CHAPTER NINE

ADSORBED GASES IN BUNDLES OF CARBON NANOTUBES: THEORY AND SIMULATION

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9.1 INTRODUCTION

The discovery of carbon nanotubes [1, 2] has led to extensive investigation of adsorption on these remarkable substrates. Much of this effort has been directed toward potential applications, such as gas storage and separation, which exploit the fact that every carbon atom of a single-wall carbon nanotube (SWNT) can provide two surfaces, inside and outside of the tube, for...
potential gas adsorption; this corresponds to a specific area of order 2500 m$^2$/g. Early claims of extraordinary hydrogen uptake (e.g., six H$_2$ molecules per C atom) stimulated a particularly intense effort to achieve practical amounts for storage applications, but those results have not been confirmed by any subsequent experiments. More modest uptake (0.5 molecule per C atom) of H$_2$ has been found to occur in some experiments and that may suffice for storage and other applications [3–9].

This chapter focuses on basic scientific questions concerning the structural, dynamical, and thermal properties of gases adsorbed in the environment shown in Fig. 9.1, a nanotube bundle. Much of the research to date has assumed that these bundles are ideal, consisting of identical, perfect, and parallel collections of tubes. More realistic analyses are based on simulations derived from distributions of tube radii (R) in typical laboratory samples [10, 11]. The role of such disorder should be taken into account when comparisons are made with the data.

Figure 9.1 exhibits the various adsorption sites accessible, in principle, to an adsorbate. The external surface region includes the so-called groove between pairs of nanotubes, an energetically favorable site because of the high coordination number of C atoms; the binding energy is typically a factor 1.7 times as large as that on graphite. Between a triad of nanotubes within the bundle lie “interstitial channels” (ICs). If not blocked at the end, the ICs are accessible to small atoms or molecules. Finally, there exists the “endohedral” region inside the individual tubes; access to this region usually requires chemical treatment to open the tube [12–15]. The subsequent sections of this chapter are organized by site.

**Figure 9.1** Simulation of adsorption of methane at 159.88 K and 0.05 bar on monodisperse and polydisperse distributions of nanotubes within bundles. (Adapted from Ref. [11].)
9.1 Introduction

This chapter describes results obtained from theoretical and simulation studies of adsorption in these geometries. Chapter 10 discusses the specific case of hydrogen adsorption, emphasizing the problems of gas storage and isotope separation. Chapter 17 deals with the results from experimental studies and compares these with relevant calculations. We confine our description to the results of the research and ignore the detailed assumptions and methods used in the calculations. At the outset, we note that most studies employ simplified model adsorption potentials, such as continuum versions of the tubes, rather than atomistic descriptions. This approach may be justified by our lack of knowledge of the geometry (e.g., polydispersity), on the one hand, and by the absence of reliable theories of adsorption potentials for the nanotube array, on the other. When we know the potential better than we do now, more sophisticated modeling will be possible (and probably necessary) for explaining experimental data.

A significant fraction of the research literature is focused on SWNTs having radius $R$ of order 0.7 nm. This is exemplified by a particular variety of tube, the so-called (10,10) “armchair” nanotube; the general ($n$, $m$) designation refers to the lattice vector of the graphene sheet identifying a line perpendicular to the hypothetical cutout employed to construct the tube. For this (10,10) species, the lattice vector is bent into a circumferential curve that is locally parallel to the C–C bonds of the tubes. This curve can pass through 20 C nuclei per revolution and corresponds to $R = 0.68$ nm. Much of the research literature makes the simplifying approximation that the tube consists of smeared-out helium, ignoring atomicity. Calculations indicate that this is usually a good approximation inside the tubes, where the coordination number of an atom is high, but it is less accurate for exohedral adsorption [16].

Nanotubes in the laboratory often exhibit an aspect ratio of 10,000, i.e., length $L$ approximately in microns. From the fundamental perspective, an important stimulus of this research is the realization that such a linear geometry provided by small $R$ nanotubes yields one-dimensional (1D) phases of matter; that description is certainly true from the phase transition perspective (since only one dimension approaches infinity in the thermodynamic limit). The subject of 1D matter has been studied as an academic problem for many years [17, 18]. An intriguing aspect of the subject is that no phase transitions occur in a strictly 1D system at finite temperature ($T$). In the nanotube environment, however, 1D lines of adsorbed molecules can interact with neighboring lines of molecules, resulting in a 3D transition at finite $T$. To this date, in fact, predictions have been made of 1D, 2D, 3D, and even 4D phases of matter in this novel environment [19, 20]. All such regimes will be discussed, to some extent, in this chapter and Chapter 15. The rich variety of phenomena has made theoretical study both enjoyable and rewarding.

The outline of this chapter is as follows: Section 9.2 discusses adsorption within the tubes; Section 9.3 addresses the subject of IC adsorption; and Section 9.3 describes adsorption on the external surface.
9.2 Endohedral Adsorption

9.2.1 General Remarks

This section deals with adsorption inside the nanotubes. Access of molecules to this region requires a sample preparation technique that leaves open the ends or the walls of the tubes, because molecules cannot tunnel through the close-packed, graphene-like tube wall (interatomic spacing 0.14 nm). The other possibility is that the tube forms around the molecules, as is likely to be the case for endohedral C$_{60}$ (the system nicknamed “peapods” [21]).

The interior of a tube is usually more attractive to an adparticle than the exterior because of the larger effective coordination experienced inside. This difference is exemplified in Fig. 9.2 for the case of Xe in a tube of radius 0.7 nm.

One may consider a wide variety of adsorbed molecules and nanotube sizes. The morphology of the adsorbed film depends on the relationship between the particle diameter ($\sigma$) and the diameter, $2R$, of the tube. This dependence stems from the potential energy function; an example is shown in Fig. 9.3 for the case of a C$_{60}$ molecule in nanotubes of different sizes [23].

Note that the energy minimum occurs on the axis, i.e., radial distance $r = 0$, for the smaller tube, while it lies near $r = 0.37$ nm for the larger tube. In the case of a Lennard-Jones (LJ) type of pair potential describing the molecule–C pair interaction, with hard-core parameter $\sigma_{\text{int}}$, the transition between these two types of behavior occurs at tube radius $R_{\text{trans}} = 1.212\sigma_{\text{int}}$ [24], where $\sigma_{\text{int}}$ is the LJ hard-core diameter of the gas–C interaction. Typically, an arithmetic combining rule is used to relate the lengths involved in the problem:

$$\sigma_{\text{int}} = \frac{(\sigma + \sigma_C)}{2}$$

![Figure 9.2](image_url) Xe atom’s interaction with a (10,10) nanotube. The left curve shows the interior region and the right curve shows the exterior region. (Adapted from Ref. [23].)
Here, \( \sigma \) is the diameter of the gas–gas interaction and \( \sigma_C \) is that of C, typically taken to have a value \( \sigma_C = 0.34 \text{ nm} \) for C atoms of graphene-like surfaces, a value based on the interlayer separation of graphite planes [25]. For the case of \( C_{60} \), this analysis predicts a crossover value \( R_{\text{trans}} = 0.8 \text{ nm} \). The potentials of Fig. 9.3, calculated by Hodak and Girifalco, are consistent with this finding. For a (10,10) tube, \( R = 0.68 \text{ nm} \); hence, the \( C_{60} \) molecule is localized near the axis; its motion at room temperature is limited to a domain of relative extent \( r/R < 0.01 \). The behavior of an ensemble of many \( C_{60} \) molecules is then well described by a 1D model, which has been employed by several authors [26–30]. In the case of a (15,15) tube, instead, \( R = 1.02 \text{ nm} > R_{\text{trans}} \), so that the potential minimum lies away from the axis. As seen in the figure, the molecule’s radial motion extends over a relative range \( \Delta r/R \sim 0.01 \) near \( r = 0.37 \text{ nm} \). Such a system of \( C_{60} \) molecules at low coverage and temperature might be well described by a 2D model, where the azimuthal motion provides the second dimension (in addition to the motion parallel to the \( z \) axis of the tube). Both continuum and lattice gas descriptions of this problem have been evaluated [29–36]. Figure 9.4 depicts the kind of interesting behavior that has been seen in simulation studies by Hodak and Girifalco [23]. At low \( T \), the system consists of two parallel strands of \( C_{60} \) molecules in nearly perfect registry. These strands disorder as \( T \) increases, but the fluctuations appear to be small at 50 K. Above 100 K, instead, the system resembles a poorly defined 1D chain of molecules. It is interesting that such a low temperature has a dramatic effect on a system for which the characteristic energy scales (gas–gas and gas–surface) are of order several tenths of an electron volt, which corresponds to \( T \sim 1000 \text{ K} \). We attribute this unstable behavior to the one-dimensionality of the peapod system, which precludes truly long-range order at any finite \( T \).

The issue of radial localization and “effective dimensionality” is somewhat different in the quantum case [16, 24, 37], as exemplified in Fig. 9.5, for the
Figure 9.4 Monte Carlo snapshot configurations of molecules inside a (15,15) nanotube at various temperatures and fixed density. (Adapted from Ref. [23].)

case $\sigma/(2R) = 0.26$. Note that the ground-state wave function of a He atom is relatively delocalized, extending over a region $\Delta r/R \sim 0.2$ because of zero-point motion. In the quantum description, single-particle wave functions are of the form

$$\psi_{mk}(r) = R(r) \exp[i(m\phi + kz)]$$

Here $R(r)$ is the ground-state radial wave function, $\phi$ is the azimuthal angle, $m$ is the azimuthal quantum number, and $k$ is the wave vector parallel to the $z$ axis of the tube. The figure also shows wave functions of a “helical” excited state (with $m = 1$) and a radial excited state. The latter states are of such high energy that they are often ignored. An interesting consequence of this spectrum is the specific heat, $C_N(T)$, shown in Fig. 9.6. In the classical case of low density depicted there, $C_N/N$ equals Boltzmann’s constant $k_B$ times the $(D/2)$, where $D$ is the dimensionality. In the present case, the behavior of the system is observed to be effectively 1D at low $T$ and 2D at higher $T$. The crossover temperature ($\sim 1\text{ K}$) is determined by the azimuthal (centrifugal) excitation energy; this varies as $<r>^{-2}$, where $<r>$ is the mean value of the radial coordinate [24].
9.2 Endohedral Adsorption

**Figure 9.5** Potential energy (dashed curve) and simplified model potential (full curve) for a $^3$He atom in a tube of radius 0.5 nm. The energies of the ground state and lowest azimuthally and radially excited states are shown as horizontal lines along with the corresponding wave functions (top to bottom). (Adapted from Ref. [37].)

**Figure 9.6** Heat capacity per atom, in units of Boltzmann’s constant, as a function of $T$ for a noninteracting gas of $^4$He atoms within a tube with $R = 0.5$ nm. The low $T$ limiting behavior is that of a 1D gas, while the high $T$ limit is that of a 2D gas. (Adapted from Ref. [24].)

One can study tubes of larger radius than those mentioned above. In such cases, adsorption occurs in a set of cylindrical shells. This kind of behavior has been explored as a general model of adsorption in porous media, using a wide variety of techniques [38–44]. For lack of space, we ignore such large-pore behavior in the remainder of this chapter.
9.2.2 Axial-Phase Transition

If the pore radius lies in an appropriate range, relative to $\sigma$, there can occur a so-called axial-phase transition. The term refers to capillary condensation in the case when a “shell” phase, bound to the wall, is gradually augmented by the appearance of a 1D “axial phase,” localized near $r = 0$. This transition is exemplified by the simulation results for $\text{H}_2$ in Fig. 9.7. One observes that at low chemical potential $\mu$ the film is localized at $r = 0.39$ nm, at close approach to the C cylindrical surface. As $\mu$ is increased above a threshold value, the axial phase appears rather abruptly. This behavior is demonstrated further in Fig. 9.8, which separates the total coverage into axial and shell contributions. At saturation, their ratio is about 6.9.

Since this transition is essentially a configurational phenomenon, similar behavior is expected for the case of a classical gas. Figure 9.9 shows an adsorption isotherm in such a case, computed with a lattice gas model in which seven “shell” sites near the tube wall surround each axial site. The figure compares results from mean field (MF) theory and Monte Carlo calculations [31, 32]. The axial “transition” is spread over a range of $\mu$ in both calculations since the temperature is above that of the MF axial-phase condensation. Although the MF results are qualitatively correct, they exhibit a spurious shell-filling transition at low $T$, seen in the figure as a coverage discontinuity near the reduced chemical potential $\mu^* = 2.2$. Similar spurious transitions arise in virtually all density functional studies of this problem, as these employ an MF approximation of the effective potential experienced by the particles; the effect of omitted fluctuations is particularly acute in 1D systems [42–44].

![Figure 9.7](image-url) Dependence on chemical potential $\mu$ of $\text{H}_2$ film density in a pore with $R = 0.7$ nm at 10 K. (Adapted from Ref. [34].)
9.2 Endohedral Adsorption

Figure 9.8 Adsorption isotherms for the case shown in Fig. 2.6; left ordinate (upper curve) depicts the shell areal density \( \theta \), while right ordinate (lower curve) shows the linear density \( N/L \) of the axial phase. (Adapted from Ref. [34].)

Figure 9.9 Adsorption isotherms for a lattice gas model consisting of shell and axial sites at the indicated temperatures (reduced by the pair interaction well depth) and various values of the reduced chemical potential. While mean field (MF) results exhibit a discontinuous shell-filling transition at \( T = 1 \), essentially exact Monte Carlo (MC) results show a near discontinuity there. (Adapted from Ref. [31, 32])

Figure 9.10 shows the specific heat at half-filling for this lattice model [31, 32]. The low \( T \) peak is due to a quasitransition of the shell phase, whereas the high \( T \) peak is due to promotion of atoms from the shell to the axial phase; the latter is analogous to heat capacity peaks on planar surfaces due to layer promotion [45, 46]. Qualitatively similar behavior was seen in a simulation of \( \text{CO}_2 \) in a (10,10) tube.
Figure 9.10  Specific heat (left scale) at half-filling for the lattice gas model shown in Fig. 9.9. Right scale denotes the contribution to $C_N$ due to promotion of atoms from shell to axial sites. (Adapted from Refs [31, 32].)

by Matranga et al. [12–15] (see Fig. 11 of that paper), which shows a similar energy increase attributed to gas evaporation from the shell phase.

9.2.3 Other Endohedral Transitions

In a bundle, 1D lines of molecules confined within one tube can interact with neighboring lines within parallel tubes. As a result, the system can undergo 3D transitions even though the molecular motion is essentially 1D. Two kinds of transition have been explored for this highly anisotropic problem. One is condensation of the vapor phase into a liquid [30, 47–50] and the other is crystallization of that liquid [51, 52]. Because these parallel lines of atoms experience weak interchannel interactions (compared with the intrachannel interactions), the transitions occur at very low temperature. Figure 9.11 exemplifies this phenomenon for the case of $C_{60}$ molecules, for which the intermolecular potential has a well depth of order 3000 K. When confined inside a bundle, the transition is manifested as van der Waals loops appearing below 500 K.

When the anisotropy is so large, the analysis is simplified, so that an analytic limiting expression can be derived. One asymptotic result of Fisher [53] has proved to be particularly useful for understanding the results of numerical calculations [30, 47–51]. The Fisher expression yields the critical temperature of an anisotropic lattice gas model, as follows:

$$K_B T_c = \frac{2J_l}{\left(\ln(1/c) - \ln[\ln(1/c)]\right)}$$

Here $J_l$ is the longitudinal interaction and $\epsilon = J_t/J_l$ is the ratio of the transverse to longitudinal interactions, where $\epsilon \ll 1$. The 1D limit $T_c^\ast = 0$ is approached only gradually (logarithmically) as $\epsilon$ goes to zero. Equivalently, the strictly 1D
9.2 Endohedral Adsorption

**Figure 9.11** 1D line pressure as a function of linear density $1/a$ for $C_{60}$ molecules, taking into account interactions between molecules in different tubes. Note the van der Waals loop below 570 K, signaling a phase transition. (Adapted from Ref. [30].)

The system is very sensitive to weak interchannel interactions, a consequence of the divergent correlation length of the 1D system at low $T$.

Figure 9.12 depicts the results of Carraro [51, 52] for showing a crystallization transition of similarly coupled 1D chains of molecules. As $T$ increases, at fixed

**Figure 9.12** Density and inverse particle displacement function, in reduced units, as described in text, as a function of reduced temperature showing crystallization of a system of coupled parallel chains of molecules. (Adapted from Refs [51, 52])
pressure, melting occurs at reduced temperature 0.15; this is manifested as a divergence of $< u^2 >$, the mean-square fluctuations of the particles about their equilibrium sites. Note that the transition is of higher than first order, because the density is continuous across the transition. The latter property also occurs in the 2D Kosterlitz–Thouless transition [54].

### 9.3 Adsorption in Interstitial Channels

When nanotubes gather spontaneously into bundles, they tend to pack into a hexagonal lattice leaving narrow ICs between the tubes where small atoms and molecules can be adsorbed. For example, in a typical (10,10) tube bundle, the distance between the center of the tubes is around 1.7 nm and the radius of the ICs is approximately 0.3 nm.

The possible realization of 1D matter when gas is adsorbed in these channels motivated the study of 1D and quasi-1D phases of several gases. For classical gases, the 1D equation of state is particularly convenient because there exists an analytical solution for the classical 1D equation of state for an arbitrary pair potential [17, 18]. There is one caveat: interactions beyond the nearest neighbor are neglected in that solution of the problem. These interactions, however, are weak and can be easily evaluated with perturbation theory, if necessary [55].

For quantum fluids, i.e., He and H$_2$, 1D studies require numerical methods. The ground-state and zero-temperature equation of state of such gases are of particular interest as these small adsorbates are the most likely to be adsorbed in the ICs [56]. In the case of 4He, the 1D ground state (minimum of the energy per atom, $E/N$) is an extremely weakly bound liquid [57–59] (Fig. 9.13); the cohesive energy is less than 3 mK; this value may be the lowest value for any many-body physical system ever studied. This situation is a consequence of the large zero-point energy. The liquid has a very low equilibrium density, corresponding to a mean interatomic spacing of about 2.5 nm. These results [59], obtained with the “exact” diffusion Monte Carlo (DMC) method, employ an empirical potential derived from 3D experiments [60]; if the conventional LJ He–He interaction were used instead, the system would not be bound at all (as is the case, incidentally, for 1D 3He). In reality, we do not know what interaction potential is appropriate for fluids adsorbed in the bundle environment. One study [61] has shown that the neighboring C atoms provide some reduction in the long-range attraction, in which case the real ground state may well be a 1D gas, rather than a low-density liquid. We note in passing that 2D liquid 4He has a binding energy of order 0.9 K, a factor $\sim 3000$ greater than the 1D result and eight times smaller than the 3D result [62].

A similar behavior was predicted for linear phases of H$_2$ and D$_2$. A system of H$_2$ molecules in a strictly 1D array and inside a narrow tube (radius $\sim 0.34$ nm) was studied using the DMC method [63]. The 1D calculation shows the existence of a self-bound state at $T = 0$ with a binding energy of 4.8 K. Very similar results
9.3 Adsorption in Interstitial Channels

![Figure 9.13](image)

Figure 9.13 Energy per $^4$He atom as a function of 1D density from the diffusion Monte Carlo (DMC) calculation (circles and full curve) of Boninsegni and Moroni [58]. Crosses are hypernetted chain results of Krotscheck and Miller [57]. Analogous DMC results were obtained by Gordillo, Boronat, Casulleras [59].

are obtained in the quasi-1D case of H$_2$ inside the tube where small transverse displacements (perpendicular to the tube axis) are allowed.

Studies of the 1D quantum gases at high density reveal the gradual development of strong interparticle correlations, manifested in the radial distribution function, corresponding to a nearly periodic structure [59, 63]. In that case, a quasicontinuous $T = 0$ liquid to solid transition was predicted. If the corrugation of the external potential is taken into account, a transition from a commensurate to an incommensurate state can also occur as the density increases [64]. An analysis following the ideas of Carraro [51, 52] would yield a genuine crystal if coupling between particles in neighboring grooves were included. Such a model calculation has not yet been undertaken however.

As discussed in Section 9.2.3, despite the apparent 1D nature of matter filling the channels, atoms in adjacent ICs of a bundle can interact with each other. In that case, a fully 3D condensation transition with a nonzero critical temperature can happen where the final condensed state is an anisotropic liquid [47–49]. This state is much more stable than the 1D liquid; for example, the binding energy of a He system [47, 48] increases from 2 to 16 mK. Although the interchannel interaction is very weak compared with the gas–gas interaction inside the channels, its presence is enough to drive the transition. On the
other hand, the critical temperature is mainly determined by the intrachannel interaction and weakly dependent on the strength of the interchannel interaction.

Another peculiar aspect of the adsorption in the ICs is the possibility that the adsorbed gas expands the lattice and/or deforms the tubes. Such changes in the structure of the bundle would happen provided the adsorption energy gain in the new environment overcomes the energy cost for deforming the lattice. In that respect, a theoretical study recently showed that hydrogen adsorption in the ICs may increase the separation between the tubes in a bundle, making the channels much more favorable for adsorption [65]. Figure 9.14 shows the dramatic effect of a small dilation (1%) in the potential and ground-state energy of a single hydrogen molecule within an IC. In that work, it is assumed that the tubes (all with the same diameter) form a perfect hexagonal lattice, and a uniform linear density of hydrogen is filling infinitely long and straight ICs. The total energy of the system, which includes the gas–gas, gas–tubes, and tube–tube interactions, is minimized to find the ground state (Fig. 9.15). It is found that the hydrogen can greatly increase its binding energy (from 280 K to 480 K) by slightly widening the ICs so that the gas condensation in the ICs at $T = 0$ involves an expansion of the bundle. This many-body effect can also be thought as a consequence of an “effective interaction” between the molecules that results from the gas–gas interaction mediated by the dilation of the lattice.

![Figure 9.14](image_url)  
**Figure 9.14** Probability density (top panel) and potential energy of $H_2$ as a function of perpendicular distance from the center of the interstial channels (IC). Dotted lines indicate the ground state energies. (Adapted from Ref. [65].)
The large increase in binding energy suggests the presence of a strong “effective interaction” that would lead to a high critical temperature for this transition. In the case of H$_2$, the critical temperature was estimated to be around 400 K. A less dramatic effect is found for smaller atoms such as He or Ne as in these cases the size of the ICs is near the optimal one. On the other hand, it is predicted that larger particles like Ar or CH$_4$ would be adsorbed in the ICs only if this dilation occurs. More recently, the results of this model have been tested using DMC techniques yielding a rather good agreement [66].

At this point, it is important to briefly review the experimental results concerning interstitial adsorption. This topic has been one of the most controversial issues in the study of gas adsorption in carbon nanotubes probably because the accessibility of the ICs may be different in different samples. For He, the ICs provide the most attractive sites of the bundle and there is at least some evidence that the atoms enter the channels [67–70]. The most recent one is based on a very high value of the isosteric heat obtained at very low coverage that can only be explained with the interstitial adsorption [71]. The case of H$_2$ is somewhat different since the binding energy in the grooves is greater than in the ICs (at least 100 K larger considering a lattice dilation). Here, a determination of the isosteric heat of adsorption of H$_2$ and D$_2$ at low coverage shows a considerable isotopic effect, a difference of about 200 K that has to be originated by a high confinement of the gas like the one that happens in the ICs [72]. Another piece of evidence comes from adsorption isotherms of H$_2$ measured at 90 K. In that case, a kink and an abrupt slope in the isotherm at nearly 40 atm seems to show a transition to higher coverage states. The authors attribute this behavior to H$_2$ permeating between the tubes that separate to allow
the interstitial adsorption [73]. Although somewhat indirect, this work would confirm the presence of the dilation-induced adsorption explained above. In addition, shifts in the Raman spectra of H₂ adsorbed in the bundles seem to indicate the population of the ICs [74].

With respect to some other gases, recent neutron scattering measurements have shown no lattice dilation when Ar or CH₄ is adsorbed in the bundle [75, 76]. However, to explain the adsorption isotherms, the authors still claim that there could be some interstitial adsorption if one considers that the adsorption happens in heterogeneous bundles (where the tubes have different diameters) of flexible tubes. In this case, the tubes would deform to accommodate these larger adsorbates [76]. In fact, a similar conclusion has been drawn from a recent computer simulation study of CH₄ adsorption on heterogeneous bundles, without considering the flexibility of the tubes [11]. On the other hand, another experimental study of gas adsorption concluded that Ne, CH₄, and Xe were not adsorbed in the ICs [77]. We note that the T = 0 K theory predicts IC adsorption of heavy gases only at very high μ, far above the threshold for groove adsorption on the external surface. For smaller gases such adsorption seems a logical concomitant of current potential models.

Different kinds of novel phenomena have been predicted when gases are adsorbed in the ICs. Among them is the possibility of using these channels as quantum sieves for separating isotopic mixtures [78]. This effect, discussed in Chapter 15, is based on the difference in binding energies of the isotopes that results from the difference in their zero-point kinetic energy that arises in confined environments. Another intriguing prediction involves the possibility of observing an unusual Bose–Einstein condensation of H₂ adsorbed in the ICs. In this case, a 4D behavior is expected for this system if tubes of different sizes are considered within a bundle [79].

9.4 External Surface

The external surface of a nanotube bundle is accessible to any adsorbate and for many gases that is the only region that needs to be considered. Such is the case of closed tubes and either blocked ICs or medium- to large-size molecules that do not fit in the ICs.

Molecules in the groove region, between two tubes, experience an attraction provided by two neighboring tubes. In that case, the heat of adsorption is nearly twice the value on graphite [56, 80–83]; the ratio is somewhat less than 2 because the tubes are convexly curved, reducing the effective coordination number of an adatom (relative to the planar surface value), and because graphite includes many underlying layers that increase the binding energy on a planar surface. Further adsorption occurs on the remainder of the external surface, which is somewhat less attractive than the surface of graphite for the same two reasons.
9.4 External Surface

The groove is a region of particular importance for fundamental reasons. Several studies of strictly 1D matter (see Section 9.3) have been undertaken in order to describe this regime of adsorption. On the other hand, simulation studies have been undertaken to describe classical adsorption on the external surface [11, 83–85]. The results tend to have common features, differing only in detail as a consequence of variable adsorption potentials [86]. As an example, Ne adsorption isotherms and density are shown in Figs 9.16 and 9.17. In these data, the ordinate $N$ refers to the number of atoms per groove within one simulation cell, of length 3 nm. Then, about $N = 9$ atoms corresponds to close-packing for 1D Ne. The isotherms show the gradual formation of the 1D film within the groove, for $N < 9$. This regime of low $\mu$ is followed by a coverage jump to a so-called three-stripe phase, with $N = 27$. The meaning of this name is evident from the density plot, i.e., the system consists of three parallel lines of Ne atoms, symmetrically arranged above the groove.

The next jump in the isotherm, which shows hysteresis, is to the complete monolayer phase. The hysteresis arises from the existence of two distinct phases, seven-stripe and eight-stripe, which have nearly equal free energies; these are seen in the density plot. Above the monolayer regime there occurs a step, of height $\Delta N = 9$, in the isotherm that is clearly seen in the density profile as a “second-layer groove phase.” Even this feature was seen in the experimental isotherm data of Migone’s group [87].

These simulation results were obtained using a simplification of the geometry: the surface was assumed to be an infinite, periodic array of parallel tubes lying on a flat surface. If a more realistic description of a nanotube bundle were used, the abrupt transitions appearing above would all become rounded. This can be seen in Fig. 9.18 for the case of $\text{CH}_4$. 

Figure 9.16  Ne isotherms at temperatures shown, depicting step-like growth and hysteresis at monolayer completion ($N \sim 70$). Coverage scale is defined in the text. (Adapted from Ref. [81].)
Figure 9.17  Density of Ne at $T = 12\,\text{K}$ and $\log P\,\text{(atm)} = -19$, $-16$, and $-9$, from top to bottom. The middle curve superimposes results for nearly degenerate seven-stripe and eight-stripe phases of the monolayer. (Adapted from Ref. [84].)

Figure 9.18  Isosteric heat of adsorption for CH$_4$ from experiments (circles) and simulations. The diamonds (squares) are for adsorption onto heterogeneous (homogeneous) bundles. (Adapted from Ref. [11].)
9.4 External Surface

These classical simulation results are not quantitatively reliable below the Debye temperature due to the onset of quantum effects. The extreme example is He, described earlier, which does not condense above $T = 0$. The other noble gases and CH₄ are of considerable experimental interest; these exhibit quantum effects below about 100 K in 3D. A number of phonon analyses have been undertaken for these gases, beginning with work of Siber [88]. Figure 9.19 shows typical data for the case of the three-stripe phase of CH₄. As this phase includes three atoms per unit cell, the spectrum includes nine branches. At low $T$, the mode denoted L₁ is the only one excited. It is seen to correspond closely to the 1D phonon mode (at the same density) at long wavelengths but exhibits an avoided crossing with another longitudinal mode (L₂) near phonon wavelength equal to 10 times the lattice constant, i.e., about 4 nm. Thus, the thermal behavior is essentially that of a 1D system ($C$ proportional to $T$) only below about 15 K [89]. The approach to fully 3D behavior (i.e., $C_N \sim 3/2Nk_B$) appears for all gases studied to date somewhat above 50 K and that classical limit is achieved above 100 K. The predictions of these phonon theories are amenable to testing with both low $T$ specific heat and inelastic or quasielastic neutron scattering measurements.

![Figure 9.19](image)

**Figure 9.19** Phonon dispersion relation (angular frequency vs. relative wave vector) for the three-stripe phase of CH₄ on the external surface of a bundle. L₁, L₂, and L₃ are longitudinal branches, i.e., molecular motion parallel to the groove. The dotted curve is the result for a 1D adsorbate at the same density. (Adapted from Ref. [89].)
Chapter 9: Adsorbed Gases in Bundles of Carbon Nanotubes: Theory and Simulation

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REFERENCES

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86. Aldo Migone and Oscar Vilches have affirmed that their data shows evidence of corresponding states behavior, where the particle diameter is scaled by the experimental diameter on a graphite surface.


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AU1 | “The next chapter” has been changed to “Chapter 10”. Please check if this is OK.
AU2 | “The subsequent hydrogen chapter” has been changed to “Chapter 15.” Please check if this is OK.
AU3 | Please clarify whether “Matranga et al. [12–15] (see Fig. 11 of that paper)” could be changed to “Matranga et al. [14] (see Fig. 11 of that article)”
AU4 | “the hydrogen chapter” has been changed to “Chapter 15”. Please check if this is OK.
AU5 | Please provide the volume number and page number.
AU6 | Please provide the complete details of Aldo Migone and Oscar Vilches. And also please advise whether we can move “have affirmed that ... graphite surface” to the text part so as to read “Aldo Migone and Oscar Vilches [87] have affirmed that ... graphite surface.”?
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