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An accurate model for the filling pressure of carbon slit-like micropores

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ABSTRACT

The Horvath–Kawazoe (HK) model that allows computing the filling pressure of micropores is traditionally used in gas porosimeters to assess the pore size distribution of microporous materials because of its simplicity, even if it is known to overestimate the pore sizes. In this study, we propose a new thermodynamic model that is able to link the filling pressure of a slit micropore to its pore size and that describes both primary and secondary filling, which is not feasible with the original HK model. The principal novelty of the pore filling model presented in this work, in comparison to its HK predecessors, is the inclusion of both pore width and pressure in the estimation of the adsorbate density in the pore. Moreover, the model is based on a simplified schematization of the adsorbed fluid that is considered as a combination of dense homogeneous fluid layers parallel to the pore walls and interacting between them and with the solid. Grand Canonical Monte Carlo simulations have been used to obtain the information concerning the number and density of fluid layers as a function of both pore width and pressure. Even if the method we propose is more general, this thermodynamic model is used in this work to compute, as a first example, the filling pressure of argon and nitrogen at 77 K in graphitic slit-like micropores and an excellent agreement is found with non local density functional theory results. Hence, the model is applied to compute, as a first test case, the pore size distribution of a carbon molecular sieve.

1. Introduction

Gas adsorption is the most widely used technique to determine the pore size distribution (PSD) of microporous materials. This characterization is usually carried out with simple gases such as nitrogen (N_2) or argon (Ar) at low temperatures, for instance at 77 K. Carbon dioxide (CO_2) or other probe molecules are also sometimes used at ambient temperatures to avoid the diffusional limitations that can be encountered for N_2 and Ar at low temperature.

The filling pressure of micropores strongly depends on their pore size and thus has been used for calculating PSD from these experimental adsorption isotherms. One of the most popular methods used in gas porosimeters to assess the PSD of microporous materials is the Horvath–Kawazoe (HK) model [1] because of its simplicity. In the original framework of the HK model, an analytical expression is obtained for the filling pressure as a function of the pore size of a microporous slit pore. However, the original HK correlation, even if widely used, is known to overestimate the pore filling pressure in comparison with density functional theory (DFT) and molecular simulation results [2,3]. Some studies have shown similar results between the HK model and more sophisticated methods such as non local DFT (NLDFT) [4,5,6]. However, Gauden et al. [6,7] have shown that this good correspondence is restricted to ultramicroporous materials where the process of primary micropore filling dominates.

Hence, for several years, there have been some attempts to modify and improve the original HK method. First, the method was extended to other pore geometries like cylindrical pores [8] or spherical ones [9]. Cheng and Yang also improved the model by taking into consideration the nonlinearity of the adsorption isotherm at high relative pressures [9,10]. Then, Rege and Young [11] argued that in the original HK method the adsorbate–adsorbate interaction was incorrectly calculated and proposed a corrected version for three pore geometries by considering for the first time the interaction between the nearby fluid layers of adsorbate molecules in the filled micropore. In the same time, Lastoskie and Dombrowski [2,3] have revisited the method after having pointed out the different errors appearing in the original HK paper [3]. They recalculated the mean free energy change of adsorption with two representations of the adsorbate density: an “unweighted” version corresponding to a uniform density of the adsorbate in the pore and a “weighted” one in which a more realistic structured profile is adopted. The unweighted version is

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surprisingly in better agreement with DFT calculations. But one has to notice that the fitted density profiles used in the weighted version seem to overestimate a lot the average density in the pore and thus the adsorbed quantities, which could explain the bad results. Ustinov and Do [12] have reconsidered the HK approach in a more rigorous thermodynamic analysis and apply it to the benzene adsorption. One limitation of their method is that they considered that the adsorbed phase could solely be represented as one or two liquidlike layers, which is not always true (see Section 3). Their method was then improved by Kowalczyk [13] by incorporating new numerical algorithms. Recently, Gauden et al. [7] proposed the application of the Dubinin–Astakhov equation in the HK model on the place of the Henry equation in order to take into account the nonideality of the adsorbate. This correction led to an improvement for the larger micropores.

It is worth noticing that the application of more rigorous theories to obtain the PSD of microporous materials such as NLDFT [4,14] or quenched solid DFT [15]. These theories are powerful but their implementation is relatively difficult for experimenters, as it requires not solely a good knowledge of the density functional theory but also of minimization techniques because obtaining the PSD from the inversion of a kernel of theoretical individual pore isotherms is an ill-posed problem. Hence, in general, they are solely used in the commercial softwares developed by the gas porosimeters manufacturers and not by the experimenters who develop their own adsorption devices. Moreover, care must be taken when using these methods in a press button way in the commercial softwares because the results depend strongly on the regularization parameter used that can drastically change the PSD. This situation leaves place to develop thermodynamic models that would be slightly less rigorous but that could be more easily used for PSD determination if they also proved to be efficient.

Hence, the principal aim of this paper is to propose a new thermodynamic model that is able to link the filling pressure of a slit micropore to its pore size in the whole micropores range, but with the aim of a relative straightforward application for PSD determination in the case of microporous adsorbents. This model is based on a simplified schematization of the adsorbed fluid that is considered as a combination of dense homogeneous fluid layers parallel to the pore walls and interacting between them and with the solid. The paper is organized as follows. A presentation of the model is made in Section 2. The new model is used in Section 3 to obtain the filling pressure of Ar and N_2 at 77 K in graphitic slit-like micropores, after a brief discussion on the average densities in the micropores. Finally, it is applied, as a first test case, to compute the PSD of a carbon molecular sieve.

2. Thermodynamic model

In order to determine the micropore filling pressure, we use the principle of equality of the chemical potential in the bulk and adsorbed phases

$$\mu^{\mathrm{bulk}} = \mu^{\mathrm{ads}} \tag{1}$$

At classical thermodynamic conditions used for microporous solid characterization (very low pressures and low or ambient temperatures), the gas in the bulk phase can be considered as ideal and thus:

$$\mu^{\mathrm{bulk}} = k_{\mathrm{B}}T\ln\left(\frac{\Lambda^3 P}{k_{\mathrm{B}}T}\right) \tag{2}$$

where k_{B} is the Boltzmann constant, T is the temperature, P is the pressure and Λ is the de Broglie thermal wavelength.

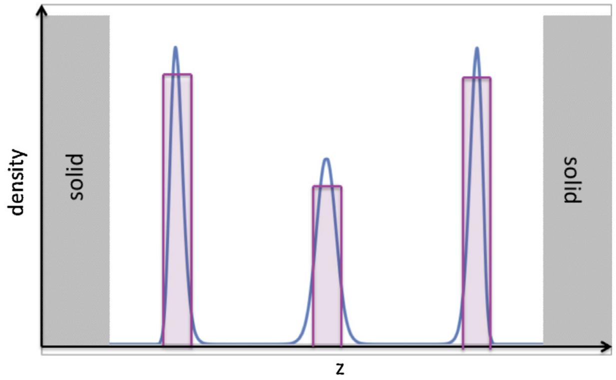

Fig. 1. Simplified schematization of the adsorbate in a slit pore. —: real fluid density. ▨: simplified model density.

Molecular simulations performed in slit shaped pores show that the adsorbed phase is classically made of several layers of dense fluid parallel to the solid walls (see Fig. 1). The number, density and positions of the layers depend on the fluid–solid pair, the pore size and the thermodynamic conditions (pressure and temperature). In this work, we use a simplified model for the adsorbed fluid by considering that this latter is made up of several homogeneous liquidlike layers parallel to the walls as indicated in Fig. 1. The numbers N and positions z of the layers were obtained from Gran Canonical Monte Carlo (GCMC) molecular simulations; it was considered that they depended not solely on the pore size, as classically done in the literature in HK type model predecessors, but in an original way also on pressure. The densities $\overline{\rho_i}$ of the homogeneous layers replacing the real peak of adsorption were taken in order to keep the net adsorption in the pore (see Section 3).

For each pore size, at each pressure the adsorbed fluid is thus considered as the sum of N homogeneous layers of density $\overline{\rho_i}$ and its chemical potential is given by:

$$\mu^{\mathrm{ads}} = \mu^{\mathrm{id}} + \sum_{i=1}^{N}\left(\mu_i^{\mathrm{rep}} + \mu_i^{\mathrm{att}} + \mu_i^{\mathrm{sf}} + \mu_i^{\mathrm{ff}}\right) \tag{3}$$

where the ideal part μ^{id} of the chemical potential is classically:

$$\mu^{\mathrm{id}} = k_{\mathrm{B}}T\ln\left(\Lambda^3\sum_{i=1}^{N}\overline{\rho_i}\right) \tag{4}$$

the hard sphere contribution μ_i^{rep} is the one of Carnahan Starling [16]:

$$\mu_i^{\mathrm{rep}} = k_{\mathrm{B}}T\left(\frac{8\eta - 9\eta^2 + 3\eta^3}{(1-\eta)^3}\right) \tag{5}$$

with the packing fraction $\eta = \pi\frac{\overline{\rho_i}\sigma_{\mathrm{ff}}^3}{6}$.

A mean field approximation is used for the attractive interaction, what gives in the case of the Weeks–Chandler–Anderson [17] potential (with the radial distribution function equal to 1 everywhere):

$$\mu^{\mathrm{att}}i = 4\pi\overline{\rho_i}\int_0^{+\infty} u^{\mathrm{att}}(r)r^2\mathrm{d}r = -\frac{32}{9}\sqrt{2}\pi\overline{\rho_i}\varepsilon_{\mathrm{ff}}\sigma_{\mathrm{ff}}^3 \tag{6}$$

The Steele's [18] potential is used to describe the interaction between a layer of fluid at z_i and the two walls of the pore: $\mu_i^{\mathrm{sf}} = V_i^{\mathrm{sf}}(z_i) + V_i^{\mathrm{sf}}(H - z_i)$ with