Short Notes

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First Evidence of Spinodal Decomposition in the Diamond Anvil Cell

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Introduction Spinodal decomposition processes have attracted considerable interest over the past decade because of their highly nonlinear transition kinetics /1/. Experimentally, the process of phase separation is usually analyzed by studying the evolution of the structure function, $S(\vec{k}, t)$. For liquid mixtures, the growth of $S(\vec{k}, t)$ following quenches into the miscibility gap has been investigated by light scattering, analogous studies of alloys have been performed by neutron or X-ray scattering. These experiments are characterized by relatively high demands on the preparation technique (e.g. for liquids the constancy of temperature in the mK range must be ensured /2/). Alternatively, phase separation in simple model systems has also been simulated in computer experiments. The specific problem of such simulations is of course the limited memory space, and they are usually very time consuming /3/.

In contrast, we propose an experimental procedure, which is very convenient for the study of spinodal decompositions in unstable liquid mixtures. The basic idea is to slow down the diffusion limited process by application of very high pressures (up to 30 kbar). The resulting decomposition evolves within a typical range of 20 min and is easily monitored by an image processing system.

Experimental The apparatus consists of four main components: the high-pressure diamond anvil cell for pressure generation; a fluorescence microscope modified for a laser input and a three-directional signal output; an image-processing system for image monitoring, combined with a digitizer for image transfer to an external computer, and an optical multichannel analyzer for spectral measurements of luminesence and absorption. It is described in more detail elsewhere /4/. The chosen thermodynamic system is a methanol-ethanol-water mixture because of its well-known high-pressure behaviour showing low freezing point eutectic compositions which have a tendency to exhibit high freezing pressures. Mixtures of these liquids tend to superpress rather than crystallize, which permits the glassy state to be achieved through a steady increase in viscosity with increase in pressure. It is commonly used as a pressure-transmitting medium up to 144 kbar in the composition range of 16:3:1 by volume /5/. For

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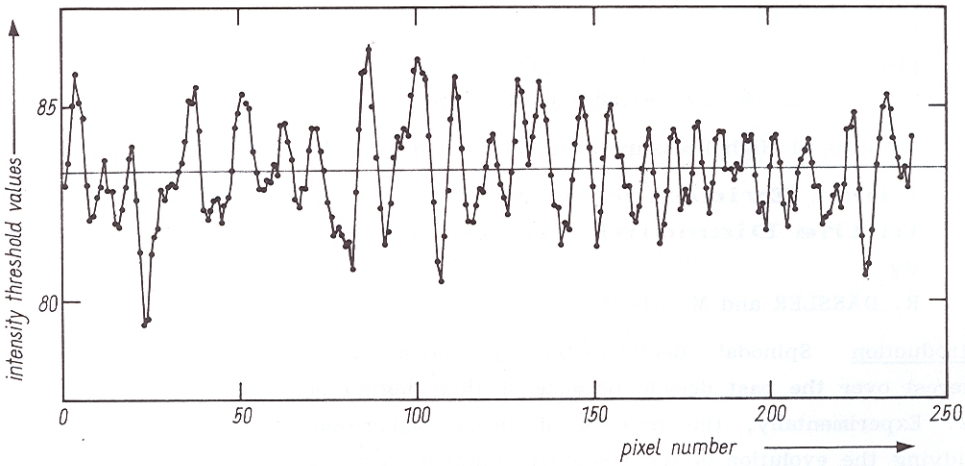

Fig. 1. Line scan through a digitized image of 512×512 pixels showing the density fluctuations $\delta c(r) = c(r) - \bar{c}$ in terms of different grey steps; the weak line shows the mean density

other composition ranges, a variety of pressure-induced phase transitions may be observed, among them nucleation and growth processes, eutectical cellular solidification (or glass formation, respectively) and spinodal decompositions. As a consequence of the employed thin film preparation method (the sample volume in the diamond anvil cell has a diameter of 200 μm and a thickness of about 20 μm) and the great thermal conductivity of the diamond anvils, the temperature may be considered in good approximation as constant during the transformation. Special attention has to be paid to the constancy of pressure depending on the deforming behaviour of the gasket material.

Results If the mixture is quenched into the thermodynamic unstable region by means of a sudden pressure jump, local density fluctuations $\delta c(r) = c(r) - \bar{c}$ arise and cause the formation of complicated domain structures of two liquid or glassy phases with different mean densities, compare Fig. 1. Thereafter, the domains begin to grow with a characteristic power law in time. This is due to a diffusion driven coarsening process which tends to minimize the total surface energy in the system. The corresponding time stamped snapshots are shown in Fig. 2. Due to the optically limited spatial resolution in the order of 1 μm, only the late separation stages are visuable. The digitized snapshots cover 512×512 = 262144 pixels with a grey scale of 256 steps yielding data files of about 260 kbytes. These files are stored on a personal computer and can be analzyed by standard numerical methods like fast Fourier transformations.

The kinetics of nonequilibrium decomposition processes is usually analyzed by means of the two-dimensional autocorrelation function $F(r, t)$,

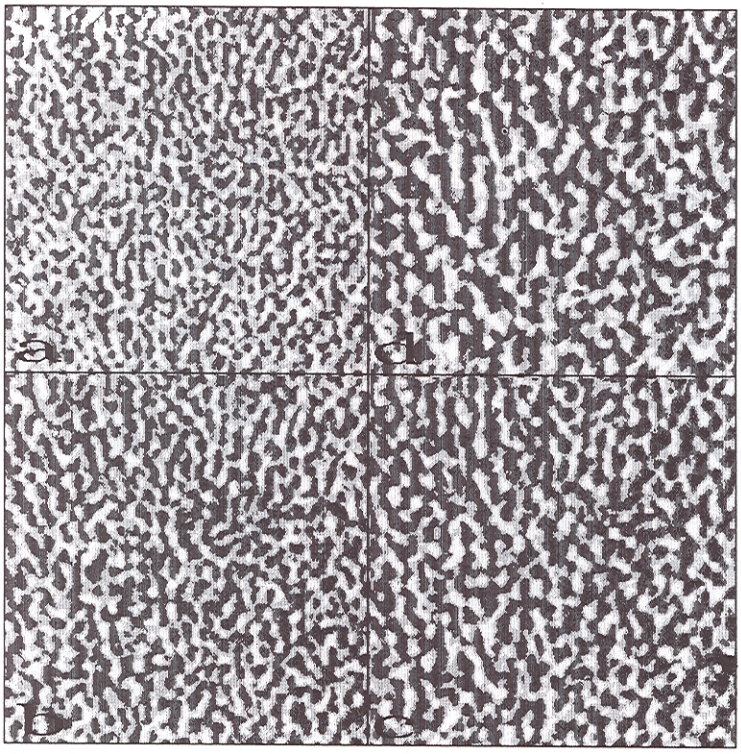

Fig. 2. The growing domain structure at different time delay Δt after initial pressure quench: Δt = 1, 3, 8, and 16 min from a to d, respectively (the images are printed with a reduced 16 grey step scale)

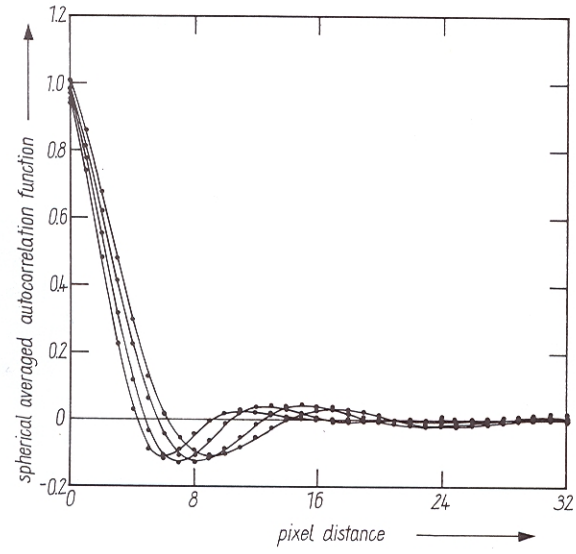

Fig. 3. Spherical averaged autocorrelation function $F(|r|,t)$ plotted for several times; Δt = 1, 3, 8, and 16 min, respectively, from left to right at zero crossing

$$F(r, t) = \sum_{r'} \delta c(r' + r)\delta c(r') \ .$$

The quantitative evaluation for the four decomposition stages of Fig. 2 show the typical time evolution behaviour of the spherically averaged autocorrelation function $F(|r|, t)$, see Fig. 3. They are comparable with recent results of a computer simulated spinodal decomposition in a two-dimensional fluid model published by Farell and Valls using a 100×100 square lattice /6/. The shift of the correlation function radius, reflecting the continuous coarsening of density domains, may be used for further quantitative examinations of different theoretical model descriptions of nonequilibrium phase transitions. The corresponding work, as well as a detailed analysis of the separating phases, is at present in progress /7/.

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