pgm: A Python package for free energy calculation

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Motivation

- Goal: thermodynamic properties of strongly anharmonic metal or inssulating solids at high T and P
- Traditional quasi-harmonic approximation (QHA)[1] method

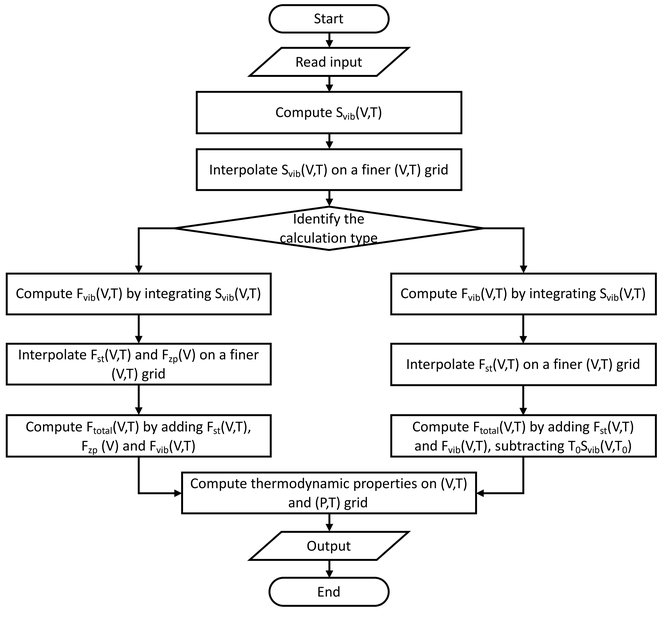
$$F(T,V) = U(V) + \frac{1}{2}\sum_{\boldsymbol{q},s} \hbar\omega_{\boldsymbol{q},s}(V) + k_B T \sum_{\boldsymbol{q},s} \ln\left(1 - \exp\left(-\frac{\hbar\omega_{\boldsymbol{q},s}(V)}{k_B T}\right)\right)$$

- Anharmonicity, electronic excitations in metals, or both, introduce an intrinsic T-dependence on the phonon frequencies → $\omega_{\boldsymbol{q},s}(V,T)$, making the QHA free energy formula inadequate

pgm Python package flowchart

Command line

```
pgm run settings.yaml
```



Input files for `pgm` code

File name	Description
`settings.yaml`	User-specified settings file for `pgm` calculation
`input-0K`, `input-300K`, `input-1000K`…	Each file contains volumes and Mermin energy, and phonon frequencies from ab initio calculation*, at its temperature as speci-fied by the input file name.

Method

Phonon Gas Model (PGM)

- Vibrational entropy

$$S_{vib}(V,T) = k_B \sum_{\boldsymbol{q},s} \Big((1+n_{\boldsymbol{q}s})\ln(1+n_{\boldsymbol{q}s}) - n_{\boldsymbol{q}s}\ln n_{qs} \Big)$$

- Bose-Einstein distribution

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

T-dependent frequencies with wave-vector **q** in branch *s*

Or *T*-independent frequencies $\tilde{\omega}_{\boldsymbol{q}s}(V)$

- PGM free energy (integration from 0 K)

$$F(V,T) = F_{st}(V,T) + \frac{1}{2}\sum_{q,s} \hbar\omega_{\boldsymbol{q},s}(V,0) - \int_0^T S_{vib}(V,T')dT'$$

- PGM free energy (integration from T > 0 K)

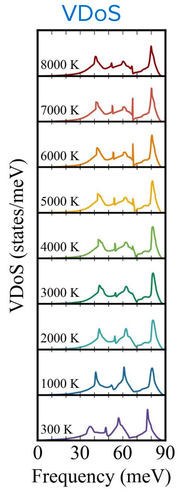
$$F(V,T) = F_{Mermin}(V,T_0) - T_0 S_{vib}(V,T_0) - \int_{T_0}^T S(V,T')dT'$$

Example – ε-Fe [2]

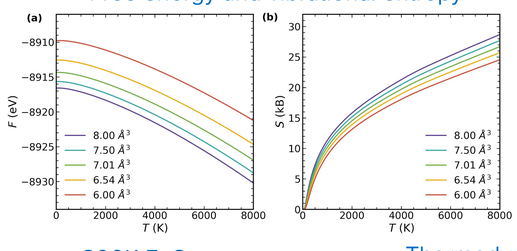
Calculation Details

- Quantum ESPRESSO
- GGA Evolutionary PAW*
- Non-spin polarization; Disregard anharmonicity
- 10 x 10 x 10 **k**-point mesh
- 4 x 4 x 4 **q**-point grid
- Brillouin zone integration 10 x 10 x 10 **k**-mesh
- 0 ≤ T ≤ 8000 K
- 0 ≤ P ≤ 500 GPa
- Small T_{ef}-dependence in phonon

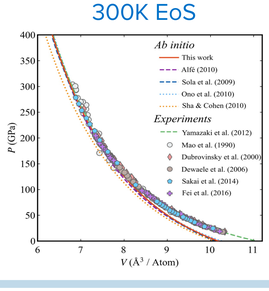
VDoS



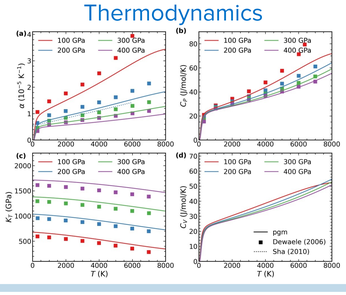
Free energy and vibrational entropy



300K EoS



Thermodynamics

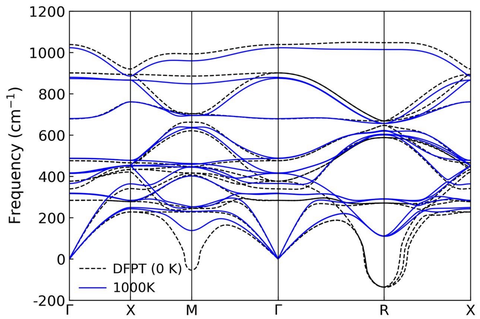


Example – CaPv [3]

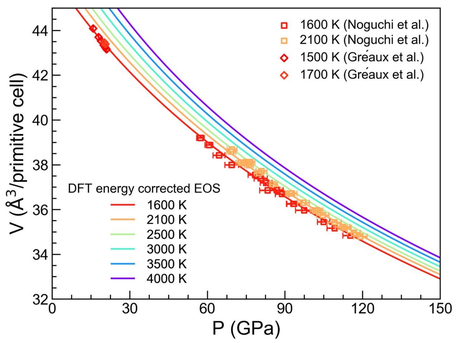
Calculation Details

- Strongly anharmonic system
- cubic phase with $Pm\bar{3}m$
- VASP, LDA-PAW
- Phonon quasiparticles
- 1500 K < T < 4000 K
- 5 volumes

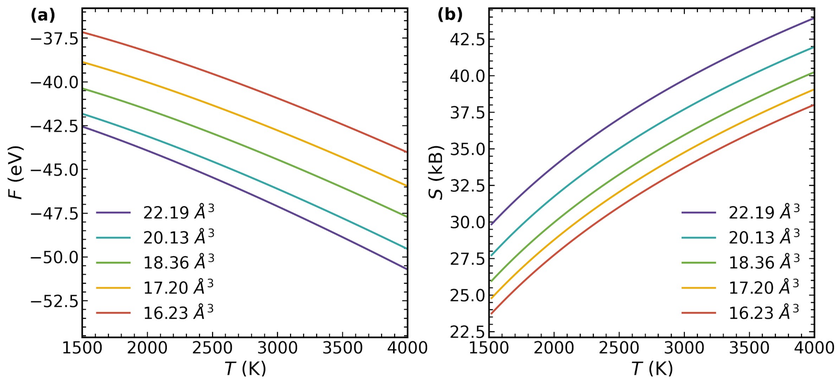
Unstable phonons stablize at high T



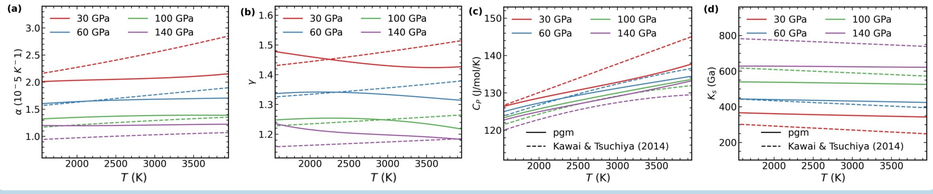
Isothermal EoS



Free energy and vibrational entropy



Thermodynamics



Reference & Acknowledgement

[1] Qin, T., Zhang, Q., Wentzcovitch, R. M., & Umemoto, K. (2019). qha: A Python package for quasiharmonic free energy calculation for multi-configuration systems. *Computer Physics Communications*, *237*, 199–207.
[2] Zhuang, J., Wang, H., Zhang, Q., & Wentzcovitch, R. M. (2021). Thermodynamic properties ε-Fe with thermal electronic excitation effects on vibrational spectra. *Phys. Rev. B*, *103*(14), 144102.
[3] Zhang, Z., & Wentzcovitch, R. M. (2021). Ab initio anharmonic thermodynamic properties of cubic $CaSiO_3$ perovskite. *Phys. Rev. B*, *103*(10), 104108.

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