SCAILD in abinit

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Outline

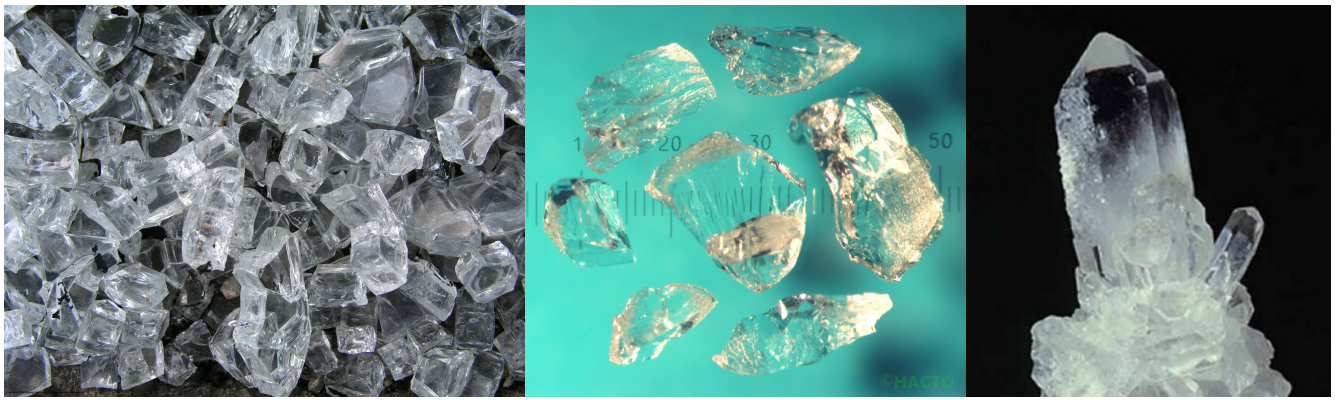
1 Motivation

2 Formalism

3 Conclusions

ab initio phase diagrams...

- How to determine the stablest phase at given conditions?
- Minimize appropriate (Gibbs) Free energy
- NVT ensemble: F=U-TS
- NPT ensemble: Gibbs=F+pV
- Works in principle for any phase transition (displacive)

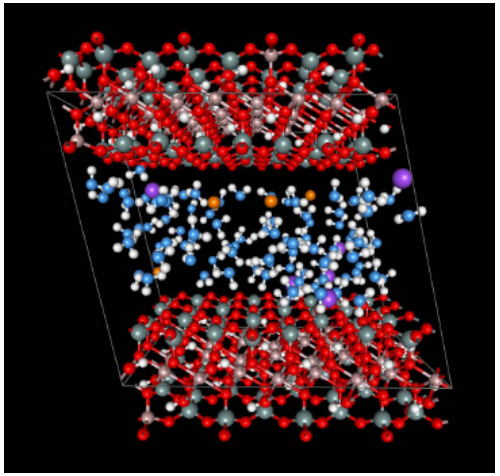


Free Energies

- Thermodynamical stability $\leftarrow$ lowest free energy
- Entropic effects can stabilize different phases for $T > 0$
- Also need candidate dynamically stable phases
- Metastable states
  - enforced by symmetry or
  - “authentic”

Standard methods I

- Do Molecular Dynamics trajectory, explore phase space
- *very* slow to get to ergodicity
- either spontaneously relaxes to correct phase
- or compare average energies



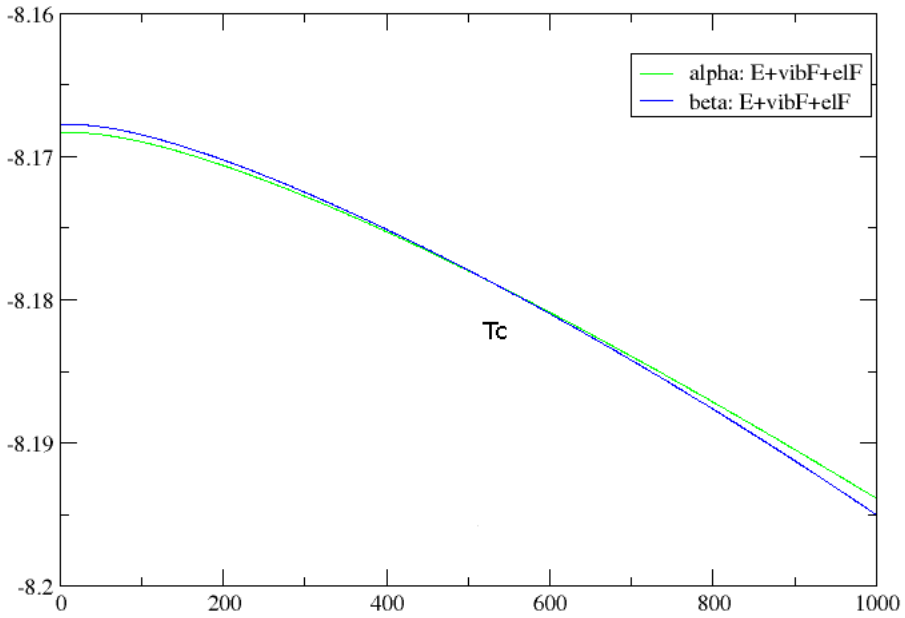
Standard methods II

- 0K EOS - suppose U(V) independent of T
- Vibrational entropy from phonons at $T = 0$, $V = V_0$
- Quasi-harmonic approximation - take V(T) into account
- Add e^- entropy (usu. negligible)
- Extrapolation of F(V,T) - fit polynomials in T
- e.g. **Albe PRB 55 6203 (1997)**

$$F^{vib} = \frac{1}{N}\sum_{i}^{3N}\frac{\hbar\omega_i}{2} + k_B T ln[1 - exp(-\frac{\hbar\omega_i}{k_B T})]$$

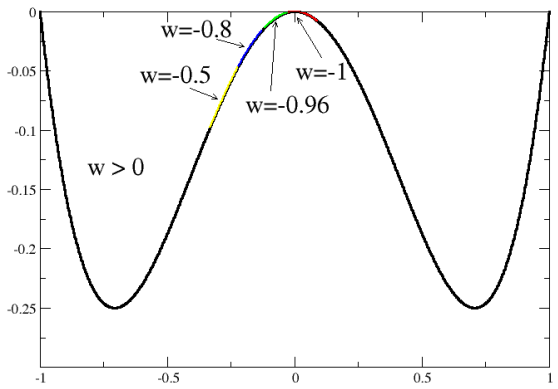
Standard methods III

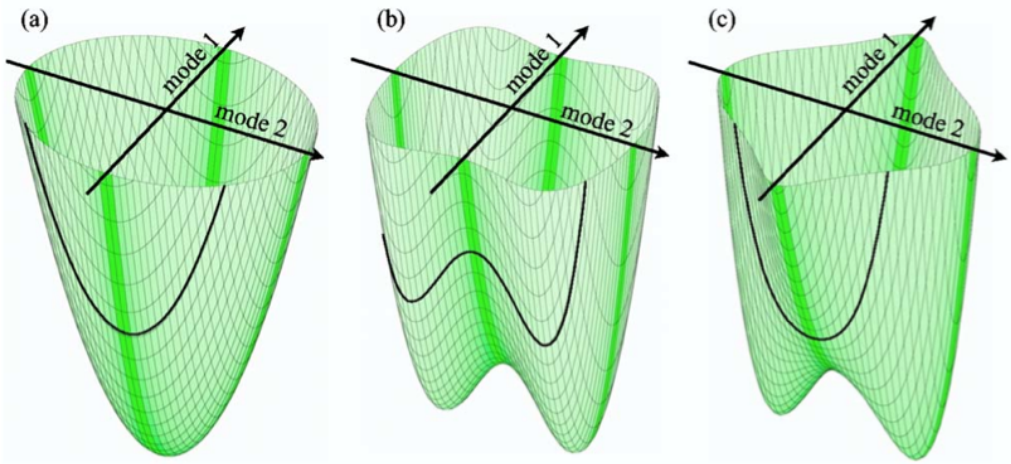
- Calculate $U(V)$ and phonons for two phases
- Add F^{vib} (T), and compare
- Thm expansion $\rightarrow$ phonons at high-T volume
- impossible with unstable phonons



Issues

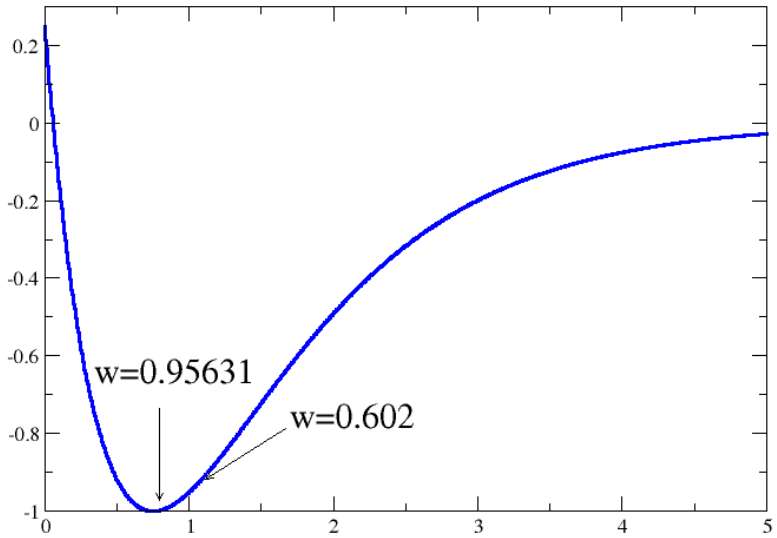
- Physically ω changes with T!
- Lack of symmetry constraints
- Finite T phonons explore anharmonicity (even 1 mode)
- Coupling of (an)harmonic phonons





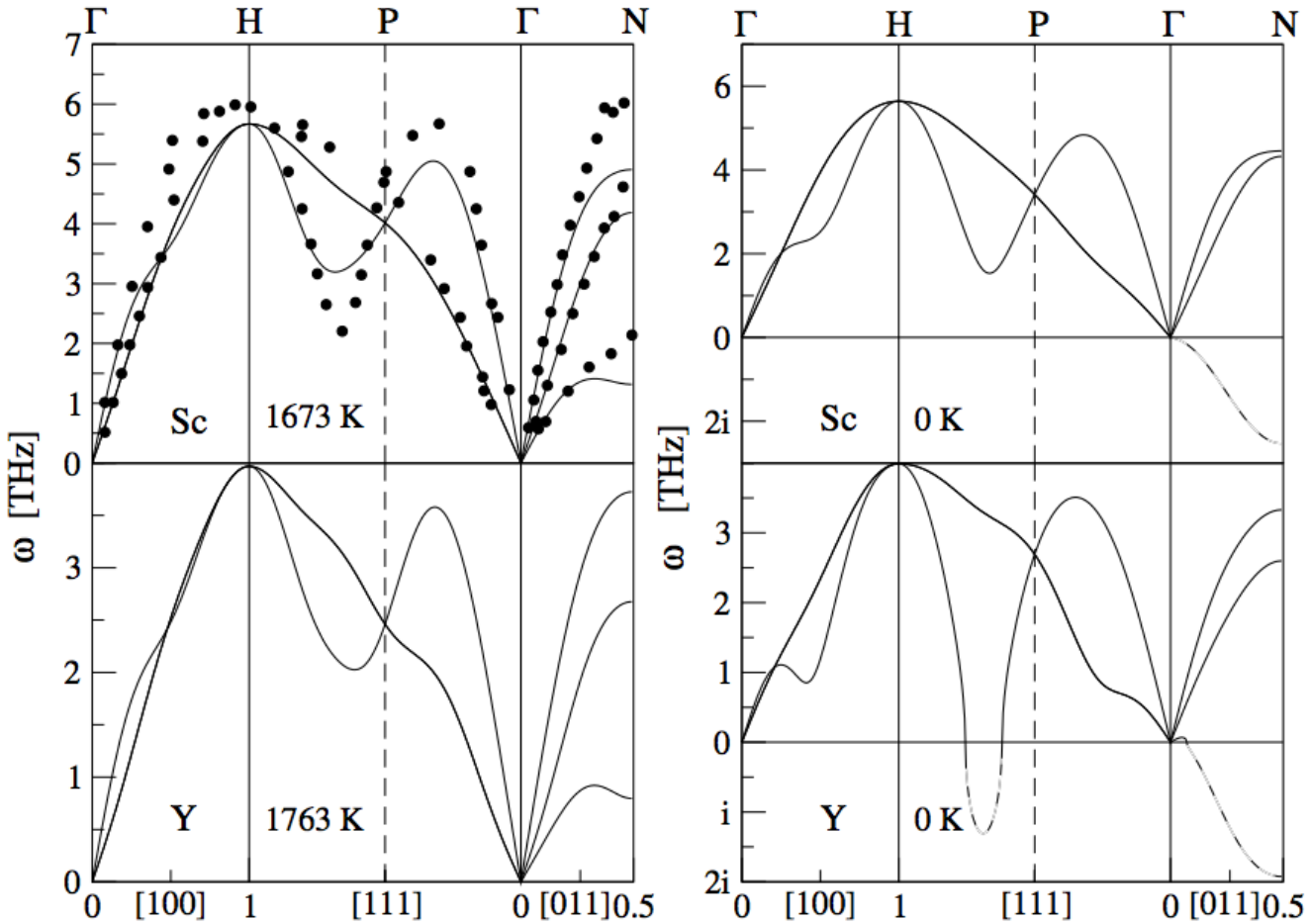
Self-consistent phonons

- Born-like method: Souvatzis et al. PRL 100 095901 (2008)
- Calculate phonons at $T > 0$ "self-consistently"
- Phonon displacements are "thermalized"
- Takes anharmonicity into account



Self-consistent phonons

- Example from Souvatzis CMS **44**, 888: high-T stability of BCC phases of Sc and Y



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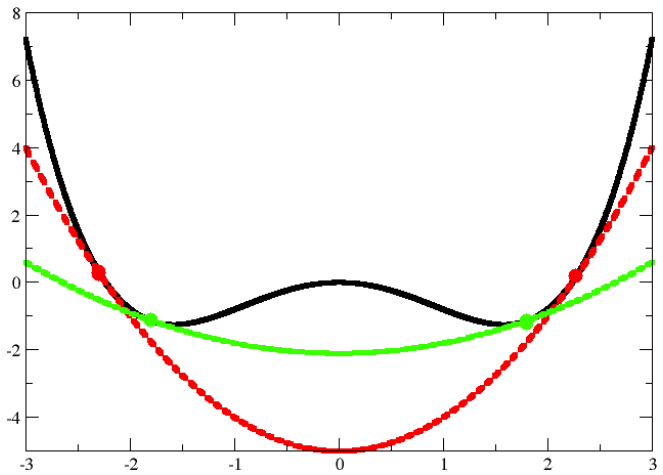
Formalism I

Relate forces and phonon frequencies:

$$\vec{F}_R = -\sum_{R'} \Phi(R - R') U_{R'} \quad \Rightarrow \quad \vec{F}_q = -\sum_s M \omega_{qs}^2 \mathcal{A}_{qs} \vec{\epsilon}_{qs}$$

FT of real space $\vec{F}$ wrt lattice vectors
beyond normal regime you pretend the well is harmonic...



Formalism II

Cartesian vs. normal modes

$$U_R = \frac{1}{\sqrt{MN}} \sum_{qs} \mathcal{Q}_{qs} \vec{\epsilon}_{qs} e^{iqR}$$

Normal modes are Boson-occupied $T > 0$

$$\langle \mathcal{Q}^{\dagger}_{qs} \mathcal{Q}_{qs} \rangle = \frac{\hbar}{\omega_{qs}} \left[\frac{1}{2} + n\left(\frac{\hbar\omega_{qs}}{k_B T}\right) \right]$$

$$\mathcal{A}_{qs} = \pm \sqrt{\frac{\langle \mathcal{Q}^{\dagger}_{qs} \mathcal{Q}_{qs} \rangle}{M}}$$

Formalism III

- Relate forces to phonon frequencies, through classical displacements

$$\omega_{qs} = \left[-\frac{1}{M} \frac{\vec{\epsilon}_{qs} \cdot \vec{F}_q}{\mathcal{A}_{qs}} \right]^{1/2}$$

- renormalized frequencies (in principle to all orders!):

$$\bar{\omega}^2_{qs} = \omega^2_{qs} \left(1 + \frac{\sqrt{M}}{2} \sum \Phi^3 \epsilon_{k_1 s_1} \epsilon_{k_2 s_2} \epsilon_{ks} \frac{\mathcal{A}_{k_1 s_1} \mathcal{A}_{k_2 s_2}}{\mathcal{A}_{ks} \omega^2_{ks}} + \dots \right)$$

Formalism IV

Cycle to “self-consistency”:

- $\omega \rightarrow$ normal mode displacements $\mathcal{A}$
- $\mathcal{A} \rightarrow$ atom displacements $\rightarrow \vec{F}$
- $\mathcal{A}$ and $\vec{F} \rightarrow$ new ω

Hypotheses

- Hyp 1: phonon polarization vectors unchanged
- Hyp 2: no phonon lifetime effects
- Hyp 3: no thermal expansion

In practice

1. Get T=0 phonons
2. Use a supercell, move atoms along normal modes
3. $\rightarrow$ displacements for given T
4. DFT forces $\rightarrow$ effective frequencies
5. $\rightarrow$ new free energy and normal modes
6. symmetrize ω
7. get configuration averaged ω

Tricks

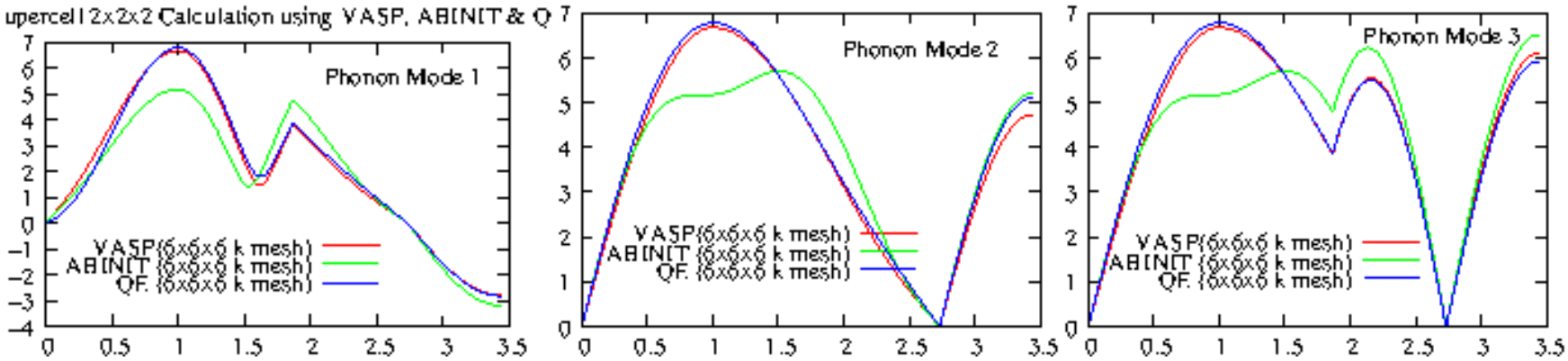
1. Running average of frequencies $\rightarrow$ config. avg.
2. Interpolation of $\bar{\omega}_{qs} \rightarrow$ better $F(T)$
3. Choice of amplitude for displacement: ± 1 (could be Gaussian)
4. Populate negative modes as though they were positive

Limitations

1. Method inherently requires large supercells (4x4x4 usually not converged)
2. no direct access to 3rd or 4th order derivatives or other info
3. no evolution of cell or ϵ
4. dielectric effects in supercell (Parlinskii) are gross

scphon adaptation

- Original VASP scripts adapted to Abinit and Qespresso by Srijan Kumar Saha
- parse abinit output for forces and feed in correct atomic positions and supercell
- remaining difference due to psp (Ti without SC states)



Abinit workflow

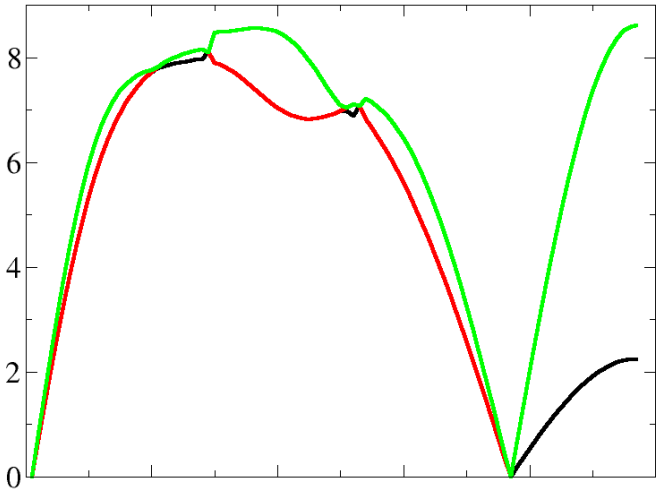
1. Run normal DFPT for q=2x2x2 MP
2. anaddb with "outscphon 1" to get:
3. xx_PCINFO, xx_PHFRQ, xx_PHVEC copied to abinit run
4. Supercell equivalent to phonon q-grid
5. Implemented in ABINIT as MD, but excluded from Guillermo's library (77_ddb dependencies)

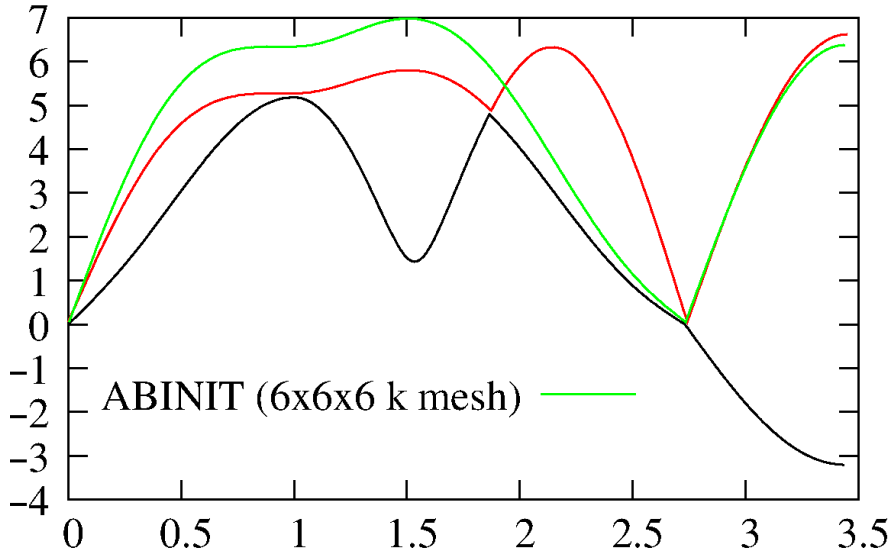
variables

ionmov 30	nsym 1	acell *= 2
scphon_temp 300 K	scphon_supercell	2 2 2

Ye goode aulde code

- Still testing after all these years
- Low T limit incorrect, bug left somewhere
- 2x2x2 supercell of Ti
- order of magnitude fine, but some tricks missing
- scphon_XX subroutines





Ye goode aulde code

- Phonons appear to be stabilized very systematically (too much?)
- Phase stability from free energy differences
-
- test v6 number 100, uses output for AI from v6 tests 85-88

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- Heavier than standard phonon calculations of F(T)
- Still easier than coding full anharmonic effects...
- Not clear if it has precision for good Tc estimation

Perspectives

- Try on ferroelectrics or geological phases
- Abinit version should have better dipole-dipole term
- lifetimes related to variance of $\bar{\omega}$?

Discussions

Ideas

- Petros Souvatzis (Uppsala)
- Karsten Albe (Dresden)
- Olle Ericsson (Uppsala)