AMORPHOUS MATERIALS: PROPERTIES, STRUCTURE, AND DURABILITY†
First-principles study of self-diffusion and viscous flow in diopside (CaMgSi$_2$O$_6$) liquid

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ABSTRACT
We have carried out equilibrium molecular dynamics simulations of CaMgSi$_2$O$_6$ (diopside) liquid as a function of pressure (up to 150 GPa) and temperature (2200 to 6000 K) using density functional theory. Self-diffusion of Mg/Ca atoms decouples most from that of framework (Si/O) atoms at 2200 K and zero pressure, and all diffusivities become increasingly similar as temperature and pressure increase. The predicted temperature variations of all transport coefficients at zero pressure closely follow the Arrhenian law with activation energies of 107 to 161 kJ/mol. However, their pressure variations show significant deviations from the Arrhenius behavior. Along the 3000 K isotherm, the Si and O self-diffusivities show non-monotonic variations up to 20 GPa and then rapidly decrease upon further compression. The melt viscosity also shows a weak anomaly in the low-pressure regime before it starts to increase rapidly with pressure. Our results agree favorably with experimental observations of low-pressure non-uniform variations of Si and O self-diffusivities and viscosity. The predicted complex dynamical behavior requires pressure-volume dependent activation volumes and can be associated with structural changes occurring on compression.

Keywords: Diopside liquid, diffusion, viscosity, first-principles simulations, high pressure

INTRODUCTION
Knowledge about molten silicates is crucial for our understanding of the cooling and crystallization of Earth’s early magma ocean as well as for our understanding of the magmatic processes at the present (e.g., Abe 1997; Solomatov 2007; Lee et al. 2010). The analysis of xenoliths (Haggerty and Sautter 1990) and seismic observations (Revenaugh and Sipkin 1994; Lay et al. 2004) suggest that melts can exist at various depths in the mantle including the core-mantle boundary and can have a broad range of composition. Despite their great geophysical and geochemical importance, experimental studies of relevant silicate melts are still limited to relatively low pressures and temperatures, particularly, in the case of transport properties. Recently, we have reported first-principles studies of self-diffusion and viscous flow for several key liquids including SiO$_2$ (Karki and Stixrude 2010a), Mg$_2$SiO$_4$ (Ghosh and Karki 2011), MgSiO$_3$ (Karki and Stixrude 2010b), and CaAl$_2$Si$_2$O$_8$ (Karki et al. 2011).

Here, we study the transport properties of diopside (CaMgSi$_2$O$_6$) liquid, which being an end-member of model basalt composition (0.64 diopside + 0.36 anorthite) and representing a tertiary (CaO-MgO-SiO$_2$) system is a key component of the most common magma (basaltic melt). Diopside liquid has a relatively depolymerized structure and is expected to show faster and simpler dynamics than highly polymerized liquids (e.g., Bottiinga and Richet 1995). Experimental data on self-diffusion and viscosity coefficients of diopside liquid currently exist at temperatures below 2500 K and pressures below 15 GPa (Dunn 1982; Urbain et al. 1982; Scarfe et al. 1987; Shimizu and Kushiro 1991; Reid et al. 2001, 2003). The estimated activation energies and volumes of self-diffusion and viscous flow vary largely among these studies thereby rendering any extrapolations to high pressures uncertain. On the other hand, first-principles approach allows us to make reasonably accurate quantitative predictions of the values of these transport coefficients over much wider pressure and temperature ranges. In addition, the simulations are expected to provide insight into underlying microscopic mechanisms in the form of the atomic trajectories. In this endeavor, a recent study has addressed the structure and thermodynamics of diopside liquid (Sun et al. 2011). By performing equilibrium molecular dynamics simulations of molten CaMgSi$_2$O$_6$, we calculate here from first-principles its self-diffusion and viscosity coefficients as a function of pressure (up to ∼150 GPa) and temperature (2200 to 6000 K).

The paper is organized as follows. First, we introduce the methodology in the context of simulations, and derivation and analysis of the dynamical properties. Then, we present the specific results and discussion on melt transport properties by comparing our predictions with relevant experimental and calculated results for other silicate melts.

METHODOLOGY
First-principles molecular dynamics method (Kresse and Furthmüller 1996) was used within the local density approximation (LDA). The projector augmented wave (PAW) method (Kresse and Joubert 1999) was used with a plane wave cutoff of 400 eV and γ point. Simulations (consisting of 80 and 160 atoms) based on the canonical (NVT) ensemble were performed to explore compression from $P/V_0 = 1.5$ to 0.45 covering pressure range of 0 to 150 GPa at 2200 to 6000 K, where $V_0$ = 81.8 cm$^3$/mol is the reference volume also used in the previous study (Sun et al. 2011). The initial structure at each volume was first melted at 6000 K and then cooled isochorically to lower temperatures. Long simulation durations ranging from 20 to...