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SELF-CORRELATION FUNCTIONS

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FIRST ORDER PHASE TRANSFORMATIONS:

SCALING RELATIONS FOR GRAIN SELF-CORRELATION FUNCTIONS

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INTRODUCTION

At high pressure many alkali halides transform from the NaCl (B1) structure to the CsCl (B2) structure. We have recently studied this transformation in polycrystalline RbI, which transforms at a critical pressure, $P_c = 3.5$ kbar.¹ By observing the time development of the neutron diffraction pattern after sudden increase of hydrostatic pressure from $P < P_c$ to $P > P_c$ we directly deduced $X(t)$, the fraction of the sample converted from metastable to stable phase, as a function of time. We showed that $X(t)$ taken at different P could be approximately scaled onto a universal growth curve by introducing an adjustable characteristic time $\tau(P)$ for each curve, such that

$$X(t, P) = x(t/\tau(P)). \quad (1)$$

This is demonstrated in Fig. 1.

We further noted that the resulting growth curve was very similar to one predicted by a simple model of nucleation and growth in which, when the pressure is instantaneously raised above P_c , infinitesimal grains of stable phase nucleate randomly within the sample at a constant rate, Γ , per unit volume. Although $\Gamma(P)$ is time independent, the

Fig. 1. The scaled growth curves, $(1-X(t))$, for RbI plotted vs. $t/\tau(P)$. Except for the highest pressure (Curve 6), they are well represented by the Kolmogorov model (solid line).

nucleation rate decreases with time in proportion to the fraction of metastable phase remaining, $(1-X(t))$. Once formed, a grain grows isotropically with constant domain-wall velocity, $v(P)$, until it is impeded by impinging on neighboring grains. An explicit expression for $X(t)$ for this model was first given by Kolmogorov,²

$$X(t) = 1 - \exp\left[-\Gamma \int_0^t V(t') dt'\right] \quad (2)$$

where $V(t')$ is the volume occupied by a hypothetical "free" grain (one that has not yet been impeded by a neighboring grain) at a time t' after nucleation. $X(t)$ given by Eq. 2 for spatial dimension $d = 3$ is shown in Fig. 1 and demonstrates a remarkable similarity to our data.

The success of the Kolmogorov model in fitting $X(t)$ suggests that comparisons of model predictions with other experimental observables be made on the system. For example, by a trivial (in principle) extension of the neutron diffraction techniques described above, one might determine the broadening of the powder diffraction peaks due to finite grain size as a function of time throughout growth. This particle size broadening is related by Fourier transformation to the grain autocorrelation function, $G_S(r,t)$, which measures the ensemble average of the overlap of grains with themselves upon translation of the grain pattern by an amount r . A quantity much studied in connection with heterogeneous reaction kinetics is $G(r,t)$, which measures the inter- as well as intra-grain correlations.³ It is often found that a scaling relation of the form

$$G(r,t) = F(r/R(t)) \quad (3)$$

is at least approximately valid. Here $R(t)$ is a measure of the dominant length scale of the evolving spatial correlations. In early stages of growth $G(r,t)$ and $G_S(r,t)$ are similar, but whereas $G(r,t+\infty)$ approaches a constant (corresponding to complete transformation to the stable phase), $G_S(r,t+\infty)$ has structure which carries information about asymptotic grain size distribution. (We assume that each grain retains its unique identity rather than merging with neighbors on contact.) At some intermediate time intergrain separation and grain size are comparable, a situation which poses complications for scaling theories for $G_S(r,t)$, since it is not clear that there is a single dominant length upon which to scale.

Fig. 2. Diagrammatic representation of domain nucleation and growth for $d = 1$. A grain is formed at P and its ends are progressively pinned at Q and R. The diagonal lines have the slope $r = vt$.

In the following sections we present some results of a study of the scaling properties of $G_s(r,t)$ for the Kolmogorov model for $d=1$ and $d=2$. Although the model is highly idealized, it is perhaps the simplest conceivable one which obeys correlation function scaling in early stages of growth and undergoes nontrivial saturation due to volume fraction effects in the late stages. A paper⁴ describing the work upon which these results are based is in progress.

AUTOCORRELATION FUNCTION SCALING FOR $d=1$.

Although it is possible that the results have practical applications for linear polymers, $d=1$ is considered here because it is possible to establish some exact results, in contrast to the computer simulations for $d=2$ considered in the following Section. $d=1$ is exceptional in that there are three distinct grain types with pinning index $\mu=0, 1$, or 2 , corresponding to the number of boundaries of the grain pinned by impingement on neighboring grains. Each grain grows with velocity $v_\mu = (2-\mu)v$. Each newly formed grain progresses from unpinned to fully pinned in a sequence shown diagrammatically in Fig. 2. Through a reasoning process similar to that used by Kolmogorov² to derive $X(t)$, it is possible to show⁴ that the probability, $P_0(t_0)$, that a grain will nucleate somewhere along a unit length between t_0 and $t_0 + dt$ is

$$P_0(t_0) = \Gamma \exp(-\Gamma A_0), \quad (4)$$

where A_0 is the area shown in Fig. 2. Similarly the probability that a grain will first encounter another grain in dt_1 about t_1 can be shown to be

$$P_1(t_1) = \Gamma \frac{dA_1}{dt} \exp(-\Gamma A_1), \quad (5)$$

and the probability that a partially pinned grain will encounter a second grain in dt_2 about t_2 is

$$P_2(t_2) = \Gamma \frac{dA_2}{dt} \exp(-\Gamma A_2). \quad (6)$$

Eqs. (4) - (6) provide the basis of a complete description of the time evolution of the $d = 1$ Kolmogorov model.⁴ In particular, the grain auto-correlation function is given by

$$G_s(r,t) = \int_r^{2vt} (l-r)N(l,t)dl \quad r < 2vt \quad (7)$$

where $N(l,t)$ is the total number of grains per unit length at time t with a length between l and $l+dl$. It is convenient to introduce a normalization such that

$$\tilde{G}_s(r,t) = G_s(r,t)/G_s(r=0,t),$$

where $G_s(r=0,t)=1-X(t)$, is the volume fraction of the stable phase. In early stages of growth, $t \ll (\Gamma v)^{-1/2}$, grains propagate freely and since $N(l,t=0) = \Gamma/2v$, Eq. 7 is easily evaluated.

$$\begin{aligned} G_s(r,t) &= \left(1 - \frac{r}{R(t)}\right)^2 & r < R(t) \\ &= 0 & r > R(t) \end{aligned} \quad (8)$$

showing that $\tilde{G}_S(r,t)$ satisfies scaling at small t , with $R(t) = 2vt$. If scaling were exact at all t , it would be possible to find an $R(t)$ for each t such that eq. (8) was satisfied. Fig. 3 shows the values of $R(t)$ which result from a least square fit to exact values of $G_S(r,t)$ determined numerically by the procedure sketched above. Fig. 4 shows $G_S(r,t)$ for various t plotted vs. the resulting values of $r/R(t)$.

Fig. 3. The scaling length, $R(t)$, for $d=1$ obtained by least square fitting of $G_S(r,t)$ to eq. 8. The time is in natural units, $z = (\Gamma v)^{1/2} t$.

Fig. 4. $G_S(r,t)$ for $d=1$ and various values of t (in natural units) vs. the scaling parameter $x=r/R(t)$. The line is the scaling prediction (Eq. 8).

Scaling predicts a single universal curve. This is not the case, as can be seen most readily by observing that eq. 8 predicts that $G_S(r,t) = 0$ for $r > R(t)$, whereas in reality it remains small but finite for $R(t) < r < 2vt$. Nevertheless eq. 8 does provide a very reasonable approximation over the entire range of t .

AUTOCORRELATION FUNCTION SCALING FOR $d=2$.

Lacking obvious means to generalize the exact $d=1$ results to higher dimensions, we performed a numerical simulation on a discrete 20×20 lattice with periodic boundary conditions. The procedure, carried out on an IBM 4860 computer with a 4.77 MHz clock cycle, consisted of iterating to completion a two-step cycle. In the nucleation step random sites were chosen as potential nuclei and discarded only if occupied (i.e. transformed in a previous cycle). In the growth step each grain, including the newly selected point nuclei of the previous cycle, was

expanded into any unoccupied nearest neighbor sites. All results were averaged over an ensemble of 16 independent trials.

For $d=2$ $G_s(r,t)$ is an anisotropic function of the vector r . It is simple to verify that an exact scaling form exists for small t . For the limiting cases of r along an edge or a diagonal of the square array, the explicit forms for $t \ll (\Gamma v^2)^{-1/3}$ and $r < R(t)$ are

$$\tilde{G}_s(r,t) = 1 - \frac{3}{2} \left(\frac{r}{R(t)_{\text{edge}}} \right) + \frac{1}{2} \left(\frac{r}{R(t)_{\text{edge}}} \right)^3, \quad (9)$$

$$\tilde{G}_s(r,t)_{\text{diag}} = \left(1 - \frac{r}{R(t)_{\text{diag}}} \right)^3. \quad (10)$$

As for $d=1$, the values of $\tilde{G}_s(r,t)$ derived from the simulation were fitted to the scaling forms suggested above by least squares adjustment of $R(t)$. The values of $R(t)$ so obtained are shown in Fig. 5, and the values of $G_s(r,t)$ plotted vs. the appropriate scale variable $r/R(t)$ are shown in Fig. 6. It is again clear that these simple scaling forms are quantitatively useful approximations, but they cannot be made exact in late stages of growth.

Fig. 5a. Scaling length, $R(t)_{\text{edge}}$, obtained by fitting $\tilde{G}_s(r,t)$ for $d=2$ to Eq. (9). The time is in natural units, $z = (\Gamma v^2)^{1/3} t$.

Fig. 5b. Scaling length, $R(t)_{\text{diag}}$, obtained by fitting $G_s(r,t)$ for $d=2$ to Eq. (10).

Fig. 6. $\tilde{G}_s(r,t)$ for $d=2$ and various t (natural units) plotted vs. the scaling parameter $x=r/R(t)$. The lines are the scaling predictions (Eq. (9)-(10)).

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