cavities at fractional pore filling f_0 a film will develop at the pore wall. In terms of this model the film thickness will increase with the fractional pore filling as

$$t = R \left(1 - \sqrt{\frac{1-f}{1-f_0}} \right). \quad (7)$$

Fig. 5 shows that the film thickness t derived from the gas adsorption data on the basis of this relation agrees with the experimental values of t over nearly the entire range of relative pressures up to pore condensation.

In conclusion, the present work shows that the thickness t of nitrogen adsorbed films and its dependence on the vapor pressure in cylindrical pores of a periodical mesoporous silica can be determined from the intensities of the leading Bragg peaks. Using neutron scattering for such studies has the advantage that the silica matrix and the adsorbed nitrogen film have similar scattering length densities, which facilitates the data analysis. On the other hand, the broad wavelength distribution of the neutron beam implies that not all Bragg peaks can be resolved separately by SANS. This is a serious disadvantage which limits the accuracy of the film thickness determination by neutron scattering. For the present sample the error in t is estimated to ca. ± 0.1 nm, but larger error bars (± 0.2 nm) were found for other samples. X-ray scattering is much preferable for such studies from this point of view, although it implies that nitrogen has to be replaced by a gas of higher electron density, such as Kr, Xe, dibromomethane or perfluorinated hydrocarbons. Recently, an X-ray small-angle diffraction study of the pore filling of SBA-15 with krypton has been performed [11] which supports the main conclusions of the present study, but also reveals significant differences in the pore filling of templated mesoporous silica with nitrogen and krypton.

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REFERENCES

- [1] S.J. Gregg, K.S. Sing, *Adsorption, Surface Area and Porosity*, Academic, London 1982
- [2] M. Kruk, M. Jaroniec, A. Sayari, *Langmuir* **13** (1997) 6267
- [3] W.H. Lawnik, U.D. Goepel, A.K. Klauk, G.H. Findenegg, *Langmuir* **11** (1995) 3075
- [4] W. Prange, W. Press, M. Tolan, C. Gutt, *Eur. Phys. J. E* **15** (2004) 13
- [5] V. Panella, J. Krim, *Phys. Rev. E* **49** (1994) 4179
- [6] B. Smarsly C. Göltner, M. Antonietti, W. Ruland, E. Hoinkis, *J. Phys. Chem. B* **105** (2001) 831
- [7] M. Impéror-Clerc, P. Davidson, A. Davidson, *J. Amer. Chem. Soc.* **122** (2000) 11925
- [8] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, *J. Amer. Chem. Soc.* **120** (1998) 6024
- [9] E. Hoinkis, *Langmuir* **12** (1996) 4299
- [10] I.G. Shenderovich, G. Buntkowsky, A. Schreiber, E. Gedat, S. Sharif, J. Albrecht, N.S. Golubev, G.H. Findenegg, H.-H. Limbach, *J. Phys. Chem. B* **107** (2003) 11924
- [11] T. Hoffmann, D. Wallacher, P. Huber, R. Birringer, K. Knorr, A. Schreiber, G.H. Findenegg, *Phys. Rev. B*, accepted

Strong light scattering upon capillary condensation in silica aerogels

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1. INTRODUCTION

Within the past decade several authors reported on the observation of light scattering in silica aerogels upon capillary adsorption or desorption of gases and vapours [1-5]. The effect has been observed for LN₂ at 125 K [1,2] as well as for sorption of 2-propanol at room temperature [5]. X-ray scattering of a high porosity (98%) silica aerogel partially filled with ⁴He at 3.6 K indicates an increase of the size of the scattering entities with the amount of ⁴He condensed; the length scale of the scatterers was found to be up to 60 nm [4]. In contrast, light scattering of a denser aerogel (porosity 87%) upon sorption revealed scattering entities on the order of 100 nm in addition to scattering from the outer sample surface [5]. The goal of this paper is to elucidate the mechanisms responsible for the scattering by analyzing the optical data in more detail.

2. EXPERIMENTAL

2.1. Sample

The silica aerogel investigated was a one-step base-catalyzed supercritically dried silica gel (TMOS). For details of the synthesis see e.g. references [5,6]. To increase the stiffness of the as-prepared sample and thus to avoid a significant volume change due to capillary forces [2] we sintered the silica aerogel to a density of about 0.29 g/cm³ (initial density 0.26 g/cm³).

For the characterization of the sample with optical and X-ray scattering methods a 1 mm thick slice was cut from the aerogel with a diamond saw. The adsorption was performed by placing the cuvette for the optical measurement holding the sample next to a reservoir of 2-propanol for several hours. The amount of 2-propanol adsorbed was determined by weighing. After each sorption step the sample was sealed in the cuvette.

2.2. Characterization of the porosity and the texture

The sample was characterized by nitrogen sorption at 77 K (ASAP 2000, software 2010, Micromeritics) to determine its total mesoporosity, the average pore size and the average size

of the particles forming the silica network. Complementary, (ultra) small angle X-ray scattering ((U)SAXS) data were taken at the beam lines BW1 (JUSIFA) and BW4 (German synchrotron facility HASYLAB, Hamburg). The elastic modulus of the aerogel was determined via an ultrasonic run time measurement.

2.3. Optical characterization

The optical properties of the silica aerogel were investigated in a light scattering set-up (see [6]) that allows the detection of the intensity of the scattered light as a function of the scattering angle. Hereby the incident beam was unpolarized light with a wavelength of 543 nm. In addition, the direct-hemispherical transmittance and reflectance of the sample was measured with a VIS-IR spectrometer (Lambda 9 by Perkin-Elmer) combined with an integrating sphere [7, 8].

3. RESULTS

3.1. Structural properties of the aerogel investigated

The nitrogen sorption and U(SAXS) data are shown in Figs. 1 and 2. In the SAXS-plot (Fig. 2) also the light scattering data are included to extend the range in scattering vector q . The nitrogen isotherm (Fig. 1) shows a typical type IV shape with a H1 hysteresis [9]. The specific surface area, the total porosity and the average pore size (BJH) determined from the experimental data are 300 m²/g, 3 cm³/g and 55 nm, respectively.

The scattering data in Fig. 2 exhibit different scattering regimes that also have been found for similar aerogels by other authors (e.g. [10]). Besides the characteristic scattering at $q > 10^{-2} \text{ \AA}^{-1}$ that can be interpreted in terms of fractal clusters [11], an additional increase of the scattered intensity is visible at small q -values. Within the framework of this paper it is important to prove that this feature is not due to a significant number of large pores:

The porosity Φ as a function of the length scale L can be expressed in terms of the integral over the intensity $I(q)$ times q^2 according to

$$\Phi(L) \propto \int_{q=1/L}^{q_{ref}=1/L_{ref}} q^2 \cdot I(q) dq \quad (1)$$

with q_{ref} the scattering vector corresponding to an arbitrary reference length scale at which the sample possesses a porosity Φ_{ref} (e.g. $L_{ref} = 2 \text{ \AA}$ corresponding to about $q_{ref} = 0.5 \text{ \AA}^{-1}$). Since Fig. 2 shows that the contribution to the integral (Eq. (1)) is negligible for scattering vectors $q \leq 10^{-3} \text{ \AA}^{-1}$ (corresponding to a length scale larger than about 300 Å) the porosity on a length scale of 300 Å and larger does not change any more. It can therefore be concluded that the forward scattering is not an indication of large pores, but can rather be explained in terms of small density fluctuations caused by the arrangement of large clusters (100–200 nm) with an aerogel substructure (see also AFM-images [10]).

Fig. 1. Nitrogen sorption isotherm taken at 77 K.

Fig. 2. Left: Scattered intensity versus scattering vector; the data plotted represent the results from light scattering ($q < 10^{-3} \text{ \AA}^{-1}$) and (U)SAXS. Right: Scattered intensity times q^2 vs. q -representation. The cartoon in the middle represents the model of an aerogel skeleton.

3.2. Optical measurements

The light scattering as a function of the scattering angle and the wavelength dependence of the direct-hemispherical transmittance of the silica aerogel are shown in Fig. 3 for various amounts of 2-propanol absorbed.

The light scattering data I_{light} were evaluated by a superposition of two “2-phase media” [12] contributions to account for scattering from the bulk (B) and the external surface (S) of the sample:

$$I_{\text{light}}(\theta) = [I(\theta, L_S) + I(\theta, L_B)] \cdot (e_{\parallel} + e_{\perp} \cdot \cos^2(\theta)), \text{ with} \quad (3a)$$

$$I(\theta, L_{S,B}) = a_{S,B} / (1 + (L_{S,B} \cdot q(\theta))^2)^2 \text{ and} \quad (3b)$$

$$q = 4\pi \cdot \sin(\theta/2) / \lambda, \quad (3c)$$

with q the scattering vector. λ and θ are the wavelength of the incident laser beam and the scattering angle, respectively. The parameter a is a factor accounting for the intensity of the incident beam and the total scattering volume; $e_{\parallel}$ and $e_{\perp}$ denote the polarization of the scattered light. L_S and L_B are the mean chord lengths characterizing the surface (roughness of the outer surface) and the bulk of the sample. For a statistically isotropic medium, the correlation length L_B is a representative measure for the extension of the inhomogeneities within a sample consisting of two phases with different electron density or dielectric constant; these properties are assumed to be constant within each phase. The results derived via a fit of the light scattering data (Fig.3) with a superposition of two 2-phase media models (Eq. (3a)) are given in Table 1.

Within the framework of this investigation the directional-hemispherical reflectance and transmittance were measured instead of the corresponding directional-directional quantities because directional-hemispherical data also contain information about the scattering of the incoming radiation. This is reflected by the fact that the directional-directional transmittance T_{dd} decreases with $\exp(\tau_0)$, whereas the directional-hemispherical transmittance T_{dh} is proportional to τ_0^{-1} for optically thick samples; hereby is τ_0^* the effective optical thickness. The effective values of the optical thickness τ_0^* and the albedo ω_0^* are related to the quantities τ_0 and ω_0 (that can be derived from direct-direct measurement) via the anisotropy factor g [13]:

$$\tau^*(\lambda) = \tau(\lambda) \cdot (1 - \omega_0(\lambda) \cdot g), \quad \omega_0^*(\lambda) = \frac{\omega_0(\lambda) \cdot (1 - g)}{1 - \omega_0(\lambda) \cdot g}, \quad (4a)$$

$$\text{with } g = \int_{4\pi} \cos \vartheta' \cdot p(\vartheta', \vartheta) d\Omega \quad (4b)$$

the probability for radiation coming in at an angle ϑ' to be scattered in the direction defined by the angle ϑ . The values of the anisotropy factor g can range from -1 (in case of pure backward scattering) to $+1$ (in case of a delta function like forward scattering). The effective scattering and the effective extinction coefficients S^* and E^* , respectively, can be determined from τ_0^* and ω_0^* via

$$E^*(\lambda) = \tau_0^*(\lambda) \cdot D \quad \text{and} \quad S^*(\lambda) = \omega_0^*(\lambda) \cdot E^*, \quad (5)$$

with D the sample thickness. The spectral variation of the effective scattering coefficient S^* is affected by the pore structure of the silica aerogel, i.e. the size and shape of the pores and porosity Π of the sample. The effective scattering coefficient

$$S^*(\lambda) = \frac{3}{2} \cdot \Pi \cdot \frac{I_{\text{scattered}}(\lambda)}{I_{\text{incident}} \cdot d} \quad (6)$$

can be calculated via the Mie-theory [15]. The effective scattering coefficient S^* determined from the experimental data (Fig.4) was fitted with an equation derived from Mie-theory [14-17] assuming individual spherical scatters [7] and two different indices of refraction, i.e. $n \sim 1.45$ for silica and 2-propanol and $n = 1$ for the air in the pores, respectively. Hereby we presumed that the volume of the scattering entities within a logarithmic diameter interval $\Delta \ln d$ is distributed according to a logarithmic normal distribution [14]:

$$f(d) \Delta \ln d = \frac{1}{\sqrt{2\pi}\sigma_g} \exp \left[-\frac{(\ln d - \ln d_M)^2}{2\sigma_g^2} \right] \Delta \ln d \quad (7)$$

The results of the fit are given in Table 1. It has to be noted that the scattering coefficient (Fig.4) shows an offset in the range of low absorption ($\lambda < 2000$ nm). This part has not been included in the fit. It is likely to originate from the larger scattering entities which have been found via the evaluation of the light scattering profile (Table 1).

Table 1

Results derived from the light scattering data (vs. scattering angle) and the direct-hemispherical spectra as described in the text. L_{surface} and L_{bulk} are the mean chord lengths of the entities causing scattering from the outer surface and the bulk of the sample, respectively. (* different sample, however taken from the same batch)

	from light scattering		from direct-hemispherical data
pore filling (pore vol %)	L_{surface} (nm)	L_{bulk} (nm)	average diameter d (nm)
0	nd	119*	nd
4	517	94	13
6	640	99	20
30	641	(61)	30

Fig.3. Left: Scattered intensity versus scattering angle for the silica aerogel with different amounts of 2-propanol adsorbed (incident beam: $\lambda = 543$ nm). The lines represent fit of the data by a two-phase model [5]. Right: direct-hemispherical transmittance for the same set of samples. The transmittance decreases with increasing amount of 2-propanol adsorbed. The two different experimental configurations are indicated by the sketches above the plots.

Fig.4. Effective scattering coefficient for the silica aerogel with different amounts of 2-propanol sorbed.

4. DISCUSSION

The light scattering data for the silica aerogel with different amounts of 2-propanol adsorbed reveal three characteristic length scales (Table 1):

- according to Wang et al. [6] the largest scattering entities ($L_{\text{surface}} \sim 500$ nm) can be attributed to scattering from the rough outer surface of the sample (caused by the sawing of the sample)
- the two other length scales of about 100 and 10 to 30 nm are related to scattering from the bulk of the silica aerogel.

The mean chord length L_{bulk} is almost constant except for the sample with 30 vol.% filling. In the latter case, however, the scattering is so strong that significant multiple scattering effects are to be expected, which will yield a broadening of the scattering profile vs. scattering angle and thus mock a decrease of L_{bulk} . If we therefore do not include the 30 vol.% value in our discussion, we have to conclude that L_{bulk} does not vary significantly with the amount of 2-propanol adsorbed.

The average diameter d , in contrast, clearly increases with increasing filling of the pores; this effect is qualitatively in accordance to the observations of Lurio et al. for the X-ray scattering of a LHe filled silica aerogel [4] with a higher porosity. One effect, however, is critical for a quantitative interpretation of our data: since the sample was not continuously kept at constant temperature, part of the optical measurements might have been taken from a sample that is in the process of desorption rather than of adsorption yielding larger scattering entities [4]. However, we believe that the experiments still provide a first glimpse at the effects involved, that is two types of scatterers being present in the bulk:

- small entities increasing with pore filling that can be interpreted as (partially) filled pores or pores of increasing size being filled
- large scatterers that do not significantly change in size but that still contribute increasingly to the extinction with increasing pore filling; these entities can be related to large aerogel clusters whose scattering contrast is increasing in the early stage of capillary condensation with the amount of 2-propanol adsorbed.

5. CONCLUSIONS

Although the experiments presented are crude in terms of controlling the sorption of 2-propanol within the sample, they indicate that the light scattering of a silica aerogel partially filled with condensed vapour has two components, i.e. scattering of small density fluctuations on a length scale of about 100 nm and scattering of liquid filled pores.

Currently, a new temperature controlled set-up is being tested that allows for simultaneous measurements of sorption and light scattering under well controlled conditions.

REFERENCES

- [1] A.P.Y. Wong, S.B. Kim, W.I. Goldburg, M.H.W. Chan, *Phys. Rev. Lett.* 70 (1993) 954.
- [2] G.W. Scherer, D. M. Smith, D. Stein, *J. Non.-Cryst. Solids* 186 (1995) 314.
- [3] A. Bisson, E. Rodier, A. Rogacci, D. Lecomte, P. Achard, *J. Non.-Cryst. Solids* 350 (2004) 230.
- [4] L.B. Lurio, N. Mulders, M. Paetkau, M. Lee, S.G.J. Mochri, M.H.W. Chan, *J. of Low Temperature Physics*, 121 (2000) 591.
- [5] G. Reichenauer, J. Fricke, J. Manara, J. Henkel, *J. Non.-Cryst. Solids* 350 (2004) 364.
- [6] P. Wang, W. Körner, A. Emmerling, A. Beck, J. Kuhn, J. Fricke, *J. Non.-Cryst. Solids* 145 (1992) 141.
- [7] J. Manara, R. Caps, F. Rather, J. Fricke, *Optics Communications* 168 (1999) 237.
- [8] J. Manara, R. Caps, J. Fricke, *International Journal of Thermophysics* 26 (2005) 531.
- [9] F. Rouquerol, J. Rouquerol, K. Sing, *Adsorption by Powders and Porous Solids* (Academic Press 1999).
- [10] C. Marliere, F. Despetis, P. Etienne, T. Woignier, P. Dieudonne, J. Phalippou, *J. Non.-Cryst. Solids* 285 (2001) 148.
- [11] A. Emmerling, R. Petricevic, A. Beck, P. Wang, H. Scheller, J. Fricke, *J. Non-Cryst. Solids* 185 (1995) 240.
- [12] P. Debye, H. R. Anderson, H. Brumberger, *J. of Appl. Phys.* 285 (1957) 679.
- [13] B.H.J. McKellar and M.A. Box, *J. Atmosph. Sci.* 38 (1981) 1063.
- [14] G. Mie, *Annalen der Physik* 25 (1908) 377.
- [15] C.F. Bohren, D.R. Huffman, *Absorption and Scattering of Light by Small Particles* (John Wiley & Sons 1983).
- [16] M. Kerker, *The Scattering of Light and Other Electromagnetic Radiation* (Academic Press 1969).
- [17] H.C. van de Hulst, *Light Scattering by Small Particles* (Dover Publications Inc. 1981).

Characterisation of porous solids from nanometer to micrometer range by capillary condensation

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A new experimental procedure based on the isothermal desorption of vapour is proposed to extend the domain of characterisation of porous solids and powders by capillary condensation until the macropore range. The set-up is based on the use of a Tian-Calvet type microcalorimeter that insures a full control of temperature gradients around the sample and allows the desorption isotherm to be determined very close to the saturation pressure. The principle of the experiment is described and the first results obtained for water desorption are compared to measurements based on gravimetry as well as to pore size distributions obtained by mercury porosimetry.

1. INTRODUCTION

The determination of pore size distributions by gas adsorption-desorption methods is probably the most commonly used method but it is admitted to be reliable only in the micro-mesopore size range (0.3-50 nm) [1]. For larger pore sizes, mercury porosimetry is a useful complementary method, notably because of its unique ability to determine pore size distributions at several scales from nm to several hundred micrometers. Unfortunately, this method is destructive for many samples that are more or less damaged by the high pressures that are required by such an experiment. Moreover, the sample, even if not damaged, cannot be recovered in many cases and this technique will be probably faced to more and more drastic rules in the future for environmental reasons. Another technique, thermoporometry, can also be used for pore size characterisation, with more or less the same range of pore size as gas adsorption [2]. Its advantage relies on its possible use for samples that cannot be dried without damage. Its disadvantages are mainly due to the fact that melting-solidification in confined medium is less well understood than capillary condensation, despite clear similarities [3]. Indeed, calculation procedures and models are not as well established and useful parameters are not directly measurable. Clearly there is a need for characterisation methods which cumulate the advantages of gas adsorption (adsorbate with low interfacial tension, well defined models with measurable parameters), mercury porosimetry (pore size determination at several scales) and thermoporometry (starting from wet state). Because of the advantages quoted above, a method based on capillary condensation, i.e. adsorption or desorption of a vapour, would be interesting provided it could be applied in a larger range of