UNIVERSALITY OF SCALED STRUCTURE FUNCTIONS IN QUENCHED SYSTEMS UNDERGOING PHASE SEPARATION

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Abstract—We present a novel heuristic "universal" formula for the scaled structure function following a quench into the miscibility gap which gives very good fits to a variety of experimental observations. The single adjustable parameter γ needed to fit data for alloys, binary fluids, polymer mixtures and computer simulation curves depends essentially only on the fraction of the volume of the minority phase. Minimizing the ratio of "surface area to volume" of the minority phase predicts a rough morphology of the system—its local character changes from spherical isolated droplets to interconnected plate-like objects as the minority fraction increases. By relating γ to this microstructure we obtain the value of γ correctly to within 10%.

Résumé—Les auteurs présentent une nouvelle formule heuristique "universelle" pour la fonction réduite de structure résultant d'une trempe dans la zone de non-miscibilité; cette formule donne un très bon accord avec un grand nombre d'observations expérimentales. Le parfamètre unique ajustable γ nécessaire pour réaliser un accord avec les données expérimentales pour les alliages, les fluides binaires, les mélanges de polymères et les courbes de simulation calculées ne dépend essentiellement que de la fraction volumique de la phase minoritaire. En minimisant le rapport de "la surface au volume" de la phase minoritaire, on prévoit une morphologie grossière du système—son caractère local passe de gouttes sphériques isolées à des objets en plaquettes interconnectés lorsque la fraction minoritaire croît. En reliant γ à cette microstructure, nous obtenons une valeur de γ correcte à 10% près.

Zusammenfassung—Wir legen eine neue heuristische "universal-" Formel für die skalierte Strukturfunktion vor, die aus Abschrecken in die Mischungslücke entsteht; sie beschreibt eine Reihe von experimentellen Beobachtungen sehr gut. Der einzige anzupassende Parameter γ, der für die Beschreibung der Daten für Legierungen, binäre Flüssigkeiten, Polymermischungen und Computersimulationen notwendig ist, hängt im wesentlichen vom Volumanteil der Minoritätsphase ab. Die Minimalisierung des Verhältnisses von "oberfläche zu Volumen" der Minoritätsphase sagt eine grobe Morphologie des Systems voraus-sein lokaler Charakter wechselt von isolierten kugelförmigen Tröpfchen zu miteinander verbundenen plattenförmigen Objekten, wenn der Volumanteil der Minoritätsphase zunimmt. Indem γ auf diese Mikrostruktur bezogen wird, erhalten wir den Wert für γ auf 10% genau.

1. INTRODUCTION

The process of phase segregation which follows the quench of an alloy, liquid or polymer from a uniform state into the miscibility gap is a problem of both theoretical and practical interest [1]. The quantity most amenable to measurement (by means of small-angle scattering of X-rays, light or neutrons) is the evolution of the structure function, $S(k, t)$, as it changes with the time following the quench. It was observed in computer simulations of this process [2] that, after some initial transients, $S(k, t)$ has the scaling form [3]

$$S(k, t) = Ak_m^{-3}(t)F[k/k_m(t)] \qquad (1)$$

where $k_m(t)$ is the position of the maximum of S at time t and A is a constant (independent of t) chosen here to make $F(1) = 1$. (1) has been checked in great variety of experiments and simulations and found to

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hold whenever long range elastic interactions between different domains (clusters) are unimportant [1].

There is no satisfactory theory for the actual form of $F(x)$ at the present time although there are various theories leading to non-linear equations for $S(k, t)$ whose numerical solutions agree (more or less well) with experiments [4–7]: we consider simulations also as experiments. Furukawa [8] has argued that $F(x)$ should become broader for off-critical quenches. He also proposed [8] an expression for F (which however did not contain the volume fraction explicitly) whose agreement with experiment is reasonable for small volume fractions, close to $\phi \approx 0.1$. Other expressions proposed for $F(x)$, mainly obtained from distributions of hard spheres, fit the experimental data only very approximately [9–11]. The only feature of $F(x)$ for which there is a heuristic theory in excellent agreement with experiment is the large x behavior. This is given by Porod's law [12], $F(x) \sim Cx^{-4}$. The derivation of Porod's law is based on a model in which there are sharp interfaces between different domains and the constant C is a measure of such

surface area per unit volume [12]. Taking this model as our clue we present here a heuristic argument for a simple approximate function $L(x)$ which turns out to represent $F(x)$ well in all systems studied.

2. MODEL FOR THE SCALING FUNCTION

We assume that at the "late stages" of phase segregation the composition at each point, $\rho(\mathbf{r})$, is either that of the A-phase or that of the B-phase with $\rho(\mathbf{r}) = 1$ or 0 respectively. The spherically averaged structure function $S(k, t)$ is then proportional to the Fourier transform of $\hat{S}(r)$ (at time t)

$$\hat{S}(r) = \left\langle \frac{1}{V} \int_V [\rho(\mathbf{u}) - \phi][\rho(\mathbf{u} + \mathbf{r}) - \phi]d\mathbf{u} \right\rangle,$$

$$\text{for} \quad V \to \infty \quad (2)$$

where the brackets denote the spherical average, $r = |\mathbf{r}|$ and ϕ is the fraction of the volume V occupied by the minority phase A. Note that $\hat{S}(0) = \phi(1 - \phi)$ which is independent of time. If the surface separating the different phases were "randomly" distributed then, following Debye et al. [14], we should have

$$\hat{S}(r) = \phi(1 - \phi)\exp(-\lambda r), \quad \lambda = \sigma/4\phi(1 - \phi) \quad (3)$$

where σ is the interface surface per unit volume; see equations (32)–(34) in [14]. However a random distribution of interfaces will not describe the morphology in the case of phase separation. The conservation of material induces a modulation with some (time dependent) wavelength D, related to the fastest growing mode [1]. Within a volume of the typical diameter D, the average concentration will remain constant. To take this into account we set

$$\hat{S}(r) = \phi(1 - \phi)\exp(-\lambda r)\frac{\sin \alpha r}{\alpha r}; \quad \alpha = \frac{2\pi}{D}. \quad (4)$$

The corresponding approximate scaling function normalized so that the maximum is at 1 will be given by the formula

$$L_1(x) = \frac{b_1}{b_1 + (x^2 - 1)^2}; \quad b_1 = \frac{4\gamma^2}{(1 - \gamma^2)^2}; \quad \gamma = \frac{\lambda}{\alpha}. \quad (5)$$

$L_1(x)$ has the correct large x behavior in agreement with Porod's law. Its width is determined by b_1 which depends on ϕ in accord with experiment. Its behavior at small x is however not in agreement with experiment where it is usually found that $F(x) \approx 0$ as $x \to 0$. In fact, Yeung [13] noted that the experimental data is consistent with an x^4 dependence when $x \to 0$ and this was confirmed recently by Furukawa [8]. We accept this and multiply L_1 by a factor $x^4/(x^4 + constant)$. After renormalizing so that the maximum is located at 1 our final approximate form for $F(x)$ is

$$L(x) = \frac{ax^4}{x^4 + c}\frac{b}{b + (x^2 - 1 + d)^2} \quad (6)$$

with

$$b = \frac{4\gamma^2}{(1 - \gamma^2)^2}(1 - d)^2;$$

$$c = \frac{d}{b - d(1 - d)};$$

$$a = (1 + c)\left(1 + \frac{d^2}{b}\right).$$

N.B. $F(x) \approx 0$ for small x is not related to $F(0) \equiv 0$, for a fixed V, which follows from the definition (2). $S(k, t) \approx 0$ for $k \approx 0$ is a statement about the magnitude of composition fluctuations on a length scale several times $2\pi/k_m$ as compared to the dominant ones. $2\pi/k_m$ is however much smaller than $V^{1/3}$ in real experiments; in computer simulations k is discrete and $S(k = 0, t) = 0$ says nothing about neighboring k-values.

3. COMPARISON TO EXPERIMENT DATA

We used $L(x)$ with two free parameters γ and d to fit data in polymers, liquids, solids and simulations: see Fig. 1. These parameters can of course be related to various features of the $L(x)$ curve, e.g. to the curvature at the maximum, to the coefficients of x^4 near $x = 0$ or of x^{-4} for $x \gg 1$. Since we do not have a good a priori theory we decided to let experiment be our guide. We found to our surprise that d is nearly universal with $d \approx 0.06$ in all cases. We do not have any good explanation for this, but we know that the fits are not very sensitive to the exact value of d. In the following we consider d as constant equal to 0.06, so that γ remains as the only fitting parameter. Comparing the three scaling curves in Fig. 1, it is apparent that γ is essentially a measure for the width of the scaling curve which increases when γ increases. The values for γ obtained by fitting equation (6) to experimental scaling functions are listed in Table 1. We observe that for all critical quenches where $\phi = 0.5$ the value for γ is around 0.3 independent of temperature, even very close to T_c. There is however a strong dependence of γ on ϕ (see also Fig. 1).

4. DISCUSSION

To get a physical interpretation of γ we note that by (3)–(5), $\gamma = \sigma D/8\pi\phi(1 - \phi)$, so that for a fixed volume fraction ϕ and a fixed characteristic length D (determined at each t by the kinetics) γ is proportional to the interphase surface per unit volume σ which in turn depends on the morphology. According to our model there are periodic modulations of A-rich and B-rich domains with an average wavelength of D. This means that at time t after the quench the average composition within cubes of length (several times) D is still the same as at time $t = 0$. The size D of these regions is time dependent and increases during the decomposition process. To calculate the amount of interphase surface within the region of size D we now consider three possible morphologies for the minority phase. First, clusters may be isolated within the majority phase, so that they will be essentially spherical. Secondly, we assume the possibility of rod- or
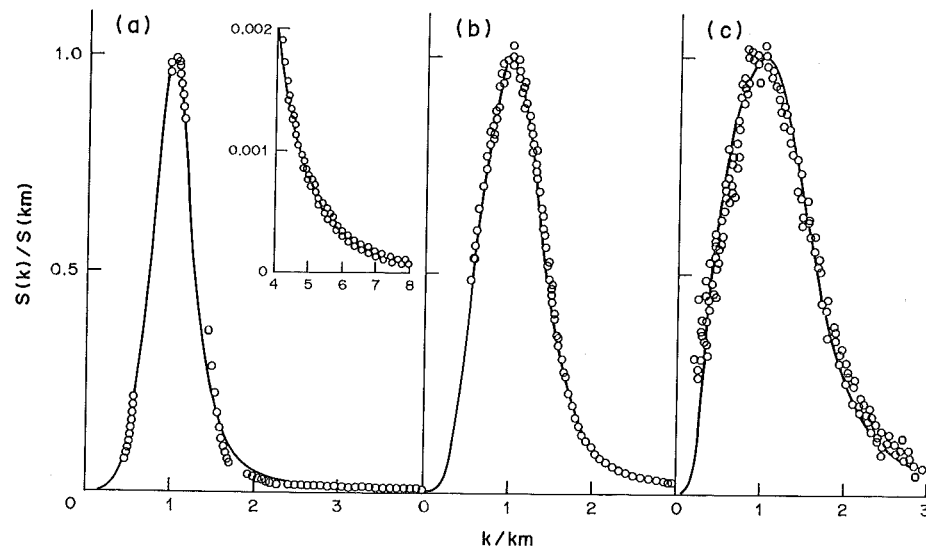
Fig. 1. Comparison of the model scaling function $L(x)$ with (a) the numerical solution of the Ginzburg–Landau equation [7], with (b) experimental data for Cu–33at%Mn [23] and (c) for Al–3.7at%(Zn,Mg) [21]. Circles represent data points and the solid lines correspond to equation (6) with (a) $\gamma = 0.30$, (b) $\gamma = 0.45$, (c) $\gamma = 0.60$.

(thirdly) plate-like objects reaching with their axis the border of the region of size D, where they will touch clusters from adjacent regions. As the plates (or the rods) in adjacent regions are randomly oriented, their touching describes a highly interconnected morphol-

Table 1. The value of γ for experimental and simulation data fitted with equation (6) is given as γ_{exp} and the corresponding value calculated from equation (7) as γ_{mod}.

System[ref]	$1 - T/T_c$	ϕ	γ_{exp}	γ_{mod}
Acid + water[15]	$3 \cdot 10^{-6}$	0.50	0.28	0.32
acid + water[15]	$2 \cdot 10^{-5}$	0.50	0.28	0.32
Lutidine + water[15]	$2 \cdot 10^{-6}$	0.50	0.28	0.32
Lutidine + water[15]	$6 \cdot 10^{-6}$	0.50	0.28	0.32
Polybutadiene[16]	$4 \cdot 10^{-2}$	0.50	0.28	0.32
PS-PMPS(polymer)[17]	$2 \cdot 10^{-4}$	a	0.45	
PS-PMPS(polymer)[17]	$6 \cdot 10^{-3}$	b	0.75	
PS-PVME(polymer)[18]	$-3 \cdot 10^{-3}$	a	0.35	
PS-PVME(polymer)[18]	$-4 \cdot 10^{-3}$	a	0.40	
PS-PVME(polymer)[18]	$-7 \cdot 10^{-3}$	a	0.40	
PS-PVME(polymer)[18]	$-2 \cdot 10^{-2}$	a	0.50	
PS-PVME(polymer)[18]	$-3 \cdot 10^{-2}$	a	0.60	
Borate glass[19]	0.22	0.50	0.45	0.32
Borate glass[19]	0.19	0.10	0.35	0.45
Al–22at%Zn(Mg)[9]	0.50	0.27	0.35	0.37
Al-5.3at%Zn[10]	0.51	0.03	0.55	0.64
Al-6.8at%Zn[10]	0.51	0.05	0.50	0.55
Al-6.8at%Zn[10]	0.40	0.04	0.50	0.59
Al-6.8at%Zn[10]	0.36	0.03	0.55	0.64
Al-6.8at%Zn(Mg)[20]	0.41	0.04	0.55	0.59
Al-10at%Zn(Mg)[20]	0.51	0.10	0.50	0.46
Al-3.7at%(Zn,Mg)[21]	0.36	0.02	0.60	0.68
Au-60at%Pt[22]	0.46	0.50	0.35	0.32
Cu-33%at%Mn[23]	0.17	0.50	0.45	0.32
Cu-46at%Ni-4at%Fe[24]	0.10	0.30	0.50[c]	0.37
Fe-34at%Cr(early t)[25]	0.08	0.24	0.50[c]	
Fe-34at%Cr(later t)[25]	0.08	0.24	0.35	0.38
$\rho = 0.075$; 3-d Ising[3]	0.41	0.06	0.50	0.52
$\rho = 0.10$; 3-d Ising[3]	0.41	0.09	0.40	0.47
$\rho = 0.20$; 3-d Ising[3]	0.41	0.19	0.35	0.40
$\rho = 0.50$; 3-d Ising[3]	0.41	0.50	0.35	0.32
$\rho = 0.50$; 3-d Ising[3]	0.21	0.50	0.40	0.32
$\rho = 0.50$; 3-d Ising[3]	0.11	0.50	0.50[c]	0.32
3-d Ginzburg-Landau[7]	1.00	0.50	0.30	0.32

[a]Critical mixture but asymmetric phase diagram: $\phi \neq 0.50$.
[b]Off-critical mixture with a very asymmetric phase diagram.
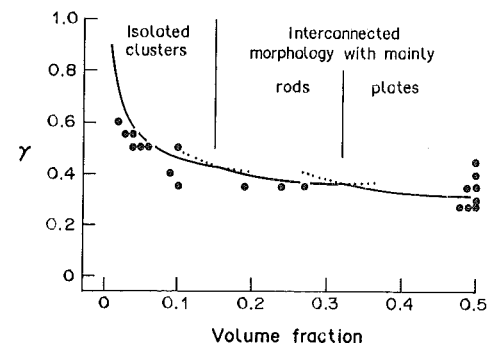[c]Probably, the asymptotic regime has not been reached.

ogy. Of course the size and the separation D of the clusters will show some dispersion throughout the sample, but their average values will be proportional for a given volume fraction ϕ (e.g. for plates the average thickness equals $D\phi$) and this will determine σ and γ

$$\gamma = \begin{cases} [4\pi\phi(1 - \phi)]^{-1} & \text{plates} \\ [4\pi^{1/2}\phi^{1/2}(1 - \phi)]^{-1} & \text{rods} \\ [2(4\pi/3)^{2/3}\phi^{1/3}(1 - \phi)]^{-1} & \text{spheres.} \end{cases} \quad (7)$$

We assume now that, within each region of size D, the system will choose the microstructure which minimizes the interphase surface per unit volume σ for a given volume fraction ϕ. For fixed ϕ and D, σ is directly proportional to γ, which is given by equation (7). The minimization of σ (or equivalently γ) predicts isolated clusters (i.e. spheres) for small values of ϕ. For $\phi \geqslant 0.15$ there will be an interconnected

Fig. 2. The theoretical value for γ (full line) as compared to experimental data (solid circles) taken from Table 1. γ has been calculated in function of ϕ using the minimum of the three expressions in equation (7): spheres for $\phi \leqslant 0.15$, plates for $\phi \geqslant 0.32$ and rods in between. The continuations of each expression to higher and lower ϕ are indicated by dotted lines.

morphology composed mainly by rods ($\phi \leqslant 0.32$) and by plates ($\phi \geqslant 0.32$). The so obtained value for γ is shown in Fig. 2 in fuction of ϕ. The fact that there are isolated clusters at small volume fractions and an interconnected morphology close to the critical composition corresponds well to observations in experiments and computer simulations [1, 6, 26]. The boundary between the two types of morphology ($\phi \approx 0.15$) is also quite reasonable. Computer simulation data on the Ising model for instance [2] showed isolated clusters for $\phi = 0.09$ and an interconnected morphology for $\phi = 0.19$. The distinction between mainly rod-like or plate-like elements in the interconnected patterns as proposed in our model is however difficult to ascertain by comparison with experimental data and we do not discuss it further.

Both in Table 1 and in Fig. 2 the theoretical value of γ is compared to the fitted γ from experimental data. A remarkable agreement is obtained in most cases. Some experimental data where only the full widths at half maximum of the scaling curve were indicated [27] are not included in the table; but there is a reasonable agreement with our theoretical model. Finally it should be noted that, when elastic interaction dominates the surface energy, our model breaks down and different features should be expected for the microstructure [28].

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