DYNAMICAL SCALING OF STRUCTURE FUNCTION IN QUENCHED BINARY ALLOYS*

JOEL L. LEBOWITZ†, J. MARRO
Division de la Physique, Cen-Saclay, 91190 Gif-sur-Yvette, France; Departamento de Física Teórica y
Departamento de Ecuaciones Funcionales, Universidad de Barcelona, Diagonal, 647, Barcelona-28, Spain

and

M. H. KALOS
Courant Institute of Mathematical Sciences, New York University,
New York, NY 10012, U.S.A.

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Abstract—We study the structure functions $S(k, t)$ obtained from computer simulations of the time
evolution of a segregating binary alloy following quenching into the miscibility gap. They are shown to
have a simple scaling behavior, $S(k, t) \propto K^{-3}(t) F(k/K(t))$. The shape of the function $F(x)$ depends some-
what on the part of the coexistence region into which the quench is made. Comparison with some recent
experiments on quenched alloys is quite satisfactory. The time evolution of $K^{-3}(t)$ appears to be linear
for late times, consistent with the Lifshitz-Slyozov theory.

Résumé—Nous étudions les fonctions de structure $S(k, t)$ obtenues à partir de simulations sur ordinateur
de l'évolution en fonction du temps d'un alliage binaire présentant une ségrégation, après une trempe
dans la lacune de miscibilité. On montre qu'elles vérifient une loi d'échelle simple $S(k, t) \propto K^{-3}(t) F(k/K(t))$. La forme de la fonction $F(x)$ depend un peu de la partie du domaine diphasé
dans lequel on fait la trempe. La comparaison avec quelques expériences récentes sur des alliages
tremps est assez satisfaisante. L'évolution de $K^{-3}(t)$ en fonction du temps est linéaire après un certain
temps, en accord avec la théorie de Lifshitz et Slyozov.

Zusammenfassung—Es werden die Strukturfunktionen $S(k, t)$ untersucht, die mit Rechnersimulation des
Segregationsverlaufes in einer in die Mischungslücke abgeschreckten binären Legierung erhalten
wurde. Diese Funktionen weisen ein einfaches maßstäbliches Verhalten auf: $S(k, t) \propto K^{-3}(t) F(k/K(t))$. Der Verlauf der Funktion $F(x)$ wird ein wenig von dem Koexistenzgebiet ab, in welches abgeschreckt.
Ein Vergleich mit neueren Experimenten ist zufriedenstellend. Der zeitliche Verlauf von $K^{-3}(t)$ scheint
für große Zeiten linear zu sein, welches mit der Theorie von Lifshitz-Slyozov übereinstimmt.

1. INTRODUCTION

The process of segregation which occurs in many
alloys, e.g. Al–Zn, following quenching from the melt
into the miscibility gap determines various properties
of the alloy and is, therefore, of great importance. The
theoretical analysis of this process, variously de-
scribed as nucleation, spinodal decomposition, coarsen-
ing, and Ostwald ripening, is based mainly on the
classical works of Cahn and Hilliard [1] and of Lif-
shitz and Slyozov [2]. The former work, as formulated
by Cook [3], describes the evolution of structure
function $S(k, i)$ while the latter considers the grain dis-
tribution $n(i, t)$; here $i$ is the time since quenching, $k$
is a reciprocal wave vector, and $i$ is a grain size. This
division corresponds directly to the two principal experi-
mental methods of study: x-ray (or neutron) scat-
tering for $S(k, t)$ and electron microscopy for $n(i, t)$.

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DOE Contract DE-AC02-76ER03077.
† Permanent address: Dept. of Mathematics and
Physics, Rutgers University, Busch Campus, New Brunswick, NJ 08903, U.S.A.
apparently real and systematic dependence of the scaling function $F(x)$ on the location of the quenched state inside the miscibility gap: $F(x)$ becomes more peaked as we move away from the coexistence line. The behavior of the characteristic wave number $K(t)$ with time seems more difficult to pin down with precision. Using an asymptotic power law dependence for $K(t)$, i.e. writing $K(t) \sim t^{-\alpha}$ for all (after the very early transients) times, the value of the exponent $\alpha$ appears to change from a $0.2 \pm 0.05$ near the center of the gap to a $0.33 \pm 0.03$ at low concentrations of one component. On the other hand for late times when scaling holds, we obtain a good fit with $K^{-1}(t) \sim A + Bt$ (See Fig. 15 and Table 3) as expected on the basis of the Lifshitz–Slyozov theory. Our guess is that the latter is indeed the right description of the phenomena for 'late times'.

The available experimental data (known to us) on real alloys is consistent with scaling behavior [10, 11]. Scaling was also found to hold in quenches of binary liquids [12]. The phenomena therefore appears to be quite general. More precise experiments are however needed to establish conclusively this scaling behavior and clarify its features.

2. DESCRIPTION OF MODEL

The model system we study has been described before in detail [7]. At each site of a simple cubic lattice of $N = L^3$ sites ($L = 30$ or $L = 50$, in our simulations) there is assumed to be either an A atom or a B atom: the occupation variable of the $i$th site, $\eta_i$, takes on the values $+1$ or $-1$ when there is an A(B) atom at the lattice position $r_i$. (The system is isomorphic to a lattice gas where each site can be either occupied or empty and to a ferromagnetic Ising spin system where $\eta_i = \pm 1$ corresponds to 'up and down' values of the spin variable). In the initial state a spin system where $\eta_i = \eta$ corresponds to an infinite temperature state with uniform composition and no correlation between atoms. This corresponds to an infinite temperature state with uniform composition and no correlation between atoms at different positions. The relative concentration of A atoms is $\rho = (\eta + 1)/2$, $0 \leq \rho \leq 1$, where $\eta = N^{-1} \Sigma_i \eta_i$ is the average 'magnetization' in the lattice (fraction of A atoms less the fraction of B atoms), which is constant in time. Evolution proceeds by choosing, at a rate $\alpha/3$, a pair of nearest neighbor sites, $i, j$, in the lattice. If the sites are occupied by different kinds of atoms there is a probability

$$P_{ij} = \exp(-\beta \Delta U_{ij})[1 + \exp(-\beta \Delta U_{ij})]^{-1}$$

that they will be interchanged (Kawasaki dynamics [13]). Here $\beta = 1/k_B T$, $k_B$ is Boltzmann's constant and $\Delta U_{ij}$ is the change in the energy of the system caused by the interchange.

For our model system the energy is assumed to be given by

$$U = -J \sum \eta_i \eta_j, \quad J > 0.$$  

The sum in equation (2) goes over all nearest-neighbor pairs of sites and $J$ is positive so that the system will segregate below a critical temperature $T_C$. We use periodic (toroidal) boundary conditions for identifying nearest neighbors.

The phase diagram of our model A-B alloy is presented in Fig. 1. For temperatures $T \geq T_C$ the system is uniform on a macroscopic scale at all values of $\rho$. For $T < T_C$ there is a range of concentrations $\rho$, inside the coexistence curve, for which the equilibrium state of the system is one of coexistence of two phases: one A-rich, $\rho = \rho_1$ and one A-poor $\rho = \rho_2$: $2\rho_1 - 1 = 1 - 2\rho_2 = m_0$, the spontaneous magnetization in spin language. The value of $T_C$ is known very accurately for this system, $4J/k_B T_C \approx 0.88686$, as is the whole coexistence curve [14]. The phase diagram is shown in Fig. 1. While the figure corresponds strictly to a macroscopic, formally infinite, system we expect that our system is sufficiently large for the quantities investigated to behave (for the times considered) in a manner qualitatively similar to their behavior in a macroscopic system. The absence of systematic differences between the $L = 30$ and $L = 50$ simulations appears to confirm this expectation.

2.1 Simulations

The dots in Fig. 1, labeled 1–7, represent, at each density, the temperature(s) inside the miscibility gap to which our model alloy was quenched from an initially random configuration (infinite temperature). They are: for $P_1$–$P_3$, $T \approx 0.59 T_C$ and fractional con-
Values of $k_1, k_2/k_1$ (see equation (14)) and

\[ m(t) = \sum_{i=1}^{N} S_i(k, t) \]

at selected values of the time (in units of $\alpha^{-1}$) for the quenches to $P_1 - P_7$. Note that $k_1$ and $k_2$ refer to the quantity $S_i(k, t)$; using the values of $m(t)$, the definition equation (13) and the values in Table 2, one can however obtain $k_1$ and $k_2$, referring to $S_{i}(k, t)$, monitored during the corresponding evolution. $L$ refers to the size of the model system, and $NR$ is the number of independent runs made at that particular phase point. We have also included for comparison values for $k_1, k_2/k_1$ and $p'(r)$ in the visible zone of $\gamma(k, r)$, computed from the data in Fig. 3 of Ref. [10] corresponding to the Au-60 at $\alpha^2$. Pt alloy quenched to $T = 0.6 T_c$ in this case $0.03 A k A 0.21 \text{Å}^{-1}$, and the values are given in c.g.s. units.
centration of A-atoms $\rho = 0.05, 0.075, 0.10, 0.20$ and 0.50 respectively. At this temperature the value of $\rho$ at the coexistence line is $\rho_c \approx 0.015$. $m_0 \approx 0.97$. The points $P_a$ and $P_r$ are at $\rho = 0.5$ and $T \approx 0.78 T_c$ and $T \approx 0.89 T_c$ respectively. At $0.78 T_c, \rho_c \approx 0.0613$, $m_0 \approx 0.877$, while at $0.89 T_c, \rho_c \approx 0.1246$, $m_0 \approx 0.75$.

The evolution of the system following quenching was observed up to a time $t$ which varied between $10^2 a^{-1}$ and $10^4 a^{-1}$ (see Table 1). $a^{-1}$ is the average time interval between two attempts at exchanging a specific site and is taken as our time unit. To make some comparison with experiment we need at least a rough idea of how to compare time scales. We do this by noting that in our model the diffusion coefficient of a single A atom in a crystal of B atoms is given by $D = \alpha/6$ since the probability that a given bond will be tried in time $dt$ is $(1/3) \alpha dt$ and if tried the probability of an exchange is 1/2. We therefore think of our time unit at temperature $T$ as comparable to $a_0 2/6 D_0(T)$ where $a_0$ is the lattice spacing and $D_0(T)$ is the diffusion constant of a real alloy at temperature $T$ in the limit of zero concentration of A atoms. The lattice spacing $a_0$ is our unit of length. The relevant parameters for the Al-Zn alloys are estimated [21] to be $a_0 \approx 3 \AA, T_c \approx 350{\degree}C$ and $D_0 \sim 10^{-14} \text{cm}^2/\text{s}$ at $T = 0.59 T_c$. According to this rough estimate, the physical time interval in our studies at $P_1$ to $P_5$, is many hours. This is however only an order of magnitude computation since defects, vacancies and other imperfections built in during quenching may greatly speed up the time in a real alloy.

2.2 Structure function

The quantity of primary interest in our observations was $S(k, t)$, the structure function at time $t$ following quenching. $S(k, t)$ is the Fourier transform of the spatial correlation function $G(r, t)$:

$$S(k, t) = N^{-1} \left\{ \sum_r \exp(ik \cdot r_j) \left[ \eta(r_j, t) - \bar{\eta} \right] \right\}$$

$$= \sum_r \exp(ik \cdot r) G(r, t),$$

$$G(r, t) = N^{-1} \sum_{r_i} \left\{ \left[ \eta(r_i, t) - \bar{\eta} \right] \left[ \eta(r_i + r, t) - \bar{\eta} \right] \right\},$$

where $r$ and $r_j$ run over the $N$ lattice sites and $k = (2\pi/L)\mu, \mu_0 = 0, \pm 1, \pm 2, \pm L/2, (\alpha = 1, 2, 3)$, specifies the first Brillouin zone. The $\langle >$ represents an ensemble average which could in principle be implemented on the computer by making many independent runs. In practice we used between one and eight independent runs and relied on the spatial averaging given in equation (4) as well as on some 'time averaging' for obtaining reliable data; see end of section.

$S(k, t)$ is periodic in each component with period $2\pi/L$: $S(k = 0, t) = 0$ and

$$N^{-1} \sum_k S(k, t) = (1 - \bar{\eta}^2).$$

The above statements hold exactly for any 'run'. We expect also, that apart from small fluctuations, each run started at $t = 0$ with a random configuration will have

$$S(k, 0) = (1 - \bar{\eta}^2), \quad k \neq 0$$

and that $S(k, t)$ will have cubical symmetry for $t > 0$.

In order to reduce our data to a manageable level as well as to compare with experiments on polycrystalline materials we define an average structure function depending only on the wave number $k = 2\pi \mu/L, \mu = 0, 1, \ldots, \sqrt{3} L/2$,

$$S(k, t) = \sum_{[k]} S(k, t) / \sum_{[k]} 1,$$

where

$$\sum_{[k]}$$

is the sum over all values of $k$ in the first octant, $k_x > 0, x = 1, 2, 3$, such that

$$(2\pi/L)(\mu - 1/2) \leq |k| \leq (2\pi/L)(\mu + 1/2).$$

Note that the average defined in equation (7) is not exactly a spherical average since the points on the boundary and in the interior of the first octant of the Brillouin zone are given equal weights. Thus if $n(k)$ is the actual number of points in the first Brillouin zone contained in the full spherical shell specified in (8), then $n(k)$ is less than $8 n_+(k)$.

$$n_+(k) = \sum_{[k]} 1$$

is 1, 6, 13, 19, 39, 55, 72, 91, 114, 169, 178, 210, 253, 306, 346, ... in successive shells. Using the sum rule equation (5) we should have

$$(1 - \bar{\eta}^2)N^{-1} \sum_{k = 0}^{3L} n(k) S(k, t) = 1.$$
where the $N = 27,000$ lattice was used, comes (in addition) from an average over eight independent runs, i.e., eight evolutions starting with independent, initial random configurations. The data at $P_1 - P_3$ (and at the other phase points mentioned in the text but not included in Fig. 1) comes from one evolution on the $N = 125,000$ lattice.

3. DISCUSSION OF RESULTS

3.1 Qualitative behavior of $S(k, t)$

In our simulations we were able to monitor $S(k, t)$ for 10 shells, $\mu = 1, \ldots, 10$, for the $L = 30$ lattice used at points $P_4$ to $P_7$ and for 14 shells in the $L = 50$ lattice used for $P_1$ to $P_3$.

Figure 2 shows plots of $S(k, t)/(1 - I^2)$ vs $k$ at different times for quenches to the point $P_1$. These plots are qualitatively similar to those obtained at other points $P_i$. At $t = 0$, the system is completely disordered and $S(k, 0)/(1 - I^2) \sim 1$ independent of $k$; see equation (6). The system is then quenched to some low temperature inside the coexistence curve. Thermal processes lead to the migration of A and B atoms, proceeding (in our model) via nearest neighbor exchanges given by the transition probability equation (1), which now drive the system towards equilibrium corresponding to segregation into A-rich and B-rich regions. As these regions grow in size, $S(k, t)$ develops a peak at $k = k_{max}(t) = \pi R(t)$ where $R(t)$ represents some characteristic length in the system at time $t$ following the quench. This length will grow in time as the single phase regions grow to macroscopic sizes so that $k_{max}(t) \rightarrow 0$ as $t \rightarrow \infty$ in a macroscopic system. (In the computer simulations we obviously have $R(t) < \frac{1}{2}L$.) For contrast we also show, in Fig. 3, the qualitatively very different behavior of $S(k, t)$ when the system is quenched to the point $P^*$, $\rho = 0.0613$, $T = 0.78 T_c$ at the coexistence curve.

One striking difference between the different quenches is the time, in units of $\tau^{-1}$, it takes the system to achieve a certain amount of segregation, as reflected in the development of $S(k, t)$. A crude but simple quantitative measure of this is obtained by considering the quantity

$$p(t) = \left[(1 - I^2)N\right]^{-1} \sum_{k=0}^{\infty} n(k)S(k, t) \quad (10)$$
Fig. 4. The quantity $p(t)$ defined in equation (10) is plotted here vs time (note that the horizontal axis is labeled in units of $100\tau^{-1}$) in the case of the quenches to $P_j = 1 - 7$. The corresponding value of $j$ identifies each line which is also identified by different symbols. Below each symbol the values of the corresponding percentage of A-atoms and of the ratio $T/T_c$ respectively, are also shown. Note that the sums defined in equations (10), (14) and (19) actually go from $k = 2\pi/L$ to $k = \frac{x}{2} \leq 0.55 \pi$; we have precisely $X = \frac{8\pi}{15}$ for $L = 30$ (so that the sum includes 8 different values) and $X = \frac{14\pi}{25}$ for $L = 50$ (14 different values).

where $X$ is some cut-off, less or equal to the largest value of $k$ studied in our simulations which was $2\pi/3$ for $L = 30$ and $14\pi/25$ for $L = 50$. At $t = 0$, $p(0)$ is just equal to the fraction of points of the first Brillouin zone which are contained in $|k| < X$. Choosing $X \geq 0.55\pi$ in both cases (dropping the last two shells for $L = 30$) this corresponds to $p(0) \approx 0.1$. As $t$ increases and the weight of $S$ shifts toward smaller values of $k$, $p(t)$ increases by the 'amount' of $S(k, t)$ which has moved into the 'observation' zone defined by the cut-off $X$. Fig. 4 shows $p(t)$ vs $t$ for different quenches. Comparisons of the graphs for points $P_1$ to $P_3$ shows that the speed of the segregation increases, in units of attempted exchanges, with the distance of the quench from the coexistence line. The same is true for the points $P_5$ to $P_7$. This accounts, in the main, for the widely different time lengths to which we ran our simulations (see Table 1). It is clear that close enough to the coexistence line at $T \approx 0.6 T_c$, the relaxation time would become so long that the system would appear, for all practical purposes, to be in a meta-stable state while close to $T_c$ the system will be in the region of critical slowing down. In either case the segregation would not be visible in our simulations.

It should be noted that the relaxation time increases rapidly as one approaches the coexistence line. There is no evidence, however, in our simulations of any abrupt change in the behavior on crossing any of the theoretical spinodal lines indicated in Fig. 1. There are some differences however in the way in which $S(k, t)$ evolves with time in different parts of the coexistence region. This can be seen in Figs 5 and 6 where we plot $S(k, t)/(1 - \bar{n}^2)$ vs $t$ for quenches to different $P_j$'s at $T \approx 0.6 T_c$ for $k = \pi/5$ and $k = 2\pi/5$. It is seen there that for quenches deep in the coexistence region $S(k, t)$ decreases strongly after reaching its maximum value while near the coexistence line it remains approximately constant for the times observed. This behavior is also true for other values of $k > k_{\text{max}}$ and results in 'cross-overs' at large $k$ seen in $S(k, t)$ vs $k$ curves, for $P_4$ in Fig. 2(a) of Ref. [7c] and for $P_5$ in Fig. 2 of Ref. [7a] but not in Fig. 2 here. Such cross-overs have been conjectured [4] to be the hallmark of quenches inside the spinodal curve and our simulations give some evidence of this. The evidence is however not entirely conclusive since the differences may be due to not waiting long enough near the coexistence line and the scatter is relatively large (see e.g. Figs 3-4 in Ref. [7a] corresponding to the quenches to $P_{j'}-P_j$).

3.2 Scaling behavior of $S(k, t)$

An inspection of Fig. 2 shows clearly that the wide...
spacings of possible $k$ values coupled with fluctuations, both due to the small size of our model system, make detailed comparisons between the $S(k, t)$ obtained from our simulations and the smooth structure functions seen in experiments [10–12] or obtained from theory [3–6] very difficult. The latter always deal with macroscopic size systems which corresponds in our model to $N \to \infty$, $k$ becoming a continuous variable and $S(k, t)$ a continuous function of $k$. Let $\mathcal{S}(k, t)$ be the limit of $S(k, t)$ as $N \to \infty$. It is this smooth function about which we would like to obtain information from our computer simulations. Hence it is essential that we look for quantitative features in our computed $S(k, t)$ which will go over smoothly to the macroscopic $\mathcal{S}(k, t)$.

In order to understand the long time behavior of $\mathcal{S}(k, t)$ we note that as $t \to \infty$ we expect that $\mathcal{S}(k, t) \to \mathcal{S}_f(k)$, the equilibrium structure function of a macroscopic system fully segregated into two pure phases. This is given by

$$\mathcal{S}_f(k) = (m_0^2 - \bar{n}^2) \delta(k) + \mathcal{S}_f(k; T)$$

where $\delta(k)$ is the sphericalized Dirac delta function at $k = 0$, $\mathcal{S}_f(k; T)$ is the equilibrium structure function on the coexistence line (by the symmetry of our model system this is the same for both pure phases) and $m_0(T)$ is the spontaneous magnetization. $m_0 = 1 - 2\rho_0 = 2\rho_1 - 1$ (equal to $\bar{n}$ on the coexistence line). As already noted, the system, after quenching, will segregate locally into regions (often referred to as grains, clusters or droplets) of A-rich and B-rich phases and then will evolve further by the growth of these segregated regions (coarsening or Ostwald ripening). We might expect that after some initial time the structure function 'within' the segregated regions will be close to its equilibrium value $\mathcal{S}_f(k; T)$. It seems therefore reasonable to consider the quantity

$$\mathcal{S}_f(k, t) = [\mathcal{S}(k, t) - \mathcal{S}_f(k; T)](m_0^2 - \bar{n}^2)^{-1},$$

which approaches $\delta(k)$ with time, as most relevant for the description of the coarsening process. This is basically the subtraction of 'background' proposed in the third reference of Ref. [5].

We shall therefore consider in our analysis also the analogous quantity for our finite system

$$S_f(k, t) \equiv [S(k, t) - S_f(k; T)](m_0^2 - \bar{n}^2)^{-1}$$

in the hope that it will more clearly reveal the essential features of the coarsening process. The function $S_f(k; T)$ was obtained, for the three different temperatures $T$ considered here, by quenching to points on the coexistence line and waiting for the system to reach equilibrium. At low temperatures there is in fact very little difference between $S$ and $S_f$ for small values of $k$ after some initial times (cf. Figs. 1 and 2; see also Table 2). The difference is therefore likely to be unimportant also experimentally; but it appears to help

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Equilibrium values of the first and second moments of $S_f(k, t)$, and the quantity

$$m \equiv \sum_{k=1}^{\infty} S(k)$$

and $p$ defined in equation (10) corresponding to quenches to the coexistence curve at the temperatures of the simulations reported in this paper.

with the proper normalization of our data at different points $P_i$. It also makes some difference for $P_i$ where $T = 0.89 T_c$ and $S_f(k; T)$ is not so negligible at the relevant $k$ values; see table 2.

A quantitative feature of $S(k, t)$ we looked at in our simulations were the moments $k_n(t) = \langle k^n \rangle$

$$k_n(t) = \frac{\sum_{k=0}^{\infty} k^n S_f(k, t)}{\sum_{k=0}^{\infty} S_f(k, t), \ n = 1, 2}$$

where $k \approx 0.55n$ as explained before (see caption for Fig. 4). These appeared to behave quite smoothly as functions of $t$. We found furthermore that $\langle k^2 \rangle / \langle k \rangle^2$ was essentially independent of $t$; see Table 1. This suggests that our $S_f(k, t)$ with discrete argument $k$ having spacings $2x/L$ might be related for late times to the macroscopic structure function $\mathcal{S}_f(k, t)$ via a smooth scaled function $\mathcal{X}$ such that

$$S_f(k, t) \approx \mathcal{X}(k, t - b(t)) \mathcal{S}_f(k; K(t))$$

where $K(t)$ is some characteristic wave vector in the system and $b(t)$ is a normalizing factor. Now if this is indeed the case, then using the fact that for large systems the number of points in the Brillouin zone contained in a spherical shell of thickness $\Delta k$ approaches $4\pi n^2 \Delta k/(2\pi L)^3$, we have from equations (9) and (12) that

$$\int_B k^2 \mathcal{S}_f(k, t) \, dk = b(t)K^3(t) \int_0^{2\pi} \mathcal{F}(x) \, dx = 2\pi^2 (m_0^2 - \bar{n}^2)^2$$

independent of $t$. The integration on the left side of equation (16) is over the first Brillouin zone and so the $x$ integration is over a cube centered at the origin with sides of length $2\pi/K(t)$. For large $t$, $K(t) \to 0$, and the integral in (16) can be taken over all space. Since $\mathcal{F}(x)$ can be expected to decay quite fast for large $x$, very little error will be made even at quite early times if we set $b(t) = 2\pi^2 K^{-3}(m_0^2 - \bar{n}^2)$ and normalize $\mathcal{F}$ so that

$$\int_0^\infty x^2 \mathcal{F}(x) \, dx = 1.$$
Fig. 7. The scaling function $F(x)$ in the case of 'deep' quenches: the triangles correspond to a quench to $P_d$ and they include times $t \geq 1500 \, \text{x}^{-1}$, the asterisks to $P_3$ and $t \geq 350 \, \text{x}^{-1}$, and the circles to $P_e$ and $t \geq 1000 \, \text{x}^{-1}$ (see also caption for Fig. 8). The dashed line represents the shape of the function $F$ at an earlier time when scaling does not yet hold: it was drawn connecting the discrete values of $F(x; r)$ for $r = 110 \, \text{x}^{-1}$ in the case $P_e$. The dotted line corresponds to a function $F^{-1} = a_1 + a_2 \, x^2$ trying to fit the experimental data for $x > x_{\text{max}}$ the location of the maximum of $F(x)$.

To test this scaling hypothesis and find the smooth $F(x)$ from our simulations we define a function of two variables, $x = k/k_1(t)$ and $t$, by the relation

$$F(x; t) = \frac{L}{\pi} \frac{k_1^2(t) S_1(kx, t)}{\sum_{k=0}^\infty k^2 S_1(k, t)}$$  \hspace{1cm} (18)

and then see whether for late times $F(x; t) \approx F(x)$ a smooth function of $x$ independent of $t$. The normalization (18) is chosen so that

$$\sum_{j=1}^{\infty} (\delta j)^2 F(j\delta; t) \delta = 1$$  \hspace{1cm} (19)

independent of $t$ for $\delta = 2\pi/k_1(t)L$. This means that if scaling is really valid then for large $N$, when equation (19) approximates the corresponding integral, it will satisfy equation (17). (Note that equation (18) is defined slightly differently, using $S_1$ rather than $S$ and multiplying by $L/\pi$, than the corresponding function for $P_2$ and $P_3$ in Ref. [8]).

The values of $F(x; t) \approx F(x)$ independent of $t$, obtained from our simulations for large times are shown in Figs 7–9 for 'deep', 'intermediate' and 'shallow' quenches. While these curves are all similar, the 'experimental' scatter within each group is signifi-
Fig. 8. The function \( F(x; t) \) defined in equation (18) is plotted here versus \( x = k/k_{s}(t) \) in the case of the ('intermediate') quench to \( P_{2} \). Every symbol (0, 1, 2, 3, ...) in the graph corresponds to a different value of the time: the first one (zero) is for \( t \approx 2500 \alpha^{-1} \), the time increasing up to \( t \approx 7300 \alpha^{-1} \) which is represented by crosses. All the values of \( F(x; t) \) in that time interval seem to lie on a common curve at different values of \( x \) (see, however, Fig. 12). The dashed line was drawn connecting the values of \( F(x; t) \) at \( t = 228 \alpha^{-1} \). The dotted line corresponds to a fit \( F^{-1} = a_{1} + a_{2} x^{4} \) to the 'tail' \( x > x_{\text{max}} \) of \( F(x) \).

Figures 7-9 also show the function \( F(x; t) \) at some earlier times as indicated. We have also included in those figures a fit of the form \( (a_{1} + a_{2} x^{4})^{-1} \) to the 'tail', \( x > x_{\text{max}} \), of the scaling function \( F(x) \) which seems to be suggested by Ref. [9]. While this is approximately the behavior of our data for \( x \geq x_{\text{max}} \), the location of the maximum of \( F(x) \), the data clearly deviates from the \( x^{-4} \) behavior at larger \( x \) values. This is shown in Fig. 10 where we have plotted \( F^{-1} \), \( x > x_{\text{max}} \) versus \( x^{4} \) in the case of the quench to \( P_{2} \).

The graphs in Fig. 10 also show that \( F(x; t) \) has not yet reached the asymptotic function \( F(x) \) at large values of \( x \) in our simulations so this may be a part of the reason for the observed deviations from the \( x^{-4} \) behavior.

As already mentioned it is a difficult task to extract from our simulations precise and reliable information.
same as Fig. 7 in the case of (‘shallow’) quenches to $P_1$, (triangles; all the data $r > 6800 \text{a}^{-1}$ is included in this case), $P_2$ (asterisks, $r \approx 4000 \text{a}^{-1}$) and $P_3$ (circles, $r \approx 1000 \text{a}^{-1}$). The dashed line is for $P_1$ and $r = 209 \text{a}^{-1}$.

Fig. 10. The inverse of the function $F(x; r)$ defined in equation (18) is plotted here, for $x > x_{\text{max}}$ vs $x^4$ in the case of the quench to $P_4$. The full ovals correspond to $t = 1519 \text{a}^{-1}$, the empty ovals to $t = 1926 \text{a}^{-1}$, the full circles to $t = 2344 \text{a}^{-1}$, and the empty circles to $t = 3140 \text{a}^{-1}$. The dashed straight line corresponds to the dotted line in Fig. 7. It is seen here that $F(x; t) \approx F(x) \sim x^4$ describes approximately our data at values of $x \leq x_{\text{max}}$, while at larger values of $x$, where scaling does not yet hold in our simulations, $F(x; t)$ is time dependent.

Fig. 10. The inverse of the function $F(x; t)$ defined in equation (18) is plotted here, for $x > x_{\text{max}}$ vs $x^4$ in the case of the quench to $P_4$. The full ovals correspond to $t = 1519 \text{a}^{-1}$, the empty ovals to $t = 1926 \text{a}^{-1}$, the full circles to $t = 2344 \text{a}^{-1}$, and the empty circles to $t = 3140 \text{a}^{-1}$. The dashed straight line corresponds to the dotted line in Fig. 7. It is seen here that $F(x; t) \approx F(x) \sim x^4$ describes approximately our data at values of $x \leq x_{\text{max}}$, while at larger values of $x$, where scaling does not yet hold in our simulations, $F(x; t)$ is time dependent.

3.3 Qualitative properties of the cluster distribution

We define a cluster in our model system as a group of A atoms linked together by nearest-neighbor bonds. This is expected to correspond, approximately, at low concentrations of the minority component, to the grains observed by microscopy in real materials; it is the latter which the conventional nucleation theories have in mind and about which we would like to obtain information from our simulations [2, 7, 16]. The computer was programmed to record periodically the ‘sizes’ and ‘energies’ (i.e. the surface areas defined as the total number of A–B bonds incident on the cluster) of all the clusters in the current configuration. The size of a cluster, $l$, is defined as the number of A atoms in the cluster.

A qualitative description of the (early) time evolution of the cluster distribution $n(l, t)$, the total number of clusters having size $l$, is given below.

- **Initial stage** ($t \leq t_{\text{eq}}$): The cluster distribution $n(l, t)$ is approximately constant for all $l$.

- **Growth stage** ($t_{\text{eq}} < t < t_{\text{max}}$): The cluster distribution $n(l, t)$ increases rapidly with increasing $l$.

- **Steady state** ($t > t_{\text{max}}$): The cluster distribution $n(l, t)$ reaches a maximum value and then plateaus.
Values of the adjustable parameters for two different fits to $k_1$: first assuming a simple power law (here all the data except the very early one is included in the fit), and then assuming a linear behavior of $k_1^{-3}$ with time (using only data for $t \geq t_0$). Here $t_0$ is the approximate time at which we observed the onset of the dynamical scaling of the structure function according to equation (15).

of clusters of size $l$, has been reported elsewhere [7e] for the case $T \approx 0.6 T_c$. For values of $\rho$ very close to $\rho_v$, the corresponding saturated vapor density, $n(l,t)$ rapidly settles down to a stationary value characteristic of a metastable state. At $\rho \approx 0.05 - 0.075$ the distribution of 'small' clusters still approaches rapidly a quasi-stationary distribution characteristic of metastable states, but there is now a measurable rate at which larger clusters develop (i.e., a finite nucleation rate). A detailed quantitative analysis of this behavior, at $\rho = 0.075$, using ideas from the Becker–Döring and Lifshitz–Slyozov nucleation theory is given in Refs. [7f] and [16]. As the density (and the supersaturation) is increased further, $\rho \approx 0.1$ at $0.6 T_c$, we observe the early appearance of relatively large loose clusters ($l > 50$) coexisting with very small clusters of size one to ten or so. The number of $A$ atoms and their relative distribution in the small clusters is close to what is observed in the $A$-poor (gas) phase equilibrium state. The system then shows a slow process of aggregation of the larger clusters into still larger compact clusters which will finally lead to a fully segregated $A$-rich (liquid) phase [5, 16]. When the density of $A$ atoms in the model system is increased further, the system undergoes percolation, i.e., the appearance of 'infinite' size clusters. This happens in our model system (simple cubic lattice) at approximately [17] $\rho = 0.31$ for atoms placed entirely randomly on the lattice (i.e., $T = \infty$), and was also observed [7a, 7c] at $P_4 - P_1$. To our knowledge this phenomena has not been investigated so far in real alloys.

A detailed analysis of the cluster distribution $n(l,t)$ at low densities will be reported elsewhere [16] on the basis of a kinetic theoretical model of the Becker–Döring type. We shall only report here some gross features of $n(l,t)$ as one varies $\rho$ at $T \approx 0.6 T_c$, namely on the time evolution of the cluster mean size defined as

$$ l_i(t) = \sum_{l > l_i} l n(l,t) \bigg/ \sum_{l > l_i} l^{-1} n(l,t), \quad i = 1, 2. \quad \text{(20)} $$

The cut-off $l_i$ is intended as a (somewhat arbitrary) separation between 'small' and large clusters. The second of these definitions (note that the notation differs from that for $k_1$ and $k_2$ in equation (14)) gives more weight to large $l$ and diminishes to some extent the relevance of the choice $l_i$. We present in Fig. 11 a plot of $l_3(t)$ vs time for $l_i = 20$ (similar results are obtained for $l_i = 50$) for quenches to $P_1 - P_3$. There is clearly a difficulty in analysing these data on the assumption of a simple power law [5] behavior with time as suggested by the Lifshitz–Slyozov theory [2]. This may however be due to the fluctuations in our single run.

![Fig. 11. The mean size $l_3(t)$, as defined in equation (20) with $l_i = 20$, is plotted here vs time (in units of $a^{-1}$) for the cases $P_1$ (crosses), $P_2$ (triangles) and $P_3$ (circles).](image-url)
We find that the ratio \( \frac{\langle k^2 \rangle}{\langle k \rangle^2} = l_2/l_1 \), which gives information about the shape of the cluster distribution \( n(k, t) \), is far from constant even for late times—unlike the corresponding quantity \( \frac{\langle k^2 \rangle}{\langle k \rangle^2} \) obtained from the structure function \( S(k, t) \). Moreover, even when the cluster distribution of the system undergoes percolation at high temperatures \( (T > T_c) \), there is no corresponding change in the equilibrium structure function \( S(k, t) \) [7, 17]. Thus it seems that attention must be paid not only to the size but also to the 'shapes', composition and distribution of the clusters and other properties of the system. Note, however, that it is possible to make other definition of 'clusters' to avoid the trouble with the percolation of clusters [5].

We finally mention that the theoretical ideas about scaling with time of \( S(k, t) \) (section 2.2) are based on the assumption [5, 6] that for late times after quenching (to temperatures far enough from \( T_c \)) the mean 'diameter' \( R \) of the grains is much larger than the (thermal) correlation length. Thus \( R \) is the only relevant length scale for fluctuations in these circumstances, and the structure function should be scaled accordingly. Moreover when \( p \) is small and the temperature is low one may assume nearly pure grains of the minority (A) phase so that \( R^2(t) \) is approximately proportional to \( l_i(t) \) and one is lead to the prediction \( k_i(t) \sim \frac{1}{l_i(t)} \). This is confirmed by Fig. 12 where we have plotted \( k_i^{-2}(t) \) versus \( l_i(t) \).

3.4 Comparison with experiment

3.4.1. Preliminary remarks. The model used in our computations certainly involves a great over-simplification of the behavior of real alloys where the processes we are interested in are greatly influenced by elastic distortions, grain boundaries, vacancies and other competing phenomena. The behavior of the model can thus only be compared with that of real materials in highly idealized conditions. Despite this, previous analysis have shown that our results are frequently very similar to experimental observations [7d]. In order to make comparison with experiments, however, care must be paid to the relation between the units and other characteristics in our model and those corresponding to real alloys. For instance, as described before, the basic unit of time \( \sigma^{-1} \) for the model evolution may correspond in real alloys to times which vary between very broad limits: e.g. from \( \sigma^{-1} \sim 50 \text{s} \) at 0.6 \( T_c \) to \( 10^{-4} \text{s} \) at 0.8 \( T_c \) in the case of aluminum alloys. Thus our simulations at 0.6 \( T_c \) can be compared with experimental observations on real alloys (where the system relaxation is typically followed for some hours) while one has to be cautious at higher temperatures, say 0.8 \( T_c \).

We note further that the typical resolution of X-ray cameras is in the range [21] of 10-1000 Å and that the inhomogeneities measured by experimentalists, e.g. the so-called 'Guinier-Preston zones', have typically linear dimensions in the range 15-200 Å. Thus, assuming \( a_0 = 3 \text{Å} \) the smallest grains measured in typical experiments contain between 30 and 150 atoms, and the largest ones about \( 3 \times 10^5 \) atoms. This may influence the comparison between experiments and simulations given the cut-off \( l_i \) in equation (20) and given that the largest clusters observed in our simulations at \( P_1-P_3 \) contain typically no more than 800 A-atoms [23].

Other causes of differences between the behavior of our model and experimental observations can be found in the quenching rate which is finite in real experiments but infinite in our model system. We have checked that the quenching process seems to influence considerably the subsequent evolution. For instance we have been able to reproduce qualitatively the 'untypical' observations by Allen et al. [19], corresponding to room temperature aging of Al-Zn, \( \rho = 0.12 \), quenched into iced water \((T \approx 0.44 T_c)\) from \( T = 0.93 T_c \). By simulating a similar double quenching of our model system the influence of the quenching process has also been reported in the case of some liquid mixtures [20].

3.4.2 Comparisons. We have analysed the data reported by Singhal, Herman and Kostorz [10] corresponding to the Au-60 at.\% Pt alloy, in particular their Fig. 3 coming from an experiment in which the sample was solutionized at around 1543 K and then quenched into iced brine; the aging at around 823 K was observed by neutron scattering during 900 s. The composition of the sample lies at the center of the miscibility gap, and \( T = 0.6 T_c \) so that the experiment may be compared with our simulations at \( P_3 \) and perhaps at \( P_6 \). Moreover, those authors estimate [10] the interdiffusion coefficient as being of order...
Fig. 13. We compare in this figure data from the computer simulation (empty symbols) with the experimental data in Fig. 3 from Ref. [10] (full symbols) corresponding to Au-60 at.
% Pt alloy quenched to $T = 0.6 T_c$. The full circles are for $t = 900$ s and the stars for $t = 360$ s, both lying on the same curve except perhaps for $x \geq 1.8$. The broken line 1 is for $t = 0$ (the initial sample was already decomposed to some extent), and the broken line 2 is for $t = 30$ s, in both cases scaling does not yet hold. The empty circles correspond to our simulation at $P_4$ while the empty squares are for $P_3$ (see Fig. 7). Only the vertical scale in Fig. 7 needed to be changed in order to obtain the present fit.

Fig. 14. The data in Fig. 9 is compared with experimental data (Ref. [11]) on an Al-15 at.
% Zn alloy quenched to 90°C (solid line) and to 110°C (dashed line) (both $T \simeq 0.6 T_c$). The vertical and horizontal scales in Fig. 9 where changed to obtain the present fit; a fairly good fit can also be obtained, however, by changing only the vertical scale in Fig. 9.

We have found a similar agreement between our scaling function $F(x, t)$ and the one reported by Guyot et al. [11] corresponding to a sample of Al-15 at.
% Zn quenched to $T \simeq 0.6 T_c$; this is shown in Fig. 14.

Finally, recent observations on binary fluid mixtures [12, 20, 22] report a behavior which is also
qualitatively similar to the one shown by our model system (note, however, when making comparisons that the diffusion coefficient is much larger for fluids, $10^{-4}$--$10^{-6}$ cm$^2$/s, than for alloys).

In particular Chou and Goldburg [12] find a scaling behavior of $S(k, t)$ with a function $F(x)$ which looks quite similar to our function.

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