

MODELLING OF GAS ADSORPTION IN SLIT-LIKE MICROPORES

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Introduction

Recent achievements in computer simulations of gas adsorption in micropores and onto heterogeneous surfaces showed that simulation techniques can be used successfully to generate adsorption isotherms for well-defined solid surfaces. In addition, these isotherms can be obtained via density functional theory calculations, which provide essentially the same data as computer simulations but in much shorter time.

There is a great interest in computer simulations and density functional theory (DFT) calculations of gas adsorption in carbonaceous pores. The simulated adsorption isotherms for these systems are useful to elaborate and examine advanced methods for characterizing nanoporous carbon materials. In the current work the simulated adsorption isotherms for argon in slit-like pores [1], obtained by Grand Canonical Monte Carlo (GCMC) method, were used to study problems associated with evaluation and interpretation of the energy distribution function $F(U)$ from adsorption data and to formulate some recommendations concerning characterization of the surface and structural heterogeneities of nanoporous materials.

Methods

GCMC simulations. Argon adsorption isotherms were simulated at 87.25 K for two types of slit-like pores: (i) slits with energetically homogeneous walls, and (ii) slits with walls from two patches of different adsorption energies. The Lennard-Jones (12-6) potential was used to describe the argon-carbon and argon-argon interactions (details are given in Ref. [1]). The argon-wall interaction potential was obtained by three-dimensional integration. The MC-box had the wall size of $6\sigma_{ArAr} \times 6\sigma_{ArAr}$

The resulting adsorption isotherms for slit-like pores with energetically homogeneous walls possess steps

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related to adsorption on the pore walls and capillary condensation inside pores [1]. The simulated isotherms for bi-patch walls show a slightly smoother increase in comparison to those obtained for homogeneous pores. A comparison of the isotherms for homogeneous and bi-patch pores of widths greater than 1.4 nm shows that the condensation pressure is very similar for both types of pores of the same width and seems to be not much influenced by the surface heterogeneity of pore walls. This result suggests that the mesopore-size distribution should not be much altered by changes in the surface heterogeneity.

Adsorption energy distribution calculations. The energy distributions were evaluated from simulated adsorption isotherms by using a regularization method (INTEG program [2]), which seems to be the most advanced method for inverting the integral equation of adsorption. The Fowler-Guggenheim equation was used to represent local adsorption isotherm. A future improvement of the INTEG method is possible by employing the DFT method to calculate the local adsorption data.

Results and Discussion

Computer simulations of adsorption in pores showed that first adsorbate molecules adsorb on the surface of pore walls and next they condense inside pores. Thus, the range of the adsorption data used in calculations of the energy distribution function influences its shape. In addition, the shape of the energy distribution depends on the micropore-size distribution and the surface heterogeneity of the pore walls. Thus, physical interpretation of the energy distributions for porous carbons is difficult due to the overlapping of the surface and structural heterogeneity effects. However, these effects (as demonstrated below) can be characterized quantitatively by analyzing the simulated adsorption isotherms.

Shown in Figure 1 are energy distributions for the 1.8 nm homogeneous slits calculated by using different ranges of the simulated adsorption isotherm. The energy distribution obtained from the low-pressure data

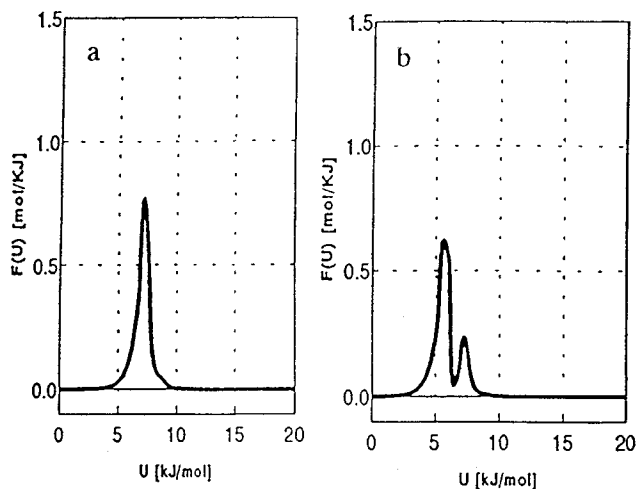


Figure 1 - Energy distributions calculated from the simulated adsorption data for a 1.8 nm energetically homogeneous slit with the degrees of filling below 33% (a) and 89% (b), respectively.

contains one sharp peak, which reflects surface heterogeneity of the micropore walls. When almost entire adsorption isotherm is used the energy distribution contains an additional peak, which characterizes energetic heterogeneity of the pore interior. Analysis of the $F(U)$ -distributions for different ranges of the pore filling demonstrates that effects associated with the surface heterogeneity and capillary condensation can be separated. The low-pressure adsorption data provide mainly information about surface heterogeneity. This information is not much altered by the multilayer formation effects if the adsorbate-adsorbent interactions are much stronger than the adsorbate-adsorbate interactions.

The pore-width effect is demonstrated in Figure 2, which contains the energy distributions for the 4.0 and 1.4 nm homogeneous slits. The $F(U)$ -functions in the upper row were calculated by using the entire isotherm, whereas the distributions in the lower row were obtained using only data points below $p/p_0=0.05$. The $F(U)$ -curves in the lower row reflect the surface heterogeneity of the pore walls (sharp peak at 7.2 kJ/mol because pore walls were assumed to be energetically homogeneous). If the slits become smaller, the energy of the peak maximum increases because of overlapping of adsorption forces from the opposite micropore walls. In addition, the $F(U)$ -distribution for micropores (e.g., the 1.4 nm slit) shows a shoulder or small peak, which appearance is caused by difficulty in separating the monolayer adsorption data from those related to multilayer formation and/or phase transitions. The $F(U)$ -functions

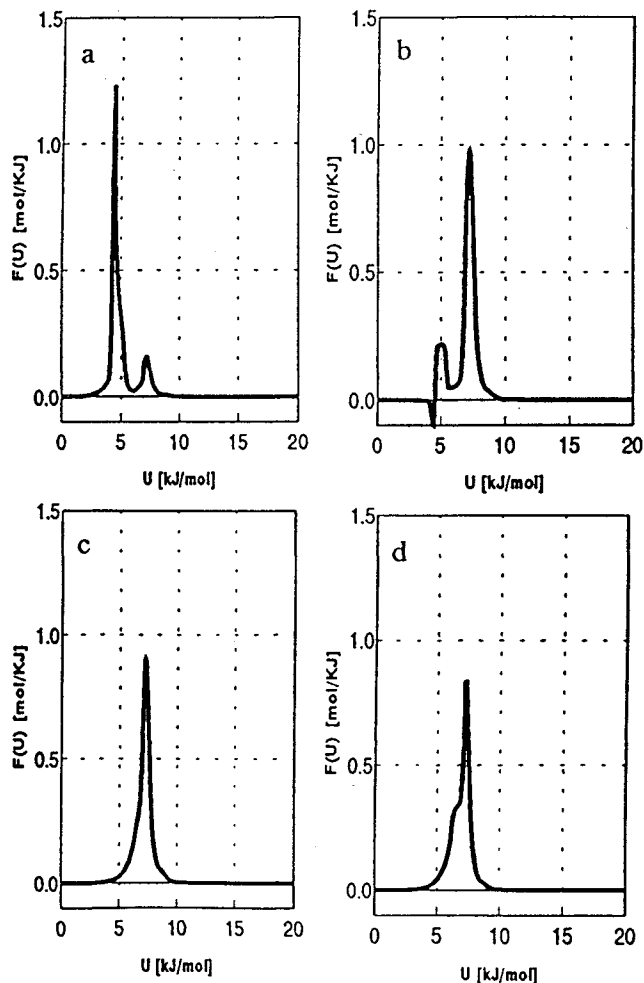


Figure 2 - Energy distributions for the 4.0 (a,c) and 1.4 nm (b, d) slits calculated by using the entire isotherm (upper row) and the data points below $p/p_0 = 0.05$ (lower row).

in the upper row of Figure 2 show, in addition to the surface heterogeneity, some details related to the capillary condensation in pores. For bi-patch pores the resolution of peaks is smaller and the $F(U)$ -analysis is much difficult.

Acknowledgment

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References

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