Coordinated Hard Sphere Mixture (CHaSM): A simplified predictive model for melts in the deep mantle with application to MgO

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Recent first-principles calculations (e.g. Stixrude, 2009; de Koker, 2013), shock-wave experiments (Mosenfelder, 2009), and diamond-anvil cell investigations (Sanloup, 2013) indicate that the compression behavior of silicate melts at deep mantle conditions is much more complex than previously appreciated. Melts undergo large structural changes with rapidly evolving oxygen coordination numbers over the mantle pressure range, strongly influencing their equations of state (e.g. Karki, 2006; 2007). Silicate melts also require significantly less energy to melt at high pressures (Stixrude, 2009), supporting the possibility of a deep whole-mantle magma ocean early in Earth's history. The evolution of this magma ocean as it cools and crystallizes is dominated by the poorly understood behavior of silicates at extreme pressures and temperatures. Probing these conditions is difficult for both theory and experiment, especially given the large compositional space (MgO-SiO_2-FeO-Al_2O_3-etc).

As a complement to first-principles methods, we have developed the Coordinated Hard Sphere Mixture model (CHaSM). We extend the standard hard sphere model, applied to silicates by Jing (2011), by incorporating the range of oxygen coordination states available to liquids. Using analytic expressions from hard sphere theory, our method rapidly predicts complex liquid structure and thermodynamics (~minutes on standard desktop computers). Given its speed, CHaSM is uniquely suited to mapping the wide compositional space relevant to early Earth evolution.

As a first application of the CHaSM approach, we have determined the thermodynamic and structural evolution of MgO liquid over a broad P-T range (0-250 GPa, 1667-7000K). We show how model parameters are calibrated using only data from crystal polymorphs, which discretely sample the spectrum of local structures available to the liquid. Thus, CHaSM is a fully predictive model that rapidly determines liquid properties as a continuous function of V and T. These calculations are validated using first-principles molecular dynamics simulations, demonstrating the accuracy of this simple approach for determining all thermodynamic quantites of interest, including isothermal compression curves, grüneisen parameter evolution, and melting curves.