DE LA RECHERCHE À L'INDUSTRIE

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a-TDEP : Temperature Dependent Effective Potential for ABINIT

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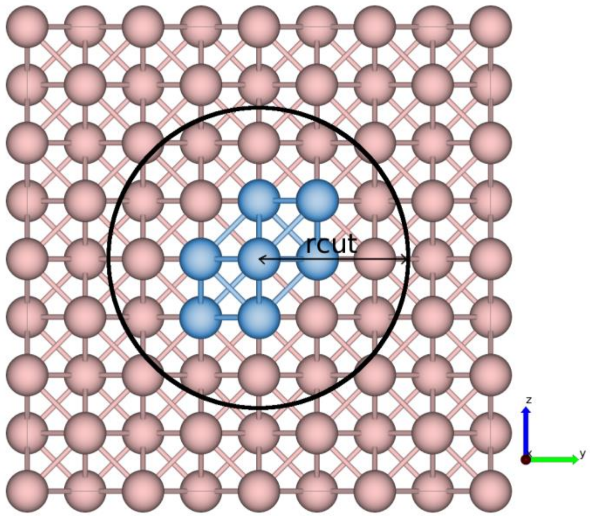
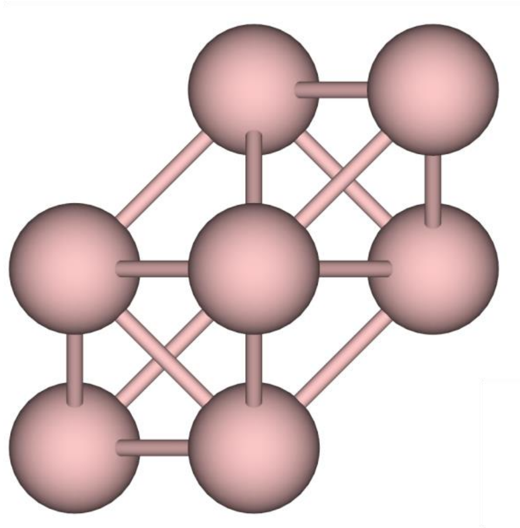
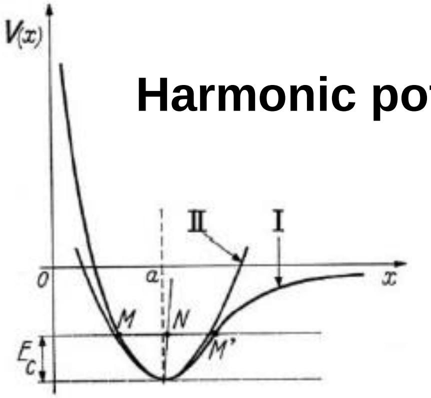




ABINIT WORKSHOP, 20-22/05 2019

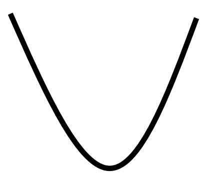
HARMONIC, QUASI-HARMONIC & ANHARMONIC



Harmonic potential

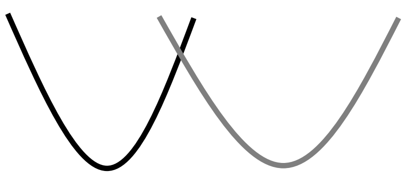
The HA gives good results in numerous cases, except when…

ω (0K, V)



Harmonic approximation
The temperature is involves only through the filling of the energy levels

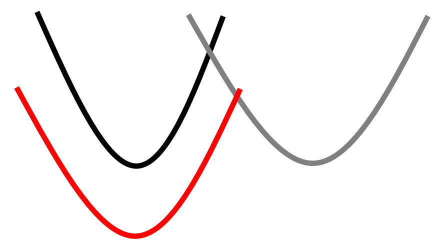
ω (0K, *V(T)*)



Quasi-harmonic approximation
Includes the thermal expansion

Calculations at 0 K (DFPT, DF…)

ω (*T*,*V* (*T*))



Anharmonic effects
The phonon spectra explicitly depends on the temperature

The temperature is explicitly taken into account (DM, MC…)

OUTLOOK

- ❑ Capabilities of a-TDEP : thermodynamic & elastic
- ❑ Some examples : Si, MgO, U, Fe, Pu

THERMODYNAMIC (I) : MACRO

Grüneisen parameter :

$$\gamma = V\left(\frac{\partial P}{\partial U}\right)_V$$

Specific heat :

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\alpha_p = \frac{\gamma C_V}{B_T V}$$

Bulk Modulus :

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$B_T = \frac{1}{\kappa_T}$$

Thermal expansion :

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

THE INTERATOMIC FORCE CONSTANTS (I)

All these quantities only depends on

Interatomic force constants (IFC),

which allow to obtain the phonon frequencies

$$\omega(V(T),T)$$

but also the thermal expansion, the Grüneisen parameter, the specific heat, the Bulk modulus, the free energy, the lattice thermal conductivity, the thermal pressure, the elastic constants, the sound velocities…

How to obtain IFC(T)?

THE INTERATOMIC FORCE CONSTANTS (II)

Taylor expansion of the potential energy around equilibrium :

$$U_{\text{model}} = U_0 + \sum_{i,\alpha} \Pi_i^\alpha u_i^\alpha + \frac{1}{2!} \sum_{ij,\alpha\beta} \Phi_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta + \frac{1}{3!} \sum_{ijk,\alpha\beta\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_i^\alpha u_j^\beta u_k^\gamma + 0(u^4)$$

In the framework of this model, the forces are :

$$\begin{aligned} \mathcal{F}_{i,\text{model}}^\alpha &= -\Pi_i^\alpha - \sum_{j,\beta} \Phi_{ij}^{\alpha\beta} u_j^\beta - \frac{1}{2} \sum_{jk,\beta\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_j^\beta u_k^\gamma + 0(u^3) \\ &= -\sum_p \frac{1}{p\,!} \sum_{j\ldots,\beta\ldots} \Theta_{ij\ldots}^{\alpha\beta\ldots}(p) u_j^\beta \ldots \\ &= \sum_{p\lambda} f_{i,\lambda p}^\alpha(\mathbf{u}) \theta^{\lambda p} \end{aligned}$$

Non-linear in u

Linear in θ

After an AIMD run, we obtain a set of ($\mathbf{F}_{MD}$; $\mathbf{u}_{MD}$) at each time step t,

so we search θ such as :

$$\mathcal{F}_{i,\text{MD}}^\alpha(t) = \sum_{p\lambda} f_{i,\lambda p}^\alpha(\mathbf{u}_{\text{MD}}(t)) \theta^{\lambda p}$$

THE INTERATOMIC FORCE CONSTANTS (III)

One can solve this system of equations by searching its least squares solution. Let us define the residual : $\mathcal{R} = \mathbf{F}_{MD} - \mathbf{f}.\boldsymbol{\Theta}$

One measure of smallness of the residual is to choose θ such that $\mathcal{S} = \min(\mathcal{R}^T.\mathcal{R}) = ||\mathbf{F}_{MD} - \mathbf{f}.\boldsymbol{\Theta}||^2$ is as small as possible.

The solution giving the lowest residual is the following least squares solution : $\boldsymbol{\Theta} = \mathbf{f}^\dagger.\mathbf{F}_{MD}$

Once the IFC obtained, we can compute the dynamical matrix :

$$D_{ij}^{\alpha\beta}(\mathbf{q}) = \frac{1}{N_a}\sum_{ab}\frac{\Phi_{ij}^{\alpha\beta}(a,b)}{\sqrt{M_i M_j}}\exp\left(i\mathbf{q}.[\mathbf{R}(b)-\mathbf{R}(a)]\right)$$

and finally the phonon modes

$$\sum_{\beta,j} D_{ij}^{\alpha\beta}(\mathbf{q})X_{js}^{\beta}(\mathbf{q}) = \omega_s^2(\mathbf{q})X_{is}^{\alpha}(\mathbf{q})$$

THERMODYNAMIC (II) : MICRO

Grüneisen parameter :

$$\gamma_i = -\left(\frac{\partial \ln \omega_i}{\partial \ln V}\right)_T = -\frac{V}{\omega_i}\left(\frac{\partial \omega_i}{\partial V}\right)_T \qquad \gamma = \frac{\sum_{i=1}^{3N_a} \gamma_i C_{V,i}}{C_V}$$

$$\gamma_s(\mathbf{q}) = -\frac{1}{6\omega_s^2(\mathbf{q})} \sum_{ijk,bc,\alpha\beta\gamma} \Psi_{ijk}^{\alpha\beta\gamma}(0,b,c) \frac{X_{is}^{\star\alpha}(\mathbf{q}) X_{js}^{\beta}(\mathbf{q})}{\sqrt{M_i M_j}} \tau_k^{\gamma} \exp\left[i\mathbf{q}.\mathbf{R}(b)\right]$$

$$\alpha_p = \frac{\gamma C_V}{B_T V}$$

Thermal expansion :

$$\alpha_p = \frac{1}{B} \sum_{i=1}^{3N_a} \left(-\frac{C_{V,i}}{\omega_i}\right) \left(\frac{\partial \omega_i}{\partial V}\right)_T$$

THERMODYNAMIC (II) : MICRO

$$\alpha_p = \frac{\gamma C_V}{B_T V}$$

Specific heat :

$$C_V = 3N_a k_B \int_0^{\omega_{max}} \left(\frac{\beta\hbar\omega}{2\sinh(\frac{\beta\hbar\omega}{2})} \right)^2 g(\omega) d\omega$$

$$g(\omega) = \frac{1}{3N_a} \sum_{i=1}^{N_a} \delta(\omega - \omega_i)$$

Bulk Modulus :

$$C_{\alpha\beta\gamma\delta} = A_{\alpha\gamma\beta\delta} + A_{\beta\gamma\alpha\delta} - A_{\alpha\beta\gamma\delta}$$

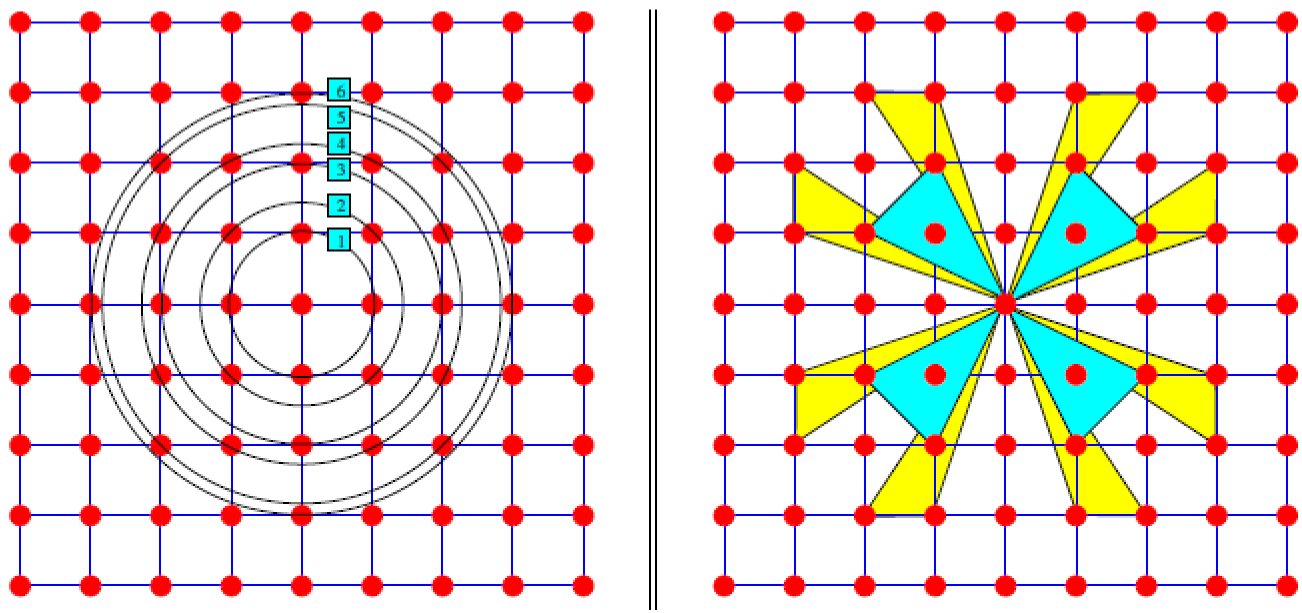
$$A_{\alpha\beta\gamma\delta} = \frac{1}{2V} \sum_{ij} \Phi_{ij}^{\alpha\beta} d_{ij}^{\gamma} d_{ij}^{\delta}$$

$$B_T = ((C_{11} + C_{22} + C_{33}) + 2(C_{12} + C_{13} + C_{23}))/9$$

« TEMPERATURE DEPENDENT EFFECTIVE POTENTIAL »

a-TDEP : 90% of the effort has been devoted to the calculation of the IFCs

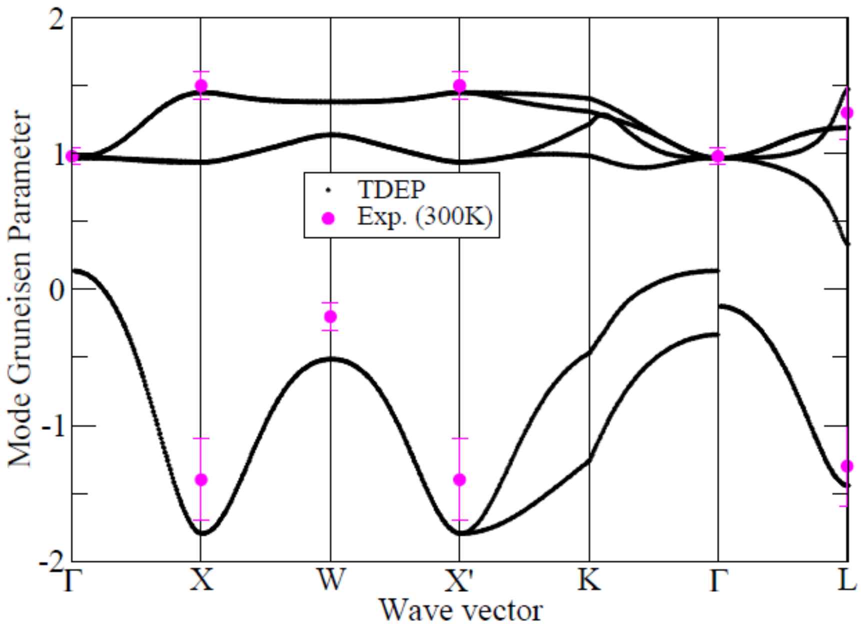
$$\Phi_{ij}^{\alpha\beta} \qquad \Psi_{ijk}^{\alpha\beta\gamma}$$

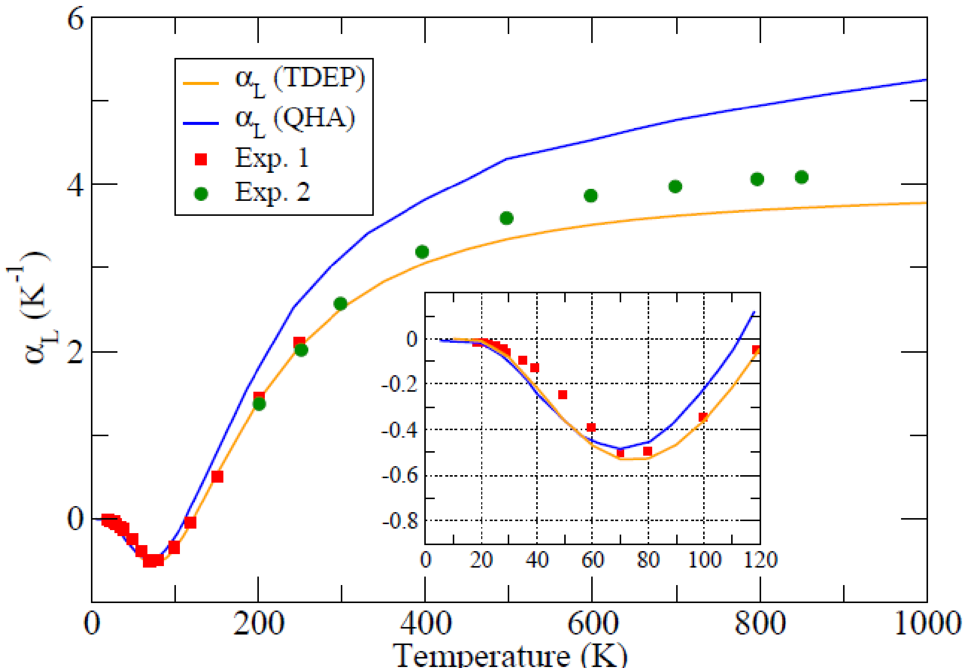


One has to take into account symmetries, invariances…

O. Hellman *et al.*, PRB **84**, 180301(R) (2011), O. Hellman *et al.*, PRB **87**, 104111 (2013).
J. Bouchet & F. Bottin, PRB **92**, 174108 (2015), J. Bouchet & F. Bottin, PRB **95**, 054113 (2017)

A negative thermal expansion at low temperature :





This result could be obtained using QHA

$$\gamma = \frac{\sum_{i=1}^{3N_a} \gamma_i C_{V,i}}{C_V}$$

$$\alpha_p = \frac{\gamma C_V}{B_T V}$$

F. Bottin, J. Bouchet & J. Bieder, to be submitted

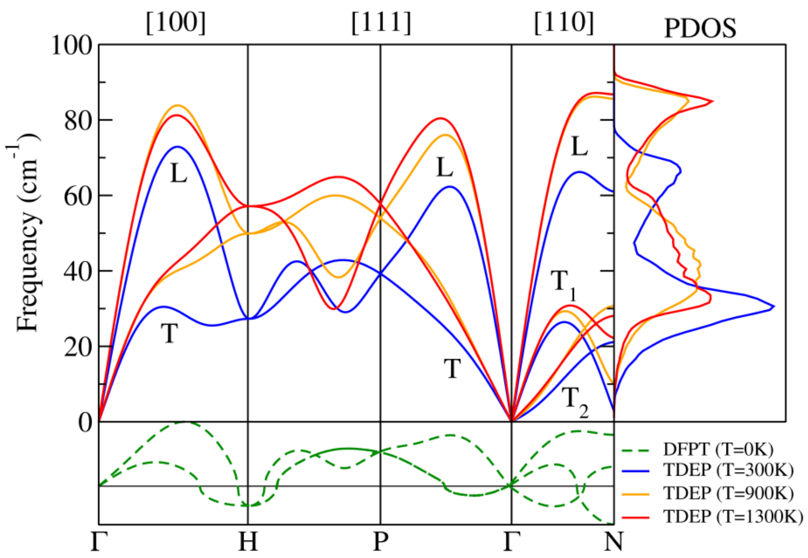
U (GAMMA) : INTRINSIC ANHARMONIC EFFECTS

Phonon frequencies depends on temperature, implicitly & explicitly : $\omega(V(T),T)$

$$\left(\frac{\partial \ln \omega}{\partial T}\right)_p = \left(\frac{\partial \ln \omega}{\partial T}\right)_V + \left(\frac{\partial \ln \omega}{\partial \ln V}\right)_T \left(\frac{\partial \ln V}{\partial T}\right)_p$$

Isochoric or intrinsic anharmonicity:

Isothermal or extrinsic anharmonicity



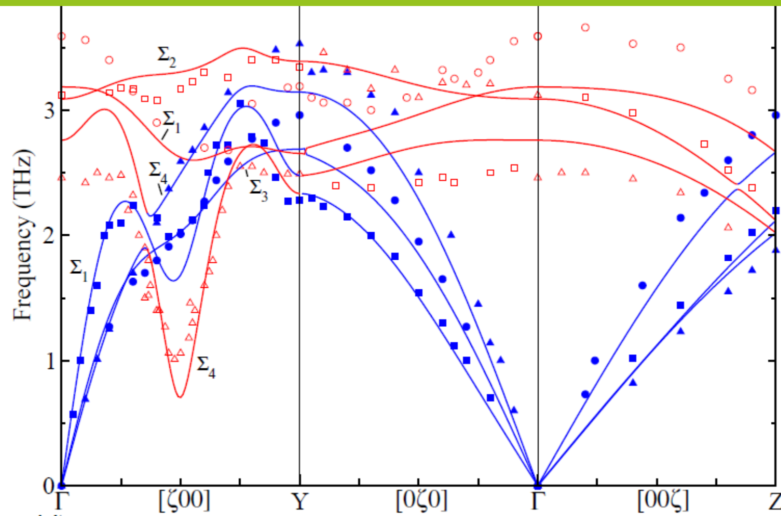
$$-\gamma = \left(\frac{\partial \ln \omega}{\partial \ln V}\right)_T$$

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

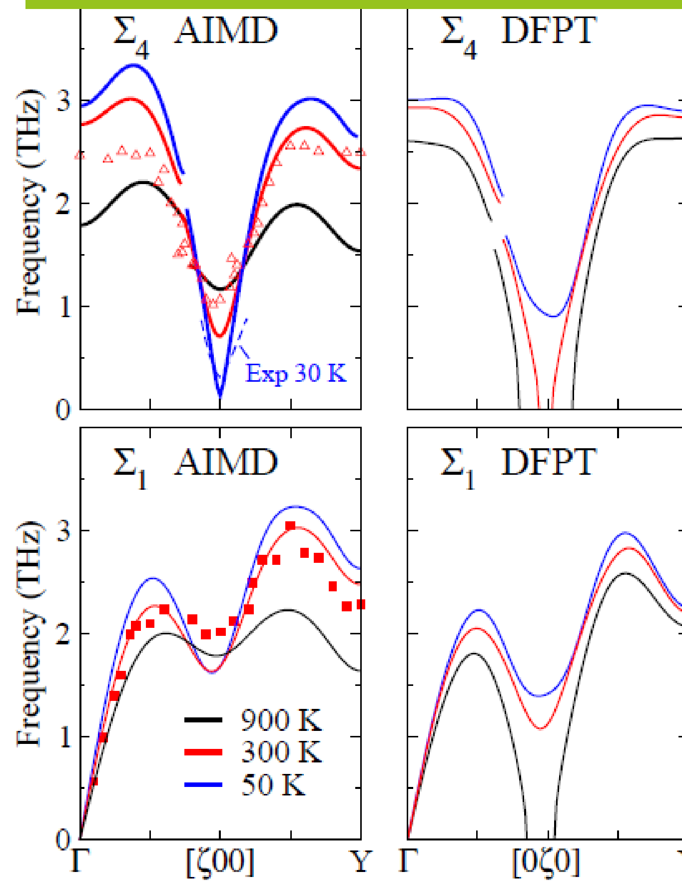
J. Bouchet & F. Bottin., PRB **95**, 054113 (2017)

U (ALPHA) : FAILURE OF THE QHA

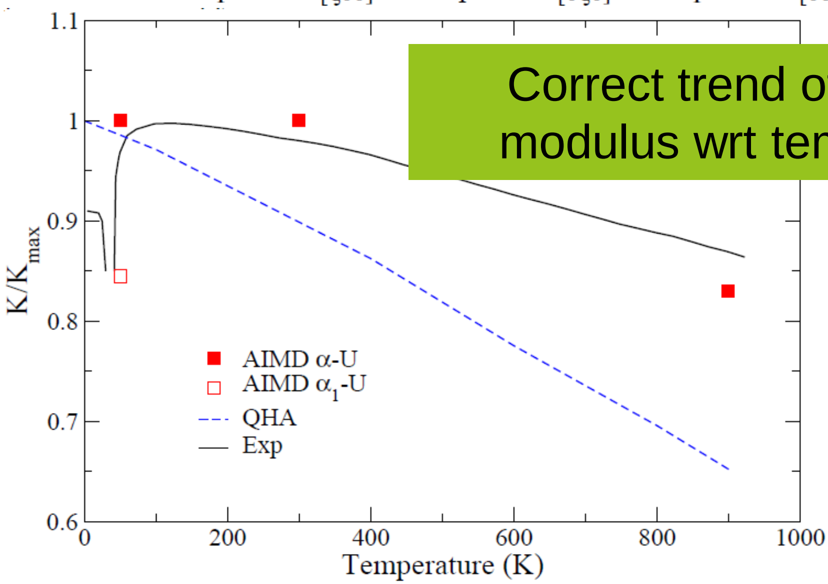
Phonon spectra in good agreement with experiments (300K)



Correct trend of the soft mode wrt temperature



Correct trend of the bulk modulus wrt temperature

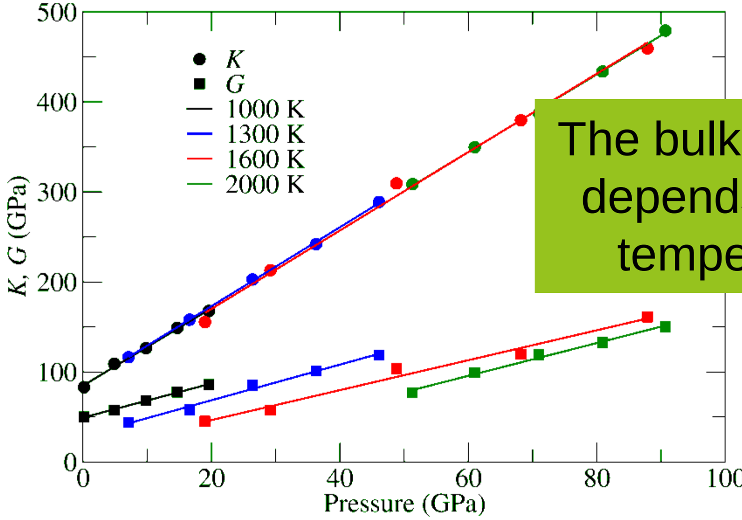


J. Bouchet & F. Bottin., PRB **92**, 174108 (2015)

URANIUM: BULK, SHEAR & PHASE DIAGRAM

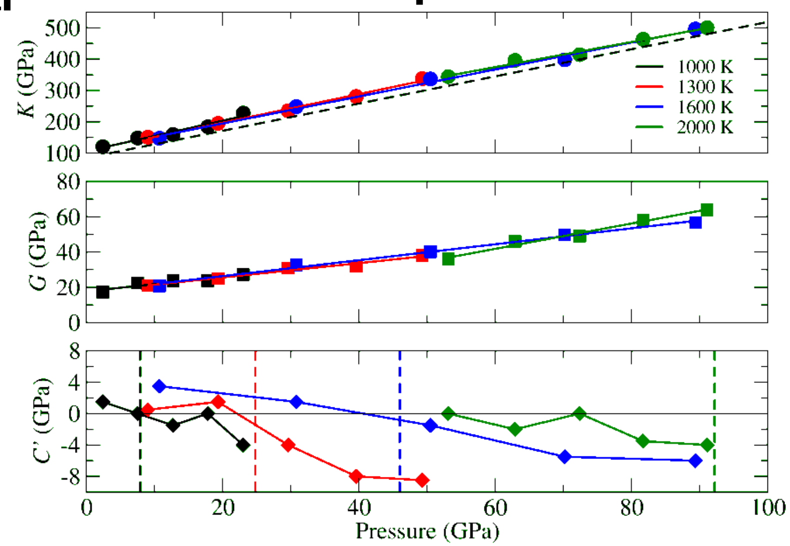
Bulk & Shear

U-α

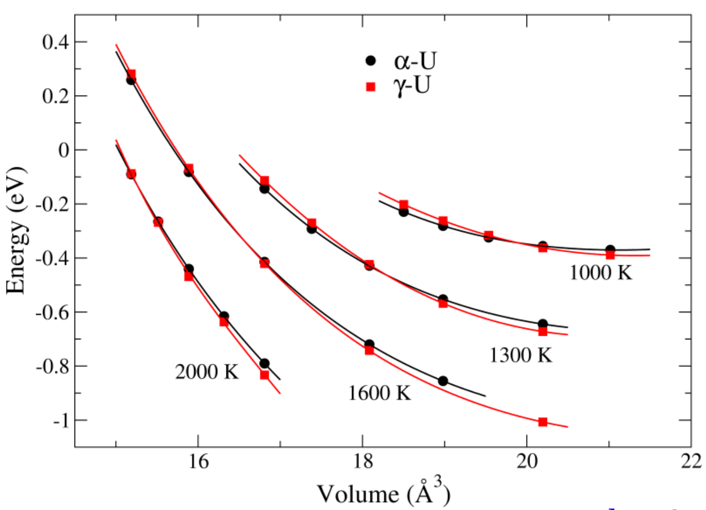


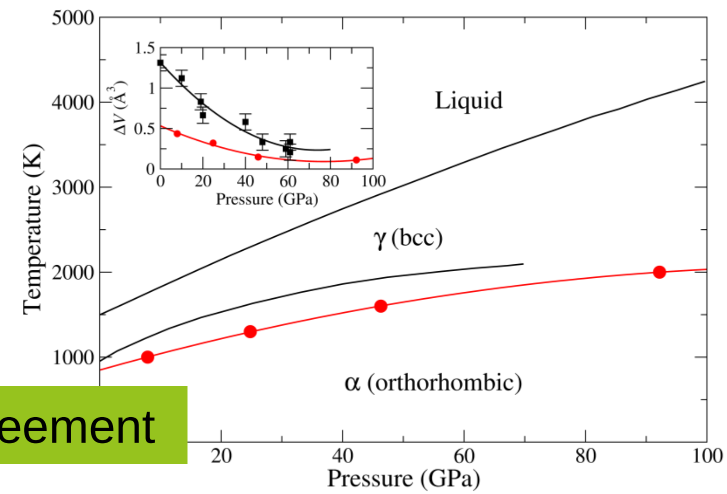
The bulk modulus depends on the temperature

U-γ



Free energy and phase diagram



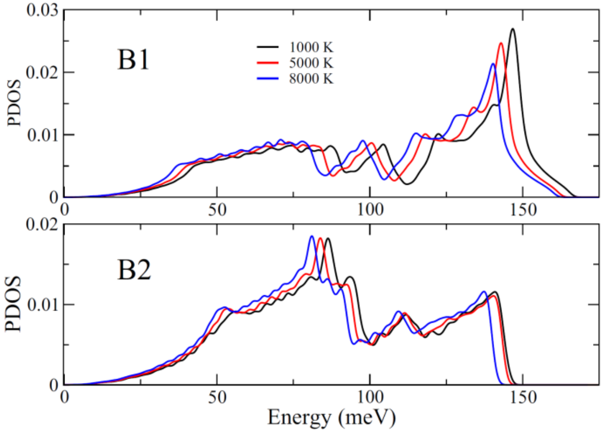


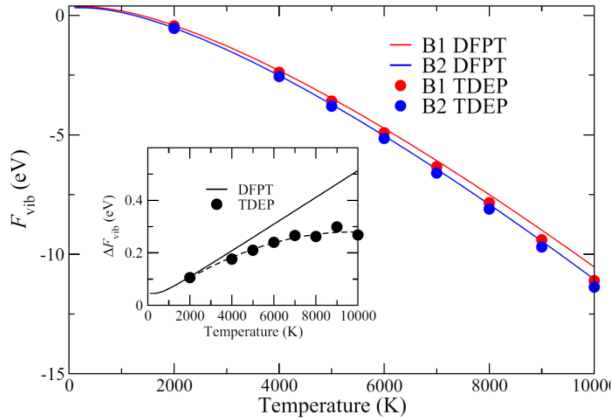
Good agreement

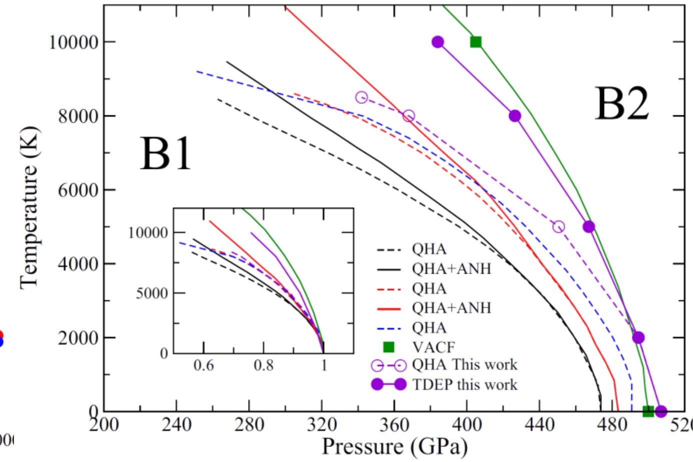
J. Bouchet & F. Bottin., Phys. Rev. B **95**, 054113 (2017)

MGO : THE B1-B2 PHASE TRANSITION

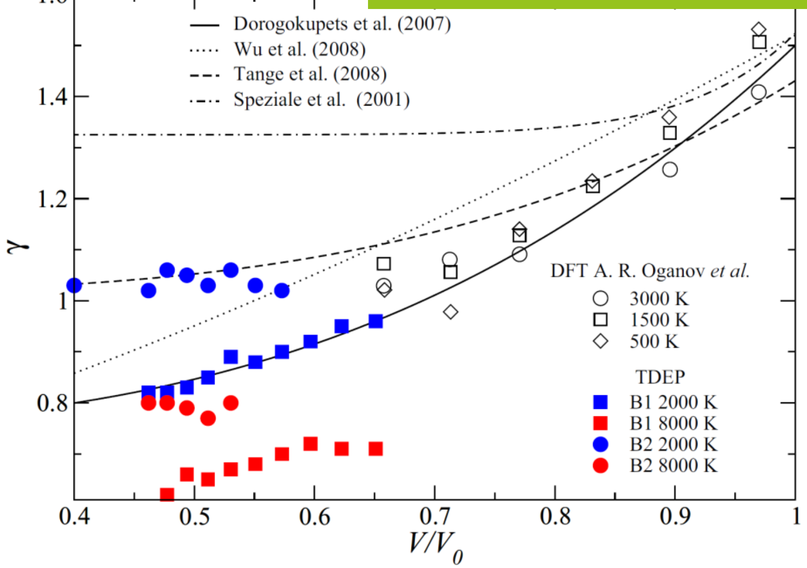
Variation wrt T along an isochore

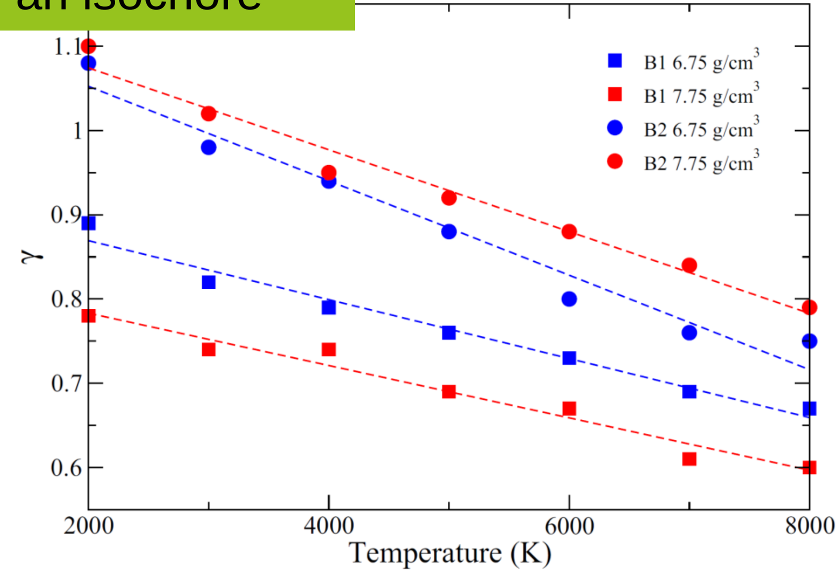






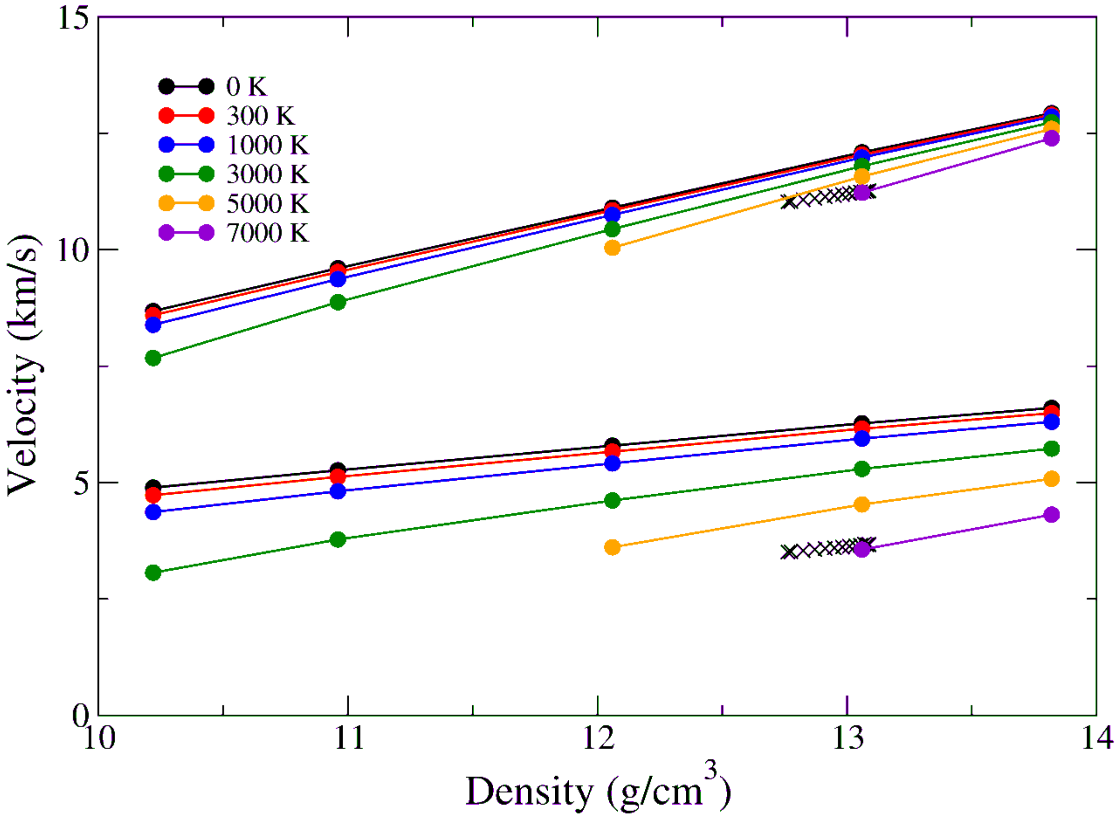
Variation wrt T along an isochore





F. Bottin, J. Bouchet, V. Recoules, F. Remus, G. Morard, R.M. Bolis & A. Benuzzi-Mounaix, PRB 99, 094113 (2019)

IRON : C_{IJ}, ELASTIC MODULI, V_P & V_S



$$K_S = K_T(1 + \alpha\gamma T)$$

$$V_p = \sqrt{\frac{K_S + 4/3G}{\rho}}$$

$$V_s = \sqrt{\frac{G}{\rho}}$$

Strong dependency of the sound velocities wrt temperature

J. Bouchet & F. Bottin, to be submitted

HOW TO RUN « A-TDEP » IN ABINIT

As usual…

```
tdep < input.files > log
```

…with 3 lines in the input.files…

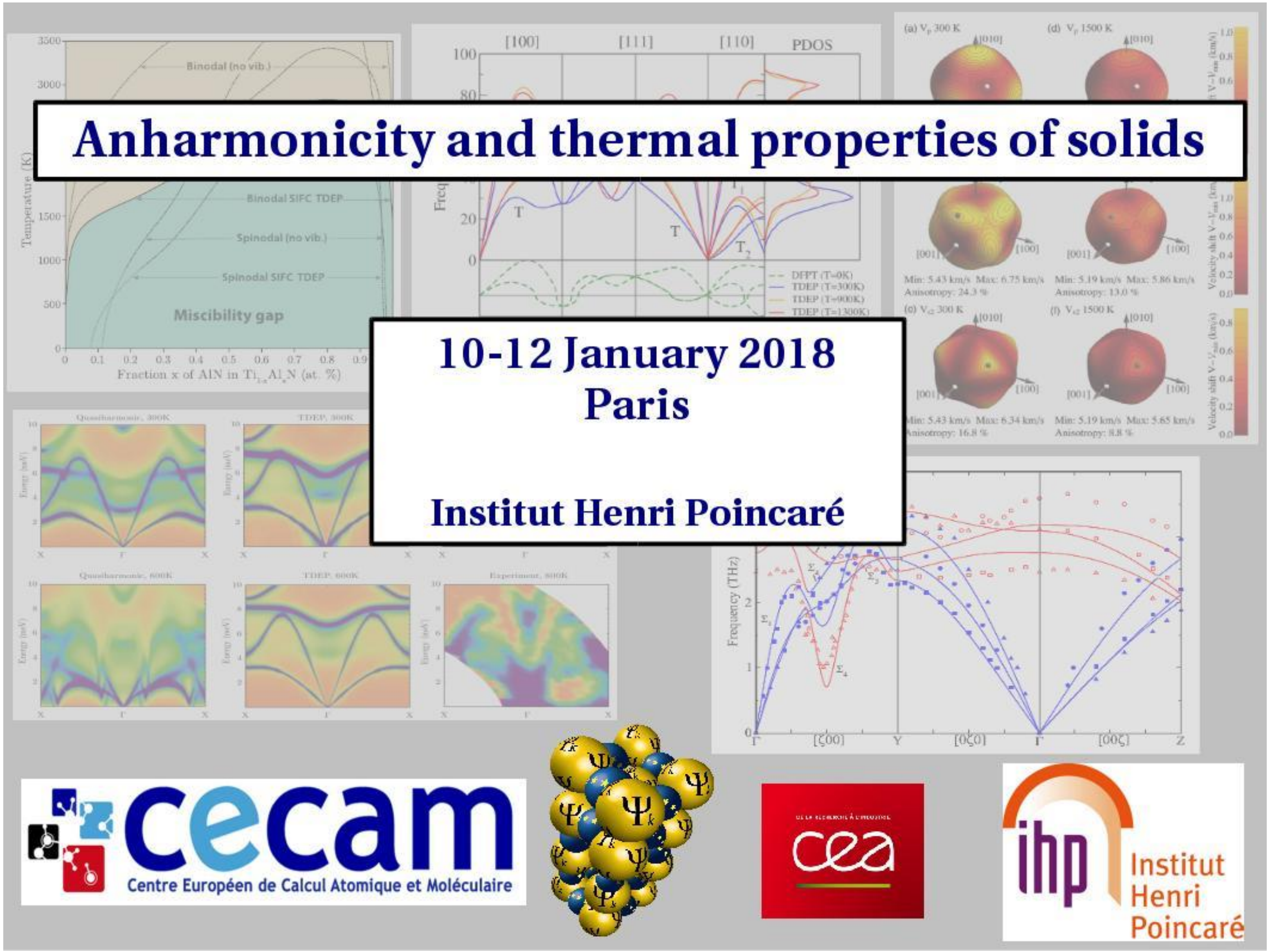
```
input.in
HIST.nc
output
```

… and a few « compulsory » variables in the input.in file (see the t37 test of the v8 suite) :

```
      NormalMode
# Unit cell definition
            brav    7    0
  natom_unitcell             5
   xred_unitcell    0.0 0.0 0.0   0.5 0.5 0.5   0.0 0.5 0.5   0.5 0.0 0.5   0.5 0.5 0.0
  typat_unitcell    3    2    1    1    1
# Supercell definition
    multiplicity    2.00    0.00    0.00    0.00    2.00    0.00    0.00    0.00    2.00
     temperature     495.05
# Computation details
       nstep_max       101
       nstep_min         1
            Rcut      7.426
# Optional inputs
           Ngqpt2 2 2 2
           TheEnd
```

For more details, see the « Topic » and « Input variables » sections in ABINIT.

CONCLUSION


Anharmonicity and thermal properties of solids
10-12 January 2018
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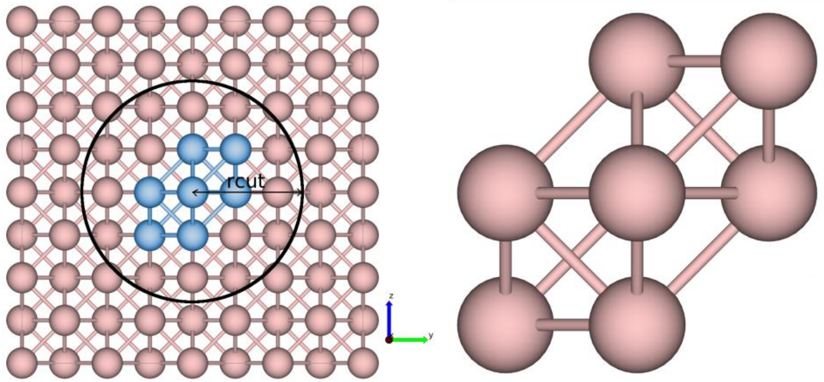
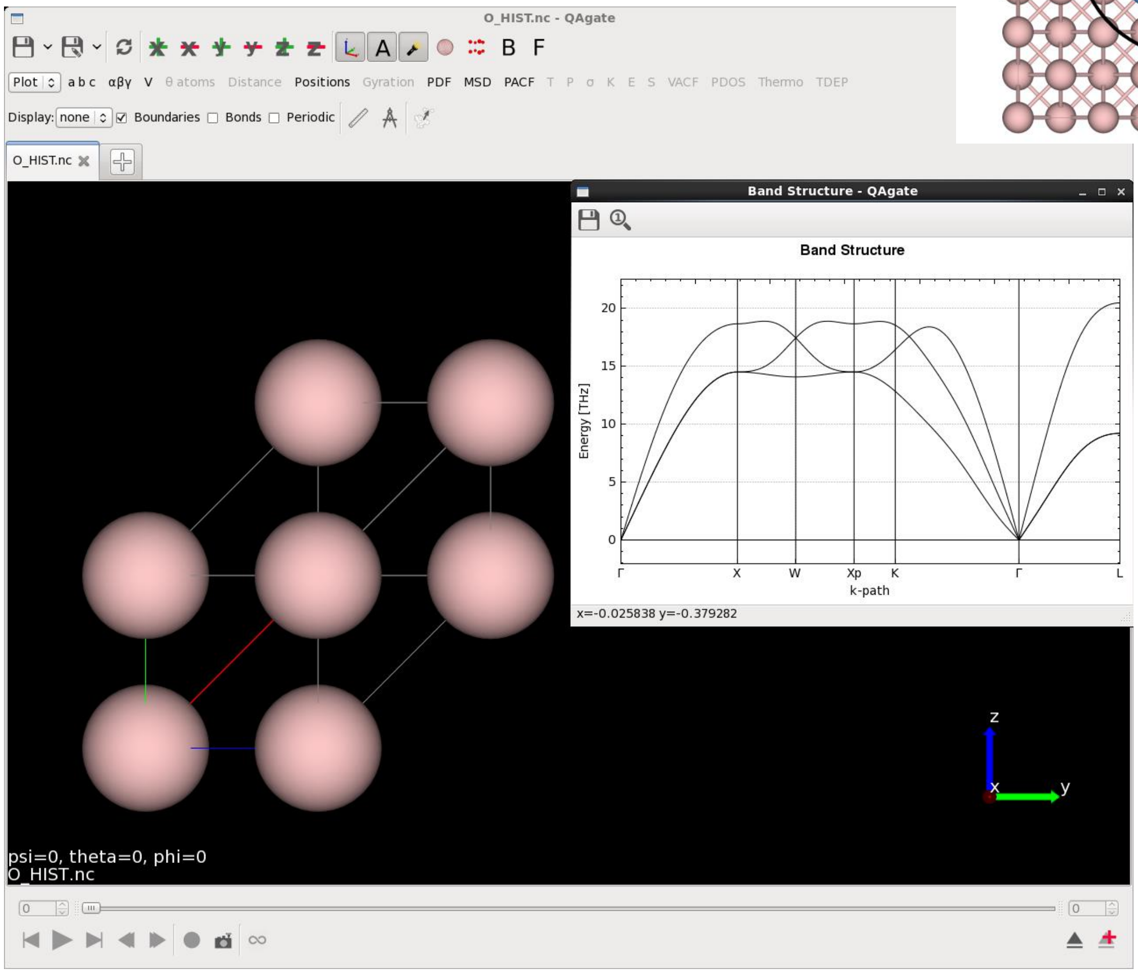
QAGATE





qAgate

Abinit Graphical

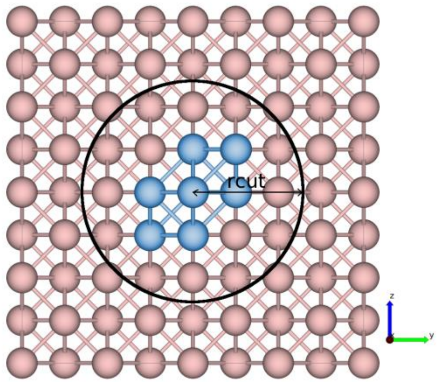
Analysis Tool Engine

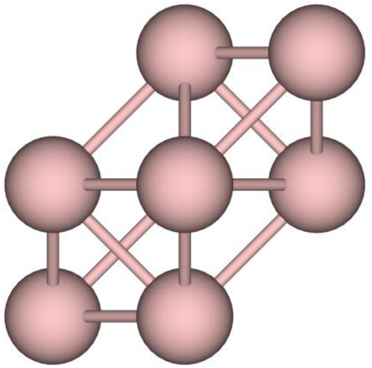
J. Bieder, to be submitted

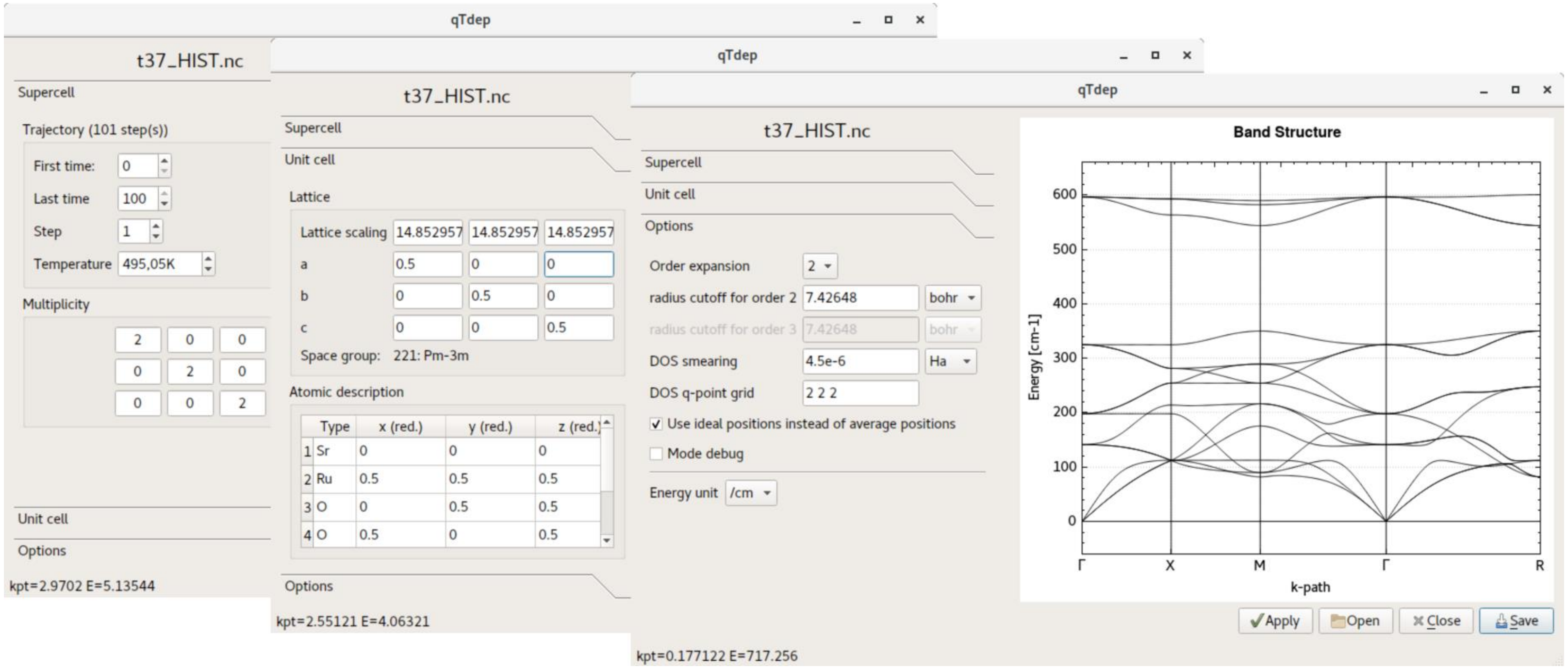
QTDEP

Graphical interface

qTdep







J. Bieder, to be submitted