

## A new approach for the equation of state of liquids under high-pressures

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Equation of state of liquids such as silicate melts plays an important role in our understanding the chemical evolution of Earth and other planets. For example, possible density cross-over at high-pressures could control the way of chemical evolution. Also, the experimental observations indicate that the Grueneisen parameter of liquids increases with compression (as opposed to decrease as observed in solids) that has an important implication for the temperature distribution in the magma ocean. In most of the previous studies in Earth science community, the equation of states of liquids under high-pressures were made using an analogy with those of solids. For example, Stixrude and Karki interpreted their observations of pressure variation of the Grueneisen parameter using the variation of Grueneisen parameter in solids. However, an inspection of existing data on a large number of liquids suggests that such an approach is not valid because the fundamental mechanisms of compression are different from those of solids. For example, (1) in a complex liquid such as a silicate melt, there exists a short-range order but a long-range order does not exist, (2) when a silicate (or an oxide) melt is compressed, the inter-atomic distances change much less than expected from the volume change, (3) the bulk moduli of silicate melts are about the same, (4) thermal expansivities of liquids are much larger than those of solids and change much less with compression than those of solids, (5) in all liquids so far studied, the Grueneisen parameter increases with compression. The observations (1) and (2) means that the main mechanism of compression is not due to the change in inter-atomic distances (as in the case for solids), but due to the geometrical processes through the modification of configuration of atomic groups (configurational entropy). When the main change in free energy is the change in internal energy and if the inter-atomic potential is central force potential, then the Birch law follows that leads to the negative dependence of the Grueneisen parameter on pressure. In these cases, equation of state such as the Birch-Murnaghan equation of state works. However, in a liquid, where configurational entropy plays a major role, a completely different approach is required. An ideal gas is a material in which the free energy is entirely of entropy origin. A model of a liquid that is based on the modification from the ideal gas model is a rigid sphere model. We will first example the properties of the rigid sphere model. In a rigid sphere model, the sole contribution to the free energy is configurational entropy. The main difference from an ideal gas is the fact that the motion of atoms (or groups of atoms) occurs only in a space that is not occupied by the atoms (spheres) (excluded volume effect). Since the main contribution to free energy in this model is configurational entropy, the thermal component of this equation of state is largely different from that of a conventional equation of state (such as the B-M equation of state). In particular, this model provides a natural explanation to all of the above listed unique features of liquids. One limitation of this rigid sphere model, however, is that it predicts a bulk modulus that is highly sensitive to the packing fraction. In order to rectify this point, we need to extend this model to allow compression of atoms (or molecules). Some properties of this deformable sphere model will also be presented.