

The effect of surface pollution on homogeneous ice nucleation: A molecular dynamics study

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Abstract

Homogeneous ice nucleation in neat and surface contaminated water has been studied by means of molecular dynamics simulations. In neat water nucleation preferentially starts in the subsurface region, which accommodates better than the bulk the volume increase associated with freezing. As models of the adsorbates we have assumed pentanol and pentanoic acid. Homogeneous ice nucleation is affected more by alcohol than by acid. Water slabs covered by a disordered layer of pentanol exhibit negligible preference for subsurface nucleation and longer nucleation times in comparison with neat water, while nucleation times are almost unaffected by the presence of pentanoic acid and the subsurface preference is only slightly decreased. The effect of adsorbates has important implications for the microphysics of formation of high altitude clouds upon conditions when a wide range of high molecular weight compounds is emitted to atmosphere during biomass burning.

Introduction

Homogeneous ice nucleation has been shown to be crucial for the microphysics of formation of high altitude cirrus clouds and polar stratospheric clouds, as well as for glaciation of thunderclouds.¹⁻⁴ There is an ongoing discussion whether homogeneous freezing starts preferentially in the aqueous bulk or at the surface of the droplets.⁵⁻⁸ If the surface or subsurface is relevant for nucleation, as is likely in particular in the case of small droplets, then pollution can be very important. However, the effects of organics on the ice nucleation behavior of upper tropospheric aerosols are not very well understood.⁹ On one hand, some laboratory studies have indicated that homogeneous freezing of low molecular weight carboxylic acids solutions is not as efficient as in aqueous sulfate aerosols, with others having found practically unaffected nucleation efficiencies.^{10,11} On the other hand, certain inorganic and organic substances were shown to possess the ability to enhance ice nucleation.¹² Amphiphilic molecules forming Langmuir monolayer films may be designed such that their hydrophilic head groups create a surface template for the future nucleated ice crystal. For example, induced freezing of drops of supercooled water covered by ordered monolayers of long chain (i.e., with more than ten CH₂ groups) aliphatic alcohols and carboxylic acids was extensively studied both experimentally¹³⁻²⁰ and theoretically.^{21,22} The ice-nucleation temperatures were found to depend on the length of the hydrocarbon chain and the even-odd parity of carbon atoms, as well as on the chemical nature of the headgroup. A systematic increase in nucleation temperature was found for long chain alcohols (but not carboxylic acids) starting from about 15 carbon atoms.¹³

Ice nucleation and freezing of aqueous droplets can be monitored experimentally or with the use of computer simulations. Measurements on supercooled water are difficult to perform because of the high probability of uncontrolled ice nucleation in samples of normal size and purity.²³ Several approaches exist for experimental investigation of freezing of smaller water droplets in the micrometer and even nanometer size range, such as those employing electrodynamic Paul-traps²⁴, free-fall tubes²⁵, emulsified droplets²⁶, and jet expansions²⁷. High-speed monitoring of the freezing process of freely suspended supercooled pure and salty water droplets has been reported for the first time employing method of

acoustic levitation combined with IR/VIS high-speed imaging.²⁸ These experiments show that nucleation starts preferentially in the interfacial region, which is in agreement with a previous study.⁸ However, laboratory measurements employing the method of electrodynamical levitation indicate that homogeneous ice freezing is a volume-proportional process with surface nucleation being potentially important for small droplets with radii below 20 μm .⁶ Volume nucleation is more probable for bigger droplets simply because many more molecules are present in the bulk than in the surface layer. It was also found that in some emulsion experiments the presence of surfactants at the oil/water interface prevents surface nucleation.⁵ In these cases volume nucleation is the favored nucleation process. These authors further proposed that for droplets in air surface nucleation is, nevertheless, the preferred nucleation process. At the moment, neither a surface nor a volume dependent nucleation processes are unequivocally supported by measurements. The analysis remains inconclusive, since the scatter in experimental data from various techniques is too large.⁷

There exist only a handful of computational studies of homogeneous ice nucleation. The first successful study was performed using the TIP4P water model²⁹, the melting point of which is 232 K, and only a single nucleation trajectory was obtained.³⁰ Soon thereafter, a six site water potential abbreviated as NE6³¹ for simulation of ice and water near the experimental melting point was developed. Employing this model ice growth from supercooled water in contact with crystal of ice was simulated at conditions close to experimental reality.³²⁻³⁴ Using the NE6 model we were able to show that in slabs of varying sizes homogeneous ice nucleation starts preferentially in the subsurface.³⁵ In that study we have also produced the first freezing trajectory employing the TIP5P model³⁶. Recently, we succeeded in simulating homogeneous ice nucleation and brine rejection in a salt solution, again using the NE6 water model.²⁸

In the present study we aim at answering the following questions. How do surface active substances affect homogeneous ice nucleation in water? Does nucleation occur preferentially in the subsurface or in the bulk of polluted water? How do adsorbates influence the time required for the formation of the ice nucleus? What is the effect of different head groups of the surface active species?

Pentanoic acid and pentanol serve as model compounds for organic acids and alcohols present in atmospheric aerosols. Monocarboxylic acids (C6-C34) have been observed in field measurements³⁷, long-chain alcohols and fatty acids have been mentioned in Ref. 38, alcanoic acids (C10-C32), and alcanols (C10-C34) in Refs 39 and 40. The investigated adsorbates are small enough to make the nucleation simulation feasible, but their aliphatic chains are at the same time long enough to ensure sufficiently low solubility in water. The maximal mole fraction of pentanoic acid in a binary mixture with water at 298.15 K is 0.65%⁴¹ and saturated water-pentanol mixture at 293.15 K contains 0.49 molar percent of pentanol.⁴² Extending our previous studies^{28,35} we have simulated homogeneous ice nucleation in slabs containing either neat water or water covered by a disordered layer of a adsorbate. Nucleation is a stochastic event, description of which requires more than a single trajectory for each system. We thus base our conclusions on a set of more than 60 successful nucleation trajectories.

Systems and force fields

MD simulations of homogeneous freezing of aqueous slabs were performed using a six-site interaction potential for water NE6³¹. This potential was optimized for simulations of water and ice near the experimental melting point T_m . Only few models yield satisfactory values of T_m , such as TIP4P/Ice⁴³ and TIP5P³⁶. The former model also provides a good description of the phase diagram involving solid phases, while TIP5P fails for this purpose.⁴⁴ A first report of T_m for the NE6 was very close to the experiment. In a recent paper, the authors refined the melting point to the range 280-285 K.⁴⁵ Two different methods were used for the calculation of T_m for the NE6 potential. The first one is a combination of a Gibbs-Duhem integration and free energy calculations and the second one determination of the melting temperature by direct coexistence. In summary, averaging the results obtained with both methods, 289 K is proposed as the most likely value of T_m .⁴⁴ The new estimate thus places the melting temperature about 16 degrees above the experimental value. For the purpose of the present study, this is an acceptable deviation which has, moreover, the advantage of yielding somewhat faster crystallization rates.³³

Pentanol and pentanoic acid were adopted as model surface adsorbates. Geometry and charge distribution of adsorbate molecules were taken from ab initio calculations at the MP2/aug-cc-pVDZ level of theory. Other force field parameters were adopted from AMBER parm99⁴⁶. Interaction energies of pairs water-adsorbate, adsorbate-adsorbate and water-water were compared with MP2/aug-cc-pVDZ results. Optimized structures of mentioned pairs are depicted in Figure 1. The NE6 water model employed here somewhat overestimates the interaction energy of the water dimer, which is the prize for achieving good bulk properties with a non-polarizable model. In the pentanol-water pair (Figure 1 d), water should be a better hydrogen bond donor than pentanol according to ab initio calculations. Reversed ordering of hydrogen bonding strength in alcohol-water pair resulting from empirical force field has been noticed previously.²² In order to fix this, partial charges and Lennard-Jones parameters on pentanol atoms were slightly modified in order to achieve the correct ordering of hydrogen-bonding strength. Parameters for pentanoic acid give satisfactory results, therefore, no adjustment was necessary here. Force-field parameters for the employed adsorbate molecules are summarized in Table 1, while Table 2 reports on comparison with MP2 calculations.

Simulation methods

The simulated aqueous systems were placed in a rectangular prismatic box extended in the z-direction, and 3D periodic boundary conditions were applied. This resulted in the formation of an infinite slab (more precisely an infinite series of practically non-interacting slabs) with bulk region in-between two surfaces in the xy-plane. The smallest unit cells with approximate dimensions 13.5 x 15.5 x 100 Å³ contained 192 water molecules. First, a unit cell with dimensions of 13.5 x 15.5 x 29.5 Å³ was chosen such as to correspond to a rectangular cell of ice Ih and, subsequently, the z-dimension was extended to 100 Å³. This size is just large enough to provide the slab with a well developed bulk-like region^{47,48}, but small enough to allow for extremely long simulations needed for capturing homogeneous nucleation in water. Larger slabs used for test calculations were constructed by doubling or tripling the width of the original cell, yielding systems with 384 or 576 water molecules in the unit cell. The z-dimension was consequently prolonged to 180 or 270 Å, respectively. Surface contaminated water slabs

were constructed by adding six pentanol or pentanoic acid molecules on each of the two surfaces, forming an incomplete and disordered layer.

Long range electrostatic interactions were accounted for using the smooth particle mesh Ewald method, employing a pseudo-2D correction for the slab geometry.⁴⁹ Non-bonded interactions had to be cut off at a relatively short distance of 6.5 Å due to the small size of the simulation cells in the x- and y-dimensions. After preparation of the liquid water systems and short preequilibration period at a given temperature, the production runs followed. Newton equations of motion were propagated with a time step of 1 fs for 100 - 1800 ns (depending on the occurrence of a nucleation event in a given trajectory).

To avoid possible problems with the quantum nature of OH vibrations we used the LINCS algorithm to constrain bonds involving hydrogen atoms.⁵⁰ This makes the calculations computationally more efficient and also leads to faster equilibration and thermalization of the unconstrained degrees of freedom. OH vibrations do not play a very important role in freezing process, because ice growth occurs at much longer time scales than OH vibrations. The slower translational and rotational/librational motions are, therefore, more relevant. Temperature was adjusted using the Nose-Hoover thermostat.⁵¹ The optimal freezing temperature and temperature coupling constant were determined in our previous work.³⁵ The fastest ice nucleation occurred at the temperature of 250 K, maintained using a temperature coupling constant of 0.5 ps. For each system we carried out about 20 simulations for the smallest cell, with additional two runs for the two larger cells, all with different starting coordinates for each run. All calculations were performed using the GROMACS 3.3 program package.⁵²

Results

The main goal of this work was to explore the differences in homogeneous ice nucleation in neat and surface contaminated water and compare these in terms of the preferred spatial location of nucleus and the time required for its formation. Homogeneous ice nucleation is a rare event, the simulation of which is extremely time consuming. Moreover, the stochastic character of this process requires large number of simulation trajectories in order to provide statistically meaningful results. Therefore, we have performed tens of simulations only for the smallest slabs which, however, already have a well

developed bulk region in between the two interfaces.^{47,48} There is an important issue of possible size effects on the results. We have also obtained several nucleation trajectories for slabs containing 384 and 576 water molecules, yielding qualitatively similar results. Increasing the size of the system in the z -direction does not change the nucleation process significantly, as shown also in our previous studies³⁵. We also considered increasing the size of the system in lateral dimension by duplicating in both, x and y direction. However, this quadruples the size of the system making the simulations more than an order of magnitude slower, therefore we were not able to collect a long enough trajectory to resolve the issue. For now, we can at least state that for the reverse (and computationally simpler) process of ice melting size effects do not play a big role. This has been satisfactorily addressed by Vega and coworkers who reported that coexistence of water and ice and melting temperature are not affected within the statistical error by system size.⁵³

Figure 2 shows four snapshots from one successful nucleation trajectory for each system under study: neat water (top), water covered by pentanoic acid (middle) and water covered by pentanol (bottom). Only the unit cell, containing 192 water molecules and, in the latter two cases also the 12 adsorbate molecules, are depicted. The shaded regions highlight the newly formed ice nucleus. In the selected trajectory for neat water, nucleus was formed in the subsurface region, which is in accord with our previous study³⁵, after ~ 160 ns. In water covered by pentanoic acid it also formed in the subsurface after ~ 250 ns, while in water covered by pentanol it took ~ 380 ns to form a nucleus close to the center of the slab. We should stress here, that this figure serves just as an illustration and we base our further conclusions on an ensemble of tens of nucleation events for each system.

The onset of crystallization can be monitored in several ways: 1. observing formation of six-membered rings as can be seen from snapshots, 2. searching for “long lasting” hydrogen bonds between four-coordinated water molecules. “Long lasting” means with life time more than 2 ns, 3. potential energy decreases during freezing period, so the beginning of this decrease indicates nucleation, 4. plotting evolution of density profile in time. The last approach was presented in Ref. 54, while the previous two were suggested by Matsumoto et al.³⁰ All four approaches were tested in the present study

and the corresponding crystallization times differ by less than two ns. For further discussion we used the first approach.

The main results of this work are visualized in Figure 3 which displays the fraction of slabs without an ice nucleus formed plotted against time. Our statistics is based on 17 nucleation trajectories for neat water, 29 for water contaminated by pentanol and 16 for water contaminated by pentanoic acid. Every symbol in the figure represents formation of a stable ice nucleus at a given time. Empty symbols correspond to a nucleus created in the subsurface, while filled symbols represent a nucleus formed in the bulk region. Nucleation preferentially starts in the subsurface in neat water (subsurface to bulk ratio of 12:5) and in water covered by acid (subsurface to bulk ratio of 10:6) with the subsurface preference slightly decreased in the latter case. There is, however, virtually no preference for subsurface nucleation for water contaminated by alcohol (subsurface to bulk ratio of 15:14). Note that by “surface” we mean the first layer (3-4 Å thick), it does not necessarily have to be the “surface” as assumed by Tabazadeh and coworkers⁵ in macroscopic experiments, their scale being different. The vapor-liquid interface of water has been studied for example in Refs. 47 and 48, mainly based on analysis of hydrogen bond network (calculating hydrogen-bonded neighbors) it was concluded that the shortest distance from the aqueous liquid-vapor interface at which one can observe bulk liquid behavior is approx. 10 Å. Using this result, our system has a 10-12 Å thick bulk region. Substraction of thickness of bulk and two “surfaces” from the whole thickness, one obtains thickness of two “subsurfaces” 12-14 Å. Volumes of the bulk region and that of the two subsurface regions are roughly the same. This is worth mentioning that the terms “surface”, “subsurface” and “bulk” do not have only geometrical meaning, but also correlate with properties of the hydrogen-bond network.^{47,48}

The next important observable is the mean time required for formation of either the subsurface or bulk nucleus. According to classical theories dealing with both volume or surface dependent nucleation^{4,55} we should obtain an exponential decrease from which we could extract the corresponding time constant. Characteristic nucleation times were obtained by least-square fit of data (bulk and subsurface together) by $\exp(-t/\tau)$, where τ is characteristic nucleation time, this is one-parameter fit. We also fitted data by

$a \cdot \exp(-t/\tau)$ (two-parametr fit), but the difference between derived nucleation times was small. In all three systems, we also fitted bulk and subsurface data separately to see eventual difference, but they were negligible which means that the time required for formation of a subsurface nucleus does not differ significantly from that needed for formation of a bulk nucleus. Nucleation times are about 220 ns for both neat water and water covered by pentanoic acid, compared to 330 ns for water covered by pentanol. Note that the decay in Fig. 3 is, not perfectly exponential. Nevertheless, it can clearly be seen that nucleation in water covered by pentanol is slower than in the other two cases.

After the nucleation event ice starts to grow. The freezing rate, which is defined as the thickness of ice formed per time unit, is for neat water approximately 1 Å/ns, which is somewhat faster than typical experimental values. This is because in macroscopic experiments freezing is slowed down by the release of latent heat, which in a MD simulation of a small system is efficiently removed by the thermostat. The simulated freezing rate is practically unaffected by adding pentanoic acid, while it is slightly slowed down close to the water/pentanol interface.

Note that homogeneous ice nucleation observed in MD simulations possessing both bulk and surface regions is not just a special feature of the NE6 model. Already in our previous work³⁵ we produced a successful nucleation trajectory employing the TIP5P model³⁶ at 240 K, which lies 35 K below its melting point. Most recently, we have obtained the first nucleation trajectory employing the TIP4P/2005⁵⁶ water model at 210 K, which is about 40 K below its melting point.

Discussion

We now discuss the different effects of pentanoic acid and pentanol on homogeneous ice nucleation. We start with the following question: How can we explain the negligible influence of pentanoic acid on the freezing process? First note that pentanoic acid is a weak one, therefore, neglecting dissociation in the simulation does not cause a large error. Carboxylic acids form stable dimers with two strong hydrogen bonds, as well as reasonably stable (but weaker) heterodimers with water, as depicted in Figure 1a, b. In the heterodimer pentanoic acid acts as a hydrogen bond donor. Pentanol dimer, in contrast to the acid one, contains only one hydrogen bond, being additionally stabilized by van der

Waals interactions of alkyl chains (Figure 1 c). Stabilization of this dimer is not as high as that of the pentanoic acid dimer. Pentanol and water form two heterodimers. The first one (Figure 1 d) with water acting as a hydrogen bond donor is slightly more stable than the second one where pentanol is the hydrogen bond donor (Figure 1 e). Summarizing these findings, it might be expected that water surface is less affected by carboxylic acid, since it interacts more likely with other carboxylic acid molecules than with water molecules. We checked this hypothesis by hydrogen bond analysis but, as a matter of fact, there is little difference between alcohol and acid in this respect. On average, one pentanoic acid molecule forms 2.3 hydrogen bonds with water (acting as hydrogen donor or hydrogen acceptor) and 0.2 hydrogen bonds with another acid, while pentanol forms 2.3 hydrogen bonds with water and 0.15 hydrogen bonds with another alcohol. Based on hydrogen bond analysis we, therefore, cannot explain the different influence of alcohol vs. acid on ice nucleation and, therefore, have to look for other explanations.

Figure 4 depicts orientation maps of water dipoles with respect to the z-axis (i.e., the axis perpendicular to the interface). Orientation map shows “intensity” (number of molecules) as a function of z (axis perpendicular to the interface) and $\cos\theta$, where θ is an angle between water dipole (pointing from oxygen to hydrogens) and z-direction. Prior to nucleation in bulk water, all orientations of water molecules have the same probability and therefore, the color of the corresponding area is uniform, but certain orientations are preferred at the interface. For example water molecules expose oxygen to the adsorbate-water interface (Figure 4 b, c), therefore probability of $\cos\theta$ having positive value (close to 1) is enhanced at lower interface and probability of $\cos\theta$ having negative value (close to -1) is enhanced at upper interface. In case of neat water hydrogens are predominantly pointing toward the gas phase.

Orientation of molecules at the interface does not change after freezing, as can be seen from upper part of Figure 5. This is because water molecules in the top layer remain unfrozen forming a quasi-liquid layer. Orientation of water dipoles of surface molecules is thus similar for the two polluted systems, but differs from that for neat water. Note also that orientation of water molecules in ice is no more random as in the supercooled liquid, but it is determined by orientation of the basal plane with

respect to the interface. Certain combinations of orientation and vertical position are more probable (brighter areas), certain less probable (dark areas) than in bulk liquid.

In all three investigated systems homogeneous nucleation typically leads to formation of a mixture of cubic and hexagonal ice, while only rarely pure cubic or pure hexagonal ice is formed. This is in agreement with conclusions of other investigators³³ who observed that, regardless of the substrate, a variable number of stacking faults appears during crystallization. Our three investigated systems do not differ in crystal structure, but rather in orientation of the basal plane with respect to the interface. This plane is on average mainly tilted in the case of neat water (Figure 5 a), both tilted and coplanar in case of water covered by pentanol (Figure 5 c), and mainly coplanar in case of water covered by pentanoic acid, which is illustrated in Figure 5 b.

The increased rotational mobility of water molecules at the interface is important for homogeneous ice nucleation in the subsurface, since it represents a kinetic advantage (faster reorientation) for ice nucleation³⁵. We have used the rotational autocorrelation function to represent mobility of interfacial water molecules, for which an almost exponential curve with fast decay was obtained for neat water, while for polluted systems rotation is more hindered. Figure 6 shows the average rotational autocorrelation function of 8 most interfacial water molecules in all three investigated systems. In case of neat water correlation time is the shortest, with water molecules being more hindered for pentanol than pentanoic acid surface pollution.

While short-chain soluble alcohols act as antifreeze agents, it has been shown that ordered monolayers of long-chain aliphatic alcohols act as efficient ice nucleators¹³⁻²⁰, which is rationalized in terms of a structural match between the monolayer and a layer of ice in the *ab* plane. The adsorbates investigated here lie in between these two limits. Pentanol molecules in our systems are strongly surface active but are not arranged in an ordered surface monolayer as in experiments with long-chain alcohols but rather form a disordered and incomplete layer, which then has slowing rather than enhancing effect on ice nucleation.

Conclusion

We have studied homogeneous ice nucleation in neat and surface contaminated water by means of extensive MD simulations. We did not want to draw conclusion from one or two trajectories, but aimed at bringing statistical averaging into this issue performing in total more than 60 simulations at the (sub)microsecond timescale. Nucleation preferentially starts in the subsurface in neat water and in water covered by pentanoic acid, with subsurface preference slightly decreased in the latter case. There is, however, virtually no preference for subsurface nucleation for water contaminated by pentanol. Nucleation time of neat water and water covered by pentanoic acid are practically the same (about 220 ns), while presence of pentanol slows down nucleation by about 50 %.

Based on our analysis of the MD trajectories we come to the following conclusion. Neat water and water covered by pentanoic acid have similar kinetics of homogenous ice nucleation but probably for different reasons. Adsorbates have an orientation effect, as demonstrated by orientation of water molecules at the interface and orientation of ice planes, which enhances ice nucleation. At the same time, adsorbates also hinder the motion of interfacial water molecules which slows down nucleation. These two effects practically compensate each other for water covered by pentanoic acid, while in the case of pentanol contamination hindering is stronger than the orientational effect, which is why the subsurface preference for nucleation is washed out and homogeneous ice nucleation is slower than in neat water.

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FIGURE CAPTIONS

Figure 1. Optimized geometries at the MP2/aug-cc-pVDZ level of pentanoic acid dimer (a), pentanoic acid-water complex (b), pentanol dimer (c) and pentanol-water complexes (d) and (e).

Figure 2. Four snapshots from a selected nucleation trajectory for each system under study: neat water (top), water covered by pentanoic acid (middle), and water covered by pentanol (bottom). Only the unit cell, containing 192 water molecules and possibly the 12 adsorbate molecules, is depicted. The shaded regions highlight the newly formed ice nucleus. In the depicted cases, nucleus was formed in the subsurface region for neat water after ~ 160 ns. In water covered by pentanoic acid it also formed in the subsurface after ~ 250 ns, while in water covered by pentanol it took ~ 380 ns to form a nucleus close to the center of the slab.

Figure 3. Fraction of slabs without an ice nucleus plotted against time. Empty symbols correspond to a nucleus created in the subsurface, while filled symbols represent a nucleus formed in the bulk region. Green circles correspond to neat water, red triangles to water covered by pentanoic acid, and blue squares to water covered by pentanol.

Figure 4. Orientation maps of dipoles of water molecules in supercooled liquid in neat water (a), water covered by pentanoic acid (b), and water covered by pentanol (c). Colour coding corresponds to probability distribution as a function of z-coordinate (z-axis perpendicular to the interface) and cosine of angle between water dipole and z-axis. Brighter color means more probable orientation. Water molecules are oriented randomly in the bulk region. Surface water molecules have preferentially dipoles almost perpendicular to the z-axis in case of neat water (a). In polluted systems (b) and (c) water dipoles are mostly parallel to z-axis with water molecules pointing with oxygen atoms toward the gas phase.

Figure 5. Orientation maps of dipoles of water molecules in frozen systems with corresponding snapshots: neat water (a), water covered with pentanoic acid (b), water covered with pentanol (c). Color coding corresponds to probability distribution as a function of the z-coordinate (perpendicular to the

interface) and the cosine of the angle between water dipole and z-axis. Preferential orientation of interfacial water molecules do not change upon freezing (compare to Figure 4). Orientation of water molecules in ice is no more random as in the supercooled liquid, but it is determined by orientation of the basal plane with respect to the interface. Certain combinations of orientation and vertical position are more probable (brighter areas), certain less probable (dark areas) than in bulk liquid.

Figure 6. Average rotational autocorrelation function of 8 most interfacial water molecules in neat water (green), water covered by pentanoic acid (red), and water covered by pentanol (blue). The correlation function was evaluated every 5 ns for the first 100 ns of the trajectory, that is why there are more lines for each system. No drift of correlation time with simulation time was observed.

Figure 1:

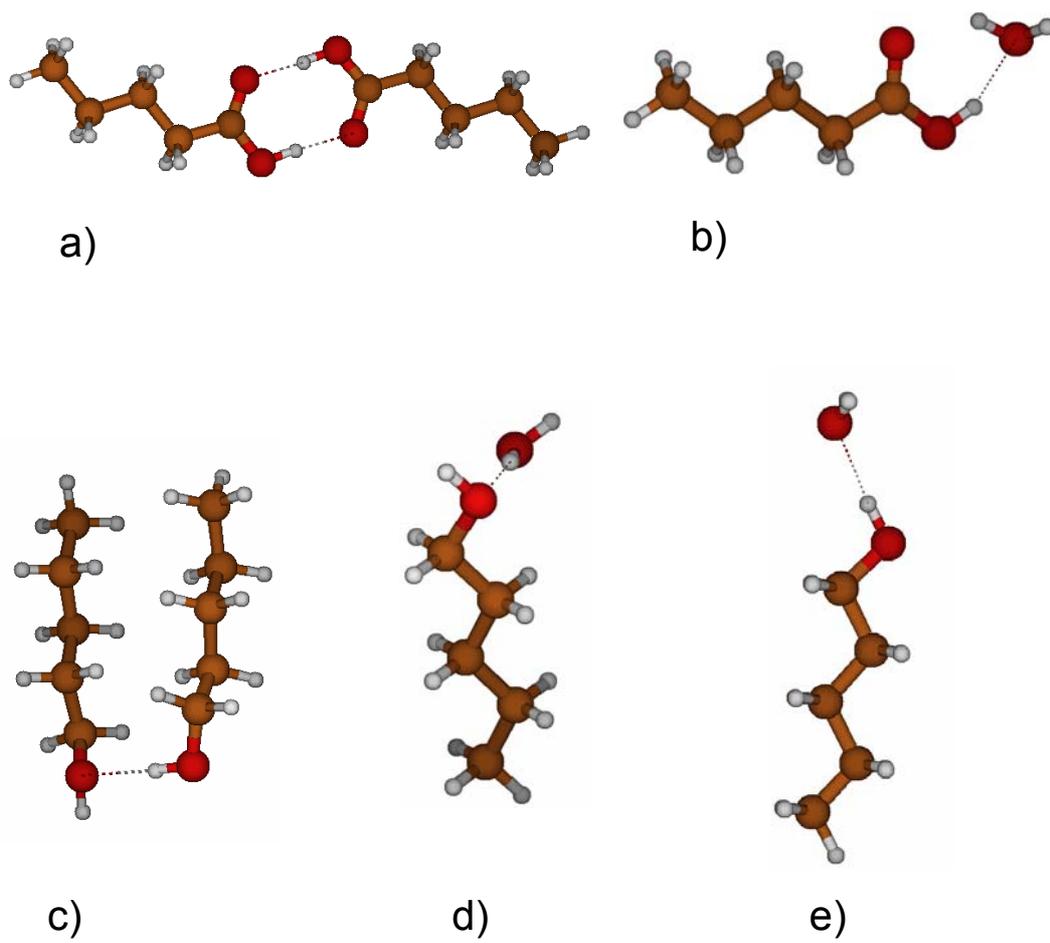


Figure 2:

