

## Isotopic effect on phase equilibria of pure fluids and mixtures: Molecular simulation, theory and experiment

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The temperature dependence of vapor – liquid and vapor – solid isotope fractionation factors was predicted by NVT-Molecular Dynamics and Gibbs Ensemble Monte Carlo simulations for atomic molecules (<sup>36</sup>Ar/<sup>40</sup>Ar, <sup>20</sup>Ne/<sup>22</sup>Ne, <sup>80</sup>Kr/<sup>84</sup>Kr) to assess the accuracy of h<sup>2</sup>-order Kirkwood-Wigner free energy expansion for specific Lennard – Jones parameterizations. In addition, the composition dependence of the corresponding fractionation factors for binary Ar–Kr mixtures was also predicted. Our simulation results compare very well with the existing experimental data. Fractionation factors were also predicted for other isotopic pairs, which have not been studied experimentally to date, including <sup>20</sup>Ne/<sup>21</sup>Ne, and <sup>132</sup>Xe/<sup>136</sup>Xe. Some premises behind the microscopic interpretation of the fractionation factors are also tested. Relevant extensions of this study to polyatomic molecular systems of geochemical interest, including O<sub>2</sub>, N<sub>2</sub>, CO, and H<sub>2</sub>O, are also discussed. The advantages of this approach over quantum mechanical calculations and the limitations of the methodology are addressed as well.

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### Reference

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## Ab initio molecular dynamics simulations of silicate liquids at high pressure

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Silicates liquids are primary agents of mass and heat transport, yet little is known of their properties over much of the vast range of pressures and temperatures that are relevant to planetary evolution. In the last few years, it has become possible to study for the first time silicate liquids with first principles quantum mechanical methods. We have applied density functional theory to the study of silicate liquids via ab initio molecular dynamics. The electronic structure, total energy, stress tensor, and forces acting on the atoms are computed self-consistently at each time step and atomic positions advanced according to Newton's equations of motion. The simulations are performed in the *NVT* ensemble with a Nose thermostat. Typical simulations consist of 80 atoms and are run for several picoseconds. We present initial results on MgSiO<sub>3</sub> liquid that span the entire pressure and temperature range of the deep earth. Preliminary results indicate that the fluid contains dominantly four-fold coordinated silicon and that the average coordination number increases gradually with increasing pressure. A surprise is that isotherms at 3000 K and 6000 K diverge on compression, behavior that is contrary to that of most crystals, and which implies a Grüneisen parameter that increases on compression. We will address issues including liquid-crystal density inversion, comparison with experiment, and analysis of the equation of state in terms of inherent structure.