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A simple equation for accurate mesopore size calculations

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ABSTRACT

A simple equation is proposed for accurate mesopore size calculations from the nitrogen adsorption isotherms without the addition of the film thickness. The validity of this equation is tested in combination with experimental data of a series of mesoporous materials.

1. Introduction

Mesoporous materials are of particular interest in several industrial applications such as: catalysis, chemical sensing, gas separation, oil recovery, nanotechnology, etc. [1]. In many instances the optimal design of these processes requires a quick determination of the mean pore size of the involved mesopore medium. To this end, adsorption techniques, mainly nitrogen adsorption at 77 K, are used on a routine basis and mesopore size calculations can be deduced by using the Kelvin equation [2]:

$$\ln\frac{p}{p_0} = -\frac{2\gamma V_L}{RTr_m} \quad (1)$$

where γ and V_L are the surface tension and the molar volume of the liquid adsorbate, R is the gas constant, T is the isothermal temperature and r_m is the mean radius of the liquid/gas interface. On the assumption of zero contact angle, the r_m for a hemispherical meniscus will be equal to r_m=r_k, where r_k is the Kelvin radius. It is well known however that the Kelvin equation and its modified forms, underestimates the pore size by about 10 Å [3]. To resolve this problem much effort has been made, especially after the discovery of ordered mesoporous materials, so as to derive a rigorous thermodynamic solution on capillary condensation/evaporation. In this passing the Kelvin approach is improved and the criticality in pores is addressed.

On the other hand computational analytical methods have been developed for reproducing adsorption isotherm and estimating pore size distribution on mesoporous and microporous materials [4,5]. Density functional theory (DFT) implies that the Helmholtz free energy of a confined fluid is represented as a functional of the spatially varying fluid energy [6,7]. Non-local density functional theory (NLDFT) is a model based on density functional theory adding some non-local correction to improve the local density approximations [8,9]. Further according to quench solid density functional theory (QSDFT), solid atoms are considered as quenched component(s) of the solid–fluid system with given density distribution(s) [10]. Grand Canonical Monte Carlo [11,12] (GCMC) simulates actual molecular microscopic configurations of the confined fluid using realistic intermolecular interaction potentials. Combination of small-angle scattering [13–15] and 3D stochastic reconstruction methods can be also proved an essential tool for visualizing the evolution of the adsorption mechanism and show how sorption alters the pore space characteristics of the material [16,17].

In the following, we introduce a new, very simple, form of the Kelvin equation and compare it against the results obtained from the most advanced calculation methods.

2. Experimental

In order to check the validity of the proposed equation a comparison has been attempted from results given in the literature, based on various techniques. To this end, we have concentrated on a number of mesoporous media such as MCM, SBA, FMS, HMS, etc.

In addition, we performed nitrogen porosimetry, X-ray diffraction (XRD) and small-angle X-ray scattering measurements (SAXS)

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on three silica based ordered mesoporous materials MCM-41 and SBA-15 which were prepared according to standard formulas [18,19]. The N_2 adsorption isotherm has been performed volumetrically at 77 K on an Autosorb-1 gas analyzer, Micropore version (Quantachrome instruments). For adsorption measurements, the sample was initially outgassed at 300 °C for 24 h under high vacuum (<10^{-6} mbar). XRD measurements were carried out on a Siemens XD-500 diffractometer, using CuKα radiation in the 2θ range 1–10°. Small-angle X-ray scattering (SAXS) measurements were carried out on a JJ X-ray with a 2D gas detector (Rigaku). The NLDFT [8,20] and BJH [21] calculations have been derived from the commercial software AS1win (provided by Quantachrome instruments) and compared with our proposed equation.

3. Results and discussion

At its simplest form, the pore radius r_p of a mesoporous material is given by:

$$r_p = r_k + t + \delta \tag{2}$$

where t is the thickness of the adsorbed film and δ is a correction term for the interaction between adsorbate and substrate. All parameters in Eq. (2) are functions of p/p_0 and a solution as for r_p demands heavy computation of a number of conditional equations. This is a major drawback and although the aforementioned advancements are highly recognized in scholar studies, the use of the Kelvin equation remains an indispensable benchmark in many practical cases. And although the inaccuracies of the standard method for nanopore structure analysis are well documented, the simplicity of the Kelvin equation still provides a strong motivation for using it against new models and characterization methods that have been proposed. Following this principle, Kruk and Jaroniec [22] have discussed the case where the Kelvin equation can be modified in an empirical way that:

$$r_c = -\frac{a'}{ln\left(c'\frac{p}{p_0}\right)} + b' \tag{3}$$

where r_c is the pore core radius, (a') is a constant that is in principle related to the surface tension, molar volume, and temperature; (c') is an additional constant that modifies the relative pressures close to saturation; and (b') is a constant correction term. By combining r_c with a t-curve an empirical equation for the relation between the capillary condensation pressure and the pore radius of cylindrical pores for argon adsorption is obtained: $r_p = r_c + t(p/p_0)$, where $t(p/p_0)$ is the film thickness as a function of p/p_0.

Based on nitrogen data we discover that there is a linear approximation between r_k and r_p and this is important because for a wide range of p/p_0 one overtakes many of the standard method limitations without loss in simplicity. In this light Eq. (2) reduces to:

$$r_p(\overset{o}{A}) = \frac{r_k}{0.72} + 7.2 \tag{4}$$

where its main advantage is that the addition of the film thickness is not required.

As a further step, both nitrogen adsorption and XRD (SAXS) measurements were performed on ordered mesoporous silica materials MCM-41 and SBA-15. These materials consist of a two-dimensional hexagonal arrangement of well-defined cylindrical pores. As a result, these materials are ideal model systems for studies of adsorption [23,24] and mesopore size determination [25,26]. It should be also mentioned that SBA-15 materials exhibit thicker silica walls than MCM-41, providing, thus, higher mechanical stability [27]. Fig. 1 illustrates the N_2 adsorption isotherms of one SBA-15 and two MCM-41 silica samples having different pore size (MCM-41a and MCM-41b). The isotherms are of type IV, according to the IUPAC classification [28]. At low pressures, a steep increase is observed in all samples due to the formation of a monolayer on the pore walls, while at higher pressures an extended multilayer region and a sharp pore condensation step can be observed. The upturn of the sorption isotherms at pressures close to the vapor pressure can be attributed to large (presumably macro-) pores formed between the silica particles. In the case of MCM-41a sample, the isotherms is reversible; as it will be further discussed, the absence of a hysteresis loop for such materials is attributed to the pore size, which lies between the margins of micro- and mesopore regions [29,30]. On the other hand, both MCM-41b and SBA-15 samples exhibit a marked hysteresis loop (type H1 by IUPAC classification) corresponding to capillary condensation and evaporation on open cylindrical pores at both ends. In addition, the higher relative pressure for the capillary condensation is related to the larger pore size [31]. In Table 1, the structural characteristics of the samples deduced from the N_2 isotherms and the XRD (SAXS) measurements are reported. The specific surface area (SSA) was determined by the Brunaver–Emmet–Teller (BET) method [32] using a_m (N_2 = 16.2 Å^2), where, a_m, is the molecular area of nitrogen at 77 K. The primary mesopore volume, V_p, was calculated from the high resolution α_s-plot method [33]. The primary mesopore diameter for materials with hexagonal arrays of uniform pores, D_{XRD}, can be obtained from the primary mesopore volume, V_p and the lattice parameter, a_0, of the mesopore lattice, deduced from XRD (SAXS) data, according to the following equation [34,35]:

$$D_{XRD} = c\alpha_0\left(\frac{\rho V_p}{1+\rho V_p}\right)^{1/2} \tag{5}$$

where $c = \sqrt{2\sqrt{3}/\pi} \approx 1.05$, ρ is the density of the silica framework (2.15 g/cm^3) and $a_0 = 2d_{100}/\sqrt{3}$, d_{100} is the XRD (SAXS) interplanar spacing. Finally the average pore sizes, D_{BJH}, D_{NLDFT} and $D_{Eq.4}$ were evaluated from the desorption branch of the isotherms according to BJH method, NLDFT and Eq. (3) respectively.

The results show an excellent agreement of the pore sizes deduced from NLDFT and Eq. (4) (within an error of less than 3%). On the other hand, the BJH approach compared with all the other methods underestimates the pore size, in consistency with previous studies [3,20]. Further, in the case of MCM-41a, Eq. (4) is in excellent agreement compared with D_{XRD}, obtained by Eq. (5); however, a small deviation (about 7%) is observed for the MCM-41b sample (see also Fig. 1). This is attributed to the fact that Eq. (5) may not be very accurate for ordered mesoporous silicas with larger pores. In addition, Eq. (5) is not valid when complementary pores in the mesopore walls are present (such as in the case of SBA-15). As a result, advanced methods of mesostructure analysis and full-profile refinement have been developed based on XRD (SAXS) structure modeling [36,37]. Recently, Jaroniec and Solovyov [38] derived from nitrogen adsorption measurements an analytical expression (improved KJS method) for extending the calculation of pore width up to ~120 Å by using SBA-15 materials. When applied to our SBA-15 sample, a small underestimation of the pore width is observed compared both to Eq. (4) and NLDFT results (Table 1). This is not surprising as the improved KJS method takes into account the presence of complementary pores. It is also noteworthy to mention that XRD [39] or in situ fluid adsorption with SAXS results [40,41] revealed that SBA-15 silica appears to deviate from an ideal matrix as the cylindrical mesopores could be surrounded by a corona that may either represent a microporous layer or results from pronounced surface corrugations. Further, analysis of in situ neutron diffraction data of adsorbed carbon dioxide on an MCM-41 sample showed the formation either of a smooth film or an outer layer (corona) of reduced density [42].

In addition, we undertook the task to compare Eq. (4) against some of the most advanced simulation techniques that have been