WARM DENSE SILICA: ANALYSIS OF PROBLEMS AND APPLICABILITY LIMITS OF THE PSEUDOPOTENTIAL APPROACH

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Advantages of the DFT+PP approach

1. Electrons are treated as quantum particles to allow evaluation of exchange and correlation contributions to energy.

2. The approach, though with some ifs, can be referred to as ab initio because its input parameters only include data on system stoichiometry.

3. Compared to other ab initio approaches, the DFT+PP is relatively inexpensive computationally (a few hundred of atoms in the systems).

4. Within Born-Oppenheimer quantum molecular dynamics, the approach allows analysis into the evolution of the system in time at finite pressures and temperatures.

DFT+PP limitations

I. From PP:

- Pressure cannot be increased arbitrarily .
- Temperature cannot be increased arbitrarily.

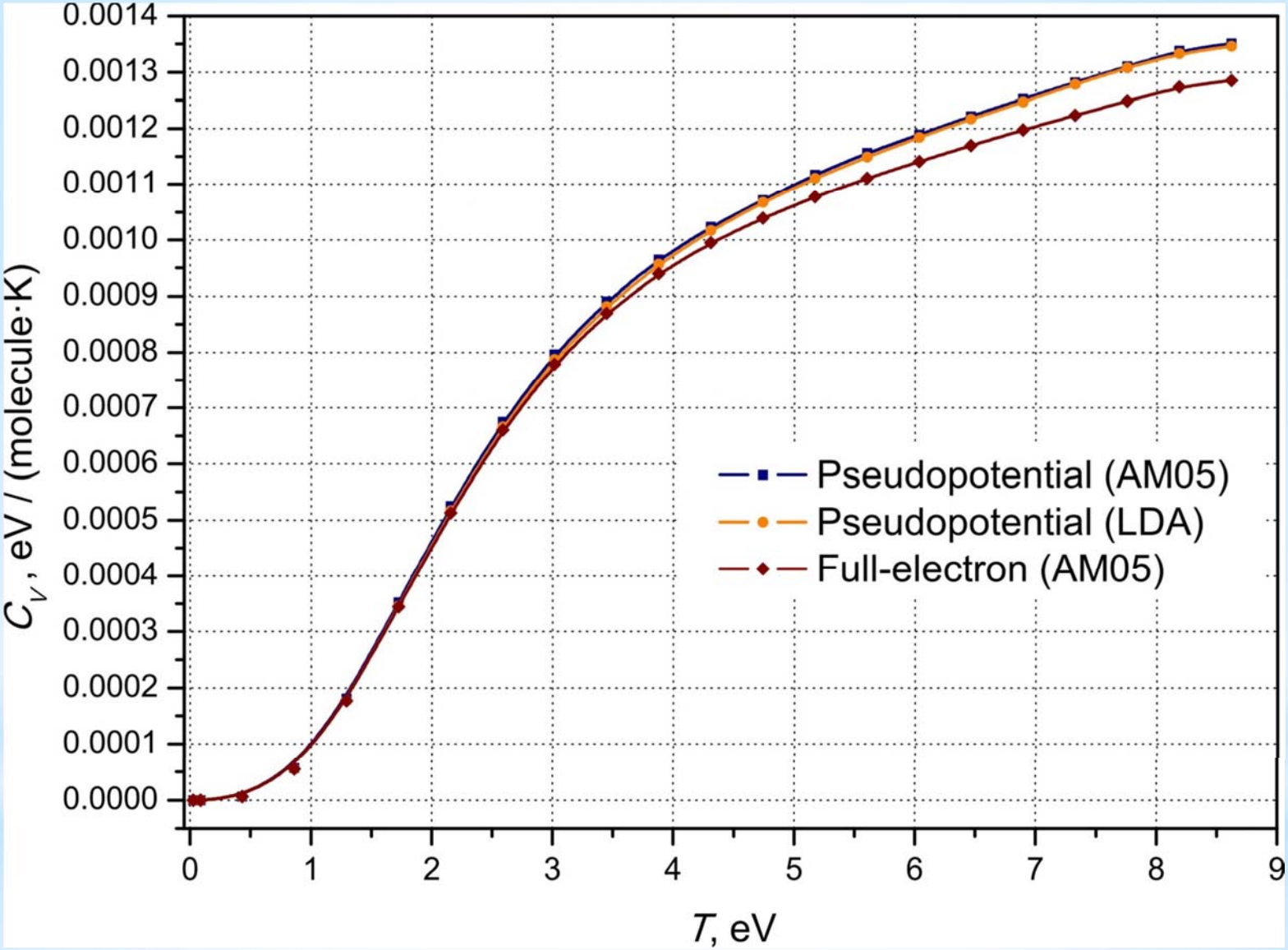
II. From DFT:

- The choice of form for the exchange-correlation functional
- Plane wave energy cutoff (basis set finiteness)

III. From Born-Oppenheimer molecular dynamics:

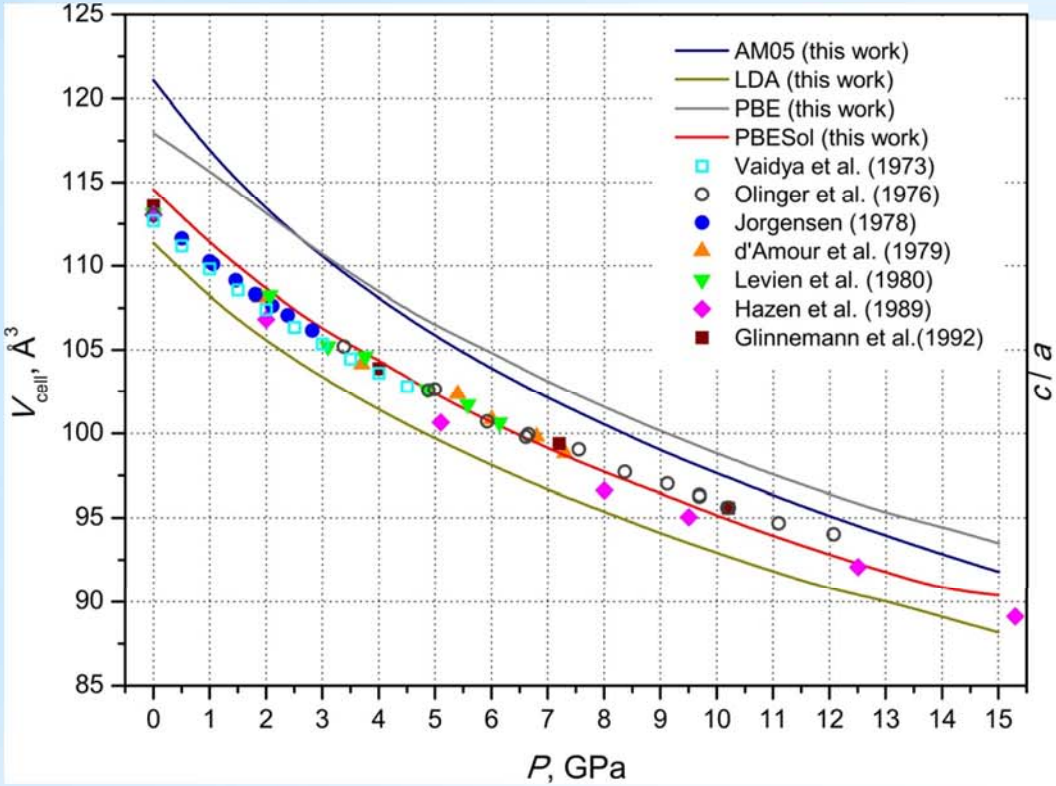
- Nuclei move as classical particles.
- The timestep significantly decreases as temperature grows.

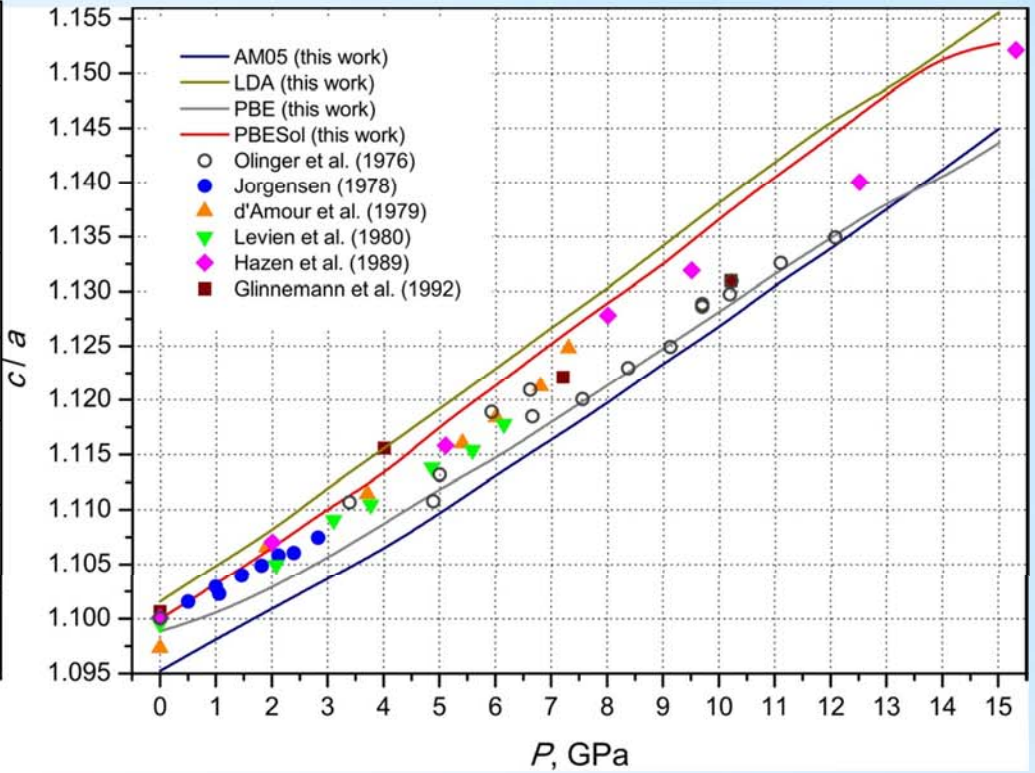
Electronic specific heat as a criterion for PP applicability boundaries in temperature



With the growing temperature the contribution of internal electrons to specific heat starts to manifest itself in the deviation of the $C_V(T)$ curves from the all-electron calculation in pseudopotential approach.

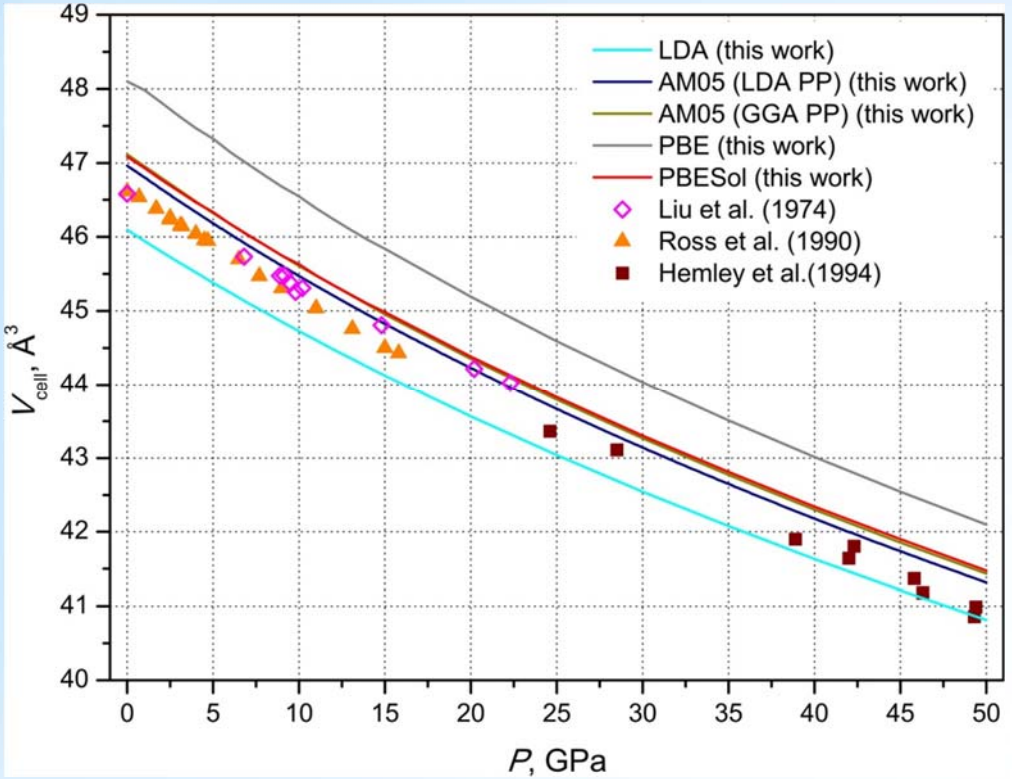
Isotherm T = 0: α-quartz

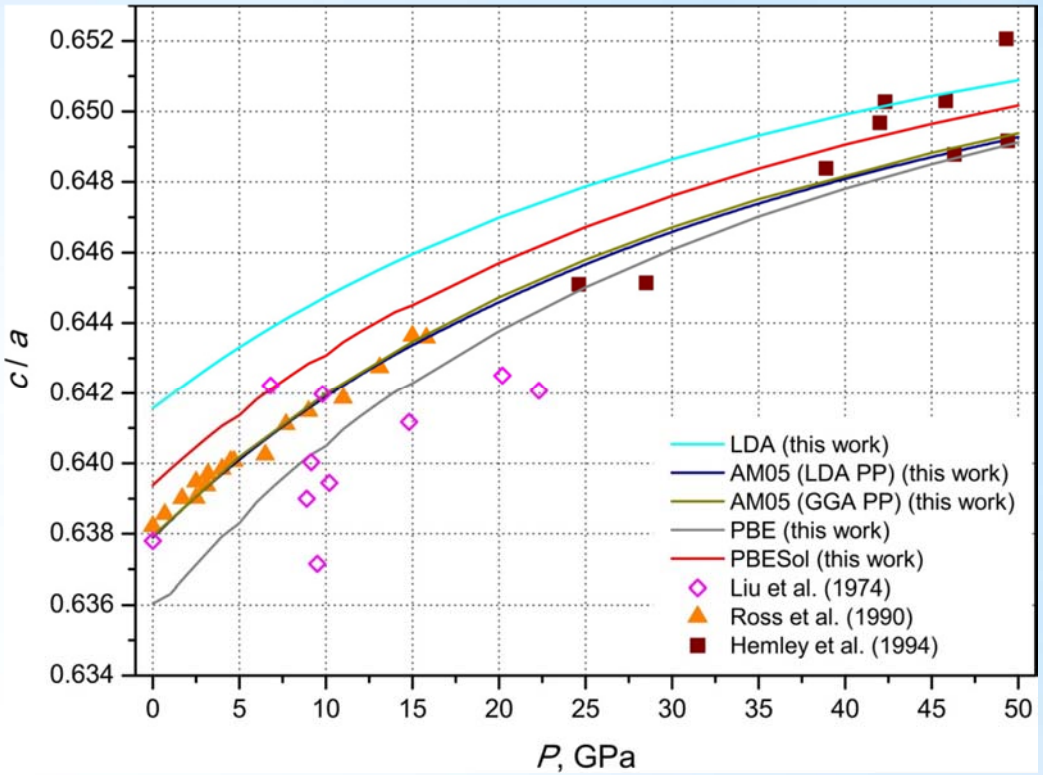




Experiment	B, GPa	B’	Calculation	B, GPa	B’
Vaidya et al. [1]	34.7±0.1	7.66±0.10	AM05	26.2±0.4	5.26±0.14
Olinger et al. [2]	38.0±2.3	5.80±0.82	LDA	32.4±0.7	5.95±0.26
Jorgensen [3]	36.4±0.4	6.49±0.40	PBE	39.5±1.5	4.12±0.35
d’Amour et al. [4]	37.5±10.3	5.55±4.81	PBESol	32.7±1.5	5.34±0.47
Levien et al. [5]	37.7±8.2	5.86±4.56	LDA [8,9]	38.1	3.90
Hazen et al. [6]	32.0±4.7	6.09±1.64			
Glinnemann et al. [7]	34.8±10.1	6.27±4.23			

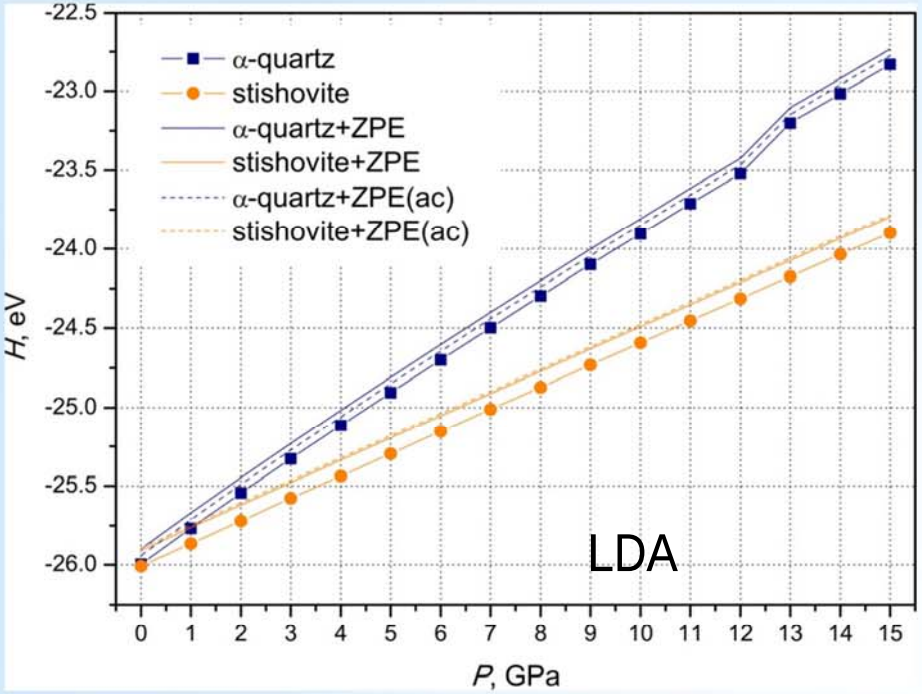
Isotherm T = 0: stishovite

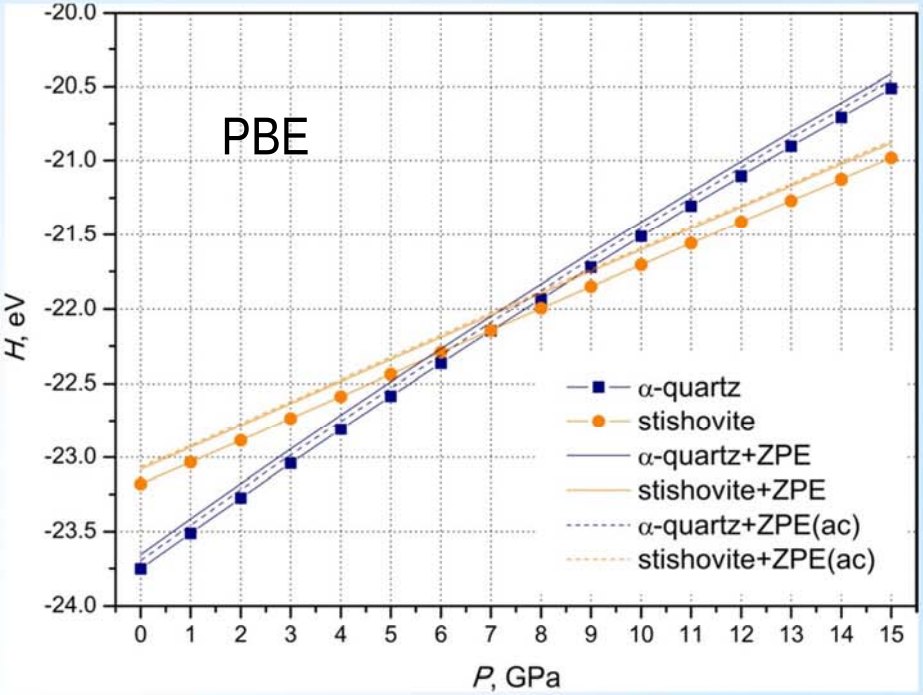


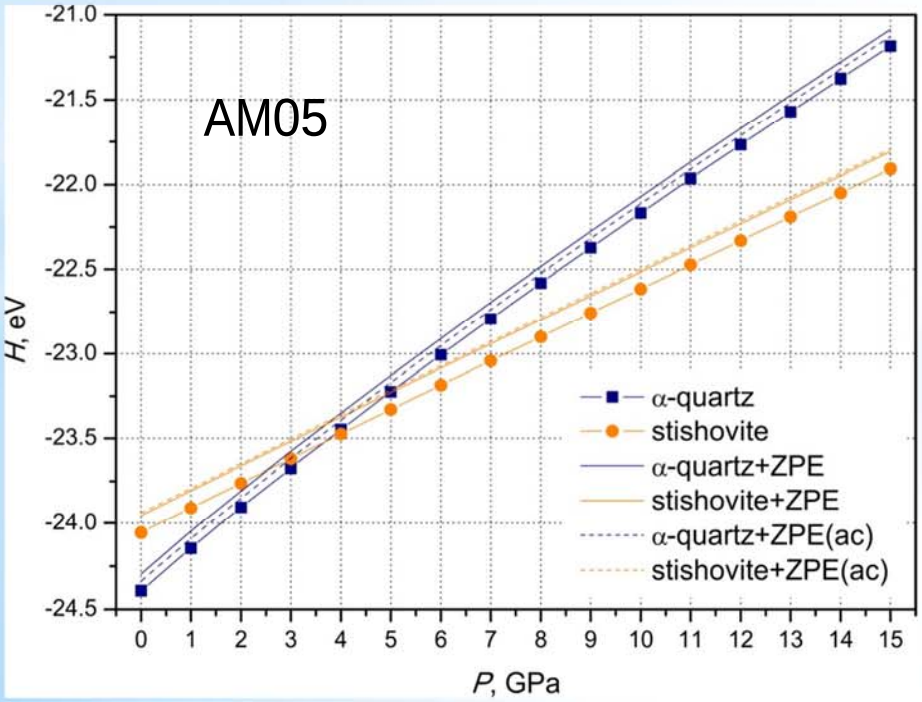


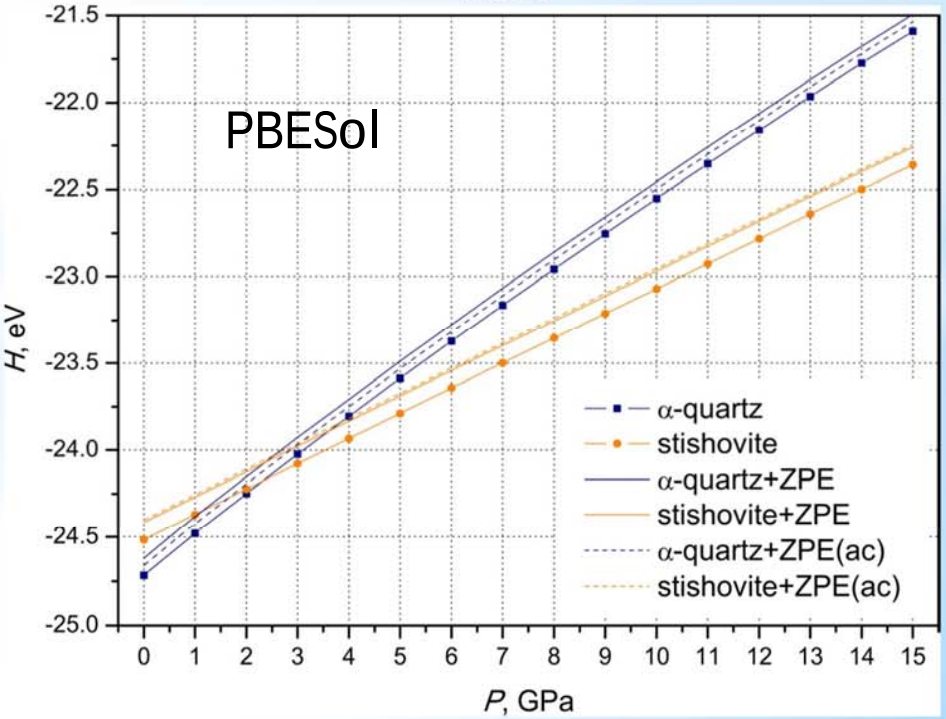
Experiment	B, GPa	B’	Calculation	B, GPa	B’
Liu et al. [10]	343.1±24.2	4.86±3.11	LDA	310.7±0.6	4.59±0.04
Ross et al. [11]	312.2±8.5	1.82±1.29	AM05 (LDA PP)	287.7±0.5	4.75±0.04
Hemley et al. [12]	327.0±43.4	2.50±1.97	AM05 (GGA PP)	286.8±1.4	4.76±0.09
Sato [13]	298.7±10.0	0.60±2.21	PBE	281.0±0.6	4.30±0.17
			PBESol	294.8±1.1	4.59±0.08

α-quartz → stishovite transition





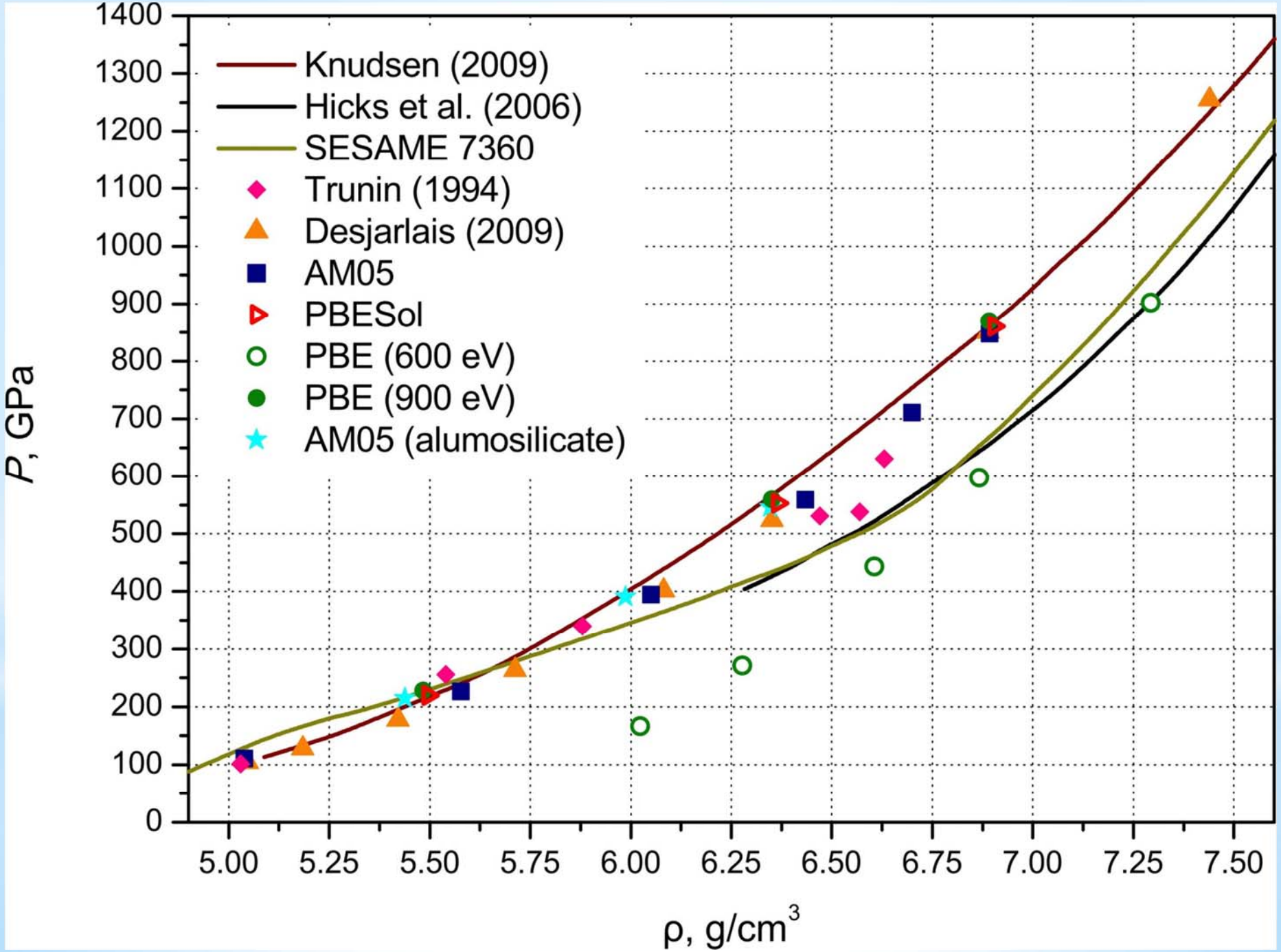




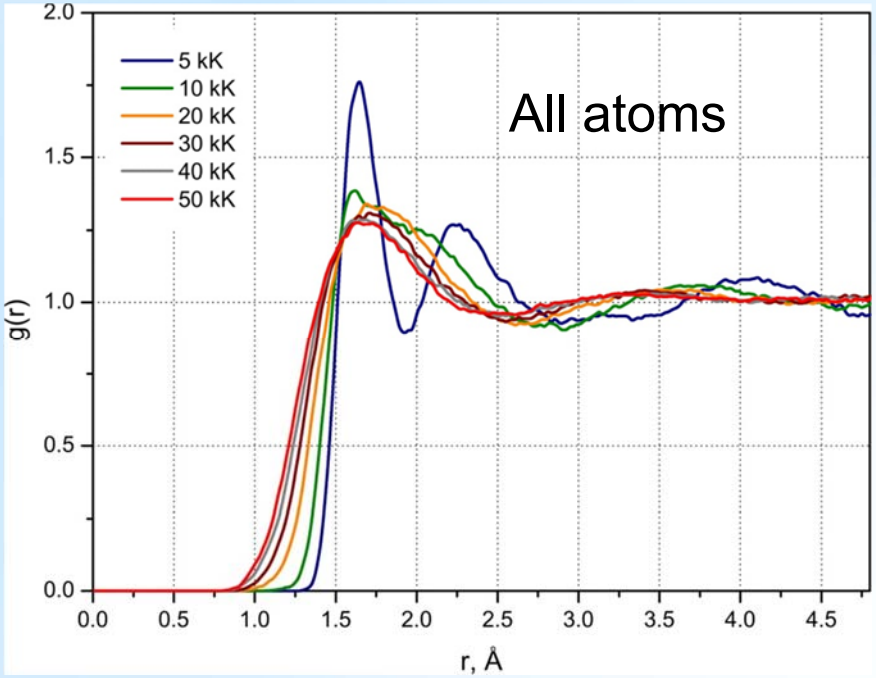
Molecular dynamics simulation

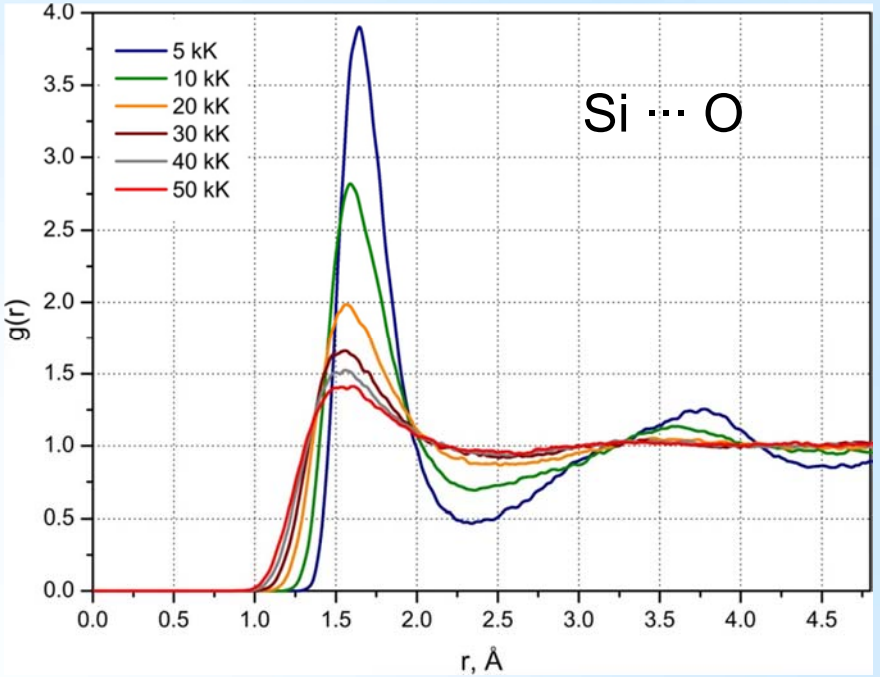
- Systems of 72 atoms (24 molecules SiO_2) were used in simulations. Test calculations with a large cell (216 atoms) did not show noticeable differences in pressure and internal energy.
- The energy cutoff for the plane wave basis was 900 eV. A number of calculations were done for E_{cut} = 600 eV.
- Reciprocal space discretization was limited to the Γ-point (after tests on a 2x2x2 grid).
- The timestep was varied with temperature but did not exceed 1 fs.
- The exchange-correlation energy was represented by the PBE, AM05, and PBESol functionals.
- The effect of the stoichiometric composition on Hugoniot waveform was evaluated with a model mixture for which we took aluminum silicate $(SiO_2)_{0.81}(Al_2O_3)_{0.19}$ with its density corresponding to that of SiO_2 under ambient conditions.
- Temperatures within 300 – 63000 K; densities within 1.585 – 7.943 g/cm^3. The reference structure for Hugoniot construction was the structure of amorphized crystals resulted from melt cooling and equilibration at T = 300 K.

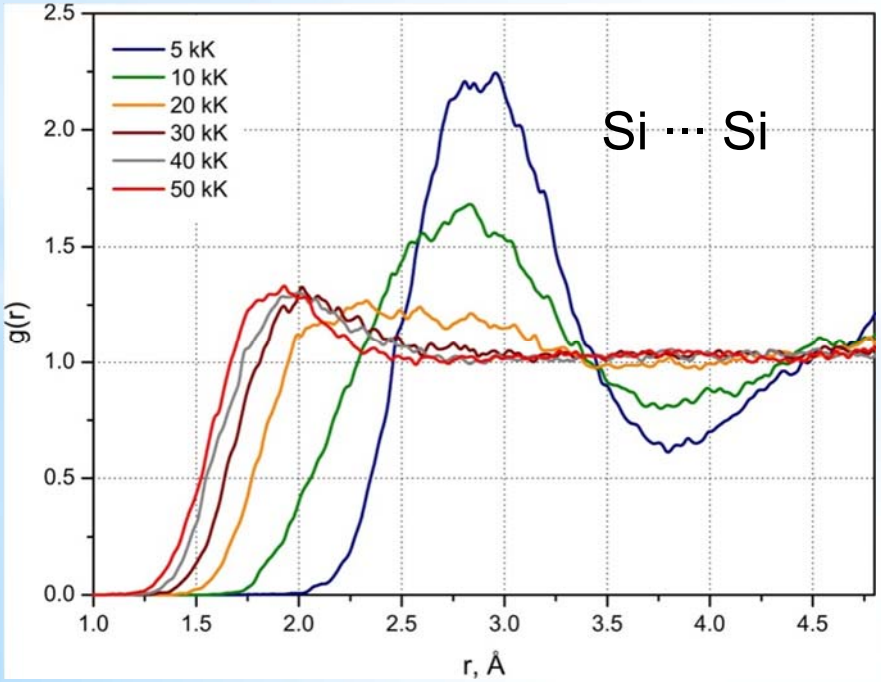
α-quartz principal Hugoniot

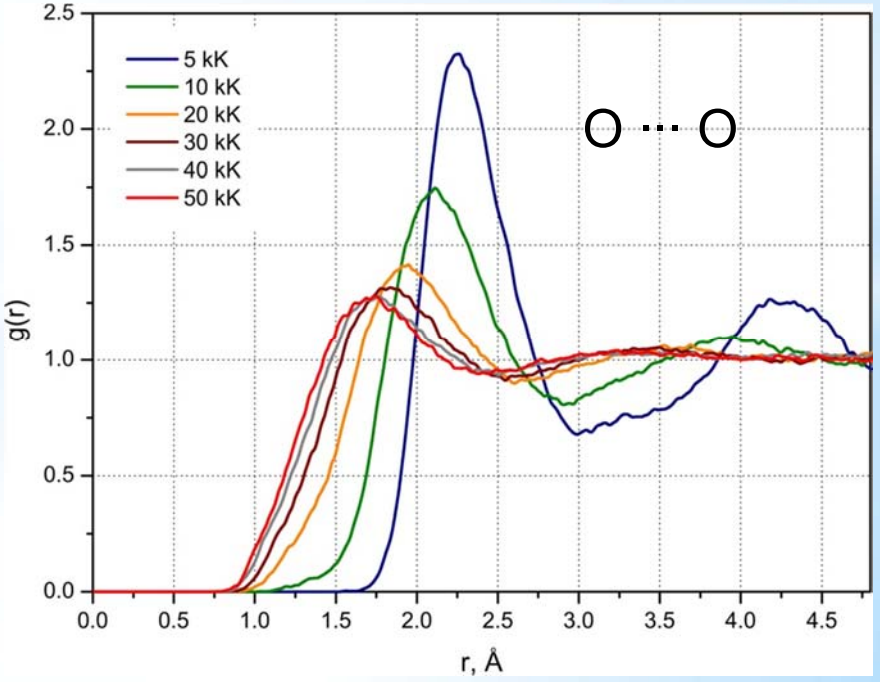


Radial distribution functions









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Thank you for your time!