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Encapsulation of methane molecules into carbon nanotubes

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ABSTRACT

Methane gas (CH_4) is a chemical compound comprising a carbon atom surrounded by four hydrogen atoms, and carbon nanotubes have been proposed as possible molecular containers for the storage of such gases. In this paper, we investigate the interaction energy between a CH_4 molecule and a carbon nanotube using two different models for the CH_4 molecule, the first discrete and the second continuous. In the first model, we consider the total interaction as the sum of the individual interactions between each atom of the molecule and the nanotube. We first determine the interaction energy by assuming that the carbon atom and one of the hydrogen atoms lie on the axis of the tube with the other three hydrogen atoms offset from the axis. Symmetry is assumed with regard to the arrangement of the three hydrogen atoms surrounding the carbon atom on the axis. We then rotate the atomic position into 100 discrete orientations and determine the average interaction energy from all orientations. In the second model, we approximate the CH_4 molecule by assuming that the four hydrogen atoms are smeared over a spherical surface of a certain radius with the carbon atom located at the center of the sphere. The total interaction energy between the CH_4 molecule and the carbon nanotube for this model is calculated as the sum of the individual interaction energies between both the carbon atom and the spherical surface and the carbon nanotube. These models are analyzed to determine the dimensions of the particular nanotubes which will readily suck-up CH_4 molecules. Our results determine the minimum and maximum interaction energies required for CH_4 encapsulation in different tube sizes, and establish the second model of the CH_4 molecule as a simple and elegant model which might be exploited for other problems.

1. Introduction

Nanotechnology promises much for the world in terms of novel nanodevices and new technologies, and many advances stemming from it are already being implemented. Two sectors that nanotechnology has the potential to revolutionize are energy and the environment. The need for cleaner fuels has become critical due to the heavy demand for products made from natural gas, and CH_4, which is the main constituent of natural gas, has been proposed as a possible source of clean energy. This idea is increasingly becoming more relevant in a world that requires sources of energy which are both renewable and environmentally sustainable. Many studies have examined the use of CH_4 as a source of energy, but more research is still needed. Most of the quantitative studies carried out deal with the storage and adsorption of CH_4 in nanotubes. The idea of expanding the size of an opening on a C_{60} using successive cage scission so as to achieve the encapsulation of CH_4 in the chemically modified cage was first proposed by Whitener et al. [1]. High temperatures and pressures are essential in making the insertion of CH_4 into the cage possible. Lee et al. [2] investigate the adsorption equilibria for CH_4 on multi-walled carbon nanotubes using the static volumetric method at different temperatures and pressures. Other studies on the adsorption of CH_4 on single-walled carbon nanotubes, for example Tanaka et al. [3], employ a functional density theory model for the adsorption of CH_4 on single-walled carbon nanotubes. They assume an homogenous cylindrical tube for the open-ended single-walled carbon nanotube and model an isolated single nanotube as opposed to aligned bundles of nanotubes which are usually found.

A more mathematical approach has been adopted by Thornton et al. [4] for which interactions between a gas molecule and a pore wall are investigated, in order to predict gas diffusion regimes for different pore sizes, shapes and compositions. Using the Lennard-Jones potential for the molecular interactions, the study also predicts transport of light gases, including CH_4, through carbon tubes and slits. Their novel approach suggests that gases can accelerate through the entrance of the pore opening due to the large molecular forces. Other novel studies include the possibility of storing CH_4 in bottle-like nanocapsules (a system of combined nanotubes forming bottle-like pores) with the added advantage of having a fill-and-lock mechanism for CH_4 storage [5]. These authors examine the effects of different tube radii and an applied electric field on the filling strengths of the nanocapsule with CH_4.

To the present authors' understanding, very little work has been carried out on the mathematical modeling describing the encapsulation and interaction of CH_4 with carbon nanotubes. The

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work presented here is aimed at developing mathematical models using classical applied mathematics to describe different orientations of a CH_4 molecule and its interactions with an open-ended carbon nanotube. The Lennard-Jones potential for non-bonded atoms and the continuous approximation, which assumes that the interatomic interactions can be modelled by smearing the atoms uniformly across the surfaces, are used to determine the molecular interaction energy for each of the atoms of the CH_4 molecule and the carbon nanotube. Carbon nanotubes of varying radii are investigated and the total interaction energy for the CH_4 molecule is obtained. We comment that the present study assumes an ideal environment, but the storage of CH_4 in nanosystems is more complex, however, and should include a study of temperature dependence of adsorption capacity. These considerations are outside the scope of this study. The Lennard-Jones potential employed in calculating the energy potential is described in the following section, and the subsequent section gives a brief derivation of the basic results of this paper. The final section provides a discussion of the results in this paper.

2. Continuous approximation and Lennard-Jones potential

In this section, we outline the techniques employed in calculating the total interaction energy between a CH_4 molecule and a carbon nanotube. We assume two different models (I) and (II) for the CH_4 molecule as shown in Fig. 1(a) and (b), respectively. The first model, which describes an orientation that is rotationally symmetric about the nanotube axis is subdivided into two configurations; one which describes a particular orientation as shown in Fig. 1(a), and the other an average of 100 distinct orientations. The CH_4 molecule is located such that the carbon atom and one of the hydrogen atoms are lying on the axis of the nanotube as shown in Fig. 1, with the other three hydrogen atoms located off the axis of the tube. We also assume that each atom of the CH_4 molecule is well defined by its coordinate position. We derive the total interaction energy as a sum of the individual interaction

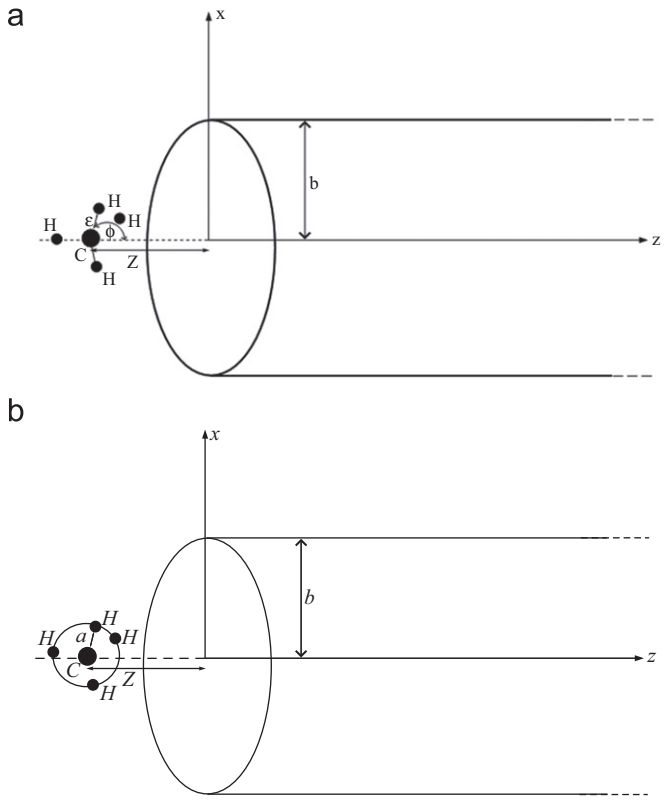

Fig. 1. CH_4 entering a carbon nanotube for models (I) and (II).

Table 1
Numerical values of constants used.

Parameters	Values
Radius of (9,5)	$b=4.813$ Å
Radius of (8,8)	$b=5.428$ Å
Radius of (10,10)	$b=6.784$ Å
Radius of hydrogen-sphere	$a=1.1$ Å
Attractive constant C–C[a]	$A=17.4$ eV Å^6
Repulsive constant C–C[a]	$B=29\,000$ eV Å^{12}
Attractive constant C–H[b]	$A=14.94$ eV Å^6
Repulsive constant C–H[b]	$B=14\,544$ eV Å^{12}
Mean surface density of hydrogen-sphere	$\eta_2=0.263$ Å^{-2}
Mean surface density of carbon nanotube	$\eta_1=0.3812$ Å^{-2}

[a] Denotes data from Ref. [6].
[b] Denotes data from Ref. [7].

energies for all the atoms in the CH_4 molecule and the carbon nanotube. We then derive a rotational matrix R, to define a general co-ordinate position which we employ to calculate the average interaction energy for 100 different orientations of the CH_4 molecule. The second model assumes that the CH_4 molecule has the carbon atom on the axis of the carbon nanotube, while the four hydrogen atoms are smeared over a spherical surface of a certain radius a ($a=1.1$ Å, C–H bond length in CH_4) which is centered on the carbon atom.

The Lennard-Jones potential function for two non-bonded atoms is given by

$$v(\rho) = -A\rho^{-6} + B\rho^{-12}, \tag{1}$$

where A and B denote the attractive and repulsive constants, respectively, as given in Table 1, and ρ is the distance between two typical surface elements. Using the continuous approximation which assumes that the carbon atoms on the carbon nanotube can be replaced by smearing the atoms over the entire surface and using a uniform atomic surface density, the total interaction energy is given by

$$E = \eta_1\eta_2 \int\int v(\rho)\, dS_1\, dS_2, \tag{2}$$

where η_1 and η_2 denotes the mean surface densities of the nanotube and the CH_4 molecule, respectively, and $v(\rho)$ is the Lennard-Jones potential function for two non-bonded atoms with typical surface elements dS_1 and dS_2. In summary, the calculation reduces to (i) calculating the interaction energy of an on axis carbon atom or hydrogen atom with a carbon nanotube, (ii) calculating the interaction energy of an offset hydrogen atom and a carbon nanotube, and this calculation may be used for the two other hydrogen atoms due to the assumption of symmetry for the hydrogen atoms of the CH_4 molecule off the axis of the tube, (iii) calculating the average interaction energy for 100 CH_4 orientations by rotating the four hydrogen atoms around the axis, and (iv) calculating the interaction energy of an on axis hydrogen shell and a carbon nanotube. Finally, to facilitate the evaluation of the integrals, we assume that the carbon nanotube is semi-infinite in length, which is reasonable for a molecule entering one opening of a carbon nanotube, because the non-bonded interactions modeled here operate over very small distances, which are of the order of a few nanometers.

3. Analysis

For the first model (see Fig. 1(a)), the total interaction energy between CH_4 and a carbon nanotube is given as the sum of the individual interaction energies. We define a Cartesian coordinate system with its origin located at the center of the open end of the carbon nanotube, and the nanotube axis co-linear with the