

ADSORPTION POTENTIALS AND SIMULATIONS IN CARBON SLITS AND CYLINDERS

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Introduction

In grand canonical ensemble Monte Carlo (GCEMC) molecular simulations of fluid adsorption in slit-shaped carbon pores, the Steele 10-4-3 potential [1] is commonly used to represent the fluid-pore wall interaction. Similar approaches have been used to simulate adsorption in cylindrical carbon pores [2]. These approaches exclude possible studies of the influence of pore wall structure on adsorption properties. However, in both carbon slits and cylinders, the pore wall structure may have significant influence on adsorption. Here we use new fluid-wall potentials that account for different pore wall structures to study adsorption in both carbon slits and cylinders. The new potentials are discussed, and GCEMC simulations of adsorption of N_2 in both carbon slits and cylinders at 77 K that incorporate these potentials are reported. As with previous studies of this kind, our work is directed to understanding adsorption in active carbons, where pores are generally slit-shaped, and in carbon nanotubes where pores are cylindrical.

Potentials and Simulations

The GCEMC method used here has been reported elsewhere [3]. In the simulations, the Lennard-Jones 12:6 potential was used to model all intermolecular interactions. The fluid-fluid LJ parameters used here for N_2 - N_2 interactions are $\sigma_{ff}=0.3572$ nm and $\epsilon_{ff}/k=93.98$ K.

For carbon slits, the fluid-wall potential U is given by

$$U(z) = u(z) + u(H - z)$$

$$u(z) = 4\pi\rho_a\epsilon_{sf}\sigma_{sf}^2 \sum_{i=0}^{n-1} \left[\frac{1}{5} \left(\frac{\sigma_{sf}}{z+i\Delta} \right)^{10} - \frac{1}{2} \left(\frac{\sigma_{sf}}{z+i\Delta} \right)^4 \right]$$

where H is the pore width, n is the number of layers in the pore wall and other parameters are as in [3]. The solid-fluid LJ parameters used here are $\sigma_{sf} = 0.3494$ nm and $\epsilon_{sf}/k = 53.22$ K.

For cylinders with walls comprising one layer of carbon atoms, the potential described by Everett and Powl [4] was used to model the fluid-wall potential. This fluid-wall potential was then summed over n layers in the wall to give

$$U(r) = 3\pi^2\rho_a\epsilon_{sf}\sigma_{sf}^2$$

$$\sum_{i=0}^{n-1} \left[\frac{21}{32} \left(\frac{\sigma_{sf}}{R+i\Delta} \right)^{10} \sum_{m=0}^{\infty} \alpha_m \left(\frac{r}{R+i\Delta} \right)^{2m} - \left(\frac{\sigma_{sf}}{R+i\Delta} \right)^4 \sum_{m=0}^{\infty} \beta_m \left(\frac{r}{R+i\Delta} \right)^{2m} \right]$$

where α and β are complex function of m [4], and R is the radius of the cylindrical pore.

Results and Discussion

Calculated fluid-wall potentials both in the case of carbon slits and cylinders show the significant influence of pore wall thickness, n (all other factors being kept constant). Figure 1 shows that the potential minimum in both slits ($H = 1.37$ nm) and cylinders ($D = 2R = 1.37$ nm) decreases rapidly for $n < 5$, but more gradually for $n > 5$. A new observation is that the influence of pore wall thickness is more pronounced in cylinders than in slits. However, the deeper potential minimum in cylinders compared with slits is as expected. These features appear generally for cylinders and slits with pores in the micropore size range.

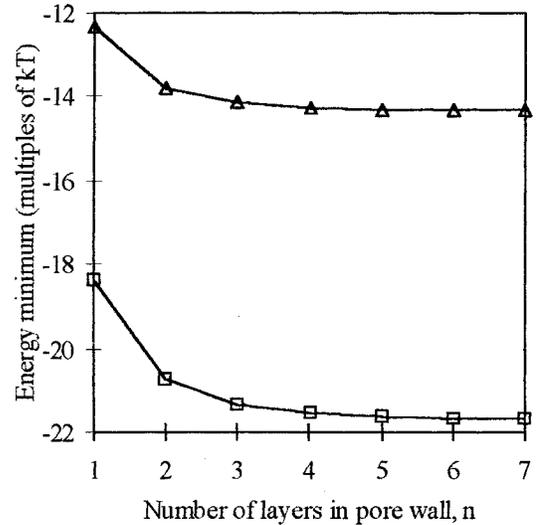


Figure 1. Energy minimum of adsorption potential as a function of pore wall thickness for an N_2 molecule at 77 K in carbon slits ($H = 1.37$ nm - triangles) and cylinders ($D = 1.37$ nm - squares).

Figures 2 and 3 show simulated N_2 adsorption isotherms at 77 K in a 2.5 nm cylinder and 2.5 nm slit with varying pore wall thickness. The y-axes of these figures are mean fluid density in pores divided by the bulk density of liquid N_2 at 77 K ($28.9 \text{ mmol cm}^{-3}$); the x-axes (on a logarithmic scale) are relative pressure.

The trends in each figure are similar. There is the formation of a monolayer at low pressures followed by pore filling or condensation at higher pressures. Another general feature is that isotherms are shifted to lower pressures for thicker pore walls. This is clearly due to enhanced adsorption potentials for $n > 1$, see Figure 1. This effect also appears to result in slightly denser (tightly packed) monolayers and condensate in pores with thicker walls. The effects on adsorption of wall thickness are most pronounced when n varies from 1 to 5. Thereafter effects of varying wall thickness are small, and pore walls are effectively infinitely thick.

Figures 2 and 3 also show that completed monolayers and filled pores occur at lower pressures in cylinders than in slits. Again this is a result of greater enhancement of adsorption potential in cylinders compared with slits. New, unexpected observations are that monolayer densities in slits are slightly lower than those in cylinders, but pore condensate densities in slits are slightly higher than in cylinders. These effects are being explored further, but at this stage we think that these effects are due to differences in how atoms pack on the surfaces and in the volumes of different shaped pores.

Concluding Remarks

Potentials and simulated isotherms for the adsorption of N_2 at 77 K in carbon slits and cylinders are influenced by pore wall thickness, especially when the number of carbon layers in walls varies in the range 1-5. Monolayers form and pores fill at lower pressures in cylinders than in slits, due to the greater enhancement of adsorption in the former geometry. There are some subtle differences between fluid densities in cylindrical and slit-shaped pores that need further exploration. The findings for cylinders have obvious implications for adsorption of gases in single- and multi-wall nanotubes.

References

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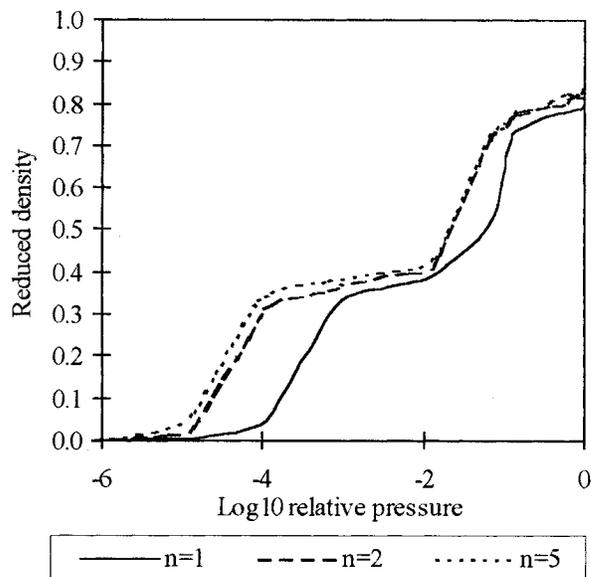


Figure 2. Simulated N_2 adsorption isotherms at 77 K in carbon cylinders of diameter $D = 2.5 \text{ nm}$, and $n = 1, 2$ and 5 layers in pore wall.

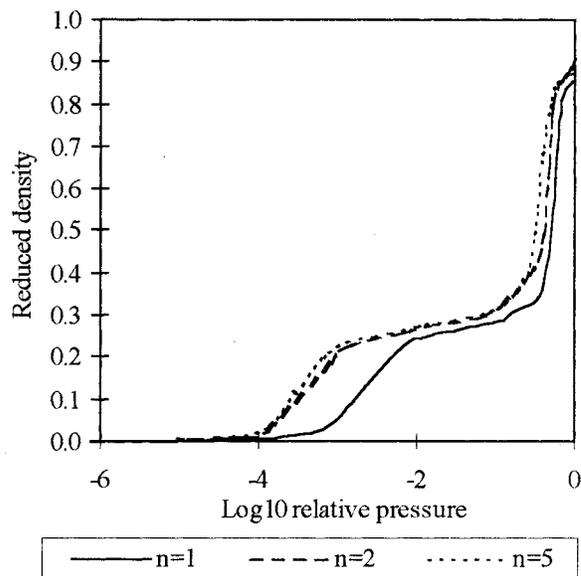


Figure 3. Simulated N_2 adsorption isotherms at 77 K in carbon slits of width $H = 2.5 \text{ nm}$, and $n = 1, 2$ and 5 layers in pore wall.