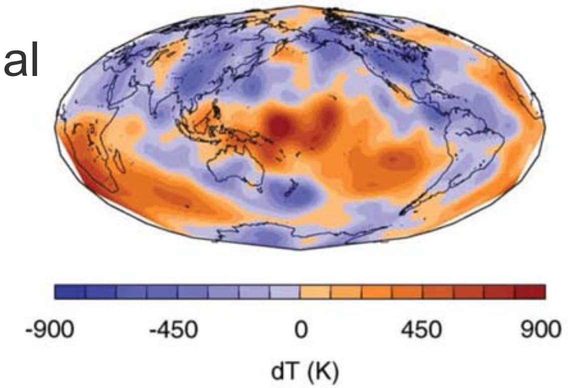
- Theoretical calculations often performed at T=0 K !

- In Earth interion minerals are commonly at T>0 K
- Measured wave velocities

$$d\ln V_p = \frac{\partial \ln V_p}{\partial T}\,dT + \frac{\partial \ln V_p}{\partial C}\,dC + \frac{\partial \ln V_p}{\partial F}\,dF$$
$$d\ln V_s = \frac{\partial \ln V_s}{\partial T}\,dT + \frac{\partial \ln V_s}{\partial C}\,dC + \frac{\partial \ln V_s}{\partial F}\,dF$$



- Numerical inversion $\Longrightarrow$
  - composition (C), temperature (T), fraction of partial melt (F)



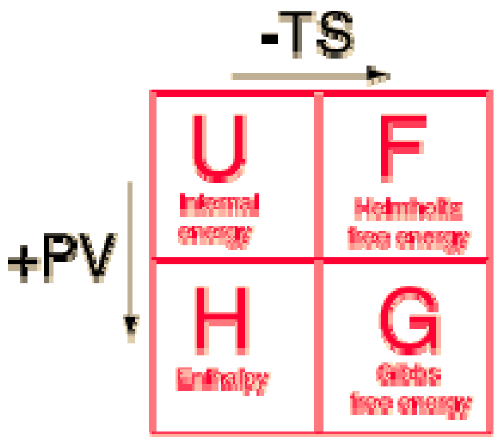
Masters, G. et. al. (2000). In Karato, S. et al. Deep Interior: Mineral Physics and Tomography from the Atomic to the Global Scale, Washington, Am. Geophys. Union.
Deschamps, F. and Trampert, J. (2003). Phys. Earth Planet. Int., 140:277–291
Deschamps F, Trampert J / Earth and Planetary Science Letters **222** (2004) 161–175

Background Thermodynamics

- Free energy *G(T,P)* is needed to calculate phase equilibria
- *G(T,P)* can be obtained from *F(T,V)*

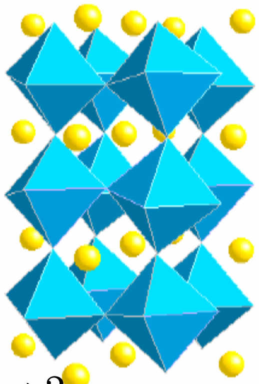
$$G(P,T) = F(V,T) + P \cdot T = \underbrace{E_{0\mathrm{K}}(V)}_{=U} + E_{\mathrm{ZP}}(V) - T \cdot S(T,V) + P \cdot V$$

- $E_{0K}(V)$ can be obtained from static calculations (geometry optimization)
- $E_{ZP}(V)$ is a (small) correction, taking into account the quantum nature of the atomic cores
- $E_{ZP}(V) - T * S(T,V)$ can be calculated from partition function



Background
Harmonic Oscillator

- Move 1 atom along 1 degree of freedom (N atoms, 3N-3 degrees of freedom)



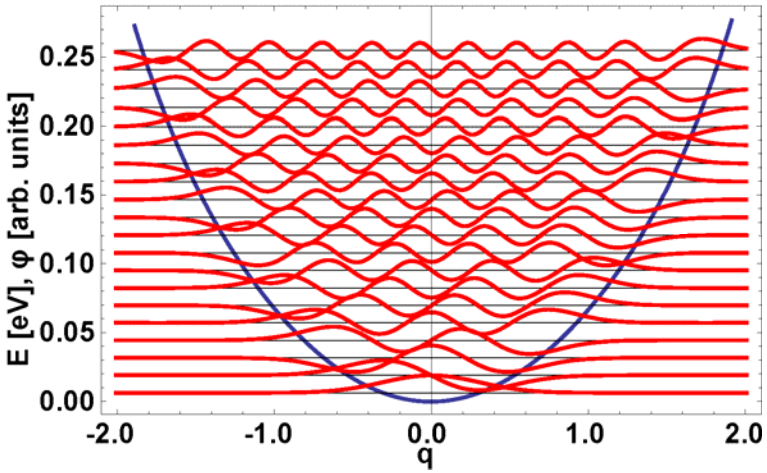
- Curvature of potential energy surface determines *all* vibrational frequencies (e.g. Wu, 2008)
- (Quasi) Harmonic approximation => atoms are "connected by springs" and experience the potential

$$U = \frac{k}{2}(q_\mu)^2$$

- Energies for harmonic potential are equidistant

$$\mu \in [1, 3N-3]$$

- Indices:
  - — Accounts for degree of freedom
  - — J accounts for energy level
- Theory breaks down for negative curvatures of potential energy surface



$$\omega_\mu = \sqrt{\frac{1}{m_\mu}\frac{\partial^2 V(q_\mu)}{\partial q_\mu^2}}\Bigg|_{q_\mu=0}$$

$$\epsilon_\mu^j = \hbar \cdot \omega_\mu \cdot \left(\tfrac{1}{2} + j\right) \text{ and } j \in \mathbb{N}_0$$

Background Thermodynamics

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- The partition function Z gives access to all thermodynamic quantities

$$Z = \sum_i e^{-\frac{\epsilon_i}{k_B T}}$$

$$A = -k_B T \ln Z$$

- The free energy is the thermodynamically relavant potential at *T*>0
- Thermodynamic energy

$$\langle E \rangle = k_B \cdot T^2 \frac{\partial \ln Z}{\partial T}$$

- Heat capacity

$$c_V = \frac{\partial \langle E \rangle}{\partial T}$$

- Elastic constant tensor

$$c_{ij}^T(T,P) = \left[\frac{\partial^2 A}{\partial \varepsilon_i \, \partial \varepsilon_j} \right]_P$$

$$G(P,T) = F(V,T) + P \cdot T = \underbrace{E_{\mathrm{0K}}(V)}_{=U} + \underbrace{E_{\mathrm{ZP}}(V) - T \cdot S(T,V)}_{A} + P \cdot V$$

Background
Phonons

- In solid, the lowest energy excitations are collective vibrations of atoms: phonons

$$\Phi = \begin{bmatrix} \frac{d^2 E}{dq_1\, dq_1} & \cdots \\ \cdots & \frac{d^2 E}{dq_\mu\, dq_\nu} \end{bmatrix}$$

- They can be obtained from force constant matrix

$$-\frac{dE}{dq_\mu} = F_\mu \Rightarrow \frac{d^2 E}{dq_\mu\, dq_\mu} = -\frac{dF_\nu}{dq_\mu}$$

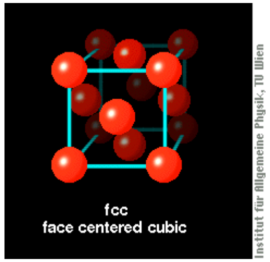
- The eigenvalues of the dynamical matrix D are eigenenergies

$$D = \begin{bmatrix} \frac{1}{\sqrt{m_1 \cdot m_1}} \frac{d^2 E}{dq_1\, dq_1} & \cdots \\ \cdots & \frac{1}{\sqrt{m_\mu \cdot m_\nu}} \frac{d^2 E}{dq_\mu\, dq_\nu} \end{bmatrix}$$

- The eigenvectors of the dynamica matrix D are the polarization vectors

Example
Dynamical matrix

> Dynamical matrix



In carthesian coordinates

$$D = -\frac{1}{\sqrt{m_\mu \cdot m_\nu}} \frac{dF_\nu}{dq_\mu} = \begin{pmatrix} -6. & 0. & 0. & 0.2 & 0.4 & 0. \\ 0. & -6. & 0. & 0.4 & 0.2 & 0. \\ 0. & 0. & -6. & 0. & 0. & 0. \\ 0.2 & 0.4 & 0. & -6. & 0. & 0. \\ 0.4 & 0.2 & 0. & 0. & -6. & 0. \\ 0. & 0. & 0. & 0. & 0. & -6 \end{pmatrix}$$

> Polarization vector

— Collective modes

$$\varepsilon = \begin{bmatrix} 0.5 \\ 0.5 \\ 0 \\ -0.5 \\ -0.5 \\ 0 \end{bmatrix} \qquad \varepsilon_i = \begin{pmatrix} 0.5 & 0.5 & 0 & 0 & 0.5 & 0.5 \\ 0.5 & -0.5 & 0 & 0 & -0.5 & 0.5 \\ 0 & 0 & 1. & 0 & 0 & 0 \\ -0.5 & 0.5 & 0 & 0 & -0.5 & 0.5 \\ -0.5 & -0.5 & 0 & 0 & 0.5 & 0.5 \\ 0 & 0 & 0 & 1. & 0 & 0 \end{pmatrix}$$

> Eigenvalue

$$D = \begin{pmatrix} 6.6 & 0. & 0. & 0. & 0. & 0. \\ 0. & 6.2 & 0. & 0. & 0. & 0. \\ 0. & 0. & 6. & 0. & 0. & 0. \\ 0. & 0. & 0. & 6. & 0. & 0. \\ 0. & 0. & 0. & 0. & 5.8 & 0. \\ 0. & 0. & 0. & 0. & 0. & 5.4 \end{pmatrix}$$

Background
Contribution of long wave-length phonons

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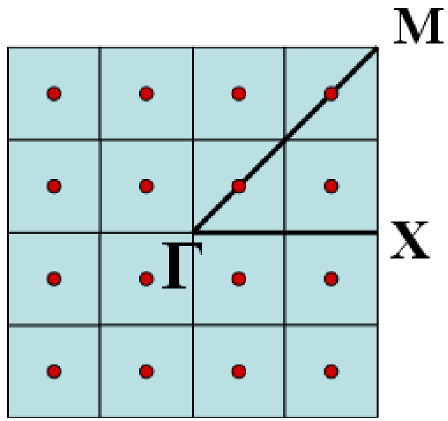
- Free energy of solid

$$A = U + \sum_{\mu} \underbrace{\frac{1}{2}\hbar\omega_{\mu} + k_B T \ln\left(1 - e^{-\frac{\hbar\omega_{\mu}}{k_B T}}\right)}_{f(\omega_{\mu})}$$

- Contribution from long wave-length phonons are important

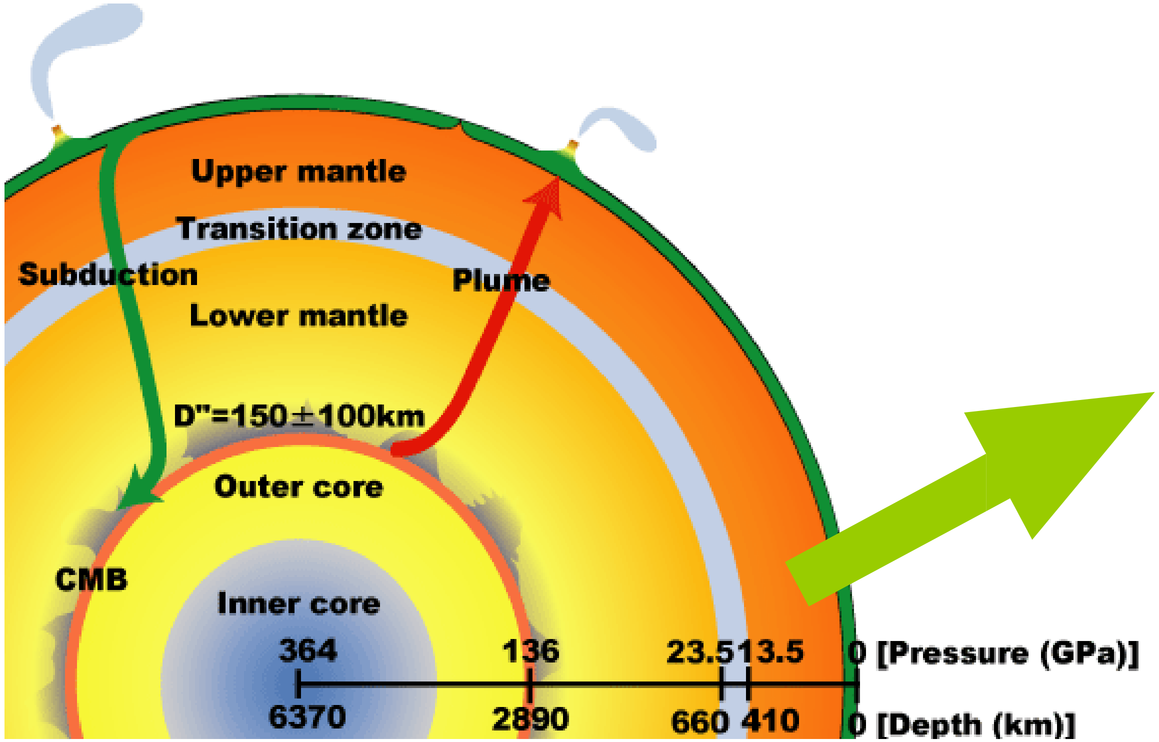
- Avoid large supercells through summation over Brillouin Zone
  - In small cell determine force constants
  - Recompute Dynamical matrix at several long wave-length phonons
  - Sum up contributions using multiplicty w_{ν}

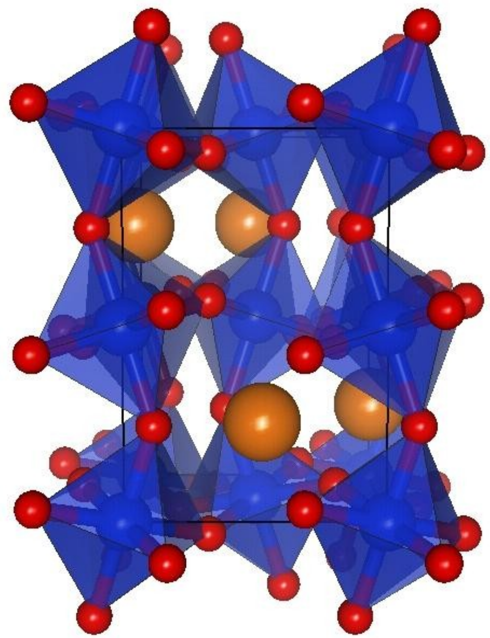


$$A \rightarrow U + \sum_{\nu << 3N-3} w_{\nu} \cdot f(\omega_{\nu})$$

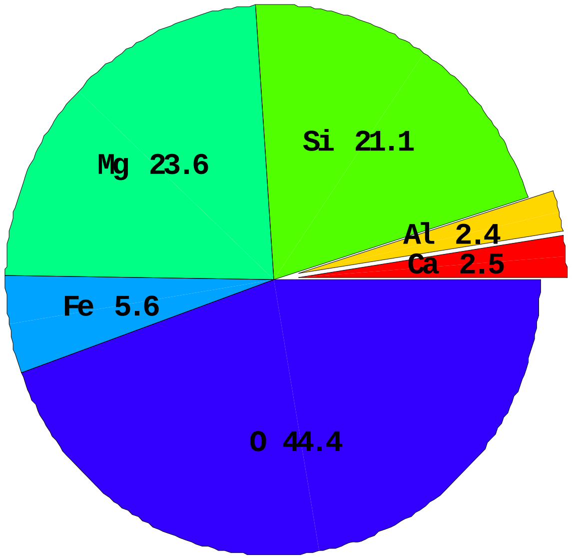
Composition of the Earth‘s (lower) mantle

- MgSiO$_3$: most abundant constituent in the Earth’s lower mantle
- Orthorhombic distorted perovskite structure (*Pbnm*)
- Its stability is important for understanding deep mantle (D” layer)





Lower mantle composition



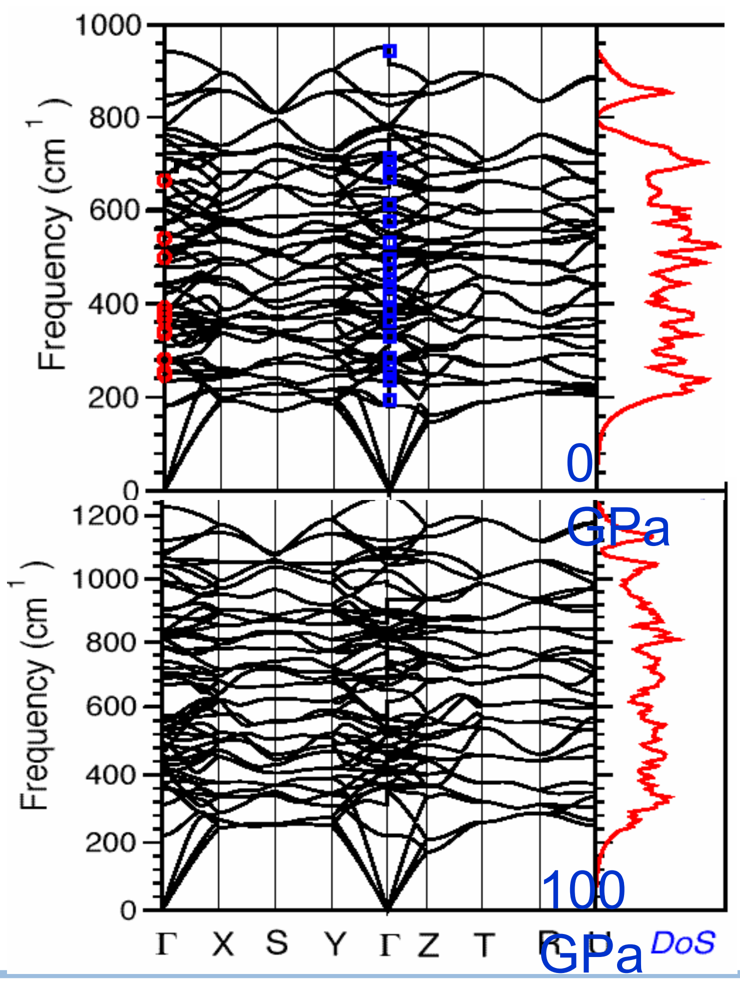
Lower mantle:

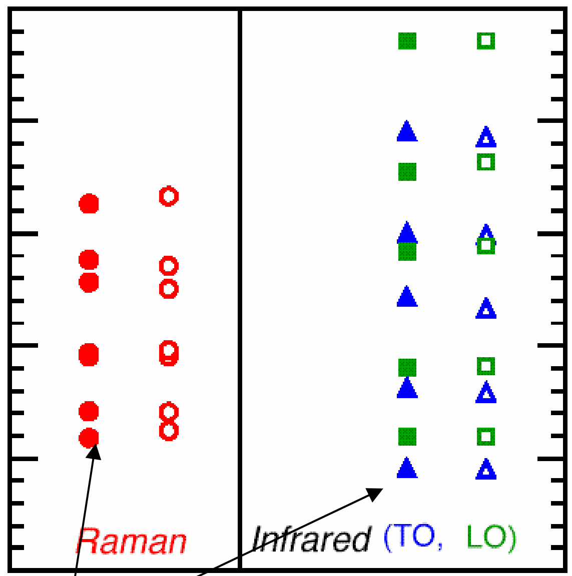
- 53 vol.% of the Earth
- 75 wt.% - $MgSiO_3$ (post)-perovskite
- 18 wt.% - (Mg,Fe)O magnesiowüstite
- 7 wt.% - $CaSiO_3$ perovskite

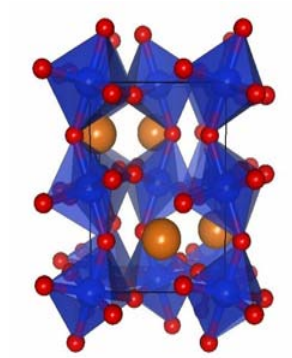
Not suitable for harmonic approximation

$(Mg_{(1-x-z)},Fe_x, Al_z)(Si_{(1-y)},Al_y)O_3$	$(Mg_x,Fe_{(1-x)})O$	$CaSiO_3$

Phonon dispersion of $MgSiO_3$ perovskite



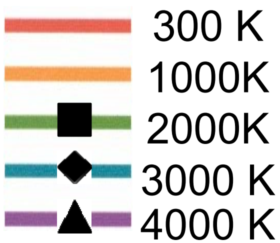




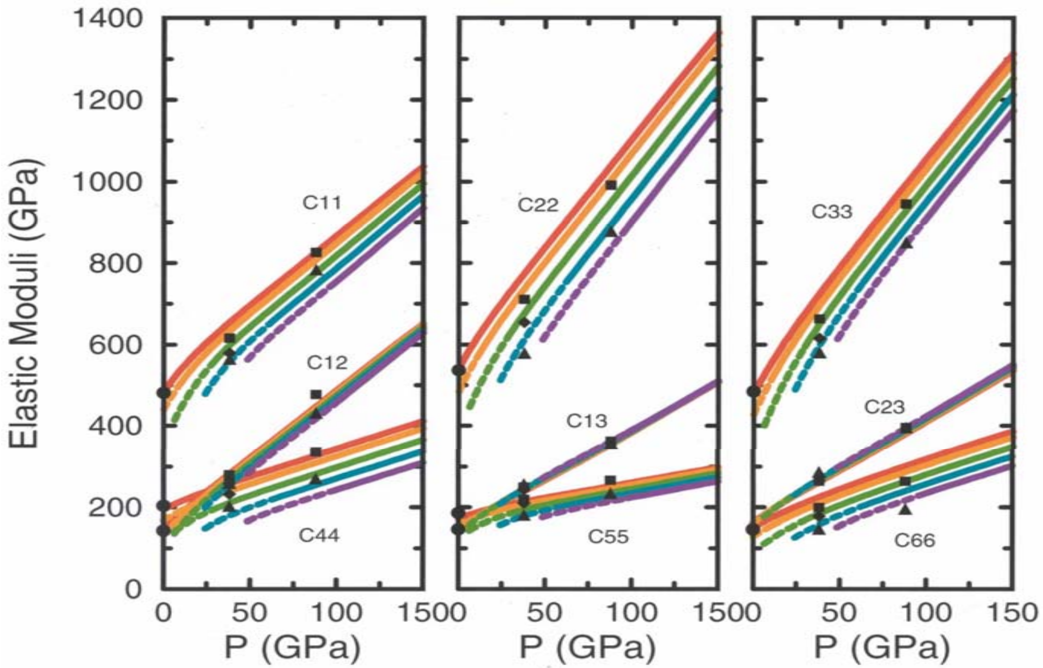
Theory: Karki, Wentzcovitch, de Gironcoli, Baroni (2000) PRB 62, 14750
Exp: Raman (Durben and Wolf, 1992)
Infrared (Lu et al. 1994)

Temperature dependent elastic constants MgSiO3 perovskite

$$c_{ij}^{T}(T,P) = \left[\frac{\partial^2 A}{\partial \varepsilon_i \, \partial \varepsilon_j}\right]_P$$



(Oganov et al,2001)



Wentzcovitch, Karki, Cococciono, de Gironcoli (2004) Phys. Rev. Lett.

Hands-on Tutorial on Phonon calculations

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- Conclusions
  - Harmonic theory treats vibrations as if they did not interact
  - System is equivalent to a collection of independent harmonic oscillators
  - Energies used to compute partition function Z and the free energy, A(T).
  - Through the free energy all properties are accessible
  - DAMA allows to calculate the free energy even for materials with dynamic instabilities
  - Dynamic instabilities are common in high temperature phases
  - Good agreement between QHA (and DAMA) and experiment, e.g. for phase transition cryolite

Dr. Donat ADAMS

University of Bern

Institute of Geological Sci.

Baltzerstrasse 1+3

CH-3012 Bern

Switzerland

Movies:

www.adams-science.com