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Molecular simulation of the effect of ionic impurities and external electric fields on rod-like water clusters in polyethylene

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ABSTRACT

Monte Carlo methods have been combined with end-bridging methods to study the solubility and structure of water in polyethylene, where the polyethylene contains a pair of oppositely charged ionic impurities. The water in the polymer is in equilibrium with pure liquid water. Both the polymer and pure water phases are exposed to an external electric field. The ions dramatically increase the solubility of water in polyethylene and induce the formation of a stable, rod-like water cluster between the ions. The solubility, the hydrogen-bond ordering of the water molecules in the cluster and the size of the cluster increase in the presence of an external field that enhances the local electric field between the ions. When the direction of the external field is reversed, and when it has the same magnitude as the local ionic field, the rod-like structure is broken up and a smaller cluster forms around each ion.

1. Introduction

The solubility and structure of water in polymers exposed to external electric fields are of great interest in high voltage cable insulations made of polyethylene. For example, water trees, which are macroscopic tree- or bush-like structures comprised of paths of water filled voids with radii of up to 5 μm, can form when the insulation is exposed to high field strengths [1]. In severe cases these voids form larger channels in the polymer which can lead to breakdown of the insulation. Relatively little is known about the molecular mechanism of water penetration and water tree propagation in the polymer, but a necessary condition is the presence of an alternating electric field. Water trees have been reported to grow [1] at external fields as low as 1.9×10^6 V/m. This is much lower than the electric field that high voltage insulators are typically exposed to, which is approximately 10^7–10^8 V/m. Defects in the electrically conducting metal or impurities in the polymer are expected to create local electric fields that are larger than 10^8 V/m [2].

Water treeing, together with the possible initiation and growth mechanisms, have been well described by Dissado and Fothergill [1], and a review of more recent work has been written by Jones et al. [3]. Also, a study performed by Radu et al. [4] concluded that the presence of water in water trees increases the electrical permittivity compared to unaffected regions, and that the water enhances the local electric field. They conclude that a water tree can have a local self-amplification of as much as 50% of the external field at the extremities of the tree. This, together with defects in the material, such as small conducting inclusions, can induce breakdown of the insulation.

An experimental study of the solubility of water in rubber was done by Southern and Thomas [5]. Rubber is much less resistant to swelling than polyethylene and can thus absorb much more water under certain conditions, but pure rubber is also hydrophobic and the solubility of water is thus low. Southern and Thomas found that rubber prepared with a small amount of impurities (sodium chloride) increased the water solubility by more than an order of magnitude and proposed that the water forms clusters around the impurities. They also repeated the experiment with a protein impurity and found similar results, demonstrating that increased solubility can be induced by different types of impurities.

An experimental study has shown that a relative humidity of about 75% is necessary for water trees to grow [6]. This value is the same as the vapor pressure over a saturated NaCl solution (the experiment was performed at 295 K), and since NaCl contamination of the polymer in normal use is unavoidable they conclude that ions play a significant role in the water treeing mechanism. This is in agreement with the fact that it is very difficult to grow water trees if polyethylene is saturated with pure water [7].

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Bulinski et al. [7] performed experiments on water tree initiation on samples saturated with salt solution. They found water tree densities that were similar for both NaCl and $CuSO_4$ solutions, and that the water tree initiation rate was not affected by the presence of oxygen, suggesting that oxidation is not a major factor in the water treeing mechanism.

These experimental studies have been complemented by modeling. However, previous models have not included all four critical components used in the experiments, namely the polymer, water, impurities and electric field. For example, Kiselev and Heinzinger [8] performed a molecular dynamics (MD) study of a Cl^- ion dissolved in liquid phase simple point charge/extended (SPC/E) [9] water, where the system was exposed to an external electric field at 300 K (a polymer matrix was not included in their simulations). They observed long range ordering of the water molecules at a field strength of 10^{10} V/m and that a weaker field of 5×10^9 V/m did not affect the water structure compared to systems that were not exposed to an external field. Their simulations also showed that the number of water hydrogen bonded to the ion decreased significantly at higher fields and that the self-diffusion coefficient decreased significantly with increasing field strength.

Monte Carlo (MC) simulations of oppositely charged ions and methane in liquid water by Jönsson, Skepö and Linse showed that the tetrahedral structure of water is replaced by a denser structure near the ions [10]. They also found that this structure decreases the solubility of methane. In addition, a MD study of SPC/E water between hydrophobic plates with a separation of 6 Å showed that the water forms a bilayer ice structure at room temperature and high pressure [11] ($P \geq 0.1$ GPa), and a MC simulation of water absorption in hydrophobic zeolites showed that water tends to form hydrogen bonded clusters around hydrophilic impurities [12]. Similar results have been reported by Di Lella et al. [13].

Jungwirth [14] used first principle methods to show that it requires at least six water molecules, arranged in two layers with three molecules in each layer, to separate a Na^+–Cl^- pair. The ion separation for the six-molecule water cluster was 4.43 Å. We have previously used MC methods to show that water in decane and polyethylene forms rod-like clusters between oppositely charged ions at much larger distances [15] (up to 20 Å). A similar rod-like water structure has also been observed by Shevkunov and Vegiri [16] in pure water clusters exposed to an external electric field of 5×10^9 V/m.

The study presented here is the first molecular level study of the combined effect of an ion pair, consisting of oppositely charged ions, and external electric fields on water solubility and structuring in polyethylene, where the water dissolved in the polyethylene is in equilibrium with pure liquid water. Similar to our previous studies [15], we model polymer-bound impurities (such as peroxides, metal particles and carbon black, and which arise during production and processing of the polymer [17]) by a Na^+–Cl^- ion pair that is fixed in the polymer matrix. We therefore focus on generic trends of water structuring due to ion pairs in the presence of external electric fields. It is also relevant that experimental studies of water treeing in polyethylene usually use polymer samples that are immersed in salt solution prior to the experiment [7]. The density of ions in the salt solution is 0.05–0.1 M [7], which is similar to the density of ions in the polymer matrix modeled here – where the Na^+ and Cl^- ions are separated by 20 Å. However, the ions are not bound to the polymer as modeled in our simulations and as is the case for some of the impurities that arise during processing of polyethylene. In addition, we simulate polyethylene in equilibrium with pure liquid water, and not a salt solution.

2. Methods

The service temperature of high voltage cable insulation [1] is approximately 350 K. However, simulations cannot be performed on polyethylene at this temperature due to the risk of polymer crystallization. To ensure a fully amorphous system it is necessary to use a temperature above the melting temperature (the experimental value for polyethylene is 412 K) and 450 K was chosen for our simulations. The pressure used in this study, 30 bar, was chosen because it is above the vapor pressure of water (≈ 10 bar at 450 K) thus ensuring that the bulk water is in the liquid phase.

The methods and potential models used here have been used and described elsewhere [15,18,19]. Briefly, we have studied equilibrium between bulk water and water dissolved in the polymer using MC in a connectivity altering osmotic Gibbs Ensemble [18,20]. Ordinary Gibbs Ensemble moves were performed on the 500 water molecules, which were represented by the SPC/E model [9]. The 10 polymer chains, each with an average length of 300 carbon units, were represented by the TraPPE model [21] (Previous simulations [18] have shown that this chain length gives converged results for water solubility in polymers in the absence of ions and an external field, and although we have not explicitly tested convergence when ions and fields are present it is expected that the trends in water clustering reported here are not sensitive to the chain length.). The polymer molecules are not allowed to transfer out of the polymer box since, in agreement with previous simulations [18], one can assume insignificant solubility of polyethylene in water. The polyethylene has been simulated using end-bridging methods [22].

Ion–ion interactions, as well as those between ions and the rest of the system (water and polymer) are based on the Dang models [23], which were developed to be used in combination with the SPC/E model. Interactions between different atom types are determined using Lorentz–Berthelot mixing rules. These models have been successfully used in previous studies of hydrocarbon–water [15,18,19] and ion–water [23] systems, and are combined here to study systems that include hydrocarbons, water and ions.

Equilibration was initiated with all water molecules in the pure liquid phase and the Na^+–Cl^- ion pair in the polyethylene phase. No trial translational (or any other) moves were attempted for the ions, which were therefore fixed at relative positions in the simulation box. The initial separation was 20 Å, and this distance increased marginally (≈ 0.05 Å) from the initial separation since absorption of water leads to expansion of the polymer phase and hence an increase in the volume of the polyethylene box. The effect of changing this separation has been studied elsewhere [15] (although this was for water in hydrocarbon in the absence of an electric field, the trends seen in that study are expected to be observed in the system studied here).

The systems were equilibrated for 1.2×10^9 MC steps. Following equilibration, the simulations were propagated for 3.0×10^9 steps for each system. Cluster analysis, which is very time consuming for these large clusters, has been restricted to a simulation length of 1.2×10^8 steps for each simulation.

The same uniform electric field strength was applied to both the polyethylene and pure water simulation boxes. The total potential energy, U, of a system with an external electric field, $\mathbf{E}$, is

$$U = U_0 - \mathbf{M} \cdot \mathbf{E} \tag{1}$$

where U_0 is the potential energy in the absence of an external field and $\mathbf{M}$ is the vector of the molecular dipole moments. Field strengths of 0, 6×10^7, 2×10^8, 6×10^8 and 2×10^9 V/m were studied. This can be compared to the magnitude of the local field midway between the bare ions, which is 2.8×10^9 V/m for the 20 Å separation used in the simulations presented here.

The external fields were applied both parallel and antiparallel to the $Na^+ \rightarrow Cl^-$ axis. The parallel fields enhance the local field between the ions and the antiparallel fields weaken the local ionic field. Both of these fields (as well as fields in other directions relative to the ion impurities) are found under alternating current

(AC) conditions that, as mentioned above, are required for water treeing. We have not explicitly considered the mechanism of restructuring of the water clusters due to changes in the field direction, which may require time-dependent techniques. Unless explicitly stated, the results reported below are for the parallel (enhancing) external field.

Analysis of the water structures in the polymer matrix was based on the definition of 'physical' clusters that has been used in previous studies of saturated water vapor [24]. According to this definition, a molecule is part of a cluster if the oxygen–oxygen (O–O) distance to another molecule in the cluster is less than 4.0 Å. This definition, which is based on that proposed by Stillinger [25], neglects the relative orientation of neighboring molecules. It was used in this study since the electric field between the ions may disrupt the hydrogen bonding (due to alignment between the water dipole and the field) even when water molecules belong to a single 'physical' cluster. The separation of 4.0 Å is chosen since this distance includes all water–water nearest neighbor separations, i.e., the first (and only) peak in the O–O radial distribution function is less than 4.0 Å (discussed below with reference to Fig. 3).

To study the effect of this definition and the extent of hydrogen bonding (H bonding) in the clusters, the results are compared to those obtained when using a definition for H-bonded clusters. The latter clusters are defined using a combined distance and energy criterion, proposed by Kalinichev and Bass [26], who have used this definition when studying cluster size and shape in supercritical water, where a water molecule belongs to a cluster if the distance between the oxygen and a hydrogen on a neighboring water molecule is less than 2.4 Å, at the same time as the intermolecular energy between the two molecules is less than −10 kJ/mol. A molecule is considered to be a member of a cluster if it has at least one H bond to another molecule in the cluster.

3. Results

As shown in Fig. 1, the average number of water molecules in the polyethylene matrix increases with increasing external field. This is opposite to the trend seen for water in pure polyethylene under large electric fields [19], where increased field strength decreases the water solubility in the polymer. Hence, it is the combined effect of the ion pair and the enhancement of the local ionic field by the external field, which leads to the increasing solubility with increasing field seen in the present simulations. It should also be noted that the presence of the ion pair (and electric field) leads to an order of magnitude increase in the solubility of water in

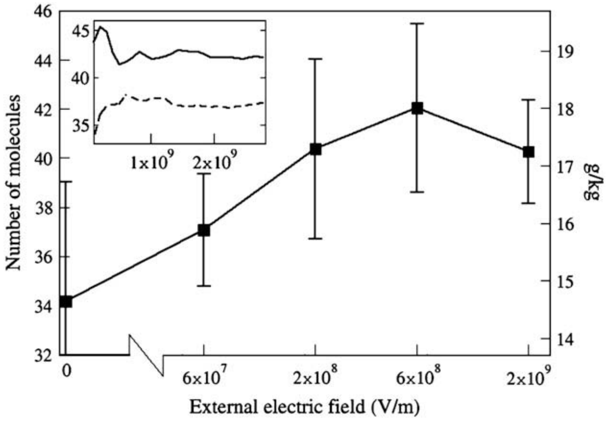

Fig. 1. Scale to the left; average number of water molecules in the polyethylene matrix as a function of external electric field. The bars indicate the standard deviation. Scale to the right; solubility of water in the polymer expressed in g water/kg polymer matrix. The insert to the figure shows the cumulated average number of water molecules as a function of number of MC steps at 6×10^7 V/m (dashed line) and 6×10^8 V/m (solid line).

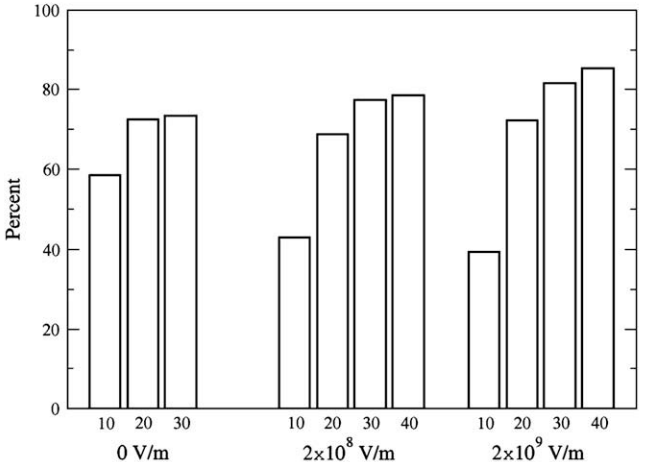

Fig. 2. Cumulative percentage of water molecules in the polyethylene that are included in hydrogen bonded clusters with a maximum size of 10, 20, 30 and 40 molecules (dimers, but not monomers, are considered as clusters). Distributions are shown for parallel external fields 0, 2×10^8 and 2×10^9 V/m (other fields are not shown for the sake of brevity). No clusters larger than 30 water molecules were observed at 0 V/m.

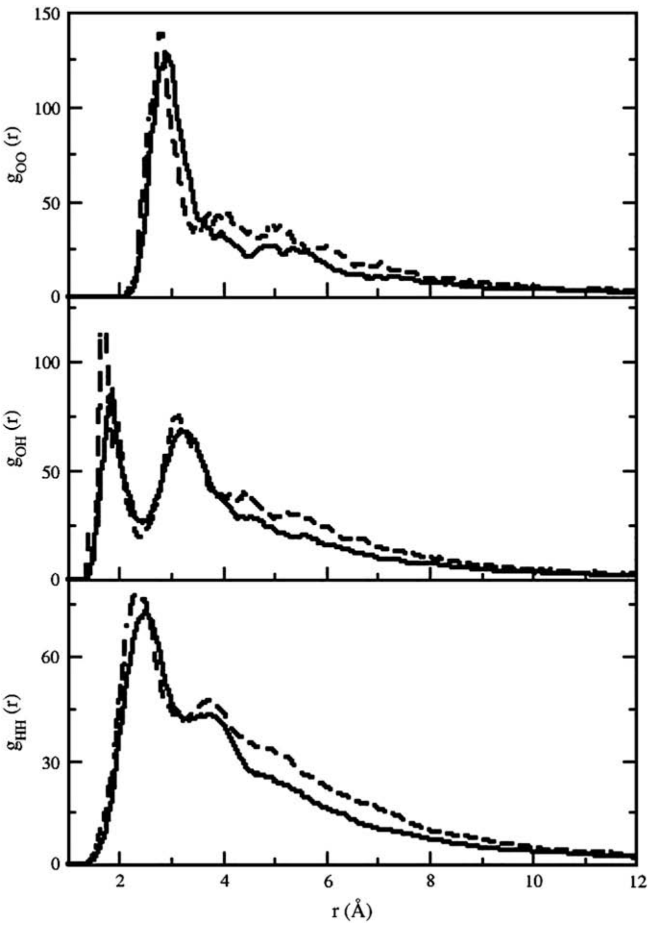

Fig. 3. Water oxygen–oxygen, oxygen–hydrogen and hydrogen–hydrogen radial distribution functions in the polymer matrix in the absence of an external field (solid line) and in a field of 2×10^9 V/m (dashed line). Distributions for the other fields studied here are not shown for the sake of clarity.

polyethylene [15]. The insert in Fig. 1 shows the cumulated average number of water molecules as a function of the number of MC steps at 6×10^7 and 6×10^8 V/m. Note that the number of water molecules have converged relatively early in the simulations. It is not clear if the reduction in the number of molecules at 2×10^9 V/m is statistically meaningful, and an investigation at even higher fields is beyond the scope of this work. However, we have noticed a decrease in water solubility in polyethylene at higher external fields in the absence of ions [19], and note that the external field of 2×10^9 V/m is similar to the local field between the ions (2.8×10^9 V/m midway between the ions). This decrease in solubility is combined with a restructuring of the liquid water phase where the molecules gradually increase their orientation in the field. It appears, therefore, that this water restructuring in the liquid water phase leads to a larger decrease in total Gibbs free energy at high electric fields than the corresponding restructuring in the polymer phase. Consistent with the increased solubility at higher fields, preliminary results from simulations where the monovalent Na^+ and Cl^- ions have been replaced by divalent ions (achieved by simply doubling the charges of the ions) show that the increased local field between the ions attracts more water molecules and the number of water molecules found in the polymer increases by a factor of two to four compared to the monovalent ions.

In addition to the large increase in solubility, the presence of the ion pair and the external field affects the clustering of the water in the polymer. When the polymer, that contains the ion pair, is exposed to parallel (enhancing) external fields, there is always one, and only one, physical cluster with a size large enough to bridge the distance between the ions (larger than 20 water molecules) in the simulated polymer matrix. Some small physical clusters (smaller than 10 water molecules) are also found, and the abundance of these small clusters decreases strongly with increasing field in agreement with previous results [19]. Also, the percentage of water molecules in the polymer matrix that are included in the single, large physical cluster increases from 96% in the absence of an external field to almost 99% when an enhancing field of 2×10^9 V/m is applied. This, together with the increase in water solubility at larger fields (Fig. 1), leads to larger physical clusters with increasing field strength. In addition, larger external fields increase the stability of the water cluster, which is seen by lower rates of fluctuations in cluster sizes in systems exposed to strong external fields. For example, for the same set of MC parameters the acceptance of attempted transfers of water molecules between the boxes is three times larger in the absence of an external field than in a field of 2×10^9 V/m.

Similar trends are seen when using the hydrogen bond definition of clusters. Increasing the field strength leads to an increase in the size of these clusters, as well as the percentage of water molecules that are included in these clusters. This is shown in Fig. 2 where it can be seen that, in the absence of an external field, almost 60% of the molecules are included in H-bonded clusters that contain at most 10 water molecules (dimers, but not monomers, are considered as clusters). This decreases to 43% at 2×10^8 V/m and 39% at 2×10^9 V/m, at the same time as the number of molecules that are included in larger clusters increases. In addition, the size of the H-bonded clusters increase with increasing external field, e.g., clusters containing between 30 and 40 water molecules are found at the field strengths shown in the figure (and there are more of these larger clusters at the larger field). Also, the percentage of water molecules in the polymer matrix that are located in H-bonded clusters (of any size) increases from 73% with no external field to 85% at a field of 2×10^9 V/m. In contrast to the physical clusters, where the vast majority of the molecules are included in one single cluster, the H-bonded clusters are smaller.

The fact that the H-bonded clusters become larger with increasing field strength, and the fact that a larger percentage of water molecules are included in these clusters, indicates that there is larger H-bonded ordering for larger field strengths. This increased ordering may be due to both alignment of the molecules due to the field, and the fact that external fields shift the water phase diagram to lower temperatures [19,27]. A decrease in the temperature leads to increased ordering of the water, and it has been observed [24], for example, that the difference between the percentage of molecules included in physical clusters and those included in hydrogen bonded clusters in saturated vapor is lower at lower temperatures.

The increased ordering of water molecules in the polyethylene with increasing field is also observed in the radial distribution functions (rdfs) of water oxygen–oxygen (O–O), oxygen–hydrogen (O–H) and hydrogen–hydrogen (H–H) separations shown in Fig. 3. For the sake of clarity, only field strengths of 0 and 2×10^9 V/m are shown. The peak in the O–O rdf is narrower when the system is exposed to an external field, and it is shifted to a smaller value by 0.2 Å. Similarly, both the first and second peaks of the O–H rdf are shifted to shorter distances when the external field is increased. For example, the second peak is shifted from 3.30 Å when no field is applied to 3.15 Å at 2×10^9 V/m. In addition, the minimum between the first and second peak is reduced by 30% when increasing from 0 to 2×10^9 V/m. A similar effect is observed when exposing systems containing a single Cl^- ion dissolved in water to external electric fields [8]. The first peak of the H–H rdf is also shifted to shorter distances when the field strength is increased, and a second peak appears at 3.8 Å when the field strength is 2×10^9 V/m. This peak is not as prominent at the weaker external fields.

In addition to showing an increased ordering of the water molecules, the shift of the peaks in the rdfs to shorter distances also reveals that the density in the cluster increases at high external fields. This has also been seen for liquid water exposed to high external fields [19,27]. It may be noted that the amplitudes of the peaks in the rdfs shown in Fig. 3 are far larger than those obtained for liquid water [8] since they are normalized to the density of water far away from the cluster, and the density of water in polyethylene is far lower than that of liquid water.

Typical snapshots of water clusters in polyethylene are shown in Fig. 4 (no external field) and Fig. 5 (field of 2×10^9 V/m). It can be seen that the external field induces a larger cluster, and that the cluster is more ordered. For example, the cluster that is exposed to 2×10^9 V/m is more compact than that in the absence of the field,

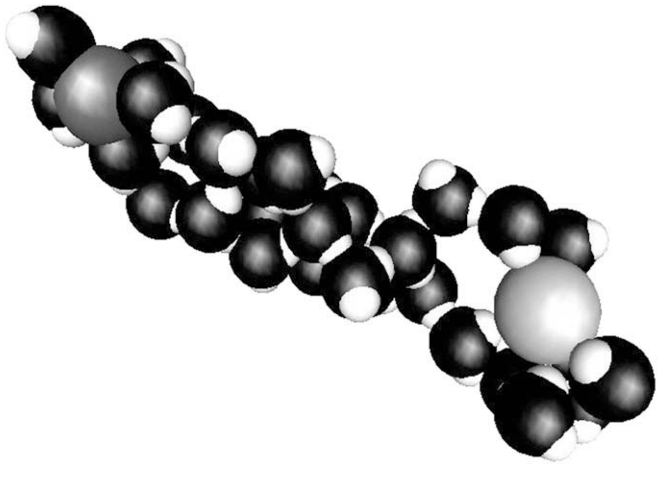

Fig. 4. Typical snapshot of a cluster in the absence of an external electric field. The Na^+ ion is shown in dark grey (upper left of the figure) and the Cl^- ion in light grey. The polymer is not shown.

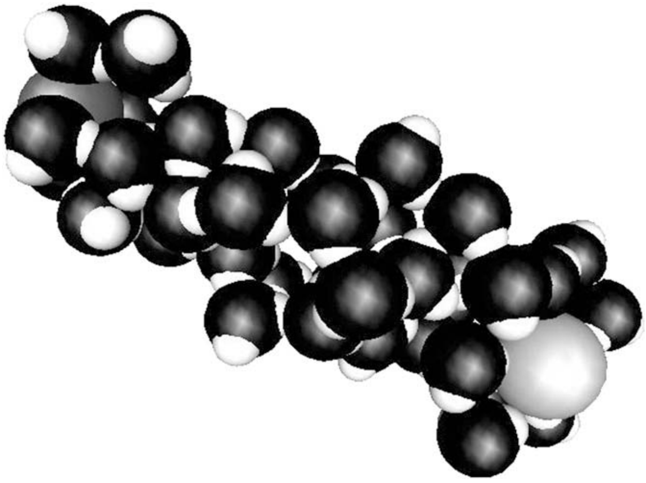

Fig. 5. Typical snapshot of a cluster in an enhancing parallel external electric field of 2×10^9 V/m. The Na^+ ion is shown in dark grey (upper left of the figure) and the Cl^- ion in light grey.

and all water molecules are located between the ions in the large field. This is not the case for weaker fields.

Application of an antiparallel field, that weakens the local ionic field, decreases the size and stability of the water cluster. In fact, when the magnitude of this external field is sufficiently high, the cluster between the ions separates into two small clusters, one around each ion. A typical snapshot of this is shown in Fig. 6 for an external antiparallel field of 2×10^8 V/m. When the strength of this external field is further increased, a single cluster forms again. However, it does not form between the original Na^+–Cl^- ion pair, but between one of the ions in the simulation box and the copy of the oppositely charged ion that exists in the neighboring simulation box (due to the periodic boundary conditions). That is, the cluster that existed between a $Na^+ \rightarrow Cl^-$ pair now exists between a $Cl^- \rightarrow Na^+$ pair, such that the field enhances the local ionic field between this new pair. The enhancement is sufficient to induce a single water cluster that spans the distance between the ions in the new ion pair, which is ≈25 Å in our simulations. We have previously shown that the local field between two ions at a separation of 25 Å is too low to form a rod-like cluster between these ions in the absence of an external electric field [15], although it should be noted that those studies were with decane instead of polyethylene, and that the temperature was 400 K. Hence, the external field is important for the formation of the cluster in the present studies. Further increasing the strength of the (antiparallel) field leads to the formation of larger clusters, containing up to 63 water molecules for the fields studied here (this is larger than that obtained for the strongest parallel field since the separation between the ions is larger).

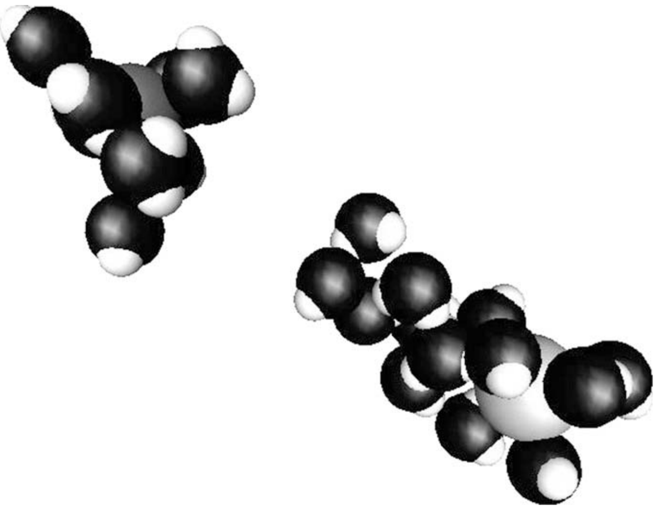

Fig. 6. Typical snapshot of a cluster in an antiparallel external electric field of 2×10^8 V/m. The Na^+ ion is shown in dark grey (upper left of the figure) and the Cl^- ion in light grey.

The simulations presented here are for ions that have fixed positions in the polymer. However, it is of interest to note that, due to the very large stability of the water clusters formed between the ions, simulations that were initialized with an equilibrated water cluster but where translations of the ions were allowed, show very small changes over long simulation runs. That is, the oppositely charged ions did not rapidly combine, but were kept apart by the water cluster. For example, a simulation where the initial ion separation was 20 Å showed that the ion separation was more than 19 Å after 4×10^9 MC steps. This was obtained in the absence of an electric field and, as discussed above, applying an electric field further increases the stability of the water cluster. Also, even though the separation between the ions decreases during the simulation, translations that increase the separation are also accepted. It is expected that the separation will continue to decrease until an equilibrium distance [14] is reached. It can also be noted that 90% of the accepted ion translations were performed on the Cl^- ion, which is expected due to the weaker interactions with the water molecules compared to the Na^+ ion. The stability and large size of the water clusters seen here are in agreement with an experimental study by Meyer and Chamel, who found that the diffusion coefficient of water is 100 times larger than that for Na^+ ions in polyethylene [28]. That is, the Na^+ ions or Na^+–Cl^- ion pairs, may be part of large water clusters that have slower diffusion rates.

The polyethylene density (excluding water and ions) is 773 kg/m^3 for the pure polyethylene but decreases to ≈760 kg/m^3 in systems with ions and water under the electric fields studied here (the density is obtained after excluding the mass of ions and water). The decreased density is due to the expansion of the polymer. That is, the absorption of the water creates cavities in the material. Although we have not explicitly analyzed the size distributions of these cavities, a typical cluster with 35 water molecules has a length of ∼25 Å and a diameter of ∼8 Å, resulting in a volume of approx 1400 Å^3. This is clearly larger than the average size of cavities in the absence of ions in external fields (since the presence of ions in external fields leads to a decrease in the polymer density). On the other hand, the geometries of the polymer molecules are not significantly affected by the absorption of water (or the presence of ions or external field), and polymer molecular bond and torsion angles are the same as those found in pure TraPPE polyethylene. Similarly, the internal energies for the polymer molecules are, within statistical uncertainties, the same as for the pure system.

The mechanical damage theory of water treeing [29] states that small voids, induced by mechanical stresses at the tip of the water tree, are subsequently filled with water. That is, voids are formed before water enters these areas of the polymer. The results presented here indicate an alternative initiation mechanism, where the formation of water clusters causes the formation and enlargement of voids. Of importance to note here, is that water trees usually grow in AC fields, with field strengths of 10^8 V/m (as mentioned above, impurities, and water in water trees, can enhance this value considerably). In this work we have shown that parallel fields of 2×10^8 V/m or larger that enhance local ionic fields can induce the formation of larger clusters than in the absence of external electric fields, which may also form voids in the polymer to allow for sufficient space for the water cluster (this was not explicitly analyzed in this work, but a decrease in the polymer density was observed). In addition, antiparallel fields of $\approx 2 \times 10^8$ V/m break the water cluster between the ions into two smaller clusters surrounding the ions (or larger fields create a new cluster between other ions – probably inducing a new void between these ions). Since typical operating frequencies of an alternating current are 50 Hz, the water can relax within each new cycle (i.e., the water cluster can reach equilibrium in fractions of 50^{-1} s for each new change in external field) but the polymer matrix, which has a relaxation time of seconds [30] cannot. Hence voids, and paths of voids, can be created by the formation of water clusters. In addition, the voids that were created by the formation of a water cluster, and that are emptied by the change in direction of the external field, are available for the absorption of additional water. Absorption of water into this empty void will restrict the original water molecules, e.g., that are located around the ions, from returning to their prior position between the ions. If this mechanism leads to a sufficiently large cluster, it may reach a critical cluster size and continue to grow without needing the influence of ions. It can also be noted that the critical cluster size is decreased considerably when applying an external electric field (by over 30% in a field 10^9 V/m) [27]. Simulations to test the mechanism proposed here is left for future work.

4. Conclusions

Monte Carlo methods in a connectivity altering osmotic Gibbs Ensemble have been combined with end-bridging methods to study the solubility and structure of water in polyethylene, where the polyethylene contains a Na^+–Cl^- ion pair separated by 20 Å, is in equilibrium with pure liquid water and where both the polymer and pure water are exposed to external electric fields.

It was found that the ions dramatically increase the solubility of water in polyethylene and induce the formation of a stable, rod-like water cluster between the ions. Exposure to parallel external fields that enhance the local electric field between the ions increase the amount of water absorbed in the polyethylene as well as the size and stability of the water cluster. In addition, increasing the field strength increases the H-bond ordering of the water molecules in the cluster. Application of a sufficiently large antiparallel field destroys the rod-like structure and separate clusters are formed around each ion.

Based on these observations an alternative mechanism for water tree formation is proposed, where new voids, on a molecular scale, are seeded by impurities in the polymer. Water molecules will aggregate between these impurities and eventually reach a critical cluster size from which the water cluster can grow to a microscopic size.

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