

Dynamics of Liquid Structure Relaxation from Criticality after a Nanosecond Laser Initiated T-Jump in Triethylamine–Water

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Due to its lower critical consolute temperature, we can use a nanosecond laser T-jump to induce spinodal demixing in the triethylamine/water binary mixture. Using a time-resolved Raman probe, we obtained direct molecular level evidence for liquid restructuring in the early stage (<200 ns) of this spinodal decomposition. From these Raman data, we concluded that in this system the early and intermediate stage spinodal dynamics were apparently over within 1 μ s. In addition to Raman spectroscopy, we developed a novel shadowgraphic microscopic time-resolved imaging system to get information about morphological changes during demixing, such as phase domain growth rate. In the microsecond time scale, the characteristic scale of length (ξ) of phase domains increased with time following a simple power law $\xi \sim t^{0.76(\pm 0.04)}$, while the structure maintained its self-similarity. In this case, the onset of late stage spinodal phase change is several orders of magnitude faster than has been reported for other simple binary mixtures because of the depth of the jump into the two-phase region brought about by our heating pulse.

1. Introduction

Compared to many chemical processes, phase change is a complex event that involves cooperative movement of molecules within a bulk medium and non-Fickian diffusion driven by chemical potential gradients that increase the concentration gradient rather than decreasing it.^{1,2} In fact, the dynamics of phase separation are governed by chemical potential minimization of the bulk that is attenuated by the energy required to sharpen a concentration gradient to form a surface. Phase splitting in a binary mixture will involve the fine balance between molecular attraction and repulsion as well as the energetics of both the surface and the bulk, and therefore a full picture of phase separation should involve directly obtained molecular level information such as spectroscopic evidence, preferably at the vibrational level.

Previous high quality works carried out on phase changing systems have reported time-resolved studies on binary or more complex mixtures. The time-resolved studies involving direct vibrational spectroscopic measurement have been limited to long time scales in relatively complex polymer/solvent mixtures.³ Vibrational spectroscopic studies on simple systems such as 2-butoxyethanol/water have also been reported under nondynamic experimental conditions.⁴ Some workers have used time and space resolved light scattering or turbidity techniques, which can probe dynamic changes to the morphology and refractive index gradients within the system, to describe events during spinodal phase separation of simple binary mixtures. In these studies, the experimental time scale was rather long, being from

hundreds of milliseconds to several hundreds of seconds due to thermal equilibration times after a pressure jump or thermal quench.^{5–11} From these works the growth rate of phase domains could be evaluated. The nucleation phase change mechanism in binary liquid mixtures was also followed using pressure and T-jump experiments.^{12–15} These workers elegantly applied Mie theory¹⁶ to scattering data to derive the growth rate of droplets during phase separation.

Since 1972, it has been known that nanosecond Raman laser T-jumps can be successfully applied to relaxation studies.¹⁷ The laser T-jump has been successfully applied in many biological studies of protein folding using infrared, Raman, and fluorescence probes. For examples, see Yamamoto et al.,¹⁸ Williams et al. and Wang et al.¹⁹ and Ballew et al.²⁰ This laser T-jump has also been applied to the study of the dynamics of aggregation and phase change, from fractions of nanoseconds to seconds, in complex mixtures such as aqueous block copolymers, micelles, phospholipid vesicles, and emulsions, probing with fixed angle light scattering techniques.^{21–29} T-jumps coupled with fluorescence probes and other absorbing molecular probes have sometimes provided alternative methods to follow phase separation in complex block copolymer and phospholipid systems.^{28,29} In the phospholipid systems, relaxations were observed with lifetimes ranging from 4 ns to 20 ms, and these included molecular level reorientation of phospholipid head and tail groups within these vesicles.²⁹

On the other hand, by far the majority of previous works on binary liquid mixtures, involving simpler molecules with less structural ordering, have concentrated on static equilibrated conditions using several probes of bulk character. These have highlighted several interesting features of the critical point, such as refractive index anomaly, ultrasound attenuation, specific heat

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anomaly, viscosity increase, critical slowing down of chemical reactions, and so on.^{30–46}

To our knowledge, except for our current works in progress, no direct vibrational spectroscopic data has yet been obtained pertaining directly to the molecular level interactions of the bulk molecules in such simple binary liquid mixtures undergoing spinodal phase separation during the early nanosecond to microsecond structural reorganization. Further, information on domain size growth rate has also not been obtained in fast laser T-jump experiments. Such information should be of interest to many chemists and physicists, especially if molecular level changes can be directly linked in time with light scattering and morphological information gained for the same system under the same condition.

With this in mind, we have chosen to study the triethylamine (TEA)/water system. The TEA–water mixture provides a classic textbook⁴⁷ model for phase separation in a relatively simple mixture. This mixture has a lower critical consolute temperature, above which it splits into a water-rich phase and a TEA-rich phase. This is convenient for inducing phase separation, because rapid heating is generally easier than rapid cooling. In the present work, we wish to address previously unexplored dynamic aspects of spinodal phase separation in this system by spectroscopically probing the process of phase change following a nanosecond laser-induced temperature jump at the same time as monitoring light scattering and by direct morphological observation under a microscope. We describe for the first time the direct vibrational spectroscopic observation of rapid changes in intermolecular interactions that occur within the bulk at short nanosecond time scales during the spinodal phase change process in a simple mixture. We show that under our conditions the early stages of spinodal decomposition are very rapid (sub-microsecond time scale).

2. Experimental Section

We generated a 1.9 μm laser pulse by Raman shifting 1 J of 1064 nm light (injection seeded Nd:YAG, Spectra Physics Quanta Ray GCR200, 10 Hz, 8 ns) after focusing ($f = 50\text{ cm}$) into a high-pressure (30 atm) hydrogen cylinder. With the use of injection seeding stimulated Raman backscatter was the dominant form of the energy conversion.^{48,49} When injection seeding was not used forward scatter dominated and the power and stability of the 1.9 μm beam were vastly inferior. With the injection seeder we could produce 300 mJ of backscattered 1.9 μm light.

This 8 ns, 1.9 μm laser pulse was used to directly excite water molecules via absorption by combination bands in a mixture of TEA (Wako >99% pure)/water (distilled) increasing the temperature of the liquid above its critical point and forcing phase separation. The TEA water mixture (0.2 mole fraction of TEA, 0.28 mole fraction of TEA, or at the lower critical consolute point of 0.08 mole fraction of TEA.⁴²) was flowed through a 300 or 200 μm cell to present a heated volume sufficiently small to produce T-jumps from 6 to 16 K. The sample absorbance at 1.9 μm was $\sim 10\text{ cm}^{-1}$, so at 0.2 mole fractions of TEA we expect a thermal gradient of around 5 K in 300 μm for a 7 K (averaged) T-jump (this gradient will be less for 0.28 TEA mole fraction and more for 0.08 TEA mole fraction). All experiments were carried out in Teflon containers using a Teflon pump so as to avoid contamination from dissolved borosilicate, which is the main cause of deviation from the coexistence curve we assumed from ref 42. As ref 42, we used a clean quartz cell. The total flowing sample volume was 150 cm^3 . All pump apparatus was preflowed with portions of the sample solution

that were then discarded. The starting temperature of the TEA/water mixture was regulated at 13, 15, or 16 $^{\circ}\text{C}$ with a water bath and measured at the liquid jet with a thermocouple.

Molecular level changes were observed and followed using time-resolved Raman scattering from a second synchronized Nd:YAG laser (Quantel Brilliant, 532 nm, 10 Hz, 8 ns) and, for comparison, bulk morphological changes were monitored by simultaneous observation of Mie scattering of the Raman probe pulse detected by photodiodes placed at 60 $^{\circ}$ and 90 $^{\circ}$ to the incident probe light path.

Microscopic images were recorded using comparable heating conditions, in a quartz cell mounted on a microscope observation stage (Olympus IX70, 40 \times objective lens, depth of focus $\sim 10\text{ }\mu\text{m}$) imaging the front face of the cell. In these experiments, the 532 nm light from the probe laser was used to excite a solution of Rhodamine dye placed above the observation stage. This provided an incoherent time-resolved probe light for obtaining images with a CCD camera. All apparatus is shown in Figure 1.

The following points should be noted when considering laser heating. Laser heating to high temperatures inevitably produces shock waves, and these shock waves can produce apparent relaxation in probe signals.^{17,50–52} A major reason for this is photoacoustic cavitation,^{17,50,51} which Wray et al.⁵⁰ have shown to become a problem to transmission measurements at T-jumps of more than 20 K to temperatures above 30 $^{\circ}\text{C}$. Typically cavitation will occur after a few microseconds.^{17,50,51} This will be especially problematic if we use a transmission method such as absorption or turbidity as a probe. However, in our case we T-Jump from 13 to 29 $^{\circ}\text{C}$ (maximum) and in any event, in the case of the Raman data we measure a scattered light signal and monitor the relative ratio of peaks so that even if cavitation does occur after a few microseconds then it will not be as problematic as in a transmission measurement.

In the case of Raman, in principle a problem can arise due to scattering and depolarization of the probe and Raman light. This can change the intensity of the depolarized to polarized peak ratios in the spectrum. This effect can in part be compensated by insertion of a depolarizer in the probe line giving circular polarization. This at least compensates for depolarization in two planes. In fact, in the present case we can be absolutely sure that none of our spectral evolution is due to any such optical artifact because we can evaluate the expected spectral change due to depolarization by simply twisting the inserted polarizer to give elliptical polarization and measuring the resulting spectral change compared to a circularly polarized probe. This defines the expected region of change in the spectrum due to scattering based depolarization phenomena. Further, we can evaluate the expected spectral change due to phase separation by making a static measurement of the Raman spectra of two phases in a phase split sample. Our Raman spectra exactly resemble the form expected due to phase separation and do not match the form expected due to depolarization from scattering giving us high confidence in our data.

Further points to note are that lateral heating inhomogeneities can also give rise to refractive index modulation leading to scattering and formation of a thermal lens. This can easily interfere with any transmission based probe method even at low-temperature rises. Again, a Raman scattering analysis based on the spectral shape will be a good choice to avoid many of these complications. We finish with a caution that with higher T-jumps, spectroscopic measurements can be affected after a few microseconds by cavitation, and we will limit our discussion to these shorter times in the discussion section. However,

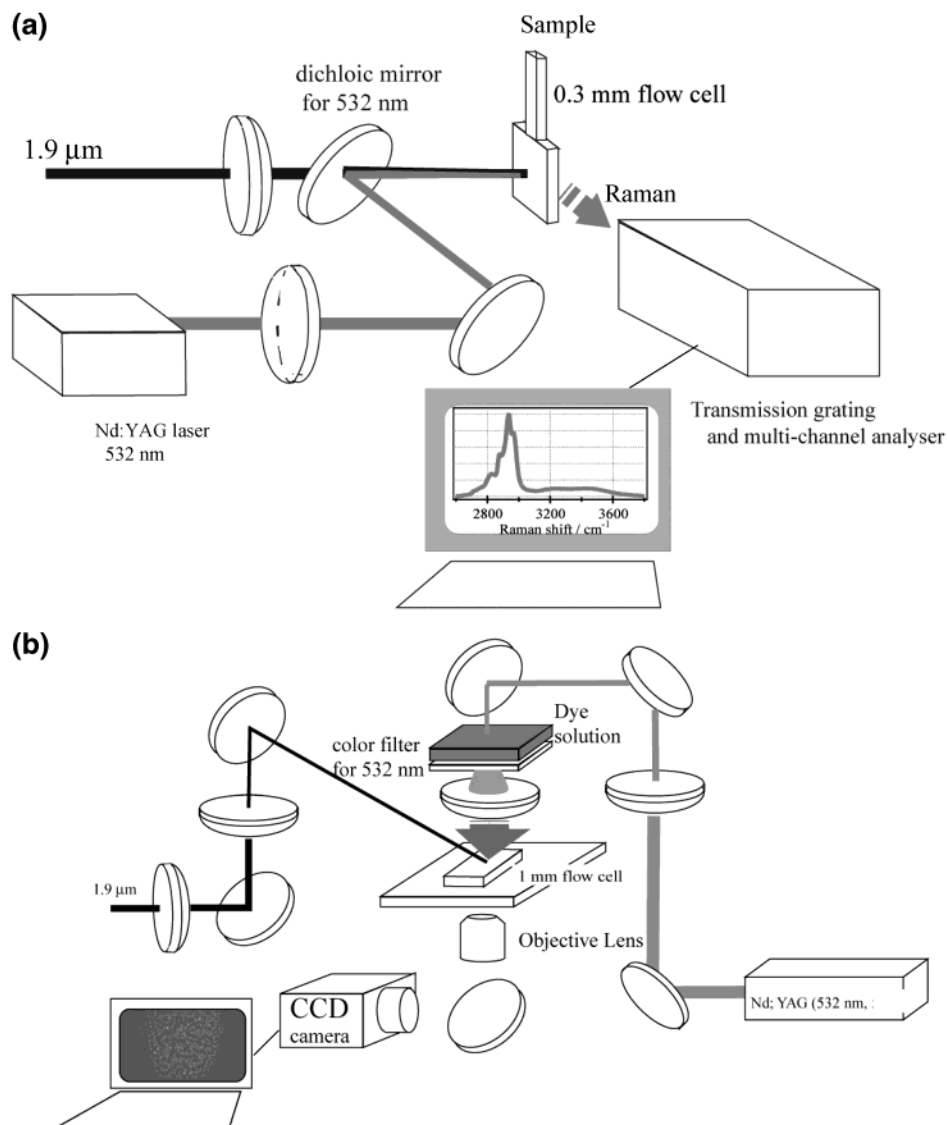


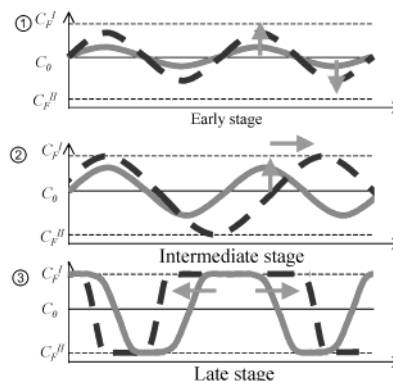
Figure 1. The apparatus for T-jump pump-probe Raman (a) and microscopic (b) measurements.

SCHEME 1

What is spinodal decomposition.

: phase separation process which requires no thermal activation energy.

- ① In the early stage, a concentration fluctuation, having some characteristic wavelength, evolves increases concentration gradient without changing this wavelength.
- ② In the intermediate stage, both the wavelength and amplitude of the concentration fluctuation increase.
- ③ In the late stage, the amplitude of the concentration fluctuation reaches the value of the equilibrium state but the fluctuation wavelength grows and interface narrows while maintaining self-similarity.



shadowgraphic measurements can be analyzed with great confidence if cavities are not apparent in the images obtained.

3. Results and Discussion

Spinodal Phase Change. To begin this discussion, we refer to the three stages of spinodal phase change shown in Scheme 1.^{53,54}

In the first stage, molecules in the critical state have instability that can be reduced by diffusion in a naturally occurring

fluctuation in the state of the liquid (pressure, density, composition, temperature). One fluctuation wavelength is naturally amplified as a concentration gradient due to mutual feedback from two factors. The first factor is the requirement for molecules to diffuse as fast as possible to region of greater stability. This factor favors the formation of short wavelength concentration fluctuations. The second factor is that short wavelength fluctuations in concentration require greater energy to create a large area of interface between phases. This factor

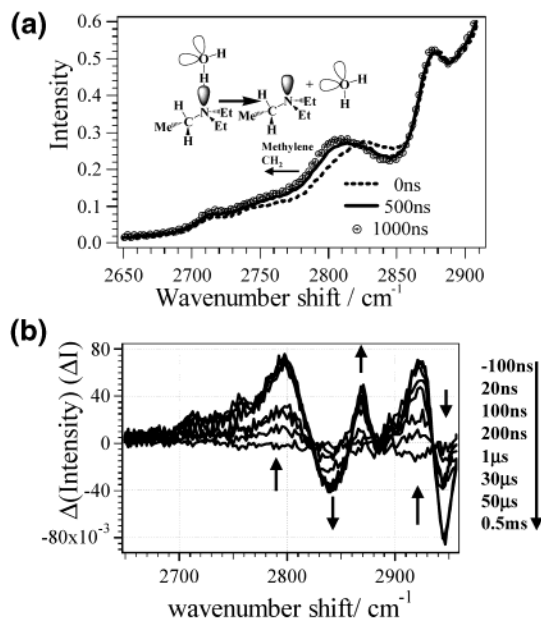


Figure 2. (a) Raman spectra of the methylene (N)C–H stretch region before and after a laser induced T-jump above the critical temperature (T-jump from 13 to 29 °C, TEA mole fraction of 0.2) and (b) Raman difference spectra determined after the same laser induced T-jump above the critical temperature.

favors the formation of longer wavelength fluctuations in concentration. In this way, a single natural characteristic scale of length becomes amplified as a concentration gradient.

In the second phase of this spinodal process, the composition of each phase continues to change at the same time as the wavelength of the fluctuation increases, until the composition is the same as the equilibrium composition. This marks the beginning of the later stage during which the composition is constant, but the phase domain wavelength increases to minimize surface energy in the manner of phase ripening.

Raman Spectroscopy. After phase splitting of this binary TEA/water mixture, a clear red shift occurs to the methylene C–H(str) mode at around 2800 cm^{-1} .⁵⁵ A typical T-jump induced spectral shift is shown in Figure 2a.

By analogy to spectral shifts assigned for methoxy groups in aqueous media,³ this shift may be due to an increase in hyperconjugation between the lone pair on the N-atom and σ^* of the C–H bond, occurring as the H-bond breaks and the molecules rearrange. Further, any interaction between the water oxygen's lone pairs and the methylene C–H would also be reduced and this is said to increase the C–H bond length.^{56,57} The exact causes of this shift are the subject of an ongoing theoretical study by our group. Initial results from this suggest that neither hyperconjugation nor C–H hydrogen bonding need to be applied to the model to obtain the observed shift. At present, we concede that the exact cause of the shift is controversial and may be an amalgamation of all of the factors we have mentioned. In any event, this clear red shift in a distinct band that is sensitive to H-bonding to water provides us with unique window to observe molecular level liquid structure reordering.

Phase separation dynamics were monitored using Raman difference spectra (Figure 2b).^{58,59} Obtaining the difference between the spectrum before the T-jump and after the T-jump separates the useful, but relatively small spectral changes from the main spectral information allowing us to finely pinpoint and interpret the shifts due to the breaking of the TEA–water hydrogen bonded complex at hypercritical temperatures. As we

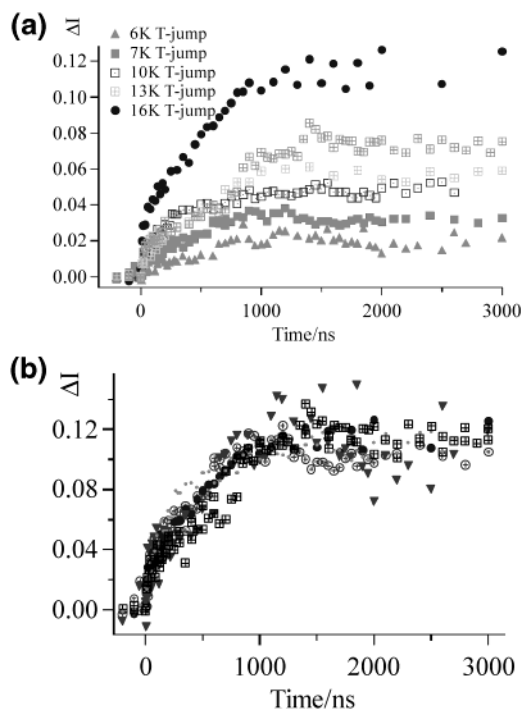


Figure 3. (a) Kinetics of phase separation for different T-jumps from 13 °C with mole fraction of TEA of 0.2. (b) The same data, but normalized.

have stressed, the spectral shifts and difference spectra obtained after the T-jump were fully consistent with the spectral shifts observed in the two individual layers in a mixture of the same composition that had been phase split using a static temperature rise equal to the predicted laser induced rise. Further, it is clear that the difference spectra have “isosbestic type” points from 0 to 10 μs , and this allows us to propose a simple two species model for this system involving the H-bonded TEA that is dominant in the monophasic and non-H-bonded TEA that dominates in the binary region of the phase diagram. The “isosbestic type” points also point to the lack of optical artifacts with our probe method, giving us higher confidence in our data.

Figure 3 shows kinetic traces for the breaking of the H-bonded TEA/water complex monitored using the peak to trough magnitude of the methylene C–H stretching band in the difference spectrum. As we can see, there is an initial rapid decrease in H-bonding occurring during the laser heating pulse, and this continues further until 200 ns. We suggest that the initial change within the pulse is due to the weakening of the hydrogen bond that is binding the TEA–water complex and the changes up to 200 ns are due to the migration of the now weakly associated molecules down natural fluctuation (P, T, density) gradients to form bicontinuous phase separated regions.^{54,60–62} After these rapid events, there is a slower kinetic region to the H-bonding decrease occurring over the next 1 μs . As can be seen from the normalized data sets in Figure 3b, within the error, the form of the kinetics of these spectral changes are not temperature dependent. However, the total final spectral shift is temperature dependent, meaning that the diffusional flux does increase with temperature. Many factors could lead to this invariant normalized rate in the early stage. It may be that this is a characteristic of homogeneous phase splitting or spinodal decomposition, which has a low activation energy.^{60–62} The size of fluctuation that is enhanced for a particular T-jump will also be a factor, since this determines the distances that must be traveled by a diffusing molecule to minimize its chemical potential and, as we shall discuss later, this fluctuation size

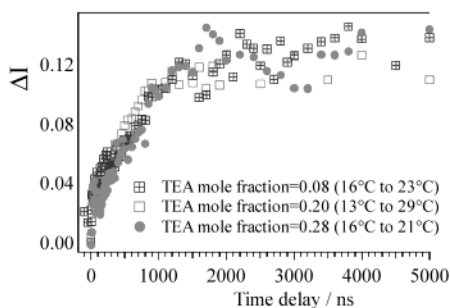


Figure 4. Kinetics of phase separation (normalized) at the lower critical consolute point (mole fraction of TEA of 0.08) compared to the kinetics at 0.2 and 0.28 mole fractions of TEA.

decreases with temperature.⁶ We note that the composition usually used in our experiments has a TEA mole fraction of 0.2 (used to reduce thermal gradients), which is close to that corresponding to the lower critical consolute temperature on the phase diagram⁴² where we expect the spinodal line to touch the binodal line.^{54,61,62} Further, when the experiment was conducted at this lower critical consolute temperature with a “deep quench” the kinetics were essentially the same (Figure 4) supporting the application of the spinodal concept in our discussion. In this latter case, it should be facile to enter the homogeneously phase separating region of the diagram after the T-jump thereby avoiding any metastable region. This suggestion is consistent with the very rapid onset of the spectral changes and the fact that there is no incubation period to H-bond reordering during which nuclei form, as we may expect to observe if we were in the binodal region. Even when the mole fraction of TEA was higher (0.28) the kinetics for the H-bond reorganization did not significantly alter, within our experimental error, as can also be seen in Figure 4. Thus, the TEA/water mixture separates spontaneously and rapidly restructures at all temperatures and compositions presently used.

Also clear from Figures 3b and 4 is that the kinetics of the slowest kinetic region from, 200 ns until 1 μ s, do not exponentially decrease. In this kinetic region, the H-bonding appears to decrease in a rather linear fashion with time up to 1 μ s. At 1 μ s, the H-bond reduction rate slows down rather abruptly with no change occurring after this time. We suggest that this slow kinetic phase of spectral evolution may be associated with the formation of more clearly defined sharpened concentration gradients as molecules continue to migrate and also to the phase ripening that occurs to minimize surface energy requirement that typifies the intermediate stage spinodal phase change.^{54,62} During the early stage of bicontinuous phase formation bulk free energy change will dominate events since interfaces and surfaces are ill defined. Later in this process surface energy changes dominate leading to phase ripening. We can consider probable reasons for the nonexponential kinetic behavior of this proposed intermediate phase. On one hand, as defined domains form, the chemical potential gradient will increase with respect to a given distance, and thermal reversibility of the phase separation will become less significant with time tending to accelerate the process. However, as phase domains form and their sizes increase, the surface contact of the water-rich phase to the TEA-rich phase will decrease and this will tend to slow the rate at which H-bonding contacts between the two phases are reduced at interfaces as the phase domain size is increasing. Also less surface contact reduces the effective transfer rate of molecules from one phase to another. Importantly, after 1 μ s no further change in the molecular level interactions occurs, which means that we can hypothesize that both the early and intermediate stages of spinodal decomposition

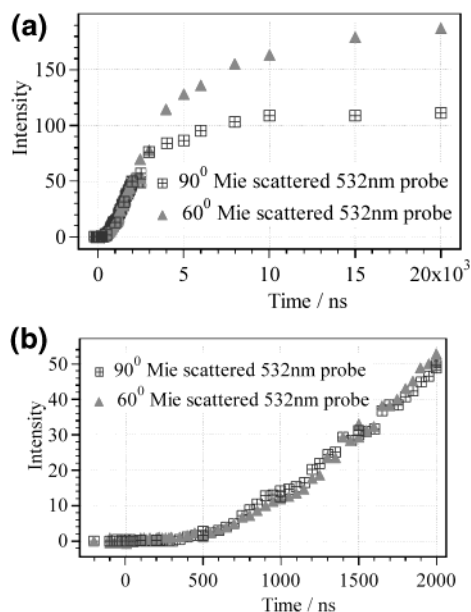


Figure 5. (a) Kinetics of morphological change monitored using light scattering on the long time scale and (b) at earlier times. T-jump from 13 to 20 °C; mole fraction of TEA was 0.2.

should be over after this time, since both early and intermediate stages involve changes in molecular composition.⁵⁴ If this hypothesis is correct then any events observed after this time should be due the late stage coarsening.

Mie Scattering. No increase in Mie scattering of the probe beam was observed from the absorption of the laser pulse until 200 ns (Figure 5). From 200 to 1000 ns, we could observe the onset of scattering of the probe beam. This further suggests that the Raman spectral changes in this time scale are due to early stage spinodal decomposition. This is reasoned because, from this light scattering of the 532 nm probe beam, we see when phase splitting is occurring on a macroscopic or morphological level. This light scattering is probing the formation of well-defined phase regions that are of sufficient characteristic length (ξ) to increase the scattering efficiency of the 532 nm probe light ($\xi > 1\%$ of λ i.e., >5 nm at minimum) and with sufficiently large gradients of refractive index to induce scattering. We suggest that prior to the observation of significant Mie scattering, with our Raman probe we are probably observing the formation of concentration gradients in a spinodal wave with ill-defined refractive index gradients.^{60–62}

In the time scales up to 3 μ s, the 60° and 90° scattered light components grow in concert indicating that any phase boundaries that form are still in the smaller range of the so-called large particle regime of Mie theory. However, after around 3 μ s the intensity of light scattered at 60° overtakes that of the 90° scattered light, indicating the formation of larger regions that favor forward scattering. This is expected simply due to the merging of regions by diffusion and collision. For the forward scatter to become favored the domain size should be of the same order as the 532 nm probe beam, in other words, in the order of hundreds of nanometers. The light scattering increased further, gaining a plateau after around 16 μ s. Note that in early times up to a few microseconds the amount of scattering was relatively low meaning that optical interferences to the Raman probe will be minimal.⁵² This light scattering data can only give a general estimate of events at this time scale as multiple scattering is obviously occurring based on the time course of scattering events.^{12–16} Also scattering depends on the number of scattering regions, the dimension of each scattering

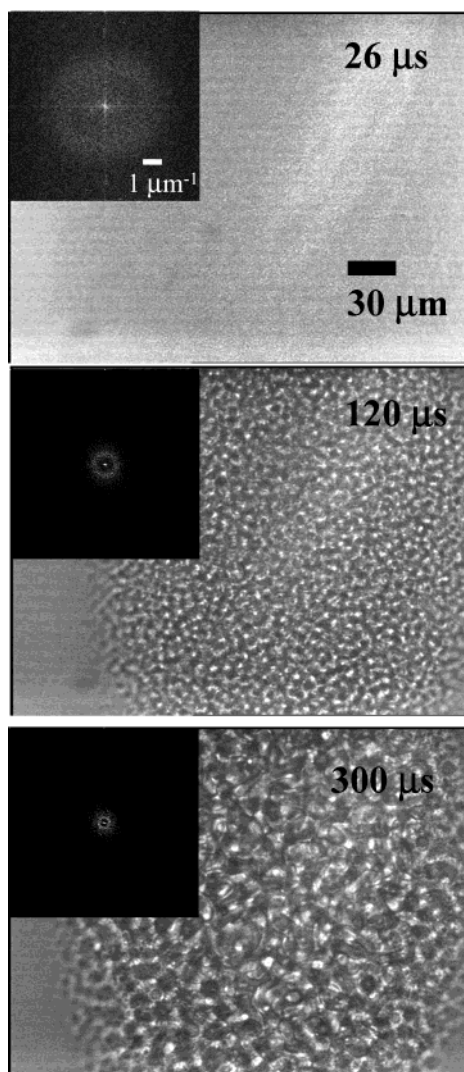


Figure 6. Time-resolved microscopic images and Fourier transforms of these images for phase separating TEA/water. Note the maximum in the implied scattering vector that is characteristic of spinodal decomposition. T-jump from 15 to 22 °C, Mole fraction of TEA was 0.2.

region as well as the refractive index gradient at the boundary of the scattering regions. Scattering measurements can also be subject to artifacts,⁵⁰ and a better more reliable probe of morphological change was required to combine with all the previous data. However, within limits the scattering measurement can potentially give some information on morphology at early nanosecond time scales, and we can get an idea of the time evolution of events from such measurements especially after comparison with data from other techniques.

Microscopic Shadowgraphy. Microscopic imaging of the phase separation was highly enlightening as from these pictures we obtained direct time dependent morphology changes of the phase domains. By Fourier transforming these images we could infer the magnitude of the scattering vector and from this we could estimate the average domain size.^{63,64} Importantly, the Fourier transform of these images revealed a maximum in the scattering vector, which supports our assignment of spinodal decomposition to our observations.^{10,54,64} Typical microscopic images and Fourier transforms are shown in Figure 6.

First these images appear to show that our probe area was laterally rather homogeneous. More importantly, from these images we could estimate the growth rate of the phase domains

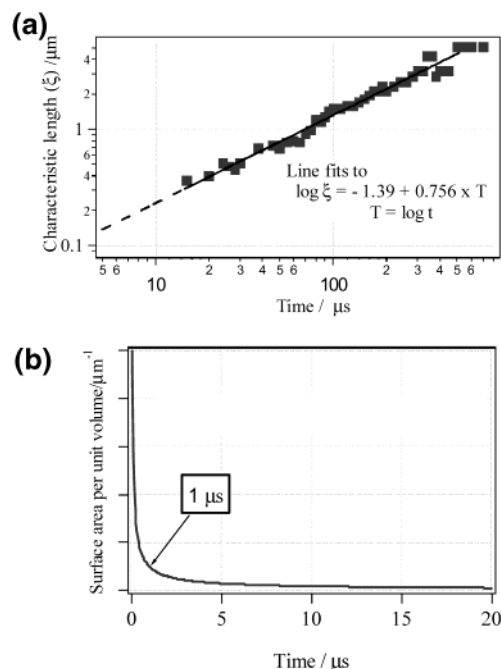


Figure 7. (a) Time scale for domain size characteristic length growth. (b) Implied surface contact change between domains with time (assuming late stage mechanism). The conditions were the same as for Figure 6.

with time, from which we found that in the microsecond time scale the scale of length (ξ) of phase domains increased with time following a simple power law $\xi \sim t^{0.76}$ while the structure evolved with self-similarity. A plot of domain size growth with time is shown in Figure 7a. From the value of 0.76 for the exponent of the domain growth with time and from the Raman data we can more clearly conclude that we are in the late stage of spinodal decomposition even in this early microsecond time scale.^{5–11,54} Further, although the resolution of our microscope limits us to measuring phase domains only after $\sim 10 \mu\text{s}$, we can extrapolate the growth rate with time, assuming that we remain in the late stage of spinodal decomposition, to earlier times. In this way, we can also estimate the rate of change of surface contact between phase domains with time at earlier times. This is useful because it allows us to estimate the time at which the rate of decrease of surface contact would become negligible in the process of H-bond contact reduction. The derived change of surface contact with time, assuming late stage dynamics and mechanism, is plotted in Figure 7b.

From Figure 7b, we can clearly see that the loss of surface contact with time plateaus at around $1 \mu\text{s}$, which is consistent with the lack of Raman spectral change observed after $1 \mu\text{s}$. At this time, the domain size has an estimated characteristic length of around 40 nm. This value is also reasonable in view of the Mie scattering data, which roughly suggested that domain sizes greater than hundreds of micrometers were only formed after 3 μs .

Overview. It is interesting to note that in our case we have kinetics for spinodal decomposition for a simple binary mixture that are several orders of magnitude faster than observed by previous authors.^{5–11} Differences in experimental protocol must account for the differences. Our quench is from a temperature well below the two-phase region and to a depth of quench far higher than possible in the previous works. Our technique is far more universally applicable as we are not limited so much in our starting and final temperatures. We do not need to wait for thermal equilibration as vibrational relaxation in water is a

picosecond time scale process.⁶⁵ We should consider that the fluctuation wavelength that dominates spinodal decomposition in the early stage is determined by the high energy required to create high-frequency waves coupled with the constraint of increased molecular diffusion times for low-frequency waves. If we jump our system to higher temperatures putting more energy into the system then higher frequency waves should be supported. We can compare our derived characteristic length of 40 nm at the onset of late stage with a typical value inferred from a previous work for which $\xi > 4.5 \mu\text{m}$.⁵⁻⁷ We draw attention to the following expression describing the early stage dynamics:^{6,53}

$$R(Q) = -[M(\chi^{-1}(T_f) + 2\kappa Q^2)]Q^2$$

For which, $R(Q)$ is the growth rate of the amplitude of the fluctuation wavenumber Q and $\chi(T_f)$ is the susceptibility. $\chi^{-1}(T_f)$ is itself related to the free energy change with changing composition (second derivative of free energy with composition). M is the molecular mobility and κ is a constant. $\chi^{-1}(T_f)$ is proportional to $(T_f - T_c)/T_f$ where subscripts f and c denote final and critical. In other words, the domain growth rate in the early stage of the phase change process will increase with quench depth. Compared to the work by Mallamace,⁵⁻⁷ our deeper quench depth should increase the initial growth rate by around 2 orders of magnitude or more based on this proportionality and by the expected increase in diffusion with temperature meaning that the onset of intermediate and late stages can also be shifted to earlier times. Also based on the work of Cahn,⁵⁴ Mallamace describes⁶ that $\chi(T_f) < 0$ in the spinodal region and that R changes sign when $Q = Q_c = 2(\kappa\chi)^{-1/2}$. The most rapidly growing value of Q can be called $Q_m = Q_c(2)^{-1/2}$; therefore, $Q_m = (2)^{-1/2}2(\kappa\chi)^{-1/2}$. This means that a higher final temperature in our T-jump will favor a larger value for the maximally amplified wavenumber Q_m since $\chi^{-1}(T_f)$ is proportional to $(T_f - T_c)/T_f$. This will also lead to an increased initial rate with our deeper quench. The apparent paradox of the similarity in the form of the kinetic from the Raman data is actually still consistent with this discussion, because even though the normalized data has apparently similar kinetics, the molecular flux in the uphill diffusion process is obviously still greater with higher temperature meaning that the amplitude of the scattering vector Q_m will in fact still grow faster. Also, even though Q_m will be larger at higher T-jumps the number of molecules that need to migrate to reequilibrate will also be increased since the extent of phase separation is also increased.

The starting condition may also be an important factor, because as we move our system to the critical point from the one-phase to the two-phase region, the characteristic length increases according to the following scaling expression until the critical point:³⁰

$$\xi \sim \xi_0[(T_c - T)/T_c]^{-\nu}$$

The conclusion that we can draw is that from this is that a binary liquid mixture T-jumped from just below its critical point may already possess some large amplitude structure compared with one T-jumped from a lower temperature. This means that fluctuations with a given wavenumber range that are already partially amplified in terms of concentration gradient, due to long-range structuring near the critical point, may have an advantage in the subsequent spinodal decomposition process following a sudden T-jump.

4. Conclusions

We provide a molecular level insight into the fast nanosecond time scale of spinodal phase decomposition of a classically studied binary mixture (TEA/water). We reveal molecular processes occurring far in advance of bulk changes observed by light scattering and microscopy. The phase separation of TEA/water at the mole fractions studied begins within the 8 ns heating pulse and occurs with no incubation time. The activation barrier to the phase change appears to be low and we propose that the spinodal mechanism dominated under our conditions. This is confirmed by microscopic imaging. In the present case, the rate of spinodal phase change is several orders of magnitude faster than previously reported for similar simple systems. The growth rate of domain size has been determined and the lifetime of all of the important phases of this process have been estimated. In the time from 0 to 200 ns the liquid structure is itself transient. In the time from 200 ns to 1 μs , we propose that restructuring and domain size increase is occurring at the same time. In the later stage after 1 μs , the size of domains increases in a regular fashion.

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