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## Adsorption Kinetics of Diatomic Molecules

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Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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The adsorption dynamics of diatomic molecules on solid surfaces is examined by using a Kinetic Monte Carlo algorithm. Equilibration times at increasing loadings are obtained, and explained based on the elementary processes that lead to the formation of the adsorbed film. The ability of the molecules to change their orientation accelerates the overall uptake and leads to competitive kinetic behaviour between the different orientations. The dependence of the equilibration time with coverage follows the same decreasing trend obtained experimentally for ethane adsorption on closed-end carbon nanotube bundles. The exploration of molecule-molecule interactions effects on this trend provides relevant insights to understand the kinetic behaviour of other species, from simpler molecules to larger polyatomic molecules, adsorbing on surfaces with different binding strength.

### Introduction

Over the last few years, many nanostructures have emerged that show potential aptitude for adsorption-based applications such as gas separation and storage. Depending on the specific application, this capacity is typically assessed in terms of adsorption properties, for example, binding energies, surface area or equilibrium selectivity.<sup>1</sup> Though definitely relevant, these characteristics are mostly based on the equilibrium properties of the adsorbed phase and are only useful if they can be efficiently exploited. Kinetic limitations, in the form of slow adsorption and/or diffusion rates or even steric restrictions imposed by pore sizes, play a fundamental role to properly account for the whole adsorption behavior of a system.<sup>2</sup> These kinetic characteristics become more relevant as the complexity of the adsorbent structure and/or the adsorbate molecule increases, due to the presence of different groups of adsorbing sites as well as the increase in the number of internal degrees of freedom of the adsorbate. A typical example of this situation occurs when considering the adsorption of polyatomic molecules such as linear alkanes in carbon nanotube bundles, which indeed has provided the initial motivation for this work as explained below.

In a number of previous studies,<sup>3-6</sup> we have explored the adsorption kinetics of mono-atomic gases in nanotube bundles. These studies were originally motivated by disagreements between theoretical predictions and experimental results regarding gas adsorption inside the interstitial channels between the tubes.<sup>5</sup> By implementing a Kinetic Monte Carlo algorithm, we reproduce the elementary processes that occur while the gas

is being adsorbed. In this way, we predict how the coverage adsorbed on the surface evolves with time, when the surface is exposed to a gas at certain pressure and temperature. We can then determine the equilibration time, that is the time that it takes for the adsorbed phase to reach the equilibrium coverage, at the pressure and temperature of the coexisting gas.<sup>3-6</sup> For a given temperature, this is done for increasing pressures, and the equilibration time is plotted as a function of the final equilibrium coverage. The qualitative trend and main features of this dependence can then be compared with its experimental counterpart. In this case, equilibration times are typically obtained from monitoring the decrease in the gas pressure as molecules are being adsorbed (which relates one-to-one to the increase in the coverage on the adsorbed phase) until the system reaches equilibrium.<sup>7,8</sup>

When we explored the kinetic behavior of atoms on heterogeneous carbon surfaces<sup>4</sup> and binary mixtures adsorbing on uniform substrates,<sup>3</sup> we found unique features stemming from the availability of sites with different binding energies. In all cases, however, the equilibration time would decrease as the equilibrium coverage increases, which was confirmed by a number of experimental results on carbon nanotube bundles.<sup>7,8</sup> We now turn our attention to non-spherical molecules, with the overall goal of exploring the effect of the internal structure and shape of the adsorbate on its adsorption kinetics behavior.

Hydrocarbon chains are among the simplest molecules that can be chosen to study films of linear (or quasi-linear) adsorbates. This family of molecules is especially well suited to systematically explore the effects of increasing molecular length on the equilibrium and dynamical properties of the

adsorbed phases. During the last decade, the adsorption behavior of linear hydrocarbons on nanotube bundles has been investigated via experiments and simulations.<sup>9-18</sup> Most of these studies are focused on equilibrium properties; only very recently has the kinetics of adsorption of linear alkanes been explored experimentally.<sup>18</sup> In that study, the equilibration time of a series of alkane molecules of increasing length (from ethane to pentane), adsorbing on the exterior of a nanotube bundle, were measured. This was done as a function of the final coverage on the surface, up to monolayer completion, and at the same relative temperature with respect to the critical temperature of the species. It was found that the decreasing trend of the equilibration time for methane and ethane was replaced by a non-monotonic function for the longer alkanes: propane, butane and pentane. In those cases, the equilibration time would initially increase, with coverage reaching some maximum value before eventually decreasing to very low values as the coverage approaches a single monolayer.<sup>18</sup> We have previously explained the occurrence of the decreasing trend in the monomer case (methane) with the aid of a simple model and simulations.<sup>5,7,8</sup> This decreasing trend basically occurs as a consequence of the increase in the external gas pressure necessary to achieve higher coverages, and that is the main cause of the accelerated adsorption seen as monolayer completion is approached.<sup>5</sup> The fact that this trend exhibits a notable qualitative change as the length of the molecule increases clearly suggests the presence of other competing effects in the equilibration process that are not present for the simpler molecules.

With the ultimate goal of providing an explanation for this change in the kinetic behavior as the length of the molecule increases, we start here by focusing on the adsorption of diatomic molecules on a lattice that represents binding sites on the external surface of a nanotube bundle. This allows us to directly compare with the experimental results mentioned above for ethane adsorption on closed-end nanotube bundles.<sup>15,18</sup> Although we will be somewhat focusing on this system as a particular example (due to the availability of experimental results for the whole alkane series), the model and results presented here are in fact relevant for the kinetic behavior of other homo-nuclear diatomic adsorbates such as  $H_2$ ,  $N_2$ , and  $O_2$ . Diatomic molecules are the shortest non-spherical adsorbates possible, and this work is a sensible first step to later analyze the increasingly larger effects of the non-spherical nature of longer molecules. Longer chains introduce many more orientation changes, which leads to more complex kinetic behavior. We hope that these more complicated cases will be easier to analyze if we thoroughly understand first the diatomic case as discussed in this work.

## Theoretical model and methods

Carbon nanotube bundles are spontaneously formed when single-walled nanotubes are produced. Due to dispersion forces between the individual tubes, they tend to self-organize parallel to each other with their axis in a typical triangular array.<sup>19</sup> Numerous studies of adsorption on closed-end nanotube bundles have shown that the equilibrium uptake on the external surface of a bundle occurs as a successive formation of lines or stripes of molecules (parallel to the axis of the tubes).<sup>20</sup> As the external pressure is increased, molecules occupy the strongest binding sites (the channel lying in between two tubes that we call the groove) and then form pairs of additional lines at both

sides of the groove (with weaker binding). Further increase in pressure makes the uptake to keep raising causing the molecules to also adsorb onto the surface of each one of the tubes to the sides, until the whole external surface is covered up (see Figure 1). The number of stripes comprising the monolayer is essentially determined by the size of the tubes and the adsorbate, typically anywhere between three lines (for a large quasi-spherical molecule like  $CF_4$ )<sup>21</sup> to seven or eight lines (for a smaller atom like Ne).<sup>22</sup>

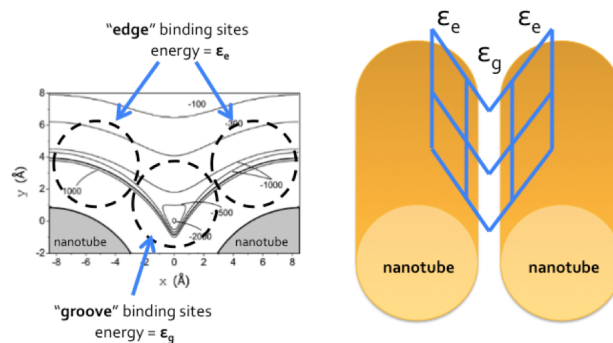


FIG. 1. On the left: Potential energy contours for a quasi-spherical molecule ( $CH_4$ ) on the external surface of a bundle. The dotted circumferences represent regions with two distinctive binding energies: the stronger "groove" flanked by stripes of lower binding ("edges"). On the right: Lattice sites representing the energy landscape shown on the left.

We begin by applying the Kinetic Monte Carlo (KMC) algorithm<sup>23</sup> to a lattice-gas model, allowing the molecules to adsorb to a one-dimensional lattice, which could represent the groove that exists between adjacent nanotubes on the exterior of the bundle or a strip formed on the external surface of a single tube (Fig. 1).<sup>4</sup> We represent the diatomic molecules as dimers, made out of two identical units where each unit is able to occupy a single site (Fig. 2).

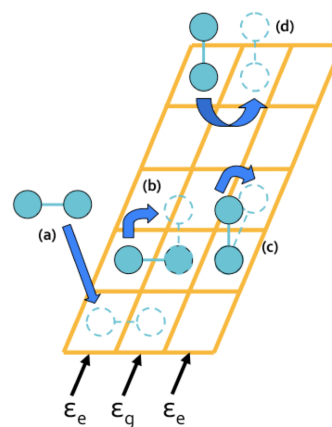


FIG. 2. Configurations and transitions of dimers on the lattice: (a) adsorption, (b) and (c) orientation change, (d) diffusion.

The dimers can either lie flat on the lattice (occupying two sites) or stand transversely to it (occupying a single site); therefore, the maximum coverage considered corresponds to a

full monolayer. This model is essentially based on numerous adsorption studies on the equilibrium properties of the adsorbed films of polyatomic molecules. In the diatomic case, the main energy difference between the possible configurations occurs between the flat and transverse orientations. Other orientations are definitely possible (and indeed occur) but in this work we use the simplest model that would let us identify the parameters that play the greatest role in the dynamics.

Next, we explore the kinetics when two more lines of sites are added to the lattice. This two-dimensional scheme better models the whole external surface of a nanotube bundle; the center strip represents the groove between adjacent nanotubes, while the outer lines model the weaker-binding sites that run alongside the groove, on the surface of the individual nanotubes (Figure 1).<sup>4</sup> In this system, the dimers have greater freedom to reorient themselves to minimize their energy. As before, they may lay flat along the groove or along the edge, but they may now also lay flat across the lines, perpendicularly to the groove. The adsorbates can also stand transversely to the lattice at all points (Figure 2). We assign binding energy values to the different configurations based on a monomer binding energy,  $\epsilon_g$  (groove site) or  $\epsilon_e$  (edge site). Therefore, a flat dimer occupies two sites, with energy  $2\epsilon_g$ ,  $2\epsilon_e$  or  $(\epsilon_g + \epsilon_e)$  while a transverse dimer occupies a single site, with energy  $1.5\epsilon_g$  or  $1.5\epsilon_e$ . Similarly, molecule-molecule interactions are built from the monomer-monomer interaction energy,  $2\epsilon_{int}$ , in the nearest-neighbor approximation.<sup>24</sup>

As done in our previous studies,<sup>4,5</sup> we start with an empty lattice in contact with an infinite reservoir of dimers at temperature  $T$  and chemical potential  $\mu$ . Per the KMC algorithm,<sup>23</sup> we calculate the probabilities of transition for a dimer to be adsorbed, desorbed or change its orientation as follows:

$$\frac{W_{ads}}{W_{des}} = \exp[-\beta(E_{TF} - \mu)] \quad (1)$$

$$\frac{W_{F \rightarrow T}}{W_{T \rightarrow F}} = \exp[-\beta(E_T - E_F)] \quad (2)$$

where  $\beta=1/(k_B T)$ , and  $E_{TF}$  are the total energy of a transverse or flat dimer adsorbed on the surface, including both the binding energy to the surface as well as interactions with neighboring molecules. Next, the selection rule prescribed by the KMC algorithm<sup>23</sup> is used to determine the state transition that occurs, and the time is advanced correspondingly. In this way, the system evolves through different states, and the process continues until the adsorbed film reaches equilibrium, that is, the number of particles on the lattice stops changing. A full account of the details of the Kinetic Monte Carlo algorithm is available in our previous publications.<sup>4,5</sup>

Following this scheme, we keep track of the number of adsorbed molecules as a function of time as the elementary processes that lead to equilibrium occur. For a given chemical

potential, we obtain the total coverage of the lattice as well as the contribution from flat and transverse molecules adsorbed on the different sites. As a result, we are able to observe how the preferred orientation of the adsorbates changes with time and coverage. The key difference in this system, compared with our previous work on the adsorption dynamics of quasi-spherical adsorbates, stems from the number of different states available in the system and from the ability of the system to go through them in its evolution towards the equilibrium state. At equilibrium, a single dimer in the flat configuration is energetically favorable, compared to a single transverse dimer, but at the cost of a reduction in the number of particles that can occupy the lattice. Conversely, the system would lower its total energy (understood as the grand potential  $\Omega(T, \mu)$ ) if the two spaces taken up by a single flat dimer were instead filled by two transverse dimers, though this requires a higher chemical potential. The orientation of the molecules in these final equilibrium states definitely depends on the final coverage, and this work explores and focuses on what are the elementary transitions (in particular orientational changes) that the system follows in order to reach these different equilibrium states.

## Results

### Adsorption Kinetics on a Single Line

We consider a single line of 200 identical sites, with  $\epsilon_g = -175$  K and  $T = 100$  K.<sup>24</sup> To simplify the analysis of the kinetic processes, no dimer-dimer interactions were considered at first but they were later added to evaluate their influence on the overall equilibration times (see Figs. 4 and 5).

In Figure 3, we show the number of molecules as a function of time, for increasing values of the chemical potential (which is typically an increasing function of the gas pressure). In order to analyze how the molecules change their orientation as the adsorbed film evolves towards equilibrium, we keep track of not only the count of molecules in each configuration that make up the film at every instant (full line), but also the orientation in which those molecules were originally adsorbed from the gas, before adopting that orientation (dotted line). Although presenting the evolution of the fractional coverage (instead of the number of particles) would be the standard choice to show these results, plotting the number of molecules let us show directly how many molecules are changing orientation; the fractional coverage shows a more indirect perspective as transverse and flat molecules do not occupy the same number of sites.

At low pressure (Fig. 3.a), the flat dimers provide the greatest contribution to the total uptake at all times, with comparatively fewer particles in the transverse state as shown by the full lines. However, the dotted lines show that more particles were originally adsorbed from the gas in the transverse orientation but some made the transition to the flat state as equilibrium was approached. Because the flat orientation is the preferred state at equilibrium and there is no competition for space at this low coverage (only about 20 % of the lattice sites



are occupied), molecules adsorbed flat will remain in that configuration and some of the originally adsorbed transverse change to flat. The initial uptake rates from the gas (dotted lines) are the same for both orientations as they share the same chemical potential; however, the number of flat dimers on the surface effectively increases more rapidly due to the transition of originally adsorbed transverse dimers to the flat state.

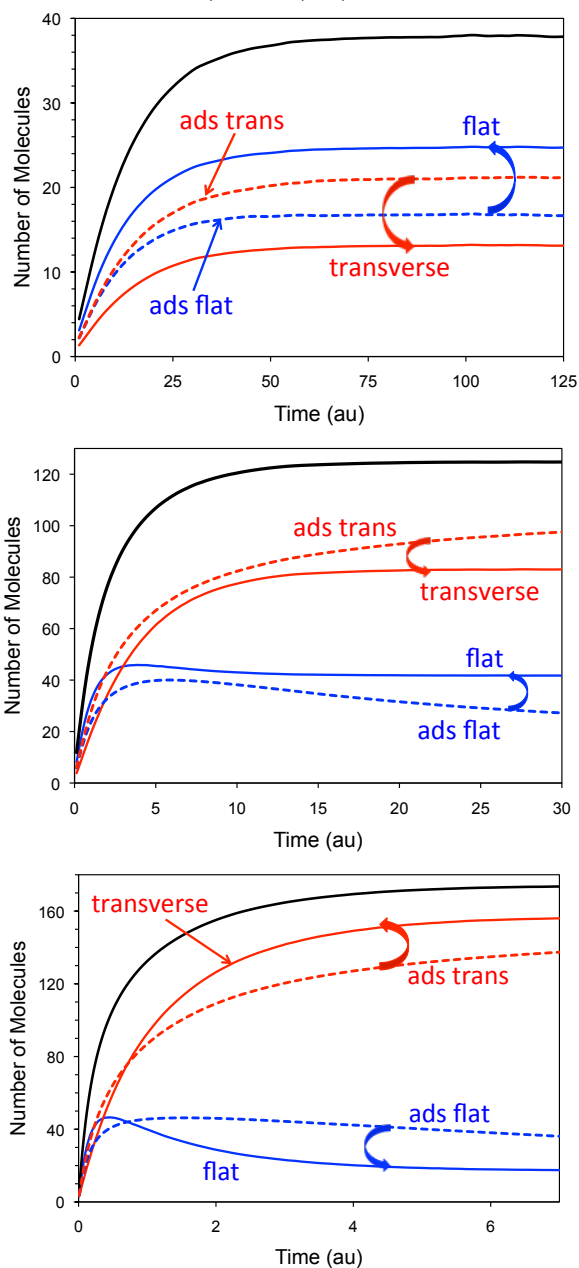


FIG. 3. Number of molecules adsorbed as a function of time at  $\beta\mu = -5, -1.7$  and  $0.34$  (200 sites,  $T=100$  K). The dotted lines correspond to molecules adsorbed directly from the gas in each configuration. These curves were obtained after averaging over hundreds of individual runs to smooth out the simulation fluctuations.

As the chemical potential rises (Fig. 3.b), we see the expected increase in overall coverage (about 60% of the lattice is covered at equilibrium). Even though the overall competition for sites favors the transverse orientation at equilibrium, the dotted lines indicate that a number of molecules that end up in the flat orientation were still first adsorbed as transverse dimers. Eventually, when the pressure is high enough (Fig. 3.c), there is an overwhelming preference for the transverse orientation; the dotted lines now show that molecules originally in the flat state transition to the vertical state as the lattice approaches 85 % of a full monolayer.

In all cases shown in Fig. 3, the total coverage of the lattice rises monotonically (full black line). However, that is not the case for the flat dimers' contribution at the higher coverages of Figs. 3.b. and 3.c., which exhibits an 'overshoot' very early in the equilibration process. The full lines in Fig. 3.c. show that there is, initially, a slight preference for the flat state but, as the lattice becomes increasingly populated more than half of those molecules stand up, substantially decreasing the initial flat contribution. This 'overshoot' behavior in the flat dimer coverage is similar to what we previously observed in the adsorption kinetics of a binary mixture:<sup>3</sup> the effect of faster adsorption rates that drive the coverage evolution at the beginning of the equilibration process is gradually replaced by the influence of the binding strength as the film gets closer to its equilibrium state. It is important to note here that, contrary to the case of binary mixtures, the overshoot behavior described for dimers adsorbing in the flat orientation is not something observable in the experiments since its effect does not show up significantly on the overall coverage evolution.

We can bring together the results from the individual evolution curves shown above to characterize the overall kinetic and equilibrium behavior of the system as function of the final equilibrium coverage. The equilibrium properties are typically displayed on the adsorption isotherm (Figure 4), while the overall kinetic behavior can be shown by plotting the equilibration time as function of the equilibrium coverage (Figure 5). In both cases, we also now show the effect of (attractive) molecule-molecule interactions of increasing strength. Based on the monomer-monomer interaction value,  $\epsilon_{\text{int}} = 0.08\epsilon_g$ , the full molecule-molecule interaction is calculated depending on their relative orientation. We chose the numerical value of 0.08 based on typical values for simple adsorbates on carbon surfaces. For example, if we consider the ethane molecule composed of two methyl groups adsorbed on the groove of a nanotube bundle,  $\epsilon_g \sim -1700$  K while  $\epsilon_{\text{int}} \sim -140$  K, for two molecules closer to their equilibrium separation. Starting from this initial value, we then consider increased values  $\alpha\epsilon_{\text{int}}$ , with  $\alpha = 0, 1, 4, 6,$  and  $8$  to evaluate its effect on the overall equilibrium and kinetic behaviors. In this work, we focused on the effect of attractive interactions mainly because we are considering sub-monolayer coverages; also, this is the kind of interaction that could lead to longer equilibration times due to effectively increasing the binding,<sup>5</sup> which is the effect observed for longer molecules.<sup>18</sup>

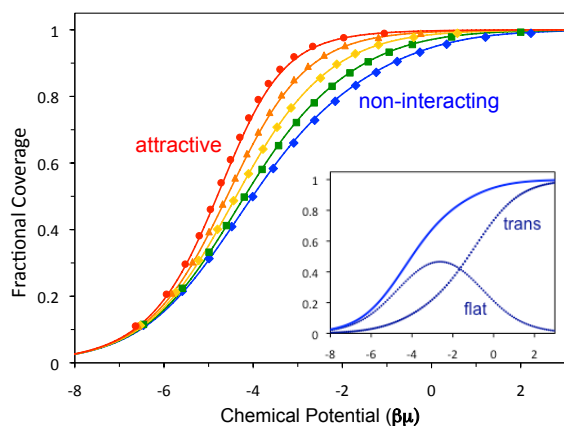


FIG. 4. Adsorption isotherms for increasing values of the interactions ( $\alpha = 0, 1, 4, 6,$  and  $8$ ). Symbols correspond to simulation results while full lines are obtained from lattice gas calculations as explained in the text. The inset shows the coverage contributions from each orientation for the non-interacting case.

Figure 4 shows the isotherms obtained from the simulation results (symbols) together with predictions from solving the corresponding lattice gas model of adsorption<sup>25</sup> for the number of adsorbed molecules (lines) as follows. We assumed a unit cell of four sites with periodic boundary conditions. We counted the different configurations in which flat and transverse dimers could be arranged on this lattice (nine in all) and calculated the total energy of each arrangement of molecules, including the adsorption energy of each molecule in the arrangement, as well as the particle-particle interaction energies, where applicable. From there we could calculate the partition function and the equilibrium values of fractional coverage and energy per site.<sup>25</sup> These calculations are an important verification of our simulation results (that the simulations provide the expected equilibrium values) and give us better insight into the parameters of the system that affect the kinetics of adsorption.

In figure 4, we show the overall equilibrium coverage as a function of  $\beta\mu$  (corresponding to the logarithm of the ideal gas pressure); the inset shows the individual contributions from the molecules with different orientation for the non-interacting case (very similar behavior is observed for the other cases). At low pressures, the majority of the coverage is due to flat dimers on the lattice. As the chemical potential increases, the contribution of the flat dimers peaks and then begins to fall, while the coverage due to transverse dimers rises sharply. Increasing the interactions has a similar effect as decreasing the temperature since it effectively increases the binding energy to the surface.

In Figure 5, we plot the overall equilibration time (defined as the time at which the system reaches equilibrium and the coverage stops changing) as a function of the final coverage adsorbed on the lattice at equilibrium. For example, from Figure 3, we can observe that it takes about 60 time units to reach a fractional coverage of 0.3, and about 15 and 7 time units to get to coverages of 0.8 and 0.98 (blue line in Figure 5). In our previous work on the adsorption kinetics of non-interacting quasi-spherical adsorbates, we found and explained

the observed decreasing linear relationship between the equilibration time and the final coverage (with steeper slopes for higher binding); basically, increasing pressure values are needed to reach larger coverages and, since each site is occupied independently from the others, this directly leads to faster adsorption rates. In this work, we found a similar dependence for the non-interacting case, as seen in Figure 5 (blue line). The equilibration time decreases monotonically as the overall equilibrium coverage increases, but we observe that the equilibration time exhibits a slight curvature, deviating from the linear behavior seen for quasi-spherical molecules. These deviations result from the new ability of the adsorbates to transition between adsorbed states with differing energies, which was not possible in the case of monomers. The decreasing trend persists for relatively large interactions and only changes to a non-monotonic behavior when  $\alpha$  is greater than about 6. In those cases, the initial rise in the equilibration time can be understood in terms of our previous finding about slower adsorption due to increased binding.<sup>5</sup> From the lattice perspective, one can think of an “effective” or “mean” energy per site that increases with coverage as neighboring sites are filled, leading to increasing equilibration times before the effect of the pressure takes over to eventually bring down the equilibration time to zero at monolayer completion. In fact, we had previously observed a similar effect (induced by the particle-particle interactions) in the equilibration times of quasi-spherical molecules.<sup>5</sup>

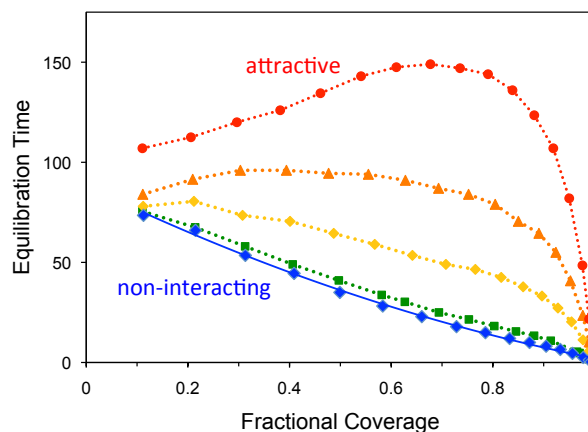


FIG. 5. Equilibration time (in arbitrary units) as function of final coverage for increasing values of the interactions (from bottom to top,  $\alpha = 0, 1, 4, 6,$  and  $8$ ). Errors are smaller than the line width. Lines are shown to guide the eye.

### Adsorption kinetics on three lines

We repeated the simulations described above on a three lines lattice ( $T = 100$  K, and  $\epsilon_c = \epsilon_g/2 = 87.5$  K),<sup>24</sup> thereby adding detail to our model of the external surface of the carbon nanotube bundle. We observed behaviors similar to those found on a single line. In these simulations, there are three possible flat configurations, represented by the three lines that are

concave down: molecules laying flat along the outside edge of the lattice (with binding energy  $2\epsilon_o$ ), dimers laying half in the groove and half out of it (with binding energy  $\epsilon_g + \epsilon_o$ ), and dimers laying along the groove (with binding energy  $2\epsilon_g$ ). We again included periodic boundary conditions in both directions, longways to represent an infinitely long nanotube bundle and shortways to represent the repeating series of grooves observed as the nanotube bundle rotates.

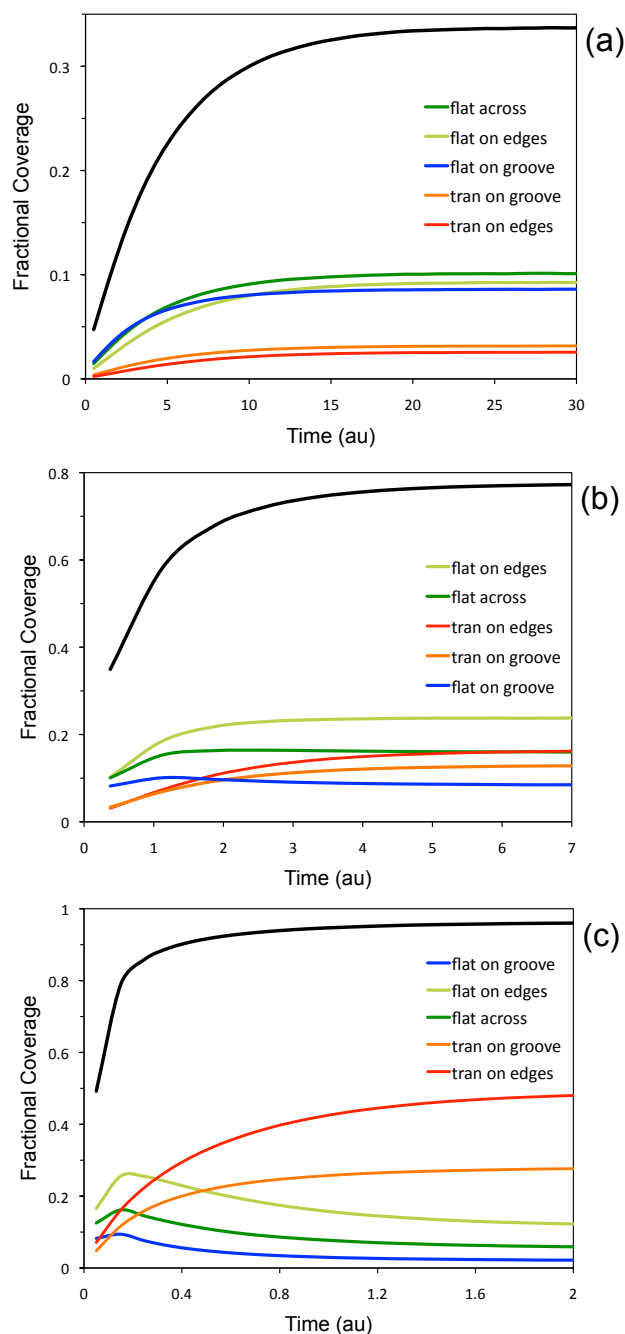


FIG. 6. Fractional coverage as a function of time for increasing values of the pressure (black); the individual contributions from molecules adsorbing with each orientation on different sites are also shown (600 sites,  $T=100$  K).

The overall evolution of the coverage together with the individual contributions of the molecules adsorbed in the different orientations is presented in Figure 6. Similarly to the single line case, at low pressure (Fig. 6.a), the flat orientation is preferred since only about 30% of the lattice sites are occupied. Again, the faster occupation rate exhibited by the flat dimers is an indication that those molecules are mostly transitioning there from other transverse configurations rather than being adsorbed directly from the gas phase. As the chemical potential increases (Fig. 6.b), competition for the strong-binding sites of the groove increases and the flat orientation on the groove is not likely, considering many groove sites are filled by dimers in other states. Least favorable is the state in which the dimer lies along the outer edge of the groove; however, this state has the greatest contribution to the overall coverage of the lattice because there are so many configurations in which the particles can fit into the outer edges, both parallel to the groove and perpendicular to it, thanks to the periodic boundary conditions imposed on the system. There is also much less transition from the transverse to the flat orientations since transverse molecules are preferred at equilibrium at this relatively high pressure. In fact, an incipient overshoot in the flat dimer population on the groove signals the occurrence of the opposite transition, from flat to transverse states. When the surface is approaching monolayer completion (Fig. 6.c), the molecules are mostly adsorbed in the transverse orientation (and stay in that configuration) or make the transition to that state as the system comes closer to equilibrium generating the overshoots in the population of the flat molecules, similarly to what we observed previously for a single line.

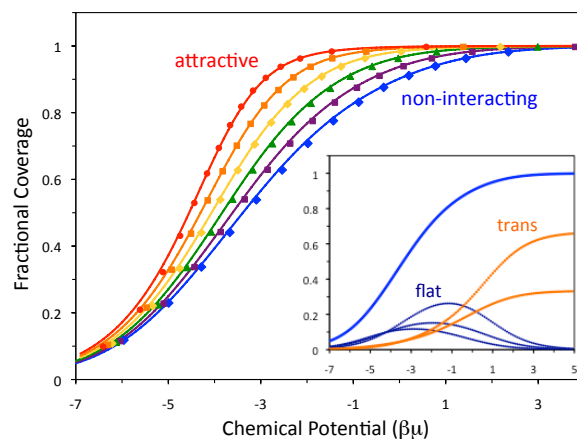


FIG. 7. Adsorption isotherms for increasing values of the interactions ( $\alpha = 0, 1, 2, 3, 4, \text{ and } 5$ ). Symbols correspond to simulation results while full lines are obtained from lattice gas calculations as explained in the text. The inset shows the coverage contributions from each orientation for the non-interacting case.

We plot the equilibrium isotherms in Figure 7; very similar behavior to the single line is observed. The inset now shows the contribution from the molecules adsorbed on the different lines in each one of the orientations. As seen before, the flat orientation is preferred at low chemical potential but then the

molecules have to stand up at the highest pressures to maximize the lattice occupation. The symbols correspond to the simulation results while the lines were calculated using standard statistical mechanics methods for solving a lattice gas model of adsorption as we did for the single line case. For these calculations, we used a 3x2 lattice, with periodic boundary conditions in both dimensions. Again, we determined all possible arrangements of the adsorbed molecules in all possible orientations (which resulted in a total of 96 configurations) and were able to find the partition function and the equilibrium coverage as before.

The overall equilibration time as a function of final coverage is shown in Figure 8. We observe that the trend is decreasing unless the molecule-molecule interactions are (artificially) enlarged more than four times over the typical value for ethane. Two important consequences are directly derived from this fact: 1) the decreasing trend obtained when we consider typical values for the ethane-ethane interaction is similar to the one obtained experimentally for this particular system,<sup>18</sup> which provides validity to our models and approach, but moreover 2) the non-monotonic behavior observed for higher interaction values suggests that the trend change observed experimentally for propane and longer molecules could be due to the increased role of molecule-molecule interactions as the chain gets longer (as explained before for the curves in Figure 5). It should also be noted that the effect of the molecule-molecule interaction on the adsorption kinetics displayed in Figures 5 and 8 shows a general tendency that is indeed relevant for many other systems as it essentially depends on the relative strength of the inter-particle interactions compared to the binding provided by the surface. For example, it could definitely be possible that the non-monotonic dependence be observed for simpler gases like methane adsorbing on weaker substrates (although the particular behavior would of course depend on the details of the system).

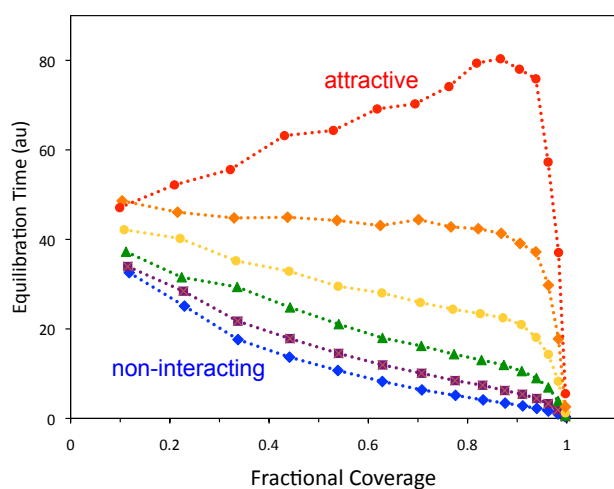


FIG. 8. Equilibration time as function of final coverage for increasing values of the interactions ( $\alpha = 0, 1, 2, 3, 4,$  and  $5$ ). Errors are smaller than the line width. Lines are only to guide the eye.

## Conclusions

The kinetics of diatomic molecules exhibits characteristics of both binary mixtures and heterogeneous surfaces systems. Similarly to the binary mixture,<sup>3</sup> there is competition for the binding sites not between different types of adsorbates, but rather between the preferences for the different orientations with respect to the surface. As in the case of the mixture, the competition starts based on the occupation rate (favoring the flat orientation) but for high enough loading, the equilibrium preferred state (transverse) takes over, forcing the molecules to stand up and generating the overshoot observed in the flat dimer population. The ability of the diatomic molecules to transition through intermediate states as the system equilibrates accelerates the adsorption of the flat dimers at low coverages because the rate of change of state is higher when the energy difference between the before- and after- states is lower. Thus, if a dimer from the gas will end up in the flat configuration, it will first pass through a transverse intermediate state (with final energy  $1.5\epsilon$ ) instead of making a single jump across a larger energy gap (since the final energy would be  $2\epsilon$ ). Similarly to the adsorption of monomers on a heterogeneous surface,<sup>4</sup> the transitions to and from these intermediate states cause a deviation of the equilibration time versus coverage from the linear trend observed for simpler monomers adsorption on uniform surfaces. The heterogeneity of the surface adds another source of intermediate states: in general, increasing the energy difference between the binding sites (relative to the thermal energy) will lower the transfer of molecules from one group of sites to another, and will typically result in the development of distinct steps in the isotherm, i.e. decreasing the coupling between the different kinds of sites.

Attractive molecule-molecule interactions have the effect of increasing equilibration times<sup>5</sup> and, if they are high enough, of changing the overall dependence on the coverage from a decreasing trend to a non-monotonic function that initially raises and then reaches a maximum before falling down closer to monolayer completion. As explained before, this can be directly traced back to the increase in the effective energy per site brought about by the attractive molecule-molecule interactions as the lattice gets progressively filled with more particles.<sup>5</sup> Increasing binding slows down adsorption and causes the equilibration times to go up initially before the pressure gets too high (closer to monolayer completion) for this effect to matter. For the particular case of ethane adsorption on closed-end carbon nanotube bundles, the decreasing trend derived from our simulations agrees with the observed experimental trend. Although not realized experimentally (for ethane), the non-monotonic trend obtained for strong molecule-molecule interactions indicates this as a potential factor for the observed trend change for propane and longer chains as the relative role of the interactions is expected to increase with the length of the molecule.



## Acknowledgements

We acknowledge the support provided by the National Science Foundation through Grants CBET-1064384 and DMR-1006428.

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- 24 We estimate the binding energy of the monomer that is far from the surface in the transverse orientation to be half of the one closest to the surface based on the typical size of the ethane molecule (two methyl groups separated by 0.23 nm) and the adsorption potential due to the carbon nanotubes. In this case,  $\epsilon_g \sim -1750$  K,  $\epsilon_e \sim \epsilon_g / 2$ , and  $\epsilon_{int} \sim -140$  K. (Parameters for the ethane interactions were taken from R. F.