Current limitations of molecular dynamic simulations as probes of thermo-physical behavior of silicate melts

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ABSTRACT

Molecular dynamic simulations offer promise as an essential tool, complementary to experiments, for expanding the reach of computational thermodynamics in igneous petrology by evaluating excess thermodynamic properties of multicomponent silicate melts. However, we present evidence suggesting that current practices in simulation may not achieve the precision needed to predict complex phase equilibria relevant to modeling the Earth’s interior evolution. We highlight the importance of quantification of the chemical short-range order in terms of cation-cation pairs in the melt and its impact on different kinetic aspects of molecular dynamic simulations. We analyze published molecular dynamic simulation studies of silicate melts to identify specific criteria and best practices for achieving and demonstrating equilibrium and producing accurate results. Finally, we propose a list of experimental and numerical investigations that need to be performed in the future to ensure full consistency between these two approaches to reduce the gap in our fundamental understanding of silicate melts between the atomic level and the macroscopic scale.

Keywords: Molecular dynamics, ab initio calculations, classical thermodynamics, silicate melts

INTRODUCTION

Our ability to describe the range of evolutionary pathways for terrestrial planets and to identify, through interpretation of available data, the particular pathway that the Earth followed depends on our understanding of the thermo-physical properties of Earth materials under a wide range of conditions. Multi-component liquid solutions of oxides, metals, and silicates, in particular, are the defining materials of magmatic processes that have driven chemical differentiation throughout planetary history and that continue to modulate ongoing dynamic processes and natural volcanic hazards. Questions whose answers depend on such liquid properties include (but are not limited to): temperature and heat flow profiles across the Earth’s mantle over time (Davies 2006, 2008); bulk chemical composition and both radial and lateral heterogeneity of mantle and crust (Solomatov and Stevenson 1993); and evolution of oxidation state and the speciation and outgassing (and ingassing) of volatile components, an essential part of the story of Earth’s habitability over time (Dasgupta and Hirschmann 2006; Hirschmann 2006).

In turn, the properties of melts and partial melts that must be predicted accurately as functions of temperature (T), pressure (P), or volume (V), and composition include elastic and thermodynamic quantities as well as dynamic transport properties such as viscosity, thermal conductivity, and chemical diffusivities (Stixrude et al. 2009). The densities of silicate melts, solids, and glasses define the driving forces by which gravity leads to physical flow and differential transport of phases (Agee 1998; de Koker et al. 2013; Lange and Carmichael 1987; McKenzie 1984, 1985; Sparks and Parmentier 1991; Stolper et al. 1981). Standard-state thermodynamic quantities and activity-composition relationships govern phase equilibria and provide the driving forces for chemical transport and differential transport of species within phases (Fei et al. 1990; Ghiorso 1985). Viscosity of melts controls many aspects of magma transport and chemical evolution of magmas (Clemens and Petford 1999; Dingwell 1996, 1998; Vetere et al. 2008; Whittington et al. 2009), although texture of multiphase aggregates is important as well (Faul et al. 1994; von Bargen and Waff 1986). Chemical and self-diffusivity of various species lead to stable isotope fractionation (Lacks et al. 2012; Lundstrom et al. 2005; Richter et al. 2003) and are often rate-limiting in crystal growth in igneous rocks (Faul and Scott 2006) and more generally in the achievement of thermodynamic equilibrium (Lesher 2010; Liang 2003).

The behavior and distribution of silicate liquids can be addressed near the surface and in both the present and the past through collection and analysis of igneous rocks (Klein and Langmuir 1987; Lee et al. 2009; Lehnert et al. 2000; Niu et al. 2011; Plank and Langmuir 1988), whereas the current distribution of melts at depth can be inferred from seismological (Forsyth 1996; Karato and Jung 1998; Lay et al. 2004; Williams and Garnero 1996) or magnetotelluric (Evans et al. 2005; Matsuno et al. 2012) measurements. However, many melting-related phenomena occur at extreme P and T, where observational and even experimental data are available only at sparsely sampled compositions and (P, T) or are lacking altogether. This creates an obvious need for theoretical or computational approaches to construct and calibrate a successful, general model of liquids, applicable to all relevant compositions and conditions and capable of predicting all thermodynamic and kinetic properties. The question is how to construct such a model. We propose that major progress can be achieved through a combination of approaches from Earth science and from engineering thermodynamics that have yet to be brought together.

The goal

An ultimate strategy to self-consistently represent and predict the thermo-physical behavior of silicate melts should link together the internal energy (U), the structure, and the equilibrium...