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Thermodynamics, self-diffusion, and structure of liquid $NaAlSi_3O_8$ 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 $NaAlSi_3O_8$ 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 $D_{Na} > D_{Al} > D_O > D_{Si}$. 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 $NaAlSi_3O_8$ at high pressure and temperature, shedding light on how microscopic structural changes influence macroscopic properties in molten aluminosilicates.

Keywords: Thermodynamics, molecular dynamics, melt, $NaAlSi_3O_8$, equation of state, self-diffusion, coordination number, internal pressure, liquid structure