Experimental Study of the Relaxation of Concentration Fluctuations in the "Critical Region" of a Binary Mixture

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The results reported here, obtained by the heterodyne technique, show unambiguously that the relaxation of concentration fluctuations *is exponential* even very close to T_c. This experimental work thus confirms Kawasaki's assumption on the shape of this relaxation.

In a previous experimental study of a binary mixture of cyclohexane and aniline,[1] we showed that there was a "critical region" in which the linewidth Γ of the spectrum of scattered light is given by the equation $\Gamma = AK^3$, where A is a constant independent of temperature. During this experimental study, it seemed to us, within the experimental precision, that the obtained spectra were no longer quite Lorentzian,[2] a result which might imply that the relaxation of concentration fluctuations was no longer exponential.

So it was of a great interest to study very carefully this "critical region" in order to determine the exact shape of the relaxation of concentration fluctuations.

One knows that, in optical spectroscopy by means of photon beating,[3,4] the spectrum obtained by the heterodyne technique gives directly the spectrum of the scattered light, whereas the spectrum obtained by the self-beating technique gives the convolution by itself of the real optical spectrum only if the statistical distribution of the scattered field is Gaussian, as was shown first by Benedek[5] and later by Cummins and Swinney[6]; it was shown also that very close to T_c this distribution might be non-Gaussian.[7]

If the relaxation of concentration fluctuations is exponential the heterodyne spectrum will be Lorentzian whatever the statistical distribution of the scattered field might be.

If the statistical distribution of the scattered field is Gaussian, then the self-beating spectrum will be the convolution of the heterodyne spectrum by itself, and, in particular, if the latter is Lorentzian, with a linewidth equal to Γ, the self-beating spectrum will be also Lorentzian with a linewidth equal to 2Γ.

Experimental device.—The cell used for this study had a rectangular shape, 2 mm thick, in order to avoid as much as possible multiple scattering. The scattered light was collected, at an angle $\theta = 170°$ with respect to the incident direction, by a photomultiplier with appropriate diaphragms. At each temperature we got, thus, a self-beating spectrum. Then by changing slightly (2 or 3° maximum) the orientation of the cell, the photomultiplier collected the inelastic light scattered in the backwards direction by the cell, as well as the light elastically scattered close to the regular reflection of the laser beam by the surface inhomogeneities of the cell. We used this elastically scattered light as a local oscillator.

We have thus a heterodyne device in which the intensity of the local oscillator is adjustable. The geometry of our device is such that it allows

Table I. Results of various experiments. In the calculations of $K\xi$ we used the following values: $\xi_0 = 2.11$ Å and $\nu = 0.62$.

	$T-T_c$ (mdeg)	$K\xi$	Γ, self-beating spectra (Hz)	Γ, heterodyne spectra (Hz)
Critical region	<3	16	1390 ± 100	626 ± 50
	4	7	1309 ± 100	635 ± 40
	7	5	1400 ± 140	625 ± 60
	10	3,8	1420 ± 140	680 ± 80
	25	2,1	1440 ± 140	639 ± 80
	48	1,3	1602 ± 140	710 ± 80
	136	0,72	2295 ± 200	1160 ± 200
	158	0,65	2210 ± 200	1095 ± 200

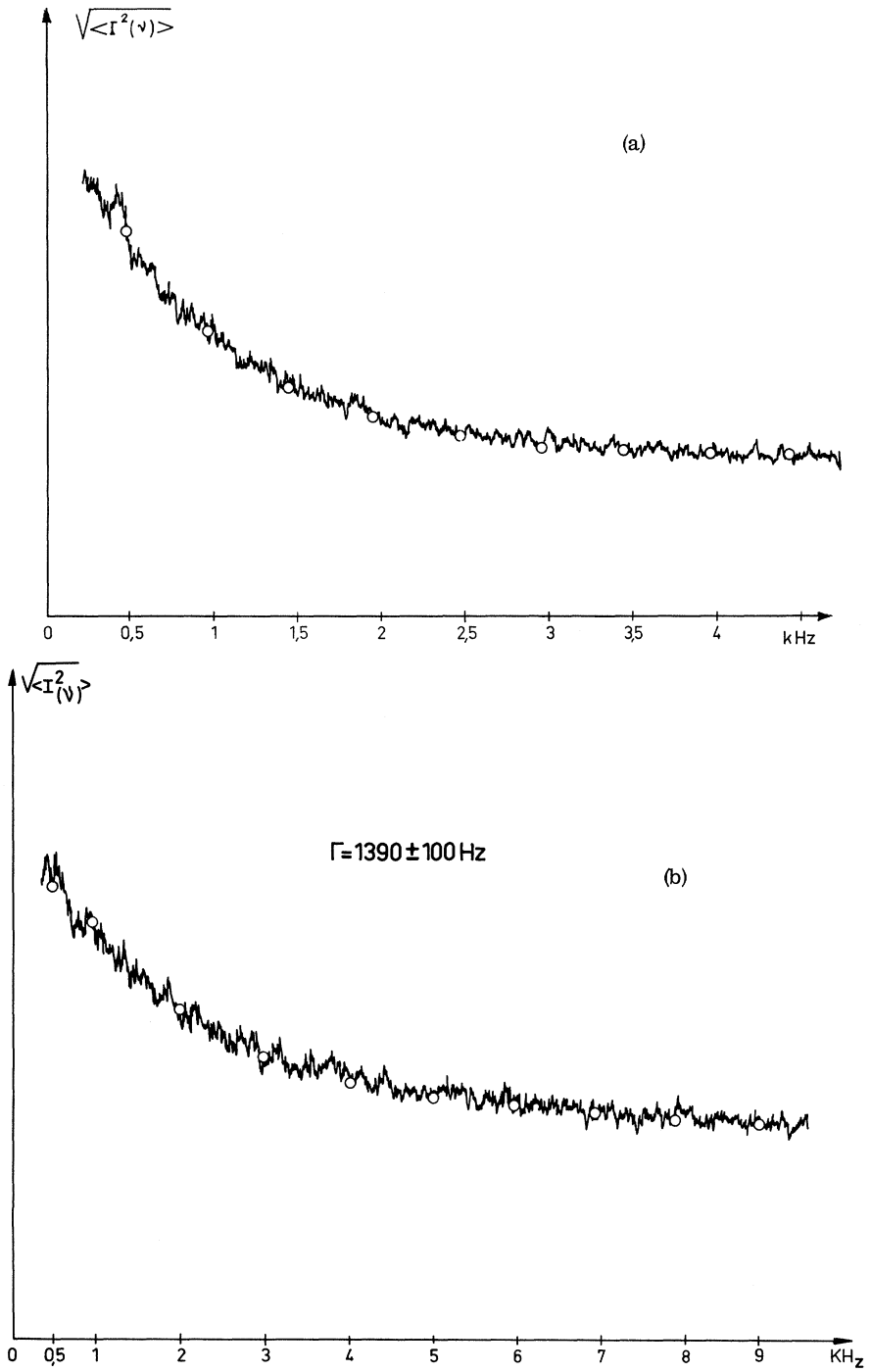

FIG. 1. (a) Heterodyne spectrum obtained at 4×10^{-3} °K. Circles denote points corresponding to the computed Lorentz line. (b) Self-beating spectrum obtained at 4×10^{-3} °K. Circles denote points corresponding to the computed Lorentz line.

us to work with practically one coherence area on the photocathode of the photomultiplier. As the intensity of the critical scattering is very strong, it is practically impossible to choose an intensity of the local oscillator much stronger than that of the light scattered by the mixture without blinding the photomultiplier. So we worked usually with ratios equal to $I_{\text{loc osc}}/I_{\text{inel scattering}} \simeq 60$ to 80. In these conditions the self-beating spectrum was not completely negli-

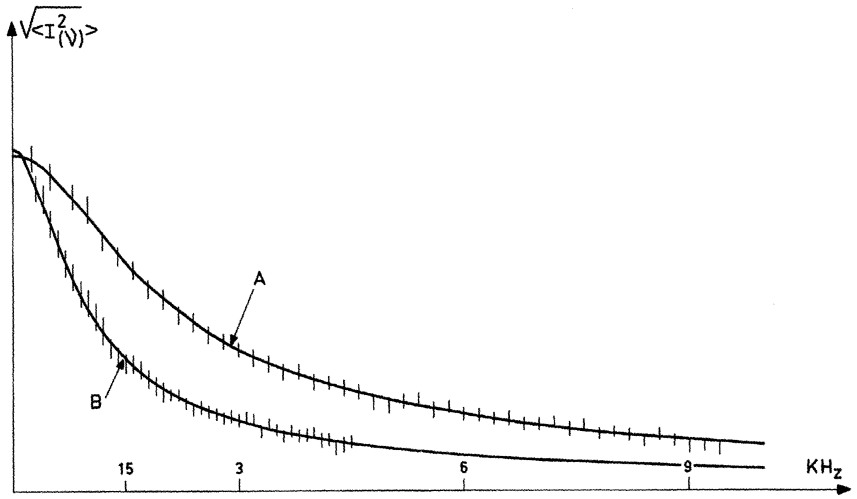

FIG. 2. Curve A, mean value of all self-beating spectra; curve B, mean value of all heterodyne spectra with the same frequency scale.

gible with regard to the heterodyne spectrum; in fact the self-beating spectrum gave a contribution of 10% maximum. Hence we corrected the spectra by subtraction before dealing with the information included in these spectra.

Experimental results.—Figures 1(a) and 1(b) give an example of a heterodyne spectrum and the corresponding self-beating spectrum, both obtained at $T-T_c = 4\times10^{-3}$°K. In fact all the experimental spectra are described by the square root of a Lorentzian line because we do not use a squaring device. The error on temperature must be taken equal to $\pm2\times10^{-3}$°K.

Table I is a résumé of the results of various experiments.

Figure 2 shows the mean value of all the self-beating spectra and the mean value of all the heterodyne spectra which we obtained in the critical region. We found

$$\Gamma_{\text{self-beating}} = 1395 \pm 60 \text{ Hz},$$

and

$$\Gamma_{\text{heterodyne}} = 649 \pm 50 \text{ Hz},$$

respectively. Examining in detail all these results we may conclude the following:

(1) All the heterodyne spectra are Lorentzian as shown in Figs. 1(a) and 2. This result shows unambiguously that the relaxation of concentration fluctuations is exponential even at $T-T_c < 3\times10^{-3}$°K. This result confirms the validity of the assumption made by Kawasaki.[8]

(2) All the self-beating spectra are Lorentzian[9]; their linewidth Γ is systematically equal to twice the linewidth of the corresponding heterodyne spectra, within our experimental precision, as is shown in Figs. 1(b) and 2.

This result seems to point out that the statistical distribution of the scattered field is Gaussian, even at $T-T_c < 3\times10^{-3}$°K. However the correlation length ($\xi \sim 5500$ Å) was much smaller than the linear dimensions of the scattering volume. Thus scattered light from a large number of uncorrelated volume elements was observed, and the distribution must be Gaussian by the central-limit theorem.

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[9]The observed discrepancy between a Lorentzian shape and the observed self-beating spectra which we noticed in a previous paper (Ref. 2) is probably due to the fact that we considered the asymptotic behavior of spectral density when $\omega \to \infty$, and in doing so we misestimated the level of the noise, which changed systematically the slope of the straight line obtained in the log-log plot.