aTDEP -- Lattice dynamics including anharmonicity

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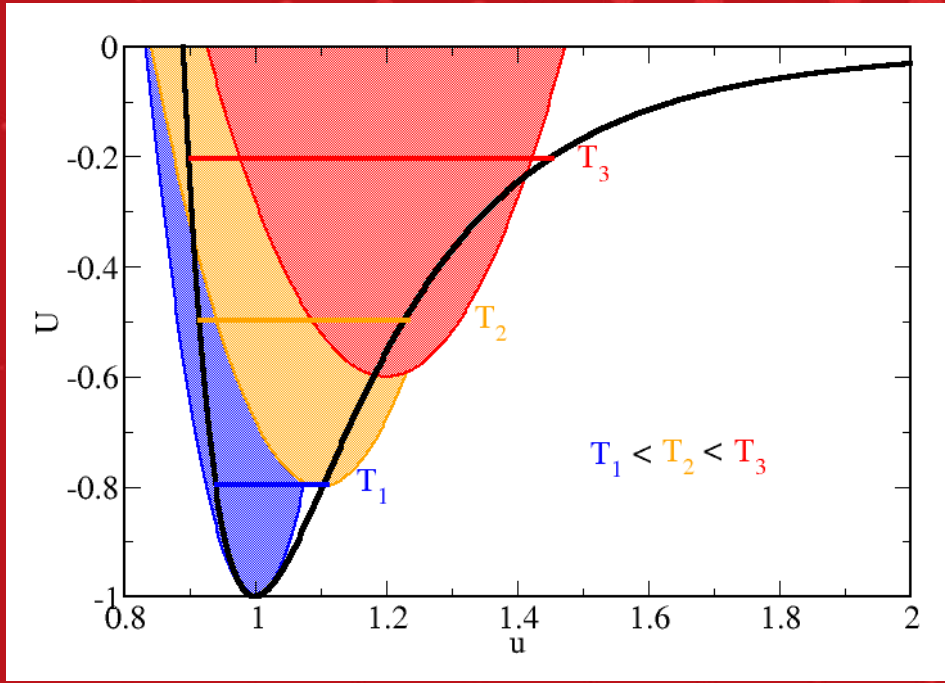
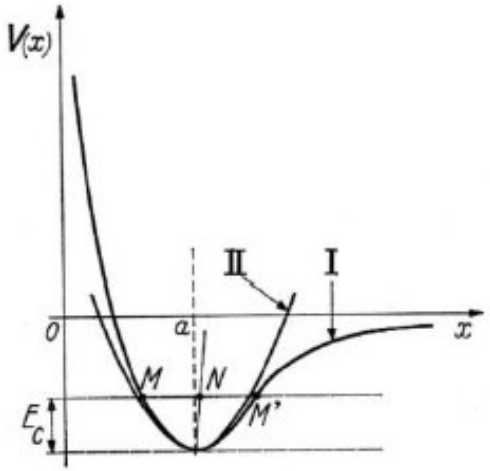
DE LA RECHERCHE À L'INDUSTRIE



ABINIT Developer Workshop May 31 - June 4, 2021



Harmonic approximation

The temperature acts only through the filling of the energy levels.

Quasi-harmonic approximation

Includes the thermal expansion. The phonon frequencies **implicitly** depend on the temperature (through the volume).

Calculations at 0 K (DFPT, FD…)

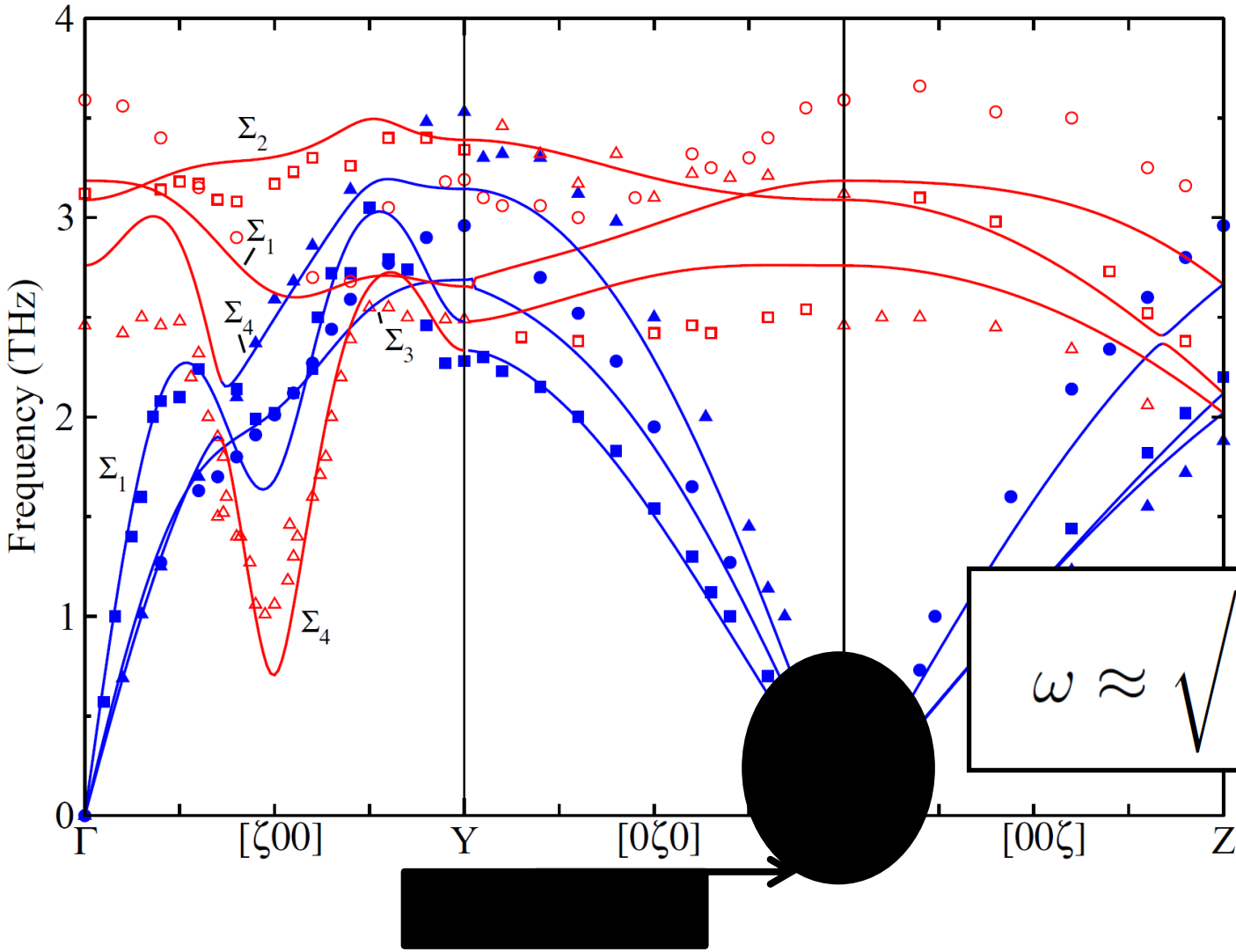
The QHA gives good results in numerous cases… except when the phonon frequencies evolve at constant V.

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

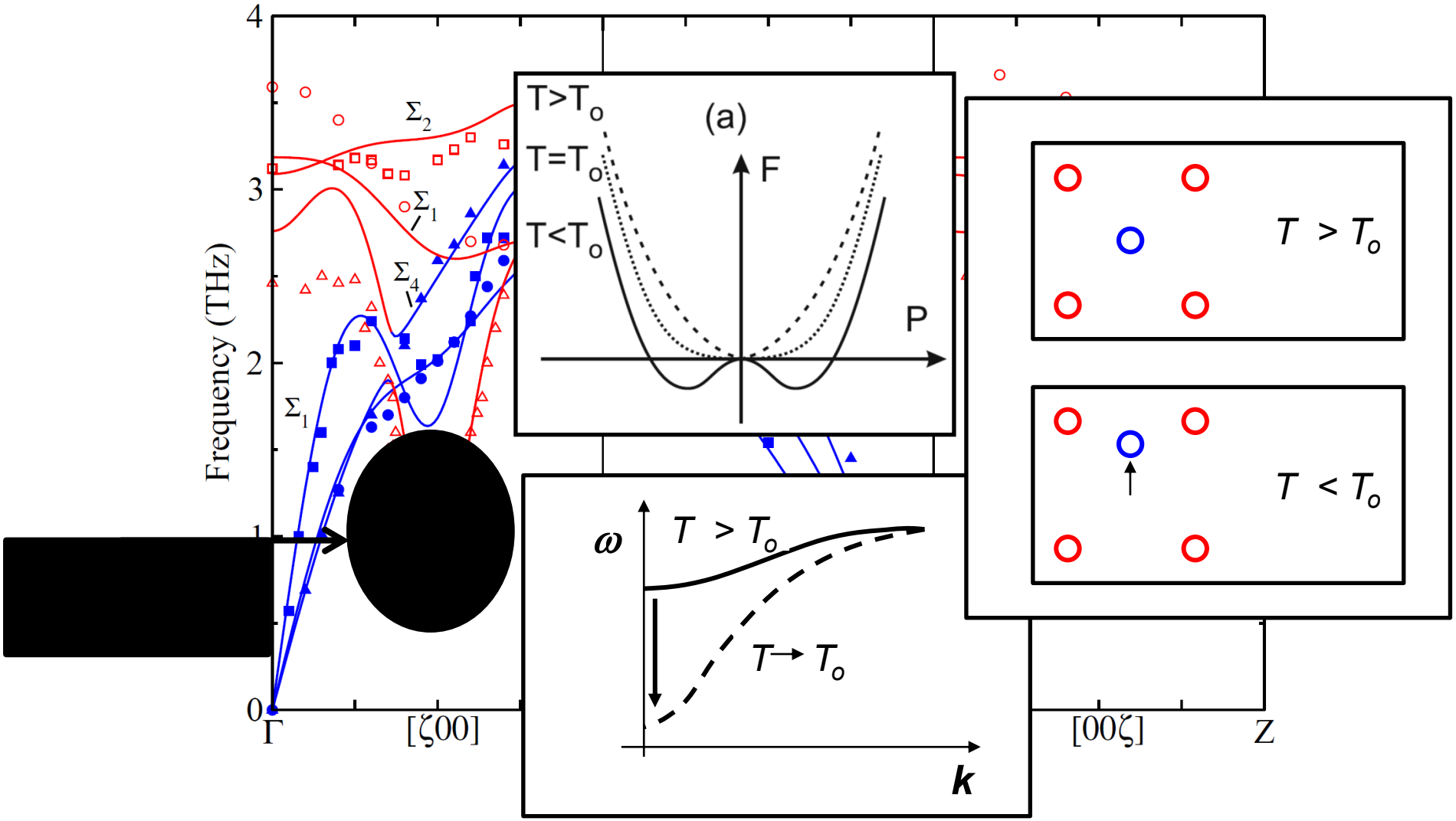
Anharmonic effects

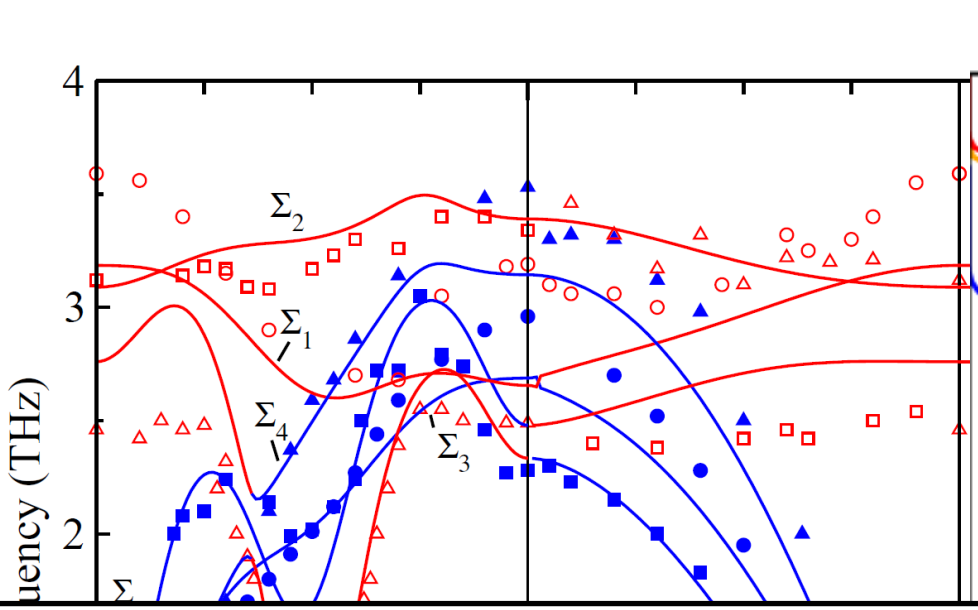
The phonon frequencies **explicitly** depend on the temperature

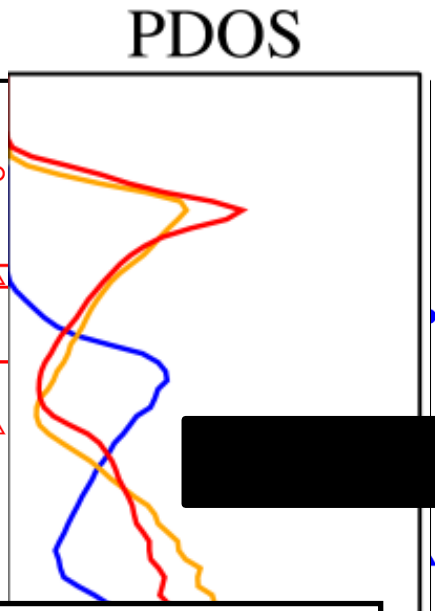
The temperature has to be explicitly taken into account (MD, MC…)



$$\omega \approx \sqrt{\frac{\lambda}{m}}\, ak$$


Frequency (THz)
4
3
2
1
0
Γ
[ζ00]
[00ζ]
Z
Σ2
Σ1
Σ4
Σ1
T>To
T=To
T<To
(a)
F
P
ω
T > To
T→ To
k
T > To
T < To





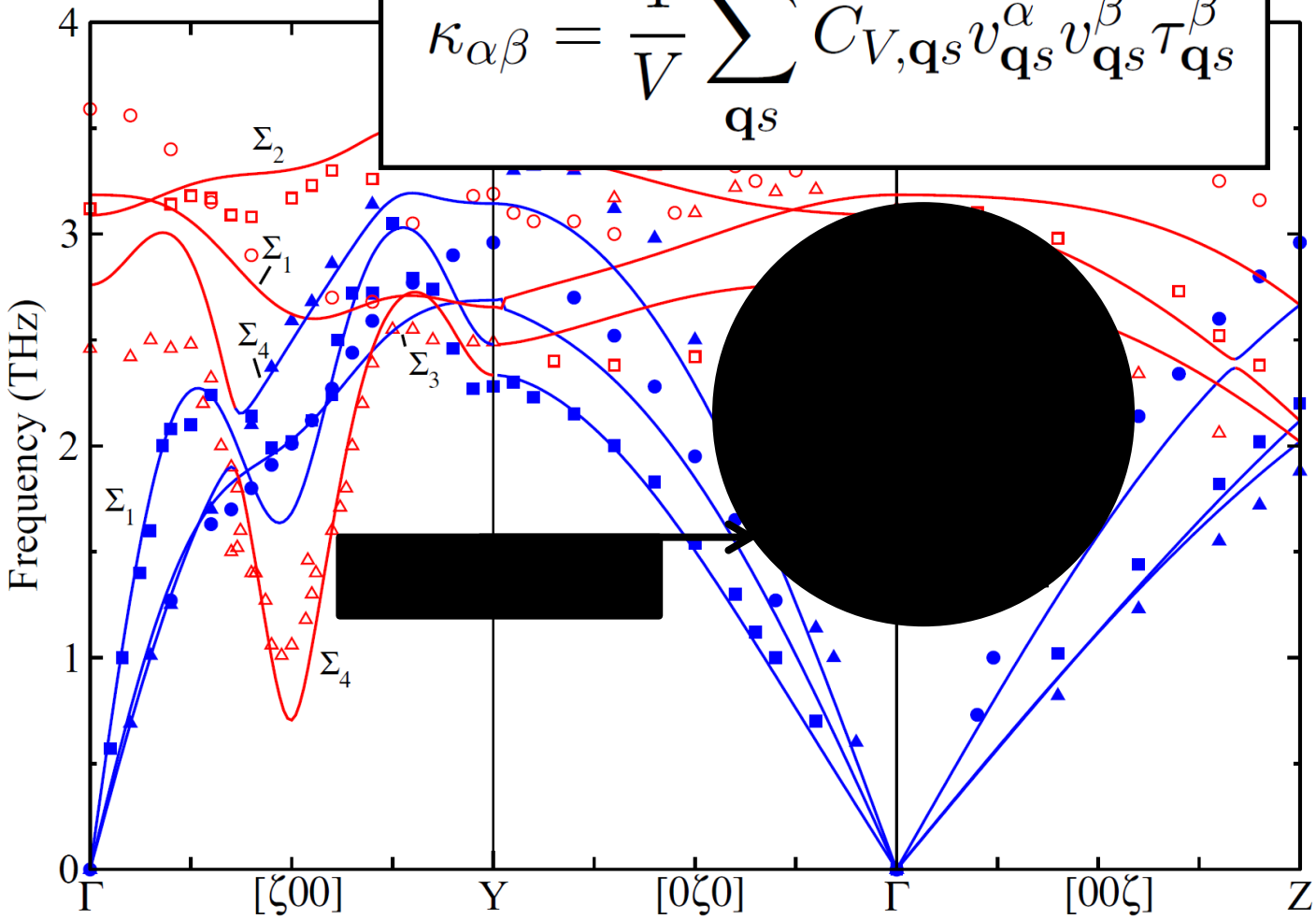
$$U = 3N_a \int_0^{\omega_{max}} \frac{\hbar\omega}{2} \coth(\frac{\beta\hbar\omega}{2}) g(\omega) d\omega$$

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

$$F_{\mathrm{vib}} = \frac{3N_a}{\beta} \int_0^{\omega_{max}} \ln\left(2\sinh(\frac{\beta\hbar\omega}{2}) \right) g(\omega) d\omega \quad \rightarrow \quad F(V,T) = U_0(V) + F_{\mathrm{vib}}(V,T)$$

$$S_{\mathrm{vib}} = 3N_a k_B \int_0^{\omega_{max}} \left[\frac{\beta\hbar\omega}{2} \coth(\frac{\beta\hbar\omega}{2}) - \ln\left(2\sinh(\frac{\beta\hbar\omega}{2}) \right) \right] g(\omega) d\omega$$

$$\kappa_{\alpha\beta} = \frac{1}{V} \sum_{\mathbf{q}s} C_{V,\mathbf{q}s} v^{\alpha}_{\mathbf{q}s} v^{\beta}_{\mathbf{q}s} \tau^{\beta}_{\mathbf{q}s}$$



Everything depends on IFC

Grüneisen parameter :

$$\gamma_i = -\left(\frac{\partial \ln \omega_i}{\partial \ln V}\right)_T = -\frac{V}{\omega_i}\left(\frac{\partial \omega_i}{\partial V}\right)_T$$

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

ecific heat :

$$^{max}\left(\frac{\beta\hbar\omega}{2\sinh(\frac{\beta\hbar\omega}{2})}\right)^2 g(\omega)d\omega$$

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

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

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

Bulk Modulus :

Thermal expansion :

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

$$\alpha_p = \frac{1}{B}\sum_{i=1}^{3N_a}\left(-\frac{C_{V,i}}{\omega_i}\right)\left(\frac{\partial\omega_i}{\partial V}\right)_T \frac{}{V}\sum_{ij}\Phi_{ij}^{\alpha\beta}d_{ij}^{\gamma}d_{ij}^{\delta}$$

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

Taylor expansion of the potential energy around equilibrium :

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

Here, the forces are :

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

Non-linear wrt u

Linear wrt θ

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

⟹ **solved using a least squares method**

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

O. Hellman *et al.,* PRB **84**, 180301(R) (2011) ; O. Hellman *et al.,* PRB **87**, 104111 (2013).
J. Bouchet & F. Bottin., Phys. Rev. B **92**, 174108 (2015) ; F. Bottin, J. Bieder & J. Bouchet CPC 254, 107301 (2020).

Using invariances (translation & rotation), symmetries of the crystal, dynamical matrix, elastic tensor, etc, the number of IFC coefficients can be strongly reduced.

For 100 atoms : → at the 2nd order : from ~ 90 000 to ~ 20

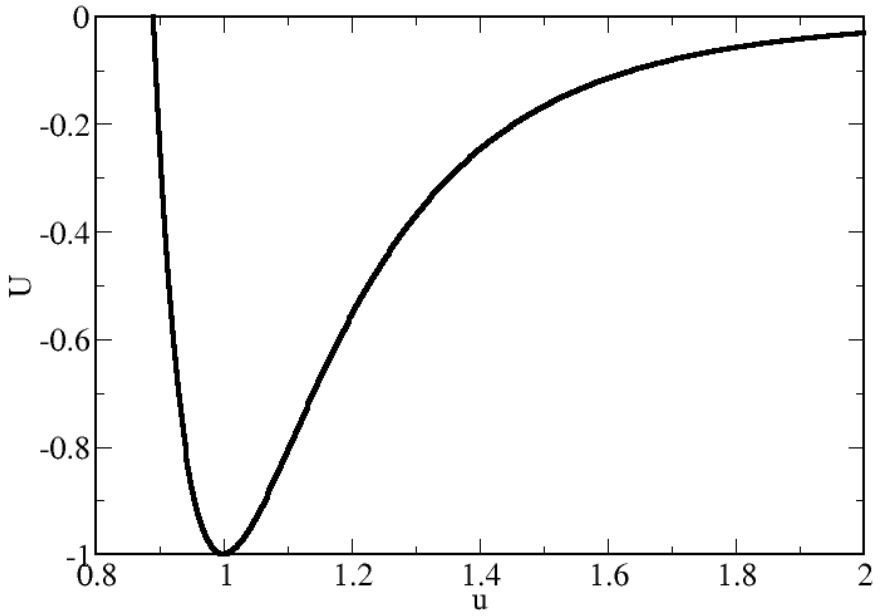
→ at the 3rd order : from ~ 27 000 000 to ~ 200

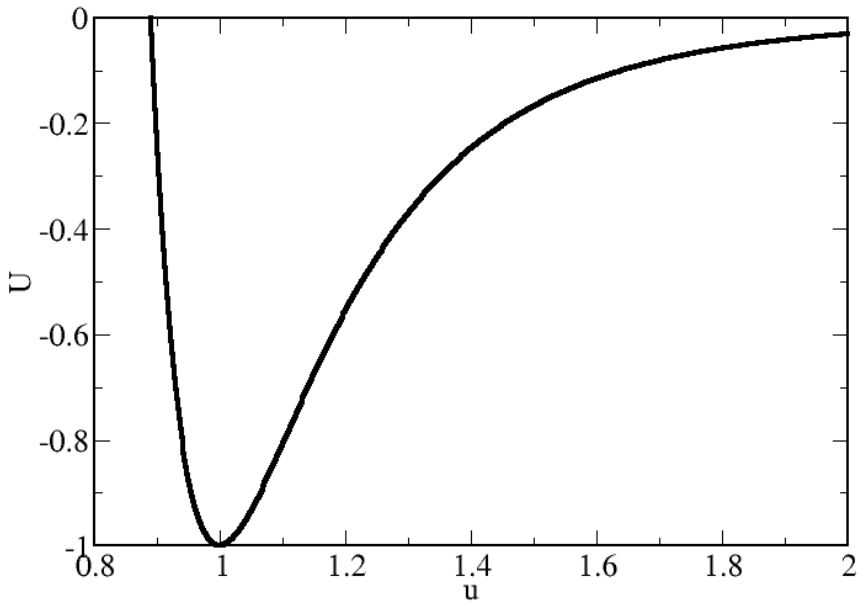
$$\begin{pmatrix} \mathcal{F}^x_1(1) \\ \vdots \\ \theta_{11} \\ \vdots \\ \theta_{p\Lambda_p} \\ \vdots \\ \mathcal{F}^z_{N_a}(N_t) \end{pmatrix} = \begin{pmatrix} f^x_{1,11}(1) & \cdots & f^x_{1,p\Lambda_p}(1) \\ \vdots & \ddots & \vdots \\ f^z_{N_a,11}(N_t) & \cdots & f^z_{N_a,p\Lambda_p}(N_t) \\ \vdots & \vdots & \vdots \\ f^z_{N_a,11}(N_t) & f^z_{N_a,12}(N_t) & \cdots & f^z_{N_a,p\Lambda_p}(N_t) \end{pmatrix}^{\dagger} \cdot \begin{pmatrix} \mathcal{F}^x_1(1) \\ \vdots \\ \mathcal{F}^z_{N_a}(N_t) \\ \vdots \\ \theta_{p\Lambda_p} \end{pmatrix}$$

$$U = U_0 + \frac{1}{2!}\sum_{ij,\alpha\beta}\Phi_{ij}^{\alpha\beta}u_i^\alpha u_j^\beta + \frac{1}{3!}\sum_{ijk,\alpha\beta\gamma}\Psi_{ijk}^{\alpha\beta\gamma}u_i^\alpha u_j^\beta u_k^\gamma + \frac{1}{4!}\sum_{ijkl,\alpha\beta\gamma\delta}\chi_{ijkl}^{\alpha\beta\gamma\delta}u_i^\alpha u_j^\beta u_k^\gamma u_l^\delta + 0(u^5)$$

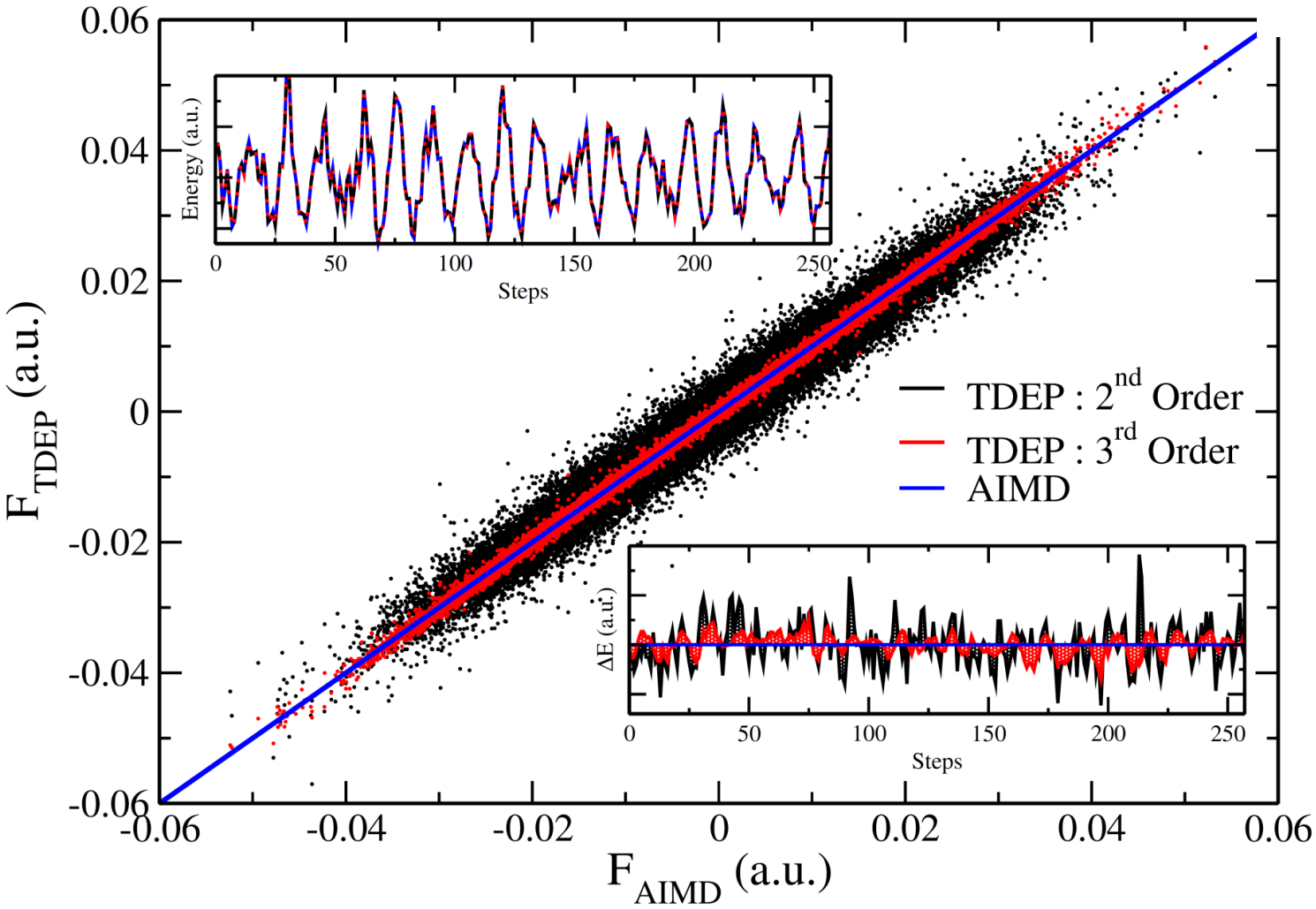
$$U = U_0 + \frac{1}{2!}\sum_{ij,\alpha\beta}\Theta_{ij}^{\alpha\beta}(T)u_i^\alpha u_j^\beta$$

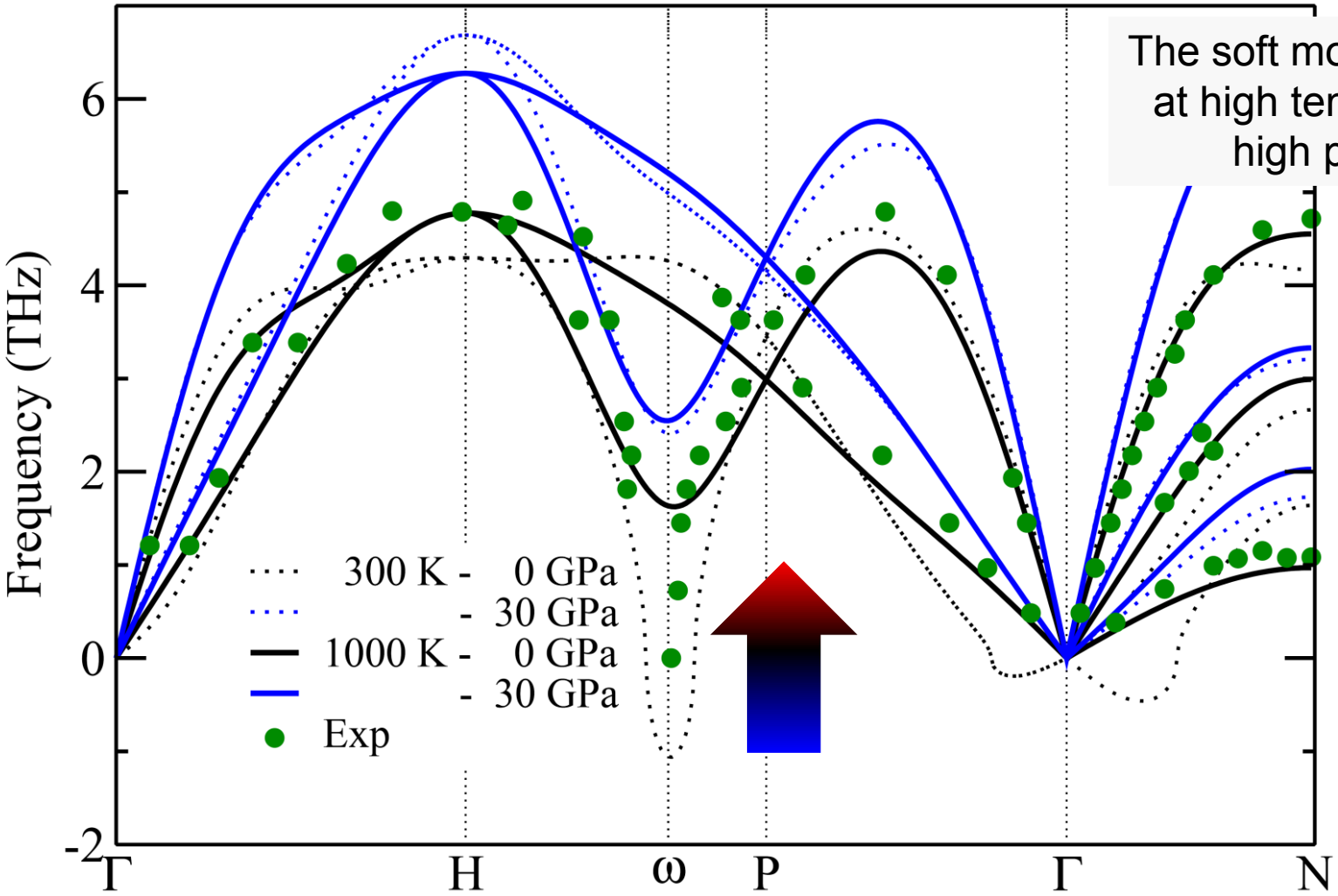
$$U = U_0 + \frac{1}{2!}\sum_{ij,\alpha\beta}\Theta_{ij}^{\alpha\beta}(T)u_i^\alpha u_j^\beta + \frac{1}{3!}\sum_{ijk,\alpha\beta\gamma}\Theta_{ijk}^{\alpha\beta\gamma}(T)u_i^\alpha u_j^\beta u_k^\gamma + \frac{1}{4!}\sum_{ijkl,\alpha\beta\gamma\delta}\Theta_{ijkl}^{\alpha\beta\gamma\delta}(T)u_i^\alpha u_j^\beta u_k^\gamma u_l^\delta$$





O. Hellman *et al.,* PRB **84**, 180301(R) (2011) ; O. Hellman *et al.,* PRB **87**, 104111 (2013).
J. Bouchet & F. Bottin., Phys. Rev. B **92**, 174108 (2015) ; F. Bottin, J. Bieder & J. Bouchet CPC 254, 107301 (2020).

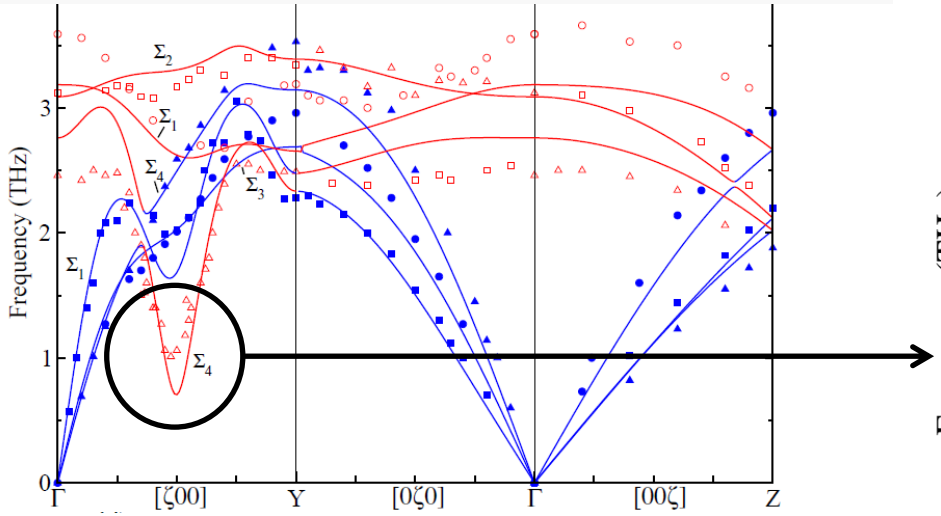

0.06
0.04
0.02
0
-0.02
-0.04
-0.06
F TDEP (a.u.)
-0.06
-0.04
-0.02
0
0.02
0.04
0.06
F AIMD (a.u.)
Energy (a.u.)
0
50
100
150
200
250
Steps
TDEP : 2nd Order
TDEP : 3rd Order
AIMD
ΔE (a.u.)
0
50
100
150
200
250
Steps



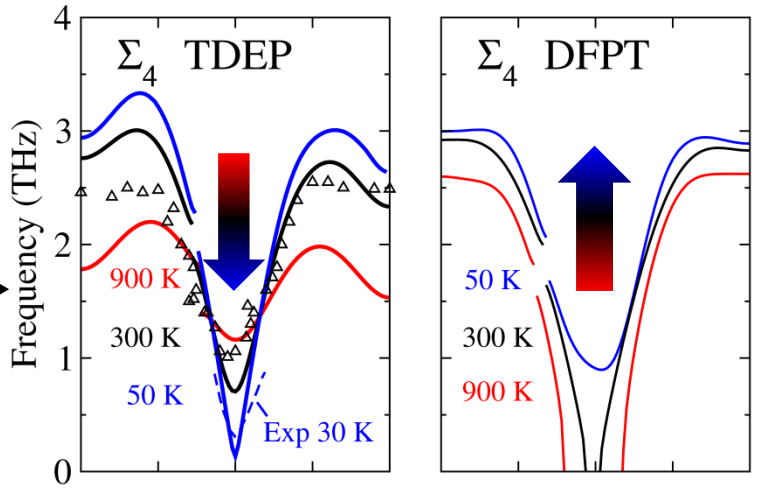
The soft mode disappear at high temperature or high pressure

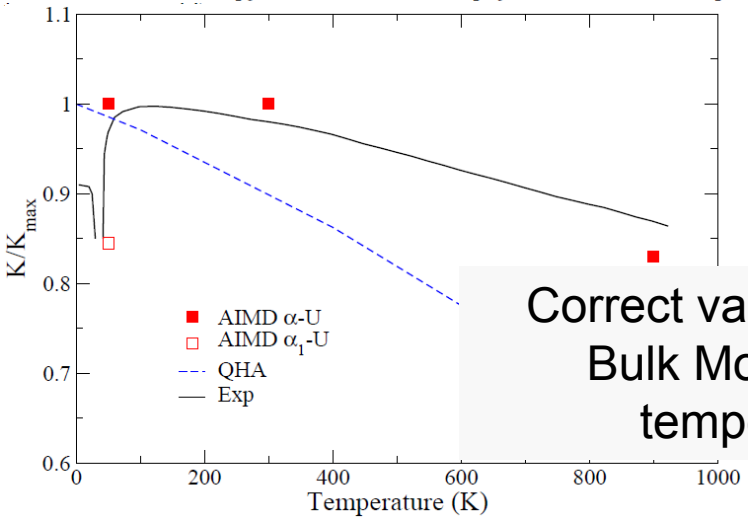
O. Hellman *et al.,* PRB **84**, 180301(R) (2011).
S. Anzellini, F. Bottin, J. Bouchet and A. Dewaele *et al.,* PRB **102**, 184105 (2020).

aTDEP phonon spectrum in good agreement with experiment (300K)



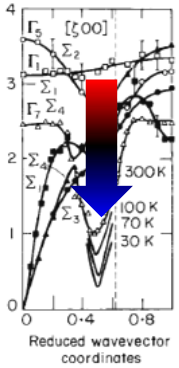
Correct variation of the phonon modes wrt temperature





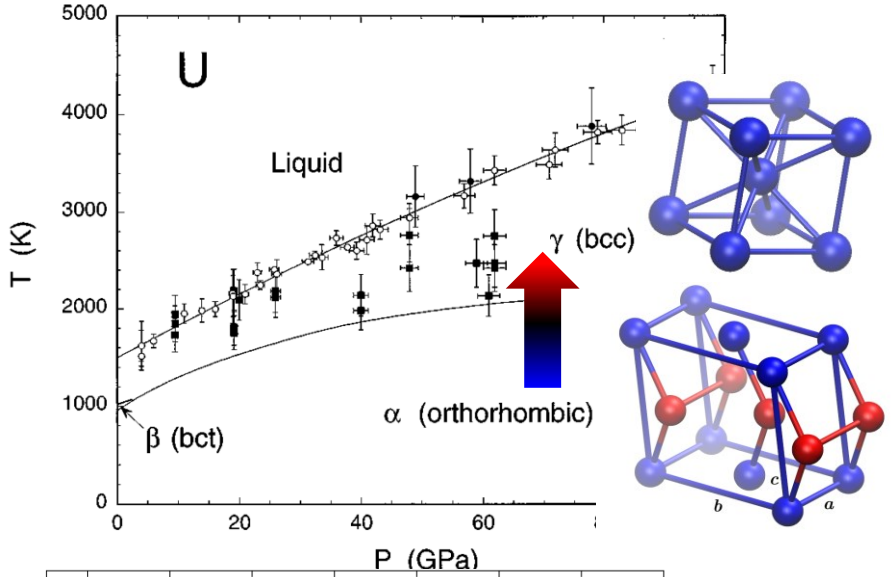
Correct variation of the Bulk Modulus wrt temperature

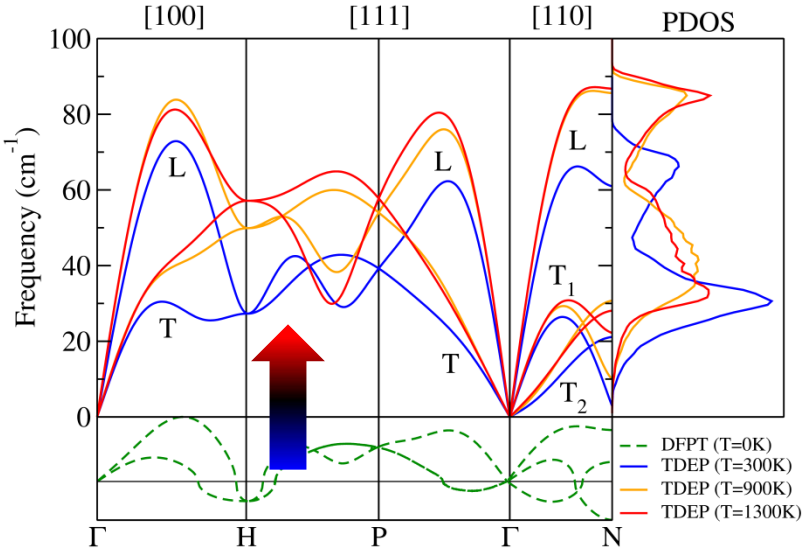
Exp

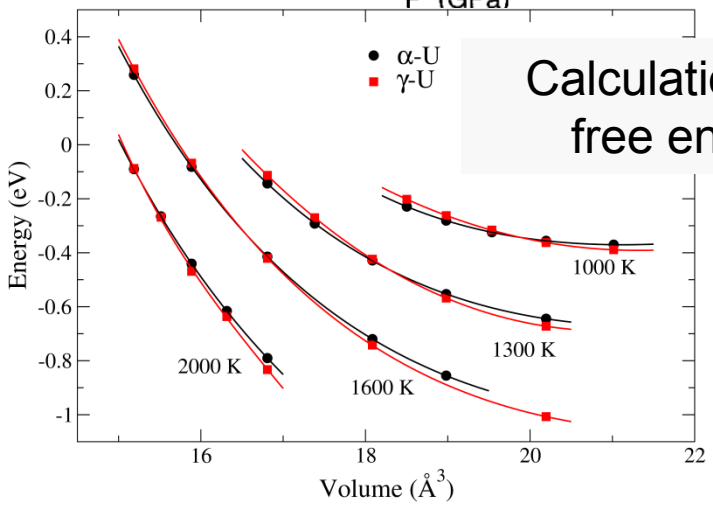


J. Bouchet & F. Bottin., Phys. Rev. B **92**, 174108 (2015)

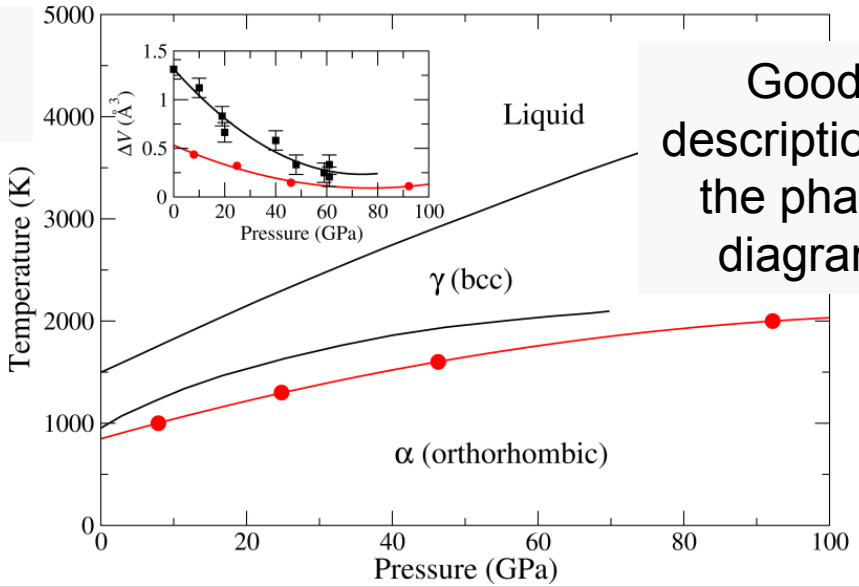
URANIUM (GAMMA) : THE PHASE DIAGRAM







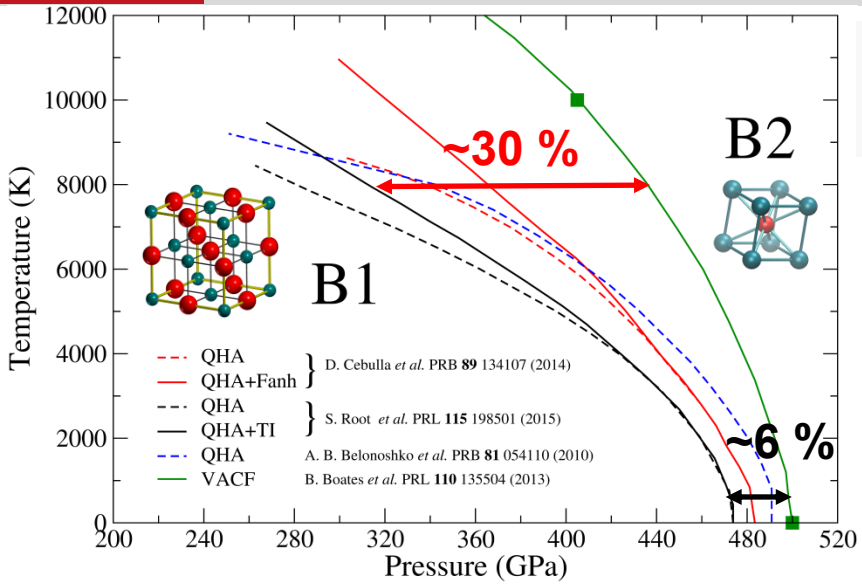
Calculation of the free energies



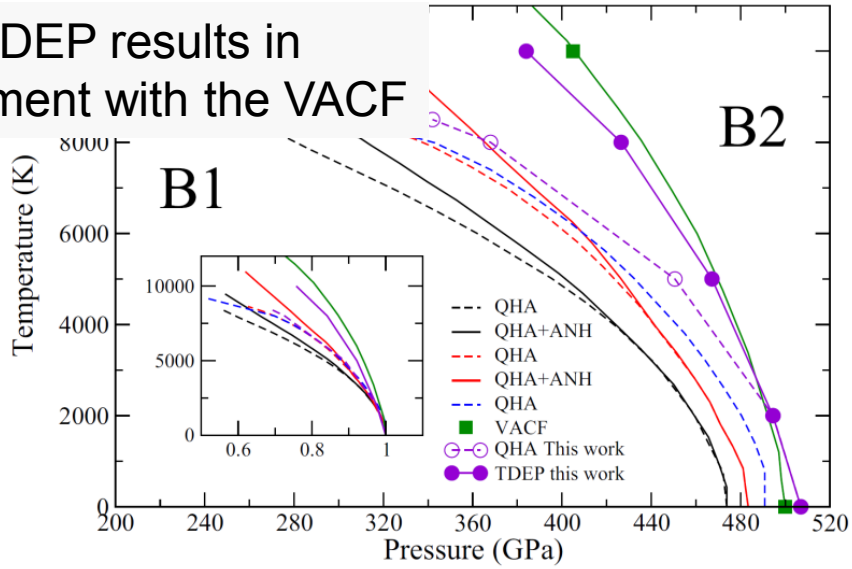
Good description of the phase diagram

C.-S. Yoo, H. Cynn, & P. Söderlind PRB **57**, 10359 (1998)
J. Bouchet & F. Bottin., Phys. Rev. B **95**, 054113 (2017)

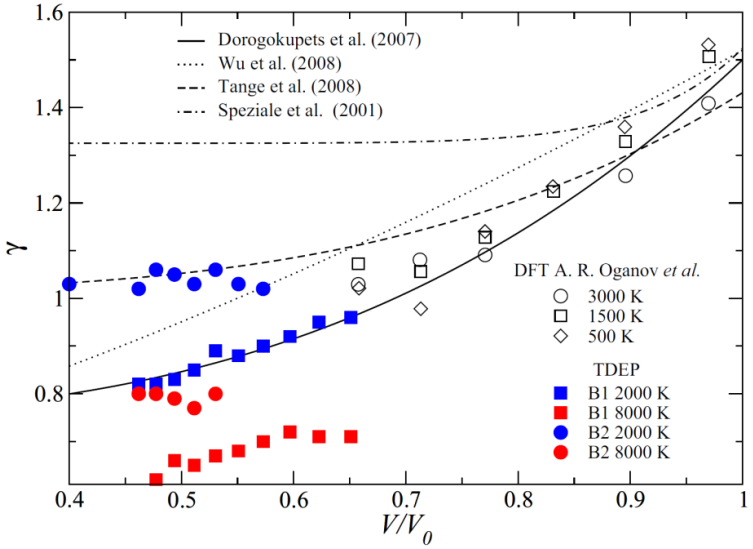
MGO : THE B1-B2 PHASE TRANSITION



TDEP results in agreement with the VACF



Variation of the Gruneisen parameter wrt temperature (along an isochoric process)



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

As usual…

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

…with 3 lines in the input.files…

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

… and a few variables in the input.in file (see the atdep 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
```

A large number of files :

- **Phonon frequencies (omega.dat)**
- **Dynamical matrices (dij.dat & DDB)**
- **Interatomic Force Constants (ifc.dat & ifc.nc)**
- **Thermodynamic data (thermo.dat)**
- **…**
- **Main output file :**

- ✓ **Implementation of the :**
  - ➢ **4th order IFCs**
  - ➢ **Dipole-dipole interaction (LO-TO splitting)**
  - ➢ **Alloy description (VCA)**
  - ➢ **Reweighting (see the presentation of A. Castellano)**
  - ➢ **Parallelisation over configurations**

- ✓ **Creation of an aTDEP series of test (around 40 tests)**
- ✓ **Improvement of the documentation for the user (see the « Topic », the « Input variables » and the « User guide »)**
- ✓ **Building of a first « aTDEP tutorial »**

ATDEP : USER GUIDE – TOPIC – INPUT VARIABLES - TUTORIAL

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The aTDEP utility ¶

The Temperature Dependent Effective Potential (TDEP) method has been developped by O. Hellman *et al.* *[Hellman2011]*, *[Hellman2013]*, *[Hellman2013a]* in 2011 and the aTDEP implementation in ABINIT has been performed and used for the first time in 2015 by J. Bouchet and F. Bottin *[Bouchet2015]*, *[Bouchet2017]*.

- User guide (in a pdf format): aTDEP guide
- Theory: aTDEP paper corresponding to the article *[Bottin2020]*

Prerequisite and theory

The approach used in this code is detailed in a publication dedicated to the development of all formula (see aTDEP paper). We strongly encourage all the users to carefully read this paper before beginning. All the vibrational, elastic and thermodynamic quantities computed by aTDEP are presented with the same writing conventions as the ones used in the output files of aTDEP. In the same manner, a comprehensive understanding of some ABINIT basic variables is also required in order to fill the input file and read the output file of aTDEP.

In addition, this paper is also useful to understand the limitations and convergences which are inherent to the present method. These particular points are sometimes discussed in the article, with some references and illustrating examples.

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CRPA
Crystal

aTDEP

This page gives hints on how to perform thermodynamic, elastic and transport properties calculations including explicit temperature effects with the ABINIT package.

- User guide: aTDEP guide
- Theory: aTDEP paper corresponding to the article *[Bottin2020]*

Introduction

The Temperature Dependent Effective Potential (TDEP) method has been developped by O. Hellman *et al.* *[Hellman2011]*, *[Hellman2013]*, *[Hellman2013a]* in 2011 and the |aTDEP| implementation in ABINIT has been performed and used for the first time in 2015 by J. Bouchet and F. Bottin *[Bouchet2015]*, *[Bouchet2017]*.

The capture of thermal effects in solid state physic is a long standing issue and several stand-alone or post-process computational codes are available. Using different theoretical frameworks, they propose to provide some thermodynamic quantities involving the so called anharmonic effects. |aTDEP| calculation can produce almost all the temperature-dependent thermodynamic quantities you want, from a single *ab initio* molecular dynamic (AIMD) trajectory and by means of a Graphical User Interface (GUI) very easy to use (AGATE).

The original TDEP method *[Hellman2011]* is implemented in ABINIT. In particular, various

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atdep input variables

This document lists and provides the description of the name (keywords) of the atdep input variables to be used in the input file for the atdep executable.

alloy

Mnemonics: ALLOY treatment
Mentioned in topic(s): topic_aTDEP
Variable type: integer
Dimensions: 3
Default value: 0
Added in version: 9.5.1

Test list (click to open). Moderately used, [1/43] in all atdep tests, [0/5] in atdep tutorials

OPTIONAL: Defines the treatment of the alloy. The first value defines the approximation used (0=nothing and 1=Virtual Crystal Approximation). The second and the third values define the [[typat_unitcell]] of the atoms which have to be alloyed.

amu

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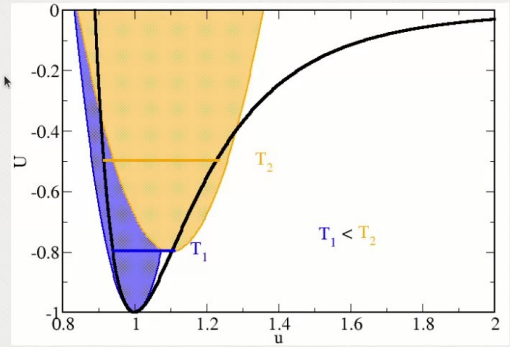
First tutorial on aTDEP



The 2^{nd} order **effective** Interatomic Force Constants

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2.1.1 The data files tatdep1_1xred.dat, tatdep1_1fcart.dat and tatdep1_1etotal.dat
2.1.2 The input file tatdep1_1.abi
2.1.3 The files file tatdep1_1.files
2.2 The output files
2.2.1 The main output file tatdep1_1.abo
2.2.2 The phonon frequencies file tatdep1_1omega.dat
2.2.3 The thermodynamic file tatdep1_1thermo.dat
2.3 Numerical convergence (accuracy and precision)