

## Observation of Dynamical Scaling in "Spinodal Decomposition" in Two Dimensions

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We present results of a helium atom beam scattering experiment on spinodal decomposition in two dimensions and for deep temperature quenches. A system with conserved order parameter and equal volume fractions of two phases is realized by deposition of 0.5 monolayer Cu on a Cu(100) surface. We find that the morphology evolves in a self-similar fashion. Growth exponents close to  $\frac{1}{4}$  are in accord with ideas of corrections to the Lifshitz-Slyozov growth law due to excess mass transport along domain boundaries in the temperature and time range covered by our experiment.

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Ordering and growth processes are very common and general phenomena in nature [1,2]. However, despite this diversity, some ideas seem to be unifying and fundamental. Dynamical scaling is expected to describe the time evolution of the morphology: The growth pattern can be characterized by a single length scale  $L(t)$ , and at a given time the pattern has an appearance similar to an appropriately magnified portion of it at an earlier time. Often the time dependence of this characteristic length  $L(t)$  obeys an algebraic law,  $L(t) = A(T)t^x$ , where  $A$  is the growth rate constant, depending on temperature  $T$ , and  $x$  the growth exponent. In analogy to equilibrium phase transitions, the value of this exponent is believed to characterize certain universality classes. There are suggestions [2] that in fact only two universality classes exist, depending only on whether the order parameter is a conserved or a nonconserved quantity.

However, especially the case of conserved order parameter, which is experimentally represented for example by a system undergoing phase separation, is not completely settled. Lifshitz and Slyozov (LS) [3] examined a two-component system with widely spaced domains of one phase growing in a matrix of the second phase. Under these conditions, growth is mediated by evaporation of monomers from small domains, long-range diffusion through the matrix, and subsequent condensation onto large domains. In that case, the theory reveals an algebraic growth law with  $x = 1/3$ . It is *a priori* not clear if this result still holds in a situation for which the volume fractions of the two phases are comparable, as is for example experimentally realized in spinodal decomposition. A near-critical quench usually results in a morphology where one has not isolated domains, but instead an interconnected and interpenetrating domain structure [1,2]. This opens the possibility for additional activated ordering mechanisms, for example, diffusion along domain boundaries. Theories and computer simulations both give contradicting results in two-dimensional (2D) systems.

Early Monte Carlo (MC) studies [4] of spinodal decomposition within the Ising model gave significantly lower power-law exponents, between 0.17 and 0.25. Langevin theories reveal either the asymptotic value  $1/4$

[5] or  $1/3$  [6]. Mazenko, Valls, and Zhang [7] predicted originally a logarithmic growth law, which has subsequently been withdrawn in favor of an algebraic law with the exponent  $1/3$ . However, the logarithmic growth law may apply for very deep temperature quenches. Huse [8] recently generalized the phenomenological LS theory for arbitrary volume fractions. He found that the influence of diffusion along interfaces leads to a significantly lower "global" exponent, when the evolution of the characteristic length is evaluated over a limited time range with an algebraic law. In contrast, the "local" exponent,  $d[\ln L(T, t)]/d(\ln t)$ , was shown to converge asymptotically against  $1/3$  for very large  $L$ . These predictions have very recently been supported by extensive MC [9] and MC renormalization-group simulations [10]. However, these studies reveal in some cases very long  $x = 1/4$  transients as well. Moreover, while in some of the computer studies spatial self-similarity has been observed [8-10], others show scaling only when a growth regime with the exponent  $1/3$  is established [11].

To our knowledge, effort on this subject for 2D systems has been devoted exclusively to theoretical studies or computer simulations. In this Letter, we present the results of a helium atom beam diffraction experiment on spinodal decomposition in 2D. Within the spirit of universality, the nature of the initial state is believed to be irrelevant for the long-time behavior of the system. In our experiment, a system in 2D with conserved order parameter, equal volume fractions of the two phases, and an interconnected domain structure is realized by adsorbing 0.5 monolayer (ML) Cu on a Cu(100) surface at low temperature. We find that the morphology of the surface evolves indeed in a self-similar fashion. The global algebraic growth exponent is confined between 0.12 and 0.25. Moreover, the ordering kinetics is governed by an activated process with a characteristic energy of 0.35 eV. These findings suggest that in the temperature and time range covered by our experiment the ordering process is largely controlled by diffusion of material along domain boundaries.

The experiments were performed in a Campargue type source helium atom beam spectrometer at a base pressure

of  $10^{-10}$  Torr. The average residual terrace length of our sample is estimated from the broadening of the specular peak in the antiphase condition to be at least 700 Å. Cu was evaporated from a high-purity, desulfurized Cu disk, radiatively heated by a W filament. The coverage has been calibrated with an estimated accuracy of better than 10% from diffraction peak oscillations in the layer-by-layer growth regime at high deposition temperatures [12].

The initial state is prepared by depositing 0.5 ML of Cu adatoms onto the Cu(100) surface at 100 K. At this temperature, thermally activated diffusion is virtually zero [13]. Hence, atoms are, at a coverage of 0.5 ML, on the average  $\langle L \rangle = 1/0.5^{1/2} = 1.4$  lattice constants apart, resulting in a structure which consists of a network of interpenetrating and interconnected domains [14]. The surface is subsequently rapidly raised to and held at a higher temperature, and the kinetics of domain growth is monitored by measuring diffraction profiles as time evolves. Most measurements were performed from about 300 sec after the upquench in temperature to about 10000 sec thereafter and repeated for six different temperatures between 212 and 266 K. Within this temperature range, ordering is fast enough to be observed reliably, but on the other hand slow enough in order to get information on the surface morphology from the diffraction patterns without invoking delicate deconvolution procedures.

The initial state at 100 K is characterized by a diffraction pattern which shows only a low-intensity specular peak, pointing to very short-range domain pair correlations [15]. After raising the temperature, additional structures in the diffraction pattern rapidly appear. Figure 1 shows typical angular distributions for upquenches to 235 K after annealing for 500 and 8000 sec. These structures move towards the specular, become narrower,

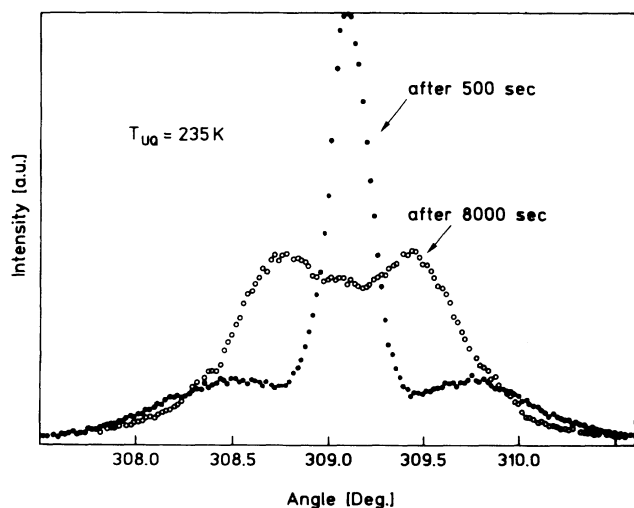


FIG. 1. Representative angular distributions, here for an upquench to  $T=235$  K. In order to determine the position of the maxima accurately, the data have been fitted with three Gaussians.

and increase in intensity as time evolves. The structure factor  $S(Q,t)$  reflects the time-dependent domain pair correlation function [8,9]. The position  $Q_{\max}$ , for which the structure factor has a maximum, is an appropriate measure of  $L(t)$  [9]. Dynamical scaling implies that, although the characteristic length changes with time, the functional form of domain pair correlations does not. This can be expressed [1,2] as

$$S(Q,t) = [Q_{\max}(t)]^{-d} F(Q/Q_{\max}(t)), \quad (1)$$

where  $d$  is the dimensionality of the system (in this case  $d=2$ ), and  $F$  a time-independent master function. In order to check for dynamical scaling, we have plotted our data according to Eq. (1). Figure 2 shows a representative example for  $T=246$  K. It is seen that dynamical scaling is followed to a very good approximation. Similar behavior is observed for other upquench temperatures, except at the highest. It is likely that there the influence of the instrument, not taken into account in the present analysis, becomes noticeable and leads to an apparent deviation from scaling.

This dynamical scaling is observed although the global growth exponent is found to be far from the LS value. Figure 3 shows the evolution of the characteristic length  $L$  as a function of time. Assuming an algebraic growth law, we obtain global growth exponents confined between 0.12 and 0.25. Except at the highest temperature exponents for the intensity are double those for the characteristic length, which is a consequence of scaling. The power-law fits are quite acceptable, although not perfect. Particularly pronounced at 222 K, the data points bend upwards. The observed deviations imply an increasing local exponent, and consequently, discard a logarithmic growth law.

Low global exponents and increasing local exponents have been found in MC simulations as well. An explanation for this behavior has been proposed in a seminal paper by Huse [8]. He argued that mass transport along

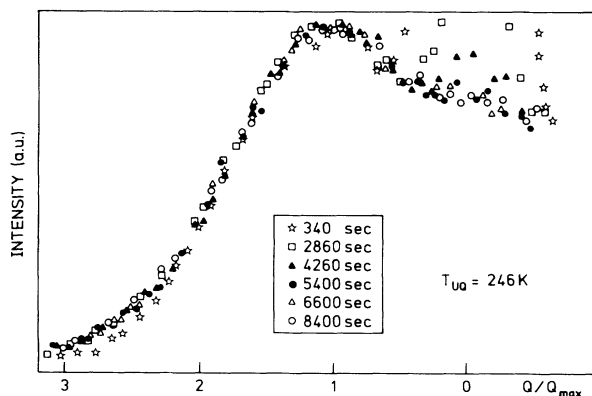


FIG. 2. Demonstration of scaling. The specular peak has not been removed from the data set. Therefore, intensity is not zero at  $Q/Q_{\max}=0$  and apparent deviations from scaling are observed in this region.

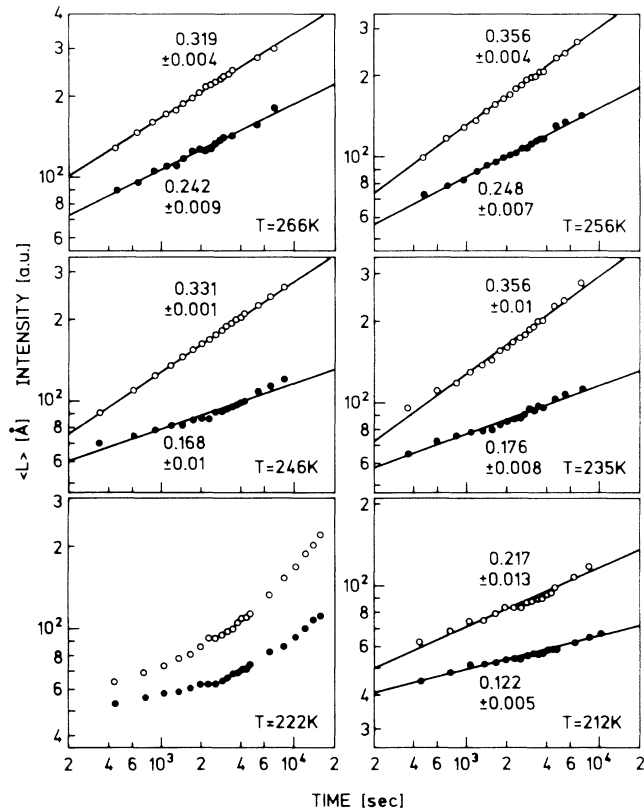


FIG. 3. Variation of the characteristic length  $L$  (●) and of the peak intensity (○) vs time for different upquench temperatures. Lines are fits with an algebraic growth law. The numbers indicate power-law exponents.

domain boundaries, which contributes in parallel with the evaporation-condensation (EC) mechanism to ordering, leads to corrections to the asymptotic LS growth law. The relative rate of these ordering mechanisms must depend on the length of the domain boundaries. Therefore, the correction can be expressed as a time-dependent domain size correction to the LS growth exponent, viz., [8],  $x = \frac{1}{3} [1 - L_0(T)/L(T, t)]$ .  $L_0$  depends on temperature roughly as  $\exp(\Delta E/k_B T)$ , where  $\Delta E$  is the difference in activation energies of both mechanisms. Consequently,  $L_0$  is expected to be very much smaller than  $L$  for quenches to high temperatures.

A quantitative comparison of measured exponents and the characteristic length  $L$  according to Huse's formula reveals that  $L_0$  is smaller than  $L$ , but of the same order of magnitude in our case. This suggests that in our experiment the ordering process is dominated by mass transport along domain boundaries. In fact, if we connect the energetics of the Cu(100) surface [16,17] to those of the 2D Ising model, we find that our experiment corresponds to very deep quenches confined between about  $0.1T_c$  and  $0.3T_c$ . Unfortunately, MC simulations with sufficiently good statistics have not been performed for this temperature range. However, it is likely that Huse's correction is

not valid when  $L_0$  becomes arbitrarily large (otherwise the exponent would become negative). Based on dimensional arguments, Mullins [18] predicts that interface diffusion by itself leads to an asymptotic algebraic growth law with the exponent  $1/4$ . This value is in good agreement with the experimentally observed exponents at the highest temperatures. The observed lower exponents at lower temperatures should therefore presumably be interpreted as corrections to this growth law due to a hitherto unidentified kinetic process.

This hypothesis is supported by experiments, in which we have adsorbed only 0.3 and 0.1 ML Cu, respectively, followed by upquenches to 252 K. If the EC mechanism were operative, we should approach, within the spirit of the LS theory, the exponent  $1/3$ . Instead, we find for 0.3 ML,  $x=0.08$ , while for 0.1 ML, growth effectively stops after a few minutes. This demonstrates that a fully connected domain structure is essential for ordering in this temperature and time range.

In general, we expect the growth law with the exponent  $1/4$  to hold only if EC is in fact strictly zero. But because both mechanisms, boundary diffusion and EC, are activated processes, the  $x=1/3$  growth law will eventually always catch up at only sufficiently long times. However, from a realistic experimental point of view, i.e., in view of the limited measuring time, the exponent  $1/4$  obtained in this particular situation of interconnected domains and for very deep quenches might be regarded as asymptotic.

It is also possible to extract information on the growth rate activation energy and hence on the process that controls growth from our data. By inspecting the growth curves at different temperatures, we have determined the various times  $\tau(T)$  needed for the characteristic length to reach a fixed value  $L_f$  [19]. Since  $L_f$  is the same for all temperatures, it follows that the average diffusional activation energy can be obtained via  $D(T) = \text{const}/\tau(T)$  [20]. This analysis gives  $E = 0.35 \pm 0.06$  eV. Ordering involves formation and migration of mobile species. The activation energy for migration of Cu adatoms on terraces has recently been determined to be 0.28 eV [13], while evaporation of kink atoms from domains onto terraces has been calculated within effective medium theory to be 0.55 eV [21]. On the other hand, the kink formation energy lies between 0.07 and 0.1 eV [16,17]. Therefore, ordering mediated by the EC mechanism would require at least 0.8 eV, while ordering by mass transport along domain boundaries takes between about 0.4 and 0.5 eV, if we assume that the migration energy of atoms along domain boundaries is comparable to migration on terraces (it is likely to be smaller). Our experimental result is compatible with the latter estimate, and confirms that the EC mechanism is negligible under the conditions of our experiment.

We feel that our experiment represents a genuine ordering mechanism, free of the influence of inhomogeneities. Impurities and defects are known to slow down

the domain growth, leading to an asymptotic logarithmic growth law [2]. This implies a decreasing local exponent with time; instead, we observe an increase of the local exponent. Moreover, the maximum value of the characteristic length is 200 Å; therefore, the influence of residual steps, at least 700 Å apart, should be negligible.

Our results suggest at least two directions for future work. With faster detection and improved resolution, it should be possible to enter the EC regime at higher temperatures. On the other hand, it would be interesting to elucidate the nature of the kinetic processes associated with the very low exponents found at the lowest temperatures. It might be that entire patches of domains drift slowly, mediated by kink diffusion. Recent experimental work on vicinal Cu surfaces indicates that such processes may be possible [17]. Mechanisms of this type have been suggested by Binder [22], and they lead to very small exponents.

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