

Modelling adsorption of a water molecule into various pore structures of silica gel

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Abstract Silica gel is widely used in commercial applications as a water adsorbent due to its properties including hydrothermally stable, high water sorption capacity, low regeneration temperature, low cost and wide range of pore diameters. Since the water sorption capacity of silica gel strongly depends on the pore size and structure, which can be controlled during synthesis, this paper study the effect of pore shapes and dimensions of silica gel upon the adsorption of a water molecule aiming at maximising the water sorption capacity. In particular, we consider three types of pore structures, namely cylindrical, square prismatic and conical pores. On using the Lennard-Jones potential and a continuum approximation, we find that the minimum radii for a water molecule to be accepted into cylindrical, square prismatic and conical pores are 4.009, 3.7898 and 4.4575 Å, respectively. For cylindrical and square prismatic pores, the critical radii which maximise the adsorption energy are 4.5189 and 4.1903 Å, respectively. Knowledge of these critical pore sizes may be useful for the manufacturing process of silica gel that will maximise the water sorption capacity.

Keywords Nanopores · Silica gel · Water adsorbents · Adsorption energy · Lennard-Jones potential

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1 Introduction

Nanopores receive considerable attention for possible industrial and medical applications, particularly their use as water adsorbents [1], vehicles for enzyme encapsulation [2], biosensors and targeted drug and gene delivery [3]. Water sorption behaviour in nanoporous materials plays an important role in the design and manufacture of advanced materials and many nanodevices. The water sorption behaviour of a sorbent depends on many factors, including the structure and the chemical composition of the nanoporous material, the presence of charged species, the type of framework structure and the hydration level. Due to the demand for materials with high sorption capacity and high selectivity toward water at different concentrations, several water adsorbents have been discovered. They can be classified into three main categories: (i) inorganic materials (zeolites, clays and silica), (ii) carbon based adsorbents (activated carbons, graphite, carbon molecular sieves and pre-shaped carbon fibres and nanotubes) and (iii) organic polymers [1]. The most studied adsorbents for water are microporous materials (zeolites), activated carbon, and silica gels. Commercially, silica gels and zeolites are the dominant hydrophilic sorbents for water sorption as they are hydrothermally stable and have high water sorption capacity and low cost. However, silica gels have advantages over zeolites due to the lower regeneration temperature, lower cost and a wider range of pore diameters, typically between 5 and 3,000 Å [1]. Commercial applications for silica gel range from water and moisture adsorbents for preservation of chemicals and foods, enzyme and protein carriers, organic acids removers, industrial gas purifiers to a preservation tool for controlling relative humidity in laboratories and in storage [2,4–9].

Silica gel is a chemically inert, nontoxic, polar and dimensionally stable amorphous form of SiO_2 . Depending on the synthesis process, silica gels have different surface areas, pore volumes and particle sizes [1]. As a result, it is possible during the manufacturing process to adjust the pore size range to best fit application needs. Adsorption of water molecules into silica gel pores can be attributed to a physical process generally referred to as physical adsorption, or physisorption, caused by van der Waals forces, or a chemical process referred to as chemical adsorption or chemisorption, involving valency forces [10,11]. In this paper, we focus on physisorption where we model the van der Waals interaction between a water molecule and a pore of silica gel using the Lennard-Jones potential and a continuum approach. For more details of this approach we refer the readers to Girifalco et al. [12] and Cox et al. [13,14].

The adsorption of liquids or gases and vapors into the pores of silica gel strongly depends on the pore size and structure [1,15]. Several researches show that the reduction in pore size of silica gels can significantly increase water sorption capability. For example, Dawoud et al. [16] explore the role of pore size of silica gels by studying sequentially the sorption capacity of commercial samples towards water vapor. They show that the water loading of microporous silica is twice higher than in mesoporous, which is explained by an increment of pore volume when the pore size is being reduced. This result is supported by Chua et al. [17] who demonstrate that the pore volume and the surface area play important roles in achieving a high water adsorption uptake in nanoporous materials. Thus to improve the sorptivity of silica gel, a decrease of pore diameter is desirable, which can be done through changing the silica

solubility during the preparation process. The question that remains is to what extent we can decrease the size without too much compromising on the sorption capacity. As such, this paper aims to determine the effective pore size that gives rise to the highest sorption capacity. Since the shape of the pores also strongly affects water sorption behaviour, this paper studies three types of pore structures, namely cylindrical, square prismatic and conical and for each pore shape, we determine the critical dimension which maximises the water sorption capacity.

In the following section, we introduce the Lennard-Jones potential and we adopt a continuum approach to model the interactions between pores of silica gel and a water molecule. To model an interaction involving a water molecule, similar to [18] we consider a water molecule as a spherical entity where we assume that an oxygen atom is situated at the centre of a sphere with two hydrogen atoms located on its surface. As such, for each type of pore structures we determine an analytical expression for the interaction energy between an atom and a spherical surface, as shown in Sects. 3 and 4. In Sect. 5 numerical results are provided, while a summary of the paper is given in the final section.

2 Lennard-Jones function and continuum approximation

We employ the Lennard-Jones potential function and a continuum approximation to determine the molecular interatomic energy between two molecules. The 6–12 Lennard-Jones potential function is given by

$$\Phi = -\frac{A}{\rho^6} + \frac{B}{\rho^{12}}, \quad (1)$$

where ρ denotes the distance between two typical points, and A and B are the attractive and repulsive Lennard-Jones constants, respectively. Equation (1) can also be written as

$$\Phi = 4\epsilon \left[-\left(\frac{\sigma}{\rho}\right)^6 + \left(\frac{\sigma}{\rho}\right)^{12} \right],$$

where ϵ denotes a well depth and σ is the van der Waals diameter, and from which we may deduce $A = 4\epsilon\sigma^6$ and $B = 4\epsilon\sigma^{12}$. The Lennard-Jones constants in the system of two atomic species can be obtained using the empirical combining laws or mixing rules [19], which are given by

$$\epsilon_{12} = \sqrt{\epsilon_1\epsilon_2}, \quad \sigma_{12} = \frac{\sigma_1 + \sigma_2}{2},$$

where 1 and 2 refer to the respective individual atoms.

Using a continuum approach, where the atoms at discrete locations on the molecule are averaged over a surface, the molecular interatomic energy is obtained by calculating integrals over the surfaces of each molecule, namely

$$E = \eta_1 \eta_2 \int_{S_1} \int_{S_2} \left(-\frac{A}{\rho^6} + \frac{B}{\rho^{12}} \right) dS_2 dS_1, \quad (2)$$

where η_1 and η_2 represent the mean surface density of atoms on each molecule. Further, we may define the integral I_n in the form of

$$I_n = \int_{S_1} \int_{S_2} \rho^{-2n} dS_2 dS_1, \quad n = 3, 6, \quad (3)$$

and therefore, $E = \eta_1 \eta_2 (-AI_3 + BI_6)$.

The van der Waals interaction force between two molecules is given by

$$F_{vdW} = -\nabla E, \quad (4)$$

where the energy E is given by (2). Due to the symmetry of problem configurations in this paper, we only need to consider the force in the axial direction. The axial force in the z -direction is obtained by differentiating the integrated Lennard-Jones potential with respect to Z , which is defined as the distance between two molecules in the z -direction, therefore (4) simplifies to

$$F_z = -\frac{\partial E}{\partial Z}.$$

In this paper, we aim to optimize the radius of the pore which gives rise to the maximum adsorption energy. Similar to the suction energy described by Cox et al. [13], the adsorption energy W defined here is the total work done by the interaction force upon a molecule entering the pore. Mathematically, this can be represented by

$$W = \int_{-\infty}^{\infty} F_z(Z) dZ. \quad (5)$$

In the case of a finite pore length, the value of the adsorption energy defined by (5) goes to zero since the work done to move the molecule from the positive to the negative directions are equal and opposite sign. Therefore, when considered the pore of finite length L , the lower and the upper limits of the integral in (5) need to be changed to $-L/2$ and $L/2$, respectively.

3 Interaction energies for different pore shapes and a single atom

In this section, we determine the adsorption behaviour of a single atom into three different pore shapes which are cylindrical, square prismatic and conical pores, as shown in Fig. 1. On using the Lennard-Jones potential function together with the continuum approximation, the total interaction energies for the three systems are derived.

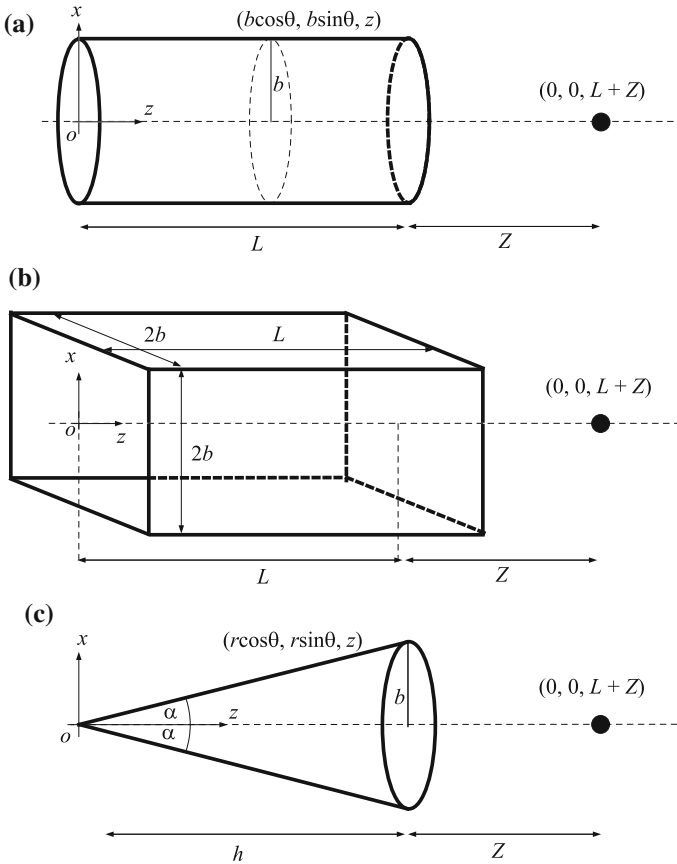


Fig. 1 Model for **a** cylindrical, **b** square prismatic and **c** conical pore shapes

3.1 Cylindrical pore shape

With reference to the Cartesian coordinate system (x, y, z) , a cylindrical pore shape is assumed to be co-axially located on the z -axis and one end centred at the origin with the length L in the positive z -direction, as shown in Fig. 1a. An arbitrary point on the surface of the pore has the coordinates $(b \cos \theta, b \sin \theta, z)$ where b is the pore radius and $-\pi \leq \theta \leq \pi$. With reference to the same Cartesian coordinate system (x, y, z) , an atom is located at $(0, 0, L + Z)$ where Z is the distance between the atom and the pore, and for positive (negative) value of Z the atom is outside (inside) the cylindrical pore. Therefore, the distance from the atom to a typical surface element on the pore is given by $\rho^2 = b^2 + (z - Z - L)^2$, and the integral I_n defined by (3) becomes

$$I_n = b \int_{-\pi}^{\pi} \int_0^L \frac{1}{[b^2 + (z - Z - L)^2]^n} dz d\theta.$$

Then we make a substitution $b \tan \psi = z - Z - L$, and we may deduce

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

and

$$\begin{aligned} & \int \cos^{2(n-1)} \psi d\psi \\ &= \frac{1}{2^{2(n-1)}} \left[\binom{2(n-1)}{(n-1)} \psi + \sum_{k=0}^{n-2} \binom{2(n-1)}{k} \frac{\sin[(2n-2k-2)\psi]}{(n-k-1)} \right], \quad (6) \end{aligned}$$

where $\binom{n}{m}$ is the binomial coefficient. By evaluating (6) at $\psi = -\tan^{-1}(Z/b)$ and $\psi = -\tan^{-1}[(Z+L)/b]$, an analytical expression for I_n may be obtained. The total interaction energy for an atom adsorbed into a cylindrical pore is given by $E_c = \eta_1(-AI_3 + BI_6)$ where η_1 denotes the mean atomic surface density of the pore.

3.2 Square prismatic pore shape

With reference to the Cartesian coordinate system (x, y, z) , the centre of a square prismatic pore is assumed to be located co-axially on the z -axis. The dimensions of the pore are assumed to be $2b$ in width, $2b$ in height and L in length, as shown in Fig. 1b. Consequently, an arbitrary point on each side of the pore has the coordinates (b, y, z) , $(-b, y, z)$, (x, b, z) and $(x, -b, z)$, and we note that b is assumed to be the radius of the pore in order to compare this result with the other two pore shapes. With reference to the same Cartesian coordinate system (x, y, z) , an atom is located at $(0, 0, L+Z)$ where Z is the distance between the atom and the pore, and for positive (negative) value of Z the atom is outside (inside) the square prismatic pore.

The interaction energy between an atom and a square prismatic pore can be thought of as an interaction energy between an atom and four planes. The distance from the atom to a typical point on each plane can be written as $\rho^2 = b^2 + s^2 + (z - Z - L)^2$ where s represents x or y for the four planes and $s \in (-b, b)$. Here we consider only the interaction energy for one plane, and the total energy of the system can be obtained by multiply by four. Therefore, I_n becomes

$$I_n = \int_0^L \int_{-b}^b \frac{1}{[b^2 + s^2 + (z - Z - L)^2]^n} ds dz.$$

Further, we define J_n in the form

$$J_n = \int_{-b}^b \frac{1}{[b^2 + s^2 + (z - Z - L)^2]^n} ds = 2 \int_0^b \frac{1}{[b^2 + s^2 + (z - Z - L)^2]^n} ds,$$

where we make the substitution $s = \sqrt{b^2 + (z - Z - L)^2} \tan \psi$ and proceed as in the previous section which produces

$$J_3 = \frac{2}{[b^2 + (z - Z - L)^2]^{5/2}} \left\{ \frac{3}{8} \tan^{-1} \left(\frac{b}{\sqrt{b^2 + (z - Z - L)^2}} \right) + \frac{3 b [b^2 + (z - Z - L)^2]^{1/2}}{8 [2b^2 + (z - Z - L)^2]} + \frac{1 b [b^2 + (z - Z - L)^2]^{3/2}}{4 [2b^2 + (z - Z - L)^2]^2} \right\},$$

and

$$J_6 = \frac{2}{[b^2 + (z - Z - L)^2]^{11/2}} \left\{ \frac{63}{256} \tan^{-1} \left(\frac{b}{\sqrt{b^2 + (z - Z - L)^2}} \right) + \frac{63 b [b^2 + (z - Z - L)^2]^{1/2}}{256 [2b^2 + (z - Z - L)^2]} + \frac{21 b [b^2 + (z - Z - L)^2]^{3/2}}{128 [2b^2 + (z - Z - L)^2]^2} + \frac{21 b [b^2 + (z - Z - L)^2]^{5/2}}{160 [2b^2 + (z - Z - L)^2]^3} + \frac{9 b [b^2 + (z - Z - L)^2]^{7/2}}{80 [2b^2 + (z - Z - L)^2]^4} + \frac{1 b [b^2 + (z - Z - L)^2]^{9/2}}{10 [2b^2 + (z - Z - L)^2]^5} \right\}.$$

Further, there are two forms of integrals needed to be determined which are

$$K_{s,t} = \int_0^L \frac{dz}{[b^2 + (z - Z - L)^2]^s [2b^2 + (z - Z - L)^2]^t},$$

$$L_s = \int_0^L \frac{1}{[b^2 + (z - Z - L)^2]^{s/2}} \tan^{-1} \left\{ \frac{b}{\sqrt{b^2 + (z - Z - L)^2}} \right\} dz,$$

where s and t are certain positive integers corresponding to the power appearing in J_3 and J_6 .

Now we consider $K_{s,t}$ and make a substitution $u = z - Z - L$, and we may deduce

$$K_{s,t} = \frac{1}{2^t b^{2s+2t}} \int_Z^{Z+L} \frac{du}{[1 + (u^2/b^2)]^s \{1 + [u^2/(2b^2)]\}^t},$$

where the integrand is a rational function which can be evaluated for specific s and t .

Next we consider L_s , and for convenience we define $\lambda = \sqrt{b^2 + (z - Z - L)^2}$. Since $(b/\lambda) < \infty$ and from Gradshteyn and Ryzhik [20] (1.644.1) we obtain

$$\tan^{-1} \left(\frac{b}{\lambda} \right) = \sum_{k=0}^{\infty} \frac{(2k)!}{2^{2k} (k!)^2 (2k+1)} \frac{b^{2k+1}}{(\lambda^2 + b^2)^{k+1/2}},$$

and then

$$L_s = \sum_{k=0}^{\infty} \frac{(2k)!}{2^{2k} (k!)^2 (2k+1)} b^{2k+1} \int_0^L \frac{dz}{[b^2 + (z - Z - L)^2]^{s/2} [2b^2 + (z - Z - L)^2]^{k+1/2}},$$

which is in the form of $K_{s/2, k+1/2}$.

Therefore, the total interaction energy between a single atom and a square prismatic pore is given by

$$E_b = 4\eta_1 \left[-2A \left(\frac{3}{8} L_5 + \frac{3b}{8} K_{2,1} + \frac{b}{4} K_{1,2} \right) + 2B \left(\frac{63}{256} L_{11} + \frac{63b}{256} K_{5,1} + \frac{21b}{128} K_{4,2} \right. \right. \\ \left. \left. + \frac{21b}{160} K_{3,3} + \frac{9b}{80} K_{2,4} + \frac{b}{10} K_{1,5} \right) \right],$$

where η_1 represents the mean atomic surface density for the square prismatic pore, and the factor 4 comes from the fact that the square prismatic pore has four identical plane sides.

3.3 Conical pore shape

In this section, we determine the interaction energy between a single atom and a conical pore, where the vertex of the cone is assumed to be located at the origin and the axis of the cone is assumed to be co-axial with the z -axis, as shown in Fig. 1c. With reference to a rectangular Cartesian coordinate system (x, y, z) with the origin located at the vertex of the cone, a typical point on the cone surface has coordinates $(r \cos \theta, r \sin \theta, z)$. The cone has vertex angle 2α with base radius b and height L , and $r = z \tan \alpha$ where $\tan \alpha = b/L$. With reference to the same coordinate system, an atom is located at $(0, 0, Z + L)$ where Z is the distance from the cone base to the atom. Therefore, the distance between a typical point on the conical pore to the atom

is given by

$$\rho^2 = r^2 + (z - Z - L)^2 = z^2 \sec^2 \alpha - 2(Z + L)z + (Z + L)^2.$$

By using the Lennard-Jones potential together with the continuum approximation, the integral I_n can be written as

$$I_n = \frac{\tan \alpha}{\cos \alpha} \int_{-\pi}^{\pi} \int_0^L \frac{z}{[z^2 \sec^2 \alpha - 2(Z + L)z + (Z + L)^2]^n} dz d\theta,$$

where $(z \tan \alpha) / \cos \alpha$ is the factor arising from the surface integral, and the derivation details can be found in [21]. Further, we may deduce

$$I_n = 2\pi \frac{\tan \alpha}{\cos \alpha} \int_0^L \frac{z}{[z^2 \sec^2 \alpha - 2(Z + L)z + (Z + L)^2]^n} dz.$$

From Gradshteyn and Ryzhik [20] (2.174), we obtain

$$I_n = \frac{\pi \sin \alpha}{(1 - n)} \left\{ \frac{1}{[z^2 \sec^2 \alpha - 2(Z + L)z + (Z + L)^2]^{n-1}} - 2(n - 1)(Z + L) \int_0^L \frac{dz}{[z^2 \sec^2 \alpha - 2(Z + L)z + (Z + L)^2]^n} \right\},$$

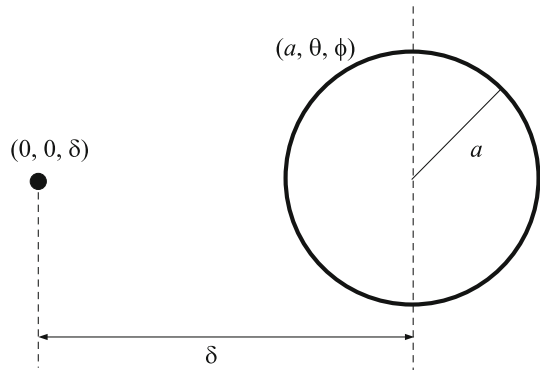
where the above integral can be determined for specific value of n . Finally, the total interaction energy between a conical pore and a single atom is given by $E_o = \eta_1(-AI_3 + BI_6)$.

4 Interaction energies for different pore shapes and a spherical molecule

In this section we determine the potential energies for a spherical molecule interacting with three different pore structures. In nature, proteins such as trypsin when folded can be viewed as spherical structures, thus the adsorption of a spherical molecule into a pore is of particular interest as it can be used to study the immobilization of proteins into porous materials [2].

Here, we first consider the interaction energy between a sphere and a point as depicted in Fig. 2. Then, we assume that the point is the atom located on the surface of a pore and as a result the total energy of the system can be determined utilizing a surface integral technique.

Fig. 2 Schematic for sphere interact with single atom



Following the work of Cox et al. [13], the interaction energy between a spherical molecule of radius a and a single atom can be given by

$$E = \frac{\pi a \eta_2}{\delta} \left\{ \frac{A}{2} \left[\frac{1}{(a + \delta)^4} - \frac{1}{(a - \delta)^4} \right] - \frac{B}{5} \left[\frac{1}{(a + \delta)^{10}} - \frac{1}{(a - \delta)^{10}} \right] \right\}, \quad (7)$$

where η_2 represents the mean atomic surface density of the sphere. By placing fractions over common denominators, expanding and reducing to fractions in terms of powers of $(\delta^2 - a^2)$, it can be shown that

$$\frac{A}{2\delta} \left[\frac{1}{(a + \delta)^4} - \frac{1}{(a - \delta)^4} \right] = -4aA \left[\frac{1}{(\delta^2 - a^2)^3} + \frac{2a^2}{(\delta^2 - a^2)^4} \right], \quad (8)$$

$$\begin{aligned} \frac{B}{5\delta} \left[\frac{1}{(a + \delta)^{10}} - \frac{1}{(a - \delta)^{10}} \right] = & -\frac{4aB}{5} \left[\frac{5}{(\delta^2 - a^2)^6} + \frac{80a^2}{(\delta^2 - a^2)^7} + \frac{336a^4}{(\delta^2 - a^2)^8} \right. \\ & \left. + \frac{512a^6}{(\delta^2 - a^2)^9} + \frac{256a^8}{(\delta^2 - a^2)^{10}} \right]. \end{aligned} \quad (9)$$

The total interaction energy between the spherical molecule and the pore is obtained by performing surface integrals for (7) over the cylindrical, square prismatic and conical pore shapes which are detailed in Sects. 4.1, 4.2 and 4.3, respectively. Further, we define

$$J_n = \int_S \frac{1}{(\delta^2 - a^2)^n} dS, \quad (10)$$

where n is a positive integer corresponding to the power of the polynomials appearing in (8) and (9), and dS is the surface element of the three different pore shapes.

4.1 Cylindrical pore shape

The schematic model for the interaction between a spherical molecule and a cylindrical pore is similar to Fig. 1a by replacing the single atom with a sphere of radius a . The distance δ from the centre of the sphere to a typical point on the surface of the cylindrical pore is given by $\delta^2 = b^2 + (z - Z - L)^2$, where b is the radius of the pore of length L , and Z is the distance from the centre of the sphere to the pore opened end. Consequently, the integral J_n becomes

$$J_n = b \int_{-\pi}^{\pi} \int_0^L \frac{1}{[b^2 + (z - Z - L)^2 - a^2]^n} dz d\theta. \quad (11)$$

By precisely the same method as in Sect. 3.1, the integral J_n can be obtained and in this case we evaluate the definite integral at $\psi = -\tan^{-1}(Z/\sqrt{b^2 - a^2})$ and $\psi = -\tan^{-1}[(Z + L)/\sqrt{b^2 - a^2}]$.

The total interaction energy for a spherical molecule adsorbed into a cylindrical pore is given by

$$E_{cc} = \pi a^2 \eta_1 \eta_2 \left[-4A (J_3 + 2a^2 J_4) + \frac{4B}{5} (5J_6 + 80a^2 J_7 + 336a^4 J_8 + 512a^6 J_9 + 256a^8 J_{10}) \right],$$

where η_1 and η_2 denote the mean atomic surface density for a cylindrical pore and a spherical molecule, respectively, and J_n is defined by (11).

4.2 Square prismatic pore shape

The total interaction energy between a spherical molecule and a square prismatic pore is four times the interaction energy between a sphere and a plane. Hence in this section, we determine the interaction energy between the plane of dimension L in length and $2b$ in width and the sphere with a radius of a . The pore is assumed to be located co-axially to the z -axis as shown in Fig. 1b, where the atom in the figure is replaced by the sphere. The distance δ from the centre of the sphere to a typical surface element on the pore is then given by $\delta^2 = b^2 + s^2 + (z - Z - L)^2$, where s represents the coordinate x or y and $s \in (-b, b)$. From (10), we may deduce

$$J_n = \int_0^L \int_{-b}^b \frac{1}{[b^2 + s^2 + (z - Z - L)^2 - a^2]^n} ds dz. \quad (12)$$

where we note that b is referred to the radius of the pore.

Using the same technique as described in Sect. 3.2, the integral J_n can be evaluated for a given value n . Consequently, the total interaction energy for a spherical molecule

and a square prismatic pore is given by

$$E_{cb} = 4\pi a^2 \eta_1 \eta_2 \left[-4A \left(J_3 + 2a^2 J_4 \right) + \frac{4B}{5} \left(5J_6 + 80a^2 J_7 + 336a^4 J_8 + 512a^6 J_9 + 256a^8 J_{10} \right) \right],$$

where J_n is given by (12), and again the factor 4 arises from the fact that a square prismatic pore comprises four sides of identical planes.

4.3 Conical pore shape

The model for the system of a spherical molecule interacting with a conical pore shape is depicted in Fig. 1c where we replace the single atom by a sphere of radius a . The vertex of the cone is assumed to be located at the origin, where the vertex angle is denoted by 2α with the cone base radius of b . Moreover, the length of the conical pore is assumed to be L where $L = b/\tan \alpha$. The distance δ is then given by $\delta^2 = z^2 \sec^2 \alpha - 2(Z + L)z + (Z + L)^2$.

By using the continuum approximation together with the surface integral method, we may deduce

$$J_n = \frac{\tan \alpha}{\cos \alpha} \int_{-\pi}^{\pi} \int_0^L \frac{z}{[z^2 \sec^2 \alpha - 2(Z + L)z + (Z + L)^2]^n} dz d\theta. \quad (13)$$

The analytical expression for the above equation can be determined utilizing the same technique as described in Sect. 3.3. Further, the total interaction energy for a spherical molecule and a conical pore shape is given by

$$E_{co} = \pi a^2 \eta_1 \eta_2 \left[-4A \left(J_3 + 2a^2 J_4 \right) + \frac{4B}{5} \left(5J_6 + 80a^2 J_7 + 336a^4 J_8 + 512a^6 J_9 + 256a^8 J_{10} \right) \right],$$

where J_n is given by (13).

5 Numerical results

In this paper, we consider the adsorption of a water molecule (H_2O) into a pore of silica gel (SiO_2). We assume that a water molecule can be thought of as a composition of a single oxygen atom at the centre and a cloud of two hydrogen atoms at the surface of the spherical water molecule. As a result, the total interaction energy of the system comprises (i) the interaction between a single atom and a pore, and (ii) the interaction between a sphere and a pore. Further, there are two different interactions for silica gel, SiO_2 , and the single oxygen atoms which are $Si-O$ and $O-O$, so that the interaction energy (i) consists of one-third for the interaction energy between $Si-O$, and two-third for the interaction energy between $O-O$ as a proportion of atoms. Similarly, there are two interactions for the silica gel and the assumed spherical hydrogen molecule, therefore the interaction (ii) comprises one-third for the interaction between $Si-H$ and two-third for the interaction between $O-H$.

The Lennard-Jones constants for hydrogen, silicon and oxygen atoms are taken from [22], and they are presented in Table 1. Moreover, the radius of a spherical hydrogen molecule is assumed to be 0.9584 \AA which is a bond length between oxygen and hydrogen atoms in a water molecule.

For the three types of pore, Figs. 3, 4, and 5 present the relation between the total potential energy and the distance Z , where the positive (negative) Z indicates that the

Table 1 Numerical values for the Lennard-Jones constants

Interaction	$\epsilon (\text{eV} \times 10^{-2})$	$\sigma (\text{\AA})$
H-H	0.5146	2.827
Si-Si	1.7400	4.295
O-O	0.9195	3.467

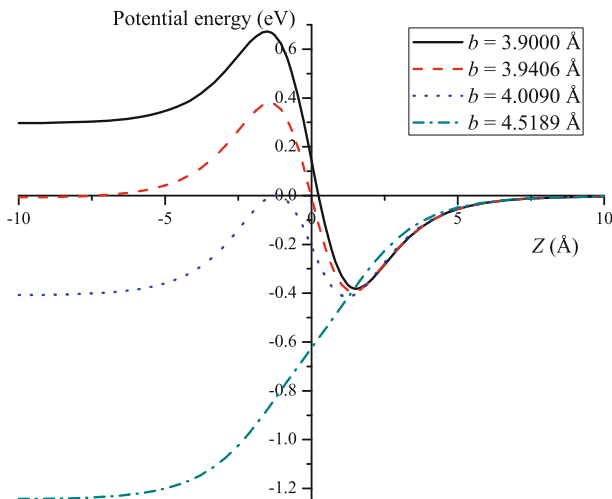


Fig. 3 Energy profiles of a water molecule absorbed into a cylindrical silica gel pore with various pore radii b and $L = 20 \text{ \AA}$

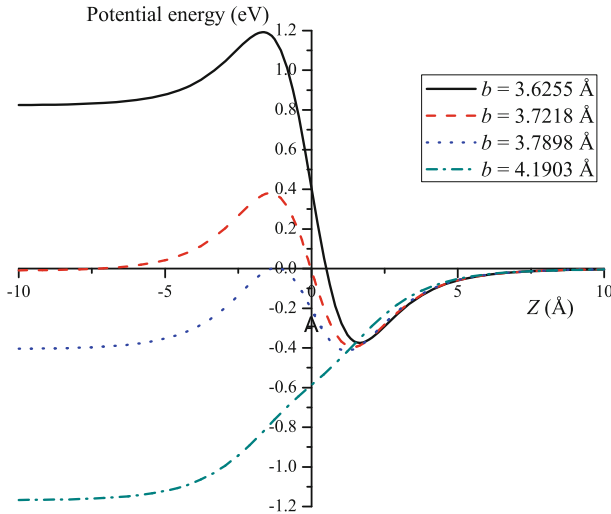


Fig. 4 Energy profiles of a water molecule absorbed into a square prismatic silica gel pore with various pore radii b and $L = 20 \text{ \AA}$

water molecule is outside (inside) the pore and the open end of the pore is located at $Z = 0$. The water molecule will be adsorbed into the pore when the energy inside the pore is lower than that outside the pore, otherwise an initial velocity is required in order for the molecule to overcome an energy barrier at the open end of the pore and to adsorb into the pore. As shown in Figs. 3 and 4, the water molecule begins to enter the cylindrical and square prismatic silica gel pores when $b = 4.009$ and 3.7898 \AA , respectively since the energy levels inside the pores are lower than those of outside. We comment that the structures of the cylindrical and square prismatic pores are similar in the sense that the radii of the pores are equal throughout the pores, whereas the radius for the conical pore decreases in the negative z -direction toward the vertex of the cone and as a result, the energy profile of the conical silica gel pore is different from those shown in Figs. 3 and 4. We can see from Fig. 5 that for a given pore size the molecule prefers to be at an equilibrium position where the energy is minimum. The energy becomes repulsive as the molecule gets further inside toward the vertex of the cone. From Fig. 5, the water molecule begins to enter the conical pore when $b \geq 4.4575 \text{ \AA}$ since the global minimum energy occurs inside the pore. To compensate for the repulsive energy received from the vertex, a larger opening radius than those of cylindrical and square prismatic pores is required for the conical pore to adsorb a water molecule.

The adsorption energy is plotted against the pore radius b for the cylindrical and square prismatic pores in Fig. 6. In this paper, the adsorption energy is referred to as the total interaction energy between a water molecule and the pore. We note that the adsorption energy for the conical pore is not determined since further along the pore there is a large repulsive force from the cone vertex which causes the infinite value of the adsorption energy. From Fig. 6, we find that the maximum adsorption energy

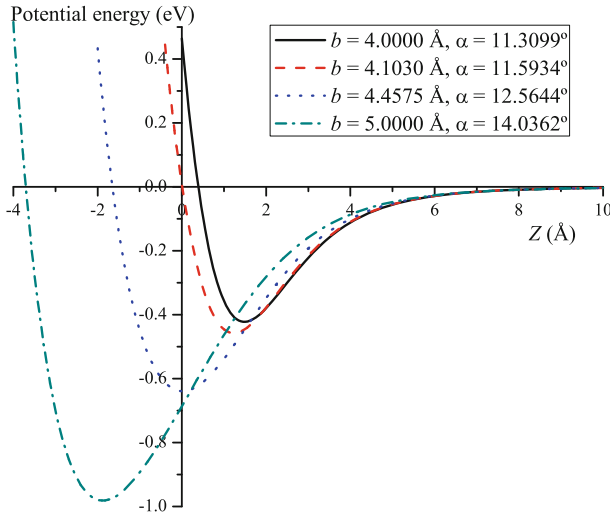


Fig. 5 Energy profiles of a water molecule absorbed into a conical silica gel pore with various pore radii b and $L = 20 \text{ \AA}$

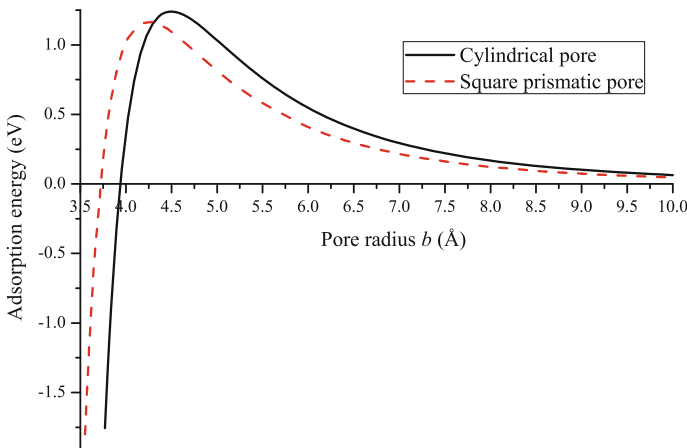


Fig. 6 Adsorption energy for cylindrical and square prismatic pores

occurs when $b = 4.5189$ and 4.1903 \AA for the cylindrical and square prismatic pores, respectively.

6 Summary

Silica gel is widely used as a water adsorbent in many commercial applications. However, pore shapes and sizes of silica gel are variable due to the synthesis processes. Since these parameters are key factors for the determination of the sorption capacity

of water into the pore, this paper considers the effect of the pore structures of silica gel upon the adsorption of a water molecule. In particular, we focus on three different shapes of silica gel pore, namely cylinder, prismatic square and cone. We note that this paper only consider the physisorption based on the van der Waals interaction between the silica gel pores and a water molecule and this interaction is modelled using the Lennard-Jones potential and a continuum approach. There is a need to reduce the pore size of silica gel for better water sorption capacity [1]. Thus, this paper provides the minimum radius required for each pore shape for adsorbing a water molecule. Our results show that among the three shapes, the square prismatic pore requires the smallest pore radius of 3.7898 Å. The minimum radii for the cylindrical and conical pores are 4.009 and 4.4575, respectively. However, the critical radii which give rise to the maximum adsorption energy for a cylindrical and a square prismatic pores are 4.5189 and 4.1903 respectively. Knowledge of these critical radii may be useful to tailor the silica gel pores to adsorb water at highest capacity and at the fastest rate. Finally, the analysis for the interaction between pores and a spherical molecule given in Sect. 4 presents a future research direction for the study of the immobilization of enzyme in pores of silica gel and the encapsulation of drugs in nanopores

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