Small-Angle X-ray Scattering Size Parameters and Higher Moments of the Particle-Size Distribution Function in the Asymptotic Stage of Ostwald Ripening

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Abstract

Small-angle X-ray scattering (SAXS) is a powerful tool to study the kinetics of phase separation in materials. A simple procedure is presented that allows one to prove if the particle-size distribution established in a system in the late stages of phase separation corresponds to the predictions of the classical Lifshitz–Slyozov–Wagner (LSW) theory for the asymptotic stage of Ostwald ripening. The method is based on the correlations between certain SAXS size parameters and the higher moments of the LSW size distribution functions for diffusion-limited or reaction-limited ripening. It is suggested that the use of these size parameters, which can be obtained with high accuracy from the scattering curve, is frequently more advantageous than a direct comparison of the experimentally obtained size distributions with the asymptotic size-distribution functions predicted by the LSW theory. The method is applicable if the suppositions made in the LSW theory that the precipitated particles should be homogeneous spheres with volume fraction tending to zero are fulfilled. The method is applied to a photochromic glass; although the silver-halide precipitates contained in the glass develop according to the power law of diffusion-limited Ostwald ripening, their size distribution is shown not to correspond to the features of the LSW size distribution. Consequently, in this case the LSW theory cannot describe quantitatively the kinetics of ripening.

1. Introduction

Phase-separation phenomena in supersaturated solid solutions (alloys or glasses) are of great practical interest and have been studied in many systems using different experimental techniques. Small-angle X-ray scattering (SAXS) (Guinier & Fournet, 1955; Glatter & Kratky, 1982) has proved to be very useful in this field (e.g. James, 1975; Gerold & Kostorz, 1978; Walter, Kranold & Lembke, 1988). Several processes can be distinguished in phase separation: nucleation and growth, spinodal decomposition and coarsening (Ostwald ripening). By means of SAXS experiments, structural parameters, including the dimensions of second-phase particles, the mean-squared electron density fluctuations, the volume fraction or number density of the particles and the interfacial area per unit volume can be determined. From these parameters, the different processes mentioned can be qualitatively distinguished by a study of the development of the phase-separation process as a function of time (Walter, Kranold & Lembke, 1988). However, a quantitative comparison of experimental results with the predictions of phase-separation theories is frequently impossible, owing to a lack of information regarding exact miscibility-gap data or other system parameters such as the effective diffusion coefficient $D$ or the interfacial energy $\sigma$.

The classical theories of nucleation and growth (Zener, 1949; Ham, 1958) and Ostwald ripening (Lifshitz & Slyozov, 1958, 1961; Wagner, 1961) predict different power laws for the evolution of the mean particle radius $\langle R \rangle$ (or the critical radius $R_c$) as a function of time, depending on whether the particle growth is controlled by long-range diffusion or by surface reactions. SAXS results can be used to distinguish between the two growth mechanisms (James, 1975; Walter, Kranold & Lembke, 1988). Moreover, in principle, it is possible to determine $D$ or $\sigma$ from the prefactors of the temporal power laws provided that one of these parameters is already known from other experiments (Zarzycki & Naudin, 1967; Lembke & Göcke, 1990). There are, however, several problems that (in investigations using this approach) may have led to incorrect results. The major problem has been that often the classical theories are unable to describe adequately the phase-separation process going on in the system under investigation. Another, more methodological, problem lies in the correct determination of the mean particle radius $\langle R \rangle$, where $\langle R \rangle$ is the first moment of the particle-size distribution function $N(R)$ of the ensemble of particles evolving in the course of the phase-separation process. Several techniques can be employed to calculate $N(R)$ from SAXS data (Walter, Kranold, Gerber, Baldrian & Steinhart, 1985). However, the accuracy obtained is frequently very limited, depending mainly on the type of scattering curve. On the other hand, various size parameters exist (Damaschun, Müller, Püschel & Sommer, 1969) that are closely connected with higher moments of $N(R)$. These parameters, which are defined in §2, can be determined from SAXS experiments more
SAXS SIZE PARAMETERS AND PARTICLE-SIZE DISTRIBUTION FUNCTION

easily and with better accuracy than \( \langle R \rangle \) from the size distribution function. Therefore, the use of these alternative size parameters promises a simpler method of testing different growth theories.

In general, in the course of a phase-separation process, the particle-size distribution function \( N(R, t) \) depends explicitly on time and is influenced, moreover, by the initial size distribution established as the result of the nucleation process. In the late stages of phase separation, i.e. in the asymptotic stage of Ostwald ripening, however, this dependence on the initial state is lost and a universal size distribution is established depending only on the mechanism of growth (Lifshitz & Slyozov, 1958, 1961; Wagner, 1961).

The universal character of this size distribution makes it possible to calculate its higher moments and thus the SAXS size parameters mentioned above, independent of any peculiarities that may influence the initial particle-size distribution for any particular experiment. In the present contribution, these calculations are performed for both diffusion-limited and reaction-limited particle growth. Using the results obtained, a very simple method is proposed to prove whether the phase-separation process in the system under investigation is properly described by the classical LSW theory of Ostwald ripening (Lifshitz & Slyozov, 1958, 1961; Wagner, 1961) or not. It should be noted that in the given approach the SAXS size parameters are interpreted for exactly the same conditions (homogeneous spherical particles with a volume fraction tending to zero) that have to be assumed for the validity of the classical LSW theory.

2. Small-angle X-ray scattering size parameters

The normalized scattered intensity \( I(s) \) obtained from a SAXS experiment, using pinhole collimation, is given by (Guinier & Fournet, 1955)

\[
I(s) = 4\pi r^2 C(r) \sin sr/(sr) \, dr, \quad (2.1)
\]

where \( C(r) \) is the autocorrelation function of the excess electron density, \( s \) stands for the magnitude of the scattering vector, given by \( s = (4\pi/\lambda) \sin (\theta/2) \), \( \lambda \) is the X-ray wavelength and \( \theta \) is the scattering angle. In the frequently used case of infinitely long slit collimation, the slit-smeared scattering curve

\[
\tilde{I}(s) = 2 \int_0^\infty I(s^2 + t^2)^{1/2} \, dt \quad (2.2)
\]

is obtained (Guinier & Fournet, 1955).

\( C(r) \) can be calculated from \( I(s) \) or \( \tilde{I}(s) \) (Walter et al., 1985). Since the function \( C(r) \) at large \( r \) values depends very sensitively on the packing density of the particles,

the validity of one of the basic assumptions of the classical LSW theory, that the volume fraction of the particle phase must tend to zero, can easily be checked. The \( r \) value \( L \) at which \( C(r) \) drops to zero represents an important structural parameter. For a ‘diluted’ system of homogeneous spherical particles, the SAXS of which shows no interparticle interference effects, \( L \) is the greatest diameter of the particles in the sample (Damaschun et al., 1969). It has been shown elsewhere (Walter et al., 1985) that under the above-mentioned assumptions the particle-size distribution function defined as

\[
N(R) = -d[C''(r)/r]_{r=2R}/dr
\]

can be determined directly from \( I(s) \) or \( \tilde{I}(s) \). Because \( N(R) \) represents the third derivative of the Fourier transform of the scattering curve, it is evident that the errors of the experimental SAXS data have a much stronger influence on the calculation of \( N(R) \) than on the computation of \( C(r) \). That is why an extraordinarily high accuracy of experimental SAXS data is required in order to compare directly the experimentally determined size distribution \( N(R) \) with the asymptotic distributions predicted by the classical LSW theory. Frequently, an accuracy of the SAXS data sufficient for this procedure cannot be obtained in investigations of solid solutions, where the particle scattering is superimposed on the scattering of the matrix phase.

A set of valuable size parameters that can be calculated directly from the scattering curves \( I(s) \) or \( \tilde{I}(s) \) consists of (Damaschun et al., 1969):

(i) the average intersection length

\[
(d) = (4/\pi) \int_0^\infty s^2 I(s) \, ds \left/ \lim_{s \to \infty} s^4 I(s) \right. \]

\[
= \int_0^\infty \tilde{s} I(s) \, ds \left/ \lim_{s \to \infty} s^3 \tilde{I}(s) \right. \quad (2.3)
\]

(ii) the correlation length

\[
(l) = \pi \int_0^\infty \tilde{s} I(s) \, ds \left/ \int_0^\infty s^2 \tilde{I}(s) \, ds \right. \]

\[
= 2 \int_0^\infty \tilde{s} I(s) \, ds \left/ \int_0^\infty s \tilde{I}(s) \, ds \right. \quad (2.4)
\]

(iii) the correlation surface

\[
(f) = 2\pi \int_0^\infty I(s) \, ds \left/ \int_0^\infty s^2 \tilde{I}(s) \, ds \right. \]

\[
= 2\pi \tilde{l}(0) \left/ \int_0^\infty \tilde{s} I(s) \, ds \right. \quad (2.5)
\]

(iv) the correlation volume

\[
(v) = 2\pi^2 I(0) \left/ \int_0^\infty s^2 \tilde{I}(s) \, ds \right. \quad (2.6)
\]
(v) the mean electron distance

\[ \langle a \rangle = \frac{(8/\pi)}{5} \left[ \int_0^\infty I(s) \, ds / I(0) \right] \left( -\lim_{s \to 0} [d[\ln I(s)] / d(s^2)] \right) \]

(2.7)

(vi) the electronic radius of gyration

\[ \langle R_g \rangle = 3^{1/2} \left( -\lim_{s \to 0} [d[\ln I(s)] / d(s^2)] \right)^{1/2} \]

(2.8)

For a diluted particle system of homogeneous spheres with the size distribution \( N(R) \), from each of the structural parameters (2.3)–(2.8) extracted from the experimental data an average radius \( R_i \) of the spheres can be obtained. It has been shown (Walter et al., 1985; Damaschun et al., 1969; Sjöberg, 1974) that these characteristic radii \( R_i \) are associated with certain ratios of various moments of the size distribution function \( N(R) \):

\[ R_d = \frac{3}{4} \langle d \rangle = \langle R^3 \rangle / \langle R^2 \rangle \]  
\[ R_l = \frac{2}{3} \langle l \rangle = \langle R^3 \rangle / \langle R^2 \rangle \]  
\[ R_s^3 = \frac{5}{4 \pi} \langle f \rangle = \langle R^3 \rangle / \langle R^2 \rangle \]  
\[ R_s^4 = \frac{3}{4 \pi} \langle v \rangle = \langle R^4 \rangle / \langle R^2 \rangle \]  
\[ R_c = \frac{35}{36} \langle a \rangle = \langle R^5 \rangle / \langle R^2 \rangle \]  
\[ R_t = \frac{1}{2L} \lim_{n \to \infty} \left[ \langle R^n \rangle \right]^{1/n} \]  

(2.9)–(2.15)

Here, the \( m \)th moment of \( N(R) \), \( \langle R^m \rangle \), is given by

\[ \langle R^m \rangle = \int_0^\infty R^m N(R) \, dR \int_0^\infty N(R) \, dR. \]

(2.17)

It should be noted that for validity of (2.9)–(2.16) the form of \( N(R) \) need not be specified.

### 3. The Lifshitz–Slyozov–Wagner theory: basic assumptions and results

In the calculation of the higher moments of the size distribution function in the asymptotic stage of Ostwald ripening, we follow here the classical Lifshitz–Slyozov–Wagner (LSW) theory (Lifshitz & Slyozov, 1958, 1961; Wagner, 1961; Slyozov & Sagalovich, 1987). Despite the fact that a number of modifications and extensions have been proposed, in particular in the last decade (Toku-yama, Kawasaki & Enomoto, 1986; Marder, 1987; Ulbricht, Schmelzer, Mahnke & Schweitzer, 1988; Grätz & Simmich, 1988; Jayanth & Nash, 1989), the main conclusions derived by Lifshitz & Slyozov and Wagner remain valid. Modifications have resulted in changes of the prefactors in the asymptotic power laws and in the form of the distribution function.

The LSW theory is based primarily on the following set of three equations (Lifshitz & Slyozov, 1958, 1961):

\[ \frac{dR}{dt} = 2\sigma D c' / (c_s^2 k T) (1/R) \left[ (1/R_c) - (1/R) \right] \]  
\[ (\partial N / \partial t) + \partial [N R] / \partial R = 0; \]

(3.1)

\[ (c_0 - c') / c' = [(c - c') / c'] \]

(3.2)

\[ + (c_s / c')(4 \pi / 3) \int_0^\infty R^3 N(R, t) \, dR. \]

(3.3)

Equation (3.1) describes the diffusion-limited growth of a particle with radius \( R \); \( \sigma \) is the interfacial energy, \( D \) the effective diffusion coefficient, \( c' \) the equilibrium concentration of the segregating component at temperature \( T \), \( c_0 \) the initial concentration and \( k \) the Boltzmann constant.

The critical radius \( R_c \) is determined by the classical Gibbs–Thomson relation,

\[ R_c = 2\sigma / [c_s k T \ln (c / c')] \]

(3.4)

where \( c \) is the actual concentration of the segregating component at a sufficient distance from the particle, and \( c_s \) is the volume concentration of the segregating component in the newly evolving phase.

Equation (3.2) represents the continuity equation for the distribution function \( N(R, t) \) with respect to particle sizes. By definition, \( N(R, t) \) is normalized to yield

\[ \int_0^\infty N(R, t) \, dR = N_v(t), \]

(3.5)

where \( N_v(t) \) is the number of particles of the new phase per unit volume.

Equation (3.3) is a consequence of the conservation of matter, where \( c_0 \) is the concentration of segregating monomers in the homogeneous initial state, corresponding to a critical particle radius \( R_{c0} \).

Introducing the new quantities

\[ x = R_c / R_{c0}, \quad u = R / R_c, \quad \tau = 3 \ln x, \]

(3.6)

and replacing \( N(R, t) \) by \( \phi(u, \tau) \) via

\[ N(R, t) \, dR = \phi(u, \tau) \, du, \quad \phi = R_c N(R, t). \]

(3.7)

we can obtain the following results for the evolution of an ensemble of particles at sufficiently large times for diffusion-limited growth:

\[ R_c^3 = \frac{2}{3} \left[ \sigma D c' / (c_s^2 k T) \right] t, \]

(3.8)

where

\[ N_v(t) = 0.24 [(c_0 - c') / c'] c_s k T / (\sigma D) (1/t), \]

\[ \phi_D(u, \tau) = (0.9 / \kappa) \exp (-\tau) P_D(u), \]

\[ \kappa = [c_s / (c_0 - c')] (4 \pi / 3) R_{c0}^2, \]

(3.9)
The size distribution for asymptotic diffusion-limited ripening is shown in Fig. 1. The region of applicability of the asymptotic solutions is given by

$$t \gg \frac{9}{8} R_c^3 \sigma c^2 kT/(\sigma Dc').$$

It follows immediately from (3.7)-(3.10) that the mean particle radius \( \langle R \rangle \) is equal to the actual value of the critical radius

$$\langle R \rangle = R_c(t).$$

Consequently, one may also write

$$\langle R \rangle ^3 = \frac{9}{8} [\sigma Dc'/(c^2 kT)] t.$$ (3.13)

If, instead of diffusion-limited growth resulting in (3.1), other growth mechanisms determine the temporal evolution of the individual particles and thus of the ensemble of particles, the outlined results are modified (Wagner, 1961; Slyozov & Sagalovich, 1987; Grätz & Simmich, 1988) to some extent. The method of derivation of the corresponding equations remains the same.

For reaction-limited growth, one has to start instead of (3.1) with

$$\frac{dR}{dt} = \frac{2D \sigma c'/(c^2 kT)(1/\ell_0)(1/R_c) - (1/R)}{},$$ (3.14)

where \( \ell_0 \) is a length of molecular dimensions. In this case, one obtains in the same way

$$R_c^2 = [\sigma Dc'/(c^2 kT\ell_0)] t,$$ (3.15)

and the asymptotic size distribution for reaction-limited growth is

$$\varphi_R(u, \tau) = A \exp (-\tau) P_R(u)$$

$$P_R(u) = \begin{cases} \frac{24u}{(2-u)^3} \exp \left[-\frac{3u}{2(2-u)}\right] & u < 2 \\ 0 & u \geq 2 \end{cases}.$$ (3.16)

The constant \( A \) can be determined from the condition of conservation of matter. This yields

$$A = \frac{3\kappa}{1} \left[u^4/(u-2)^2\right] \exp \left[g(u)\right] du,$$ (3.17)

with

$$g(u) = -3 \ln [(2-u)/2] - [3u/(2-u)],$$ (3.18)

which results in \( A = 1.045/\kappa \).

In Fig. 1, the asymptotic size distribution for reaction-limited ripening is compared with the size distribution for the asymptotic stage of diffusion-limited ripening. Both distribution functions are strictly valid only for a very low volume fraction of the particle phase.

4. Comparison of higher moments of different size distribution functions with SAXS data

To calculate higher moments of a size distribution function \( N(R, t) \), we start with

$$\langle R^m \rangle = \int_0^\infty R^m N(R, t) dR / \int_0^\infty N(R, t) dR,$$ (4.1)

which with (3.7) can be written

$$\langle R^m \rangle = R_c^m \int_0^\infty u^m \varphi(u, \tau) du / \int_0^\infty \varphi(u, \tau) du.$$ (4.2)

For diffusion-limited growth, \( R_c \) and \( \varphi(u, \tau) \) are given by (3.8) and (3.9), and in the case of reaction-limited growth, \( R_c \) and \( \varphi(u, \tau) \) are defined according to (3.15) and (3.16).

Now, the average radii \( R_i \) defined by (2.9)-(2.16) can be calculated. According to (3.12) and (4.2), this yields

$$R_i = K_i R_c = K_i \langle R \rangle,$$ (4.3)

with the parameters \( K_i \) given in Table 1 for diffusion-limited growth and reaction-limited growth.

Taking into account diffusive interactions between growing or dissolving particles and the resulting correlations (Tokuyama, Kawasaki & Enomoto, 1986; Marder, 1987; Jayanth & Nash, 1989) or deviations of the growth rate due to the nonstationary character of the concentration profile (Grätz & Simmich, 1988), in agreement with experimental observations one would obtain more symmetric and broader distributions than the
Table 1. Parameters $K_i$ for the asymptotic size distributions of diffusion-limited ripening and reaction-limited ripening according to the LSW theory

<table>
<thead>
<tr>
<th>$K_i$</th>
<th>Diffusion-limited growth</th>
<th>Reaction-limited growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_d$</td>
<td>1.080</td>
<td>1.076</td>
</tr>
<tr>
<td>$K_l$</td>
<td>1.106</td>
<td>1.134</td>
</tr>
<tr>
<td>$K_f$</td>
<td>1.116</td>
<td>1.156</td>
</tr>
<tr>
<td>$K_v$</td>
<td>1.125</td>
<td>1.176</td>
</tr>
<tr>
<td>$K_p$</td>
<td>1.151</td>
<td>1.233</td>
</tr>
<tr>
<td>$K_a$</td>
<td>1.159</td>
<td>1.249</td>
</tr>
<tr>
<td>$K_g$</td>
<td>1.165</td>
<td>1.263</td>
</tr>
<tr>
<td>$K_t$</td>
<td>1.5</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 2. Parameters $K_i$ of the Gaussian size distribution (4.4) calculated according to (4.6)-(4.14) for different ratios $R/(R)

<table>
<thead>
<tr>
<th>$K_i$</th>
<th>$R/(R)=0.185$</th>
<th>$R/(R)=0.5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_d$</td>
<td>1.066</td>
<td>1.400</td>
</tr>
<tr>
<td>$K_l$</td>
<td>1.097</td>
<td>1.536</td>
</tr>
<tr>
<td>$K_f$</td>
<td>1.111</td>
<td>1.592</td>
</tr>
<tr>
<td>$K_v$</td>
<td>1.125</td>
<td>1.645</td>
</tr>
<tr>
<td>$K_p$</td>
<td>1.166</td>
<td>1.804</td>
</tr>
<tr>
<td>$K_a$</td>
<td>1.179</td>
<td>1.853</td>
</tr>
<tr>
<td>$K_g$</td>
<td>1.191</td>
<td>1.920</td>
</tr>
<tr>
<td>$K_t$</td>
<td>$\infty$</td>
<td>$\infty$</td>
</tr>
</tbody>
</table>

The values of $K_i$ calculated for $R/(R)$ equal to 0.185 and 0.5 are given in Table 2.

In order to distinguish between the different types of size distributions in Fig. 2, the normalized parameters $K_i = R_i/R_t$ are drawn versus the values of $K_i$ for the size distribution in the case of asymptotic reaction-limited ripening. For both asymptotic LSW size distributions, linear plots are obtained. However, for a Gaussian type of size distribution, the parameters $R_i/R_t$ that can be obtained using the values of $R_i$ detected experimentally by SAXS always exhibit a nonlinear course in such a plot. The slope of the curved lines for Gaussian distributions increases with increasing standard deviation of the distribution.

It has to be mentioned, however, that the analytical results (4.6)-(4.13) correctly describe the parameter $K_i$ of the Gaussian distribution only for small standard deviations $R/(R) \leq 0.5$. The reason for this is that for large values of $R/(R)$ the size distributions of real particle systems become asymmetric in consequence of the condition that $N(R)=0$ for $R<0$. This condition can be considered for computing the exact solutions, which are much more complicated than (4.7)-(4.13). That is why it is intended to discuss these exact solutions graphically only, by means of Fig. 3. As can be deduced from the curves $R_i=f(R/(R))$ shown in Fig. 3 also in the case of large ratios $R/(R)$ a plot according to Fig. 2 should exhibit a significant curvature. In principle, this behaviour even intensifies with rising standard deviation $\beta$ of the Gaussian distribution. However, beyond $R/(R)=3$, the asymmetric Gaussian distribution is no longer an appropriate model for real particle-size distributions.
In Fig. 2, the curves predicted for different types of theoretical size distributions are also compared with the normalized parameters $R_i/R_t$ determined from a phase-separated photochromic glass sample (PC glass). The $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ base glass was melted with a small amount of AgBr and CuO in the batch. Initially, the undercooled melt is homogeneous but supersaturated with silver halide. The glass becomes photochromic after a heat treatment at intermediate temperatures owing to silver-halide droplets being precipitated. In the specimen investigated, this phase separation was obtained after treating the PC glass isothermally at 883 K for 8 h. The SAXS curve $I(s)$ was recorded by a Kratky camera using the conditions of infinitely long slit collimation (Glatter & Kratky, 1982). From the SAXS data, a volume fraction of 0.0056 has been extracted, representing the saturation value of the precipitated silver-halide phase. This maximum phase volume was already reached after 2 h at 883 K. That means that the system of precipitated particles in the sample investigated is already in the stage of Ostwald ripening. Additional evidence for this behaviour is given in Fig. 4, which illustrates a dependence of $R_i \propto t^{1/3}$. The procedure of data evaluation and further information about the growth kinetics are described elsewhere (Lembke & Göcke, 1990).

Considering the very low volume fraction of the dispersed particle phase, we see that the PC-glass sample fulfils the condition of a diluted system and interparticle interferences can be neglected. As is typical for a standard SAXS measurement, only the size parameters are considered in Fig. 2, which can be determined directly from the slit-smeared scattering curve $I(s)$, i.e. no desmearing procedure has been applied to the measured scattering curve. The error bars in curve (e) of Fig. 2
indicate the uncertainties of the ratios $R_i/R_t$ with the assumption of noise of 3% superimposed on the scattering curve $I(s)$. This corresponds to $10^3$ counts per measuring point and should be the limit of uncertainty for every serious SAXS experiment. As has been shown by model computations (Walter et al., 1985), in this case the size parameters can deviate as follows: $\delta R_d/R_d = 4\%$, $\delta R_f/R_f = 1\%$, $\delta R_G/R_G = 3\%$, $\delta R_c/R_c = 2\%$.

Curve (e) in Fig. 2 indicates a course that is significantly different from that expected from the LSW theory for diffusion-limited Ostwald ripening. This can be clearly realized even in the case in which the maximum deviations of the size parameters $R_i$ are taken into account.

5. Discussion

Relation (4.3) shows that for the asymptotic particle-size distributions (3.10) and (3.16) predicted by the LSW theory for the late stage of Ostwald ripening, each of the characteristic SAXS size parameters (2.9)--(2.16) is connected with the critical radius $R_c$ only by a numerical factor. Consequently, each of them measured as a function of time can be used directly for an experimental testing of the theoretically predicted temporal power laws (3.8) and (3.15). This result has already been applied by Zarzycki & Naudin (1967) using only $R_r$ and $R_G$. It is worth mentioning that frequently, through the possibility of using various SAXS parameters $R_i$ for the calculation of the critical radius $R_c$, the time interval in which the development of $R_c$ can be observed will be increased.

A quantitative comparison of experimental results with the predictions of the LSW theory or a determination of the diffusion coefficient $D$ from the prefactors in the temporal power laws (3.8) and (3.15) using experimentally obtained values for the interfacial energy $\sigma$ (see Zarzycki & Naudin, 1967; Lembke & Göcke, 1990) requires that the asymptotic stage of ripening is reached. In order to prove the applicability of the classical LSW theory to real systems, a very simple method is proposed using a plot as illustrated in Fig. 2. In practice, the experimentally determined $R_i$ should be normalized to $R_{i0}$, which has the highest accuracy, and the $R_i/R_t$ values obtained have to be drawn versus the $K_i$ values given in Table 1 for reaction-limited ripening. If one of the asymptotic size distributions (3.10) or (3.16) predicted by the LSW theory has been established in the sample investigated, the plot of $R_i/R_t$ versus $K_i$ should result in a straight line with a slope like curve (a) or (b) in Fig. 2. Since the experimental SAXS parameters $R_i$ given by (2.9)--(2.16) and, consequently, the $R_i$ values calculated from $R_{i0}$ by means of (4.3) using the $K_i$ values in Table 1 will be obtained with different accuracy (see Walter et al., 1985), a weighted-average value should be determined as an optimum value of $R_c$. This optimum value of $R_c$ should be used for an intended computation of $D$ or $\sigma$ from the power laws.

Furthermore, in the case where the SAXS data are not in correspondence with the LSW theory, it can be decided from the plot of $R_i/R_t$ versus $K_i$ whether a Gaussian distribution of the particle size can be assumed. Obviously, small size distributions of Gaussian-like type (curve c in Fig. 2) are not easily distinguishable from the LSW distributions for the asymptotic ripening stage. In this case, the deviations of the experimental ripening kinetics from the LSW theory are small and a quantitative evaluation of the ripening velocity corresponding to (3.13) or (3.15), guided by the time evolution of a measured size parameter $R_i = K_i(R)$ according to (4.3), should yield reliable results.

In the case of broad size distributions and a shape far from that of the LSW distributions, a plot of $R_i/R_t$ in accordance with Fig. 2 leads to a significant curvature and a steeper slope with regard to the LSW graphs (see curve d). Curve (e) represents an experimental example for such findings. Even though the volume fraction of the silver halide phase is very small and has reached its maximum value already after 2 h and although, obviously, $R_i(t)$ obeys the power law of diffusion-limited ripening (Fig. 4), the result of the plot in Fig. 2 strictly forbids quantitative use of (3.8). The existence of a Gaussian-like size distribution in the present sample can be interpreted in terms of a transient stage between independent particle growth and asymptotic ripening.

This behaviour of the size distribution is well known from experimental investigations in phase-separating glasses (Zarzycki & Naudin, 1967) and has been studied by model computations (Bartels, Lembke, Pascova, Schmelzer & Gutzow, 1991). The transient stage is characterized by a rearrangement of the size distribution and it is frequently observed in systems with high viscosity.

The applicability of the procedure presented is limited to very small volume fractions of the particle phase (up to
about 1–2%). Increasing phase volume leads to modified asymptotic size distributions, whereas the critical radius is relatively insensitive to the volume fraction (Yao, Elder, Guo & Grant, 1993). Additionally, the SAXS data are affected by a higher concentration of the particle phase in such a way that interparticular interference effects disturb the correlations between the measured size parameters and the higher moments of the size distribution described in (2.9)–(2.16).

6. Concluding remarks

The procedure presented provides a simple means to prove if the particle-size distribution established in a phase-separated system corresponds to the predictions of the classical LSW theory for the asymptotic stage of Ostwald ripening. The method is based on the correlations between certain SAXS size parameters and the higher moments of the LSW size distribution functions for diffusion-limited or reaction-limited ripening. Normally, most of these size parameters can be calculated from the measured SAXS data more easily and with better accuracy than the size distribution itself. The applicability of the method is restricted to particle systems that satisfy the same suppositions that must be fulfilled for the validity of the LSW theory: homogeneous spherical precipitates with volume fraction tending to zero.

The method has been applied to a sample of a photochromic glass containing a system of silver-halide particles in the stage of Ostwald ripening. It has been shown that after considerable treatment times from the beginning of ripening the asymptotic size distribution predicted by the LSW theory is not yet established. Therefore, the experimental example demonstrates the case in which one cannot make use of the relations between the growth rate in the ripening stage and the thermodynamic parameters of the material given by the classical LSW theory.

References


