work was performed under the terms of the agreement on association between Max-Planck-Institut für Plasmaphysik and EURATOM.

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Dynamics of Entropy Fluctuations in a Critical Binary Mixture

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(Received 15 September 1975)

Using a very sophisticated light-beating spectrometer and a new correlation technique, we have measured the relaxation time of entropy fluctuations in a critical binary mixture in the reduced temperature range of $4\times10^{-6}\leq t\leq10^{-1}$. In the hydrodynamic regime this relaxation time, which is proportional to the specific heat at constant pressure and critical concentration, is found to behave as $t^{-\alpha}(1+Bt^{+x})$ with a critical exponent $\alpha=0.059\pm0.003$ and $x=1.05\pm0.15$.

Light-beating spectroscopy has provided numerous important results regarding the dynamics of concentration fluctuations in liquid mixtures especially near the critical point. As a result of both the strong divergence of the intensity of the light scattered from these fluctuations and their critical slowing down, large signal-to-noise ratios can be achieved which allow a precise determination of the decay rate of concentration fluctuations Γ_c.

In critical binary mixtures the dynamics of entropy fluctuations is basically as important as the dynamics of concentration fluctuations. In the hydrodynamic regime, the decay rate of entropy fluctuations is $\Gamma_s'=D_s'q^2$ where q is the wave number of fluctuations and D_s' is a diffusion coefficient given by the ratio of Λ', a noncritical kinetic coefficient, to $C_{p,c}$ the specific heat per unit volume, at constant pressure and critical concentration.

Because of the coupling between entropy and concentration fluctuations, Λ' is slightly larger than the thermal conductivity Λ, except at the critical point where $\Lambda=\Lambda'$.[1] As the temperature T approaches T_c, $C_{p,c}$ is theoretically expected to follow the temperature dependence

$$C_{p,c}=At^{-\alpha}[1+Bt^{x}]+C,$$

where $t=\Delta T/T_c=(T-T_c)/T_c$. $At^{-\alpha}$ describes the asymptotic behavior of the specific heat and Bt^{x} is the first nonanalytic correction term predicted by renormalization-group theory.[2] The coefficients A, B and the regular part C of $C_{p,x}$ may be weakly temperature dependent (analytic functions of t). The critical exponent α and the subcritical one x are expected to be about 0.125 and 0.640,[3] respectively, for the three-dimensional Ising model.

Careful measurements of the D_s' can therefore lead to a determination of the value of α and may provide a test of renormalization-group theory for corrections to asymptotic scaling.[4] Unfortunately near the critical point, the intensity of the light scattered from entropy fluctuations diverges very weakly, as $t^{-\alpha}$, and the corresponding spectrum is consequently generally completely hidden by the wings of the concentration-fluctuation spectrum, which varies as $t^{-\gamma}$ with $\gamma = 1.22$. For this reason, even if the entropy-fluctuation spectrum has been detected in a critical binary mixture,[5] no experimental work has been published on its temperature dependence. In this Letter we show that using a very sophisticated light-beating spectrometer and a new correlation technique this temperature dependence can indeed be obtained with a good accuracy, at least in the case where the critical opalescence is not too strong.

All the measurements reported here were obtained on the nitroethane–3-methylpentane mixture, for which numerous critical data, and in particular the critical concentration, are well known.[6] The refractive indices of the two liquids are respectively $n^N = 1.3917$ and $n^3 = 1.3765$ at $T = 20°\mathrm{C}$ and $\lambda = 589.3$ nm.[7] Even if $n^N - n^3 = 0.0152$ is comparatively weak, scattering from concentration fluctuations is quite important near T_c and measurements become difficult with usual correlators because of their restricted dynamic range. Nevertheless, as shown in Fig. 1, the spectrum of entropy fluctuations is observable.

Reference grade 3-methylpentane for gas chromatography and synthesis grade nitroethane were obtained commercially. The nitroethane was dried and purified by fractional distillation and its purity controlled by gas chromatography. Both liquids were carefully filtered and a cylindrical fused quartz cell, with two optical windows, was filled with the critical mixture (0.499 mole fraction of nitroethane), cooled at liquid-nitrogen temperature, and sealed in vacuum. The critical refractive index, calculated from the Lorentz–Lorenz formula, is $n = 1.378$ and interferometric measurements have shown that $dn/dT = -(5.31 \pm 0.06) \times 10^{-4}\ \mathrm{K}^{-1}$.

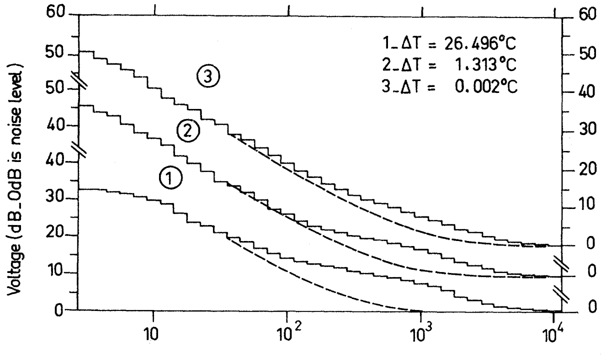

FIG. 1. Typical spectra of light scattered from the critical nitroethane–3-methylpentane mixture ($P \simeq 200$ mW, $\lambda = 514.5$ nm). The broken lines represent the tails of the concentration spectra.

The cell which is 1 cm long and 2 cm in diameter is contained horizontally in a massive copper oven whose temperature is controlled to ±0.5 mK for several days. The cell is oriented at the Brewster angle with respect to the laser beam to avoid spurious reflections in the inside. Near the cell the diameter of the laser beam was approximately 1.3 mm, its full divergence 0.80 mrad, and its height adjusted to pass through the sample at the level where the meniscus appears at T_c. Elastic scattering from dust on the cell walls provides a local oscillator. The light scattered from the sample and the cell walls is detected by a photomultiplier whose collection angle is 1.6 mrad and the direct laser beam is measured by a photodiode. The output currents from the two photodetectors are arranged to be equal and subtracted from one another in a differential amplifier. Thus the signal arising from spurious modulations of the laser light is almost completely eliminated[8] from the amplifier output; the output is applied through a tunable band-pass filter to a digital voltage correlator.

An unusually large dynamic range is required because the concentration line diverges near T_c (Fig. 1). The corresponding spectrum might be eliminated by means of a high-pass filter. Unfortunately near the critical temperature, the cutoff frequency must be set so high that the filter alters the self-correlation function[9] which must be then deconvoluted from the filter memory curve. The resulting accuracy is poor.

In order to avoid this drawback we have developed a new correlation method in which the signal is cross correlated with its own time derivative performed by a single RC filter chosen so that $1/RC \simeq \Gamma_s'$. It can easily be shown[9] that, for positives times only, the cross-correlation function is similar to the self-correlation function in which the relative intensity of the correlation function of concentration fluctuations is reduced by a factor of $2\Gamma_c/\Gamma_s'$. At low scattering angles, at which the measurements were made, this factor is about 10^{+2} at $\Delta T = 30$ K and 10^{+5} at $\Delta T = 2$

mK. This technique was widely checked and a complete report will be given elsewhere.[9]

The accuracy of this new correlation technique was estimated as follows. First, a 2-cm-long optical cell was filled with pure liquids and the decay rates Γ_s of entropy fluctuations were measured many times, using both the usual self-correlation techniques and the new technique. Within ± 1% the results were the same. A second cell, 2 mm long, containing 0.5-μm-diam latex spheres suspended in ethanol was then placed against one of the walls of the first cell. The particle concentration was adjusted to give a spectrum similar to the one of the critical mixture at $\Delta T \simeq 1$ mK. Under these conditions, our new correlation technique still gave the same values for Γ_s with a 2% standard error.

All the measured correlation functions have been plotted on semilogarithmic scales, after subtraction of the background due to the short-time behavior of concentration fluctuations. When the cross-correlation technique is used, this background is easily determined because it is simply a straight horizontal line. These plots show that the entropy fluctuations decay exponentially with time in the temperature range of 2 mK $\leqslant \Delta T \leqslant 30$ K. For $\Delta T \leqslant 1$ K the data were only obtained by means of the cross-correlation technique at $q = 2680 \pm 90$ cm^{-1}, corresponding to a 15.9 ± 0.6 mrad scattering angle in the sample for $\lambda = 514.5$ nm. Although the correlation length is about 0.4 μm at $\Delta T \simeq 2$ mK, all the data are in the hydrodynamic regime. For $\Delta T \geqslant 1$ K the measurements performed by means of the two techniques, under both the Brewster and the normal incidences, show that the decay rate Γ_s' is proportional to q^2 in the range 2500 cm$^{-1} \leqslant q \leqslant 5000$ cm^{-1}.

The results were found to be independent of both the incident power level ranging from 50 to 300 mW and the height of the beam in the sample within 2 mm either side of the meniscus level. Since both the Brewster and the scattering angles were held constant during the course of the experiment, the experimental accuracy is about ± 6% for Γ_s' whereas it is ± 9% for D_s' mainly because of the error in the Brewster angle.

Figures 2 and 3 show that the thermal diffusion coefficient D_s' decreases by about 35% when the temperature is lowered from $\Delta T = 10$ K to $\Delta T = 2$ mK. We attribute the slight decrease of D_s' for $T \leqslant 10$ K to a slowing down of entropy fluctuations of 3-methylpentane near its boiling temperature $T_b = 63$°C, i.e., $\Delta T = 36.5$ K. Indeed we have measured the thermal diffusivities of the pure components in the temperature range of 19°C $\leqslant T \leqslant 56.5$°C and found that the thermal diffusivity of 3-methylpentane is $D_s^3 = (0.85 \pm 0.01) \times 10^{-3}$ cm^2/sec at $T = 26.5$°C and decreases linearly with increasing temperature with a coefficient $dD_s^3/dT = -(3.1 \pm 0.3) \times 10^{-6}$ cm^2/sec K. On the contrary the thermal diffusivity of nitroethane $D_s^N = (1.03 \pm 0.01) \times 10^{-3}$ cm^2/sec was found to be nearly temperature independent. The broken line in Figs. 2 and 3 represents the thermal diffusivity $D_s^{id} = [(0.93 \pm 0.01) - (2.0 \pm 0.2) \times 10^{-3}\, \Delta T] \times 10^{-3}$ cm^2/sec of an ideal mixture of critical concentration, calculated from these data.

The data of Figs. 2 and 3 were fitted with the

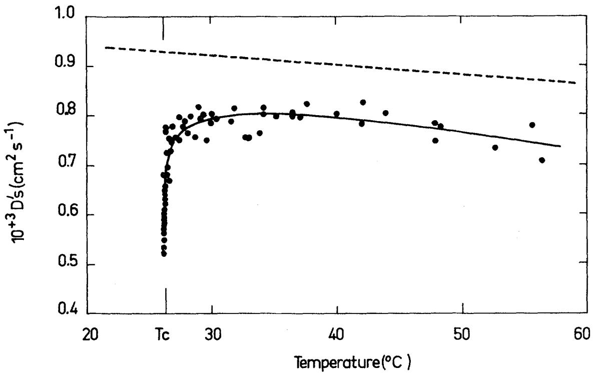

FIG. 2. The diffusion coefficient D_s' of entropy fluctuations in the critical nitroethane–3-methylpentane mixture (full circles). The broken line represents the thermal diffusivity of an ideal mixture of critical concentration.

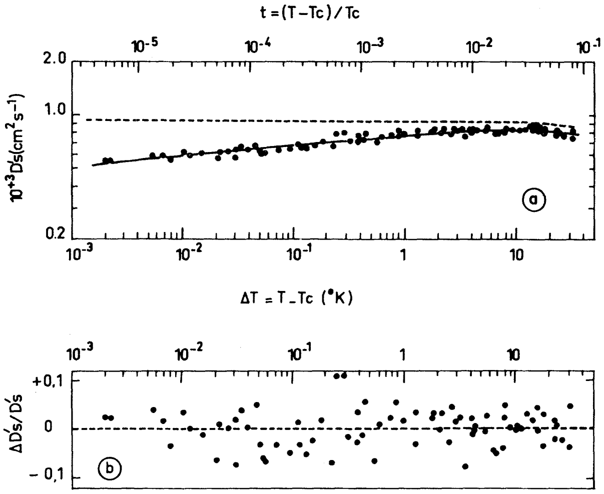

FIG. 3. (a) As in Fig. 2 but on log-log scales. The line represents the best fit through the data. (b) Deviations from this fit.

theoretical expression

$$D_s'=\Lambda'/[At^{-\alpha}(1+Bt)^x+C]$$

using a statistical refining program of Tournarie.[10] In this program, all the parameters are varied together and the given errors are always larger than one standard deviation because systematic errors are taken into account. The ratio Q of the statistical error to the total one is also given.

The best fit is obtained when the possible temperature dependences of A/Λ' and B are neglected and when C is fixed at zero. The results are

$$\alpha=0.059\pm0.003,$$

$$A/\Lambda'=(0.92\pm0.02)\times10^{+3}\ \mathrm{sec/cm^2},$$

$$x=1.05\pm0.15,\quad B=2.5\pm5.0,$$

with $Q=0.981$. The experimental deviations from this fit are shown in Fig. 3. The standard error is about 4%. The self-consistency of the fit was checked both by decreasing the number of data from $\Delta T\simeq30$ K to $\Delta T\simeq1.7$ K and by allowing C to vary freely. In any case the results were found to be constant within two standard deviations and C negligibly small ($C/C_{p,c}=0\pm10^{-7}$).

This study of the dynamics of entropy fluctuations in a critical binary mixture shows that (i) these fluctuations decay exponentially with a decay rate proportional to the square of their wave number in the hydrodynamic regime. (ii) The thermal diffusion coefficient D_s' follows the theoretically expected temperature dependence. (iii) The critical exponent $\alpha=0.059\pm0.003$ is significantly different from zero and consequently a logarithmic divergence of the specific heat $C_{p,c}$ cannot describe the data.[11] In order to verify the scaling laws where α is involved, we have also measured the decay rate of concentration fluctuations near T_c, but still in the hydrodynamic regime.[12] After correction for the temperature dependence of the viscosity[13] we obtain a critical exponent $\nu=0.644\pm0.005$. The scaling law $3\nu=2-\alpha$ gives then $\alpha=0.068\pm0.015$ in perfect agreement with our value. Furthermore our value agrees also with $\alpha=0.08\pm0.03$ inferred from the other scaling law $\alpha+2\beta+\gamma=2$, using experimental values[6] for the two other exponents. (iv) The background part C of $C_{p,c}$ is negligible for this mixture. We believe that the high temperature decrease of D_s' could prevent it from being estimated, but it should be noted that at the present time there is no firm experimental evidence of any backgrounds in binary systems, contrary to the case for pure fluids. (v) These data cannot be well described without the term Bt^x but its physical meaning remains somewhat ambiguous because $x\simeq1$. For $x\equiv1$ we find $Bt=(7.6\pm1.3)\times10^{-3}\Delta T$ with the same values and errors for the other parameters ($Q=0.979$). A similar study far from T_c of another mixture has not shown such a strong decrease of D_s'. Even if Bt is approximately three times greater than the temperature coefficient of D_s^{id} we believe that this term describes the temperature dependence of the coefficient A/Λ' rather than the predicted confluent singularity. If a linear temperature dependence is assumed for A/Λ' we find that the confluent singularity is completely negligible.

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