

A Simulation Study on the Adsorption Properties of Linear Alkanes on Closed Nanotube Bundles

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Abstract

Adsorption onto carbon nanotube bundles may find use in various applications such as gas pre-concentration and separation, and as a result it is of great interest to study the adsorption properties of such bundles. The adsorption of linear alkanes, with their systematic variation through chain length, is particularly useful to explore the effects of molecular length on adsorption characteristics. We have conducted Grand-Canonical Monte Carlo simulations of light linear alkanes adsorbing onto closed nanotube bundles in order to explore these effects in a systematic manner. Our results demonstrate how adsorption into the grooves of the bundle is favoured with alignment of the alkanes along the nanotube axis. We describe in detail the effects of competition for adsorption in the grooves and on the bundle as a whole, and highlight how selectivity can be tuned through careful choice of pressure and temperature. Finally, we describe how it is possible to derive a systematic relation between the length of the alkane and its loading on the bundle, and discuss its usefulness in applying Ideal Adsorbed Solution Theory (IAST) to predicting competitive mixed adsorption over a wide range of pressures. We also focus in turn on the ability of IAST to capture adsorption-saturation effects.

Introduction

There is great interest in using carbon nanotubes for applications such as molecular sensors^{1,2} or as pre-concentrators,³ since their large area-to-mass ratio offers a significant number of potential adsorption sites. Such a large number of potential sites promotes strong interaction between the molecules and the nanotubes, with subsequent positive implications for the desired measurement or effect. Rather than being isolated in nature however, nanotubes almost always form bundles, and this alters the adsorption of molecules, compared to isolated nanotubes. Whereas such isolated nanotubes would offer completely isotropic adsorption around the cylindrical axis, the presence of a number of different adsorption sites in the bundle makes the adsorption cylindrically anisotropic (figure 1). In addition, the greater number of close-range carbon atoms surrounding a pore increases interaction with the gas molecules and enhances the adsorption beyond that of an isolated

carbon surface.^{4,5} Since each type of adsorption site has slightly different adsorption strength and confinement characteristics, each site can be expected to display its own unique adsorption properties which could be exploited for application purposes.

Nanotube bundles have long been of interest for adsorption applications, and early studies focussed on the characterisation of the bundle pores, in order to understand more about their properties and influence on adsorption. For example, small molecules, able to penetrate into even the small interstitial pores, have been used to explore adsorption characteristics both on an experimental and theoretical basis.⁶⁻¹⁰ Among other things, this highlights the enhanced adsorption that arises due to the presence of the pores. Furthermore, the nature of the adsorption has been shown to be unusual, with “1D” alignment of molecules within the grooves of the bundle.¹¹⁻¹³ A number of characterisation studies have also been conducted with gases such as methane at low-temperature;¹⁴⁻¹⁶ the low temperatures accentuating the effects on adsorption by the different sites.

In order to examine the selectivity of nanotube bundles in a systematic fashion, the study of alkane and alkene adsorption onto bundles has become of increasing interest. Since alkanes interact with the carbon atoms of nanotubes through the relatively-simple van der Waals (VDW) interactions, and since linear alkanes differ only by the length of their carbon chain, such alkanes offer a clear insight into the effects of molecular length on adsorption in bundles. As a result, during recent years a number of studies have considered such adsorption, particularly using molecular simulation, since this offers clear detail about the location and energies of molecular adsorption. For example, adsorption of pure alkanes and competitive adsorption of mixed alkanes have been examined, showing how inside the bundle, large alkanes can be replaced by small alkanes at high pressure due to entropic effects.¹⁷ In general however where competition between species is negligible (eg, at low pressures), larger alkanes adsorb more strongly than smaller alkanes, due to their greater VDW interaction.¹⁸ When considering the outer surface of the bundle, such adsorption occurs more strongly in the grooves if they are accessible, compared to the ridges of the bundle,^{4,5} although the strongest adsorption of alkanes over the whole bundle occurs inside the nanotubes

themselves, if they are open and accessible.^{19,20} Further comparisons of adsorption between alkanes and their corresponding alkenes have highlighted the sensitivity of such pores, allowing differences in adsorption characteristics to be generated simply by the saturation (or lack thereof) of molecular bonds.^{21,22}

While a number of theoretical studies have offered valuable information about the internal adsorption characteristics by considering infinitely-periodic bundle systems (considering inner-nanotube and interstitial sites only),^{17,23} a number of studies have highlighted that inclusion of the outer surface of the bundle in simulations greatly assists in obtaining closer agreement with experiment, and that this can be important when considering competition between different adsorbing species.^{24–28} When growing nanotubes in the form of mats or films, for example, the sparse nature of the nanotubes will cause them to form isolated bundles,²⁹ and therefore the outer surface of these bundles plays a deciding role in the adsorption characteristics. As a result, in order to enhance the realism of simulations, it is important to include this outer surface. Furthermore, in an aim to obtain greater correlation between simulation and experiment, some authors have shown that the simulation of a heterogeneous range of nanotube diameters within the bundle (resulting in non-ideal packing of the nanotubes, and subsequently larger interstitial pores)^{14,15,30} as well as assuming some of the nanotubes are open³¹ can be helpful in improving agreement between simulation and experiment. It can in many cases however be preferred to have completely closed nanotubes, since the process of oxidation that leads to the opening usually introduces unwanted defects. As a result, the “N” sites in figure 1 are often inaccessible to the adsorbing molecules.

When considering the adsorption of molecules such as alkanes onto bundles of small closed nanotubes, surface effects will dominate the adsorption and selectivity. While it is clear that alkanes will generally favour groove sites, it is not yet clear to what extent this can be used to separate similar molecules such as alkanes. Furthermore, it is of interest to consider what quantitative relation there is between the adsorption of the alkanes and their chain-length in a realistic system, and to examine to what extent prediction of mixed adsorption is possible. In order to investigate these issues, we have conducted Grand-Canonical Monte Carlo (GCMC) simulations of pure and

mixed adsorption of small alkanes onto closed nanotube bundles, and have examined the nature of the adsorption, as well as the potential for selectivity, and the predictability of such results.

This paper is organised as follows: After detailing the simulation system, we describe the adsorption characteristics of the alkanes onto the nanotube bundle, both in terms of pure alkanes and in terms of alkane mixtures competing for adsorption. We then turn to the predictability of the adsorption of pure and mixed alkanes, before making a summary of the results.

Simulation details

Adsorption of linear alkanes from methane to hexane have been considered (C_nH_{2n+2} where $n=1\dots6$, referred to in an abbreviated form of “ C_n ” throughout this paper), using Grand-Canonical Monte Carlo (GCMC) simulations. The system is prepared in the following way: A nanotube bundle consisting of 7 nanotubes is prepared in the formation shown earlier in figure 1. Each nanotube is a (10,10) armchair nanotube and is 13.56Å in diameter. Separation between the nanotubes is set so that the minimum distance corresponds to the VDW radius of 3.21Å for carbon-carbon interactions (taken from the work of Werder et. al.³²). This study will therefore represent results for a bundle in a tightest-packing scenario. Furthermore, while the bundle is the smallest possible constructible, the results should hold for larger bundles too as the size and shape of the pores will not change significantly. The carbon atoms are fixed in position for all simulations, since framework flexibility has been shown in general to have a minor influence on adsorption.³³ Using periodic boundary conditions, the nanotubes are essentially infinite in length, and the interior of the nanotubes (“N” sites in figure 1) is blocked to molecular adsorption in order to reproduce the realistic condition of an unopened bundle. The presence of periodic boundary conditions also prevents any adverse finite-size effects. A system length of 44Å is used as it represents a system which is statistically sufficient (no difference in results is observed when the length is doubled) whilst maintaining reasonable computational cost. Since the interest is in an isolated bundle, the cartesian axes perpendicular to the direction of the bundle are around 85Å in length, giving approximately 50Å

between periodic images. This is sufficient for the bundle to be considered isolated and allows examination of surface adsorption. The TraPPE-UA potentials are used to describe the interaction between the alkanes,³⁴ which treat the molecules flexibly, combining hydrogen atoms with their corresponding carbon atoms to form a chain of single-site pseudo-atoms. Lorentz-Berthelot combining rules³⁵ are meanwhile used for non-bonded heterogeneous atomic interaction.

For a given simulation, the reservoir surrounding the system is at constant temperature, pressure and chemical potential. As with any GCMC simulation, the probability of accepting an insertion of a molecule into the system depends both on the parameters of the coupled bath, and the energy of the proposed insertion location in the system. Any insertion attempts inside the nanotubes are rejected through an applied blocking potential, since they are considered to be closed. For the insertion of the alkane chains, the Configurational-Bias Monte Carlo (CBMC) method is used.³⁴ In addition to insertion and deletion trial moves, translation and rotation trial moves are also permitted, as well as regrowths of the molecules. In addition to complete regrowths, the regrowths can also be partial, in which case only part of the molecule undergoes regrowth trials, reproducing internal degrees of freedom. Each simulation consists of 20,000 initialisation cycles, and then 20,000 measurement cycles. Each cycle consists of a number of trial moves equal to the number of alkane molecules in the system (with a minimum of 20 moves), so on average, each cycle will see each molecule attempt one trial move. In order to establish an isotherm, adsorption is measured for a given temperature over a range of pressures, from 0.01kPa up to 1000kPa for Methane (“C1”) and Ethane (“C2”), and up to the pressure at which saturation occurs for Propane (“C3”) and larger molecules. Tests reveal no hysteresis, and therefore calculations at the various pressures can be run in parallel.

In order to further enhance the realism of the simulations, gases are not assumed to be ideal; ie, the pressure is not equal to the fugacity. This requires knowledge of the relation between chemical potential (or fugacity) and pressure, which is achieved through the Redlich-Kwong equation of state.³⁶ For the simulation of alkane mixtures, the Lewis and Randall rule³⁷ is used to calculate the chemical potential (or fugacity) of each species in the mixture at the given pressure. For further

details of the simulation method, the reader is referred to papers by Dubbeldam et. al.³⁸ and Vlugt et. al.³⁹

Results and discussion

Adsorption of pure and mixed alkanes

Figure 2 shows how the pure alkane adsorption varies with alkane length and pressure, at 300K. As expected, a longer alkane results in greater adsorption, arising because the greater number of carbon atoms in a given alkane chain induces a stronger VDW interaction. Although a blocking potential is not applied to the interstitial pores as it is inside the nanotubes, their small size is observed to permit no adsorption, and so all adsorption here is on the surface of the bundle. The linear shape of the isotherm is consistent with other surface studies of light molecules,¹⁹ although interestingly of marked contrast to the type V isotherms that arise when adsorption inside the nanotubes is permitted,¹⁷ with sudden filling occurring over a short pressure range, preceded and followed by a slow increase in adsorption with pressure. This highlights how the form of the isotherms can give valuable information regarding the nature of adsorption by the bundle. Furthermore, in contrast to earlier experimental studies of low-temperature methane adsorption where distinctive stages of adsorption could be observed due to the presence of the groove, here no inflection points are observed, and the adsorption is quite linear; a result of the higher temperature. While the lack of experimental data limits comprehensive comparison of these results to experiment, the general increase in adsorption strength with alkane length is consistent with the trend observed in experiment.²⁰

In order to examine the ability of the bundle to separate alkanes, a mixture of alkanes, C1 to C5 is considered. The composition of the molecules in the gas phase is in the ratio 5:4:3:2:1 for C1 to C5 respectively (ie, the composition is at approximately equal mass ratio). Figure 3 demonstrates how, at low loading, larger alkanes adsorb more strongly. At high pressures, since larger alkanes have lower saturation pressures, a change in the ratio of the loading occurs. Furthermore, there is

no evidence of hysteresis as our tests indicate that a sudden increase to the prescribed pressure and a gradual increase give the same results.

In order to isolate the effects of the grooves, the same mixed adsorption isotherm is calculated for a single (35,35) armchair nanotube of similar diameter and surface-area to the bundle. Comparing the adsorption of C2-C5 against that for C1 (figure 4), the presence of the grooves can be seen to increase the selectivity between the alkanes at lower pressures, while at higher pressures there is no difference in the relative adsorption. The grooves assist selectivity at lower pressures because they are filled preferentially by the stronger-interacting larger molecules at the expense of the weaker-interacting smaller molecules, forcing them to adsorb onto outer sites which also have weaker adsorption properties than the grooves. At higher pressure there is greater overall adsorption, which negates the special nature of the grooves as competition for all sites increases, and leads to no difference in selectivity between the bundle and the large single nanotube. The saturation of the larger alkanes at high pressures acts to reduce the rate of increase in adsorption with pressure, and when combined with competition for space and entropic effects within the grooves can result in a decrease in the amount of adsorption, as demonstrated for C5 in figure 5.

As competition for adsorption sites becomes greater, one might expect compression effects to reduce the end-to-end length of the alkanes, however this is not the case; the length remains constant at all pressures (not shown here). The angle of the alkanes relative to the nanotube axis is however very-much dictated by the presence of the grooves, as is shown for the alignment of C5 (pentane) at 100kPa in the mixed solution (figure 6). As could be expected, alkanes are strongly aligned with the nanotubes at the base of the groove, and as molecules are positioned further out of the grooves, the orientation becomes progressively more random. Interestingly, just beyond the mouth of the groove (just beyond a distance of 0\AA in figure 6), moderate promotion of aligned orientation occurs again, corresponding to the alignment of alkanes side-by-side. The induced alignment then becomes weaker as the distance outside the bundle increases further.

The adsorption of the alkanes onto the bundle occurs because the thermal energy is not sufficient to escape the VDW attraction to the carbon atoms of the nanotubes. By reducing the temper-

ature, the thermal energy is reduced, and hence more adsorption is expected. What is interesting to consider is how this effects the adsorption characteristics in contrast to those already observed at 300K. Again using 100kPa and 300kPa for comparison, figure 8 shows the dramatic effect that temperature can have on the adsorption-selectivity of the bundle. While the previous results at 300K showed C5 being replaced by smaller molecules, at 340K the order in loading from C1 to C5 is restored. At lower temperature however, the opposite is true; at 260K, not only does C5 experience saturation but so does C4, leaving C3 with the greatest loading. This demonstrates clearly that by careful cycling of both temperature and pressure, it is possible to selectively adsorb chosen alkanes.

Predictability of alkane adsorption

Pure adsorption

As mentioned earlier, one motivation for the study of alkane adsorption is that each alkane differs in a systematic manner from the next (ie, by the simple addition of carbon atoms). As a result, it allows study of the adsorption in a methodical manner and may allow a relation to be derived between the length of the alkane and its adsorption characteristics. We have therefore examined the predictability of the loading of pure alkanes onto the nanotube bundle, as a function of the alkane length. This has been performed both at 300K and the lower temperature of 260K, in order to examine the effects of temperature too. Isotherms for pure alkanes were shown earlier in figure 2 for 300K, and in this style a best-fit line can be applied to reproduce this data for each pure alkane at each temperature. Not only can this be done for loading as a function of pressure, as in the case of figure 2, but it can also be done as a function of fugacity in a similar manner.

In fact, for the current purposes of predicting pure alkane adsorption, there is a clear advantage to predicting this in terms of fugacity rather than pressure. This is because that unlike at 300K where the number of molecules becomes computationally expensive as the phase changes and the free space around the bundle is filled, the loading of pure molecules such as C4 and C5 at 260K saturates only in the local volume around the bundle. Since the molecules do not fill the free

space away from the bundle, it is clear that the bundle is required for favourable adsorption at this temperature. If one assumes that the gas is ideal (ie, fugacity = pressure), as is done in some works,^{40,41} then it is impossible to apply a simple isotherm to describe the loading with pressure, because such a simple description can not capture the levelling-off of the loading at 260K during saturation. If one treats the gas as non-ideal however, then even as the loading as a function of pressure saturates, the loading as a function of fugacity does not, and therefore a simple isotherm is sufficient to describe the adsorption over the full range of fugacity, which can then subsequently be converted back to pressure. For this reason pure adsorption predictability is studied in terms of fugacity.

A number of isotherm forms exist for the description of loading vs pressure or fugacity at constant temperature, however two which combine simplicity with accuracy are the Langmuir isotherm⁴² of the form $n = \frac{n_s k f}{1 + k f}$ and the Freundlich isotherm⁴³ of the form $n = a f^b$, where n is the number of adsorbates, f is the fugacity, n_s is the saturation loading and k , a and b are constants. Note that for the relations to be thermodynamically correct, n needs to be proportional to f at low pressure, and so strong deviation of the value of b from unity in the Freundlich isotherm is undesired. Of the two isotherms, the Freundlich isotherm proved to fit the data most accurately. Since the Langmuir isotherm is developed based on the principle of a single site, it was considered whether this could be improved by a double-langmuir isotherm to represent two sites, however this led to no improvement of the fit. A double-Freundlich isotherm meanwhile produced only a marginal improvement in the already-good fit, at a cost of doubling the number of variables, and was therefore disregarded.

So each alkane isotherm can be described in the form of a Freundlich isotherm, $n = a f^b$, with correlation coefficients between the predicted and actual data of $R^2 = 0.999$ or higher for all alkanes. The values of a and b as a function of alkane length (number of carbon atoms), fitted over all pressures, are shown for both temperatures in 9. The variation of these constants can both be described by exponential functions of the form $a = j_1 j_2^{n_c}$ and $b = j_3 j_4^{n_c}$ where n_c is the number of carbon atoms in the alkane chain and $j_{1...4}$ are constants. The values of the constants for 300K are

found to be $j_1 = 1.99 \times 10^{-7}$ Pa, $j_2 = 4.71$, $j_3 = 1.16$ and $j_4 = 0.93$, while for 260K the values are $j_1 = 6.44 \times 10^{-7}$ Pa, $j_2 = 5.73$, $j_3 = 1.09$ and $j_4 = 0.92$ for a final equation of the form

$$n = (j_1 j_2^{n_c}) f(j_3 j_4^{n_c}) \quad (1)$$

While the increase in the values of a and b is largely smooth at 260K, this is not the case at 300K. The trend for C1 and C2 seems out of line with the trend observed for all the larger alkanes; there is a discontinuity between C2 and C3. It can be considered that the value of a in the Freundlich isotherm is essentially the gradient of the loading with fugacity (so a larger value leads to a greater increase of loading per unit fugacity-increase) and the value of b describes the curve of the gradient (so a value greater than 1 describes a curve upwards, while a value less than 1 describes a more asymptotic trend of loading with fugacity). If the trend of a for alkanes C3 to C6 at 300K is extrapolated back for C2 and C1 in figure 9, then C1 and C2 can be seen to have larger-than-expected values of a : they have a stronger increase in adsorption with fugacity than expected. Similar extrapolation for b meanwhile shows that C1 and C2 have a lower value of b than would otherwise be expected: in other words, they display slightly sharper asymptotic behaviour than expected.

Figure 10 shows how the adsorption into the grooves for C1 and most of C2 is linear (non-saturating), while C3 and longer alkanes experience clear saturation of adsorption in the grooves during the pressure-range investigated here. This corresponds well with the notion that C1 and C2 experience a stronger adsorption increase per unit fugacity-increase than would otherwise be expected, since the adsorption into the grooves is more favourable than outside the grooves. Furthermore, although the curve for C1 and C2 is almost straight (giving a value of b near unity), the fact that b is slightly lower than would be expected is consistent with minor saturation in the confined grooves, compared to the freer adsorption outside the grooves.

In order to confirm the role of the grooves in the inflection in a and b at 300K, one can calibrate the Freundlich isotherm for larger alkanes using only lower pressures, before complete filling of the grooves occurs. For C1 this corresponds to pressures up to 1000kPa (ie, all pressures considered

in this study), for C2 this is up to 300kPa and for C3 this is up to just 40kPa. For alkanes C4 and larger, groove-saturation occurs for even very low pressures, and therefore only C1 to C3 are considered. The values for a and b derived from these lower pre-groove-saturation pressures are also shown in figure 9, demonstrating clearly how the inflection point in the trend now disappears. This demonstrates conclusively that the presence of the grooves of the bundle has an important impact in enhancing adsorption of the smallest molecules.

The trend in the values of a and b at 260K meanwhile can be understood to simply be an extension of these effects. It has been highlighted how alkanes at 260K adsorb more strongly onto the bundle, and this is reflected in the value of a which sees an increase in value for all alkanes. Greater asymptotic behaviour is meanwhile suggested by the decrease in value of b , consistent with the requirement of the presence of the bundle for adsorption into the system, and the resulting reduction in freedom of the molecules to adsorb elsewhere within the system. The slight inflection observed for C1 at this temperature arises as a result of greater groove-based adsorption over the range of pressures studied, compared to the larger alkanes.

Mixed adsorption

Beyond prediction of pure-alkane isotherms, it is of interest to extend the models developed for pure adsorption to predict the adsorption characteristics of mixed alkanes. The advantage of such predictability is that only individual pure adsorption isotherms are required, and then any combination of alkanes at the given temperature can be calculated. For the purpose of predicting mixed adsorption isotherms based on pure isotherms, Ideal Adsorbed Solution Theory (IAST) is often used, and has been shown to hold for a wide range of different absorption situations, such as in hydrogen isotope separation using nanotubes,⁴⁴ CO_2 separation from N_2 for environmental applications using Metal-Organic-Frameworks (MOF's)⁴⁵ and ethane separation from a mixture of natural gas,⁴⁶ but to name a few. The background to IAST and its derivation is well detailed in the original work⁴⁷ as well as those more recent.^{40,48}

Obtaining the pure adsorption data for the purposes of predicting the mixed adsorption can be

achieved either through experiment or simulation at the desired temperature and pressure. It can be observed from figure 2 earlier however that at 300K, pure adsorption data is limited, since beyond a certain pressure, phase change and complete filling of the simulation cell occurs. The limit for mixed adsorption is much higher however (figure 3), since complete filling of the simulation cell by individual species does not occur. This is where the $n = af^b$ models derived in the previous section for pure alkane adsorption are particularly useful: by extending the model for pure adsorption to higher pressures, we are able to predict mixed adsorption beyond the limit of pure adsorption data.

Figure 11 shows the predictive ability of IAST for the adsorption of a C1-C5 alkane mixture on the nanotube bundle at both 260K and 300K. Close agreement is generally observed between the predicted and measured isotherms for the mixture. Furthermore, the saturation in the adsorption is also captured well by IAST, showing the wide range of applicability of IAST to various situations. Deviation in the accuracy of IAST in reproducing the mixed adsorption isotherm stems from small deviations in describing the pure loading through the Freundlich isotherm; agreement could therefore be improved with more accurate prediction of the pure-component isotherms.

Conclusion

The adsorption of small linear alkanes onto a closed nanotube bundle has been studied using Grand-Canonical Monte Carlo simulations. The adsorption of pure alkanes has been shown to be well-described by Freundlich isotherms, while selectivity of alkanes in a mixture has shown to be possible through careful choice of temperature and pressure, utilising differing saturation pressures of alkane species. The grooves of the bundle have been shown to play an important role in enhancing selectivity at lower pressures, while at higher pressures the grooves become less important as confinement is experienced at all sites. The replacement of larger alkanes by smaller alkanes at high pressures, particularly in the grooves, has also been discussed. In general, adsorption has been shown to strongly favour the grooves of the bundle, and alkanes have been shown to promote alignment with the bundle deep in the groove and, less expectedly, at the mouth to the

groove too.

The predictability of adsorption has also been discussed for both pure and mixed alkanes. The adsorption of pure alkanes with fugacity has been shown to be quantitatively predictable through the number of carbon atoms, n_c , in the form $n = (j_1 j_2^{n_c}) f^{(j_3 j_4^{n_c})}$, and this has helped highlight the enhanced adsorption at 300K of methane and ethane arising through relatively high groove-saturation pressures. The applicability of Ideal Adsorbed Solution Theory (IAST) in predicting mixed alkane adsorption from pure isotherms has also been considered, showing close agreement with mixed-alkane simulations, including the capturing of adsorption-saturation as well as the competition for adsorption in the mixture. The usefulness in using pure-alkane models for the extension of IAST to higher pressures has been highlighted, and the importance of the accuracy of these pure isotherms for the predictive accuracy of IAST has also been discussed.

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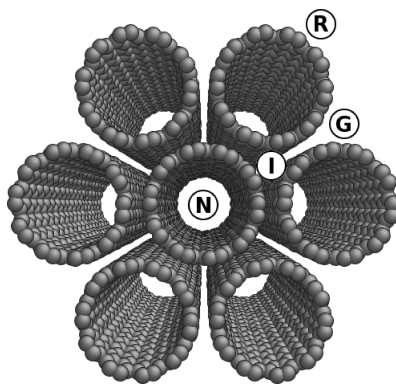


Figure 1: The four principle adsorption sites of a hexagonal nanotube bundle consist inner-nanotube sites (N), interstitial sites (I), groove sites (G) and ridge sites (R).

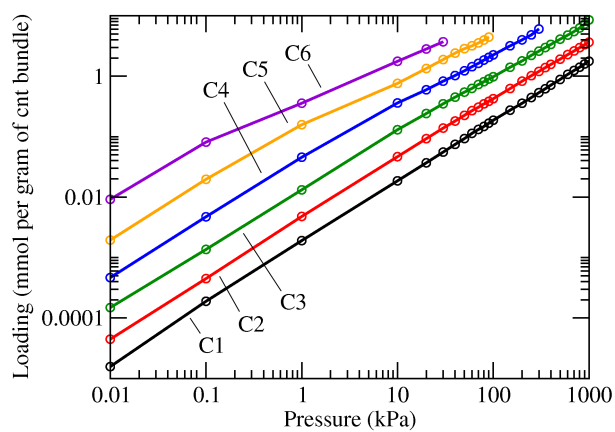


Figure 2: Adsorption of each pure alkane onto the nanotube bundle, from methane (“C1”) to hexane (“C6”), at 300K. The strongest adsorption can be observed for the largest alkane.

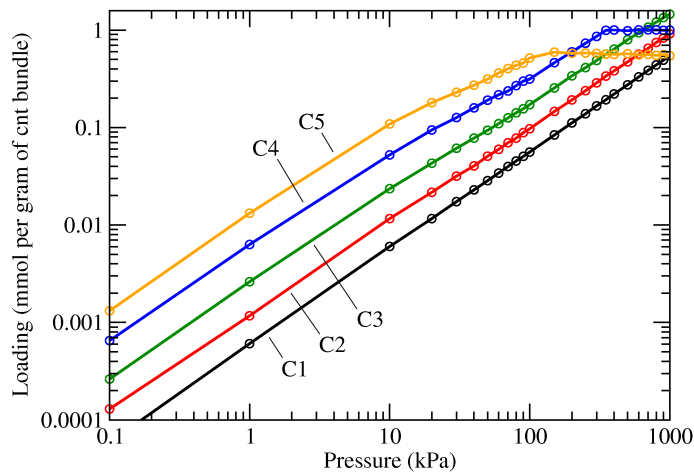


Figure 3: Adsorption of an equi-mass mixture of alkanes at 300K from methane (“C1”) to pentane (“C5”). At lower pressures, as in the case of pure alkanes, the larger alkanes adsorb more strongly, but saturation of large alkanes at higher pressures begins to reverse this trend.

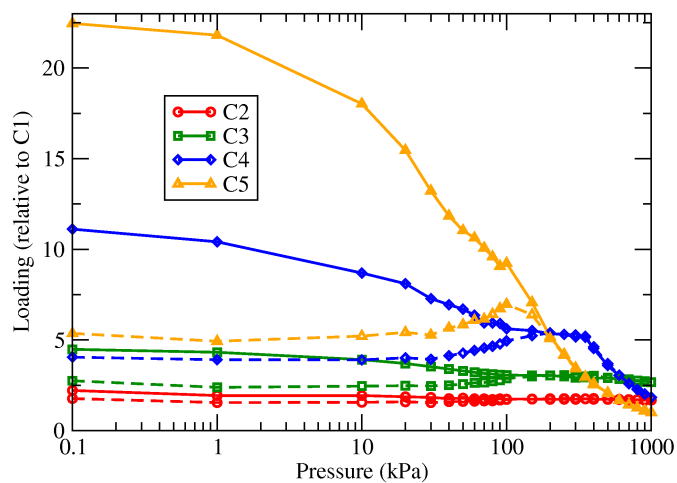


Figure 4: Adsorption of C2 to C5 relative to C1 for the bundle (solid lines) and a smooth large nanotube (dashed lines) with a diameter and surface area similar to that of the bundle. The presence of the grooves can be seen to increase the selectivity at lower pressures.

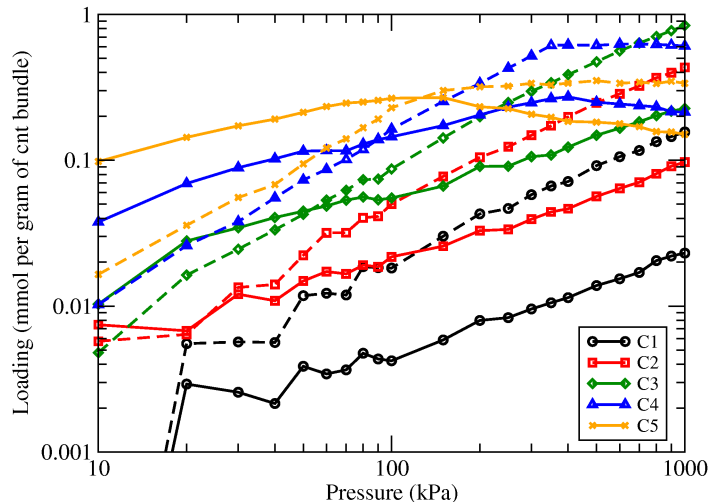


Figure 5: Average loading of molecules inside the grooves (solid lines) and immediately outside the nanotube bundle (dashed lines) in the C1-C5 equi-mass alkane mixture. Adsorption saturation of C4 and C5 is observed in correspondence with that shown in 3. Replacement of the large alkanes inside the grooves is also observed at high pressures.

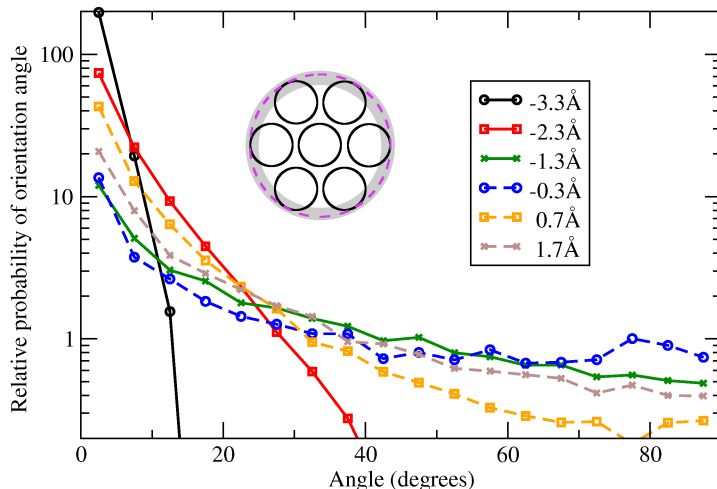


Figure 6: The orientation of C5 (pentane) molecules in the C1-C5 equi-mass mixture at 300K and 100kPa, for given distances from the edge of the bundle. The edge is marked in the inset schematic with a dashed line, and the range of distances (-3.3\AA to 1.7\AA) is indicated by the shaded region. Therefore, a negative position corresponds to a position inside the groove. An angle of 0° corresponds to alignment with the nanotube axis, while that of 90° corresponds to cross-orientation. The relative probability of the orientation angle is calculated by taking the observed probability derived from simulation snapshots, and dividing it by the probability that would be expected if the orientation were completely random. Therefore a relative probability greater than 1 corresponds to an increased probability of that orientation occurring. Each angle is split into 5° bins for statistical analysis.

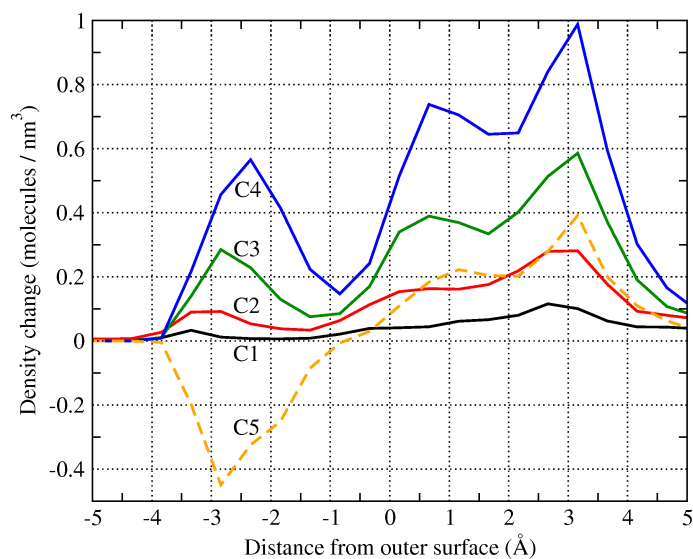


Figure 7: The difference in average radial density between 100kPa and 300kPa for the C1-C5 alkane equi-mass mixture. A positive value indicates an increase in density with pressure. The increase in C5 is much reduced due to its reaching saturation pressure. When this is combined with competition for space and entropic effects within the grooves, this results in a decrease in the amount of C5, while other alkanes continue to experience an increase. Zero on the x-axis is the outer edge of the bundle (as in the inset of figure 6), so a negative position corresponds to a location in the groove.

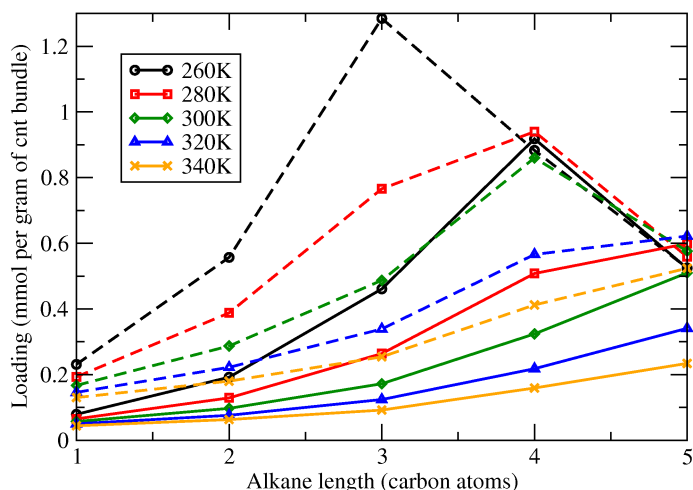


Figure 8: The influence of temperature on bundle loading for a C1-C5 equi-mass alkane mixture. Solid lines are at 100kPa, while dashed lines are at 300kPa.

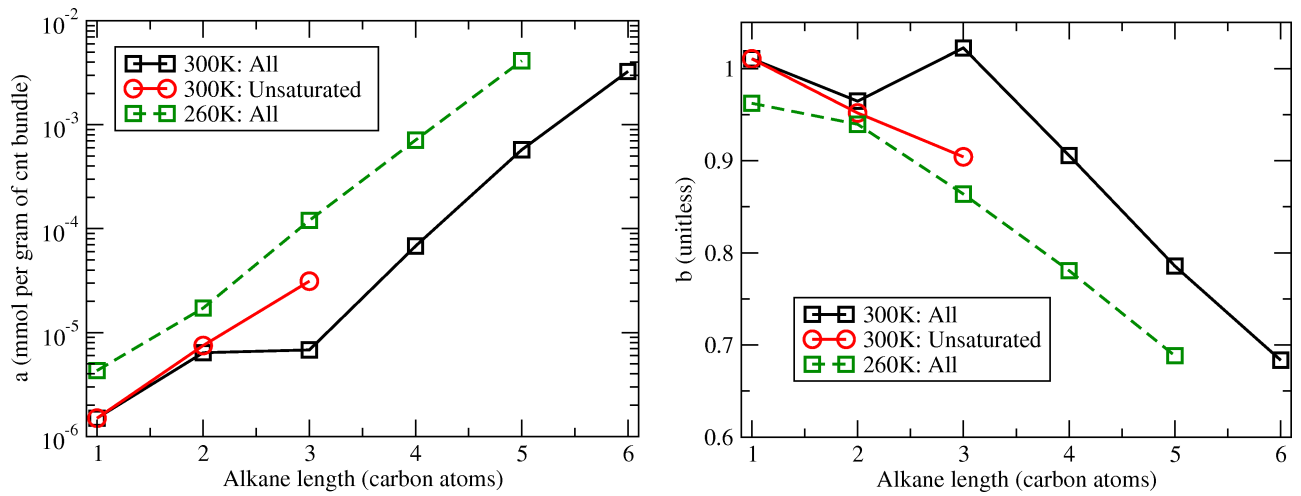


Figure 9: Variation of the value of constant a (left) and b (right) within the Freundlich-isotherm fit $n = F^b$ describing pure-alkane adsorption. “All” corresponds to a and b values derived from a fit over all data, while “Unsaturated” corresponds to fits based only on lower pressures where complete filling (saturation) of the grooves has not yet occurred (see main text for more details).

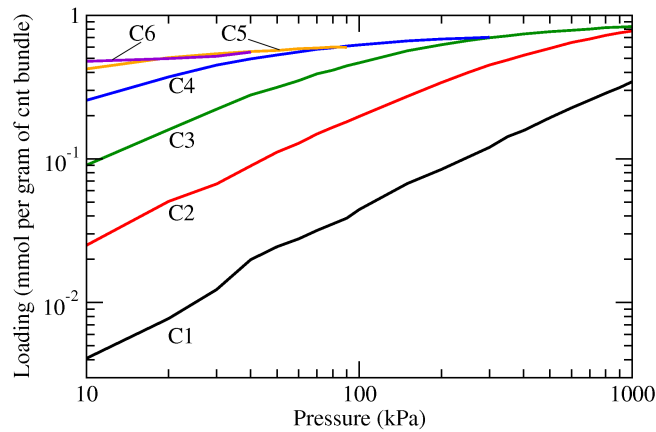


Figure 10: The loading of molecules in the grooves of the bundle for pure-alkane adsorption at 300K.

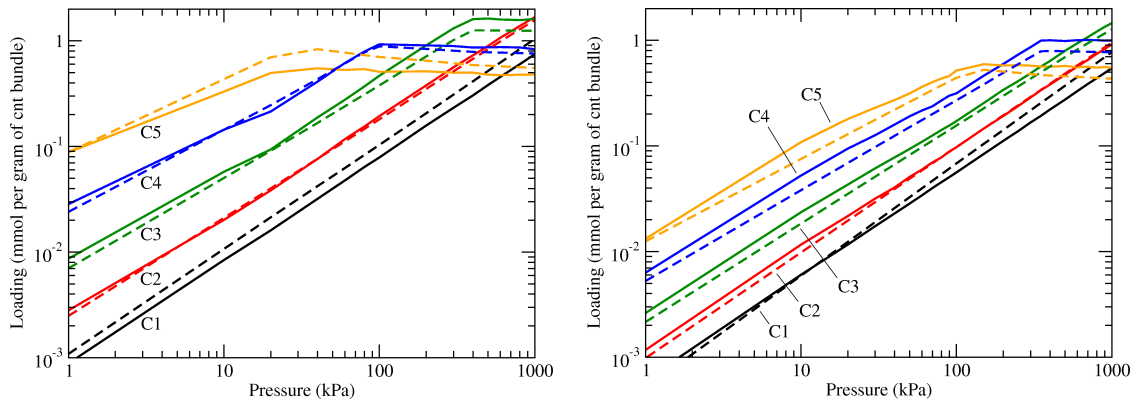


Figure 11: Actual adsorption isotherms (solid lines) for a C1-C5 mixture and the corresponding isotherms predicted through IAST (dashed lines), for 260K (left) and 300K (right), based on the pure adsorption models developed in the previous section.

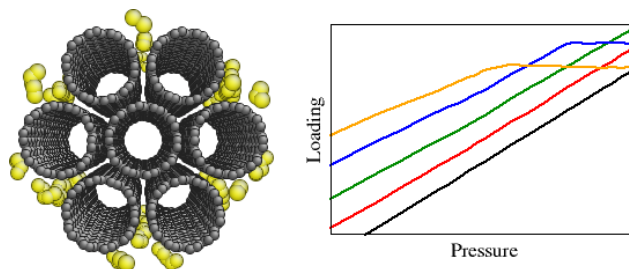


Figure 12: Table of contents image