Quantum Monte Carlo Study of the Elastic Instability of Stishovite Under Pressure

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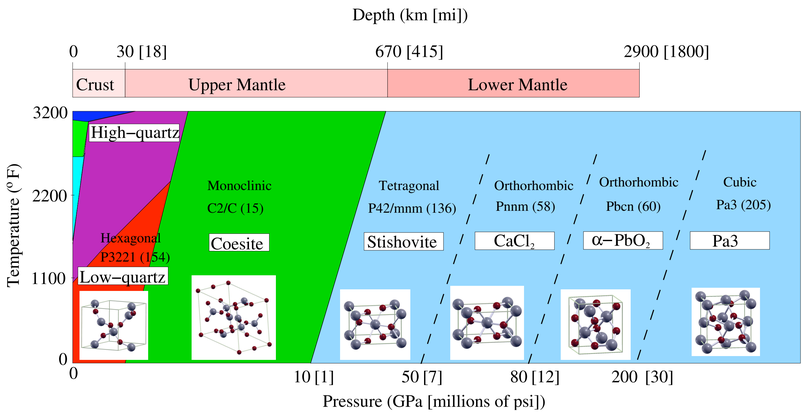
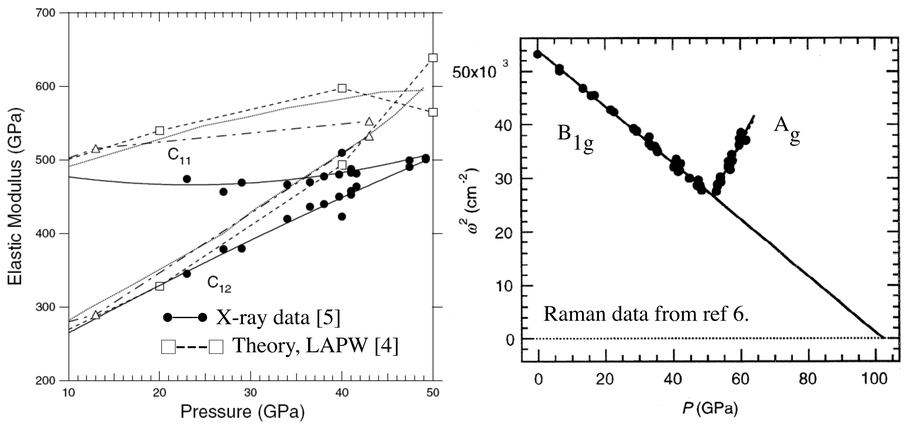
Introduction: Silica



•Silica, the simplest of Earth's silicates, exhibits a rich phase diagram including rutile structured phases, such as stishovite, that are common among several minerals.
•Diamond anvil cell measurements can be challenging due to pressure and temperature gradients in samples, but have provided accurate data for silica.
•Theoretical efforts to study silica require accurate, first principle methods in order to make reliable predictions.
•Density Functional Theory (DFT) predictions can strongly depend on the functional form for some silica properties, such as transition pressures [1], but have generally been reliable.
•The accuracy of the many-body method, Quantum Monte Carlo (QMC) [2], can make reliable predictions of high-pressure silica phases and other minerals where experimental measurements are scarce. QMC is 100-1000 times more costly than DFT.
•In this work we test the feasibility of QMC to calculate the elastic constants and predict the softening of the shear modulus under pressure in the stishovite to $CaCl_2$ transition.

Previous Work: Shear Modulus Softening in Stishovite



• At 50 GPa stishovite transforms to a $CaCl_2$-type structure [3].
• Stishovite to $CaCl_2$ transition is driven by instability of the elastic shear modulus, c_{11}-c_{12} [4].
• X-ray diffraction experiments show the shear constant, c_{11}-c_{12}, vanishes under pressure [5].
•The instability is due to softening of the B_{1g} Raman mode, changing to the A_g mode at 50 GPa [6].
•In general, tetragonal rutile-type crystals, such as stishovite, exhibit anomalous B_{1g} mode softening with increasing pressure. B_{1g} induces a structural phase transition at pressure p_T to a orthorhombic $CaCl_2$-type structure by coupling with the shear elastic constant [7].

$$c_{11} - c_{12} \propto p - p_T \propto \omega^2_{B_{1g}}$$

Quantum Monte Carlo Method

Trial Wave Function and Jastrow Factor

$$\Psi_T = \exp(J(r_{ij})) \sum_n D_n^{\uparrow} D_n^{\downarrow}$$

•A Jastrow factor multiplies orbitals providing particle correlation.
•J includes two and three body correlation terms and plane wave expansion in electron-electron separation to fill out corners of the simulation cell.
•Density functional theory provides the Slater determinant of orbitals (D), which contains the exchange part of the wave function.
•Two freely available DFT codes, ABINIT and PWSCF, produce orbitals for QMC in the b-spline basis.

Variational Monte Carlo (VMC) and Wave Function Optimization

•Our work utilizes the CASINO [8] QMC code with pseudopotentials.
•VMC uses Monte Carlo integration to calculate energies of Ψ_T and optimizes Ψ_T via the variational principle.
•Minimizing the variance of the energies optimizes the Jastrow parameters.

$$E_{vmc} = \int |\Psi|^2 \frac{H\Psi}{\Psi} dR = \int |\Psi|^2 E_L(R) dR = \frac{1}{M} \sum_{i=1}^{m} E_L(R_i)$$

Diffusion Monte Carlo (DMC)

•DMC uses a many-body Hamiltonian to stochastically project out the ground state from Ψ_T

$$\Psi(R) = \lim_{n\to\infty} \sum_{i=1}^{n} \exp[-\Delta\tau_n (H - E_T)] \Psi_T(R)$$

•Calculation of elastic constants requires total energies with small statistical error bars.

Calculating Elastic Constants with Strain-Energy Relations

Strain the crystal lattice

$$R' = [I + \varepsilon] R$$

•The crystal lattice vectors are strained by a few per cent for several different cell volumes.
•Volume-conserving strains avoid pressure correction terms for easier computation of pressure dependence on elastic constants [4].

Strain-energy relation for a volume conserving strain [9]

$$\frac{E}{V} = \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl}$$

•Volume conserving strain of the tetragonal stishovite lattice corresponds to changing one lattice vector by δ and another by -δ (ε11=δ, ε11=-δ).
•Changing the magnitude of δ, produces a energy vs. strain curve.

Elastic constants are proportional to the curvature of E(ε)

•Solving the strain-energy relation for the elastic constants yields a depence on the second derivative of the energy with respect to strain (i.e. the curvature of an E vs. strain curve).

$$c_{ijkl} = \frac{1}{V} \frac{\partial^2 E}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}}$$

•Fitting a polynomial to computed E(ε) points and determining the curvature of the fit at zero strain for each volume gives the elastic constants.

References

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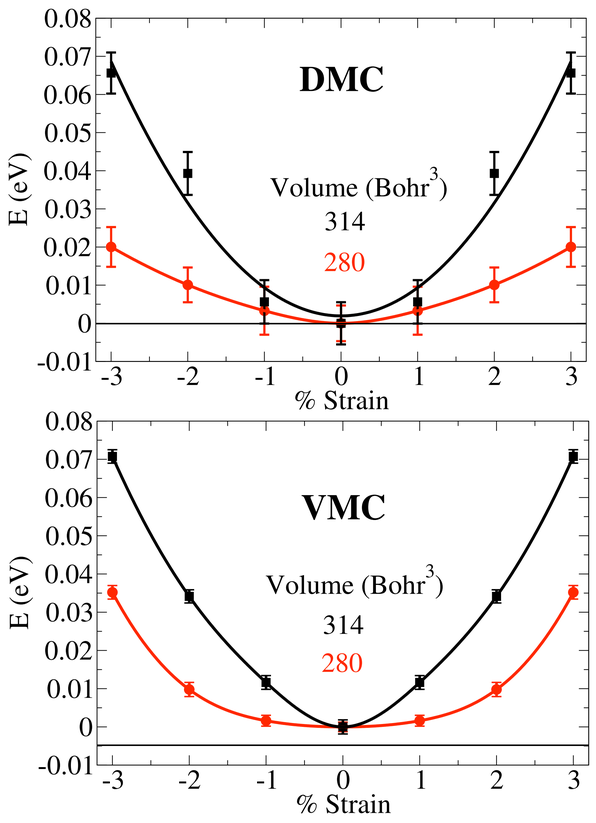
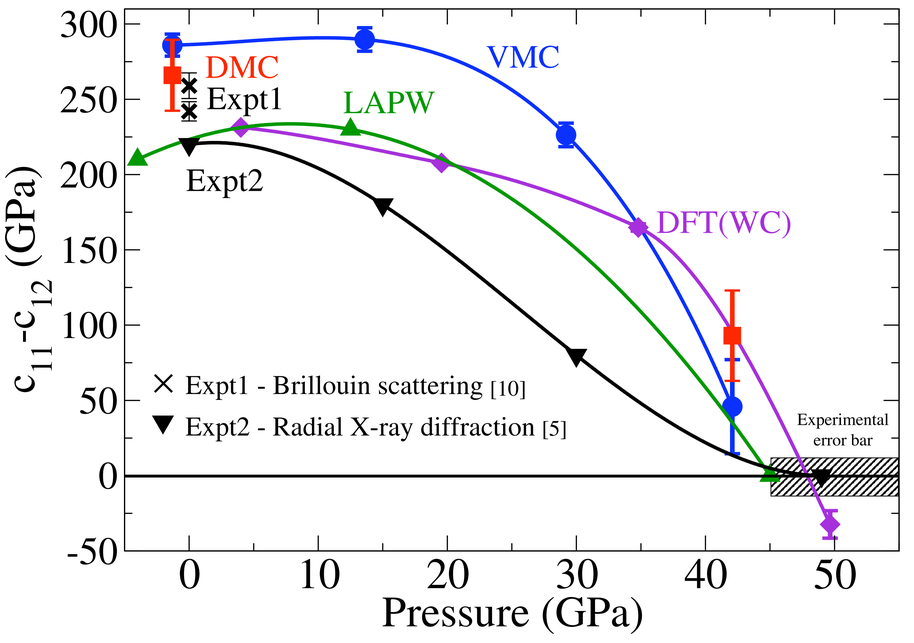
VMC and DMC Energy vs. Strain Curves



•The volume of 280 $Bohr^3$ corresponds to a pressure near the transition to $CaCl_2$ (pressure of 50 GPa).
•The volume of 314 $Bohr^3$ corresponds to stishovite at zero pressure.
•QMC error bars must be ~1 meV in order to determine curvature accurately.
•At this accuracy level, QMC is 1200 times more expensive than DFT.

QMC Benchmarks Shear Modulus Softening: Stishovite to $CaCl_2$



•QMC benchmarks DFT for shear modulus softening of stishovite.
•The shear modulus disappears near the transition pressure (50 GPa) in both QMC and DFT.
•Radial X-ray values tend to lie below theoretical values, agreeing best near 0 and 50 GPa.
•DMC agrees best with zero pressure Brillouin scattering.
•QMC results required 3 million CPU at hours at NERSC.
•The high computational expense of DMC prohibited calculations at intermediate pressures.

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