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Henry constant and Isosteric Heat at Zero-Loading for Gas Adsorption in Carbon Nanotubes

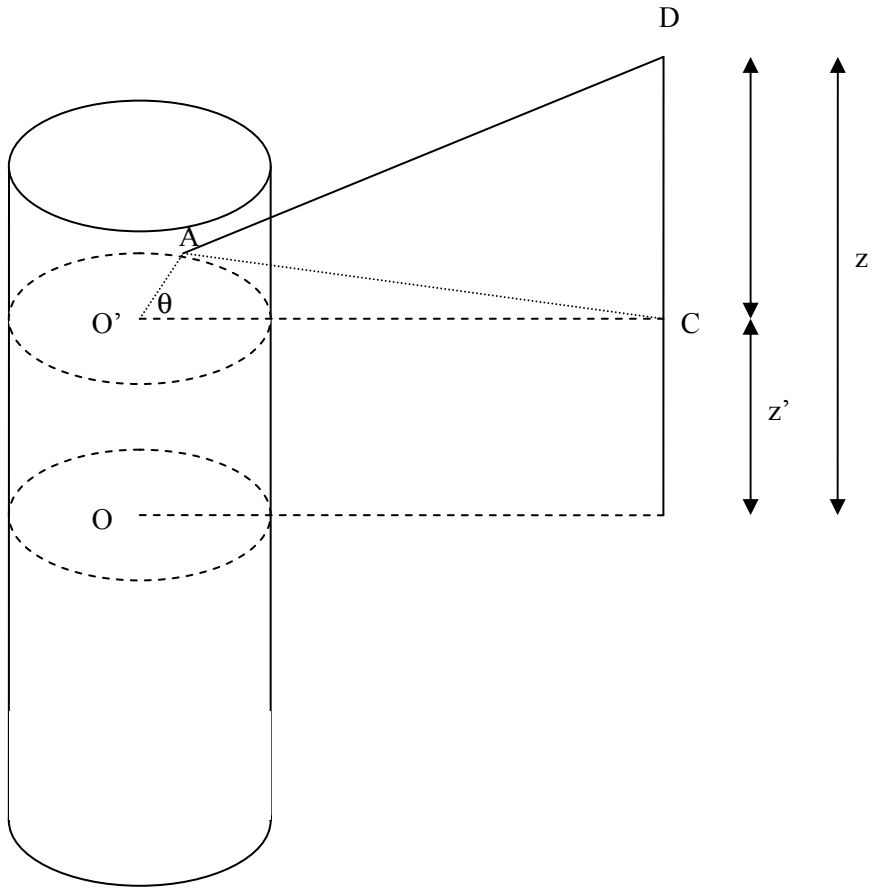
by

D. D. Do[a]*, H. D. Do[a], A. Wongkoblap[a] and D. Nicholson[a,b]

a.School of Engineering, University of Queensland, St. Lucia, Qld 4072, Australia
b. Theory and Simulation Group, Department of Chemistry, Imperial College, London SW7 2AY,UK.

Supplementary Material

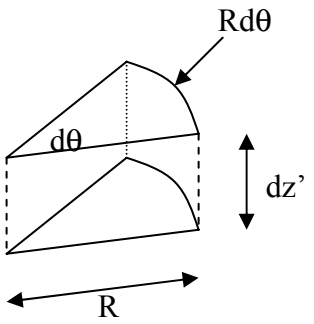
Solid-Fluid potential for a finite cylindrical pore



We choose the origin at the centre of the finite cylinder whose radius and length are R and L, respectively. Let D be the position of a point in space and A be an arbitrary point on the cylinder. The plane orthogonal to the cylinder defines the various points and an angle as shown in Figure A1.1. The coordinates of the point D are r and z. The distance AC is calculated from $d_{AC}^2 = r^2 + R^2 - 2rR\cos\theta$, and therefore the distance between the adsorbate and an arbitrary point D on the carbon nanotube is

$$d_{AD}^2 = r^2 + R^2 - 2rR\cos\theta + (z - z')^2 \qquad \text{(A1.1)}$$

Consider a differential area around the point A as shown with a length dz' and an angle dθ. The area is $dA = R\,d\theta\,dz'$. Let ρ_s be the surface carbon atom density, the number of carbon atoms in this differential area is $dN_C = \rho_s R\,d\theta\,dz'$.



Therefore the potential energy of an adsorbate with all carbon atoms in the differential area dA is (assuming pairwise additivity):

$$d\varphi = \rho_s R d\theta dz' \left\{ 4\varepsilon^{(\alpha,\beta)} \left[\left(\frac{\sigma^{(\alpha,\beta)}}{d_{AD}} \right)^{12} - \left(\frac{\sigma^{(\alpha,\beta)}}{d_{AD}} \right)^{6} \right] \right\} \qquad \text{(A1.2)}$$

for $-L/2 \le z' \le L/2$ and $0 \le \theta \le 2\pi$. Substituting the distance d_{AD} of eq. (A1.1) into eq. (A1.2) and then integrating with respect to z' and θ, we obtain the potential energy between a single particle and the finite carbon nanotube.

$$\varphi = 4\varepsilon^{(\alpha,\beta)} \rho_s R \int_0^{2\pi} \int_{-L/2}^{L/2} \sum_{n=3,6} a_n \frac{\left[\sigma^{(\alpha,\beta)}\right]^n}{\left[(z-z')^2 + R^2 + r^2 - 2rR\cos\theta \right]^n}\, d\theta dz' \qquad \text{(A1.3)}$$

where $a_3 = -1$ and $a_6 = 1$. Interchanging the integration and summation operation, we get:

$$\varphi = 4\varepsilon^{(\alpha,\beta)} \rho_s R \sum_{n=3,6} a_n \left[\sigma^{(\alpha,\beta)}\right]^{2n} \int_0^{2\pi} I(\theta; r, z; n, R, L)\, d\theta \qquad \text{(A1.4)}$$

Here the integrand $I(\theta; r, z; n, R, L)$ is a function of θ, and the above integral can be integrated numerically. This integrand I is:

$$I = \int_{-L/2}^{L/2} \frac{1}{\left[(z-z')^2 + R^2 + r^2 - 2rR\cos\theta \right]^n} dz' \qquad \text{(A1.5)}$$

Depending on the value of $r^2 + R^2 - 2rR\cos\theta$, the integrand I can be evaluated analytically as below. For $r^2 + R^2 - 2rR\cos\theta = 0$, the function I takes the form:

$$I = (1-2n)^{-1}\left[\left(\frac{L}{2}-z\right)^{1-2n} + \left(\frac{L}{2}+z\right)^{1-2n}\right] \qquad \text{(A1.6a)}$$

When $r^2 + R^2 - 2rR\cos\theta \neq 0$, the function I is:

$$I = \frac{H(x_2;n) - H(x_1;n)}{\left(R^2 + r^2 - 2rR\cos\theta\right)^{n-(1/2)}} \qquad \text{(A1.6b)}$$

where x_1 and x_2 are given by:

$$x_1 = \frac{-\left(\frac{L}{2}+z\right)}{\sqrt{R^2 + r^2 - 2rR\cos\theta}}; \qquad x_2 = \frac{\left(\frac{L}{2}-z\right)}{\sqrt{R^2 + r^2 - 2rR\cos\theta}} \qquad \text{(A1.6c)}$$

The function H(x;n) is given by:

$$\begin{aligned} H(x;n) &= \int (1+x^2)^{-n}\, dx \\ &= \frac{x}{(2n-1)} \sum_{j=1}^{n-1} \frac{(2n-1)(2n-3)\cdots(2n-2j+1)}{2^j\,(n-1)(n-2)\cdots(n-j)(1+x^2)^{n-j}} + \frac{(2n-3)!!}{2^{n-1}(n-1)!}\arctan(x) \end{aligned} \qquad \text{(A1.6d)}$$

When the pore becomes infinite, the potential can be expressed in terms of the hypergeometric function [1]. It has the form:

$$\varphi = 4\pi^2 \rho_s \left[\sigma^{(\alpha,\beta)}\right]^2 \varepsilon^{(\alpha,\beta)} (I_6 - I_3) \qquad \text{(A1.7a)}$$

where I_6 and I_3 are given by

$$I_6 = \frac{63}{128}\left(\frac{\sigma^{(\alpha,\beta)}}{R}\right)^{10}\left[1-\left(\frac{r}{R}\right)^2\right]^{-10} \times F\left[-\frac{9}{2}; -\frac{9}{2}; 1; \left(\frac{r}{R}\right)^2\right] \qquad \text{(A1.7b)}$$

$$I_3 = \frac{3}{4}\left(\frac{\sigma^{(\alpha,\beta)}}{R}\right)^{4}\left[1-\left(\frac{r}{R}\right)^2\right]^{-4} \times F\left[-\frac{3}{2}; -\frac{3}{2}; 1; \left(\frac{r}{R}\right)^2\right] \qquad \text{(A1.7c)}$$

Here R is the pore radius and r is the distance from the center to the adsorbate center.

The potential energy equation of (A1.7) has been used by a number of workers [2-6] in their analysis of solids having cylindrical pores, such as carbon nanotube and MCM-41.

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