

Molecular dynamics simulations of pure water and aqueous NaCl solutions at high pressure by Kawamura program

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Introduction

Water is the most abundant volatile element in the Earth's interior, and gives effects on many phenomena. Kawamoto et al. (Journal of Chemical Physics, 2004) reported Raman spectra of pure water under high pressure and temperature, and suggested that its structure changes as increasing pressure. They suggested that its structure changes from low density water to high density water at around 0.4GPa at 298K. Aqueous fluids which can be carried into the Earth's mantle by subducting slabs are not pure water but sea water. Therefore, we carried out a molecular dynamics (MD) simulation in pure water and NaCl solution in a pressure from 0.0001GPa to 1.0GPa in order to understand the behavior of water and sea water under high pressure.

Experiments

In this study, all MD simulation has been carried out at 300K with system containing. 1000 water molecules or 1000 water molecules + 32 NaCl molecules. The calculations were done with a pressure interval of 0.1GPa; in the range of 0.3-0.5GPa, a pressure interval was 0.02GPa. We determined the O-O pair-distribution function (PDF), density and angular of hydrogen bonding and covalent bonding of water molecules. PDF shows a relation between the length of two given atoms and their correlation. A wave pattern of PDF reflects structure of those two atoms. We will compare these calculated values of pure water with those of NaCl solution.

Results

In both simulation of pure water and NaCl solution, density and PDF have similar changes with increasing pressure. Density increases with pressure successively without any kink as suggested by Raman spectra in the previous spectroscopic study (Kawamoto et al., 2004). The wave patterns of O-O PDF also changes as a function of pressure; at atmosphere pressure, the wave pattern has a peak at about 2.8Å, which represents a length of hydrogen bonding and the other peak at about 4.5Å, which represents a length of a edge of a tetrahedron composed of hydrogen bonded molecules (Salah et al., J.Phys.Chem., 2006). But, as increase pressure, the peak at about 4.5Å becomes weak and a new peak at about 3.3Å appears. This new peak represents interstitial structure of water molecules (Saitta and Datchi, Phys.Rev.Lett., 2003). These structural changes are continuous.

The angulars of hydrogen bondings and covalent bonding of water molecules decrease as increasing pressure. Unlike density, their variation patterns change linearly to a pressure point and then change their slope. This pressure values are located in the range of 0.3-0.4GPa. These can be correspond to the kink observed in a pressure dependence of Raman frequencies (Kawamoto et al., 2004) and may indicate change of structure from low-pressure water to high-pressure water.

Comparison of the calculation results of pure water with those of NaCl solution indicates that NaCl solution has a structure similar to structure of pure water at higher pressure. This is consisting with the findings by neutron diffraction experiments (Leberman and Soper, Nature, 1995). The effect by addition of NaCl on the pressure increase is smaller at higher pressure.