
Large-Scale Nanosecond Simulations of the Dynamics of the Xe + H₂O System

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Large-scale molecular dynamics simulations of the high-pressure transformations of the xenon/water system were performed involving special purpose molecular dynamics machines. We investigated several systems of different sizes and geometry at the suitable simulational conditions (density, temperature, etc.), which are similar to the experiments conducted on the xenon hydrates. A binary mixture (ice water + Xe) undergoes at high pressure a long evolution and the Xe-guest atoms, enclosed inside the water molecules, were observed and analyzed. Even for the thin slabs, starting with the capture of the guest atoms by the water molecules, the water clusters around the xenon atoms are formed. The results show that such a hydrate-like formation preserves its structural stability over a long period of the simulation time of order of nanosecond. The molecular dynamics simulations were performed on a basis of the MDGRAPE-2 modifications of the DL_POLY general purposes package, with the efficient treatment of the Ewald real and reciprocal-space components of the Coulombic and Van der Waals forces. The MDGRAPE-2 accelerates the calculations of the Coulomb and Van der Waals forces, without applying a spherical cut of a fixed distance.

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1. Introduction

Understanding mechanisms of the high pressure-temperature reactions of gases with water is one of fundamental topics in hydrate phenomena [1–5]. The most challenging question, regarding hydrates, is the formation of the hydrates [3, 4, 6]. The hydrates kinetics, as a basically time-dependent phenomena, is generally characterized through the nucleation, growth, and dissociation processes. It is worth noting that the time-dependent hydrate formation phenomena are

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substantially more challenging than time-dependent phenomena of structure and thermodynamics [4, 7–14].

The initial process of the hydrates formation in the system guest molecule/water is a topic of the intense research and it is a task of great practical interest. The formation of gas hydrate possesses a stochastic nature, the hydrate crystallization process demands a very long timescale to observe. One of the most powerful tools in the theoretical studies on the hydrate phenomena is molecular dynamics (MD) method [2, 4, 10–16]. The aim of our present work is to investigate, through the large-scale nanosecond MD simulations, the initial stage of the gas(xenon)/water interaction process. We will consider the high pressure conditions, closely to the experimental situations, which are conducted on the xenon hydrates.

It is worth noting that MD method has been used widely in the hydrate studies from the different aspects. MD simulations have been performed in [10–12] on the hydrate lattice stability, where the calculation results have been used to estimate the macroscopic and spectroscopic properties. The approaches employed in these studies include the Raman spectra along with the estimation of the electronic and vibrational properties of the guest atoms in a clathrate hydrate, etc. The structural stability aspects and the effects of the guest molecules on the host lattice structure were studied in [13, 14], through the molecular dynamics, and in [15, 16], using the lattice dynamics method. In Ref. [15] the motion of the host and the guest within cages, depending on the guest size ratios (larger than methane within the 5^{12} cavity), was investigated. Some other findings, regarding the application of the MD in hydrates, cover the investigation of the affect of water molecules outside the cavity, the hydrate lattice stretch in correlation with the guest size, the vibrations of guests within the different cavities, the guest–guest interactions, the hydrogen bonding in the hydrate and in the hydrate crystal interface, and others [4, 17–20].

Our goal is to present clustering processes of the water around the guest (xenon) molecules and on the time-dependent behavior of the hydrate-like formation in the gas/water system. In the xenon hydrate experiments (see, for example [5]), structure I xenon clathrate was observed to be stable up to 1.8 GPa. In the case of Xe hydrates, the cavities are filled with $46\text{H}_2\text{O}$ molecules and eight guest molecules. At the room temperatures, growth of crystals from the initial $\text{Xe} + \text{H}_2\text{O}$ mixture was observed by increasing pressure to 0.7–0.8 GPa. In the present MD study large-scale transformations of the xenon and water system were investigated for different sizes and geometry. To compare the system behavior at different pressures, we simulated the xenon/water dynamics at the low and high gas densities. The evolution of the initial configuration of the xenon + water mixture was estimated at the temperatures 240 K and 280 K. The several events of hydrate-like formation are observed at both temperatures. Once the guest xenon atom has been captured by the water molecules, a hydrate-like formation preserves

a structural stability over a timescale of order of nanosecond. In the calculations we used a special purpose MD machine MDGRAPE-2, with the efficient treatment of the Ewald real- and reciprocal-space components of the Coulombic and Van der Waals forces [21].

The paper is organized as follows. First, we present model and the simulation method, then calculation results and finally, we summarize the key points of this paper and discuss the results.

2. Simulation method and systems

2.1. Systems

The MD simulations have been performed on five model systems of xenon and water. In Fig. 1 the snapshots of the five simulated systems (numbered I, II,

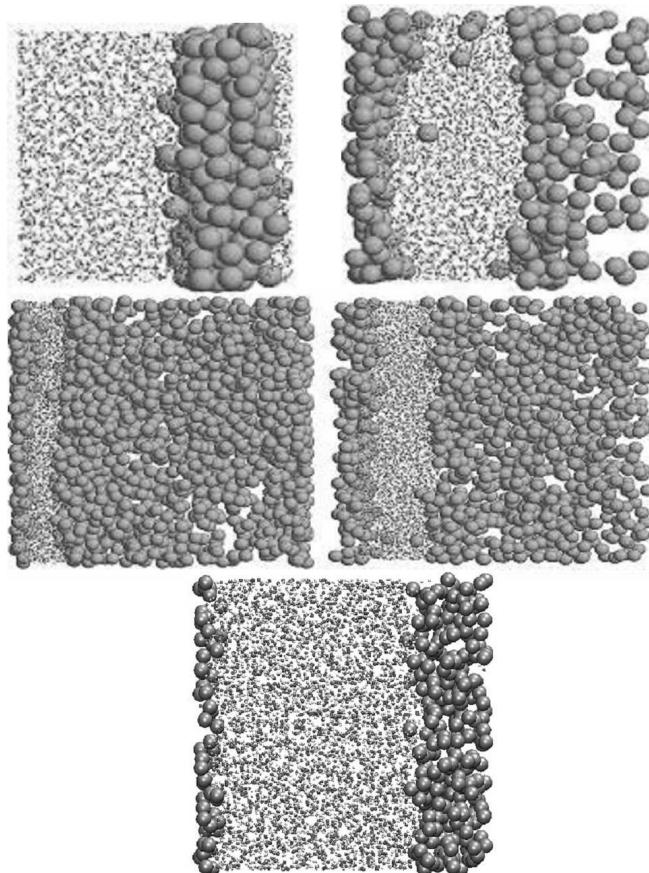


Fig. 1. Five configurations of the water + Xe mixtures are shown. As described in the text, the top figures are systems I (left) $t = 75$ ps and II (right) $t = 315$ ps; the middle figures are systems III (left) $t = 29$ ps and IV (right) $t = 21$ ps and the bottom is system V $t = 10$ ps. The water molecules are shown as dots, the xenon as large gray circles.

III, IV, V) are presented. The first two pictures (systems I and II, top) are the slabs of the Xe + water mixtures, contained in the volumes of $V = L^3 = (42 \text{ \AA})^3$ and $V = L^3 = (82 \text{ \AA})^3$, respectively ($L = L_x = L_y = L_z$). For these two configurations we have the same number of particles: the TIP4P water molecules = 2240, the Xe atoms = 320 (9280 total atomic sites). The xenon for the system I is a high density gas, for the system II — a low density gas. The initial water/gas volume proportions in these configurations are: water = 5/6(V), Xe gas = 1/6(V). For the next two pictures (system III and IV, middle) we have the same volume $V = L^3 = (82 \text{ \AA})^3$, but different numbers of particles: the water molecules = 2560, the Xe atoms = 1920 (12160 total atomic sites, left figure); the water molecules = 4480, the Xe atoms 1280 (19200 total atomic sites, right). The last simulated system (system V) was contained in the volume of $V = L^3 = (43 \text{ \AA})^3$, with 2240 TIP4P water molecules and 320 Xe atoms which gives 9280 total atomic sites.

2.2. Simulation method

We have used the Lenard–Jones potential and TIP4P water model to describe Xe–Xe and Xe–water interactions. The equations of motions were integrated using Verlet algorithm and the temperature was controlled by a Nosé–Hoover thermostat. The trajectories were generated in the (N, V, T) ensemble, with the integration time step of 1 fs, and the periodic boundary conditions were applied in all directions. The Ewald method was used for calculation of the electrostatic forces. In all performed MD simulations, the water + Xe system was gradually equilibrated at a given temperature in a step of 10 K and for the several hundred time steps.

3. Simulation results

In Fig. 2, the results of the MD simulations, performed at 280 K on the system I, are presented. The calculations have been done for about one million time steps. During the system's evolution several Xe atoms are seen to be surrounded by the water molecules. The events of water clustering around the xenon atoms have been monitored in real time. The mobility of the Xe atoms, which are captured in the water phase, are essentially low in comparison with the atoms in the gas phase. Once the Xe was enclosed by the water molecules, a hydrate-like structure has been formed, which preserves a stability over a long period of simulation time (the timescale in Fig. 2 is of an order of nanosecond).

We investigated in detail the above Xe + water clustering formation by the crystal CERIUS2 Visualiser. In Fig. 3 the structure of the Xe + water cluster, surrounded by a hydrogen-bond network, is shown. This structure, as analysis shows, closely resembles a hydrate-like formation (Fig. 3). However, the systems temperature seems too be too high to form a crystal, with a good structural stability. For system I we have performed the same simulation also at the temperature of 240 K. Nevertheless, no events of the water clustering around the xenon atoms have been observed.

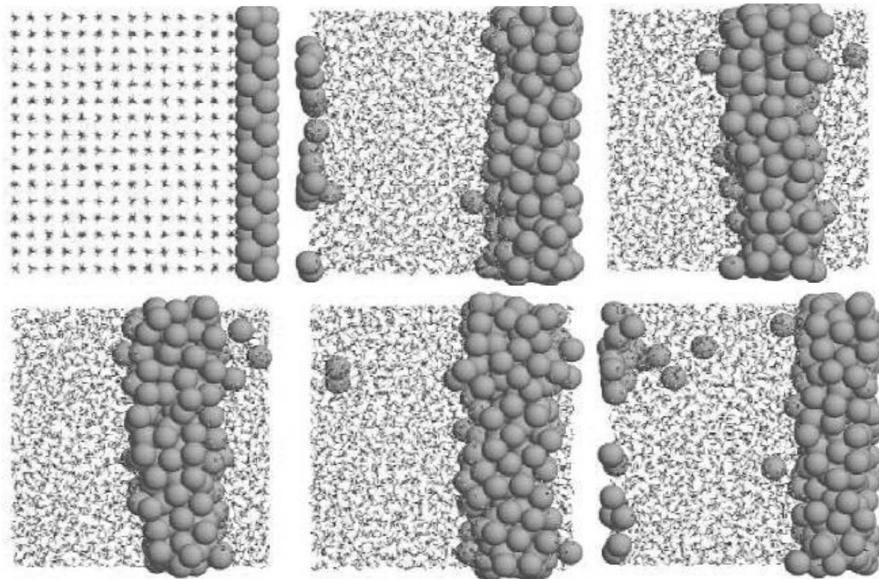


Fig. 2. The six sequential snapshots of the MD simulation are shown for the system I as described in the text. The temperature is 280 K. The water molecules are shown as dots, the xenon as large gray circles. The initial configuration $t = 0$, $t = 1.5$ ns is the final state, the other snapshots correspond to 0.3 ns, 0.6 ns, 0.9 ns, 1.2 ns.

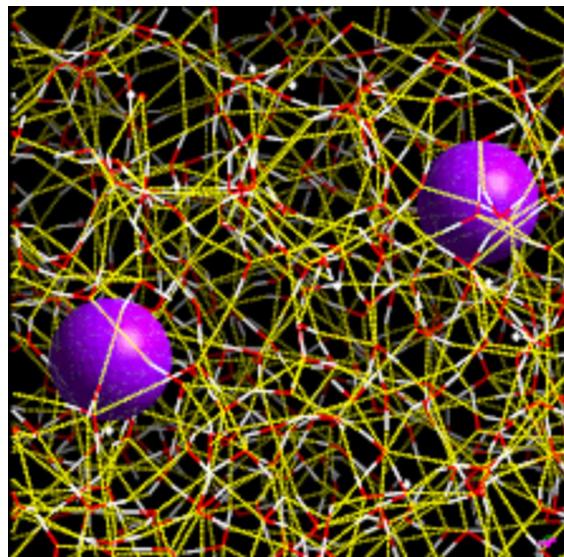


Fig. 3. The Xe + water clustering structure is presented. The Xe atoms (large circles) with the water molecules (red oxygen, white hydrogen), surrounded by hydrogen bonds (yellow dotted line), are shown.

About 1.5 nanosecond calculations showed no results, like those presented in Figs. 2 and 3. Probably, at lower temperatures for this system a much longer simulation is necessary for the hydrate to form.

In Fig. 4 the results of MD simulations are presented for the system II at 240 K. The calculations have been performed for $N_{\text{step}} > 10^6$ time steps. Starting with the well-separated states, the pockets of Xe enclosed by water inside the slab are formed.

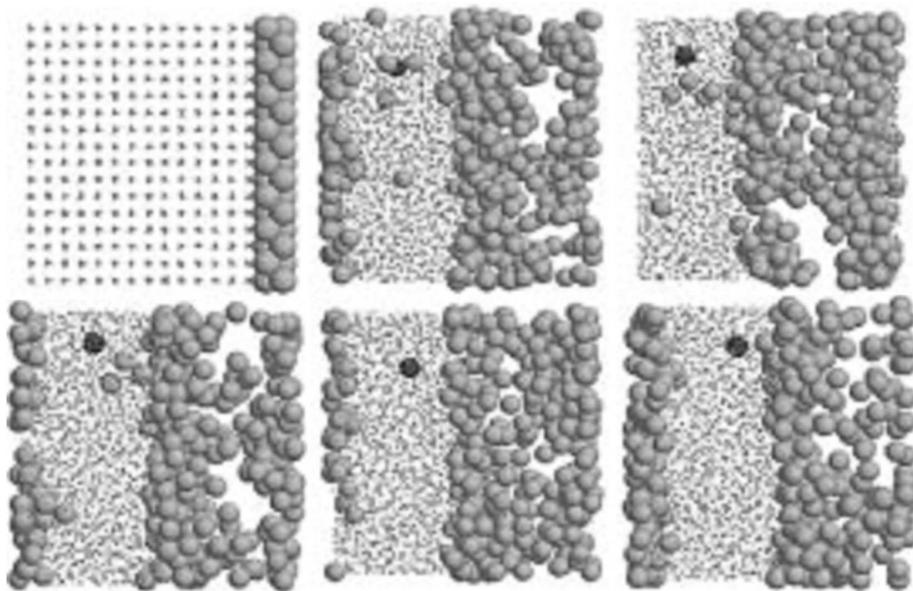


Fig. 4. Six sequential snapshots of the MD simulations are shown for the system II, as described in the text. The temperature is 240 K. The final configuration is for time moment of 1.7 nanosecond. The water molecules are shown as dots, the xenon as large gray circles. The initial configuration $t = 0$, $t = 1.5$ ns is the final state, the other snapshots correspond to 0.3 ns, 0.6 ns, 0.9 ns, 1.2 ns.

The number of the Xe atoms, clustering in the water phase, changes with time. For some Xe atoms from the water–gas interface there is a possibility to return back to the gas phase. However, those Xe atoms, which are surrounded by the water molecules at the center of the slab, are “long-lived” objects. For example, the Xe, which is marked in black in Fig. 4, has remained in the water phase during about 1 million time steps of the system’s dynamics. (The final configuration in Fig. 4 corresponds to a 1.5 nanosecond state.) The Xe atoms, surrounded by the water molecules, possess a very low mobility, in comparison with the atoms in gas phase.

Figure 5 demonstrates the position diagram of the selected Xe (was shown in Fig. 4 in black) inside the water cage. As it is seen from Fig. 5, at the initial stage

of water clustering around the Xe, the Xe still possesses a high mobility, as the variation of its coordinates is large. Nevertheless, with time the Xe coordinates change more and more slowly, so that the Xe atom seems to be confined inside the water cluster. For about 700000 simulation steps, starting from the point 0.5 ns and until 1.2 ns in Fig. 5, the Xe spatial coordinates are close to constant values. In other words, the Xe reaches a “frozen” state inside the cage. With regards to the systems III and IV, the simulations show the similar features of the clustering and cage formations, as for the above two systems, but in a longer timescales. A more detailed analysis of the results, obtained for the models III and IV, will be the subject of our following studies.

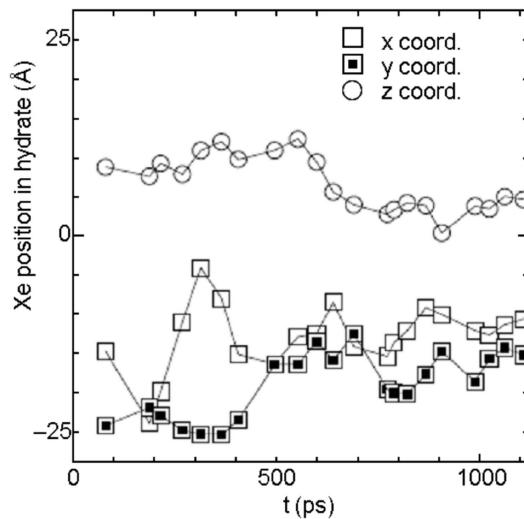


Fig. 5. The Xe position diagram inside the hydrate-like formation of Fig. 4 is presented. For the selected Xe a “frozen” state inside the cage is shown. Starting from the initial stage of the cage formation, the variation of the Xe spatial coordinates will decrease with time. The values of the Xe spatial coordinates, within the 700000 time steps in the interval of [0.5–1.2] ns, remain closely constant.

Simulation for system V has been performed at the pressure of 0.4 GPa at a temperature of 260 K for 260 ps. In comparison to other systems the latter simulation is a rather short time dynamics, nevertheless, the obtained results show the formation of at least one short-lived water cluster. This water + Xe formation has been observed as a stable object between 40 and 60 ps. In general, the system V shows a structure that might be characterized as an initial stage for the stable, long-lived object.

Figure 6 presents the position diagram of the selected Xe atom. The Xe coordinates change slowly starting from the point 40 ps, and at this point we found Xe atom in the water cluster. We can also see the cluster stabilization at

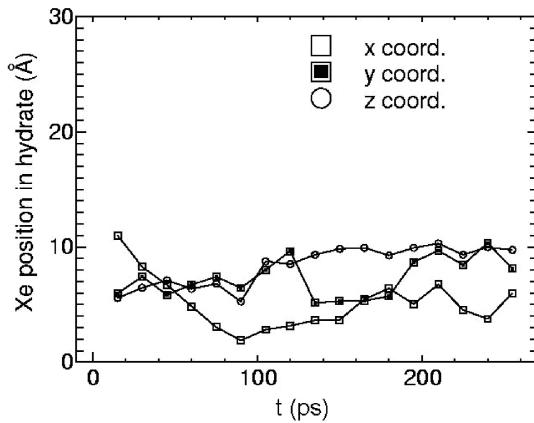


Fig. 6. This diagram presents positions of selected Xe atom in system V.

the point of 120 ps on the diagram but the analysis did not yet reveal a hydrate-like (crystallic behavior) formation at this stage. The event occurs within a very short simulation time and it possesses a quite low stability.

4. Discussion

In conclusion, we have performed large-scale nanosecond molecular dynamics simulations of the high-pressure transformations of the xenon/water system. We investigated several systems at the suitable simulational conditions, similar to the xenon hydrates experiments. The Xe + water system undergoes at high pressure a long evolution and the Xe-guest atoms, enclosed by the water molecules, have been observed and analyzed. The results show that a hydrate-like formation preserves its structural stability over a long period (of order of nanosecond) of the simulation time. We think that it would be interesting to continue researches in similar systems applying even longer simulation times and different configurations. The MD simulations have been performed on a special purpose MDGRAPE-2 machine using the DL.POLY general purposes code. The DL_POLY/MDGRAPE-2 accelerates the calculation of the Coulomb and Van der Waals forces, without applying a spherical cut off at a fixed distance.

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References

- [1] D.W. Davidson, in: *Water: A Comprehensive Treatise*, Ed. F. Pranks, Plenum, New York 1973, p. 115.
- [2] Y.P. Handa, J.S. Tse, D.D. Klug, E. Whalley, *J. Chem. Phys.* **94**, 623 (1991).
- [3] Y.A. Dyadin, E.G. Larionov, T.V. Mikina, L.I. Starostina, *Mendeleev Commun.* **7**, 74 (1997).
- [4] E.D. Sloan, Jr., *Clathrate Hydrates of Natural Gases*, Marcel Dekker, Inc., New York 1998.
- [5] C. Sanloup, H.-K. Mao, R.J. Hemley, *Proc. Natl. Acad. Sci. USA* **99**, 25 (2002).
- [6] J.P. Long, E.D. Sloan, *Mol. Simul.* **11**, 145 (1993).
- [7] J.P. Long, E.D. Sloan, *Int. J. Thermophys.* **17**, 1 (1996).
- [8] L.A. Baez, P.A. Clancy, *Ann. New York Acad. Sci.* **715**, 177 (1994).
- [9] J.S. Parent, M.Sc. Thesis, University of Calgary, 1993.
- [10] J.S. Tse, M.L. Klein, *J. Phys. Chem.* **91**, 5789 (1987).
- [11] J.S. Tse, M.A. White, *J. Phys. Chem.* **92**, 5006 (1988).
- [12] J.S. Tse, *Ann. New York Acad. Sci.* **715**, 187 (1994).
- [13] P.M. Rodger, *J. Phys. Chem.* **94**, 6080 (1990).
- [14] P.M. Rodger, *Mol. Simul.* **5**, 315 (1990).
- [15] K. Koga, H. Tanaka, *J. Chem. Phys.* **104**, 263 (1996).
- [16] K. Koga, H. Tanaka, K. Nakanishi, *Mol. Simul.* **12**, 241 (1994).
- [17] K.A. Sparks, J.W. Tester, *J. Phys. Chem.* **96**, 11022 (1992).
- [18] M.J. Hwang, Ph.D. Thesis, University of Pittsburgh, Pittsburgh (PA) 1989.
- [19] M.J. Hwang, G.D. Holder, S.R. Zele, *Fluid Phase Equil.* **93**, 437 (1993).
- [20] T. Carver, M. Drew, M. Rodger, in: *Proc. 2nd Int Conf. on Natur. Gas Hydrat., Toulouse 1996*, Ed. J.P. Monfort.
- [21] K. Kholmurodov, W. Smith, K. Yasuoka, T. Ebisuzaki, *Comput. Phys. Commun.* **125**, 167 (2000); in: *Proc. 6th World Multiconf. SCI'2002, Orlando (USA) 2002*.