



# Statistical mechanical lattice models of endohedral and exohedral xenon adsorption in carbon nanotubes and comparison with Monte-Carlo simulations

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## ABSTRACT

Adsorption of xenon in carbon nanotubes has been investigated by Kuznetsova et al. [A. Kuznetsova, J.T. Yates Jr., J. Liu, R.E. Smalley, *J. Chem. Phys.* 112 (2000) 9590] and Simonyan et al. [V. Simonyan, J.K. Johnson, A. Kuznetsova, J.T. Yates Jr., *J. Chem. Phys.* 114 (2001) 4180] where endohedral adsorption isotherms show a step-like structure. A matrix method is used for calculation of the statistical mechanics of a lattice model of xenon endohedral adsorption which reproduces the isotherm structure while exohedral adsorption is treated by mean-field theory.

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## 1. Introduction

The discovery of carbon nanotubes [1,2] occurred almost two decades ago, yet despite much effort, unresolved questions remain about the adsorption properties of these materials and nanotubular structures in other forms [3] of carbon (for a review of nanotubular adsorption see [4]). Such materials exhibit potential for numerous applications due to their microscopic structure. It is expected that matter adsorbed in such nanochannels [5] might exhibit unusual behaviour due to the reduced dimensionality. Inert gases are of particular interest and adsorption of xenon in carbon nanotubes has been investigated both experimentally by Kuznetsova et al. [6] and theoretically by Simonyan et al. [7]. Adsorption isotherms obtained by Monte-Carlo simulation for endohedral xenon adsorption in isolated carbon nanotubes [7] show a step-like structure (see Fig. 1) while exohedral adsorptions isotherms are more conventional. Here, we present the results of matrix based statistical mechanical calculation [8–12] of a lattice model of endohedral xenon adsorption in a narrow nanotube considered as sites on the walls of a cylinder using a matrix method, while exohedral adsorption is treated by mean-field theory. For a range of interaction parameters the model reproduces the unusual features in the adsorption isotherms. We find a step in the xenon adsorption isotherm caused by intermolecular interactions and the energetic cost of packing atoms into the same neighbourhood.

This work parallels similar work by Trasca et al. [13] and Trasca et al. [14] and that by Gubbins and co-workers [5]. The agreement with the Monte-Carlo simulations of Simonyan et al. [7] gives us confidence in our model and method thereby allowing us to vary rapidly to calculate a series of isotherms at a range of temperatures and at much less computer time than the simulations.

We focus in this paper on narrow-bore (10,10) nanotubes (diameter 13.56 Å) shown in Fig. 2 which may be expected to differ significantly in properties from those with larger diameters. Recent work by Jiang et al. [15] has presented simulated isotherms for alkane adsorption in wide-bore (40.68 Å diameter) carbon nanotubes with smooth walls. These isotherms do show evidence for condensation phenomena probably due to the large diameter and intermolecular interactions.

We consider an ideal xenon vapour phase at ambient pressure and temperature  $P$ ,  $T$  in equilibrium with an adsorbed phase of atoms in the nanotube. In our lattice model we separate the problem into two non-interacting systems, one exohedral and the other endohedral both at the same chemical potential as the vapour phase.

Lattice models of adsorbed fluids have been widely discussed [10–12,16–21] and can successfully model unusual adsorption features displayed by porous materials. In order to have confidence in our results for the one-dimensional endohedral adsorbed phase an accurate statistical treatment of is essential. Here the Grand Partition function for the endohedral adsorbed component in a nanotube is evaluated using a matrix method [10–12]. The exohedral phase is modeled as adsorption on a two-dimensional layer which is a reasonable approximation for a nanotube of sufficient diameter.

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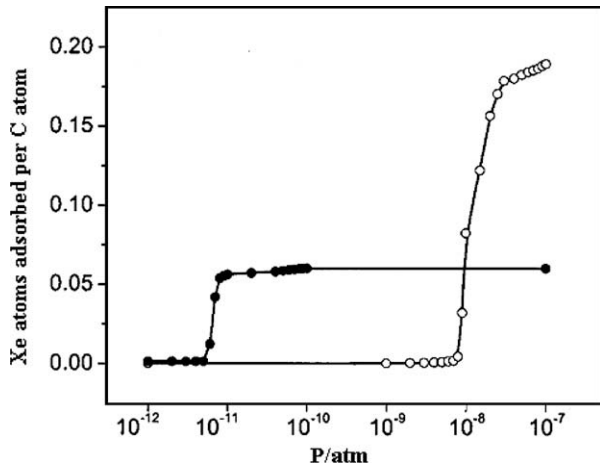


Fig. 1. Adsorption of xenon at 95 K on the endohedral and exohedral (filled and open spheres surfaces, respectively) of an isolated (10,10) carbon nanotube (adapted from Simonyan et al., Ref. [7]).

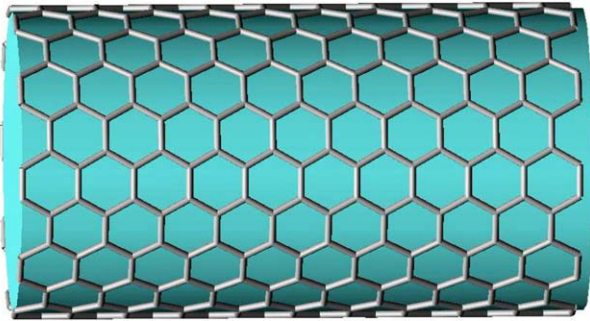


Fig. 2. Structure of a (10,10) carbon nanotube (reproduced from <http://www.jcrystal.com/steffenweber>).

## 2. Matrix method for grand partition function for endohedral adsorption

In our lattice fluid model, it is assumed there are groups of adsorption sites along the nanotube walls. At the highest density the tube would contain along the tube repeating units of 4 Xe atoms as shown in Fig. 4 of Ref. [7]. This is not an exact representation of the adsorbed phase but is thought to realistically mimic the adsorption sites in the pore. Each adsorption site can be occupied by an adsorbed atom or is vacant (occupied by a ‘hole’). We ignore any issues arising from the corrugation of the tube, treating the nanotube wall as smooth.

We present the theory for our model for the general case of  $N$  rings each with  $n = 4$  adsorption sites along the nanotube so that there are  $nN$  adsorption sites on the inside of the nanotube. All 4 sites on a ring are assumed to be energetically accessible to xenon atoms. We assume cyclic boundary conditions and consider the possible configurations of species with 0, 1, 2, ..., 4 identified by the index  $i$  on a chain of  $N$  rings. Each ring with  $n = 4$  sites may be occupied by  $i$  atoms in a variety of configurations each of which represents one of  $g_i = n!/(n-i)!!$  types of cluster of class  $i$ . We assume that following Simonyan et al. [7] that the potential energy of a single adsorbed xenon atom is  $U$  ( $-2800$  k, where  $k$  is Boltzmann’s constant). To simplify the analysis we will assume that all clusters of atoms of type  $i$  in the same ring have an energy  $B_i$  which arises from interactions between species on the same ring and we treat all such clusters in the same class as a single species

with degeneracy  $g_i$ . The  $B_i$  interaction parameters ( $i = 0, 1, \dots, 4$ ) are critical for controlling the isotherm steps and implicitly take into account the loss of free energy when a pair of non-spherical atoms is pushed together at short range. For clusters composed of 2 atoms ( $B_2 = \epsilon$ ), for 3 atoms per cluster ( $B_3 = 3\epsilon$ ) and for 4 atoms per cluster ( $B_4 = 6\epsilon$ ). The clusters on nearest-neighbour rings also interact. The parameter  $J_{\mu\nu}$  is the interaction energy between pairs of clusters  $\mu, \nu$  on nearest-neighbour rings and is calculated using the estimate  $J_{\mu\nu} = \mu\nu\epsilon$  where  $\epsilon$  ( $-221$  k) is the well-depth in a Lennard–Jones potential for pairs of xenon atoms. The product  $\mu\nu$  is a measure of the number of pair interactions between clusters.

The vibrational and translational degrees of freedom of a heavy adsorbed xenon atom confined inside the nanotube contribute a factor to the partition function of the endohedral phase which is assumed to be small and negligible.

The Grand Partition function  $\Xi$  for the endohedral adsorbed phase is given by

$$\Xi = \sum_{M=0}^{\infty} \exp\left(\frac{\mu M}{kT}\right) Q(M, nN, T) \quad (1)$$

$\mu$  is the chemical potential.  $Q(M, nN, T)$  is the canonical partition function for  $M$  interacting atoms adsorbed over  $nN$  sites in a nanotube. We assume that occupation of sites by pairs of atoms is energetically forbidden so that we have

$$\Xi = \sum_{M=0}^{nN} \exp\left(\frac{\mu M}{kT}\right) Q(M, nN, T) \quad (2)$$

There are now at most  $nN$  atoms on the lattice. By inspection it can be seen that  $\Xi$  may be written as the sum of the products of  $N$  factors given by

$$\Xi = \sum_{(\alpha=0,1,2,3,4)} \sum_{(\beta=0,1,2,3,4)} \cdots \sum_{(\omega=0,1,2,3,4)} A_{\alpha\beta} A_{\beta\gamma} A_{\gamma\delta} \cdots A_{\omega\alpha} \quad (3)$$

The factors above are given by

$$A_{\mu\nu} = (\phi_{\mu}\phi_{\nu})^{\frac{1}{2}}\phi_{\mu\nu} \quad (4)$$

$$\phi_0 = 1 \quad (5)$$

$$\phi_i = g_i \exp\left[\frac{[i \cdot (\mu - U) - B_i]}{kT}\right] \quad (6)$$

$$\phi_{\mu\nu} = \exp\left(\frac{-J_{\mu\nu}}{kT}\right) \quad (7)$$

Using the inner product rule  $D_{ij} = \sum B_{ik}C_{kj}$  for matrix multiplication of a pair of matrices  $\mathbf{B}$  and  $\mathbf{C}$  the Grand Partition function can be expressed as

$$\begin{aligned} \Xi &= \sum_{(\alpha=0,1,2,3,4)} (A^N)_{\alpha\alpha} = \text{Trace}(A^N) \\ &= (\lambda_1)^N + (\lambda_2)^N + (\lambda_3)^N + (\lambda_4)^N + (\lambda_5)^N \end{aligned} \quad (8)$$

where  $\lambda_1, \lambda_2, \dots, \lambda_5$  are the eigenvalues of the matrix  $\mathbf{A}$  whose elements are defined above.

For macroscopically large  $N$  we then obtain

$$\Xi = (\lambda_{\max})^N \quad (9)$$

where  $\lambda_{\max}$  is the largest eigenvalue of the above matrix which can be obtained numerically.

The mean number of adsorbed atoms  $\rho$  given by the relation

$$\rho = \frac{kT}{n} \cdot \frac{\partial}{\partial \mu} \ln(\lambda_{\max}) \quad (10)$$

The chemical potential of a component in an ideal gas is given by [22–24]

$$\mu = \mu^0 + kT \cdot \ln(P) \quad (11)$$

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