

## Dielectric-constant anomaly near the critical solution point in polystyrene + cyclohexane

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We present measurements of the static dielectric constant  $\epsilon$  near the liquid-liquid critical point in polystyrene + cyclohexane. The data show an anomalous decrease in  $\epsilon$  as a function of temperature as the critical temperature is approached from the one-phase region at the critical composition. The anomaly reaches an amplitude of about  $7 \times 10^{-5}$  in  $\epsilon$  at a few millikelvins from the critical temperature. The data are consistent with the theoretical predictions of a critical exponent for  $\rho^{-1}\epsilon$  of  $(1-\alpha)$ , where  $\rho$  is the density and  $\alpha$  is the specific-heat exponent.

## I. INTRODUCTION

Microscopic<sup>1-3</sup> and phenomenological<sup>3,4</sup> arguments predict that in the one-phase region near a liquid-gas or liquid-liquid critical point, the static dielectric constant  $\epsilon$  as a function of temperature should have a cusplike anomaly with a critical exponent of  $(1-\alpha)$ , where  $\alpha$  is the exponent which describes the divergence of the heat capacity at constant volume at a liquid-vapor critical point.<sup>5</sup> Sengers *et al.*<sup>3</sup> have shown that correction terms<sup>6,7</sup> may be added for an extended temperature range, yielding, along a path of constant near-critical composition for a liquid-liquid critical point, a predicted functional form:

$$\rho^{-1}\epsilon = A_1 + A_2\Delta T + A_3(\Delta T)^{1-\alpha} + A_4(\Delta T)^{1-\alpha+\Delta_1} + \dots, \quad (1)$$

where  $\rho$  is the density,  $\Delta T = (T - T_c)/T$ ,  $T$  is the temperature,  $T_c$  is the critical temperature,  $\Delta_1 = 0.50$  is the correction exponent,<sup>8</sup> and  $\alpha = 0.1098$ .<sup>8</sup>  $\Delta T$  is slightly different from the more common reduced temperature  $t = (T - T_c)/T_c$  and is expected to be more closely related to the fundamental statistical mechanics.<sup>9,10</sup>

Experimental evidence for such an anomaly at either liquid-gas or liquid-liquid critical points has been difficult to obtain due to the usual experimental problems at critical points.<sup>3</sup> Gravity effects, in particular, can cause difficulties at fluid critical points.<sup>11-13</sup> In the case of the liquid-liquid critical point, the measurements are not done at constant volume and the well-known  $(1-\alpha)$  anomaly in the

density<sup>12,13</sup> can mask the  $\epsilon$  anomaly. In many fluids, conducting impurities<sup>14</sup> can complicate the measurements of  $\epsilon$ .

The best work to date along the critical isochore for nonpolar pure fluids at liquid-gas critical points has shown no evidence of an anomaly.<sup>3,15-18</sup> Pestak and Chan<sup>19</sup> have recently observed an anomaly in  $\epsilon$  for the polar fluid carbon monoxide; the anomaly appears as an increase in  $\epsilon$  of 0.1%. The CO anomaly is consistent with Eq. (1) with four terms, but  $\alpha$  is not well determined by the data, since a change in  $\alpha$  from 0.1 to 0.3 makes no significant change in the goodness of fit.

The best work on  $\epsilon$  at liquid-liquid critical points to date has been that of Hollecker *et al.*<sup>20</sup> and Thoen *et al.*<sup>14</sup> on the polar mixture benzonitrile + isooctane. These workers give convincing evidence of an anomaly of about  $5 \times 10^{-3}$  of the background  $\epsilon$ , but the amplitude and shape of the anomaly could not be determined well because of the superposition of a density anomaly<sup>20</sup> and of strong background terms in  $\epsilon$  due to the large dipole moment of the benzonitrile. The data are consistent with Eq. (1), but do not determine the parameters in Eq. (1) with precision.

Sengers *et al.*<sup>3</sup> have recently made a careful review of the theoretical and experimental aspects of the dielectric constant at fluid critical points. We refer the reader to that paper for a detailed analysis and historical references.

We have measured  $\epsilon$  and  $\rho$  at a near critical composition of the mixture polystyrene + cyclohexane, which is very nearly nonpolar. We were able to avoid the above-mentioned experimental

difficulties. Gravity effects are negligible in this particular mixture.<sup>21,22</sup> Our density measurements have shown the thermal expansion anomaly to be negligible for this system.<sup>22</sup> Conducting impurities were not a problem. As a result, we were able to make unambiguous measurements of  $\epsilon$  which show an anomalous negative deviation from background of about  $7 \times 10^{-5}$  at a few millikelvins from  $T_c$ . We are able to fit Eq. (1) to the  $\rho^{-1}\epsilon$  data; the data are consistent with this function and with the theoretical value of  $\alpha$ . Because the anomaly is so small, the parameters in Eq. (1) are still not determined as well as we would like in order to have a quantitative test of the theory.

## II. EXPERIMENTAL METHODS

### A. Sample preparation

The sample consisted of 16.29 weight percent polystyrene in cyclohexane.<sup>21</sup> Density measurements in the two-phase region<sup>23</sup> indicated that this concentration was within 0.1 weight percent of the critical one. The polystyrene was National Bureau of Standards Standard Reference Material 1478, with a number average molecular weight  $M_N$  of 35 800; the ratio of  $M_N$  to the weight-average molecular weight  $M_w$  was 1.045. The cyclohexane was Mallinkrodt spectrophotometric grade, used without further purification. The volume of the sample in the cell (see below) was about 60 cm<sup>3</sup>. About 5 cm<sup>3</sup> of air was above the sample in the cell.

### B. Density measurements

Density measurements above  $T_c$  were made using a magnetic suspension balance<sup>24</sup> and have been described in a separate publication.<sup>22</sup> The density of 16.29% polystyrene in cyclohexane was measured with an accuracy of 100 ppm and a precision of 20 ppm. The data were described by the analytical function:

$$\rho = C_1 + C_2 T + C_3 T^2, \quad (2)$$

where  $T$  is in °C,  $\rho$  in g/cm<sup>3</sup>,  $C_1 = 0.834 863$ ,  $C_2 = -0.000 885$ , and  $C_3 = -0.000 003 7$ . The anomalous contribution to  $\rho$  can be estimated by assuming two-scale-factor universality<sup>22</sup>; it is  $10^{-3}$  of the analytical thermal expansion and will therefore be negligible. This estimate is consistent with our density measurements, which showed no anomaly at the precision of 20 ppm.

### C. Dielectric constant measurements

The dielectric constant cell, which has been described in a separate publication,<sup>25</sup> was a cylindrical capacitor made of Teflon and stainless steel. The cell was guarded and used in a three-terminal mode with a General Radio (GR) 1615-A capacitance bridge, a Hewlett-Packard 3311A function generator, and a Princeton Applied Research 5204 lock-in amplifier. The excitation signal was 1 V rms sinusoidal voltage at frequencies between 2 and 30 kHz. The standard deviation of the  $\epsilon$  measurements was 5.7 ppm. The accuracy in  $\epsilon$  is expected to be about 100 ppm.

The conductance of the sample in the cell was  $10^{-4} - 10^{-5} \mu\Omega^{-1}$ , which corresponds to a conductivity of  $10^{-10} - 10^{-11} \text{ m}^{-1} \Omega^{-1}$ . This parallel conductance was easily balanced by the GR 1615-A bridge and was not a source of difficulty. The conductance was not determined with great accuracy and showed no interesting features. A detailed analysis of the conductivity itself was, therefore, not deemed worthwhile.

### D. Temperature control and measurement

The temperature control was achieved with a vacuum thermostat in which three concentric cylindrical shells surrounded the capacitance cell. The first shell around the cell was a gold-plated copper radiation shield,  $\frac{1}{16}$  in. in wall thickness. The next shell was of  $\frac{1}{4}$ -in.-thick aluminum, wrapped with a copper heater wire. The third and outer shell was a brass can wrapped with  $\frac{1}{4}$ -in. copper tubing. A circulating water bath pumped water through this tubing, controlling the temperature of the outer shell to  $\pm 0.1$  K. The outer shell was set at a temperature about 0.5 K below the desired cell temperature. An ultrastable thermistor<sup>26</sup> on the heater shell was used in a dc bridge to control the temperature at the shell. The stages of the thermostat were isolated from one another with nylon standoffs. All electrical leads were thermally anchored between stages. The space between the stages was evacuated to about  $10^{-3}$  mm Hg (133 mPa) with a mechanical pump.

Another ultrastable thermistor<sup>26</sup> mounted on the cell was used in an ac ratio transformer bridge to measure the sample temperature. This thermistor was calibrated on the International Practical Temperature Scale of 1968 to 0.01 K. The precision of the temperature measurements was 0.001 K.

We tested for temperature gradients by placing

matched thermistors on the top and bottom of the cell. The gradient observed was less than 1 mK across the entire cell.

#### E. Procedures

The procedure for an experimental run was to heat the sample to about ten degrees above  $T_c$ , stir it thoroughly by shaking the entire thermostat, then cool down step by step, measuring  $\epsilon$  at each step. The rate of cooling was limited by the long time constant of the thermostat; data points were usually taken about once a day.

We expected no complications due to gravity effects in this mixture from the report of Nakata *et al.*<sup>21</sup> and from our own density experiments.<sup>22</sup> In the course of the density measurements, we had searched for gravity effects by measuring the density along the height (about 6 cm) of the sample; we

saw no density gradient within our resolution of 20 ppm, even within a few millikelvins of  $T_c$ . During the  $\epsilon$  measurements, we checked for the development of density gradients near  $T_c$  by shaking the entire thermostat to stir the sample. Any gradient should appear as a change in  $\epsilon$  upon stirring. When the sample had not been stirred for several weeks while the data were being taken near  $T_c$ , we sometimes observed a decrease in  $\epsilon$  after stirring. These changes were quite small—barely outside our experimental uncertainty. We have discarded any data where such gravity effects might have been present.

There was no evidence of a drift with time in  $T_c$  or in  $\epsilon$ . The measurements were quite reproducible, as can be seen by an examination of the data for runs 1 and 2 in Table I or in the figures, which we discuss below.

TABLE I. Measurements of the dielectric constant  $\epsilon$  of polystyrene + cyclohexane along a path of constant, near-critical composition above the critical point. Two different runs are indicated by \* and  $\circ$ . Data are given at three different frequencies. The density is indicated by  $\rho$ .

Point	Run	$T(^{\circ}\text{C})$	2 kHz		10 kHz		30 kHz	
			$\epsilon$	$\rho^{-1}\epsilon$ ( $\text{cm}^3/\text{g}$ )	$\epsilon$	$\rho^{-1}\epsilon$ ( $\text{cm}^3/\text{g}$ )	$\epsilon$	$\rho^{-1}\epsilon$ ( $\text{cm}^3/\text{g}$ )
1	$\circ$	13.238	2.10206	2.55570	2.10208	2.55572	2.10182	2.55540
2	*	13.243	2.10206	2.55572	2.10204	2.55569	2.10178	2.55537
3	$\circ$	13.258	2.10204	2.55574	2.10206	2.55576	2.10180	2.55544
4	*	13.262	2.10203	2.55574	2.10201	2.55571	2.10177	2.55541
5	*	13.281	2.10200	2.55576	2.10198	2.55573	2.10174	2.55544
6	*	13.303	2.10197	2.55579	2.10195	2.55576	2.10171	2.55547
7	$\circ$	13.303	2.10199	2.55581	2.10199	2.55581	2.10175	2.55552
8	*	13.311	2.10200	2.55585	2.10196	2.55580	2.10171	2.55549
9	*	13.315	2.10199	2.55584	2.10194	2.55578	2.10171	2.55550
10	*	13.334	2.10194	2.55585	2.10193	2.55584	2.10169	2.55554
11	*	13.352	2.10190	2.55585	2.10189	2.55584	2.10163	2.55552
12	*	13.371	2.10191	2.55592	2.10187	2.55588	2.10161	2.55556
13	*	13.379	2.10188	2.55591	2.10186	2.55588	2.10161	2.55559
14	$\circ$	13.386	2.10187	2.55591	2.10187	2.55592	2.10163	2.55562
15	*	13.400	2.10186	2.55596	2.10184	2.55593	2.10158	2.55561
16	$\circ$	13.529	2.10167	2.55611	2.10166	2.55610	2.10139	2.55578
17	*	13.599	2.10156	2.55619	2.10152	2.55615	2.10127	2.55583
18	$\circ$	13.721	2.10138	2.55635	2.10138	2.55635	2.10112	2.55604
19	*	13.796	2.10127	2.55645	2.10125	2.55642	2.10099	2.55611
20	$\circ$	13.920	2.10109	2.55661	2.10109	2.55661	2.10084	2.55630
21	*	14.000	2.10094	2.55667	2.10094	2.55668	2.10070	2.55638
22	$\circ$	15.025	2.09935	2.55791	2.09939	2.55795	2.09916	2.55768
23	*	15.999	2.09789	2.55917	2.09786	2.55912	2.09763	2.55885
24	$\circ$	17.009	2.09630	2.56040	2.09635	2.56046	2.09612	2.56019
25	*	17.997	2.09482	2.56173	2.09480	2.56171	2.09456	2.56142
26	*	19.993	2.09172	2.56437	2.09170	2.56434	2.09144	2.56403

### III. RESULTS AND ANALYSIS

Data taken on two experimental runs at three frequencies (2, 10, and 30 kHz) are listed in Table I. Data were taken at 26 temperatures in the range  $3.3 \times 10^{-6} < \Delta T < 2.3 \times 10^{-2}$ .

A plot of all the  $\epsilon$  data at a given frequency as a function of  $T$  or  $\Delta T$  looks to the eye quite straight. We must consider the small deviations from a straight line in order to find the critical anomaly. Figure 1 shows the deviations of the data from straight lines determined by fits to the eight points farthest from  $T_c$ . The deviations become increasingly large and negative near  $T_c$ , indicating the presence of an anomaly. At a few millikelvins from  $T_c$ , the amplitude of the deviations is  $(7-9) \times 10^{-5}$ . We concluded that a very small anomalous decrease in  $\epsilon$  near  $T_c$  is present and proceeded to try to describe the data by the predicted function, Eq. (1), using Eq. (2) for  $\rho$ .

All data analysis was done on a microcomputer using a nonlinear least-square fitting routine in the Basic language. This routine is similar to the well-known Fortran routine CURFIT.<sup>27,28</sup> The uncer-

tainty in  $\rho^{-1}\epsilon$  was at all frequencies taken to be  $1.2 \times 10^{-5}$ , from the propagation of the error in  $\epsilon$ . The uncertainties at 2 and 30 kHz are actually slightly larger ( $\sigma$  for  $\rho^{-1}\epsilon$  should be  $1.8 \times 10^{-5}$  at 2 kHz and  $1.3 \times 10^{-5}$  at 30 kHz, for  $\chi^2_\nu$  to be unity in the best fits) due probably to the increased dielectric loss to be balanced out at 2 kHz and the loss in precision of the bridge 30 kHz. The uncertainty in  $T$  was taken to be 1 mK.

$T_c$  was determined from an expanded plot of  $\epsilon$  vs  $T$  which included some data in the two-phase region below  $T_c$ . (The two-phase data are not given here.) As we have discussed,  $\epsilon$  decreases anomalously as  $T_c$  is approached from the one-phase region. Upon the appearance of the meniscus, the decrease in  $\epsilon$  for the sample halted and the plot of  $\epsilon$  vs  $T$  became quite flat. We took the temperature at which the  $\epsilon$  vs  $T$  plot changed shape to be  $T_c$ . This value was not well determined, but was in the range 286.386 to 286.396 K. In the analysis of the data, we used  $T_c = 286.386$  K (13.236°C). We tested the dependence of the analysis upon  $T_c$  by trying fits with  $T_c = 286.396$  K; we found that, within this 10 mK range, the

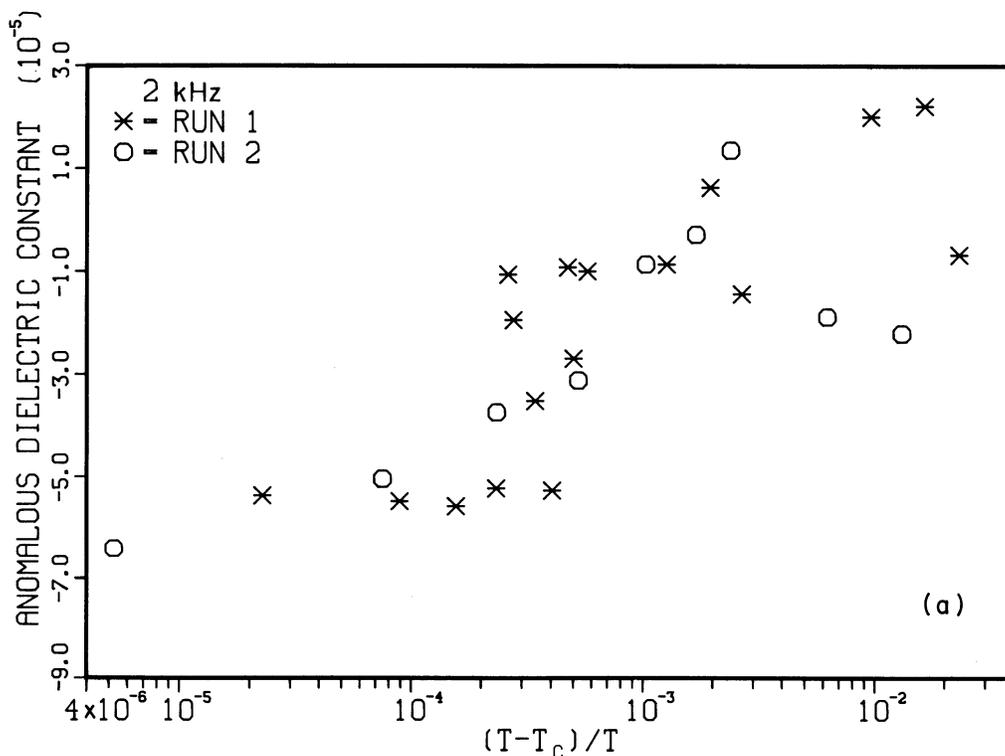


FIG. 1. Deviations of  $\epsilon(\Delta T)$  [where  $\Delta T = (T - T_c)/T$ ] from straight lines determined by the eight points farthest from  $T_c$ . The "anomalous dielectric constant" is  $\epsilon(\text{expt}) - \epsilon(\text{fit})$ . The presence of an anomaly is indicated by the increase in deviations near  $T_c$ .

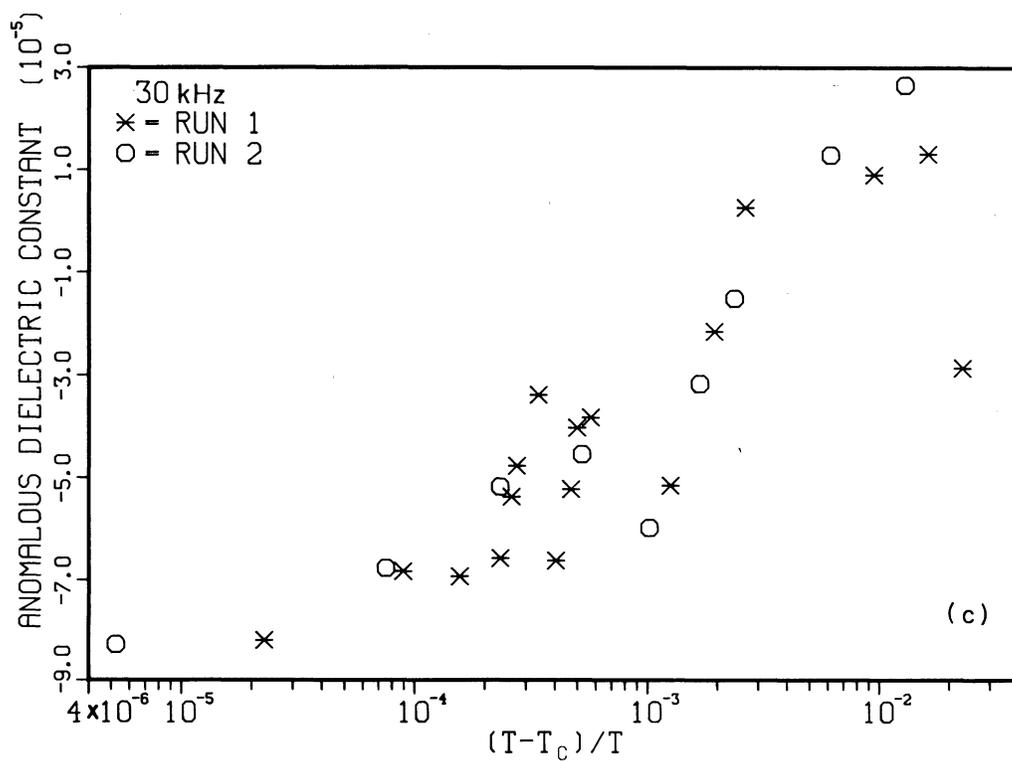
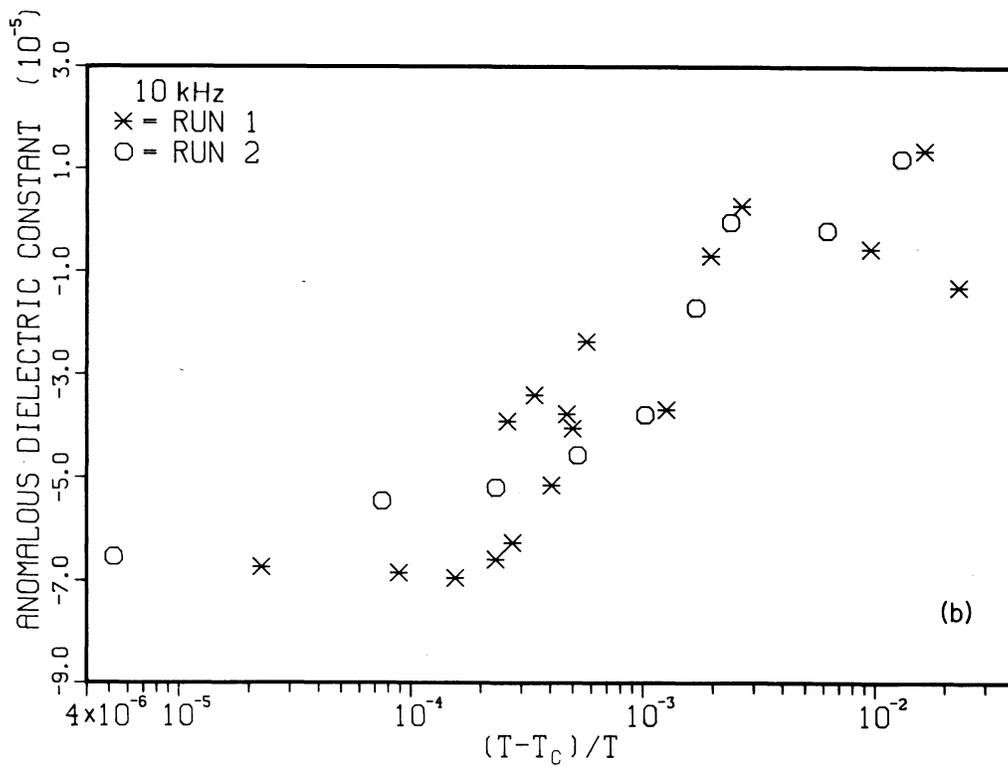


FIG. 1. (Continued).

TABLE II. Results of fits to  $\rho^{-1}\epsilon$  for a mixture of polystyrene + cyclohexane near the liquid-liquid critical point, where  $\rho$  is the mass density and  $\epsilon$  is the static dielectric constant.  $\Delta T$  is  $(T - T_c)/T$ , where  $T$  is the temperature and  $T_c$  the critical temperature. In these fits,  $T_c$  was fixed at 286.386 K,  $\alpha$  at 0.11,<sup>a</sup> and  $\Delta_1$  at 0.50.<sup>a</sup> The uncertainty  $\sigma$  for each parameter is its standard deviation and  $\chi^2_\nu$  is a measure of goodness of fit.<sup>b</sup> The data were in the range  $3.3 \times 10^{-6} < \Delta T < 2.3 \times 10^{-2}$ . A blank space indicates that term was omitted in the function for that fit.

Fit no.	Frequency (kHz)	$\rho^{-1}\epsilon = A_1 + A_2\Delta T + A_3(\Delta T)^{1-\alpha} + A_4(\Delta T)^{1-\alpha+\Delta_1} + \dots$								$\chi^2_\nu$
		$A_1$	$\sigma_{A_1}$	$A_2$	$\sigma_{A_2}$	$A_3$	$\sigma_{A_3}$	$A_4$	$\sigma_{A_4}$	
1	2	2.555 712	$5 \times 10^{-6}$			0.158	0.002	0.59	0.02	2.7
2	2	2.555 745	$1 \times 10^{-5}$	0.483	0.026	-0.074	0.017			9.2
3	2	2.555 697	$8 \times 10^{-6}$	-0.194	0.080	0.253	0.039	0.82	0.095	2.2
4	10	2.555 681	$4 \times 10^{-6}$			0.162	0.002	0.57	1.01	1.2
5	10	2.555 713	$9 \times 10^{-6}$	0.467	0.022	-0.063	0.014			6.3
6	10	2.555 672	$5 \times 10^{-6}$	-0.116	0.050	0.218	0.026	0.70	0.06	1.0
7	30	2.555 371	$4 \times 10^{-6}$			0.166	0.002	0.54	0.01	1.1
8	30	2.555 403	$8 \times 10^{-6}$	0.449	0.018	-0.051	0.012			4.2
9	30	2.555 371	$6 \times 10^{-6}$	0.0045	0.059	0.164	0.029	0.54	0.07	1.2

<sup>a</sup>Reference 8.

<sup>b</sup>Reference 27.

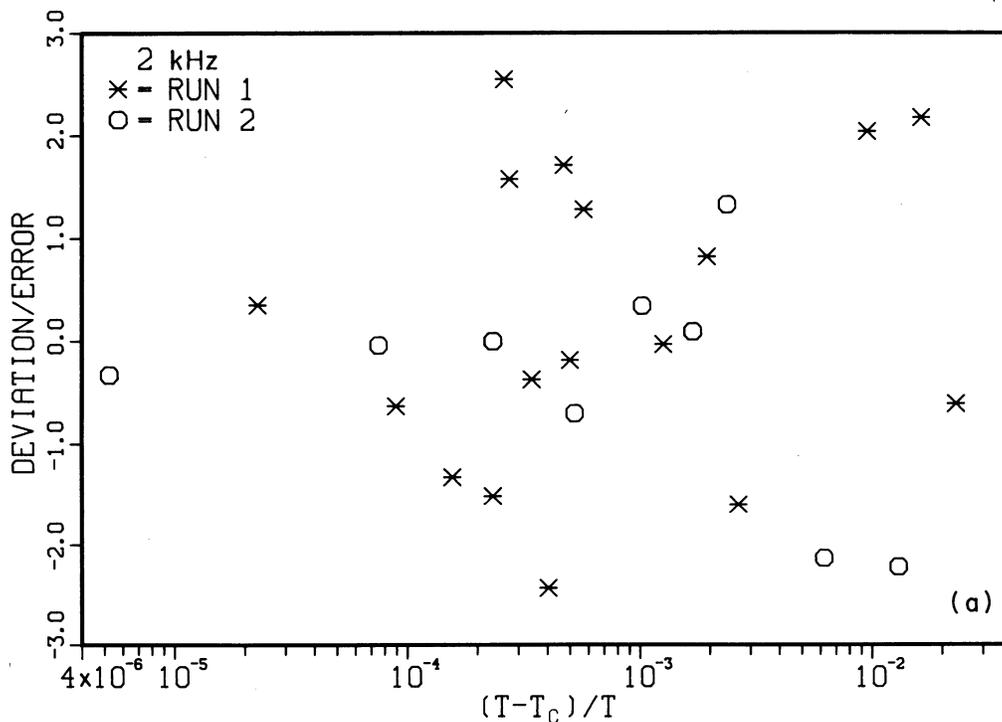


FIG. 2. Residuals of fits of the equation  $\rho^{-1}\epsilon = A_1 + A_2\Delta T + A_3\Delta T^{1-\alpha} + A_4\Delta T^{1-\alpha+\Delta_1}$ , where  $\Delta T = (T - T_c)/T$ ,  $\alpha = 0.11$ ,  $\Delta_1 = 0.50$ , and  $T_c = 286.386$  K, to data on the ratio of the dielectric constant  $\epsilon$  to the density  $\rho$  for polystyrene + cyclohexane. See Table II, fits 3, 6, and 9, for parameters.

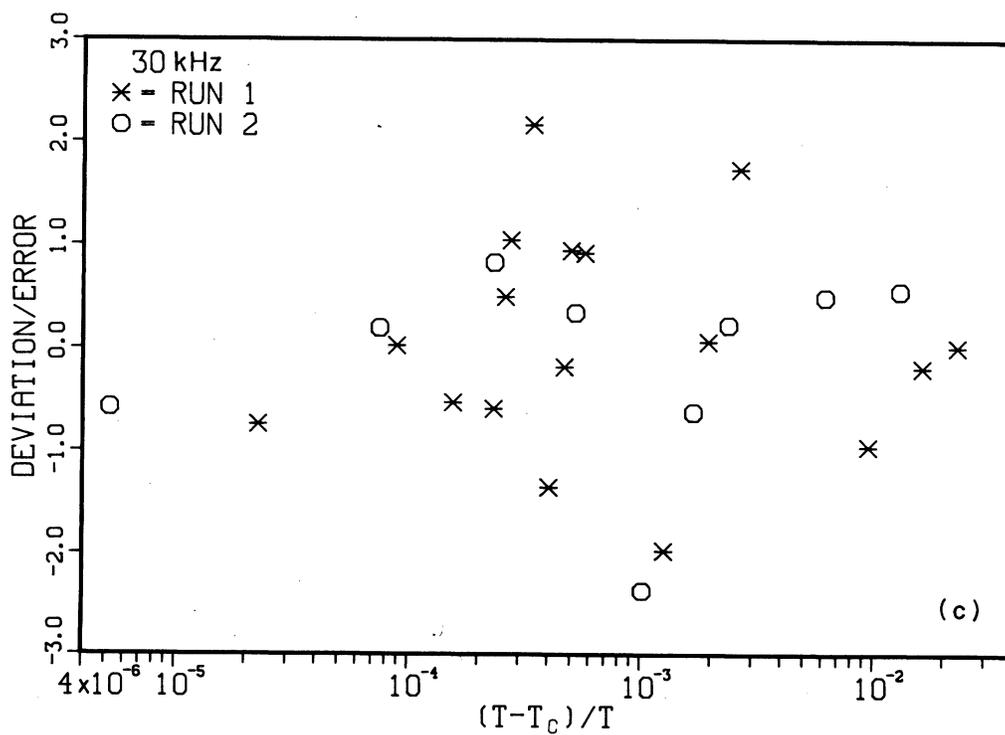
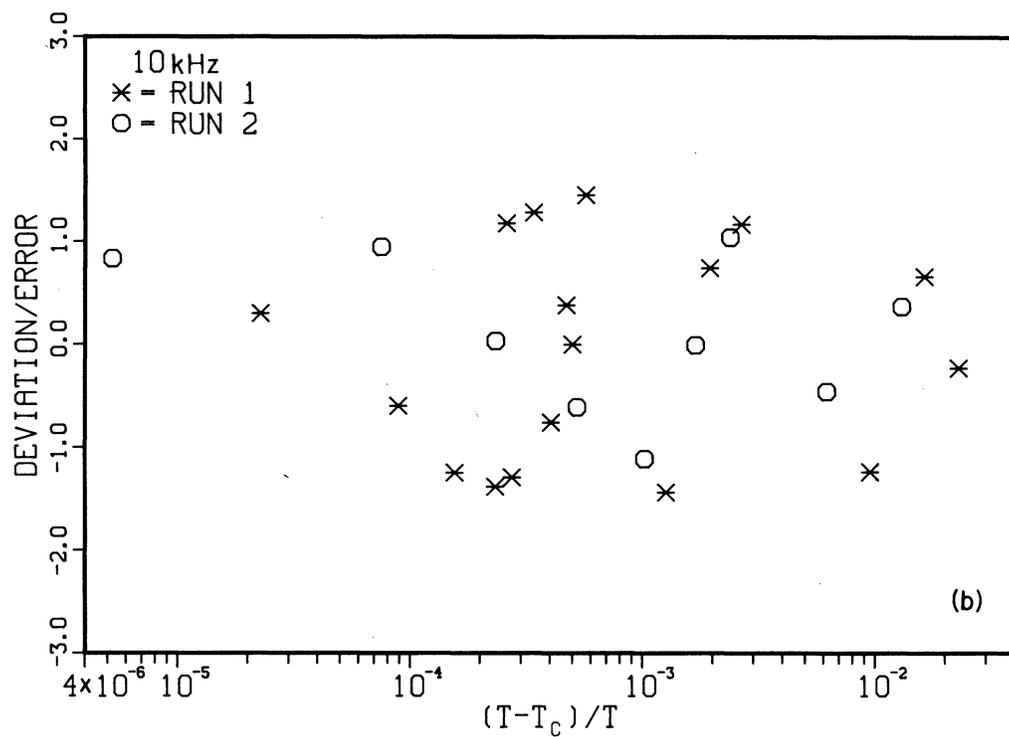


FIG. 2. (Continued).

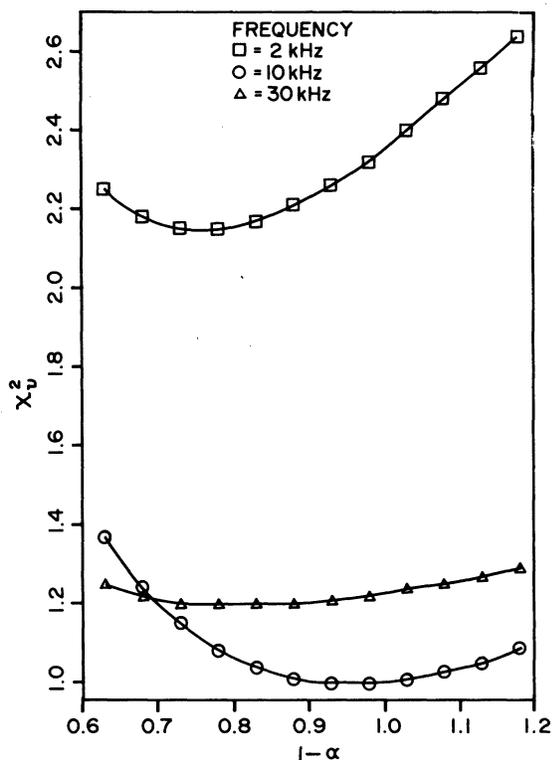


FIG. 3. Reduced chi square  $\chi_v^2$  as a function of fixed values of  $(1-\alpha)$  for fits of the equation  $\rho^{-1}\epsilon = A_1 + A_2\Delta T + A_3(\Delta T)^{1-\alpha} + A_4(\Delta T)^{1-\alpha+\Delta_1}$  with  $\Delta_1=0.50$  and  $T_c=286.386$  K to data for polystyrene + cyclohexane.

value of  $T_c$  did not affect the fits significantly.

In comparing the data to Eq. (1), the questions to be considered are (a) Will equation (1) describe the data? (b) How many terms are needed? (c) Does it make any difference if  $t = (T - T_c)/T_c$  is substituted for  $\Delta T = (T - T_c)/T_c$ ? (d) Do the fits depend upon the frequency (2–30 kHz) at which the measurements were made? (e) How well do the data determine the value of the leading anomalous exponent,  $(1-\alpha)$ ?

In Eq. (1), using four terms, there are four coefficients and two exponents. If all these parameters were allowed to vary in the least-squares analysis, there would be a number of (possibly very different) combinations of parameters which would fit the data equally well. Since we have theoretical estimates<sup>8</sup> for  $\alpha$  and  $\Delta_1$ , we have chosen to hold these exponents fixed in the first set of fits, given in Table II. From Table II, we can begin to answer the questions listed above.

(a) Yes, the data can be described by Eq. (1). Fits

3, 6, and 9 describe the data quite satisfactorily, as indicated by the residual plots in Fig. 2.

(b) The data require four terms in Eq. (1), if the linear term is included (i.e.,  $A_2 \neq 0$ ). It is possible to fit the equations to the data with  $A_2 = 0$  (see fits 1, 4, and 7), but there is no reason to expect  $A_2 = 0$ . Fits 2, 5, and 8 give systematic residual plots and indicate that one anomalous term is not sufficient, but two must be used. We also attempted to fit the "simple scaling" function

$$\rho^{-1}\epsilon = C_1\Delta T^{C_2} \quad (3)$$

to the data, but such a function would not fit the entire set of data. Nor could analytic functions of the form

$$\rho^{-1}\epsilon = C_1 + C_2\Delta T + C_3\Delta T^2 + C_4\Delta T^3 + \dots \quad (4)$$

be fitted to the data, confirming the presence of a nonanalytical term.

(c) Fits using the variable  $t$  were not significantly different from those using  $\Delta T$ .

(d) The various fits in Table II are quite alike for the three frequencies, with one exception. At 30 kHz, for fit 9,  $A_2$  is positive, whereas in the analogous fits for 2 and 10 kHz (see fits 3 and 6),  $A_2$  is negative. We judge this result insignificant because  $A_2$  is determined very inaccurately in fit 9.

(e) It is clear from Table II that there are large uncertainties in the fitted coefficients. The given uncertainties are, in fact, underestimates, since they ignore correlations among parameters.<sup>27</sup> We suggest that the best way to determine the uncertainty in  $(1-\alpha)$  is not by letting  $\alpha$  be a free parameter and extracting the standard deviation to a fit, but by varying  $(1-\alpha)$  stepwise in fits of the data to Eq. (1) with four terms. The width of the minimum of  $\chi_v^2$  as a function of  $\alpha$  will then be a measure of the uncertainty in  $(1-\alpha)$ .

Plots of  $\chi_v^2$  vs  $\alpha$  are given in Fig. 3. The 30-kHz data show a very broad minimum. The 2-kHz data show a minimum in the range  $0.7 < (1-\alpha) < 0.8$ . The 10-kHz data show a minimum in the range  $0.9 \leq (1-\alpha) \leq 1.0$ . We consider the 10-kHz data to be the best data, least subject to instrumental effects. We note that a leading exponent of 0.65 has been found for the critical anomaly in the resistivity,<sup>29</sup> which might be expected to be related to that in  $\epsilon$ ; such an exponent is excluded by our 10-kHz data, but not by the 2- and 30-kHz data. The theoretically predicted value of  $(1-\alpha)=0.89$  (Refs 3 and 8) is consistent with all the data, as noted above and in Table II.

## IV. CONCLUSIONS

We have found that there is a very small (70 ppm) anomalous decrease in the static dielectric constant of the system polystyrene + cyclohexane as the liquid-liquid critical point is approached by varying the temperature along a path of constant, near critical composition, in the one-phase region. The data on this anomaly are consistent with the predicted<sup>1-4</sup> leading critical anomaly, having an exponent  $(1-\alpha)$ , where  $\alpha=0.11$ .<sup>8</sup> The values of the leading exponent and of the other parameters required to describe the data are not well determined because of the small size of the anomaly and the complexity of the function. It may be possible to achieve a better test of the theory by choosing for study a liquid mixture in which at least one component is very polar, in the expectation that the strong polarity will amplify the anomaly.<sup>14,20</sup> Such a mixture must also, as mentioned above and

in Ref. 3, show negligible gravity effects, contain no conducting impurities,<sup>14</sup> and have a well-determined (preferably negligible) thermal expansion anomaly.

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- <sup>1</sup>G. Stell and J. S. Høye, *Phys. Rev. Lett.* **33**, 1268 (1974).
- <sup>2</sup>J. Goulon, J. -L. Greffe, and D. W. Oxtoby, *J. Chem. Phys.* **70**, 4742 (1979).
- <sup>3</sup>J. V. Sengers, D. Bedeaux, P. Mazur, and S. C. Greer, *Physica (Utrecht)* **104A**, 573 (1980).
- <sup>4</sup>L. Mistura, *J. Chem. Phys.* **52**, 4563 (1973).
- <sup>5</sup>H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford, New York, 1971).
- <sup>6</sup>F. Wegner, *Phys. Rev. B* **5**, 4529 (1972).
- <sup>7</sup>M. Ley-Koo and M. S. Green, *Phys. Rev. A* **16**, 2483 (1977).
- <sup>8</sup>J. C. LeGuillou and J. Zinn-Justin, *Phys. Rev. B* **21**, 3976 (1980).
- <sup>9</sup>J. M. H. Levelt Sengers and J. V. Sengers, in *Perspectives in Statistical Physics*, edited by H. J. Raveché (North-Holland, Amsterdam, 1980).
- <sup>10</sup>S. S. Leung and R. B. Griffiths, *Phys. Rev. A* **8**, 2670 (1973).
- <sup>11</sup>M. R. Moldover, J. V. Sengers, R. W. Gammon, and R. J. Hocken, *Rev. Mod. Phys.* **51**, 79 (1979).
- <sup>12</sup>R. L. Scott, in *Specialist Periodical Reports, Chemical Thermodynamics*, edited by M. L. McGlashen (Chemical Society, London, 1978), Vol. II, p. 238ff.
- <sup>13</sup>S. C. Greer, *Accts. Chem. Res.* **11**, 427 (1978).
- <sup>14</sup>J. Thoen, R. Kindt, and W. Van Dael, *Phys. Lett.* **76A**, 445 (1980).
- <sup>15</sup>T. Doiron and H. Meyer, *Phys. Rev. B* **17**, 2141 (1978).
- <sup>16</sup>M. H. W. Chan, *Phys. Rev. B* **21**, 1187 (1980).
- <sup>17</sup>B. J. Thijsse, T. Doiron, and J. M. H. Levelt Sengers, *Chem. Phys. Lett.* **72**, 546 (1980).
- <sup>18</sup>B. J. Thijsse, *J. Chem. Phys.* **74**, 4678 (1981).
- <sup>19</sup>M. W. Pestak and M. H. W. Chan, *Phys. Rev. Lett.* **46**, 943 (1981).
- <sup>20</sup>M. Hollecker, J. Goulon, J. -M. Thiebaut, and J. -L. Rivail, *Chem. Phys.* **11**, 99 (1975).
- <sup>21</sup>M. Nakata, T. Dobashi, N. Kuwahara, and M. Kaneko, *Phys. Rev.* **18**, 2683 (1978).
- <sup>22</sup>S. C. Greer and D. T. Jacobs, *J. Phys. Chem.* **84**, 2888 (1980). This paper lists references to all previous work on polystyrene + cyclohexane.
- <sup>23</sup>S. C. Greer and D. T. Jacobs (unpublished).
- <sup>24</sup>S. C. Greer, M. R. Moldover, and R. Hocken, *Rev. Sci. Instrum.* **45**, 1462 (1974).
- <sup>25</sup>D. T. Jacobs and S. C. Greer, *Rev. Sci. Instrum.* **51**, 994 (1980).
- <sup>26</sup>Type S-1, 4k $\Omega$ , Thermometrics, Inc., Edison, N. J.
- <sup>27</sup>P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969).
- <sup>28</sup>See also William Bennett, Jr., *Scientific and Engineering Problem Solving with a Computer* (Prentice-Hall, Englewood Cliffs, 1976).
- <sup>29</sup>C. -H. Shaw and W. I. Goldberg, *J. Chem. Phys.* **65**, 4906 (1976); J. Ramakrishnan, N. Nagarajan, A. Kumar, E. S. R. Gopal, P. Chandrasekhar, and G. Ananthakrishna, *ibid.* **68**, 4098 (1978); A. Kumar and E. S. R. Gopal, *Pramana* **12**, 511 (1979); *Chem. Phys. Lett.* **62**, 306 (1979).