qha: A Python package for quasi-harmonic free energy calculation for multi-configuration systems [1]

Qi Zhang [1] Renata Wentzcovitch[1,2]

[1]Applied Physics and Applied Mathematics Department, Columbia University, New York, NY

[2]Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY

[1] Qin, T. *et al. Computer Physics Communications.* 2018.

Quasi-harmonic approximation (QHA)

- a useful tool to compute materials thermodynamic properties at high T, P
- a good approximation when T is not too close to T_{M}
- Born–Oppenheimer approximation: static contribution + vibrational contribution (QHA on phonon spectra)
- deal with multiple configuration systems

Multi-configuration systems that qha may apply

- the order-disorder phase boundary between ice-VIII and ice-VII [2]
- the relative stability of hydrous defects in Mg_2SiO_4-forsterite at high P and T [3]
- the effect of disorder and iron concentration on the spin crossover diagram of Fe^{3+}-bearing $MgSiO_3$-bridgmanite [4]

[2] Umemoto, K. *et al. Chemical Physics Letters.* 2010.
[3] Qin, T. *et al. American Mineralogist.* 2018.
[4] Shukla, G. & Wentzcovitch, R. M. *Physics of the Earth and Planetary Interiors.* 2016.

Methods

- single configuration system:

$$Z(T,v) = \exp\big(-E(v)/k_BT\big)\prod_{\boldsymbol{q},s}\frac{\exp(-\hbar\omega_{\boldsymbol{qs}}(v)/2k_BT)}{1-\exp(-\hbar\omega_{\boldsymbol{qs}}(v)/k_BT)}, \tag{1}$$

$$F(T,v) = -k_BT\ln Z(T,v). \tag{2}$$

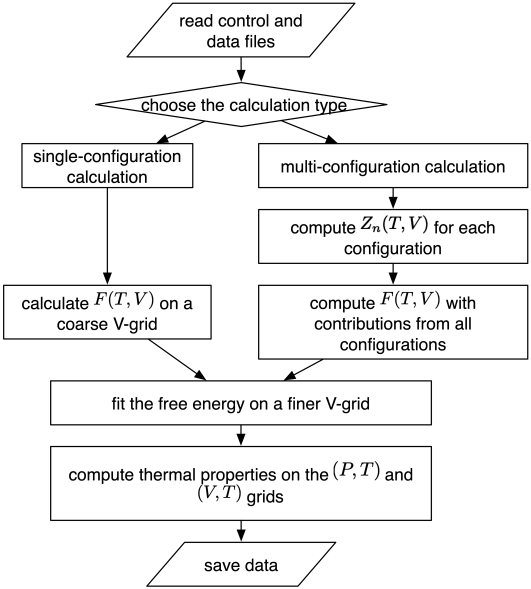
- multi-configuration systems:

$$Z(T,v) = \sum_{n=1}^{N_c} g_n Z_n(T,v), \tag{3}$$

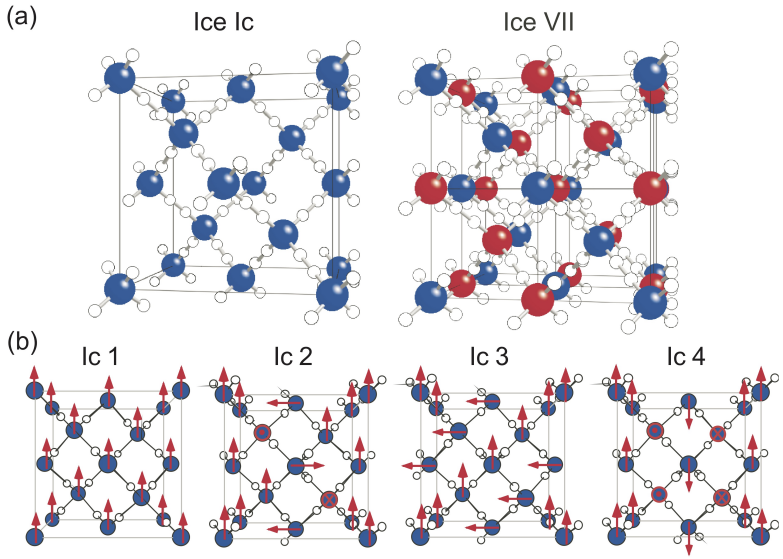
$$F(T,v) = -k_BT\ln Z(T,v). \tag{4}$$

- finite strain equation of state fitting to string $\{F(T,v)\}$'s to a continuous function $F(T,V)$

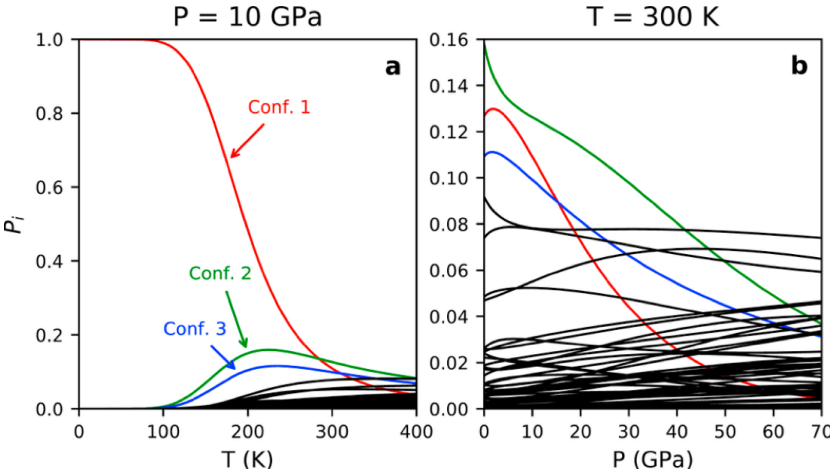
Flow chart


read control and data files
choose the calculation type
single-configuration calculation
multi-configuration calculation
compute $Z_n(T,V)$ for each configuration
calculate $F(T,V)$ on a coarse V-grid
compute $F(T,V)$ with contributions from all configurations
fit the free energy on a finer V-grid
compute thermal properties on the (P,T) and (V,T) grids
save data

Ice VII(disordered)-VIII(ordered) phase transition I



Ice VII(disordered)-VIII(ordered) phase transition II



Possibilities $P_i(V,T) = \frac{g_i \exp\left(\frac{-E_i(V)}{k_B T}\right)}{Z(V,T)}$ of the 52 configurations

Ice VII(disordered)-VIII(ordered) phase transition III

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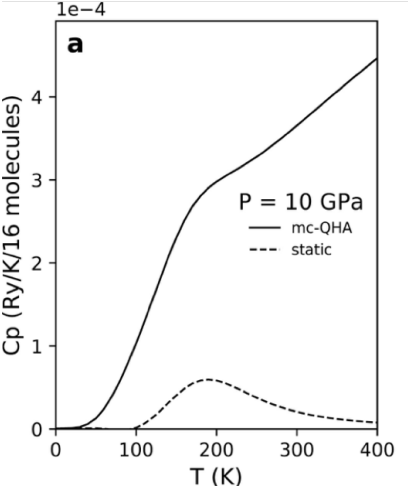
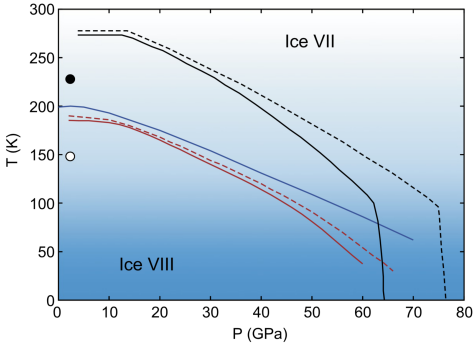




[2]Blue line: static, red lines: QHA results, black lines: experimental results, solid lines: H_2O, dashed lines: D_2O

[2] Umemoto, K. *et al. Chemical Physics Letters.* 2010

Comparisons with other codes

`qha`

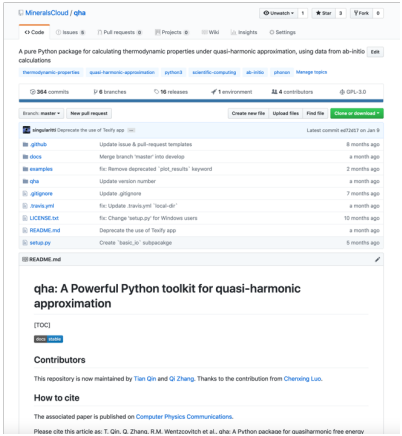
- addresses the thermodynamic properties of multi-configuration systems
- directly samples the free energy in Brillouin zone
- balances the speed and flexiblility

other codes

- address single configuration systems
- integrate the vibrational density of states $g(\omega)$ to get F [5]
- less flexible and extensible [6]

[5] Petretto, G. *et al. Scientific Data.* 2018
[6] `https://github.com/dalcorso/thermo_pw`

Applications or extensibilities



https://github.com/MineralsCloud/qha

- Extensibilities to materials research
  - thermoelastic properties of materials [7]
  - metals with phonon frequencies varying at different electronic temperatures (introduced in seission H17.00005, Tuesday)
  - calculate the geotherm and isentrope [8]

[7] Wu, Z. & Wentzcovitch, R. M. *Physical Review B*. 2011
[8] Cardona, J. J. V. *et al. Geophysical Research Letters*. 2017

Conclusion

- qha is a fast, user-friendly Python package for tranditional QHA calculations
- qha can calculate multi-configuration system's equation of state and other thermodynamic properties
- qha is extensible and will form a more complete toolchain in the near future

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References I

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5. Shukla, G. & Wentzcovitch, R. M. Spin crossover in $(Mg, Fe^{3+})(Si, Fe^{3+})O_3$ bridgmanite: Effects of disorder, iron concentration, and temperature. *Physics of the Earth and Planetary Interiors* **260,** 53–61 (2016).

References II

6. Umemoto, K., Wentzcovitch, R. M., de Gironcoli, S. & Baroni, S. Order–disorder phase boundary between ice VII and VIII obtained by first principles. *Chemical Physics Letters* **499,** 236–240 (2010).

7. Wu, Z. & Wentzcovitch, R. M. Quasiharmonic thermal elasticity of crystals: An analytical approach. *Physical Review B* **83,** 184115 (May 2011).