Molecular simulation on adsorption of helium by activated carbon in 4-10 K

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Abstract. In the liquid helium temperature region, the specific heat of helium increases rapidly, so adsorption behavior of helium on activated carbon is expected to be used in the regenerator of 4-K class cryocoolers to improve the performance of the refrigerator. In this paper, we use Grand Canonical Monte Carlo method to simulate the adsorption of helium on the amorphous carbon in 4-10 K. And the structural parameters of amorphous carbons and the effect of temperature, pressure, graphite slice’s size and density of amorphous carbon on the adsorption amount were analyzed. The results show that the amorphous carbon constructed from the larger size graphite slice has a smaller specific surface area and a larger pore volume. And as the temperature decreases and the pressure increases, the amount of adsorbed helium increases. In addition, we have found that mixed-filled amorphous carbon can obtain higher specific surface area and pore volume, and has better comprehensive properties.

1. Introduction
In recent years, the 4K-class regenerative cryocoolers have been successfully used in many fields owing their mechanical simplicity and high reliability, such as low temperature physics, cryo-electronics, superconducting magnets and space missions’ detectors, etc [1-2]. However, in the liquid helium temperature, the specific heat of the regenerator material is much smaller than that of the helium gas, which increases the loss of the regenerator. Considering that activated carbon can adsorb a large amount of gas molecules at low temperature, using activated carbon with adsorbed helium as regenerator material to reduce the loss is proposed by some scholars [3-4]. Further analysis requires adsorption characteristics date of helium on activated carbon. And due to the complexity of low temperature experimental systems, molecular simulation is a better way to choose. This method can easily construct different kinds of activated carbons, and analyse the influence of structure, temperature and pressure on...
the adsorption amount and isosteric heat from the molecular level. In this paper, amorphous carbon structures were modelled, and the grand canonical Monte Carlo (GCMC) method was used to simulate adsorption of helium on these amorphous carbons in 4-10 K to provide reference for the further analysis of activated carbon used in regenerators.

2. Simulation method and result

2.1. Activated carbon model

Activated carbon has characteristics of various type and wide sources. It’s complicated internal structure and irregular pore size distribution make modeling of activated carbon difficult. Many scholars have done a lot of research in this area. Commonly used models include the slit-pore model, carbon nanotube and amorphous carbon structures [5-8]. The former two models are relatively simple in structure, mainly used to analyze the influence of pore structure on adsorption, however, these models have a great limitation in the study of the internal structure and chemical complexity. Since activated carbon is an amorphous-based material mainly composed of graphite-like crystallites and hydrocarbon, it is disordered and is generally considered to be amorphous carbon. The third model is closer to the actual activated carbon. In our work, three different size of graphite slices were used to construct amorphous carbon structures and analyzed structural parameters. These three types of graphite slices (7 rings, 19 rings and 37 rings) are showed in figure 1 and they contain 24, 54 and 96 carbon atoms, respectively.

![Graphite slices](image)

**Figure 1.** Graphite slices.

Different density and filling patterns amorphous carbons were built, partial models (density=0.5 g/cm3) are shown in the figure 2. Then the Atom Volume & Surface tool was used to obtain the specific surface area and pore volume of amorphous carbon. The figure 3 describes the result, the blue part represents the free volume, the red part is the volume occupied by solid carbon.
Figure 2. Amorphous carbon structures.

Figure 3. Free volume distribution of amorphous carbon.

The figure 4 shows the structural parameters of these amorphous carbon. It can be seen that as the density increases, the specific surface area and pore volume decrease. When the density is constant, the amorphous carbon constructed by the 7 rings graphite slice has the largest specific surface area, and the amorphous structure of the 37 rings graphite slice has the smallest value. On the contrary, the pore volume decreases as the size of the graphite slice decreases. The reason for these results may be that the pore size of amorphous carbon structure composed of a small size graphite slice is smaller.

Figure 4. Structural parameters of amorphous carbon.
2.2. Simulation method
The GCMC is a numerical simulation method based on probability statistics. In the grand canonical system (the volume, temperature and chemical potential are specified), a large number of movement, insertion and deletion operations of the particles in the system are taken to balance the system, and then properties are obtained. Hence, the GCMC simulation is a powerful method for gas-solid physical adsorption process [9-10]. We use Material Studio 7.0’s sorption model to simulate the adsorption isotherms and isosteric heats at 4 K, 6 K and 10 K.

2.3. Result
The figure 5 shows the adsorption sites of helium adsorbed by different amorphous carbon. ((a) is 7 rings, 6 K and 500 kPa; (b) is 7 rings, 6 K and 2000 kPa; (c) is 19 rings, 6 K and 2000 kPa).

![Figure 5. Adsorption sites of helium on amorphous carbon.](image)

The adsorption amount of helium on amorphous carbon (filled with 7 rings graphite slice) shown in the figure 6 and figure 7. It is obvious that when the size of graphite slice is unchanged, as the temperature and density decreases, the adsorption amount decreases, and as the pressure increases, the adsorption amount increases and tends to a maximum value.

![Figure 6. Adsorption amount of helium on amorphous carbon at 4 K](image)

![Figure 7. Adsorption amount of helium on amorphous carbon at 6 and 10 K.](image)
The figure 8 shows adsorption amount of helium on amorphous carbons constructed by 7 rings and 19 rings graphite slices at 6 K. It can be seen that the same density amorphous carbon structures filled with 7 rings or 19 rings graphite slice have almost the same adsorption amount of helium in the same pressure and temperature. For this phenomenon, we should combine the structural features of the previous part of the paper for analysis. Obviously, the adsorption amount of porous materials has a great relationship with its specific surface area and pore volume. As can be seen from the figure 4, when the density is the same, the amorphous carbon constructed by the 7 rings graphite slice has the larger specific surface area and lower pore volume than that filled with 19 rings graphite slice. These factors counteract each other and cause almost the same amount of adsorption.

![Figure 8](image_url)

**Figure 8.** Adsorption amount of helium on different filled pattern amorphous carbon.

The figure 9 shows the isosteric heat of different structures amorphous carbons at 6 K. These data indicate the isosteric heat increases as the adsorption amount, density and graphite slice’s size increases.

![Figure 9](image_url)

**Figure 9.** Isosteric heat of helium on different amorphous carbons.

3. **Effect of mixed filling method on amorphous carbon**

In addition, we have also studied the mixed filling of amorphous carbon. We use different sizes of graphite slices to build amorphous carbon according to a certain amount of proportion and compared it
with the amorphous carbon used in the previous simulation. The figure 10 shows the structural parameters of these two kinds of amorphous carbons (a₁: a₂: a₃ means the ratio of the number of 7 rings, 19 rings and 37 rings graphite slices).

![Figure 10](image)

**Figure 10.** Structural parameters different filling pattern amorphous carbons.

For the mixed-filled amorphous carbon structure, its structural parameters are mainly affected by the graphite slice with the largest filling amount, and it also has the structural characteristics of other sizes graphite slices. For example, when the proportion is 2:1:1, the specific surface area of the structure is higher, and the pore volume is not very low. It can be seen that the amorphous carbon structure obtained by the mixed filling method can have both a higher specific surface area and a higher porosity.

4. Conclusions

In this paper, a variety of amorphous activated carbons were constructed first, and then the adsorption amount and isosteric heat of helium adsorbed by activated carbon in the range of 4-10 K were simulated by the GCMC method. The specific conclusions are as follows:

1. The amount of adsorption increases as the temperature decreases, and increases to a maximum as the pressure increases. At the same density, the amount of helium adsorbed by amorphous carbon constructed from 7 rings or 19 rings graphite slices is very similar.

2. The larger the adsorption amount and the size of the filled graphite slice, the larger the isosteric heat.

3. For an amorphous carbon structure composed of a single type of graphite slice, the smaller the size of the graphite slice, the larger the specific surface area and the smaller the pore volume. The mixed-filling method is advantageous for obtaining amorphous carbon with high specific surface area and pore volume.

5. References

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