Amplitude of the anomaly in the mass density near a liquid-liquid critical point

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We address two questions with respect to the amplitude of the critical anomaly in the mass density (or the thermal expansion) as a function of temperature in the one-phase region near a liquid-liquid critical point. First, is this amplitude proportional to the difference in density between the two pure liquid components of the mixture? A consideration of data from the literature on 11 liquid-liquid systems shows no such correlation, nor is any such correlation expected from theory. Second, is this amplitude, as directly measured, thermodynamically consistent with measurements of the heat capacity at constant pressure and composition \( C_P \), on the same system? Data from the literature on 5 systems show that, in relating the critical coefficient of the density anomaly to the critical coefficient of \( C_P \), we cannot make a direct calculation of one from the other. If we try to test the consistency among the critical behaviors of the thermal expansion \( C_P \), and the dielectric constant \( \varepsilon \), then the required data are available for only one system and are not consistent. We attribute these problems to the behavior of \( C_P \), and also to the importance of terms other than the critical terms. We caution that the interpretation of the amplitudes of small critical anomalies, such as in the density, must be done with care.

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I. INTRODUCTION

We wish to address two questions with respect to the amplitude of the anomaly in the mass density as a function of temperature \( \rho(T) \) [or in its derivative with respect to temperature, the thermal expansion, \( \frac{\partial \rho}{\partial T} \)] in the one-phase region approaching a liquid-liquid critical point. First, is this amplitude proportional to the difference in density between the two liquids in the mixture? Second, is this amplitude, as directly measured, thermodynamically consistent with measurements of the heat capacity at constant pressure on the same system?

The first question is prompted by recent work by Hamelin et al. [1], who sought to measure the intrinsic anomaly in the dielectric constant near the liquid-liquid critical point in methanol+cyclohexane. The mass density as a function of temperature is expected to have the form [2,3]

\[
\rho = \rho_c + R_1 t + R_2 t^{1-a} + R_3 t^{1-a+\Delta} + \cdots
\]

\[
= \rho_c [1 + (R_1/\rho_c) t + (R_2/\rho_c) t^{1-a} + (R_3/\rho_c) t^{1-a+\Delta} + \cdots]
\]

where \( \rho \) is the mass density in g/cm\(^3\), \( \rho_c \) is the mass density at the critical point, \( T_c \) is the critical temperature, \( t \) is the reduced temperature \((T-T_c)/T_c\) for an upper consolute point and \((T_c-T)/T_c\) for a lower consolute point, and the exponents are fixed at their theoretical values [4] of \( a=0.11 \) and \( \Delta=0.5 \). Thus \( R_2 \) is the amplitude of the leading critical anomaly in the density. The functional form for the dielectric constant \( \varepsilon \) is the same as Eq. (1), but with different values of the amplitudes and of the constant [2,3]. Since the density and the dielectric constant have the same functional form for the intrinsic critical behavior, measurements of \( \varepsilon \) will reflect the anomaly in the density and must be corrected for the density effect if the intrinsic anomaly in \( \varepsilon \) is to be analyzed. Indeed, previous workers have found several systems in which the critical anomalies in the density are negligible and/or measured, and the measured intrinsic critical anomalies in \( \varepsilon \) are then consistent with the predicted functional form for \( \varepsilon \) [5–10].

Hamelin et al. [1] sought to find a system for which the critical anomaly in the density is negligible in order to analyze better the critical anomaly in \( \varepsilon \). They state that “the contribution of the thermal expansion divergence is related to the mass density difference \( \Delta \rho \) between the two phases.” We take “between the two phases” to mean “between the two pure components.” The experiment they present is predicated on the assumption that, if the difference in density between the two pure components is small, then the critical anomaly in the density is small and a measurement of the dielectric constant is not “contaminated” by the anomaly in the density. This assumption of a correlation between \( \Delta \rho \) and the amplitude of the critical anomaly in the density bears close consideration since it is not a prediction of any theory of which we are aware [11]. Moreover, as we show below, we find no such correlation in the available data.

The second question that we address is that of the thermodynamic consistency of measured values of the thermal expansion with measured values of the heat capacity at constant pressure. We begin with the exact thermodynamic relation [12],

\[
C_{P,x} - C_{V,x} = T (\partial V / \partial T)_{P,x} (\partial P / \partial T)_{V,x},
\]

where \( C_{P,x} \) is the heat capacity at constant pressure \( (P) \) and composition \( (x) \), \( C_{V,x} \) is the heat capacity at constant molar volume \( (V) \) and temperature \( (T) \), and the partial derivatives are as indicated. (For liquids, one actually measures the heat capacity at the saturated vapor pressure rather than at constant pressure, but this distinction is insignificant.) For a liq-
uid mixture at its critical concentration, \( x \) is \( x_c \). Close enough to \( T_c \), \( C_{V,x} \) is finite, \( C_{P,x} \) is weakly diverging, and \((\partial V/\partial T)_{P,x}\) becomes the constant \((dT_c/dP)_x\), so that \([13,14]\)

\[
(\partial V/\partial T)_{P,x} = -(\partial p/\partial T)_P \rho^2_c \approx C_{P,x}(dT_c/dP)/T_c. \tag{3}
\]

Equation (2) is thermodynamically exact and must always be true. Equation (3) can be expected to hold only close enough to the critical point that the behavior of \( C_{V,x} \) is not important.

We can write a function for \( C_{P,x} \) in the one-phase region near the critical point \([15]\)

\[
C_{P,x} = C_{P,x}^0 + (A_{P,x}/\alpha) t^{-\alpha}[1 + \cdots], \tag{4}
\]

where \( C_{P,x}^0 \) is a “background” contribution. The contribution of \( C_{P,x}^0 \) is very important (e.g., \( C_{P,x}^0 \) is 91% of \( C_{P,x} \) at \( t = 10^{-4} \) for methanol+cyclohexane \([16]\]). If Eq. (3) is true, then it can be used to relate the amplitude of the critical anomaly in the mass density \( R_2 \) to that in \( C_{P,x} \),

\[
(A_{P,x}/\alpha) = \pm [(1 - \alpha)R_2]/(\rho_c (dT_c/dP)), \tag{5}
\]

where the plus sign applies for a lower consolute point and the minus sign applies for an upper consolute point.

The problems with the range of validity of Eq. (3), and thus the range of validity of Eq. (5), were discussed 20 years ago by Subramanyam, Ramachandra, and Gopal \([17]\) and by Morrison and Knobler \([12]\), and more recently by Anisimov \([16]\). Sometimes Eq. (5) seems to work \([18]\) and sometimes it does not work \([17]\). Anisimov \([16]\] has asserted that \( C_{V,x} \) will have behavior that can be described by a \( t^{-\alpha} \) anomaly in all the experimentally accessible regions and that therefore Eq. (3) will not be valid in the experimentally accessible region.

We present here a review of the direct experimental determinations of \( R_2 \), compared to the direct measurements of \( A_{P,x} \) for the same systems, and a consideration of one case where information is also available on the behavior of \( C_{V,x} \). We find that the value of \( R_2 \) obtained by the fits to the data is usually greater than the value predicted from Eq. (5). A test of the consistency among the critical behaviors of the density, \( C_{P,x} \) and \( C_{V,x} \), using Eq. (2) for the one system for which all the data are available, fails to show the expected relationship. We attribute these problems not only to the behavior of \( C_{V,x} \), but also to the importance of terms other than the critical terms.

II. CORRELATION BETWEEN THE AMPLITUDE OF THE DENSITY ANOMALY AND THE DIFFERENCE IN DENSITY

We can test whether there is any experimental evidence for a correlation between the difference in density between the pure components \( \Delta \rho \) and the amplitude of the density anomaly \( R_2 \) by plotting \( R_2 \) as obtained from fits to published measurements of \( \rho(t) \) or of the thermal expansion, versus \( \Delta \rho \). For simplicity, we consider only direct experimental measurements of the mass density or of the thermal expansion and do not include indirect measurements such as the refractive index \([18]\). Equation (1) has been used to fit all data sets, with the exponents fixed at the theoretical values. We fit Eq. (1) to data using a nonlinear least-squares routine that is designed to include in the estimation of errors the correlations among the amplitudes of the terms in the fitted equation \([19]\). However, it is important to note that the fitted amplitudes in Eq. (1) can depend on the choice of terms to include in the equation \([18]\). In particular, the value of \( R_2 \) can depend on the choice of a “fourth” term as either a term in \( t^{1-\alpha+\Delta} \) or an analytic background term in \( t^\alpha \). It is also important for our purposes that we propagate error consistently: We report all fitted uncertainties at the 99% confidence level. When a term in \( t^{1-\alpha+\Delta} \) yields a different \( R_2 \) than does an analytic background term in \( t^\alpha \), we use the average of \( R_2 \) between the two fits and take the deviation from the mean as the uncertainty. We determine \( \Delta \rho \) from handbook values \([20]\) of the densities of the pure components, extrapolated to \( T_c \). The various parameters and amplitudes are listed in Table I.

For six systems—benzonitrile+isooctane, triethylamine +water, 2.6-lutidine +water, polystyrene+diethyl malonate, and polystyrene+cyclohexane—Eq. (1) was used in the original publications and the published amplitudes could be used for our purposes. For benzonitrile+isooctane \([21]\), Eq. (1) described the data with three terms. For a fit with a fourth term, \( R_3 \) was undetermined, but \( R_2 \) was unchanged \([22]\); thus we use the published amplitude. For triethylamine+water, we use the published values \([18,23]\). For 2.6-lutidine +water, Eq. (1) was used in the original publication; we take an average over fits given for the two samples near \( T_c \) for \( R_2 \). For polystyrene+diethyl malonate \([24]\), the original analysis found no significant magnitude for \( R_2 \); we use the upper limit of \(-0.022 \pm 0.027 \). For polystyrene+cyclohexane \([25]\), no significant critical anomaly was found; we use \( R_2 = 0 \). We caution that for polystyrene+diethyl malonate and for polystyrene+cyclohexane, we take \( \Delta \rho \) between a solid pure component \([26]\) and a liquid pure component, as opposed to between two liquids for the other systems. For nitroethane +cyclohexane, we use the published amplitude \([8,27]\), but note that neither the original data nor the details of the fitting were published.

For two systems, we have ourselves fitted Eq. (1) to the published data. For nitroethane +3-methylpentane \([28]\), we find that \( R_2 \) depends on the choice of the fourth term; we use an average value to obtain \( R_2 = -0.025 \pm 0.007 \). For isobutyric acid +water, we have fitted Eq. (1) to the published data converted to density \([12]\); no fourth term is required and we obtain \( R_2 = +0.0388 \pm 0.0001 \).

For three systems, we have fitted the derivative of Eq. (1) to the published measurements of the thermal expansion and converted the coefficient of the leading anomalous term to the equivalent \( R_2 \). For methanol+cyclohexane \([29]\), the fit is again sensitive to the fourth term; we use an averaged \( R_2 = -0.06 \pm 0.01 \), essentially the same as the value obtained by Scheibner et al. \([29]\). For cyclohexane+acetic anhydride \([30]\), the fit is also sensitive to the fourth term; we use an averaged \( R_2 = -0.64 \pm 0.12 \) and \( \rho_c \) is estimated from the composition (assuming an ideal solution) to be 0.87. For methanol+heptane \([31,32]\), the fit is sensitive to the fourth term; we use an averaged \( R_2 = -0.43 \pm 0.08 \) and \( \rho_c \) is estimated from the composition (assuming an ideal solution) to be 0.72.

Figure 1(a) is a plot of \( R_2/\rho_c \) versus \( \Delta \rho \) and Fig. 1(b) is a plot of \( |R_2/\rho_c| \) versus \( \Delta \rho \), where \( \Delta \rho \) is the difference in mass density of the pure components at \( T_c \), for the 11 liquid-liquid
TABLE I. Parameters of liquid-liquid systems: $\Delta \rho$ is the difference in density between pure components at $T_c$; $\rho_c$ is the mass density at the critical point; $R_2$ is the experimental amplitude of the critical anomaly in the mass density in the one-phase region; $dT_c/dP$ is the derivative of the critical temperature with respect to pressure; $A^+=\text{expt}$ is the experimental amplitude of the heat capacity at constant pressure in the one-phase region; and $A^+(\text{calc})$ is the amplitude of the heat capacity at constant pressure in the one-phase region, as calculated from Eq. (5). Uncertainties are given at the 99% confidence interval. See the text for further discussion.

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>$\Delta \rho$ ($\text{g/cm}^3$)</th>
<th>$\rho_c$ ($\text{g/cm}^3$)</th>
<th>$R_2(\text{expt})$ ($\text{g/cm}^3$)</th>
<th>$dT_c/dP$ (mK/atm)</th>
<th>$A^+_x$ (J/cm$^2$ K)</th>
<th>$R_2(\text{calc})$ ($\text{g/cm}^3$)</th>
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<td>methanol</td>
<td>0.013</td>
<td>0.7536$^a$</td>
<td>$-0.06^b$</td>
<td>33.9$^c$</td>
<td>0.0077$^d$</td>
<td>$-0.020$</td>
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<td>cyclohexane</td>
<td>$\pm 1 \times 10^{-4}$</td>
<td>$\pm 0.01$</td>
<td>$\pm 0.4$</td>
<td>$\pm 0.004$</td>
<td>$\pm 0.001$</td>
<td>$\pm 0.001$</td>
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<td>isobutyric acid</td>
<td>0.035</td>
<td>0.993 00$^e$</td>
<td>$+0.0388^f$</td>
<td>$-50^g$</td>
<td>0.0042$^h$</td>
<td>$+0.021$</td>
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<td>water</td>
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<td>$\pm 5$</td>
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<td>$-0.02^h$</td>
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<td>$\pm 0.027$</td>
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<td></td>
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<td>2,6-lutidine</td>
<td>0.085</td>
<td>0.988 33$^i$</td>
<td>$+0.017^j$</td>
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<td>0.021$^j$</td>
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<td>$\pm 0.004$</td>
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<tr>
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<td>$\pm 0.02$</td>
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<td>$-11.9^l$</td>
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<td>0.792 01$^u$</td>
<td>$-0.025^u$</td>
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<td>3.67$^v$</td>
<td>0.03$^w$</td>
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<td>$\pm 1 \times 10^{-5}$</td>
<td>$\pm 0.007$</td>
<td>$\pm 0.09$</td>
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<td>0.03</td>
<td>$\pm 0.009$</td>
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<td>0.864 845$^x$</td>
<td>$-0.0294^x$</td>
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<td>15.03$^x$</td>
<td>0.0282$^x$</td>
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<td>$\pm 0.04$</td>
<td></td>
<td>$\pm 0.0004$</td>
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</table>


systems discussed above. We note that neither plot shows any correlation between $R_2/\rho_c$ and $\Delta \rho$. Thus there is no experimental evidence that $R_2/\rho_c$ is correlated to $\Delta \rho$.

III. THERMODYNAMIC CONSISTENCY OF THE DENSITY AND THE HEAT CAPACITY

We next address the following questions: (i) Does Eq. (5) hold true for the relationship between the amplitude of the critical anomaly in the density in the one-phase region and the amplitude of the critical anomaly in the heat capacity ($A^+/\alpha$)? (ii) When $R_2$, $A^+_x$, $A^+_{V,x}$, and $dT_c/dP$ are all known from experiments, do the data satisfy Eq. (2)?

We have been able to find the necessary information for the first comparison—measurements of $dT_c/dP$ and measurements of the heat capacity at constant pressure—for only five systems: methanol + cyclohexane, isobutyric acid + water, triethylamine + water, nitroethane + 3-methylpentane, and nitroethane + cyclohexane. As in Sec. II, we consider only measured parameters and do not consider parameters derived from other critical properties [33,34]. Since the functional behavior of the heat capacity is a divergence rather than a cusp, there is less ambiguity in the determination of $A^+_x$ from fits to heat capacity data than in the determination of $R_2$ from fits to density data. Therefore, we use the amplitudes as reported in the original experiments or in subsequent analyses, always with $\alpha=0.11$. The values used are given in Table I.

In Fig. 2(a), we plot the ratio of the value $R_2^+$ as obtained from measurements (Sec. II above and Table I) to the value of $R_2$ as calculated from Eq. (5), using the values of $dT_c/dP$ and $A^+_x$ given in Table I, versus $[R_2(\text{expt})/\rho_c]$, for the five systems for which all the information is available. We note that the experimental value of $R_2$ is usually 1.3–3.0 times the calculated value of $R_2$. This trend suggests that the small critical amplitudes are difficult to determine and that the use of Eqs. (3) and (5) is therefore problematic. Another factor in this discrepancy can be the behavior of $C_{V,x}$, which we discuss below.

While Eqs. (3) and (5) are approximations that need not always be true, Eq. (2) is an exact thermodynamic relationship that must always be true. There is only one liquid-liquid system for which all the quantities in Eq. (2) have been published near a liquid-liquid critical point: methanol + cyclohexane, for which $C_{P,x}$ [35], $C_{V,x}$ [36], and the thermal expansion [29] have all been measured. As Anisimov et al. point out [16,36], the behavior of $C_{V,x}$ may for some
systems be very similar to that of $C_{P,x}$ in the experimentally accessible range of reduced temperature. Both sets of data can be described by a $t^{-a}$ critical anomaly. We can write a function like Eq. (4) for $C_{V,x}$:

$$C_{V,x} = C_{V,x}^0 + (A_{V,x}^+/\alpha) t^{-a} [1 + \cdots].$$

(6)

Anisimov et al. [16] finds $A_{P,x}^+/A_{V,x}^+$ for methanol + cyclohexane to be $1.8 \pm 0.2$. Thus, while the apparent divergence in $C_{V,x}$ for methanol + cyclohexane is smaller than the divergence for $C_{P,x}$, it is hardly negligible. For

FIG. 1. (a) Coefficient of the leading critical anomaly in the mass density $R_2$ divided by the critical density $\rho_c$ as a function of the magnitude of the difference in mass density $\Delta \rho$ between the two pure components at the critical temperature, for 11 liquid-liquid systems. (b) Magnitude of the ratio of the coefficient of the leading critical anomaly in the mass density $R_2$ to the critical density $\rho_c$ as a function of the magnitude of the difference in mass density $\Delta \rho$ between the two pure components at the critical temperature, for 11 liquid-liquid systems. The systems are (1) methanol + cyclohexane, (2) isobutyric acid + water, (3) polystyrene + diethyl malonate, (4) 2,6-lutidine + water, (5) methanol + heptane, (6) polystyrene + cyclohexane, (7) triethylamine + water, (8) cyclohexane + acetic anhydride, (9) benzonitrile + isooctane, (10) nitroethane + trimethylpentane, and (11) nitroethane + cyclohexane.

FIG. 2. (a) Ratio $R_2(\text{expt})$, the coefficient of the leading critical anomaly in the mass density as obtained from fits to measurements (see Sec. II and Table I), to $R_2(\text{calc})$, as calculated from Eq. (5) using the values of $dT_c/dP$ and $A_{P,x}$ given in Table I, versus the amplitude of $R_2(\text{expt})$ divided by the critical density $\rho_c$. (b) Ratio $R_2(\text{expt})$ to $R_2(\text{calc})$ versus the dimensionless product $[\rho_c R (dT_c/dP)]^2$, where $\rho_c$ is the critical density, $R$ is the gas constant, and $dT_c/dP$ is the dependence of the critical temperature on pressure. Both plots include the five systems (1) methanol + cyclohexane, (2) isobutyric acid + water, (3) triethylamine + water, (10) nitroethane + trimethylpentane, and (11) nitroethane + cyclohexane. The system numbering is consistent with Table I and Fig. 1.
We caution that the equating of the coefficients of like terms implies that the coefficients are not significantly correlated and that higher-order terms can be ignored. For methanol + cyclohexane, using the information in Table I, the ratios of the terms on the right-hand side to the term on the left-hand side are 0.55 for the first term [16] and 3.0 for the second term. Moreover, if we consider the signs of these terms (Table I), we see that the inclusion of the $A_{V,s}$ actually makes the agreement worse rather than better. Thus the experimental behavior of methanol + cyclohexane does not satisfy Eq. (7).

IV. DISCUSSION AND CONCLUSIONS

We set out to address two questions with respect to the amplitude of the critical anomaly in the mass density (or the thermal expansion) as a function of temperature in the one-phase region near a liquid-liquid critical point. First, is this amplitude proportional to the difference in density between the two pure liquid components of the mixture? Second, is this amplitude, as directly measured, thermodynamically consistent with measurements of the heat capacity at constant pressure on the same system?

For the first question, after considering data on 11 liquid-liquid systems, we find no experimental evidence for a dependence of the critical anomaly in the mass density upon the difference in density between the components. We cannot claim to have proven the absence of such a correlation, for the determination of amplitudes from fits to data is complicated. However, with our present best evaluation of the amplitudes, there is no experimental evidence in favor of such a correlation between the amplitude of the anomaly in $\rho$ and the amplitude of $\Delta \rho$ and one should not be used to predict the other. We are likewise aware of no theoretical argument in support of such a correlation.

The second question is the following: Is the amplitude of the anomaly in the mass density, as directly measured, thermodynamically consistent with measurements of the heat capacity at constant pressure on the same system? We considered first the approximation given by Eqs. (3) and (5), which neglect $C_{V,s}$ near the critical point. We found that these equations do not, in general, work. The experimental value of the critical amplitude of the density anomaly is, for the systems we considered, generally larger than the calculated amplitude.

We conclude that the amplitude of the critical anomaly in $C_{P,s}$ and the amplitude of the density anomaly cannot be used, one to predict the other. This conclusion had been reached previously by other workers considering the particular systems isobutyric acid + water [12] and methanol + heptane [17]. We have extended their observations to all the available data. We note that the problems come both from the non-negligible behavior of $C_{V,s}$, and from the inherent difficulties in determining small amplitudes accurately.

Recent analysis by Anisimov et al. [38] indicates that the difference between $C_{P,s}$ and $C_{V,s}$ is larger for a liquid-liquid system if the isothermal compressibility is larger. Anisimov et al. [38] suggest that a measure of the compressibility of weakly compressible liquid mixtures is the dimensionless quantity $[\rho R (dT_c/dP)]^2$, where $R$ is the gas constant: If $[\rho R (dT_c/dP)]^2$ is smaller, then the compressibility is expected to be larger, the right-hand side of Eq. (2) to be smaller, and thus Eqs. (3) and (5) should be more accurate. Figure 2(b) shows the ratio (from Table I) of $R_2$ as obtained by direct experiments to that calculated from Eq. (3), as a function of $[\rho R (dT_c/dP)]^2$. The expected approach of $R_2(\text{expt})/R_2(\text{calc})$ to unity as $[\rho R (dT_c/dP)]^2$ gets smaller is not observed.

We then considered consistency of the data with the full thermodynamic relationship given in Eq. (2). We have only one liquid-liquid system, methanol + cyclohexane, for which all the necessary data are available. Those data are not mutually consistent. We do not want to overinterpret data on just one system when systematic errors in just one of the data sets could cause the discrepancy. Moreover, there are many problems with such comparisons. The background contributions to $C_{P,s}$ and $C_{V,s}$ for methanol + cyclohexane are 91% and 97%, respectively [35,36], leaving a small critical contribution to be studied. The fitted experimental amplitudes can depend on the exact choice of the function. The fitted experimental amplitudes could depend on the exact sample composition and on the level of impurities in the samples, although work by Anisimov et al. [35,36] indicates that these effects are not significant for $C_{P,s}$ and $C_{V,s}$ of methanol + cyclohexane and no such effect is seen on the amplitude of the coexistence curve for methanol + cyclohexane [39,40].

Our analysis suggests several experiments that would be worthwhile. Table I indicates that measurements of $dT_c/dP$ for lutidine + water would allow further analysis of that system. A new measurement of the mass density for methanol + cyclohexane, including measurements on the deuterated mixtures used by Hamelin et al. [1], would help to clarify issues. There exist measurements of $C_{P,s}$ for nitroethane + isooctane [37], for which measurements of $dT_c/dP$ and of the mass density would be complementary.

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