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Electrical-conductivity fluctuations in binary liquid mixtures near the critical point: The effects of fluid flow

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We have measured dc electrical conductivity fluctuations in isobutyric-acid—water (I-W) and 2,6-lutidine-water (L-W) mixtures near the critical temperature T_c. The noise was measured in a capillary separating two reservoirs initially filled to slightly different heights. Power spectra $S_V(f)$ encompassed the frequency (f) range $0.01 \leq f \leq 100$ Hz and the temperature (T) range $1 \leq |T-T_c| \leq 1100$ mK. Very close to T_c the spectra for L-W and I-W (at early times after mixing the sample) are consistent with the assumption that the noise is generated by flow. The temperature dependence of the noise can be represented by a power law $S_V(f,T) \propto |T-T_c|^{-\gamma}$, with $\gamma=1.0\pm0.1$. This value of γ, being smaller than the Ising value of 1.25, suggests that the composition fluctuations are suppressed by the shear flow in the capillary. We cannot explain the appreciable noise which persists after the flow has ceased. An ac method of determining $S_V(f)$ yields results identical with those of the dc method. Finally, we demonstrate, through a direct test, that the noise in a binary mixture near T_c has a negligible nonlinear component.

I. INTRODUCTION

It might be expected that $1/f$ noise can be more easily understood in fluids than in the bulk solids or thin films because effects like strains and imperfections are absent.[1] Binary fluids near the critical temperature T_c are novel systems in which to study $1/f$ noise. First, universal scaling laws[2] reduce the number of variables involved and second, very large noise exists near T_c, allowing a rigorous and quantitative comparison with calculations of various sources of noise. These considerations motivated us to study[3] the power spectrum $S_V(f)$ of conductivity fluctuations in a critical binary mixture of isobutyric acid-water (I-W), through which a small dc current was flowing. Our findings[3] were, however, only qualitatively explained by analytical calculations of $S_V(f)$ based on the assumption that the noise was produced by the diffusing relaxation of composition fluctuations. Typically, the measured spectra at frequencies of the order of 0.1 Hz were 100 times larger than the calculated values near the critical point. As predicted,[3] however, $S_V(f)$ was observed to diverge as $\epsilon^{-\gamma}[\epsilon=(T-T_c)/T]$, γ being the critical exponent[2] which describes the divergence of fluctuations in the order parameter. Theoretically γ is 1.25 for binary fluids,[2] but we found $\gamma \simeq 1$. As will be seen below, this discrepancy is understandable in terms of shear-flow effects.[4]

It was noted in passing in Ref. 3 (henceforth referred to as I) that $S_V(f)$ decreased (at frequencies from 0.04—4 Hz) over a few hours after the sample (I-W) was mixed. This decrease in $S_V(f)$ was attributed to possible leaching of impurities from the Pyrex walls of the capillary. Our new investigations, and a fresh look at the earlier data, force us to a different conclusion, viz., the noise was produced by flow. Flow noise should appear even if the two reservoirs connected by the capillary are filled to only slightly different heights (see Fig. 1 in I). In both I-W and 2,6-lutidine-water (L-W), flow noise dominates all other sources of noise in the frequency range 0.04—4 Hz. The present experiments establish that the spectra $S_V(f,T)$ are in fairly good agreement with the analytical values for the flow noise and that the diffusive relaxation of composition fluctuations are a relatively small contribution unless fluid flow is reduced to an extremely small value. In this paper noise spectra were measured in isobutyric acid-water and 2,6-lutidine-water (L-W). Both ac and dc methods were used. The purpose of the ac source was to assure that electrode polarization effects were unimportant.

To examine the possibility that the solution responds nonlinearly, a search was made for an (unrectified) low-frequency voltage variation resulting from a high-frequency driving current. No such noise was observed in either I-W or in carbon and metal film resisitors.[5]

Section II contains experimental details, and in Sec. III our theoretical calculations are summarized. Our results are presented and analyzed in Sec. IV and summarized in Sec. V.

II. EXPERIMENTS

A. Sample cell

The Pyrex sample cells were the same as we described earlier (Fig. 1 in I) and are identical to those used by Feher and Weissman.[6] The cell is formed by two cylindrical reservoirs joined at the bottom by a capillary. The capillary dimensions were length $2l \simeq 1$ mm, and radii $a = 18$ μm (L-W) and 50 μm (I-W). The resistance of the mixtures, and hence the noise, is dominated by this small-capillary volume. The capillary radii were measured by three methods: with a microscope, by measuring resistance of a standard $0.1N$ KCl solution in the channel, and by noting the time for the difference in levels of the two reservoirs (h) to decrease a given amount. All three methods give equivalent results within 10%. The samples were configured so that the reservoirs are brought together at the top for remixing the solutions. Thus there is no difference in pressure above the fluid in the two reservoirs.

The sample cells were placed in a well-stirred water bath, whose temperature is stable to within 0.2 mK over a few hours (see I). We used a quartz thermometer to measure temperature with a resolution of 0.1 mK. The water bath and amplifiers rest on a vibration-free table to avoid spurious vibrations.

B. Samples

The binary I-W and L-W mixtures were of critical composition (c_c). The L-W mixture was doped with 0.5 wt. % of KCl, which depressed T_c from 33.94 to 31.69 °C. This salt was added to reduce the resistance of the solution and hence suppress the Johnson noise $S_J = 4k_B TR$ where R is the resistance across the capillary. While the addition of KCl markedly changes the resistance of the mixture, it should have little effect on $[(1/R)(\partial R/\partial c)]$, to which the noise power is proportional.[3] Furthermore, such a small amount of impurity does not affect the values of the critical exponents, amplitude ratios, etc.[2,7] Unfortunately the doping of KCl lengthened the time for complete phase separation to occur, making it difficult to check for a possible shift in the critical composition.[8] Prior to transfer, the samples were filtered with Millipore filters (0.2-μm size). The filtering prevented blocking of the capillary by dust. In both mixtures T_c steadily decreased by ~ 0.5 mK/d, necessitating its remeasurement before each run. L-W, unlike I-W, has an inverted coexistence curve, i.e., the components become miscible in all proportions *below* the critical temperature. All the spectra were recorded when the samples were in the one-phase region.

C. Method of measuring noise

The dc noise was measured using the four-wire configuration (I). All electrodes were platinized. A mercury cell in a series with a wire-wound resistor ($R_s = 9 \times 10^6$ Ω) was connected to the outer pair of electrodes. This series resistance was several times larger than the resistance R across the inner electrode pair, so that the noise appeared as a fluctuation in voltage at constant current. The inner pair of electrodes was connected to a low-noise preamplifier (PAR113) operated in the ac mode with a low-frequency cutoff of 0.03 Hz. After further amplification, the randomly fluctuating voltage was fed to a spectrum analyzer (PAR4512) which yielded the power spectrum $S_V(f)$ in V^2/Hz with a ten-bit dynamic range. Typically, the frequency resolution was 0.02 Hz. The voltage V_0 across the inner electrode pair was 1.0 V, unless otherwise noted.

The resistance fluctuations, hence, voltage fluctuations, can also be observed by passing an ac current through the sample. In our experiments these fluctuations, which modulate the driving signal, were detected by a square-law or a synchronous detector. In carbon or thin-film resistors, the resulting noise spectra are found to be inversely proportional to Δf ($1/\Delta f$ noise), where Δf is the difference between the driving frequency and the measuring frequency. Assuming that the system is linear, $S_V(f) \propto S_V(\Delta f)$, where the latter is the power spectrum obtained in an ac experiment. The proportionality constant depends on the detection scheme used.[9] In the present experiments the detector was a standard lock-in amplifier (PAR126).

Apart from completely suppressing the background noise above the Johnson level, an ac method enables one to measure noise to very low frequencies. In this way $S_V(f)$ was measured down to 0.01 Hz. With the dc method we were unable to go below 0.04 Hz, the crucial limitation being dc drift. Primarily we measured $1/\Delta f$ noise to avoid the possible electrode polarization effects in the dc method.

The driving frequencies (f_c) in the ac experiments were 10 and 100 Hz. Even though these frequencies were in the vicinity of the inverse lifetime of the composition fluctuations near T_c, the matching of the driving frequency with the frequency of the decay of composition fluctuations does not lead to any singular contribution to R or to $S_V(f)$.[10]

In all of the measurements, the current flow through the mixture was small enough to produce negligible local heating within the capillary; an approximate calculation shows the temperature rise to have been $\lesssim 0.5$ mK. A temperature difference between the fluid in the capillary and the reservoirs would have revealed itself as an apparent difference in phase-separation temperature in these two regions under conditions of current flow. This effect was searched for but not found.

III. THEORY

It was demonstrated in I that the theoretically expected contribution to $S_V(f)$ at low frequencies (0.04–4 Hz) from density fluctuations and temperature fluctuations[6,11,12] in binary-liquid mixtures is even smaller than the (frequency-independent) Johnson noise $S_J = 4k_BTR$ (V^2/Hz). Hence, the experiments were analyzed by assuming the composition fluctuations were the sole source of the resistance fluctuations.

In the absence of nonlinear effects[5] the squared voltage fluctuations across a resistance R are given by

$$\langle \Delta V^2 \rangle = V_0^2 \beta_c^2 \langle \Delta c^2 \rangle_\Omega / c_c^2 \ , \tag{1}$$

where $\beta_c = (c_c/R)(\partial R/\partial c)_{T,c_c}$, with

$$\frac{\langle \Delta c^2 \rangle_\Omega}{c_c^2} \simeq \frac{k_B T}{N_a} \frac{1}{c_c} \left[\frac{\partial c}{\partial \mu} \right]_{T,P} . \tag{2}$$

Here c is the molecular density of one of the components, c_c is its value at the critical composition, Ω is the sample volume, and $N_1 = c_c\Omega$ is the number of molecules of this component in Ω. In these experiments Ω may be taken as the capillary volume. The chemical potential $\mu = \mu_1 - \mu_2$, where μ_i refers to the two molecular species. The osmotic compressibility $(\partial c/\partial \mu)_{T,P}$ diverges[2,13] at T_c as

$$\frac{k_B T_c}{c_c} \left[\frac{\partial c}{\partial \mu} \right]_{T,P} = \Gamma \epsilon^{-\gamma} \ , \tag{3}$$

where Γ is a sample-dependent constant and $\epsilon \equiv |T - T_c| / T_c$. The critical exponent γ in a binary fluid is found to be close to the theoretical prediction[2] of 1.25 for an Ising model. Equations (1)–(3) give

$$\frac{\langle \Delta V^2 \rangle}{V_0^2} = \frac{\beta_c^2}{N_a} \Gamma \epsilon^{-\gamma} . \tag{4}$$

The composition fluctuation spectrum $S_c(f)$ is the Fourier transform of the correlation function of composition fluctuations $\langle c(0)c(t) \rangle_\Omega$; it is related to the power spectrum $S_V(f)$ by

$$\frac{S_V(f)}{V_0^2} = \beta_c^2 \frac{S_c(f)}{c_c^2} . \tag{5}$$

In the normalization used here,

$$\int_0^\infty S_c(f) df = \langle \Delta c^2 \rangle_\Omega \ ,$$

and

$$\int_0^\infty S_V(f) df = \langle \Delta V^2 \rangle_\Omega . \tag{6}$$

It is evident from Eq. (4) that voltage fluctuations become large at small ϵ, i.e., near the critical point.

In I the power spectrum for composition fluctuations was derived, assuming that they relax diffusively. One finds that $S_V(f) \propto 1/f^{3/2}$ in the frequency range $D/l^2 \ll f \ll D/\xi^2$. Here D is the composition diffusion constant and ξ is the correlation length characterizing the composition fluctuations. Both D^{-1} and ξ diverge strongly as the critical point is approached.[2] The above restriction was well satisfied over the frequency and temperature range spanned by the earlier experiments and the present ones. Since the measured spectra do not conform to this simple power law, further discussion of the calculation is unnecessary.[3]

Consider next the contribution of the fluid flow to $S_V(f)$. Assuming a uniform velocity of flow v_x within the capillary and neglecting diffusional relaxation of the composition fluctuations, one finds that[3]

$$\frac{S_V(f)}{V_0^2} = \frac{4\beta_c^2 \Gamma \epsilon^{-\gamma}}{N_a \omega_0} \left[\frac{\sin \omega/\omega_0}{\omega/\omega_0} \right]^2 , \tag{7}$$

where $\omega_0 = v_x/l$ and $\omega = 2\pi f$. In the situation of interest here, where $v_x(r)$ has the radial dependence of Poiseuille flow, the oscillations in Eq. (7) are partially suppressed, and one obtains the following expression on averaging Eq. (7) over the cross-sectional area πa^2 of the capillary:

$$\frac{S_V(f)}{V_0^2} = \frac{K}{A} \int_b^\infty \frac{\sin^2 y}{y^3} dy \ , \tag{8}$$

where $K = 4\beta_c^2 \Gamma \epsilon^{-\gamma}/N_a$, and $b = \omega/A$, with $A = \Delta P a^2 / 8 l^2 \bar{\eta}$. Here ΔP is the pressure difference between the two ends of the capillary, and $\bar{\eta}$ is the viscosity of the fluid mixture. In Sec. IV, this result will be compared with our measurements.

IV. RESULTS

Figure 1 shows how the power spectrum in L-W (18-μm cell) varies with flow rate, i.e., with the initial difference in height, h of the mixture in the two reservoirs. The capillary is sufficiently narrow that Δh did not change during the course of the spectral measurements. The solid lines in this log-log plot correspond to $\Delta h = 0.1$ and 1.0 cm, as indicated. Both spectra were recorded at $T_c - T = 10$ mK. They spanned the frequency interval $0.04 \le f \le 100$ Hz.

The resistance of the mixture R was 6 MΩ, so that the Johnson noise

$$S_J = 4k_B TR = 10^{-13.0} \text{ V}^2/\text{Hz} .$$

This noise contribution, which was not subtracted out, is responsible for the leveling off of the spectra at the high-frequency end.

It is clear from Fig. 1 that the spectra do not have a simple power-law form; rather a knee appears at a characteristic frequency f^*, above which $S_V(f) \sim 1/f^{\psi}$ with $\psi \gtrsim 2$. This knee frequency is seen to increase with increasing flow rate, as expected if the noise is produced by flow.

To determine whether the spectra in Fig. 1 span a large enough frequency range to exhaust the sum rule, Eq. (6), we have evaluated the integral

$$I(\Delta h; f_2, f_1) = \int_{f_1}^{f_2} [S_V(f) - S_J] df .$$

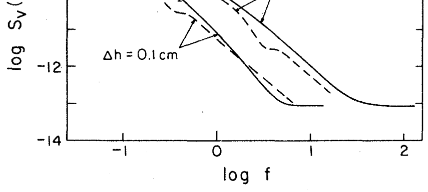

FIG. 1. Solid lines: $S_V(f)$ vs f for L-W in an 18-μm cell at $\Delta h = 1$ and 0.1 cm. Sample was in one phase at 10 mK below the critical point. Voltage V_0 across the capillary was 1.0 V in all of the dc measurements. Dashed lines: $S_V(f)$ calculated from Eq. (8).

Taking $f_2 = 24$ Hz and $f_1 = 0.04$ Hz, one finds $I(1.0 \text{ cm}; 24 \text{ Hz}, 0.04 \text{ Hz}) = 3.6 \times 10^{-10}$ V^2 and $I(0.1 \text{ cm}; 24 \text{ Hz}, 0.04 \text{ Hz}) = 2.3 \times 10^{-10}$ V^2. These two integrals are approximately equal in spite of the factor of 10 difference in the two flow rates and the consequent difference between the two spectra of Fig. 1. It thus appears that the noise power is almost entirely contained between 0.04 Hz and 24 Hz. We assume this to be so in order to obtain an estimate of Γ in Eq. (4), since this parameter has not been measured in L-W. Since $V_0 = 1$ V,

$$\begin{aligned} V_0^{-2} I(\Delta h; 24, 0.04) &\simeq 3 \times 10^{-10} \\ &= V_0^{-2} \int_0^{\infty} S_V(f) df \\ &= \beta_c^2 \Gamma \epsilon^{-\gamma} / N_a . \end{aligned}$$

The latter equality is obtained by combining Eqs. (1)–(3) and Eq. (6).

From the known dimensions of the capillary, one finds $N_a = 2 \times 10^{15}$, assuming the two components contribute additively to the total volume. The other factors entering Eq. (4) are β_c and γ. Since β_c has not been measured in L-W, we use the I-W value,[3] viz., $\beta_c = 2.2$. As discussed below, the temperature dependence of the noise yields the exponent $\gamma = 1.0$ rather than the Ising value 1.25. Inserting the above constants and the measured values of I in Eq. (6) gives $\Gamma = 4 \pm 1$. This value is roughly consistent with theoretical expectations, though an order of magnitude larger than that previously deduced from noise measurements in I-W.[3]

The dashed theoretical curves in Fig. 1 are plots of Eq. (8) with $\Delta h = 1$ mm and 1 cm. The viscosity $\bar{\eta}$ was taken to be 0.02 P,[14] and the remaining parameters were assigned the values stated above, i.e., $\gamma = 1$, $\Gamma = 4$, $\beta_c = 2.2$, and $N_a = 2 \times 10^{15}$. The satisfactory agreement between the measured and calculated spectra in Fig. 1 provide strong evidence that the noise is dominated by flow, even when Δh is as small as 1 mm. As discussed in I, diffusion-generated noise should be negligible in the frequency range of our measurements. Furthermore, diffusion spectra should have the simple power-law form $S_V(f) \propto f^{-3/2}$ in the frequency range of Fig. 1. Both flow and diffusion noise diverge as the critical point is approached. Strictly speaking, of course, flow noise and diffusion noise are not distinguishable; they merely represent solutions to the diffusion equation in the extreme limits where either the $D\vec{\nabla}^2 c$ term or the $(\vec{v} \cdot \vec{\nabla})c$ term is negligible.[3] It is perhaps useful to think of flow noise as being generated by correlation volumes, $\xi^3 \propto (T - T_c)^{-3\nu}$ randomly entering and leaving the capillary.

Measurements similar to those in Fig. 1 were also carried out in I-W ($a=50$ μm), and agreement with Eq. (8) was equally good. Figure 2 shows the temperature dependence of $S_V(f)$ in L-W for $f=0.1$, 1.0, and 4 Hz at $\Delta h=1.0$ cm. The background noise $S_0(f)$, measured at $V=0$, has been subtracted, removing the Johnson noise S_J and a low-frequency contribution originating in the amplifier. All three sets of measurements conform to the equation $S_V(f)\propto\epsilon^{-\gamma}$ with $\gamma=1.0\pm0.1$. An identical value of this exponent was extracted from the earlier noise experiments in I-W.[3]

It is reasonable to explain the decrease of γ from its usually observed Ising value[2] $\gamma=1.25$, to its mean-field value[15] $\gamma=1$, as the result of shear flow within the capillary. Shear is indeed expected to suppress the order-parameter fluctuations and produce mean-field behavior, provided the shear rate $S\equiv\partial v_x/\partial y$ is large compared to the inverse lifetime $\Gamma_\xi(=k_BT/16\pi\bar{\eta}\xi^3)$ of the composition fluctuations.[4] In the situation of interest here, the y axis is along a capillary radius, and the flow v_x is along its axis.

In L-W ($a=18$ μm), the average shear rate $\bar{S}=\bar{v}_x/a\simeq200$ Hz at $\Delta h=1$ cm; in I-W ($a=50$ μm), $\bar{S}\simeq60$ Hz at $\Delta h=0.1$ cm. (In the I-W experiments described in I, Δh was kept to a minimum and never exceeded 1.0 mm.) Using the known value of $\bar{\eta}$ and ξ in L-W,[8,14,16] one finds $S>T_\xi$ when $\epsilon<2\times10^{-5}$. Thus most of the data in Fig. 2 lie in the "strong-shear regime," where γ should be unity.[4]

Strong shear should also produce a slight shift in T_c by an amount[4]

$$\Delta T_c(S)\equiv T_c(S)-T_c(0)$$
$$=\mp0.0832T_c(0)\epsilon'\tilde{\tau}_s(S)\ , \tag{9}$$

where $-$ and $+$ signs refer to systems with normal and inverted coexistence curves, respectively. In the above equation $\epsilon'=4-d=1$ (d is the dimensionality) and $\tilde{\tau}_s(S)=(16\bar{\eta}\xi_0^3S/k_BT_c)^{1/3\nu}$. The correlation length $\xi=\xi_0\epsilon^{-\nu}$. Using the known values of ξ_0, ν, and $\bar{\eta}$ in L-W (Refs. 14 and 16) and I-W,[17] one obtains $\Delta T_c^{\text{I-W}}=-1.4$ mK and $\Delta T_c^{\text{L-W}}=+1.6$ mK. Experimentally, this shift in T_c, as well as the strong-shear value of γ, has been observed in a binary mixture,[18] and the results provide strong support for the theory of Onuki and Kawasaki.[4]

By simultaneously monitoring the noise in the channel and light scattering in one of the reservoirs, it was possible to detect a slight shift in T_c under conditions of flow at $\Delta h=1$ cm. On quenching the mixture a small fraction of a mK through T_c, there appears a sharp increase in the noise from the capillary and in the scattering from the reservoir. Since the flow rate in the reservoir is negligible, the temperatures at which the increases occur are presumably $T_c(S)$ (capillary) and $T_c(0)$ (bulk). The measurements showed ΔT_c (200 Hz) to be $+0.8$ mK, in satisfactory agreement with Eq. (9). Throughout this paper the reduced temperature ϵ was calulated using the zero-shear value of T_c.

Figure 3 shows how $S_V(f)$ varies with temperature in L-W ($a=18$ μm), with $\Delta h=1.0$ cm. It is apparent that the knee frequency $\tilde{f}$ in these spectra is almost temperature independent. Were the spectra diffusive in origin, $\tilde{f}=f_D=D(\epsilon)/2\pi L^2$ with $D\propto\epsilon^\nu\sim\epsilon^{2/3}$. Here the characteristic length L might be length of the capillary ($2l$), or its radius (a), if end effects were dominant.[3] For $f>f_D$ (always less than 10^{-3} Hz in these experiments) $S_V(f)\propto f^{-3/2}$ in the diffusive case.[3] It is clear, then, that the measurements in Fig. 3 cannot be explained by diffusion.

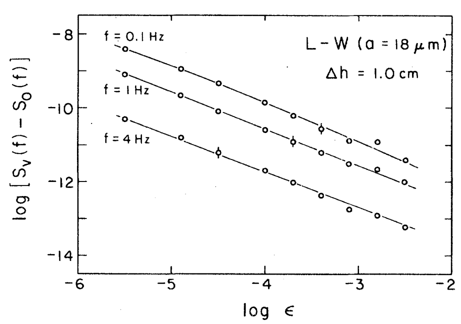

FIG. 2. $S_V(f)$ as a function of reduced temperature $\epsilon=|(T-T_c)/T_c|$ at three frequencies. Data are for L-W (18-μm cell) with $\Delta h=1$ cm. Three spectra fit the equation $S_V(f)\propto\epsilon^{-1.0\pm0.1}$. Background noise $S_0(f)$ has been subtracted.

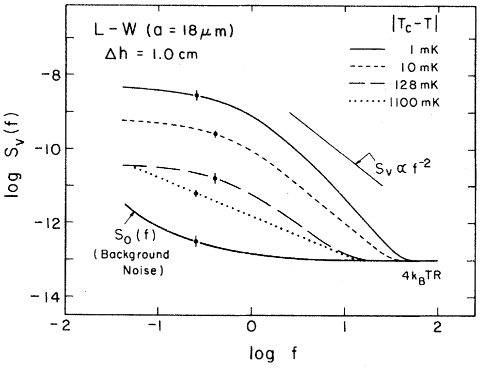

FIG. 3. Power spectra $S_V(f)$ vs f in L-W (18-μm cell) at four different temperatures below T_c (one-phase region).

The background noise $S_0(f)$ in Fig. 3 includes the frequency-independent term S_J and a contribution from the PAR113 amplifier. This latter part is insignificant above 2 Hz. Note that if the noise is produced by flow $\tilde{f} = A \propto 1/\bar{\eta}$. Thus the knee frequency should exhibit only the weak temperature dependence of the viscosity.[14] Indeed all those spectra in Fig. 3 recorded near the critical point ($T_c - T \lesssim 130$ mK) have inflection points at roughly the same frequency ($f \simeq 3$ Hz).

Far from T_c, i.e., at $|T_c - T| = 1.1\,^\circ\mathrm{C}$, $S_V(f) \propto f^{-\psi}$ with $\psi = 1.2$. Previously reported noise measurements in a critical mixture of isobutyric acid and water ($\Delta h < 0.1$ cm) also yielded spectra of this shape far from the critical point. [We will see that, in this noncritical regime, $S_V(f)$ is independent of Δh.]

Figure 4 shows a series of spectra using a cell with a capillary of sufficient diameter ($a = 50\ \mu$m) so that the flow rate decreases appreciably within several hours. The critical mixture was I-W, with $\Delta h \equiv \Delta h(0) < 0.1$ cm, $(T - T_c) = 4$ mK. The four spectra were recorded at the times (t) indicated. Note the persistent shift of the shoulder to a smaller characteristic frequency (ω_0) as t increases, i.e., as v_x decreases. This shift is further evidence that the noise is dominated by flow. After an interval of nearly 8 h, $S_V(f)$ has fallen to its steady-state values, which is well above the background contribution $S_0(f)$.

The relaxing pressure drop across the capillary results in an exponentially decaying flow rate with time constant $\tau = 8\bar{\eta}(2l)R^2/ga^4$. Here g is the gravitational constant and R is the radius of the cylindrical reservoir. With the I-W cell ($a = 50\ \mu$m, $R = 0.6$ cm) this equation gives $\tau \simeq 1$ h, in approximate agreement with the measured decay rate of $S_V(f)$ seen in Fig. 4. The calculated time needed for the flow noise [from Eq. (8)] to fall to the Johnson noise value S_J is 6 h for the 50-μm cell (I-W) and 20 d for the 18-μm cell (L-W). Again, our observations are in accord with these estimates.

The features associated with the time variation of $S_V(f)$ are better articulated in Fig. 5, where we plot the time variation of $S_V(f)$ in I-W under conditions in which the initial flow rate was chosen to be large. Here $\Delta h(0) = 2.0$ cm and $(T - T_c) = 11$ mK. Note that the flow noise extends to much higher frequencies than in Fig. 4, where $v_x(0)$ was at least one decade smaller.

The data in Fig. 6 provide information about the flow-independent noise component. The measurements are in I-W ($a = 50\ \mu$m) at $(T - T_c) = 100$ mK. The single line in Fig. 6 summarizes spectral measurements which commenced at a time ($t = 4$ h) after the fluid heights in the reservoirs were visually set to be equal. The last spectrum was recorded at $t = 24$ h. In this time interval, any remnant flow produced by a reservoir height difference had presumably disappeared, leaving only a small, steady-state fluid velocity produced by electro-osmosis.[3] Because the background noise S_0 is no longer negligible above $f \simeq 1$ Hz, this contribution was subtracted out. All spectra summarized in Fig. 6 fit satisfactorily to a straight line, i.e., $(S - S_0) \propto 1/f^{\psi}$, with $\psi = 1.7 \pm 0.2$. For purposes of comparison, we have drawn a short line segment of unity slope in Fig. 6.

The "zero-flow" noise spectrum, typified by the measurements in Fig. 6, is weakly dependent on $(T - T_c)$, though there is measureable increase in ψ and in the noise power as $(T - T_c) \to 0$. For example, at $(T - T_c) = 1.5$ K, $\psi = 1.5 \pm 0.2$, while at $(T - T_c) = 10$ mK, $\psi = 2.0 \pm 0.2$. And at $f = 10^{-1}$ Hz, the noise power is only 5 db smaller at the former temperature than at the latter.

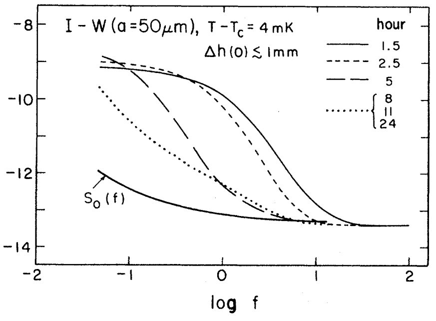

FIG. 4. $S_V(f)$ as a function of time of recording data after mixing the I-W sample (50-μm cell). Here $|T - T_c| = 4$ mK and $\Delta h \lesssim 0.1$ cm.

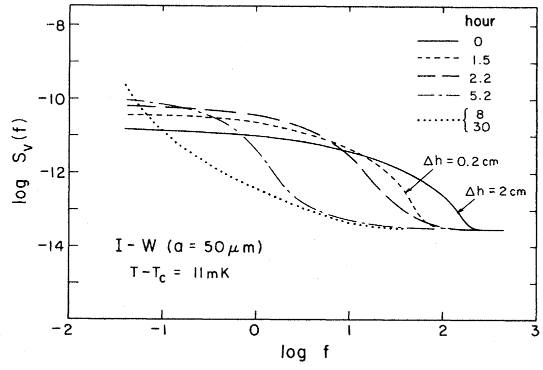

FIG. 5. Time dependence of $S_V(f)$ for I-W (50-μm cell) at $T - T_c = 11$ mK. In the course of the measurements, Δh decreased from 2.0 to 0.2 cm.

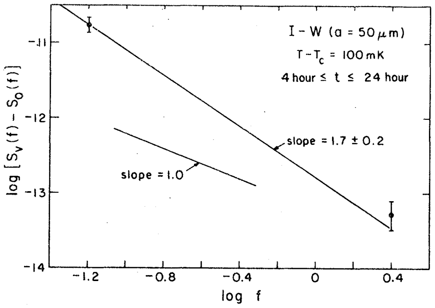

FIG. 6. Flow-independent noise in I-W (50-μm cell) at $T-T_c=100$ mK. Levels in the two reservoirs were equalized at $t=0$, but measurements did not commence until flow had almost ceased. Straight line is a good fit to all the data. Uncertainty in $S_V(f)$ was several db.

Figure 7 exhibits the temperature dependence of "zero-flow noise" in I-W ($a=50\ \mu$m) at two frequencies, $f=0.08$ and 1.0 Hz. The spectra were recorded at $t \gtrsim 5$ h. Note the weak temperature dependence of $S_V(f)-S_0(f)$; the straight lines drawn by the eye through the data points have slopes, -0.33 ± 0.2 and -0.2 ± 0.1 at the lower and higher frequencies, respectively. There is little we can say about this noise other than that it is only weakly related to the critical fluctuations in composition. Its temperature dependence seems to be only slightly stronger than that of the specific-heat singularity in Ising-like systems; in such systems the specific heat is expected to diverge[2,15] as $\epsilon^{-\alpha}$ with $\alpha=0.110$.

Mention has already been made of noise measurements in which the driving current was an ac source rather than a battery. If the driving frequency f_0 is greater than the maximum noise frequency of interest, the rectified voltage across the sample is linearly related to the (slow) fluctuations of sample resistance. Fourier analysis of this detected signal yields a spectrum $S_V(\Delta f)$, which is proportional to the dc-determined spectrum $S_V(f)$.[5,9] This will be true only if the system is linear, i.e., if the sample resistance is independent of the current flowing through it. Measurements of $S_V(\Delta f)$ were made in I-W at $f_0=100$ Hz, using a two-wire configuration. The driving signal $V_{\rm app}$ across the current-carrying electrodes was 0.33 V rms. The rectifier was a lock-in amplifier whose bandwidth was set below 100 Hz. There was no measureable difference between the spectra determined by the dc and ac methods. With the ac scheme, one escapes the low-frequency noise originating in the preamplifier which follows the bridge. The disadvantage of the ac scheme is that the sample must be operated in a bridge configuration, whose balance must be maintained to at least a part in 10^4 to prevent overloading of the amplifier chain by the driving signal. It was difficult to maintain this balance for more than 1 h.

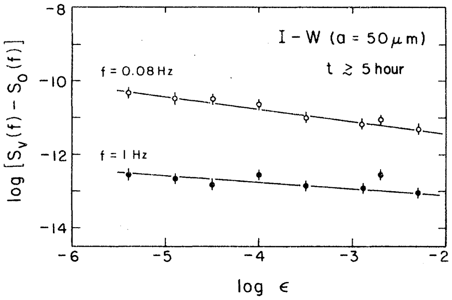

FIG. 7. Temperature dependence of steady-state spectra ($\Delta P \simeq 0$) in I-W (50-μm cell) at 0.08 and 1 Hz.

To assure that the I-W solution behaved linearly, spectra $S_V(\Delta f)$ were measured as a function of $V_{\rm app}$. Figure 8 shows such measurements at the three indicated values $\Delta f=0.12$, 0.4, and 1.2 Hz. Within experimental uncertainty, the slopes of these lines confirm the expected linear variation of $S_V(\Delta f)$ with $V_{\rm app}^2$. The straight line drawn by the eye through the data points are of the form $S_V(\Delta f) \propto V^n$, with $n=2.0\pm0.3$, 2.1 ± 0.2, and 1.95 ± 0.2 at $\Delta f=0.1$, 0.4, and 1.2 Hz, respectively.

Finally, a sensitive search was made for a nonlinear contribution in the I vs V_0 response of a critical binary mixture. The I-W sample was in one arm of the bridge, which was driven by signal of the form

$$V(t)=V_0(\cos 2\pi f_1 t+\cos 2\pi f_2 t)$$

(plus small harmonic terms). The two phase-locked frequencies $f_1=1000$ Hz and $f_2=1010$ Hz, were derived from a single square-wave source, as shown

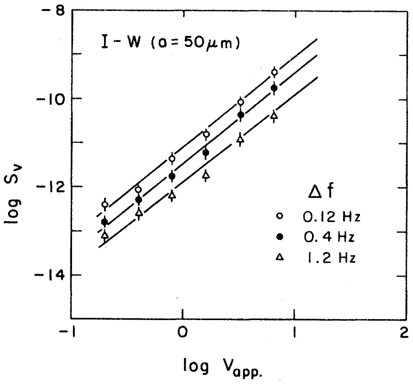

FIG. 8. $S_V(\Delta f)$ vs $V_{\rm app}(5.6)$ in I-W. Driving frequency was 100 Hz with $T-T_c=1$ mK.

schematically in Fig. 9. The filter F strongly attenuates the harmonics of f_1 and f_2. The amplifier A, which follows the bridge B, was set to block all frequencies above 30 Hz. A peak in the output of the wave analyzer (W) was searched for at $f = |f_1 - f_2| = 10$ Hz. Such a beat signal could appear only if the mixture (or the amplifier) were slightly nonlinear.

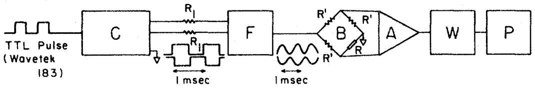

FIG. 9. Experimental arrangement employed to test for nonlinearity in I-W near T_c. Various components are C frequency splitter; R_1, isolation resistors (39 KΩ, metal film); F, Krohnhite filter; R', metal-film resistors; R, sample; A, amplifier chain; W, spectrum analyzer; P, interactive digital plotter.

To produce the phase-locked pulses, the circuit component C divided down the input signal, which consisted a 1-MHz pulse train supplied by a crystal-controlled function generator.

Our most sensitive test for the presence of a nonlinear contribution to $S_V(f)$ was made under transient conditions; the I-W had just been quenched several mK through the critical point, thereby producing resistance fluctuations orders of magnitude larger than the equilibrium value. This "nucleation noise" was observed to persist for many minutes. At $f = 10$ Hz and $V_{\rm app} = 1$ V, S_V was more than 60 dB smaller than that generated by an equal dc voltage at this same frequency. In contrast, previous measurements, using carbon resistors, showed this type of nonlinear noise to be proportional to the dc-generated noise and only 10–20 dB smaller.[19–21] We also failed to detect unrectified noise[5] in I-W at $f = 10$ Hz under conditions of thermal equilibrium several mK above the critical temperature.

In an effort[5] to repeat the previously reported observation of unrectified noise in semiconducting materials,[19–21] the I-W sample was removed from the bridge and replaced with 1-KΩ and 1-MΩ carbon resistors. (The noise from the remaining three metal-film resistors in the bridge was negligible.) All the bridge components were in a metal box that virtually removed a spurious signal at the 10-Hz mixing frequency. Within our experimental error, no peak was detectable at 10 Hz at $V_0 \simeq 2$ V. We could infer[5] from this experiment that in these carbon resistors, the power spectrum at 10 Hz (integrated between 8 and 12 Hz) was at least 140 dB smaller than the mean-square voltage across the 1-KΩ sample.

V. SUMMARY

The present experiments demonstrate that, in binary mixtures, macroscopic flow can produce low-frequency noise. Flow noise, like diffusion noise, diverges strongly near the critical point. In the present experiments the critical exponent γ, which characterizes the divergence of $S_V(f)$, is reduced to unity, presumably because strong shear within the capillary suppresses the critical fluctuations.[4,18] (In thermal equilibrium[2,15] $\gamma \simeq 1.25$.)

As discussed in I, the relaxation of composition fluctuations by diffusion should also produce low-frequency noise, but its power should be concentrated at frequencies much below those explored in the present study and the previous one.[3] The remnant of diffusion noise which should exist above 10^{-2} Hz would have a spectrum of the form $S_V(f) \propto 1/f^{3/2}$, contrary to our findings.

Both the earlier measurements and the present ones reveal a contribution to $S_V(f)$, which persists after flow has ceased, and hence after the steady state is reached. This noise has neither the frequency signature of diffusion noise, nor its expected strong temperature dependence. If end effects are neglected,[3] diffusion noise should diverge as $\epsilon^{-1.25}$ at each frequency, whereas we observe zero-flow spectra under dc excitation to have the form $S_V(f) \propto \epsilon^{-\theta}$, with $\theta \simeq 0.2$.

Finally, a sensitive search was made for a nonlinear current versus voltage response of the binary mixture I-W, and of carbon resistors. No such contribution was found.

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