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Computer simulation of hexagonal ice[a)]

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The oxygen atoms in ordinary hexagonal ice are simply arranged. These atoms form two interpenetrating hexagonal-close-packed lattices. Every oxygen has four nearest neighbors, from the other HCP lattice, such that the four neighbors lie at the vertices of a regular tetrahedron. The arrangement of the hydrogen atoms is more complicated. Pauling[1] explained that each nearest-neighbor pair of oxygen atoms has associated with it a hydrogen atom which lies closer to one or the other oxygen. Hydrogen atoms in the crystal occupy these positions randomly with the overall restriction that each oxygen have exactly two nearby hydrogens. Two other hydrogen atoms, farther away, form hydrogen bonds with each oxygen. This description of the structure is generally accepted because the entropy associated with the random arrangement[2] is in agreement with experiment.[3]

Computer simulation of microscopic systems has reached the stage at which ice can seriously be considered.[4] In any such simulation the problem of arranging the hydrogen atoms must first be solved. This problem is analogous to that of filling three-dimensional space with peculiarly-shaped dominoes. We have gone to considerable effort to generate ice structures, random in Pauling's sense, which satisfy two additional constraints important to computer simulation. Because these same structures, which we intend to apply to a study of frac-

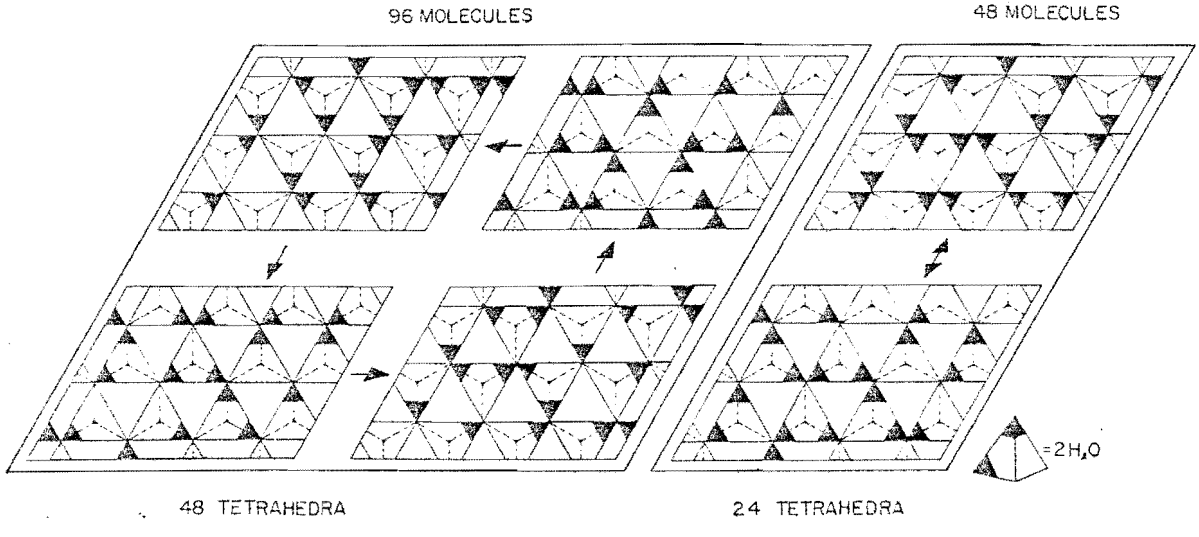

FIG. 1. Periodic hexagonal ice.

ture[5] and flow in ice, should also be useful to workers concerned with equilibrium thermodynamic and lattice dynamical properties of ice we record two of them here. The additional constraints we have made are these: first, the structure must satisfy periodic boundary conditions. This is necessary to minimize small-system surface effects. Second, the structure should have the minimum possible multipole moments.[6] This is necessary to reduce long-range forces between parts of a fracturing crystal and is also desirable, we believe, to reduce number dependence of equilibrium ice-crystal properties.

To generate the crystals shown in Fig. 1 we first produced 22000 layers of 12 ice tetrahedra each. These tetrahedra are centered on the oxygens of one of the two interpenetrating lattices. Because two of the four hydrogens in each H_4O_2 tetrahedron will be close to the vertices and two will be close to the center, there are six possible types of tetrahedra in a given layer. We have required that (1) each type occur twice in each layer, and (2) each layer be consistent with the ice structure. It is necessary to examine about 10000 layers which satisfy requirement (1) in order to find layers which will pack together to form 48-molecule, or larger, periodic crystals. Figure 1 shows bottom views of layers making up 48- and 96-particle crystals. In the figure the bases of the tetrahedra making up the layers have been shaded to indicate vertices with nearby hydrogen atoms. The crystals contain no recognizable regularities other than the restrictions mentioned above. It is noteworthy that these restrictions cause the dipole, quadrupole, and octupole moments of these crystals to vanish.

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