

# Molecular dynamics simulation of thermodynamic and transport properties of H-bonded low-temperature substances

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The results of modeling of isotopic water mixture clusters in nitrogen and argon cryomatrices are presented. Earlier, our experimental studies of water mixture in cryomatrix have shown that changes in the concentration of analyte in matrix leads to a splitting of the absorption bands characteristic frequencies of the molecules in the IR spectrum. Moreover the multiplicity of characteristic absorption bands in the IR spectrum remained unchanged during heating of the samples from the condensation temperature to the sublimation temperature of the matrix element. In order to find out what structure of clusters is responsible for the immutability of the absorption bands in the vibrational spectrum during thermal cycling of the samples, computer research of water molecules enclosed in nitrogen and argon cryomatrices by the molecular dynamics simulation was conducted. For this purpose, theoretical studies were carried out using computer software packages, that implement used by us semi empirical and *ab initio* molecular dynamics methods. As a result of the research, the data must be obtained are of theoretical interest for summarizing the physical and chemical properties of systems, consisting of water molecules, and their combination with inert gases for studying the properties of molecular crystals composed of small molecules.

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## 1. Introduction

“Water clusters”, groups of water molecules held together by hydrogen bonds, have been the subject of a number of intense experimental and theoretical investigations [1–5] because of their importance in understanding of cloud and ice formation, solution chemistry, and a large number of biochemical processes. In this contribution, we discuss the applicability of the methods of computational chemistry for the theoretical study of ice crystal formation. Besides, hydrogen bonds are very important for understanding molecular and crystal structures. Even though they are not as strong as covalent bonds, they contribute much to molecular mobility. All through the paper there will be a lot talk about hydrogen bonding in water.

Studies of the properties of molecular crystals have a special place in solid state physics. The relative simplicity and understanding of Van der Waals forces that bind the molecules in the lattice caused the interest that shows the

theory to molecular crystals. The substances selected by us as objects of the study belong to the simplest Van der Waals crystals. Due to the nature of their structure cryocrystals are closest to the models, considered by the theory, and are ideal objects for studying the fundamental solid-state physics [6].

The purpose of this paper is to obtain thermodynamic and structural characteristics of cluster systems formed by heavy water vapor and Ar and N<sub>2</sub> gases are based on the results of computer simulation. The infrared absorption spectra for these systems will be calculated, as well as the movement of molecules in clusters will be studied.

The remainder of this article is organized as follows. Experimental procedures and results are described in Sec. 2. In Sec. 3 we explain the computational model and methods used to carry out the simulations and report their results. The results are discussed and interpreted in Sec. 4 based on the spectra computed in our simulations.

## 2. Experimental procedure

The basis of experimental method for obtaining the information about the state of isotopic water mixture molecules in nitrogen cryomatrix lies on the analysis of absorption bands amplitude corresponding to vibrations of heavy water molecules in unbound state. The measurements were carried out using the setup the scheme and experimental method of which is described in detail by the authors [7]. In this work we used the isotopic mixture of water with the ratio (10% — H<sub>2</sub>O, 40% — D<sub>2</sub>O, 50% — HDO).

After film deposition at  $T = 16$  K the IR spectrum were measured, after which the substrate temperature is gradually increased until reaching the matrix evaporation temperature. In [8] the experimental data of the isotopic mixture of water during heating were shown.

Figure 1 shows the spectrum of the cryocondensates of isotopic water mixture in nitrogen cryomatrix, taken in concentration of 1 to 10%, compared to 100% of the isotopic mixture into a solid state. In this frequency range stretching vibrations of OH and OD bonds of heavy water, and deformation vibrations of nonbounded water are observed. Clear difference observed at spectra of isotopic water mixture molecules isolated in nitrogen cryomatrix is in presence of multiplicity of the absorption bands of vibrational spectrum compared with the spectrum of pure mixture.

Appearance of multiplicity of the characteristic absorption bands of heavy water in nitrogen cryocondensates and increasing of spectrum multiplicity with the decrease in the concentration of water mixture in the matrix observed in Fig. 1 are due to the formation in cryocondensates of polyaggregates with different sizes. This issue is discussed in detail in our previous studies [8]. According to [9] in cryocondensates with the lowest concentration of the investigated substance in a matrix small clusters are formed with the size of primarily dimers, trimers, etc.

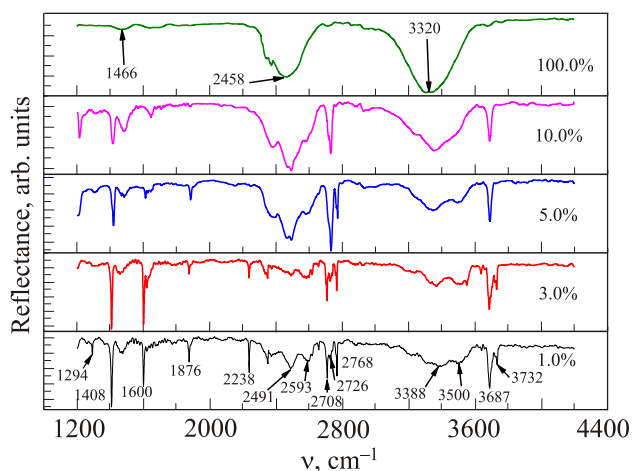


Fig. 1. (Color online) IR-spectra of isotopic water mixture in nitrogen cryomatrix in frequencies interval 1200–4400 cm<sup>-1</sup>.

Also in [10] shown that films with a higher concentration of water in nitrogen (10%) contribution of microcrystallites vibrations is very significant, while in the low temperature the condensates with the least concentration of the test mixture (1%), the contribution of small clusters vibrations increases. This fact is confirmed in our studies, in the case of consideration the isotopic water mixture as the investigated substance, the spectrum of which is shown in Fig. 2.

At a later stage, we investigated the resulting sample of the cryocondensate film of heavy water in nitrogen cryomatrix during heating to a temperature  $T = 34$  K. The results of this study are presented and analyzed in detail in [8]. Thus becomes evident the absence of changes in the spectrum of the vibrational frequencies of water in the matrix as the temperature increases, i.e., the multiplicity of the system is unchanged, until the value corresponding to the matrix evaporation temperature. The question is why there is no change in the structure of the crystallites and absence of their associations into larger clusters. We have suggested that the observed phenomenon is due to formation by water molecules in the matrix of stable clusters with certain size by hydrogen bonds between them. That is why it was decided to test this hypothesis by computer modeling of the system using molecular dynamics methods. The algorithm and the results of the study are presented below.

## 3. Technique of molecular dynamics simulation

The intermolecular Van der Waals potentials between atoms  $i$  and  $j$  on different molecules are taken as a sum of Lennard-Jones (LJ) and electrostatic point charge interactions. The Lennard-Jones  $\sigma_{ij}$  and  $\epsilon_{ij}$  parameters are generally taken from AMBER force field. The dynamics and hydrogen bonding calculations at each temperature and pressure were studied with a standard algorithm of microcanonical ensemble NVE (i.e., at constant number of particles, the

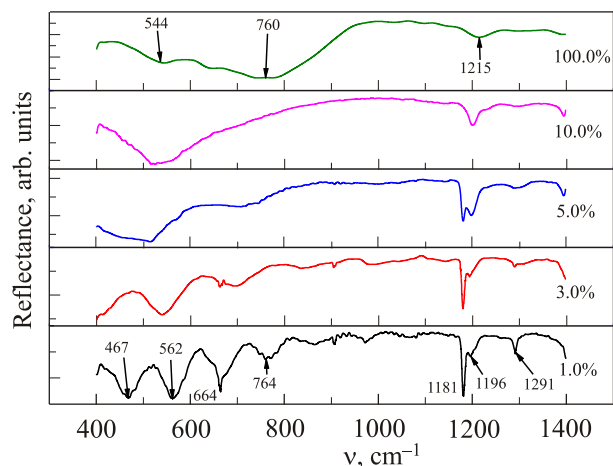


Fig. 2. (Color online) IR-spectra of isotopic water mixture in nitrogen cryomatrix in frequencies interval 400–1400 cm<sup>-1</sup>.

volume of the system and the total energy per particle) [11]. The researched system consisted of  $N = 3\text{--}20$  of water molecules in a cubic basic cell, the size of which varies from calculation to calculation to set the required density.

Potential parameters or force fields are defined for each molecule and constructed to take all important interactions between molecules into account. Intermolecular pair-potentials are expressed as:

$$U(r_{ij}) = \frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right].$$

In order to avoid surface and finite-size effects, periodic boundary conditions were used. Integration of the equations of motion was carried out on the basis of Verlet algorithm with a time step of 0.1 fs. The water molecules used to solvate a solute comes from Jorgensen's Monte Carlo equilibrated box of 215 molecules, described by the TIP3P potential function [12]. This box is cubic and 18.70 Å on a side. When the requested box fits into this, it is just carved out of the basic Jorgensen box. When a bigger box (more than 216 water molecules or perhaps an elongated box) is required, then the basic 216 molecule box is duplicated to create  $3 \times 3 \times 3 \times 216$  water molecules in a box 56.10 Å on a side and the required box is carved of this.

The integrated infrared band intensity for the  $k$ th fundamental is defined [12] as:

$$A_k = \frac{1}{CL} \int \left( \ln \frac{I_0}{I} \right) d\vartheta,$$

where  $C$  is concentration (in moles liter<sup>-1</sup>),  $L$  is optical path length (in cm),  $\vartheta$  is wavenumber in cm<sup>-1</sup>, and  $I_0$  and  $I$ , respectively, are the intensities of incident and transmitted light. Assuming electric and mechanical harmonic,  $A_k$  may be approximated by:

$$A_k = \frac{\pi N_a g_k}{3000c^2} \left| \frac{\partial \mu}{\partial Q_k} \right|^2,$$

where  $N_a$  is the Avogadro number (mol<sup>-1</sup>),  $c$  is the light velocity,  $g_k$  is the degeneracy factor, and  $\partial \mu / \partial Q_k$  is the dipole-moment derivative with respect to the  $k$ th normal coordinate  $Q_k$ .

Also, we performed first-principles, MD simulations of  $\text{H}_2\text{O}_n$  with  $n = 2, 4, 6$  at two different temperatures by using a pseudopotential, plane wave approach in conjunction with a gradient corrected exchange-correlation functional Becke–Lee–Yang–Parr (BLYP), as implemented in the density-functional theory (DFT) package of the program. The choice of the BLYP functional was motivated by its excellent performance in describing the structural, energetic, and vibrational properties of small water clusters, as compared to higher level quantum chemical MP2 calculations [12]. Of particular importance to this study is the ability of BLYP to

reproduce harmonic intermolecular vibrational frequencies 1000 cm<sup>-1</sup>. Atomic positions and electronic wave functions were evolved at finite temperature with the Car–Parrinello algorithm [13]. The electronic fictitious mass was set to a value of 250 a.u., and equations of motion were integrated with a time step of 5 a.u. Trajectories were initially equilibrated by means of a Nose–Hoover thermostat [12] for about 1–2 ps, followed by microcanonical runs of up to at least 25 ps. Statistical averages were typically collected in the last 20 ps of the simulation.

#### 4. Results and discussion

Interactions between water molecules are far more complicated than those between particles of simple liquids. This complexity displays itself in the ability of  $\text{H}_2\text{O}$  molecules to form hydrogen bonds, making water an associated liquid.

It is worth noting here that the use of simple water models requires careful attitude to the results and their interpretation, as well as perfect agreement with the experimental data should not be expected in this case. However, even with these limitations many important properties can be found from the description of atomistic structure and thermodynamics using MD methods, especially if the trajectories of atoms are considered to obtain the information on physical mechanisms behind experimentally observed phenomena.

Clusters formed by  $\text{D}_2\text{O}$  molecules are more stable and resistant in comparison with clusters of water due to the deuterium isotope effects caused by twice heavier mass of deuterium. Furthermore  $\text{D}_2\text{O}$  structure is similar to the structure of water molecules with only one difference in the lengths of covalent bonds. These effects result in the fact that the hydrogen bonds formed by deuterium atoms

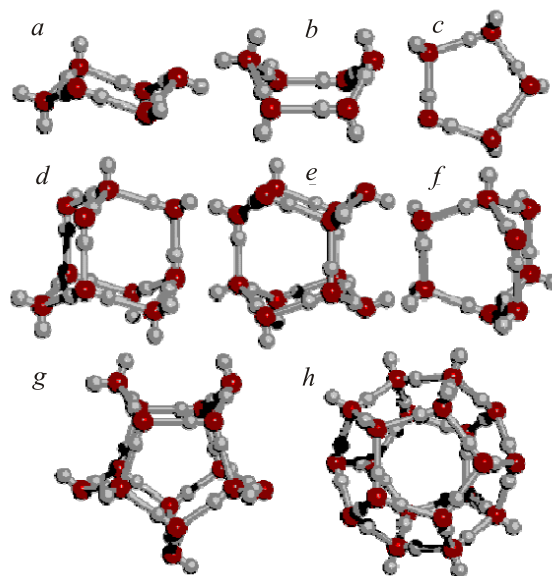


Fig. 3. (Color online) Cluster formation between heavy water molecules through the hydrogen bonds [14].

vary in strength and energy of hydrogen bonds in the normal water. In general, many authors noted that the isotope effects stabilize the hydrogen bonds with deuterium, which ultimately leads to the formation of stable associates of D<sub>2</sub>O molecules [14].

As shown by computer modeling, the clusters are able to interact with one another through the outer surfaces exposed to hydrogen bonds (Fig. 3). Combined, they can form a more complicated structure of from 5 to 20 or more molecules of H<sub>2</sub>O. In clusters through cooperative interactions between hydrogen bonds can occur proton migration to the relay mechanism, leading to proton delocalization within the cluster.

Computer modeling using molecular dynamics method designed the structure and energy of water clusters. For structures with the lowest energy the dependence of energy on the clusters temperature are obtained and dependence of the heat capacity and vibrational energy are identified.

Extensive *ab initio* calculations have been performed using the 6–31 G basis sets for several possible structures of water clusters. It is found that the most stable geometries arise from a fusion of pentameric rings (Fig. 4).

Figure 5 shows the total potential energy during the time of MD-simulation for the system of 20 heavy water molecules. We can observe four exact stages in the condensation process: (1) a long period with relatively constant potential energy (for about  $t = 15$  ns); (2) a very short period with slowly decreasing potential energy; (3) a period with rapid decrease of the potential energy; and (4) a final period during which the potential energy remains relatively constant and we can say, that the structure of ice at this stage fully forms. The fact that the system explores the overall relatively flat potential energy landscape for a considerable time before entering the fast growing period agrees with the predictions of basic nucleation theory [12].

Table 1 lists the scaled frequencies with maximum intensities for some of these clusters along with the frequencies of a single water molecule. The H–O–H angle deformation frequency is observed to generally increase on cluster formation. The O–H stretching frequencies, on the other hand, generally decrease with increasing cluster size. Also, it is noticed from Table 1 that the intensities of all these vibrations are enhanced on cluster formation.

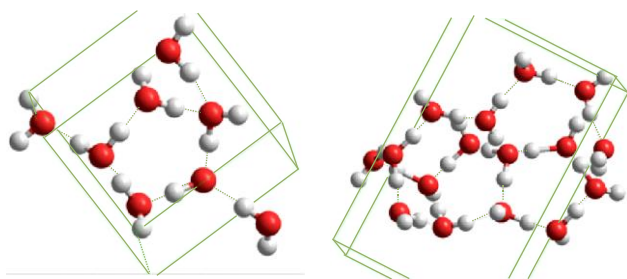


Fig. 4. (Color online) Water pentamers.

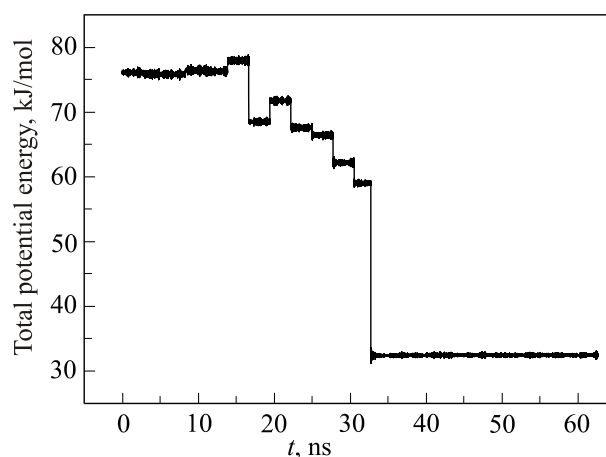


Fig. 5. The total potential energies of the instantaneous structures in the trajectory for 20 molecules after quenching from  $T = 280$  K to 16 K.

$$S = k_B T \frac{\partial \ln Q}{\partial T} + k_B \ln Q, \quad U = k_B T^2 \frac{\partial \ln Q}{\partial T},$$

$$C_v = \frac{\partial U}{\partial T}, \quad F = H - TS = -k_B T \ln Q.$$

where  $S$  is the entropy,  $U$  is the internal energy,  $C_v$  the constant volume heat capacity,  $F$  is the Helmholtz free energy, and  $k_B$  the Boltzmann constant. In the harmonic approximation, one approximates the normal modes of the system to be a set of  $3N$  harmonic oscillators, so that the partition function  $Q$  can be expressed in term of the partition function  $q_i$  for the individual modes [15]. For a continuous distribution of normal modes, the partition function  $Q$  can be shown to be related to DOS( $\mathcal{G}$ ) by [15]:

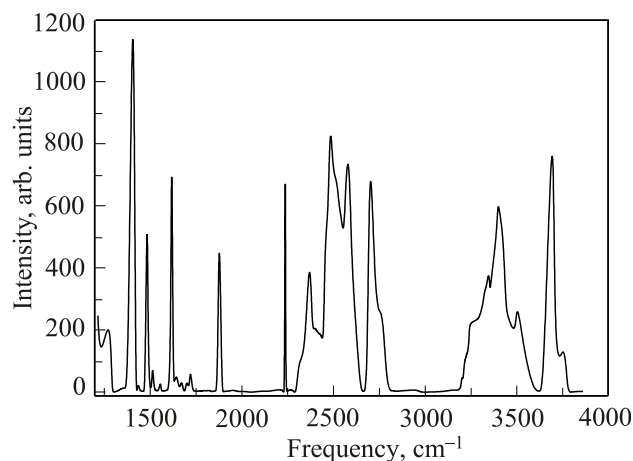


Fig. 6. Linear vibrational absorption spectrum of ice formed by 20 molecules at  $T_c = 16$  K calculated using the PM3 method. Three intramolecular modes are preserved in ice, the bending vibration and the overlapped symmetric and asymmetric stretching vibrations and one intermolecular mode (librations).

Table 1. Vibrational frequencies calculated at program for (H<sub>2</sub>O)<sub>n</sub>

Structure code	Scaled frequency, cm <sup>-1</sup>	Intensity, arb. units	Type
H <sub>2</sub> O	1770	65	Bending
	4153	204	Stretching
(H <sub>2</sub> O) <sub>3</sub>	862.18	93.72	Librations
	1622.37	55.4	Bending
	2422	944	Combination (bending+libration)
	3701	151.6	Stretching
(H <sub>2</sub> O) <sub>8</sub>	845.9	58.5	Librations
	1637	33.02	Bending
	3662	234.03	Stretching
(H <sub>2</sub> O) <sub>10</sub>	842	103.79	Librations
	1664	236.15	Bending
	2045	573.02	Combination (bending+libration)
	3663	438.2	Stretching
(H <sub>2</sub> O) <sub>11</sub>	846	105.7905	Librations
	1688	50.22	Bending
	3660	260.23	Stretching

$$\ln Q = \int_0^\infty \text{DOS}(\vartheta)W(\vartheta)d\vartheta,$$

where  $W(\vartheta)$  is the relevant weighting function. Here, the  $\text{DOS}(\vartheta)$  is obtained from the Fourier transform of the atomic velocity autocorrelation functions

$$\text{DOS}(\vartheta) = \lim_{\tau \rightarrow \infty} \frac{1}{2kT} \int_{-\tau}^{\tau} \sum_{j=1}^N \sum_{k=1}^3 m_j \langle \vartheta_j^k(t'+t) \vartheta_j^k(t) \rangle,$$

where  $\langle \vartheta_j^k(t'+t) \vartheta_j^k(t) \rangle$  is the  $k$ th component of the velocity autocorrelation function of atom  $j$  at time  $t$ . Physically,  $\text{DOS}(\vartheta)$  represents the density of normal modes of the system at frequency  $\vartheta$ .

We can observe that the dependence between  $\log P$  and  $C_v$  is linear as predicted by the theory:

$$\frac{dp}{dT} = \frac{r}{T(V'' - V')},$$

$$\frac{dp}{pdT} = \frac{r}{pT(V'' - V')},$$

$$\log p = \int \frac{r}{RT^2} dT = C_v.$$

The assignment of the absorption bands at Fig. 6 around  $\nu = 3310, 1600$  and  $800 \text{ cm}^{-1}$ , respectively, to the stretching, bending and libration vibrations and is not in doubt.

We started our simulations from the known ground state structures for the dimer and the tetramer cyclic. At our BLYP level of theory, the ring structure (Fig. 4) has the lowest energy among other degenerate geometries. The obtained binding energies of the dimer, pentamer, and hexamer ring, calculated after full relaxation of the atomic positions without inclusion of quantum effects, are 0.09, 0.27, and 0.30 eV per molecule, respectively [16–18].

Calculations also showed that due to the ability of water molecules to form hydrogen bonds this system has a great variety of structures with substantially different binding energy and heat capacity. Most stable ring structures among them is pentamer ring structure shown in Fig. 4, which has only one proton molecules involved in the formation of hydrogen bonds. Orientation of such clusters in cryomatrix of nitrogen and argon is shown at Fig. 7.

### 5. Conclusions

Experimentally shown that in isotopic water mixture in nitrogen and argon matrices multiplicity of absorption bands appears in the IR spectra of the samples with a decrease in their concentration, which, in our opinion, is due

Table 2. Thermodynamic parameters of water clusters with different number of molecules at 16 K

Simulation type	Number of molecules in cluster	$T, \text{ K}$	$\log P$	$V, 10^{-10} \text{ m}^3$	$S, \text{ kJ}/(\text{mol}\cdot\text{K})$	$F_{\text{vib}}, \text{ kJ}/\text{mol}$	$C_v, \text{ kJ}/\text{mol}$
NVE	3	16	-2.01	539.94	0.061	513.3	0.167
NVE	5	16	-4.09	778.65	0.15	920.88	0.202
NVE	8	16	-5.69	906.86	0.639	1115.4	0.488
NVE	10	16	-7.68	1212.17	0.9	1557	1.116
NVE	20	16	-8.19	2326.64	1.364	2253.3	1.205

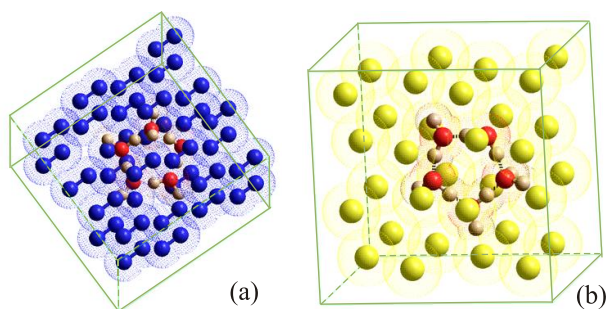


Fig. 7. (Color online) Pentameric rings of heavy water in cryomatrices of nitrogen (a) and argon (b).

to the formation of small clusters of isotopic water mixture molecules (dimers, trimers, etc). Computer model of this system has shown that the formation of the cluster structure occurs at the time of condensation mixture. Calculation of change in the total energy of the system in time confirms the assumption of the model. According to the results of molecular dynamics calculations the following conclusions can be formulated.

1. Analysis of the research results showed that the change of crystal structure of the matrix element occurring in heating process of the sample from the condensation temperature  $T_c = 16$  K to the sublimation temperature of the matrix molecules do not affect the multiplicity of absorption bands at characteristic frequencies of water molecules.

2. The vibrational spectrum obtained by calculation of the sample's computer model also reveals the presence of characteristic absorption bands of free OH-bonds in water molecules at cryomatrix.

3. Using the molecular dynamics method it has been found that water molecules isolated in nitrogen, argon cryomatrices at  $T_c = 16$  K, form nanoclusters with stable structure. Among them, the most stable structure is a pentamer with the form of pentagon, and it was noted that increasing the concentration of the mixture of molecules ( $n \geq 20$ ) leads to the formation of two-dimensional pentagons.

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1. F. Sedlmeir, D. Horinek, and R.R. Netz, *J. Stat. Phys.* **2**, 145 (2011).
2. A. Wallqvist and B. Berne, *J. Phys. Chem.* **9**, 99 (1995).
3. G.G. Malenkov, *J. Phys.: Condens. Matter* **21**, 283101 (2009).
4. B. Barbiellini and A. Shukla, *Phys. Rev. B* **66**, 235101 (2002).
5. N. Giovambattista, H.E. Stanley, and F. Sciortino, *Phys. Rev. E* **72**, 044515 (2005).
6. W.L. Jorgensen, J. Chandrasekhar, J.D. Madura, A.M. Bass, and H.P. Broida, *J. Chem. Phys.* **79**, 926 (1983).
7. А. Дробышев, А. Алдияров, Д. Жумагалиулы, В. Курносов, Н. Токмолдин, *ФНТ* **33**, 627 (2007) [*Low Temp. Phys.* **33**, 472 (2007)].
8. А. Дробышев, А. Алдияров, К. Катпаева, Е. Коршиков, В. Курносов, А.О. Шинбаева, *ФНТ* **40**, 1281 (2014) [*Low Temp. Phys.* **40**, 1002 (2014)].
9. А. Алдияров, А. Дробышев, Ш. Сарсембинов, *ФНТ* **28**, 297 (2002) [*Low Temp. Phys.* **28**, 210 (2002)].
10. А. Алдияров, А. Дробышев, М. Арюткина, В. Курносов, *ФНТ* **37**, 659 (2011) [*Low Temp. Phys.* **37**, 524 (2011)].
11. J. Abascal and C. Vega, *J. Chem. Phys.* **123**, 234505 (2005).
12. Г.Н. Саркисов, *УФН* **176**, 833 (2006).
13. R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
14. И. Игнатов, О. Мосин, Ю. Великов, *Математические модели, описывающие структуру воды, Интернет-журнал «Науковедение», №3* (2013).
15. S. Maheshwary, N. Patel, N. Sathyamurthy, A.D. Kulkarni, and S.R. Gadre, *J. Phys. Chem.* **105**, 10525 (2001).
16. C.J. Tsai and K.D. Jordan, *J. Phys. Chem.* **97**, 5208 (1993).
17. H.E. Stanley and J. Teixeira, *J. Chem. Phys.* **73**, 3404 (1980).
18. J. Carrasco, A. Michaelides, M. Forster, S. Haq, R. Raval, and A. Hodgson, *Nature Mater.* **8**, 427 (2009).