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Energy Barriers at the Ends of Carbon Nanotube Bundles: Effects on Interstitial Adsorption Kinetics

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We investigate the presence of adsorption sites and energy barriers near the ends of carbon nanotube bundles to determine their consequences on gas adsorption in the interstitial channels between the tubes. In the case of H_2 molecules adsorbing in bundles of closed (10,10) tubes, a high binding energy site followed by a potential barrier lie right before the entrance to the interstitial channels, producing a dramatic slowing down of interstitial adsorption kinetics.

Gas adsorption on carbon nanotube bundles has been actively investigated since the discovery of these nanostructures in 1991 [1]. The increasing interest in this topic is based not only on potential practical applications to problems such as gas storage and separation, but also on the related fundamental questions that this system originates as a consequence of its unusual geometry. Single walled carbon nanotubes are hollow tubes made out of carbon atoms. Typically, their diameter is of the order of 1 nm and their length is 1000 times larger than their diameter. Tubes with nearly the same radii can gather spontaneously into bundles or ropes of 10 to 100 tubes, following a triangular lattice pattern [2]. Several adsorption sites can be identified in such a rope. Inside the bundle, gas may be adsorbed in the interior of the tubes (if their ends are open) and within the narrow interstitial channels (ICs) formed between the tubes. On the exterior of the bundle, the external surface of the tubes and the grooves formed where two adjacent tubes meet can also hold physisorbed particles [3–5].

Numerous experimental and theoretical investigations of gas adsorption on nanotube bundles have aimed to determine the binding energies of the adsorption sites, the phases present in the adsorbed film, and the characteristics of the adsorption isotherms, among other equilibrium properties [3–24]. In most of these studies it is assumed that adsorption occurs on bundles containing infinitely long tubes. While this hypothesis does not alter the adsorption behavior on the external surface in any significant way, the accessibility and eventual occupation of the adsorption sites within the bundle will occur only if the appropriate gas transport through the ends of the bundle takes place. As a matter of fact, even though there exists considerable consensus about the adsorption properties of the bundles, a controversy still remains regarding interstitial adsorption [25]: Although several theoretical (equilibrium) studies predict H_2, Ne, and He adsorption in the ICs [3,4,13–17],

experimental observations have failed to provide a conclusive confirmation of this basic prediction [5–7,18–23]. This disagreement may have a possible explanation based on the characteristics of the samples (for example, the presence of blocking elements at the entrance of the channels), but it may also be related to the time scale involved in the adsorption process and/or the properties of the adsorption kinetics in the whole bundle. To shed light on this latter possibility, we have explored the potential energy surface near the ends of a bundle to determine the presence of adsorption sites and/or potential barriers that may obstruct or slow down the entrance of the gas to the interior of the bundle. In this Letter, we especially focus on the case of H_2 adsorbing on tubes with radius $R = 6.9$ Å [the so-called (10,10) tubes]. In the case of bundles with closed tubes, we find a high binding energy site right before the entrance of the IC, followed by a potential barrier at the beginning of the channel. Moreover, this site provides the strongest binding in the bundle for this gas, thanks to the favorable combination of the largest carbon-gas attractive potential (where three tubes meet) with a reduced confinement effect that lowers the zero point motion of the adsorbed particles. In addition to the intrinsic interest of this new identified adsorption site, we perform a kinetic Monte Carlo simulation [26] to prove that its presence drastically alters the adsorption kinetics within the IC, with important consequences for the experimental observation of interstitial adsorption.

We consider a bundle of three rigid, parallel, and perfect (with no holes) carbon nanotubes. For simplicity, we assume that all the ends (closed or open) are at the same height. Other arrangements do not alter significantly our conclusions. The closed tubes are capped with spherical surfaces. We compute the potential energy of a H_2 molecule near the bundle's end summing the contributions from the three tubes. As in our previous work [8–10], the potential is derived as a sum of Lennard-Jones gas-carbon

interactions, adopting typical parameters and a continuous distribution of carbon atoms.

Figure 1 shows the potential energy of H_2 in a bundle of closed tubes. The interior of the channel corresponds to negative values of the z coordinate. The most remarkable feature of the energy landscape is the presence of a deep minimum at the entrance of the channel that happens when the potential minima of every tube meet at some height z, *outside* the channel. This energy minimum is realized somewhere outside the channel where the separation between the tube walls can be larger than inside the IC. In addition, a potential barrier is evident at the channel entry. Figure 1 also shows that a molecule initially adsorbed on the external groove would encounter another barrier while diffusing towards the IC. The potential energy corresponding to bundles with open tubes (not shown) exhibits a similar minimum outside the IC but in this case its energy is higher than the IC energy minimum. This feature suggests a better situation for IC adsorption in open tube bundles as confirmed below.

The values of the diffusion barriers for light molecules like H_2 in confined environments are affected by zero point motion effects. Therefore, we compute the ground state energy E_0 of a H_2 molecule at the end of the bundle by solving the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r, z) \right]\psi(r, z) = E_0\psi(r, z) \qquad (1)$$

using the diffusion method [27]. In this equation, $V(r, z)$ is the azimuthally averaged adsorption potential along the IC; r denotes the distance from the center of the channel, and z is the distance from the IC entry. The ground state energy is $E_0 = -730.7$ K for a state localized at the entrance of the channel, as shown in Fig. 2. Since the ground state of the

molecule *inside* the channel [14] is -281.5 K, one can estimate a diffusion barrier height to entry the channel of around 450 K. This turns out to be much larger than the difference between the potential energy minima corresponding to the inner and outer sites (≈ 120 K) or even the potential barrier shown in Fig. 1 (≈ 200 K). This result is a direct consequence of zero point effects: For a molecule adsorbed on the outer site, not only is the potential more attractive, but also the zero point energy is greatly decreased with respect to the interior of the channel since the confinement is much smaller. Moreover, the probability density maximum is ≈ 0.5 Å away from the position of the potential minimum, indicating the tendency of the molecule to be in the loosest environment compatible with the greatest binding. In the case of open tubes, the ground state energy outside the channel is $E_0 = -266.4$ K which, in contrast to the closed tubes case, is higher than the ground state inside the channel. Thus, opening the tubes will certainly speed up the interstitial adsorption process.

It is important to keep in mind that these results rely on the values of the potential parameters and depend on the geometry of the system (radii and separation between the tubes). The most critical factors in the case of interstitial adsorption are the length parameter for the gas-carbon interaction (σ_{gc}) and the radii of the tubes. Since the values of σ_{gc} are not known with certainty, we show in Fig. 3 the range of values of σ_{gc} and radii of the tubes that would lead to the presence of the outer adsorption site while IC adsorption is also possible. Decreasing the tube's radius and/or increasing σ_{gc}, reduces the effective radius of the IC. For any value of σ_{gc}, at large radius, the only adsorption site is inside the IC but as the radius decreases the outer adsorption site appears. Further decrease in the radius prevents adsorption inside the IC and only the external site can be occupied. We indicate in Fig. 3 the value of σ_{gc} used in this work obtained with semiempirical combining rules [3] and also the value derived by Wang *et al.* (WSW) [28] based on the interaction of H_2 with planar graphite. The problem of determining which value is more
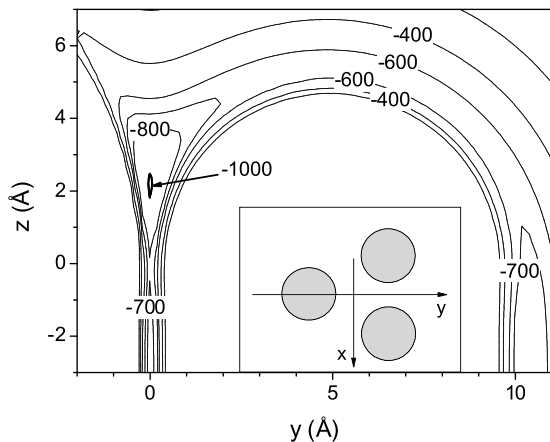

FIG. 1. Potential energy (in K) of a H_2 molecule near the end of a bundle with three closed tubes. The origin of the y axis lies at the center of the interstitial channel. The z axis coincides with the axis of the channel and its origin indicates the entrance to the channel. Positive values of z indicate positions outside the IC. See Fig. 2 for a more detailed picture of the region near the IC.
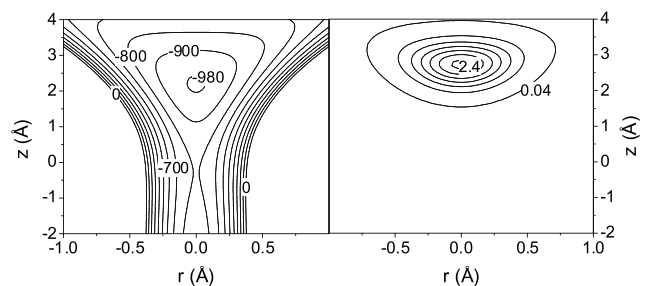

FIG. 2. Ground state of a H_2 molecule at the end of the bundle. Left panel: Potential energy (same geometry used in Fig. 1). Right panel: Probability density. Note that the probability maximum is shifted from the minimum of the potential energy to take advantage of the less confined environment.

realistic is still an open question that requires more experimental evidence to be answered. In any case, Fig. 3 shows that there *always* exists a range of the radii of the tubes for which the phenomenon described in this work will occur, with either set of parameters. The outer adsorption site could still be observed in bundles with slightly ($\approx 10\%$) narrower tubes if the alternative value of σ_{gc} is considered.

To assess the effects of this state at the ends of the channels on the adsorption kinetics, we consider gas adsorption on a one-dimensional lattice with a total of N_s adsorption sites. The sites at both ends of the chain, with energy $E_{end} = -731$ K, represent the sites at the entrance of the IC [29]. The internal sites are inside the channel and have energy $E_{IC} = -282$ K. Rather than providing a detailed description of the kinetics, our goal in this work is to compare the rate of adsorption of this system with the corresponding rate of a homogeneous chain where every site has the same adsorption energy E_{IC}. To study the adsorption kinetics [30], we use the kinetic Monte Carlo scheme described in Ref. [26]. Starting from any state i of the system, the time evolution of the system is determined by the transition probabilities $W_{i \to j}$, $j = 1, 2, \ldots, n_{states}$ where n_{states} is the total number of accessible states from the state i. These transition probabilities are chosen so that the detailed balance principle is satisfied. For particle displacements along the chain,

$$\frac{W_{i \to j}}{W_{j \to i}} = \exp\left(-\frac{E_j - E_i}{k_B T}\right), \qquad (2)$$

where T is the temperature of the system and k_B is the Boltzman constant. In addition, the end sites have the possibility of adsorbing or desorbing particles according to the adsorption (desorption) probabilities $W_{ads(des)}$ that verify

$$\frac{W_{ads}}{W_{des}} = \exp\left(-\frac{E_{end} - \mu}{k_B T}\right) \qquad (3)$$

where μ is the chemical potential of the gas in contact with the adsorbing chain. Figure 4 shows the evolution of the coverage $n = \langle N \rangle / N_s$ as a function of time for different temperatures and equilibrium coverages n_{eq}. The top panel corresponds to $T = 200$ K, and $T = 100$ K for the curves in the bottom panel. We compare the rates dn/dt when the system has reached half of its equilibrium coverage. At $T = 200$ K, the rate of the inhomogeneous system is only 2 times slower but at $T = 100$ K, which is closer to the typical temperatures in H_2 adsorption experiments, the rate has decreased approximately 20 times. This dramatic kinetic effect may explain why it is so difficult to observe interstitial adsorption. Moreover, we can also explore the consequences of the fact that the adsorption occurs only through the ends of the channel. For example, we can compare the coverage evolution of the inhomogeneous system in two cases: when adsorption is allowed only through the end sites and when adsorption occurs at every site of the chain (as on the exterior of the bundle). A drastic reduction on the rate, which decreases almost 300 times (at
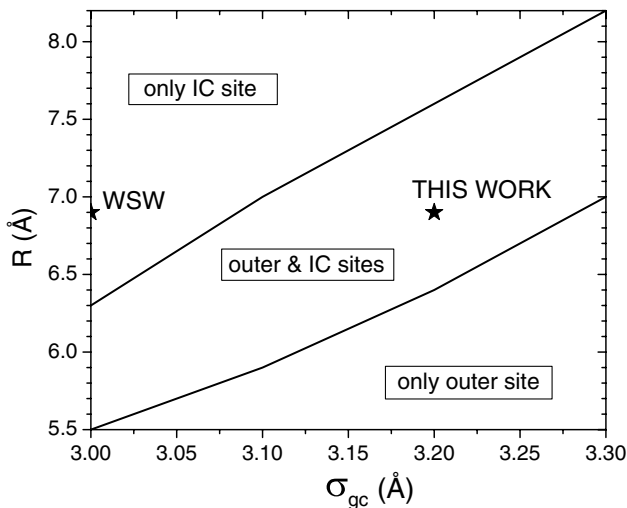

FIG. 3. Sensitivity of the presence of the outer adsorption site to the value of σ_{gc} and tube radius R. The region enclosed by the lines corresponds to systems that exhibit both IC and outer adsorption sites. For any given σ_{gc}, if the radius is too large, the outer adsorption site disappears while no adsorption is possible inside the IC if the radius is too small. We indicate with star symbols the values of the parameters used in this work and the ones corresponding to Ref. [28] (WSW).
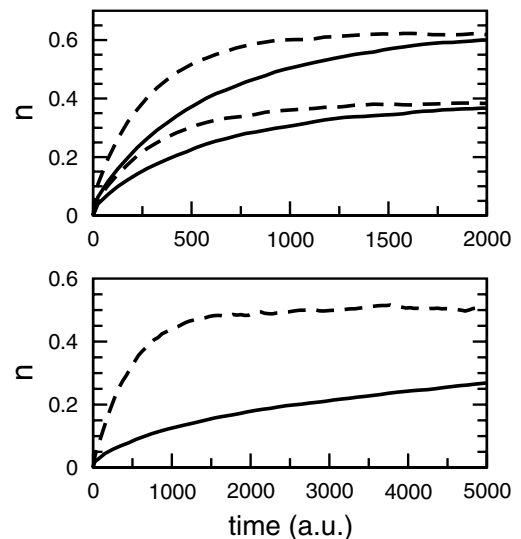

FIG. 4. Mean coverage $n = \langle N \rangle / N_s$ of H_2 as a function of time. The dashed lines correspond to the homogeneous IC chain (no entry sites) and the full lines correspond to the IC with high binding energy sites at the ends. Top panel: $T = 200$ K; the chemical potential is $\mu/(k_B T) = E_{IC}/(k_B T) + 0.5$ for the two upper curves ($n_{eq} \approx 0.62$) and $\mu/(k_B T) = E_{IC}/(k_B T) - 0.5$ for the two lower curves ($n_{eq} \approx 0.38$). Bottom panel: $T = 100$ K and $\mu = E_{IC}$ ($n_{eq} \approx 0.5$).

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$T = 200$ K), occurs when adsorption happens only through the ends. This means that adsorption on the external grooves could be much faster than in the interstitial channels. In fact, if we consider the groove as a homogenous chain where every site has an energy $E_{\text{groove}} = -615$ K [3], the adsorption rate is 50 times higher than in the channels, at $T = 200$ K. Lowering the temperature will result in an even larger effect.

In summary, exploring the potential energy surface near the ends of a nanotube bundle has led us to two important discoveries. First, we have identified a new possible adsorption site at the entrance of the channel that, in the case of H_2, provides the greatest binding in the whole bundle. Then, we established that the presence of this site certainly slows down the adsorption. At low temperatures, the adsorption rate may decrease by 1 order of magnitude, making the interstitial adsorption an extremely slow process and therefore difficult to detect experimentally. Opening the tubes can somewhat reduce this effect, since in the open tubes case the internal sites have higher binding energy. Adsorption on the external grooves happens much more quickly than in the interstitial channels. This is likely to be true even for the gases that do not find energy barriers at the entrance of the channel. In that case, it is possible that some obstruction at the ends of the bundle is caused by the same gas adsorbing on its exterior. This issue will be further investigated in future work.

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