

Can thin disk-like ice clusters be more stable than compact droplet-like ice clusters?

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Abstract

The relative stability of water clusters of two different morphologies has been examined with the size N ranging from 54 to 864; the first one is a circular fragment of bilayer ice (a disk-like cluster), and the second one is a spherical fragment of normal cubic ice (a droplet-like cluster). We found a crossover at $N_c \approx 1000$, below which the disk-like cluster becomes more energetically favorable. The crossover arises because the potential energy (per molecule) for the droplet-like cluster decreases linearly with $N^{-1/3}$ whereas it decreases by $N^{-1/2}$ for the disk-like cluster. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Nanoscale clusters are particularly fascinating because they offer several significant benefits. First, these clusters provide a bridge between microscopic single atoms or molecules and macroscopic condensed matters. Second, they play a central role in condensed phase nucleation. Third, they offer new materials whose characteristics can be tuned via changing the cluster size [1]. A current interest in cluster science is to determine the cluster size at which the transition from the embryonic to bulk crystalline forms occurs. Van der Waals clusters are known to be more stable with icosahedral symmetry

than with lattice-based symmetry [2,3]. Covalent clusters have special sizes (e.g., C_{60} for carbon) at which the stability of cluster is greatly enhanced [4]. Hydrogen-bond nanoclusters, however, have been studied less. The hydrogen-bond strength lies in between those of van der Waals and covalent bonds. Here we report a novel nanocluster of water molecules out of which a bulk crystalline form could occur. This hydrogen-bonded cluster is disk-like with all constituent molecules exposed to the vacuum. Yet, this cluster is more stable than a spherical fragment of bulk cubic ice [5] over the size ranging from 100 to 1000 molecules.

Recently, we demonstrated by molecular dynamics (MD) simulation of the TIP4P water [6] that when the water is confined between two plane-parallel hydrophobic walls, it can freeze into a defect-free bilayer ice crystal [7]. Each layer of the bilayer ice is

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composed of rows of distorted hexagons; the two layers are stacked in complete registry. Every molecule has four hydrogen-bonded neighbors, three in the same layer and one in another layer. The new water cluster we propose is a disk-like portion of the bilayer ice crystal in vacuum. Although this water cluster is quasi two-dimensional and without normal cubic ice symmetry, most of the hydrogen bonds in the cluster are saturated. This unique feature confers on the disk-like cluster a more favorable morphology compared to the spherical portion of normal cubic ice of the same size, despite the fact that the latter has a much smaller surface area exposed to the vacuum.

In general, the relative stability of various morphologies of clusters can be examined via calculating the potential surface [8,9]. The stable morphologies correspond to the local minima on this surface. For nanoclusters with hundreds of molecules, it is nearly impossible to identify the most stable morphology (the global minimum in configuration space). On the other hand, in the large-size cluster limit, the most stable cluster should be a spherical fragment of bulk crystal, which has the fewest molecules on its surface. In this sense, the most stable cluster of water should be, at a certain size, a spherical fragment of crystalline cubic ice which has a minimum number of molecules on its surface. Such a cluster composed of several thousands water molecules has indeed been observed by an electron diffraction experiment [10]. Here we consider specifically the relative stability of the quasi two-dimensional bilayer ice clusters and the three-dimensional cubic ice clusters. The basic strategy is to calculate and compare, over a wide range of sizes, the potential energy of the two kinds of ice clusters.

2. Results and discussion

To examine the stability of two kinds of clusters, we calculated the potential energy of clusters made from the bilayer ice and cubic ice. Both kinds of ice are proton-disordered, and thus there are many possible arrangements as to the positions of protons. We generated 100 configurations for each bilayer and cubic ice. Water clusters that we studied were made from those ice crystals. The appropriate number of

water molecules were cut out from each kind of generated ice crystals taking the molecules in the order of the distance from an arbitrarily chosen center. The numbers of water molecules in clusters N were 54, 108, 216, 324 and 864. Each cluster was quenched to the local minimum structure (attainable at 0 K) [11]. This quenching was performed for both kinds of clusters with five different sizes, each of which has 100 different forms of proton-ordering.

First, we examined the stability of the crystalline bilayer ice whose flat surfaces are exposed to vacuum. It is found that the bilayer ice structure remains stable at temperature 0 K even when the two parallel walls are removed. The potential energy in this condition is -53 kJ mol^{-1} , which is close to that under high pressure (e.g. 1 GPa) [7]. This value is a little higher (by 3 kJ mol^{-1} only) than that of the cubic ice I, -56 kJ mol^{-1} , despite the fact that two planes of the bilayer are exposed to the vacuum, which possess a wide surface area. Note that these surfaces contain no broken hydrogen bonds.

Second, we compared the stability of the quasi two-dimensional bilayer ice cluster and the three-dimensional cubic ice cluster at 0 K. When the peri-

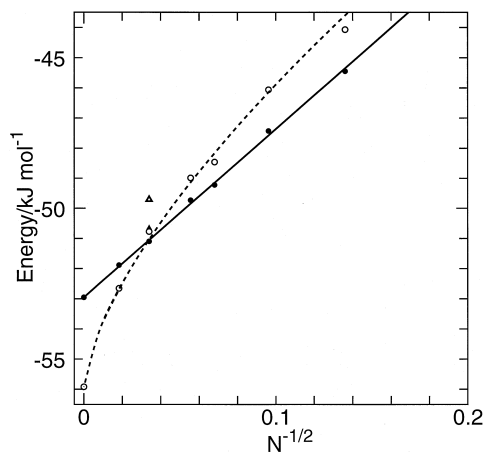


Fig. 1. Potential energy of water clusters divided by the number of participating water molecules N as a function of $N^{-1/2}$. Filled circle: thin disk-like cluster; open circle: spherical droplet-like cluster. Solid line: the fitting curve for disk-like clusters to $b_0 + \Delta b N^{-1/2}$; dashed line: the fitting curve for droplet-like cluster to $c_0 + \Delta c N^{-1/3}$. The extrapolated curves are shown in the inset and a crossover is seen at about $N=1000$. Open triangle: spherical droplet derived from the low-density bulk liquid; filled triangle: spherical droplet derived from the high-density bulk liquid.

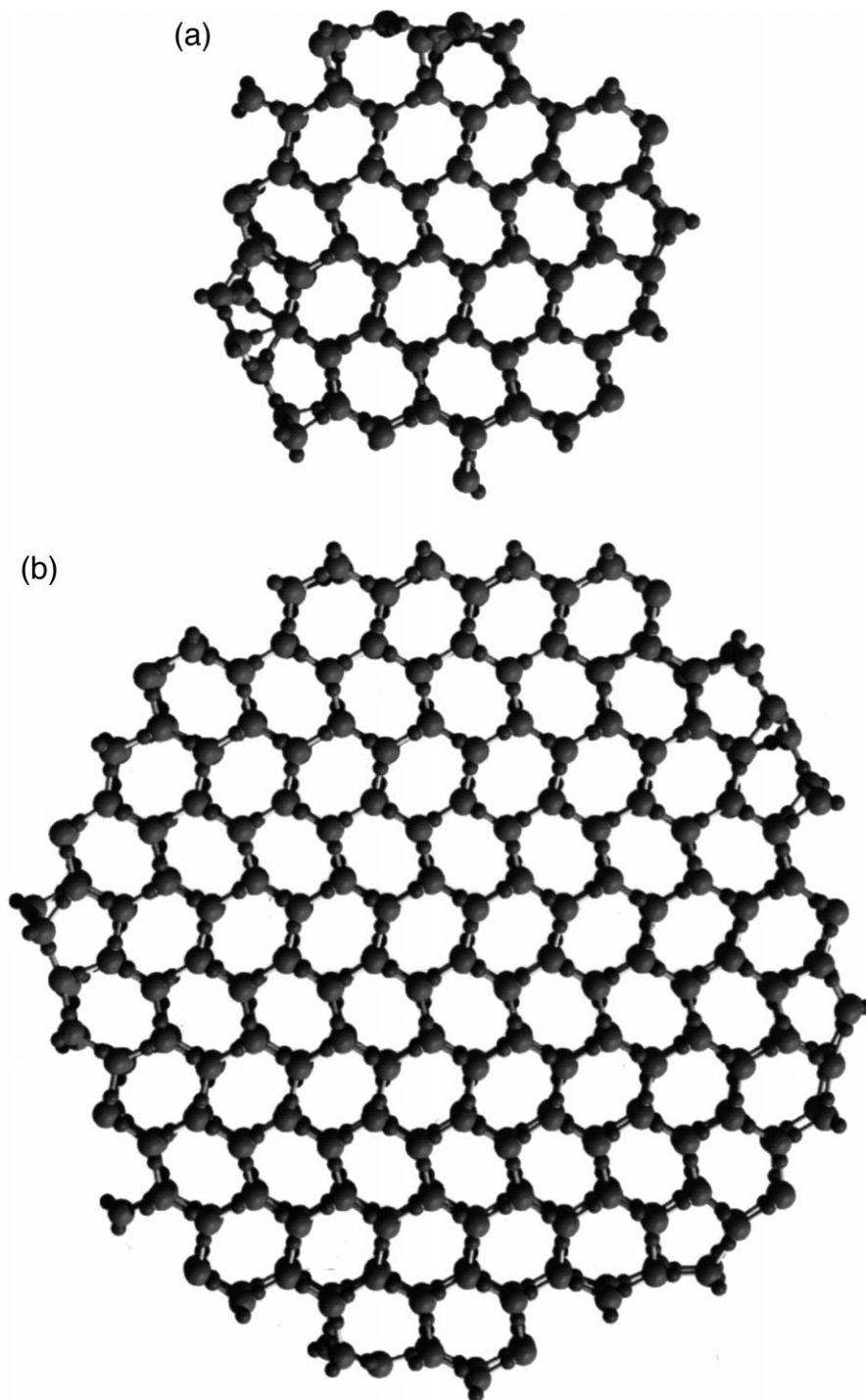


Fig. 2. Structure of disk-like clusters, (a) $N = 108$ and (b) $N = 324$, and droplet-like clusters, (c) $N = 108$ and (d) $N = 324$.

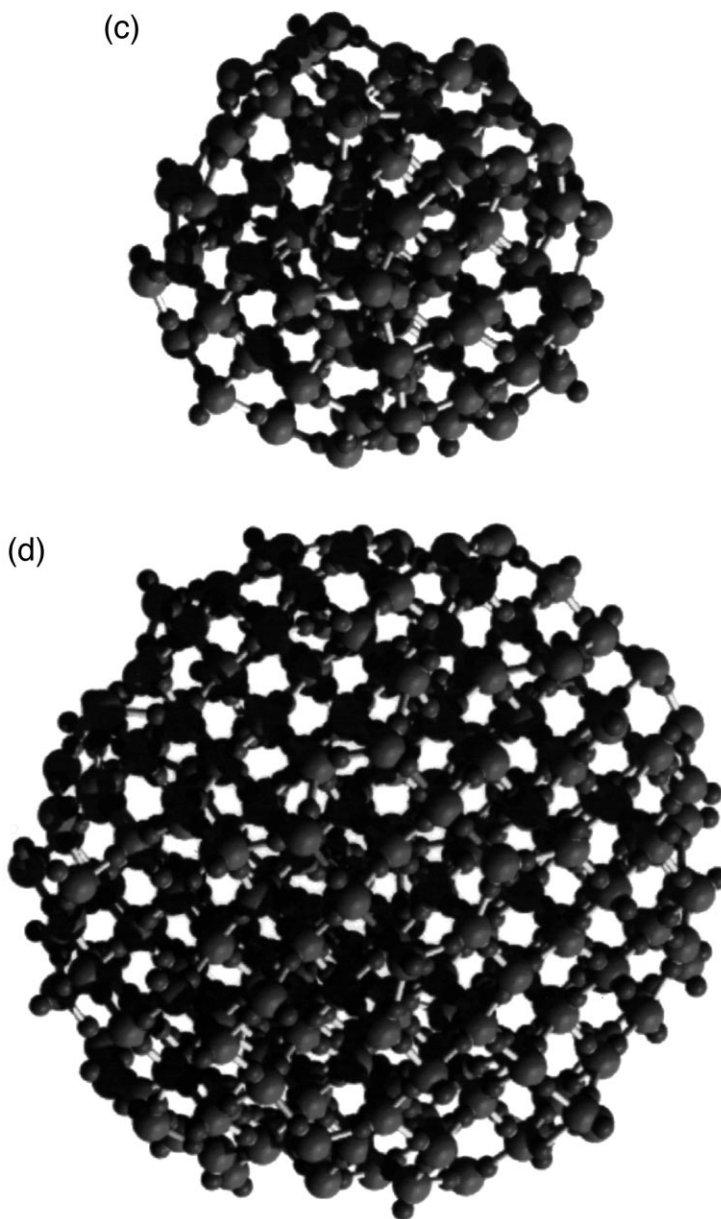


Fig. 2 (continued).

odic boundary condition is removed, the bilayer and the cubic ices become a thin disk-like and a droplet-like clusters, respectively (in the vacuum). Both clusters contain some broken hydrogen bonds. When the number of broken hydrogen bonds is minimized, it is proportional to $N^{1/2}$ for the thin disk cluster and $N^{2/3}$ for the spherical droplet cluster in the

large N limit. Consequently, the droplet-like cluster is expected to possess a higher energy than the disk-like cluster with the same size, which suggests the latter at intermediate size is more favored energetically in the low temperature regime. It is thus sensible to argue that the potential energy per molecule is asymptotically proportional to $N^{-1/2}$ for

disk-like clusters and $N^{-1/3}$ for droplet-like clusters. With this argument, it is straightforward to show that an energy difference maximum would appear, at certain cluster size. The energy difference would change sign at a certain value of N larger than that at the maximum energy difference because the potential energy of the disk-like clusters is higher (though by only 3 kJ mol⁻¹) than that of the droplet-like clusters in the large N limit.

In Fig. 1, the potential energy (total potential energy divided by N) of both kinds of clusters at 0 K is plotted against $N^{-1/2}$. For all cluster sizes examined initially, the disk-like clusters are more stable than the droplet-like ones. However, with increasing N , the energy difference decreases gradually. The energy values can be well fitted respectively to $b_0 + \Delta bN^{-1/2}$ and $c_0 + \Delta cN^{-1/3}$, where b_0 and c_0 correspond to the energies of infinitely large clusters, and Δb and Δc are the fitting parameters [7]. The fitting suggests that a crossover would appear at a cluster size of approximately 1000. To confirm this, a further calculation was made for clusters with 3000 molecules. We indeed find that at 0 K the energy of the droplet-like cluster, -52.68 kJ mol⁻¹, is lower than that of the disk-like cluster, -51.89 kJ mol⁻¹.

It was also found by extensive MD simulation of the TIP4P water that the potential energy and other properties in supercooled water change abruptly at around 210 K [12,13]. Various anomalies of water, such as divergences of heat capacity and some dynamic properties in supercooled state [14], were accounted for by associating them with either the critical behaviour [12] or the phase transition between two liquid states [13]. The potential energy of supercooled liquid water below 210 K is found to be only slightly higher than that of ice in its local minimum structure [13]. This liquid has no long-range order but contains several defects in the hydrogen-bond network. Those defects may be utilized to reduce the surface energy when a cluster is prepared from this liquid water. Thus, we also examined the stability of the droplet-like clusters originated from bulk liquids, both at high- and low-density states [13]. The energies of 864 clusters made from the liquids are also given in Fig. 1. For the clusters made from low-density liquid, the potential energy is almost the same as that from cubic ice.

Typical clusters with 108 and 324 water molecules are shown in Fig. 2a,b for disk-like clusters and in Fig. 2c,d for droplet-like clusters. These show that molecules at the edge region and surface region are irregularly arranged whereas the core region remains intact. The size of core region increases with increasing N . The distribution of potential energy per individual water molecule in the clusters is plotted in Fig. 3. For the bilayer bulk ice, the energy distribution splits to two peaks whereas for the cubic ice it exhibits a unimodal and broad peak. Upon removal of the periodic boundary condition and subsequent quenching, high-energy surface molecules show up, which correspond to a peak at about -70 kJ mol⁻¹ in Fig. 3. Note that the separation of the high- from the low-energy peak is more conspicuous for the disk-like clusters. Evidently, as N grows, the relative population of high-energy surface molecules decreases and, eventually, the disk-like clusters becomes less stable relative to the droplet-like cluster.

The stability of two kinds of clusters with 216 molecules was also examined at 30 and 60 K with MD simulation. The temperature was kept constant by simple rescaling of the molecule velocities. After 100000 time steps of MD simulation, which corresponds to a 50 ps annealing period, the system was quenched to the potential energy minimum structure. This procedure was applied for both kinds of cluster, each with 100 different proton-disordered configurations. After annealing at 30 K, the average quenched energy for disk-like clusters is -49.11 kJ mol⁻¹ and that for droplet-like clusters is -48.74 kJ mol⁻¹. These values are comparable with those without annealing (given in Fig. 1), i.e. -49.22 kJ mol⁻¹ for the disk-like clusters and -48.46 kJ mol⁻¹ for the droplet-like clusters. Even after annealing at 60 K, the energy for disk clusters is -48.93 kJ mol⁻¹ and that for droplet clusters is -48.72 kJ mol⁻¹. We conclude that the disk-like clusters can be energetically more stable than the droplet-like one at finite, although low, temperatures.

Finally, we note that when N is small (≤ 100) is small, there could be still more stable forms of water clusters other than the disk- or droplet-like clusters. Indeed, small water clusters up to 20 molecules have been extensively investigated by either *ab initio* quantum-mechanical calculation or MD simulations. It was shown that the fused cubic and stacked pen-

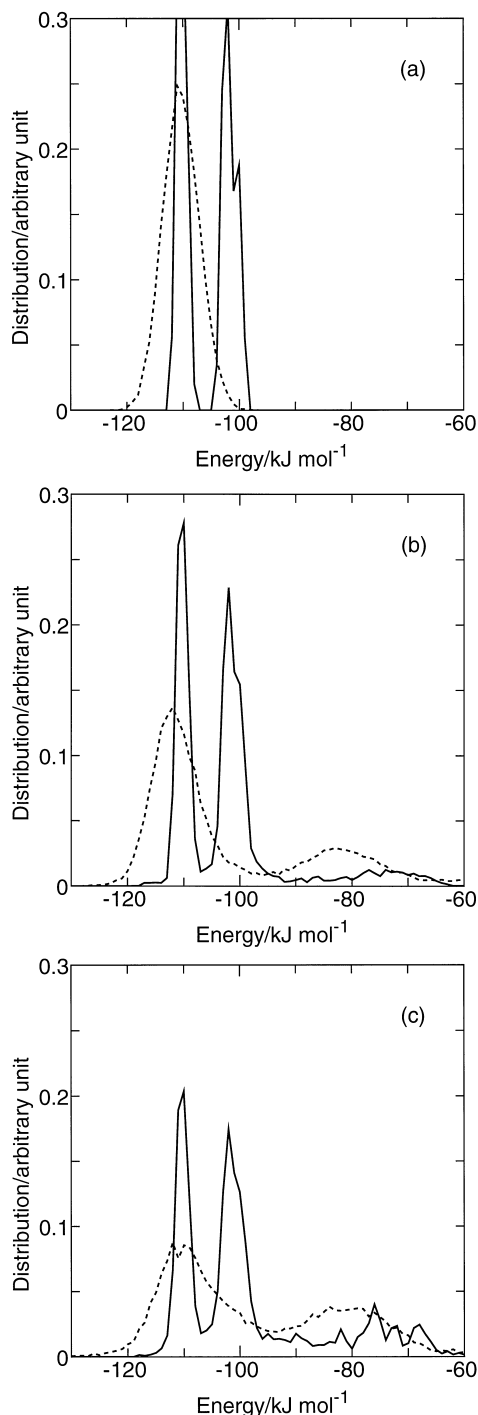


Fig. 3. Binding energy distribution for disk-like (solid lines) and droplet-like (dashed lines) clusters. (a) $N = \infty$, (b) $N = 864$, (c) $N = 216$.

tagonal ring structures are more stable than the cage structures [15,16]. The basic components in those small clusters are four- or five-membered rings. The fused cube may be another candidate for the large stable cluster, since it forms a one-dimensional ice cluster and also has four hydrogen-bonded neighbours. Tsai and Jordan examined the stable morphology of small water clusters ranging from 8–20 molecules [15]. The potential energy for fused cubes is well fitted to the function, $a_0 + \Delta aN^{-1}$. The asymptotic energy a_0 is approximately -47 kJ mol^{-1} , which is much higher than the energy of two-dimensional ice -53 kJ mol^{-1} because the distortion is rather large in the fused cubic clusters whose four-membered rings are formed at the cost of a fairly large energy penalty. Therefore, the crossover should exist at small size. Indeed, Wales and Ohmine found a more stable structure made from pentagonal rings than the fused cube for a $(\text{H}_2\text{O})_{20}$ cluster [16]. The pentagonal rings, however, cannot tile a plane solely by themselves. It is therefore conceivable that a large cluster ($N \geq 100$) made from stacked hexagonal rings, such as the disk-like cluster derived from the bilayer ice, could have the lowest potential energy.

Although the precise value of N_c may be affected by the choice of potential models, the general trend that the disk-like cluster of bilayer ice can be more stable than the droplet-like cluster of cubic ice for a certain range of N ($\sim 10^2$) seems generic.

Most of the theoretical studies on the stability of various morphologies for water clusters have been made in terms of the potential energy. It is, however, much more desirable even at the lowest temperature limit that the stability of water clusters is examined by evaluating not only the potential energy but also the zero-point energy of the intermolecular vibrations. Calculation of the zero-point energy is now under way.

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