Interfacial tension of fluids near critical points and two-scale-factor universality

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Data for the surface tension of pure fluids near critical points and for the interfacial tension between coexisting liquid phases of binary mixtures near consolute points are reviewed using recent theoretical values for the critical exponents and the concept of two-scale-factor universality [D. Stauffer, M. Ferer, and M. Wortis, Phys. Rev. Lett. 29, 345 (1972)]. The data are used to estimate the universal amplitude ratios relating the interfacial tension amplitude \( \sigma_0 \) to the specific-heat divergence and to the correlation length near \( T_c \). The amplitude ratios for a wide variety of fluid systems including polymer solutions are consistent and, in the most favorable cases, have an accuracy approaching \( \pm 5\% \) of \( \sigma_0 \). The experimental amplitude ratios do not agree with recent theoretical estimates from either Monte Carlo simulations of the Ising model or the \( \epsilon \) expansion. The theoretical values of \( \sigma_0 \) are about 65% of the experimental values. I have no explanation for this inconsistency. In the process of reviewing surface-tension data for pure fluids, it was observed that the capillary-length data for many fluids deviate by less than 2% from the experimental relationship

\[
T \sim \sigma_0^2 a_0^2 (1 - T/T_c)^{0.935}
\]

when \( T \) varies from the triple point to 0.99 \( T_c \). (The exponent 0.935 is expected to be accurate only asymptotically close to \( T_c \).) This observation implies that the scale factors for the critical anomaly in the free energy of these liquid-vapor systems can be estimated from measurements of the densities of the coexisting phases at all temperatures and a measurement of the capillary rise near the triple point.

I. INTRODUCTION

The van der Waals theory of interfacial tension\(^1\) provides a direct connection between the thermodynamic properties of a fluid and the energy of an interface between coexisting phases of the same fluid. To the extent that equations of state obey a law of corresponding states, the van der Waals theory implies that the interfacial tension also obeys a law of corresponding states. This idea has been frequently exploited to correlate the surface tension of liquid-vapor systems at low and moderate reduced temperatures.\(^2,3\) Such corresponding-states correlations may use the critical parameters \( T_c \) and \( V_c \) to scale the surface-tension data or they may use the parameters \( \sigma \) and \( \epsilon \) characterizing model intermolecular potentials as scale factors. If an additional parameter such as the "acentric factor" or the molecular weight is introduced, surface-tension data for an extraordinarily wide variety of liquid-vapor systems can be correlated.\(^4,5\)

In contrast with earlier correlations, the present work is focused on the behavior of the interfacial tension in the critical region. Furthermore, the present work treats the interfacial tension between coexisting phases of binary liquid mixtures near consolute points on the same basis as the surface tension of a liquid-vapor system. The underlying ideas can be traced to Fisk and Widom,\(^6\) who extended the theory of van der Waals by incorporating the nonanalytic behavior of thermodynamic properties near the critical point to predict the behavior of the surface tension near the critical point. Fisk and Widom\(^6\) concluded that universal ratios should exist between the amplitude \( \sigma_0 \) (which characterizes the vanishing of the interfacial tension in the critical region) and the amplitude \( \xi_0 \) (which characterizes the divergence of the correlation length) and a combination of amplitudes which characterize the nonanalytic part of the free energy near the critical point. Although the ratios were predicted to be universal, the amplitudes themselves are not and their values have no obvious connection with the critical parameters or the parameters for model intermolecular potentials. Stauffer et al.\(^7\) introduced the concept of two-scale-factor universality which asserts that the singular part of the free energy belonging to a volume \( \xi_0^d \) (\( \xi_0 \) is the correlation length, \( d \) is the dimensionality) is a finite quantity which is also universal for fluids. They concluded that separate universal ratios should exist between \( \sigma_0 \) and \( \xi_0 \) and between \( \sigma_0 \) and each of the amplitudes characterizing the divergence of the specific heat per unit volume. The existence of separate ratios leads to a very useful result: A measurement of the interfacial tension, the correlation length, or the specific-heat divergence leads to knowledge of all three quantities on the coexistence curve and its extension. These separate ratios are the primary subject of this paper.

In this paper data from the literature are used to estimate three "universal" amplitude ratios for a wide variety of fluids. The experimental amplitude ratios are indeed internally consistent (within about \( \pm 5\% \) of \( \sigma_0 \)) and are also consistent with the ratios previously found for polymer solutions. The numerical values of the amplitude ratios do not agree with recent calculations based on field theory or with simulations of the Ising model. The differences between theory and experiment exceed plausible systematic errors in the experiments. Despite this problem, the internal consistency of the experimental values of the amplitude ratios means that they will be useful in the future for relating measurements of the interfacial tension
to data for any of the three properties: the correlation length, the heat-capacity anomaly, or the equation of state.

This paper is organized as follows. First, the notation is introduced and the values of the critical exponents which are assumed for the analysis of the data are listed. Then the principal results concerning amplitude ratios are stated. A description of the data sources and processing procedures follows. There, it is pointed out that for liquid-vapor systems the capillary length often has a remarkably simple temperature dependence. In this systems separate correlations of the capillary length and the coexisting densities are preferred to correlations of the interfacial tension. The analysis of the data is followed by a discussion of systematic errors. In concluding sections some comments are made concerning discrepant data and possible applications.

II. NOTATION AND EXPONENTS

The customary power-law temperature dependence will be used for the interfacial tension, the difference between the densities of coexisting phases, the isothermal compressibility, the specific heat, and the correlation length:

\[ \sigma = \sigma_0 (-T)^{\mu(1 + \cdots)} , \]
\[ \Delta \rho = 2\rho_c B_0 (-T)^{\mu[1 + B_1 (-T)^{\Delta_1} + \cdots]} , \]
\[ P_e \cdot (\partial \rho / \partial \mu)^{\frac{T}{\sigma}} = 1 + \rho_c^2 T^{-\gamma(1 + \cdots)} , \]
\[ C^+ / R = A_0^+ | t |^{-\alpha(1 + A_1^+) | t |^{\Delta_1} + \cdots} , \]
\[ \xi^+ = \xi_0^+ | t |^{-\gamma(1 + \cdots)} . \]

Here \( R \) is the gas constant, and \( T_c, \rho_c, \) and \( P_c \) are the critical temperature, mass, density, and pressure, respectively. The reduced temperature is defined by \( t \equiv (T - T_c) / T_c \), except in the case of lower critical solution temperatures where \( t \equiv (T_c - T) / T_c \) is used. The superscripts + and - refer to the critical isochore (or iso-pleth) in the homogeneous and inhomogeneous regions, respectively. The specific heat \( C \) is the molar heat capacity at constant volume for liquid-vapor systems and the molar heat capacity at constant pressure and composition for liquid-liquid systems. \( \mu \) is the chemical potential.]

The capillary length is defined by

\[ a^2 = 2\sigma / (\Delta \rho g) , \]  
(2)

where \( g = 9.81 \text{ m/sec}^2 \) is the acceleration due to gravity. The capillary length has the representation

\[ a^2 = a_0^2 | t |^{\Phi(1 + \cdots)} . \]  
(3)

The critical exponents are assumed to have the values calculated via the renormalization group,\(^8,9\) namely

\[ \alpha = 0.110, \ \nu = 0.630, \ \gamma = 1.241, \ \beta = 0.325 . \]

In three dimensions Widom's scaling law\(^10\) for the interfacial tension gives

\[ \mu = 2\nu = 1.26 . \]

From the definition of \( a^2 \) it follows that

\[ \phi = \mu - \beta = 0.935 . \]

I shall use data to estimate three amplitude ratios. They relate the interfacial-tension amplitude to one of the two heat-capacity amplitudes or to the correlation-length amplitude in the homogeneous phase. For the liquid-vapor systems \( \sigma_0 \) was obtained from separate data for the capillary length and the coexisting densities. Thus each amplitude ratio has two possible forms, one using \( \sigma_0 \) and one using \( a_0^2 \):

\[ R_{\sigma A}^\pm = \left( \frac{A_0^\pm \rho_c N_0}{M} \right)^{2/3} \frac{k_B T_c}{\sigma_0} , \]

\[ = \left( \frac{A_0^\pm \rho_c N_0}{M} \right)^{2/3} \frac{k_B T_c}{a_0^2 \rho_c \sigma_0} . \]  
(7)

\[ R_{\sigma \xi}^\pm = \frac{\sigma_0 (\xi_0^\pm)^2}{k_B T_c} = \frac{a_0^2 B_0 \rho_c \sigma_0 (\xi_0^\pm)^2}{k_B T_c} . \]  
(8)

\( N_0 \) is Avagadro’s constant, \( k_B \) is Boltzmann’s constant, and \( M \) is the average molecular weight of the fluid system.

FIG. 1. The amplitude ratio \( \sigma_0 (\xi_0^\pm)^2 / (k_B T_c) \) for various fluids. The experimental values of this ratio cluster near 0.386. Renormalization-group (RG) calculations and two simulations of the Ising model (MC1 and MC2) lead to smaller values of this ratio.
III. RESULTS CONCERNING AMPLITUDE RATIOS

The experimental information concerning $R^{+\sigma}_{\sigma A}$ and $R^{+\sigma}_{\sigma A}$ is displayed graphically in Figs. 1 and 2. More detailed information is presented in Tables I—III.

Figure 1 shows that the experimental values of $\sigma_0(\xi_0^+)^2/k_BT_c$ are scattered about the value 0.386, which is represented by the solid horizontal line. Three theoretical estimates for this amplitude ratio are shown on Fig. 1. All three are much smaller than the experimental values.

The theoretical estimate denoted by RG in Fig. 1 is obtained by evaluating, at $\epsilon = 1$, a one-loop renormalization-group (RG) calculation\textsuperscript{11} of $\sigma_0(\xi_0^+)^2/k_BT_c$ and an $\epsilon$-squared calculation\textsuperscript{12} of $\xi_0^+ / \xi_0^-$. The error attributed to the combination includes only the error in the one-loop calculation estimated by Brezin and Feng.\textsuperscript{11}

The theoretical estimate of $\sigma_0(\xi_0^+)^2/k_BT_c$ denoted by MC1 in Fig. 1 is obtained by combining the results of Binder's\textsuperscript{13} Monte Carlo (MC) simulation of the simple-cubic (sc) Ising model ($\sigma_0=1.05\pm0.05$ $k_BT_c/a^2$) with the value $\xi_0^- = 0.478a$ obtained by Tarko and Fisher\textsuperscript{14} from a Padé analysis of a high-temperature series for this model. (a is the lattice constant of the model.) The theoretical estimate denoted by MC2 in Fig. 1 is obtained by combining the results of Mon and Jasnow's\textsuperscript{15} Monte Carlo simulation ($\sigma_0=1.20\pm0.12$ $k_BT_c/a^2$) with the same series result $\xi_0^- = 0.478a$.

The phenomenological Fisk-Widom theory leads to the ratio $\sigma_0(\xi_0^+)^2/k_BT_c = 0.45$ if the parameter $\kappa$ in that theory is taken to be 0.143 as calculated by Rowlinson and Widom\textsuperscript{6} and if literature values are used for $\xi_0^+ / \xi_0^-$. 

FIG. 2. Amplitude ratios relating the heat capacity to the interfacial tension for various substances. • denotes ratios based on direct measurements of heat capacity; ○ denotes ratios based on equation-of-state data. The theoretical estimates of $R^{+\sigma}_{\sigma A}$ are 1.5—1.6; the theoretical estimates for $R^{-\sigma}_{\sigma A}$ are 2.2—2.4.

<table>
<thead>
<tr>
<th>Fluid(s)</th>
<th>$T_c$ (K)</th>
<th>$\sigma_0$ (mN/m)</th>
<th>$\xi_0^+$ (nm)</th>
<th>$\sigma_0(\xi_0^+)^2$/$k_BT_c$</th>
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</thead>
<tbody>
<tr>
<td>Ar</td>
<td>150.73</td>
<td>31.35</td>
<td>0.137</td>
<td>0.283</td>
</tr>
<tr>
<td>Xe</td>
<td>289.73</td>
<td>45.69</td>
<td>0.184</td>
<td>0.387</td>
</tr>
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<td>CO$_2$</td>
<td>304.13</td>
<td>70.05</td>
<td>0.153</td>
<td>0.391</td>
</tr>
<tr>
<td>SF$_6$</td>
<td>318.69</td>
<td>47.85</td>
<td>0.188</td>
<td>0.386</td>
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<tr>
<td>C$_2$H$_6$</td>
<td>305.33</td>
<td>45.95</td>
<td>0.180</td>
<td>0.354</td>
</tr>
<tr>
<td>TEA-W</td>
<td>291.6</td>
<td>142</td>
<td>0.10</td>
<td>0.353</td>
</tr>
<tr>
<td>NE-3MP</td>
<td>299.6</td>
<td>33</td>
<td>0.216</td>
<td>0.372</td>
</tr>
<tr>
<td>IBA-W</td>
<td>299.0</td>
<td>31$^a$</td>
<td>0.362</td>
<td>0.987</td>
</tr>
<tr>
<td>CY-AN</td>
<td>302.7</td>
<td>31.5</td>
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<td>0.452</td>
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<tr>
<td>Six Polymer</td>
<td>0.8—7.1</td>
<td>1.4—0.5</td>
<td>0.33—0.49</td>
<td></td>
</tr>
</tbody>
</table>

Median fluid
sc Ising model$^b$ 1.05$k_BT_c/a^2$ 0.478$^a$ 0.23—0.25
sc Ising model$^c$ 1.20$k_BT_c/a^2$ 0.478$^a$ 0.25—0.30
Renormalization group
Fisk and Widom

$^a$Reference 46.
$^b$Reference 84.
$^c$References 13 and 14.
$^d$References 15 and 14.
**TABLE II.** Specific-heat amplitudes and their correlation with capillary-rise data.

<table>
<thead>
<tr>
<th>Fluid(s)</th>
<th>$M$ (g/mol)</th>
<th>$\rho_c$ (kg/m$^3$)</th>
<th>$T_c$ (K)</th>
<th>$B_0$</th>
<th>$a^+_\sigma$ (mN/m)</th>
<th>$\sigma_0$</th>
<th>$A^-$</th>
<th>$A^+$</th>
<th>$A^-/A^+$</th>
<th>$R_{\sigma A}^+$</th>
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<tbody>
<tr>
<td>Ar</td>
<td>39.944</td>
<td>535</td>
<td>150.73</td>
<td>1.47</td>
<td>4.06</td>
<td>31.35</td>
<td>9.26</td>
<td>4.94</td>
<td>1.87</td>
<td>1.18</td>
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<tr>
<td>C$_2$H$_6$</td>
<td>32.10</td>
<td>206.5</td>
<td>305.33</td>
<td>1.57</td>
<td>14.42</td>
<td>45.95</td>
<td>11.09</td>
<td>6.02</td>
<td>1.84</td>
<td>1.13</td>
</tr>
<tr>
<td>Xe</td>
<td>131.3</td>
<td>1110</td>
<td>289.73</td>
<td>1.42</td>
<td>2.96</td>
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<td>4.80</td>
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<td>CO$_2$</td>
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<td>467.8</td>
<td>304.13</td>
<td>1.60</td>
<td>9.52</td>
<td>70.05</td>
<td>13.30</td>
<td>7.05</td>
<td>1.89</td>
<td>1.16</td>
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<td>SF$_6$</td>
<td>146.07</td>
<td>730</td>
<td>318.69</td>
<td>1.74</td>
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<td>47.85</td>
<td>15.02</td>
<td>8.12</td>
<td>1.85</td>
<td>1.17</td>
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<td>$^3$He</td>
<td>4.003</td>
<td>69.60</td>
<td>5.19</td>
<td>1.04</td>
<td>0.85</td>
<td>0.61</td>
<td>3.25</td>
<td>1.62</td>
<td>2.01</td>
<td>1.24</td>
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<tr>
<td>TEA-W</td>
<td>24.47</td>
<td>930</td>
<td>291.6</td>
<td>1.05</td>
<td>0.70</td>
<td>0.30</td>
<td>2.00</td>
<td>1.02</td>
<td>1.96</td>
<td>1.00</td>
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<td>NE-3MP</td>
<td>80.62</td>
<td>792</td>
<td>299.6</td>
<td>33.0</td>
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<td>3.20</td>
<td>1.73</td>
<td>1.28</td>
<td>0.89</td>
<td>0.27</td>
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<td>IBA-W</td>
<td>25.70</td>
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<td>11.6</td>
<td>0.71</td>
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</tbody>
</table>

Median value for fluids

Renormalization group

The experimental estimates are in reasonably good agreement ($\pm$10% of $\sigma_0$) with the theoretical values obtained for the Ising model and from the renormalization group.

IV. ANALYSIS OF DATA

To estimate the experimental value of the amplitude ratios from data I had to review separate measurements of the interfacial tension, the correlation length, the specific heat, and the equation of state. In this section I shall list the sources of the data used and the procedures followed to obtain the amplitudes which appear in the tables.

Because different procedures were used to estimate $\sigma_0$ near liquid-vapor critical points and liquid-liquid critical points, the discussion of the interfacial-tension data for

**TABLE III.** Equation-of-state parameters and their correlation with the capillary-length amplitude via Eqs. (7) and (16).

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$P_c$ (MPa)</th>
<th>$\rho_c$ (kg/m$^3$)</th>
<th>$T_c$ (K)</th>
<th>$a^+_\sigma$ (mm$^2$)</th>
<th>$B_0$</th>
<th>$\Gamma^+_\sigma$</th>
<th>$R_{\sigma A}$</th>
<th>$R_{\sigma A}^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe</td>
<td>5.840</td>
<td>1110</td>
<td>289.73</td>
<td>2.96</td>
<td>1.42</td>
<td>0.058</td>
<td>1.185</td>
<td>0.761</td>
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<tr>
<td>CO$_2$</td>
<td>5.735</td>
<td>468</td>
<td>304.13</td>
<td>9.52</td>
<td>1.59</td>
<td>0.046</td>
<td>1.268</td>
<td>0.809</td>
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<td>SF$_6$</td>
<td>3.761</td>
<td>730</td>
<td>318.69</td>
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<td>0.838</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>1.250</td>
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</table>

Optical data

PV $\tau$ data

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<th>Fluid</th>
<th>$P_c$ (MPa)</th>
<th>$\rho_c$ (kg/m$^3$)</th>
<th>$T_c$ (K)</th>
<th>$a^+_\sigma$ (mm$^2$)</th>
<th>$B_0$</th>
<th>$\Gamma^+_\sigma$</th>
<th>$R_{\sigma A}$</th>
<th>$R_{\sigma A}^+$</th>
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<tbody>
<tr>
<td>H$_2$O</td>
<td>22.046</td>
<td>323</td>
<td>647.07</td>
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<td>0.0607</td>
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<tr>
<td>C$_2$H$_6$</td>
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<td>13.90</td>
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<td>0.0581</td>
<td>1.192</td>
<td>0.782</td>
</tr>
<tr>
<td>C$_4$H$_6$</td>
<td>3.629</td>
<td>226</td>
<td>407.84</td>
<td>12.71</td>
<td>1.641</td>
<td>0.0542</td>
<td>1.201</td>
<td>0.788</td>
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<tr>
<td>Mean</td>
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<td></td>
<td></td>
<td>1.190</td>
<td>0.781</td>
</tr>
</tbody>
</table>
these two cases is separated. The rest of the data is discussed without such a division.

The amplitude ratios in Fig. 1 and in Table I for polymer solutions are taken from Fig. 11 of Shinozaki et al.\(^{18}\) These authors used the same exponents we are using to analyze data for six solutions of polystyrene in methycyclohexane. Each solution contained polystyrene with a different molecular weight. The six solutions span the molecular-weight range \(9 \times 10^3 - 1.3 \times 10^5\). The amplitude ratios for the polymer solutions agree with the experimental ratio for ordinary fluids. (Note: The ordinate of Fig. 11 of Ref. 18 must be divided by 1.38 to convert the data plotted therein to the ratio \(R_{d}^{\sigma} \).)

A. Interfacial-tension data for liquid-vapor systems

To estimate \(\sigma_{0}\) for liquid-vapor systems I have combined separate measurements of the temperature-dependent capillary length (which is measured via capillary rise) with measurements of the density difference between coexisting phases. The capillary-length data will be described first; then will be the density-difference data. Finally, the resulting values of \(\sigma_{0}\) will be compared with the limited supply of capillary-wave data in the literature.

1. Capillary-length data

In Fig. 3 I have plotted the capillary length (measured via capillary-rise experiments) for ten pure fluids as a function of \(-t\). It is clear from Fig. 3 that \(a^{2}/|t|^{0.935}\) is an extraordinarily weak function of \(t\), even very far from \(T_{c}\). Perhaps this weak temperature dependence occurs because the effective value of \(\phi = 2\nu - \beta\) only changes very slightly from 0.935 near \(T_{c}\) towards 1.00 far from \(T_{c}\) (where effective exponents are expected to approach their mean-field values).

Rathjen and Straub\(^{19}\) have clearly documented that the temperature dependence of \(a^{2}/|t|^{0.935}\) is much weaker than the temperature dependence of \(\sigma /|t|^{1.26}\) for six refrigerants (including the nonpolar fluids \(SF_{6}\) and the highly polar fluids CHClF\(_2\) and CCIF\(_3\) plotted in Fig. 3). Thus, in the many cases in which surface-tension data do not exist very close to \(T_{c}\), it is preferable to estimate \(a_{0}^{2}\) rather than \(\sigma_{0}\) from the data.

For most fluids, \(a_{0}^{2}\) was estimated by averaging the values of \(a^{2}/|t|^{0.935}\) in the vicinity of \(|t| = 10^{-6}\). For \(C_{2}H_{4}\) and \(i-C_{4}H_{10}\) there are no \(a^{2}\) data in the critical region. For \(C_{2}H_{4}\), I averaged \(a^{2}/|t|^{0.935}\) from the data of Maass and Wright\(^{20}\) in the range \(0.34 < -t < 0.43\). For \(i-C_{4}H_{10}\), I averaged the data of Coffin and Maass\(^{21}\) in the range \(0.27 < -t < 0.42\). If data so far from \(T_{c}\) were used for \(H_{2}O\), \(a_{0}^{2}\) would have been underestimated by 22%. For the other liquid-vapor systems examined (with the exceptions of \(^{3}\)He and \(^{4}\)He) the apparent value of \(a_{0}^{2}\) changes by less than 2% upon changing \(-t\) from 0.34 to 0.01.

The \(CO_{2}\) data of Grigull and Straub\(^{22}\) and the \(C_{2}H_{6}\) data of Katz and Saltmann\(^{23}\) closest to \(T_{c}\) are not consistent with the relation \(a^{2} \propto |t|^{0.935}\). This may have occurred because the criterion used to select \(T_{c}\) was not appropriate for the particular fluid samples under study. In these cases the data closest to \(T_{c}\) were neglected.

I have obtained \(a_{0}^{2}\) from the following authors: argon and nitrogen from Stansfield,\(^{24}\) \(C_{2}H_{6}\) from Maass and Wright\(^{20}\) and from Katz and Saltmann,\(^{20}\) xenon from Smith et al.,\(^{25}\) \(^{4}\)He from van Urk et al.,\(^{26}\) \(^{3}\)He from Zinov’eva,\(^{27}\) water from Vargaftik et al.,\(^{27}\) \(n\)-hydrogen from Blagoi and Pashkov,\(^{28}\) and \(SF_{6}\) from Rathjen and Straub.\(^{29}\)

2. Densities of coexisting liquid and vapor phases

The most precise values of the densities of coexisting liquid and vapor phases near \(T_{c}\) have been obtained from the index of refraction and/or dielectric-constant measurements. Balzarini and Orhn\(^{30}\) used optical techniques to demonstrate that the difference between the liquid and vapor densities approaches an asymptotic form near \(T_{c}\) very slowly. This is now understood to be a consequence of the small correction to scaling exponent \(\Delta_{1} \approx 0.5\). A representation for the density difference that is now widely used is

\[
\frac{\rho_{\text{liquid}} - \rho_{\text{vapor}}}{\rho_{c}} = 2B_{0}(-t)^{0.325}[1 + B_{1}(-t)^{\Delta_{1}} + \cdots].
\]

The limited evidence available is consistent with \(B_{1}\) being greater than zero and of order unity. Thus the first correction term contributes about 1% to the density difference at \(-t = -10^{-4}\). The values of \(B_{0}\) which have been compiled in Table I were obtained by dividing the density difference measured at \(-t = 10^{-4}\) by \((10^{-4})^{0.325}\).
thus the tabulated values of $B_0$ are likely to be $0\% \pm 2\%$ too large. In some cases the data extend to smaller values of $-\tau$; however, they do not determine $B_0$ more accurately.

I obtained $B_0$ from optical data from the following sources: for $C_2H_6$ the data of Balzarini and Burton,\textsuperscript{31} for xenon the data of Balzarini and Mouritsen,\textsuperscript{32} for $CO_2$ the data of Levelt Sengers et al.,\textsuperscript{25} for $SF_6$ the data of Rathjen and Straub,\textsuperscript{33} and for $^3He$ the data of Edwards.\textsuperscript{34}

I obtained $B_0$ for argon from the specific-heat measurements that Voronel et al.\textsuperscript{35} made especially for this purpose. For $^3He$ the dielectric-constant data of Pittman et al.\textsuperscript{36} were used.

It is possible to estimate the systematic errors in $B_0$ in the few cases where two sets of data with the necessary resolution exist. For $C_2H_6$, optical measurements of the density difference are within 1% of pressure-volume-temperature (P-V-T) data\textsuperscript{37} at $-\tau = 10^{-2}$.

In a region of overlap the index-of-refraction data of Balzarini and Mouritsen\textsuperscript{32} for xenon appear to differ from those of Garside et al.\textsuperscript{38} by an amount equivalent to 3% of $B_0$. For $SF_6$ the situation is unusually embarrassing for experimentalists. Dielectric-constant data for the coexisting phases have been published by Thijsse\textsuperscript{39} and appear in the thesis by Weiner.\textsuperscript{40} Index-of-refraction data for coexisting phases have been published by Rathjen and Straub\textsuperscript{33} and by Balzarini and Ohrn.\textsuperscript{30} Thijsse's review of the discrepancies (which amount to 13% of the effective $B_0$ at $t = 10^{-4}$) does not resolve them. My selection of the Rathjen and Straub data was based on two criteria: The raw data are readily available for reanalysis, and the experimental procedure does not rely on a confined geometry. (Recent studies of wetting layers near critical points indicate confined geometries may lead to systematic errors which were not suspected at the time of the measurements in question.)\textsuperscript{41}

3. Capillary-wave measurements of interfacial tension

In this subsection the measurements of interfacial tension very close to $T_c$ via capillary waves are compared with the measurements via capillary rise. Such a comparison is possible for the three liquid-vapor systems for which both types of data have been published: xenon, $CO_2$, and $SF_6$. We shall find the data sets are in agreement; however, a reexamination of the capillary-wave data might be useful.

The interfacial-tension data for $CO_2$ and xenon near their critical points are plotted in Fig. 4. The data closest to $T_c$ (Herpin and Meunier\textsuperscript{42} for $CO_2$ and Zollweg et al.\textsuperscript{43} for xenon) were obtained from spectral analysis of quasielastic scattering from the liquid-vapor interface. The points plotted further from $T_c$ were obtained by combining measurements of capillary rise with measurements of the difference in density of the coexisting phases as determined from index-of-refraction data.

The capillary-wave data for xenon are consistent with the capillary-rise data when the latter are converted to interfacial tensions using the index-of-refraction data of Garside et al.\textsuperscript{38} (as recommended by Zollweg et al.\textsuperscript{43}). Both sets of data are more nearly consistent with the temperature dependence $\sigma \propto |t|^{1.26}$ predicted by theory and adopted in this review. We speculate briefly on the reason for the discrepancy. As $T_c$ is approached, short capillary waves become overdamped. Then the interfacial tension derived from the scattering data becomes sensitive to the viscosities of the coexisting fluid phases, instead of the difference in densities of the coexisting phases. The capillary-wave data for xenon were analyzed with the assumption that the effective viscosity is a linear function of temperature. If they were reanalyzed today, the weak divergence of the viscosity near $T_c$ would be incorporated into the analysis.\textsuperscript{44} This would increase $\sigma$ for the data nearest $T_c$ and would change the apparent temperature dependence of $\sigma$ towards that assumed here.

The curve marked "this work" in Fig. 4 is obtained by combining the value of $a_0^2$ for xenon (from the data of Smith et al.\textsuperscript{44} near $-t = 0.04$) with the temperature-dependent density-difference data of Balzarini and Mouritsen.\textsuperscript{32} Because Balzarini and Mouritsen use $\beta = 0.325$, this curve has the asymptotic temperature dependence $\sigma \propto |t|^{1.26}$. This curve misses the data of Smith et al. because the index-of-refraction data of Balzarini and Mouritsen are inconsistent with those of Garside et al.\textsuperscript{37} (as noted in Sec. IV A 2).
If the capillary-wave data for SF₆ of Wu and Webb had been plotted in Fig. 4 they would have overlapped the xenon data. The capillary-wave data for SF₆ agree extremely well (within 1%) with the capillary-rise data of Rathjen and Straub. Our remarks concerning the apparent temperature dependence of the interfacial tension and viscosity of xenon also apply to the SF₆ data.

The CO₂ data in Fig. 4 are plotted as interpreted by the original authors. The capillary-wave data lead to a surface tension which, according to the authors, is higher than that obtained from the capillary-rise data far from Tₑ. This difference, apparent in Fig. 4, would be reduced if another choice of Tₑ were made in the capillary-rise data. The CO₂ capillary-wave data have sufficiently great scatter that the viscosity anomaly was not detected in the analysis.

B. Interfacial-tension data for liquid-liquid mixtures

The measurement of interfacial tension near the consolute point of binary liquid mixtures appears to be subject to systematic errors which are not fully understood. To illustrate this, we note that the interfacial tension of the system perfluoromethylcyclohexane + methylcyclohexane (PMCH + MCH) has been measured near Tₑ by three groups. The most recent group summarized the results in the following words: “In the temperature range in which the data overlap, the [Heyd and Cahn] measurements of σ for PMCH + MCH display nearly identical temperature dependence but the values are about 40% smaller than ours [Howland et al].” [Sunquist and Oriani], who determined the interfacial tension by the sessile drop method, found a steeper variation with temperature; their value is 10% higher than ours at T – Tₑ = 20 K and 16% smaller at T – Tₑ = 10 K.” Thus we cannot expect the interfacial-tension data for binary mixtures to determine σ₀ with the same accuracy that the liquid-vapor data define σ₀ of ³/₈.

Interfacial-tension data for four binary mixtures are plotted in Fig. 5. For these mixtures, measurements of Cₚ and/or σ have been published. In the lower half of Fig. 5 the straight lines represent the functions \((σ/σ₀)₁/³₈ = (Tₑ – T)/Tₑ\), where Tₑ was determined by the original authors. For these three mixtures the authors report the measurement of Tₑ with a precision of a few mK (corresponding to \(|t| < 10^{-3}\)). The lines correspond to σ₀ = 33 dyn/cm for nitroethane + 3-methylpentane (NE-3MP), 32 dyn/cm for isobutyric acid + water (IBA-W), and 31.5 dyn/cm for cyclohexane + aniline (CY-AN). It is clear that the straight line for the CY-AN data of Attack and Rice is a poor representation of the data. Attack and Rice showed that the difference in density between the coexisting liquid phases of CY-AN has the expected \(|t|^{0.33}\) behavior in the temperature range encompassed by Fig. 5. Thus we must conclude that the asymptotic behavior of σ for the CY-AN system is confined to \(|t| < 3\times10^{-3}\) or that there is an unknown systematic error in the capillary-rise measurement itself.

The data for triethyamine + water (TEA-W) mixtures shown on the top of Fig. 5 are taken farther from Tₑ and a precise value of Tₑ is not reported. The value \(σ₀ = 142\text{ dyn/cm}\) was obtained by fitting a straight line to the six points in the range 0 < \(-t\) < 0.015.

I have not attempted to obtain σ₀ near the consolute points of liquid-liquid mixtures from separate correlations of the density difference and the capillary constant. Near consolute points of liquid-liquid mixtures appropriate choices for the order parameter include the volume fraction of one component and the number density of one component. One expects the temperature dependence of the order parameter to be characterized by the exponent \(β\) over a reasonable range of \(-t\). The temperature dependence of the difference between the mass densities of the coexisting phases will also be characterized by \(β\) very close to \(Tₑ\); however, further from \(Tₑ\) the density difference can be dominated by the difference in the thermal expansion between the pure components and the temperature-dependent excess volume of mixing. This surely will be the case if the two pure components have nearly the same density. Thus it is not surprising that Warren and Webb find \(β = 0.88\) in the range 3\(\times 10^{-4} < -t < 3\times 10^{-2}\) in the mixture methanol + cyclohexane (ME-CY). This mixture has pure components whose densities are matched to one part in 100 far from Tₑ.
In Fig. 4 the interfacial tension obtained from capillary-rise data are compared with the interfacial tension obtained from quasielastic scattering from capillary waves for NE-3MP mixtures. The agreement is fair. McClure and Pegg observed independent measurements of the viscosity of this system and they did include the viscosity's weak divergence in their analysis of the capillary-wave data. It is encouraging that their data are consistent with the expected \( |t|^{1.25} \) temperature dependence.

C. Measurements of the correlation-length amplitude

The correlation-length amplitude \( \xi^0 \) has been obtained using diverse optical techniques. These include measurements of turbidity, measurements of the intensity of light scattered at fixed angles, and analysis of the quasielastic spectrum of scattered light. The turbidity and intensity measurements are comparatively easy to interpret; however, they are subject to a variety of systematic errors. The quasielastic spectra are easier to measure; however, the critical anomaly in the viscosity or diffusion coefficient must be carefully considered in the analysis.

I have used values of \( \xi^0 \) from published sources where \( v=0.63 \) was obtained from or assumed in the original authors' analysis. In most cases the optical data that are most significant in determining \( \xi^0 \) occur near \( t=10^{-3} \). There, the corrections to asymptotic behavior of thermodynamic quantities are small.

Quasielastic spectra have been used by Chang and Dorey \(^{25} \) to obtain \( \xi^0 \) for \( \text{C}_2\text{H}_6 \) and by Burstyn et al. \(^{23} \) to obtain \( \xi^0 \) for NE-3MP. Turbidity measurements have been used by Beysens et al. \(^{16} \) to obtain \( \xi^0 \) for IBA-W and for CY-AN.

From intensity measurements I have used the value \( \xi^0 = 0.10 \pm 0.01 \text{ nm} \) reported by Bloemen et al. \(^{54} \) for TEA-W and supported by the review of Furrow and Greer. \(^{55} \) (Beysens et al. \(^{17} \) have obtained the substantially different value \( \xi^0 = 0.128 \pm 0.005 \text{ nm} \) from turbidity measurements for this same system.) The intensity measurements of Guttinger and Cannell \(^{56} \) were used to obtain \( \xi^0 \) for xenon. For CO\(_2\) the intensity measurements of Lunecek and Cannell \(^{57} \) were used. For SF\(_6\) the intensity and turbidity measurements of Cannell \(^{58} \) were used. In these latter two cases the published value of \( \xi^0 \) was “corrected” via the relation

\[
\xi^0 = \xi^0_{\text{exp}} \left( \frac{t}{t^*} \right)^{0.63 - \nu}.
\]  

(Here \( \xi^0_{\text{exp}} \) and \( \nu \) were the published values of \( \xi^0 \) and \( \nu \) and \( t \) is the geometric mean of the temperature range spanned by the data.) For argon \( \xi^0 \) was obtained by Chandrasekhar and Schmidt \(^{39} \) from a sophisticated analysis of small-angle x-ray scattering.

D. Specific-heat data

The specific-heat data (\( C_p \) on the critical isochore for liquid-vapor systems and \( C_{px} \) at the critical concentration for liquid-liquid systems) is usually represented by the original authors in one of the forms

\[
C/R = A |t|^{-\alpha + B + \cdots},
\]

(12)

\[
C/R = A |t|^{-\alpha} + B + \cdots.
\]

(13)

In early analyses Eq. (12) was often used; in recent analyses Eq. (13) is often used. The presence of the constant term \( B \) or \( B \) means, in effect, that the data determine \( A \) from the derivative \( dC/d\bar{t} \) of \( C \).

The expected correlation between \( A \) and \( \alpha \) is obtained by evaluating \( dC/d\bar{t} \) at a value of \( |t| \) where the data are most significant. From Eq. (12) we obtain

\[
-t \frac{d(C/R)}{d\bar{t}} = \alpha A |t|^{-\alpha}.
\]

(14)

Thus a plot of \( \log_{10}(\alpha A |t|^{-\alpha}) \) versus \( \alpha \) will have a slope of \( \log_{10} |t| \). This is illustrated in Fig. 6. Each point on the plot represents corresponding values of \( A \) and \( \alpha \) determined by the original authors using various “additional terms.” The line through the ethane parameters has slope \(-3 \). It is evident that the four sets of data have nearly the same slope. Indeed, \( |t| = 10^{-3} \) is roughly the geometric mean between the maximum and minimum values of \( |t| \) used by the original authors to fit their data.

From Eq. (14) and Fig. 6 we obtain a recipe which will yield \( \alpha A \) at \( \alpha = 0.11 \) when \( A \) has been published for another value of \( \alpha \), say \( \alpha_p \).

\[
\alpha P = \left( \frac{\alpha_p}{0.11} \right) |t|^{-\alpha_p + 0.11}.
\]

(15)

In Eq. (15) the geometric mean of the range spanned by the data, either above or below \( T_c \), was used for \( |t| \).

This recipe has been used with the \( C_p \) data for CO\(_2\) published by Lipa et al. \(^{60} \) (recent unpublished \(^{61} \) \( C_p \) data for CO\(_2\) yield values of \( A \) which are roughly 7% larger than the values in Table II) and the \( C_p \) data for the mixtures nitroethane-3-methylpentane, \(^{52} \) methanol-cyclohexane, \(^{6} \) and isobutyric acid-water. \(^{64} \) It was also applied to the unpublished xenon data of van Kann \(^{65} \) in preference to the earlier xenon data published by Edwards et al. \(^{46} \). These unpublished xenon data originate from the same laboratory as earlier xenon data and have the advan-

![FIG. 6. The dependence of the specific-heat amplitude \( A \) upon the exponent \( \alpha \) used to fit the data for various fluids. The line has slope \(-3 \). Thus the values \( A \) and \( \alpha \) for ethane are determined by data with \( \log_{10} |t| \approx -3 \).](image-url)
tages of lower scatter, a smaller gravitationally rounded region (because a flat calorimeter was used), and greater certainty in the heat capacity of the empty calorimeter. The SP₆ parameters were adapted from the very high quality data in a recent thesis by Lange.

The C₆ data of argon and ethane⁶⁰ were published with values of A⁵⁶ corresponding to α = 0.11. They are listed in Table II without adjustment. The C₆ data for the mixture triethylamine-water were reanalyzed by the original authors in a subsequent publication⁶⁰ to yield the value of A⁵⁶ corresponding to α = 0.11. To estimate A⁻ for this mixture we assumed that the ratio A⁻/A⁺ equals 1.75 in the triethylamine-water mixture. This is the value for A⁻/A⁺ measured for the triethylamine-heavy water mixture by the same authors.

The tabulated values of A ± for ⁴He were obtained by my reanalysis⁶⁹ of the original data with α⁻ = α⁺ = 0.11. For ³He, the data of Brown and Meyer⁷⁰ were used with a minor adjustment.

E. Equation-of-state data in liquid-vapor systems

The thermodynamic scale factors for the temperature and the chemical potential can be determined from the equation of state. If the scaling function were known and if pressure could be measured with sufficient resolution, a precise measurement of the pressure (as a function of T) along the critical isochore and (as a function of ρ) along the critical isotherm would suffice. In practice, the scale factors have been determined by correlating equation-of-state data from a wide variety of thermodynamic paths using approximate scaling functions chosen for their simplicity. The effort required to correlate the data is too large to be repeated here. Thus the present section is restricted to those few fluids for which correlations of the equation of state exist with the constraints β = 0.325 and ν = 0.630 (or equivalently α = 0.110). First, I shall consider the equation-of-state data that were obtained by studying the stratification of a fluid in the earth's gravitational field. Then the correlations of conventional pressure-density-temperature data will be considered.

Hocken and Moldover⁷¹ measured the derivative of the index of refraction with respect to height at various temperatures extremely close to the critical points of CO₂, SF₆, and Xe. At equilibrium in the earth's gravitational field the chemical potential of the fluids varies linearly with height. The index-of-refraction data were analyzed to yield (∂ρ/∂ψ)ψ with the help of the "cubic-model" equation of state. The data were confined to a region so close to the critical point (roughly |t| = 3x10⁻⁵) that corrections to the asymptotic equation of state are negligible. The optical data were reexamined by Sengers and Moldover,¹⁵ among others, who imposed the constraints β = 0.325 and ν = 0.630. The scale factors determined by Sengers and Moldover were expressed in terms of B₀ and Γ⁺.

For the cubic model used, the amplitudes A ± can be found by

\[ A⁻ = 0.985 \frac{PᵥB₀^2}{R²T_cΓ⁺} \]
\[ A⁻/A⁺ = 1.944 \]  \hspace{1cm} (16)

The amplitudes A ± obtained from the Hocken-Moldover data via Eqs. (16) are listed in Table III. The values for A⁻ and A⁺ are 1-12% larger than those obtained from the C₆ data for the same fluids. The ratios Rₒ₄ and Rₒ₆ found by comparing these optical equation-of-state data with the interfacial-tension data (Table III) are, on the average, 4% larger than those listed in Table II.

The small differences between the amplitudes A ± obtained from the optical equation-of-state data and A ± obtained from the C₆ data are somewhat larger than one would expect upon combining the authors' estimates of errors. Perhaps small, undetected systematic errors occur in either or both kinds of measurements. Another explanation should be considered: namely, the true equation of state differs from the cubic-model equation of state. Because the optical experiment measures the derivative of the equation of state, such a difference may be amplified.

Conventional pressure-volume-temperature (P-V-T) measurements near the critical points of 17 different fluids have been reviewed and correlated by Leveld Sengers, Sengers, and various co-workers,⁷² using three different scaled equations of state. Because of the limitations of pressure measurement, the P-V-T data have useful resolution in regions where, in a rough sense, |t| ≈ 10⁻². There, corrections to the asymptotic equation of state are important. The earlier correlations of such data used critical exponents and scaling functions which differ significantly from those that are presently accepted and cannot be used for reliable estimates of A ±; however, the values of Pᵥ, ρᵥ, and Tᵥ from this early work are satisfactory.

Recently Balfour et al.⁷³ and Sengers and Leveld Sengers²⁴ have used the "linear-model" scaling function together with the critical exponents β = 0.325 and ν = 0.630 to describe the P-V-T data for H₂O, C₃H₄, and i-C₄H₁₀. These correlations also include a correction to the asymptotic equation of state which had the characteristic exponent Δ₁ = 0.5, in agreement with theory (the amplitude ratios of the correlation function have not been compared with theory). The results of these recent correlations for Γ⁺ and B₀ are listed in Table III. One can obtain A ± from Γ⁺ and B₀ for the linear model using

\[ A⁻ = 0.964 \frac{PᵥB₀^2}{RT_cΓ⁺} \]
\[ A⁻/A⁺ = 1.880 \]  \hspace{1cm} (17)

The resulting values of Rₒ₄⁺ and Rₒ₄⁻ for H₂O, C₃H₄, and i-C₄H₁₀ are shown in the lower part of Table III. Three features concerning these ratios deserve comment. First, the spread in the three values for each ratio is only ±1%. Second, these ratios are only 5% larger than the median ratios Rₒ₄⁺ and Rₒ₄⁻ listed on the top of Table I. This result was quite unexpected. It is especially remarkable upon recalling that A₀ for C₃H₄ was determined using data spanning the range 0.34 < |t| < 0.43 and A₀ for i-C₄H₁₀ was determined using data spanning the range 0.27 < |t| < 0.42. (For H₂O, data near |t| = 0.02 determined A₀.) If these results are more than coincidences, it follows that capillary-rise data quite far from Tᵥ taken to-
gether with data for the coexisting densities near \( T_c \) can be used to estimate (perhaps within 5\%) the two scale factors for the critical-point anomaly in the equation of state that was used by Balfour et al. and by Sengers and Levelt Sengers. In effect, the capillary-rise data are substitutes for more expensive specific-heat data or for detailed equation-of-state data.

V. SYSTEMATIC ERRORS

We now consider the sensitivity of the experimental amplitude ratios to the values that were assumed for the critical exponents and to the fact that the data used are not taken asymptotically close to the critical point.

In a typical case the tabulated value of \( R_{\frac{2}{3}} \) is based on measurements of the densities of the two phases at \( t \approx -10^{-4} \), the specific heat at \( t \approx 10^{-3} \), and the capillary constant at \( t \approx -10^{-2} \). If the same data were used with different choices of the critical exponents the values of \( R_{\frac{2}{3}} \) would vary in the fashion displayed in Fig. 7. Along the curve marked 1.0, these ratios would be unchanged. Along the curve marked 1.1, both ratios would be increased by 10\%, etc. From Fig. 7 one can see that changing the exponents \( \alpha \) and \( \beta \) within rather wide limits (\( \pm 0.02 \)) changes the apparent values of \( R_{\frac{2}{3}} \) implied by the data by less than 30\%. Thus the difference between the theoretical and experimental values of these ratios cannot be resolved by making other reasonable choices for the critical exponents.

To obtain the amplitudes \( B_0 \), \( A^\pm \), etc., the contributions of the subdominant singularities to the measured quantities were ignored. Thus \( B_0 \) is overestimated by a factor on the order of \( 1 + B_1(10^{-4})^{\alpha_1} \), \( A^\pm \) is overestimated by a factor on the order of \( 1 + A_1(t^{\alpha_1})^{\beta_1} \), etc. The limited evidence available\(^\text{25}\) is consistent with \( 0.5 < B_1 < 1.5 \) for \( \text{He}, \text{Ne}, \text{N}_2, \text{and Xe} \). Lange\(^\text{67}\) finds \( A_1^{\pm} < 1 \) in SF\(_6\). Edwards\(^\text{61}\) finds \( A_1^{\pm} < 1 \) in CO\(_2\). These results imply that the neglect of subdominant singularities leads to errors in the experimental values of \( R_{\frac{2}{3}} \) which are less than 2\%. There is little information concerning the amplitudes of the subdominant singularities for \( a^2 \) beyond that in Fig. 3.

VI. DISCREPANT DATA

One of the most interesting aspects of any correlation of data is the attempt to explain (away) discrepant data. We now consider these representative examples: a microemulsion system and two binary liquid mixtures.

Microemulsion systems can separate into coexisting microemulsion phases which become identical at a critical point. Kim et al.\(^\text{76}\) have used optical techniques to measure both \( \sigma \) and \( \xi^{-} \) for such a system as a critical point was approached by varying salinity. The data are consistent with the relation \( \sigma (\xi^{-})^{-2} / k_B T_c = 1.5 \). If \( \xi_0^+ / \xi_0^- \) is near 1.95, this result is 15 times larger than the median value for the fluids examined above and 30 times larger than the theoretical value for three-dimensional systems with a scalar order parameter. Recent neutron scattering studies\(^\text{77}\) near critical points of microemulsions have emphasized that a second length, namely, the size of the molecular aggregates that comprise the microemulsion is comparable to the correlation length that is measured optically. Thus a reinterpretation of the optically measured values of \( \xi^{-} \) is necessary.

Measurements of the specific heat,\(^\text{78}\) correlation length,\(^\text{79}\) and capillary constant\(^\text{80}\) have been published for binary mixtures of methanol and cyclohexane near the consolute point. Our analysis of the specific-heat data yields \( A^- = 1.37 \) and \( A^+ = 0.65 \). Various optical techniques have led to values of \( \xi_0^+ \) spanning the range 0.24–0.47 nm. The corresponding values of \( R_1^+ \) (0.20–0.39) include the theoretical value 0.27; thus, the specific-heat data and the correlation-length data seem to be consistent. The two specific-heat amplitudes can be combined with our estimates of \( R_{\frac{2}{3}} \) to obtain two estimates of \( \sigma_0 \). They are 17 and 19 mJ/m\(^3\). Both are five times smaller than the value 100 mJ/m\(^3\) reported by Warren and Webb\(^\text{80}\) (with the exponent \( \mu = 1.23 \)). I conjecture that most of the factor of 5 arises from the fact that Warren and Webb approximated the density of the mixtures by a linear function of composition (at each temperature) in order to estimate the densities of the coexisting phases. The present correlation can be combined with the capillary-length data of Warren and Webb [they are consistent with the relation \( a^2 = 14(\xi^+)^0.935 \text{ cm}^2 \) to estimate that this density difference is approximately \( \Delta \rho = 0.0026(\xi^+)0.325 \text{ g/cm}^3 \). It will be a real challenge to measure such very small density differences directly. (A datum by Schmidt and Moldover\(^\text{8}^1\) far from \( T_c \) is consistent with an unusually small coefficient for \( \Delta \rho \)).

Binary mixtures of isobutyric acid and water have also been studied extensively near the consolute point. Baysens et al.\(^\text{37}\) report \( \xi_0^+ = 0.3625 \text{ nm} \). The specific-heat data of Pegler et al.\(^\text{64}\) are consistent with \( A^+ = 0.12 \) if \( \alpha \) is forced to be 0.11. Thus \( R_1^+ = 0.24 \), a value very close to the theoretical value 0.27. Again the optical and specific-heat data appear to be consistent. The densities of the coexist-
ing phases measured by Greer are close to the densities obtained by Khosala and Widom. The capillary length has been measured by Howland et al. When $\beta$ and $\phi$ are set at 0.325 and 1.26, respectively, the density and capillary-length data imply $\sigma_0 = 31 \text{ mJ/m}^2$ as shown in Fig. 5. This value is almost three times as large as the value that would be needed to obtain $R_{\sigma_0}$ and $R_{\sigma_A}$ close to median values for other fluid systems. Recent measurements of $\sigma_0$ in this same mixture using a different technique have yielded the preliminary result $\sigma_0 = 11.6 \pm 1 \text{ mJ/m}^2$. This preliminary result leads to amplitude ratios in good agreement with those for other fluids. If the preliminary result is confirmed, one must presume that a systematic error is present in the capillary-length data reported by Howland et al.

VII. CONCLUSIONS

We have reviewed the measurements of interfacial tension in the critical region of a wide variety of fluids. The data are analyzed using theoretical values of the critical exponents to obtain amplitude ratios. Much of the data are consistent within a few percent of $\sigma_0$ with the values $R_{2G} = 0.39$, $R_{\sigma_A} = 0.77$, and $R_{\sigma_A} = 1.88$. A comparison of these ratios with theoretical ratios from a field-theory calculation and from a simulation suggests that these theoretical values of $\sigma_0$ are about half the experimental values. This dilemma is the central problem raised by this review.

It would be desirable to examine the ratios involving $\sigma_0$ for a wider variety of fluid systems. Binary mixtures of gallium and lead have an upper consolute point at 879 K.

The interfacial-tension data below $T_c$ are consistent with $\sigma_0 = 190 \text{ mJ/m}$, if this metallic mixture behaves like the median fluid system, we expect $A^+ \approx 1.07$, $A^- \approx 2.00$, and $\xi_0^+ \approx 0.15 \text{ nm}$. A test of such expectations would be most welcome. The internal consistency of the fluid results suggests that interfacial-tension measurements could be helpful for obtaining equations of state in the critical region of liquid-vapor systems.

The thermodynamic consequences of near criticality become much less conspicuous when multicomponent mixtures are studied with density-like variables held constant. In such systems the predicted universality of $R_{2G}$ may still be useful for correlating interfacial-tension data with correlation-length data.

Note added. After this manuscript was submitted for review, I received a preprint by Gießen, Verbeke, and Thoen, in which new capillary-rise data are reported for Ar, CH$_4$, N$_2$, O$_2$, and CO$_2$. The new data as well as previously published data are analyzed to obtain universal amplitude ratios. The conclusions of Gießen et al. are in excellent agreement with those presented here.

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