ABOUT THE CORRELATION DISTANCE OBTAINED BY SMALL ANGLE X-RAY SCATTERING IN CONCENTRED TWO-PHASE SYSTEMS

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- ABSTRACT: The correlation distance, as determined by small angle X-Ray scattering (SAXS) in systems which scatter according to the Debye, Anderson and Brumberger (DAB) model, is compared with the classical Porod's inhomogeneity length. Both parameters have the same value and the same physical means in compact two-phase systems. The inherent problems to fit the Porod's law in DAB model systems, as well as the deviation in the determination of the associated Porod's inhomogeneity length, are discussed .

- KEYWORDS: Small angle X-Ray scattering; Porod's inhomogeneity length; Debye, Anderson and Brumberger (DAB) correlation distance.

Introduction

The structural parameter often obtained by small angle X-Ray scattering (SAXS) in non-particulate systems in the colloidal dimension range is a certain correlation distance.[1] Direct experimental determination of the correlation distance in isotropic systems requires an appropriate theoretic model fitting the scattering intensity I(h) data as a function of the modulus of the scattering vector $h = 4\pi \sin(\varepsilon/2)/\lambda$, being ε the scattering angle and λ the radiation wavelength. Porod's law[1] and the Debye, Anderson and Brumberger (DAB) model[2] are classical ones frequently fitting the data of porous systems. However, the exact physical meaning of the DAB correlation distance in dense packing systems and its relationship with the classical Porod inhomogeneity length are not always understood.[3]

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In this work, direct determination of the DAB correlation distance, without desmearing the data from studies under experimental conditions of slit collimation, is considered, and the relationship of this parameter with that Porod inhomogeneity length is discussed together with the inherent difficulties expected to fit the Porod's law in a typical DAB model system.

Scattering by isotropic porous systems

The small angle X-ray scattering power I(h) by an isotropic porous system is related with the Fourier-Transform of the correlation function $\gamma(r)$, which is defined as the mean value of the product of the local fluctuations in electronic density, with respect to some average value, separated by the distance r. The limite $\gamma(r \Rightarrow 0)$ gives the interface surface area by unity volume of the irradiated sample.[2]

$$(S/V) = -4\phi(1-\phi)\,\gamma'(0) \qquad (1)$$

where ϕ is the pore volume fraction.

Under experimental conditions of ''linear and infinite'' cross section beam collimation (slit collimation), the observed scattering intensity is a certain smeared value $\tilde{I}(h)$ due to the infinite height of the beam, which is described by a variable t, and will be given by the following integration along t[4]:

$$\tilde{I}(h) = \int_{-\infty}^{+\infty} I[(h^2 + t^2)^{1/2}]\,dt \qquad (2)$$

The Porod's law

According to Porod's law, under slit collimation conditions, the assymptotic dependency of $\tilde{I}(h)h$ at large values of h decreases proportional to the reciprocal thirth power of h^4:

$$\lim_{h\to\infty} \tilde{I}(h) = \tilde{K}_{p/h^3} \qquad (3)$$

where $\tilde{K}_p$ is the so-called Porod-law constant for slit collimation. The Porod-law constant is related to the surface/volume ratio of the irradiated sample as it follows[6]

$$(S/V) = 4\,\phi\,(1-\phi)\tilde{K}_p/\tilde{Q} \qquad (4)$$

where

$$\tilde{Q} = \int_0^{\infty} h\,\tilde{I}(h)\,dh \qquad (5)$$

is the integrate intensity over the h space, a parameter so-called invariant which is helpful when the intensity measurements are obtained in relative units. One defines the Porod inhomogeneity length[6]

$$l_p = \tilde{Q}/\tilde{K}_p \qquad (6)$$

which yields the average sizes of the solid phase (l_s) and pores (l_v), if the pore volume fraction is known, with the help of the equations[1]:

$$l_p = (1-\phi)\,l_s = \phi\,l_v \quad \text{or:} \quad \frac{1}{l_p} = \frac{1}{l_s} + \frac{1}{l_v} \qquad (7)$$

The Debye, Anderson and Brumberger (DAB) model

According to Debye, Anderson and Brumberger,[2] when the porous system shows a distribution of holes of random shape and size, so $\gamma(r)$ is an exponential function:

$$\gamma(r) = \exp(-r/a) \qquad (8)$$

where a is the DAB correlation distance. The system will scatter according to the law:[2] $I_{DAB}(h) = A/(1+a^2h^2)^2$, where A is a constant. Under slit collimation conditions, this law yields,[7] after the appropriate integration throught equation (2),

$$\tilde{I}_{DAB}(h) = B/(1 + a^2h^2)^{3/2} \qquad (9)$$

where $B=\pi/2a$. The plot of $\tilde{I}^{-2/3}$ *vs.*h^2 is linear and the correlation distance a can be obtained from the slope-intercept ratio directly without smearing the data.

By using the correlation function of the equation (8), equation (1) becomes[2]

$$(S/V) = 4\,\phi(1-\phi)/a \qquad (10)$$

From equations (4), (6) and (10) one concludes that the correlation distance in the DAB model is equivalent to the Porod inhomogeneity length, or

$$a \equiv l_p \qquad (11)$$

Another evidence of this result can be obtained directly from the calculus of $\tilde{K}_p$ and $\tilde{Q}$ for a DAB system, i.e., a system which scatter according to the equation (9). So, from equations (3) and (5) we have

$$\tilde{K}_p = \lim_{h \to nf} \tilde{I}_{DAB}(h)h^3 = B/a^3 \qquad (12)$$

and

$$\tilde{Q} = \int_0^\infty h\,\tilde{I}_{DAB}(h)\,dh = B/a^2 \qquad (13)$$

and by using these last equations in the equation (6) it yields the equation (11) again.

Discussion

The DAB correlation distance obtained by SAXS for non-particulate systems have a precise physical meaning which is closely related with the mean size of individual phases, as it is the Porod inhomogeneity length. Porod's law is more generic than the DAB model and so the calculation of l_p is almost always possible for isotropic two-phase systems with sharp boundaries interface. The advantage in the application of the DAB model, when it is possible, is that the value of the DAB correlation distance can be obtained even at regions of small h values, where a more accurate measurement of the intensity is possible. Experimental determination of DAB correlation distance can be carried out directly under slit collimation measurements without smearing the data.

Finally, we speculate if both models could be successful to fit the scattering data from a typical DAB system and what about the experimental difficulties to carry it out. In addition, we consider if the positive deviation[8] from Porod's law found in some cases might be due to and inappropriate choosen for the Porod's law regime in a supposed DAB model system.

For a system with tridimensional electronic density fluctuations, the Porod's law can be written as[8]

$$\lim_{h \to \infty} \tilde{I}(h) = \frac{\tilde{K}_{p'}}{h^3} + b \qquad (14)$$

where $\tilde{K}_{p'}$ is the apparent Porod-law constant and b is the fluctuation magnitude. So, equation (14) could apparently be a reasonable fit to the experimental data from a DAB system if the h-range is relatively small. The Figure 1 shows $\tilde{I}(h)h^3$ *vs.* h^3 plots for DAB scattering systems with several a values. This interval covers the a-range values found in the systems studied in ref. 2. Rigorously, the Porod's law could be observed just for $ah >> 1$. Often, that law is fitted in a h-range so that $ah \gtrsim 2\pi$. Fitting equation (14) in a typical experimental h-range comprised between h_1=2.15 nm^{-1} and h_*= 3.0 nm^{-1}, it yields the parameters in Table I.

Table I – Fitting equation (14) in a fixed h-range between h_1 = 2.15 nm^{-1} and h_* = 3.0 nm^{-1} for distincts DAB model systems

a/nm	$\tilde{K}_{p'}$ / a.u.	b/a.u.	linear correlation coefficient	$\tilde{Q}'$ / a.u.	l'_p / nm	$\frac{l'_p - a}{a}$ (%)	ah_1
3.00	3.55	3.52	0.978	11.0	3.11	3.7	6.5
2.00	11.4	25.3	0.977	24.6	2.17	8.5	4.3
1.50	25.1	99.3	0.978	42.7	1.70	14.0	3.2
1.25	40.4	230.	0.979	60.0	1.48	19.0	2.7
1.00	69.7	620.	0.981	88.8	1.27	27.0	2.2

$\tilde{Q}' = \int_0^{h_*} h\tilde{I}_{DAB}\,dh + \frac{\tilde{K}_{p'}}{h_*} - \frac{bh_*^2}{2}$ ≡ apparent invariant value

$l_{p'} = \tilde{Q}'/\tilde{K}_{p'}$ ≡ apparent inhomogeneity length

The experimental data in the Porod's law regime are often within about 5% in error. The resulting parameter $l_{p'}$ obtained from the approximation by the equation (14) would be within the same experimental error if an adequate h-range had been choosen for the Porod's law fit. The condition $ah \gtrsim 2\pi$ is just held for the straight line fitting the curve e) in Figure 1. Meanwhile, if the fit is carried out in a wrong h-interval, the resulting error in the apparent $l_{p'}$ value can be relevant in precise works. However, even in the last case, that is yet a reasonable estimation of the correlation distance of the heterogeneities.

The Figure 1 shows that there is not a distinct crossover on passing from a regime described by the equation (9) to another by the equation (3) in a DAB model system. So, the distinct crossover for h = 2.06 nm^{-1} as appearing in Figure 2 from a sample of tin oxi-hydroxide wet gel[9] could not be associated to a sharp transition to the Porod's law regime (equation (3)) of a simple DAB model system (following the equation (9)), despite the good fit of both equations yielding a=0.95 nm and l_p=1.31 nm. The simultaneous observation of both regimes (eq. (9) and eq. (3)) in a typical $\tilde{I}^{-2/3}$ *vs.* h^2 plot would be incompatible for a simple DAB model system.

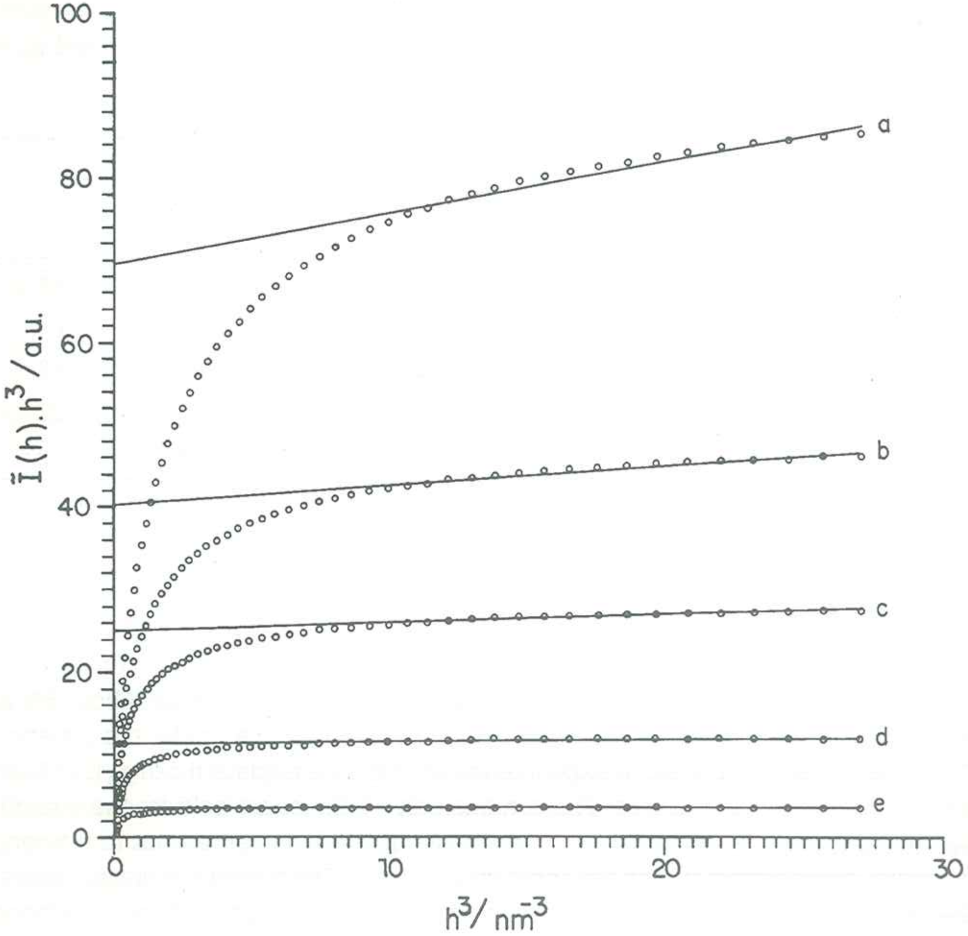

FIGURE 1 – Porod's law plots for typical DAB systems with (a) a=1.0 nm, (b) a=1.25 nm, (c) a=1.5 nm, (d) a=2.0 nm and (e) a=3.0 nm.

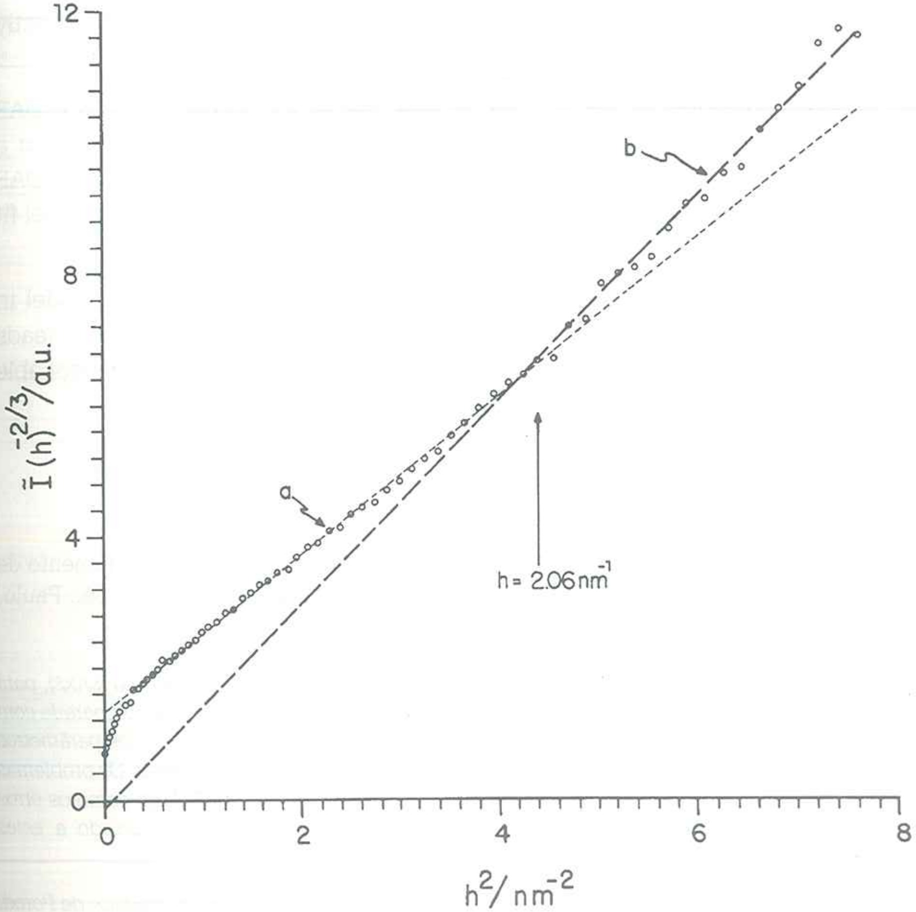

FIGURE 2 – Slit collimation DAB model plot from a wet sample of tin oxi-hydroxide gel[9]. (a) DAB model fitting (a=0.95 nm) (b) Porod's law fitting (l_P=1.31 nm).

Conclusions

i) The DAB correlation distance which is obtained for systems with a distribution of pores of random shape and size have the same value of the inhomogeneity length defined by the classical Porod's law when the scattering intensity is measured in relative units.

ii) Experimental determination of DAB correlation distance can be done directly under linear and infinite collimation conditions without smearing the data.

iii) A sharp crossover in the $\tilde{I}^{-2/3}$ *vs.* h^2 plot due to the transition from a DAB scattering behaviour (eq. (9)) to a Porod's law regime (eq. (3)) is not expected for a simple DAB model system. In this case, adequate Porod's law fits depends on the DAB correlation distance and on the h-intervals to fit the data, while direct DAB model fit is prefered.

iv) Assuming a wrong tridimensional electronic density fluctuations model in an inadequate interval for the Porod's law fitting a typical DAB scattering system, leads us to an inhomogeneity length which is greater than the real value, but yet a reasonable estimation of the size of the heterogeneities.

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- *RESUMO: A distância de correlação obtida por espalhamento de Raios X a baixo ângulo (SAXS), para sistemas que espalham segundo o modelo de Debye, Anderson e Brumberger (DAB), é comparada com o clássico comprimento de inhomogeneidade de Porod. Fica evidenciado que ambos os parâmetros têm o mesmo valor e o mesmo significado físico nos sistemas compactos de duas fases. Os problemas de ajuste da lei de Porod em sistemas que espalham segundo o modelo de DAB, bem como os erros acarretados na determinação do comprimento de inhomogeneidade de Porod associado a estes sistemas, também são discutidos.*

- *UNITERMOS: Espalhamento de Raios X a baixo ângulo; comprimento de inhomogeneidade de Porod; distância de correlação de Debye, Anderson e Brumberger (DAB).*

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