

カーボンナノチューブ束へのアルカンの吸着特性： グランドカノニカルモンテカルロシミュレーション

Adsorption characteristics of alkanes onto carbon nanotube bundles: Grand Canonical Monte Carlo simulation

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The separation of alkanes is important for a range of applications such as oil refinement, filtration and gas separation. Carbon nanotubes, with their large surface area are highly promising for applications utilising alkane adsorption and separation. Rather than remaining isolated however, nanotubes tend to bundle together, and the adsorption properties of such bundles and subsequent potential for practical alkane separation is not yet entirely clear. For this reason, we have undertaken Grand Canonical Monte Carlo simulations in order to study the adsorption properties of alkanes on nanotube bundles. Our results show how precise control of temperature and pressure allows selective adsorption of certain alkanes, and we describe in detail the reasons behind this.

Key Words : Gas, Adsorption, Separation, Alkane, Simulation

1. Introduction

With their large area-to-mass ratio, carbon nanotubes have long been of interest for use in applications which utilise the adsorption of molecules. This could include using the nanotubes for example as gas sensors [1], pre-concentrators [2] or for filtration and separation [3]. Rather than being isolated in nature however, nanotubes are usually found in bundles, resulting in a number of different adsorption sites inside and outside the bundle (figure 1). In order to understand the implications of these different adsorption sites, simulations and experiments examining the adsorption of various molecules have been performed during the last two decades. Light atoms, for example, able to penetrate into the smallest pores, have been used to explore the nature of the pores [4,5]. The use of linear alkanes has also been particularly popular [6,7], since they consist only of a simple chain of carbons, allowing systematic study of the effects of molecule length on the adsorption properties. For example, it has been shown that larger alkanes generally adsorb more strongly onto a carbon surface than smaller alkanes [8], but when confinement is significant, the opposite can be true as the molecules compete for space [6].

Studying adsorption using alkanes can not only give

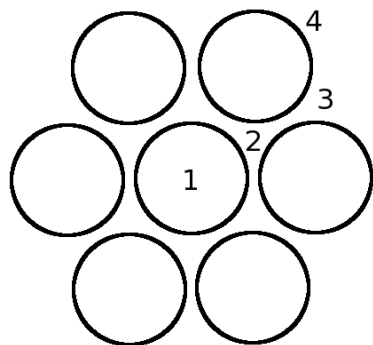


Fig. 1 A bundle made of nanotubes (circles) features adsorption sites classed as Internal nanotube (1), Interstitial (2), Groove (3) and Ridge (4) sites.

information about the ability to separate these important molecules, but can also give an insight into the potential bundles have in general for separation of molecules based on molecular length. When considering the separation of alkanes using nanotube bundles, realistic simulations of bundle adsorption need to be undertaken to answer a number of outstanding questions: Firstly, what capacity is there for the separation of alkanes, and by extension, separation based on molecular size? Can alkane adsorption be tailored through variation of pressure and temperature? What characteristics of the bundle effect adsorption? In order to answer these questions, we have undertaken Grand Canonical Monte Carlo simulations of the adsorption of Methane, Ethane, Propane, Butane and Pentane (denoted C1-5, respectively) onto a carbon nanotube bundle.

2. Simulation design

A nanotube bundle consisting of 7 nanotubes was prepared in the hexagonal formation shown in figure 1, with separation between the nanotubes corresponding to the carbon van der Waals (VDW) minimum potential distance of 3.2\AA . Periodic boundary conditions are employed in all 3 cartesian directions, so the nanotubes can be considered to be infinitely long in the z-plane. The simulation cell is 44\AA in length. In order to ensure that the bundle can be considered to be isolated, the simulation cell is made large enough that there is a distance of 50\AA between periodic images. The bundle itself has about 35\AA in width in the cross-axial planes. Each simulation consists of 20,000 equilibration cycles and a further 20,000 cycles for measurement. At each cycle trial moves of molecular insertion, deletion, translation and rotation are attempted, depending on the probability relevant for the given pressure and temperature, as well as the local energy at the position of interest. Bias arising from alkane length during insertion is taken account of through Rosenbluth weighting. Since, realistically, nanotubes are often found in their closed form, alkanes are prevented from entering the nanotube interiors (site (1) in figure 1).

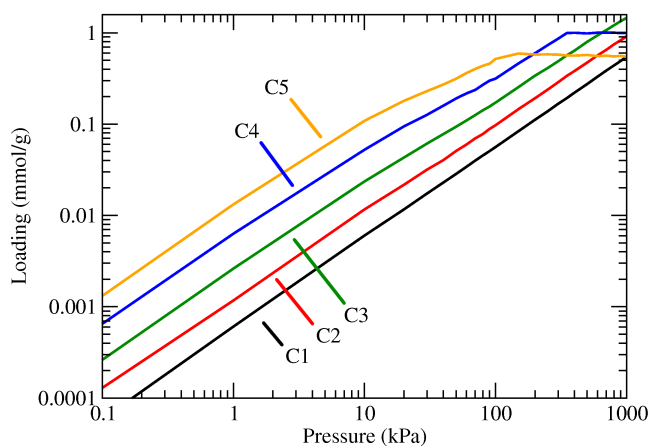


Fig. 2 An isotherm showing competitive adsorption of alkanes from Methane (C1) to Propane (C5) on the nanotube bundle. At high pressures, saturation of the largest alkanes can be observed as competition for adsorption inside the groove sites increases.

3. Results

Initial testing was conducted with separate adsorption of pure alkanes onto the bundle at 300K, and as expected, larger alkanes were found to adsorb more strongly compared to smaller alkanes. Interstitial sites inside the bundle are not sufficiently large for alkanes to enter, so adsorption is entirely on the surface. Figure 2 shows the contrasting situation when a mixture of alkanes adsorb onto the bundle; above a certain pressure, saturation can be observed, first in Pentane (C5) and then in Butane (C4) at slightly higher pressure. The origin of this saturation and the slight decrease of adsorption with pressure by large alkanes in the high-pressure region can be examined through comparison of the adsorption at 100kPa and 300kPa (figure 3). A decrease in the adsorption in the grooves is clearly observed for C5, highlighting how this is being replaced by smaller molecules. Thus the grooves are playing a highly important role in the adsorption characteristics at these pressures.

In addition to pressure, another environmental parameter that can be controlled is temperature, and it is interesting to consider how a combination of these parameters can be used for precise adsorption control. In principle, the adsorption of the alkanes occurs as the thermal energy is insufficient to escape the potential energy well at the nanotube bundle. Decrease of the temperature reduces the thermal energy, and so it is expected that a decrease in temperature will result in an increase in adsorption. Figure 4 demonstrates that this is indeed the case, and also that this effects the competition for adsorption in interesting ways. For example, at 260K, the greatest adsorption occurs for C3, since greater competition between the alkanes exists, reducing adsorption for the two largest alkanes. Higher temperatures however reduce the overall adsorption as well as competitive adsorption effects, resulting in a conventional increase in adsorption with alkane length.

4. Conclusion

We have conducted realistic Grand-Canonical Monte Carlo simulations into the adsorption properties of alkanes onto carbon nanotube bundles. Our results have demonstrated how nanotubes have the potential to separate alkanes and other molecules based simply on their size. Adsorption characteristics have been seen to be strongly influenced by the presence of the grooves and the competition for adsorption within them. No adsorption was observed inside the interstitial pores of the bundle. The results demonstrate how careful choice of pressure

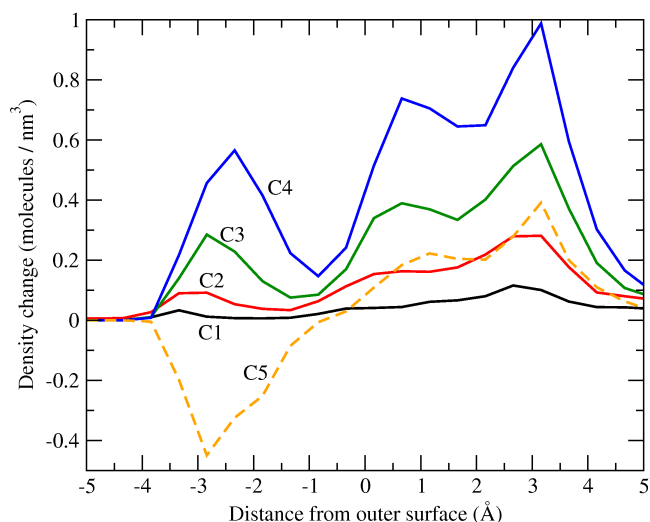


Fig. 3 Difference in adsorption amounts between 100kPa and 300kPa as a function of distance from the edge of the bundle. Negative positions are inside the grooves. C5 is seen to experience a reduction in the number of molecules in the groove when increasing the pressure to 300kPa, being replaced by the other alkanes.

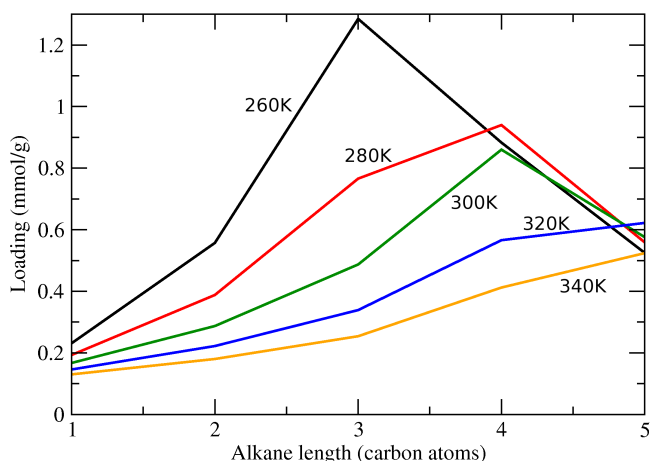


Fig. 4. Temperature dependence of alkane adsorption on the bundle at 300kPa. Reducing the temperature is seen to cause greater adsorption along with greater saturation effects of large alkanes.

and temperature allows adsorption onto the bundle to be tailored as desired, which may be useful in practical applications.

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