ORIGINAL PAPER

Modelling of carbon dioxide: methane separation using titanium dioxide nanotubes

Duangkamon Baowan

Abstract The separation of carbon dioxide (CO_2) and methane (CH_4) mixture is of considerable interest in order to purify natural gas, and one suggestion is that titanium dioxide (TiO_2) nanotubes might be exploited to separate a gaseous mixture of methane and carbon dioxide. In this study, we employ both Coulomb's law and the Lennard–Jones potential to determine the total energy of adsorption CO_2 and CH_4 into a TiO_2 nanotube. The CH_4 is a nonpolar molecule, and therefore the Coulombic interaction may be neglected. The total energy of the systems is evaluated utilizing the continuous approximation, which assumes that the two gas molecules are spheres of certain radii, while the tube is modelled as a cylinder. Further, both electrostatic and van der Waals potentials are determined and expressed in the exact analytical formulae. The numerical results predict that a single molecule of CO_2 or CH_4 can be encapsulated into the tube. On assuming both gases may form clusters with the same proportion of atom species, a cluster of CO_2 will not be adsorbed into the tube when its radius exceeds 3.32 Å. On the other hand, a cluster of CH_4 can be encapsulated into an appropriate radius of TiO_2 nanotube. These results indicate that TiO_2 nanotubes may be useful in the purification of CH_4.

Keywords Gas separation · Lennard–Jone potential · Coulombic interaction · Mathematical model

D. Baowan (✉)
Department of Mathematics, Faculty of Science, Mahidol University,
Rama VI Rd., Bangkok 10400, Thailand
e-mail: scdbw@mahidol.ac.th

D. Baowan
Centre of Excellence in Mathematics, CHE, Si Ayutthaya Rd., Bangkok 10400, Thailand

1 Introduction

Methane (CH_4) is a major component of natural gas and it is a colorless, odorless and nontoxic gas. On combustion CH_4 releases carbon dioxide (CO_2) and water (H_2O), and CO_2 is presently considered to be the cause of the greenhouse gas effect. In addition, CO_2 is found as an impurity in natural gas. Accordingly, the separation of CH_4/CO_2 mixture using an appropriate adsorbent would be practical in order to purify the natural gas, and to store the CO_2 and not allow emissions into the atmosphere [1].

Baborao et al. [1] studied silicalite, C_{168} schwarzite and IRMOF-1 as adsorbents to separate a binary gas mixture of CO_2 and CH_4, and they showed that the IRMOF-1 has the highest adsorption capacity amongst the three adsorbents. Huang et al. [2] employed Monte Carlo simulations to extensively study the adsorption behaviour of CO_2/CH_4 into carbon nanotubes in various environments. Their results predicted that the adsorption selectivity of CO_2 exceeds that of CH_4 under all conditions. Further, Pent et al. [3] used canonical Monte Carlo simulations to study the encapsulation of CO_2 and CH_4 in the binary combinations of $CH_4 - CO_2$ and $N_2 - CO_2$ onto C_{60} fullerenes. They also found that the carbon fullerene is an outstanding material to adsorb CO_2. Moreover, a number of other studies have examined the adsorption of CH_4 and CO_2 on or into carbon nanostructures, and most conclude that the CO_2 molecule is more likely to be adsorbed by carbon nanostructures than the CH_4 molecule [3–8]. We refer the reader to Keller and Staudt [9] and to Catlow et al. [10] for a comprehensive summary of experimental and simulation studies in this area.

In this paper, we consider the separation of CO_2 and CH_4 using TiO_2 nanotube. The formation of TiO_2 nanotubes was firstly reported by Kasuga et al. [11] in 1998 with potential applications as adsorbents and as deodorants, especially for metallic, inorganic and organic materials [11]. Moreover, TiO_2 nanostructures are believed to improve dye sensitized solar cells performance [12]. In this paper we provide the critical dimensions necessary when using a TiO_2 nanotube membrane to separate a gaseous mixture of CH_4 and CO_2. In particular, we provide the critical radii of the nanotubes which will allow CH_4 to pass, but will prevent CO_2 from passing through. This theoretically-derived data will allow experimentalists to focus their work within a restricted range of nanotube radii and lengths. We employ both Coulombic and Lennard–Jones potential functions to determine the adsorption of CO_2 and CH_4 into the nanotube, while the continuous approach is utilized to determine the total potential energy of the system, which can be analytically evaluated in closed form. We note that the CH_4 molecule has no electrostatic charge, and therefore the Coulombic term may be neglected.

The present paper is organised as follows. The coulomb and Lennard–Jones terms as well as all parameters used in the model are presented in the next section. Following that the mathematical derivations for the total energy of the system are given in Sect. 3. Numerical results are presented in Sect. 4 and finally some concluding remarks are made in Sect. 5.

2 Electrostatic and Lennard–Jones potential functions

The total potential energy in the model is assumed to be given by

$$E^* = \sum_{i \neq j} \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r_{ij}} + \sum_{i \neq j} \left(-\frac{A}{r_{ij}^6} + \frac{B}{r_{ij}^{12}} \right),$$

where the first term represents the electrostatic energy and the second term is the van der Waals energy for atoms i and j at a distance r_{ij} apart. In this equation, q_1 and q_2 are the electrostatic charges of the two atoms where opposite signs produce an attractive potential, otherwise we have a repulsive potential, ϵ_0 denotes the electrical permittivity of space, and A and B are the attractive and repulsive Lennard–Jones constants, respectively.

Using the continuous approach, which assumes that the atoms at discrete locations on the molecule are averaged over a surface, so that the molecular interatomic energy is obtained by calculating integrals over the surfaces of each molecule, and is given by

$$E = \eta_1 \eta_2 \frac{1}{4\pi\epsilon_0} \int_{S_1} \int_{S_2} \frac{q_1 q_2}{r} dS_1 dS_2 + \eta_1 \eta_2 \int_{S_1} \int_{S_2} \left(-\frac{A}{r^6} + \frac{B}{r^{12}} \right) dS_2 dS_1,$$

where η_1 and η_2 represent the mean atomic surface densities of atoms on each molecule. Further, we may define the integrals I_n of the form

$$I_n = \int_{S_1} \int_{S_2} \frac{1}{r^n} dS_1 dS_2, \tag{1}$$

where here n takes the values $n = 1, 6$ and 12.

The numerical values of the Coulombic potential parameters for CH_4 and CO_2 are taken from the work of Babarao et al. [1] while those for TiO_2 are utilized from TiO_2-II structure which can be found in [13]. The numerical values of the Lennard–Jones parameters used for nonbonded interaction for each atom element are taken from the work of Mayo et al. [14]. Moreover, the usual Lorentz–Berthelot mixing rules [15] are used to calculate the cross interaction parameters. All the numerical values of the parameters used in this model are presented in Table 1. Both the CO_2 and CH_4 molecules are modelled as spheres with a carbon atom at the centre, and where the radius of oxygen (hydrogen) sphere is assumed to be 1.163 (1.100) Å, which gives rise to a mean surface density of 0.1177 (0.2613) Å^{-2}. We note that the radius of the oxygen (hydrogen) sphere is taken from a bond length between the carbon (carbon) atom and the oxygen (hydrogen) atom in CO_2 (CH_4) molecule which are approximating values under the continuous approach. The value of the mean atomic surface density for the TiO_2 nanotube is 0.0750 Å^{-2} [16]. Specifically, there are two different interactions from the TiO_2 nanotube which are a titanium site and an oxygen site, so that the total energy may be obtained as a proportional ratio of the mean surface density, namely

Table 1 Numerical values for parameters ($A = 2D_0 R_0^6$ and $B = D_0 R_0^{12}$ for Lennard–Jones constants, and units are converted to Å and eV)

	Site–site	R_0 (Å)	D_0 (kcal/mol)	q (e)
TiO_2	Ti	4.5400	0.0550	+1.153
	O	3.4046	0.0957	−0.577
CO_2	C	3.8983	0.0951	+0.576
	O	3.4046	0.0957	−0.288
CH_4	C	3.8983	0.0951	0
	H	3.1950	0.0152	0

one-third titanium and two-thirds oxygen. The results of this model, total interaction energy, will be obtained as a function of a gas molecule radius and a nanotube radius, therefore different values of the radii can be used and they are a part of determination.

3 Mathematical derivation

The interaction energies between the assumed spherical CO_2 and that of the CH_4 with the TiO_2 nanotubes comprise:

(i)   The interaction energy between a point of carbon atom and the cylindrical tube,
(ii) The interaction energy between a sphere and the cylindrical tube,

and the model formation is as shown in Fig. 1. The tube is assumed to be $2L$ in length with a radius b and centred at the origin of the Cartesian coordinate system, which has a typical surface element of the cylinder at $(b \cos \theta, b \sin \theta, z)$ where $\theta \in (-\pi, \pi)$ and $z \in (-L, L)$. Further, the centre of the spherical molecule of radius a is assumed to be located at $(0, 0, Z)$. Using the same Cartesian coordinate system, a typical point on the
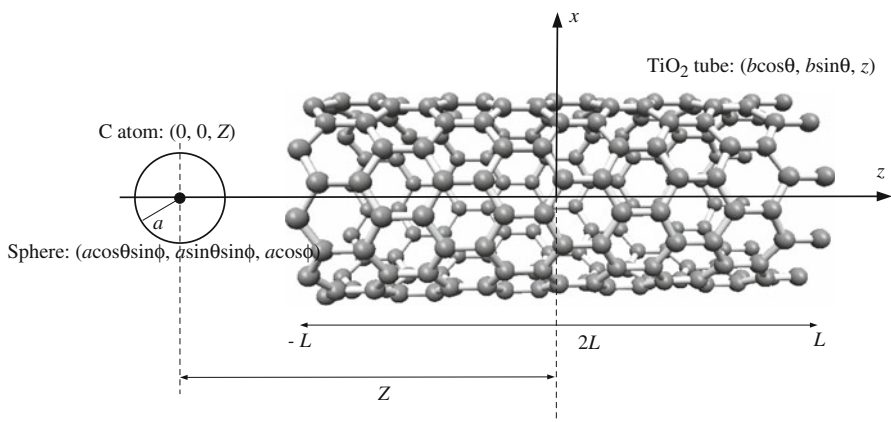

Fig. 1 Model formation for spherical CO_2 or CH_4 interacting with TiO_2 nanotube

sphere has coordinates $(a \cos \theta_1 \sin \phi, a \sin \theta_1 \sin \phi, a \cos \phi + Z)$ where $\theta_1 \in (-\pi, \pi)$ and $\phi \in (0, \pi)$.

Next we consider the integral I_n defined by Eq. (1) for the interaction between a point and the cylinder with $r^2 = b^2 + (z - Z)^2$. By a straightforward integration, we may deduce that

$$I_n = \frac{2\pi}{b^{n-2}} \int_{-\tan^{-1}[(L+Z)/b]}^{\tan^{-1}[(L-Z)/b]} \cos^{n-2} \psi \, d\psi,$$

which may be evaluated in closed form for all values of n, noting that we have the formulae

$$\int \frac{1}{\cos x} dx = \ln (\sec x + \tan x) + \text{constant},$$

$$\int \cos^{2n} x \, dx = \frac{1}{2^{2n}} \binom{2n}{n} x + \frac{1}{2^{2n-1}} \sum_{k=0}^{n-1} \frac{\sin(2n - 2k)x}{2n - 2k} + \text{constant},$$

where $\ln(x)$ is the logarithm to the base e. Thus, the total interaction energy between a point and a cylindrical tube takes the form

$$E_p = \frac{\eta_1}{4\pi \epsilon_0} q_1 q_2 I_1 + \eta_1 (-A I_6 + B I_{12}), \tag{2}$$

where η_1 denotes the mean atomic surface density of the TiO$_2$ nanotube. Again, we note that for the system of CH$_4$ and TiO$_2$ the Coulombic potential is zero due to the nonpolar nature of the CH$_4$ molecule.

In terms of the interaction energy between a spherical molecule and a cylindrical nanotube, we firstly determine the surface integral for the sphere interacting with a point, and then the total energy for the system can be obtained by performing a second surface integration over a cylinder.

For the case of a sphere interacting with a point, the distance r appearing in (1) is the distance from a typical surface element of the sphere to the point $(0, 0, \rho)$ located on the cylinder of radius b. Hence, the integral I_n becomes

$$I_n = \int_0^\pi \int_0^{2\pi} \frac{a^2 \sin \phi}{[a^2 \sin^2 \phi + (a \cos \phi - \rho)^2]^{n/2}} d\theta d\phi = \frac{\pi a}{\rho} \int_{(\rho-a)^2}^{(\rho+a)^2} \frac{1}{t^{n/2}} dt,$$

where we have made the substitution $t = a^2 + \rho^2 - 2a\rho \cos \phi$. For $n = 1$, we may deduce $I_1 = 4\pi a^2/\rho$, while for $n = 6$ and 12, the integral I_n takes the form

$$I_n = \frac{\pi a}{\rho[(n/2) - 1]} \left[\frac{1}{(\rho - a)^{n-2}} - \frac{1}{(\rho + a)^{n-2}} \right].$$

Next the other surface integral for the cylindrical tube is evaluated, where the distance from a typical surface element on the tube and the centre of the sphere is given

by $\rho^2 = b^2 + (z - Z)^2$. Firstly, we determine the Coulomb interaction for $n = 1$ which may be written as

$$J_1^* = \int_{-L}^{L} \int_0^{2\pi} b I_1 d\theta dz = 4\pi a^2 b \int_{-L}^{L} \int_0^{2\pi} \frac{1}{[b^2 + (z - Z)^2]^{1/2}} d\theta dz$$

$$= 8\pi^2 a^2 b \ln \left[\frac{\sqrt{b^2 + (L - Z)^2} + (L - Z)}{\sqrt{b^2 + (L + Z)^2} - (L + Z)} \right].$$

Following the work of Cox et al. [17], I_6 and I_{12} can be shown to become

$$I_6 = 4\pi a^2 \left(J_3 + 2a^2 J_4 \right),$$

$$I_{12} = \frac{4\pi a^2}{5} \left(5 J_6 + 80a^2 J_7 + 336a^4 J_8 + 512a^6 J_9 + 256a^8 J_{10} \right),$$

where we further define integrals J_n by

$$J_n = \int_S \frac{1}{(\rho^2 - a^2)^n} dS = b \int_{-L}^{L} \int_0^{2\pi} \frac{1}{[b^2 + (z - Z)^2 - a^2]^n} d\theta dz,$$

where here n is a positive integer corresponding to the power of the polynomials appearing in integrals I_6 and I_{12}, and dS is the surface element for the nanotube. Using a simple transformation, the integral J_n can be obtained as

$$J_n = \frac{2\pi b}{(b^2 - a^2)^{n-1/2}} \int_{-\tan^{-1}[(L+Z)/\sqrt{b^2-a^2}]}^{\tan^{-1}[(L-Z)/\sqrt{b^2-a^2}]} \cos^{2n-2} \psi \, d\psi,$$

and for the above specific values of n this integral may be analytically determined. Therefore, the total interaction energy between a spherical molecule and a cylindrical nanotube is given by

$$E_s = \frac{\eta_1 \eta_2}{4\pi \epsilon_0} q_1 q_2 J_1^* + 4\pi a^2 \eta_1 \eta_2 \left[-A(J_3 + 2a^2 J_4) + \frac{B}{5}(5 J_6 + 80a^2 J_7 + 336a^4 J_8 \right.$$
$$\left. + 512a^6 J_9 + 256a^8 J_{10}) \right], \tag{3}$$

where η_2 is a mean atomic surface density of the spherical surface.

Finally, the total interaction between a CO_2 and a CH_4 molecule with a TiO_2 nanotube is the sum of E_p and E_s, which are given by Eqs. (2) and (3), respectively.

4 Numerical results

The suction energy or the encapsulation energy is defined as the total energy or the work done generated by the interaction of a particular molecule as a consequence of being sucked into the nanotube [17], and for the CO_2 and CH_4 molecules this is graphically shown in Fig. 2. We find that the suction process becomes favourable for a molecule of CH_4 when the tube radius is greater than $b = 3.596$ Å and the suction energy reaches a maximum, 0.0693 eV, at $b = 4.090$ Å, where we require a larger tube radius to encapsulate a molecule of CO_2. The suction process for a molecule CO_2 becomes favourable when $b > 3.748$ Å and the maximum suction energy, 0.0777 eV, is reached when $b = 4.232$ Å. Our finding is in a good agreement made by Thornton et al. [8] where they used carbon and silica nanotubes as nanopores in order to predict gas diffusion regime.

The binding energy between a single CO_2 molecule and a single CH_4 molecule is 0.0189 eV which is approximately 4 times less than the maximum suction energies arising from the nanotubes to encapsulate CH_4 and CO_2 molecules. In other words, the suction energy from the TiO_2 nanotube overcomes the van der Waals interaction between CH_4/CO_2 in a mixture. Consequently, the TiO_2 nanotube might be thought of as a potential candidate to separate a cluster of this binary gas mixture.

The interaction energy between the CH_4 molecule and the adsorbent involves only the Lennard–Jones potential since there is no net charge of carbon and hydrogen atoms in the molecule. However, the CO_2-adsorbent intermolecular interaction involves a combination of Lennard–Jones and Coulomb potential. Assuming that the gas molecules may form a larger cluster with the same proportion of atomic species, the suction
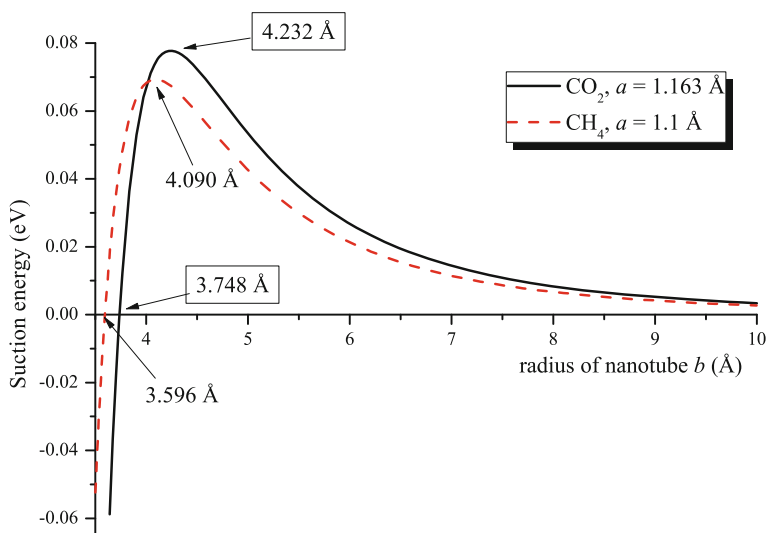

Fig. 2 Suction energy for single CO_2 molecule ($a = 1.163$ Å) and single CH_4 molecule ($a = 1.1$ Å) encapsulated into TiO_2 nanotubes
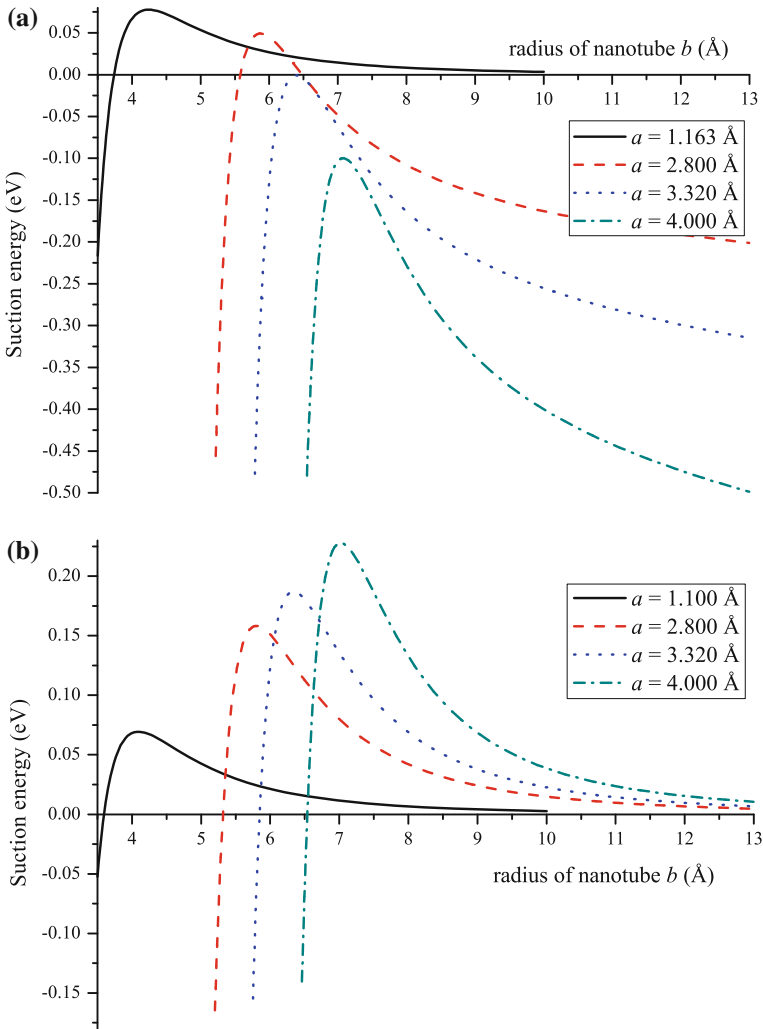
Fig. 3 Suction energy for **a** CO_2 and **b** CH_4 encapsulated into TiO_2 nanotube for four values of molecule radii

behaviour for the system of CO_2 and that of CH_4 encapsulated into the TiO_2 nanotubes is shown in Fig. 3. From Fig. 3a, we observe that when the radius of the CO_2 cluster exceeds the value of 3.32 Å, it will not be encapsulated into the tube since the suction energy is less than zero. This is due to the net repulsive Coulombic term dominating the system as the distance between the gas and the absorbent increases, and the larger radius of the gas cluster gives rise to a longer distance between two interacting atoms. On the other hand, the suction energy increases as the radius of the CH_4 cluster increases since the number of molecules increases which gives rise to a larger total van der Waals interaction as indicated in Fig. 3b.

5 Summary

Here, we employ applied mathematical modelling to determine the total interaction energy for the encapsulation of CO_2 and CH_4 into TiO_2 nanotubes, with the aim to purify a mixture of CO_2/CH_4. The interaction between CO_2 and the nanotube is modelled using both Coulombic and Lennard–Jones potential functions, while the interaction between CH_4 and the tube involves only Lennard–Jones terms. Analytical expressions for the two systems are obtained in closed form. Further, the suction energy for the various gas molecule radii are determined, and we find that the suction energy varies inversely with the radius of the CO_2 molecule, and when its radius is larger than 3.32 Å the gas molecule has no prospects of encapsulation into the TiO_2 nanotube due to the net repulsive interaction from Coulomb potential dominating the van der Waals interaction. However, for any given radius of CH_4 an appropriate nanotube radius can be determined to achieve the maximum suction energy, and the suction energy depends linearly on the assumed radius of CH_4 molecule. In consequence, the TiO_2 nanotubes provide an exciting prospect as an adsorbent material to separate and store CO_2 and CH_4 molecules, and these preliminary calculations might serve to focus further experimentation. To-date there are no TiO_2 nanotubes available with smaller pore sizes, and so the testing of our model predictions with experimental results for the optimum nanotube radius and the maximum suction energy is not possible.

References

1. R. Babarao, Z. Hu, J. Jiang, S. Chempath, S.I. Sandler, Storage and separation of CO_2 and CH_4 in silicalite, C_{168} schwarzite, and IRMOF-1: A comparative study from Monte Carlo simulation. Langmuir **23**(2), 659–666 (2007)
2. L. Huang, L. Zhang, Q. Shao, L. Lu, X. Lu, S. Jiang, W. Shen, Simulations of binary mixture adsorption of carbon dioxide and methane in carbon nanotubes: temperature, pressure, and pore size effects. J. Phys. Chem. C **111**(32), 11912–11920 (2007)
3. X. Peng, D. Cao, W. Wang, Computational study on purification of CO_2 from natural gas by C_{60} intercalated graphite. Ind. Eng. Chem. Res. **49**(18), 8787–8796 (2010)
4. C. Matranga, L. Chen, M. Smith, E. Bittner, J.K. Johnson, B. Bockrath, Trapped CO_2 in carbon nanotube bundles. J. Phys. Chem. B **107**(47), 12930–12941 (2003)
5. B.-U. Choi, D.-K. Choi, Y.-W. Lee, B.-K. Lee, S.-H. Kim, Adsorption equilibria of methane, ethane, ethylene, nitrogen, and hydrogen onto activated carbon. J. Chem. Eng. Data **48**(3), 603–607 (2003)
6. M. Bienfait, P. Zeppenfeld, N. Dupont-Pavlovsky, M. Muris, M.R. Johnson, T. Wilson, M. DePies, O.E. Vilches, Thermodynamics and structure of hydrogen, methane, argon, oxygen, and carbon dioxide adsorbed on single-wall carbon nanotube bundles. Phys. Rev. B **70**, 035410 (10pp), (2004)
7. X. Peng, W. Wang, R. Xue, Z. Shen, Adsorption separation of CH_4/CO_2 on mesocarbon microbeads: experiment and modeling. AICHE J. **52**(3), 994–1003 (2006)
8. A.W. Thorntona, T.A. Hilder, A.J. Hill, J.M. Hill, Predicting gas diffusion regime within pores of different size, shape and composition. J. Membr. Sci. **336**, 101–108 (2009)
9. J.U. Keller, R. Staudt, *Gas Adsorption Equilibria: Experimental Methods and Adsorptive Isotherms* (Springer, New York, 2004)
10. C.R.A. Catlow, B. Smit, R.A. van Santen, *Computer Modelling of Microporous Materials* (Elsevier, Amsterdam, 2004)
11. T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, Formation of titanium oxide nanotube. Langmuir **14**(12), 3160–3163 (1998)

12. X. Pan, C. Chen, K. Zhu, Z. Fan, TiO$_2$ nanotubes infiltrated with nanoparticles for dye sensitized solar cells. Nanotechnology **22**, 235402 (7pp), (2011)
13. V. Swamy, J.D. Gale, Transferable variable-charge interatomic potential for atomistic simulation of titanium oxides. Phys. Rev. B **62**(9), 5406–5412 (2000)
14. S.L. Mayo, B.D. Olafson, W.A. Goddard III, A generic force field for molecular simulations. J. Phys. Chem. **94**, 8897–8909 (1999)
15. J.O. Hirschfelder, C.F. Curtiss, R.B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954)
16. D. Baowan, W. Triampo, D. Triampo, Encapsulation of TiO$_2$ nanoparticles into single-walled carbon nanotubes. New J. Phys. **11**, 093011 (13pp), (2009)
17. B.J. Cox, N. Thamwattana, J.M. Hill, Mechanics of atoms and fullerenes in single-walled carbon nanotubes. I. Acceptance and suction energies. Proc. R. Soc. A **463**, 461–476 (2007)