Vol 12 No 2, February 2003
1009-1963/2003/12(02)/0208-03

Chinese Physics

© 2003 Chin. Phys. Soc.
and IOP Publishing Ltd

Positive deviation from Debye's theory in small-angle x-ray scattering*

Li Zhi-Hong(李志宏)[a], Gong Yan-Jun(巩雁军)[a], Wu Dong(吴 东)[a]†, Sun Yu-Han(孙予罕)[a], Zhao Hui(赵 辉)[b], Dong Bao-Zhong(董宝中)[b], and Wu Zhong-Hua(吴忠华)[b]

[a] *State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan* 030001, *China*
[b] *Beijing Synchrotron Radiation Laboratory, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing* 100039, *China*

(Received 3 June 2002; revised manuscript received 28 August 2002)

The small-angle x-ray scattering (SAXS) resulting from a non-ideal two-phase system having sharply defined phase boundaries but with micro-fluctuations of electron density within any phase shows a positive deviation from Debye's theory. We have found a simple method suitable for fitting the slit-smeared SAXS data and correcting the positive deviation. The validity of this procedure is tested on porous ZrO_2 xerogel prepared using the sol-gel process.

Keywords: small-angle x-ray scattering, positive deviation from Debye's theory, porous ZrO_2 xerogel
PACC: 6110, 6140

Small-angle x-ray scattering (SAXS) originates from spatial fluctuations of the electronic density within a medium.[1−5] Since the past few years, in many research branches, SAXS has become a popular technique. In a SAXS experiment, the result is the scattering intensity showing decay against the scattering angle. One of the main theories in the SAXS is Debye's theory,[6−8] which gives a general treatment of the scattering by an inhomogeneous material whether the scattering objects (particles or pores) in it is dilute or not. It shows how a scattering measurement can be used to obtain the average square of the fluctuations in electron density and a correlation function that measures the degree of correlation between two fluctuations as a function of their separation. Debye's theory is applicable only to ideal two-phase systems having constant sharply defined phase boundaries, but different electron density in different phase. In practice, if the electron density in any phase of a two-phase system is inhomogeneous (i.e. with micro-fluctuation), although its phase boundary is sharp, then the scattering will show deviation from Debye's theory. In this case, the theory needs a correction. To the best of our knowledge, we have not found this kind of study in the literature.

In this short communication, we have two goals: the first is to extend Debye's equation from an ideal two-phase system to a non-ideal two-phase system, in any phase of which the electron density is inhomogeneous (i.e. with micro-fluctuations) except that the phase boundary is sharp; and the second is, to correct the deviation from Debye's theory and lead to the information of the microstructure of the system under examination.

It is well known that for an ideal two-phase system having sharply defined phase boundaries and with constant but different electron density in different phase, according to Debye's theory,[6−8] the observed slit-smeared scattering intensity is given by

$$J_{\rm obs}(q) = A(1 + a_{\rm c}^2 q^2)^{-3/2}, \tag{1}$$

i.e.

$$J_{\rm obs}(q)^{-2/3} = A^{-2/3} + A^{-2/3} a_{\rm c}^2 q^2, \tag{2}$$

where q is the scattering vector, $q{=}4\pi \sin\theta/\lambda$, 2θ is the scattering angle, λ is the incident x-ray wavelength, $J_{\rm obs}(q)$ is the observed slit-smeared scattering intensity, A is a constant and $a_{\rm c}$ is the correlation distance,

*Project supported by the National Natural Science Foundation of China (Grant No 29973035), by the National Key Basic Research Special Foundation of China (Grant No G200000480) and by the National Natural Science Priority Project Research Special Foundation of China (Grant No 20133040).

†Author to whom correspondence should be addressed. E-mail: wudong@public.ty.sx.cn Fax: 86-351-4041153.

which is a measure of the phase size. Equation (2) implies that the plot of $J_{\rm obs}(q)^{-2/3}$ versus q^2 is linear in the whole experimental range of scattering angle with a positive slope.

For a non-ideal (pseudo) two-phase system having sharply defined phase boundaries but with micro-fluctuations of electron density within any phase which give rise to some additional scattering, the whole scattering will show deviation from Debye's theory, i.e. the plot of $J_{\rm obs}(q)^{-2/3}$ versus q^2 will no longer be linear but present a downward-concave curve. This might be named a positive deviation from Debye's theory in analogy with that named in the deviation from Porod's law.[2,9−11] By proper tests, we conclude that the slit-smeared scattering showing a positive deviation from Debye's theory could be fitted with the equation

$$J_{\rm obs}(q) = A(1 + a_{\rm c}^2 q^2)^{-3/2}\exp(bq^2), \qquad (3)$$

where the physical meaning of $\exp(bq^2)$ remains ambiguous, it might represent the positive deviation due to the micro-fluctuations of electron density within any phase, and b could be a parameter related to the average size of the regions with micro-fluctuations in electron density.

It should be mentioned that the above Eq. (3) may be valid only in of q lower than $3{\rm nm}^{-1}$ at the incident x-ray wavelength λ of 0.154nm.

In order to evaluate the value of b, Eq.(3) is transformed into a tractable form

$$\exp(2/3bq^2)J_{\rm obs}(q)^{-2/3} = A^{-2/3} + A^{-2/3}a_{\rm c}^2 q^2. \qquad (4)$$

By introducing an appropriate value of b, the plot of $\exp(2/3bq^2)J_{\rm obs}(q)^{-2/3}$ versus q^2 should be (or statistically be) linear, and then A and $a_{\rm c}$ may be determined from the intercept and the slope respectively. Therefore, Debye's theory may be recovered by adding a correction of the positive deviation due to the existence of the micro-fluctuations of electron density within any phase of the non-ideal two-phase system with sharply defined phase boundaries using the following equation

$$J(q)^{-2/3} = \exp(2/3bq^2)J_{\rm obs}(q)^{-2/3} \qquad (5)$$

or

$$J(q) = \exp(-bq^2)J_{\rm obs}(q), \qquad (6)$$

where $J(q)$ is the positive-deviation-corrected scattering intensity which obeys Debye's theory and can be used to study the microstructure of the system under examination.

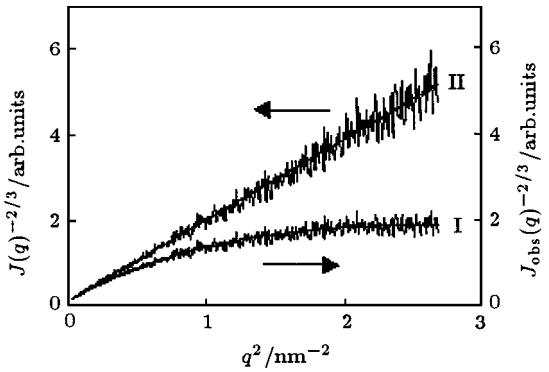


Fig.1. A typical positive deviation from Debye's theory (I) and the deviation-corrected Debye plot (II) of mesoporous ZrO_2 xerogel.

The validity of the preceding statement is tested for porous ZrO_2 xerogel, which was prepared using a sol-gel process as follows: zirconium n-propoxide (75% in propanol, Strem Chemicals) was added to the diglycol solution of ethanol, and another solution containing ethanol and deionized water and non-ionic alkylpolyethyleneoxide $CH_3(CH_2)_n(OCH_2CH_2)_9OH$ (AEO_9) surfactant was slowly introduced into the above solution to obtain a homogeneous mixture with the compositions of $Zr(OC_3H_7)_4$: $3H_2O$: $3O$ $(C_2H_4OH)_2$: $0.1AEO_9$:$65C_2H_5OH$ (in molar ratio); then the mixture was transferred into a stainless autoclave lined with Teflon for thermal treatment at 230°C for 72h. Finally, the resulted precipitation was filtered, washed and dried at 50°C for overnight. N_2 adsorption-desorption measurement indicated that this sample is a kind of mesoporous material with polydispersive pores in nano-sized scale. It is these pores that give rise to the small-angle x-ray scattering.[2,8,10] The phase boundaries between the pores and the solid skeleton should be sharp under the preparing condition. Figure 1 shows a typical Debye plot of the sample. A SAXS experiment was performed using synchrotron radiation as the x-ray source with a long-slit collimation system at Beijing Synchrotron Radiation Laboratory, Chinese Academy of Sciences. The incident x-ray wavelength λ was 0.154nm. The scattered x-ray intensities were recorded using the imagery plate technology. The air scattering and the absorption of the sample were corrected. The plot I ($J_{\rm obs}(q)^{-2/3}$ versus q^2) in Fig.1 deduced from the originally measured data presents a downward concave curve. It is obvious that the scattering shows a positive devia-

tion from Debye's theory, suggesting that there exists micro-inhomogeneity of electron density within the solid phase of ZrO_2 xerogel. This may be due to the incomplete crystallization below 230°C and the amorphous matter still existing in the skeleton, i.e. the sample is in semicrystalline state as confirmed by x-ray diffraction (XRD) pattern in Fig.2. The fitted line across curve I in Fig.1 is obtained according to Eq.(3). Obviously, the scattering data showing a positive deviation from Debye's theory might be well fitted with Eq.(3). In order to study the structure of the pores in the sample, additional scattering due to the micro-inhomogeneity of electron density should be removed first. Therefore, the performance of the positive deviation correction is necessary to recover Debye's theory, as shown by the linear plot II ($J(q)^{-2/3}$ versus q^2) in Fig.1, which should be the pure scattering of pores. An approximate agreement is found between the average pore size, 3.81nm (supposing the pores are global) obtained from the positive deviation corrected SAXS data, and 4.21nm obtained from N_2 adsorption data. Similar analysis is performed on mesoporous silica with templates remaining in the pores and carbon fibres prepared under different temperatures. It seems that the preceding statement is valid for these cases.

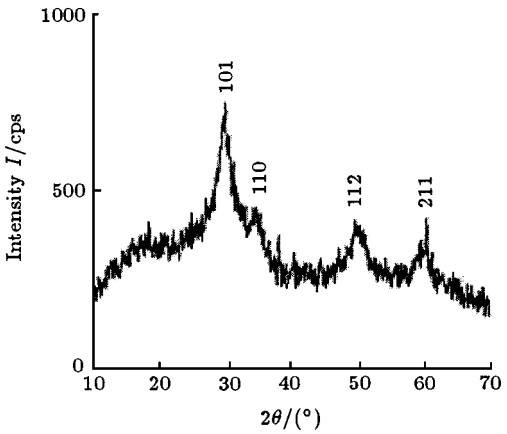


Fig.2. XRD pattern of mesoporous ZrO_2 xerogel.

References

[1] Glatter O and Kratky O 1982 *Small Angle x-ray Scattering* (New York: Academic)

[2] Li Z H, Gong Y J, Zhang Y, Wu D, Sun Y H, Wang J, Liu Y and Dong B Z 2001 *Chin. Phys.* **10** 429

[3] Li Z H, Sun J H, Zhao J P, Wu D, Sun Y H, Liu Y, Sheng W J and Dong B Z 2000 *Acta Phys. Sin.* **49** 775 (in Chinese)

[4] Li Z H, Sun J H, Wu D, Sun Y H, Liu Y, Sheng W J and Dong B Z 2000 *Acta Phys. Sin.* **49** 1312 (in Chinese)

[5] Li Z H, Gong Y J, Wu D, Sun Y H, Wang J, Liu Y and Dong B Z 2001 *Acta Phys. Sin.* **50** 1128 (in Chinese)

[6] Debye P, Anderson H R and Brumberger H 1957 *J. Appl. Phys.* **28** 679

[7] Brown D S, Warner F P and Wetton R E 1972 *Polymer* **13** 575

[8] Li Z H, Gong Y J, Pu M, Wu D, Sun Y H, Wang J, Liu Y and Dong B Z 2001 *J. Phys. D: Appl. Phys.* **34** 2085

[9] Koberstein J T, Morra B and Stein R S 1980 *J. Appl. Cryst.* **13** 34

[10] Li Z H, Zhao J P, Wu D, Sun Y H, Wang J, Liu Y and Dong B Z 2000 *Acta Chim. Sin.* **58** 1147

[11] Meng Z F 1996 *Theory and Application of Small Angle x-ray Scattering* (Changchun: Jilin Science and Technology Press) (in Chinese)