

Termodinámica *ab initio* de sólidos cristalinos

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Content

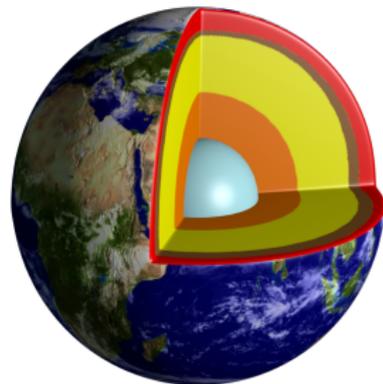
- 1 First-principles thermodynamics of solids
- 2 A model system: magnesium oxide
- 3 Gibbs2: a program for first-principles thermodynamics of solids
- 4 Conclusions



Thermodynamics of solids

Importance of thermodynamic properties of solids.

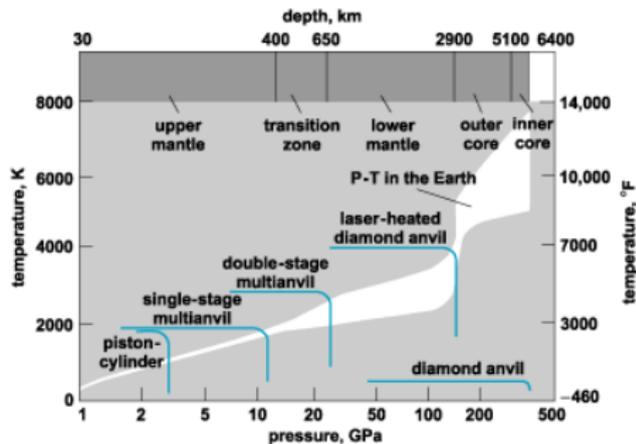
- Equations of state: determine the volume (and geometry) of a phase under a given pressure and temperature. Many electronic, magnetic, optical and chemical properties depend critically on volume.
- Phase diagrams, transition pressures,... Open question: predicting phase structures without experimental input. Design of ultrahard materials,...
- Mechanical properties are important in geophysics. Bulk and shear moduli and sound velocities of mantle materials important to interpret seismic data. MgO, MgSiO₃, silicates, Fe,...
- Materials modelling: accurate determination of thermal expansivities, heat capacities,... very important for technological applications.
- Properties of alloys and solid solutions from the pure components.
- Databases of thermodynamic properties: CALPHAD.



Thermodynamics of solids

Why first-principles instead of experimental?

- **Confirm** the accuracy of experimental results.
 - **Explain** experimental observations.
 - **Predict** properties outside the experimentally accessible pressure-temperature region.
-
- Avoids the use of expensive and time-consuming experimental techniques.
 - Ensures the internal consistency of thermodynamic data.



First-principles approach: pressure effects are easily applied but thermal effects require quite more effort. Using only the crystal structure of one or more phases of a solid. In cases, only the composition.

The standard model of materials science

The thermodynamic properties of a solid under a given hydrostatic pressure (p) and temperature (T) are determined by the general Gibbs energy:

$$G^*(V, \mathbf{x}; p, T) = E(V, \mathbf{x}) + pV + F_{vib}^*(V, \mathbf{x}; T) + \dots$$

where \mathbf{x} represents the internal geometry of the crystal, V is the cell volume, E is the electronic energy. The Helmholtz free energy F_{vib}^* term includes the contribution from lattice vibrations. Other terms: free electrons in metals, configurational and magnetic degrees of freedom, etc.

$E(V, \mathbf{x})$ and $p = -dE/dV$ are obtained directly from a first-principles calculation and are the source of the *static* approach, quite useful for a first analysis of the high pressure solid properties.

The calculation of F_{vib}^* requires a **thermal model** to represent the vibrations of the crystal.



The standard model of materials science

Given pressure and temperature conditions, the equilibrium geometry of the crystal corresponds to a minimum of G^* . Considering volume, this implies the **mechanical equilibrium condition**:

$$\frac{\partial G^*}{\partial V} = 0 = -p_{sta} + p - p_{th}$$

A second corollary:

At a given pressure and temperature, the stable phase of a solid is the one that minimizes G^* . Metastable phases correspond to local minima of G^* .

When the equilibrium volume $V(p, T)$ is known, standard thermodynamic relations can be applied to calculate the rest of the properties (α , C_p , C_v , B_T , B_S, \dots).

In general, it is too expensive to calculate directly G^* because this involves sampling the energy and vibrations of the whole potential energy surface. Several **approximations** are required.



The statically constrained approximation

The thermodynamic properties of a solid under a given hydrostatic pressure (p) and temperature (T) are determined by the general Gibbs energy:

$$G^*(V, \mathbf{x}; p, T) = E(V, \mathbf{x}) + pV + F_{vib}^*(V, \mathbf{x}; T) + \dots$$

The following are equivalent statements of the statically constrained approximation:

- F_{vib}^* depends exclusively on volume.
- $\mathbf{x}(p, T) = \mathbf{x}_{sta}(V(p, T))$.
- El efecto de la temperatura se traduce únicamente en un efecto de volumen representado por la presión térmica. Principio de Neumann.
- The sampling of G^* is reduced to the static path ($V, \mathbf{x}_{sta}(V)$).

The effect of relaxing this approximation has been studied recently in the perovskite mineral (MgSiO_3). In general, too expensive to avoid and the corrections are minor. Effect on elastic and mechanical properties: bulk modulus, shear modulus, elastic constants, sound velocities,...



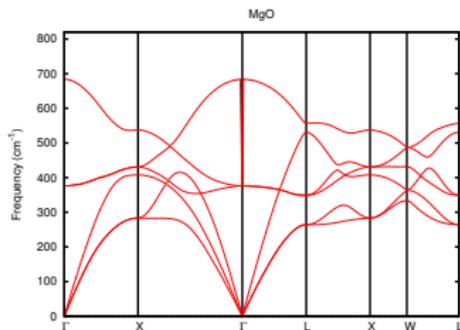
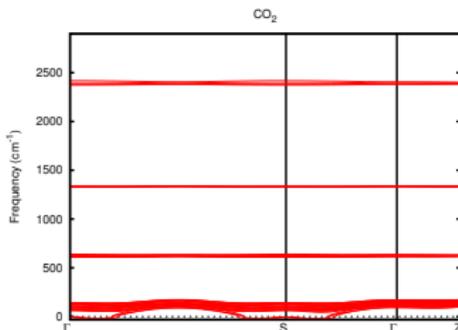
The quasiharmonic approximation (full)

Quasiharmonic approximation (QHA): at any crystal geometry, the atoms are subject to a harmonic potential. These potentials change depending on the crystal structure including some anharmonicity, hence the quasiharmonic name.

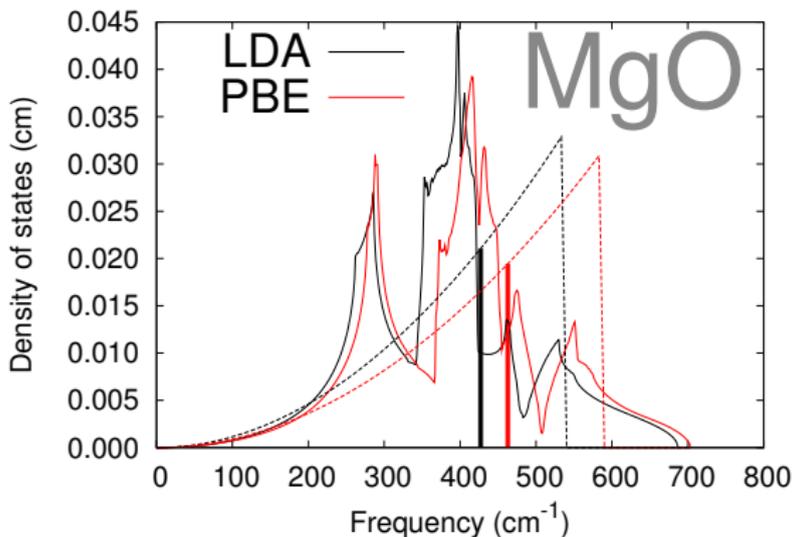
- Works well at low temperatures.
- Includes purely quantum vibrational effects (zero-point).
- Breaks down at higher temperatures due to the lack of anharmonicity. Impossible to model a melting process.

Statistical thermodynamics,

$$F_{vib}^* = \int_0^{\infty} \left[\frac{\omega}{2} + k_B T \ln \left(1 - e^{-\omega/k_B T} \right) \right] g(\omega; V, \mathbf{x}) d\omega$$

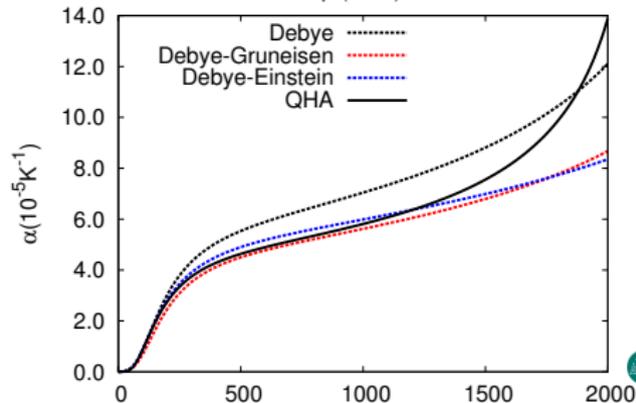
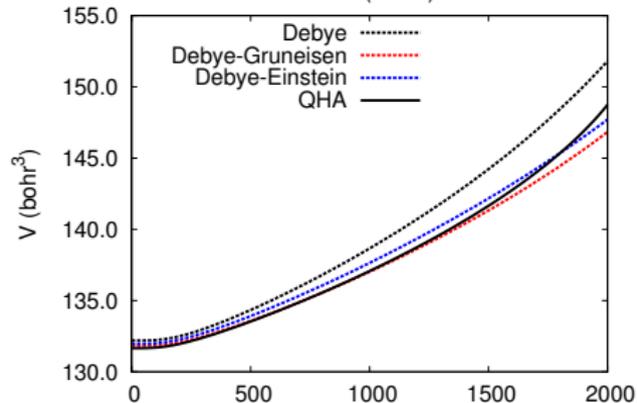
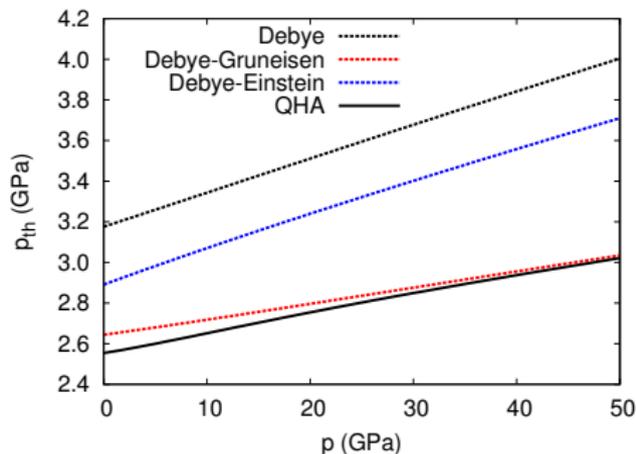
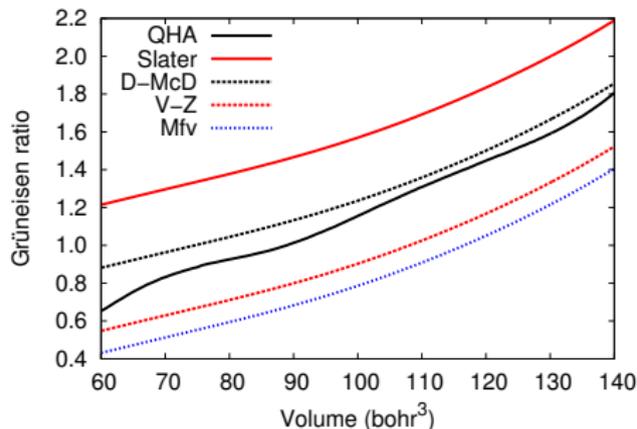


The quasiharmonic approximation (simplified models)



- Debye-Slater: $E(V)$ and σ , Poisson ratio erroneously assumed to be constant. Poor quasiharmonicity.
- Debye-Grüneisen: $E(V)$ and σ , a generalization of Debye-Slater where quasiharmonicity is introduced through an approximate gamma.
- Debye-Einstein: $E(V)$, σ and $\omega_i(\Gamma; V_0)$, same as Debye-Slater for the acoustic part but the optic branches are represented by ω_Γ . Good for molecular crystals.

The quasiharmonic approximation (simplified models)



The exchange-correlation functional approximation

The reference method for solid-state calculations is the **Density Functional Theory (DFT)**. We assume a periodic solid.

- 1 There is a one-to-one correspondence between the ground state electron density ρ of a system and the external potential imposed by the nuclei.
- 2 There is a variational principle that applies to the energy functional of the density.

The *exact* electron density of the system is the one that minimizes the functional:

$$E[\rho] = T[\rho] + \int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{\text{xc}}[\rho]$$

that gives rise to the *Kohn-Sham* equations:

$$\left\{ -\frac{1}{2}\nabla^2 + \hat{V}_n + \hat{V}_H + \hat{V}_{\text{xc}} \right\} \psi_i(\mathbf{x}) = \varepsilon_i\psi_i(\mathbf{x})$$

The exchange-correlation functional is **unknown** and approximations are used instead (LDA, GGA,...). Very active field of research. Jacob's ladder of functionals.



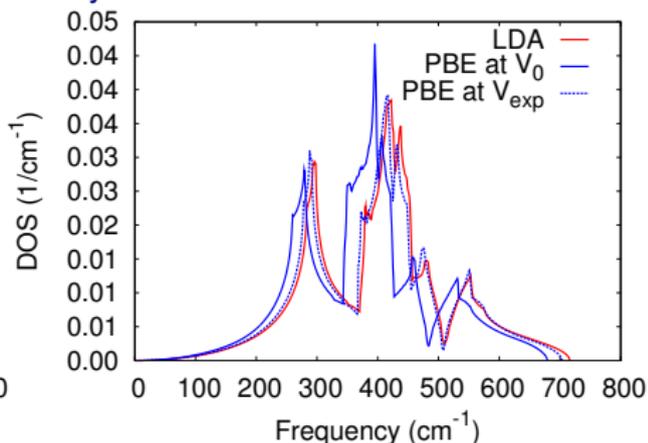
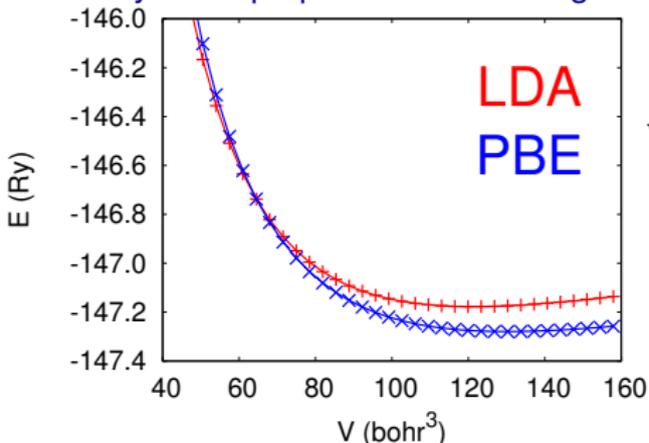
The exchange-correlation functional approximation

The QHA needs the shape of the atomic harmonic potentials:

- Second derivatives of the energy with respect to individual atomic displacements, the **force-constant matrix**,
- or its Fourier-transform, the **dynamical matrix**.

One method: the **Density Functional Perturbation Theory (DFPT)**, where the first-order perturbative correction to the electron density is calculated when the system is subject to an infinitesimal atomic displacement.

Summary: DFT imposes an **additional approximation** to the calculation of thermodynamic properties. Results significantly different.



A model system: magnesium oxide

Magnesium oxide

- Very simple system. Benchmark for many purposes implies wide availability of experimental data.
- Minority component of the Earth's mantle, in solid solution with FeO (magnesiowüstite).
- Possible use as pressure scale for extreme- pT diffraction experiments: extremely wide stability range (B1 phase) and chemical inertness. This application requires a very accurate EOS, $V(p, T)$. The calibration range is outside experimental bounds.

Summary of approximations

- Quasiharmonic approximation.
- Statically constrained approximation (**not** present).
- Density functional approximation.

Starting point

Grid of volumes (174) where the energy and the phonon DOS is calculated.

Functionals: LDA and PBE.



Step 1: the equation of state

The traditional EOS. Used in the experimental field to extrapolate to wide regions of pressure and temperature. Physical underlying principles. Non-linear fits and strong parameter correlation. Convergence problems. BM4:

$$f = \frac{1}{2} \left[(V_r/V)^{2/3} - 1 \right], \quad E = \sum_{k=0}^3 c_k f^k, \quad x = V/V_r$$

$$E = E_0 + \frac{9}{16} V_0 B_0 \frac{(x^{2/3} - 1)^2}{x^{7/3}} \{x^{1/3} (B'_0 - 4) - x(B'_0 - 6)\}$$

$$p = \frac{3}{8} B_0 \frac{x^{2/3} - 1}{x^{10/3}} \{3B'_0 x - 16x - 3x^{1/3} (B'_0 - 4)\}$$

Other EOS: Murnaghan, BMn, Poirier-Tarantola, Vinet, Holzapfel AP2, Baonza et al.

The traditional EOS do not yield stable values of the equilibrium volume and the energy derivatives. Extrapolation vs. interpolation.

	V_0 (bohr ³)	B_0 (GPa)	B'_0	B''_0 (GPa ⁻¹)
BM3	129.6757	158.70	3.9457	-0.0242
BM4	130.0741	151.23	4.1001	-0.0279
Vinet	130.7726	132.25	4.8306	-0.0584
AP2	130.0648	147.98	4.3026	-0.0367

Step 1: the equation of state

Polynomial EOS. Taylor expansion of the strain energy. Linear polynomial fits to any order. Averaging method that produces error bars, and is excellent for interpolation and energy derivatives.

$$E_n = \sum_{k=0}^n c_k f^k \Rightarrow P_{\text{average}} = \sum_{k=0}^n w_n E_n / \sum_{k=0}^n w_n \quad ; \quad w_i = \exp(-[N_i/n_i][S_i/S_{\min}])$$

<i>strain</i>	<i>EOS</i>	<i>f</i>	<i>f</i> _{(n+1)V}	<i>f</i> _{1V}
<i>Eulerian</i>	<i>BM</i>	$\frac{1}{2} (x^{-2/3} - 1)$	$(3n+2)sf_{nV}$	$-\frac{x^{-2/3}}{3V}$
<i>Lagrangian</i>	<i>Thomson</i>	$\frac{1}{2} (x^{2/3} - 1)$	$(3n-2)sf_{nV}$	$-\frac{x^{2/3}}{3V}$
<i>Natural</i>	<i>PT</i>	$\frac{1}{3} \ln x$	nsf_{nV}	$\frac{1}{3V}$
<i>Infinitesimal</i>	<i>Bardeen</i>	$1 - x^{-1/3}$	$(3n+1)sf_{nV}$	$\frac{(1-f)^4}{3V_r}$
x^3		x^3	$(3n-1)sf_{nV}$	$\frac{x^{1/3}}{3V}$
V		V	0	1

$$x = V/V_r, \eta = x^{1/3}.$$

Step 1: the equation of state

Different equations of state yield different and non-equivalent results. No criterion to choose the correct result. This problem translates to the free energy fits, and hence the calculation of thermodynamic properties.

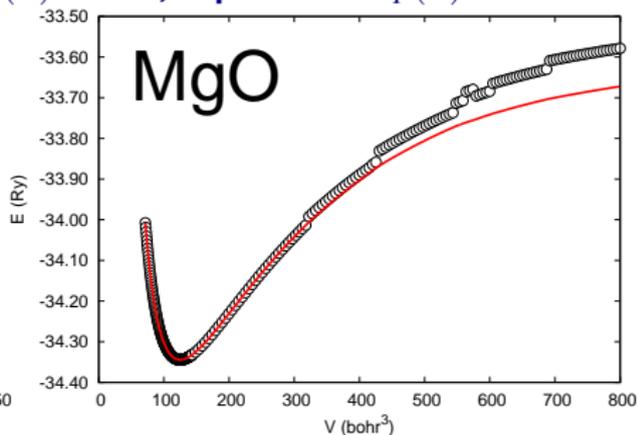
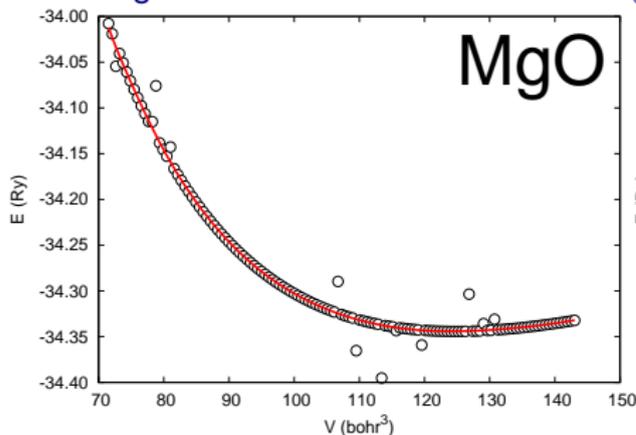
	V_0 (bohr ³)	B_0 (GPa)	B'_0	B''_0 (GPa ⁻¹)
BM3	129.6757	158.70	3.9457	-0.0242
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Vinet	130.7726	132.25	4.8306	-0.0584
AP2	130.0648	147.98	4.3026	-0.0367
avBM	130.0792(50)	150.49(26)	4.1284(91)	-0.0266(22)
avPT	130.0839(115)	150.34(24)	4.1284(169)	-0.0246(35)
avLagr	130.0806(205)	150.20(44)	4.1428(562)	-0.0237(139)
avInf	130.0815(49)	150.39(22)	4.1290(94)	-0.0255(31)

- Robust linear fit. When the non-linear fit converges, the results are identical for lower order-polynomials.
- Results of different strain families are equivalent.
- Statistics with polynomials allow establishing an error bar for calculated properties. Error bars statistically verified (bootstrap).
- Good quality derivatives of the (free) energy. Can not extrapolate, but it is possible to generate V_0 , B_0 for lower order EOS.
- Detection of noise and bad quality of data.



Step 1: the equation of state

The polynomial average technique is relatively insensitive to noisy data. It can also be augmented to treat discontinuous $E(V)$. **Also, experimental $p(V)$ data.**



May not be very interesting from the point of view of theory, but can be used to great success in fits to experimental data. E.g. obtaining equilibrium properties of an EOS (V_0, B_0, B'_0, \dots). Careful with overfitting.



Step 1: the equation of state

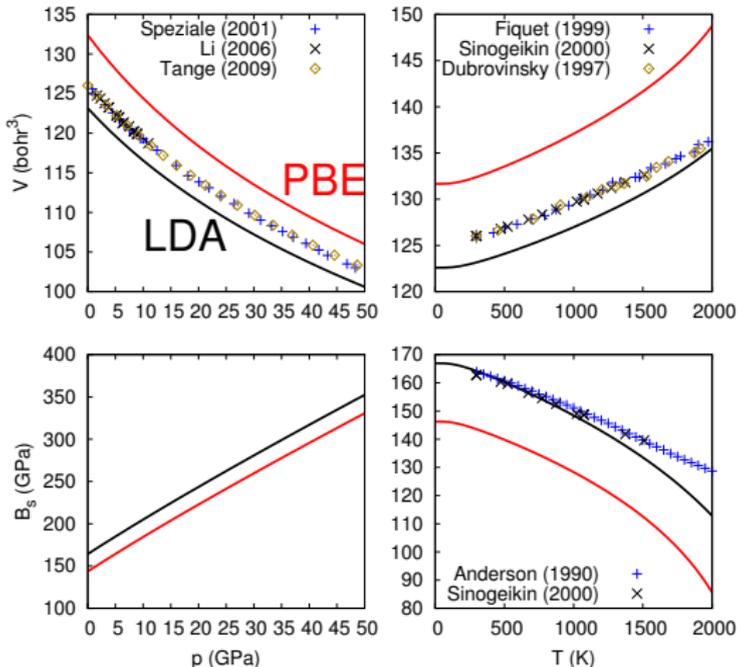
Asturfit: a free octave package for $E(V)$ and $p(V)$ data fits. Product of `gibbs2` prototyping.

- Octave fitting routines.
- Automatic fit of polynomial average to $E(V)$ data and $p(V)$ data (experimental).
- Determination of the equilibrium parameters.
- A number of traditional EOS can also be used, either in non-linear or linear fits where available.
- Statistical measure of the quality of the data, the fit and the error bars by the bootstrap technique.
- Bootstrap for noisy and discontinuous datasets.
- Same techniques included in the `gibbs2` code.
- Simple and comfortable use.
- Published under open license. Soon to be available in the MALTA web page.



Step 2: empirical energy corrections

- Choice of xc: source of uncertainty in DFT.
- Known tendencies in solids of popular functionals: LDA overbinds and PBE underbinds.
- No systematic ways of improving the results. **Not predictive.**



Step 2: empirical energy corrections

The systematic deviations in the exchange-correlation functionals can be corrected by using one or two accurate experimental results: ambient conditions volume (V_{exp}^0) and bulk modulus (B_{exp}^0). The corrections apply to the **static energy** and **require a thermal model to work**.

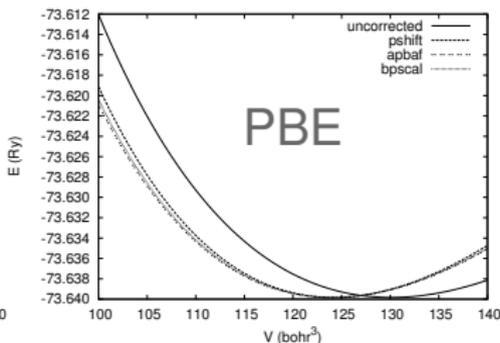
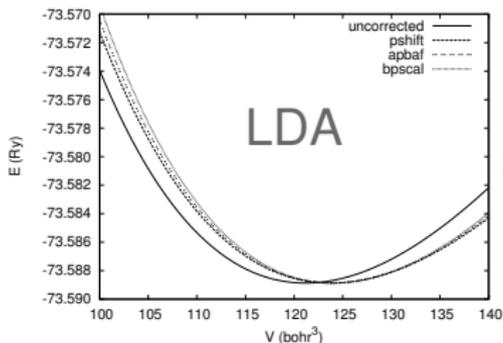
We explored several choices:

pshift

$$\tilde{E}_{\text{sta}}(V) = E_{\text{sta}}(V) + \Delta p V \quad ; \quad \Delta p = p(V_{\text{exp}}^0, T^0) = p_{\text{sta}}(V_{\text{exp}}^0) + p_{\text{th}}(V_{\text{exp}}^0, T^0)$$

apbaf

$$\tilde{E}_{\text{sta}}(V) = E_{\text{sta}}(V) + \frac{\alpha}{V} \quad ; \quad \alpha = -p(V_{\text{exp}}^0, T^0)(V_{\text{exp}}^0)^2.$$



Step 2: empirical energy corrections

Kunc and Syassen's observation: p/B_0 vs. V/V_0 transferable with V_0 and B_0 the static equilibrium volume and bulk modulus.

$$\frac{\tilde{E}'_{sta}(V)}{B_{exp}} = \frac{E'_{sta}\left(V \frac{V_0}{V_{exp}}\right)}{B_0}$$

The **bpscal** EEC is:

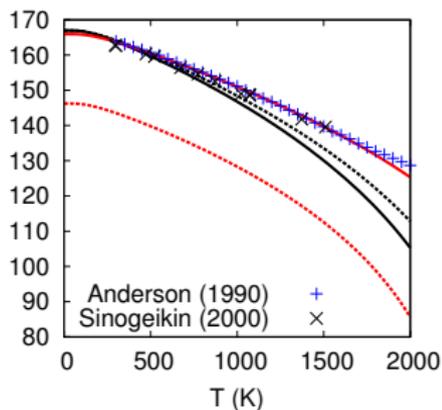
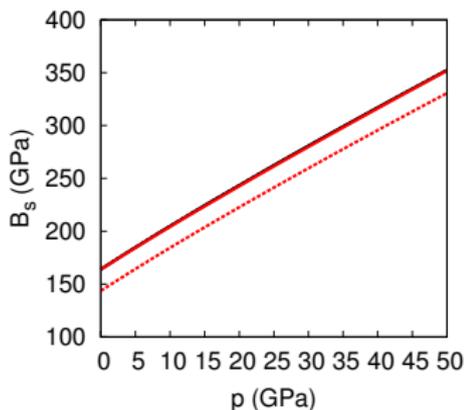
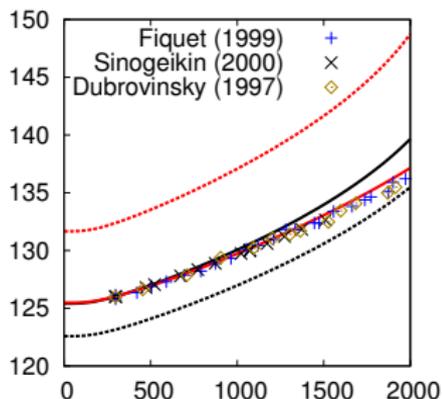
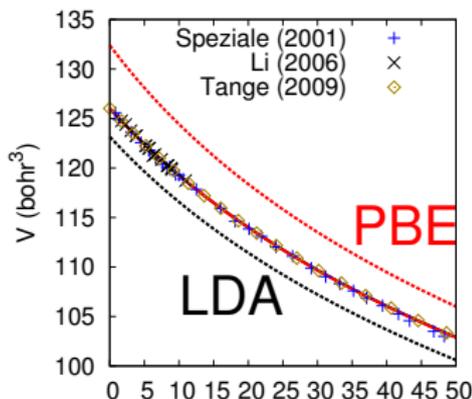
$$\tilde{E}_{sta}(V) = E_{sta}(V_0) + \frac{B_{exp}V_{exp}}{B_0V_0} \left[E_{sta}\left(V \frac{V_0}{V_{exp}}\right) - E_{sta}(V_0) \right]$$

The V_{exp} and B_{exp} are experimental parameters extrapolated to static conditions. Their value is chosen so that the static energy coupled with the thermal model reproduces the experimental room temperature values V_{exp}^0 and B_{exp}^0 .

$$B_{exp} = -B_0 \frac{p_{th}(fV_0, T^0)}{p_{sta}(fV_0)} \quad ; \quad f = \frac{V_{exp}^0}{V_{exp}}$$



Step 2: empirical energy corrections



Result: thermodynamic properties of MgO

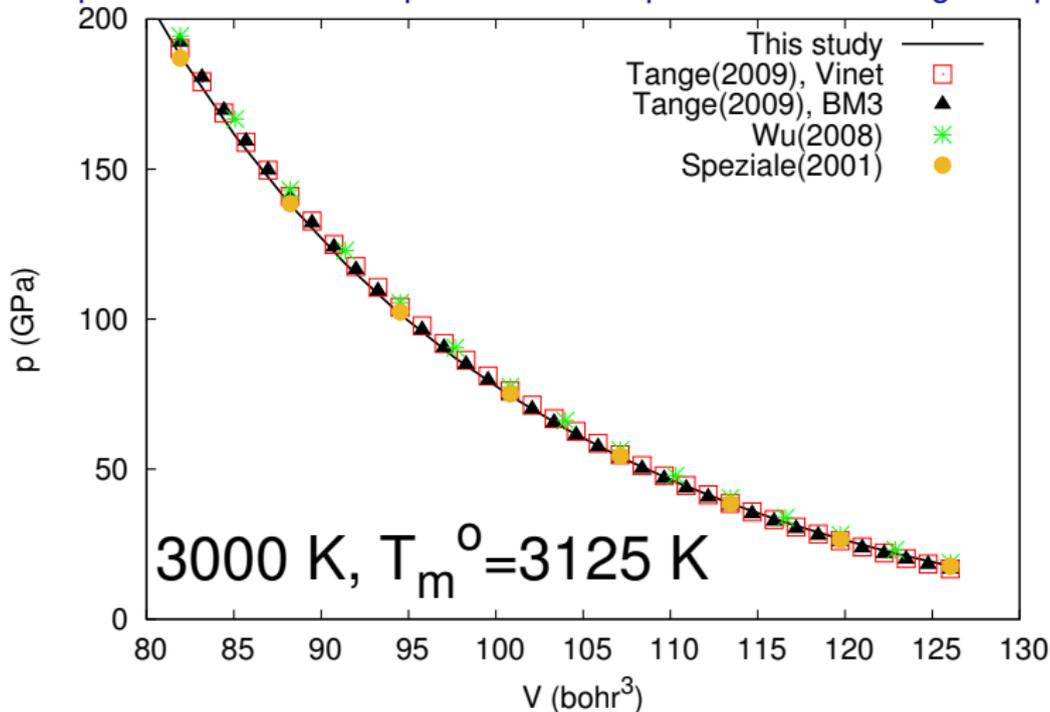
The three steps: (free) energy fitting, full QHA and empirical energy corrections allow us to predict thermodynamic properties with unprecedented accuracy in a wide range of pressures and temperatures.

	Room (0 GPa and 298.15 K)		(0 GPa and 1000 K)	
	PBEcorr	expt.	PBEcorr	expt.
V (bohr ³)	126.024(19)	126.025	129.708(84)	129.6
F_{vib} (kJ/mol)	11.4236(47)		-31.613(59)	
S (J/mol K)	27.0028(88)	27.18	82.853(56)	82.24
p_{th} (GPa)	2.624(15)	0.717	6.943(67)	4.96
B_T (GPa)	161.43(50)	161.3	141.2(20)	141
B_S (GPa)	163.72(50)	163.9	151.6(20)	151.1
α ($1 \cdot 10^{-5}$ K)	3.1002(97)	3.12	4.680(68)	4.47
C_V (J/mol K)	36.6821(50)	36.9	48.5530(28)	47.61
C_p (J/mol K)	37.2023(57)	37.409	52.132(55)	50.87
B'_T	4.173(43)		4.53(12)	
B''_T (GPa ⁻¹)	-0.0333(28)		-0.089(24)	
γ	1.53435(24)	1.54	1.5751(11)	1.54



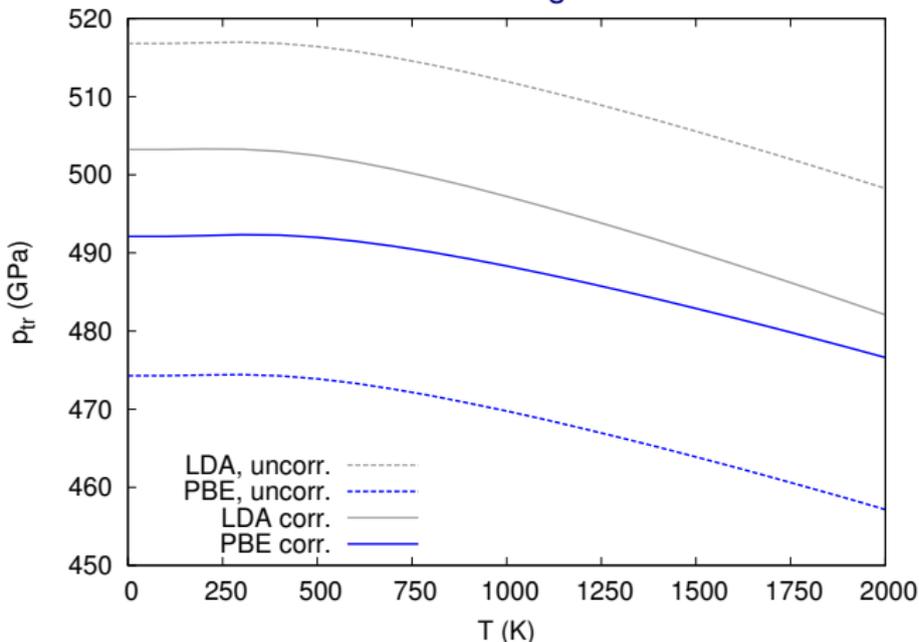
Result: a pressure scale for MgO

First principles equation of state of magnesium oxide: pressure scale for extreme pressure-temperature diffraction experiments. Comparison with existing extrapolations:



Result: phase diagram of MgO

Possible drawbacks of the empirical energy correction scheme: lack of experimental data. The B1 \rightarrow B2 transition of MgO is an excellent test.

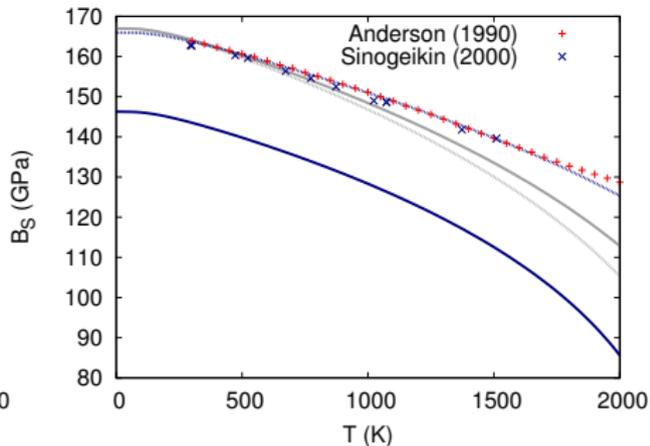
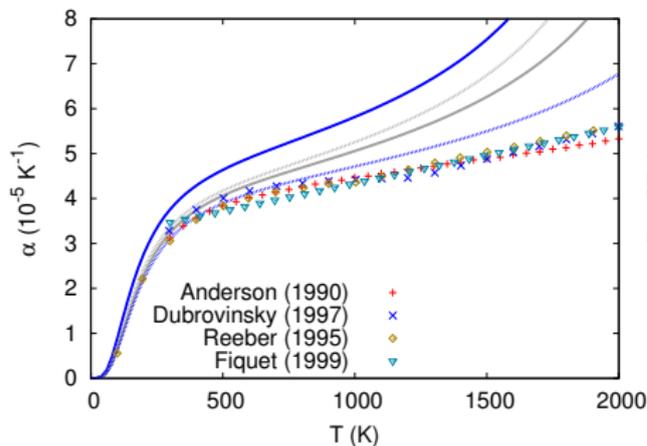


What if no room temperature experimental data are available? Use data at different p, T or transfer from a stable phase (van de Walle and Ceder).



Result: the quasiharmonic limit of validity

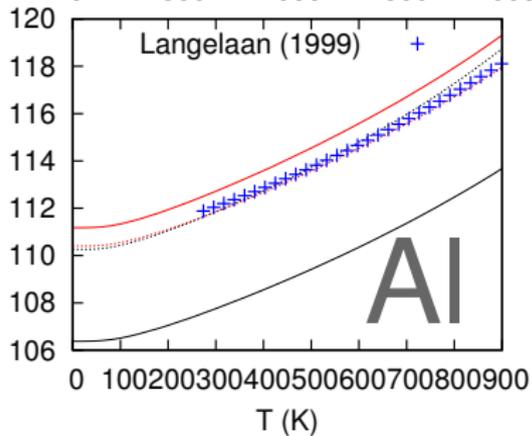
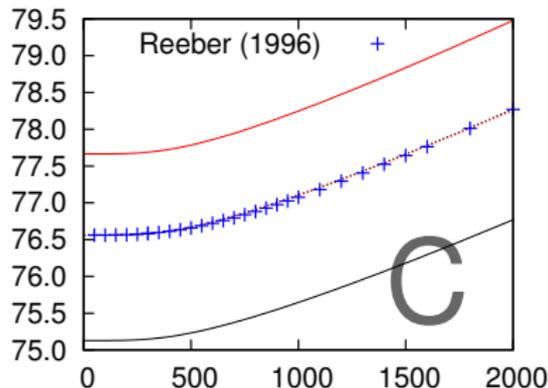
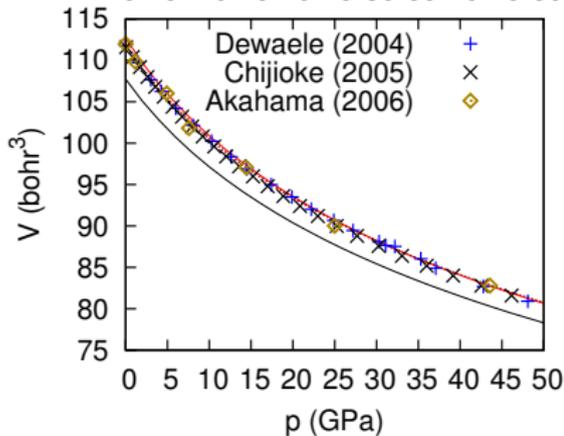
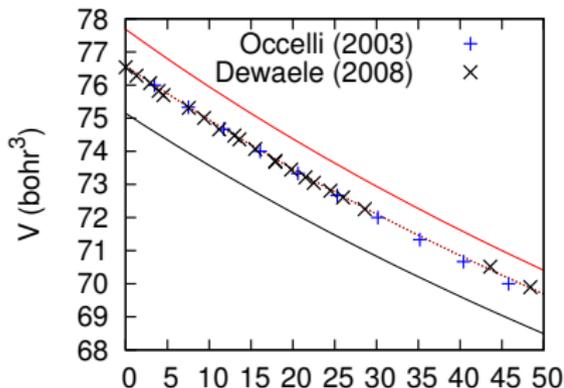
The QHA breaks down at high temperatures because of the lack of anharmonic effects.
Wentzcovitch criterion: use the point where $\alpha''(T) = 0$. Too restrictive for EOS or B_S ,
for example.



The unphysical softening at higher temperatures cancels with the LDA underbinding.
Explanation of LDA popularity in geophysics? The limit of validity of PBE is extended
by the energy correction. Risk of a very bad extrapolation.



Results for other systems



Summary: rigorous treatment of first-principles thermodynamics data

It is not possible to blindly predict the equation of state of a simple solid using the uncorrected DFT data alone.

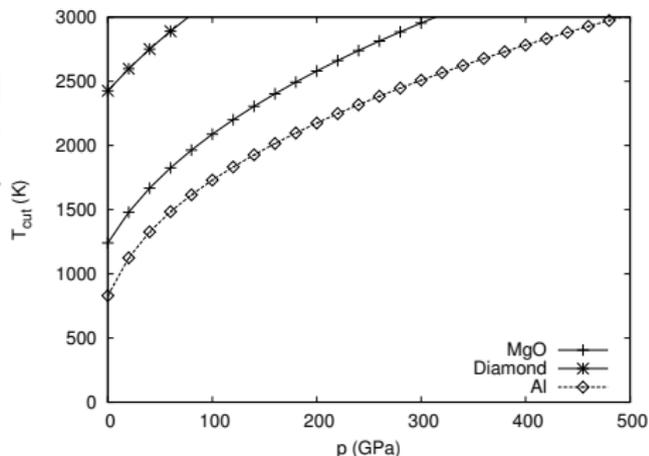
Three steps are key to make QHA+DFT a predictive tool:

- A good quality dataset ($E(V)$ and $g(\omega; V)$). Garbage in-garbage out still applies.
- Statistically sound fitting techniques to obtain static and free energy derivatives.
- Empirical energy corrections to rectify systematic deviations caused by the functional.

A wide range $V(p, T)$ can be proposed for the studied material using a Mie-Grüneisen-Debye fit to the QHA+DFT data in its region of validity.

$$p(V, T) = p_{T_0}(V) + \Delta p_{\text{th}}(V, T)$$

$$\Delta p_{\text{th}}(V, T) = \frac{3nR\gamma}{V} [D_3(\theta_D/T) - D_3(\theta_D/T_0)]$$



The Gibbs2 program

The original Gibbs is a very popular program that implements the Debye model approximation to QHA in solids. The intent with gibbs2: modernizing the original code. However, we implemented many new features.

- Rewritten in fortran90. New interface.
- New thermal models, including the full QHA. Varying degrees of accuracy and input requirements.
- Careful study of (free) energy fits. A number of EOS have been implemented. A companion code: `asturfit`.
- Empirical energy corrections.
- Automatic calculation of phase transitions, thermodynamic properties. Simple and efficient use.
- Published under open license. Soon to be available for the MALTA group.



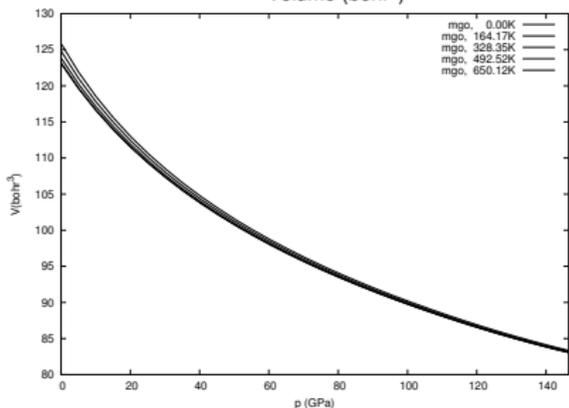
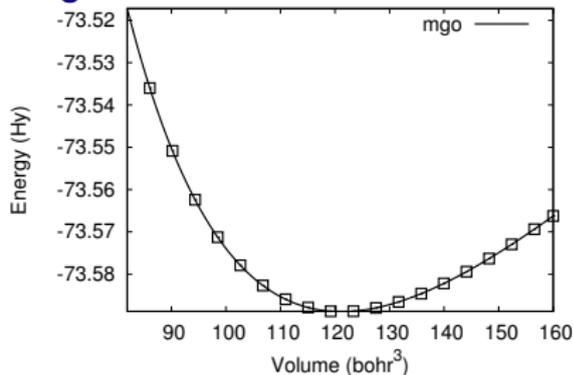
Use of gibbs2

Simplest use of gibbs2

```

1 mm 40.3044
2 vfree 2
3 phase mgo
4 81.88836 -73.51716594
5 86.03588 -73.53601334
6 ...
7 156.54373 -73.56937912
8 160.00000 -73.56625122
9 endphase

```

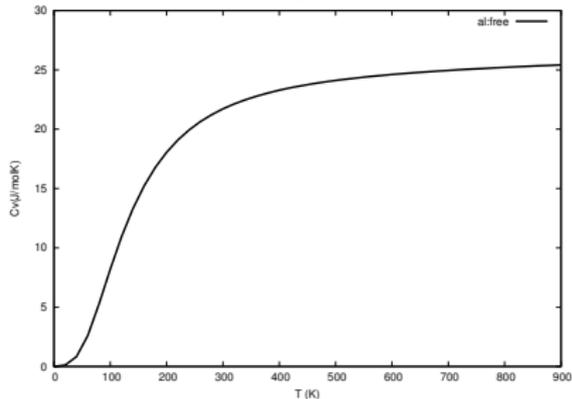
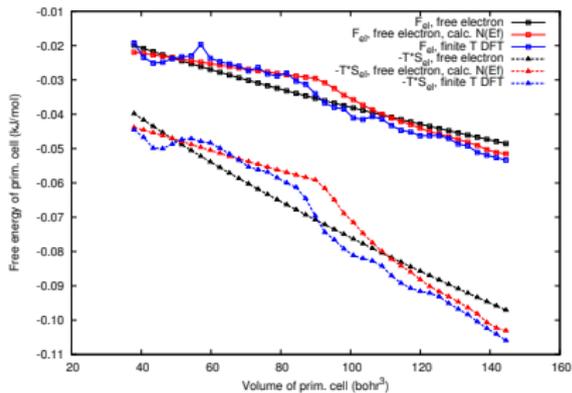


Use of gibbs2

Input for fcc Al.

```

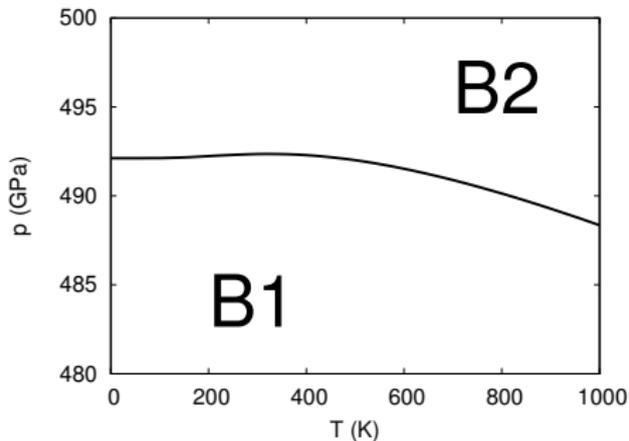
1 # Aluminium
2 mm 26.981538
3 vfree 1
4 pressure 0
5 temperature 0 20 900
6
7 # free electron model
8 phase Al:free file al.res \
9   tmodel debye_gruneisen dm \
10  units energy ry \
11  eec bpscal 112.04 72.7 \
12  elec sommerfeld free nelec 3
13 end
  
```



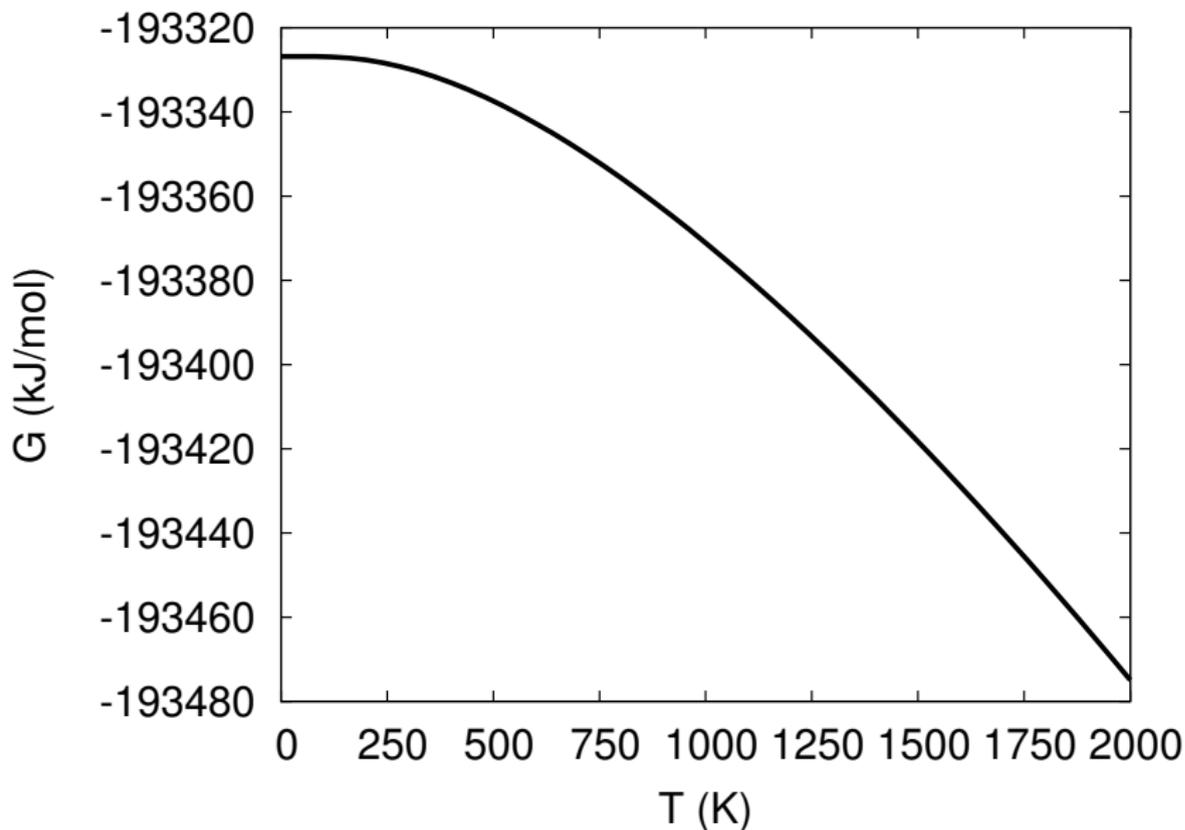
Use of gibbs2

Input for MgO phase diagram.

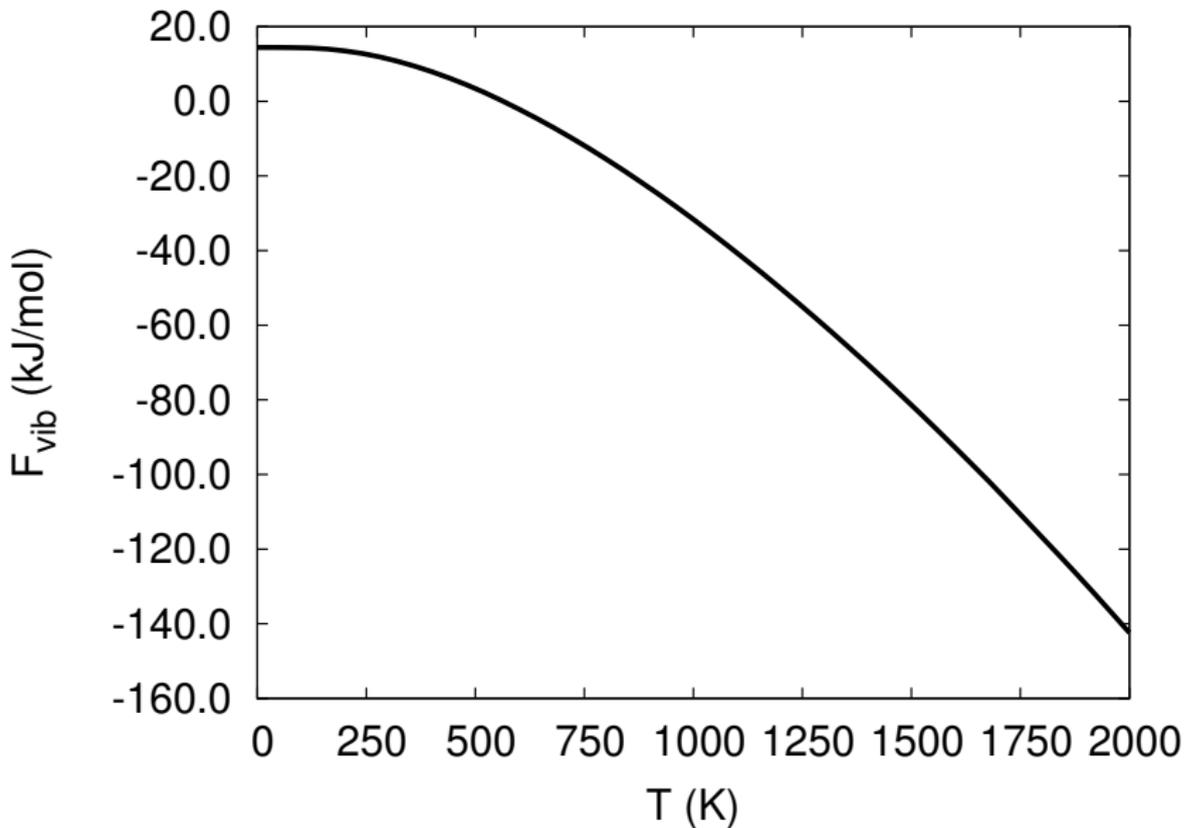
```
1 mm 40.3044
2 vfree 2
3 pressure 0 25 600
4 temperature 0 20 1000
5
6 phase B1 \
7   file ../dat/b1/b1.res \
8   tmodel qha \
9   units energy ry freq cm-1 \
10  prefix ../dat/mgo_pbe/ \
11  eec bpscal 126.025 161.3
12
13 phase B2 \
14   file ../dat/b2/b2.res \
15   tmodel qha \
16   units energy ry freq cm-1 \
17   prefix ../dat/mgob2_pbe/ \
18   eec use 1
19
20 end
```



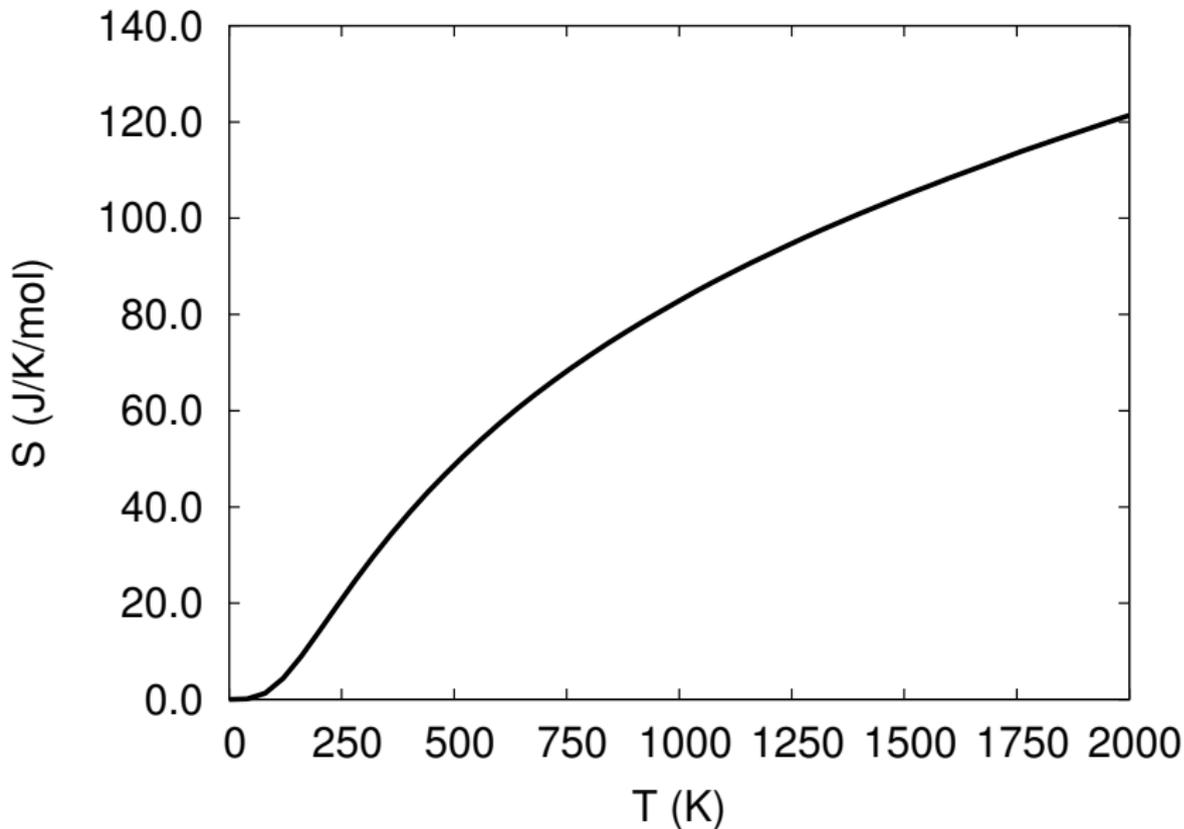
Thermodynamic properties gallery



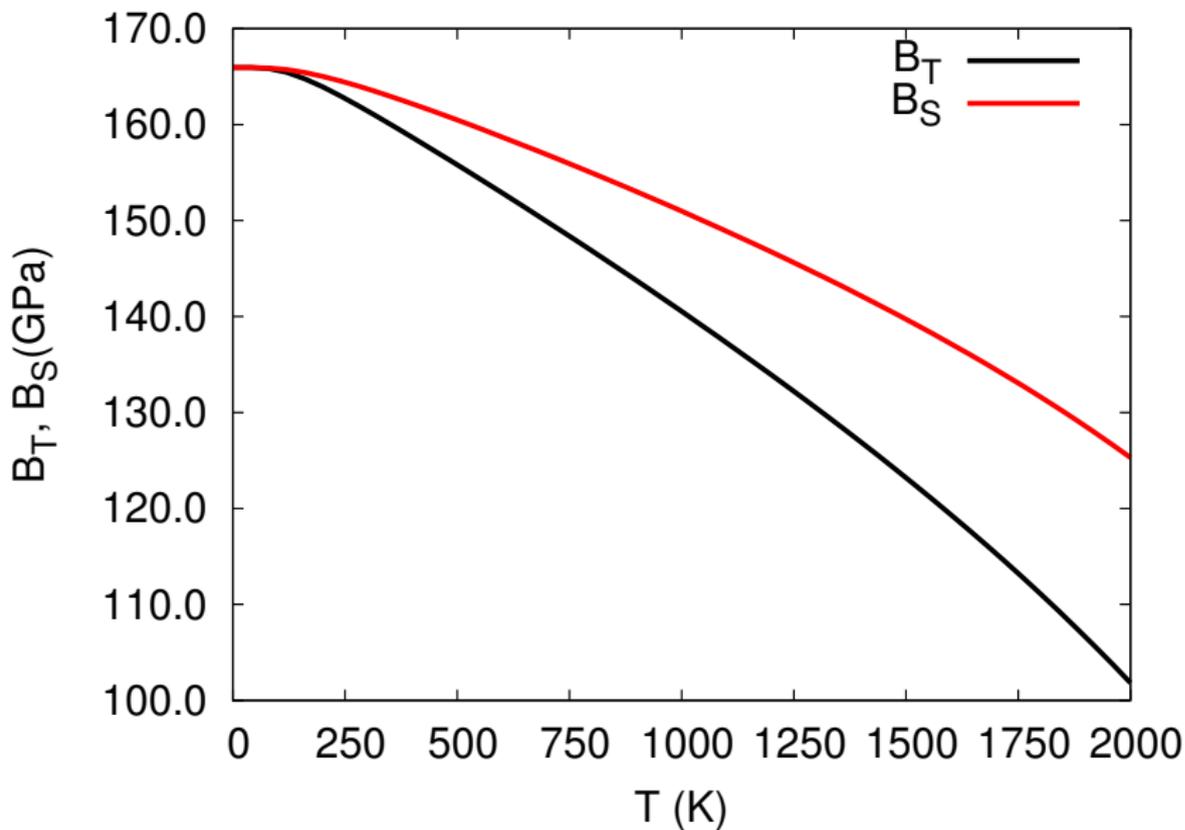
Thermodynamic properties gallery



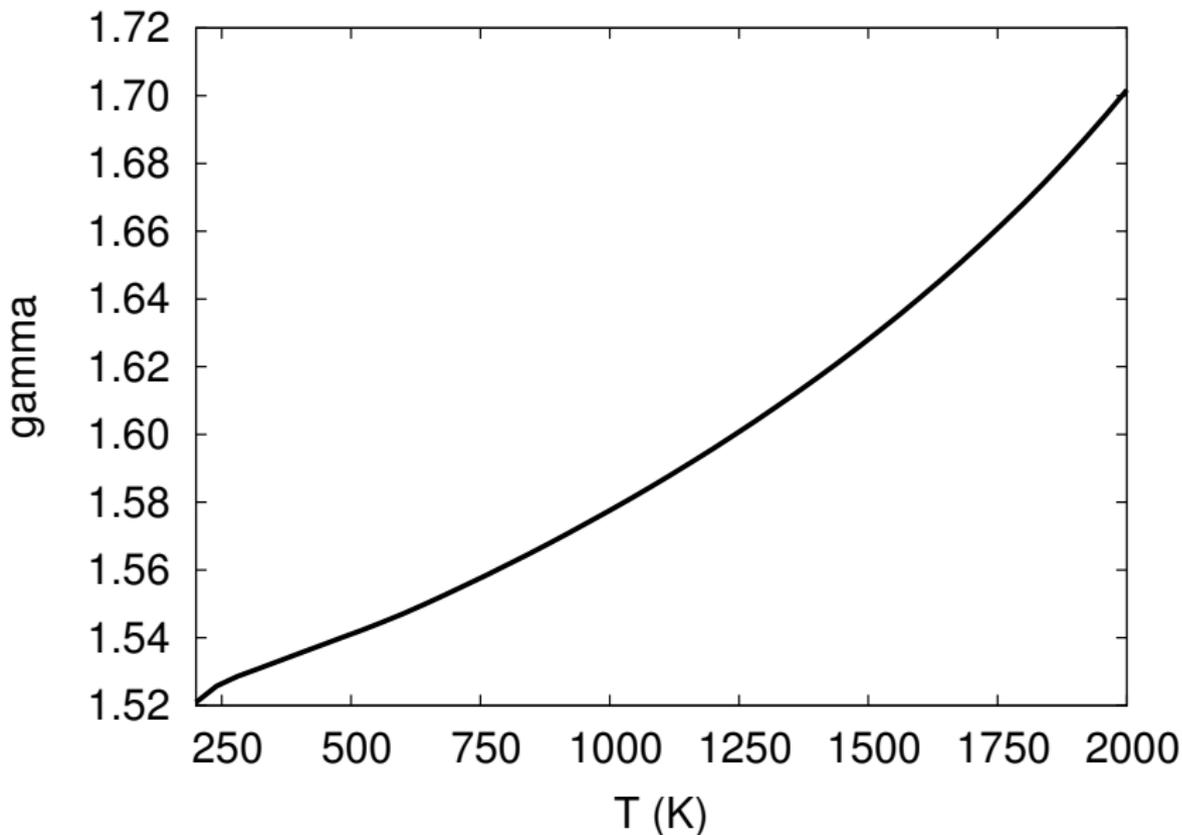
Thermodynamic properties gallery



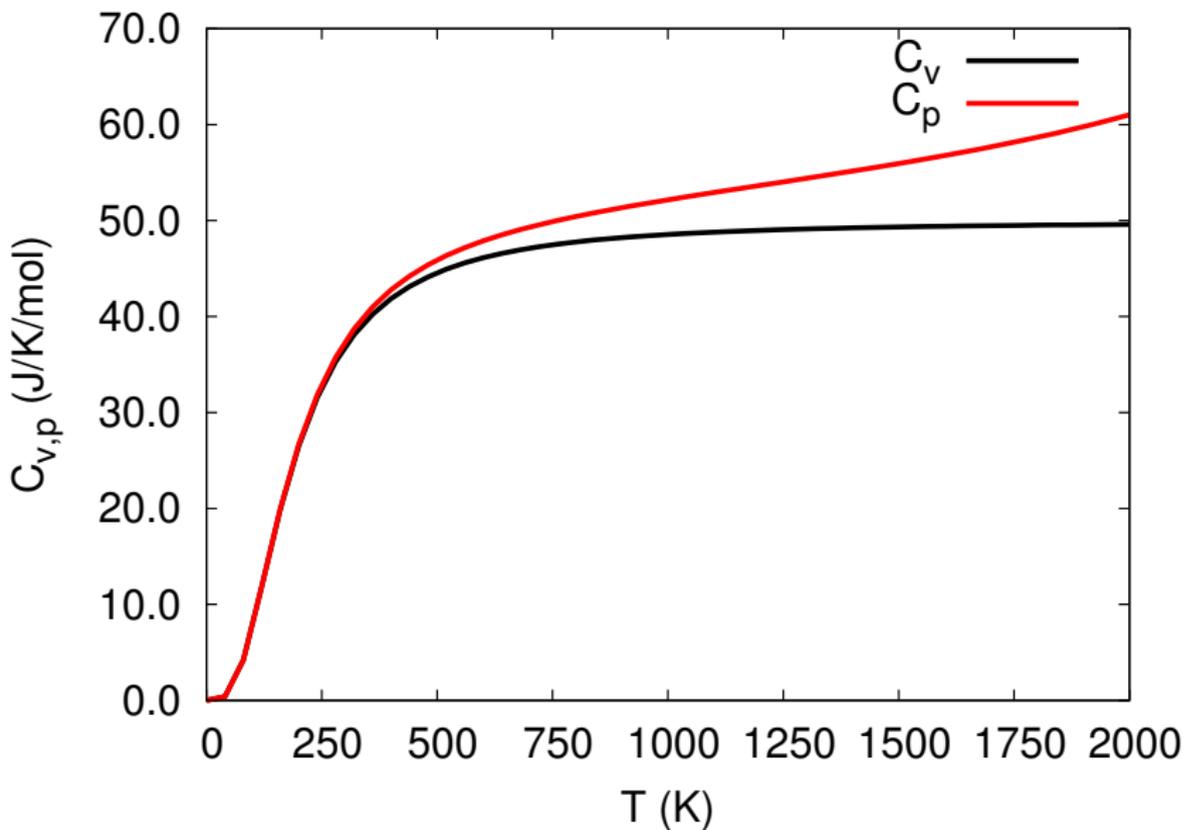
Thermodynamic properties gallery



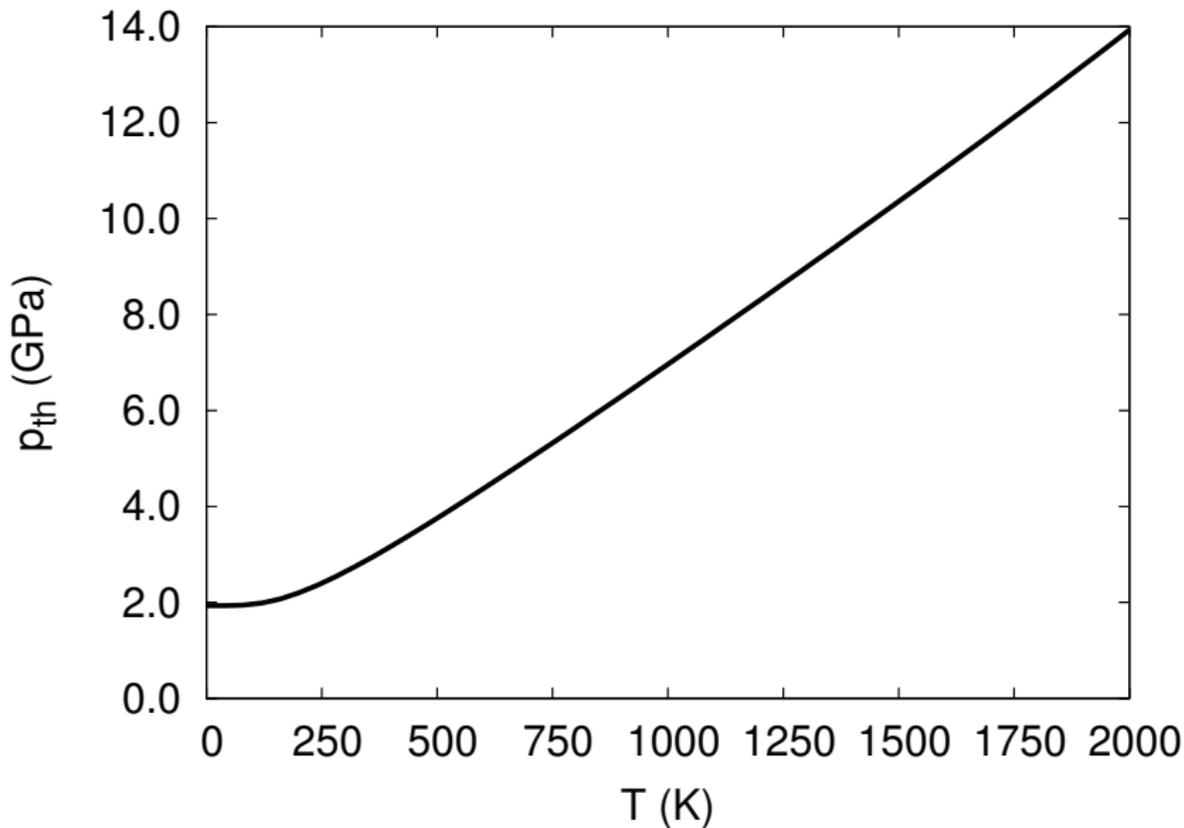
Thermodynamic properties gallery



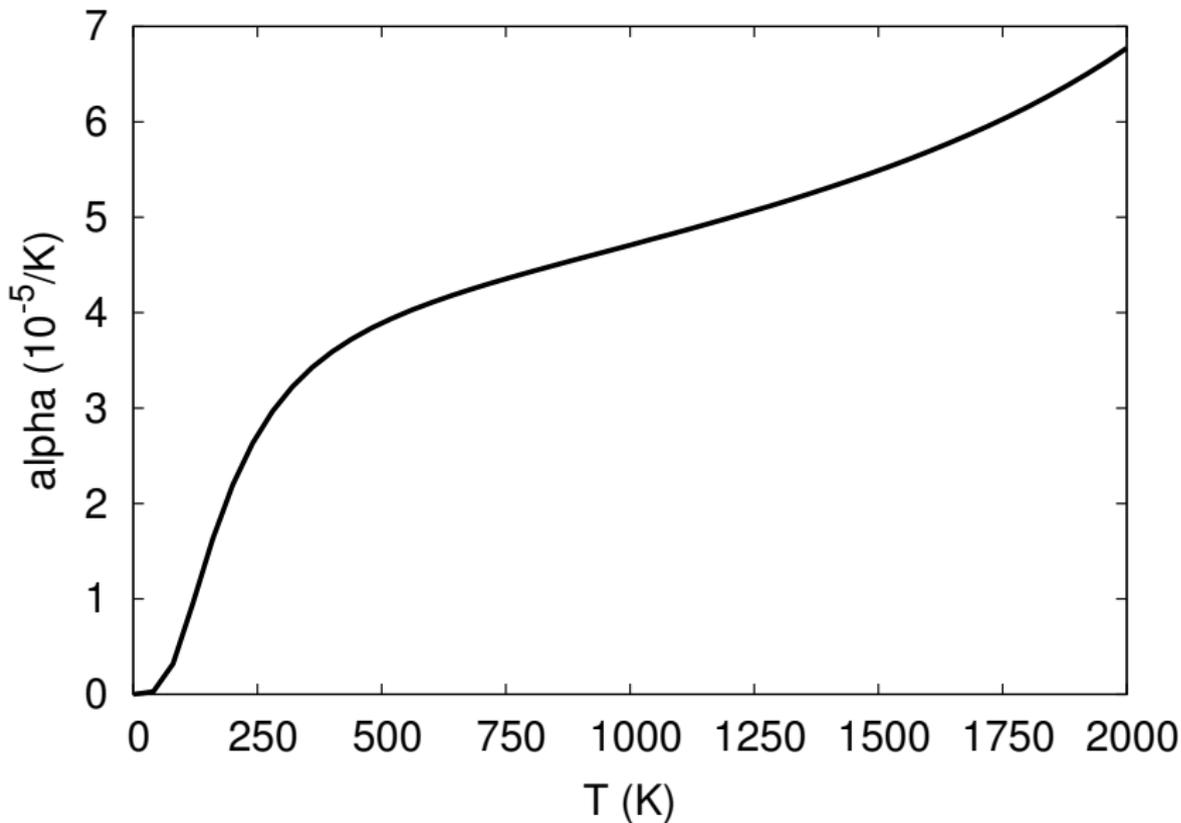
Thermodynamic properties gallery



Thermodynamic properties gallery



Thermodynamic properties gallery



Availability

- Any method able to provide static $E(V)$ data and phonon DOS as a function of volume can be used. Among the *ab initio* open source electronic structure codes: Quantum Espresso, abinit, siesta, ...
- The codes for fitting and for doing the complete analysis described here are open source and publicly available:
 - GIBBS2: *A new version of the quasi-harmonic model code. I Robust treatment of the static data.* Comput. Phys. Commun. **182** (2011) 1708.
 - GIBBS2: *A new version of the quasi-harmonic model code. II. Thermal models, features and implementation.* Comput. Phys. Commun. (2011, in press, doi:10.1016/j.cpc.2011.05.009).
- The technique and results have been described in:
 - *Equations of State in Solids. Fitting theoretical data, possibly including noise and jumps.* Comput. Theor. Chem. (2011, in press, doi:10.1016/j.comptc.2011.03.050)
 - *Rigorous treatment of first-principles data for quasiharmonic thermodynamics of solids: the case of MgO.* Phys. Rev. B (2011, in press)
 - *Very accurate equations of state and thermodynamics of solids using empirical corrections in the quasiharmonic approximation.* Phys. Rev. B (2011, submitted)



Conclusions

- First-principles calculations of thermodynamic properties is essential in the modelling of materials, geophysics,... as an alternative to experimental techniques.
- The vanilla QHA+DFT used in the literature today is not able to predict the equation of states or thermodynamic properties with accuracy.
- By using averages of strain polynomials to high order it is possible to remove the uncertainties caused by the equation of state used to represent the numerical $E(V)$ grid.
- The energy fitting techniques have been implemented in a easy to use octave interface (*asturfit*), that allows rapid processing of the data.
- The empirical energy corrections rectify systematic errors caused by the approximate exchange-correlation functional. PBE works systematically better than LDA.
- The QHA breaks down at high temperatures, but this limit can be estimated and p - V - T EOS can be used to extend the equation of state beyond this limit. It is possible to calculate state-of-the-art equations of state this way, and we have done it for diamond, fcc Al and MgO.
- All the above techniques have been implemented in the `gibbs2` program.

