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Observation of the Anomalous Refractive Index of a Critical Binary Fluid*

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We report the first observation of the anomaly in the real part of the refractive index of a critical binary fluid (methanol-cyclohexane). A theoretical relation was obtained for the refractive index of a binary mixture in the vicinity of its critical point which agrees with the experimental results within the experimental error. More precise experiments are in progress.

A number of theoretical predictions have been made of an anomalous increase in the refractive index of a pure fluid near its critical point,¹⁻⁴ and preliminary evidence of such an anomaly has been found in xenon.^{2,5} We wish to report the measurement of such an anomalous refractive index for the binary mixture methanol-cyclohexane in the single-phase region near its critical mixing point. We also report the results of a theoretical description of the anomaly based on a simple model for a critical binary mixture. The real part of the refractive index is described in terms of the critical parameters ν , ξ_0 , and η . The theory together with the experimental results can provide values for these three parameters.

The measurement technique employs a Fabry-Perot etalon with the fluid under study contained between the interferometer flats. The flats are oriented vertically and an expanded and collimated horizontal beam from a 0.5-mW He-Ne laser illuminates the mirrors at normal incidence. The mirrors are adjusted to a slight tilt such that a series of three or four vertical "equal-thickness" fringes are observed from the opposite side of the flats by a measuring telescope. The change in refractive index with temperature is determined by measuring the lateral shift of the fringes at a fixed vertical position in the cell. The lateral fringe shift $\delta(x_N)$ of the N th-order fringe is related to the change in refractive index δn by $\delta(x_N) \cong N(\lambda_0/2 \tan \theta) \delta n/n^2 = (N\Delta x/n) \delta n$, where $N = d/(\lambda_0/2n) \cong 2650$, d is the distance between the flats at the position of the N th-order fringe ($d \cong 0.06$ cm), λ_0 is the free-space wavelength of the incident radiation ($\lambda_0 \cong 6328$ Å), n is the refractive index of the fluid ($n \cong 1.41$), Δx is the fringe spacing ($\Delta x \cong 0.4$ cm), and θ is the angle between

the flats.

The fluid cell containing the mirrors is mounted inside an aluminum heat shield and the cell and shield are mounted inside a brass vacuum envelope. The cell, shield, and vacuum envelope are mutually isolated from heat conduction and heat is transferred principally through radiation. Corrections for the normal expansion of the cell with temperature change are made.

The cell temperature is controlled by a thermistor in a 33-Hz Kelvin bridge.⁶ Temperature measurements were performed by use of a platinum resistance thermometer in a separate similar type bridge circuit. A third separate system controls the heat shield to ± 0.01 K. We could consistently measure the cell temperature with a resolution of 0.1 mK. Since the platinum thermometer was uncalibrated we could determine our absolute temperature only to ± 0.2 K. By monitoring the position of the fringes themselves at fixed control-bridge settings, we determined that our cell temperature was typically stable to about ± 0.1 mK/day. All temperatures were measured relative to the critical temperature ($T_C = 45.15^\circ\text{C}$) which was measured absolutely only to ± 0.2 K. T_C is considered that temperature at which the fringes just disappear after becoming progressively dimmer, broader, and stippled as the temperature is decreased toward T_C . T_C was located before and after each set of measurements of the refractive index and was typically reproducible to ± 1 mK from one day to the next. However, T_C was located to within ± 0.2 mK for the measurements made in the range $0.3 \text{ mK} \leq T - T_C \leq 3 \text{ mK}$.

The fluid composition of the mixture was (29.97 \pm 0.03)% methanol compared with the reported

value⁷ of 28.1%. Even with this difference in composition our apparent T_c should only be shifted down by about 1 mK.

The homogeneity and stability of the system is grossly determined by the straightness of the fringes and finely determined by their motion. For example at $T - T_c = 1$ mK, if we accept our measured value of the refractive index, a fringe shift of 4×10^{-4} cm (the precision of locating the fringe at this temperature) corresponds to a temperature change of 0.05 mK. Equilibrium was considered attained when the fringe settled to a fixed value $\pm 8 \times 10^{-4}$ cm and remained in this range for *at least* 1 h. The fact that no change in the fringe straightness, nor any rotation of the fringes from verticality, was observed to *within* 0.3 mK of T_c enables us to estimate that temperature variations over the 1.5-cm-diam cell were less than 0.2 mK and that no gravitation-induced concentration variations with height were observed.

Measurements were made within the temperature interval $0.3 \text{ mK} \leq T - T_c \leq 97 \text{ mK}$. In order to avoid difficult averaging procedures for the various overlapping refractive-index curves and the problem of piecing these curves together, the value of the average derivative $\delta n / \delta T$ for each incremental temperature change δT was plotted versus $T - T_c$ in Fig. 1.

Data were obtained by scanning temperature in both directions. Hysteresis could be avoided if temperature changes were kept small, the size of the temperature increments depending upon

$T - T_c$. In the range $30 \text{ mK} \leq T - T_c \leq 97 \text{ mK}$, temperature steps of 10 mK were taken, each requiring about 1.5 h for system stability to be attained; in the range $3 \text{ mK} \leq T - T_c \leq 10 \text{ mK}$, 1-mK steps were taken; while between $0.3 \text{ mK} \leq T - T_c \leq 3 \text{ mK}$, 0.7-mK and 0.4-mK steps were taken with a waiting time of about 3 h. The precision of locating a fringe was $\pm 4 \times 10^{-4}$ cm for $T - T_c \leq 3 \text{ mK}$ and $\pm 2 \times 10^{-4}$ cm for higher temperatures, corresponding to $\delta n = \pm 5 \times 10^{-7}$ and $\delta n = \pm 2.5 \times 10^{-7}$, respectively. However, the actual precision of the refractive-index measurements was about 2×10^{-6} . This was due to a slight change in the angle between the flats caused by long-term relaxations in the Teflon seals and the Kel-F diaphragm supporting the movable flat in the temperature range above 3 mK. It was due principally to the uncertainty in $T - T_c$ in the range less than 3 mK.

We develop an expression for the index of refraction of a critical binary mixture using an initial approach similar to that employed for a single-component critical fluid by Larsen, Mountain, and Zwanzig.¹ We consider a model system consisting of a spherically symmetric inhomogeneous medium containing two species of polarizable molecules with respective effective polarizabilities α_1 and α_2 . We assume that the *anomalous* part of the refractive index arises from *single* scattering from concentration fluctuations. We further assume that the total number density $\rho_1(\vec{x}_i) + \rho_2(\vec{x}_i)$ is a constant. (Note that this constraint does allow mass-density fluctua-

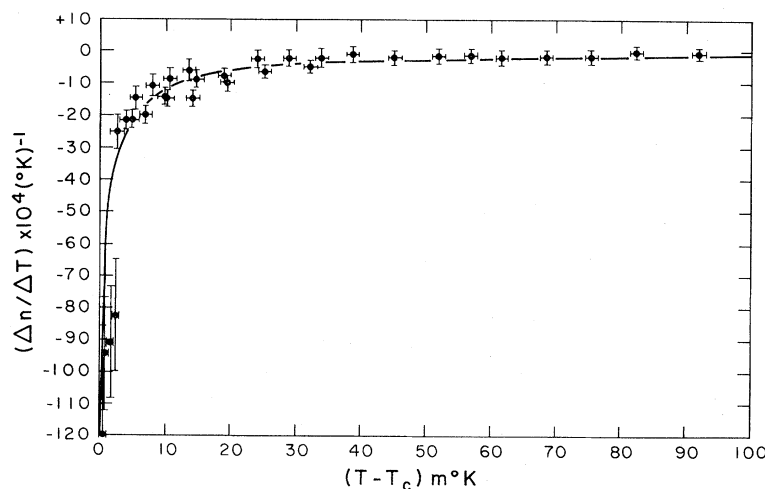


FIG. 1. The anomalous change in the derivative of the real part of the refractive index. Solid curve is a theoretical fit to the data with $\nu = 0.60$, $\xi_0 = 4.7 \text{ \AA}$, and $\eta = 0$.

tions.) In terms of the pair correlation functions, this constraint requires that

$$\rho_1^2 g_{11}(R) + \rho_1 \rho_2 g_{12}(R) = (\rho_1 + \rho_2) \rho_1, \quad (1)$$

with a similar equation relating $g_{22}(R)$ and $g_{12}(R)$. With these assumptions and for an induced electric field $\langle \vec{E}(\vec{x}_j) \rangle = \langle \vec{E} \rangle \exp(-in\vec{k}_0 \cdot \vec{x}_j)$, where $\langle \vec{E} \rangle$ is a constant and n can be identified as the refractive index, one can show that

$$n^2 = [1 + (\alpha_1 \rho_1 + \alpha_2 \rho_2)^{2/3} \epsilon_0 + B(n)] / [1 - (\alpha_1 \rho_1 + \alpha_2 \rho_2)^{1/3} \epsilon_0 - B(n)] \quad (2)$$

From this point, our development parallels that of Hocken and Stell.² In particular our Eq. (2) is the analog of their Eq. (1.6a), and the justification for the fact that the polarizabilities appear as constants is discussed by them and will not be repeated. The contribution of the concentration fluctuations to the complex refractive index is contained in

$$B(n) = \left(\frac{k_0^3}{i3\epsilon_0} \right) \frac{\rho_1 \rho_2 (\alpha_1 - \alpha_2)^2}{(\alpha_1 \rho_1 + \alpha_2 \rho_2)} \int_0^\infty dR R^2 [1 - g_{12}(R)] [2h_0(k_0 R) j_0(nk_0 R) + h_2(k_0 R) j_2(nk_0 R)], \quad (3)$$

where $h_m(k_0 R)$ and $j_m(nk_0 R)$ are spherical Hankel and Bessel functions, respectively.

We use Eq. (1) to express $g_{12}(R)$ in terms of the concentration correlation function for species 1, $g_{11}(R) - 1 = A \exp(-\kappa R) / R^{1+\eta}$, where $\kappa^{-1} = \xi$ is the correlation length, η is the critical exponent introduced by Fisher,⁸ and A is a constant. We find

$$B(n) = \rho_1^2 (\alpha_1 - \alpha_2)^2 A k_0^{1+\eta} [2I_0(n) + I_2(n)] (\alpha_1 \rho_1 + \alpha_2 \rho_2) \epsilon_0 / 3, \quad (4)$$

where Hocken and Stell have evaluated $I_0(n)$ and provided an approximate representation for $\text{Re}I_2(n)$. Using their results we find $|B(n)| \ll (\alpha_1 \rho_1 + \alpha_2 \rho_2) / 3\epsilon_0$. Thus, we can find an approximate expression for n in terms of n_b , the index of refraction in the absence of fluctuations, and $B(n)$. Further, since $B(n)$ is small, we can replace $B(n)$ by $B(n_b)$, where n_b is assumed real, and incorporating the results for $\text{Re}I_0(n)$ and $\text{Re}I_2(n)$ we find

$$\text{Re}(n - n_b) \cong \left(\frac{(n_b^4 + n_b^2 - 2)\rho_1^2 (\alpha_1 - \alpha_2)^2 A k_0^{1+\eta} \Gamma(1 - \eta)}{18n_b \epsilon_0 (\alpha_1 \rho_1 + \alpha_2 \rho_2)} \right) \left(1 + \frac{n_b^2}{2(5 - n_b^2)(1 - \exp[-b/(3 - n_b^2)]) + n_b^2} \right) \\ \times \frac{1}{\eta} \left\{ [b^2 + (n_b + 1)^2]^{1/2} \sin \left[\eta \arctan \left(\frac{n_b + 1}{b} \right) \right] + [b^2 + (n_b - 1)^2]^{1/2} \sin \left[\eta \arctan \left(\frac{n_b - 1}{b} \right) \right] \right\}. \quad (5)$$

Examination of this result shows that in agreement with the result for a simple fluid,² $\text{Re}(n - n_b)$ for a critical binary mixture remains finite as $\xi \rightarrow \infty$ at T_c and behaves as $b = (\xi k_0)^{1-\eta}$ far from T_c .

In Fig. 1 we show a best-fit theoretical curve of the average derivative of Eq. (5) to our data with A_r [the first factor in large parentheses in Eq. (5)], ξ_0 , and η as adjustable parameters. Wong and Huang⁹ obtained $\nu = 0.60 \pm 0.01$ for a critical mixture of methanol-cyclohexane. Fixing $\nu = 0.60$ in our computer program yields $\xi_0 = 4.7 \text{ \AA}$, $\eta < 10^{-7}$, and $A_r = 89.7$. On the other hand, if we fix ξ_0 at 3.5 \AA and η at 0.10 , we obtain an equally good fit with $\nu = 0.61$ and $A_r = 90.1$. The flexibility allowed by the large error bars on our measurements and the large number of adjustable parameters indicate that higher measurement accuracy is required and that additional independent measurements of ν and ξ_0 may be useful. We have redesigned our experimental

system and intend to pursue these measurements further with the specific intention of obtaining a reasonably good value for η .

No evidence of gravitationally induced concentration gradients was observed above the critical temperature, although thermodynamic considerations¹⁰ lead one to believe that they should be present near the critical temperature. As discussed earlier, the observed fringes in the experiment were oriented vertically and would display concentration gradients in the liquid since the index of refraction of the binary mixture is a strong function of concentration. A small concentration gradient in our system would have masked our observations of the anomaly in $\text{Re}(n)$. It is presumed that an extremely long time would be required for its establishment. Any thermal convection in the system would tend to oppose the development of such a gradient.

In conclusion, a refractive-index anomaly in the region of a critical point has been observed. However, measurements are not yet sufficiently precise to specify the critical parameters that should be obtainable (i.e., ν , ξ_0 , and η) with adequate accuracy. Our observations are fitted by our theoretical relationship for the refractive index within the accuracy of our preliminary measurements.

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Onset Phenomena in Superfluid Helium*

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Onset phenomena in superfluid helium have been studied by measuring the rotational decay constant of a levitated, superconducting niobium sphere coated with an unsaturated superfluid film. The novel features of onset that were observed are discussed. Previous observations of a two-layer-thick solid phase of helium underlying the film have been confirmed.

Onset phenomena associated with unsaturated liquid He II film—specifically, onset of superfluidity,¹⁻⁷ superfluid density,^{8,9} and solid layers^{10,11}—have recently stimulated a great deal of interest in the scientific community. This Letter reports some novel observations of onset phenomena obtained by measuring the rotational decay time constant α of a rotating sphere coated with an unsaturated superfluid film. We believe this to be the first complete set of observations free of extensive extrapolation.

The apparatus and technique used have been described previously.¹⁰ The rotating sphere was an ultrapure, superconducting, niobium ball of 1 in. diameter and 5 μ in. sphericity. An unsaturated superfluid film in equilibrium with its own vapor at a pressure below the saturated vapor pressure was formed on the sphere's surface. The film thickness¹² is given by

$$d = [(RT/\Gamma M) \ln(P_0/P)]^{-1/3}, \quad (1)$$

where Γ is a constant,¹⁰ M is the molecular weight of He, R is Boltzmann's gas constant, T is the temperature of the sphere, P is the pres-

sure of the vapor in equilibrium with the film, and P_0 is the saturated vapor pressure. The angular velocity ω of the sphere was always kept low enough (6 to 15 rpm) that the rotational decay time constant is given by¹³

$$\alpha = -\omega^{-1} d\omega/dt. \quad (2)$$

Experimental measurements of α as a function of d were taken 1 h after the temperature and pressure had stabilized. In each set of measurements, we started with a saturated film and then slowly reduced the film thickness by removing He gas from the chamber. The results for six sets of measurements in the temperature range 1.165 to 2.08 K are summarized in Fig. 1. The points are experimental values; the solid lines are best-fit curves and do not represent any theory at this time.

We chose to analyze the data by assuming two major components in each measured value of α : the classical component that we have reported previously¹⁰ and the superfluid component unique to He II films. Figure 2 shows the experimental curve for 1.91 K (from Fig. 1) and the two com-