Structure, thermodynamic, and transport properties of molten \( \text{Mg}_2\text{SiO}_4 \): 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 \( \text{Mg}_2\text{SiO}_4 \) 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\(_2\)O-CaO-MgO-Al\(_2\)O-SiO\(_2\) 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 isochors spanning the density range 2754–4500 kg/m\(^3\). 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 \( \text{Mg}_2\text{SiO}_4 \) 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 (\( \rho < 3400 \text{ kg/m}^3 \)) but decreasing as \( T \) rises at high density (\( \rho > 3400 \text{ kg/m}^3 \)); hence, the integrated form of the Mie-Grüneisen EOS is only approximately valid for liquid \( \text{Mg}_2\text{SiO}_4 \), 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 \( \text{Si} \) 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\(_2\)O\(_4\) 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\(^3\)/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 \( \times 10^{-3} \text{ Pa s} \) 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 \( \text{Mg}_2\text{SiO}_4 \) 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

Introduction

An understanding of the equation of state (EOS), atomic structure, and transport properties of molten silicates in geochemical systems is central to many aspects of planetary dynamics. Quantitative information bearing on the shear viscosity, self-diffusion coefficients, and thermal and ionic conductivities of molten silicates, including the relationship between atomic level structure and macroscopic property variation with pressure (\( P \)) and temperature (\( T \)), is indispensable in the analysis of geochemical processes. For example, understanding the cooling and crystallization of Earth’s early magma ocean requires knowledge of the thermodynamic and transport properties of MgO-rich silicate liquids at \( P \) and \( T \) in the range 0–135 GPa and 2000–6000 K, respectively. The state of the mantle following magma ocean solidification sets the initial conditions for growth and subsequent evolution of the lithosphere, continental and oceanic crust, the hydrosphere and the atmosphere, and impacts the start of subduction and the plate tectonic cycle on Earth (e.g., Anderson 2007). Because silicate liquids are generally more compressible than crystals of the same composition, a density crossover between magma and crystals might be anticipated at high pressure. It is possible, therefore, that crystalline olivine accumulated in a region of neutral buoyancy in the Earth’s primitive magma ocean during and immediately following Earth accretion and Moon-forming impact. Arguments have been presented for the

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