Linking the internal structure and volume of silicate melts to their thermodynamic properties

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The magmatic processes that define the formation and evolution of the Earth and terrestrial planets are controlled by the structural and thermo-physical properties — density, internal energy, viscosity, thermal and chemical diffusivity — of multicomponent silicate melts and aspects of their coexistence with solid solutions — e.g., melting points and major and trace element partitioning — across a wide range of pressure (P), temperature (T), and redox conditions. These properties need to be accurately known and then incorporated in large scale numerical models of magmatic processes like partial melting, crystallization, and melt-crystal segregation in order to define pathways of planetary evolution.

Numerical experiments based on density functional theory (DFT) coupled to classical molecular dynamic (MD) simulations have enabled, recently, considerable progress in such characterization of silicate melts even at extreme P, T conditions. However, these simulations are insufficient when trying to predict phase equilibria and self-consistent thermodynamic properties as they cannot access directly the Helmholtz or Gibbs free energy. They also suffer from expense and inherent errors due to approximations made in the DFT, the need for thermodynamic integration, and kinetic limitations associated with the motion of atoms in MD.

For these reasons, DFT calculations have to be coupled to other modelling approaches to identify potential strategies to accurately evaluate thermo-physical properties and ultimately to compute equilibrium states of multicomponent-multiphase systems. Classical thermodynamic models based on analytical definition of the Helmholtz or Gibbs free energy are therefore an essential complement to atomic-level simulation, if the macroscopic models can be made sufficiently accurate through incorporation of microscopic information.

In this work, we discuss in detail the importance of explicitly linking the internal structure and volume to the thermodynamic description of multicomponent silicate melts using a quasichemical approach. We propose self-consistent excess models based on DFT calculation results to incorporate the effect of pressure in the description of the excess Gibbs energy. We compare this method to existing models such as the stoichiometric and associated solution models and highlight the predictive limitations of other approaches.