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Experimentally determined growth exponents during the late stage of spinodal demixing in binary liquid mixtures

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Spinodal demixing was initiated in two systems, with critical and off-critical compositions, using nanosecond pulsed laser-induced temperature jumps (T-jumps) of various magnitude. In this way, deep quenches could be imposed on the systems. One system was the simple triethylamine (TEA)/water mixture and the other was the ionic mixture of 2-butoxyethanol (2BE)/water/KCl. The demixing process was followed using the technique of nanosecond time-resolved microscopic shadowgraphy. The growth of the evolving phase-separated domains followed a simple power law with respect to time in every case. For a given composition, the magnitude of the T-jump had little effect on the growth exponent, however the composition was found to influence the rate of domain growth. At off-critical mole fractions of 0.2 with respect to TEA, the domains grew according to the following expression: $L_{(t)}=t^{0.70}$ (where $L_{(t)}$=the domain size) whereas at the critical TEA mole fraction of 0.08 the domains grew as $L_{(t)}=t^{0.52}$. 2BE/water/KCl mixtures quenched at the just off-critical composition of 0.05 mole fraction with respect to 2BE evolved as $L_{(t)}=t^{0.63}$. These results will be compared to theoretical models and simulations and discussed in terms of estimated Reynolds numbers as well as the consumption and conversion of the available surface energy that fuels the demixing process.

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I. INTRODUCTION

The early stages of the process of spinodal demixing have been thoroughly studied both theoretically [1,2] and experimentally [3–10] and are well understood. Despite this, the domain growth in the late stage of this process is less well understood, as detailed in two reviews on this subject [11,12]. The late stage of spinodal demixing is characterized by coarsening of the domain structure with the domain growth typically following a power law with respect to time.

Several growth exponents have been theoretically predicted for systems evolving into two coexisting phases, such as binary liquid mixtures. According to the mechanism of evaporation and condensation proposed by Lifshitz-Slyozov and Wagner [13,14] for dilute mixtures in which the minority phase concentration is 1–4%, the growth exponent will be $\frac{1}{3}$. Direct droplet recombination may occur in more concentrated mixtures, which will also result in a growth exponent of $\frac{1}{3}$, unless the mixtures are sufficiently concentrated that the phases can become interconnected. Siggia showed that when this happens, hydrodynamic effects will govern the coarsening, and the late-stage growth exponent should become 1 [15]. The concentration of the minority phase at which percolation may occur is suggested to be around 15%. The major difference between the mechanisms yielding exponents of $\frac{1}{3}$ and 1 is that in the former case diffusion is required for droplets to merge or for molecules to move from one domain to another, whereas in the case where the phases are percolating there are long tubes of liquid in which narrower sections or necks will be squeezed into wider sections due to surface tension. However, the percolating phases will not break up into a series of droplets because the bulk pressure and surface tension will feed back to prevent this from happening since spheres do not pack efficiently. The energy that drives the coarsening is originally stored as the surface energy in the interconnected high spatial frequency phases. This surface energy gets converted into kinetic energy to drive the drift and motion of the phase domains.

Making the assumption that phase separation proceeds isothermally, Furukawa predicted that when the Reynolds number (R_e) is large enough and the surface tension is large, then inertial effects and turbulence will make the growth exponent cross over from 1 to $\frac{2}{3}$. Also if the R_e is large and the surface tension is small, then he predicted that the growth exponent would be $\frac{2}{5}$ [12,16]. These scenarios are expected to occur when the system experiences a deep quench. However, real systems exhibiting growth exponents of $\frac{2}{3}$ and $\frac{2}{5}$, in which R_e is sufficiently large, are not reported, meaning that these exponents remain a theoretical possibility. This is because the deep quenches required to enter this inertial regime are experimentally hard to achieve. It is, however, clear that experimental evidence for what occurs following a deep quench is desirable. In particular, some knowledge of the scenarios in which turbulent effects are important and when they are not important is required. This is especially highlighted by the fact that in recent times, inertial effects have become a ripe subject of discussion between different theoretical groups of researchers [17–21].

A few experiments have been carried out to investigate late-stage coarsening in real binary liquid mixtures quenched at the critical composition starting from just away from the critical temperature [6–10]. Close to the critical point, from a practical viewpoint, it is easy to access the spinodal region, since at this point the binodal and spinodal line touch and

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*Email address: jonathan@orgphys.chem.tohoku.ac.jp even small temperature changes can send the system into the percolating region of the phase diagram. In most cases, the expected exponent of 1, proposed by Siggia for the late stage of domain growth, was found [6–10,15].

Off-critical quenches have also been studied [22–25], for which experimentally determined late-stage growth exponents of $\frac{1}{3}$ are generally reported, as expected [22,23,25]. However, Wiltzius *et al.* reported a growth exponent of $\frac{1}{2}$ [24] for off-critical demixing liquid polymer blends. With deeper quenches, the growth exponent for this system also had the expected value of $\frac{1}{3}$. Wiltzius *et al.* [25] also reported an anomalous growth exponent of $\frac{3}{2}$ which they attributed to the effect of the vessel wall. Wong and Knobler [22] studied both critical and off-critical quenches for isobutyric acid/water. They reported late-stage growth exponents of 1 for critically quenched mixtures and $\frac{1}{3}$ for off-critical quenches, which is consistent with most theoretical works [13–15].

Since Furukawa proposed the inertial regime for deep quenches in which growth exponents of $\frac{2}{5}$ and $\frac{2}{3}$ are predicted [16], the $\frac{2}{3}$ growth exponent has been observed in simulations and numerical studies of the demixing process [26,27], as has the diffusive exponent of $\frac{1}{3}$ ($\frac{1}{2}$ in two dimentions) [26–31] and the hydrodynamic exponent of 1 [27,32]. In other simulations, Cates *et al.* placed the crossover from the hydrodynamic to the inertial regime at an R_e of 20 [21], whereas Grant and Elder suggested that R_e cannot continue to grow unchecked and that at a large enough value, turbulent remixing of the interfaces will occur [17]. They predict that this will limit the growth of R_e, and the exponent they suggest in this regime is $\frac{1}{2}$. Their upper value R_e was estimated to be 10–100 [17].

As mentioned, despite predictions of inertial effects, experimental evidence for the $\frac{2}{3}$, $\frac{2}{5}$, or even the $\frac{1}{2}$ growth exponent has been elusive [11]. One group reported $\frac{1}{3}$ and 1 growth exponents in a three-dimensional polymer mixture undergoing demixing, which modified to $\frac{1}{3}$ and $\frac{2}{3}$ in a two-dimensional experiment with restricted geometry [33]. However, in this two-dimensional viscous polymer, the μm size domains that were observed must have an R_e that is far too low for inertial terms to become significant.

Recently, Gonzales-Segredo *et al.* carried out three-dimensional lattice Boltzmann simulations for 50:50 binary immiscible fluids that yielded growth exponents that increased from ~0.55 to ~0.72 as R_e increased from 0.18 to 37 [34]. These authors discussed this result based on the transient crossover of the growth exponent from $\frac{1}{3}$ (diffusive) to 1 (hydrodynamic).

In the current work, we explore the possibility of entering the inertial regime using a deep quench induced by a nanosecond IR laser temperature jump (T-jump). We present experimentally determined late-stage growth exponents of between 0.5 and 0.7 for critical and off-critical systems in which the domains percolate. Critical quenches gave growth exponents of around 0.5, whereas off-critical mixtures had growth exponents closer to 0.7. These growth exponents differ from most other experimentally determined values, but the off-critical values of around 0.63–0.7 are close to the predicted, experimentally elusive, $\frac{2}{3}$ growth exponent for the inertial regime predicted by Furukawa [16]. They are also close to the values observed in simulations for the diffusive to inertial regime crossover at higher R_e values [34]. These values are discussed in terms of the available literature and current theories, and the applicability of inertial effects [16] or transient crossover [34] will be shown to be inappropriate in this case even though the quenches produced and the resulting values of R_e are very much greater than in any previous experimental studies.

II. EXPERIMENTAL

The apparatus used in this study has been described previously [35,36], but briefly relies on the absorption of a 1.9 μm, 8 ns laser pulse by water molecules in the binary mixture, which causes a rapid T-jump. The sample was presented in a quartz flow cell of thickness 100–300 μm. The binary liquid mixture was thermostatically controlled to below the temperature at which demixing occurs, and the laser pulse heated the system to above this temperature. The arrival of the heating pulse at the sample was synchronized with the arrival of a 532 nm laser pulse from a second Nd-YAG laser. This second pulse induced fluorescence in a solution of rhodamine dye, which generated an incoherent nanosecond strobe light. This strobe light was used to illuminate the sample on a microscope stage, in transmission mode, at a given variable time delay after heating. In this way, we could capture images of events occurring during phase separation using a gated CCD camera. In this work, we studied TEA/water mixtures having mole fractions of 0.2 and 0.08 with respect to TEA as well as 2BE/water/KCl mixtures with compositions of 0.05 and 0.01 with respect to 2BE and KCl, respectively. Static Raman measurements were made to estimate the phase diagram of the 2BE/water/KCl system using a gated Hamamatsu PMA-50 detector fitted to a Kaiser Optics Holospec spectroscope. The probe light for Raman scattering measurements was the 532 nm second harmonic from the Nd-YAG laser. To determine the phase diagram of 2BE/water/KCl, we measured the Raman spectra of the individual gravitationally separated phases equilibrated over a range of temperatures. The composition of each phase could be determined from the relative intensities of the water OH stretch and the 2BE CH stretch bands in the region around 3000 cm^{-1}. The phase diagram of TEA/water was obtained from the literature [37].

III. RESULTS

The phase diagrams for TEA/water [37] and 2BE/water/KCl are shown in Fig. 1. As can be seen, the mole fractions of the components used in this study correspond to both critical and off-critical compositions.

From shadowgraphs obtained as a function of time after the imposed T-jump in all TEA/water and 2BE/KCl/water mixtures, we could only observe the formation of bicontinuous phases, which characterize spinodal demixing, as shown in Fig. 2. Hence the expected late-stage growth exponent in the absence of inertial effects was 1 in every case. The insets

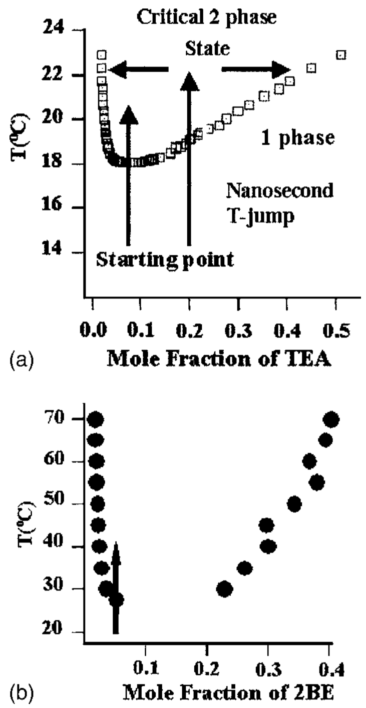

FIG. 1. The phase diagram for (a) TEA/water and (b) 2BE/water/KCl.

show the Fourier transforms of these images, which exhibit ring structures with radii that decrease in diameter with time, indicating that the domain growth was isotropic. From the ring size, we could estimate the characteristic wave number of the domains, and from this we could estimate the domain size as a function of time.

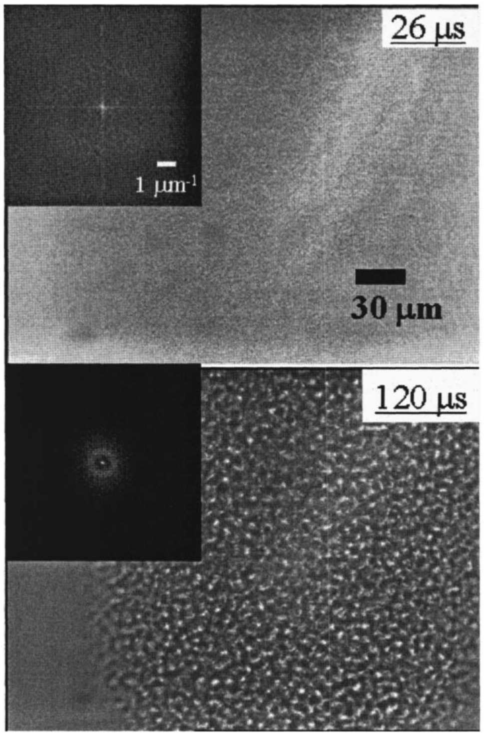

FIG. 2. Spatial patterns of spinodal decomposition measured using shadowgraphy for TEA/water at a mole fraction of 0.2.

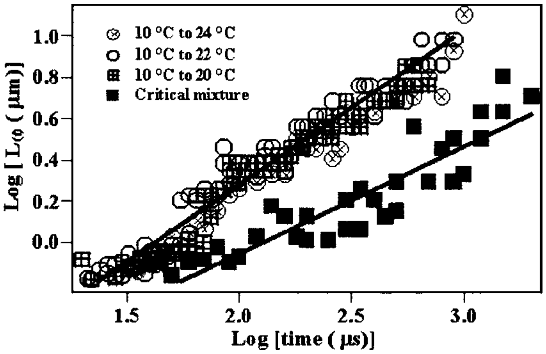

FIG. 3. Domain growth as a function of time (log-log plot) for 0.2 mole fraction TEA in water and 0.08 mole fraction TEA in water with fits (solid lines) to exponents 0.7 and 0.5, respectively ($L_{(t)}$=the domain size).

In Fig. 3, we show the domain growth as a function of time (log-log plot) on the time scale from 10 until 1500 μs for the 0.08 TEA mole fraction critical mixture compared to the 0.2 TEA mole fraction off-critical mixture. It is apparent that the rate of the domain growth for the off critical mixture was not significantly faster for the higher-temperature jumps employed. The domain growth obeyed a simple power law with exponents determined to be around 0.70. In the case of the critical mixture, the domain growth again obeyed a power law, but the growth exponent for this composition was 0.52.

The time scale of the domain growth (log-log plot) for mixtures quenched at different temperatures at the critical composition are shown in Fig. 4. In this figure, it is apparent that increasing the quench depth had a greater effect upon the rate of domain growth at the critical composition of 0.08 mole fraction of TEA than it did when the TEA mole fraction was 0.2, however the log-log plot was always consistent with a slope of around 0.5.

For comparison, we determined growth exponents for 2BE/water/KCl mixtures with a composition that was just off-critical. Again a bicontinuous phase evolved during the entire time course of the experiment. A plot of the domain growth against time (log-log plot) for the 2BE/water/KCl system is shown in Fig. 5. In this case, higher-temperature jumps resulted in coarsening that was clearly

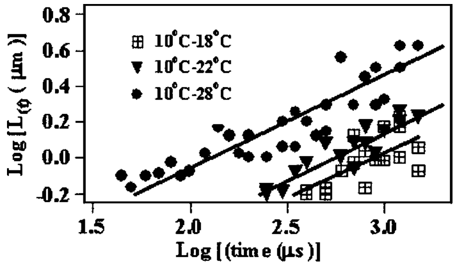

FIG. 4. Domain growth as a function of time (log-log plot) at different quench depths for 0.08 mole fraction of TEA in water with fits (solid lines) to 0.52 ($L_{(t)}$=the domain size).

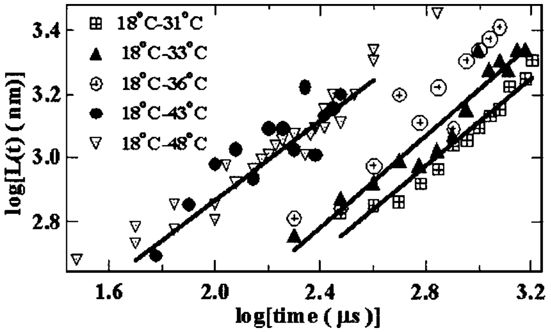

FIG. 5. Domain growth as a function of time (log-log plot) at different quench depths for 0.052 mole fraction of 2BE in an aqueous KCL solution with fits (solid lines) to 0.61, 0.65, and 0.64 (respectively for increasing T) ($L_{(t)}$=the domain size).

faster, however the growth exponents again showed no clear trend with respect to the magnitude of the temperature jump. The averaged exponent for these different quench depths was 0.63.

IV. DISCUSSION

Critically quenched TEA/water

First we will discuss the case of the critically quenched TEA/water mixture with the 0.08 mole fraction of TEA. The most striking result here is that the late-stage growth exponent for the percolating phases is around 0.52, which is very different from the expected value of 1 for the hydrodynamic regime or even the value of $\frac{1}{3}$ expected for the diffusive regime, which have been previously reported experimentally [6–10,22–25].

To examine the possible causes of this result, we will consider the differences between our study and those of other workers, such as the quench depth, viscosity, and the resulting time scale of the de-mixing process. In most previous experimental works on critical binary liquid mixtures, the quench depth achieved was only of the order of mK in magnitude. This means that in our case the density difference between the phases will be bigger, as will the surface tension between the domains. Further, in our case, the empirically determined rate of the demixing process is several orders of magnitude faster than in previous studies. Since the domain sizes in the other studies are similar to ours, this means that R_e in our case is several orders of magnitude bigger [6–10,22–25]. Also compared with the polymer systems studied by Cumming *et al.* [24] and Haas *et al.* [33], the viscosity is expected to be much lower in our case, meaning that R_e is again larger in our case. Indeed, since we imposed relatively deep quenches, it is tempting to try and explain our results by invoking inertial effects proposed by Furukawa to suggest an expected growth exponent of 0.4 (low surface energy and large R_e), which is closer to our experimental value of 0.52 than is the hydrodynamic exponent of 1 [16]. Taking into account the coarsening rate, the domain sizes, and the expected viscosities, we can easily get a rough estimate of R_e as given by $R_e=(\rho L_{(t)}/\eta)dL_{(t)}/dt$ (where ρ=density, η=viscosity, $L_{(t)}$=characteristic length, $dL_{(t)}/dt$ =characteristic velocity). We estimated that $R_e \sim 0.005$ growing to ~ 0.04, for this critical mixture of TEA/water, over our measurement time range, if η/ρ (the kinematic viscosity) is $\sim 0.5\times 10^{-2}$ cm^2/s (a reasonable value based upon Refs. [37–41] taking into account volume fractions), with $dL_{(t)}/dt \sim 0.36-0.26$ cm/s as obtained from the rate of domain growth at different times, and with $L_{(t)} \sim 7\times 10^{-5}$ cm growing to 9×10^{-4} cm as measured experimentally. According to Furukawa's prediction, the inertial regime giving a growth exponent of 0.4 would be seen for systems having a relatively small amount of surface energy to convert to kinetic energy as well as an $R_e > 1$. This means that inertial effects are unlikely to account for our findings since our R_e values are too low and the available surface energy is expected to be large for such dissimilar phases experiencing a deep quench. From the results of simulations of symmetrical quenches, it was reported that, depending on the R_e, the expected growth exponents of $\frac{1}{3}$ (diffusive) and 1 (viscous) cross over through long-lived intermediate values [34]. However, we note that the R_e used in this simulation, for which this long crossover region was observed, were between 0.18 (exponent of 0.545) and 37 (exponent of 0.717), whereas those estimated from our experimental data are at least five times lower in the best case. Also for TEA/water mixtures with deep quenches, the intermediate stage of coarsening should be over after 1–2 μs [35]. It is therefore clear that our data points span a time range that is clearly outside the time domain of the intermediate stage of domain growth where diffusive behavior can be expected. A transient crossover from $\frac{1}{3}$ to 1 therefore can be easily ruled out.

Deeper quenches in mixtures at the critical composition will lead to bigger density differences between the two types of phase, meaning that gravity effects [15] may become prominent at earlier times, however gravity may be expected to increase the growth exponent to greater than 1, not decrease it to less than 1. We can therefore rule out gravity effects as being responsible for the lower than expected growth exponent determined in this study.

Off-critical quenches

In the following paragraphs, we will consider the off-critical quenches in TEA/water and 2BE/water/KCl, for which percolating phases were also observed, meaning that the expected late-stage growth exponent in the absence of inertial effects is 1. In these cases, the experimentally determined growth exponent values of ~ 0.7 for TEA/water and 0.63 for the 2BE/water/KCl system are similar to the $\frac{2}{3}$ growth exponent predicted by Furukawa [16] for the inertial regime where $R_e > 1$ and a relatively large amount of energy is available in the form of surface tension.

For the TEA/water off-critical mixture, a similar discussion can apply as was used in the case of the critical quench. In other words, the increased domain drift velocity and low viscosity could result in a higher R_e, and inertial effects could become significant compared to viscous ones. In fact, we found that the R_e for this off-critical TEA/water system will be $\sim$10 times higher than for the critical mixture. We estimated that $R_e \sim 0.03$ growing to $\sim$0.3 for our off-critical mixture if $\rho/\eta \sim 5 \times 10^{-3}$ cm^2/s (a reasonable value based upon Refs. [37–40] taking into account volume fractions) and with $dL_{(t)}/dt \sim 1.7$ cm/s decreasing to 1.6 cm/s, and with $L_{(t)} \sim 1 \times 10^{-4}$ cm growing to 9×10^{-4} cm.

Although for this off-critical quench the R_e values are evidently higher than for the critical TEA/water system, and several orders of magnitude higher than any previous experimentally studied systems, it is notable that they are still less than 1, and further, they are small compared with the value of 20 which has been suggested as the threshold for the crossover from the hydrodynamic to the inertial regime [21].

In the case of 2BE/water/KCL, the R_e values are in fact harder to estimate due to a lack of literature for this system. However, if we use values of $dL_{(t)}/dt$ extracted from our graphs of between 0.12 cm/s for small T-jumps to 0.35 cm/s for higher T-jumps and using a very rough kinematic viscosity of 0.5×10^{-2} cm^2/s (pure water is 1×10^{-2} cm^2/s whereas that of pure 2BE is 0.362×10^{-2} at 20 °C and 0.283×10^{-2} at 25 °C; the effect of KCl is not reported), we can estimate that $R_e \sim 0.0018 - 0.02$. Although the 0.63 growth exponent is superficially similar to that predicted by Furukawa, it must be concluded that the estimates of R_e (albeit with their obvious limitations) are so low as to suggest that inertia again has no significance in this system.

In both of the above off-critical cases, we can rule out gravity effects, which would speed up the domain growth, as well as a transition between the diffusive to inertial regimes since the intermediate stage of domain growth for these systems is again over much earlier than the observation range currently reported [35,36].

Overview

Anomalous growth exponents were observed in critical and off-critical binary liquid mixtures. In all of the experiments reported, the crossover from the diffusive to the inertial regime can be ruled out as the reason for the observed exponents because the time scale is wrong [35,36]. Gravity effects can also be ruled out since the growth exponent is lower than that expected for the hydrodynamic late-stage value of 1 and not higher. Gravity effects will also be minor in the case of fast demixing as there is little time for convection to occur [15].

It is obvious that the values of R_e will be tending toward small (<1) in all of the current cases since the domain sizes involved are of μm order and the velocities of the domains are inherently slow. This is despite the fact that the values reported in this current experimental work are much higher than those that can be inferred from the results of previous works. Although we observe growth exponents that are close to the value of $\frac{2}{3}$ expected in the inertial regime, the corresponding values of R_e are too low [16,21]. In the case of an R_e of between 0.03 and 0.3, which was the estimated range for the TEA/water off-critical mixture, it is expected that inertia will only be of marginal importance overall even at the latest time of the measurements with the largest R_e of 0.3. For lower values of $R_e < 0.01$, it is hard to imagine any inertial contribution to the growth mechanism.

The question still remains as to what factors can be affecting our results to give us lower than expected growth exponents. Having ruled out transient crossovers [34], gravity [15], and inertial effects [16,21], we must consider the differences between the experiments which we report and the experiments and theoretical works of others. One difference is that in our case the domain evolution is in fact faster than the thermal diffusion rate within the heated area. This means that the phase change should be adiabatic over our measurement time scale since heat will not significantly flow into or out of the extended phase-changing region. This in turn means that the demixing process may not necessarily be isothermal. Note that it was assumed that demixing occurred isothermally in the theory of Furukawa [16]. Further, there are inevitable differences in heat capacity between two dissimilar phases resulting in possible thermal gradients leading to convective flows within the evolving domains. Heating, convective flows, and heat transfer may consume a small part of the surface energy otherwise available for conversion into the kinetic energy required for domain ripening, and this could slow down the coarsening rate. Heating in a high heat capacity fluid is energetically costly so perhaps it is significant that the lowest growth exponent of 0.52 was found for the critical TEA/water mixture, which has the higher water content and higher heat capacity.

We can consider the energy conversion in our current system. First, the laser energy is converted into heat as the mixture's temperature is raised. Next the fluid demixes chemically over $1-2$ μs [35,36], which is an endothermic process, so the temperature will drop. After $1-2$ μs, there exists a finely structured labyrinth of phase domains having a high surface energy. This surface energy will be converted into kinetic energy to force the domains to coarsen. Since the coarsening rate is fast in our case, it is possible that some heat will be generated due to fluid motion within and between the domains. In fact, heat will be the eventual form of the energy in this process since in the end all domain motion ceases. This means that the isothermal assumption cannot be guaranteed in this case.

It should be considered whether it will be possible to achieve a condition to experimentally test Furukawa's theory. In order to achieve a higher R_e than we currently have, we would need to impose a T-jump in the liquid even further into the two-phase region. If this occurred, then we would induce even faster demixing than in the present case. This means that the isothermal assumption would be even less likely to hold. It is therefore clear that there is still a large mismatch between current theory, simulation, and experiment in terms of validating the $\frac{2}{3}$ growth exponent of the inertial regime. This remains a future challenge.

CONCLUSION

We present experimental data from which we derive new growth exponents of 0.52, 0.63, and 0.7. Although these values are roughly consistent with the experimentally elusive $\frac{2}{5}$ and $\frac{2}{3}$ exponents predicted by Furukawa [16], the corresponding values of R_e are far too low. A possible explanation for the current observations is that the mixture is demixing faster than the thermal diffusion time so that it cannot beguaranteed that the system is isothermal. Further, thermal gradients may exist between the nano- and microdomains. Such heating effects may then suppress the growth rate.

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