

## **Structure, thermodynamic, and transport properties of molten Mg<sub>2</sub>SiO<sub>4</sub>: Molecular dynamics simulations and model EOS**

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### **ABSTRACT**

Molecular dynamics simulations have been used to study the structure, equation of state (EOS), self-diffusion, and shear viscosity of molten Mg<sub>2</sub>SiO<sub>4</sub> for pressures and temperatures in the range 2.5–110 GPa and 2100–5060 K, respectively. The transferable pair-potential parameters of Matsui (1998) for the system Na<sub>2</sub>O-CaO-MgO-Al<sub>2</sub>O-SiO<sub>2</sub> have been used accounting for Coulomb, Born, and van der Waals forces. Simulations have been carried out in the microcanonical (NEV) ensemble at 63 state points along 12 isochores spanning the density range 2754–4500 kg/m<sup>3</sup>. Thermodynamic properties including the isochoric heat capacity, isobaric expansivity, isothermal compressibility, thermal pressure, and the Grüneisen parameter ( $\gamma$ ) are computed directly from MD results. A density crossover between molten Mg<sub>2</sub>SiO<sub>4</sub> and forsterite crystals occurs at ~15 GPa at 2100 K. We find the Grüneisen parameter to be a function of temperature ( $T$ ), increasing with increasing  $T$  at low density ( $\rho < 3400$  kg/m<sup>3</sup>) but decreasing as  $T$  rises at high density ( $\rho > 3400$  kg/m<sup>3</sup>); hence, the integrated form of the Mie-Grüneisen EOS is only approximately valid for liquid Mg<sub>2</sub>SiO<sub>4</sub> since  $\gamma$  varies by ~20% over the  $T$  range along an isochore. Radial distribution functions for all atoms around all other atoms were used to generate coordination statistics as a function of pressure ( $P$ ) and  $T$ . Oxygen about Si coordination increases from fourfold coordination at low pressure to sixfold at higher pressure; the abundance of distorted trigonal bipyramidal fivefold polyhedra, Si(V) maximizes at 30 GPa at 3500 K. Interestingly, O about O increases to a maximum of 13 at low  $P$  before decreasing with increasing pressure to ~10. The mean coordination number (CN) of Si around oxygen increases from 1.2 to 1.5 consistent with an increasing abundance of Si<sub>2</sub>O<sub>7</sub> dimers as pressure increases. Self-diffusion of Mg, Si, and O was calculated at each state point giving activation energies of 67, 79, and 76 kJ/mol and activation volumes of 1.42, 1.10, and 1.32 cm<sup>3</sup>/mol, respectively. Shear viscosity of the liquid calculated at 12 state points using the Green-Kubo formulation provides an excellent Arrhenian fit. Viscosity varies by a factor of ~20 ( $1.5 \times 10^{-3}$  Pa s to 0.03 Pa s) from 1 to 100 GPa. The validity of the Stokes-Einstein and Eyring expressions for atom mobility and shear viscosity is examined in detail. Characteristic lengths for atom mobility are consistent with ionic radii to within a factor of ~1.5–2 for all atoms. An equation of state and thermodynamic model for Mg<sub>2</sub>SiO<sub>4</sub> liquid is developed consistent with the fundamental measure functional theory of Rosenfeld and Tarazona (1998). Our model reproduces the  $E$ - $P$ - $V$ - $T$  relations and the derived thermodynamic properties obtained from the MD simulations to within the reported uncertainty.

**Keywords:** Forsterite liquid, equation of state, molecular dynamics, Grüneisen parameter, structure, viscosity, diffusion