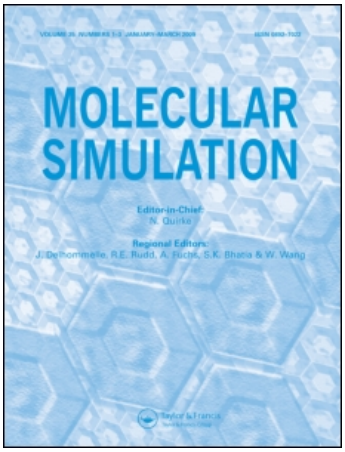

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Electrodissociation of clathrate-like structures

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Electrodissociation of clathrate-like structures

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In the present work, we develop molecular dynamics (MD) simulations in the NPT (isobaric–isothermic) ensemble to analyse the effect of an external electrostatic field over a cubic methane hydrate crystallite. The amplitude of the field is in the range 0.5–3.0 V/nm. For the simulations, we used the SPC/E rigid water model and a single-site model for methane at a temperature of 248 K and a pressure of 20 bar. When the external electrostatic field is applied, the water dipoles are oriented in such a way that the methane molecules can diffuse far away from the water cages, hence the clathrate dissociation takes place. This last phenomenon was observed for intensities above 1.5 V/nm. Taking the final configuration of each run as input, we develop a new set of MD simulations, and we observe that the stable clathrate is not recovered immediately when the external electrostatic field is turned off due to limitations in the simulation time.

Keywords: methane hydrates; external electric field; molecular simulation; coordination number; radial distribution function

PACS: 31.15.xv; 36.40.Ei; 36.40.Sx

1. Introduction

In the last decade, there have been several papers devoted to analysing the formation and the structure of natural gas hydrates. These structures consist in a kind of 'cage' built by water molecules and such arrangement allocates gas molecules, namely 'guest' molecules. These so-called 'cages' are supported by the effect of the hydrogen bonds of the water molecules [1]. Currently, the mechanisms of natural gas hydrate crystallisation and dissociation are poorly understood [2], and it is desirable to improve our knowledge about them, to enhance our capability of developing new inhibition techniques. This could result in economic incentives to the oil and gas industry due to the concern of hydrate blockage in pipelines and the possibility of using methane hydrates as a source of energy.

On the other hand, since water is a polar fluid, it is important to study the effect of an external electrostatic field in the stability of the clathrate hydrate of methane. In the literature, it is possible to find molecular dynamics (MD) simulations that have been used to study structural properties [3–7], nucleation [8–10], crystallisation and dissociation of methane hydrates [11–17], but only a few of them include an external physical perturbation. In particular, English and MacElroy [13] have performed MD simulations of methane hydrate under the influence of an external electromagnetic field in a range from microwave to far-infrared frequencies (5–7500 GHz), and they noticed dissociation when the external fields break the hydrogen bonds of the water arrangements in the hydrates. Other simulations have focused on the effect of an external static electric field in the bulk water [18–24] which attempts to reorient the water dipoles along the field direction resulting in the perturbation of the molecular position and break-up of the hydrogen bond arrangements. These effects have been possible in simulations through the assistance of an external static electric field in the range 1.0–5.0 V/nm at 243 K. Experimentally, fields up to 50 V/nm can be routinely obtained by the application of potentials of 1.0–5.0 kV over tips of radius of 10–100 nm [25]. On the other hand, computer simulations of water implemented by Shevkunov and Vegiri [23] in the presence of an external static electric field in the range 0.5–7.0 V/nm have shown the destruction of the normal solid- or liquid-like state of the cluster, in a process that has the characteristic of a first-order phase transition.

The above-mentioned studies show that water can suffer structural changes in the presence of an external electrostatic field in the range from 1.0 to 8.0 V/nm and temperatures around 240 K. These observations support the idea that the clathrate structure may be altered enough to be dissociated by means of an external perturbation, and this could be used in a new technique to dissociate clathrate structures in pipelines and microfluidic devices [26]. The present work addresses the problem whether a simple constant electric field applied on methane hydrates is enough to observe the dissociation phenomena. For this purpose, the radial distribution functions (RDFs) of water–methane and methane–methane were calculated in a stable thermodynamic state. In addition to these

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properties, the coordination number, the orientation of the total dipole moment and the methane diffusion were also estimated.

This paper is laid out as follows: in Section 2, some aspects of the simulation are mentioned; in Section 3, our relevant results are included and also a brief discussion around them; finally, in Section 4, conclusions and perspectives of this work are included.

2. Methodology

In the present work, we have used the rigid/non-polarisable SPC/E water potential [27] and a single-site methane model consisting of a Lennard-Jones (LJ) 12-6 interaction [5]. The SPC/E water potential was chosen because of its good performance to reproduce the dissociation of the methane hydrate system that was observed in a previous work [28], where the comparison between different rigid water model behaviour in MD simulations showed that such model was the most convenient to reproduce the transition from a stable to unstable clathrate structure. In addition, the three-site model showed an excellent agreement with the experimental results, specifically around the phase transition line. On the other hand, the simulations were developed using the GROMACS MD package [29–31]. For the long-range electrostatic interaction, particle mesh Ewald was used with a cut-off radius of 1.0 nm, for van der Waals interactions the spherically truncated and shifted LJ was implemented with a cut-off radius of 1.0 nm and the Lorentz–Berthelot mixing rules were applied for the interaction between different atom species. The simulations were developed in the NPT ensemble, with a time step of 1.0 fs for 1.0 ns, and we also used three-dimensional periodic boundary conditions [32]. The initial configuration for our simulations was based on the results of the X-ray diffraction study made by McMullan and Jeffrey [33] for the structure type I of the ethylene oxide hydrate, which provides the positions of the oxygen atoms in each water molecule and the mass centres in the unitary cell for the methane molecules. The orientations of the hydrogen atoms in the water molecules were randomly set, and subsequently a short MD simulation (50 ps at 50 K and 1 bar) allows the water hydrogen atoms to be settled into the correct orientations consistently with the Bernal–Fowler rules [34]. The unit cell of side 1.203 nm was replicated 2^3 times to form a cubic cell of side 2.406 nm which includes 368 molecules of water and 64 molecules of methane; this means that the water 'cages' in the methane hydrate are completely occupied. The total energy of the systems was taken in agreement with the work of James et al. [35] as follows:

$$U_{\text{total}} = \sum U_{ab} - Ee\sum q_i z_i, \tag{1}$$

where E is the field strength applied in the z-direction, z_i is the z Cartesian coordinate of partial charge q_i and e is the electron charge. U_{ab} includes the electrostatic and LJ contributions. The strength of the external static electric field was taken in the range 0.5–3.0 V/nm with a temperature and a pressure of 248 K and 20 bar, respectively. In all cases, the coordination number between methane and water molecules was calculated and estimated using the following formula [36]:

$$n(d) = 4\pi\rho\int_0^d x^2 g(x)\mathrm{d}x, \tag{2}$$

where $g(x)$ is the RDF, ρ is the density number of water molecules and the integral is calculated in the first coordination shell that is demarcated by the distance d.

Concerning the dynamics, the methane molecular mobility, in the presence of an external static electric field, is described through the diffusion coefficient as a result of the limiting slope of the mean-square displacement (MSD) of the methane molecules via the fluctuating Einstein relationship [32]

$$\langle [r(t) - r(0)]^2 \rangle = 6Dt, \tag{3}$$

where D is the diffusion coefficient and $r(t)$ is the molecule position at time t.

3. Results and discussion

In this section, the relevant results of our simulations are shown. First, the effect of an external static electric field on the clathrate hydrate structure is reviewed. After that, a new series of simulations are carried out but now with the external static electric field turned off. These last simulations were performed using the final configurations obtained under the influence of the external fields as an input.

3.1 The clathrate hydrate under an external electrostatic field

We have selected a temperature of 248 K and a pressure of 20 bar, since experimental evidence has shown that the system is stable under these thermodynamic conditions [1]. In Figure 1, we present a snapshot of the initial configuration of the system with the clathrate structure. In Figure 2, the centre–centre CH_4—H_2O RDF for several external static electric field strengths is shown. The system that is free of an electric field supplies a curve very similar to that in figure 4 of [13], and it corresponds to the stable structure of the clathrate. We can note that the structure starts to disappear for fields larger than 1.0 V/nm because the area below the RDF in the first coordination shell decreases (RDFs derived from fields greater than

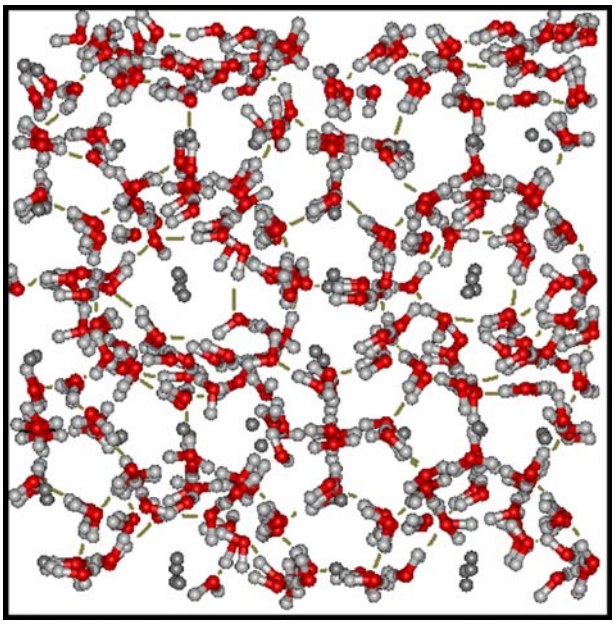

Figure 1. Snapshot of methane clathrate formation without an external electrostatic field for a pressure of 20 bar and a temperature of 248 K, where we have highlighted the methane molecule inside a rigid cage arrangement.

1.0 V/nm are omitted because these are very similar to the RDF obtained with a field of this same intensity). The difference between the two structural states is the number of water molecules surrounding a methane molecule in the first coordination shell. In Figure 3, the average coordination number of CH_4—H_2O is shown. This number

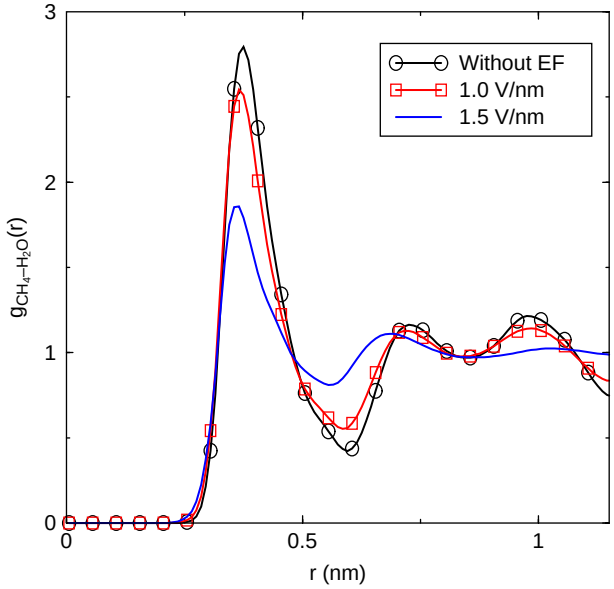

Figure 2. RDF of CH_4—H_2O for a pressure of 20 bar and a temperature of 248 K for different values of an external electrostatic field (EF).

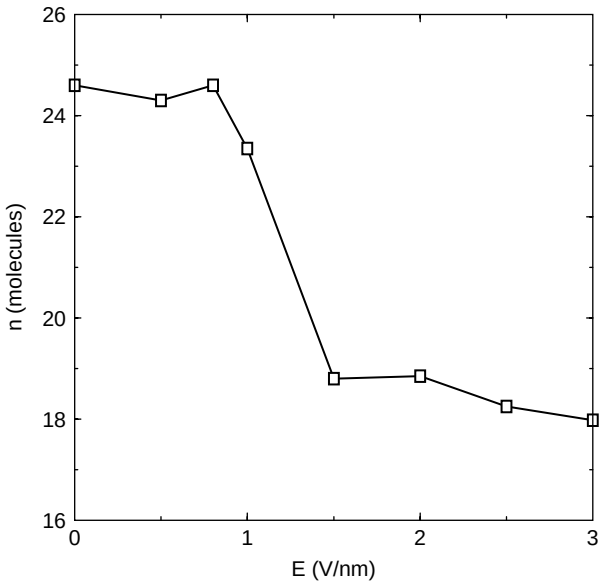

Figure 3. Variation of the coordination number of water molecules around methane molecules in the first coordination shell for a pressure of 20 bar and a temperature of 248 K with the external electrostatic field applied.

decreases below 20 for fields up to 1.5 V/nm. It is important to remember that 20 corresponds to the coordination number of a pentagonal dodecahedron which is the smaller cavity for a clathrate type I [1]. This means that a field with this strength can orient the water molecules in such a way that methane molecules can dissociate from the water cages and the clathrate hydrate phase does not maintain its structural integrity.

There is also evidence of structural changes in the RDF of CH_4—CH_4, which are shown in Figure 4, with and without an electric field. The continuous line denotes the typical separation between two methane molecules for a stable state of clathrates. Also, we can note that this curve is quite similar to that in figure 5 of [13]. In the same figure, it is evident that the effect of an external field induces the appearance of a peak at 0.4 nm. On the other hand, we observe that, for magnitudes of electric fields of 1.0 V/nm, there is breaking in the original structure and, for 1.5 V/nm, the first peak is enhanced, which can be interpreted as the methane molecules leave the water cages and they can remain closer to each other as a consequence of the applied field. Concerning the spatial arrangement of clathrates, we carried out some extra simulations using a $3\times3\times3$ cell in order to analyse a possible restriction due to the periodic boundary conditions (not shown), and no significant difference was found in the data obtained for structural properties.

On the other hand, as was mentioned above, in order to quantify the diffusion of the methane molecules in the dissociation process, we calculated the MSD of the methane molecules. In Figure 5, the MSD is shown for

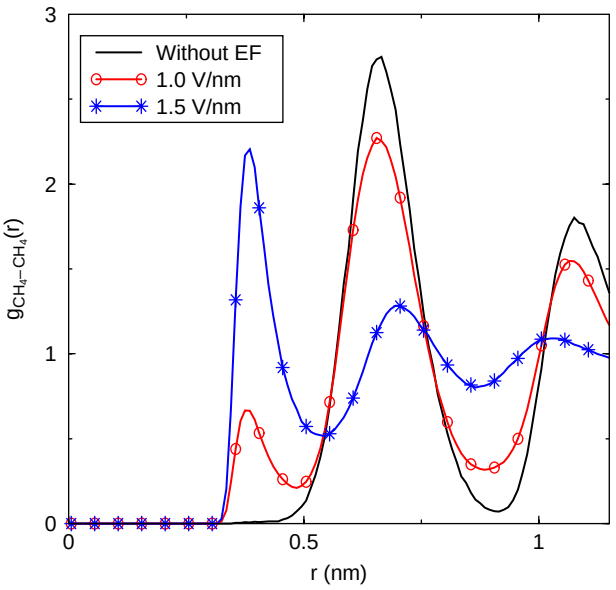

Figure 4. RDF of CH_4—CH_4 molecules for a pressure of 20 bar and a temperature of 248 K with the external electrostatic field applied.

different field intensities. The open circles correspond to the curve without the electric field. This behaviour could be considered as the displacement on behalf of the methane inside the water cage. Concerning the curve derived for a field intensity of 1.0 V/nm, such curve shows a smooth increment on the slope, and this result allows to set up that this intensity in the electric field is not enough to cause the dissociation of the system in a complete way.

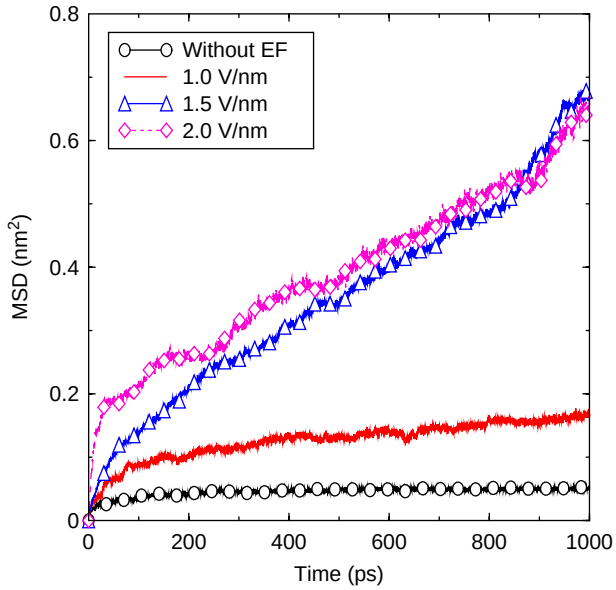

Figure 5. The MSD of the methane molecules for a pressure of 20 bar and a temperature of 248 K when the external electrostatic field is applied.

In the same figure, we can observe that the MSD values of the methane molecules increase considerably in the system when the electric field magnitude is 1.5 V/nm, i.e. qualitatively, the value of the diffusion coefficient increases from $1.7 \times 10^{-7}\,cm^2/s$, under an electric field magnitude of 1.0 V/nm, to $1.5 \times 10^{-6}\,cm^2/s$ when the electric field magnitude is 1.5 V/nm. This value is only one order of magnitude smaller than the higher MSD for methane molecules in a clathrate hydrate system heated from 250 to 400 K, as reported by Yasuoka and Murakoshi [12]. This result suggests that the conformation of the hydrate must suffer considerable structural decomposition when an electric field of these magnitudes is applied leading to a structural phase transition.

Another important aspect to analyse is the influence of the external electric field on the orientation of the water dipole moment vector inside the simulation box. It is convenient to remember that, initially, in the unit cell, the hydrogen protons are randomly allocated, and then, by a short simulation at 10 K and 20 bar, such protons become oriented in such a way that the clathrate is obtained. After this procedure, the clathrate type I was already formed and simulations at 20 bar for different temperatures were performed. The obtained configuration is used as an input in simulations in order to analyse the influence of the external field on the dipole moment. In Figure 6, the dipole moment components as well as the total dipole moment of clathrate are shown. Such dipolar moments correspond to the system under the influence of an external electric field

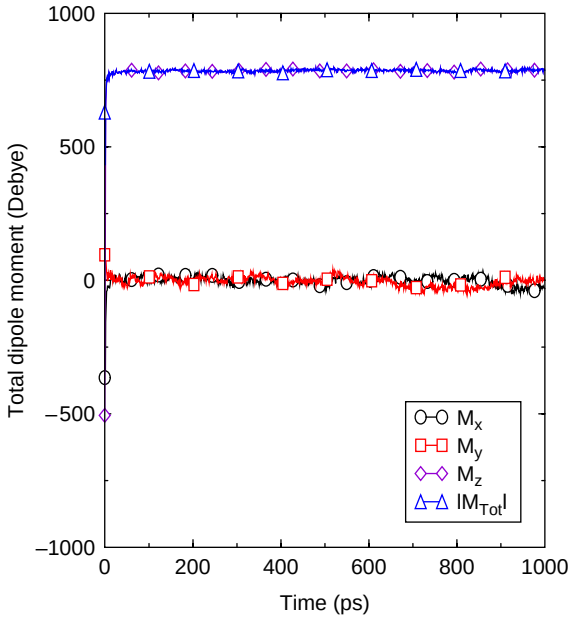

Figure 6. Magnitudes of the dipole moment components on each axis and a total dipole moment vs. time for an external electric field of 3.0 V/nm at a pressure of 20 bar and a temperature of 248 K.

of 3.0 V/nm and applied in the z-direction. The evidence shows that the field intensity is high enough to align the water dipole. In addition to this, it can be observed immediately that the total dipole moment is aligned along the z-axis, and the corresponding x and y components approach zero.

3.2 *Turning off the external electrostatic field*

In Figure 7, a snapshot of the methane clathrate configuration at a temperature of 248 K and a pressure of 20 bar is shown. This spatial arrangement was obtained after the application of a 3.0 V/nm external electrostatic field, which shows the water molecules orientated in the field direction. After applying the external electrostatic field, the final configuration of each run is used to develop a new series of simulations but now with the external electrostatic field turned off, to verify how the system could evolve. The immediate question would be whether the system returns to its original structural state or the disorder in the same system is increased. Figure 8 presents the RDF of CH_4—H_2O molecules. The open diamonds correspond to the curve obtained when the electric field is not present, and this result corresponds to the clathrate in a stable state. The open circles and the continuous line are the results obtained from those configurations where the electric field was applied before and later on it was turned off. Moreover, it can be seen that the system does not recover its stable structure immediately. In Figure 9, the coordination number of each simulation box is shown, but now without an external electrostatic field. All these runs were developed in a stable thermodynamic state for type I clathrate (248 K and 20 bar), according to the experimental evidence. However, the coordination number takes values below 20, and this result indicates that the stable structure of the methane hydrates is not recovered. Concerning this last point, we can mention that the simulation time used here could not be enough to capture the clathrate reorganisation.

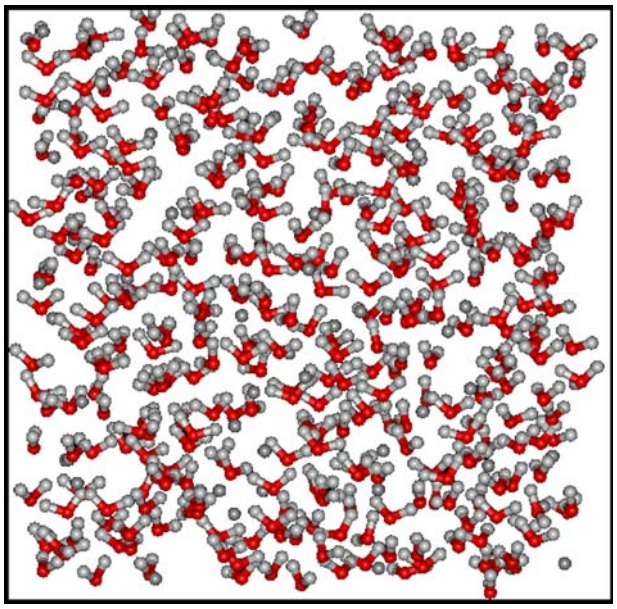

Figure 7. Snapshot of the clathrate dissociated with water molecules orientated in the direction of an applied external electrostatic field of magnitude 3.0 V/nm.

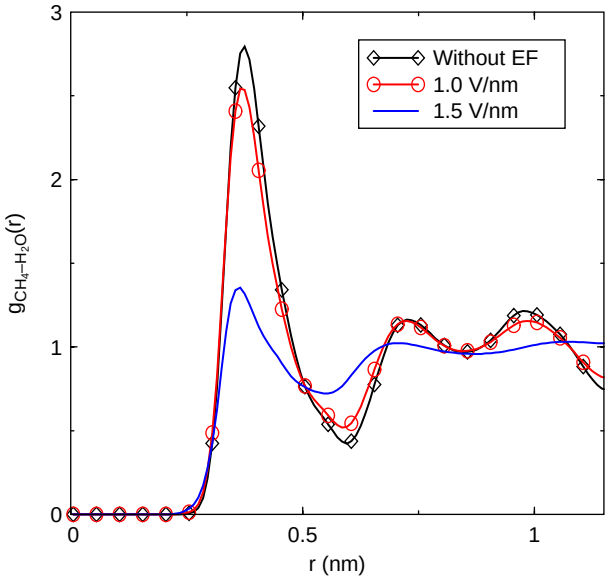

Figure 8. RDF of CH_4—H_2O molecules for a pressure of 20 bar and a temperature of 248 K with the external electrostatic field turned off.

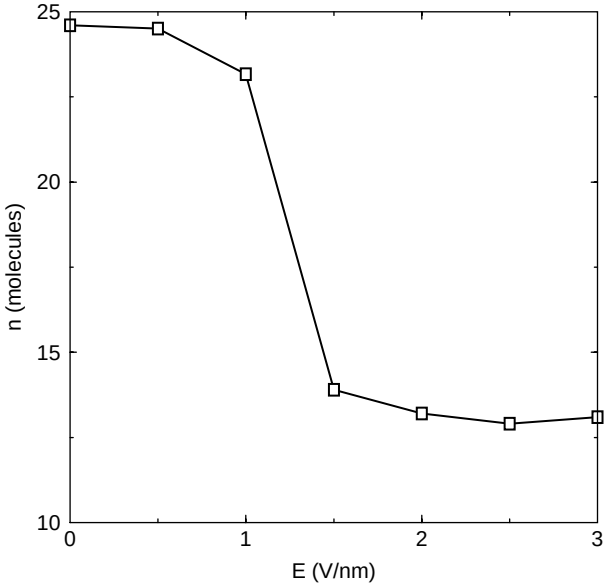

Figure 9. Variation of the coordination number of the water molecules around methane molecules for a pressure of 20 bar and a temperature of 248 K after the external electrostatic field was turned off.

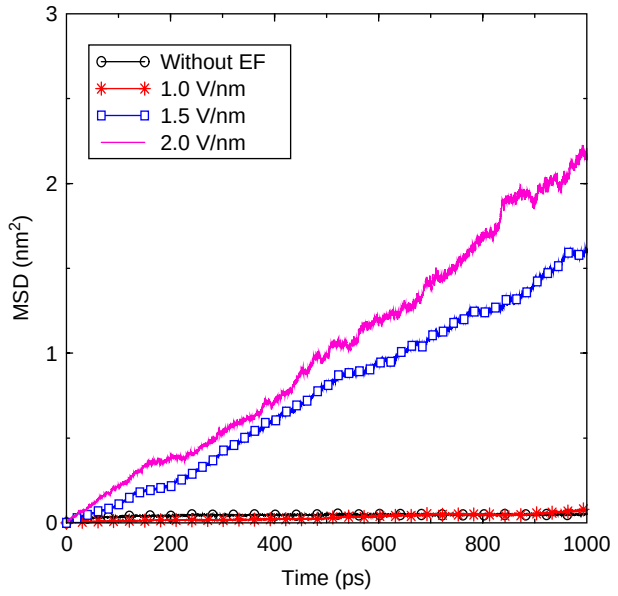

Figure 10. MSD of the methane molecules as a function of time step. The runs performed when the system was under the influence of an external field were continued but now with the external electric field turned off, for a given pressure of 20 bar and a given temperature of 248 K. The open circles are the results for the MSD without the electric field.

Finally, Figure 10 displays the estimated MSD of the methane molecules after the external electrostatic field is turned off. We can observe that the structural transition suffered by the system, under an external electric field larger than 1.5 V/nm, is such that even when the field is turned off, there is no more stable clathrate structure retained; hence, the methane molecules escape from the water cages and they cannot re-enter. As a relevant result, we can mention that the MSD increases considerably, as well as the diffusion coefficient increases, from 1.5×10^{-6} to $6.34\times10^{-6}\,\mathrm{cm^2/s}$, for those cases whose 1.5 V/nm external electrostatic field was applied and then turned off. The above-mentioned results suggest that water molecules of the system become oriented in the direction of the strength field, which induces an important mobility on methane molecules. This tendency on mobility increases when we continue the runs with the external electric field turned off, resulting in the lack of the stable structural arrangement.

4. Conclusions

The structural arrangement of methane hydrates which is under the influence of an external field was analysed by means of the MD. The considered intensity is in the range from 0.5 to 3.0 V/nm, keeping the temperature and pressure constant. The external field applied over clathrates induces the ordering of the water molecules on the field direction and thus the breaking of the hydrogen bond arrangements. This process leads to the dissociation of the methane hydrate conformation produced by structural changes which have the characteristics of phase transitions. On the basis of our obtained results, we can mention that an external static electric field sufficiently intense (up to 1.5 V/nm) causes that the system tends to a state where the CH_4 molecules leave the water cages (dissociated system) and the methane molecules do not return immediately into the cages even when the field is turned off. This situation takes place probably because the computational time is not enough to recover the stable clathrate. In a future work, we would like to analyse the effect of the external static electric field on the clathrate system, incorporating salt into the system. An additional problem to be addressed is to estimate the reaction rates of nucleation in terms of the interactions between the particles in order to incorporate the cooperativity between methane and water [37].

Acknowledgements

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