

Ultrafast laser-induced molecular and morphological changes during spinodal demixing of water/2-butoxyethanol/KCl

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We initiated morphological and molecular level changes in the spinodal decomposition (SD) of H₂O/2-butoxyethanol/KCl with a pulsed ir laser. Transient Raman spectra gave us a molecular level view of the early stage of this process that could be linked to later morphological events. Chemical changes during SD, such as reorganization of H bonds and forced hydrophobic interactions, ended after 1 μ s; however, phase domains continued to grow with self-similarity after 30 μ s. The growth of the phase domains satisfied the power law $L(t) \sim t^{0.55}$ and was consistent with the late stage of SD. The time scale for the onset of late stage SD is many orders of magnitude faster than previously reported in ionic and nonionic conditions.

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This work describes the early nanosecond to microsecond dynamics of spinodal decomposition (SD) in a binary liquid mixture with added electrolytes. We present molecular level spectroscopic and morphological evidence that late stage SD begins ~ 6 orders of magnitude faster than in previous reports [1–7]. We link the time scales of early molecular level events and later morphology changes.

Demixing can proceed via SD, after a deep enough quench into the two-phase region [1–7]. SD can be split into three time zones [1,2,6]. In the early stage, changes in intermolecular attraction are the trigger for SD. Destabilized molecules migrate down natural fluctuation gradients minimizing their chemical potential in an uphill diffusion process. Concentration gradients between the phases form and sharpen whilst concentration fluctuation wavelengths remain constant [8,9]. In the intermediate stage, concentration gradients sharpen more whilst concentration fluctuation wavelengths also increase [6]. In the late stage, phase domains have constant concentration but the domains coarsen, minimizing their surface energy [6].

The morphological and molecular structures of liquids at their critical points have been studied using many techniques, including neutron [10,11], x-ray [10,12], and Raman scattering [13]. Dynamic measurements have been limited to long time scales, because cooling or heating from the one-phase to the two-phase region is slow due to the technical limit of heat exchange. Alloys and polymer blends [6,14] have been well studied because the characteristic time scale of SD is long so measurement is easier. Fewer works report the dynamics of phase separation for simple binary mixtures [1–5,7] and when they are reported, although the data is of great quality, the time scales of the measurement are from the late ms to late minutes time scale. However, small molecules in solution rapidly diffuse, so to study molecular level reordering we should have short nanosecond time resolution with a spectroscopic probe. To overcome the technical limit

of fast heating we developed a nanosecond microscopic shadowgraphy and a time resolved Raman pump-probe system, allowing us to T jump by more than 100 K and follow the resulting events during the phase change [15].

The 2-butoxyethanol (BE)/H₂O binary system has a lower critical temperature of 322 K at a BE mole fraction of 0.052 [1]. The liquid structure depends on the mole fraction of BE according to Raman [13] and x-ray scattering studies [12]. Subcritical mixtures are said to have morphological and molecular structure, with BE behaving as a micelle or hydrophobic surfactant. The addition of salt lowers the lower critical temperature of a binary mixture [11,16]. In a 0.052 mole fraction BE/H₂O mixture the addition of 0.01 mole fraction KCl reduces the critical temperature from 322 K to 301 K without dramatically altering the shape of the coexistence curve.

The experimental setup is shown in Fig. 1. A 1.9 μ m pulse was made by Raman shifting a 1064 nm, 8 ns laser pulse [Spectra Physics GCR200, Nd-YAG (yttrium aluminum garnet) 1 J/pulse] in 35 atm of H₂ gas. Raman backscatter of 300 mJ/pulse was obtained when using the injection seeder of the pump laser [17,18]. A subcritical mixture of H₂O (distilled)/BE (0.052 mole fraction, 99.0% Kanto

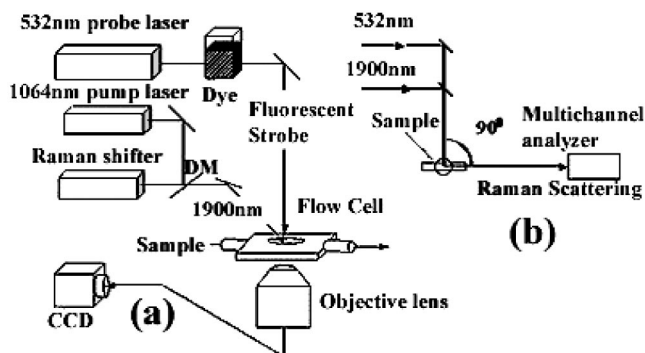


FIG. 1. Apparatus for (a) shadowgraphy and (b) Raman measurement. DM=1064 nm dichroic mirror.

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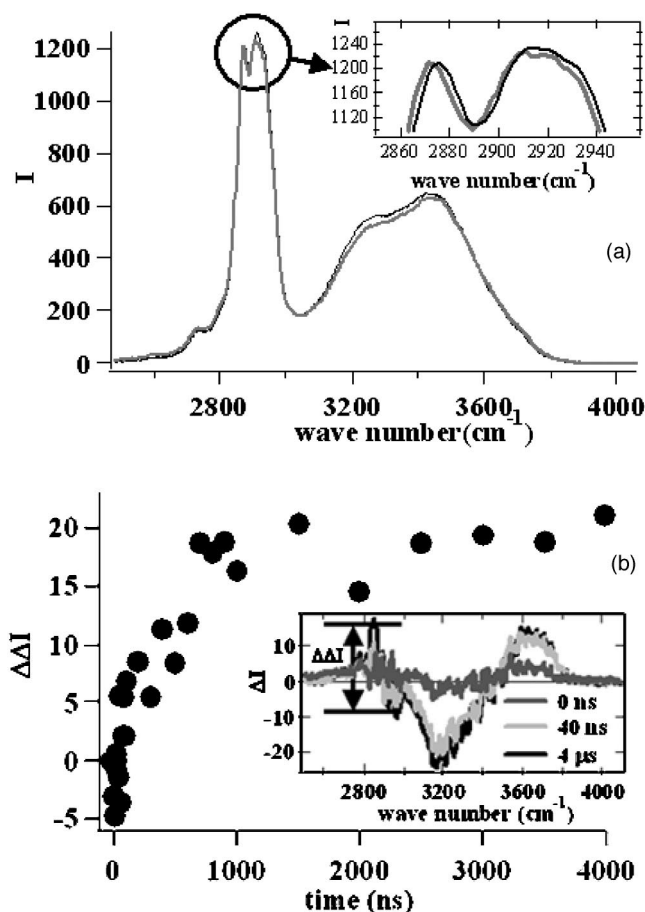


FIG. 2. (a) Raman spectra during SD. Inset: red shifting from -10 ns to 500 μ s. (b) Difference spectra.

Chemical Industry)/KCl (0.01 mole fraction, Wako Pure Chemical Industry) was heated from 291 K using the 1.9 μ m pulse. The front face of the liquid was estimated to be 321 K after the T jump by comparing of the OH region of Raman spectra obtained after the T jump with spectra obtained with static heating [15]. The sample was flowed to provide a fresh mixture between laser pulses in a quartz cell (1 mm thick for shadowgraphy, flow < 5 ml/min, and 200 μ m thick for Raman, flow 50 ml/min). The mixture's absorption coefficient at 1.9 μ m meant that phase separation only occurred in the front 100 μ m in each case. The incoherent strobe for shadowgraphy was fluorescence from a Rhodamine B solution, emitted after excitation by an 8 ns, 532 nm laser pulse (Quantel Brilliant Nd-YAG). This illuminated the cell mounted on a microscope stage (Olympus IX70, $40\times$ objective lens, focal depth 10 μ m). Transmitted light images were obtained with one shot by a charge-coupled device (CCD) camera. Raman scattering was accumulated from the 532 nm probe (Kaiser Optics spectrograph, Hamamatsu PMA-50 gated photodetector). Pump-probe synchronization was achieved with a delay generator (Stanford Instruments DG535). From Raman spectra we extracted the difference in Raman intensity before and after $t=0$. The C-H stretching region is sensitive to changes in H-bonding and hydrophobic interactions [19] so we could monitor molecular level interactions as shown in Fig. 2(a).

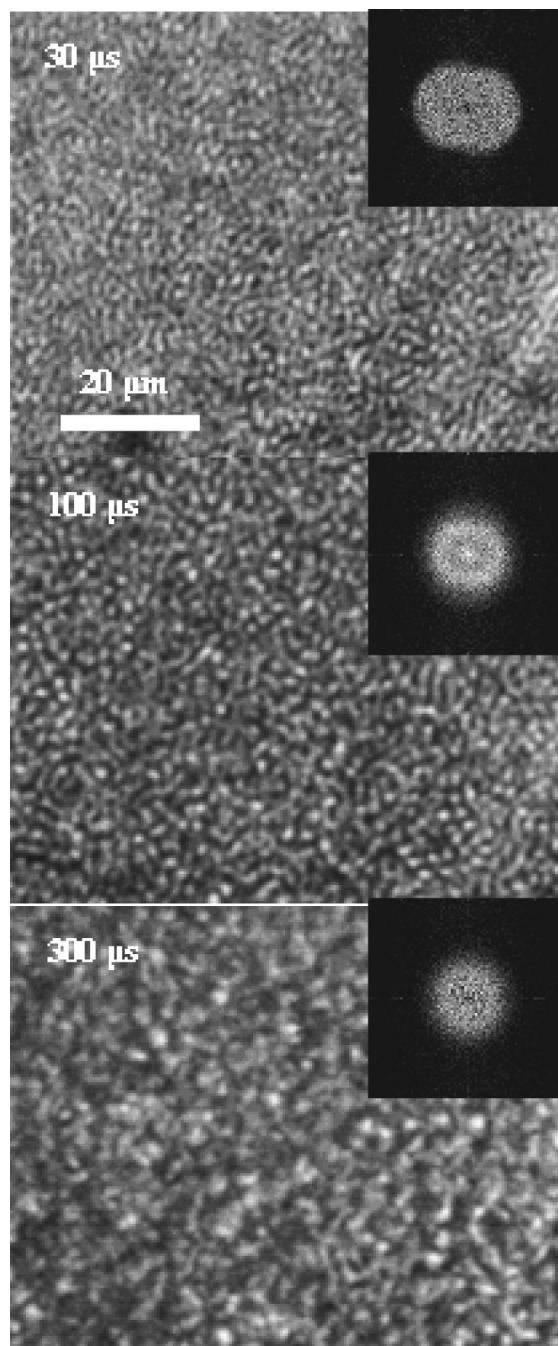


FIG. 3. Shadowgraphs and two-dimensional fast Fourier transforms, taken after a T jump.

Apparent from Fig. 2(b) is that the molecular level change ended 1 μ s after the T jump, suggesting that the early and intermediate stages of SD are also over in 1 μ s, since these both involve composition changes within the phase domains that would lead to spectroscopic change. Also within 1 μ s, phase ripening must have reached a stage where any reduction in interphase surface contact would not reduce the number of forced H-bond or hydrophobic interfacial contacts further. Considering surface area and volume ratios, this occurs for phase domains lengths $[L(t)]$ of > 50 nm.

After the 30 μ s we obtained shadowgraphic images of phase ripening as shown in Fig. 3. From these images we

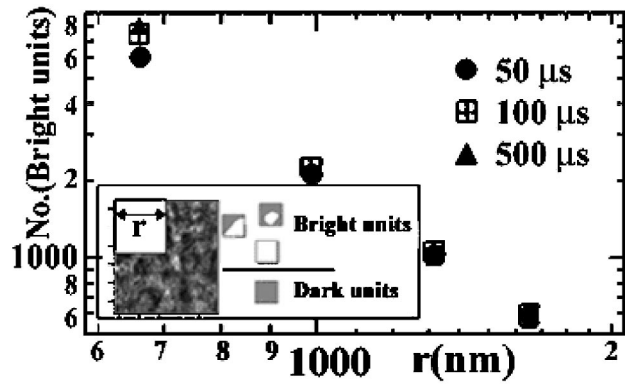


FIG. 4. Self-similar growth of phase domains shown by fractal analysis at different times.

deduced that the morphology maintained self-similarity over time. Referring to Fig. 4, we defined unit areas of dimension r within the image and determined whether they contained bright regions (bright units). We found that from unit lengths of a few hundred nm to a few μm , the summed area of bright units could be expressed as the same fractional power of r satisfying the power law: (No. bright units) $\sim r^{-1.8}$. This means that domains grow with self-similarity with a fractal dimension of 1.8.

By Fourier transforming these images we obtained the wave number of the scattering vector (see Fig. 3) and $L(t)$ of the phase domains [14,20]. The Fourier transforms had spinodal rings appearing to validate the use of the SD mechanism to describe our system, with a caution that uniform growth of similar size droplets would also give this result. The change of $L(t)$ with time (Fig. 5) follows the power law $L(t) \sim t^{0.55}$. Recall that the analysis of time resolved Raman spectra suggested that molecular level events ended after 1 μs , suggesting that at 1 μs late stage phase ripening had begun and that $L(t)$ was already >50 nm. To test this hypothesis we extrapolated $L(t)$ back to 1 μs , obtaining a value of 65 nm, which is close to the 50 nm expected.

The focal depth of the microscope objective is 10 μm and that shadowgraphic images were taken from the front face of the sample, whereas Raman spectra are an average of the full sample depth. Despite this, by comparing difference spectra over a range of known static temperatures and considering the exponential heating profile after a T jump, we can state

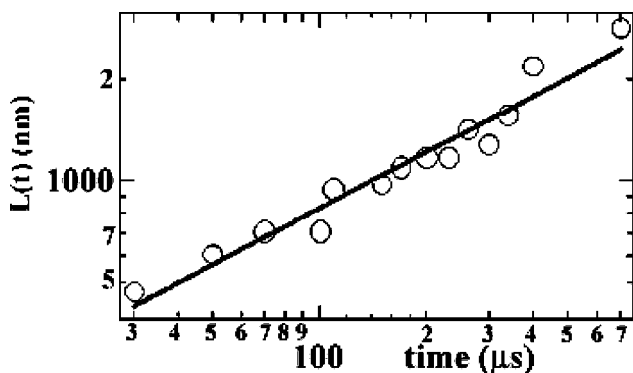


FIG. 5. The time evolution of $L(t)$.

that the main contribution to the Raman difference spectra after a T jump is also from the front face of the sample rather than the entire 100 μm undergoing SD. This is because the extent of molecular separation is greater where the sample is hotter (at the front face of the cell) giving a larger contribution to the spectral difference. Thus the two data sets follow events from similar regions validating the comparison.

Compared to previous research on $\text{H}_2\text{O}/\text{BE}$ systems [1] and to other work on ionic [1,2] and nonionic systems [3–5,7], the onset of the late stage is ~ 6 orders of magnitude faster. However, our experiment has two differences compared with those of other researchers. One is that we do not need to wait for thermal equilibration as this occurs in a few ps [21]. Also, if we jump to higher temperatures than previously achieved then shorter fluctuations can evolve, although current theory needs to advance to cover such large T jumps. Our extrapolated value of $L(t) = 65$ nm at the onset of the late stage can be compared to values from previous works of >4.5 μm [1,2] for ionic surfactants, ~ 5 μm [4], and >2 μm for nonionic samples [5]. That a smaller $L(t)$ will give faster kinetics is implied by the following expression for early stage SD [1,22]:

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

with the caution that, strictly speaking, this expression applies to systems with no long-range interactions. We justify its application here because the behavior of ionic surfactants can also be described by this expression [1,2]. In Eq. (1), $R(Q)$ is the growth rate of the amplitude of the wave number Q that is amplified. $\chi^{-1}(T_f)$ is the second derivative of the free energy change with composition. $\chi^{-1}(T_f) \propto (T_f - T_c)/T_f$. κ is a constant and M is the molecular mobility. T_c and T_f are, respectively, the critical and final temperature after a T jump. The value of Q that amplifies depends on T_c and T_f . Consider the interpretation given by Mallamace, Micali, and Trusso [1] based on the work of Cahn [22], 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 and $Q_m = Q_c(2)^{-1/2}$; therefore, $Q_m = (2)^{-1/2}2(\kappa\chi)^{-1/2}$. This means that higher T_f 's favor a larger amplified Q_m [smaller $L(t)$'s], and larger $R(Q)$ since $\chi^{-1}(T_f) \propto (T_f - T_c)/T_f$. Other groups used quench depths of ~ 0.05 K compared to 21 K in our case, giving us an expected 400-fold increase in the initial rate (early stage) of SD from the first term in Eq. (1). So the intermediate stage could reasonably start 400 times sooner as could the late stage. This still leaves several orders of magnitude difference between our rate and previous rates. However, $Q_m \propto [\chi^{-1}(T_f)]^{1/2}$ so a deeper quench will alter Q_m by a factor of the ratio of $[(T_f - T_c)/T_f]^{1/2}$ from each study, so values of Q_m in our work can be 20 times larger [$L(t)$ 20 times smaller]. Notably, scaling down the $L(t)$ values from other studies by 20 gives values of ~ 75 nm at the beginning of the intermediate stage and around ~ 125 nm in the early part of late stage [1,2] which are broadly consistent with our derived $L(t)$ values at the beginning of the late stage. Considering Q_m 's value, $R(Q_m)$ will further increase in our case by Q_m^2 in the first term (400 times), and Q_m^4 in the second term

(1.6×10^5 times) of Eq. (1), so that the overall rate increase is expected to be less than 5 orders of magnitude, considering that M also increases with temperature. This makes our work consistent with that of Mallamace on BE/H₂O and ionic surfactants [1,2] and with other works [4,5].

$$L(T) \sim L(0) [(T_c - T)/T_c]^{-\nu}. \quad (2)$$

In the one phase region, as the temperature rises towards the binodal line, Eq. (2) holds [23–25] [empirically $\nu = 0.61$ and $L(0) = 0.45$ nm for a 0.0661 mole fraction BE/H₂O mixture] [25], meaning that a mixture just below its critical point already has a finite amplitude $L(T)$ so the initial condition can be a factor.

Comparing our morphology to simulations of SD [26,27] we find some qualitative similarity, although the simulations do not consider the presence of ions, which may affect the structure. Indeed, arguably, our structures appear less bicontinuous than some simulations.

To conclude, we showed that a pump-probe laser T -jump system can induce and follow nanosecond events during SD. We followed SD spectroscopically to see events such as H-bond weakening, molecular migration, and changes in intermolecular attraction and in repulsive contacts as domains grew. These data were linked in time to morphological kinetics. These kinetics were ~ 6 orders of magnitude faster than similar systems undergoing SD [1,2,4,5] or nucleation [28]. $L(t)$ at the start of the late stage is tens to hundreds of nanometers compared to a few μm in previous reports [1,2,4,5]. Our future work will cover a range of T jumps from less than 1 K to several Kelvin to both accommodate and attempt to advance the current theory.

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- [1] F. Mallamace, N. Micali, and S. Trusso, *J. Phys.: Condens. Matter* **8**, A81 (1996).
- [2] F. Mallamace, N. Micali, S. Trusso, and S. H. Chen, *Phys. Rev. E* **51**, 5818 (1995).
- [3] K. Kubota, N. Kuwahara, H. Eda, and M. Sakazume, *Phys. Rev. A* **45**, 3377 (1992).
- [4] K. Kubota and N. Kuwahara, *Phys. Rev. Lett.* **68**, 197 (1992).
- [5] Y. C. Chou and W. I. Goldburg, *Phys. Rev. A* **20**, 2105 (1979).
- [6] F. S. Bates and P. Wiltzius, *J. Chem. Phys.* **91**, 3258 (1989).
- [7] J. S. Huang, W. I. Goldburg, and A. W. Bjerkaas, *Phys. Rev. Lett.* **32**, 921 (1974).
- [8] J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **28**, 258 (1958).
- [9] J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **31**, 688 (1959).
- [10] T. Takamuku *et al.*, *J. Phys. Chem. B* **105**, 6236 (2001).
- [11] K. Yoshida *et al.*, *J. Chem. Phys.* **113**, 2343 (2000).
- [12] Y. F. Yano, *J. Chem. Phys.* **116**, 8093 (2002).
- [13] N. Ito, T. Fujiyama, and Y. Udagawa, *Bull. Chem. Soc. Jpn.* **56**, 379 (1983).
- [14] Q. Tran-Cong, T. Ohta, and O. Urakawa, *Phys. Rev. E* **56**, R59 (1997).
- [15] A. Takamizawa, S. Kajimoto, J. Hobley, K. Hatanaka, K. Ohta, and H. Fukumura, *Phys. Chem. Chem. Phys.* **5**, 888 (2003).
- [16] V. Balevicius and H. Fuess, *Phys. Chem. Chem. Phys.* **1**, 1507 (1999).
- [17] R. Yamamoto, T. Ebata, and N. Mikami, *J. Chem. Phys.* **114**, 7866 (2001).
- [18] R. Yamamoto, T. Ebata, and N. Mikami, *Eur. Phys. J. D* **20**, 403 (2002).
- [19] Y. Maeda, *Langmuir* **17**, 1737 (2001).
- [20] H. Hoppe, M. Heuberger, and J. Klein, *Phys. Rev. Lett.* **86**, 4863 (2001).
- [21] H. K. Nienhuys, S. Wotersen, R. A. van Santen, and H. J. Bakker, *J. Chem. Phys.* **111**, 1494 (1999).
- [22] J. W. Cahn, *J. Chem. Phys.* **42**, 93 (1965).
- [23] J. D. Gunton, M. San Miguel, and P. S. Sahni, *Dynamics of First Order Transition, Phase Transitions and Critical Phenomena*, edited by C. Domb and J. Libowitz (Academic Press, London, 1983), Vol. 8.
- [24] H. Eugene Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Clarendon Press, Oxford, 1971).
- [25] St. Fusenig, D. Woermann, *Ber. Bunsenges. Phys. Chem.* **97**, 583 (1993).
- [26] Y.-L. Tang and Y.-Q. Ma, *Phys. Rev. E* **65**, 061501 (2002).
- [27] N. S. Martys and J. F. Douglas, *Phys. Rev. E* **63**, 031205 (2002).
- [28] R. Steinhoff and D. Woermann, *J. Chem. Phys.* **103**, 8985 (1995).