

# Restoration of spatial structure during spinodal decay of a liquid solution

A. V. Antonov, N. F. Bunkin, A. V. Krasnoslobodtsev, A. V. Lobeev, G. A. Lyakhov, and A. I. Malyarovskii

*Institute of General Physics, Russian Academy of Sciences, 117942, Moscow*

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When a stratifying solution (2,4,6-trimethylpyridine plus water) is put in the labile region on the phase diagram under conditions of retarded convection, one observes changes in the structure of the spinodal decay which are quasiperiodic in time. This deviation of the decay from equilibrium results from a flow mechanism for the spatial separation of the phases.

A physical solution can be in three qualitatively different states.<sup>1</sup> The regions in which the states are realized on the phase diagram are bounded by a binode and a spinode. Since the diffusion coefficient is negative in the labile region (inside the spinode), the ground state is spatially nonuniform. It is difficult to observe a realization of this state (spinodal decay) because of convection. Simply determining the position of the spinode on the phase diagram requires the use of either extrapolation methods,<sup>2</sup> which work only near the critical point  $T_c$ , or nontrivial methods involving rapid changes (induced by light<sup>3</sup> or by intense mixing<sup>4</sup>) in parameters. The requirements on the rate of the transition to the decay state stiffen with increasing depth in the labile region,  $\Delta T$ . Specifically, in a cell  $\sim 1$  cm in size the solution stratifies in 15 min at  $\Delta T \sim 10^{-3}$  K, while it stratifies in 1 s at  $\Delta T \sim 1$  K. The rate at which the ordered decay structure spreads out as a result of the convective counterflow of the light and heavy phases decreases with increasing viscosity of the solution or with decreasing difference between the densities of the conjugate phases. These parameters, however, are uncontrollable.

A way out of the difficulty is to use a thin-layer vertical geometry for the cell holding the solution of interest. In this case, convection is slowed by surface-tension forces; the lifetime of the spinodal-decay structures increases to tens of minutes at  $\Delta T \sim 1$ –10 K. It becomes possible to study the decay kinetics in addition to detecting the ordered structure (the first observation<sup>5</sup> of this structure was carried out in a centimeter-size cell holding a solution of methanol and cyclohexane). In particular, the conclusion that the decay dynamics is monotonic in time is justified only in a brief time interval. On the other hand, the decay theory of Ref. 6 is limited by the assumption that the deviations of the concentration from its equilibrium value are small. The nonlinear kinetics (incorporating a dependence), on the other hand, may be nontrivial, as it is in other self-organization systems.<sup>7</sup>

An experiment to observe spinodal decay was carried out with an aqueous solution of 2,4,6-trimethylpyridine (TMP), which is a member of the biologically important class of azines (nucleotides of DNA and RNA, several vitamins and medicinal compounds). The physical properties of TMP solutions are determined by the kinetics

of the N...H hydrogen bonds, which are responsible for the stratification that occurs as the temperature is raised (the lower critical point is  $T_c=5.7^\circ\text{C}$ ). The kinetics of the mixing of a solution of critical concentration (97 mole %  $\text{H}_2$ ) in a thin cell (with a distance  $d=50\ \mu\text{m}$  between windows) is determined by diffusion alone, so an ordinary constant-temperature chamber is sufficient to put the system deep in the labile region (to  $25\text{--}30^\circ\text{C}$ ). The relaxation to thermal equilibrium in the solution takes  $\sim 10$  min.

The experimental apparatus includes a single-mode He-Ne laser with a plane-parallel beam of Gaussian profile (the diameter of the spot formed by a telescope and a "soft iris" is  $\sim 1.5$  cm). The beam from this laser is incident on the cell holding the test solution. The light passes through a converging lens ( $f=4$  m, with an aperture  $22.5$  cm in diameter), which captures the rays scattered by both large- and small-scale structures, and then a mask which blocks the zeroth maximum to a TV camera with an aperture  $2$  cm in diameter. Various regions of the cell are projected by a microscope onto a second TV camera for parallel observation of the dynamics of the structures and the angular spectrum of the scattering by them. Using the microscope, we find that a spinodal-decay wavefront, which moves across the cell, appears  $1$  min after the constant-temperature chamber is turned on. Behind this front we can discern some small cellular structures  $1\text{--}10\ \mu\text{m}$  in size. Later, the structures enlarge to  $100\ \mu\text{m}$  along the entire observation field ( $t=2.9$  min; see the photograph in Fig. 1). These  $100\text{-}\mu\text{m}$  cells finally combine to form clusters  $\sim 1$  cm in size.

The scattering-spectrum signals from the TV camera are sent through an analog-to-digital converter to a computer for processing. The computer determines the brightness of the frame along a selected line of the television raster. An analog signal is written at time intervals of either  $1$  or  $5$  s over  $20$  min. The size of the scattering structure is determined by replacing the cell by a diffraction grating with a known period. The processing system uses a mask to detect structures with sizes from  $20$  to  $300\ \mu\text{m}$ .

The resulting densitometer traces of the angular spectrum typically reveal the following picture of the development of spinodal decay (Fig. 1). Up to a time  $t\sim 1$  min the concentration is uniform. The beginning of decay corresponds to the appearance of reflections over the entire field of the TV camera (Fig. 1a). As time elapses, the small structures disappear, and the only reflections which are visible are those from structures with dimensions of  $300\text{--}60\ \mu\text{m}$  (Fig. 1b). These structures later become so large that the reflection from them is covered by the mask (Fig. 1c). The densitometer traces corresponding to longer times demonstrate that the process is periodic: Large-scale structures with dimensions of  $50\text{--}300\ \mu\text{m}$  reappear ( $t=3.5$  and  $12.8$  min), and then (at  $t=6.2$  and  $16.1$  min) the pattern with three clearly expressed reflections is restored.

Analysis of a file of  $240$  or  $1200$  densitometer traces of angular spectra like those in Fig. 1 reveals the intensity dynamics of the light scattering by structural features of a given size. For the structures  $60\ \mu\text{m}$  in size (Fig. 2a), the rise and fall of the intensity alternate in an unsteady thermal regime (the times  $t\approx 2$  and  $6$  min correspond to the appearance of the three characteristic reflections in Fig. 1) and also in a steady-state regime in terms of the temperature: At  $t\geq 10$  min, we also see a rise, a fall, and an approach to a quasiconstant level (the time of the return to the three-reflection spec-

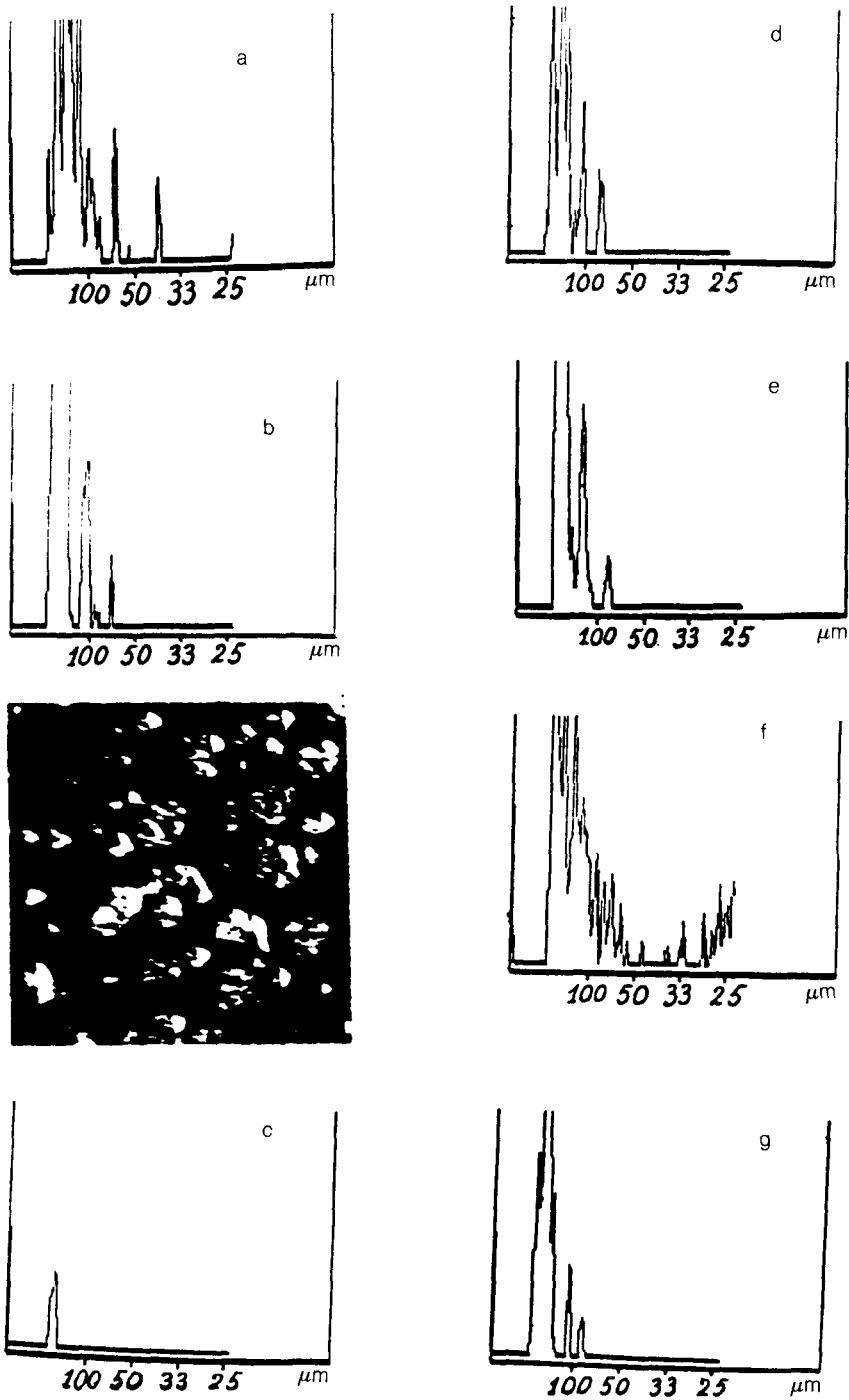


FIG. 1. Dynamics of the angular spectrum of the scattered light during the spinodal decay. *a*—The time after the beginning of the heating is  $t=1.5$  min; *b*—2.8; *c*—2.9; *d*—3.5; *e*—6.2; *f*—12.8; *g*—16.1 min. The photomicrograph of the decay structure shown here corresponds to a time of 2.9 min.

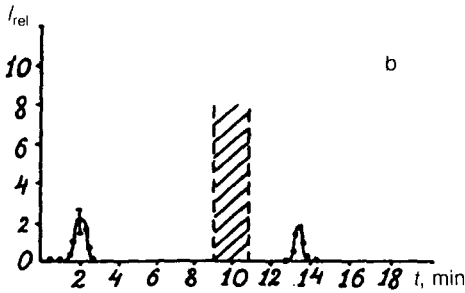
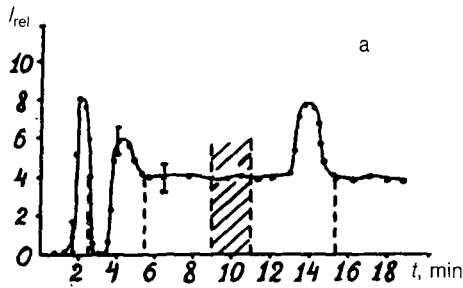


FIG. 2. Time evolution of the intensity of the reflection from a structure of fixed size scale. *a*— $60 \mu\text{m}$ ; *b*— $30 \mu\text{m}$ . The instant at which thermal equilibrium is reached is guaranteed to fall in the time interval shown by the hatching.

trum is  $t \sim 16$  min). The dynamics of the intensity of the scattering from structures  $30 \mu\text{m}$  in size is qualitatively the same (Fig. 2*b*), while the quasiperiod of the spinodal decay depends on the size of the decaying structure. The finite thickness of the layer solution in the cell ( $50 \mu\text{m}$ ) may play a role here. Some important conclusions can be drawn. First, the dynamics of the spectra is essentially independent of the process by which the thermal regime is established. Second, the spinodal decay clearly demonstrates the "restorability" which is familiar in the physics of nonlinear systems.<sup>7</sup> This is a nonlinear effect, since diffusion processes, rather than wave processes, govern the decay. A description of this effect requires a generalization of the theory of Ref. 6 to allow for a concentration dependence of the parameters.

The starting point for this generalization is the free-energy functional

$$F = \int dV [f(u) + K(\text{grad } u)^2], \quad (1)$$

where  $u$  is the concentration of one component of the mixture. In contrast with the case of macroscopically equilibrium phase transitions, a variation of (1) does not immediately give us the equation of motion for the order parameter:  $V^{-1} \cdot \delta F / \delta u = \mu_1 - \mu_2$ , which is the difference between the chemical potentials of the two components. The mass flux  $\mathbf{J}_1 = -L \text{grad}(\mu_1 - \mu_2)$ , where  $L$  is the mobility, and the continuity equation  $\partial_t \mu = -\text{div } \mathbf{J}_1$  lead to the diffusion equation

$$u_t = L \nabla^2 (\partial f / \partial u - 2K \nabla^2 u). \quad (2)$$

A linearization,  $f = -(a/2)u^2$ , makes it possible to determine only the boundary of the  $(u, T)$  region of the spinodal decay.<sup>6,7</sup> To study the kinetics of this decay we need to allow for the nonlinearity of  $f$ :  $f(u) = -(a/2)u^2 + (b/3)u^3 + (d/4)u^4$ , where  $d > 0$ , and the sole temperature-dependence coefficient  $a = \alpha(T - T_c)/T_c$  changes sign at the critical point.

Steady-state ( $u_t = 0$ ) solutions of (2) can be derived analytically in a one-dimensional model ( $\text{grad } u = u_x$ ). Their overall form is periodic:

$$u_\infty = [u_2 - u_1 m \text{sn}^2(k, \lambda x)] / [1 - m \text{sn}^2(k, \lambda x)]. \quad (3)$$

Here  $m = (u_3 - u_2)/(u_3 - u_1)$ ;  $\lambda^2 = (d/8K)(u_4 - u_2)(u_3 - u_1)$ ;  $\text{sn}(k, \lambda x)$  is the elliptic sine of modulus  $k^2 = (u_3 - u_2)(u_4 - u_1)/[(u_4 - u_2)(u_3 - u_1)]$ ;  $u_i$  are the roots of the potential  $u_x^2 = K^{-1}f(u) + Au + B$  numbered in order of increasing size; and  $A$  and  $B$  are constants of the boundary conditions. The spatial oscillations of the concentration in (3) occur between the values  $u_2$  and  $u_3$  with a period  $X = (2/\lambda)\mathcal{R}(k)$ , where  $\mathcal{R}(k)$  is the complete elliptic integral.

To analyze nonlinear diffusion problem (2), we take the approach of introducing a "slow period": We assume that the time-varying solution has the spatial dependence in (3) with a variable period  $X(t)$ . Introducing  $Z(t) = 1 - k^2(t)$ , we thus have

$$u = u_\infty [x, Z(x, t)]. \quad (4)$$

The conditions for the applicability of the slow-period approximation are

$$|\partial \ln Z / \partial x| \ll X^{-1}, \quad |\partial \ln Z / \partial t| \ll (L/X^2) |\partial f / \partial (u^2)|, \quad LK/X^4. \quad (5)$$

Substituting (4) into (2) and taking an average over the period  $X$ , using (5), we find an equation of the Airy type for a perturbation  $Z$  of the Gaussian profile. Solving this equation, we find the result which we have been seeking:

$$Z \sim (p_3 q t)^{-1/3} \text{Ai}[(x + p_1 q t)(p_3 q t)^{-1/3}], \quad q = 0.13(\mu/\Delta). \quad (6)$$

The spatial period of the concentration distribution varies in a quasiperiodic fashion in time, asymptotically approaching a steady-state value. The quasiperiod  $\mathcal{S}$  varies slowly in time:

$$\mathcal{S}_n = 7.7 y_n (p_3/p_1^4)^{1/3} (\Delta^{7/6}/\mu), \quad (7)$$

where  $y_1 = 2.30$ ,  $y_2 = 2.70$ ,  $y_3 = 4.05, \dots$  are the zeros of the Airy function. By measuring this quasiperiod (which depends on the boundary conditions through  $\Delta$  and  $\mu$ ), we find yet another (in addition to  $X$ ) combination of unknown constants of the phase-transition model ( $p_1 \sim L(-a + 2bu_1 + 3du_1^2)$ ,  $p_3 \sim KL$ ).

A stratifying solution in the labile region thus exhibits, in addition to a "rising" diffusion, a quasiperiodic temporal "restorability." This property of nonlinear systems is atypical of the diffusion processes used to model equilibrium phase transitions. Accordingly, a detailed study of a wide range of corresponding physical problems looks promising for refining the overall mechanism for the deviation from equilibrium. The restorability property in spinodal decay should also be exhibited by other systems which undergo phase transitions. Apparently a necessary condition for observing this property is that the phase-separation mechanism be nonlocal. A more general analysis

of model (1) is obviously necessary; the non-one-dimensional geometry should be taken into account, as should the explicit (and time-varying) temperature dependence of the parameters of the model. A natural approach to this generalization is to use the slow-period approximation.

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