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Corrections to Tabulated Anomalous-Scattering Factors

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Abstract

Z-dependent energy-independent corrections to the relativistic anomalous-scattering factors tabulated by a number of workers are given. These corrections are most significant for medium-Z and high-Z atoms, but are experimentally observable even in low-Z elements. Examples of use of the correction factors are provided for the real anomalous-scattering factor f' and for the differential elastic scattering cross section $d\sigma/d\Omega$.

Introduction

We give here a tabulation (Table 1) of the correction factors $\delta f'$ which should be added to the relativistic anomalous-scattering factors f' of Cromer & Liberman (1970*a*, *b*, 1976, 1981), Cromer (1974, 1983) and Henke, Lee, Tanaka, Shimabukuro & Fujikawa (1981, 1982), as discussed by Parker & Pratt (1984) and more recently, and in greater detail, by Smith (1987). This issue does not arise in a non-relativistic theory, in which f' vanishes in the high-energy limit. The correction, of relativistic origin, is Z dependent but energy independent; it is most significant in heavier elements. It has been observed experimentally, as Parker & Pratt (1984) noted in mentioning the systematic discrepancies which had been reported by Creagh (1975, 1980); more extensive comparisons and references are given by Smith (1987).

The problem arose from Cromer & Liberman's use of a dipole approximation in estimating relativistic corrections to the high-energy limit of forward scattering. Higher multipoles in fact become important at high energy. Jensen (1979, 1980) identified this as a problem, but did not succeed in calculating the corrections. In fact, $(5/3)(E_{tot}/mc^2)$, enumerated in Table II of Cromer & Liberman (1970*b*), is better replaced by (E_{tot}/mc^2), where E_{tot} is the total binding energy of the atomic electrons. The later Cromer (1983) program, incorporating the first Jensen (1979) term, should not be used unless the Jensen term is then explicitly subtracted out. The correct high-energy limit had actually been obtained earlier in other contexts. It appears to be contained, for example, in the relativistic modified form-factor approximation of Franz (1936). The Coulomb K-shell result was given by Levinger & Rustgi (1956), more generally by Goldberger & Low (1968) and Florescu & Gavrila (1976). The general result for a central potential was obtained by Levinger, Rustgi & Okamoto (1957). Beginning with the relativistic dispersion relation, Wang (1986) derived a form of the relation accurate to order $(Z\alpha)^2$ suitable for numerical evaluation.

Numerical multipole calculations based on the second-order S matrix began with the work of Brown,

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Table 1. *High-energy-limit corrections to the real part of the anomalous-scattering factor $f'(\omega)$ for neutral atoms*

The Z-dependent energy-independent correction $\delta f' = f'(\infty) - f'_{CL}(\infty)$, where $f'_{CL}(\infty)$ is the high-energy limit of the real anomalous-scattering factor given by Cromer & Liberman (1970*b*, 1981). The high-energy limit of the S-matrix anomalous-scattering factor for neutral atoms is taken as $f'(\infty) = g(0) - Z$ (see Table 2), where Z is the atomic number and $g(0)$ is the value of the relativistic modified form factor at zero momentum transfer as computed by Schaupp, Schumacher, Smend, Rullhusen & Hubbell (1983).

Z	$g(0)$	$f'(\infty)$	$f'_{CL}(\infty)$	$\delta f'$	Z	$g(0)$	$f'(\infty)$	$f'_{CL}(\infty)$	$\delta f'$
1	1·000	0·000			51	50·680	−0·320	−0·575	0·255
2	2·000	0·000			52	51·665	−0·335	−0·602	0·267
3	3·000	0·000	−0·001	0·001	53	52·650	−0·350	−0·631	0·281
4	3·999	−0·001	−0·001	0·000	54	53.634	−0·366	−0·660	0·294
5	4·999	−0·001	−0·002	0·001	55	54·618	−0·382	−0·690	0·308
6	5·998	−0·002	−0·003	0·001	56	55·602	−0·398	−0·721	0·323
7	6·997	−0·003	−0·005	0·002	57	56·585	−0·415	−0·753	0·338
8	7·996	−0·004	−0·007	0·003	58	57·568	−0·432	−0·786	0·354
9	8·995	−0·005	−0·009	0·004	59	58·550	−0·450	−0·819	0·369
10	9·993	−0·007	−0·011	0·004	60	59·532	−0·468	−0·854	0·386
11	10·992	−0·008	−0·014	0·006	61	60·513	−0·487	−0·889	0·402
12	11·990	−0·010	−0·018	0·008	62	61·494	−0·506	−0·925	0·419
13	12·987	−0·013	−0·021	0·008	63	62·475	−0·525	−0·962	0·437
14	13·985	−0·015	−0·026	0·011	64	63·455	−0·545	−1·000	0·455
15	14·982	−0·018	−0·030	0·012	65	64·435	−0·565	−1·039	0·474
16	15·979	−0·021	−0·035	0·014	66	65·414	−0·586	−1·079	0·493
17	16·976	−0·024	−0·041	0·017	67	66·393	−0·607	−1·119	0·512
18	17·973	−0·027	−0·047	0·020	68	67·371	−0·629	−1·161	0·532
19	18·969	−0·031	−0·053	0·022	69	68·349	−0·651	−1·204	0·553
20	19·965	−0·035	−0·060	0·025	70	69·326	−0·674	−1·248	0·574
21	20·960	−0·040	−0·068	0·028	71	70·303	−0·697	−1·293	0·596
22	21·956	−0·044	−0·075	0·031	72	71·279	−0·721	−1·338	0·617
23	22·951	−0·049	−0·084	0·035	73	72·255	−0·745	−1·385	0·640
24	23·946	−0·054	−0·093	0·039	74	73·230	−0·770	−1·433	0·663
25	24·940	−0·060	−0·102	0·042	75	74·205	−0·795	−1·482	0·687
26	25·935	−0·065	−0·113	0·048	76	75·179	−0·821	−1·532	0·711
27	26·929	−0·071	−0·123	0·052	77	76·153	−0·847	−1·583	0·736
28	27·922	−0·078	−0·135	0·057	78	77·126	−0·874	−1·636	0·762
29	28·915	−0·085	−0·146	0·061	79	78·099	−0·901	−1·689	0·788
30	29·908	−0·092	−0·159	0·067	80	79·071	−0·929	−1·743	0·814
31	30·901	−0·099	−0·172	0·073	81	80·043	−0·957	−1·799	0·842
32	31·893	−0·107	−0·186	0·079	82	81·014	−0·986	−1·856	0·870
33	32·885	−0·115	−0·200	0·085	83	81·985	−1·015	−1·914	0·899
34	33·877	−0·123	−0·215	0·092	84	82·955	−1·045	−1·973	0·928
35	34·868	−0·132	−0·231	0·099	85	83·924	−1·076	−2·033	0·957
36	35·859	−0·141	−0·247	0·106	86	84·893	−1·107	−2·095	0·988
37	36·850	−0·150	−0·264	0·114	87	85·861	−1·139	−2·157	1·018
38	37·840	−0·160	−0·282	0·122	88	86·829	−1·171	−2·221	1·050
39	38·830	−0·170	−0·300	0·130	89	87·796	−1·204	−2·287	1·083
40	39·819	−0·181	−0·319	0·138	90	88·762	−1·238	−2·353	1·115
41	40·809	−0·191	−0·338	0·147	91	89·728	−1·272	−2·421	1·149
42	41·797	−0·203	−0·359	0·156	92	90·694	−1·306	−2·490	1·184
43	42·786	−0·214	−0·380	0·166	93	91·658	−1·342	−2·561	1·219
44	43·774	−0·226	−0·401	0·175	94	92·622	−1·378	−2·633	1·255
45	44·762	−0·238	−0·424	0·186	95	93·585	−1·415	−2·707	1·292
46	45·749	−0·251	−0·447	0·196	96	94·548	−1·452	−2·782	1·330
47	46·736	−0·264	−0·471	0·207	97	95·510	−1·490	−2·858	1·368
48	47·723	−0·277	−0·496	0·219	98	96·471	−1·529	−2·936	1·407
49	48·709	−0·291	−0·521	0·230	99	97·432	−1·568		
50	49·695	−0·305	−0·547	0·242	100	98·391	−1·609		

Peierls & Woodward (1955), Brenner, Brown & Woodward (1955), and Brown & Mayers (1956, 1957), and has continued in the work of Cornille & Chapdelaine (1959), Johnson & Feiock (1968) and Johnson & Cheng (1976), and more recently in the Pittsburgh group (*e.g.* Kissel, Pratt & Roy, 1980; Kane, Kissel, Pratt & Roy, 1986). Lin, Cheng & Johnson (1975) numerically investigated the importance of fourth-order terms of the S matrix for scattering in helium. These S-matrix predictions currently represent the best available calculations for atomic scattering of X-rays and low-energy γ-rays. They yield the amplitude for elastic scattering of a photon from a specified atomic subshell, within the framework of external-field quantum electrodynamics and a description of independent bound atomic electron states in a relativistic self-consistent central potential. The S-matrix approach is based on Furry's extension of the Feynman–Dyson formulation of quantum electrodynamics, in which the

Table 2. *Forward-angle scattering amplitudes for selected neutral-atom subshells demonstrating the approach of the S-matrix amplitude (values at finite energy) to that predicted by the modified relativistic form-factor approximation (value at infinite energy)*

The quantity $\hbar\omega/\varepsilon$ indicates the ratio of the photon energy to the corresponding electron binding energy. The numbers in parentheses indicate the associated power of ten.

	Sub-shell	$\hbar\omega$ (keV)	$\hbar\omega/\varepsilon$	Re $A(\omega,0)$	Im $A(\omega,0)$
^{10}Ne	K	1·66	2	−2·3179	1·4636
		4·14	5	−2·2339	2·8813 (−1)
		8·28	10	−2·0923	7·3756 (−2)
		16·6	20	−2·0283	1·7325 (−2)
		41·4	50	−2·0020	2·3115 (−3)
		82·8	100	−1·9972	4·8181 (−4)
		166	200	−1·9958	1·0102 (−4)
		248	300	−1·9954	4·2000 (−5)
		∞	∞	−1·9952	0·0
^{36}Kr	L_{II}	17·5	10·3	−1·8489	4·4193 (−2)
		33·6	20	−1·9800	8·9590 (−3)
		84·0	50	−1·9866	8·7051 (−4)
		168	100	−1·9865	1·5384 (−4)
		336	200	−1·9863	3·1638 (−5)
		504	300	−1·9863	1·4202 (−5)
		∞	∞	−1·9862	0·0
^{54}Xe	N_V	2·99	50	−6·4579	2·1764 (−1)
		5·98	100	−5·8049	4·6496 (−2)
		12·0	200	−5·9865	7·5864 (−3)
		17·9	300	−5·9926	2·3667 (−3)
		∞	∞	−5·9942	0·0
^{86}Rn	K	197	2	−1·8832	8·1459 (−1)
		492	5	−1·7590	2·0552 (−1)
		984	10	−1·7089	9·0955 (−2)
		1970	20	−1·6929	4·2711 (−2)
		4920	50	−1·6895	1·7460 (−2)
		9840	100	−1·6892	8·6902 (−3)
		∞	∞	−1·6987	0·0

interaction of electrons and positrons with the atomic field is included in the unperturbed Hamiltonian.

We illustrate in Table 2 that numerical S-matrix calculations appear at forward angles to approach the relativistic modified form factor at high energy; no proof of this fact has yet been given. Our results tabulated in Table 1 are in fact based on the relativistic modified form-factor approximation, as computed by Schaupp, Schumacher, Smend, Rullhusen & Hubbell (1983), tested against S-matrix calculations in selected cases (see also Kissel *et al.*, 1980).

Examples

We may illustrate the use of our table and the significance of the correction with a couple of examples. We begin by noting that the anomalous-scattering factors are conventionally defined as the real energy-dependent angle-independent quantities f' and f'' such that for a given atom

$$\frac{d\sigma}{d\Omega}(\omega,0)=r_0^2|N+f'(\omega)+if''(\omega)|^2, \qquad (1)$$

where N is the number of bound electrons in the atom (for a neutral atom $N=Z$), and $d\sigma(\omega,\Theta)/d\Omega$ is the unpolarized elastic-scattering cross section at photon energy $\hbar\omega$ and scattering angle Θ (the angle between the incident and scattered photon directions); $\Theta=2\theta$, where θ is the Bragg angle. Note that the anomalous-scattering factors are defined at forward angle. It is known that, in a relativistic theory, the high-energy limit for forward scattering from bound electrons is not exactly $(Nr_0)^2$, so that $f'(\infty)$, as defined above, is not equal to zero (*e.g.* Levinger *et al.*, 1957). What we are listing in Table 1 is the difference of $f'(\infty)$ from the value $f'_{CL}(\infty)$ computed by Cromer & Liberman:

$$\delta f'=f'(\infty)-f'_{CL}(\infty). \qquad (2)$$

This difference arises from the inclusion of higher multipoles. At finite energy, the corrected value of the real anomalous forward-angle scattering factor is given by

$$f'(\omega)=f'_{CL}(\omega)+\delta f' \qquad (3)$$

where $f'_{CL}(\omega)$ is the value predicted by Cromer & Liberman (1970*a*, *b*, 1976, 1981), Cromer (1974, 1983) or Henke *et al.* (1981, 1982), and $\delta f'$ is the Z-dependent energy-independent high-energy-limit correction listed in Table 1. [Note we are taking the energy dependence of $f'(\omega)$ as that given by $f'_{CL}(\omega)$ rather than that from the S-matrix calculations. This is due to the strong energy dependence of scattering near threshold, where $f'_{CL}(\omega)$ have used experimental threshold energies.]

As mentioned earlier, E_{tot}/mc^2 is an approximation to the high-energy limit $f'(\infty)$ shown in Table 1. This approximation is very good for low-Z atoms, but the difference of E_{tot}/mc^2 from $f'(\infty)$ grows with increasing Z, becoming 2% for $Z=20$, 6% for $Z=40$, 9% for $Z=60$, 13% for $Z=80$, and 15% for $Z=100$. Note that the definition of E_{tot} as given, for example, by Cromer & Liberman is not simply the sum of the individual orbital binding energies.

As a concrete example, consider the case of Ag $K\alpha_1$ radiation ($\lambda\simeq 0{\cdot}5593$ Å, $\hbar\omega\simeq 22{\cdot}16$ keV) scattered by ^{14}Si. The value $f'_{CL}=0{\cdot}042$ is given by the *FPRIME* code (Cromer & Liberman, 1970*a*; Cromer, 1983*) and from Table 1 we obtain the value $\delta f'=0{\cdot}011$ for $Z=14$. Thus the corrected relativistic anomalous scattering factor is given by (3) as $f'=0{\cdot}042+0{\cdot}011=0{\cdot}053$. This value can be compared with experimental values of $0{\cdot}0545\pm 0{\cdot}003$ (Deutsch

* The version of the *FPRIME* code described in Cromer (1983) differs from the version described in Cromer & Liberman (1970*a*) by the inclusion of an energy-dependent term due to Jensen (1979), which is identified explicitly in the output produced by the code. Our values listed in Table 1 do not include this 'Jensen term' and users of the 1983 version of *FPRIME* must first remove the contribution from the Jensen term before applying our correction $\delta f'$. Generally, the contribution from this Jensen term should be ignored.

Table 3. *Illustration of the importance of the high-energy correction $\delta f'$ on the differential cross section for 59·54 keV photons scattered by* ^{82}Pb

RFF indicates relativistic form factor only; RFF+CL indicates relativistic form factor plus anomalous-scattering factors of Cromer & Liberman (1970*b*, 1981) ($f'_{CL} = -2{\cdot}201, f''_{CL} = 1{\cdot}304$); RFF+CCL indicates relativistic form factor plus high-energy corrected anomalous-scattering factors ($f'_{CL} + \delta f' = -2{\cdot}201 + 0{\cdot}870 = -1{\cdot}331, f''_{CL} = 1{\cdot}304$); SM indicates *S*-matrix predictions; EXP indicates experiment. The numbers in parentheses indicate the associated power of ten. In both cases the anomalous factors are taken as angle independent. Also, $x = \lambda^{-1} \sin(\Theta/2)$ where the scattering angle $\Theta = 2\theta$; θ is the Bragg angle.

			$d\sigma/d\Omega$ (r_0^2/sr)				
Θ (°)	x (Å^{-1})	$f(q)$	RFF	RFF+CL	RFF+CCL	SM	EXP
0	0	82·000	6·72 (3)	6·37 (3)	6·51 (3)	6·49 (3)	
20·6	0·859	34·378	1·11 (3)	9·73 (2)	1·03 (3)	1·02 (3)	1·03 ± 0·10 (3)*
30	1·243	24·457	5·23 (2)	4·35 (2)	4·69 (2)	4·63 (2)	4·52 ± 0·37 (2)*
45	1·838	16·487	2·04 (2)	1·54 (2)	1·74 (2)	1·70 (2)	1·66 ± 0·16 (2)*
60	2·401	13·185	1·09 (2)	7·65 (1)	8·89 (1)	8·63 (1)	8·43 ± 0·88 (1)* 8·80 ± 0·35 (1)†
75	2·923	10·807	6·21 (1)	4·04 (1)	4·88 (1)	4·74 (1)	4·86 ± 0·18 (1)†
90	3·396	8·876	3·94 (1)	2·31 (1)	2·93 (1)	2·86 (1)	2·77 ± 0·25 (1)* 2·98 ± 0·10 (1)†
105	3·810	7·495	3·00 (1)	1·59 (1)	2·12 (1)	2·09 (1)	2·22 ± 0·08 (1)†
107	3·860	7·354	2·93 (1)	1·53 (1)	2·06 (1)	2·03 (1)	2·09 ± 0·21 (1)*
120	4·159	6·601	2·72 (1)	1·32 (1)	1·84 (1)	1·81 (1)	1·89 ± 0·06 (1)†
135	4·437	6·053	2·75 (1)	1·24 (1)	1·80 (1)	1·75 (1)	1·85 ± 0·06 (1)†
150	4·639	5·726	2·87 (1)	1·24 (1)	1·84 (1)	1·76 (1)	1·79 ± 0·08 (1)†
180	4·802	5·502	3·03 (1)	1·26 (1)	1·91 (1)	1·81 (1)	

* Eichler & de Barros (1985).
† Schumacher & Stoffregen (1977).

& Hart, 1988), 0·0537 ± 0·0025 (Deutsch & Hart, 1984), 0·060 ± 0·003 (Creagh, 1984), and 0·0568 ± 0·0026 (Cusatis & Hart, 1975). In this case, experiment clearly distinguishes the corrected value of f' from the uncorrected value computed by *FPRIME*. The importance of this correction has also been illustrated for ^{14}Si and ^{20}Ca, 6–22 keV by Smith (1987), for ^{14}Si, 5–40 keV by Deutsch & Hart (1988), and for ^{9}F, ^{11}Na, ^{14}Si, ^{17}Cl, ^{19}K and ^{20}Ca, 5–22 keV by Wang & Chia (1988*a*). However, Deutsch & Hart (1988) note residual differences between experiment and corrected f' values of the order of 0·01 for ^{14}Si at energies higher than about 25 keV (wavelengths shorter than about 0·5 Å).

While the anomalous-scattering factors are defined at forward angle, it is even more important to correct relativistic form-factor predictions at finite angles. Although the anomalous-scattering factors have angular dependence, it is not that given by the form factors, total atom or subshell, as has sometimes been previously speculated (*e.g.* Templeton, 1962). In comparison with our *S*-matrix predictions in the X-ray regime, we find that for photon energies near and below the *K*-shell photoeffect threshold it is better to assume no angular dependence for f' and f'' than any model we have yet devised based on the form factor. (However, see an alternative model based on angle-independent quantities g', g'' discussed later in a footnote.) For large-angle experiments near the *K*-shell photoeffect thresholds of ^{36}Kr and ^{54}Xe (Smend, Schaupp, Czerwinski, Schumacher, Millhouse & Kissel, 1987), angle-independent anomalous-scattering-factor predictions agreed at the 10% or better level with *S*-matrix predictions and experiment. At the 10% or better level, it is expected that angle-independent anomalous-scattering-factor predictions will generally agree with *S*-matrix predictions near and below the *K*-shell photoeffect threshold. (At energies well above the *K*-shell photoeffect threshold, the angular dependence of the anomalous-scattering factors cannot be ignored since for larger momentum transfers such factors will dominate the form-factor term.) In this angle-independent approximation, the unpolarized elastic-scattering cross section, differential in scattering angle Θ ($\Theta = 2\theta$, where θ is the Bragg angle), may be written as

$$\frac{d\sigma}{d\Omega}(\omega, \Theta) = \frac{r_0^2}{2}(1 + \cos^2\Theta)|f(q) + f'(\omega) + if''(\omega)|^2, \tag{4}$$

where $f(q)$ is the value of the relativistic form factor (*e.g.* Hubbell & Øverbø, 1979) at momentum transfer

$$\hbar q = (2\hbar\omega/c)\sin(\Theta/2). \tag{5}$$

For forward angle, (4) gives the same result as that given by (1). [Typically, form factors are tabulated as a function of the variable $x = \lambda^{-1}\sin(\Theta/2)$; $x \simeq 20{\cdot}61\,q$, when x is in inverse ångströms and q is in mc units. Also, $r_0 = e^2/mc^2 \simeq 2{\cdot}82 \times 10^{-15}$ m; $r_0^2 \simeq 0{\cdot}0794 \times 10^{-28}$ m^2.] In Table 3 we compare finite-angle predictions with experiment for scattering of 59·5 keV photons by Pb. The relative importance of the correction $\delta f'$ generally becomes more important at finite angles because we have taken $\delta f'$ as angle independent and $f(q)$ always decreases relative to $f(0)$ with

increasing q (*i.e.* increasing Θ). In extreme cases, the anomalous-scattering factor f' can be of equal magnitude, but opposite in sign to $f(q)$, resulting in complete cancellation (Kane, Basavaraju, Lad, Varier, Kissel & Pratt, 1987).*

There are also consequences of the correction to f' in the total cross section (integrated over angles), sometimes greater than those for forward angles, as the anomalous terms become more important away from the forward direction. For 59·5 keV photons scattered by Pb, the total cross section is 2150 r_0^2 (RFF - relativistic form factor only), 1740 r_0^2 (RFF+CL - relativistic form factor with Cromer & Liberman anomalous-scattering factors), and 1900 r_0^2 (RFF+CCL - relativistic form factor with high-energy-corrected Cromer & Liberman anomalous-scattering factors). The RFF+CCL result is in good agreement with the S-matrix result of 1870 r_0^2.

Other corrections

We note that other corrections to the Cromer-Liberman tables may be needed in some circumstances. For example, as discussed by Wang & Pratt (1983), ignoring the contribution of bound-bound transitions can cause errors for carbon and other light elements. This problem becomes more serious for ions, where more bound-bound transitions are allowed. On the other hand, the Cromer-Liberman tabulation imposes experimental threshold positions and is consequently more accurate near threshold than S-matrix calculations in potential models which do not well reproduce threshold positions, since f' is generally rapidly varying near threshold. In some cases, solid-state effects will be important (Wang & Chia, 1988*b*). In other cases, details in the choice of the atomic model should be observable (Kissel & Pratt, 1987; Wang & Chia, 1988*c*). Finally, strong anisotropy has been observed in anomalous scattering near atomic thresholds due to orientation of an atom in a molecule (*e.g.* Templeton & Templeton, 1988). In their analysis, Templeton & Templeton found it necessary to generalize the anomalous-scattering factors f' and f'' from scalars to tensors.

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* Similar to the $\delta f'$ that we defined for use with the relativistic form factor $f(q)$, we can also define a correction factor $\delta g'$ for use with the modified relativistic form factor $g(q)$ (*e.g.* Schaupp *et al.*, 1983). Instead of the quantity $f(q)+f'(\omega)+if''(\omega)$ in (4), we can substitute the quantity $g(q)+g'(\omega)+ig''(\omega)$, where $g'(\omega)=f'_{CL}(\omega)+\delta g'$, and $g''(\omega)=f''_{CL}(\omega)$. To the extent that $g(0)$ does in fact have the correct high-energy limit, then $\delta g'=-f'_{CL}(\infty)$ (*e.g.* Smend *et al.*, 1987). For forward scattering the two formalisms are identical. At finite angle it may be somewhat better to assume that g', g'' are angle independent rather than f', f'', though the numerical data do not fully support either assumption.

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Small-Angle Techniques for the Asymptotic Analysis of X-ray Diffraction Peaks

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Abstract

Any wide-angle X-ray scattering (WAXS) peak, relevant to a powder sample of crystallites with negligible internal disorder, is the Fourier transform of the so-called oriented stick probability function (oSPF) of the filled part of the sample, with the stick orientated along the reflexion direction. From this observation the following consequences are obtained: the correlation function used in small-angle X-ray scattering (SAXS) is the average of the former oSPF's over all possible stick orientations; any peak profile asymptotically vanishes as $S_r h^{-2}$, where S_r is the (specific) area of the interphase surface presented by the sample along the reflexion direction; oscillatory deviations, behaving as $S_{r,\|} \cos(hL) h^{-2}$, are present only when a subset (having area $S_{r,\|}$) of the interface, after having been translated by L along the reflexion direction, superposes on itself; the angularity of the interphase surface can be measured by a natural modification of the Porod integral relation. For samples really isotropic, the above quantities should not depend on the reflexion direction and thus they should be equal to those measured by SAXS experiments. These results are applied to three ideal isotropic powder samples made up, respectively, of monodisperse spherical, cubic and cylindrical crystallites as well as to the analysis of two WAXS peaks diffracted by two real samples of zirconia powders.

I. Introduction

The aim of this paper is to point out that many of the ideas used for analysing the asymptotic behaviour of small-angle X-ray scattered intensities (SAXS) can be usefully applied, *mutatis mutandis*, in the realm of wide-angle scattering (WAXS) in order to assess the behaviour of the peak intensities in the tail regions. Although the practical application of this method suffers two serious limitations, *i.e.* the powder samples must be made up of crystallites with negligible internal disorder and the measured WAXS peaks must not fall so close to each other as to make the observation of an asymptotic tail region impossible, the results of our analysis are interesting for two reasons: they allow one to appreciate the geometrical implications hidden in the functional forms usually assumed in best-fitting observed peaks and to unify the procedures used in interpreting small- and wide-angle experimental results.

The plan of the paper is the following. In the next section (§ II), the general theoretical expressions on which our analysis is based as well as the conditions for the samples we shall deal with will be written down. In § III, we shall discuss in detail the relationship between the WAXS peak profiles and the so-called oriented stick probability functions (oSPF). We also show how to obtain along the way the SAXS idealization of a sample. It turns out that the SAXS intensity is *essentially* the 000 WAXS reflexion and that the corresponding correlation function is the angular average of the aforesaid oSPF's. In this way it becomes clear that many of the techniques used for analysing SAXS intensities can be applied also to WAXS profiles. In § IV, some recent theoretical results relating the continuity properties of the derivatives of the oSPF's to some geometrical features of the crystallite boundaries will be recalled, while in § V we show how these continuity properties determine the asymptotic behaviour of WAXS profiles.

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