How does the shape and surface energy of pores affect the adsorption of nanoconfined fluids?

Harry Cárdenas | Erich A. Müller

Department of Chemical Engineering, Imperial College London, U.K.

Correspondence
Erich A. Müller, Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, U.K.
Email: e.muller@imperial.ac.uk

Funding information
Engineering and Physical Sciences Research Council, Grant/Award Numbers: EP/E016340, EP/J014958, EP/P020194, EP/G036888/1

Abstract
We report a systematic molecular simulation study of the behavior of Lennard–Jones fluids inside nanopores of diverse shapes, focusing on the effect that the pore geometry and the local energetic environment have on the adsorption isotherms. Infinitely long pores with polygon (triangle, square, pentagon, hexagon, octagon, decagon, and circle) cross sections are considered. Three different pore sizes commensurate with the molecular diameters along with three different values of fluid–solid energy interactions are chosen to perform Grand Canonical Monte Carlo simulations at a subcritical temperature. Overall, the effect of nanoconfinement on the adsorption of fluids is seen to be a delicate balance between the geometric packing restrictions imposed by the hard cores of the molecules and the surfaces, the excess adsorption induced by the presence (or absence) of energetically favored “hot spots” and the overall ratio of surface/bulk fluid volume present in the pore.

KEYWORDS
adsorption, angular pores, corners, Grand Canonical Monte Carlo, molecular simulation, nanopores, templated materials

1 | INTRODUCTION

It is expected that the specific and unique details of the interactions between the molecules of a fluid have a big impact on their adsorption and diffusion under confinement.\(^5\)\(^-\)\(^8\) However, in addition to the fluid–fluid interactions, the detailed characteristics of the adsorbate material play an equally important role on the ultimate behavior of the confined fluid.\(^4\) Both natural and anthropogenic nanoporous materials have a plethora of pore geometries and sizes and it is precisely the subtleties in the local geometries that has a profound influence on the interfacial and transport properties of confined fluids. Fine-tuning the specifics of porous material geometry, something which is now in the realm of material sciences (cf. Figure 1), provides for avenues to tailor adsorbents to particular applications as has been exemplified in the rectification of ionic currents, \(^7,\)\(^8\) in the detection of nanoparticles, \(^9\) for capillary condensation/evaporation in materials, \(^10\) and in gas storage, \(^11\) among others.

Theoretical and semiempirical models used to predict the adsorption isotherms of gases require assumptions to be made on the pore geometry and the topology of the existing pore network. The most common workhorse models are based on simplified scenarios, typically either cylindrical\(^12\)\(^-\)\(^17\) or slit-like\(^18\)\(^-\)\(^23\) pore geometries. In contrast with these idealized conformations, a detailed analysis of porous materials (e.g., montmorillonite, silica, carbons, clays, etc.) through techniques such as atomic force microscopy, scanning electron microscopy, and transmission electron microscopy (TEM) reveal the widespread presence of steps, angles and wedges.\(^24\)\(^-\)\(^28\) In particular, the presence of angular pores (or wedges) in materials can affect the
behavior of confined fluids as evidenced by changes in filling transitions,29,30 the rise of a liquid and bubbles in a tube,31 unexpected adsorption of liquids,32 formation of solid phases,33 and the nucleation kinetics due to orientational order effects.28 In a similar way, the effect of the roughness of natural surfaces on adsorption has been considered in several molecular-based studies.34–37

Prof. Keith E. Gubbins, to whom this manuscript is dedicated, has been a pioneer in the use of molecular simulations to study the behavior of confined fluids. In his early papers, he commented on how “the use of classical thermodynamics to investigate fluids in narrow pores is suspect, because of the highly inhomogeneous nature of the fluid. An understanding of such systems must come from the use of statistical mechanics.”39 Some of his seminal papers in the area (which in spite of being over 30 years old are still pertinent) describe the use of Grand Canonical Monte Carlo (GCMC) methods to study adsorption isotherms of Lennard–Jones fluids in cylindrical pores,39 and the contrasting effects of pore geometry (between slit-pore and cylindrical models) on the adsorption isotherms.11 Clearly, both then and now, molecular simulations provide for an unequivocal approach to studying the general traits of ultraconfinement in fluids. More recently, Sarkisov and Monson40 quantified the effect of pore geometry in the hysteresis phenomena by comparing adsorption and desorption using molecular dynamics (MD) simulations. They considered a slit pore (with and without a closed end), a triangular pore (wedge), and an ink bottle geometry, concluding that different geometries lead to different adsorption isotherms types and different hysteresis loops. Coasne et al.41 explored the adsorption of Argon on silica surfaces and nanopores using molecular simulations. In terms of pore geometry, their work compared the adsorption inside cylindrical and hexagonal pores, showing that both isotherms are similar in shape. However, the condensation and evaporation pressures for the cylindrical pore were smaller than the pressures for the hexagonal pore. They concluded that the individual local geometries such as the pore mouth, a constriction or adding a blind end do not affect the shape of the adsorption isotherm significantly. Sun et al.44 employed elliptical cross sections, which gradually transition from circles to slit-like cross sections by manipulating the aspect ratio, finding that both geometry and surface energetics affect the transport of water through nanopores.

As seen above, the presence of irregular pores seems to play a role in the behavior of confined fluids, although we are not aware of any systematic study elucidating the structure–adsorption relationship. In spite of this, most researchers and modelers exclusively employ the cylindrical pore (or a slit pore) as an approximation of the more realistic random-shaped pores found in natural amorphous porous materials. There is an implicit presumption that the general shape and overall characteristics of the adsorption isotherm will not be affected by the shape of the pore, as long as the pore surface and volume are retained. We here question if this is a valid assumption. The core of this manuscript reports GCMC simulations of model fluids in well-defined pores in order to study the effect that the pore geometry has on the adsorption isotherms. The chosen pores have regular structures with different cross-sectional shapes but identical pore cross-sectional areas. The proposed pores have triangle, square, pentagon, hexagon, octagon, decagon, and circular cross-sectional area of different sizes (probing different surface/bulk fluid ratios) and surface energies to quantify the effect that these energetical and morphological heterogeneities have on adsorbed fluid behavior.

2 | METHODOLOGY

The model for both the fluid–fluid and the fluid–solid interactions is based on the Mie potential,45 which is a generalized form of the Lennard–Jones (LJ) potential:

$$u_{Mie}(r) = \frac{\lambda_r}{\lambda_s - \lambda_0} \left( \frac{\lambda_s}{\lambda_0} \right)^{\lambda_s/(\lambda_s - \lambda_0)} \varepsilon \left[ \left( \frac{r}{\lambda_r} \right)^{\lambda_s} - \left( \frac{r}{\lambda_s} \right)^{\lambda_s} \right]$$  \hspace{1cm} (1)

where $\sigma$ is a length scale that corresponds loosely with an effective segment diameter, $r$ is the distance between the centers of the particles, $\lambda_r$ and $\lambda_0$ are the repulsive and attractive exponents which are the repulsive and attractive exponents which are the repulsive and attractive exponents which are the repulsive and attractive exponents which
modulate the range of the potential, and $\varepsilon$ is the energy scale corresponding to the minimum potential well depth.

For all the simulations, the parameters for the fluid–fluid interaction are arbitrary chosen to provide measurable quantities, with the potential depth $\varepsilon/k_B = 100$ K (with $k_B$ the Boltzmann constant) and the molecular diameter $\sigma = 0.3$ nm.\textsuperscript{46} The values for the repulsive, $\lambda_r$, and attractive, $\lambda_a$, exponents are 12 and 6, respectively, corresponding to a single-sphere Lennard–Jones molecule. Lennard–Jones, and Mie fluids in general, show a conformal behavior.\textsuperscript{47} In practice, this means that the thermophysical properties may be scaled (reduced) appropriately, for example, the temperature, $T$, may be represented as $T^* = k_BT/\varepsilon$, where $k_B$ is Boltzmann’s constant, and the number density, $\rho$, may be scaled as $\rho^* = \rho\sigma^3$. Other properties can be similarly scaled. The behavior of a fluid, expressed in these reduced units, is accordingly universal (to within the validity of the corresponding states principle\textsuperscript{48}). In this sense, the results in this paper can be taken as representative of a whole family of model isotropic fluids.

The model pore geometries considered in this work are displayed in Figure 2, showing the corresponding triangle, square, pentagon, hexagon, decagon, and circular cross-sectional areas. All the different pore geometries used have the same cross-sectional area in order to preserve equivalent pore volumes. The solid porous materials are built using spherical segments with $\sigma = 0.2$ nm, placed in a square lattice at a center-to-center distance of 0.1 nm in order to obtain a close-to-smooth surface in a multilayer formation. This guarantees that the density of the solid material is identical for all the pore structures.

The interaction between the fluid particles and the solid walls follows the Mie potential (Equation (1)), where the repulsive, $\lambda_r$, and attractive, $\lambda_a$, exponents are 11 and 5, respectively.\textsuperscript{35,49} For the fluid–solid interaction, three different values of potential depth, $\varepsilon_{w}$, are employed, labeled weak, medium, and strong (Table 1). Furthermore, three different pore areas are employed for the simulations, as shown in Figure 3: 0.78, 3.14, and 12.56 nm$^2$ (from left to right). As a reference, the smaller circular pores have a diameter of 1 nm, while the larger ones, are of 2 and 4 nm in diameter. The length of each pore in the axial ($z$) direction was 4 nm; however, the system has periodicity in the $z$ direction, essentially making the pores infinite in length. The number of beads used for the solid material depends on the pore geometry and the pore size. For the small, medium, and big pores, the numbers of beads are approximately 60,000; 85,000; and 150,000, respectively. The number of particles in the fluid phase will depend on the chemical potential and the pore size, but the upper limit for the bigger pores at the highest pressures is approximately 1,200 molecules.

In order to speed up the simulations, the values of the Mie potential for the fluid–solid interactions are tabulated using a two-dimensional grid. This grid is built by dividing the system in 1,500 slabs along both $x$ and $y$ coordinates, leading to a spacing of $\sim0.003$ nm. During the simulation, linear interpolations between the nodes are used to calculate the energy values corresponding to the interaction between the fluid molecules and the solid wall.

### Table 1

| Interaction        | $\sigma$ (nm) | $\varepsilon/k_B$ (K) | $\lambda_r$ | $\lambda_a$ |
|--------------------|---------------|-----------------------|-------------|-------------|
| Strong (solid–fluid) | 0.25          | 12                    | 11          | 5           |
| Medium (solid–fluid) | 0.25          | 8                     | 11          | 5           |
| Weak (solid–fluid)  | 0.25          | 4                     | 11          | 5           |
| Fluid–fluid        | 0.30          | 100                   | 12          | 6           |

FIGURE 2 Pore structures considered in this work: triangle, square, pentagon, hexagon, decagon, and circular cross-sectional areas.

FIGURE 3 Representation of the different pore dimensions used in this work, labeled small, medium, and large (from left to right). Pores are drawn to scale relative to a fluid molecule of diameter $\sigma$. [Color figure can be viewed at wileyonlinelibrary.com]
Simulations are performed in the GCMC ensemble\textsuperscript{50,51} to obtain the number of particles adsorbed in the system. In this ensemble, the number of particles is allowed to vary at a fixed temperature and chemical potential. Each type of move (translation, deletion, and insertion) is chosen with equal probability. Acceptance ratio for translations is targeted at 30%. Each system is allowed to equilibrate discarding the first $10^7$ configurations, and the samples for the number of particles adsorbed inside the pore were taken over the following $10^7$ configurations. For all the cases analyzed in this work, the temperature $T$ is fixed to 100 K (corresponding to $T^\ast = 1$, below the bulk critical point). The cut-off radius for both fluid–fluid and fluid–solid intermolecular potentials is taken to be 1.5 nm ($\approx 5\sigma$).

It is customary to represent experimental data for adsorption isotherms as the adsorbed amount as a function of the pressure of the bulk gas in equilibrium. In GCMC simulations, it is the chemical potential that is specified instead of the equilibrium pressure. In order to relate the chemical potential to the external pressure $P$, the same chemical potential used for adsorption is used for simulations of a bulk phase at the same temperature and at an arbitrary volume. From the output of the latter, the bulk pressure is determined by calculating the virial.\textsuperscript{51}

3 | RESULTS

This section showcases the results obtained from GCMC simulations for the adsorption of a single-bead LJ fluid on pores of different geometries with constant cross-sectional area at the subcritical temperature of 100 K.

3.1 | Large pores

The large pores use as a reference a cylindrical pore with diameter 4.0 nm, leading to a cross-sectional area of 12.56 nm$^2$. Pore radius (and other distances) is measured from the center axis of the simulation cell up to the plane formed by the center of the outmost particles in the wall. The different pore geometries are built based on this cross-sectional area in order to retain the same volume in all the pore structures; triangle, square, pentagon, hexagon, octagon, decagon, and circular section.

Figure 5 shows three sets of adsorption isotherms, where each individual plot corresponds to a different value of fluid–solid energy interaction (cf. Table 1). For the weak wall interaction (Figure 5a) all isotherms have a Type III shape.\textsuperscript{52} The adsorption into the triangular pore shows the highest uptake in the gas region; however, after the first-order transition, in the liquid phase, the adsorbed density is the lowest for all the geometries. The adsorption in the pore with square shape is lower than the triangular geometry in the gas region, but higher in the liquid region. The isotherms for the pentagon, hexagon, octagon, and decagon continue the trend gradually converging to curves that seem indistinguishable from those of the cylindrical pore. On the other hand, at higher wall energies (Figure 5b,c), a Type IV isotherm is observed, where the triangular-shaped pore sees a higher uptake across the whole pressure range. As the number of vertices increase, the curves tend to converge to a single result coinciding with the cylindrical pore. This behavior can be rationalized with help from the energy maps in Figure 4, where for the polygonal pores it is possible to observe a concentration of higher energy sites at the vertices. As the number of vertices increases, the strength of this concentrated energy in the corners decreases and effectively smears out, with a limiting case in the circular pore section, where the entire wall has a homogeneous energy distribution.

From the adsorption isotherms displayed in Figure 5, it is possible to observe that the medium and strong interactions induce Type IV isotherms,\textsuperscript{52} which are characterized for the presence of capillary condensation. These adsorption types are often associated with the presence of hysteresis. Desorption simulations are performed for these cases, where the initial configuration employed an equilibrium high-density state and the chemical potential is decreased gradually to emulate the desorption process. Figure 6 displays in black symbols the isotherms corresponding to adsorption branch for the strong adsorption energy case while in red symbols the desorption branch is provided, with special emphasis in the zone surrounding the pore saturation. For the triangular pore no hysteresis is observed, which can be explained by the considerable enhanced adsorption. The effective high energy observed in this pore shifts the curve to the $y$-axis and seems to provide more stability when comparing adsorption and desorption. By increasing in a small amount the fluid–solid energy interaction or slightly decreasing the pore size, this isotherm will resemble a Type I (which does not exhibit hysteresis loops). For the square and pentagonal pores, we can observe the presence of a small hysteresis

![Figure 4](Image) Example energy maps, $u(x,y)$, of the fluid–solid interaction for pore geometries used in this work. The pore size corresponds to the largest pore with area 12.56 nm$^2$, and the potential depth is chosen as the strong fluid–solid interaction, $\varepsilon_w/k_B = 12.0$ K for each fluid particle interacting with a particle from the wall [Color figure can be viewed at wileyonlinelibrary.com]
loop. For the hexagon, octagon, decagon, and circle, the hysteresis loops observed are slightly larger. Similar trends in the hysteresis loops are seen for all systems studied where capillary filling is observed.

3.2 Medium pores

The medium size pores are based on a cylindrical pore with 2.0 nm diameter as reference, leading to a cross-sectional area of 3.14 nm². The energy density distribution in these pores (Figure 7) for the strong fluid–solid interaction resembles that seen in the larger pores (Figure 4): the triangular geometry has the highest energy anisotropy with the highest energy in the corners, while the distribution flattens out in the limiting case of the circular pore. While in the larger pores (Figure 4), the center of the pore experiences almost no attractive energy from the wall (evidenced by the white regions where \( \varepsilon_w/k_B \approx 0 \)), in the energy maps for the medium size pores, this central (white) area is seen to be significantly smaller (almost inexistent), which means that the effect of the wall potential extends over the whole volume inside the pore.

Figure 8 displays the collection of isotherms corresponding to the medium size pores for different pore geometries and fluid–solid interactions. A progression analogous to that seen with the large pores can be observed; the adsorption inside the triangular pore is noticeably larger than that of the other geometries. An important difference seen in these medium size pores is that in the condensed fluid region (i.e., at high-pressures) the adsorbed density is slightly different for

![Figure 5](image-url)  
**Figure 5** Adsorption isotherms at 100 K for large size pores for three different fluid–solid interactions: (a) weak \( \varepsilon_w/k_B = 4.0 \) K, (b) medium \( \varepsilon_w/k_B = 8.0 \) K, and (c) strong \( \varepsilon_w/k_B = 12.0 \) K [Color figure can be viewed at wileyonlinelibrary.com]

![Figure 6](image-url)  
**Figure 6** Adsorption/desorption isotherms in large pores of different geometries at 100 K, for the strong fluid–solid interaction, \( \varepsilon_w/k_B = 12.0 \) K. Black filled symbols represent the adsorption process, red filled symbols represent the desorption process [Color figure can be viewed at wileyonlinelibrary.com]
each pore geometry for the three different strengths of fluid–solid interactions. The limited volume (area) available for adsorption becomes more relevant for smaller pores, and the effect of confinement on the fluid packing begins to be considerable. For the case of the strong interaction energy, Figure 8c, we observe that the adsorption in the triangular pore is the highest, the uptake keeps descending as the number of sides is increased and the lowest limit is the cylindrical pore, following the same trend as the more energetic adsorption results in the big size pores (Figure 5c). We presume this is related to a favorable layering order induced by the underlying expected solid phase, which would have its highest packing in an FCC or BCC lattice. These solid structures are incompatible with the increasingly curved surfaces, but are enhanced by the presence of flat surfaces, which are more prominent the less angles the pore has. Figure 9 displays snapshots of equilibrium molecular configurations in the case of the triangular, hexagonal, and circular cross sections. The fluid in the middle region is removed in order to show only the first layer formed in the area next to the solid surface. Density profiles as a function of the distance from the surface are displayed for these systems in order to visualize the first two peaks corresponding to the first and second layer formed in the dense regions inside the pore. The highest density in the first peak of the profiles corresponds to the triangular cross section, and the smallest density represents the adsorption inside the cylindrical pore. This agrees with the results observed in Figure 8c, where in the saturation region, the adsorption hierarchy for these systems was: triangle > hexagon > circle. Isolating the first adsorbed layer of fluid (adjacent to the solid surface), allows us to calculate the hexagonal in-plane order parameter, $\psi$, that quantifies the structure of the layer. This order parameter is defined as

$$\psi = \frac{1}{N} \sum_{i=1}^{N} \exp(i\theta_i)$$

where $\theta_i$ is the angle formed between the vector joining the centers of two adjacent beads and a randomly taken director in the plane and the sum is taken over all $N$ beads. The order parameter can take values from 0 to 1, from the unordered to the fully ordered state, respectively. Figure 10 showcases Voronoi diagrams from unraveled sections of the first layers of the triangular, hexagonal, and circular pores. An interesting aspect of these diagrams is the alignment of the molecules along the direction of the vertices of the triangular and hexagonal pore (from top to bottom in the figure), which presumably is a consequence of the templating of the fluid by the surface. The values of the planar order parameter are also given in Figure 10, where we can observe that the order in the triangular pore is the highest, with around 71% of order, followed closely by the hexagonal pore with 69% of order. For the circular pore, the...
order parameter is significantly lower than the values obtained from the other two structures, with 60% of order in the first layer close to the solid wall.

In the case of the weak interaction, Figure 8a, the adsorption in the triangular pore is the highest for the gas region (low pressure), while the adsorption in the cylindrical pore is the lowest.
The adsorption isotherms for the other polygons place themselves between both the triangular and cylindrical pore. After the first-order transition, for the liquid region we can observe that all the isotherms lead to different values of density, but the order is inverted if we compare it with the strong interaction case (Figure 8c). If the strength of the wall interaction is low, the wall will become increasingly nonwetting and the fluid molecules will prefer to be removed from there. At these conditions, the uptake inside the pore becomes a geometric problem, where the available free volume is lower for the triangular pore and higher for the decagonal cross section. For the medium interaction, Figure 8b shows that all the isotherms converge to a similar value in the liquid region, as for this condition both the filling imposed by the geometry and the wall order induced by the enhanced energy are equally important.

3.3 | Small pores

The small size pores use a cylindrical pore with 1 nm diameter as reference, leading to a cross-sectional area of 0.78 nm². For the small pores, only the weak fluid–solid interaction is presented, as for the medium and strong interactions, a solid phase is induced due to the ultra-confinement effect, which increases the effective strength of the fluid–solid interactions. Figure 11 displays the energy maps for the different geometries of small pores, and it is possible to observe the high energy inside the pore, a consequence of the superposition of the attractions between neighboring walls causing the whole internal space to be strongly affected by the attraction of the solid walls.

Figure 12 displays the adsorption isotherms for the weakest fluid–solid interaction for the seven different pore geometries. All the curves exhibit a Type V isotherm shape. In this figure, we can observe that the difference between all the liquid phase densities is enhanced, where the lowest uptake is for the triangular pore and the largest uptake is for the decagonal pore, placing the other isotherms for the polygons in between. This case is similar to the lowest energy of the medium pore, when the adsorption depends on a subtle balance between the packing induced by the straight sections of the walls and the reduced "bulk" volume provided by the corners: the angles of 60° from the corners of the triangle are less accessible than the 90° angles the square, and so on. The results for the cylindrical pore seem to be an average between the square and the decagon.

Recently, Song et al. presented simulation results relating to the effect of pore shape on the adsorption of methane in graphitic media. Their results, which span only the very confined spaces up to 1.15 nm, are consistent with our findings for the smaller geometries.

3.4 | Patches

In order to illustrate the effect of high-energy vertices in isolation to the effects of having regions of flat surfaces, we employ a cylindrical pore and add three patches in a triangular configuration. This analysis
is made using the large pore system. Figure 13b displays a schematic representation of the cylindrical pore with the three equidistant patches. Each patch was built by changing the value of $\epsilon_W$ in a row of particles from the first layer of the solid pore (the one closest to the fluid). In 3D, the patches are essentially “stripes” along the length of the surface of the pore in the axial direction. This hybrid pore exhibits the morphology of a cylindrical pore, where the extent of the flat surfaces is minimal and the available bulk volume for the fluid is maximal (as there are no corners). However, instead of having a distributed surface–fluid interaction, there is an extreme energetic heterogeneity (a signature of the triangular cross section). The regular wall particles (gray color in the schematic from Figure 13b) have the strong interaction, which corresponds to the strong solid–fluid interaction (Table 1), while the patches (blue particles in Figure 13b) have an even stronger interaction of $\epsilon_{W, \text{patch}}/k_B = 200$ K for each particle in the patches. Figure 13a shows the energy map for the system used, where it is possible to observe that the energy is higher in the regions around the patches. The rest of the wall has a homogeneous energy, which corresponds to the same energy interaction that was used for the results presented in Figure 5c.

The adsorption isotherm obtained from this system is presented in Figure 13c, where three isotherms are compared, the cylinder with patches (blue crosses) with the adsorption in the triangular pore (black filled triangles), the regular cylindrical pore (red filled circles) (cf. Figure 5c). From this figure, we can observe that the isotherm obtained from the system with the patches lies in between the isotherms from the adsorption in the triangular pore and the one in the regular cylindrical pore. If we compare this with the results for the strong interaction for large pores, Figure 5c, the isotherm from the patchy system behaves similar to the adsorption into the square pore (green symbols), but the uptake is higher for low pressures, and as the pressure is increased, the isotherm converges to that of the square pore. Figure 13c clearly shows that the role of the energetical heterogeneities is only partially responsible for the change in adsorption behavior. The presence of edges, corners, and flat wall regions has an equivalently profound effect on the overall shape of the isotherm.

4 | CONCLUSIONS

This work shows the effect that different pore geometries, pore sizes, and fluid–solid energy interactions have on the adsorption of fluids in nanoconfinement. At pore sizes equal (or larger) than 4 nm (the “large” pores in this work, roughly 13 times the molecular diameter), the effects of the specific pore shape starts to become irrelevant. This, in itself, is a particular interesting result which explains the rationale behind the success of simple models (e.g., slit pores, cylindrical pores) in being able to represent commonly encountered natural and synthetic heterogeneous nanoporous materials, such as catalysts, membranes, shale rocks, etc., where pore size distributions are biased toward the micropore regions.

For pores of an equivalent 2 nm of diameter (roughly six molecular diameters), the detailed geometry starts playing an important role. The presence of acute corners provides for localized sites with a very high relative surface energy which enhances the capillary condensation. For the geometries where flat surfaces dominate (triangle, square), these flat regions provide templates that facilitate the arrangement into very high-density patches that further enhance the uptake. This is further evidenced upon employing a cylindrical pore with three energetic patches placed mimicking the vertices of a triangle within the pore, it is seen that it is not possible to obtain the same adsorption isotherm than the one obtained in the triangular pore, even though the energy used on the regions around the patches was higher. The effect of nanoconfinement on the adsorption is seen to be a delicate balance between the geometric packing restrictions imposed by the hard cores of the molecules and the surfaces, the excess adsorption induced by the presence (or absence) of energetically favored “hot spots” present in acute corners and the overall ratio of

FIGURE 13 Pore structure with three patches placed inside a cylindrical nanopore. (a) Energy map, $u(x,y)$, for the fluid–solid interaction for the same system. (b) Schematic representation of the pore. Blue stripes show the regions (patches) of enhanced adsorption. (c) Adsorption isotherm for a cylindrical pore of diameter 4.0 nm with three energetic patches of $\epsilon_{W, \text{patch}}/k_B = 200$ K each [Color figure can be viewed at wileyonlinelibrary.com]
surface/bulk fluid volume present in the pore. This has an important implication in the modeling of adsorbents with very tight pores, for example, activated carbons and shale oils. In this case, and seen with this perspective, density functional kernels based on slit pores and simulations based on collections of planar subunits will be better posed to represent the acute angles and pore geometries seen in carbonaceous materials.

In the limit of ultraconfined fluids, the realm of pores of 1 nm of effective diameter (with only two or three molecular diameters in span), the wall energetics dominate the adsorption and a continuous smooth uptake is observed, leading to Type V isotherms. For these pores of 1 nm or less, the particular geometry is very relevant, as some of the pore volume becomes inaccessible by the acute angles formed by the walls. In these cases, it would be unrealistic to describe the adsorption complex geometries with the simple kernels discussed above.

ACKNOWLEDGMENTS

Computations were performed employing the resources of the Imperial College High Performance Computing Service and the U.K. Materials and Molecular Modelling Hub, which is partially funded by Engineering and Physical Sciences Research Council (EPSRC; No. EP/P020194). The snapshots shown in this work are produced using visual MD (VMD). H. C. gratefully acknowledges the U.K. Materials and High Performance Computing Service and the Computational College High Performance Computing Service. The snapshots shown in this work are produced using visual MD (VMD). H. C. gratefully acknowledges the U.K. Materials and Molecular Modelling Hub, which is partially funded by Engineering and Physical Sciences Research Council (EPSRC) (EP/E016340). E. A. M. acknowledges support from EPSRC through research grants to the Molecular Systems Engineering group (Grant Nos. EP/E016340 and EP/J014958).

CONFLICTS OF INTEREST

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

AUTHOR CONTRIBUTIONS

Conceptualization and supervision, Erich A. Müller; investigation, software, data curation, Harry Cárdenas; writing, Erich A. Müller and Harry Cárdenas.

ORCID

Erich A. Müller https://orcid.org/0000-0002-1513-6686

REFERENCES

1. van Baten JM, Krishna R. Entropy effects in adsorption and diffusion of alkane isomers in modernite: an investigation using CBMC and MD simulations. Micropor Mesopor Mater. 2005;84:179-191. https://doi.org/10.1016/j.micromeso.2005.05.025.
2. Jang J, Sandler SI. Monte Carlo simulation for the adsorption and separation of linear and branched alkanes in IRMOF-1. Langmuir. 2006;22:5702-5707. https://doi.org/10.1021/la060506g.
3. Cárdenas H, Müller EA. Molecular simulation of the adsorption and diffusion in cylindrical nanopores: effect of shape and fluid-solid interactions. Molecules. 2019;24:1-13. https://doi.org/10.3390/molecules24030608.
4. Adebajo MO, Frost RL, Kloprogge JT, Carmona O, Kokot S. Porous materials for oil spill cleanup: a review of synthesis and adsorbing properties. J Porous Mater. 2003;10:159-170. https://doi.org/10.1023/A:1027484117065.
5. Liu K, Lihter M, Sarathy A, et al. Geometrical effect in 2D nanopores. Nano Lett. 2017;17:4223-4230. https://doi.org/10.1021/acs.nanolett.7b01091.
6. Wu S, Zheng H, Jia S, et al. Three-dimensional structures of magnesiuim nanopores. Nanotechnology. 2016;27:125603. https://doi.org/10.1088/0957-4484/27/12/125603.
7. Kubell C, Bund A. The role of nanopore geometry for the rectification of ionic currents. J Phys Chem C. 2011;115:7866-7873. https://doi.org/10.1021/jp111377h.
8. Luan B, Zhou R. Atomistic-scale fluidic diodes based on triangular nanopores in bilayer hexagonal boron nitride. Nano Lett. 2019;19:977-982. https://doi.org/10.1021/acs.nanolett.8b04208.
9. Davenport M, Healy K, Pavarnik M, et al. The role of pore geometry in single nanoparticle detection. ACS Nano. 2012;6:8366-8380. https://doi.org/10.1021/nn303126w.
10. Casanova F, Chiang CE, Ruminsky AM, Sailor MJ, Schuller IK. Controlling the role of nanopore morphology in capillary condensation. Langmuir. 2012;28:6832-6838. https://doi.org/10.1021/la204933m.
11. Cracknell RF, Gordon P, Gubbins KE. Influence of pore geometry on the design of microporous materials for methane storage. J Phys Chem. 1993;97:494-499. https://doi.org/10.1021/j100104a036.
12. Zhu HY, Ni LA, Lu GQ. A pore-size dependent equation of state for multilayer adsorption in cylindrical mesopores. Langmuir. 1999;15:3632-3641. https://doi.org/10.1021/la981515v.
13. Travalloni L, Castier M, Tavares FW, Sandler SL. Thermodynamic modelling of confined fluids using an extension of the generalized van der Waals theory. Chem Eng Sci. 2010;65:3088-3099. https://doi.org/10.1016/j.ces.2010.01.032.
14. Travalloni L, Castier M, Tavares FW. Phase equilibrium of fluids confined in porous media from an extended Peng-Robinson equation of state. Fluid Phase Equilib. 2014;362:335-341. https://doi.org/10.1016/j.fluid.2013.10.049.
15. Barbosa GD, Travalloni L, Castier M, Tavares FW. Extending an equation of state to confined fluids with basis on molecular simulations. Chem Eng Sci. 2016;153:212-220. https://doi.org/10.1016/j.ces.2016.07.033.
16. Franco LFM, Economou IG, Castier M. Statistical mechanical model for adsorption coupled with SAFT-VR Mie equation of state. Langmuir. 2017;33:11291-11298. https://doi.org/10.1021/acs.langmuir.7b02686.
17. Cárdenas H, Müller EA. Extension of the SAFT-VR Mie equation of state for adsorption. J Mol Liq. 2019;294(111639):1-12. https://doi.org/10.1016/j.molliq.2019.111639.
18. Rangarajan B, Lira CT, Subramanian R. Simplified local density model for adsorption over large pressure ranges. AIChE J. 1995;41:838-845. https://doi.org/10.1002/aic.690410411.
19. Yu Y-X, Wu J. Density functional theory for inhomogeneous mixtures of polymeric fluids. J Chem Phys. 2002;117:2368-2376. https://doi.org/10.1063/1.1491240.
20. Tripathi S, Chapman WG. Microstructure of inhomogeneous polyatomic mixtures from a density functional formalism for atomic mixtures. J Chem Phys. 2005;122(094506):1-11. https://doi.org/10.1063/1.1853371.
21. Martínez A, Castro M, McCabe C, Gil-Villegas A. Predicting adsorption isotherms using a two-dimensional statistical associating fluid theory. J Chem Phys. 2007;126(074707):1-10. https://doi.org/10.1063/1.2483505.
22. Wang G, Jiang J, Sun K, Wu J. An improved theoretical procedure for the pore-size analysis of activated carbon by gas adsorption. Chin J Chem Eng. 2018;26:551-559. https://doi.org/10.1016/j.cjche.2017.09.021.

23. Kong L, Adidharma H. Adsorption of simple square-well fluids in slit nanopores: Modelling based on generalized van der Waals partition function and Monte Carlo simulation. Chem Eng Sci. 2018;177:323-332. https://doi.org/10.1016/j.ces.2017.11.025.

24. Velev OD, Jede TA, Lobo RF, Lenhoff AM. Porous silica via colloidal crystallization. Nature. 1997;389:447-448. https://doi.org/10.1038/38921.

25. Zhao D, Feng J, Huo Q, et al. Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores. Science. 1998;23:548-552. https://doi.org/10.1126/science.279.5350.548.

26. Tanner M, Or D, Dudley LM. Adsorption and capillary condensation in porous media: liquid retention and interfacial configurations in angular pores. Water Resour Res. 1999;35:1949-1964. https://doi.org/10.1029/1999WR900098.

27. Töyüz H, Lehmann CW, Bongard H, Tesche B, Schmidt R, Schütt F. Direct imaging of the surface topology and pore system of ordered mesoporous silica (MCM-41, SBA-15, and KIT-6) and nanocast metal oxides by high resolution scanning electron microscopy. J Am Chem Soc. 2008;130:11510-11517. https://doi.org/10.1021/ja803362s.

28. Diao Y, Harada T, Myerson AS, Hatton TA, Trout BL. The role of nanopore shape in surface-induced crystallization. Nat Mater. 2011;10:867-871. https://doi.org/10.1038/nmat3117.

29. Bernardino NR, Parry AO, Romero-Enrique JM. The order of filling transitions in acute wedges. J Phys Condens Matter. 2012;24:1-6. https://doi.org/10.1088/0953-8984/24/18/182202.

30. Malijevsky A, Parry AO. Density functional study of complete, first-order and critical wedge filling transitions. J Phys Condens Matter. 2013;25:1-11. https://doi.org/10.1088/0953-8984/25/30/305005.

31. Bico J, Quéhé D. Rise of liquids and bubbles in angular capillary tubes. J Colloid Interface Sci. 2002;247:162-166. https://doi.org/10.1016/j.jcis.2001.08.002.

32. Rascón C, Parry AO. Geometry-dominated fluid adsorption on sculpted solid substrates. Nature. 2000;407:986-989. https://doi.org/10.1038/35039590.

33. Cámara LG, Bresme F. Liquids confined in wedge shaped pores: non-uniform pressure induced by pore geometry. J Chem Phys. 2004;120:11355-11358. https://doi.org/10.1063/1.1764771.

34. Jagiello J, Olivier JP. 2D-NLDFT adsorption models for carbon slit-shaped pores with surface energetic heterogeneity and geometrical corrugation. Carbon. 2013;55:70-80. https://doi.org/10.1016/j.carbon.2012.12.011.

35. Forte E, Haslam AJ, Jackson G, Müller EA. Effective coarse-grained solid-fluid potentials and their application to model adsorption of fluids on heterogeneous surfaces. Phys Chem Chem Phys. 2014;16:19165-19180. https://doi.org/10.1039/C4CP00670D.

36. Kern J, Johannsen M. Modeling adsorption on energetically heterogeneous surfaces with an extended SAFT-VR approach. J Supercrit Fluid. 2018;133:70-76. https://doi.org/10.1016/j.supflu.2017.07.014.

37. Ravigpati S, Galindo A, Jackson G, Haslam AJ. An investigation of free-energy-averaged (coarse-grained) potentials for fluid adsorption on heterogeneous solid surfaces. Phys Chem Chem Phys. 2019;21:25558-25565. https://doi.org/10.1039/C9CP02601K.

38. Peterson BK, Walton JPRB, Gubbins KE. Fluid behaviour in narrow pores. J Chem Soc Faraday Trans. 1986;82:1789-1800. https://doi.org/10.1039/F29868201789.

39. Peterson BK, Gubbins KE. Phase transitions in a cylindrical pore. Mol Phys. 1987;62:215-226. https://doi.org/10.1080/00268978700102151.

40. Sarkisov L, Monson PA. Modeling of adsorption and desorption in pores of simple geometry using molecular dynamics. Langmuir. 2001;17:7600-7604. https://doi.org/10.1021/la015521u.

41. Coasne B, di Renzo F, Galarneau A, Pellenq RJM. Adsorption of simple fluid on silica surface and nanopore: effect of surface chemistry and pore shape. Langmuir. 2008;24:7285-7293. https://doi.org/10.1021/la080056g.

42. Sedghi M, Piri M, Goual L. Molecular dynamics of wetting layer formation and forced water invasion in angular nanopores with mixed wettability. J Chem Phys. 2014;141(194703):1-12. https://doi.org/10.1063/1.4901752.

43. Wallacher D, Künzner D, Kovalev D, Knorr N, Knorr K. Capillary condensation in linear meso-pores of different shape. Phys Rev Lett. 2004;92(195704):1-4. https://doi.org/10.1103/PhysRevLett.92.195704.

44. Sun Z, Wu K, Shi J, et al. Effect of pore geometry on nanoconfined water transport behaviour. AIChE J. 2019;452:e16613-e16611. https://doi.org/10.1002/aic.16613.

45. Mie G. Zur kinetischen theorie der einatomigen körper. Ann Phys. 1903;316:657-697. https://doi.org/10.1002/andp.19033160126.

46. For comparison purposes, the LJ parameters that would represent Argon are σ = 0.34 nm, ε/k_B = 120 K, λ_r = 12 and λ_a = 6 as used by Ref 41. Similarly, the parameters representing the xy wall resemble those of a carbon wall, σ = 0.34 nm, ε/k_B = 28 K, λ_r = 12 and λ_a = 6 as used by Song Ref. 53.

47. Ramrattan NS, Avendano C, Müller EA, Galindo A. A corresponding-states framework for the description of the Mie family of intermolecular potentials. Mol Phys. 2015;113:932-947. https://doi.org/10.1080/00268976.2015.1025112.

48. Reed TM, Gubbins KE. Applied Statistical Mechanics: Thermodynamic and Transport properties of Fluids. 1st ed. New York, NY: McGraw-Hill; 1973.

49. Jiménez-Serratos G, Cárdenas H, Müller EA. Extension of the effective solid-fluid Steele potential for Mie force fields. Mol Phys. 2019;117:3840-3851. https://doi.org/10.1080/00268976.2019.1669836.

50. Frenkel D, Smit B. Understanding Molecular Simulation: From Algorithms to Applications. 2nd ed. London: Academic Press; 2002.

51. Allen MP, Tildesley DJ. The Computer Simulation of Liquids. 2nd ed. Oxford: Clarendon Press; 1977.

52. Thommes M, Kaneko K, Neimark AV, et al. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC technical report). Pure Appl Chem. 2015;87(1-19):1051-1069. https://doi.org/10.1515/pac-2014-1117.

53. Song W, Yao J, Ma J, et al. Grand canonical Monte Carlo simulations of pore structure influence on methane adsorption in micro-porous carbons with applications to coal and shale systems. Fuel. 2019;215:196-203. https://doi.org/10.1016/j.fuel.2017.11.016.

54. Ravikovitch PI, Vishnyakov A, Russo R, Neimark AV. Unified approach to pore size characterization of microporous carbonaceous materials from N_2, Ar and CO_2 adsorption isotherms. Langmuir. 2000;16:2311-2320. https://doi.org/10.1021/la991911c.

55. di Blase E, Sarkisov L. Systematic development of predictive molecular models of high surface area activated carbons for adsorption applications. Carbon. 2013;64:262-280. https://doi.org/10.1016/j.carbon.2013.07.061.

56. Marsh H, Rodriguez-Reinofo F. Activated Carbon. 1st ed. Amst.sterdam: Elsevier Science & Technology Books; 2006.

57. Humphrey W, Dalke A, Schulten K. VMD: visual molecular dynamics. J Mol Graph. 1996;14:33-38. https://doi.org/10.1016/0267-7855(96)00018-5.