Ab initio thermodynamics of solids under the quasiharmonic approach

Víctor Luaña (†) & Alberto Otero-de-la-Roza (‡)
(†) Departamento de Química Física y Analítica, Universidad de Oviedo
(‡) Universidad de California at Merced

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The need for a molecular engineering tool

- Columbus, Ohio (May 11, 2013) Chemical Abstracts Service (CAS) records 64,576,136 substances in CAS REGISTRY. The 50th entry was registered on sept. 7th, 2009.
- The 50th entry was registered on may. 24th, 2011.
- Some 12000 new entries are added everyday.
- The properties of most substances will remain unknown unless there is some previous hint of their importance.

- (January 1, 2013) The Cambridge Structural Database (CSD) records the crystal structure of 638598 different compounds (mostly organic and organometallic).
- The structure of most compounds will remain unknown, including the effect of $p$ and $T$ conditions.
“A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts.”

Albert Einstein (ca.1949)
Some Applications in Geophysics and Material Science
1. Molecular engineering tools

2. *ab initio* Thermodynamics of Crystals
   - The Standard Model of Material Science
   - Practical calculation of thermodynamic properties under QHA

3. Analytical Equations of State

4. DFT calculation of the electronic structure

5. Empirical Energy Corrections

6. Conclusions

7. Acknowledgements

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

\[
G(p, T, x) = E(V, x) + pV(x) + A_{vem}(V, T, x)
\]

(1)

where \( x \) represents the internal geometry of the crystal, \( V \) is the cell volume, \( E \) is the electronic energy. The Helmholtz energy \( A_{vem} \) term includes the contribution from lattice vibrations, free electrons in metals, magnons in paramagnetic materials, etc.

\( E(V, x) \) and \( p = -dE/dV \) is the source of the static approach, quite useful for a first analysis of the high pressure solid properties. Three steps are fundamental in the full thermal treatment:

- Fit an analytical Equation of State (EOS) to the \( E(V, x) \) discrete set of data.
  Objectives: (1) determine the equilibrium properties \( (V_0, E_0, B_0, B'_0, ...) \); (2) interpolate; (3) derive the curve; and perhaps (4) extrapolate.
- Scale the data if agreement with the experiment is critical.
- Determine thermal effects (including zero point energy).
Practical calculation of thermodynamic properties under QHA

- **HA (harmonic approximation):** Given an equilibrium configuration of the crystal (i.e. zero forces: \( \nabla q E = 0 \)), where \( q_i = \sqrt{M_i(R_i - R_0^i)} \) for atom \( i \) each atom moves in an harmonic potential \( K = \nabla q \otimes \nabla q E \).

- **QHA (quasiharmonic approximation):** The force constant matrix depends on the crystal volume: \( K(V) \).

- At difference from HA, the QHA solid expands when the temperature is raised.

- Density Functional Perturbation Theory [1] produces analytically the \( ab initio \) \( K \) matrix.

- Frequencies and vibrational modes (phonons) are obtained by diagonalizing \( K \). Sampling the frequencies on the first Brillouin zone produces the phonon-Density of States (\( \phi \)-DOS).

**Vibrational free energy in QHA:**

\[
A_{vib}(V, x, T) = \int_0^\infty g(\omega; V, x) \left[ \frac{\hbar \omega}{2} + k_B T \ln \left( 1 - e^{-\frac{\hbar \omega}{k_B T}} \right) \right] d\omega.
\]  

(2)
Molecular engineering tools

**ab initio Thermodynamics of Crystals**

**Analytical Equations of State**
- The Murnaghan EOS
- The Birch-Murnaghan EOS family
- Non-linear fitting and convergence of results
- BM as a polynomial strain family
- BM linear fitting procedure
- An indefinite number of polynomial strain families
- Average of polynomials and predicted error bars
- Do the different average strain families converge and agree?
- Resampling error bars

**DFT calculation of the electronic structure**

**Empirical Energy Corrections**

**Conclusions**
The Murnaghan EOS

Murnaghan historical paper [2] is based on the principle of conservation of mass combined with Hooke's law for an infinitesimal variation of stress in the solid. An equivalent result, however, can be simply obtained by assuming a linear variation of the bulk modulus with pressure, \( B(p) = B_0 + B'_0 p \), to integrate \( B = -V \left( \frac{\partial p}{\partial V} \right)_T \):

\[
V(p) = V_0 \left( 1 + \frac{B'_0}{B_0} p \right)^{-1/B'_0} \tag{3}
\]

which can be inverted to

\[
p(V) = \frac{B_0}{B'_0} \left[ \left( \frac{V_0}{V} \right)^{B'_0} - 1 \right]. \tag{4}
\]

The hydrostatic work equation, \( dW = -pdV \), can then be used to integrate:

\[
E = E_0 + \frac{B_0 V}{B'_0} \left[ \frac{(V_0/V)^{B'_0}}{B'_0 - 1} + 1 \right] - \frac{B_0 V_0}{B'_0 - 1} \tag{5}
\]

for the volume dependent energy under null temperature conditions.
The Birch-Murnaghan EOS family

**Origin:** Taylor expansion of the strain energy \( E = \sum_{k=0}^{n} c_k f^k \).

**Eulerian strain:** \( f = \frac{1}{2} \left[ \left( \frac{V_r}{V} \right)^{2/3} - 1 \right] \)

**Conditions:** \( \lim_{f \to 0} \left\{ V; E; p = -\frac{dE}{dV}; B = -V \frac{dp}{dV}; B' = \frac{dB}{dp}; \ldots \right\} = \{ V_0; E_0; 0; B_0; B'_0; \ldots \} \)

**Results:** \( V_r = V_0; \)
  
  \( c_0 = E_0; \)
  
  \( c_1 = 0; \)
  
  \( c_2 = \frac{9}{2} V_0 B_0; \)
  
  \( c_3 = \frac{9}{4} V_0 B_0 (B'_0 - 4); \)
  
  \( c_4 = \frac{3}{8} V_0 B_0 \{ 9[B_0 B'_0 + (B'_0)^2] - 63B'_0 + 143 \}; \ldots \)

**BM2:** Let \( x = \left( \frac{V}{V_0} \right) \).

\[
E = E_0 + \frac{9}{8} B_0 V_0 (x^{-2/3} - 1)^2, \quad p = \frac{3}{2} B_0 \left( x^{-7/3} - x^{-5/3} \right). \tag{6}
\]

**BM3:**

\[
E = E_0 + \frac{9}{16} V_0 B_0 \frac{(x^{2/3} - 1)^2}{x^{7/3}} \left\{ x^{1/3} (B'_0 - 4) - x(B'_0 - 6) \right\}, \ldots \tag{7}
\]
Non-linear fitting and convergence of results

Test system: Rock-salt phase of MgO.

Calculations: QUANTUM ESPRESSO [3] LDA using plane-waves and norm-conserving pseudopotentials. Very strict conditions: cutoff energy (80 Ry), $k$-mesh (shifted $4 \times 4 \times 4$ Monkhorst-Pack grid) and $q$-mesh ($6 \times 6 \times 6$).

Data points: linear grid of 129 points in the volume range 72–143 bohr$^3$.

### Equilibrium properties of the rock-salt phase of MgO.

<table>
<thead>
<tr>
<th>EOS</th>
<th>$V_0$ (bohr$^3$)</th>
<th>$B_0$ (GPa)</th>
<th>$B'_0$</th>
<th>$B''_0$ (GPa$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Murn.</td>
<td>124.885</td>
<td>177.23</td>
<td>3.505</td>
<td></td>
</tr>
<tr>
<td>Vinet</td>
<td>124.783</td>
<td>165.42</td>
<td>4.524</td>
<td></td>
</tr>
<tr>
<td>BM3</td>
<td>124.824</td>
<td>170.04</td>
<td>4.116</td>
<td>$-0.0236$</td>
</tr>
<tr>
<td>PT3</td>
<td>124.637</td>
<td>160.80</td>
<td>5.212</td>
<td>$-0.0904$</td>
</tr>
<tr>
<td>BM4</td>
<td>124.821</td>
<td>169.27</td>
<td>4.171</td>
<td>$-0.0254$</td>
</tr>
<tr>
<td>PT4</td>
<td>124.847</td>
<td>169.24</td>
<td>4.089</td>
<td>$-0.0162$</td>
</tr>
</tbody>
</table>

The dispersion of fitting parameters is very large (17 GPa for $B_0$). The five parameter EOS (BM4 and PT4) are more in agreement, but we can do better with our excellent input data. Converging BM3 and BM4 is easy, BM5 is difficult, who wants to try BM10?
BM as a polynomial strain family

The big question: If the BM family comes from assuming a polynomial $E(f)$ equation, why do not use a linear fit for the polynomial coefficients?

Is the result of linear and nonlinear fittings identical?

<table>
<thead>
<tr>
<th>Model</th>
<th>Fit</th>
<th>$V_0$</th>
<th>$E_0$</th>
<th>$B_0$</th>
<th>$B'_0$</th>
<th>$B''_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM3</td>
<td>nonlin.</td>
<td>124.823661</td>
<td>-34.344311</td>
<td>170.0414</td>
<td>4.115715</td>
<td>—</td>
</tr>
<tr>
<td>BM3</td>
<td>lin.</td>
<td>124.823661</td>
<td>-34.344311</td>
<td>170.041394</td>
<td>4.115715</td>
<td>-0.023630</td>
</tr>
<tr>
<td>BM4</td>
<td>nonlin.</td>
<td>124.821340</td>
<td>-34.344283</td>
<td>169.2683</td>
<td>4.171190</td>
<td>-0.025412</td>
</tr>
<tr>
<td>BM4</td>
<td>lin.</td>
<td>124.821340</td>
<td>-34.344283</td>
<td>169.268283</td>
<td>4.171190</td>
<td>-0.025412</td>
</tr>
<tr>
<td>BM12</td>
<td>lin.</td>
<td>124.824369</td>
<td>-34.344285</td>
<td>169.319792</td>
<td>4.151925</td>
<td>-0.024118</td>
</tr>
</tbody>
</table>

- Linear BM fittings can be done precise and efficiently to any order required by the data
- Linear fittings can be generalized to many strain definitions.
BM linear fitting procedure

1. Get the eulerian strain $f = ((V/V_r)^{-2/3} - 1)/2$. $V_r$ is a reference volume.

2. Linear fitting to the $E(f) = \sum_{0}^{n} c_k f^k$ polynomial.

3. Get minimum of $E(f)$ to determine the equilibrium properties.

4. Get the derivatives $E_{nf} \equiv d^n E/df^n$.

5. Determine $f_{nv} = d^n f/dV^n$. For the eulerian strain:

   $$f_{(n+1)V} = -(3n + 2)f_{nv}/(3V), \quad f_{1V} = -(1/3V)(V_r/V)^{2/3}, \quad n = 1, 2, 3, ...$$ (8)

6. Obtain $E_{nv} = d^n E/dV^n$:

   $$E_{1V} = E_{1f} f_{1V};$$ (9)

   $$E_{2V} = f_{1V}^2 E_{2f} + f_{2V} E_{1f};$$ (10)

   $$E_{3V} = f_{1V}^3 E_{3f} + 3f_{1V} f_{2V} E_{2f} + f_{3V} E_{1f};$$ (11)

   $$E_{4V} = f_{1V}^4 E_{4f} + 6f_{1V} f_{2V} E_{3f} + (4f_{1V} f_{3V} + 3f_{3V}^2) E_{2f} + f_{4V} E_{1f}; ...$$ (12)

7. Finally

   $$p = -E_{1V}; \quad B = VE_{2V}; \quad B_p' = -\frac{VE_{3V}}{E_{2V}} - 1; \quad B''_p = E_{2V}^{-3} [V(E_{4V}E_{2V} - E_{3V}^2) + E_{3V} E_{2V}]; ...$$ (13)
An indefinite number of polynomial strain families

<table>
<thead>
<tr>
<th>strain</th>
<th>EOS</th>
<th>( f )</th>
<th>( f_{(n+1)V} )</th>
<th>( f_{1V} )</th>
<th>( s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>eulerian</td>
<td>BM</td>
<td>( \frac{1}{2} \left( x^{-2/3} - 1 \right) )</td>
<td>(3(n)+2)(sf_{nV})</td>
<td>(-\frac{x^{-2/3}}{3V})</td>
<td>(-\frac{1}{3V})</td>
</tr>
<tr>
<td>lagrangian</td>
<td>Thomson</td>
<td>( \frac{1}{2} \left( x^{2/3} - 1 \right) )</td>
<td>(3(n)-2)(sf_{nV})</td>
<td>(-\frac{x^{2/3}}{3V})</td>
<td>(-\frac{1}{3V})</td>
</tr>
<tr>
<td>natural</td>
<td>PT</td>
<td>( \frac{1}{3} \ln x )</td>
<td>( nsf_{nV} )</td>
<td>( \frac{1}{3V} )</td>
<td>(-\frac{1}{V} )</td>
</tr>
<tr>
<td>infinitesimal</td>
<td>Bardeen</td>
<td>( 1-x^{-1/3} )</td>
<td>(3(n)+1)(sf_{nV})</td>
<td>( \left(1-f\right)^4 )</td>
<td>(-\frac{1}{3V} )</td>
</tr>
</tbody>
</table>

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

**BM:** Birch-Murnaghan [2, 4, 5]; Thomson [6]; **PT:** Poirier-Tarantola [7]; Bardeen [8].
Average of polynomials and predicted error bars

Idea:

Produce a better polynomial by averaging several strain polynomials according to their efficiency.

- The square sum of residuals: \( S_i = \sum_k [E_k - E(V_k)]^2 \).
- \( w_i = [N_i/n_i][S_i/S_{\text{min}}] \), where \( N_i \) is the number of data, \( n_i \) is the degree of the polynomial, and \( S_{\text{min}} = \min_i S_i \).
- A normalized probability distribution is defined as \( P_i = e^{-w_i}/(\sum_k e^{-w_k}) \) (method 1), or \( P_i = e^{-w_i^2}/(\sum_k e^{-w_k^2}) \) (method 2).
- The \( P_i \) are used to: (1) average the polynomial coefficients, thus defining an average polynomial; and (2) average the equilibrium properties of the individual polynomials, determining in this way the probability distribution of the properties (mean, standard deviation, skew, kurtosis, etc).
- Use bootstrap sampling when data is noisy.

This method can be used with arbitrary strain polynomial families.
Do the different average strain families converge and agree?
The results are stable (within the predicted error bars) for the many experiments that we have done: (1) decreasing the 129 volume points to 65, 33, 17, or increasing them to 257, 1025, 2049; (2) moving the grid points; (3) changing the volume range up to 1/2 or 2 times; ...

The different strain families agree.

For a good set of data, the error bars are small, orders of magnitude better than the errors currently assumed by using BM3, BM4 or Vinet.

**Equilibrium properties of MgO**

<table>
<thead>
<tr>
<th>EOS</th>
<th>(V_0) (bohr(^3))</th>
<th>(B_0) (GPa)</th>
<th>(B'_0)</th>
<th>(B''_0) (GPa(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM3</td>
<td>124.823661</td>
<td>170.0414</td>
<td>4.115715</td>
<td></td>
</tr>
<tr>
<td>BM4</td>
<td>124.821340</td>
<td>169.2683</td>
<td>4.171190</td>
<td></td>
</tr>
<tr>
<td>Vinet</td>
<td>124.783430</td>
<td>165.4184</td>
<td>4.524436</td>
<td></td>
</tr>
<tr>
<td>avg14BM</td>
<td>124.82372(83)</td>
<td>169.314(20)</td>
<td>4.1593(58)</td>
<td>-0.02461(85)</td>
</tr>
</tbody>
</table>

Contrary to the current opinion, the average of strain polynomials produces a significative value for \(B_0\), \(B'_0\), and \(B''_0\). In the case of \(B'''_0\) the error bar is larger than the predicted value.
The *resampling* method (aka Monte Carlo statistics) is a standard technique for (a) estimating the precision of sample statistics by using subsets of available data (*jackknifing*) or drawing randomly with replacement from a set of data points (*bootstrapping*); and (b) validating models by using random subsets (*bootstrapping*, cross validation).

### MgO: BM6 fitting to a resampling of the 129 data points.

<table>
<thead>
<tr>
<th>sample</th>
<th>points</th>
<th>( V_0 ) (bohr(^3))</th>
<th>( B_0 ) (GPa)</th>
<th>( B'_0 )</th>
<th>( B''_0 ) (GPa(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^2)</td>
<td>50–76</td>
<td>124.82385(36)</td>
<td>169.3117(78)</td>
<td>4.1618(13)</td>
<td>-0.02489(17)</td>
</tr>
<tr>
<td>(10^3)</td>
<td>48–79</td>
<td>124.82381(34)</td>
<td>169.3105(82)</td>
<td>4.1620(12)</td>
<td>-0.02491(15)</td>
</tr>
<tr>
<td>(10^4)</td>
<td>45–84</td>
<td>124.82381(34)</td>
<td>169.3107(75)</td>
<td>4.1620(11)</td>
<td>-0.02491(15)</td>
</tr>
<tr>
<td>(10^5)</td>
<td>39–89</td>
<td>124.82381(34)</td>
<td>169.3107(75)</td>
<td>4.1620(11)</td>
<td>-0.02491(15)</td>
</tr>
<tr>
<td>(10^6)</td>
<td>39–91</td>
<td>124.82381(34)</td>
<td>169.3107(75)</td>
<td>4.1620(11)</td>
<td>-0.02491(15)</td>
</tr>
<tr>
<td>avg14BM</td>
<td></td>
<td>124.82372(83)</td>
<td>169.314(20)</td>
<td>4.1593(58)</td>
<td>-0.02461(85)</td>
</tr>
</tbody>
</table>

The error bars of the strain polynomials average method are conservative.
1 Molecular engineering tools

2 ab initio Thermodynamics of Crystals

3 Analytical Equations of State

4 DFT calculation of the electronic structure
   - Density Functional Theory
   - The Kohn-Sham method
   - The Jacob’s ladder metaphor

5 Empirical Energy Corrections

6 Conclusions

7 Acknowledgements

8 Bibliography
The solid state physics approach: Density Functional Theory

Much is due to the seminal work of J.C. Slater and coworkers (Xα and APW methods, for instance), Wigner-Seitz (cellular method), Philips-Kleinman (pseudopotentials), . . . However, nowadays is common to start from the Hohenberg-Kohn theorems (1964):

- **HK1:** The ground state electron density, \( \rho_0(\mathbf{r}_1) \), of a bound system of interacting electrons in some external potential, \( V_{\text{ext}} \), determines this potential uniquely.

  In consequence, the ground state electron density is sufficient to construct the full Hamilton operator and hence to calculate, in principle, any ground state property of the system. In other words, any ground state property can be expressed in terms of the ground state electron density \( \rho_0 \).

  Typically \( V_{\text{ext}} \) represents the Coulomb potential of a set of nuclei.

  The theorem can be extended to the time-dependent domain to develop time-dependent density functional theory (TDDFT), which can be used to describe excited states.

- **HK2:** The functional \( \mathcal{E} \) for the ground state energy is minimized by the ground state electron density \( \rho_0 \). I.e.: \( \mathcal{E}[\rho] \geq \mathcal{E}[\rho_0] \) for every trial electron density \( \rho \).

  This enables calculating \( \rho_0 \) variationally.
The Kohn-Sham method

DFT is, in principle, an orbital-free method: minimize the energy

\[ E[\rho] = T[\rho] + \int_{\mathbb{R}^3} V_{\text{ext}}(r) \rho(r) dr + \frac{1}{2} \int_{\mathbb{R}^6} \frac{\rho(r) \rho(r')}{|r - r'|} d^3r d^3r' + E_{\text{xc}}[\rho] = T[\rho] + E_n[\rho] + E_H[\rho] + E_{\text{xc}}[\rho] \]

(14)

by varying \( \rho \) over all densities containing \( N \) electrons. However, \( T[\rho] \) an essential component of the total energy (\( T[\rho] = -E[\rho] \) by the virial theorem), is unknown, and HK1 demands that the electron density comes from a well behaved wave function (\( N \)-representability).

Most DFT calculations follow the Kohn-Sham route: \( \rho(r) = \sum_{\lambda} n_{\lambda}^{\text{oct}} |\psi_{\lambda}|^2 \), where the spinorbitals are the result of solving, self-consistently, the KS equations:

\[ \left\{-\frac{1}{2} \nabla^2 + \hat{V}_n(r) + \hat{V}_H(r, [\rho]) + \hat{V}_{\text{xc}}[\rho]\right\} \psi_{\lambda}(r) = \epsilon_{\lambda} \psi_{\lambda}(r) \]

(15)

- \( \hat{V}_n \): nuclear electrostatic potential (or sum of pseudopotentials of the chemical kernels);
- \( \hat{V}_H(r) = \int_{\mathbb{R}^3} \frac{\rho(r') dr'}{|r - r'|} \): Coulomb potential due to the (possibly valence) electron density.
- \( \hat{V}_{\text{xc}} \): Exchange and correlation term.
There is no systematic way of improving the xc functional...

... but J. P. Perdew has popularized the Jacob’s ladder metaphor.

- **First rung (LDA/LSDA) [Local (spin) density approach]:** Based on the Quantum Monte Carlo solution of an homogeneous electron gas. Ex: VWN91.

- **Second rung (GGA) [Generalized gradient approach]:** Determined by the value of the electron density and its gradient on each point. Ex: PW91, PBE, ...

- **Third rung (meta-GGA):** Depends on the local density, gradient, and kinetic energy. Ex: TPSS, ...

- **Fourth rung, Hybrid functionals:** Mix of several kinds. Typically, the Hartree-Fock exchange (exact exchange) is mixed with GGA. In other words, the functional depends on the occupied orbitals. Ex: B3LYP, ...

- **Fifth rung, Double hybrid functionals:** Depends on the virtual and occupied orbitals. Ex: XYG3, ...

**Increasing cost:** \( L(S)DA \approx GGA \ll \text{meta-GGA} \ll \text{hybrid} \ll \text{double-hybrid.} \)
Molecular engineering tools

ab initio Thermodynamics of Crystals

Analytical Equations of State

DFT calculation of the electronic structure

Empirical Energy Corrections
- Systematic errors in the DFT results
- Empirical correction of the systematic errors
- Does the EEC really works?
- Any thermodynamic property can be obtained
- MgO as a high pT pressure scale
- Performance of the method for other crystals
- Availability

Conclusions

Acknowledgements
DFT calculations on MgO

Problems that prevent true accuracy:

- Choice of xc: source of uncertainty in DFT.
- Known trends in solids: LDA overbinds, PBE underbinds.
- No systematic ways of improving the results. **Wait for a hypothetical perfect functional?**
- Fitting of the $E(V)$ and $A(V; T)$ curves. **Solved!!!**

![Graph showing LDA and PBE results compared to experimental data](image-url)
Empirical Energy Corrections (EEC)

The systematic deviations in the exchange-correlation functionals can be corrected by using one or two accurate experimental results: ambient conditions volume ($V_{\text{exp}}^0$) and bulk modulus ($B_{\text{exp}}^0$).

Kunc and Syassen's observation: $p/B_0$ vs. $V/V_0$ is transferable, $V_0$ and $B_0$ being the static equilibrium volume and bulk modulus, respectively.

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

(16)

The \textbf{bpscal} EEC is:

$$E_{\text{sta}}(V) = E_{\text{sta}}(V_0) + \frac{B_{\text{exp}} V_{\text{exp}}}{B_0 V_0} \left[ E_{\text{sta}} \left( V \frac{V_0}{V_{\text{exp}}} \right) - E_{\text{sta}}(V_0) \right]$$

(17)

The experimental $V_{\text{exp}}$ and $B_{\text{exp}}$ extrapolated to static conditions are missing, and are treated as parameters to fit the experimental data.
Does the EEC really work?

![Graph showing the comparison between different models and experimental data for the properties of solids under different pressures and temperatures. The graph includes data points and curves for LDA, PBE, and EEC models, along with experimental results from Speziale (2001), Li (2006), Tange (2009), Fiquet (1999), Sinogeikin (2000), and Dubrovinsky (1997).]
Any thermodynamic property can be obtained (MgO)

The three steps: (1) energy fitting, (2) full QHA, and (3) empirical energy corrections allow us to predict thermodynamic properties with unprecedented accuracy.

<table>
<thead>
<tr>
<th>Property</th>
<th>Room (0 GPa and 298.15 K)</th>
<th>(0 GPa and 1000 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PBEcorr</td>
<td>expt.</td>
</tr>
<tr>
<td>$V$ (bohr$^3$)</td>
<td>126.024(19)</td>
<td><strong>126.025</strong></td>
</tr>
<tr>
<td>$F_{\text{vib}}$ (kJ/mol)</td>
<td>11.4236(47)</td>
<td></td>
</tr>
<tr>
<td>$S$ (J/mol K)</td>
<td>27.0028(88)</td>
<td>27.18</td>
</tr>
<tr>
<td>$p_{\text{th}}$ (GPa)</td>
<td>2.624(15)</td>
<td>0.717</td>
</tr>
<tr>
<td>$B_T$ (GPa)</td>
<td>161.43(50)</td>
<td><strong>161.3</strong></td>
</tr>
<tr>
<td>$B_S$ (GPa)</td>
<td>163.72(50)</td>
<td>163.9</td>
</tr>
<tr>
<td>$\alpha$ ($1 \cdot 10^{-5}$ K)</td>
<td>3.1002(97)</td>
<td>3.12</td>
</tr>
<tr>
<td>$C_V$ (J/mol K)</td>
<td>36.6821(50)</td>
<td>36.9</td>
</tr>
<tr>
<td>$C_P$ (J/mol K)</td>
<td>37.2023(57)</td>
<td>37.409</td>
</tr>
<tr>
<td>$B'_T$</td>
<td>4.173(43)</td>
<td></td>
</tr>
<tr>
<td>$B''_T$ (GPa$^{-1}$)</td>
<td>-0.0333(28)</td>
<td></td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1.53435(24)</td>
<td>1.54</td>
</tr>
</tbody>
</table>
MgO as a high pT pressure scale

Magnesium oxide has been proposed as pressure scale for diffraction experiments at extreme pressure and temperature. This requires a very precise knowledge of the $p(V, T)$ EOS.

This study
Tange(2009), Vinet
Tange(2009), BM3
Wu(2008)
Speziale(2001)

3000 K, $T_m^0 = 3125$ K
Performance of the method for other crystals

- Occelli (2003) +
- Dewaele (2008) ×

- Dewaele (2004) +
- Chijioke (2005) ×
- Akahama (2006) ♦

- Reeber (1996) +
- Langelaan (1999) +
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:

- The technique and results have been described in:
The conventional procedure of fitting nonlinearly an analytical low order EOS (BM3, Vinet, ...) introduces a significant error in the equilibrium properties and in the derivatives calculated from $E(V)$ theoretical data.

The average of strain polynomial method: is efficient, numerically stable, can be extended to any order required by the data, and provides an estimation of the accuracy, in the form of error bars, that can be translated to any thermodynamic property.

An empirical energy correction (EEC) can be used to remove the systematic error in DFT calculations due, mainly, to the defects in the exchange-correlation functional.

The quasiharmonic approximation, improved with the EEC and a careful fit of the $E(V)$ and $A(V)$ curves, can predict the thermodynamic properties of a crystal in a very wide range of pressures and temperatures.

Genetic algorithms and other methods of random sampling can be used to predict new metastable phases and conformations of solids.

Chemical bonding properties in a solid do depend heavily on the pressure and, to a lesser extent, the temperature conditions.
Acknowledgements

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- Original artwork has been provided by Andrea Victoria Luaña Lafuente (aka Anvi).
Muchas gracias por su atención ...
... ¿Alguna pregunta?
References I


