

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 σ_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 σ_0 . The experimental amplitude ratios do not agree with recent theoretical estimates from either Monte Carlo simulations of the Ising model or the ϵ expansion. The theoretical values of σ_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 expression $a^2 = a_0^2(1 - T/T_c)^{0.935}$ when T varies from the triple point to $0.99T_c$. (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 tension¹ 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 σ and ϵ 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 Widom⁶ concluded that universal ratios should exist between the amplitude σ_0 (which characterizes the vanishing of the interfacial tension in the critical region) and the amplitude ξ_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 ξ^d (ξ 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 σ_0 and ξ_0 and between σ_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 σ_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 principle 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 such 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:

$$\begin{aligned}\sigma &= \sigma_0 (-t)^\mu (1 + \dots), \\ \Delta\rho &= 2\rho_c B_0 (-t)^\beta [1 + B_1 (-t)^{\Delta_1} + \dots], \\ P_c^{-1} (\partial\rho/\partial\mu)_T^+ &= \Gamma^+ \rho_c^2 t^{-\gamma} (1 + \dots), \\ C^+ / R &= A_0^+ |t|^{-\alpha} (1 + A_1^+ |t|^{\Delta_1} + \dots), \\ \xi^+ &= \xi_0^+ |t|^{-\nu} (1 + \dots).\end{aligned}\quad (1)$$

[Here R is the gas constant, and T_c , ρ_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 isopleth) 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. μ is the chemical potential.]

The capillary length is defined by

$$a^2 = 2\sigma / (\Delta\rho g), \quad (2)$$

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

$$a^2 = a_0^2 |t|^\phi (1 + \dots). \quad (3)$$

The critical exponents are assumed to have the values calculated via the renormalization group,^{8,9} namely

$$\alpha = 0.110, \quad \nu = 0.630, \quad \gamma = 1.241, \quad \beta = 0.325. \quad (4)$$

In three dimensions Widom's scaling law¹⁰ for the interfacial tension gives

$$\mu = 2\nu = 1.26. \quad (5)$$

From the definition of a^2 it follows that

$$\phi \equiv \mu - \beta = 0.935. \quad (6)$$

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 σ_0 was obtained from separate data for the capillary length and the coexisting densities. Thus each amplitude ratio has two possible forms, one using σ_0 and one using a_0 :

$$\begin{aligned}R_{\sigma A}^\pm &\equiv \left(\frac{A_0^\pm \rho_c N_0}{M} \right)^{2/3} \frac{k_B T_c}{\sigma_0} \\ &= \left(\frac{A_0^\pm \rho_c N_0}{M} \right)^{2/3} \frac{k_B T_c}{a_0^2 B_0 \rho_c g},\end{aligned}\quad (7)$$

$$R_{\sigma \xi}^+ \equiv \frac{\sigma_0 (\xi_0^+)^2}{k_B T_c} = \frac{a_0^2 B_0 \rho_c g (\xi_0^+)^2}{k_B T_c}. \quad (8)$$

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

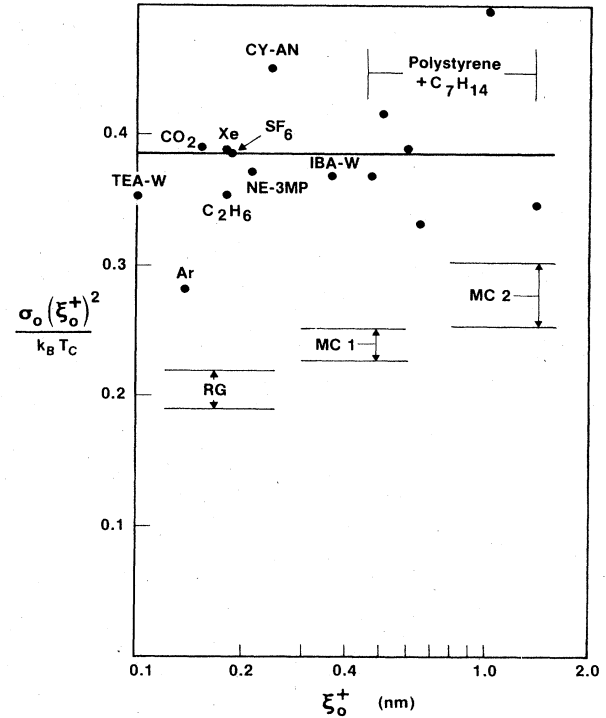


FIG. 1. The amplitude ratio $\sigma_0(\xi_0^+)^2/(k_B T_c)$ for various fluids. The experimental values of this ratio cluster near 0.386. Renormalization-group (RG) calculations and two simulations of the Ising model (MC1 and MC2) lead to smaller values of this ratio.

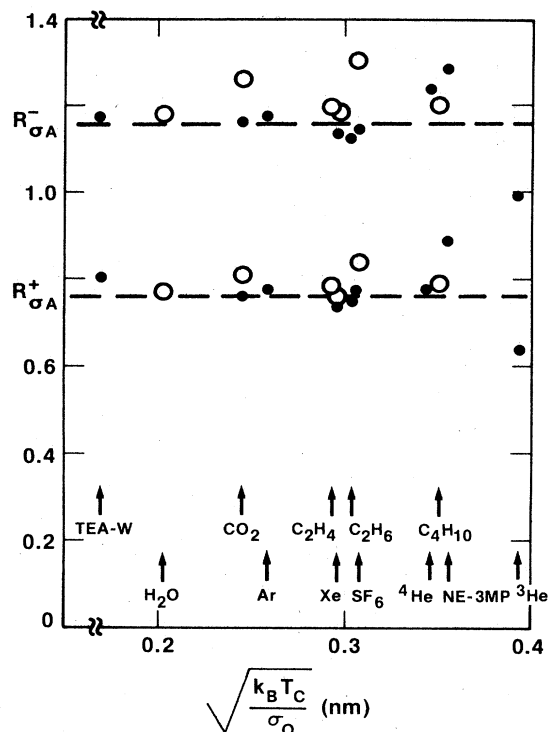


FIG. 2. Amplitude ratios relating the heat capacity to the interfacial tension for various substances. ● denotes ratios based on direct measurements of heat capacity; ○ denotes ratios based on equation-of-state data. The theoretical estimates of $R_{\sigma_A}^+$ are 1.5–1.6; the theoretical estimates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

III. RESULTS CONCERNING AMPLITUDE RATIOS

The experimental information concerning $R_{\sigma_{\xi}}^+$ and $R_{\sigma_A}^+$ 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 $\sigma_0(\xi_0^+)^2/k_B T_c$ 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) calculation¹¹ of $\sigma_0(\xi_0^+)^2/k_B T_c$ and an ϵ -squared calculation¹² of ξ_0^+/ξ_0^- . The error attributed to the combination includes only the error in the one-loop calculation estimated by Brezin and Feng.¹¹

The theoretical estimate of $\sigma_0(\xi_0^+)^2/k_B T_c$ denoted by MC1 in Fig. 1 is obtained by combining the results of Binder's¹³ Monte Carlo (MC) simulation of the simple-cubic (sc) Ising model ($\sigma_0=1.05\pm 0.05 k_B T_c/a^2$) with the value $\xi_0^+=0.478a$ obtained by Tarko and Fisher¹⁴ 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's¹⁵ Monte Carlo simulation ($\sigma_0=1.20\pm 0.12 k_B T_c/a^2$) with the same series result $\xi_0^+=0.478a$.

The phenomenological Fisk-Widom theory leads to the ratio $\sigma_0(\xi_0^+)^2/k_B T_c=0.45$ if the parameter κ in that theory is taken to be 0.143 as calculated by Rowlinson and Widom⁶ and if literature values are used for ξ_0^+/ξ_0^- ,

TABLE I. Surface tension and correlation-length amplitudes and the amplitude ratio $R_{\sigma_{\xi}}^+$ for various systems. TEA-W denotes triethylamine + water, NE-3MP denotes nitroethane + 3-methylpentane, IBA-W denotes isobutyric acid + water, and CY-AN denotes cyclohexane + aniline.

Fluid(s)	T_c (K)	σ_0 (mN/m)	ξ_0^+ (nm)	$\frac{\sigma_0(\xi_0^+)^2}{k_B T_c}$
Ar	150.73	31.35	0.137	0.283
Xe	289.73	45.69	0.184	0.387
CO ₂	304.13	70.05	0.153	0.391
SF ₆	318.69	47.85	0.188	0.386
C ₂ H ₆	305.33	45.95	0.180	0.354
TEA-W	291.6	142	0.10	0.353
NE-3MP	299.6	33	0.216	0.372
IBA-W	299.0	31 ^a	0.362	0.987
		11.6 ^b		0.369
CY-AN	302.7	31.5	0.245	0.452
Six Polymer solutions		0.8–7.1	1.4–0.5	0.33–0.49
Median fluid				0.386
sc Ising model ^c		$1.05 k_B T_c/a^2$	$0.478a$	0.23–0.25
sc Ising model ^d		$1.20 k_B T_c/a^2$	$0.478a$	0.25–0.30
Renormalization group				0.19–0.22
Fisk and Widom				0.45

^aReference 46.

^bReference 84.

^cReferences 13 and 14.

^dReferences 15 and 14.

TABLE II. Specific-heat amplitudes and their correlation with capillary-rise data.

Fluid(s)	M (g/mol)	ρ_c (kg/m ³)	T_c (K)	B_0	a_0^2 (mm ²)	σ_0 (mN/m)	A^-	A^+	A^-/A^+	$R_{\sigma_A}^-$	$R_{\sigma_A}^+$
Ar	39.944	535	150.73	1.47	4.06	31.35	9.26	4.94	1.87	1.18	0.77
C ₂ H ₆	32.10	206.5	305.33	1.57	14.42	45.95	11.09	6.02	1.84	1.13	0.75
Xe	131.3	1110	289.73	1.42	2.96	45.69	9.19	4.80	1.92	1.14	0.74
CO ₂	44.01	467.8	304.13	1.60	9.52	70.05	13.30	7.05	1.89	1.16	0.76
SF ₆	146.07	730	318.69	1.74	3.84	47.85	15.02	8.12	1.85	1.17	0.77
⁴ He	4.003	69.60	5.19	1.04	0.85	0.61	3.25	1.62	2.01	1.24	0.78
³ He	3.016	41.45	3.31	1.05	0.70	0.30	2.00	1.02	1.96	1.00	0.64
TEA-W	24.47	930	291.6			142	(11.57)	6.61	(1.75)	1.17	(0.80)
NE-3MP	80.62	792	299.6			33.0	5.54	3.20	1.73	1.28	0.89
IBA-W	25.70	993	299.0			31.0 ^a		0.12			0.27
						11.6 ^b					0.71
Median value for fluids									1.88	1.17	0.77
Renormalization group									1.82	2.2–2.4	1.5–1.6

^aReference 46.^bReference 84.

Γ^+/Γ^- and R_{ξ}^+ defined in Eq. (9). Thus, the Fisk-Widom theory slightly overestimates $R_{\sigma_A}^+$.

Experimental estimates for the two ratios $R_{\sigma_A}^+$ and $R_{\sigma_A}^-$ are represented graphically in Fig. 2 for a variety of fluid systems. The solid dots in Fig. 2 result from combining the specific-heat amplitudes with the experimental values of σ_0 (Table II). The circles result from combining equation-of-state amplitudes with the same values of σ_0 (Table III). The ratios from these very different kinds of measurements are nearly coincident and can be approximated by the horizontal lines in Fig. 2: $R_{\sigma_A}^+ = 0.77$ and $R_{\sigma_A}^- = 1.17$. The theoretical values for $R_{\sigma_A}^+$ and $R_{\sigma_A}^-$ from both the renormalization-group calculation and the Ising model are about 65% larger than the experimental values. Thus all three amplitude ratios are consistent with this statement: The Ising-model simulations and the renormalization-group calculations of σ_0 are 65% of the experimental values.

Previously published work has established that data for liquid-vapor systems¹⁶ and for binary liquid mixtures¹⁷ yield consistent estimates for the amplitude combination:

$$R_{\xi}^+ = \xi_0^+ (\alpha A_0^+ \rho_c N_0 / M)^{1/3}. \quad (9)$$

The experimental estimates are in reasonably good agreement ($\pm 10\%$ of ξ_0^+) with the theoretical values obtained for the Ising model and from the renormalization group.⁹ This agreement leads one to research for systematic errors in the experimental or theoretical values for σ_0 rather than in ξ_0^+ or A^\pm . Some comments on systematic errors in experiments are made in Secs. V and VI. I am not aware of errors which can explain the differences between the experiments and the Ising-model or field-theory results.

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 σ_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).

Fluid	P_c (MPa)	ρ_c (kg/m ³)	T_c (K)	a_0^2 (mm ²)	B_0	Γ_0^+	$R_{\sigma_A}^-$	$R_{\sigma_A}^+$
				optical data				
Xe	5.840	1110	289.73	2.96	1.42	0.058	1.185	0.761
CO ₂	7.375	468	304.13	9.52	1.59	0.046	1.268	0.809
SF ₆	3.761	730	318.69	3.84	1.62	0.046	1.305	0.838
Mean							1.250	0.803
				P-V-T data				
H ₂ O	22.046	323	647.07	34.72	1.980	0.0607	1.178	0.773
C ₂ H ₄	5.040	214	282.35	13.90	1.544	0.0581	1.192	0.782
C ₄ H ₁₀	3.629	226	407.84	12.71	1.641	0.0542	1.201	0.788
Mean							1.190	0.781

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 methylcyclohexane. Each solution contained polystyrene with a different molecular weight. The six solutions span the molecular-weight range $9 \times 10^3 - 1.3 \times 10^6$. 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 $R_{\sigma_f}^+$.)

A. Interfacial-tension data for liquid-vapor systems

To estimate σ_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 σ_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

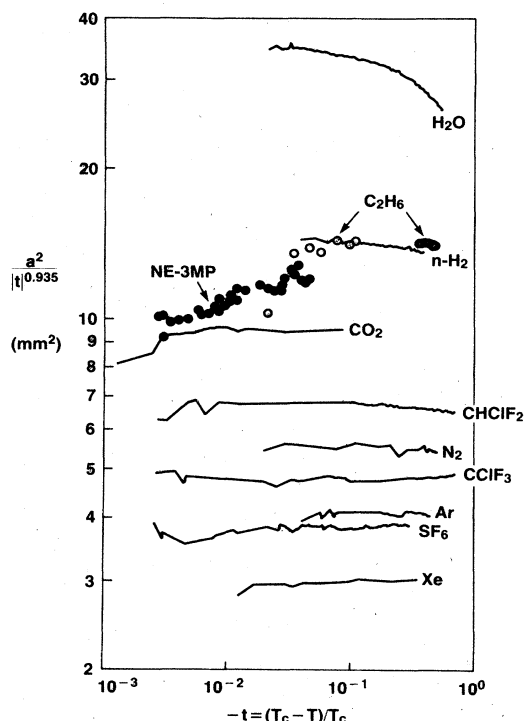


FIG. 3. Square of the capillary length as a function of the reduced temperature for various fluid interfaces. For most liquid-vapor systems, $a^2/|t|^{0.935}$ has a very weak dependence upon $|t|$, even for values of $|t|$ as large as 0.1. In contrast, the data for the binary liquid mixture NE-3MP show a stronger $|t|$ dependence. The lines connect data which are too close together to plot individually.

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 Straub¹⁹ 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 CClF_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 σ_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 $|t| = 10^{-2}$. For C_2H_4 and $i\text{-C}_4\text{H}_{10}$ there are no a^2 data in the critical region. For C_2H_4 , I averaged $a^2/|t|^{0.935}$ from the data of Maass and Wright²⁰ in the range $0.34 < -t < 0.43$. For $i\text{-C}_4\text{H}_{10}$, I averaged the data of Coffin and Maass²¹ in the range $0.27 < -t < 0.42$. If data so far from T_c were used for H_2O , a_0^2 would have been underestimated by 22%. For the other liquid-vapor systems examined (with the exceptions of ^3He and ^4He) 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 Straub²² and the C_2H_6 data of Katz and Saltmann²⁰ 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,²³ C_2H_6 from Maass and Wright²⁰ and from Katz and Saltmann,²⁰ xenon from Smith *et al.*,²⁴ ^4He from van Urk *et al.*,²⁵ ^3He from Zinov'eva,²⁶ 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 Orhn³⁰ 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

$$(\rho_{\text{liquid}} - \rho_{\text{vapor}})/\rho_c = 2B_0(-t)^{0.325} [1 + B_1(-t)^{\Delta_1} + \dots] \quad (10)$$

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 0–2% too large. In some cases the data extend to smaller values of $-t$; 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,³¹ for xenon the data of Balzarini and Mouritsen,³² for CO_2 the data of Levelt Sengers *et al.*,³³ for SF_6 the data of Rathjen and Straub,²⁹ and for 4He the data of Edwards.³⁴

I obtained B_0 for argon from the specific-heat measurements that Voronel *et al.*³⁵ made especially for this purpose. For 3He the dielectric-constant data of Pittman *et al.*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 measurements³¹ of the density difference are within 1% of pressure-volume-temperature (P-V-T) data³⁷ at $-t = 10^{-2}$.

In a region of overlap the index-of-refraction data of Balzarini and Mouritsen³² for xenon appear to differ from those of Garside *et al.*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 Thijsse³⁹ and appear in the thesis by Weiner.⁴⁰ Index-of-refraction data for coexisting phases have been published by Rathjen and Straub²⁹ and by Balzarini and Ohrn.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.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 Meunier⁴² for CO_2 and Zollweg *et al.*⁴³ for xenon) were obtained from spectral analysis of quasi-elastic 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.*³⁸ (as recommended by Zollweg *et al.*⁴³). Both sets of data are more nearly consistent with the temperature dependence $\sigma \propto |t|^{1.30}$ rather than the depen-

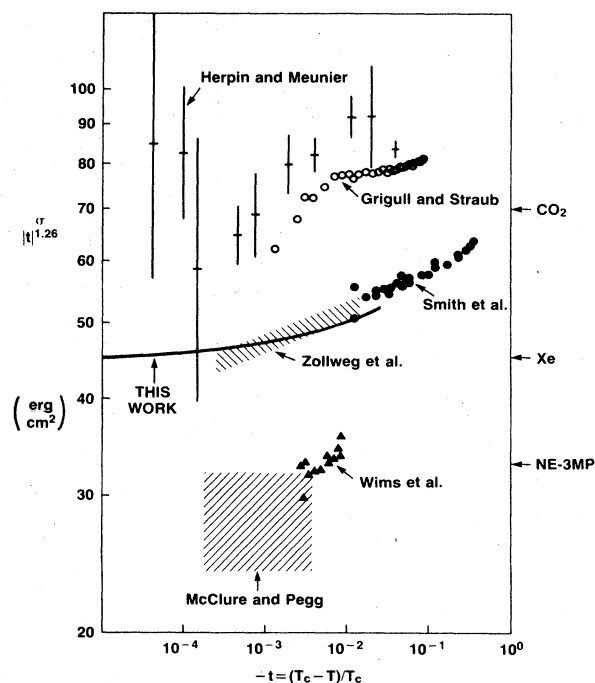


FIG. 4. Interfacial tension as a function of the reduced temperature. The capillary-wave method was used by Herpin and Meunier (CO_2), by Zollweg *et al.* (Xe), and by McClure and Pegg (NE-3MP). The capillary-rise method was used by Grigull and Straub (CO_2), by Smith *et al.* (Xe), and by Wims *et al.* (NE-3MP). The solid curve is obtained by combining the capillary-rise data of Smith *et al.* with the index-of-refraction data of Balzarini and Mouritsen. The arrows indicate the values of σ_0 used in this correlation.

dence $\sigma \propto |t|^{1.26}$ 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.⁴⁴ This would increase σ for the data nearest T_c and would change the apparent temperature dependence of σ 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.*²⁴ near $-t = 0.04$) with the temperature-dependent density-difference data of Balzarini and Mouritsen.³² Because Balzarini and Mouritsen use $\beta = 0.325$, this curve has the asymptotic temperature dependence $|t|^{1.26}$. 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.*³⁷ (as noted in Sec. IV A 2).

If the capillary-wave data for SF₆ of Wu and Webb⁴⁵ 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.¹⁹ 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-wave⁴² data lead to a surface tension which, according to the authors, is higher than that obtained from the capillary-rise data²² far from T_c . This difference, apparent in Fig. 4, would be reduced if another choice of T_c 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 T_c by three groups. The most recent group⁴⁶ summarized the results in the following words. "In the temperature range in which the data overlap, the [Heady 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 $T - T_c = 20$ K and 16% smaller at $T - T_c = 10$ K." Thus we cannot expect the interfacial-tension data for binary mixtures to determine σ_0 with the same accuracy that the liquid-vapor data define $a_0^2 B_0 \rho_c g$.

Interfacial-tension data for four binary mixtures are plotted in Fig. 5. For these mixtures, measurements of C_{px} and/or ξ have been published. In the lower half of Fig. 5, the straight lines represent the functions $(\sigma/\sigma_0)^{1/1.26} = (T_c - T)/T_c$, where T_c was determined by the original authors. For these three mixtures the authors report the measurement of T_c with a precision of a few mK (corresponding to $|t| < 10^{-5}$). The lines correspond to $\sigma_0 = 33$ dyn/cm for nitroethane + 3-methylpentane⁴⁷ (NE-3MP), 32 dyn/cm for isobutyric acid + water⁴⁶ (IBA-W), and 31.5 dyn/cm for cyclohexane + aniline⁴⁸ (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 $|t| < 3 \times 10^{-3}$ or that there is an unknown systematic error in the capillary-rise measurement itself.

The data for triethylamine + water⁴⁹ (TEA-W) mixtures shown on the top of Fig. 5 are taken farther from T_c and a precise value of T_c is not reported. The value

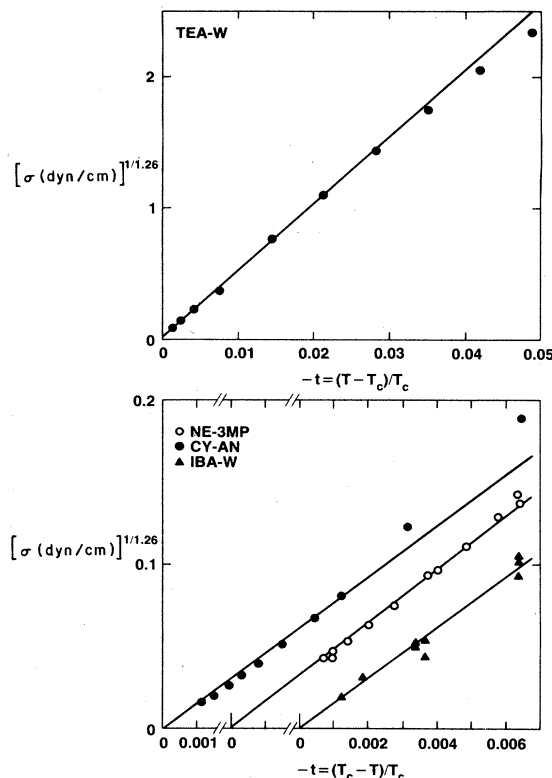


FIG. 5. Interfacial tension as a function of the reduced temperature for four binary liquid mixtures. The lines correspond to the values of σ_0 used in Tables I and II. The values displayed in the lower half of this figure were obtained by fitting the data shown with the constraint that $\sigma = 0$ at the value of T_c determined by the original authors. For TEA-W (upper curve), the data closest to T_c was fit with a straight line without requiring $\sigma = 0$ at the author's value of T_c .

$\sigma_0 = 142$ 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 σ_0 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 T_c ; however, further from T_c 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 Webb⁵⁰ find $\phi = 0.88$ 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 T_c .

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 Pegg⁵¹ did 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 $|t|^{1.26}$ temperature dependence.

C. Measurements of the correlation-length amplitude

The correlation-length amplitude ξ_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 ξ_0^+ from published sources where $\nu \approx 0.63$ was obtained from or assumed in the original authors's analysis. In most cases the optical data that are most significant in determining ξ_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 Doiron⁵² to obtain ξ_0^+ for C_2H_6 and by Burstyn *et al.*⁵³ to obtain ξ_0^+ for NE-3MP. Turbidity measurements have been used by Beysens *et al.*¹⁶ to obtain ξ_0^+ for IBA-W and for CY-AN.

From intensity measurements I have used the value $\xi_0^+ = 0.10 \pm 0.01$ 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 $\xi_0^+ = 0.128 \pm 0.005$ nm from turbidity measurements for this same system.) The intensity measurements of Guttinger and Cannell⁵⁶ were used to obtain ξ_0^+ for xenon. For CO_2 the intensity measurements of Lunacek and Cannell⁵⁷ were used. For SF_6 the intensity and turbidity measurements of Cannell⁵⁸ were used. In these latter two cases the published value of ξ_0 was "corrected" via the relation

$$\xi_0^+ = \xi_{0p}^+ (t)^{0.63 - \nu_p} \quad (11)$$

(Here ξ_{0p}^+ and ν_p were the published values of ξ_0^+ and ν and t is the geometric mean of the temperature range spanned by the data.) For argon ξ_0^+ was obtained by Chandrasekhar and Schmidt⁵⁹ from a sophisticated analysis of small-angle x-ray scattering.

D. Specific-heat data

The specific-heat data (C_v 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

$$C/R = A^\pm |t|^{-\alpha} + B^\pm + \dots, \quad (12)$$

$$C/R = A^\pm |t|^{-\alpha(1 + D^\pm |t|^{\Delta_1} + \dots)} + B. \quad (13)$$

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

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

$$-t \frac{d(C/R)}{d|t|} = \alpha A^\pm |t|^{-\alpha}. \quad (14)$$

Thus a plot of $\log_{10}(\alpha A^\pm)$ versus α will have a slope of $\log_{10}|t|$. This is illustrated in Fig. 6. Each point on the plot represents corresponding values of A^\pm and α 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 A^\pm at $\alpha = 0.11$ when A_p^\pm has been published for another value of α , say α_p :

$$A^\pm = A_p^\pm \left[\frac{\alpha_p}{0.11} \right] |t|^{-\alpha_p + 0.11}. \quad (15)$$

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_v data for CO_2 published by Lipa *et al.*⁶⁰ (recent unpublished $^{61}C_v$ data for CO_2 yield values of A^\pm which are roughly 7% larger than the values in Table II) and the C_p data for the mixtures nitroethane-3-methylpentane,⁶² methanol-cyclohexane,⁶ and isobutyric acid-water.⁶⁴ It was also applied to the unpublished xenon data of van Kann⁶⁵ in preference to the earlier xenon data published by Edwards *et al.*⁶⁶ These unpublished xenon data originate from the same laboratory as earlier xenon data and have the advan-

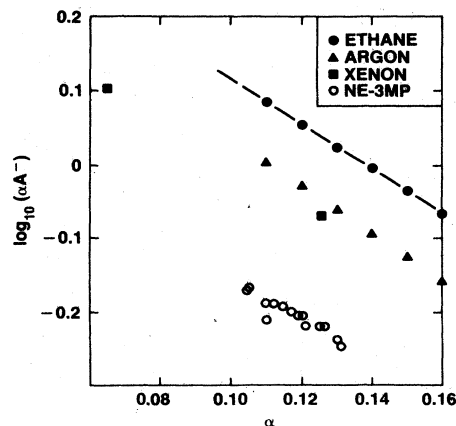


FIG. 6. The dependence of the specific-heat amplitude A^- upon the exponent α used to fit the data for various fluids. The line has slope -3 . Thus the values A^- and α for ethane are determined by data with $\log_{10}|t| \approx -3$.

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 SF_6 parameters were adapted from the very high quality data in a recent thesis by Lange.⁶⁷

The C_v data of argon and ethane⁶⁸ were published with values of A^\pm corresponding to $\alpha=0.11$. They are listed in Table II without adjustment. The C_p data for the mixture triethylamine-water were reanalyzed by the original authors in a subsequent publication⁵⁴ to yield the value of A^+ corresponding to $\alpha=0.11$. 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^\pm for 4He were obtained by my reanalysis⁶⁹ of the original data with $\alpha^- = \alpha^+ = 0.11$. 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 $\beta=0.325$ and $\nu=0.630$ (or equivalently $\alpha=0.110$). 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 CO_2 , SF_6 , 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 $(\partial\rho/\partial\mu)_T$ with the help of the "cubic-model" equation of state. The data were confined to a region so close to the critical point (roughly $|t| \approx 3 \times 10^{-5}$) that corrections to the asymptotic equation of state are negligible. The optical data were reexamined by Sengers and Moldover,¹⁵ who imposed the constraints $\beta=0.325$ and $\nu=0.630$. The scale factors determined by Sengers and Moldover were expressed in terms of B_0 and Γ^+ .

For the cubic model used, the amplitudes A^\pm can be found by

$$A^- = 0.985 \frac{P_c V_c B_0^2}{RT_c \Gamma^+}, \quad (16)$$

$$A^-/A^+ = 1.944.$$

The amplitudes A^\pm 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 C_v data for the same fluids. The ratios $R_{\sigma A}^-$ and $R_{\sigma A}^+$ 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^\pm obtained from the optical equation-of-state data and A^\pm obtained from the C_v data are somewhat larger than one would expect upon combining the authors's 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 Levelt 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, $|t| \approx 10^{-2}$. 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^\pm ; however, the values of P_c , ρ_c , and T_c from this early work are satisfactory.

Recently Balfour *et al.*⁷³ and Sengers and Levelt Sengers⁷⁴ have used the "linear-model" scaling function together with the critical exponents $\beta=0.325$ and $\nu=0.630$ to describe the P - V - T data for H_2O , C_2H_4 , and i - C_4H_{10} . These correlations also include a correction to the asymptotic equation of state which had the characteristic exponent $\Delta_1=0.5$, 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 B_0 are listed in Table III. One can obtain A^\pm from Γ^+ and B_0 for the linear model using

$$A^- = 0.964 \frac{P_c V_c B_0^2}{RT_c \Gamma^+},$$

$$A^-/A^+ = 1.880. \quad (17)$$

The resulting values of $R_{\sigma A}^+$ and $R_{\sigma A}^-$ for H_2O , C_2H_4 , and i - C_4H_{10} 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 $\pm 1\%$. Second, these ratios are only 5% larger than the median ratios $R_{\sigma A}^+$ and $R_{\sigma A}^-$ listed on the top of Table I. This result was quite unexpected. It is especially remarkable upon recalling that a_0^2 for C_2H_4 was determined using data spanning the range $0.34 < -t < 0.43$ and a_0^2 for i - C_4H_{10} was determined using data spanning the range $0.27 < -t < 0.42$. (For H_2O , data near $-t=0.02$ determine a_0^2 .) If these results are more than coincidences, it follows that capillary-rise data quite far from T_c 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 $R_{\sigma A}^{\pm}$ is based on measurements of the densities of the two phases at $t \approx -10^{-4}$, the specific heat at $t \approx \pm 10^{-3}$, 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 $R_{\sigma A}^{\pm}$ 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 α and β within rather wide limits (± 0.02) changes the apparent values of $R_{\sigma A}^{\pm}$ 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 $1 + B_1(10^{-4})^{\Delta_1}$, A^{\pm} is overestimated by a factor on the order of $1 + A_1^{\pm}(10^{-3})^{\Delta_1}$, etc. The limited evidence available⁷⁵ is consistent with $0.5 < B_1 < 1.5$ for ^3He , Ne , N_2 , and Xe . Lange⁶⁷ finds $A_1^{\pm} < 1$ in SF_6 . Edwards⁶¹ finds $A_1^{\pm} < 1$ in CO_2 . These

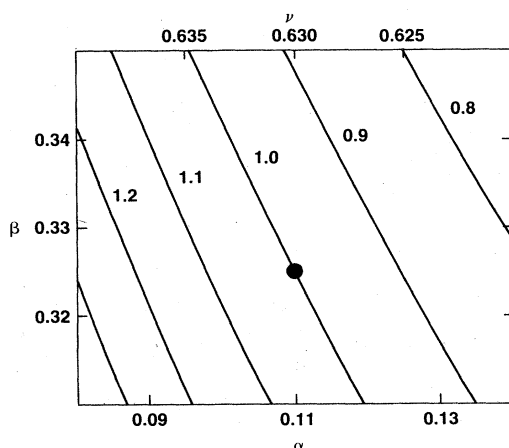


FIG. 7. Sensitivity of the ratios $(A^{\pm}\rho_c)^{2/3}/(\sigma_0/k_B T_c)$ to the choice of critical exponents. On the curve labeled 1.0, the ratios determined by the data will be the same as those listed in Tables II and III. On the curve labeled 1.1, the ratios will be 10% greater than the ratio determined by the data using $\alpha=0.110$ ($\nu=0.630$) and $\beta=0.325$.

results imply that the neglect of subdominant singularities leads to errors in the experimental values of $R_{\sigma A}^{\pm}$ 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.*⁷⁶ have used optical techniques to measure both σ and ξ^- 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 ξ_0^+/ξ_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 studies⁷⁷ 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 ξ^- is necessary.

Measurements of the specific heat,⁷⁸ correlation length,⁷⁹ and capillary constant⁸⁰ 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 ξ_0^+ spanning the range 0.24–0.47 nm. The corresponding values of R_{ξ}^+ (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 $R_{\sigma A}^{\pm}$ to obtain two estimates of σ_0 . They are 17 and 19 mJ/m². Both are five times smaller than the value 100 mJ/m² reported by Warren and Webb⁸⁰ (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 $a^2 = 14(-t)^{0.935}$ cm²] to estimate that this density difference is approximately $\Delta\rho = 0.0026(-t)^{0.325}$ g/cm³. It will be a real challenge to measure such very small density differences directly. (A datum by Schmidt and Moldover⁸¹ 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. Beysens *et al.*¹⁷ report $\xi_0^+ = 0.3625$ nm. The specific-heat data of Pegler *et al.*⁶⁴ are consistent with $A^+ = 0.12$ if α is forced to be 0.11. Thus $R_{\xi}^+ = 0.24$, 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 Greer⁸² are close to the densities obtained by Khosala and Widom.⁸³ The capillary length has been measured by Howland *et al.*⁴⁶ When β and ϕ are set at 0.325 and 1.26, respectively, the density and capillary-length data imply $\sigma_0=31$ mJ/m² as shown in Fig. 5. This value is almost three times as large as the value that would be needed to obtain $R_{\sigma\xi}$ and $R_{\sigma A}^+$ close to median values for other fluid systems. Recent measurements⁸⁴ of σ_0 in this same mixture using a different technique have yielded the preliminary result $\sigma_0=11.6\pm 1$ mJ/m². 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 σ_0 with the values $R_{\sigma\xi}^+=0.39$, $R_{\sigma A}^+=0.77$, 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 σ_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 σ_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 data⁸⁵ below T_c are consistent with $\sigma_0=190$ mJ/mm. If this metallic mixture behaves like the median fluid system, we expect $A^+\approx 1.07$, $A^-\approx 2.00$, and $\xi_0^+\approx 0.15$ 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 $R_{\sigma\xi}^-$ 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 Gielen, Verbeke, and Thoen,⁸⁶ in which new capillary-rise data are reported for Ar, CH₄, N₂, O₂, and CO₂. The new data as well as previously published data are analyzed to obtain universal amplitude ratios. The conclusions of Gielen *et al.* are in excellent agreement with those presented here.

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