at a given temperature is predicted to decrease to 1 as $|t|$ goes to zero, a result not supported by experiments, one must view this explanation with some skepticism.

Once the model parameters have been fixed, as in Table I, it is possible to run "computer experiments" on samples of fixed compositions, similar to those used in the light-scattering experiments, and to predict meniscus heights and relative scattering intensities as a function of temperature. We found that by choosing compositions close to those reported for the experiments we could obtain reasonable agreement for meniscus heights and somewhat worse agreement for intensities in the three-phase region, but that the model was not nearly as good in the two-phase regions adjoining the three-phase region. Details of these calculations will be published separately.

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Light Scattering and Sum Rules in Three Phases of a Liquid Mixture near Its Tricritical Point

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Measurements of light-scattering intensity and correlation lengths in all three coexisting phases in the mixture water + benzene + ethanol + ammonium sulfate are reported for temperatures near the tricritical point. A comparison with two sum rules predicted by a classical theory shows fairly good agreement in one case and significant deviations in the other. Possible explanations of the latter are discussed.

Tricritical points are the only multicritical points which have thus far been observed in ordinary liquid mixtures.[1-5] Light scattering is a useful probe for studying tricritical points, and in the case of ordinary mixtures it provides direct information about fluctuations in the principal order parameter. The interpretation of previous studies[2,3] of intensity and linewidth has been hindered, however, by the fact that these quantities depend not only on the temperature, but also, in a fairly complicated way, on the precise composition of the liquid sample, a variable which is not easy to measure or to control.

In this Letter we report measurements of intensity and correlation length in *each* of three coexisting phases near the tricritical point in the system[4,5] water + ethanol + benzene + ammonium sulfate, and analyze the data with use of two sum rules predicted by the classical theory[6] of tricritical points and derived in the accompanying Letter.[7] These rules predict that, independent of composition, certain functions of measured quantities should be invariant (first rule) or depend only on the temperature (second rule) near the tricritical point as long as three phases are present. A test of these rules provides a test of the classical theory on which they are based, and deviations may be a useful way of searching for nonclassical corrections to tricritical behavior.

Our observations indicate noticeable deviations from the first sum rule for both the intensities and the correlation lengths. In the case of intensities, the deviation seems to be due, at least in part, to variations in the dependence of the dielectric constant ϵ on the order parameter ψ in the vicinity of the tricritical point. The second sum rule appears to be obeyed to within experimental precision, and provides a method for estimating the tricritical temperature from measurements in a sample whose composition differs from the tricritical composition.

Our experimental studies were carried out independently on two different samples (A and B), in two different laboratories (University of Pittsburgh and University of Maryland). The procedure described in more detail elsewhere,[3,8] was in essence the following. A sample of the following composition in mass fractions was prepared and sealed in a cylindrical sample cell of 1.53 cm i.d. (A), 1.28 cm i.d. (B): ammonium sulfate 0.0175 (A), 0.0179 (B); water 0.351 (A), 0.3534 (B); ethanol 0.450 (A), 0.4471 (B); benzene 0.181 (A), 0.1817 (B). The cell was placed in a temperature bath that was controlled to ± 0.002 mK (A), ± 0.003 mK (B). A He-Ne laser beam illuminated the sample. The intensity of light scattered at various angles was monitored with a photomultiplier tube. The intensity of the forward beam before and after traveling through the sample was measured using two photodiodes (A), photomultiplier tubes (B), allowing corrections to be made for intensity variations and for turbidity. The vertical position of the samples was adjustable, so that scattering data could be obtained in each of the phases. Subsidiary measurements of the refractive index n were performed in each of the phases in order to define the scattering wave vector q at angle θ, $q = (4\pi n/\lambda)\sin(\theta/2)$.

For sample A, the temperature was measured

TABLE I. Test of first sum rule.

SAMPLE	T(°C)	I_α (arbitrary units)	I_β	I_γ	R_I	ξ_α 10^{-8}cm	ξ_β 10^{-8}cm	ξ_γ 10^{-8}cm	R_ξ
A	47.55	1959±55	2595±38	256±7	1.18±.02	365±20	494±12	304±18	1.35±.06
	47.78	3211±267	4100±385	340±31	1.17±.06	454±17	624±9	344±19	1.28±.04
	48.03	10636±796	10039±256	487±21	1.25±.04	777±45	875±21	364±42	1.30±.08
B	47.80	4080±218	9540±456	2590±137	1.17±.04	326.63±21	697.85±28.9	553.40±37	1.26±.08
	47.95	4790±149	11430±558	3340±142	1.19±.04	355.47±10.10	733.31±37.9	625.17±29.30	1.34±.08
	48.00	5210±154	12160±865	3510±114	1.19±.05	366.53±11.6	799.80±53.40	648.50±20.50	1.27±.09
	48.10	7180±458	16890±427	4880±148	1.19±.03	453.20±34.70	885.82±24.4	722.26±19.5	1.33±.06
	48.20	10280±559	23350±1352	6490±173	1.19±.04	516.96±28.6	955.17±80.6	822.86±26.10	1.40±.13
	48.30	18390±700	33610±2174	7300±711	1.21±.05	651.54±24.50	1049.50±77.20	836.19±74.80	1.41±.13
	48.325	21630±1207	35110±1885	8480±949	1.27±.05	684.70±43.90	1081.90±67.90	826.59±155.10	1.40±.17
	48.40	37910±2414	59880±3544	12730±1374	1.26±.05	880.75±74.70	1339.10±84.50	919.39±134.60	1.34±.14

using a quartz thermometer. A mercury thermometer with 0.01 °C divisions was used as a transfer instrument and compared with a calibrated platinum thermometer at the National Bureau of Standards. Absolute temperatures are believed to be accurate to ≈ 0.01 K, while temperature differences are accurate to 2 mK. For sample B, temperature differences are accurate to 3 mK, but the absolute temperature assignment may be in error by as much as 0.15 K.

The scattering intensities at a given temperature in a particular phase were analyzed with the Ornstein-Zernike formula

$$I(q)=I(0)/(1+q^2\xi^2), \tag{1}$$

where $I(q)$ and $I(0)$ are the scattered intensities at wave vectors q and 0 corrected for attenuation, and ξ is the correlation length. The inverse intensity was fitted as a function of q^2. This fit yields, for each phase, values for $I(0)$ hereafter denoted by I, and for the correlation length ξ. Following Widom's convention[9] we label the top, middle, and bottom phases and their properties with α, β, and γ. For sample A, corrections for double scattering were made at 90° angle with the method of Bray and Chang.[10] It was assumed that these corrections went linearly to zero at 0° angle in an Ornstein-Zernike plot. The double-scattering corrections increased the ξ values for sample A by 4–8%; in testing the sum rules, however, these corrections largely cancel.

The results of the Ornstein-Zernike analysis of the scattering data are summarized in Table I. The errors indicated represent the largest deviation from the mean of the two or three repeat runs, or the standard deviation of the least-squares fit, whichever quantity is larger. For two temperatures out of eight for sample B, no repeat run was available and the standard deviation of the fit was reported as the error.

If the major fluctuations in the dielectric constant near the tricritical point are associated with fluctuations in the order parameter ψ, which is a reasonable assumption, the I should be given by the formula

$$I=\text{const}\times k_BT(d\epsilon/d\psi)^2\chi, \tag{2}$$

where χ is the susceptibility for the order parameter, equal in a classical theory to the inverse of $d^2\Psi/d\psi^2$, where Ψ is the Landau free energy.[6] Furthermore the classical theory yields

$$\xi=\text{const}(g\chi)^{1/2}, \tag{3}$$

where g is the coefficient of the $(\nabla\psi)^2$ term in a Landau-Ginzburg theory. If near the tricritical point we can replace $d\epsilon/d\psi$ and g by their tricritical values, and if a_4 in the classical theory[6] is set equal to a constant times T_t-T, with T_t the tricritical temperature, the sum rules[7]

$$\chi_\alpha^{1/2}+\chi_\gamma^{1/2}-\chi_\beta^{1/2}=0, \tag{4}$$

$$\chi_\alpha^{-1/2}+\chi_\gamma^{-1/2}-\chi_\beta^{-1/2}\propto T_t-T \tag{5}$$

have as consequences

$$I_\alpha^{1/2}+I_\gamma^{1/2}-I_\beta^{1/2}=0, \tag{6}$$

$$\xi_\alpha+\xi_\gamma-\xi_\beta=0 \tag{7}$$

and

$$I_\alpha^{-1/2}+I_\gamma^{-1/2}-I_\beta^{-1/2}\propto T_t-T, \tag{8}$$

$$\xi_\alpha^{-1}+\xi_\gamma^{-1}-\xi_\beta^{-1}\propto T_t-T. \tag{9}$$

In particular, (6) and (7) predict that the ratios

$$R_I\equiv(I_\alpha^{1/2}+I_\gamma^{1/2})/I_\beta^{1/2}, \tag{10}$$

$$R_\xi\equiv(\xi_\alpha+\xi_\gamma)/\xi_\beta \tag{11}$$

should be constant everywhere in the three-phase region near the tricritical point and equal to 1. The experimental results, Table I, are consistent with R_I constant and equal to about 1.2, and R_ξ constant and equal to about 1.3.

The deviations of these values from 1 are well outside the estimated experimental errors, and may be indicative of a breakdown of classical theory. On the other hand, they may indicate that the assumptions required to go from (4) to (6) and (7) are not fulfilled. In fact, a calculation[7] based upon the Clausius-Mossotti formula and a classical model fitted to the composition data of Lang and Widom[5] indicates that deviations of $d\epsilon/d\psi$ from its tricritical value could produce an R_I as large as 1.18 at a temperature of 47.55 °C. However, this calculation also predicts that the maximum value of R_I will decrease linearly to 1 as T_t-T goes to zero, while the experimental ratios for both samples have a tendency to *increase*, be it barely outside the estimated experimental error. To explain the corresponding deviation of R_ξ from 1, one might suppose that g in (3) is a function of ψ. Calculations based on this hypothesis[7, 11] have a rather *ad hoc* character and are not very convincing.

It is thus not implausible that the data for R_I and R_ξ in Table I are indicative of departures from classical theory. Calculations of nonclassical corrections[12] indicate that, to lowest order, the sum rules (6) and (7) should be unaffected![13] Hence at present there does not seem to be a

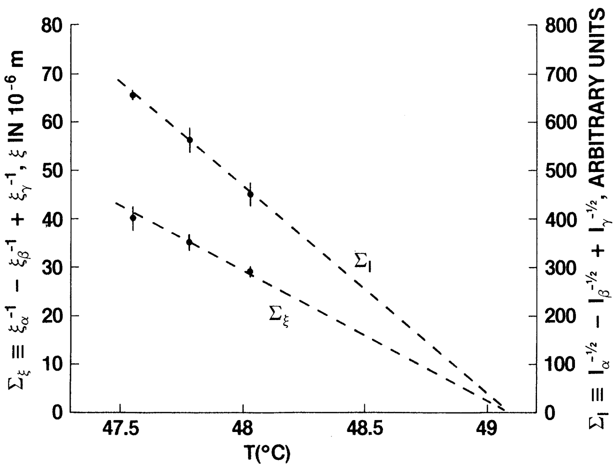

FIG. 1. Test of the second sum rule, $I_\alpha^{-1/2} - I_\beta^{-1/2} + I_\gamma^{-1/2} \simeq \xi_\alpha^{-1} - \xi_\beta^{-1} + \xi_\gamma^{-1} \propto T_t - T$, in sample *A*. The two sums extrapolate linearly to a common intercept, which is consistent with the Lang-Widom data. The extrapolation was done graphically; no least-squares fits were performed.

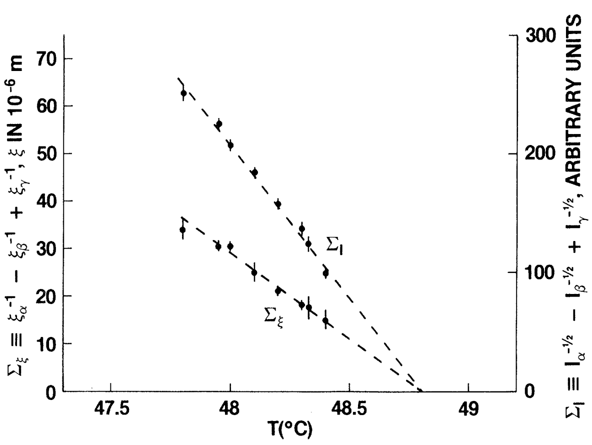

FIG. 2. Test of the second sum rule in sample *B*. Again, the two sums extrapolate linearly to a common intercept. The extrapolation was done graphically; no least-squares fits were performed.

satisfactory theoretical explanation for our observations.

A test of the second sum rule is provided by the plots of the left-hand sides of (8) and (9) as a function of temperature in Fig. 1 (Sample *A*) and Fig. 2 (Sample *B*). In each graph straight lines can be drawn through the points determined by the intensities and correlation lengths so as to extrapolate to a consistent tricritical temperature. That these temperatures are not the same for Samples *A* and *B* may simply reflect the fact that for the latter the absolute temperature calibration was not known to better than ± 0.15 °C. The tricritical temperature of 49.1 °C determined this way for Sample *A* exceeds that of Lang and Widom by 0.2 °C. However, the model calculation by Kaufman, Bardhan, and Griffiths[7] indicates that the Lang and Widom data are probably consistent with a tricritical temperature as high as 49.3 °C, and so we do not consider this discrepancy as too serious. One should, of course, treat the sum rules (8) and (9) with caution in view of the failure of (6) and (7) discussed above.

In summary, our tests of the two sum rules predicted by the classical theory indicate deviations from the first rule which are greater than the ex perimental errors. While this probably indicates a deficiency in the classical theory, we have not been able to rule out the possibility that, even though the correlation lengths are tens of nanometers, we have still not arrived at the asymptotic region where this rule applies. The second sum rule seems consistent with our data, to within the experimental errors.

R. B. Griffiths communicated his "sum rules" to us prior to publication. M. Kaufman and R. B. Griffiths calculated the dielectric constant as a function of the order parameter. R. F. Chang calculated the double-scattering correction. M. Stephen advised on logarithmic corrections, S. C. Greer on sample preparation. We acknowledge advice from M. S. Green, J. S. Huang, D. Jasnow, J. C. Lang, Jr., M. R. Moldover, and B. Widom.

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Acoustic Anomalies in Amorphous Thin Films of Si and SiO_2

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The ultrasonic absorption and variation of the sound velocity have been measured in sputtered films of amorphous silicon and amorphous silicon oxide from 0.5 to 300 K at a frequency of 300 MHz. A Rayleigh surface wave propagating along the surface of a piezoelectric crystal, which is covered by a thin film of amorphous SiO_2, allows a measurement of the well-known acoustic anomalies originating from two-level tunneling systems. In clear contrast, films of *a*-Si do not exhibit these typical anomalies.

The well-known anomalies[1,2] of the acoustic properties of amorphous materials at very low temperatures have been attributed to the scattering of sound waves by certain low-energy excitations in the disordered solid. A very successful phenomenological description[3,4] has been given in terms of two-level tunneling systems (TLS) which have a broad distribution of energy splittings. It is of particular interest to know whether these TLS are also present in amorphous solids which can only be prepared in film form. Notable among these are amorphous Si and Ge, as well as many of the metallic glasses.

Acoustic measurements require in general sizable sample dimensions, which excludes the study of thin amorphous films by conventional ultrasonic techniques. The acoustic properties of a film deposited on a suitable substrate can, however, be studied by means of surface acoustic waves (SAW). The effects of such films on surface-wave propagation have been studied extensively, primarily at ambient temperature.[5] Recent studies by Hartemann, Doussineau, and Levelut[6] and Haumeder, Strom, and Hunklinger[7] demonstrated that the surface-wave technique is useful even below 4.2 K. Furthermore, low-temperature dielectric measurements have been performed by Golding, Graebner, and Haemmerle[8] on *a*-Si films at frequencies $\sim 10^3$ Hz. However, no low-temperature acoustic properties have been previously reported for amorphous silicon films which were deposited onto surface-wave devices.

We present here the first measurement of the low-temperature acoustic properties of sputtered amorphous films of Si, $SiO_{0.7}$, and SiO_2. Our results provide evidence for the lack of TLS in sputtered amorphous Si films. The results further demonstrate that the acoustic properties of thin sputtered films of SiO_2 are similar (but not identical) to those of bulk glassy SiO_2.

The experiments were carried out on polished *YZ*-cut $LiNbO_3$ surface-wave devices with interdigital transmitting and receiving transducers spaced 10 mm apart.[9] Using water-cooled substrates, thin films of Si, $SiO_{0.7}$, and SiO_2 were sputtered from a Si target in a hydrogen-free argon atmosphere of 1×10^{-2} Torr (with oxygen partial pressures of 1×10^{-4} Torr for $SiO_{0.7}$ and 2×10^{-3} for SiO_2; background pressure 1×10^{-6} Torr) onto the entire space between the transducers. The films have been checked by x-ray diffraction to be fully amorphous. An identical surface-wave path on the same substrate was left without a film in order to eliminate the contribution of the crystal differentially. The variation of the attenuation and sound velocity in the deposited films were measured at temperatures between 0.4 and 300 K at a frequency of 300 MHz employing standard ultrasonic techniques.

In Fig. 1 the temperature-dependent absorption (after subtraction of the residual absorption at 0.4 K) is shown for three representative amorphous films of approximately 1-μm thickness. We discuss first the curve obtained for *a*-SiO_2