

actual ϕ value differs by a small amount from the value on the section this is given on the chart. In practice this means that the point representing the appropriate (hkl) $[uvw]$ lies either just above or just below the given section.

As referred to earlier, some ambiguity exists for the ideal orientations $(001)[u0]$ and these appear as points on all sections. Fig. 3 shows the $\theta=0$ section which gives the lines representing these orientations.

Fig. 4 shows the positions of (hkl) lines for all ψ values. These are the lines which appear as constant- θ on the constant- ϕ sections.

Using these sets of charts, ideal orientations can be attributed to the high density regions of crystallite orientation distribution function plots both rapidly and unambiguously. This will enhance the understanding of the data contained in the plots as well as permitting comparison with textural data obtained by more conventional methods (Dillamore & Roberts, 1965).

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Small-Angle Scattering of Two-Phase Systems: Determination and Significance of Systematic Deviations from Porod's Law

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Density transition of finite width between the phases and density fluctuations within the phases produce systematic deviations from Porod's law, which can be detected by suitable intensity plots. These plots permit the correction of the intensity and the determination of structural parameters related to the causes of the deviations.

Introduction

The theory of small-angle scattering by isotropic two-phase systems (Porod, 1951, 1952*a*, *b*) predicts a decrease of the intensity proportional θ^{-4} at large values of θ , known as Porod's law. Assuming a single scattering process and the applicability of the kinematic scattering theory, the scattering intensity I is given by

$$I = \mathcal{F}(\Delta\rho^{*2})$$

where $\Delta\rho$ is the difference between the local electron density and the average, \mathcal{F} is a three-dimensional Fourier transform

$$\int_v (\Delta\rho^{*2}) \exp \{2\pi i \mathbf{r} \cdot \mathbf{s}\} d\mathbf{v}_r$$

and *2 stands for self-convolution or autocorrelation.

With this normalization of I , Porod's law takes the form

$$I(s \rightarrow \infty) = \frac{S}{8\pi^3 s^4 (\rho_1 - \rho_2)^2}$$

where $s = 2\theta/\lambda$ and S is the total area of the interface between the phase with density ρ_1 and the phase with density ρ_2 .

Very often the intensity is not determined in absolute units and Porod's law is used in the form

$$\lim_{s \rightarrow \infty} \frac{2\pi^3 s^4 I(s)}{4\pi \int_0^\infty s^2 I ds} = \frac{S}{4c(1-c)V} = \frac{1}{l_p}$$

where S/V is the area of the interface per unit volume, c the volume fraction of one of the phases and l_p the 'range of inhomogeneity', a parameter related to

the average sizes of regions occupied by phase 1 and by phase 2.

S/V and l_p are parameters with a simple and unambiguous meaning for dilute systems as well as for dense systems, in contrast to the radius of gyration (Guinier, 1939) and the 'length of coherence' l_c ; an accurate determination of these parameters is thus highly desirable.

A further interest in an accurate determination of the asymptotic behaviour of I at large values of s is the possibility of computing the intersect distribution function from the difference between s^4I and $\lim_{s \rightarrow \infty} s^4I$ (Porod, 1965; Méring & Tchoubar, 1965, 1966).

In practice this determination is rather difficult. In many cases plots of s^4I as a function of s (or s^3I versus s for measurements with an infinite slit) do not permit an unambiguous determination of the limit and $\log I - \log s$ plots show non-integral exponents of s . This is frequently attributed to background scattering of some kind and this assumption may be correct in some cases. However, there are other causes for deviations from Porod's law, which are related to structural particularities of the two-phase system studied.

The aim of this paper is to discuss two types of such systematic deviations and the possibilities of determining and eliminating them.

Finite width of the density transition

A basic assumption in the theoretical treatment of the two-phase system is an infinitely sharp density transition from one phase to the other. As a result of this assumption the characteristic function

$$\gamma(r) = \frac{\Delta \varrho^{*2}(r)}{\Delta \varrho^{*2}(0)}$$

has the form $1 - |r|/l_p$ for small values of r .

In practice, the density transition cannot be infinitely sharp but should have at least the width produced by the electron distribution of the basic structural elements of the phases. Hosemann & Bagchi (1962) have shown that the effect of a finite width of the density transition can be conveniently represented by a convolution of the ideal density distribution ϱ with a (three-dimensional) 'smoothing' distribution h so that the observed density distribution ϱ_{obs} becomes

$$\varrho_{\text{obs}} = \varrho * h.$$

Taking into account the relationship between ϱ and γ one finds

$$\gamma_{\text{obs}} = \gamma * h^{*2}$$

and from this

$$I_{\text{obs}} = I \cdot H^2$$

where

$$H = \mathcal{F}(h).$$

The width of h should be small compared with the average extent of the regions of constant density (*i.e.*

small compared with l_p) if the definition 'two-phase system' is to remain meaningful. In this case, the width of H will be considerably larger than that of I so that the intensity distribution is essentially only affected at larger s values, *i.e.* in the region of the validity of Porod's law.

If the variance of the 'smoothing' distribution is σ^2 perpendicular to the interface, H can be approximated by

$$H = 1 - 2\pi^2\sigma^2s^2$$

for small values of σs . The intensity measured with a pin-hole system becomes thus

$$I_{\text{obs}} = I(1 - 4\pi^2\sigma^2s^2).$$

This indicates that a practical way of detecting the effect of a finite width of the density transition is an $s^4I_{\text{obs}} - s^2$ plot, which should show, at large values of s , a linear relationship with the slope

$$-\frac{2k\sigma^2s^2}{\pi l_p}.$$

This slope extrapolated towards $s=0$ intersects the s^4I_{obs} scale at

$$\frac{k}{2\pi^3 l_p}$$

where

$$k = \Delta \varrho^{*2}(0) = 4\pi \int_0^\infty s^2 I ds = Vc(1-c)(\varrho_1 - \varrho_2)^2.$$

Such a plot permits the determination of the correct value of l_p together with the parameter σ^2 related to the finite width of the density transition, which can be used to calculate I for all values of s . In many cases the intensity measurements are carried out with an 'infinite' slit height (Kratky camera). The corresponding observed intensity J_{obs} is given by

$$J_{\text{obs}} = 2 \int_0^\infty I_{\text{obs}}(\sqrt{s^2 + y^2}) dy;$$

thus

$$J_{\text{obs}} = 2 \int_0^\infty I(\sqrt{s^2 + y^2}) H^2(\sqrt{s^2 + y^2}) dy.$$

To evaluate the integral we have to assume a definite form for H . A reasonable assumption for the 'smoothing' function is a Gaussian distribution, thus

$$H = \exp \{-2\pi^2\sigma^2s^2\}.$$

With

$$I = \frac{k}{2\pi^3 s^4 l_p}$$

one obtains

$$J_{\text{obs}} = \frac{k}{4\pi^2 s^3 l_p} \times$$

$$[(1 - 8\pi^2\sigma^2s^2)\text{erfc}(2\pi\sigma s) + 4/\pi \sigma s \exp \{-4\pi^2\sigma^2s^2\}]$$

where erfc is the complementary error function.

For small values of σs this can be approximated by

$$J_{\text{obs}} = \frac{k}{4\pi^2 s^3 l_p} (1 - 8\pi^2 \sigma^2 s^2) ;$$

an $s^3 J_{\text{obs}} - s^2$ plot can thus be used in a similar way as the $s^4 I - s^2$ plot discussed above to determine l_p and σ^2 , and to calculate the corrected intensity J , *e.g.* for the computation of the intersect distribution function.

In some cases (*e.g.* anisotropic systems) the scattering intensity is given in the form of the projection of I onto a straight line, which we denote $\{I\}_1$. Taking H as above one finds for such one-dimensional projections

$$\{I_{\text{obs}}\}_1 = \frac{k}{2\pi^2 s^2 l_p} E_2(4\pi^2 \sigma^2 s^2)$$

where E_2 is the exponential integral of order two. For small values one can use the approximation

$$E_2(4\pi^2 \sigma^2 s^2) = [1 - 4\pi^2 \sigma^2 s^2 (1 - \gamma - \ln 4\pi^2 \sigma^2 s^2)]$$

where γ is the Euler constant (0.5772).

In this case the determination of l_p and σ^2 , although possible, is less easy than for I_{obs} or J_{obs} .

The approximations given above enable us to estimate the maximum value of s up to which the intensity distribution can be considered unaffected within a given limit of error. If one takes this limit equal to 5% one finds

$$s_{\text{max}} = \frac{0.036}{\sigma} \quad \text{for } I_{\text{obs}},$$

$$s_{\text{max}} = \frac{0.025}{\sigma} \quad \text{for } J_{\text{obs}}$$

and

$$s_{\text{max}} = \frac{0.016}{\sigma} \quad \text{for } \{I_{\text{obs}}\}_1.$$

As expected, the range of validity of Porod's law decreases with increasing σ for a given type of intensity measurement and decreases for a given σ from I_{obs} to J_{obs} to $\{I_{\text{obs}}\}_1$.

Density fluctuations within the phases

Another basic assumption in the theoretical treatment of the two-phase system is to consider the electron density within the phases as strictly invariant within the phase boundaries. This assumption holds for phases with a high degree of order or for voids; in many practical cases, however, the phases can be non-crystalline or composed of imperfect crystals so that this assumption is no longer valid. The density fluctuations within the phases can be considered to produce additional intensity components in the small-angle region due to the internal structure of the phases. Provided there is no correlation between the density fluctuation of one phase and that of the other nor between the fluctuation of a phase and the shape and size of

its boundaries, the corresponding intensity components are simply additive to the small-angle scattering of the ideal system. With the appropriate normalization of these components one finds

$$I = k \mathcal{F}(\gamma) + V_1 \varrho_1 [\text{Fl}]_1 + V_2 \varrho_2 [\text{Fl}]_2$$

where k has the value already given in the last section, V_1 and V_2 are the total volumes of phase 1 and phase 2, respectively, and $[\text{Fl}]_1$ and $[\text{Fl}]_2$ stand for the normalized intensity component of the density fluctuations within phase 1 and phase 2, respectively.

For three-dimensionally homogeneous fluctuations (Zernike & Prins, 1927) $[\text{Fl}]$ is given by

$$[\text{Fl}] = \text{Fl}_3 = \frac{\langle N^2 \rangle_v - \langle N \rangle_v^2}{\langle N \rangle_v}$$

where N is the number of electrons and the average is taken over a volume which is large compared with the interaction between the atoms and molecules within a given phase. A fluctuation is considered homogeneous when its value becomes invariant for averaging volumes of dimensions larger than these interactions. Homogeneous fluctuations exist, for example, in liquids and gases. Since X-ray diffraction does not distinguish between the time average and the space average of the density, amorphous substances with 'frozen-in' liquid structures (Levelut & Guinier, 1967) as well as crystalline substances with a gas-type distribution of foreign atoms or vacancies will also show homogeneous density fluctuations.

In the case of strongly anisotropic disorder, however, the density fluctuations become inhomogeneous and $[\text{Fl}]$ is no longer a constant. If, for example, the disorder is essentially one-dimensional and the fluctuation of the density projected onto a straight line parallel to the direction of the disorder is Fl_1 , one finds

$$[\text{Fl}] = \frac{\tau \text{Fl}_1}{2\pi s^2}$$

where τ is the surface density of electrons in the two-dimensional entities which participate in the fluctuation. Such fluctuations have been found in disordered layer structures such as graphitic carbons (Schiller & Méring, 1967) and non-graphitic carbons (Perret & Ruland, 1968, 1969).

Similarly, if the disorder is essentially two-dimensional and Fl_2 the fluctuation of the density projected onto a plane parallel to the direction of the disorder, one finds

$$[\text{Fl}] = \frac{\xi \text{Fl}_2}{2s}$$

where ξ is the linear density of electrons in the one-dimensional entities which participate in the fluctuation. Such fluctuations have not yet been observed. A more detailed discussion on the anisotropic density fluctuations will be given in a separate paper.

If the intensity distribution is measured with a slit

system of 'infinite' height the component due to one-dimensional fluctuations becomes

$$[F] = \frac{\tau F I_1}{2s}.$$

For the components due to two-dimensional and three-dimensional fluctuations the 'infinite' slit height approximation can no longer be used and the actual transmission function $W(y)$ of the slit system has to be considered. With this one finds for the component due to two-dimensional fluctuations

$$[F] = \xi F I_2 \int_0^\infty \frac{W(y)}{\sqrt{s^2 + y^2}} dy$$

and for three-dimensional fluctuations

$$[F] = F I_3 2 \int_0^\infty W(y) dy.$$

The separation of the scattering due to the contours of the phases and that due to the fluctuation of the density within these phases is relatively simple when both phases show the same type of fluctuation or when the fluctuation term is negligibly small for one phase. In this case one can use a plot of $s^4 I$ versus a parameter u in the case of a pin-hole system and a plot of $s^3 J$ versus u (Luzzati, Witz & Nicolaieff, 1961) in the case of a slit-system of finite height to produce a linear relationship which permits the separation. The values of the parameter u as a function of the type of fluctuation are given in Table 1. Having found a linear relationship in one of these plots, the type of fluctuation is defined, the magnitude of the fluctuation is obtained from the slope and the corrected asymptotic value is given by the extrapolated value of the linear relationship at $u=0$.

Table 1. Values of the parameter u

$[F]$	u for $s^4 I$	u for $s^3 J$
One-dimensional	s^2	s^2
Two-dimensional	s^3	$s^3 \int_0^\infty \frac{W(y)}{\sqrt{s^2 + y^2}} dy$
Three-dimensional	s^4	s^3

If the two phases show fluctuations of different types trial and error methods could be used for the separation.

Conclusions

Systematic deviations from Porod's law can be detected by using appropriate intensity plots of $s^4 I$ or $s^3 J$. The finite width of the density transition produces negative deviations, the density fluctuations within the phases positive deviations. This may lead, in exceptional cases, to partial or even total compensation. The quantitative measurement of the parameters determining the deviations permits the computation of the corrected intensity distribution necessary for the determination of l_p and S/V and of the intersect distribution function and thus increases the range of the applicability of the evaluation methods developed for two-phase systems. Furthermore, supplementary structural information is obtained which may, in some cases, be of equal or higher interest than the information obtainable from the ideal intensity distribution only.

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