Molecular dynamics simulations of properties of a (001) methane clathrate hydrate surface

Viorel Chihaia 1, Stefan Adams, Werner F. Kuhs *

GZG, Abt. Kristallographie, Universität Göttingen, Goldschmidtstr. 1, D-37077 Göttingen, Germany

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Abstract

The results of molecular dynamics simulations of a (001) methane clathrate hydrate surface interfaced with methane gas involving 2944 water and 512 methane molecules are reported for a temperature of 270 K. The water–water, water–methane and methane–methane interactions are evaluated using the flexible potential KKY. The program MXDORTO was used for the MD calculations and a newly developed code HBTOPOLOGY for the analysis of hydrogen bonds and the oxygen network. The oxygen and carbon surface z-density profiles present regular and periodic peaks that permit the decomposition of the system in slabs. On both surfaces, the external oxygen peak is depleted, indicating the formation of adlayers by water molecules on the surface. Various structural parameters for water molecules (orientational order and coordination) and oxygen atoms (mean-square-displacement, translational order, radial distribution function and ring distribution) are analysed in the different slabs. The distribution of the torsion angle between water dipole of neighbouring water molecules is introduced as a measure of the water molecules' rearrangement on the surface. The analysed MD data indicate that rearrangements at the surface are mainly induced by adsorbed water molecules with a tendency to complement the open large cages. The analysis of jump frequencies (typically 3 ps) and distances (between 1.5 and 6 Å) indicates that the water molecules' mobility should be observable in a time-of-flight quasi-elastic neutron scattering experiment. © 2005 Elsevier B.V. All rights reserved.

Keywords: Gas hydrate; Surface; Molecular dynamics

1. Introduction

Clathrate hydrates, also known as gas hydrates, are a special class of gas inclusion compounds with face-sharing small and large cavities, formed by water molecules (WMs) in similar arrangements as the carbon atoms in 20, 24, 28 or 36 buckyballs. Depending on the size and nature of enclosed gas as well as on the thermodynamic conditions, clathrate hydrates are formed in three main types of structure (sI, sII and sH). They are formed under pressure, at moderately low temperatures and are abundant in nature in (sub)permafrost regions and in the sea-floor of continental margins; the most abundant enclosed gas is methane. Methane hydrate is a possible source of energy but also a considerable geological and climatic hazard upon decomposition by de-stabilizing the seafloor and emitting greenhouse gases [1]. Moreover, they represent a major nuisance by blocking oil and gas pipelines. Nucleation and growth of clathrate hydrate may be prevented or reduced by modifying the thermodynamic conditions or using kinetic inhibitors [2,3].

Due to the importance of these issues, many research groups from academia and industry have developed special research programs over the last years.
dedicated to the characterization, formation and decomposition of clathrate hydrates. Despite great efforts to establish macroscopic models capable of describing the growth or decomposition of clathrate [4] or predicting their stability and thermodynamic properties [5], many questions related to the various phenomena at microscopic level remain to be answered. The growth of clathrate hydrates takes place in super-saturated solutions of water with guest molecules, at the water-guest interfaces (in gas phase or liquid) or at the ice-hydrate interfaces [6], thus the interface characterization is an important step in establishing the growth mechanisms. The diffusion of water molecules and of guest species on the surface plays a crucial role in the growth or the decomposition of the clathrates. These processes depend on thermodynamic conditions \( (P, T) \) and on the nature of the clathrate-liquid or clathrate-vapour interface. Thus, a detailed knowledge of molecular arrangements and mobility at the clathrate surface appears to be highly important. Most common experimental surface techniques that use high vacuum are not applicable to the study of the surface of clathrate hydrates because of the gas atmosphere formed by the guest molecules. Other techniques (like infrared and Raman spectroscopy) have insufficient surface sensitivity or are difficult to set up due to high gas pressures (like ellipsometry or surface diffraction). However, experimental techniques like quasi-elastic neutron scattering can in principle give access to the dynamics of water molecules (profiling from the large incoherent cross-section of hydrogen) when sufficiently large areas are provided in a bulk sample [7]. Gas hydrates can provide such large areas; we know from electron microscopic work that due to a sub-micron porous structure (with a pore size between 20 and 500 nm) specific surface areas of several tens of m\(^2\)/g are typical [8]. In preparation for quasi-elastic neutron scattering experiments we have performed the molecular dynamics simulations presented here.

Because the interaction of guests with host water molecules is weak and based on the structural similarity of clathrate hydrates with ice, it may be expected that the surface phenomena are not very different in both systems and dominated by the interactions between water molecules. Accordingly, one may speculate about what happens on the clathrate hydrate surface starting from the better-investigated case of the ice surface. There is accumulated evidence that the first surface layers of ice melt below the bulk melting temperatures \( T_{\text{surf}}^m < T_{\text{bulk}}^m = 0 \degree \text{C} \). The ice surfaces are covered with a thin liquid-like layer, called quasi-liquid layer (QLL), which plays an important role in the growth and decomposition of ice [9]. The thickness of the QLL depends on the crystal face [10] and increases with temperature [9,11]. The absolute values found for the \( T_{\text{surf}}^m \) and for the thickness of the QLL are, however, not well defined. Rather, they depend on the nature of the experimental technique used (see discussion in [12,13]).

Computer simulations have been successfully applied to study the ice surface [10,12–17], the interfaces of water and ice [16] and the ice deposition on different substrates [17]. They predict that water molecules at the surface keep the bulk translational and orientational order at very low temperatures \( (T < T_{\text{surf}}^m) \) [10,16]. At somewhat higher temperatures, the surface water molecules tend to form an increased number of hydrogen bonds (HBs): In hexagonal ice, the surface of the basal plane is terminated by a full-bilayer, for which WMs are 3-coordinated, in comparison to the less stable half-bilayer, for which WMs are 1-coordinated [18]. At higher temperatures, some molecules from the first surface layer may lose their orientational order and move from their ideal sites to form an adlayer on top of first surface layer. Close to the surface melting point \( T_{\text{surf}}^m \), the adlayer loses its identity by mixing with the first surface layer. At \( T_{\text{surf}}^m \), the long-range order is lost in several surface layers; this disordered portion corresponds to the QLL. The experimental uncertainty regarding the thickness of the QLL and \( T_{\text{surf}}^m \) is present also in case of the computer simulations; the results depend on the method of total energy calculation [13,19], and on the calculation schemes [20] of the molecular dynamics (MD) or Monte-Carlo simulations. Constant pressure MD studies of bulk ice structures with different proton orderings established significant differences of the melting temperatures [21].

Due to the complexity of the clathrate crystal structure and its interface with water or gas, extensive calculations in time and space are required. The large number of water and guest molecules in the unit cell makes ab initio studies very difficult [22]. Therefore, total energy calculations usually have to rely on empirical potentials. Various bulk phenomena (homogeneous formation [23], stability [24,25], structural and dynamical properties [26], cage occupancies [27–29], vibration spectra [30]) have been approached by computer simulations but only a few studies were dedicated to phenomena at interfaces and surfaces of clathrate hydrates. The nucleation of clathrate hydrates is a very slow stochastic process and requires several hundreds of water and guest molecules just for the homogeneous formation of a critical nucleus; this makes any straightforward MD simulation of this process unpractical at present. The inhibitor effects are usually studied by simplified models of the clathrate surface, focusing on effects of blocking the growth when adding inhibitors [31,32]. However, two studies of methane clathrate nucleation and of the polyvinylpyrrolidone (PVP) as growing inhibitor by long MD simulation, using large systems have been performed [2,3].
Rodger et al. [33] investigated the interface between methane gas and the (001) surface of clathrate hydrates at temperatures in the range of 250–300 K for low (1 MPa) and high pressure (100 MPa) by MD simulations using the SPC potential. They found that the surface melts at higher temperatures (above 270 K at 1 MPa) than in the case of ice melts at higher temperatures (above 270 K at 1 MPa), and that pressure stabilizes the surface with melting occurring above 280 K at 100 MPa. The surface layer is disordered even at 250 K and changes gradually with the increase of temperature from hydrate to a liquid. At 270 K and 1 MPa, it becomes a liquid film. Pratt et al. [34] investigated the interface of clathrate sH with water in a microcanonical ensemble corresponding to a temperature of about 185 ± 10 K by a 300 ps MD simulation. It was observed that the interface is extended to about 20–30 Å and is characterized by a gradual decrease of the rotational and translational disorder from liquid water to clathrate. Rodger [35] approached the melting and memory effect of the interface methane gas–methane hydrate by MD modelling at 290 K. A large system consisting of 4140 water molecules and 250 methane molecules was used. He identified an almost constant width of the interface (about 10–15 Å) with a clathrate decomposition rate of ca. 5 Å/100 ps. There was no evidence of clustering of water molecules, indicating that the memory effect is not related to long-lived clathrate structures. Apart from these facts, there is no direct information about the surface structure and molecular mobilities on the clathrate hydrate surface itself.

In the present study, we are in particular concerned with the properties of the (001) surface of methane clathrate hydrate. The system is investigated by MD simulations using the flexible empirical potential KKY [36]. The results of the study, particularly the mean-square displacement of the oxygen atoms, will help us to interpret the water surface mobility determined by planned quasi-elastic neutron scattering experiments. We have limited ourselves in this study to only one temperature $T = 270$ K, being below the melting temperatures of ice Ih for KKY potential, which is about 290 K at 0.1 MPa [13]. At this temperature, we expect by analogy with hexagonal ice the onset of water mobility, which is measurable in quasi-elastic neutron scattering experiments. It was one of the goals of our work to verify this possible analogy. In order to investigate the melting mechanism of the (001) surface, simulation runs at higher temperatures are under way. The paper is organized as follows: In Section 2, the crystal structure of methane clathrate hydrate is presented and details of the surface construction and computational issues are discussed. In Section 3, the main results related to the structural and dynamic properties of the (001) surface of the methane clathrate hydrates are outlined, which are summarized in Section 4.

2. Models and simulation method

2.1. Methane clathrate structure

In clathrate hydrates (as in ice), each water molecule is 4-coordinated, donating two protons to two neighbouring water molecules and accepting two protons from two other neighbouring water molecules. The crystal structures depend on the nature (in particular on the size) of guest molecules and the thermodynamic conditions. At low pressure the methane hydrate adopts a von Stackelberg type sI structure, which transforms to crystallographically different phases upon increasing pressure [37–39]. In the present study, we investigate the (001) surface of the low-pressure methane hydrate sI. The oxygen atoms of the water molecules in type sI clathrate form a cubic structure (Pm3n) with a lattice constant of about 12 Å. The unit cell contains 46 oxygen atoms, which form two dodecahedral cages (polyhedra determined by 12 pentagonal rings and denoted $5^{12}$) and six tetrakaidecahedral cages (polyhedra determined by 12 pentagonal rings and two hexagonal rings, denoted $5^{12}6^2$). There are 48 pentagonal and 6 hexagonal rings per unit cell (a ratio of 8:1). Three symmetry types characterize the nodes of the network of oxygen atoms: m (24 atoms; the notation for these nodes is $k$), 3 (16 atoms; notation: $i$) and 42m (6 atoms; notation: $c$) – see Fig. 1. The centre of the two small cages (notated as $a$) has the symmetry m3 and the centre (notated $d$) of the six large cages has the symmetry 42m. Each node belongs to two perpendicular 6-membered rings and has four neighbour nodes of type $k$. The nodes $c$ have no neighbours of type $i$. Each node belongs to six rings which are of different size in agreement with their type: a node $i$ belongs only to six 5-membered rings, a node $k$ belongs to five 5-membered rings and a 6-membered ring and the nodes $c$ to four 5-membered rings and two 6-membered rings.

A small $5^{12}$ cage is placed in the centre of the unit cell and the other is rotated by 90° with respect to the first one and placed in one corner of the unit cell. In the unit cell there are two large $5^{12}6^2$ cages along each lattice direction $x, y, z$, each paired by sharing one hexagonal ring and forming a column. These columns of hexagonal rings form layers and in the successive layers, the hexagonal channels are rotated by 90°.

The methane molecules are enclosed in both types of cages. The cage occupancy depends on temperature and pressure [40]. Due to the weak interaction of methane molecules with the encaging water molecules methane rotates almost freely [41]. The C–H vibration is slightly affected, the vibration frequencies being shifted to smaller values in comparison to the values for methane molecule. The effect is more pronounced for methane molecules enclosed in the large cages [40,42].
2.2. Computational methods

The molecular dynamics MXDORTO package [43] has been employed in this study. The interaction between particles is modelled by the flexible empirical potential KKY developed by Kawamura et al. [36,44,45]. It consists of two-body components for the interaction of all atom pairs and three-body components for hydrogen–oxygen–hydrogen in water molecules and hydrogen–carbon–hydrogen in the methane molecules. The KKY potential may be considered as a polarizable potential as the molecules are changing their dipole moment by adapting the internal geometry to their chemical environment, but it does not include an explicit polarization term. It was tested [46,47] and extensively used for water bulk systems (liquid water [46], ice [45,47,48] and clathrate hydrates [25,28,49,50]). The potential was employed successfully also for the investigation of the surface of hexagonal ice [13]. It describes the energetic and geometric properties of ice Ih and II better than the classical potentials SPC and TIP4P [51]. The predicted vibrational spectra of ice are in good agreement with the experimental spectra [44]. The KKY potential is able to treat the proton transfer between water molecules [52]. Therefore, we have inspected the molecular species from the system at each MD time step but in the present thermodynamic simulation conditions, we did not detect any dissociation of the water or methane molecules. The parameters of the KKY potential used in this work are obtained from the authors of the potential and are presented in Appendix A.

The force calculation is the most CPU-time-consuming part of the MD simulation calling for an efficient computational handling. In the original version of MXDORTO code, the atomic interactions are evaluated by looping over all pairs of atoms and excluding those pairs located at distances larger than the cut-off radius \( r_{\text{cut}} \). This method scales as \( N^2 \), where \( N \) is the number of the atoms in the system. For large systems (in our case \( N = 10,368 \)) the linked-list method [53] is less CPU-consuming, scaling as \( N \cdot \cdots \cdot M \), where \( M \) is the number of cells that divide the system. Unfortunately, the method is less efficient for surface models, as many of the cells are empty. To speed up calculations, we implemented a Verlet neighbour list [54] and the linked-list methods in MXDORTO code. The tests for various chemical systems with various sizes show identical results for the two variants of MXDORTO codes. The cut-off radius used in the present study is \( r_{\text{cut}} = 15 \, \text{Å} \), large enough to consider also the interaction between methane molecules from the gas phase and their interaction with the surface atoms.

Fig. 1. Atomic arrangement in the unit cell of a type I clathrate hydrate. Labelled atoms correspond to oxygen atoms (c, k and i) and carbon atoms (a for the centre of small cages and d for the centre of large cages). Unlabelled atoms correspond to atoms in other unit cells. For the sake of clarity, the hydrogen atoms of the water and methane molecules are not presented. The hexagonal rings are outlined for an easier recognition of the large cages. VHR and HHR designate vertical and horizontal rings. V and H indicate the adsorption sites located on VHR or below HHR, respectively.
Table 1
Fractional coordinates of the oxygen atoms of the water molecules \((i, k, d)\) and of the centre of small \((a)\) and large cages \((d)\) occupied by carbon atoms from methane molecules (see [55]). The lattice constant is \(a = 12.03 \text{ Å}\)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Point</th>
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<th>Fractional coordinates</th>
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<td></td>
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<tr>
<td>Oxygen</td>
<td>(i)</td>
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<tr>
<td></td>
<td>(k)</td>
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<tr>
<td></td>
<td>(c)</td>
<td>6</td>
<td>0.2500</td>
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<tr>
<td>Carbon</td>
<td>(d)</td>
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An orthorhombic \(4 \times 4 \times 4\) supercell was used to simulate the CH₄ clathrate hydrate, containing 2944 water molecules that form 128 (64 unit cells \(\times 2\) cages/unit cell) small and 384 (64 unit cells \(\times 6\) cages/unit cell) large cages occupied by methane molecules. The initial positions of the oxygen atoms are taken from X-ray diffraction data [55]. The 512 methane molecules occupy all cages. They are arranged in the centre of the cage with random orientation. The fractional coordinates of oxygen and carbon atoms in the asymmetric unit are presented in Table 1. Periodic boundary conditions are applied for all three directions. The two hydrogen atoms of each water molecule have to be arranged along the direction of two out of four neighbouring oxygen atoms. Because of the difficulty to generate such a large supercell [56] when a zero total dipole moment is required, we preferred to build the supercell by the multiplication of a single unit cell with zero dipole moment.

A velocity scaling method controlling the temperature fixed to \(T = 270\) K was used throughout this study. The Verlet algorithm was used for numerical integration of Newton’s equations. The integration time step is set to 0.4 fs. The conservation of the total linear momentum is assured by fixing the mass centre of the system during the MD runs.

The bulk structure is equilibrated for 50 ps in an iso-thermal-isobaric NPT ensemble \((P = 0.006\) GPa) using a scaling method for the pressure control. The NPT calculations are followed by equilibration in the canonical NVT ensemble for another 50 ps. The equilibration was checked monitoring the thermodynamics quantities (energy, temperature and pressure) as well as the convergence of radial distribution functions for different pairs of chemical species.

### 2.3. Surface model

Two surfaces are created, keeping the three-dimensional periodical boundary conditions, by cutting the system with a plane parallel to the \((001)\) surface and by introducing a void space between the two faces obtained (see Fig. 2). The \(x\)-, \(y\)- and \(z\)-directions are chosen along the supercell axes, with the \(z\)-direction taken as normal to the surface. For clarity of presentation, we will call the planes that contain the \(z\)-axis vertical planes and the \(x\)-\(y\) planes horizontal planes. In order to eliminate the direct interaction between the two surfaces, the size of the void space in the direction perpendicular to surface has been chosen to be four times larger than the size of bulk supercell. In addition, for this size of the void space, a good description of the long-range electrostatic potential is obtained in the three-dimensional Ewald summation [57] implemented in the MXDORTO code. Because the direct distance between the two surfaces is large (about 48 Å), a perturbation of one surface will not affect the other surface. An artificial dissociation of water and methane molecules lying near the cutting plane is avoided by translating hydrogen atoms along the \(z\)-direction to the side where the oxygen or carbon atoms from the same molecule are placed.

The free surface energy depends on the position of the cutting plane along the \(z\)-axis [32] and may be related to the number of cut hydrogen bonds. For an ideal structure, the cutting plane positioned at the limit of the unit cell intersects a minimal number of hydrogen bonds (see Figs. 1 and 2). As the surfaces are created from the equilibrated bulk system, the water molecules are not in the ideal positions but located around them. Therefore, not all WMs near the limit of the unit cell are contained in the cutting plane; some WMs are below or above. Systems with completely closed large cages may be created but we preferred to have a reactive surface by creating incomplete surfaces to promote structural rearrangements at the surface. WMs from the last MD step in the bulk equilibration, located near the cutting plane at the limit of the unit cell, were considered as belonging to the inferior/superior surface if they were above/below the cutting plane. They are divided up almost equally: 47 are assigned to the inferior surface and the other 49 to the superior surface.

The cutting plane divides the intersected vertical hexagonal rings (VHR) into equal parts, which belong to different faces. While most of the horizontal hexagonal rings (HHR) from the cutting plane are split into fragments localized on either face, two HHRs remain localized on the superior surface. The HBs between water molecules from each pair of neighbouring nodes \(k\) (denoted \(V_k\) – see Fig. 1) are destroyed. The HBs formed between two neighbouring WMs on a HHR or one WM localized on a HHR in a site \(c\) or \(k\) and another
from a node below/above HHR (denoted H, or H, – see Fig. 1), which are intersected by the cutting plane, are also destroyed. Therefore, because of the chosen way of surface construction, the number of broken HBs is higher (equal to the number of fragments from HHRs) than in case of keeping intact the large cage on one face. The WMs concerned from nodes V, H, or H become 3-coordinated. The WMs from HHRs will be 1- to 3-coordinated.

The surface system was equilibrated in several steps. Initially, a NVT simulation of the whole system was done for 40 ps. To make sure that the temperature-scaling technique does not affect the results we did calculations also for uncontrolled temperature. The results are almost identical, so we applied the temperature-scaling method to the whole system in order to force its equilibration. The 72 evaporated methane molecules evaporated from open cages in the first steps of the simulation and form a gas atmosphere in the available volume void space. Using the equation of state of an ideal gas, we estimate for $T = 270$ K a pressure of methane in the gas phase of about 0.6 MPa. To speed up the equilibration of the methane gas, the atoms of the water and methane molecules from the hydrate cages have been frozen in a NVT equilibration for 20 ps. The gaseous methane molecules will interact with themselves and with the frozen atoms of the hydrate structure. Finally, the full system was equilibrated for another 80 ps followed by a production run of 40 ps. The average values of different structural parameters are calculated using the atomic coordinates, saved every 20 fs. The characterization of the hydrogen bonds and the analysis of different structural parameters have been performed by a newly developed in-house code called HBTOPOLOGY.

3. Results and discussions

3.1. $z$-density profile

To investigate the structural changes we start with the analysis of the $z$-density profile of oxygen and carbon atoms, defined as
peaks may be distinguished. They are determined by oxygen atoms from horizontal hexagonal rings which join two large cages along $z$-direction. Between two successive peaks, several peaks are partly overlapping, determining two groups of peaks, symmetrically arranged between the small and large peaks of $C_L$. These two groups are also present near the surface. They are very similar to the peaks from interior slabs, slightly relaxed. Each one is bordered by a small peak corresponding to the original $C_S$ position but destroyed by surface creation. These peaks are depleted, indicating that the water molecules in external surface zones rearrange themselves forming an “adlayer” on either surface.

Considering the $z$-density profiles, it is useful for the following analysis to divide the system along the $z$-direction in eight slabs limited by the centre of the $C_S$ peaks. The six central slabs are interior slabs and the other two external slabs on each side of the system are surface slabs. On top of each surface, an additional slab was introduced to take into account adsorbed molecules on the surface. To reduce the fluctuations of water molecules between slabs, we shift the slab boundaries toward the centre of the system to include the peaks shared by the slabs. The two central slabs will thus have a common domain; therefore the incomplete central slab (slab $I_4$ in Fig. 3) will be neglected in the analysis. For each time step, the atoms are assigned to slabs depending on their $z$-coordinate, and a water molecule is assigned to the slab where its oxygen atom is located.

4. Diffusion

The centre-of-mass of a water molecule is concentrated in the oxygen, atom thus we will consider the mean-square displacement (MSD) of oxygen atoms as a measure of the water molecules’ mobility. The in-slab MSD indicates the tendency of moving of the atoms within different slabs. It is defined as

$$\langle r^2(t) \rangle_s = \frac{1}{N_{t0}} \sum_{i=0}^{N_{t0}} \sum_{s} (\mathbf{r}_i(t) - \mathbf{r}_i(0))^2,$$

where $t$ is the time, $N_{t0}$ is the number of reference time steps $0$ used in the time averaging, $N_s$ is the number of oxygen atoms localized in the slab $s$ at the time $0$, $\mathbf{r}_i$ is the position vector of the atom $i$.

The in-slab MSDs and their components parallel and perpendicular to the surface are presented in Fig. 4. The curves were plotted in a log–log scale in order to show the main features of MSD as a function of time. It may be observed that the MSDs for surface slabs and adlayers are, respectively, about two and six times higher than the same entities corresponding to the interior layers. The difference in the MSDs of the oxygen atoms from the two surface slabs and from the two adlayers...
suggests that the surface behaviour slightly depends on the cutting of the surface but overall they have the same trend. For adlayers, the perpendicular components on the surface are smaller than the parallel components, indicating a confined motion of the water molecule on top of the surface. In addition, an anisotropy of MSD components parallel to the surface was observed for the adsorbed layer with a faster diffusion along y-axis than along the x-axis. Similar anisotropies have been observed in SPC simulations of the methane clathrate surface [35] as well as for the basal surface of hexagonal ice [13].

For different time intervals, the in-slab total MSDs may be fitted by a power function $(r^2(t))/S = c + a \cdot t^\alpha$. The parameter $c$ has no physical significance but it is necessary for accurate fitting in different time domains. At very short times ($t < 0.2$ ps), $c = 0.000$ and $a = 2.000$ for all curves indicating a ballistic regime. The maximum value of MSD gives the amplitude of the thermal vibrations. For intermediate and longer times, the MSDs for interior and surface slabs turn out to be almost flat ($a < 0.0001$). The oxygen atoms are trapped in a limited space, performing displacements smaller than 0.28/0.34 Å in interior/surface slabs, as they have not enough energy to break the hydrogen bonds with the neighbouring WMs (“cage effect”). For intermediate times, the MSDs of the oxygen atoms from adlayers, behave sublinearly with the fitting parameters $\alpha = 0.891$ and 0.834 corresponding to adlayer 1 and 2, respectively. For longer time scales, they converge to a linear time dependence ($\alpha = 1.494/1.813$, $\alpha = 0.179/0.141$, $\alpha = 0.960/0.998$ for A1/A2). The investigation time is too short for accurate determination of the diffusion coefficients.

Closer inspection of the motion of the water molecules from the adlayer will elucidate the origin of the anomalous sub-diffusion in adlayers for the intermediate times. For a low surface coverage, one may suppose that the adsorption of WMs on top of the nodes V and H are energetically equally favourable. Some small differences are expected because of a different environment of the nodes and of a difference in the type of hydrogen bonds. At higher surface coverage, the adsorption on top of the Hc and Hk sites will be preferred because the adsorbed WMs may form additional hydrogen bonds with the other adsorbed neighbours. Indeed, analyzing the trajectories of the oxygen atoms from adlayers one observes that the WMs adsorbed in neighbouring H sites (cf. Fig. 1) form HBs between them, with the tendency to fill the HHRs. The low-coordinated WMs diffuse on the surface and are adsorbed on top of a V or H site, forming HBs. The WMs adsorbed on top of a V node will form in short time an additional HB with the water molecule below the next neighbour site V. A WM adsorbed on top of a V node forms an additional HB with the WM from the neighbouring V node, after a short time. The WMs adsorbed on top of H nodes try to close the incomplete large cages but they are usually not forming well-defined HHR except for one case on the inferior face. The
adsorbed water molecules tend to increase the number of hydrogen bonds. Therefore, no short chains consisting of only two or three WMs were observed in the equilibrated state.

The water molecules on the adsorption sites have a hindered rotation, coupled with jumps from one adsorption site to another. The analysis of mean residence times and mean jump distances gave values between 2 and 4.5 ps and a typical value of about 3 ps and distances between 1.5 and 6 Å. The residence time on an adsorption site depends on the local environment, especially on the possibility to form a high number of hydrogen bonds. If in a certain configuration the adsorbed water molecules have strong hydrogen bonds, they remain in that configuration for a long time. Therefore, the long waiting time of the adsorbed WMs in adsorption sites is the source of the anomalous diffusion of oxygen atoms in adlayers for the intermediate times. A similar sub-diffusion of the water molecules has been found in confined water molecules in pores [58] or in shells around proteins [59].

Recently, Ikeda-Fukazawa and Kawamura [13] investigated the full-bilayer basal surface of hexagonal ice (ice Ih) by MD simulations, using also the KKY empirical potential. They estimated the amplitude of vibration of water molecules located in different areas from the maximum values of oxygen and hydrogen MSDs in the ballistic domain, decomposed as a function of the distance from the surface. Identifying the first and second layer of the first bi-layer with the adlayers and surface slabs, respectively, and the other bi-layers with the interior slabs, we observe for the same temperature \( T = 270 \) K that the ratio of vibration amplitude of oxygen atoms from adlayers and interior for the hydrate surface is much higher than in the case of the ice surface. The ratio of the perpendicular and parallel components of MSDs of oxygen atoms from adlayers is over-unitary (1.69) for ice and sub-unitary (0.72) in the case of methane clathrate, indicating a different behaviour of the water molecules on ice and clathrate surfaces at this temperature. The parameters of the KKY potentials used in our study and in the work of Ikeda-Fukazawa and Kawamura are slightly different but these minute differences cannot explain the differences in MSD ratios. We shall give a tentative explanation in Section 5.

4.1. Translational and orientational order

The melting of the crystal, characterized by the loss of its long-range order, may be monitored by a translational order parameter. In order to investigate the degree of the crystalline order in different slabs, we evaluated the in-slab translational order parameter of the oxygen atoms as

\[
S_i(\mathbf{k}) = \left( \frac{1}{N_s} \sum_{i=1}^{N_s} \left[ \left( \sum_{j=1}^{N_i} \cos(\mathbf{k} \cdot \mathbf{r}_i) \right)^2 + \left( \sum_{j=1}^{N_i} \sin(\mathbf{k} \cdot \mathbf{r}_i) \right)^2 \right] \right)^{1/2},
\]

where \( \mathbf{k} \) is a vector from the reciprocal lattice, \( \mathbf{r}_i \) is the position of an oxygen atom \( i \) in the slab \( s \), \( N_i \) is the instantaneous number of the oxygen atoms from the slab \( s \). The angular brackets indicate averaging over the time. For a perfect ordering of oxygen atoms, the order parameter is equal to 1 while it tends to the average \( N_s^{-1} \) for a completely disordered structure.

The translational order parameters corresponding to different slabs are calculated for two reciprocal space vectors \( \mathbf{k}_x = (2\pi/b_x, 0, 0) \), \( \mathbf{k}_y = (0, 2\pi/b_y, 0) \). Here, \( b_x \) and \( b_y \) are the lattice constants along \( x \)- and \( y \)-directions. The high values of in-slab translational order parameters (about 0.91) for the two reciprocal vectors and for all slabs indicate that the system is keeping its crystalline structure.

The orientational ordering of the water molecules in slabs is characterized by the distribution of two orientational angles \( \psi = \phi \) and \( \theta \), formed by the normal direction of water plane and the water dipole moment, respectively with the \( z \)-axis (see Figs. 5 and 6). The angular distributions are calculated by a histogram method based on counting and binning of the angles \( \psi = \phi \) and \( \theta \):

\[
O_s(\psi) = \left( \frac{1}{N_s} \sum_{i=1}^{N_s} \delta(\psi_i - \psi) \right),
\]

where the distribution is given as a percentage.

Fig. 5. The distribution of the angle \( \phi \) between the normal direction of the water molecule’s plane with the \( z \)-axis after equilibration, averaged over 40 ps. The curve labels represent A – adlayers, S – surface slabs and INT – average over interior slabs.
where \( N_s \) is the instantaneous number of the oxygen atoms from the slab \( s \) and \( \delta \) is the Kronecker delta function. They are normalized by \( N_s \) – the instantaneous number of water molecules in the slab \( s \) and then averaged over the simulation time steps. Because the plane of the water molecule is not oriented, the angle \( \phi \) takes values in the range \( 0–90^\circ \), while \( h \) values range from \( 0^\circ \) to \( 180^\circ \).

In Figs. 5 and 6, the average distributions vs. \( \phi \) and \( \theta \) angles are presented for the 40 ps simulation of the equilibrated system. The distribution of \( \phi \) angles of the water molecules from internal layers show two broad peaks at \( \phi = 60^\circ \) and \( 90^\circ \). The last one corresponds to an arrangement of the WMs in vertical hexagonal rings. There are no water molecules located in the horizontal plane \( (\phi = 0^\circ) \), i.e. no WM has both protons lying along the edges of the horizontal hexagonal rings. The distributions of the angle \( \theta \) formed by the dipole moment of the water molecules with the \( z \)-axis show several sharp peaks, arranged symmetrically around \( \theta = 90^\circ \). Two pairs of broad peaks located at \( \theta = 49^\circ/131^\circ \) and \( 75^\circ/105^\circ \) can be observed and several sharp peaks are seen between \( \theta = 81^\circ \) and \( 99^\circ \). The highest peak \( (\theta = 90^\circ) \) corresponds to two arrangements of the water molecules in which a WM is lying in a vertical hexagonal ring or is contained in a pentagonal ring in a \( k \) node. The other sharp peaks are formed by WMs that have the oxygen atoms located in a node of intersection between the pentagonal and hexagonal rings. No WM has the dipole moment along the \( z \)-axis \( (\theta = 0^\circ \) or \( 180^\circ) \), a situation that corresponds to a water molecule with the oxygen atom located in a type \( c \) node, common to two vertical hexagonal rings, and the hydrogen atoms, oriented to the two neighbouring nodes of type \( k \).

The WMs from surface slabs tend to maintain the orientation as in the internal slabs, around the weakly developed peaks located at \( \theta = 49^\circ \) and \( 131^\circ \). The two surface distributions are mirrored, reflecting the anti-symmetrical arrangement of the water molecules in two successive slabs. As a general trend, the WMs from the adlayers have similar orientations as the WMs from the internal slabs. The WMs from the first adlayers have high peaks around \( \theta = 90^\circ \); in particular the WMs from the second adlayer have the highest peaks in this area. The well-defined peaks of the internal layers in the range \( \theta = 49^\circ/131^\circ \) and \( 75^\circ/105^\circ \) are only weakly indicated in the case of the first and the second adlayers, respectively.

### 4.2. Oxygen network topology

In order to find out the structural changes in the slabs we have investigated the distribution of the \( n \)-membered primitive rings \( (n = 3–6) \) formed by oxygen atoms. The definition of a primitive ring and the algorithm of their determination are presented in Appendix B. Because there are rings located in more than one slab, we have to assign for each slab the fraction of nodes located in it. The formation of 3- and 4-membered rings in the interior slabs is a very rare event and when such a ring is formed it has a very short lifetime. From Fig. 7, it can be observed that the 5-membered rings are dominant in the interior slabs, representing \( 88.877\% \) (i.e. very close to the value \( 88.889\% \) corresponding to the ideal structure). In the surface slabs, small rings are observed \( (2.34\%/3.19\% \text{ are } 3\text{-rings and } 5.41\%/6.49\% \text{ are } 4\text{-rings in } S1/S2) \) but the predominant rings are still pentagonal \( (81.77\%/79.88\% \text{ in } S1/S2) \) and hexagonal \( (10.49\%/10.42\% \text{ in } S1/S2) \). In the

![Fig. 6. The distribution of the angle \( \theta \) between the water dipole moments and the \( z \)-axis after equilibration, averaged over 40 ps. The curve labels represent A – adlayers, S – surface slabs and INT – average over interior slabs.](image)

![Fig. 7. The number of \( n \)-membered rings \( (n = 3–6) \) in the network formed by oxygen atoms located in different slabs. For the labelling of slabs see Fig. 3.](image)
adlayers the oxygen atoms are forming a different network than in interior slabs: small rings (15.00%/15.06% are 3-membered rings and 21.50%/22.02% are 4-membered rings) are competing with the larger rings (37.35%/35.70% 5-membered rings in S1/S2 and 26.14%/27.22% 6-membered rings in S1/S2).

From these numbers, it might appear that a marked rearrangement takes place in surface slabs. At closer analysis, however, it is observed that the cages partly destroyed by surface creation are stable and preserve their initial structure. It is expected that for temperatures higher than those in the present study, the cages may become more distorted because of the higher kinetic energy of WMs. The presence of 3- and 4-membered rings is a signature of WMs entering from the adlayer.

Our previous ab initio investigations of 20 and 24 buckyball water clusters indicate that WMs may flip; one or two water molecules can even enter the cage to increase the number of their hydrogen bonds to four, but the oxygen network still preserves the cage shape [60]. Moreover, we investigated in calculations at the B3LYP/6-311++G** and MP2/6-31++G** levels several partly open small and large cages obtained by elimination of a pentagonal and hexagonal water ring, respectively. It was found that the opened cages are locally stable structures and their energy depends on the hydrogen configuration at the boundary formed by cutting. It may happen that one water molecule enters the cage to form four hydrogen bonds but without destroying the overall shape of the partly open cage. In case of a hydrate surface, the partly open cages are stabilized additionally by HBs between the WMs that form the cage and neighbouring WMs.

4.3. In-slab radial distribution function

The relative arrangement of the atoms in slabs can be inspected by the radial distribution function (RDF) of the particles that belong to each slab. The in-slab radial distribution function of oxygen atoms is defined as

\[ g_s(r) = \left\langle \frac{V_s}{N_s \cdot (N_s - 1)} \sum_i \sum_j \delta(r - r_{ij}) \right\rangle, \tag{5} \]

where \( V_s \) is the volume of slab s, \( N_s \) is the instantaneous number of oxygen atoms in slab s and \( \delta \) is the Kronecker delta function. The angular brackets indicate the averaging over time.

By construction, the slabs have the same volume but may contain different numbers of oxygen atoms. When we compare \( g_s \) for different slabs we should realize that two factors contribute in different ways to \( g_s \), compensating each other. In surface slabs or in adlayers there are fewer atoms than in internal slabs, thus increasing the RDF by decreasing the denominator. At the same time, there are less \( i-j \) pairs and the summation for the numerator will have fewer terms as compared to the interior slabs. Moreover, because of the limitation of slabs size in the z-direction, \( g_s \) does not approach unity at large distances.

The in-slab oxygen–oxygen RDFs are presented in Fig. 8. The RDF peak of the first internal slabs is broad and asymmetric towards large values of oxygen–oxygen distance \( d_{OO} \). A geometrical analysis of the inter-atomic distances in the oxygen network reveals small differences for O–O pairs from nodes with different type (\( k-c, c-k, k-i \) and \( i-i \)). The second peak is formed by contributions of the next-nearest neighbour oxygen atoms from pentagonal (\( d_{OO} \cdot \sin(36^\circ) \)) and hexagonal (\( \sqrt{3} \cdot d_{OO} \)) rings. The third peak is determined mainly by the pairs of oxygen atoms arranged on the diagonal of the hexagonal rings.

Regarding the positioning of the peaks of the oxygen–oxygen RDF, we can see that they are in the same position for surface and interior slabs (2.78/4.53 Å for first/second peak) but at larger distances for adlayers (2.80/4.86 Å for the first adlayer and 2.80/4.93 Å for the second adlayer). Other peaks are not present in the adlayers suggesting a clustering of WMs. The oxygen–oxygen in-slab RDFs for surface slabs have similar features as for the interior slabs but with somewhat reduced amplitudes and a slight broadening. The effect is rather small because only a minor fraction of the WMs in the surface plane is non 4-coordinated. In the case of adlayers, the first peak in RDF for both adlayers is much higher than the one of the other slabs.

4.4. Water molecule coordination

Having determined the water arrangements near the surface, we turn our attention to the hydrogen bonds
formed between the water molecules. For this, we have performed an analysis of the hydrogen bond population in different slabs. We adopted a geometrical definition of the hydrogen bond: (i) two water molecules are connected by a hydrogen bond if the oxygen–oxygen distance is less than 3.50 Å (corresponding to the maximum limit of the first peak in the O–O RDF, determined in the present study for methane clathrate), (ii) the oxygen–hydrogen distance along the hydrogen bond is less than 2.40 Å (corresponding to the maximum limit of the second peak in the O-H RDF) and (iii) the OH CO angle has values between 160 and 200 degrees.

In Fig. 9, the hydrogen bond coordination of the water molecules is presented averaged for the first ps after surface creation and during the production run of 40 ps. In the interior layers no significant changes appear, where about 95% of water molecules participate in four hydrogen bonds and less than 5% in three hydrogen bonds. The distribution of 4-coordinated WMs is reduced in the surface slabs (to about 74%) in comparison to the interior slabs. Very small changes appear in the surface slabs, mainly by disappearance of the monocoordinated water molecules and by a small reduction of the 3-coordinated water molecules that become about 23%. Large changes appear in the adlayers: While initially 55% (45%) of the WMs in adlayer 1 (adlayer 2) are 2-coordinated their number is reduced to 35% in both adlayers after equilibration, whereas the number of 3-coordinated water molecules rises from initially 30% in adlayer 1 and 41% in adlayer 2 to 53% in both adlayers. In adlayers, 4-coordinated water molecules appear in even smaller numbers (7.1% in adlayer 1 and 4.5% in adlayer 2) after equilibration. The number of water molecules that form only one hydrogen bond, is reduced (from 15% and 12% in adlayer 1 and 2, respectively to half of these values). We can observe that even if by the accidental way of cutting the surface the hydrogen bond coordination of the WMs in the two adlayers is initially different, they become very similar after equilibration. The presence of a small number of 5-coordinated WMs in the surface slabs and adlayer indicates that the adsorbed water molecules move into the incomplete cages to form extra hydrogen bonds with partners that are already 4-coordinated in a tetrahedral arrangement. However, the trajectory analysis shows that such “adsorbed” WMs remain in the incomplete cavities only for periods <5 ps.

4.5. Torsion angle distribution

From different ab initio or empirical potential calculation schemes it appears that the nearest neighbour water–water interactions are the dominant contributions to the total energy of water clusters or water bulk systems, mainly via electrostatic interactions. The most stable isomer of the water dimer is the trans-linear configuration where two water molecules are connected by a hydrogen bond. For a fixed oxygen–oxygen distance, the strength of the hydrogen bond in a free linear dimer depends on the torsion angle \( \tau \) around the hydrogen bond as \( 1 + \cos(\tau) \), similar as in dipole–dipole interaction. The KKY potential, in the parameterisation used in the present study, predicts a difference of 1 kcal/mol between the energies corresponding to a water dimer in trans- and cis-linear arrangements. For small and medium clusters of 3-coordinated water molecules, the stability of different isomers with the same number of hydrogen bonds increases with the number of trans-linear water dimers. Moreover, the electronic and geometric features may well depend on the relative arrangement of the water dimers in the system and the number of protons donated by each molecule \([60,61]\). The importance of the higher-order interaction increases with the size of the water system and they are responsible for the oxygen–oxygen contraction in bulk systems \([62]\). The three-body interaction, the major many-body component, is mainly contributed by the polarization and charge transfer components \([63]\).

At low temperature, the water molecules maximize the number of the hydrogen bonds forming tetrahedral networks as in ice and clathrate hydrates. In an ideal tetrahedral arrangement, the torsion angle \( \tau \) between the dipole moments of two hydrogen bonded water molecules is 60° (gauche-linear dimer) or 180° (trans-linear dimer). In case of clathrates, some small deviations around these values appear, depending on which sites \( i, k \) or \( c \) are occupied by the two oxygen atoms and along which oxygen site–site directions the protons are arranged.
Some empirical potential studies indicate that the stability [64] and the melting point [21] of hexagonal ice depends on the proton arrangements, i.e., on the fraction of trans-linear HBs. The TIP4P MD simulations indicate different average oxygen–oxygen distances for ferroelectric (2.85 Å) and antiferroelectric (2.79 Å) ice structures [15]. The main effect of the torsion angle should be observed in the librational motions. Itoh et al. determined in a KKY MD simulation of ice XI (the proton-ordered ice Ih), four peaks in the librational spectra in contrast to the librational spectra of hexagonal ice, which exhibits a broad band [45,65,66].

It is not possible to build a clathrate structure with WMs arranged only in trans-linear connectivity, as on pentagonal rings at least two water molecules have to be connected as in gauche-linear dimer. However, it is possible to form clathrate hydrate only by WMs connected by gauche-linear hydrogen bonds. Based on a combinatorial analysis on fragments of clathrate hydrates, Kirov estimated the minimum number of trans-linear HBs as zero, the average as 34% and the maximum limited to 65%; the others are gauche-linear hydrogen bonds [65].

In ice and clathrate hydrates the water molecules are orientationally frustrated: they are on average 4-coordinated and have to break three hydrogen bonds to flip around one hydrogen bond in order to transform the hydrogen bond in trans-linear arrangement. Moreover, depending on the arrangement of the neighbour WMs, the flipping may increase the number of gauche-linear hydrogen bonds. After the flipping of a WM, a pair of Bjerrum defects type L and D appears. The defects are propagated in the system by additional reorientations of neighbouring WMs. Another possible mechanism of changing the HB type is the proton transfer between hydrogen-bonded water molecules, which will generate ionic defects H$_3$O$^+$ and OH$^-$. Koga and Tanaka [66] have shown by an analysis of the dipole–dipole correlations of the individual water molecules and by a calculation of the distribution function of waiting times that the reorientations of the WMs are rare events in clathrate hydrates which encage polar guests. At the surface, where the WMs are mainly 3-coordinated or less and have a higher kinetic energy than in bulk, they may flip to form stronger HBs. In buckyballs the water molecules are 3-coordinated and in a way, they represent a model surface with the cyclic boundary conditions of Born-Von Kármán. However, this cyclic condition is more likely for bilayer terminated hexagonal ice where the WMs from the top of the surface are 3-coordinated rather than in our case where only a small part of WMs from the top of surface are 3-coordinated. For buckyballs of 20 and 24 water molecules, the equivalents of small and large clathrate cages, the WMs prefer to make trans-linear hydrogen bonds with their neighbours [60].

To see to what extent the two types of hydrogen bonds, gauche- and trans-linear, are involved in our system, we calculated the distribution of the hydrogen bond arrangement as a function of the torsion angle decomposed on slabs. If the hydrogen bond links water molecules whose oxygen atoms are located in different slabs, half of the hydrogen bond is assigned to each slab concerned.

The torsion angle distributions for water dimers shown in Fig. 10 exhibit a broad central peak at $\tau = 60^\circ$ corresponding mainly to gauche-linear hydrogen bonds and a sharper peak at $\tau = 180^\circ$ representing the
trans-linear hydrogen bonds. These angles correspond to the two possible torsion angles for an arrangement of two water molecules in an ideal clathrate structure. The distribution around $\tau = 60^\circ$ is broader for surface slabs and more diluted in the case of the adlayers, whereas the peaks around $\tau = 180^\circ$ are narrower and higher than in internal layers. These tendencies are more prominent in the case of the two adlayers. Torsion angles around $\tau = 0^\circ$ and $120^\circ$ are avoided in interior slabs but appear to be quite frequent in surface slabs and adlayers. Hydrogen bonds are formed predominately by WMs from adlayers with WMs from the surface slabs.

The percentages of trans-linear HBs in different slabs obtained are presented in Fig. 11. It can be seen that the values are very similar in the internal slabs and increase in the surface slabs and adlayers. The water molecules from interior slabs are in an orientational frustration and reorientations rarely occur. It is clear that in adlayers the water molecules have freedom and enough kinetic energy to rotate, thus the number of the hydrogen trans-linear bonds ($\tau = 180^\circ$) increases. This justifies the reduction of the peak at $60^\circ$ (see Fig. 10). The changes of shape of hydrogen bond distributions corresponding to the surface slabs is mainly due to the adsorbed water molecules that enter in surface slabs. The WMs from the top of this cage have large amplitude vibrational motions, so that the HBs may break allowing the WMs to flip. This might cause the increase in the number of trans-linear HBs. Fig. 12 gives an example of the rearrangement by a flipping of the WMs from the top of the large cage that remain intact after surface creation and along the MD runs.

The increase in the percentage of trans-linear hydrogen bonds in surface slabs and adlayers does not necessarily indicate that the trans-linear arrangement is preferred. At best, they indicate that the trans and gauche arrangements have similar probabilities. Longer MD runs at higher temperatures are required to check whether the tendency of forming trans-linear hydrogen bonds propagates to the interior slabs.

5. Conclusions

The MD simulations presented were made at a nominal temperature of 270 K, i.e. approximately 20 K below the bulk melting point of hexagonal ice as established in [13] using the KKY interaction potential also employed in our work. We have discussed the analysis of the surface structure, of the hydrogen bond topology and the dynamic behaviour of surface and bulk of methane clathrate hydrate. In terms of the thermal stability of methane hydrate the nominal simulation temperature corresponds to a temperature several tens of degrees below decomposition for any pressure compatible with our simulation, resulting in a still fairly ordered arrangement of the surface molecules and a well-defined slab structure with internal and surface slabs as evidenced by the regular peaks in the $z$-density profile. Water molecules from fragments of hexagonal rings (artificially disrupted by surface creation) form adlayers on top of the surface slabs. The high values of the in-slab translational order parameters indicate that the water molecules are arranged periodically also in the slab surfaces and adlayers. The WMs are mainly 4-coordinated ($\approx 75\%$) in surface slabs and 3-coordinated ($\approx 50\%$) in adlayers. The time dependence of the mean-square-displacements of oxygen atoms in the adlayers indicates a sublinear diffusion of the corresponding water molecules; mean residence times have been estimated as ca. 3 ps. This behaviour finds its explanation in the long adsorption times of adlayer
water molecules above 3-coordinated water molecules belonging to surface slabs.

In the case of a basal surface water bilayer in hexagonal ice, the WMs in the outer layer of the surface bi-layer are 3-coordinated and they rearrange locally to increase the number of the surface hydrogen bonds. This explains the different ratios of the oxygen MSDs from adlayer and interior slabs, which were observed in clathrate hydrate and hexagonal ice; it seems that the structural rearrangements penetrate somewhat deeper into the surface in the case of ice Ih leading to a more gradual variation of MSDs between adlayer, surface and interior. In the internal and surface slabs the water network remains quite rigid. On the other hand, the water molecules in the adlayers form 3- to 6-membered rings, both among themselves and with water molecules in the top part of the surface slabs. The study of the distribution function of the torsion angle of two water molecules shows that in surface slabs and especially in adlayers the water molecules occasionally flip, frequently resulting in an increase of the number of the trans-linear hydrogen bonds.

The open cages at the surface remained stable throughout the simulation. WMs from adlayers are preferentially adsorbed on 3-coordinated WMs from surface slabs, located in nodes Vₖ, Hₖ and Hₖ. The water molecules from adlayers have the tendency to cluster on top of open cages from surface slabs (sites Hₖ and Hₖ) closing them. Isolated WMs prefer to adsorb on two Vₖ neighbour sites, where they form two HBs. Typical distances between preferential adsorption sites are in the range from 1.5 to 6 Å.

In this study, we presented the results of MD simulations of a methane clathrate hydrate surface interfaced with methane gas. We established that the water surface mobility at ca. 253 K (corresponding to the KKY simulation temperature of 270 K) should be experimentually accessible to time-of-flight quasi-elastic neutron scattering. Such experiments are now under way on IN6 at the HFR of ILL (Grenoble).

Acknowledgements

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Appendix A

The parameters of the KKY potential used in the present study. The values in parentheses are used in Kawamura’s MD investigations [50]. The notation of parameters correspond to the one used by the authors of the KKY potential [36].

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Appendix B. Ring search algorithms

Several ring search algorithms have been proposed [67] but they are not implemented in public codes. Therefore, we had to develop our own code, applicable to periodical structures, trying at the same time to make an efficient code. It starts with the fast construction of the connectivity list of the oxygen atoms (considered as nodes here) based on the Verlet neighbour list [54] and the linked-list [53] methods. Two oxygen atoms are taken as connected if the distance between them is in the domain of 1.75–3.50 Å. In order to avoid the discontinuity of rings at the boundaries of the periodic structures, the minimum-image-convention is employed.

We define a path as a continuous sequence of edges, which starts and finishes in two preset nodes; the first one is called starting-node and the last one end-node. The length of a path is equal to the number of edges along the path. A closed path (the starting-node coincides with the end-node) of length n is called an n-member ring or simply an n-ring. A ring may contain two or
more smaller rings inside. A ring is called a primitive ring if the ring cannot be decomposed into smaller rings. It is non-primitive when two nodes of the ring are connected by a shorter path than along the ring in question.

The enumeration of the nodes of a ring depends on the starting-node and the direction of circulation in the ring. Thus, in order to have a unique enumeration we introduce the following convention: the enumeration of nodes starts from the node with the minimum index and the direction of circulation is from this node through the neighbouring node with the smallest index (out of the two neighbours within the ring). The other neighbouring node will thus become the last node in the list of ring nodes.

The search for rings is performed on the basis of the connectivity of the nodes and considering successively each node \( i = 1, n \) (\( n \) – total number of nodes) as starting-node. The paths that start from node \( i \) share some edges and form a tree that has the node \( i \) as root. Exploring the branches of the currently analysed tree node by node, all the possible paths that start from node \( i \) may be identified.

In order to reduce the number of trials in the identification of the closed paths that start from \( i \), the exploration along a branch of the tree is cancelled if (1) the circulation from the starting-node is not through the neighbouring node with the smallest index; (2) the currently explored node has a lower index than \( i \); (3) two non-successive nodes along the path are connected; (4) the path is not closed and its length is higher than 5 (6 is the upper limit of the analysed rings in our study); or (5) if a node appears more than once in the list of the path’s nodes. Case (1) is exploited by presetting the last node of the ring: the pair of nodes \( j \) and \( l \) (\( j \neq l \) as the second and the last node, respectively), which are the neighbours of node \( i \), is established before starting the identification of the path. The edges \( l-i \) and \( i-j \) may be contained in a number of paths but both edges are contained in very few only. If the path arrives in the preset node \( l \), a new ring is found and the length and the nodes of rings are recorded. After all the paths that contain the pair \( l \) and \( j \) have been explored, a new triad is investigated. In situation (5) a portion of path forms a ring; this ring is identified in a cycle corresponding to another starting-node.

The next to last node before the current end-node, we will call previous-node. The length of the paths is increasing or decreasing, depending on the direction of the exploration of the tree’s branches. The exploration goes ahead analysing the next neighbour of the current node (the end-node becomes the previous-node and the investigated node becomes the end-node) when none of the situations (2)–(5) occurs, or it is going back by exploring the path that is going through the next neighbour of the previous-node (the node before the previous-node along the path becomes the previous-node and the investigated and accepted node becomes the end-node) [68]. Once all the neighbouring nodes of the end-node have been explored, the procedure going-back by one node is applied. If the end-node coincides with the preset node \( l \), then one ring is identified and its nodes are recorded; the procedure going-back by one node is applied. The track of the path is kept recording the length and the nodes along the path, as well as the last explored neighbouring node of each node of the path.

In this way, all the branches that start from \( i \) are investigated and the procedure is continued considering the next starting-node. The ring detection procedure stops when all the nodes have been considered as starting-node and all the trees that start from them are explored. From the list of detected rings, the non-primitive rings are excluded.

References

[68] In the going-back procedure there are situations when the next neighbour of previous-node is the prior node along the path of the previous-node. This case is automatically excluded according to case (5): the node occurs twice along the path.