Quasiharmonic approximation and thermodynamics Renata Wentzcovitch

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Body wave (acoustic) velocities

- Longitudinal waves (P-waves) (compressive waves)
- •Transverse waves (S-waves) (shear waves)







1D-Seismic Model



Making sense of mantle heterogeneities (Seismic Tomography)



Parameter: vs | depth: 1500 km | ref: mean | threshold: <6.63 (dashed red), >6.73 (solid blue)

GLAD-M25 δV_s

(*Lei, Tromp, et al., 2021*)

S-model

Thermochemical convection (need ρ , K, α , C_P, μ , κ)



(McNamara et al., 2014)

The Ultimate Vision



The Quasi-Harmonic Approximation (QHA)

- A simple approximate treatment of thermodynamical behavior
- It treats vibrations as if they did not interact
- System is equivalent to a collection of independent harmonic oscillators
- These establish the quantum mechanical energy levels of the system
- The levels are used to compute the partition function, Z, and the Helmoltz free energy, F(T,V). From the latter, all thermodynamic functions can be derived.

Helmholtz Free Energy:

$$E = internal energy$$

 $F = -k_{B}T\ln Z$

$$S = entropy$$

Z is the partition function

Z = sum of Boltzman factors of all energy levels

$$Z = \sum_{i} e^{-\frac{\varepsilon_i}{k_B T}} \quad \varepsilon_i = \text{ eigenvalues of energy operato}$$

For a single oscillator with freq. ω_i , the energy levels are:

$$\frac{1}{2}\hbar\omega_i, \frac{3}{2}\hbar\omega_i, \frac{5}{2}\hbar\omega_i, \dots$$

Helmholtz Free Energy:

Therefore:

$$Z_i = e^{-\frac{\hbar\omega_i}{2k_BT}} \sum_{s=0}^{\infty} e^{-\frac{s\hbar\omega_i}{k_BT}} = \frac{e^{-\frac{\hbar\omega_i}{2k_BT}}}{1 - e^{-\frac{\hbar\omega_i}{k_BT}}}$$

$$(h \equiv \hbar -)!!$$

$$F_i = \frac{1}{2} \hbar \omega_i + k_B T \ln \left(1 - e^{-\frac{\hbar \omega_i}{k_B T}} \right)$$

For a lattice of normal modes of vibration with frequencies ω_i :

$$F = \sum_{i} F_{i}$$
 is the vibrational free energy

Helmholtz Free Energy of all oscillators:

$$F = U + \sum_{i} \frac{1}{2} \hbar \omega_{i} + k_{B} T \sum_{i} \ln \left(1 - e^{\frac{-\hbar \omega_{i}}{k_{B} T}} \right)$$

As a solid compresses, deforms, etc..., U and ω_i 's change

From $F(T, V, \varepsilon_1, \varepsilon_2, ...)$ all the thermodynamical behavior can be deduced.

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V} \qquad \qquad P = -\left(\frac{\partial F}{\partial V}\right)_{T}$$

E = F + TS H = E + PV G = F + PV

Note:

- This (or a more complete) quantum treatment is required at "low T"
- The QHA is not appropriate at "high T" because of phonon-phonon interactions
- This (or a more complete) quantum treatment is required at "low T"

 $T_{low} < \theta_{Debye} < T_{high} < T_{melt}$

- Phonon frequencies must be accurate (ab initio)
- Phonon sampling must be thorough

Integration (summation) over the Brillouin Zone



- 1) Compute and diagonalize the dynamical matrix at few \dot{q} 's (CPU intensive procedure)
- 2) Extract "force constants"
- 3) Recompute dynamical matrices at several q' points using those force constants
- 4) Summation over tetrahedral volume elements is very accurate for DoSs

Earth's Lower Mantle:



(Mg_x,Fe_(1-x))SiO₃

 $(Mg_x, Fe_{(1-x)})O$



Phonon Dispersion in MgO

(Karki, Wentzcovitch, de Gironcoli and Baroni, PRB 61, 8793, 2000)



Zero-Point Motion Effect:



Phonon Dispersion in MgSiO₃ perovskite:





Comparison with Experimental Data

ρ (gr/cm⁻³)	V (A ³)	K _T (GPa)	d K _T /dP	d K _T ²/dP² (GPa⁻¹)	d K _T /dT (Gpa K⁻¹)	10 ⁻⁵ Κ ⁻¹		LDA
3.580	18.80	159	4.30	-0.030	-0.014	3.12	Calc.	рс
3.601	18.69	160	4.15	~	-0.0145	3.13	Exp.	рс
4.210	164.1	247	4.8	-0.016	-0.031	2.1	Calc.	Ρv
4.247	162.3	246 266 (256)	3.7 4.0	~	-0.02 -0.07	1.7 2.2	Exp.	Pv

Exp.: [Ross & Hazen, 1989; Mao et al., 1991; Wang et al., 1994; Funamori et al., 1996; Chopelas, 1996; Gillet et al., 2000; Fiquet et al., 2000]

Validity of QHA



Thermal Expansivity and the QHA

 α provides an *a posteriori* criterion for the validity of the QHA



Validity of QHA



a Boehler and Ross, EPSL 153, 223 (1997).
b Shaner et al., in High pressure in science and technology, p. 137 (1984).

c Vocadlo and Alfe, PRB 65, 214005 (2002).

a: Zerr and Boehler, Nature 371 506 (1994). b: Strachan et al., Phys. Rev. B6, 15084 (1999).

Umemoto, **2005**

<u>Always check if possible</u>:



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Murakami at al, Science 2004 Tsuchiya et al, EPSL 2004 Ogonav and Ono, 2004



Dissociation phase boundary: $MgSiO_3 \rightarrow SiO_2 + MgO?$





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Software for calculation of relevant properties Systematic DFT study of structural properties of minerals with express:

Q. Zhang, J. Zhuang, H. Gu, and R. Wentzcovitch,







Material	Formula	Space Group
Albite	NaAlSi ₃ O ₈	P-1
Coesite	SiO ₂	C2/c
Diopside	CaMgSi ₂ O ₆	C2/c
Bridgmanite	MgSiO ₃	Pbnm
Stishovite	SiO ₂	P4 ₂ /mnm
Akimotoite	MgSiO ₃	R-3
Lime	CaO	Fm-3m
Corundum	Al ₂ O ₃	R-3c

Software for calculation of relevant properties 🙀 Systematic DFT study of structural properties of minerals with express

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QHA at 300 K Birch-Murnaghan EOS

How to distinguish DFT vs. anharmonic effects?



Wu et al., J. Geophys. Res. 113, B06204 (2008)

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$$F(V,T) = \begin{bmatrix} U(V) + \sum_{qj} \frac{\hbar \omega_{qj}(V)}{2} \end{bmatrix} + k_B T \sum_{qj} \ln(1 - e^{\hbar \omega_{qj}(V)/k_B T}) \qquad P = -\frac{\partial F}{\partial V} \Big|_T$$

$$P_{ZP} = \frac{-\partial F_{ZP}(V,T)}{\partial V} \Big|_{T'} \quad \text{and} \quad P_{th} = \frac{-\partial F_{th}(V,T)}{\partial V} \Big|_{T'}$$

Crystal structure and phonon frequencies depend on volume only!

Therefore, if $V_1(P_1,T_1) = V_2(P_2,T_2) = V$, then $\rightarrow crystal structures and phonons$ at (P_1,T_1) are the same as at (P_2,T_2)

Carrier et al., PRB 76, 064116 (2007)



Carrier et al., PRB 76, 064116 (2007)

X-ray diffraction: T = 300 K

Pbnm perovskite: Mg_y, Mg_x, etc





Carrier et al., PRB 76, 064116 (2007)





Carrier et al., PRB 76, 064116 (2007)





Cause:
$$P_{th}$$
 is not isotropic
$$\delta \sigma_i = P_{QHA}(V,T) - \sigma_i^{int}$$
$$\sigma_i^{int} = \frac{\partial F}{\partial e_i} \Big|_{\sim P}$$

Carrier et al., PRB 76, 064116 (2007)

<u>Cause</u>: P_{th} is not isotropic





Carrier et al., PRB 76, 064116 (2007)



- So far we have used the QHA on a single structure
- We can also use the QHA to investigate "multi-configuration" systems
- Example: Order-disorder transition in H₂O-ice



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- We can also use the QHA to investigate "multi-configuration" systems
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- Example: Order-disorder transition in H₂O-ice (Umemoto *et al.*, Chem. Phys. Lett. **499**, 236-240 (2010))



- Let's calculate the free energy of a disordered ice VII system represented by 16 molecules (supercell)
- There are 8100 possible configurations of which only 52 are symmetrically distinct

- Free energy of an ensemble of configurations:

$$\begin{aligned} Z_{\text{static}}(V,T) &= \sum_{i=1}^{52} w_i \exp\left(-\frac{E_i(V)}{k_B T}\right) \qquad (\sum_{i=1}^{52} w_i = 8100) \\ Z_{\text{QHA}}(V,T) &= \sum_{i=1}^{52} w_i \sum_{n_{s,i}=0}^{\infty} \exp\left\{-\frac{1}{k_B T} \left(E_i(V) + \sum_{s=1}^{144} \frac{1}{2} \hbar \omega_{s,i}(V)\right)\right\} \\ &\times \exp\left(-\frac{1}{k_B T} \sum_{s=1}^{144} n_{s,i} \hbar \omega_{s,i}\right) \\ &= \sum_{i=1}^{52} w_i \exp\left\{-\frac{1}{k_B T} \left(E_i(V) + \sum_{s=1}^{144} \frac{1}{2} \hbar \omega_{s,i}(V)\right)\right\} \\ &\times \prod_{s=4}^{144} \left\{1 - \exp\left(-\frac{\hbar \omega_{s,i}(V)}{k_B T}\right)\right\}^{-1}, \end{aligned}$$

-(Umemoto et al., Chem. Phys. Lett. 499, 236-240 (2010))

- Order-disorder transition is more easily identified as a peak in C_P



Figure 2. (a) Static heat capacity calculated at 10 GPa for 4, 8, and 16 molecule supercells. (b) Heat capacity calculated at 10 GPa: full C_p including the vibrational contribution to the free energy, including ZPM contribution only and pure static calculations. The dashed vertical line denotes peak position with inclusion of ZPM energy only. (Umemoto *et al.*, Chem. Phys. Lett. **499**, 236-240 (2010))

- Order-disorder transition in H₂O and D₂O



Figure 4. Calculated ice VII–VIII phase boundaries (blue line: static, red lines: QHA results). Black solid and dashed lines are experimental phase boundaries for H_2O and D_2O by Song et al. [10]; their nearly vertical parts are phase boundaries between ice VIII and VII[']. Black and white dots are T_c calculated using the BLYP-type XC functional by Refs. [15,16] and [17,18], respectively. (For interpretation of references to colors in this figure legend, the reader is referred to see the web version of this article.)

- Transition mechanism
- Distribution of energies



Figure 5. Histograms of the total energy $E_i(V)$ at several volumes at (a) 10.32 cm³/mol (~5 GPa) and (b) 6.79 cm³/mol (~50 GPa).

- Transition mechanism
- Probability of occurrence of a configuration: $p_i(V,T) = \frac{w_i \exp(-\frac{w_i}{T})}{T}$



Figure 7. Probabilities of the 52 symmetrically inequivalent configurations generated by the 16-molecule supercell at: (a) 10 GPa and (b) 300 K. The most likely configurations are represented by color lines. Conf. 1 is ice VIII and consists of ice Ic 1 with the dipole moment $\mathbf{d} = (0, 0, 8)$ and Ic 1 with $\mathbf{d} = (0, 0, -8)$. Conf. 2(3) consists of Ice Ic 1 with $\mathbf{d} = (0, 0, 8)$ in one sub-lattice of ice VII, and Ic 3 (Ic 2) with $\mathbf{d} = (0, 4, -4)(\mathbf{d} = (0, 0, -4))$ in the second sub-lattice (see Figure 1 for the definition of ice Ic configurations).

(Umemoto et al., Chem. Phys. Lett. 499, 236-240 (2010))

Module #2: Equations of state (EoS)

- Finite strain expansion of energy and equations of state (EOS)
- Vinet EOS
- A brief review of classical thermodynamics
- Quasi-harmonic approximation (QHA)
- Debye model and the high temperature Mie-Debye-Gruneisen EOS (skip)
- Resources:
 - Jean-Paul Poirier, Introduction to the Physics of the Earth's Interior (Cambridge)

(Chaps. 1 and 4)