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Molecular simulation of the adsorption and structure of benzene confined in mesoporous silicas

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Abstract Grand Canonical Monte Carlo simulations are used to study the adsorption of benzene at 298 K in an atomistic cylindrical silica nanopore of a diameter 3.6 nm. The adsorption involves a transition from a partially filled pore (a two layers thick film at the pore surface) to a completely filled pore configuration. Strong layering of the benzene molecules at the pore surface is observed. It is found that the layering decays as the distance to the pore surface increases. The position of the peaks for the density of the C, H atoms and the center of mass of the molecules shows that benzene molecules prefer an orientation in which their ring is perpendicular to the pore surface. This result is corroborated by calculating orientational order parameters and examining the distribution of the distances between the H and C atoms of the benzene molecules and the H and O atoms of the silica substrate.

Keywords Benzene · Capillary condensation · Monte Carlo simulation · Nanoporous material

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1 Introduction

The behavior of fluids confined within nanometric pores (size of a few molecular diameters) significantly differs from that of the bulk. In particular, the effect of confinement, surface forces, and reduced dimension affects the phase transitions (condensation, freezing, etc.) (for reviews, see Gelb et al. 1999 and Alba-Simionesco et al. 2006). Significant shifts in transitions (e.g. pressure, temperature) are observed and, in some cases, new types of phase transitions (layering, wetting, etc.) can also be found for these inhomogeneous systems. Understanding such confinement and surface effects on the thermodynamics of fluids is of crucial interest for both fundamental research and potential applications. Among nanoporous solids, the siliceous MCM-41 and SBA-15 are important materials because of their possible uses as adsorbents or catalytic supports for gas adsorption, phase separation, catalysis, preparation of nano-structured materials, drug delivery, etc. (Soler-Illia et al. 2002). The pore diameter distribution is narrow with an average value that can be varied from 2 up to 20 nm, depending on the synthesis conditions. From a fundamental point of view, MCM-41 and SBA-15 are considered as model materials to investigate the effect of nanoconfinement on the thermodynamic properties of fluids. In particular, the simple cylindrical geometry of the pores in these materials makes it possible to address in a simple way the effect of confinement on the adsorption, capillary condensation, and freezing/melting of fluids in nanopores.

Most simulation and theoretical studies on fluids confined in MCM-41 or SBA-15 have been performed for simple adsorbates, i.e. non polar and near spherical molecules (Maddox et al. 1997; Ravikovitch et al. 2004; Gelb 2002; Neimark et al. 2003; Coasne and Pellenq 2004a, 2004b;

Coasne et al. 2006a). These works have provided significant insights on the existence and nature of phase transitions for these simple probe molecules. In contrast, the behavior of more complex fluids confined in atomistic models of these materials has received less attention (Gallo et al. 2002; Morineau et al. 2002; Alba-Simionesco et al. 2003; He and Seaton 2003; Schumacher et al. 2006) and remains to be clarified. The aim of the present work is to investigate by means of molecular simulation the behavior of benzene confined within an atomistic silica nanopore of MCM-41. The all-atom model developed by Jorgensen and Severance (Jorgensen and Severance 1990) for benzene has been used so that we can address the orientation and conformation of the adsorbate near the silica surface of the pore and within the pore center. Grand Canonical Monte Carlo (GCMC) simulations are used to determine the adsorption isotherm and isosteric heat of adsorption curve. We also investigate the structure of benzene confined in the silica nanopore and compare it with its bulk counterpart.

2 Computational techniques

The GCMC technique consists of determining the properties of a system at a constant volume V (the pore with the adsorbed phase) in equilibrium with an infinite fictitious reservoir of particles imposing its chemical potential μ and its temperature T (Frenkel and Smit 2002). The silica pore used in this work was prepared according to the method proposed by Pellenq and Levitz to build numerical Vycor samples (Pellenq and Levitz 2002). This procedure allows cutting out portions of an initial silica volume in order to obtain different porous matrices. In order to model the pore inner surface in a realistic way, we removed all silicon atoms being in an incomplete tetrahedral environment and all non-bonded oxygen atoms. The electroneutrality of the simulation box is ensured by saturating all oxygen dangling bonds with hydrogen atoms; the partial charges carried by the atoms of the substrate are $q_O = -1e$, $q_{Si} = +2e$ and $q_H = +0.5e$. Regular or irregular cylindrical pores can be easily prepared with this procedure (Coasne et al. 2004, 2006b). The pore model considered in this work is a unique cylindrical nanopore of a diameter $D = 3.6$ nm and a length $L = 6.417$ nm. Due to the use of periodic boundary conditions, the length of this pore can be considered as infinite; in particular, this implies that the pore has no opening towards the external phase.

Benzene was described in our simulations using the all-atom model by Jorgensen and Severance (Jorgensen and Severance 1990). In this model, each C and H atom of the rigid benzene molecule possesses a partial charge that interacts through the Coulombic interaction. In addition, each site of the molecule is a center of repulsion/dispersion interactions which interact through the Lennard–Jones potential. Interactions between the C and H atoms of benzene and the Si, O, and H atoms of the silica nanopore were calculated using the PN-TraZ potential as reported for rare gas adsorption in zeolite (Pellenq and Nicholson 1994) or in porous silica glass (Pellenq and Levitz 2002). The intermolecular energy is written as the sum of the dispersion interaction with a repulsive short-range contribution and an induction term due to the interaction of the adsorbed atom with the local field created by the partial charges of the atoms in the substrate. The choice of the PN-TrAZ model to describe the benzene/silica interaction was motivated by the good transferability of this model in the case of water in porous silica (Puibasset and Pellenq 2004). The Coulomb energy was computed without the use of Ewald summation due to the large size of the simulation box, absence of isolated charge, and absence of dipolar moment of the adsorbate. A Monte Carlo step in the present work corresponds to a molecule displacement or rotation attempt and either a deletion or a creation attempt. The system was first allowed to equilibrate in the course of a first GCMC run. Afterward, the number of particles in the system and the isosteric heat of adsorption, which fluctuate about a steady value, were averaged using 10^5 Monte Carlo steps per particle.

3 Results

3.1 Adsorption isotherms

The simulated benzene adsorption isotherm obtained at 298 K for the cylindrical nanopore MCM-41 with $D = 3.6$ nm is shown in Fig. 1. Adsorbed amounts are reported as the total number of molecules adsorbed in the pore as a function of the relative pressure P/P_0 ($P_0 \sim 12040$ Pa is the experimental saturated vapor pressure). At low pressures, the pore surface is covered by a quasi-homogeneous layer of benzene molecules (see the typical molecular configuration obtained at $P/P_0 = 3.2 \times 10^{-3}$ in Fig. 2). At low pressures, the adsorbed amount increases rapidly with pressure; this regime corresponds to the continuous filling

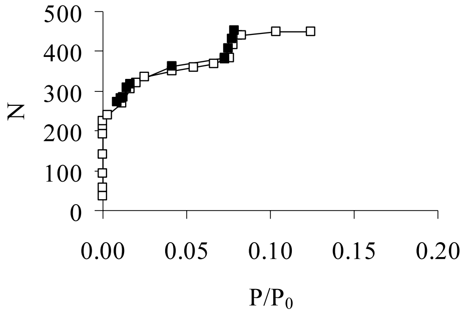

Fig. 1 Adsorption isotherm of benzene at 298 K in a MCM-41 silica nanopore with $D = 3.6$ nm. *Open* and *closed symbols* correspond to the adsorption and desorption data, respectively

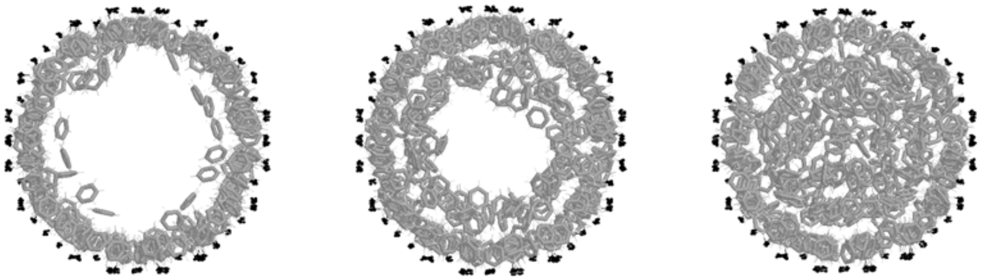

Fig. 2 Typical configurations of benzene adsorbed at 298 K in a MCM-41 nanopore with $D = 3.6$ nm. The pressure P is $3.2 \times 10^{-3} P_0$ (*left*), $2.5 \times 10^{-2} P_0$ (*middle*), and $8.3 \times 10^{-2} P_0$ (*right*). *Grey sticks* are the C–C bonds of the benzene rings while *black spheres* are hydrogen atoms that delimit the pore surface (the hydrogen atoms of benzene are not shown for the sake of clarity)

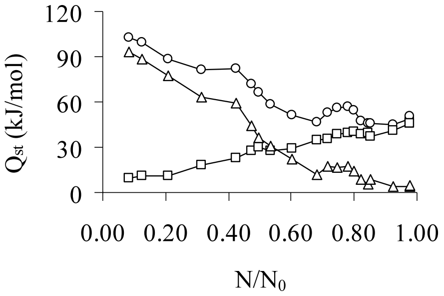

Fig. 3 Isosteric heat of adsorption Q_{st} as a function of the filling fraction N/N$_0$ for benzene confined at 298 K in a MCM-41 nanopore with $D = 3.6$ nm. The *circles* correspond to the overall isosteric heat of adsorption. *Triangles* and *squares* are the fluid-wall and fluid-fluid contributions to the isosteric heat of adsorption, respectively

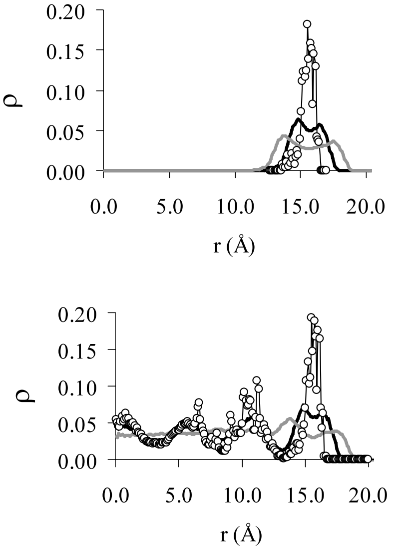

Fig. 4 Density profile of benzene confined at 298 K in a MCM-41 nanopore with $D = 3.6$ nm: (*top*) $P = 3.3 \times 10^{-6} P_0$ and (*bottom*) $P = 0.12 P_0$. The *circles* correspond to the overall density that was calculated by considering the center of mass of the molecules. The *black* and *grey lines* are the density profiles of the C and H atoms of the molecules, respectively

of the first layer adsorbed at the pore surface. At higher pressures, the adsorption isotherm exhibits two steps located at about $P \sim 1.5 \times 10^{-2} P_0$ and $P \sim 7.8 \times 10^{-2} P_0$, respectively. The first step in the adsorption isotherm corresponds to the filling of the second layer at the pore surface. This result is confirmed by the inspection of the simulation snapshots in Fig. 2 which shows that the pore surface at $P = 2.5 \times 10^{-2} P_0$ is covered by two layers of benzene molecules. The second step in the adsorption isotherm corresponds to capillary condensation in the pore (the simulation snapshot in Fig. 2 shows that the pore is completely filled at $P = 8.3 \times 10^{-2} P_0$). As can be seen in Fig. 1, both the filling of the second layer and the pore center are reversible. These results show that the adsorption of benzene in the MCM-41 nanopore involves a transition from a partially filled pore (a two layers thick film adsorbed at the pore surface) to a completely filled pore configuration.

We also report in Fig. 3 the isosteric heat of adsorption, Q_{st}, for benzene in the silica nanopore with $D = 3.6$ nm. This quantity has two components: the adsorbate/adsorbate and the adsorbate/substrate contributions. This type of isosteric heat curve is usually interpreted as being characteristic of adsorption in an energetically heterogeneous environment. The decrease in Q_{st} as the loading increases is due to the decrease of the adsorbate/silica contribution; the adsorbate/adsorbate contribution is, of course, an increasing function of loading. Q_{st} decreases down to a value that is close to the heat of liquefaction of bulk benzene, ~34 kJ/mol.

3.2 Structure of adsorbed benzene

We now discuss the structure of benzene adsorbed in the silica nanopore with $D = 3.6$ nm. The density profile of benzene adsorbed at low and high pressures are shown in Fig. 4. We report the density profile of the center of mass of the molecules and those of the C and H atoms. These density profiles confirm that a molecular layer of benzene is adsorbed at the pore surface at low pressure. The position of the peaks for the density of the C and H atoms shows that the benzene molecules tend to orientate themselves perpendicularly to the pore surface. The precise arrangement of the benzene molecules towards the O and H atoms of the silica

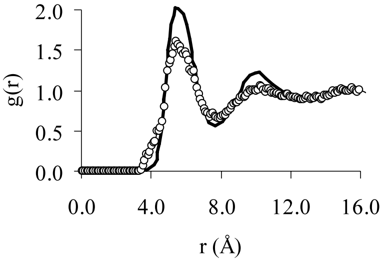

Fig. 5 Pair correlation function g(r) for the center of mass of the benzene molecules: (*open circles*) confined benzene and (*black thick line*) bulk benzene. The data for bulk benzene correspond to the simulations by Jorgensen and Severance (1990)

substrate will be discussed in detail below. The density profile of the center of mass of the benzene molecules when the pore is completely filled shows density oscillations that are characteristic of non-uniform fluids. Such a spatial ordering of fluids in the vicinity of surfaces or confined in porous materials has been discussed in detail in the literature (for a review, see Evans 1990). As for the case of the density profile obtained at low pressure, the density profiles for the C and H atoms of the benzene molecules adsorbed in the first layer at high pressure show that these molecules remain significantly orientated perpendicularly to the pore surface. On the other hand, the density profiles for the C and H atoms of the benzene molecules in the pore center (starting from the second layer) show that these molecules do not exhibit orientational order, in contrast to those located in the first layer.

The pair correlation function g(r) of the center of mass of the confined benzene molecules when the pore is completely filled is shown in Fig. 5. We also report the pair correlation function of the bulk liquid at the same temperature (which has been calculated by Jorgensen and Severance for the same model of benzene molecules, Jorgensen and Severance 1990). We also show in Fig. 6 the partial pair correlation corresponding to the C–C and C–H contributions. These curves are also compared with their bulk counterpart (liquid phase). All the pair correlation functions for the confined fluid have been corrected for excluded volume effects (Gallo et al. 2002; Morineau and Alba-Simionesco 2003) according to the method reported by Gallo et al. The pair correlation function for the center of mass of the molecules in the pore shows that the confined fluid has a liquid-like structure as only short range positional order is observed. This result is consistent with experimental data for benzene confined in MCM-41 pores having a diameter smaller than 4.7 nm (Dosseh et al. 2003). It is found that the peaks of the g(r) function for the confined molecules are located at the same position as those for the bulk fluid. On the other hand, the amplitude of these peaks for the confined fluid are smaller than those for the bulk. This result suggests that the confined fluid is less ordered than in the bulk phase, due to the strong interaction with the pore wall. It appears that the confined fluid adopts a less organized liquid structure in order to optimize its molecular arrangement near the pore wall. In contrast, the partial correlation functions for the C–C and C–H pairs are very similar to those for the bulk liquid. In particular, the results above suggest that the correlation length for the bulk and confined fluids are both of a few molecular diameters.

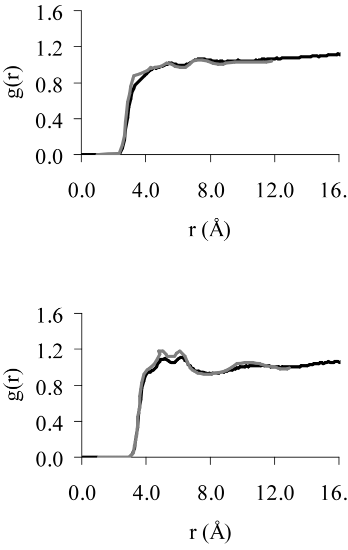

Fig. 6 Partial pair correlation function g(r) for confined benzene (*black line*) and for bulk benzene (*grey line*): (*bottom*) C–C contribution and (*top*) C–H contribution. The H–H contribution is not shown. The data for bulk benzene correspond to the simulations by Jorgensen and Severance (1990)

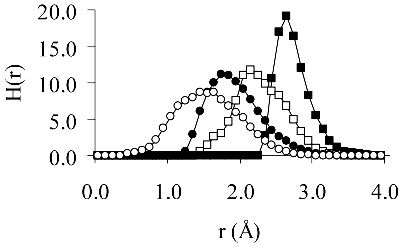

Fig. 7 Histogram of the shortest distances between the H and C atoms of the benzene molecules and the H and O atoms of the silica substrate at $P = 4.0 \times 10^{-6}$ P_0: H_{C6H6}–$H_{subs.}$ (*open circles*), H_{C6H6}–$O_{subs.}$ (*closed circles*), C_{C6H6}–$H_{subs.}$ (*open squares*), C_{C6H6}–$O_{subs.}$ (*closed squares*)

Figure 7 shows the distribution of the distances between the H and C atoms of the benzene molecules (O_{C6H6} and H_{C6H6}) and the H and O atoms of the silica substrate ($O_{subs.}$ and $H_{subs.}$). Each of the following distances have been calculated H_{C6H6}–$H_{subs.}$, H_{C6H6}–$O_{subs.}$, C_{C6H6}–$H_{subs.}$, and C_{C6H6}–$O_{subs.}$. In order to consider only the local structure of the molecules in the vicinity of the pore surface, these distributions have been calculated at very low pressures ($P = 4.0 \times 10^{-6}$ P_0). The distributions in Fig. 7 show

Table 1 Order parameter S for the layers of benzene confined at different pressures in a MCM-41 nanopore with $D = 3.6$ nm. Contact layer corresponds to the layer in contact to the pore surface

P/P_0	Nb. of layers	S (contact layer)	S (second layer)	S (third layer)	S (fourth layer)
3.2×10^{-3}	1	−0.36	–	–	–
2.5×10^{-2}	2	−0.31	−0.01	–	–
1.2×10^{-1}	4	−0.28	−0.02	0.01	0.04

that the shortest distance between benzene and the silica surface is the H_{C6H6}–$H_{subs.}$ distance (d ~ 1.5 Å). The second, third, and fourth shortest distances between benzene molecule and the silica surface are the H_{C6H6}–$O_{subs.}$ (d ~ 1.8 Å), C_{C6H6}–$H_{subs.}$ (d ~ 2.2 Å), and C_{C6H6}–$O_{subs.}$ (d ~ 2.6 Å) distances, respectively. The fact that the H atoms of benzene point towards the H atoms of the silica surface is surprising as the H_{C6H6}–$H_{subs.}$ interaction is repulsive as both H_{C6H6} and $H_{subs.}$ carry positive charges. A possible explanation is that the CH bond of the benzene molecules tend to be orientated in a direction parallel to the OH bonds of the silica surface so that the attractive H_{C6H6}–$O_{subs.}$ and C_{C6H6}–$H_{subs.}$ interactions overcompensate the repulsive C_{C6H6}–$O_{subs.}$ and H_{C6H6}–$H_{subs.}$ interactions. Taking into account the average distances reported above and the charges carried by the atoms, a simple estimate of the balance between the attractive and repulsive Coulombic interactions shows that such a conformation of the benzene molecules in the vicinity of the silica surface is favorable, i.e. $\sum_{\substack{i=C,H \\ j=O,H}} q_i q_j / d_{ij} < 0$.

This interpretation is consistent with the density profiles reported in Fig. 4, which shows that benzene adsorbed at the pore surface is perpendicular to the pore surface. We confirmed this result by calculating the following orientational order parameter for each layer of confined adsorbate:

$$S = \left\langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \right\rangle \tag{1}$$

where θ is the angle between the normal vector to a benzene molecule and the normal vector to the pore surface. The brackets in the equation above denote an average over all of the adsorbed molecules. S ~ −0.5 and ~1 for benzene molecules perpendicular and parallel to the pore surface, respectively. On the other hand, S ~ 0 for adsorbed molecules having no particular orientation with respect to the pore surface. Table 1 reports the values of the order parameter S for the layers of benzene confined at different pressures in the nanopore with $D = 3.6$ nm. For all loadings, it is found that S ~ −0.3 for the molecules located in the contact layer. This results confirms that the molecules prefer an orientation in which their ring is perpendicular to the pore surface. The fact that S is not strictly equal to −0.5 is due to the thermal activity of the molecules which introduces some disorder in the organization of the adsorbate. Interestingly, S for the contact layer decreases when molecules get adsorbed in the second, third, and fourth layers, i.e. the molecules that are not located in the vicinity of the silica surface induce a perturbation in the arrangement of the molecules in the contact layer. In contrast to the results for the contact layer, we found that the molecules in the second, third, and fourth layers have no preferred orientation with respect to the pore surface, i.e. S ~ 0. We also calculated the distribution of angles, $\theta' = (\text{CH}, \text{HO})$, between the CH bond of a benzene molecule and the closest OH group of the pore surface. Calculations for the angle θ' were limited to benzene molecules located at a distance of less than 4 Å in order to consider only molecules within the first layer (in contact with the pore walls). The largest probability is obtained for $\theta' = 0°$ (distribution not shown). This result shows that the perpendicular orientation of benzene at the pore surface is mainly driven by the attractive H_{C6H6}–$O_{subs.}$ and C_{C6H6}–$H_{subs.}$ electrostatic interactions. This result is consistent with the distribution of distances between the H and C atoms of the benzene molecules and the H and O atoms of the silica substrate (see Fig. 7 and discussion above).

4 Conclusion

This work reports a molecular simulation study of the adsorption of benzene in an atomistic nanoporous silica pore of a simple geometry. Capillary condensation in this pore involves a transition from a partially filled pore (a two layers thick film at the pore surface) to a completely filled pore configuration; as the pressure increases, the adsorbed film collapses in the pore center. The density profiles of confined benzene show the strong layering of the adsorbate at the pore surface. As expected, it is found that the layering decays as the distance to the pore surface increases. The position of the peaks for the density of the C, H atoms and the center of mass of the molecules shows that benzene molecules prefer an orientation in which their ring is perpendicular to the pore surface. This result is corroborated by looking at the distribution of the distances between the H and C atoms of the benzene molecules and the H and O atoms of the silica substrate ($O_{subs.}$ and $H_{subs.}$). These results are also confirmed by calculating order parameters that characterize the orientation of the benzene molecules with respect to the silica surface and the OH silanol groups.

In future work, we plan to study the adsorption of benzene on silica surfaces and nanopores (Coasne et al. 2007) and compare with available experimental data (Dosseh et al. 2003; Ribeiro Carrott et al. 2001). We will investigate the effect of the surface chemistry by varying the density of OH groups of the silica substrate. We will also address the effect of the pore length on the adsorption and desorption mechanisms by comparing the results for an infinitely long pore and a pore of a finite length opened at both ends towards a bulk reservoir. Finally, we will also address the effect of temperature on the adsorption and structure of benzene in the vicinity of silica surfaces by considering two temperatures (298 K and 323 K). Starting from well-equilibrated configurations of confined benzene, we will also determine the evolution of the structure/density of confined benzene as the temperature decreases in order to study freezing of such an adsorbate. We will also perform Molecular Dynamics simulations to obtain information regarding the dynamics of the confined fluid. This will provide useful information regarding the nature of the confined phase, such as its diffusion coefficient and relaxation time.

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References

Alba-Simionesco, C., Dosseh, G., Dumont, E., Frick, B., Geil, B., Morineau, D., Teboul, V., Xia, Y.: Confinement of molecular liquids: consequences on thermodynamics, static and dynamical properties of benzene and toluene. Eur. Phys. J. E **12**, 19–28 (2003)

Alba-Simionesco, C., Coasne, B., Dosseh, G., Dudziak, G., Gubbins, K.E., Radhakrishnan, R., Sliwinska-Bartkowiak, M.: Effects of confinement on freezing and melting. J. Phys. Condens. Matter **18**, R15–R68 (2006)

Coasne, B., Pellenq, R.J.-M.: Grand Canonical Monte Carlo simulation of argon adsorption at the surface of silica nanopores: effect of pore size, pore morphology, and surface roughness. J. Chem. Phys. **120**, 2913–2922 (2004a)

Coasne, B., Pellenq, R.J.-M.: A Grand Canonical Monte Carlo study of capillary condensation in mesoporous media: effect of the pore morphology and topology. J. Chem. Phys. **121**, 3767–3774 (2004b)

Coasne, B., Gubbins, K.E., Pellenq, R.J.-M.: A Grand Canonical Monte Carlo study of adsorption and capillary phenomena in nanopores of various morphologies and topologies: testing the BET and BJH characterization methods. Part. Part. Charact. Syst. **21**, 149–160 (2004)

Coasne, B., Hung, F.R., Pellenq, R.J.M., Siperstein, F.R., Gubbins, K.E.: Adsorption of simple gases in MCM-41 materials: the role of surface roughness. Langmuir **22**, 194–202 (2006a)

Coasne, B., Galarneau, A., Di Renzo, F., Pellenq, R.J.M.: Gas adsorption in mesoporous micelle-templated silicas: MCM-41, MCM-48, and SBA-15. Langmuir **22**, 11197–11105 (2006b)

Coasne, B., Alba-Simionesco, C., Audonnet, F., Dosseh, G., Gubbins, K.E.: Adsorption and structure of benzene on silica surfaces and nanopores. *Langmuir* (2007, to be submitted)

Dosseh, G., Xia, Y., Alba-Simionesco, C.: Cyclohexane and benzene confined in MCM-41 and SBA-15: confinement effects on freezing and melting. J. Phys. Chem. B **107**, 6445–6453 (2003)

Evans, R.: Fluids adsorbed in narrow pores: phase equilibria and structure. J. Phys. Condens. Matter **2**, 8989–9007 (1990)

Frenkel, D., Smit, B.: Understanding Molecular Simulation, 2nd edn. Academic, New York (2002)

Gallo, P., Ricci, M.A., Rovere, M.: Layer analysis of the structure of water confined in Vycor glass. J. Chem. Phys. **116**, 342–346 (2002)

Gelb, L.D.: The ins and outs of capillary condensation in cylindrical pores. Mol. Phys. **100**, 2049–2057 (2002)

Gelb, L.D., Gubbins, K.E., Radhakrishnan, R., Sliwinska-Bartkowiak, M.: Phase separation in confined systems. Rep. Prog. Phys. **62**, 1573–1659 (1999)

He, Y., Seaton, N.A.: Experimental and computer simulation studies of the adsorption of ethane, carbon dioxide, and their binary mixtures in MCM-41. Langmuir **19**, 10132–10138 (2003)

Jorgensen, W.L., Severance, D.L.: Aromatic-aromatic interactions: free energy profiles for the benzene dimer in water, chloroform, and liquid benzene. J. Am. Chem. Soc. **112**, 4768–4774 (1990)

Maddox, M.W., Olivier, J.P., Gubbins, K.E.: Characterization of MCM-41 using molecular simulation: heterogeneity effects. Langmuir **13**, 1737–1745 (1997)

Morineau, D., Alba-Simionesco, C.: Liquids in confined geometry: how to connect changes in the structure factor to modifications of local order. J. Chem. Phys. **118**, 9389–9400 (2003)

Morineau, D., Xia, Y., Alba-Simionesco, C.: Finite size and surface effects on the glass transition of liquid toluene confined in cylindrical mesopores. J. Chem. Phys. **117**, 8966–8972 (2002)

Neimark, A.V., Ravikovitch, P.I., Vishnyakov, A.: Bridging scales from molecular simulations to classical thermodynamics: density functional theory of capillary condensation in nanopores. J. Phys. Condens. Matter **15**, 347–365 (2003)

Pellenq, R.J.-M., Nicholson, D.: Intermolecular potential function for the physical adsorption of rare gases in zeolite. J. Phys. Chem. **98**, 13339–13349 (1994)

Pellenq, R.J.-M., Levitz, P.E.: Capillary condensation in a disordered mesoporous medium: a Grand Canonical Monte Carlo study. Mol. Phys. **100**, 2059–2077 (2002)

Puibasset, J., Pellenq, R.J.M.: A Grand Canonical Monte Carlo simulation study of water adsorption on Vycor-like hydrophilic mesoporous silica at different temperatures. J. Phys. Condens. Matter **16**, S5329–S5343 (2004)

Ravikovitch, P.I., Vishnyakov, A., Neimark, A.V.: Density functional theories and molecular simulations of adsorption and phase transitions in nanopores. Phys. Rev. E **64**, 011602 (2004)

Ribeiro Carrott, M.M.L., Candeias, A.J.E., Carrott, P.J.M., Ravikovitch, P.I., Neimark, A.V., Sequeira, A.D.: Adsorption of nitrogen, neopentane, n-hexane, benzene and methanol for the evaluation of pore sizes in silica grades of MCM-41. Microporous Mesoporous Mater. **47**, 323–337 (2001)

Schumacher, C., Gonzalez, J., Wright, P.A., Seaton, N.A.: Generation of atomistic models of periodic mesoporous silica by kinetic Monte Carlo simulation of the synthesis of the material. J. Phys. Chem. B **110**, 319–333 (2006)

Soler-Illia, G.J. de A.A., Sanchez, C., Lebeau, B., Patarin, J.: Chemical strategies to design textured materials: from microporous and mesoporous oxides to nanonetworks and hierarchical structures. Chem. Rev. **102**, 4093–4138 (2002)