Equation of state for complex fluids

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Approach

On the basis of the Helmholtz free energy A, for neutral species like H_2O, CO_2, CH_4, H_2, N_2, O_2, Ar etc., equations of state (EOS) are available (e.g. [1, 2]). By differentiation of A in respect of temperature T and density ϱ, all thermodynamic properties can be derived. For the formulation of these EOS, A is split into an ideal gas term A^o and a residual term A^r. These EOS have been proven to be precise and extrapolatable to high temperatures and densities relevant for the upper mantle, but are for pure fluids only. The necessary parameters for A^r are not based on physical properties but are empirical. Mixing parameters have to be fitted therefore separately [3].

Another breed uses perturbation theory and expands A^r considering electrical moments, polarizabilities, and deviations from spherical symmetry for repulsion (e.g. [4, 5, 6]) using spherical harmonics. A simple EOS formulation has been published by Churokov & Gottschalk [7, 8], but the full approaches of Twu & Gubbins [4] and Moser *et al*. [5] are more sophisticated. These approaches are extendable to mixtures.

EOS

Applying [4, 5, 6], an EOS for A in the system H-He-C-N-O-Ne-Ar-Kr-Xe is presented. Instead of approximating the *Lennard-Jones* part of A^r by hard-spheres, a direct approach is applied by using the EOS for a *Lennard-Jones* fluid by Thol *et al*. [9]. The necessary dipole-, quadrupole-, octupole-moments, the polarizabilities, and the heat capacities were taken either from literature or calculated by *ab initio* methods. The remaining parameters for the *Lennard-Jones* fluid for each species ε_i, σ_i, and any non-spherical contributions are fitted by generating numerous A-values as a function of T and ϱ from the precise EOS for pure fluids (e.g. [1, 2]). For mixtures respective mixing rules are available. Because of the physical approach an extension to electrolytes is possible.

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