Volume-Fraction Dependence of the Scaling Function for Phase-Seperating Systems

BY PETER FRATZL
Institut für Festkörperphysik der Universität Wien, Strudlhofgasse 4, A-1090 Wien, Austria

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Abstract
In the last decades, the kinetics of phase separation following a quench into the miscibility gap have been studied in a variety of systems by small-angle scattering techniques. A scaling behavior in the late stages of coarsening, first observed in computer simulations, was found to be a 'universal' feature of the small-angle scattering intensity \( S(k,t) \) with \( S(k,t) \approx S(k_m(t),t)F(k/k_m(t)) \), where \( k_m(t) \) is the value of the modulus \( k \) of the scattering vector at which \( S(k,t) \) has its maximum. Furthermore, it was observed recently that, for many systems ranging from liquid and polymer mixtures to solid alloys and computer simulation models, the scaling function \( F(x) \) does not change appreciably from one system to another when the volume fraction is kept constant. This paper first reviews work carried out jointly with J. L. Lebowitz and O. Penrose, discussing various features of the scaling function leading to a simple analytical expression suitable to fit experimental data. New small-angle X-ray scattering results on the shape of the scaling function for dilute Al-Ag and Cu-Fe systems are then presented and compared with the predictions of the model.

1. Introduction
The separation process of a uniform mixture into two phases after a quench into the miscibility gap is a problem of theoretical and enormous practical interest (Gunton, San Miguel & Sahni, 1983; Furukawa, 1985; Komura & Furukawa, 1988; Binder, 1990), precipitation hardening being one of the essential tools for materials design. Besides electron microscopy, small-angle scattering (SAS) of X-rays, neutrons or light is the most frequently used method to investigate the microstructure of liquids or solids undergoing phase separation (see Komura & Furukawa, 1988). SAS allows the time-dependent structure function \( F \) leading to a simple analytical expression suitable to fit experimental data. New small-angle X-ray scattering results on the shape of the scaling function for dilute Al-Ag and Cu-Fe systems are then presented and compared with the predictions of the model.

2. Model for the scaling function
In the time-scaling regime of the decomposition process, all relevant length scales (e.g. size or distance distributions of the monophase domains) grow proportionally to a single length scale which could be (for example in a dilute system) the average droplet size \( \bar{R} \).

For very dilute systems (almost infinite distance between droplets), a scaling of the droplet size distribution has already been proposed in the theory of Ostwald ripening (Lifshitz & Slyozov, 1961; Wagner 1961). In most realistic systems, however, droplets have a finite distance and, for large volume fractions \( \varphi \) of minority phase, they even touch each other.
forming complicated interconnected patterns. Despite this large variety in possible microstructures, time scaling of the structure function is observed for dilute as well as concentrated systems and the scaling function \( F(x) \) looks quite similar in all cases: it typically decreases to 0 when \( x \to 0 \), exhibits a single maximum and then decreases as \( x^{-4} \) at large \( x \). The latter is known as Porod's law (see for example Porod, 1983) and expresses the fact that there are sharp interfaces between the monophase regions. The existence of a maximum indicates a certain periodicity or typical distance in the arrangement of the monophase domains. The fact that \( F(x) \to 0 \) when \( x \to 0 \) means that there are no correlations extending over distances larger than several times the typical distance between monophase domains (Fratzl, Lebowitz, Penrose & Amar, 1991). This last property might be connected to the fact that, owing to diffusion limitations, individual atoms will not be able to travel distances larger than some value \( D(t) \) during the time \( t \); in a system evolving from an initially homogeneous mixture one does not expect, therefore, correlations over distances larger than several times \( D(t) \). In fact, an analysis of the nonlinear diffusion equation for spinodal decomposition due to Cahn & Hilliard (Cahn, 1961) yields an \( x^{-4} \) dependence at small \( x \) (Yeung, 1988; Furukawa, 1989).

Following the procedure given by Fratzl & Lebowitz (1989), one can use this property together with Porod's law to construct, in a heuristical way, an analytical expression for the structure function \( F(x) \). Debye, Anderson & Brumberger (1957) have derived an exponential expression for the correlation function \( g \) of a two-phase system containing randomly distributed interfaces. If the periodicity induced by the conservation of material within regions of size \( D(t) \) is further taken into account by a cosine-like spatial variation (averaging this cosine over all possible directions), one may set

\[
g(r,t) = \varphi(1 - \varphi) \left\{ \sin[\alpha(t)r]/\alpha(t)r \right\} \exp[-\lambda(t)r] \quad (2)
\]

with

\[
\alpha(t) = 2\pi/D(t)
\]

and

\[
\lambda(t) = \sigma(t)/[4\varphi(1 - \varphi)],
\]

where \( \sigma(t) \) is the interfacial area per unit volume. This is in fact the same expression as that used by Teubner & Strey (1987) to describe the (equilibrium) structure of surfactant stabilized microemulsions, which is geometrically quite similar to the case of an unmixing system.

The corresponding structure function \( S(k,t) \) may be calculated by taking the Fourier transform of \( g(r,t) \). \( S \) then has a maximum in \( k \) and a \( k^{-4} \) decrease at large \( k \) in agreement with Porod's law, but it does not have the required behavior at small \( k \). This can be forced without affecting the structure function at large \( k \) by multiplying it by \( k^4/(k^4 + \delta) \), where \( \delta \) is a constant \( \ll 1 \). After normalizing the obtained structure function, the final expression for the model scaling function is

\[
L(x) = \frac{ax^4}{x^4 + c} \quad \frac{b}{b + (x^2 - 1 + d)^2} \quad (3)
\]

with

\[
a = (1 + e) \left( 1 + \frac{d^2}{b} \right); \quad b = \left[ \frac{2\gamma(1 - d)}{1 - \gamma^2} \right]^2;
\]

\[
c = \frac{d}{b - d(1 - d)}; \quad \gamma = \frac{\lambda}{\alpha}.
\]

It has been shown that \( L \) can be used to fit many different experimental data with \( d \) fixed at 0.06 (Fratzl & Lebowitz, 1989). This value ensures the \( x^4 \) behavior at small \( x \), but is small enough not to affect the scaling function at large \( x \) significantly. Consequently, there remains just one free parameter, which is

\[
\gamma = \frac{\lambda(t)}{\alpha(t)} = \frac{\sigma(t)D(t)}{8\pi\varphi(1 - \varphi)}.
\]

Note that the product \( \sigma D \) must be independent of time because \( L(x) \) does not depend on time. \( \sigma \) may finally be estimated using a simple model for the structure of the two-phase system:

(i) In the case of dilute systems, the minority phase will form spherical droplets. After the initial nucleation period there will be competition between neigh-

\begin{align*}
0 \leq \varphi & \leq \frac{4\pi}{81} \quad \frac{4\pi}{81} \leq \varphi \leq \frac{1}{4} \quad \frac{1}{4} \leq \varphi \leq 0.5
\end{align*}

Fig. 1. Microstructural model as discussed in the text. (a) A spherical droplet is located inside a box of edge length \( D \); (b) a cylinder or (c) a plate crosses the box to meet differently oriented cylinders or plates in the neighboring boxes, forming interconnected patterns. The interphase surface inside the box (black in the figure) is smallest for droplets when \( \varphi < 4\pi/81 \), for plates when \( \varphi > 1/\pi \) and for cylinders in between.
boring nucleation sites and one may estimate that within the typical diffusion distance $D(t)$ of individual atoms just one such nucleus remains. This is shown in Fig. 1(a), where a spherical droplet is represented inside a box of edge length $D$. With this model, it is easy to calculate the amount of interfacial area inside the box and therefore the specific surface $\sigma$.

(ii) At $\varphi$ larger than $\sim 0.15$, the surface of the sphere in the box is larger than the surface of a cylinder with the same volume crossing the box (Fig. 1b) and extending into the neighboring boxes to touch other cylinders oriented differently. As the system has a tendency to reduce the interfacial area, such a structure, constituting a very crude approximation of interconnected patterns, will be more probable than isolated droplets.

(iii) At $\varphi \geq 0.31$, plates crossing the box have an even smaller surface than the cylinders (Fig. 1c) and the morphology might change from interconnected cylinders to interconnected plate-like objects.

With the model outlined in Fig. 1, $\sigma$ may be calculated as a function of $\varphi$:

$$\sigma D = \begin{cases} 
\frac{4\pi(3\varphi/4\pi)^{2/3}}{2\pi(\varphi/\pi)^{1/2}} & 0 < \varphi < 4\pi/81 \\
2 & 4\pi/81 < \varphi < 1/\pi \\
1/\pi < \varphi , 
\end{cases}$$

and consequently $\gamma$ is defined via (4), leaving no more adjustable parameters in the model scaling function $L(x)$.

$L(x)$ has already been compared with many experimental data in a previous paper (Fratzl & Lebowitz, 1989). The values for the full width at half-maximum (FWHM) of experimental scaling curves analyzed are reproduced here by full circles in Fig. 2, together with the FWHM estimated from the model (full line in Fig. 2). There is quite a good overall agreement, but one may notice the absence of data in the region of very small $\varphi$, where the strongest dependence of the FWHM on $\varphi$ is predicted by the model.

3. Experimental determination of the scaling function for dilute systems

3.1. The system $\text{Al}_{1-x}\text{Ag}_x$

Although a collection of data from several investigators on the system Al–Zn, carried out by Hoyt & de Fontaine (1989) (see also Kostorz, 1991) supports the idea that the width of the scaling function increases towards smaller $\varphi$, no experimental test using a single system and experimental set-up has been reported up to now. Recently, Langmayr (1991) obtained results on the scaling function for $\text{Al}_{1-x}\text{Ag}_x$ at 393 K, with $x = 1, 2$ and 5 at.%. This corresponds to values of $\varphi = 0.02, 0.04$ and 0.09, respectively, using the miscibility gap reported by Naudon & Caiasso (1974), which – in the temperature range around 393 K – is consistent with the more recent determination by Dubey (1990). Structure functions were measured for several annealing times by X-ray SAS with a conventional X-ray source and a pinhole camera. They were rescaled using (1) and plotted in Fig. 3. Full lines in this figure represent the model scaling function (3) calculated with the known values for $\varphi$, i.e. without any adjustable parameter. Besides the curve for $\varphi = 0.02$, where the agreement is approximate, the model scaling function describes the data almost perfectly, giving therefore strong...
experimental support to the ideas on the microstructure outlined in Fig. 1. As expected, the FWHM increases strongly when the volume fraction \( \varphi \) becomes very small and these FWHM values are plotted as open squares in Fig. 2.

3.2. The case of Cu\(_{0.99}\)Fe\(_{0.01}\)

It is well known that spherical precipitates of pure \( \gamma \) iron are formed upon heating dilute Cu–Fe alloys (Wada, Yuchi, Uemori, Tanino & Mori, 1988). The decomposition of Cu\(_{0.99}\)Fe\(_{0.01}\) was very recently investigated by SAS at the JUSIFA beamline of the synchrotron source in Hamburg, using anomalous scattering to enhance the contrast between Fe and Cu (for a description of the beamline see Haubold, Gruenhagen, Wagener, Jungbluth, Heer, Pfeil, Rongen, Brandenberg, Moeller, Matzerath, Hiller & Halling, 1989). In addition, the amount of precipitated \( \gamma \) iron was determined by high-temperature Mössbauer spectroscopy, yielding \( \varphi = 0.005 \) at 973 K. A preliminary account of the scaling function measured in this system at 973 K is given in Fig. 4.

The most surprising fact which can be deduced from Fig. 4 is that no decrease of the structure function \( S(k,t) \) towards small \( k \) is observable in the experimentally accessible \( k \) range (here \( k = 4\pi \sin \theta /\lambda \), where \( \theta \) is half the scattering angle and \( \lambda \) the wavelength of the incident radiation). The data could therefore not be normalized with \( k_{m}(t) \) as in (1) and the radius of gyration (Guinier & Fournet, 1955) \( R_{g}(t) \) was used instead. To interpret this absence of a maximum in the structure function, one may refer to the rapid divergence of the FWHM predicted for the model scaling function \( L(x) \) (see Fig. 2). The maximum of \( F(x) \) being fixed at \( x = 1 \), this is equivalent to saying that, for a given width of the structure function \( S(k,t) \), the maximum position \( k_{m}(t) \) shifts to very small \( k \) (and therefore eventually outside the experimentally accessible \( k \) range) when \( \varphi \to 0 \).

4. Concluding remarks

By heuristic arguments a simple analytical expression has been constructed for the scaling function. This expression depends explicitly on the volume fraction \( \varphi \) and contains no more adjustable parameters. Within this model, a strong increase of the peak width of the structure function is to be expected for small \( \varphi \). This effect was confirmed by carrying out X-ray SAS experiments with Al–Ag alloys. For very dilute systems (typically \( \varphi \leq 0.01 \)), the model predicts a divergence of the width of \( F(x) \), the maximum
being located at $x = 1$. This is equivalent to saying that the maximum in the structure functions should approach $k_m = 0$ when $q \to 0$. The structure functions measured by synchrotron SAS for Cu$_{0.99}$Fe$_{0.01}$ at 923 K (where $q = 0.005$) did not show any maximum, in agreement with these expectations. Furthermore, the data agreed almost perfectly with the scaling function calculated using the droplet size distribution predicted by the theory of Lifshitz & Slyozov for the case $q \to 0$.

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References
