The diamond Equation of State

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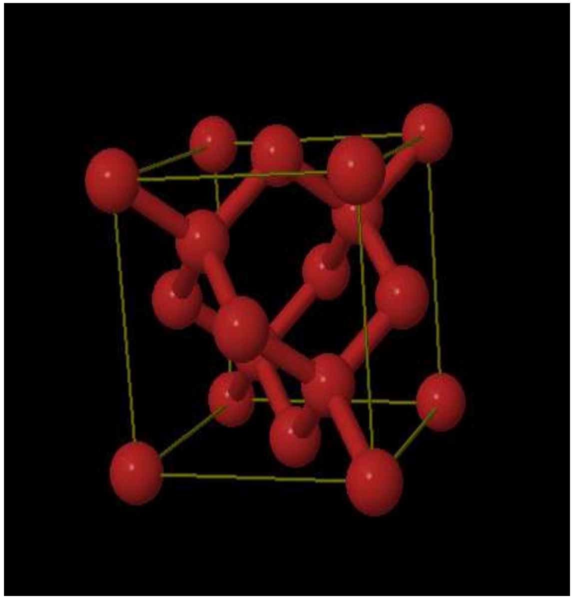
Introduction

- 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

Property		Application
Thermal	Highest known thermal conductivity (4-20W/cm/K)	Heat spreader
Chemical	Unreactive below 300°C	
Optical	Transparent	Wear-resistant optical windows
Mechanical	Hardest known material	Drills, diamond anvil cells
Electronic	Electrical insulator	Insulator in high voltage circuits, high speed switch
Acoustic	Highest known sonic velocity	High performance surface acoustic wave devices



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_{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)

$$P = -\partial E / \partial V$$

  - 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)

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

- 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, $r=3/2[B_0'-1][(V/V_0)^{1/3}-1]$
- 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.

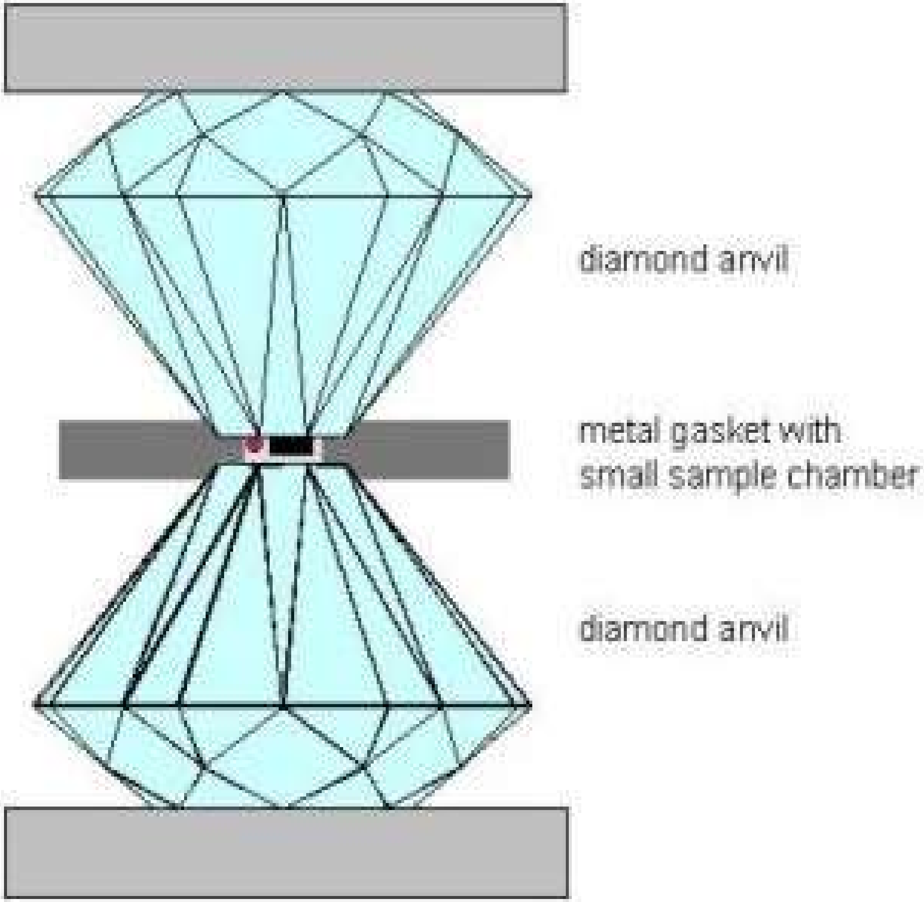
Which one to use?

- 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

Method	B_0'
Ultrasonic, up to 0.2GPa, McSkimin and Andreatch (1972)	4.0(5)
X-ray diffraction and Raman scattering, up to 140GPa, F. Occelli, P. Loubeyre, and R. LeToullec (2003)	3.0(1)
LDA Fahy et al, Chelikowsky et al, Pavone et al, Kunc et al, Crain et al	3.5, 3.54, 3.63(3), 3.24, 4.22
GGA Kunc et al, Ziambaras et al	3.67(3), 3.71, 3.72, 3.70, 3.97

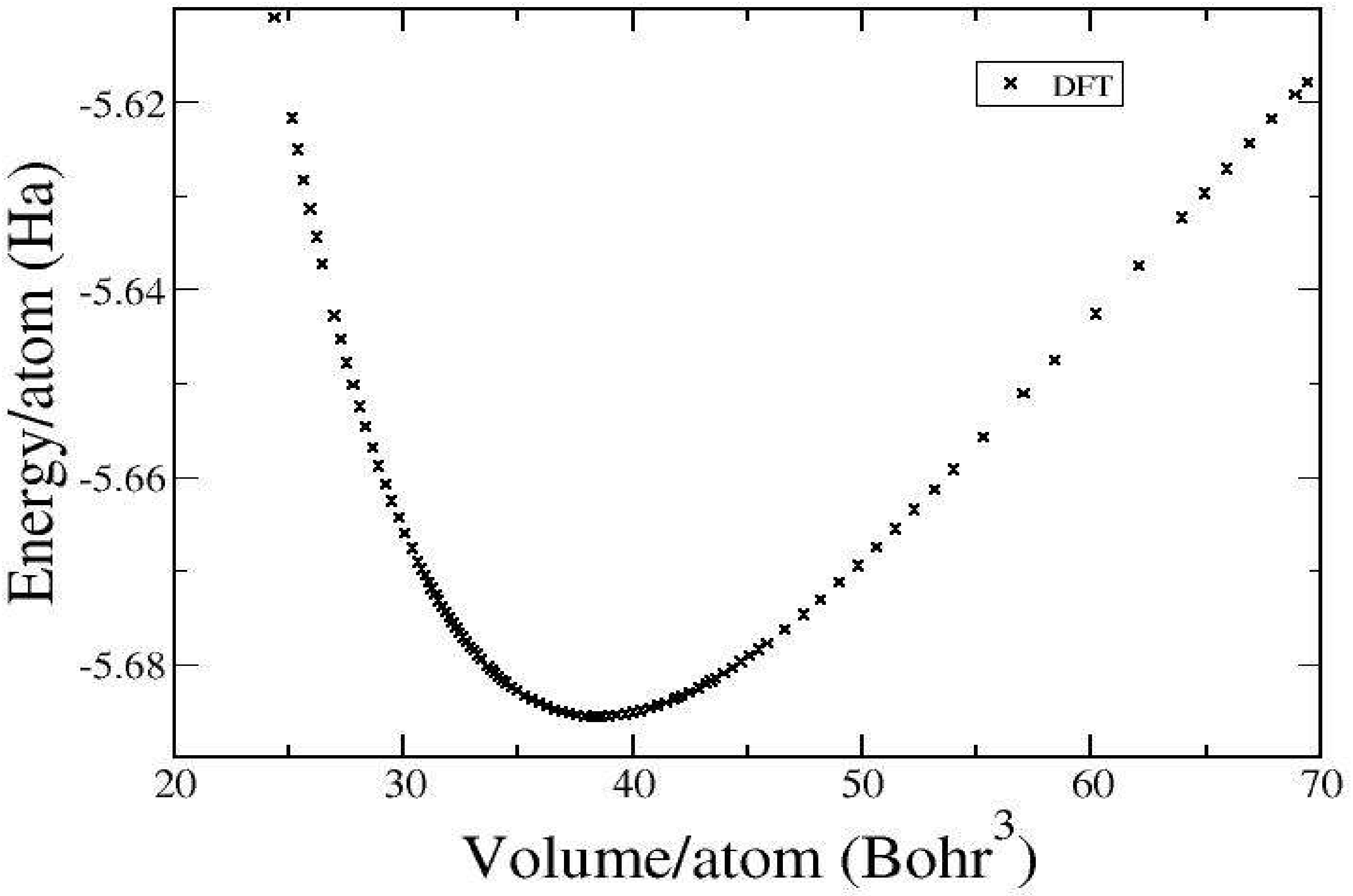
Pressures

0.5	Pa	Atmospheric pressure on Pluto
1	KPa	Atmospheric pressure on Mars
101	KPa	Atmospheric pressure on Earth at sea level
100	MPa	Pressure at the bottom of Mariana Trench, 10km below ocean surface
2	GPa	Ultrasonic measurement by McSkimin
10	GPa	Diamond forms
15	GPa	Large Anvil Cells
140	GPa	X-ray, Raman scattering by Occelli with Diamond Anvil Cells
240	GPa	Highest pressure in present QMC study
330	GPa	Pressure at mantle-core boundary
450	GPa	Highest pressure in future QMC study

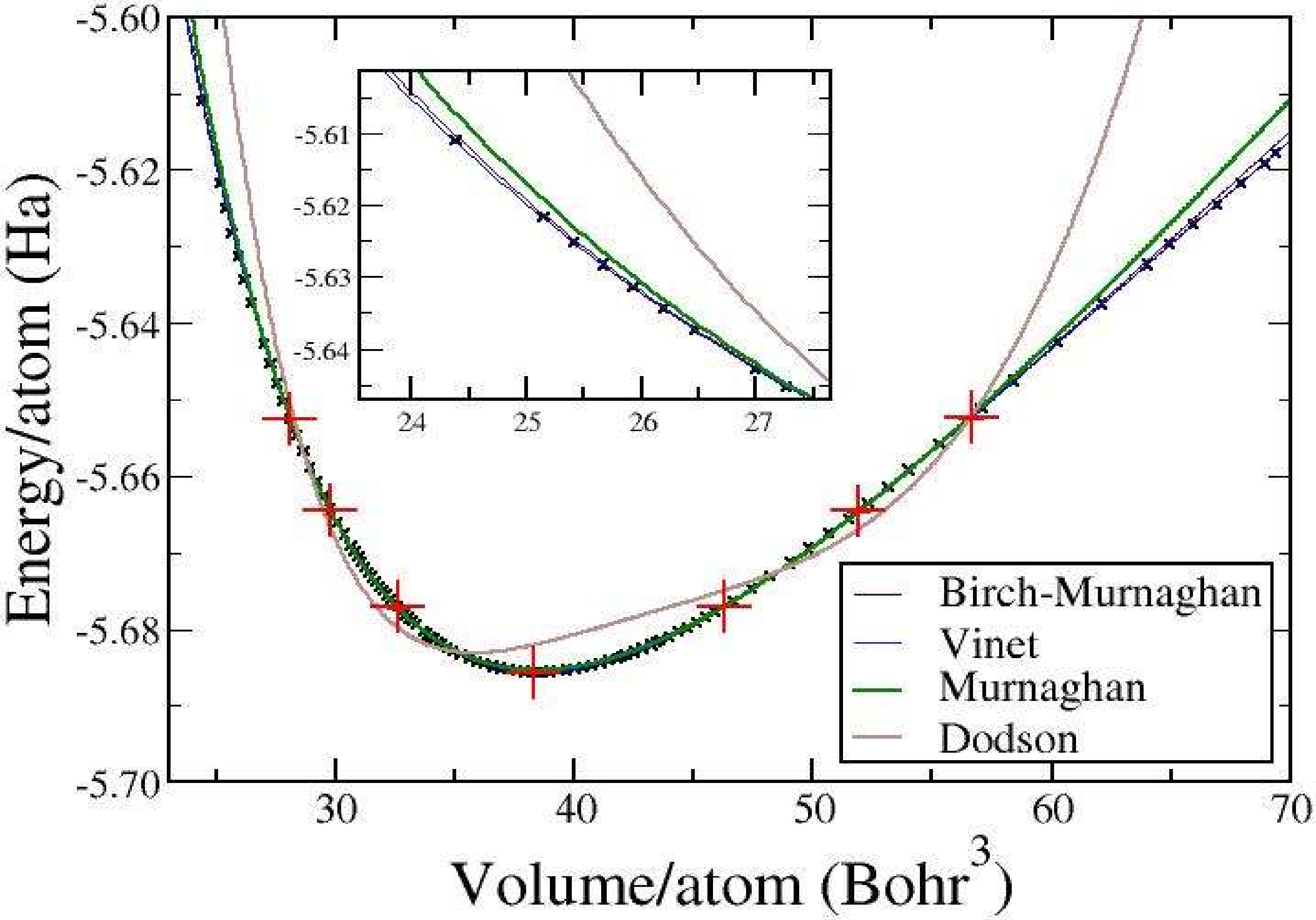
DFT calculations

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

Energy vs volume



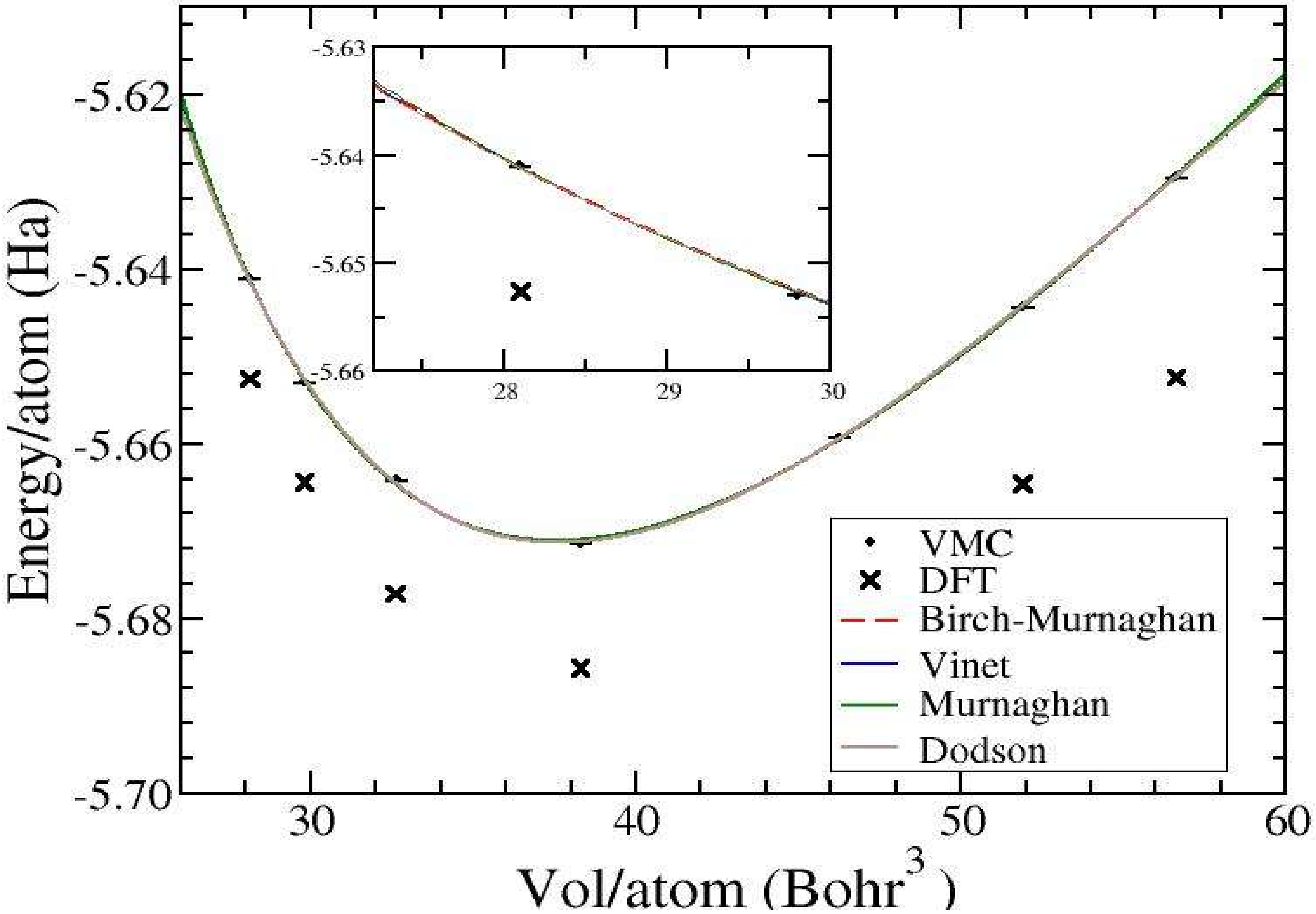
E(V) - different EoS



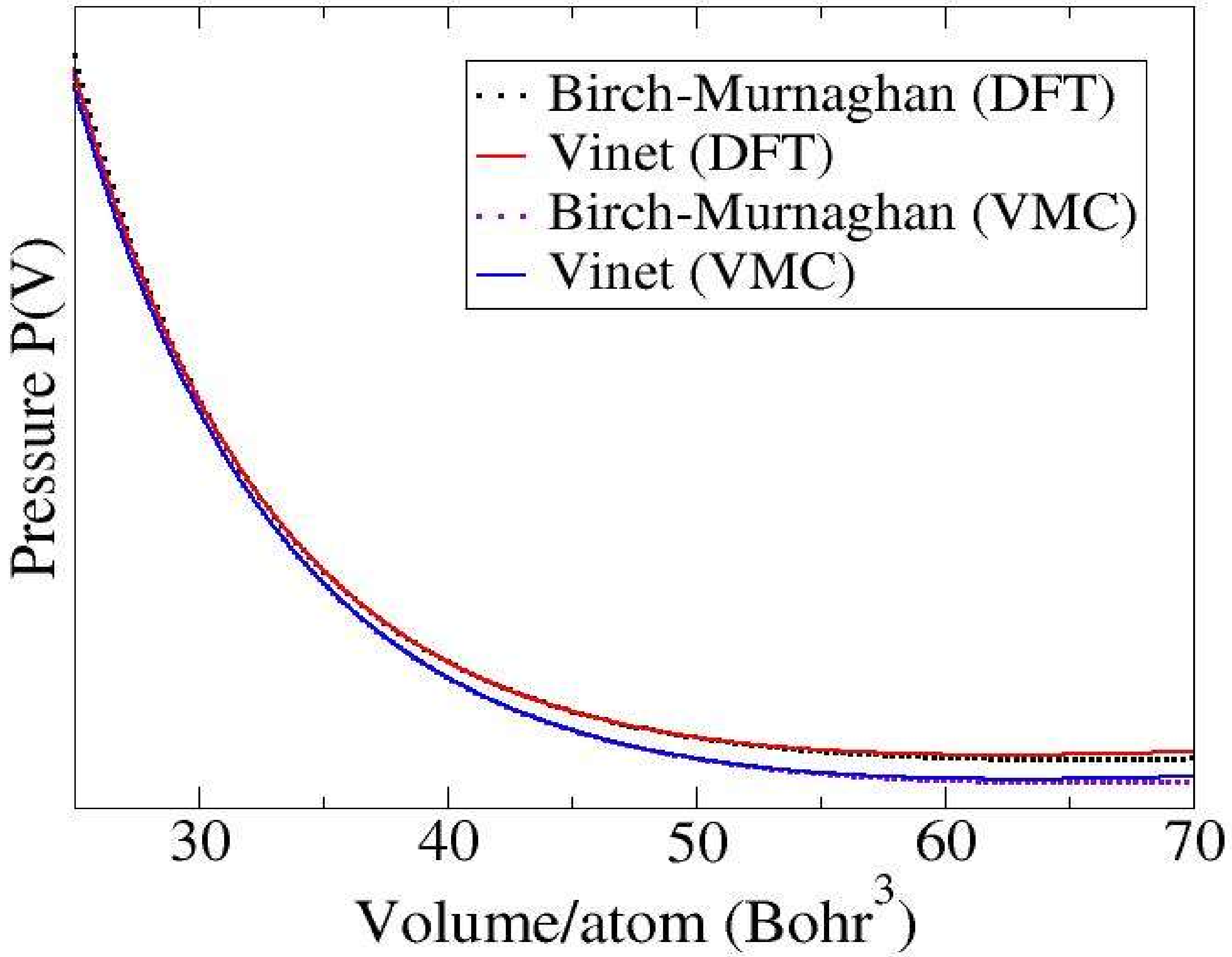
QMC calculations

- 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)


Energy/atom (Ha)
-5.62
-5.64
-5.66
-5.68
-5.70
Vol/atom (Bohr^3)
30
40
50
60
-5.63
-5.64
-5.65
-5.66
28
29
30
VMC
DFT
Birch-Murnaghan
Vinet
Murnaghan
Dodson

Pressure


Birch-Murnaghan (DFT)
Vinet (DFT)
Birch-Murnaghan (VMC)
Vinet (VMC)
Pressure P(V)
30
40
50
60
70
Volume/atom (Bohr^3)

EoS parameters (DFT)

	Vinet	B-M	Murnaghan	Dodson	DFT GGA (from lit.)	Expt
Lattice constant (Å)	3.573	3.573	3.573	3.488	3.55, 3.568, 3.565	3.567, 3.5668
Bulk Modulus (Mbar)	4.31	4.26	4.09	4.66	4.33(2), 4.32, 4.22, 4.36, 4.32, 4.35	4.42, 4.43, 4.52, 4.448(8), 4.46(1), 4.45, 4.69 (at 0K)
Pressure deriv. of the bulk modulus	3.70	3.73	3.79	11.80	3.67(3), 3.71, 3.72, 3.70	4.0(5), 3.0(1)

EoS parameters (VMC)

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

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)