Theories of fluids at extreme conditions

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Introduction

In this contribution two completely different methods to estimate by means of theory properties of fluids at conditions encountered in geochemical applications will be presented and discussed.

It is been well known that at these conditions most of compounds can be treated fairly well by a softly repulsive EXP6 potential. Consequently, common theories of fluids making use, either directly or indirectly, of the properties of the fluid of hard spheres (HS) are inapplicable in this case. Following the recently established idea of a uniform view of fluids [1] we have developed a theory, called augmented van der Waals theory [2], based on a Yukawa reference. Within this theory the EXP6 fluid may be described either directly by means of a 2-Yukawa model or by a simple Yukawa-based van der Waals equation, vdW (Y), with a simple mean field term. Both methods make use of the knowledge of theory-based analytic expressions for the thermodynamic properties of the Yukawa fluids.

The other method follows the common experimental setup, namely, to operate at fixed temperature, T, and pressure, P, and is based on P-explicit analytic equations of state for both pure HS fluids [3] and general hard-body fluid mixtures [4]. It is shown that the volume, as a function of T and P, estimated by means of the hard body equations captures extremely well the behavior of real fluids and that the additional mean field term is sufficient to bring theoretical results to agreement with experiment.

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First-principles simulations of alkali aluminosilicate liquids

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We have investigated the thermodynamics, diffusion, and structure of alkali aluminosilicate liquids at mantle conditions using first-principles molecular dynamics. Results for $NaAlSi_2O_6$ and $NaAlSi_3O_8$ liquid have been obtained at temperatures of 3000-6000 K and pressures up to 150 GPa. We find that fourth order finite strain expansions are required to account for the pressure-volume equations of state. Thermodynamic properties derived from simulation results agree well with experimental measurements. Isochoric heat capacity decreases with pressure, but the Grüneisen parameter increases with pressure. Liquid structure changes continuously with pressure, showing trends in mean coordination numbers and relative abundances of distinct coordination species consistent with previous studies of other silicate liquids. Self-diffusivities for Si and O increase with pressure below 16 GPa at 3000 K, while low-pressure diffusivities of Na are 3–6 times higher than values for other components. Activation volume for Na diffusion is much larger than that for Al, Si, and O diffusion, so that Na diffusivities become comparable to those of the other components at lower mantle pressures. This disappearance of mobility contrast implies that alkali-rich silicate liquids associated with low degree melting in Earth's interior are unlikely to have high electrical conductivity and will be more difficult than previously expected to detect by magnetotelluric sounding.