Molecular simulation study on the radon adsorption behavior in carbon nanotube bundles

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Abstract. As we know radon is harmful to people because of its radioactivity. Focusing on the technical requirements of radon mitigation by adsorption, the radon adsorption behavior of carbon nanotube bundles was studied under different diameter tube bundles and different tube spacing using the grand canonical ensemble Monte Carlo (GCMC) simulation method. The results show that the (10:10) type nanotubes have the strongest ability to adsorb radon with a tube spacing of 1 nm, followed by (7:7) type nanotubes with a tube spacing of 1 nm. The bundle of carbon nanotubes of the (8:8) type has the worst adsorption capacity. Moreover, the nanotube bundles of each type of tube have an increased ability to adsorb radon as the tube spacing increases.

1. Introduction

Radon and its progeny are the main sources of human radiation exposure from natural radiation. Under normal circumstances, humans receive an annual natural radiation dose of about 2.4mSv, of which 50% of the contribution comes from the exposure of radon and its progeny [1]. Research on indoor radon concentration control methods has already begun in the 1960s. From the point of view of radon mitigation, there are two main types, one is to prevent radon from entering the room, and the other is to remove the radon in the room. There are more studies on the first type of methods than the second type, but these methods have the disadvantages of higher cost and inconvenient operation. For the study of the second method, the effect of ventilation radon reduction measures is affirmed, but it is often not well implemented in practice (such as weather, building structure constraints, etc.). There have been some research reports on the use of ordinary air purifiers to reduce radon[2-3]. Another way to remove radon in room is adsorption radon by porous material which needs to well understand the radon adsorption behaviour in different adsorbent. Although there are several studies on radon adsorption in several material such as zeolite[4-5], it is interesting thing to study radon adsorption capability in carbon nanotubes for finding new radon adsorbent.

Instead of taking experimental measurement in radon room to investigate radon adsorption in carbon nanotubes, we use the simulation method to study radon adsorption behavior. In recent years, the use of molecular simulation methods, such as grand canonical ensemble Monte Carlo (GCMC) and molecular dynamics simulation, to study the adsorption law of gas or liquid on porous materials has been paid more and more attention[6-8]. Its advantage is that it is not limited by adsorption materials and experimental conditions. The adsorption mechanism, the structure and performance of the adsorbent, and the adsorption operating conditions were investigated in detail at three levels: micro-meso-macro. This article will use this research method to make a more in-depth discussion on the
adsorption behavior of radon in carbon nanotubes. It can systematically and efficiently study the adsorption of radon, and provide theoretical guidance for the development and utilization of adsorbed radon technology.

2. Simulation method of grand cononical ensemble Monte Carlo(GCMC)
GCMC simulation method is usually used to simulate fluid adsorption. This method is based on the principle of statistical thermodynamics. Under the condition of fixed chemical potential, temperature and volume, the number of fluid molecules in the simulation box is obtained by establishing a statistically significant configuration and performing ensemble averaging [9].

2.1. Monte Carlo simulation principle of grand cononical ensemble
Grand cononical ensemble, its partition function can be expressed as:

\[ Q(\mu, V, T) = \frac{1}{\lambda^3 N!} \int \int \ldots \int \exp(-\phi_i/kT) dr_i \ldots dr_N \]

Where \( N \) is the number of molecules in the ensemble system; \( r_i \) is the vector coordinate of the \( i \) molecule; \( \lambda \) is the de Broglie wavelength. Therefore, the average ensemble \( \langle \rangle \) of thermodynamic quantities \( X \) can be expressed as

\[ \langle X \rangle = \frac{1}{Q(\mu, V, T)} \sum_{n=0}^{\infty} \exp(N\mu/kT) \int \int \ldots \int \exp(-\phi_i/kT) dr_i \ldots dr_N \]

Dimensionless \( dr_i, d\tau_i = \frac{dr}{V} \) then,

\[ \langle X \rangle = \frac{1}{Q(\mu, V, T)} \sum_{n=0}^{\infty} \exp(N\mu/kT) \int \int \ldots \int X \exp(-\phi_i/kT) d\tau_i \ldots d\tau_N \]

Equations (1) to (3) are the basic equations for simulation.

In the specific implementation of the simulation, each step of the loop contains the following three attempts: insert a molecule into the simulation box, delete a molecule from the simulation box, and move the molecule from one position to another position in the simulation box. In the simulation, the molecular algorithm of equal weight selection is used, so that the possibility of such attempts as insertion, deletion and movement are the same). After a certain attempt, the acceptance probability is as follows:

When inserting a molecule, its acceptance probability \( p_{ins} \) is

\[ p_{ins} = \min\left(1, \frac{V}{\lambda^3 (N+1)} \exp[\frac{\mu - \Delta\phi}{kT}] \right) \]

When deleting a molecule, its acceptance probability \( p_{del} \) is:

\[ p_{del} = \min\left(1, \frac{\lambda^3 N}{V} \exp[-\frac{\mu + \Delta\phi}{kT}] \right) \]

When moving a molecule, its acceptance probability \( p_{mov} \) is:

\[ p_{mov} = \min\left(1, \exp[-\frac{\Delta\phi}{kT}] \right) \]

For non-spherical molecules, there are movement methods such as rotation.

2.2. Calculation of chemical potential
In the GCMC simulation, the chemical potential is fixed. However, under actual physical conditions, pressure is a relatively intuitive physical quantity. According to thermodynamics, there is a one-to-one
correspondence between chemical potential and pressure. This correspondence can be obtained by means of simulation [10], or by the equation of state of the fluid [11]. In this paper, the Peng-Robinson equation of state is used to calculate the relationship between chemical potential and pressure. In the simulation, the pressure is input as a parameter, and the pressure is converted into a chemical potential according to the corresponding relationship program, and then the simulation calculation is implemented.

2.3. Potential energy calculation

In molecular simulation, the choice of force field is very important. It can be said that at present, the molecular simulation method framework is relatively mature. In order to improve the accuracy of simulation, people are now investing a lot of experience in the analysis and research of the force field. As far as Monte Carlo molecular simulation is concerned, every step needs to calculate the potential energy of the system, which is also the main place where the computing resources are consumed. Generally, the potential energy of the molecular system is decomposed into the sum of the following four items:

$$E = \sum_A E^\text{stretch}_A + \sum_A E^\text{bend}_A + \sum_A E^\text{torsion}_A + \sum_A \sum_B E^\text{non-bonded}_{AB}$$ (7)

Among them, the first, second, and third items correspond to the stretching potentials, bending potentials, and torsion potentials, all of which are bonding potentials. The four terms are non-bonding potentials.

The stretching and bending potentials correspond to the stretching and bending vibrations of molecules, respectively. In most cases, they can be regarded as harmonic oscillators, which are described by Hook's law.

$$E^\text{stretch}(r) = \frac{1}{2} k^\text{stretch}(r - r^\text{eq})^2$$
$$E^\text{bend}(\alpha) = \frac{1}{2} k^\text{bend}(\alpha - \alpha^\text{eq})^2$$ (8)

Among them, $r$ and $\alpha$ refer to the bond length and bond angle respectively; $r^\text{eq}$ and $k^\text{bend}$ refer to the bond length and bond angle in the equilibrium configuration, which can be obtained by experimental methods or quantum chemical calculations; $k^{\text{stretch}}$ and $k^{\text{bend}}$ are the force constants and the bending force constant respectively.

The torsional potential is roughly divided into three categories, the normal dihedral angular potential; the reversal potential used to force the conjugate plane; the coupling term between different internal coordinates is considered. The torsional potential is usually written as a trigonometric cosine function, such as:

$$E^\text{torsion}_A = \frac{N}{2} \sum_{n=0} V \left[ 1 + \cos(n\omega - \gamma) \right]$$ (9)

In the formula, $\omega$ is the twist angle.

Non-bonded interactions between atoms are generally divided into two categories: coulombic interaction and van der Waals interaction potential (VDW).

$$E^\text{non-bonded}(r) = E^\text{VDW}(r) + E^\text{coulombic}(r)$$ (10)

The van der Waals interaction potential $E^\text{VDW}(r)$ is used to describe the long-range interaction potential, usually written as the sum of attractive potential and repulsive potential, and described by Lennard-Jones (12-6) potential:

$$E^\text{VDW}(r) = \epsilon \left[ \left( \frac{r^\text{eq}}{r} \right)^{12} - 2 \left( \frac{r^\text{eq}}{r} \right)^6 \right]$$ (11)
Among them, \( r \) is the distance between non-bonded atoms, and \( \varepsilon \) and \( \varepsilon_{eq} \) represent the potential depth and equilibrium distance parameters respectively.

The coulombic interaction potential \( E_{\text{coulombic}}(r) \) is expressed in Coulomb:

\[
E_{\text{coulombic}}(r) = \frac{q_1 q_2}{r}
\]  

(12)

Where \( r \) is the distance between non-bonded atoms, and \( q \) refers to the partial charges of the particles.

3. Calculation method

3.1. Carbon nanotube bundle modeling
Carbon nanotubes (Carbon nanotubes, CNTs) is a carbon structure discovered in 1991. It is a cage-like "fiber" made of one or several layers of carbon atoms in graphite. The inside is empty, and the outside diameter is only a few nanometers to tens of nanometers. The ideal carbon nanotube is a seamless, hollow tube made of graphene sheets formed of carbon atoms. Such a material is very light but strong. Its density is 1/6 of steel, but its strength is 100 times that of steel. According to different graphene winding methods, carbon nanotubes can be divided into three types: armchair type, zigzag type and spiral type. The chiral vector of carbon nanotubes is defined as \( \mathbf{r} = n \mathbf{a} + m \mathbf{b} \), where \( n, m \) is an integer and \( \mathbf{a}, \mathbf{b} \) is two-dimensional unit vector of hexagonal lattice. Different types of carbon nanotubes can be described by a pair of parameters, and their diameter can be expressed as (see Figures 1-2):

\[
d = 0.783\sqrt{n^2 + nm + m^2}.
\]

Figure 1. Schematic diagram of carbon nanotube formation.

The carbon nanotube bundle is formed by arranging a certain number of carbon nanotubes in sequence. The carbon nanotube model established in this paper is composed of 7 carbon nanotubes. Six of them are located at the six corners of the regular hexagon, and one is located at the center of the hexagon.

The carbon nanotube bundle structure modeling program used in this paper is based on the wrapping program developed by Maruyama [12], which is modified and perfected. Figure 3 is a schematic diagram of the nanotube bundles of simulated carbon nanotubes with a tube spacing of 0.4 nm.

3.2. Calculation procedure
In order to ensure the credibility of the results, it is best to use a proven and reliable simulation program. To this end, we adopted the simulation program MUSIC (Multipurpose Simulation Code) [13] developed by Professor Snurr's research group of Northwestern University. The MUSIC program is a multifunctional molecular simulation program currently under development, with modules such as GCMC, MD and hybrid simulation. Based on this program, a series of high-level papers have been published [14]. We modified the code based on its 4.0 version to make it suitable for the structural model we built. The main modification is to couple the MUSIC adsorption simulation module with the
carbon nanotube structure input module, so that it can perform adsorption simulation calculations on the all-atom structure model we established.

4. Calculation results and discussion
In the simulation, periodic boundary conditions are used in all three directions. The size of the simulation box is determined by the method shown in Figure 4 [15]:

\[ L_x = 3(D + S) \]
\[ L_y = 2\left(\frac{3D}{2} + S\sin\left(\frac{\pi}{3}\right)\right) + S \] (13)

Figure 3. Carbon nanotube bundle structure.
The length of the box in the x and y directions is:

In the simulation calculation, the bundles of single-walled carbon nanotubes with (7:7), (8:8), and (10:10) diameters were calculated respectively, and the corresponding tube diameters were 0.95, 1.08, and 1.36 nm. The spacing between the single-walled carbon nanotubes in the nanotube bundle is taken to be 0.4, 0.7, and 1.0 nm, respectively.

4.1. Effect of tube diameter
Figures 5-7 are adsorption isotherms of nanotubes with different tube diameters when the tube spacing is the same under two temperature conditions of 273K and 298K. It can be seen from the figure that the corresponding absolute adsorption amount of the larger tube diameter is larger, but the value of the adsorption amount varies with the pressure, for example, at a lower pressure at 273K, (8:8) the adsorption capacity of the tube bundle is lower than that of the (7:7) tube bundle, but when the pressure rises to a certain value, its adsorption capacity will exceed that of the (7:7) tube bundle. When the temperature is low, the adsorption capacity is close to saturation when the pressure is low, and the adsorption isotherm changes gradually after the pressure further increases.

For convenience, the method of nanotube diameter and tube spacing is used for the structure of nanotube bundles. For example, (774) indicates that the nanotubes are (7:7) type nanotubes and the tube spacing is 0.4 nm.

4.2. Effect of tube spacing
In addition to the tube diameter, the tube spacing is also an important factor that affects the nanotube bundle radon adsorption capacity. Figures 8-10 show the calculation results of the nanotube bundle radon adsorption capacity when the tube spacing is different. From the calculation results, although the nanotube bundles formed by several nanotubes with different structures have some gaps in the amount of adsorption, the tendency of the adsorption amount to change with the tube spacing is basically the same: when the pressure is low, the tube spacing is mediate, the nanotube bundles have the strongest radon adsorption capacity, followed by the smallest tube spacing, and the largest tube spacing adsorption capacity. With the increase of pressure, the adsorption capacity of the large tube spacing continues to increase, which in turn exceeds the minimum tube spacing and the center of the tube spacing for the same pressure and structure, the radon adsorption capability is decreasing with the temperature increasing.
Figure 5. Calculation results of nanotube bundles with different diameters with tube spacing 0.4 nm.

Figure 6. Calculation results of nanotube bundles with different diameters with tube spacing 0.7 nm.

Figure 7. Calculation results of nanotube bundles with different diameters with tube spacing 1 nm.

Figure 8. Calculation results of different tube spacings of (7:7) type nanotubes.
4.3. Comparison of adsorption capacity

In order to compare the adsorption capacity of nano-carbon under different structures, we introduce the concept of excess adsorption to compare the adsorption capacity of radon under various structural models. The absolute adsorption amount can be converted into the excess adsorption amount by the formula (14)\cite{15}.

$$n_{\text{excess}} = n_{\text{absolute}} - V_p \rho_{\text{bulk}}$$

In the formula (14), $n_{\text{excess}}$ is the excess adsorption amount, $n_{\text{absolute}}$ is the absolute adsorption amount per unit mass of adsorbent, $V_p$ is the total pore volume, and $\rho_{\text{bulk}}$ is the macroscopic density of the adsorbate in the corresponding state, which can be calculated by the relevant state equation.

Using the above method, the adsorption capacity of carbon nanotube bundles with different tube diameters and tube spacings was compared. Here, the adsorption data at a temperature of 298K and a pressure of 100kPa will be analyzed as an example. The calculation results are shown in Figure 11.

**Figure 9.** Calculation results of different tube spacings of (8:8) type nanotubes.

**Figure 10.** Calculation results of different tube spacings of (10:10) type nanotubes.

**Figure 11.** Comparison of adsorption capacity of different structural models.
It can be seen from the figure that in terms of the adsorption capacity of the carbon nanotube bundle, the difference in the combination of the tube diameter and the tube spacing, the ability to adsorb radon is different. In terms of the nine combinations studied in this paper, (10:10) nanotubes, the nanotube bundle with a tube spacing of 1 nm has the strongest ability to adsorb radon, followed by (7:7) nanotubes with a tube spacing of 1 nm. The tube bundle composed of (8:8) carbon nanotubes has the worst adsorption capacity. Moreover, the ability of nanotube bundles composed of each tube type to adsorb radon increases as the tube spacing increases.

5. Conclusion
Radon mitigation by means of adsorption is very useful in specific occasions, but the selection of adsorption materials and determination of the optimal adsorption conditions are very important. In this paper, we studied the adsorption behavior of radon on carbon nanotube bundles by means of molecular simulation, investigated the influence of nanotube diameter and tube spacing on adsorption, and obtained a regular understanding. The corresponding absolute adsorption amount of the larger tube diameter is larger, but the value of the adsorption amount varies with the pressure. When the pressure is low, the tube spacing is medium, the nanotube bundles have the strongest radon adsorption capacity, followed by the smallest tube spacing, and the largest tube spacing adsorption capacity. With the increase of pressure, the adsorption capacity of the large tube spacing continues to increase, which in turn exceeds the minimum tube spacing and the medium of the tube spacing. For the same pressure and structure, the radon adsorption capability is decreasing with the temperature increasing. It is important to choose the best carbon nanotubes structure (such as tube diameter, tube spacing) for radon mitigation by adsorption in certain temperature and pressure.

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