

Low-power laser driving of a binary liquid

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We have investigated the interaction of a laser beam with a near-critical binary liquid by observing how the growth of the concentration gradient due to gravity (the barodiffusion gradient) is modified by the presence of the beam. We observe definite evidence of laser driving in the system: The size of the steady-state barodiffusion gradient increases with increasing laser power, and the system exhibits different dynamical behaviors in the limit of high and low powers. Since our results cannot be explained by a purely diffusive model, we conclude that convection must be important in the system and present an estimate of the laser power at which convection should become significant. [S1063-651X(98)10510-X]

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I. INTRODUCTION

The interaction of laser beams with delicate systems such as microemulsions, liquid crystals, and near-critical liquids has attracted much recent interest. For example, the interaction of a laser with strongly absorbing samples has been investigated in a series of papers that describe the interesting dynamics of the “heartbeating” of the laser beam’s profile after passing through a sample near an interface [1]. Further, near-critical binary liquids have also been suggested as possible model systems for the study of nonlinear optical phenomena because they may exhibit nonlinear properties at lower laser powers than are required in more traditional experiments. The theory of the nonlinear propagation of a Gaussian beam through such a binary mixture has been presented [2]; however, the treatment neglects convection, which should almost certainly be present since any absorption of energy from the laser will create horizontal density gradients in the system, which will introduce convection.

When a light beam passes through an absorbing liquid mixture, the laser modifies the structure of the liquid (and therefore its index of refraction) through thermal and electrostrictive effects [2]. The temperature field set up in the liquid by the laser affects the index of refraction n directly through the temperature dependence of n and also indirectly by changing the local concentration of the liquid by creating Soret diffusion (diffusion due to temperature gradients). Electrostrictive effects also contribute to changes in the local concentration.

Two of these processes are enhanced when the mixture is held near a critical point. As a binary liquid approaches its critical point, the index of refraction should remain well behaved, while the concentration gradients due to Soret diffusion diverge [3]. The concentration and index of refraction gradients due to electrostriction should also diverge since the electrostriction is proportional to the osmotic compressibility of the mixture, which diverges near the critical point [2]. The electrostrictive contribution also depends directly on factors such as the size of the laser beam. For the particular beam geometry, intensities, and distance from the critical point used in the experiment we are reporting, the theory of Ref. [2] shows that electrostriction should not be an important effect. Thus we will restrict our discussion

to the temperature and diffusive effects of the beam.

While work on theory for the propagation of light in critical mixtures has been done, there has not been extensive experimental work. One set of workers, Giglio and Vendramini, reported the modification of the shape of a laser beam after passing through a near-critical binary liquid [4]. The two main results were (i) that the beam diameter increased linearly with intensity until (ii) as the power was increased further, the originally Gaussian beam became asymmetric and the behavior deviated from linearity. The work was mainly qualitative because the authors did not know the precise distance of the system from its critical temperature, but it still convincingly introduced the idea of self-lensing due to Soret diffusion within the laser beam.

We have studied the interaction of a laser beam with a near-critical binary liquid by observing how the laser modifies a small concentration gradient in the mixture called the barodiffusion gradient. The barodiffusion gradient, a vertical concentration that appears when the liquid mixture is at rest in a gravitational field, has been studied on several occasions [5–7]. The general flux equation for a binary liquid is given by

$$\mathbf{j} = -\rho D \left(\nabla c + \frac{k_T}{T} \nabla T + \frac{k_p}{p} \nabla p \right), \quad (1)$$

where \mathbf{j} is the mass flux of one component, ρ is the mass density, D is the mutual diffusion coefficient, c is the mass fraction concentration of the component, p and T are the pressure and temperature, and k_p and k_T are the barodiffusion and thermodiffusion ratios. The ∇c term is the flux due to concentration diffusion, the ∇T term is the flux due to Soret diffusion mentioned earlier, and the ∇p term is the flux due to barodiffusion. All three of the fluxes have the same characteristic timescale, determined by the diffusivity D . At equilibrium with no temperature gradients, a small vertical concentration gradient, the barodiffusion gradient, will be present in the mixture, given by

$$\nabla c = -\frac{k_p}{p} \nabla p = \frac{k_p}{p} \rho \mathbf{g}. \quad (2)$$

The second equality holds since the Earth's gravitational field \mathbf{g} provides the pressure gradient in the sample. Like the Soret gradients, the size of barodiffusion gradients also diverges on approaching the critical point [6,7]. For small gravitational fields and small heights (conditions that hold in the experiment reported here), the equilibrium concentration profile is linear.

Any nonequilibrium effects in a liquid, such as convection or temperature diffusion, could modify the size of this vertical concentration gradient away from its equilibrium value. We specifically became interested in the effect of the laser beam in critical mixtures while studying the effect of buoyancy-driven convection on the growth of the barodiffusion gradient [5]. The question of the interaction of the laser with liquids is also important in laser techniques that are used in measuring diffusion coefficients [8] as well as in thermal lens spectrometry [9]. Laser techniques have also recently been used to study spinodal decomposition of binary liquids [10].

In this paper we report observations of the modification of the barodiffusion gradient by a horizontal low-power laser beam. The technique uses the laser beam both as the probe and the perturber of the system. Our results show definite evidence of laser driving even at very low powers. A purely diffusive treatment of the problem cannot explain the results and we conclude that convection must be present in the sample to explain the observed behavior. We also estimate the laser power above which convection should begin to modify the barodiffusion gradient significantly and compare this estimate to our results.

II. EXPERIMENT AND RESULTS

We use the same experimental apparatus and procedure as described in greater detail in a previous paper [5]. A single-phase mixture of aniline and cyclohexane is held about 200 mK above its critical temperature T_c in a thermostat. The sample is prepared in a well-mixed state with mechanical stirring. When the stirring ceases, a barodiffusion gradient grows in the sample and is observed using a beam deflection technique. The expected diffusion time for the growth of the gradient is given by the expression [5]

$$\tau = \frac{h^2}{\pi^2 D}, \quad (3)$$

where h is the height of the sample. At 200 mK from T_c , the diffusivity $D = 8.3 \times 10^{-8}$ cm²/s [11] and we expect the growth time to be $\tau = 3.4$ h. Accordingly, the concentration gradients are allowed to evolve for 16 h in order to reach a steady value.

To observe the vertical concentration gradients in the mixture, a beam from a 3-mW He-Ne laser is passed through a variable attenuator and then through the sample, which is held in a slot 10 mm wide and 1 mm tall. The dimension of the sample parallel to the laser beam is 20 mm. When the laser beam reaches the sample, its radius R (the $1/e^2$ radius, within which 86.5% of the power lies) is 0.42 mm; approximately 2% of the beam power is apertured by the slot. Changes in the index of the refraction of the sample perpendicular to the beam path (for instance, due to concentration

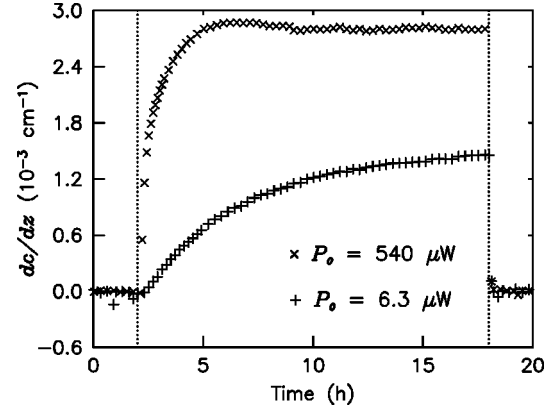


FIG. 1. Two runs at high and low intensities. During intervals 0–2 h and 18–20 h, the mechanical stirring is on, creating a well-mixed system; the interval 2–16 h shows the growth of the barodiffusion gradient.

variations) will cause a deflection of the beam. The vertical concentration gradients dc/dz are related to the vertical displacement of the beam Δz by the expression [6]

$$\frac{dc}{dz} = \left(\frac{\partial n}{\partial c} \right)_{p,T}^{-1} \frac{\Delta z}{lL}, \quad (4)$$

where again c is the mass fraction concentration of aniline, n is the index of refraction of the mixture, l is the depth of the sample along the beam path, and L is the distance to the detector. Thus the beam deflection and the vertical concentration gradient are directly related through a constant of proportionality. Since the beam has a finite size, it actually measures a spatial average of the index of refraction variations in the beam path.

The intensity and vertical position of the beam are measured after it passes through the sample by a position sensing photodiode. The photodiode voltage has been calibrated using a power meter tuned to the He-Ne wavelength in order to get an absolute power reading for the transmitted beam. Since the incident intensity was not measured during each run, the transmittance of the sample was measured for a series of laser powers at the end of the data set, allowing us to deduce the incident power P_0 for each run. We estimate the error in the calibration to be about $\pm 10\%$ for the powers used in the experiment. (The calibration assumes that the opacity of the sample does not vary with time; the validity of this assumption will be addressed later in Sec. III.)

The data presented here consist of a series of runs that observe the growth of the barodiffusion gradient for varying incident laser powers (between 6.3 and 1300 μW). Two typical runs, one at a low power and one at a high power, are shown in Fig. 1. In each run, the mechanical stirring remains on until time 2 h, at which point it ceases. The barodiffusion gradient dc/dz grows until time 18 h, when the mechanical stirring resumes, destroying the concentration gradient. The points, taken every 6 min, have been thinned in the plots for clarity. The smoothness of the two runs in the figure is characteristic of all the other data.

A summary of all the runs is shown in Fig. 2, which plots the size of the concentration gradient at the resumption of stirring versus the incident laser power. The average distance

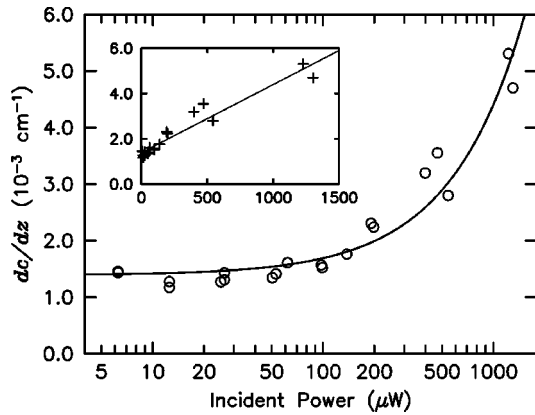


FIG. 2. Summary of measured barodiffusion gradient dc/dz versus incident laser power. The inset shows the same data with a linear scale for the power. The solid curve in each plot is a linear fit to the data.

from T_c for the runs is 204 ± 6 mK. The inset in the figure shows the same data plotted with a linear rather than a logarithmic intensity axis. We also have another data set taken with a different sample, but for which we had not calibrated the detector to measure an absolute intensity. The qualitative features of the two sets are identical.

III. DISCUSSION

Figures 1 and 2 show definite evidence of laser driving in the system. The observed concentration gradient dc/dz varies roughly linearly with the incident power as shown in Fig. 2. A linear fit to the data is also shown in the figure. The scatter in the data appears to increase as the intensity increases, but below about $50 \mu\text{W}$, the scatter begins to become indistinguishable from our expected experimental error of $\pm 0.15 \times 10^{-3} \text{ cm}^{-1}$ [12]. This suggests that there is an experimentally “safe” region at low powers in which we can measure equilibrium values of the barodiffusion gradient. The value of the slope ($3.0 \times 10^{-6} \text{ cm}^{-1} \mu\text{W}^{-1}$) should depend on the absorbance of the sample because it is the energy absorbed from the laser that perturbs the system. In some cases we have observed that the absorbance tends to increase over the lifetime of the sample (several months), by a factor of as much as 2. Thus some of the scatter in the data could be due to the changing absorbance of the sample. We believe that the intercept as the intensity goes to zero, $1.39 \times 10^{-3} \text{ cm}^{-1}$, yields the best measure of the equilibrium barodiffusion gradient because it should be independent of the absorbance.

Further evidence for the laser driving can be found in Fig. 1. Notice that the run performed at $P_0 = 540 \mu\text{W}$ reaches its steady value much faster than the $P_0 = 6.3 \mu\text{W}$ run. This trend is reflected in all the results. We can find a characteristic growth time τ at each intensity by fitting an exponential growth curve to each data run. The runs match the exponential form well and the characteristic growth time is plotted versus the incident power in Fig. 3. While the behavior of dc/dz with the incident power suggests an experimentally safe region below $P_0 \approx 50 \mu\text{W}$, the behavior of τ suggests that the laser continues to influence the dynamics of the system strongly even at very low powers.

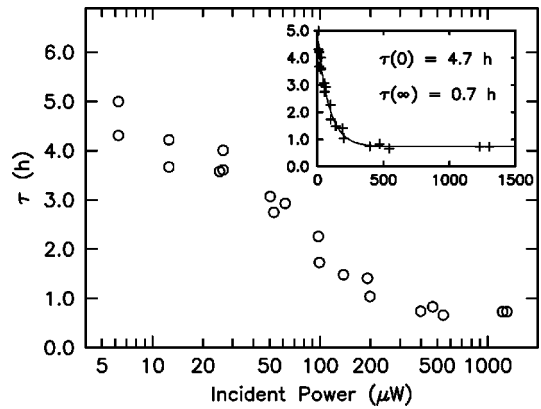


FIG. 3. Observed time constant τ for growth of the barodiffusion gradient plotted versus incident power. The inset shows the same data on a linear scale; the solid curve shows a nonlinear least-squares fit to an exponential decay. The y intercept of the fit is $\tau = 4.7$ h, while the asymptotic limit is $\tau = 0.7$ h.

The values of τ show evidence of two limiting regimes: a low-power limit in which diffusion across the entire slot dominates and a high-power limit in which diffusion within the laser beam dominates the behavior. In order to extract these limits, we performed a nonlinear least-squares fit of a decaying exponential to the data, shown by the solid curve in the inset of Fig. 3. In the limit of low laser power, τ should reflect the diffusion time for growth of the barodiffusion gradient over the entire height of the sample since the system is undriven. While the expected time of 3.4 h does not exactly match the observed limiting value of 4.7 h, it is certainly consistent with it, especially considering the fact that previous studies of barodiffusion have reported widely varying degrees of agreement with expected diffusion times [5].

As the laser power increases, the laser beam creates temperature gradients in the system, which in turn drives Soret diffusion within the beam, changing the local composition of the liquid. Near the critical point, the index of refraction gradients and density differences resulting from the Soret diffusion are much larger than those resulting solely from thermal expansion [4]. Thus the concentration gradients formed by Soret diffusion within the beam should dominate the behavior of the system. The characteristic time for this Soret diffusion is smaller than the bulk diffusion time (the low-power limit) by a factor of $(h/R)^2$ (again h is the height of the sample and R the radius of the laser beam). Using the appropriate values $h = 1.0$ mm and $R = 0.42$ mm predicts that $\tau(P_0 \rightarrow 0)$ should be about 5.7 times as large as $\tau(P_0 \rightarrow \infty)$. We observe a ratio of $4.7/0.7 = 6.7$, consistent with this proposed mechanism of Soret diffusion within the laser beam.

As is noted in the Introduction, any amount of heating by a laser should induce convection in a liquid. In a liquid mixture, the density (and therefore buoyancy forces) depends on both the temperature and the concentration. The Soret effect in the aniline-cyclohexane system acts such that the lighter component, cyclohexane, is drawn towards regions of higher temperature [3]. So both effects of the laser (thermal expansion and Soret diffusion) tend to make the liquid in the center of the beam rise.

One could imagine a situation in which the convection is

so slow that it should not significantly alter the behavior of the system. However, a nonflowing, purely diffusive approach that models the laser as a Gaussian-shaped temperature source and that includes both Soret and barodiffusion cannot explain our observations. Soret diffusion does alter the local concentration field, but the effect is symmetric about the center of the beam, so that the average concentration gradient (i.e., what we measure) remains unchanged. We have numerically solved the partial differential equation for the system to verify this. Thus we conclude that convection must be present in our system: There must be a plume of low-density liquid rising from the laser that enhances the observed dc/dz .

We have used the numerical results from the nonflowing system to try to get a rough estimate of how much convection the laser beam introduces into the system. The nonflowing results give us an estimate for the size of horizontal concentration gradients in the path of the beam, which drive the convection. (We are close enough to the critical point that the buoyancy forces are dominated by the Soret rather than the temperature gradients.) We then use scaling arguments to estimate the size of the resulting velocity field and how much this field should modify the barodiffusion gradient by advection. Assuming an absorption coefficient of 10^{-3} cm^{-1} , this approach, presented in greater detail in the Appendix, predicts that laser powers of order 1 μW should introduce significant convection into the system. This estimate is comparable to the lowest powers we used in the experiment; we present it mainly to show that one may expect to see convective effects due to laser driving even at surprisingly small intensities in such delicate systems as near-critical liquids.

IV. CONCLUSIONS

In this paper we have shown that a near-critical binary liquid is readily susceptible to laser driving, even at very low laser powers. The laser driving affects both the statics and dynamics of the system. In the data we have presented, the size of the steady-state vertical concentration gradient appears to vary linearly with the incident laser power and the time scale for the growth of the gradient appears to decrease exponentially with the incident power.

The dynamics of the system exhibit two limiting behaviors. The limiting low-power dynamics are consistent with a diffusive growth of the barodiffusion gradient across the entire height of the slot and the high-power dynamics appear to be dominated by Soret diffusion within the beam.

Previous work in this field has either neglected convection [2] or has even tried to explain some results by proposing an onset of convection [4]. However, there should be no threshold for convection in the system and our results cannot be explained without the presence of convection. An order of magnitude estimate suggests that convection could be expected to have a significant effect on the system at laser powers as low as 1 μW (intensities of about 1 $\mu\text{W}/\text{mm}^2$ in our experiment).

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APPENDIX: ESTIMATE OF THE IMPORTANCE OF CONVECTION

This is an order of magnitude estimate of the laser power necessary to modify the equilibrium barodiffusion gradient significantly. First we take a characteristic value of the horizontal concentration gradient in the beam from the numerical solution of the nonflowing model introduced in Sec. III. Using a value for the Soret coefficient of $k_T = 60$ [3], the model predicts a scaling for the horizontal concentration gradients in the beam of $c_x \sim 10^{-4}(aP_0)$, where c_x is the horizontal concentration gradient measured in mm^{-1} , a is the absorption coefficient of the mixture measured in mm^{-1} , and P_0 is the incident power of the beam measured in μW . Then, balancing the viscous dissipation term in the Navier-Stokes equation with the buoyancy term due to concentration differences [13,14] gives rise to a vertical velocity u that scales as

$$u \sim \frac{g\beta(c_x R)h^2}{\nu}.$$

Here g is the acceleration due to gravity, β is the volumetric expansivity of the mixture, R is the radius of the laser beam, h is the height of the sample, and ν is the kinematic viscosity. We are able to neglect the buoyancy due to temperature differences because we estimate the ratio of the temperature-driven buoyancy forces to those driven by concentration, $\alpha\Delta T/\beta\Delta c$, to be about 10^{-2} ; here α is the thermal expansivity of the mixture and ΔT and Δc are characteristic temperature and concentration differences within the beam. (We use the following values for the above properties: $\alpha = 0.99 \text{ K}^{-1}$ [15], $\beta = 0.32$ [16], and $\nu = 1.7 \times 10^{-2} \text{ cm}^2/\text{s}$ [17].)

The velocity field should then modify the barodiffusion gradient through advection of concentration. Thus, to estimate the importance of convection in the system, we compare the advective term with the concentration-diffusion term in the concentration equation [13]. This yields

$$\frac{\text{advection}}{\text{diffusion}} \sim \frac{g\beta(c_x R)h^3}{\nu D},$$

where D is the diffusivity of the system. When the above ratio, which can be interpreted as a Rayleigh number for the laser-driven system, becomes of order unity, the convection field will begin to modify the barodiffusion gradient significantly. Values of the absorption coefficient for our mixture are not readily available. However, benzene has an absorption coefficient of order 10^{-3} cm^{-1} in the He-Ne region [18] and we expect that a mixture of pure aniline and cyclohexane should have a similar value. It should be noted that

any contamination in the mixture (for example, any discoloration of the liquids due to oxidation) can increase this absorbance substantially (even by one or two orders of magnitude), making the system even more susceptible to laser

driving. Using the estimated absorption coefficient of the pure fluids ($a \approx 10^{-3} \text{ cm}^{-1}$), our approach predicts that a laser power of $P_0 \approx 1 \text{ } \mu\text{W}$ will introduce significant convection, as reported in the body of the paper.

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- [1] G. Gouesbet and E. Lefort, *Phys. Rev. A* **37**, 4903 (1988), and references therein.
- [2] B. Jean-Jean, E. Freysz, A. Ponton, A. Ducasse, and B. Pouligny, *Phys. Rev. A* **39**, 5268 (1989).
- [3] M. Giglio and A. Vendramini, *Phys. Rev. Lett.* **34**, 561 (1975).
- [4] M. Giglio and A. Vendramini, *Appl. Phys. Lett.* **25**, 555 (1974).
- [5] F. B. Hicks, T. C. Van Vechten, and C. Franck, *Phys. Rev. E* **55**, 4158 (1997).
- [6] M. Giglio and A. Vendramini, *Phys. Rev. Lett.* **35**, 168 (1975).
- [7] G. Maisano, P. Migliardo, and F. Wanderlingh, *J. Phys. A* **9**, 2149 (1976).
- [8] K. J. Zhang, M. E. Briggs, R. W. Gammon, and J. V. Sengers, *J. Chem. Phys.* **104**, 6881 (1996).
- [9] E. F. Simó Alfonso, M. A. Rius Revert, M. C. García Alvarez-Coque, and G. Ramis Ramos, *Appl. Spectrosc.* **44**, 1501 (1990).
- [10] N. F. Bunkin, A. V. Lobehev, and G. A. Lyakhov, *Usp. Fiz. Nauk* **40**, 1019 (1997).
- [11] P. Berge, P. Calmettes, B. Volochine, and C. Laj, *Phys. Lett.* **30A**, 7 (1969).
- [12] There are two main sources of error in dc/dz . The first contribution results from any mismatch of the baselines of the well-stirred system at the beginning and end of each run, which generally agree within $0.1 \times 10^{-3} \text{ cm}^{-1}$. The second contribution results from the expected variation of dc/dz with distance from the critical temperature T_c . The barodiffusion gradient is expected to scale with distance from T_c as $|T - T_c|^{-1.2}$ (see Ref. [5]). For the temperature range of the data, we expect this contribution to be about $\pm 5\%$ for the points taken at low intensities.
- [13] See, for example, D. J. Tritton, *Physical Fluid Mechanics*, 2nd ed. (Clarendon, Oxford, 1988), Chap. 14, for a discussion of the equations of motion governing convection.
- [14] The approximation of neglecting the inertial terms in the Navier-Stokes equation is further justified by the fact that the ratio of the kinematic viscosity to the thermal diffusivity (the Prandtl number) is large, about 20 for our system.
- [15] A method for finding an approximate value of α is described in T. C. Van Vechten and C. Franck, *Phys. Rev. E* **48**, 3635 (1993).
- [16] J. Timmermans, *Physico-Chemical Constants of Binary Systems* (Interscience, New York, 1959), Vol. 1.
- [17] G. Arcovito, C. Faloci, M. Roberti, and L. Mistura, *Phys. Rev. Lett.* **22**, 1040 (1969).
- [18] M. S. Burberry and A. C. Albrecht, *J. Chem. Phys.* **71**, 4631 (1979).