The diamond Equation of State

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30\textsuperscript{th} July 2005
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- DFT results
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Introduction

- People involved – Ryo, Neil, Mike, Richard
- Aims – determine the lattice constant, bulk modulus and the pressure derivative of the bulk modulus of diamond
- The study will be carried out up to very high pressures (beyond experimental range).
## Industrial uses of diamond

<table>
<thead>
<tr>
<th>Property</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal</td>
<td>Heat spreader</td>
</tr>
<tr>
<td>Chemical</td>
<td>Unreactive below 300°C</td>
</tr>
<tr>
<td>Optical</td>
<td>Wear-resistant optical windows</td>
</tr>
<tr>
<td>Mechanical</td>
<td>Drills, diamond anvil cells</td>
</tr>
<tr>
<td>Electronic</td>
<td>Insulator in high voltage circuits, high speed switch</td>
</tr>
<tr>
<td>Acoustic</td>
<td>High performance surface acoustic wave devices</td>
</tr>
</tbody>
</table>
Equation of state (I)

- Useful in geo, planetary, solar and stellar physics
- Data consisting of pressure, temperature and volume are parameterized to a functional form. A correct form helps us predict the high-pressure properties of solids
- For $E(V)$, parameters are $V_0$, $B_0$, $B_0'$, $E_{\text{offset}}$
- Many different forms for isothermal data – Vinet, Birch, Murnaghan, B-M, Dodson, Taylor, Holzapfel, Kumari-Dass, Parsafar-Mason...
- No EoS approaches the correct theoretical values at extreme compressions
Equation of state (II)

Three forms:

- **Derivative form (B-M, PM, Vinet)**
  \[ P = -\frac{\partial E}{\partial V} \]

- **Volume-integral form (Dodson)**
  \[ P = -\int_{V_0}^{V} B(V)/V \, dV \]

- **Pressure-integral form (Murnaghan and KD)**
  \[ \frac{V}{V_0} = \exp\left[ -\int_{0}^{P} \frac{1}{B(P)} \, dP \right] \]
Birch-Murnaghan EoS (1944)

\[
E(V) = -\frac{9}{16} B_0 \left[ (4 - B_0') \frac{V_0^3}{V^2} - (14 - 3 B_0') \frac{V_0^{7/3}}{V^{4/3}} + (16 - 3 B_0') \frac{V_0^{5/3}}{V^{2/3}} \right] + E_0
\]

- Derived from the Taylor series expansion of the bulk modulus \( B = B_0 + B_0' P \)
- Assumes the underlying interatomic potential as a series in \( 1/r^{2n} \)
- 2nd order truncated form gives the Birch EoS (accurate up to \( V/V_0 = 0.4 \))
The Vinet EoS (1987)

\[ E(V) = \frac{-4B_0V_0}{(B_0'-1)^2} \left[ 1 - \frac{3}{2}(B_0'-1) \left( 1 - \left( \frac{V}{V_0} \right)^{1/3} \right) \right] \times \exp \left[ \frac{3}{2}(B_0'-1) \left( 1 - \left( \frac{V}{V_0} \right)^{1/3} \right) \right] + E_0 \]

- Assumed the interatomic interaction in solids can be expressed as \( A(1+r) \exp(-r) \)
- From expt data, \( r = 3/2 \left[ (B_0'-1) \left( (V/V_0)^{1/3} - 1 \right) \right] \)
- Accurate up to about \( V/V_0 = 0.2-0.3 \) (or 10TPa)
- Total energy tends to a constant in extreme compression instead of infinity
Other equations of state

- Murnaghan (1944)
  - Truncated Taylor-series. Good for small compressions, therefore widely used to analyze experimental data, accurate up to $V/V_0 = 0.7$
  - Extensions:
    - Dodson (1987) – assumes
    - KD (1990) – higher-order terms are taken into account, assuming $B_0^{(n+1)} / B_0^{(n)} = -B_0''$ for $n > 1$
- Holzapfel (1996)
  - Designed for extreme compression.
Which one to use?

- For strains less than 30% [Jeanloz (1988), Cohen et al (2000)], it doesn't really matter which EoS you use.
- Parameters are better determined with the Vinet equation [Cohen et al (2000)]
- For large strains, the Vinet equation is best.
- At extreme compressions, the Holzapfel equation may be required.
Experiments

- LAC, DAC, shock compression
- Techniques include X-ray diffraction, Raman scattering, Brillouin scattering, ultrasonic.
- Hydrostatic pressure up to 140 GPa (2003)
- High temperatures – laser heating in DAC (max pressure 200GPa, 4000K)
Diamond Anvil Cells
Difficulties in experiments

- Sample chamber becomes very thin (<10μm)
- Separation of diamond signal from signal of diamond anvils
- Pressure above 140GPa leads to breakage of diamond anvils
- Calibration of the pressure (underestimates pressure by 11% in ruby calibration?)
# Pressure derivative of the bulk modulus

<table>
<thead>
<tr>
<th>Method</th>
<th>$B'_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrasonic, up to 0.2GPa, McSkimin and Andreatch (1972)</td>
<td>4.0(5)</td>
</tr>
<tr>
<td>X-ray diffraction and Raman scattering, up to 140GPa, F. Occelli, P. Loubeyre, and R. LeToullec (2003)</td>
<td>3.0(1)</td>
</tr>
<tr>
<td>LDA</td>
<td>3.5, 3.54, 3.63(3), 3.24, 4.22</td>
</tr>
<tr>
<td>GGA</td>
<td>3.67(3), 3.71, 3.72, 3.70, 3.97</td>
</tr>
<tr>
<td>Pressure (GPa)</td>
<td>Description</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>0.5</td>
<td>Atmospheric pressure on Pluto</td>
</tr>
<tr>
<td>1</td>
<td>Atmospheric pressure on Mars</td>
</tr>
<tr>
<td>101</td>
<td>Atmospheric pressure on Earth at sea level</td>
</tr>
<tr>
<td>100</td>
<td>Pressure at the bottom of Mariana Trench, 10km below ocean surface</td>
</tr>
<tr>
<td>2</td>
<td>Ultrasonic measurement by McSkimin</td>
</tr>
<tr>
<td>10</td>
<td>Diamond forms</td>
</tr>
<tr>
<td>15</td>
<td>Large Anvil Cells</td>
</tr>
<tr>
<td>140</td>
<td>X-ray, Raman scattering by Occelli with Diamond Anvil Cells</td>
</tr>
<tr>
<td>240</td>
<td>Highest pressure in present QMC study</td>
</tr>
<tr>
<td>330</td>
<td>Pressure at mantle-core boundary</td>
</tr>
<tr>
<td>450</td>
<td>Highest pressure in future QMC study</td>
</tr>
</tbody>
</table>
DFT calculations

- Code: CASTEP (plane waves)
- GGA (PBE)
- Energy cutoff 100 Ha (converged to $5 \times 10^{-5}$ Ha/atom)
- 32 kpts (converged to within $1 \times 10^{-5}$ Ha/atom)
- Calculate $E(V)$ for volumes up to 440GPa
- Choose lattice points for QMC calculations
Energy vs volume
E(V) - different EoS
QMC calculations

- 4x4x4 cell, blip basis set, calculations at 7 lattice coordinates
- Pressure up to 240GPa
- Tested convergence of basis set
- Jastrow factor optimization
- VMC calculation
VMC E(V)
Pressure

![Graph showing the relationship between pressure and volume per atom (Bohr^3)]

- Birch-Murnaghan (DFT)
- Vinet (DFT)
- Birch-Murnaghan (VMC)
- Vinet (VMC)
# EoS parameters (DFT)

<table>
<thead>
<tr>
<th></th>
<th>Vinet</th>
<th>B-M</th>
<th>Murnaghan</th>
<th>Dodson</th>
<th>DFT GGA (from lit.)</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bulk Modulus (Mbar)</strong></td>
<td>4.31</td>
<td>4.26</td>
<td>4.09</td>
<td>4.66</td>
<td>4.33(2), 4.32, 4.22, 4.36, 4.32, 4.35</td>
<td>4.42, 4.43, 4.52, 4.448(8), 4.46(1), 4.45, 4.69 (at 0K)</td>
</tr>
<tr>
<td><strong>Pressure deriv. of the bulk modulus</strong></td>
<td>3.70</td>
<td>3.73</td>
<td>3.79</td>
<td>11.80</td>
<td>3.67(3), 3.71, 3.72, 3.70</td>
<td>4.0(5), 3.0(1)</td>
</tr>
</tbody>
</table>
# EoS parameters (VMC)

<table>
<thead>
<tr>
<th></th>
<th>Vinet</th>
<th>B-M</th>
<th>Murnaghan</th>
<th>VMC (Murnaghan) [Fahy et al]</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (Å)</td>
<td>3.547</td>
<td>3.546</td>
<td>3.545</td>
<td>3.54(3)</td>
<td>3.567, 3.5668</td>
</tr>
<tr>
<td>Bulk Modulus (Mbar)</td>
<td>4.83</td>
<td>4.81</td>
<td>4.64</td>
<td>4.2(5)</td>
<td>4.42, 4.43, 4.52, 4.448(8), 4.46(1), 4.45, 4.69 (at 0K)</td>
</tr>
<tr>
<td>Pressure deriv. of the bulk modulus</td>
<td>3.43</td>
<td>3.47</td>
<td>3.63</td>
<td>-</td>
<td>4.0(5), 3.0(1)</td>
</tr>
</tbody>
</table>
Conclusions and Future Work

- Investigated different forms of EOS
- Performed DFT (GGA) and VMC calculations on diamond to determine \( a, B_0 \) and \( B'_0 \)
- DMC calculations
- Higher pressure regime (up to 450 GPa)
- Phonon frequencies (using frozen phonon method)