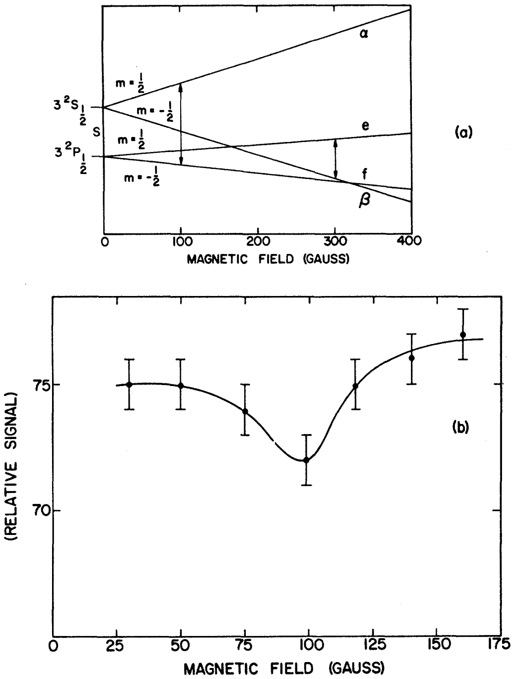

FIG. 2. (a) Relevant energy-level diagram with arrow showing the regions of observation. (b) α-β resonance signal when the energy of (HHH^+) was 400 ±20 keV with $2d$ (a period) = 0.97 cm, corresponding to an effective frequency seen by the moving hydrogen atom at 520 MHz with $E \sim 10$ V/cm.

reaction $Li^7(p,n)Be^7$ at 1.88 MeV and the magnetic field was measured by a Hall-effect gaussmeter. The motional electric field $\vec{v}\times\vec{B}/c$ is a special difficulty here. No special attempt was made to eliminate a possible small transverse component of the magnetic field. Since our beam-particle velocity is extremely high, a 2° misalignment of the Helmholtz coil can cause an E field and account for the discrepancy between our observation and that of Lamb and Sanders.[3]

We believe that this preliminary experimental result shows that one can observe a fine-structure energy separation by passing a beam of high-velocity atomic particles through potential barriers. Since it is conceivable that by using metallic gratings one can construct periodically varying electric fields with frequencies as high as 10^{12} Hz for the typical beam-particle velocities of 5×10^8 cm/sec, this technique may be useful for a great variety of resonance experiments where generation of such tunable high-frequency fields with reasonable power is beyond the present-day technology. The use of periodic potentials for the study of the Lamb shift was suggested independently by Sellin.[8]

We express our appreciation for the help of Henn Oona, Peter Stoss, and the members of the machine shop for their excellent cooperation for speedy construction of the various necessary components. One of the authors (T.H.) expresses his appreciation for the hospitality of the Physics Department of the University of Arizona during his leave of absence from Berkeley.

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†On leave from Lawrence Radiation Laboratory, Berkeley, Calif.

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LIGHT-SCATTERING MEASUREMENT OF CONCENTRATION FLUCTUATIONS IN PHENOL-WATER NEAR ITS CRITICAL POINT*

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The temperature dependence of the diffusion coefficient in phenol-water has been measured by analysis of scattered light. The data are compared with measurements in other liquid mixtures and pure fluids, and attention is drawn to interesting similarities.

In this Letter we report a study of the temperature dependence of the lifetime of concentration fluctuations in a critical mixture of phenol and water near its critical mixing temperature, T_c. The study includes what we believe to be the first extensive lifetime measurements in the two-phase region of a liquid mixture.[1] When compared with the experimental results of Swinney and Cummins on CO_2,[2] the data provide further evidence of the striking similarity between pure fluids and liquid mixtures near their critical points. This similarity appears to exist not only with regard to the critical exponents, but also with regard to ratios of parameters describing both the static and dynamic properties of the systems above and below T_c.

The experimental method used is the same as that described previously in a preliminary report on the phenol-water system.[3] Intensity fluctuations in light scattered by the concentration fluctuations are analyzed by a photon-correlation spectrometer, which measures the intensity autocorrelation function of the light $\langle I(t)I(t+\tau)\rangle$ by operating as a delayed coincidence circuit. For light scattered by thermally induced fluctuations which decay diffusively,

$$\langle I(t)I(t+\tau)\rangle = \langle I(t)\rangle^2(1+\beta e^{-2\Gamma\tau}),$$

where β is a constant $\lesssim 1$, and Γ, the quantity measured in this experiment,[4] is the inverse lifetime of the Fourier component of fluctuation causing the scattering. The same physical information can also be obtained using the "self-beat" method, which measures the Fourier transform of $\langle I(t)I(t+\tau)\rangle$.[5] For concentration fluctuations,

$$\Gamma = DK^2(1+K^2\xi^2), \tag{1}$$

where D is the mutual diffusion coefficient and ξ is the Ornstein-Zernike correlation length. The momentum transfer is $\hbar K$ with $K = (4\pi n/\lambda_0) \times \sin\frac{1}{2}\theta$.[6] Here n is the index of refraction of the mixture, λ_0 is the wavelength of the incident light, and θ is the scattering angle.

The phenol-water mixture was estimated to have impurity less than 2 parts in 10^4. According to the manufacturer (Mallinckrodt), the most abundant impurity in the phenol is H_3PO_4, which is added to suppress oxidation. It was removed by repeated washings with distilled water under a nitrogen atmosphere. The ultimate purity of our samples could be estimated from a knowledge of the phenol-water phase diagram, the assumed solubility of H_3PO_4 in each of the components, and the number of washings which were used. The sample tubes were sealed in vacuo to prevent oxidation of the phenol.[7] The critical concentration was found to be 35.0 ± 0.5 wt% phenol with an absolute accuracy of 1%. The critical temperature was 65.50 ± 0.005°C and the measurement was reproducible to within ±0.01°C over a period of months. The absolute accuracy of all temperature measurements was 0.2°C.

Measurements were made at $\theta = 33.0 \pm 0.5°$ both above T_c and in each of the two phases below T_c. These results are shown in Fig. 1 (curves A, C, and D), where $\Gamma_c/\pi \equiv (\Gamma/\pi)K_0^2/K^2$ is plotted as a function of $|T-T_c| \equiv |\Delta T|$ and $|T-T_c|/T_c$. Here K_0 is the wave number in the one-phase region. The corrected inverse lifetime Γ_c is introduced to take into account the small variation of refractive index with concentration (and hence temperature) in the two-phase region.

At $\theta = 33°$ and $T-T_c > 0.5$°C, the $K^2\xi^2$ term in Eq. (1) is observed to be negligible, and $\Gamma_c = DK_0^2$. From this equation and the data in Fig. 1, the temperature dependence of D may be found. The first row of Table I gives the results which were obtained by a least-squares fit of the data by the equation $D = D_0|\Delta T|^{\gamma^*}$. The quoted errors are generous and include values of D_0 and γ^* which result when T_c is left as an adjustable parameter in the least-squares fit. To investigate the possibility that the critical concentration had not been correctly located, measurements were made for $T > T_c$ on a sample of concentration 36.0 wt% phenol. The phase separation temperature of this sample was not measurably different from 65.50°C, and the data points lay well on curve A of Fig. 1.

On curve A of Fig. 1 the deviation from linearity at small ΔT is thought to be due to the Fixman term $K^2\xi^2$ in Eq. (1). As shown in curve B, this deviation from linearity becomes large at

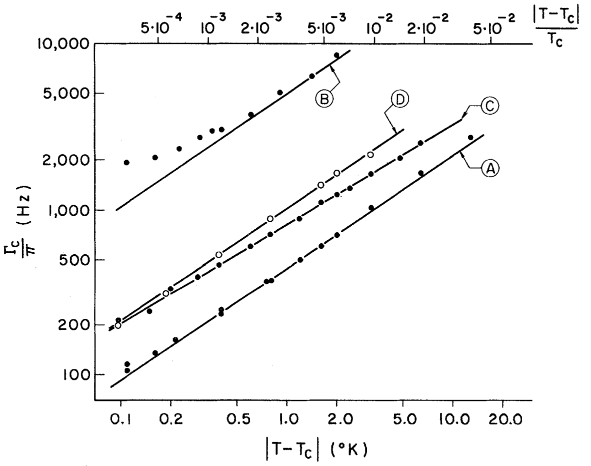

FIG. 1. Temperature dependence of the inverse lifetime Γ_c of the concentration fluctuations in phenol-water. A, $T > T_c$, $\theta = 33.0 \pm 0.5°$. B, $T > T_c$, $\theta = 145.2 \pm 0.5°$. C, $T < T_c$, $\theta = 33.0$, high-density phase. D, $T < T_c$, $\theta = 33.0°$, low-density phase (water rich).

Table I. Tabulation of data on phenol-water, CO_2, and SF_6. See text for explanation of symbols. The numbers in parentheses represent experimental errors. In phenol-water the low-density phase is water rich.

	$T>T_c$		$T<T_c$ Low-density phase					$T<T_c$ High-density phase				
	D_0 or χ_0 [a]	γ^*	D_0 or χ_0 [a]	γ^*	R_1	R_2	R_3	D_0 or χ_0 [a]	γ^*	R_1	R_2	R_3
Phenol-water	2.22 (0.05) $\times10^{-7}$	0.68 (0.03)	5.09 (0.15) $\times10^{-7}$	0.68 (0.03)	2.29 (0.13)	4.7 (0.5)	2.05 (0.30)	4.09 (0.1) $\times10^{-7}$	0.60 (0.02)	1.84 (0.09)	4.0 (0.5)	2.18 (0.26)
CO_2 (Ref. 2)	1.81 (0.05) $\times10^{-5}$	0.73 (0.02)	3.60 (0.3) $\times10^{-5}$	0.66 (0.05)	1.99 (0.23)	4.4 [b] (?)	2.21 (>0.30)	3.48 (0.25) $\times10^{-5}$	0.72 (0.05)	1.93 (0.19)	4.4 [b] (?)	2.28 (>0.25)
SF_6 (Ref. 11)	8.84 (0.28) $\times10^{-6}$	1.26 (0.02)	4.69 (0.03) $\times10^{-5}$	0.632 (0.002)				4.50 (0.05) $\times10^{-5}$	0.635 (0.003)			

[a] $D=D_0|\Delta T|^{\gamma^*}$ and $\chi=\chi|\Delta T|^{\gamma^*}$ have units of cm^2 sec^{-1}.

[b] See Ref. 15.

$\theta=145.2°$ as would be expected for the Fixman term at large K. It was found, however, that multiple scattering was appreciable for $T>T_c$ and $\Delta T\lesssim0.4°C$. The effect of multiple scattering on lifetime measurements is difficult to estimate except in the limits of $\theta\simeq0°$ and $\theta\simeq180°$.[8] In view of this, no attempt was made to extract the temperature dependence of ξ from these data. It should be noted, however, that at $\theta=33°$, $\ln\Gamma_c$ was proportional to $|T-T_c|$ even when multiple scattering was large. This suggests that the nonlinearity in curve B may be entirely due to the Fixman term.

Swift[9] has argued that the behavior of the diffusion coefficient in a binary mixture near its critical mixing point is similar to the behavior of the thermal diffusivity χ of a pure fluid near its gas-liquid critical point. For both systems Kadanoff and Swift predict $\gamma^*\simeq0.67$.[9,10] Only three extensive measurements of $\chi(\Delta T)$ or $D(\Delta T)$, including the present one, have been made both above and below T_c.[2,11] The results appear in Table I. With the exception of $\gamma^*\simeq1.26$ for SF_6 above T_c, for which no explanation has yet been given, the results are in good qualitative agreement with the theoretical prediction. A number of measurements in other systems for $T>T_c$ also yield $\gamma^*\simeq\frac{2}{3}$.[6,12] Nevertheless, contrary to present theoretical expectations, we find a significant difference between the measured values of γ^* in the two phases for $T<T_c$. It is, however, possible that this difference is due to concentration-dependent effects which would vanish on close enough approach to T_c. A smaller dissymmetry between the two phases was observed by Swinney and Cummins in CO_2.[2]

Further similarities between phenol-water and CO_2 are found when one considers ratios of certain parameters evaluated at a given temperature interval above and below T_c. Firstly, from Table I it can be seen that the ratios of the diffusion coefficients $R_1=D(-\Delta T)/D(\Delta T)$ in phenol-water and of the thermal diffusivities $R_1=\chi(-\Delta T)/\chi(\Delta T)$ in CO_2 have roughly the same value $\simeq2$.

The second similarity involves the ratio of the isothermal compressibilities $R_2=\kappa_T^{-1}(-\Delta T)/\kappa_T^{-1}(\Delta T)$ and its binary mixture counterpart[13]

$$R_2=\frac{(\partial\mu/\partial c)_{-\Delta T}}{(\partial\mu/\partial c)_{\Delta T}}.$$

Here μ is an appropriately defined chemical potential[14] and c is the concentration. In a recent analysis of thermodynamic data, R_2 has been evaluated for CO_2.[15] For phenol-water we have made a rough measurement of R_2 at $\Delta T=\pm1°C$,[16] using the fact that the scattered light intensity at small angles is inversely proportional to $\partial\mu/\partial c$.[6] In both systems $R_2\simeq4.4$ (see Table I). Similar values of R_2 have been obtained in He^4, Xe,[15] and methanol-cyclohexane.[17] Classical mean-field theories give $R_2=2$,[17] whereas the three-dimensional Ising model predicts $R_2\simeq5.2$.[18]

Using the equation $D=(\partial\mu/\partial c)\alpha^*$ [3] and its analog for a pure fluid,[11] the above results can be used to evaluate the ratios $R_3=\alpha^*(\Delta T)/\alpha^*(-\Delta T)$ or $R_3=\Lambda(\Delta T)/\Lambda(-\Delta T)$. Here the concentration conductivity α^* and the thermal conductivity Λ are dynamic variables, possibly of more fundamental interest than the corresponding diffusivities D and χ. The values of R_3 calculated from the above-mentioned values of R_1 and R_2 are tabulated in Table I. It can be seen that $R_3 = 2$ to within the experimental error in all cases. To our knowledge there is at present no theoretical prediction for this ratio. It is obvious that more experimental work must be done to determine if similar results are found in other systems.[19]

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LINEAR PARAMETRIZATION OF THE EQUATION OF STATE NEAR THE CRITICAL POINT

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A linear parametrization of the equation of state near the critical point, proposed by Schofield, is tested. From the available experimental data in the critical regions of a number of magnets ($CrBr_3$, Ni, Gd) and fluids (Co_2, Xe, He^4) we find evidence of systematic deviations from an assumption of linearity.

Recently, Schofield[1] and Josephson[2] have proposed parametric representations for the equation of state in the critical region in terms of reduced thermodynamic coordinates. By an intuitively simple and particularly attractive transformation to such variables, Schofield suggested that the reduced order parameter as a function of a single variable "is very nearly linear to within