PHASE AND STRUCTURE TRANSFORMATIONS  
IN WATER MICROCLUSTERS

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The behavior of 12- and 14-molecule water microclusters with ST2 potential in the range of 50-325 K is studied by the molecular dynamics method. Structure and phase transitions, including evaporation of molecules from the clusters and transition through the percolation threshold via hydrogen bonds, were found. Topological, temporal, and energy characteristics of the bond network are analyzed based on the dynamic criterion of hydrogen bonding.

Microclusters (MC) are a special state of substance with a strong dependence of structure and properties on the number of the constituent atoms or molecules. The MC possess increased chemical activity due to a large number of noncompensated intermolecular bonds on their surface and play an important role in the nucleation processes. Besides, MC are systems with relatively few degrees of freedom in which phase transitions take place. The small number of particles makes it possible to investigate these processes in detail at the molecular level by computer simulation methods.

Most publications on this subject are devoted to studies of MC of argon-like substances [1-3]. It was established that the most stable configurations are atomic configurations with icosahedral type of symmetry. Upon variation of temperature (kinetic energy of atom motion), transitions between the solid- and liquid-like states occur. The transitions take place in a finite temperature range. If the global minimum of potential energy differs considerably in energy from the other minima, phase coexistence is observed [1]: at a certain constant temperature the cluster makes spontaneous transitions between the solid- and the liquid-like states.

A distinctive property of water molecule systems are strong directed H-bonds. Due to this, structural chemical aspects in phase transition studies increase in importance. The existence of steep deep minima on the potential energy surface enhances the cluster's nonequilibrium state since its structure largely depends on the preparation procedure, and the accessible region of the configuration space, on the initial state.

The molecular dynamic study of an MC in the form of a pentagonal dodecadron of 20 water molecules [4] showed that it is stable up to 200 K. Then a change of structure took place, which was assigned to melting based on the shape of its caloric curve. An important result is that a free isolated MC does not evaporate and water molecules in it do not dissociate up to 300 K, although this possibility was not excluded since the modeling was carried out using the atom-atom potential of central forces. In any case, it did not happen during modeling at any temperatures. A clathrate-like structure of MC with all pentagonal faces is considered to be the most stable because the HOH angle in a water molecule is approximately equal to the angle of a regular pentagon, and each molecule participates in formation of three H-bonds.

The transition from the solid- to the liquid-like state was also observed by the Monte-Carlo method in a cubic water octamer [5]. The higher face strain in the initial configuration as compared with the pentagonal dodecadron led to a lowering of temperature down to 120-130 K at which the initial structure is destroyed and melting of the cluster begins. In the modeling, the Jorgensen potential TIP3p was used.

The present paper is devoted to molecular dynamic simulation of 12- and 14-water molecule MC with ST2 potential in a wide temperature range. Formation of a local pentagonal symmetry is considered and the possibility of spontaneous transitions to clathrate-like structures is estimated. The change of the H-band network topology is investigated.


CALCULATION PROCEDURE

The simulation was performed with a program realizing the molecular dynamics method for polar molecule systems with a fixed point distribution of masses and effective charges. For calculation of intermolecular interaction, the Stillinger potential, ST2, [6] was chosen. The Gear algorithm was used. For integration of the equations of rotatory motion, Sonnenschein's second-order quaternion method [7] was employed. A time step is $10^{-15}$ sec, the number of steps at each temperature ranged from 12,000 to 30,000. The calculation was performed at a constant total kinetic energy; this was achieved by combined scaling of rates of both the translation and rotatory motions so as not to artificially violate the zero value of the total angular momentum of the system. The MC behavior during stepwise heating by 25 K was studied.

To analyze the intensity of molecular motions and detect structural rearrangements, the standard deviations of the center of mass positions and molecular orientations [8] were calculated. The configurations corresponding to local minima on the potential energy surface or the F-structures [9] were calculated by lowering the temperature stepwise. A change of cluster structure was also observed visually. Instantaneous configurations were represented at different observation angles.

As the initial configuration in a cluster of 12 molecules, a fragment of an ideal hexagonal structure was taken (Fig. 1). Two stabilizing molecules were added into the other MC; as a result, each molecule participated in three H-bonds.

The hydrogen bonds between molecules were detected using the dynamic criterion [10], whereby a bond is identified by the mean value of the potential energy of molecular interaction during a period of time of the order of translational oscillation period. We used an averaging time of 0.5 psec. At each averaging, a pair interaction matrix was calculated. The choice of the threshold value of the interaction energy of two molecules resulted in a certain type of topological connectivity matrix. The matrix was used to calculate the number of 3-, 4-, 5-, and 6-membered rings, a mean life-time of a bond, and some other characteristics reflecting the structure and the dynamics of the hydrogen bonds network.

TRANSITION DYNAMICS AND CALORIC CURVES

The initial MC configurations are schematically represented in Fig. 1. The circles denote oxygen atoms. Positions of hydrogen atoms (protons) were chosen according to the Bernal–Fowler rule.

For the first MC, an F-structure of the initial configuration was preliminarily obtained. Its only distinction is that the mean distance between oxygen atoms increases by about 3%. Thus, the initial fragment of hexagonal ice is structurally stable. It is noteworthy that this conclusion concerns only the given configuration. With a different orientation of molecules, the changes may be more significant. For example, new H-bonds may arise. This follows from the fact that the respective minimum of potential energy is very shallow.

![Fig. 1. Structure of 12- and 14-molecule water clusters. The circles stand for oxygen atoms. The white circles correspond to two added molecules of the second MC. For other explanations, see the text.](image-url)