Optical Measurements of Gravitationally Induced Concentration Gradients near a Liquid-Liquid Critical Point*

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(Received 21 May 1975; revised manuscript received 24 June 1975)

Using a laser-beam deflection technique and a 1-mm-high sample, we have determined, for the first time, the magnitude of the steady-state concentration gradient due to the gravitational field in a binary mixture near a consolute critical point. The data have been taken, as a function of $T - T_c$, along the critical isochore. A strong γ-type divergence is observed. A comparison with the values calculated by use of our own set of osmotic compressibility data is also presented.

When a binary liquid mixture is brought close to a consolute critical point, large concentration gradients (and therefore density gradients) are expected to form, as a consequence of the gravitational field.[1] According to the theory, the magnitude of the steady-state gradient, at the height where the concentration attains its critical value, should diverge as a function of $T - T_c$ in the same way as the osmotic compressibility $(\partial c/\partial \mu)_{P,T}$ which is known to exhibit a γ-type divergence. Although qualitative observations of gravitationally induced concentration gradients were first reported by Lorentzen and Hansen,[2] and Blagoi, Sokhan, and Pavlichenko,[3] no systematic measurements of steady-state gradients have been attempted so far. Recently Greer, Block, and Knobler[4] have performed a series of density profile measurements in a sample of nitroethane + 3-methylpentane, utilizing a magnetic densitometer. Because of the height of the sample (76 mm), steady state could not be approached. Consequently the study was confined to the initial time evolution of the density profile, for a unique value of $T - T_c$, and only qualitative conclusions were drawn.

In this Letter we present, for the first time, measurements of the gravitationally induced steady-state concentration gradients, as a function of $T - T_c$, in a mixture of aniline and cyclohexane prepared at the critical concentration. These measurements have been performed by use of a laser-beam deflection technique in connection with a very thin sample in order to attain the steady-state concentration profile in a reasonably short time. We have also measured, as a function of $T - T_c$, the turbidity of the sample and consequently we have derived the temperature dependence of the osmotic compressibility $(\partial c/\partial \mu)_{P,T}$. From the values of $(\partial c/\partial \mu)_{P,T}$ we have then calculated the values for the steady-state concentration gradients, and these values have been compared with those determined experimentally.

The cell is made of an aluminum alloy, which proves to be quite inert when in contact with aniline, and at the same time has a reasonably good thermal diffusivity. The cell is rather massive in order to avoid temperature gradients which could cause spurious effects due to thermodiffusion processes.[5] The main body of the cell is made of two rectangular blocks, 46 mm long, sandwiched together. The lower block has a flat recess milled on it, 15 mm wide and 1 mm deep. Indium is used as a packing material between the two blocks, and also between the two flat optical windows tightened against the main body by means of two massive aluminum flanges. Filling is done through two small horizontal holes drilled on the lower block, and all the fluid sample is confined within a height of 1.1 mm. The temperature control of the cell is achieved by means of a two-stage temperature controller, utilizing a Peltier heat pump. Typical temperature drifts over one day are ± 0.5 mdeg. The mixture was prepared at the critical concentration, using aniline and cyclohexane of AnalaR quality. Filling was performed with the fluid in one phase, and the critical temperature T_c was determined by observing the appearance of the meniscus. Because of the greatly reduced transmittance of the sample, visual observations were hard to perform near the critical point, and the critical temperature could be determined to ± 5 mdeg only.

The optical setup is practically identical to the one described in a previous work.[5] A strongly attenuated He-Ne laser beam falls on a beam splitter. The transmitted beam power is monitored by a power meter, while the reflected beam is spatially filtered and mildly focused in the midplane of the sample. Because of the gravitationally induced concentration gradient, a refractive index gradient (dn/dz) is present inside the sample, and, consequently, the beam is deflected downward. At a distance $L = 80$ cm from the cell the beam is intercepted by a slit photomultiplier system mounted on a vertical driving stage. At each temperature, the steady-state beam center position $Y(T - T_c)$ can be located on the slit plane within ± 0.01 mm by scanning the vertical distribution of the beam power. The magnitude of dn/dz is then derived according to the equation

$$dn/dz = [Y(T - T_c) - Y_0]/IL , \qquad (1)$$

where I is the length of the fluid sample and Y_0 is the position of the beam center when no gradients are present. Measurements were performed in the temperature region $0.050°\text{C} \leq T - T_c \leq 2.303°\text{C}$. The value for Y_0 was determined by taking measurements away from T_c, at $T - T_c \geq 10°\text{C}$. In this temperature region, the gradients are too weak to be appreciated with our experimental technique.

It should be pointed out that when the sample temperature was varied in a controlled way by means of the thermostat, the beam never lost its Gaussian profile, and the time evolution of the beam center position could be easily followed. We found that while the sample attains the new temperature in a very short time (a few minutes), the gravitationally induced concentration gradients (evaluated in the center of the sample) evolve on a substantially longer time scale. The time constant characterizing this slow evolution is consistent with the value $\tau = a^2/\pi^2 D$, where a is the height of the sample and D is the diffusion coefficient at the final temperature. That is, the time constant for mass diffusion when the system is subject to pressure gradients is identical to that already observed in the case of temperature gradients[5] (Soret effect). We find typically, at $T - T_c = 0.134°\text{C}$, $\tau = 1.85 \times 10^4$ sec, from which $D = 6.6 \times 10^{-8}$ cm^2/sec, in agreement with the literature data.[6]

Values for the steady-state concentration gradient (dc/dz) were derived from dn/dz, according to the relation[7]

$$\frac{dc}{dz} = \left(\frac{\partial n}{\partial c}\right)_{P,T}^{-1} \frac{dn}{dz} , \qquad (2)$$

where $(\partial n/\partial c)_{P,T}$ has been taken from the literature.[8] The data for dc/dz as a function of $T - T_c$, are reported in Fig. 1 (c is the mass fraction concentration of aniline). A strong γ-type divergence can be observed. By fitting the data with a single power law we find $\gamma = 1.16 \pm 0.06$. Such a divergence is in agreement with the relation[9]

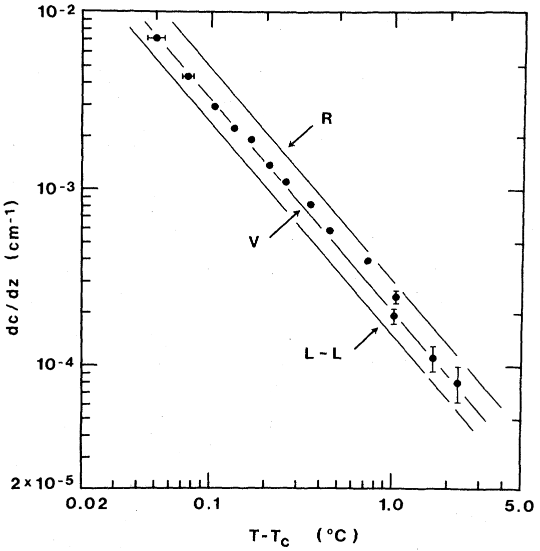

FIG. 1. Plot of the steady-state gravitationally induced concentration gradient (dc/dz) as a function of $T - T_c$, along the critical isochore. The solid lines represent the values for dc/dz obtained from turbidity measurements by taking for dn/dc the Lorenz-Lorentz value (L-L), the Vuks value (V), and the Rocard value (R).

$$\frac{dc}{dz} = \frac{g}{\rho}\left(\frac{\partial \rho}{\partial c}\right)_{P,T}\left(\frac{\partial c}{\partial \mu}\right)_{P,T} , \qquad (3)$$

since $(\partial \rho/\partial c)_{P,T}$ is known to be well behaved near the critical point. In order to check whether our experimental results for dc/dz are consistent with the numerical values calculated according to Eq. (3), we have performed absolute turbidity measurements since the osmotic compressibility $(\partial c/\partial \mu)_{P,T}$ is related to the turbidity κ through the expression

$$\kappa = \frac{8}{3}\frac{\pi^3}{\lambda_0^4 \rho}\left(2n\frac{dn}{dc}\right)^2 k_B T \left(\frac{\partial c}{\partial \mu}\right)_{P,T} , \qquad (4)$$

where λ_0 is the light wavelength. Equation (4) is valid provided $k\xi \ll 1$, where k is the light wave number and ξ is the long-range correlation length. Measurements of κ have been taken in the temperature region $0.5°\text{C} \leq T - T_c \leq 10°\text{C}$ where the condition $k\xi \ll 1$ is satisfied.[10] A difficulty, however, is encountered in trying to derive the numerical value of $(\partial c/\partial \mu)_{P,T}$ from turbidity data. Indeed, it is not yet clear which value for dn/dc should be used in Eq. (4). A choice which is made very often is to use the refractometric value, which practically coincides with that obtained by differentiation of the Lorenz-Lorentz equation (L-L). Such a procedure has been critized by Rocard[11] (R) and also by Vuks[12] (V) who have suggested alternative expressions. In all three cases dn/dc is a simple algebraic function of n. Using cgs units, we find that $(\partial c/\partial\mu)_{P,T}=A(T-T_c)^{-\gamma}$, where $\gamma=1.20\pm0.05$ and the values for A are $A_{\text{L-L}}=(5.75\pm0.7)\times10^{-7}$, $A_{\text{V}}=(7.73\pm0.9)\times10^{-7}$, and $A_{\text{R}}=(11.70\pm1.4)\times10^{-7}$. By extrapolating the behavior of $(\partial c/\partial\mu)_{P,T}$ we have calculated dc/dz for the different choices of dn/dc (see Fig. 1, where error bars have been omitted for clarity). The following conclusions can be drawn. The experimental values for dc/dz are of the correct order of magnitude. They also indicate, although somewhat qualitatively, that L-L and R values for dn/dc are either too high or too low. Better agreement is found when using Vuks's theory.

Finally, it seems appropriate to make here a few comments on the work of Greer, Block, and Knobler.[4] In their Fig. 1 they report density profiles at $T-T_c=0.785°\text{C}$ for various times, together with the theoretical steady-state profile, calculated by use of the parametric equation of state in conjunction with experimentally determined critical exponents (a reasonable choice was made for the reduction parameter of the chemical potential). According to the reported data, after only 15 days, the density gradient, at the center of the sample, is comparable with the indicated steady-state value. Incidentally we would like to point out that such a value is in fair agreement with the value one obtains by using turbidity data,[13] Eqs. (3) and (4), and Vuks's theory for dn/dc. If we take into account that[14] $D=5.9\times10^{-7}$ cm^2/sec, the time constant $\tau=a^2/\pi^2D$ comes out to be about 115 days. Therefore, the approach to steady state in the center of the sample observed by Greer, Block, and Knobler is considerably faster than that observed in our measurements when proper scaling of sample heights is taken into account. We have not been able to find a reasonable explanation for this discrepancy. Furthermore, an inconsistency can be noticed in the data of Greer, Block, and Knobler. Indeed, their experimental values for $d\rho/dz$ near the bottom and the surface of the sample are larger than the steady-state value. This is an inconsistent result, since one can show with quite general arguments that the value of $d\rho/dz$ at the boundaries must assume very rapidly a constant value equal to the equilibrium value. In fact, at the boundaries the mass flow is by definition equal to zero, and consequently the density gradient is the steady-state one.[15]

We would like to thank F. T. Arecchi, V. Degiorgio, L. Mistura, and H. L. Swinney for helpful suggestions. Discussions with S. C. Greer are also gratefully acknowledged.

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*Work partially supported by Consiglio Nazionale delle Ricerche.

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[7] Strictly speaking, $(\partial n/\partial c)_{T,\mu}$ should appear in Eq. (2) instead of $(\partial n/\partial c)_{T,P}$ since, at steady state, it is the chemical potential μ which is constant over the height of the fluid, while P changes because of the hydrostatic effect. The difference between the two derivatives, however, becomes vanishingly small near the critical point. See Ref. 1.

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[9] Expressions for the barodiffusion ratio k_P, from which dc/dz is immediately derived, can be found, for example, in L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, London, 1959). See also Ref. 1; M. Papoular, J. Chem. Phys. 60, 86 (1974).

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[15] This is the idea on which the so called "Archibald technique" is based. See C. Tanford, *Physical Chemistry of Macromolecules* (Wiley, New York, 1961).