Scaling Function for the Structure Factor in First-Order Phase Transitions

P. A. Rikvold[(a)] and J. D. Gunton[(a)]

Département de Physique Théorique, Université de Genève, CH-1211 Genève 4, Switzerland

(Received 2 April 1982)

A simple, phenomenological theory is presented for the scaling function of a phase-separating binary system. The model describes a gas of spherical droplets of the minority phase, surrounded by depletion zones, and involves a simple approximation for the two-point distribution function. Reasonable agreement is found with the structure factors for the kinetic Ising model, binary alloys, and binary liquids.

PACS numbers: 64.60.-i, 05.50.+q, 64.75.+g, 81.40.Cd

In systems undergoing phase separation following a quench into the two-phase region, the time-dependent structure factor has been found to satisfy a scaling law $S(q,t)=Cq_s^{-d}(t)\mathfrak{F}(q/q_s(t))$, where $q_s(t)$ is a time-dependent characteristic wave number, d is the dimensionality, and C is a proportionality constant. In many systems the scaling function $\mathfrak{F}(x)$ is reasonably time independent. This scaling appears rather universal in that it applies to such different systems as the Ising spin-exchange model,[1] binary liquids,[2,3] binary alloys,[4] glasses,[5] and tricritical systems.[6,7]

This scaling was implicit in a droplet theory proposed by Binder and Stauffer,[8] and subsequently by Binder, Billotet, and Mirold.[9] However, there exists no first-principles theory which predicts the form of the scaling function for systems with conserved order parameter. In view of the evident difficulties involved in obtaining such a theory, it seems useful at this stage to have a phenomenological theory for the scaling function. Hennion, Ronzaud, and Guyot[4] have proposed one form for the structure function, based on an equilibrium hard-sphere correlation function. As we point out below, this is inaccurate for small wave numbers. The most detailed phenomenological theory is due to Furukawa.[10] His theory (which contains three adjustable parameters) gives a numerical solution for $S(q,t)$ which is in good agreement with the Monte Carlo simulations of Lebowitz, Marro, and Kalos (LMK)[1] at two different quench positions, one critical and one off critical. The agreement with the data for binary liquids of Knobler and Wong (KW)[2] at an off-critical quench is also quite good.

In this Letter we present an approximate theory which yields an explicit, analytic form for the scaling function. We consider a simple, phenomenological model with no adjustable parameters, which we believe describes the essential physics of most phase-separating systems, close to the coexistence curve. We envisage a gas of droplets of the minority phase, occupying a fraction v of the total volume. The volume fraction v is the only way in which the quench position (temperature and average concentration) enters into our model. Each droplet is surrounded by a region in which the minority concentration is below its average value. In the literature such regions are often referred to as "depletion zones." Somewhat similar physical pictures have also been suggested by other authors.[3,4,8-11] The model ignores complicated physical effects, such as strain and anisotropy in alloys. It also neglects interesting hydrodynamic effects in liquids, except to the extent that they modify the scaling length. In spite of its simplicity this model provides a satisfactory description of the major features of experiments over a wide range of times where the dynamics is highly nonlinear.

We assume scaling with one single length scale, $R(t)$, which we take as the average droplet radius. Although we make no explicit assumptions about the time dependence of $R(t)$, the region of validity of the model approximately coincides with the Lifshitz-Slyozov-Wagner regime,[12] in which $R \sim t^{1/3}$. We further assume that the droplet surfaces are sharply defined and smoothly curved. This restricts us to low v, and determines the asymptotic behavior $S(q,t)\sim q^{-(d+1)}$ for large q.[10] In the theory of small-angle scattering this is known as Porod's law.[13] At higher v, where percolation effects become important, we expect our model to give much less accurate results.

The structure factor $S(q,t)$ (after subtraction of a weakly q-dependent background) can be expressed in terms of the conditional probability $V^{-1}P(|\vec{r}||R,R')$ of finding two droplets a distance $|\vec{r}|$ apart. In the monodisperse approximation $R\equiv R'\equiv R(t)$ the normalized scaling function $\mathcal{S}(Q)$

$=C^{-1}R^{-3}S(Q/R,t)$ is found to be (for $d=3$)

$$\mathcal{S}(Q)=\frac{2}{3\pi(1-v)}\psi^2(Q)\left\{1-\frac{3v}{4\pi R^3}\int[1-P(|\vec{r}|)]e^{-i\vec{Q}\cdot\vec{r}/R}d^3r\right\}, \tag{1}$$

where $Q=qR$ and $\psi(Q)=3(\sin Q-Q\cos Q)/Q^3$ is proportional to the form factor of a sphere. The first term in the brackets arises from single-droplet scattering, while the second term is due to pair correlations. The normalization is chosen so that $\int_0^\infty Q^2\mathcal{S}(Q)dQ=1$. In the late-stage coarsening regime v has essentially reached its equilibrium value, as given by the lever rule. $\mathcal{S}(Q)$ is then time independent, as can be seen from (1).

In the absence of a detailed theory for the nonequilibrium two-point distribution function $V^{-1}P(|\vec{r}||R,R')$, we here use a simple approximation, which we believe expresses the essential features of the spatial droplet distribution. We can easily find the limits of P for large and small $|\vec{r}|$: Since the centers of two different droplets cannot coinicide $P(0|R,R')=0$, while statistical independence at large distances yields $P(\infty|R,R')=1$.

We now invoke local conservation of density, which has often been overlooked in previous treatments of this problem. This requires the structure factor to vanish at $q=0$. For brevity we present this argument here only for the monodisperse case. The Fourier transform in (1) can be written as an excluded volume times a function $\varphi(Q)$ which approaches unity as $Q\to 0$. We can write the term in brackets in (1) as $1-v(R_e/R)^3\varphi(Q)$, where R_e is the radius of the excluded volume. Local conservation requires $\mathcal{S}(0)=0$, which yields $R_e=v^{-1/3}R$. Thus the excluded volume is simply the average volume per droplet. This excluded volume corresponds to the "depletion zone" mentioned above. It should be noted that this implies a long-range nonequilibrium correlation function. Whether this feature will be present in a more microscopic theory remains to be seen.

$R(t)$ cannot be directly measured in scattering experiments. For comparison with experimental data we therefore introduce the normalized scaling function $\mathcal{F}(x)=Q_{\max}{}^3\mathcal{S}(Q_{\max}x)$, where $Q_{\max}$ is the peak position of $\mathcal{S}(Q)$, and $x=Q/Q_{\max}=q/q_{\max}$. We have tried several approximate forms for $P(|\vec{r}|)$, but we find that although $\mathcal{S}(Q)$ depends on the choice, $\mathcal{F}(x)$ is relatively insensitive to it. We therefore have adopted the simplest possible form, namely $P(|\vec{r}|)=0$ for $|\vec{r}|<R_e$ and $P(|\vec{r}|)=1$ for $|\vec{r}|>R_e$. This yields

$$\mathcal{S}(Q)=[2/3\pi(1-v)]\psi^2(Q)[1-\psi(v^{-1/3}Q)]. \tag{2}$$

We have also extended this argument to the polydisperse case and obtained an averaged structure factor, assuming the Lifshitz-Slyozov-Wagner distribution for R. It should be noted that $P(|\vec{r}|)$ differs from the Ashcroft-Lekner equilibrium hard-sphere correlation function employed by Hennion, Ronzaud, and Guyot.[4] The latter yields a finite value for $\mathcal{F}(0)$.

As a result of the problem of obtaining reliable data at very small and very large wave numbers, experimental results are expressed in terms of a scaling function $F(\tilde{x})$, normalized on some finite interval $[A,B]$. The variable $\tilde{x}=q/\tilde{q}=Q/\tilde{Q}$, where $\tilde{q}$ and $\tilde{Q}$ are scaling wave numbers which may depend on $[A,B]$. Theoretical predictions are, however, more conveniently expressed in terms of $\mathcal{F}(x)$, which is normalized on $[0,\infty]$. To be able to compare results from different experiments with each other, as well as with theory, we relate the experimental and theoretical scaling functions by

$$\mathcal{F}(x)=(Q_{\max}/\tilde{Q})^3\left[\int_{A\tilde{Q}}^{B\tilde{Q}}Q^2\mathcal{S}(Q)dQ\right]F(xQ_{\max}/\tilde{Q}). \tag{3}$$

This equation is exact if $\mathcal{S}(Q)$ is chosen such that $\mathcal{F}(x)$ is the correct scaling function. For KW, $\tilde{Q}=Q_{\max}$, while for LMK, $\tilde{Q}$ is the truncated first moment of $\mathcal{S}(Q)$. We have used Eq. (3) to compare the scaling functions obtained by KW and LMK to our theoretical $\mathcal{F}(x)$. The experimental half-widths $\tilde{\Delta}$, peak heights $F_{\max}$, and moment ratios $\tilde{x}_2/\tilde{x}_1{}^2$ are also related to their theoretical counterparts by relations easily derived from (3). For LMK $(Q_{\max}/\tilde{Q})\neq 1$, which leads to a rescaling of both the horizontal and the vertical scales. Although this rescaling is necessary for comparison with KW and with theory, it makes it difficult to assess whether disagreements are due to real, physical differences, or simply reflect the approximate nature of $\mathcal{S}(Q)$, which defines the rescalings.

Our main results are displayed in the figures. In Fig. 1 is shown $\mathcal{F}(x)$ at $v=0.0855$ for the polydisperse case, together with rescaled data from LMK's quench P_3 and KW's quench K, which are made at approximately the same v. The agreement between theory and experiment seems reasonably good. The agreement with the Monte Carlo results becomes better for the quenches P_2 and P_1, which are at lower v. As shown by

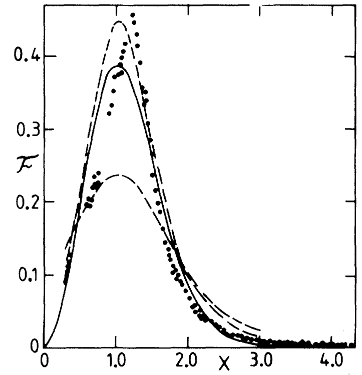

FIG. 1. Scaling function $\mathfrak{F}(x)$ for $v = 0.0855$ (full line), together with experimental data from LMK's quench P_3 at $v = 0.088$ (dots) and from KW's quench K at $v = 0.083$ (broken lines). The LMK data are from Fig. 8 of Ref. 1. The KW data are from Fig. 2 of Ref. 2. The two curves represent limits for the experimental scaling function and show to which extent scaling is obeyed. Both data sets are rescaled according to Eq. (3).

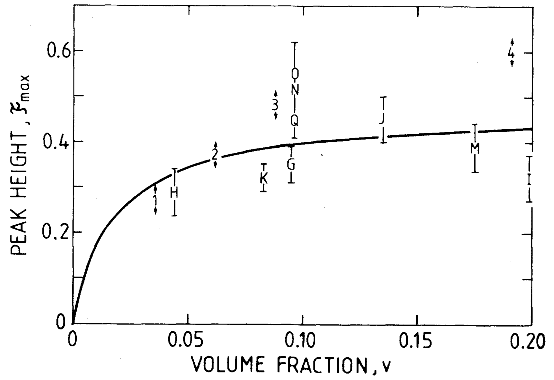

FIG. 2. Peak height $\mathfrak{F}_{\max}$ vs volume fraction v. Data for LMK's quenches $P_1 - P_4$ (numbers) are from Figs. 7–9 of Ref. 1. Data for KW's quenches $G-Q$ (letters) are from Table I of Ref. 2. Both data sets are rescaled according to Eq. (3), using the polydisperse $\mathcal{S}(Q)$. It should be noted that the "error" bars include the effect of the weak time dependence of the experimental scaling functions.

LMK, the Monte Carlo data also agree reasonably well with the results of Hennion, Ronzaud, and Guyot for the Zn-Al binary alloy. In Fig. 2 is shown the peak height $\mathfrak{F}_{\max}$ vs v. $\mathfrak{F}_{\max}$ increases with increasing v, while the moment ratio x_2/x_1^2 and the half-width Δ both decrease. This corresponds to both the experimental and theoretical scaling functions becoming higher and narrower as v increases. The agreement between the experimental and theoretical results is quite satisfactory for both the peak height and the moment ratio, especially for the liquid data. The theoretical predictions for the half-width are somewhat less satisfactory, although not unreasonable. We have not been able to explain the poorer agreement with the Monte Carlo data, unless it is due to the above-mentioned uncertainty in the rescaling. We have also made similar plots using the monodisperse approximation (2) for $\mathcal{S}(Q)$. We find that the polydisperse scaling function yields a somewhat better agreement both between the two sets of rescaled experimental data, and between theory and experiment. A more sensitive test of our basic assumptions about the behavior of $P(|\vec{r}|)$ would require scattering data at smaller v than currently available.

Since v is the only quench parameter which enters into our theoretical $\mathfrak{F}(x)$, we have displayed the data as functions of v only. If there is an additional dependence on quench temperature this may be misleading, as the data belong to considerably different temperatures. The liquid quenches generally are much closer to T_c than are the Monte Carlo simulations. For the critical $v = 0.5$, where we would expect our model to be inadequate, the experimental scaling functions certainly are temperature dependent, even after rescaling.

In conclusion we remark that in comparing our theory with that of Furukawa one should note that he has focused on the dynamics of the phase separation through obtaining an approximation for the cluster gas free energy functional. We have focused on taking into account the effect of the depletion zones through a simple approximation for the correlation function. The two approaches are complementary in that Furukawa obtains dynamical information, but no explicit analytical form for the scaling function[14] while we obtain an explicit scaling function with no adjustable parameters, but no dynamical information. We also believe that the normalization procedure is essential for reliable comparison between experimental data from different systems, and between experiments and theory. Finally it should be noted that a scattering intensity in the form of a "collapsing halo" is often considered to be a hallmark of spinodal decomposition. However, our results for the structure factor show that such a halo is equally consistent with growth of localized droplets.[9]

We wish to acknowledge the kind hospitality of the Département de Physique Théorique, Université de Genève, and the Institut für Festkörperforschung der Kernforschungsanlage Jülich. This work was partially supported by the Swiss National Science Foundation and by the National Science Foundation under Grant No. DMR-8013700. One of us (P.A.R.) acknowledges a fellowship from the Norwegian Research Council for Science and the Humanities.

---

[a] Permanent address: Department of Physics, Temple University, Philadelphia, Pa. 19122.

[1] J. L. Lebowitz, J. Marro, and M. H. Kalos, Acta Metall. 30, 297 (1982).

[2] C. M. Knobler and N. C. Wong, J. Phys. Chem. 85, 1972 (1981).

[3] Y. C. Chou and W. I. Goldburg, Phys. Rev. A 23, 858 (1981).

[4] M. Hennion, D. Ronzaud, and P. Guyot, Acta Metall. 30, 599 (1982).

[5] A. Craievich and J. M. Sanchez, Phys. Rev. Lett. 47, 1308 (1981).

[6] D. N. Sinha and J. K. Hoffer, Physica (Utrecht) 107 B+C, 155 (1981). Th. Benda, P. Alpern, and P. Liederer, unpublished.

[7] P. S. Sahni and J. D. Gunton, Phys. Rev. Lett. 45, 369 (1980); P. S. Sahni, J. D. Gunton, S. L. Katz, and R. H. Timpe, Phys. Rev. B 25, 389 (1982).

[8] K. Binder and D. Stauffer, Phys. Rev. Lett. 33, 1006 (1974).

[9] K. Binder, C. Billotet, and P. Mirold, Z. Phys. B 30, 183 (1978).

[10] H. Furukawa, Phys. Rev. A 23, 1535 (1981).

[11] E. D. Siggia, Phys. Rev. A 20, 595 (1979).

[12] I. M. Lifshitz and V. V. Slyozov, J. Phys. Chem. Solids 19, 35 (1961); C. Wagner, Z. Elektrochem. 65, 581 (1961).

[13] A. Guinier and G. Fournet, *Small Angle Scattering of X Rays* (Wiley, New York, 1955).

[14] Furukawa does, however, have an explicit form for the scaling function for large x, which asymptotically has the same x^{-4} behavior as we find.