# Fast-Mode Kinetics in Surface-Mediated Phase-Separating Fluids

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We present time-resolved elastic light scattering results of structure determination in phase-separating mixtures of guaiacol and glycerol-water constrained to lie between plates 0.5 mm apart. The structure functions show two peaks with different kinetics: A slow mode with $L(t) \sim t^{1/3}$ and a "fast mode" with $L(t) \sim t^b$, where $b$ ranges from 1.1 for a quench of depth $\Delta T = 0.01°C$ to 1.5 when $\Delta T \geq 0.15°C$. A similar fast mode was observed in a polymer system [A. Cumming, P. Wiltzius, F. S. Bates, and J. H. Rosedale, Phys. Rev. A **45**, 885 (1992)]. The observation of the fast mode in a low-molecular-weight, Ising-like system establishes it as generic to phase-separating fluids, and not peculiar to polymers.

Quenched binary fluid mixtures afford a useful class of systems with which to study the kinetics of phase transitions. Over the years, many experimental investigations into the nature of the phase separation which follows quenches from the thermodynamically stable, one-phase region of the phase diagram, to the unstable, two-phase region, have been carried out. Early light scattering work by Goldburg and co-workers [1] and Knobler and co-workers [2] in simple fluid systems such as lutidine and water, and isobutyric acid and water, served to identify the phenomenon and illustrate the notions of pattern selection and coarsening as they apply to this problem. The past decade has seen a strong interest in phase-separation kinetics in polymer mixtures [3–6]. The viscosity of these systems, which slows the phenomena of interest, has enabled investigators to acquire precise structure data, by neutron and light scattering. This work, coupled with notable theoretical [7–10] and numerical [11,12] investigations, has yielded a fairly complete understanding of the bulk, three-dimensional pattern selection and growth in phase-separating binary fluid systems.

Here, we seek to understand the role played by the walls of the container holding a critical, Ising-like mixture of simple fluids. It is well known that there is a transition to complete wetting by one of the coexisting phases in a two-phase system as the critical temperature is approached [13,14]. We expect this wetting behavior to have an effect on the domain morphology and growth law near the wall. Optical microscopy studies of this effect at late times in a density-matched simple fluid system were undertaken by Guenoun, Beysens, and Robert [15]. More recently, light scattering was used by Wiltzius and Cumming [16] on a quenched binary polymer system, wherein a new "fast mode" with an $L(t) \sim t^{3/2}$ growth law was discovered and characterized. The fast mode was attributed to a wetting effect, but in the absence of a theoretical framework within which to interpret the data, the nature of the physical process responsible for the anomalously fast kinetic exponent of $\frac{3}{2}$ was not apparent.

We now report on a series of experiments similar to those carried out on the polymer samples, but in a simple fluid mixture of guaiacol and glycerol-water. This system has been studied in some detail, starting with the work of McEwen [17] and Poppe [18]. Johnston and co-workers [19] have investigated its critical behavior. Pure guaiacol and pure glycerol are miscible. If, however, a small amount of water is added (approximately 1.4% as a fraction of the glycerol mass), a miscibility gap opens over a range of temperatures centered at approximately 63 °C. If $x$ [= (mass of water)/(mass of water + glycerol)] is increased to 5% or more, the lower critical solution temperature $(T_c)$ falls at 26 °C or lower, which is convenient for room temperature studies. For $x \geq 5\%$, the system is known to have Ising-model critical exponents [19]. The high viscosity (compared to the lutidine-water and isobutyric-acid–water systems of [1,2]) of these samples has been essential to our observation of the kinetics of phase separation over a wide range of quench depths, while looking at early enough times to see the fast mode.

The basic design parameters of the light-scattering apparatus have been described elsewhere [20]. For these studies, a more recent charge coupled device (CCD) chip was employed having 1024×1024 pixels, each with sixteen bits of dynamic range. Also, a new temperature-quench technique was employed which allowed quenches to be carried out in approximately 4 sec, about equal to the amount of time needed for heat to diffuse across the sample itself.

The sample cells consisted of a sandwich of a fused quartz window and a sapphire window separated by a Teflon gasket, and conveniently clamped in a carrier. The windows were both 1 mm thick and 21 mm in diameter, and the Teflon gasket thickness, hence the thickness of the sample itself, was fixed at 0.50 mm. The quartz window was exposed to the air in the room, while the sapphire window was exposed to a circulating bath of water, regulated in temperature.

Separate water baths with independent circulation pumps and thermal regulation circuitry were set up at two temperatures; the anneal temperature $T_a < T_c$ and the quench temperature $T_q > T_c$. A pair of four-way ball valves were interconnected in such a way so as to allow us to switch the temperature of the water being circulated

on the sapphire side of the sample from $T_a$ to $T_q$ in a period of approximately 4 sec. This scheme allowed for a minimal exchange volume between the two temperature baths (less than 30 ml, as compared to the 20 liters of water in each regulated bath) while keeping the majority of the plumbing with constant temperature flow. By using a two-stage temperature control system consisting of a Neslab RTE220 bath/circulator and a secondary circuit controlled by a Lakeshore DRC-93C, we achieved stability in $T_a$ of $\pm 5$ mK and in $T_q$ of $\pm 2$ mK over the duration of the experiment.

Many samples of various compositions $x$ and $\phi$ [$=$ (mass of guaiacol)/(mass of guaiacol+glycerol+water)] were prepared. The phase diagram for this system was measured and confirmed to be consistent with that measured by Johnston et al. [19]. For the present experiment, a single sample with $x = 5.90\%$ and $\phi = 47.92\%$ was used throughout, yielding a critical temperature of approximately 24.6 °C. Before each quench, the sample was annealed for several hours at $T_a = T_c - 0.10$ °C. Quenches to various depths $\Delta T$ ($= T_q - T_c$) ranging from 0.01 to 0.22 °C were performed on the sample, and the structure function $S(q)$ was measured as a function of time for 633 nm laser light. We employed light polarized perpendicular to the scattering plane with angle of incidence normal to the glass of the sample cell. The standard meaning was attributed to the quantity **q**, the scattering vector

$$\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i \,,$$

where $\mathbf{k}_f$ and $\mathbf{k}_i$ are the incident and scattered light wave vectors. We have assumed elastic scattering, allowing us to simply relate the momentum transfer $q = |\mathbf{q}|$ to the scattering angle $\theta$ via the relation

$$q = (4\pi n/\lambda_0)\sin(\theta/2)\,,$$

where $\lambda_0$ is the wavelength of the incident light in vacuo, and $n$ is the average refractive index of the scattering medium. At some point in the first 6 to 10 sec, depending on the quench depth, a peak emerged in the structure function, as phase separation started and domains of a characteristic size began to form and to coarsen, as indicated by the peak's movement to lower $q$. As more time passed, this peak began to split into two distinct peaks. The high-$q$ peak moved slowly towards the beam stop, while the low-$q$ peak moved rather quickly to smaller momentum transfer, by comparison. These peaks are attributable to the fast and slow modes, respectively. Figure 1 shows the structure function at various times after a quench of $\Delta T = 0.126$ °C, and after the two peaks have just become distinguishable. The raw CCD data have been collected, ten to a bin in $q$ space, in order to suppress the effect of laser speckle. The solid lines in Fig. 1 are five-parameter fits with the sum of Gaussian and Furukawa [21] line shapes, modeling the fast and slow modes, respectively:
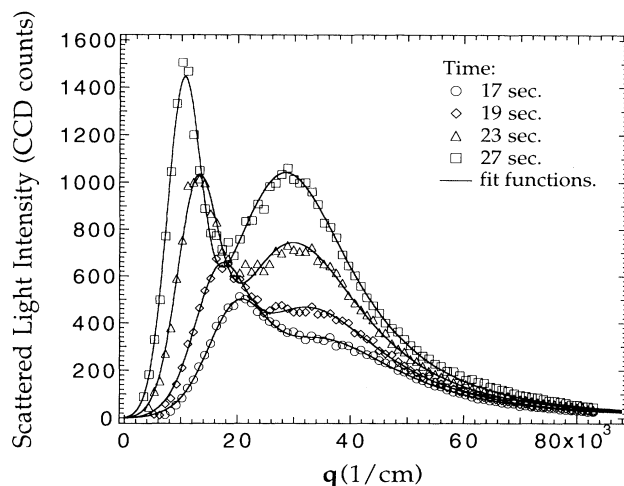


FIG. 1. Scattered intensity vs photon momentum transfer for the structure evolving from a phase-separating mixture of guaiacol+glycerol+water at 17, 19, 23, and 27 sec after a quench of 0.126 °C. The open symbols are binned CCD data, and the solid curves are fits with a model function consisting of the Furukawa line shape (for the high-$q$, slow-mode peak) and a Gaussian (the fast mode). Within the window of time depicted here, the slow mode hardly moves, while the fast-mode peak can be seen to move towards $q = 0$.

$$S(q) = I_f \exp\left[\frac{(q - q_f)^2}{2\sigma^2}\right] + I_s \frac{(\frac{1}{2}\gamma + 1)(q/q_s)^2}{\frac{1}{2}\gamma + (q/q_s)^{2+\gamma}}\,,$$

where $\gamma = d + 1 = 4$ in this case, $d$ being the dimensionality of the scatterer. The five fitting parameters are $I_f$ and $I_s$, the intensity prefactors of the two modes, $q_s$ and $q_f$, the peak positions in $q$ space of the two modes, and $\sigma$, the width of the Gaussian which models the fast-mode peak.

The dynamical scaling hypothesis, if obeyed independently for both modes, says that a single mode-dependent scale $q_j^{-1}$ determines the structure function through the relation $S(q) = q_j^{-d_j} F(q/q_j)$, where $j = f, s$ is a mode index and $d_j$ is the dimensionality of the scattering structure associated with that mode. This sort of behavior was observed with the fast mode; $\sigma = a q_f$, with $a$ independent of quench depth ($a = 0.40 \pm 0.05$ as measured), effectively reducing the number of independent fitting parameters to four. The main beam forward intensity $i_f$ was monitored as a measure of multiple scattering. A first-order correction to multiple scattering was made and dynamical scaling in the fast mode established by plotting $I_f/i_f$ vs $q_f$ on logarithmic axes. Linear fits yielded $d_f = -2.0 \pm 0.3$, indicating the scattering structure to be approximately two dimensional. Multiple scattering spoiled our ability to observe dynamical scaling for quenches of sufficient depth or of sufficiently long duration that $i_f(t)/i_f(0) < 0.4$. It is notable that the choice $\gamma = 4$ in the Furukawa function is consistent the Porod law [22] for a three-dimensional scattering structure,
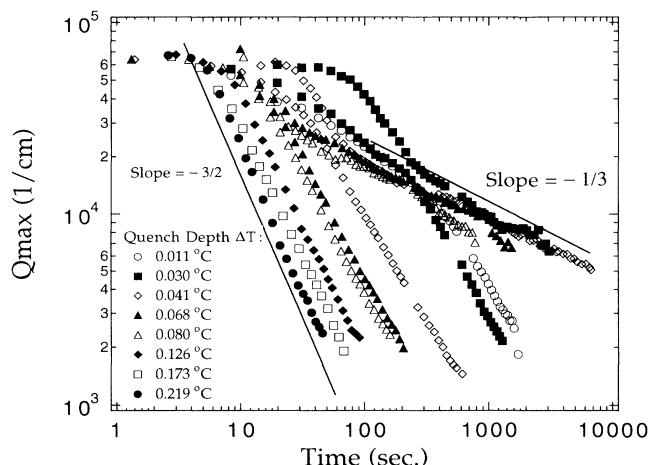
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FIG. 2. The peak positions of the peaks shown in Fig. 1, as a function of time. The slope of the curve for the low-$q$ peak (fast mode) is between $-1.1$ and $-1.5$. The slope of the curve for the high-$q$ peak (slow mode) is $-\frac{1}{3}$.

meaning that there is a well-defined interface between the phases in the bulk. We were not able to make the Furukawa function fit the fast-mode peak as well as the Gaussian, regardless of the choice of $\gamma$.

The most robust parameters of the fits were the positions of the two peaks in $q$ space. The existence of well-defined length scales in the scattering structures are responsible for the existence of these peaks, and by following the time evolution of their positions, we could infer the growth kinetics of the two modes. Figure 2 shows $q_s$ and $q_f$ plotted as a function of time, on logarithmic axes, for quenches of various depths in the range 0.01 °C $< \Delta T < 0.22$ °C. The fast and slow modes are readily
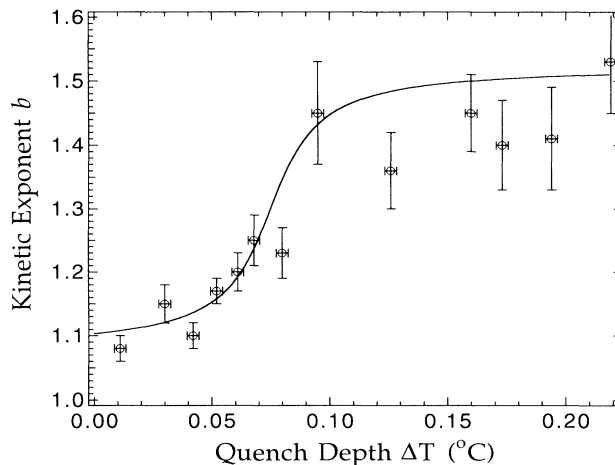


FIG. 3. The kinetic exponent of the fast mode plotted as a function of quench depth for the guaiacol-glycerol-water system with quartz and sapphire sample-cell windows. For deeper quenches, the kinetics are fast, and the couple of seconds uncertainty in the quench time translates into an uncertainty in slope on the logarithmic plot (such as shown in Fig. 2) of nearly 0.1. The solid curve is a guide to a plausible trend in the data.

visualized in this plot. The slow mode follows $q_s \sim t^{-1/3}$ behavior, as expected for diffusion-limited growth with a conserved order parameter [23], and the fast mode follows $q_f \sim t^{-b}$, where $b$ depends on the quench depth, $\Delta T$. Figure 3 shows $b$ plotted as a function of $\Delta T$. For very shallow quenches, $b$ tends toward unity, while for quenches exceeding 0.12 °C, $b$ exceeds 1.4 and tends to the value $\frac{3}{2}$, the fast-mode kinetic exponent which was observed in a mixture of polyisoprene and poly(ethylene-propylene) [16,20] for quenches exceeding 0.15 °C.
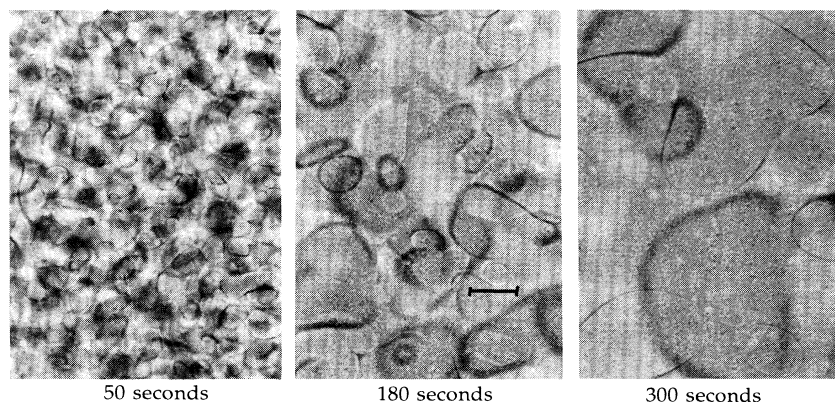


50 seconds  180 seconds  300 seconds

FIG. 4. Photomicrographs of the phase-separating mixture 50, 180, and 300 sec after a quench of 0.30 °C. In the latter two, both the fast mode (large scale) and the slow mode (small scale) can be discerned in the micrographs. The bar is 50 $\mu$m in length. Starting at 180 sec, and certainly out to 300 sec and beyond, there is evidence of the large scale structure being associated with the surfaces. The objective is focused on the near boundary of the sample, and one set of the large-domain interfaces is sharp. By adjusting the focus to the far boundary, the complementary set of large structures comes into focus and the ones on the near boundary become correspondingly defocused.

This experiment relies on the high viscosity (approximately $350 \pm 20$ cP as determined independently by an Ubbelohde viscometer and by the Stokes falling-sphere method) of our system. On the basis of optical microscopy studies, examples of which are shown in Fig. 4, we interpret the fast mode as a wetting transition as one phase of the emerging two-phase pattern takes its energetically favorable position against the glass or sapphire wall of the container. This happens quite early in the phase-separation process. It would be difficult to undertake quench experiments with a more abrupt temperature step than we have carried out here. Here, the limiting rate is the time it takes for heat to diffuse across the sample, as would be the case if we were to quench the pressure or some other thermodynamic field. Deeper quenches than those reported were not possible because the fast mode emerged and became macroscopic on time scales comparable to the quench time, introducing a prohibitively large uncertainty in the origin of time. Time-origin uncertainty is also responsible for the larger error bars in Fig. 3 for $\Delta T > 0.1\,°C$. We therefore feel that it is not likely to be possible to detect the fast mode in low-viscosity mixtures such as lutidine and water.

The present experiment establishes the fast-mode phenomenon as generic to a broad category of fluid mixtures, having been seen in both a polymer system and a low-molecular-weight Ising-like critical mixture. An understanding of the interplay between a phase-separating fluid and the surface is crucial to the broad picture of the kinetics of phase transitions. The observation of the fast mode in the guaiacol-glycerol-water system and the quench-depth dependence of the kinetic exponent will be useful to other experimenters and investigators working towards a theory of this phenomenon.

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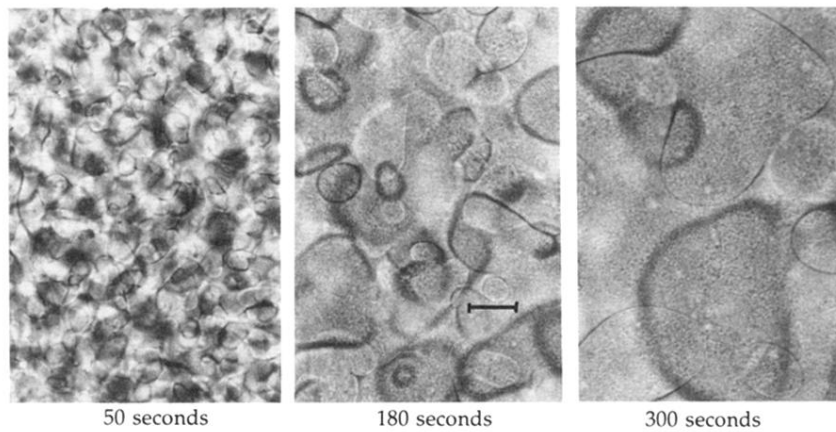
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