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Molecular Simulation Study of Water (H_2O) Adsorption on Carbon Nanotubes

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Abstract: In this study, the adsorption behavior of single-walled carbon nanotubes (SWCNTs) on water molecules under different pressure conditions was systematically investigated by molecular dynamics simulation, focusing on the effect of pressure change on water molecule adsorption. The simulation results show that the adsorption of water molecules on the surface of carbon nanotubes increases significantly with the increase of pressure, and the distribution and dynamic behavior of water molecules inside the tubes also change significantly. At 1 MPa, the water molecules are mainly adsorbed in a monolayer, and a multilayer adsorption structure is formed with the increase of pressure. In addition, the increase in pressure enhanced the interaction energy between water molecules and carbon nanotubes, and the adsorption stability was improved.

Keywords: Carbon nanotubes, Adsorption, Molecular modeling.

1. Introduction

Carbon nanotubes occupy an important position in nanomaterials science due to their unique structure and excellent physicochemical properties. Their high specific surface area, excellent mechanical properties, and good chemical stability make them show a wide range of applications in the fields of adsorption, catalysis, energy storage, etc[1, 2].

The adsorption behavior of water molecules is a key issue in the application of single-walled carbon nanotubes. Understanding the interaction mechanism between water molecules and carbon nanotubes, especially the effect of external conditions (e.g., pressure) on the adsorption behavior, is crucial to optimize the performance of carbon nanotubes in practical applications[3]. Molecular dynamics simulation, as a powerful computational tool, can reveal the adsorption process and dynamic behavior of water molecules on the surface of carbon nanotubes at the atomic scale [4], and it has been shown that pressure is one of the important external factors affecting the adsorption performance of carbon nanotubes[5]. For example, it was found through experiments and simulations that pressure changes significantly alter the filling behavior and dynamic properties of water molecules within carbon nanotubes[6]. In addition, it was shown that the number of adsorbed layers of water molecules inside carbon nanotubes increased under high pressure conditions and the adsorption energy was significantly increased[7]. However, systematic studies on the adsorption behavior of single-walled carbon nanotubes for water molecules under different pressure conditions are still limited, especially the effect of pressure on the adsorption mechanism when the diameter is constant has not been fully elucidated.

This study focuses on the adsorption behavior of single-walled carbon nanotubes on water molecules under different pressure conditions, keeping the diameter of carbon nanotubes constant, and systematically investigates the effects of pressure changes on the adsorption amount, heat of adsorption, and distribution characteristics of water molecules. The results not only help to understand the interaction between carbon nanotubes and water molecules, but also provide important references for experimental research and practical applications.

2. Model Construction

2.1. Graphene Model Construction

The carbon nanotube model established is a single-walled carbon nanotube, rigid and undoped. The model is of the armchair type (n=m), with a diameter of 4.068 nm and a length of 2.46 nm (Figure 1).

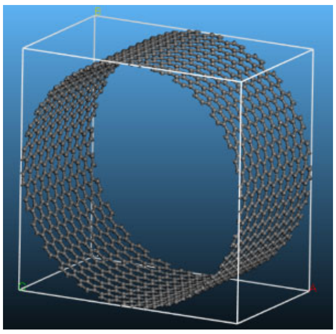


Figure 1. Carbon Nanotube Model

2.2. Water Molecule Model Construction

The water molecule model was manually drawn in the Visualizer window, using the SPC/E water type. The structural parameters are as follows: O-H bond length of 1.00 Å, H-O-H bond angle of 109.47°, hydrogen atom charge of 0.4238 e, and oxygen atom charge of -0.8476 e [8]. The drawn water molecule model was optimized in the Forcite module.

3. Simulation Method

The simulation was conducted in the Sorption module, with force field parameters selected from the Universal force field. The Fix Pressure task was chosen, employing the Metropolis method. Long-range electrostatic interactions and van der Waals interactions were calculated using the Ewald and Atom based methods, respectively. The temperature was set at 293.15 K, with pressures of 1, 3, 5, 7, and 9 MPa. The total simulation steps were 1×10^7 Monte Carlo steps, with the first 5×10^6 steps used for system equilibration and the latter 5×10^6 steps for adsorption calculation.

4. Results

4.1. Adsorption Capacity

The adsorption capacity obtained from the software is in units of molecular/u.c, which is the number of molecules adsorbed per unit cell. According to formula (1), it was converted to the international unit cm³/g.

$$n_{ab} = \frac{x \times 18000}{M} \quad (1)$$

In the formula, n_ab is the absolute adsorption capacity in cm³/g; x is the adsorption capacity obtained from the software in molecular/u.c; *M* is the molar mass of the pore framework in g/mol.

The adsorption capacity of water molecules on carbon nanotubes with a pore diameter of 4.068 nm at different pressures is shown in Figure 2.

At a pore diameter of 4 nm, the adsorption capacity increases with increasing pressure. As the pressure increases, the adsorption capacity of water molecules gradually increases, but there is a noticeable inflection point around 3 MPa; the growth of adsorption capacity slows down thereafter, indicating that the influence of pressure on the adsorption of water molecules in carbon nanotubes diminishes after 3 MPa.

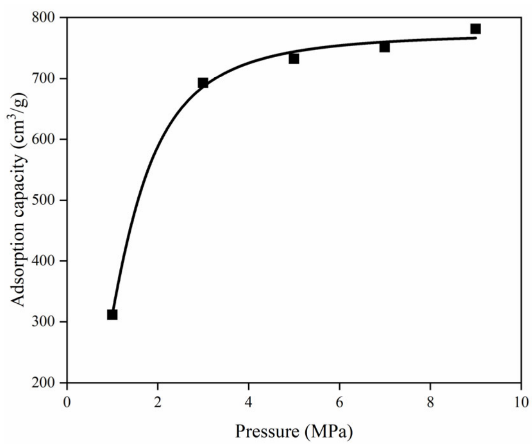


Figure 2. Variation of Adsorption Capacity with Pressure

4.2. Adsorption Heat

Adsorption heat is the heat generated during the adsorption process, and its magnitude indicates the strength of adsorption. The greater the adsorption heat, the stronger the adsorption capacity.

The adsorption heat was calculated according to the Clausius-Clapeyron equation [9]:

$$Q_i = -R\left[\frac{\partial(lnP)}{\partial(1/T)}\right] \quad (2)$$

In the formula, Q_i is the adsorption heat in kJ/mol; P is the pressure in MPa; T is the temperature in K; R is the thermodynamic constant, 8.314 J/(mol·K).

The adsorption heat of water molecules on carbon nanotubes with a pore diameter of 4.068 nm at different pressures is shown in Figure 3.

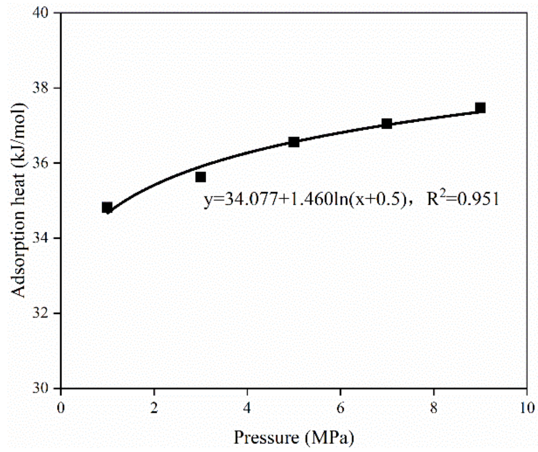


Figure 3. Variation of Adsorption Heat with Pressure

From Figure 3, it can be seen that at 298.15 K, the adsorption heat of water molecules on carbon nanotubes increases logarithmically with increasing pressure, ranging from 34.819 kJ/mol to 37.476 kJ/mol. It is inferred that under these conditions, the adsorption of water molecules on carbon nanotubes is physical adsorption[10], and the change in adsorption heat is not significant after the pressure increases to 3 MPa.

4.3. Adsorption Energy

Adsorption energy is the adsorption capacity of the adsorbent for the adsorbate, representing the energy released from the beginning to the end of adsorption. The adsorption energy between carbon nanotubes and water molecules can be expressed as:

$$E = E_A + E_B - E_{Total} \quad (3)$$

In the formula, E is the adsorption energy between carbon nanotubes and water molecules in kJ/mol; E_A is the energy between carbon nanotubes in kJ/mol; E_B is the energy of the adsorbed H_2O molecules in kJ/mol; E_{Total} is the total energy of carbon nanotubes adsorbing H_2O molecules in kJ/mol.

The adsorption energy of water molecules on carbon nanotubes with a pore diameter of 4.068 nm at different pressures is shown in Figure 4.

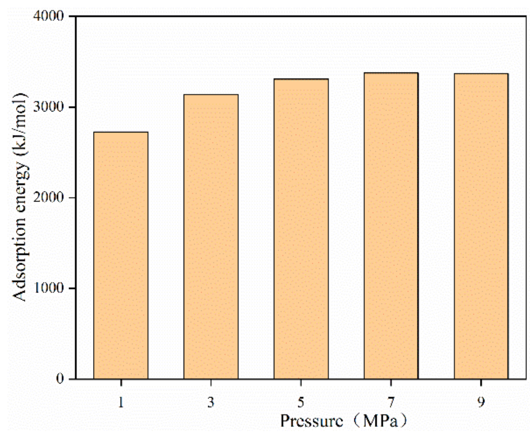
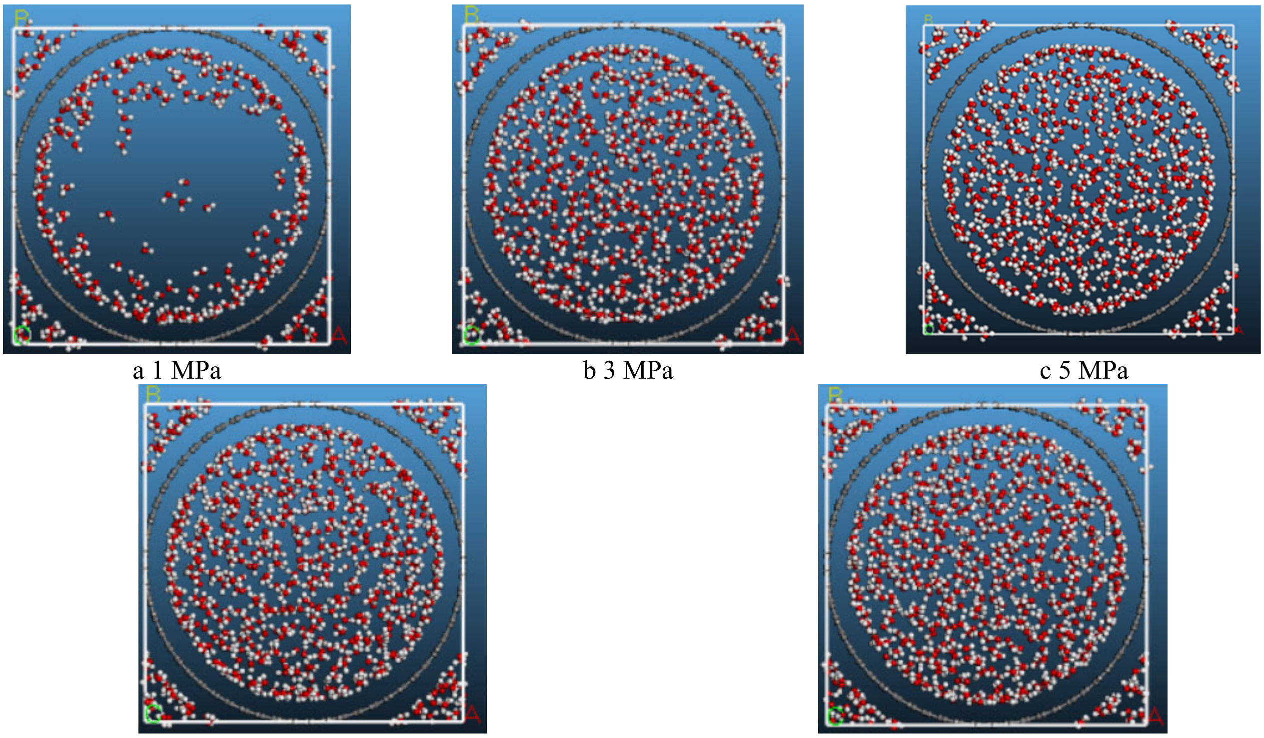


Figure 4. Variation of Adsorption Energy with Pressure

As the pressure increases, the adsorption energy between water molecules and carbon nanotubes increases logarithmically, and the change in adsorption energy is not significant after the pressure reaches 5 MPa, stabilizing around 3370 kJ/mol. At a pressure of 7 MPa, the adsorption energy between water molecules and carbon nanotubes reaches a maximum of 3375.07 kJ/mol, indicating that the system is more stable after adsorption at a pressure of 7 MPa for water molecules in a pore diameter of 4.068 nm.

4.4. Distribution of Water Molecules

From Figure 5, it can be seen that at a carbon nanotube pore diameter of 4.068 nm and a pressure of 1 MPa, water molecules form only one adsorption layer inside the carbon nanotube, with other water molecules existing in a free state. As the pressure further increases, more water molecules enter the carbon nanotube, and the adsorbed water molecules become new adsorption sites, forming a new adsorption layer. At this point, water molecules form two adsorption layers inside the carbon nanotube, coexisting in both free and adsorbed states. After the pressure increases to 3 MPa, the number of adsorption layers of water molecules in the carbon nanotube remains at two, without forming new adsorption layers. This indicates that at a carbon nanotube pore diameter of 4.068 nm and a pressure of 3 MPa, the adsorption of water molecules in the carbon nanotube is close to saturation, and the influence of pressure on the adsorption of water molecules is minimal.



a 1 MPa b 3 MPa c 5 MPa d 7 MPa e 9 MPa

Figure 5. Adsorption of Water Molecules in Carbon Nanotubes at Different Pressures

5. Results

(1) With the increase of pressure, the adsorption of water molecules in carbon nanotubes first rises rapidly and then tends to level off.

(2) Elevated pressure led to enhanced interaction between water molecules and carbon nanotubes, and both heat of adsorption and adsorption energy increased, suggesting that the interaction between water molecules and carbon nanotube walls became more pronounced with increasing pressure, which improved the adsorption stability.

(3) At 1 MPa, the distribution of water molecules inside the carbon nanotubes was relatively sparse, mainly concentrated near the tube wall; and with the increase of pressure to 3 MPa, the water molecules were more uniformly distributed inside the tubes and formed a multilayer adsorption structure.

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