Modelling gas storage in molecular nanosystems

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Dedication

To the almighty Lord, Daddy, Mummy, Niyi&family, Bukola&family, Folake&family, Ayo, the Bamigboyes and to the memory of Samuel Okusanya.

Author's publications

1. O. O. Adisa, B. J. Cox, and J. M. Hill. Encapsulation of methane molecules into carbon nanotubes. *Physica B*, 406:88–93, 2011.

2. O. O. Adisa, B. J. Cox, and J. M. Hill. Packing configurations for methane storage in carbon nanotubes. *The European Physical Journal B*, 79:177–184, 2011.

3. O. O. Adisa, B. J. Cox, and J. M. Hill. Modelling the surface adsorption of methane on carbon nanostructures. *Carbon*, 49:3212–3218, 2011.

4. O. O Adisa, B. J. Cox, and J. M. Hill. Open carbon nanocones as candidates for gas storage. *Journal of Physical Chemistry C*, 115:24528–24533, 2011.

5. O. O. Adisa, B. J. Cox, and J. M. Hill. Encapsulation of methane in nanotube bundles. *Micro and Nano Letters*, 5:291 – 295, 2010.

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7. O. O. Adisa, B. J. Cox, and J. M. Hill. Methane storage in molecular nanostructures. *Nanoscale*, 4:3295-3307, 2012.

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Abstract

In this thesis, we develop models for the adsorption of gases in various nanocontainers. We exploit the Lennard-Jones potential together with the continuous approximation, which assumes that discrete molecular structures may be approximated by replacement over the entire surface with a uniform atomic surface density. We first develop an entirely new model for a methane molecule which avoids needing to take into account the detailed atomic orientations and thus provides a major simplification to the numerical calculations, and which compares favourably with a detailed discrete formulation. This model is subsequently employed in a number of problems investigated throughout the thesis. Methane adsorption is examined in various molecular structures, which have been proposed as possible containers for methane storage; namely carbon nanotubes, carbon and silicon nanotube bundles (including interstitial and groove sites), graphite and carbon nanocones. Analytical expressions are obtained for the interaction energies and forces, the volume available for adsorption, the adsorption isotherms as well as for the probabilities for adsorption on the internal surfaces of these nanocontainers.

Computational simulation and mathematical modelling play important roles in predicting and verifying experimental outcomes which are often expensive and time consuming. Even though recent advances have greatly improved computations, due to the large number of atoms and force field calculations involved, computational simulations can still be time consuming as compared to the rapid evaluation of an analytic mathematical modelling solution. On the other hand, underlying an ideal mathematical model, there are many assumptions and approximations, but

such models often reveal the key physical parameters and optimal configurations. Here, we model the mechanics of gas storage and predict critical parameters such as the maximum and minimum geometric parameters for successful gas storage in these nanostructures, the presence or absence of energy barriers in the encapsulation process, as well as the total work done by the gas molecules during encapsulation. We determine the equilibrium distances in relation to the nanostructure surface, which are derived at the minimum energy configuration, for specific molecular structures such as graphite, a phenomenon which is essential to understanding the dynamics of the interaction. Storage in some of these molecular structures has already been investigated through either experiments or molecular dynamics simulations, and for those cases for which experimental data exists, the modelling presented in this thesis compares favourably. The major findings relate to gas encapsulation and packing in nanostructures, and the results presented here give, for the first time, accurate numerical values of minimum energies, equilibrium locations, gravimetric uptakes as well as volumes and probabilities for adsorption of gases onto these nanostructures.