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Articles

Hexagonal $\mathrm{I_h}$ Ice and Water Clusters. Mpemba Effect. Entropic Parameters of Hydrogen Bonds

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Abstract

The importance of ice in sustaining life on our planet is difficult to underestimate. Ice significantly influences the living conditions and activities of plants, animals, and various human activities. By covering water and ice, due to its low density, plays the role of a floating screen in nature, protecting rivers and reservoirs from further freezing and preserving the life lives of underwater inhabitants.

The utilization of ice for various purposes (snow retention, construction of ice crossings and isothermal warehouses, ice filing of storage, and mines) constitutes the subject of several branches of hydro-meteorological and engineering sciences.

Natural ice is used for storing and cooling food products and biological and medical preparations, for which it is specifically produced and harvested, and melt water obtained during ice melting.

The study of ice, including its hexagonal structure (Ice $\mathrm{I_h}$), highlights its intricate properties. Furthermore, investigations of the Mpemba effect, where warm (37-60°C) and hot water (>60°C) freeze faster than cold water, shed light on the interplay between entropy and hydrogen bond energies. Understanding these phenomena contributes to scientific knowledge and impacts practical applications in various industries and environmental contexts.

In summary, the importance of ice transcends mere natural phenomena, deeply intertwining with human activities, scientific endeavors, and sustenance of life across the planet, serving as a cornerstone in various ecological and industrial domains.

Keywords: hexagonal, water clusters, ice, entropy.

1. Introduction

At the corners of the crystalline lattice of ice, the oxygen (O) atoms are symmetrically arranged. They form regular hexagons. Hydrogen atoms occupy different positions and bond with

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the oxygen atoms through hydrogen bonds. Figure 1 illustrates a hexagonal structure of the ice (Ignatov, Mosin, 2014).

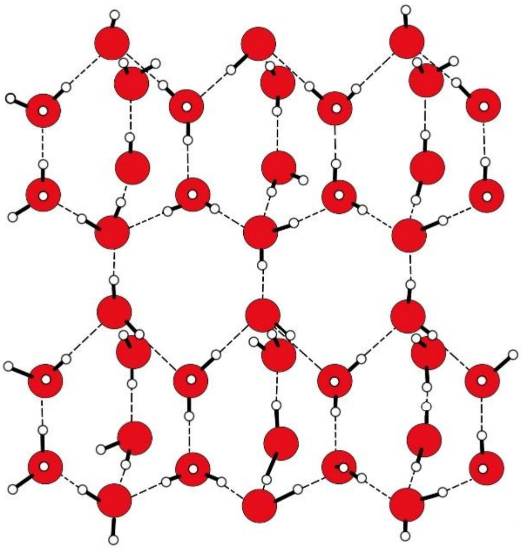

Fig. 1. Hexagonal structure of ice I_h

Research reveals that the $(H_2O)_6$ cage and $(H_2O)_{20}$ dodecahedron water clusters have a hydrogen bond topology that can be described in liquid and ice phases. The two clusters exhibit approximately the same hydrogen bond arrangement in water's liquid and solid phases (Gao et al, 2021; Iliev et al., 2023). $(H_2O)_6$ features 27, and $(H_2O)_{20}$ has 30 026 symmetry-distinct hydrogen bonds (Kuo et al., 2001).

The study used the discrete evaporation of water drops with the spectral methods NES and DNES clusters (Antonov, 1995; Todorova, Antonov, 2000; Ignatov, Valcheva, 2023).

2. Materials and Methods

Spectral methods Non-equilibrium energy spectrum (NES) and Differential non-equilibrium energy spectrum (DNES)

According to (Luck, 1980), the water molecules are bound with the energy of hydrogen bonds with energy (-E). When the water molecules are not connected with hydrogen bonds, the energy is E=0. This is recognized as the two-state model of Luck (Kontogeorgis et al., 2022; Vega, Lovell, 2016).

In a specific volume of water and our experiments, we study water drops the water, interlinked by van der Waals forces and electromagnetic hydrogen bonds, is considered an associated liquid (Antonov, 1995).

The investigation of water drops was performed in a hermetic camera with an optic system to research the wetting angle θ (Antonov et al., 1989). The parameters of the wetting angle are connected with the parameters of hydrogen bonds with a formula (Todorov et al., 2008; Todorov et al., 2010).

$\Theta = \arccos(-1+bE)$, where $b = I(1+\cos\theta_0)/C\gamma o$ (1)

The range of the parameters of the hydrogen bonds is the following:

$E=(-0.0912)-(-0.1387)$ eV; 736-1117 cm^{-1}; $\lambda = 8.9 - 13.6$ μm

In (1) θ is the wetting angle, and b is a temperature-dependent parameter. E is the energy of hydrogen bonds between one water molecule's oxygen atom and another's hydrogen (Gramatikov et al., 1992; Kumbhakkhane et al., 2013).

The function f(E) is estimated as an *energy distribution spectrum*. A non-equilibrium process of evaporation of water droplets is the energy spectrum of water. The value of NES and DNES is eV^{-1}. (Antonov, 1995; Todorova, Antonov, 2000; Mehandjiev et al., 2023).

DNES is the difference between the NES spectrum of the water sample and the NES of a control water sample.

Δf(E)=f(water sample)-f(control water sample) (2)

DNES is studied in eV^{-1}

Note: In our experiments, the water temperature is 1°C because the NES and DNES methods of research are with liquid water.

3. Results and discussion

3.1. Mathematical problem – a hexagonal structure of the ice.

One of the co-authors, Gluhchev, created the following mathematical problem. The regular hexagon is the only regular polygon whose distance from the center to any vertex equals the distance between two adjacent vertices. Let's consider a regular polygon with center point O and points P and Q as two adjacent vertices. We'll denote the side length as R and α as the central angle ORQ, equal to 360°/p. Let point M be the midpoint of side PQ. From the right triangle OMR, we have:

$MP/OP = R/(2OP) = \sin(\alpha/2) = \sin(360^o/2n)$

$OP = R/2\sin(360^o/2n)$

3a OP = R the result is

$R = R/2\sin(360^o/2n)$

or

$\sin(360^o/2n) = 1/2$ или $360^o/2n = 30^o$ или $n = 6$.

With this, the theorem has been proven.

Corollary: If p < 6, then α > 60°, and OR < R; if p > 6, then α < 60°, and OR > R.

Hypothesis: In a planar ring-like structure of a water cluster with p < 6, having an H atom at the center is impossible due to the limitation of permissible distances between atoms. With p > 6, the distance from the central atom to the atoms at the vertices is greater than the distance between two adjacent atoms of the polygon, resulting in a weaker bond.

Conclusion: A hexagon is the most stable configuration of a planar cluster, representing a regular polygon with an atom at the center.

In water, hydrogen bonds are an example of negative entropy in freezing water. At low temperatures, water forms stable structures of hydrogen bonds, leading to a negative entropy of these bonds.

Negative entropy indicates an organized and structured system.

The results for different types of hexagonal water clusters for the wavenumbers ṽ are 929, 992, 1117, 3072, and 3171 cm^{-1}. There are wavenumbers of hexagonal water clusters with different combinations of water molecules for n=6 (Table 1) (Heine, 2013).

Table 1. Wavenumbers of hexagonal water clusters with different combinations of water molecules for n=6

Combinations Hexagonal water clusters	ṽ (cm^{-1})	ṽ (cm^{-1})	ṽ (cm^{-1})	ṽ (cm^{-1})	ṽ (cm^{-1})
1st combination	929	992	1117	3072	3171
2d combination	929	992	1117	3072	
3rd combination	929	992	1117		
4th combination	929		1117		
5th combination			1117		

Table 1 shows that in the combinations of water clusters exists a peak at ṽ=1117 cm^{-1}. This peak corresponds with the energy of hydrogen bonds between water molecules.

3.2. Entropy. Effect of Mpemba

In 1963, Tanzanian high school student Erasto Mpemba observed an intriguing phenomenon. Hot water freezes faster than cold water. This phenomenon, known as the "Mpemba effect," was actually noted much earlier by historical figures such as Aristotle, Francis Bacon, and Rene Descartes. Numerous independent experiments have since confirmed this unusual property of water.

In 1969, experiments were conducted with the freezing rates of water. For the freezing rate of water at 42°C the result was 3 h 25 min 30 sec. For the freezing rate of water at 18°C the result was 4 h 40 min 15 sec (Kell, 1969).

From the perspective of one of the co-authors, Ignatov lies in the concept of the Differential Non-equilibrium Energy Spectrum (NES). Hot water possesses a DNES with a lower average energy at room temperature. As a result, the hot water requires less energy to initiate the structuring of crystals and undergo the freezing process.

According to one of the co-authors, Ignatov, the manifestation of the Mpemba effect is associated with the state of water's entropy depending on the energy of the hydrogen bonds.

According to one of the co-authors, Ignatov, the manifestation of the Mpemba effect

The result of DNES from 20° to 1°C is

$\Delta E = (-0.1160) - (-0.1120) = - 0.004$ eV

The result of ΔS from 20° to 1°C is

$\Delta S = \Delta E/T = -0.004/19=-0.00026$ eV/K$=-21.10^{-5}$ eV/K

The result of DNES from 100° to 1°C is

$\Delta E = (-0.1120) - (-0.1160) = +0.004$ eV

The result of ΔS from 90° to 1°C is

$\Delta S = \Delta E/T = 0.004/99= +0.00008$ eV/K$=+4.04.10^{-5}$ eV/K

The theoretical entropy value of ice I_h is $\Delta S =3.493.10^{-5}$ eV/K (Cherodov, 2020). When water freezes, the entropy aligns with that ice. The obtained experimental results correspond with the theoretical calculations. In absolute terms, the entropy change is 5.2 times greater from 20° to 1°C than from 90° to 1°C. In entropy terms, the change in entropy is smaller when warm water freezes compared to when cold water does

4. Conclusion

The study delves into various aspects of water properties, mainly focusing on hydrogen bonds and their influence on ice formation and the Mpemba effect. Several crucial findings emerged by exploring the spectral methods NES and DNES and the mathematical insights into hexagonal structures of liquid and solid phases of water.

1. Hydrogen Bonds and Hexagonal Ice Structures. Investigating the hydrogen bond topology in water clusters $(H_2O)_6$ and $(H_2O)_{20}$ provided compelling evidence of their similarity in liquid and ice phases. The regular hexagonal structure of ice (I_h) demonstrated a stable arrangement of oxygen and hydrogen atoms, revealing insights into the organization of water molecules.

2. The Mpemba Effect and Differential Energy Spectrum (DNES). The Mpemba effect, where warm and hot water freezes faster than cold water, remains a fascinating scientific observation. The DNES spectrum suggested a lower average energy in hot water, correlating with faster crystalline structuring and freezing.

3. Mathematical Insights into Hexagonal Structures. Mathematical deductions affirmed the stability of the hexagonal structure in planar water clusters. This analysis added a theoretical dimension to understanding water's molecular arrangements, highlighting the intricate stability within water clusters.

4. Entropy and Ice Formation. Entropy measurements revealed intriguing patterns during ice formation, particularly aligning with the theoretical entropy values of ice I_h.

5. The comparison of entropy changes from different temperatures demonstrated intriguing variations in entropy alterations during water freezing.

This study amalgamates spectral methods, mathematical deductions, and empirical observations to deepen our understanding of water's molecular behavior, especially concerning hydrogen bonds, ice formation, and the Mpemba effect. These findings provide crucial insight into fundamental properties governing water's behavior in various environmental and scientific contexts.

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