Thermodynamics, self-diffusion, and structure of liquid NaAlSi$_2$O$_8$ to 30 GPa by classical molecular dynamics simulations

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ABSTRACT

Understanding the thermodynamics of liquid silicates at high pressure and temperature is essential for many petrologic problems, and sodium aluminosilicates are an important component of most magmatic systems. We provide a high-pressure equation of state (EOS) for liquid NaAlSi$_2$O$_8$ based upon molecular dynamics (MD) simulations. The resulting thermodynamic properties have changes in pressure and temperature correlative to trends in diffusion and atomic structure, giving insight to the connections between macroscopic and microscopic properties. Internal pressure shows a maximum in attractive interatomic forces at low pressure, giving way to the dominance of repulsive forces at higher pressure. Self-diffusion coefficients ($D$) typically order $D_{\text{Na}} > D_{\text{Al}} > D_{\text{Si}} > D_{\text{O}}$. At the lowest temperature, self-diffusivity (anomalously) increases as pressure increases up to ~5–6 GPa for Al, Si, and O. Diffusion data outside this “anomalous” region are fit by a modified Arrhenius expression, from which activation energies are calculated: 85 kJ/mol (Na) to 140 kJ/mol (Si). The amount of AlO$_4$ and SiO$_4$ polyhedra (tetrahedra) decreases upon compression and is approximately inversely correlated to the abundance of five- and sixfold structures. Average coordination numbers for Al-O, O-O, and Na-O polyhedra increase sharply at low pressure but start to stabilize at higher pressure, corresponding to changes in interatomic repulsion forces as measured by the internal pressure. High-pressure repulsion also correlates with a close-packed O-O structure where ~12 O atoms surround a central O. Self-diffusivity stabilizes at higher pressures as well. Relationships between the internal pressure, self-diffusion, and structural properties illustrate the link between thermodynamic, transport, and structural properties of liquid NaAlSi$_2$O$_8$ at high pressure and temperature, shedding light on how microscopic structural changes influence macroscopic properties in molten aluminosilicates.

Keywords: Thermodynamics, molecular dynamics, melt, NaAlSi$_2$O$_8$, equation of state, self-diffusion, coordination number, internal pressure, liquid structure

INTRODUCTION

Thermodynamic and transport properties of liquid silicates at high pressure ($P$) and temperature ($T$) play fundamental roles in petrologic systems, such as magmatic processes, mantle dynamics, phase transitions, and planetary differentiation. For example, heat capacity plays an important role in estimating the total heat flux of Earth (Stacey 1995; Lay et al. 2008). The fundamental nature of these material properties may be explained by an appeal to the atomic structure of the melt. Understanding the relationship between short-range liquid structure (atomic arrangement) and thermodynamics illuminates the underlying microscopic controls on macroscopic properties of silicate liquids.

Classical molecular dynamics (MD) simulations have enabled geologists and geophysicists to explore thermodynamic properties of liquid silicates at $P$ and $T$ conditions beyond those accessible in the laboratory. Since the work of Woodcock et al. (1976), high-$T$ and high-$P$ thermodynamic properties, self-diffusion, and melt structure have been studied for various compositions using classical MD simulations (e.g., Angell et al. 1982; Bryce et al. 1999; Oganov et al. 2000; Saika-Voivod et al. 2000; Ghiorso 2004a; Lacks et al. 2007; Spera et al. 2011; Cremer 2012). Because the position of all ions is known during MD simulation, the structural arrangement of atoms can be “observed” concomitantly with the $P$- and $T$-dependencies of thermodynamic and transport properties. While laboratory experiments provide standards for material properties, only MD simulations can fully explore the connection between the structure and thermodynamics of silicate melts at extreme $P (>10$ GPa) and $T (>2000$ K). Recent computational advancements and improvements in the pair-potential parameters strengthen the statistical mechanics of MD calculations, offering greater precision and accuracy to thermodynamic models. Although investigated by MD simulations in previous decades (e.g., Stein and Spera 1995, 1996; Bryce et al. 1999), liquid NaAlSi$_2$O$_8$ (albite composition) has not been explored in the detail currently available for classical MD simulations.

In the present work, an equation of state (EOS) for liquid NaAlSi$_2$O$_8$ is developed for the $P$-$T$ range 0–30 GPa and 3100–5100 K from classical MD simulations with the effective pair-potential of Matsui (1998). A table summary of the MD