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THE STATE OF THE CRITICAL STATE OF FLUIDS

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Abstract - A review is given of recent progress in the understanding of critical phenomena in fluids and fluid mixtures. The topics discussed are: critical exponent values; the Wegner expansion for corrections to scaling, and its application in pure fluids and binary liquid mixtures; weak critical anomalies in binary liquid mixtures; symmetric and asymmetric tricritical points; interfaces and nucleation.

INTRODUCTION

In this lecture some of the accomplishments of the modern theory of critical phenomena will be discussed. Although I will occasionally draw upon my own work, most of the material for my talk has been contributed by the participants in my poster session, which has made my task both easier and more enjoyable.

The topics I want to touch upon include the thermodynamic behavior of near-critical fluids and fluid mixtures, and the critical behavior of interfaces. The foundation for the treatment of each of these topics was laid in the past century in three monumental papers by van der Waals: his thesis on the equation of state in 1873, his generalization to mixtures in 1890, and his theory of interfaces in 1894. These papers contain a complete description of what is presently called a "classical" or "mean field" approach to critical phenomena. It was already known in van der Waals' own days that this classical picture has some essential flaws but it took to well into the 1960's to remedy this problem. The cause of the trouble is rather easy to understand. The theory of critical opalescence, developed by Ornstein and Zernike in 1914-1917, had made it clear that near a critical point long-range density fluctuations are becoming very likely because of the large compressibility. Imagine now the classical parabolic coexistence curve. According to a criterion developed by Ginzburg, the classical description will have to fail at that distance from T_c where the density fluctuations become comparable with, and therefore wash out, the density difference of coexisting phases. Fluctuations become more important the lower the dimensionality; in four dimensions classical theory would still be valid, but in three dimensions the fluctuations win when the critical point is approached. This leads to the characteristic flattening of the top of the coexistence curve which makes it look more like a cubic than a parabola. Since the critical anomalies are due to large-range fluctuations, not to short-range molecular interactions, these anomalies are expected to have a mathematical character that is substance-independent. It is described by the term "critical-point universality" and it pertains to a much wider class of phase transitions than those in fluids only. Much effort in the past 15 years has been devoted to developing a universal non-classical description of the critical behavior of fluids, ferromagnets and antiferromagnets. Some of the results of this effort will be summarized here, and illustrated with examples from my own work and from the posters.

The extension of the non-classical description to fluid mixtures in the 1970's by Griffiths and Wheeler led to some surprises that could have been anticipated from the formally-analogous treatment of thermodynamic anomalies in pressurized superfluid helium in the late 1950's and early 1960's by Pippard, Buckingham, and Fairbank. Most of the material presented in my poster session pertains to the subtle anomalies present near the critical line of fluid mixtures, and roughly half of the lecture will be devoted to this topic. In the area of fluid mixtures, a thermodynamic curiosity called a tricritical point has been studied in the past decade. Contrary to a normal critical point, at a tricritical point, where three fluid phases become simultaneously identical, the difference in properties of coexisting phases grows so rapidly below the critical point that it cannot be swamped by the fluctuations, so that classical theory is expected to hold. The interest in this fluid tricritical point derives in no small manner from the fact that it is a member of a respectable family with two branches, the symmetric branch and the nonsymmetric branch. Fluid tricritical points are nonsymmetric. Well-known members of the symmetric branch are the tricritical point in mixtures of superfluid helium-4 and helium-3, and the point at which a transition turns from second-order to first-order in certain antiferromagnets. The theory for the latter case was developed by Landau in

1937 and has been recently extended to the nonsymmetric case by Griffiths. My poster session boasts members of each class, which will be introduced and described in this lecture. The lecture will close with some notes on interfaces and nucleation. In parallel with the development of nonclassical thermodynamics, the classical theory of interfaces had to be similarly modified, which was achieved by Widom and coworkers. A number of interesting developments followed, some of which are to be sketched in my talk. Those included the prediction of the divergence of the interface thickness; that of the so-called Cahn non-wetting to wetting phase transition; and the prediction of the behavior of the surface tension at the non-critical interface in the vicinity of a critical-point phase transition, which prediction was recently confirmed, as demonstrated in a poster in my session. I will not be able to restrain myself from communicating how a conceptual difficulty, that of the subcritical interface becoming infinitely thick on approach to the critical point, while the gravity-induced density gradient in the supercritical phase becomes infinitely sharp, has been recently resolved.

The last topic of my lecture, that of nucleation, developed along a similar pattern, in that the classical Becker-Döring theory of nucleation had to be adapted in order to accommodate the nonclassical behavior of density, surface tension and diffusion, as these properties enter into the equations for nucleation rate and droplet growth. The problem in this field has been a sequence of experiments that all seemed to indicate failure of the Becker-Döring theory in that the theoretical degree of undercooling seemed too small. Only very recently has this problem been resolved by an elegant experiment, displayed in the poster session, that carefully separates the events of nucleation and of droplet growth.

The seeds planted by van der Waals a century ago have been fertile beyond expectation. They have grown into a forest in which the new and unexpected is still encountered at every turn of the road. The paths I will take into this forest will be those clearly marked and laid out by its founder: fluids, fluid mixtures and interfaces.

CRITICAL EXPONENTS, CRITICAL AMPLITUDE RATIOS, SCALING

Anomalous critical behavior is described by means of power laws. Thermodynamic derivatives such as the compressibility K_T, the expansion coefficient α_P and the specific heat C_P in the pure fluid or the osmotic susceptibility $(\partial x/\partial\mu)_{PT}$ in a binary liquid diverge sharply. We write $K_T = \Gamma^{\pm}|\Delta T|^{-\gamma}$, where $\Delta T=T-T_c$, $\Gamma^{\pm}$ the amplitude of the anomaly above (+) or below (-) T_c and γ the critical exponent; $\gamma=1$ in classical theories of the type of Van der Waals, close to 5/4 for Ising-like systems such as uniaxial ferromagnets and fluids. Coexisting phases I, II have the same "field-like" properties, such as temperature T, pressure P and chemical potentials μ_1, μ_2 ..., but differ in "density-like" properties such as volume V, concentration x, entropy S, energy U, dielectric constant ε and refractive index n. These differences approach zero at the critical point. We write x_I-x_{II}, $\rho_I-\rho_{II}$, etc. $= B|\Delta T|^{\beta}$, with $\beta=1/2$ in classical theory, close to 1/3 in fluids. The relation of a density and the conjugate field on a path of constant field is characterized by the critical exponent δ; for instance: $|\mu-\mu_c|=D|\Delta\rho|^{\delta}$ at $T=T_c$, with $\Delta\rho=\rho-\rho_c$. In classical theory $\delta=3$, in fluids it is close to 5. Finally, there are properties which are predicted not to diverge in classical theory, but which *do* show weak anomalies near the critical point. Thus, the specific heat at constant volume C_V and the adiabatic compressibility K_S in the one-component fluid; C_{Px}, α_{Px}, K_{Tx} in a binary mixture, are weakly divergent, which is represented by relations such as $C_V=(A\pm/\alpha)|\Delta T|^{-\alpha}$ on the path $\rho=\rho_c$, with $\alpha\sim0.1$. The character of the divergence of the correlation length ξ follows from the Ornstein-Zernike theory and is represented as $\xi=\xi_o|\Delta T|^{-\nu}$, with $\nu=1/2$ in classical theory, almost 2/3 in Ising-like systems such as fluids. The smallest critical exponent, η, describes the slight departure from Ornstein-Zernike behavior for the r-dependence of the correlation function G(r), as $|r|^{-1+\eta}$ at the critical point; η equals about 0.03.

The results of the modern theory of critical phenomena may be summarized as follows. (a) All systems with short-ranged interparticle forces and in the same universality class (d,n) specified by the dimensionalities of the space, d, and of the order parameter, n, have the same set of critical exponents. (b) Of these critical exponents, only two are independent, the others follow from exponent equalities such as $\gamma=\beta(\delta-1)$, which are valid irrespective of the universality class. (c) Of the corresponding critical amplitudes, again only two are independent (two-scale-factor universality), the others follow from the so-called universal amplitude ratios, such as Γ^+/Γ^-, that are the same for all systems within a universality class. (d) Techniques developed from the renormalization-group approach have yielded accurate values for the critical exponents and critical amplitude ratios within each universality class.

The renormalization-group results for the critical exponents are summarized in Table 1 for the n=1, d=3 universality class; the predicted critical amplitude ratios are given in Table 2. The exponent values derived from series-expansion analyses of the Ising model have tended to differ sufficiently from those given in Table 1 to put the hyperscaling relation (Table 1) in doubt. At the 1980 NATO Summer Institute at Cargèse, however, close scrutiny of the two methods led to a resolution of most of the outstanding difficulties, Ref. (4).

TABLE 1. Critical exponents (n=1, d=3)

	Classical		Nonclassical
	Critical	tricritical	Ref. (1)
α	0	0 $T>T_c$ 1/2 $T<T_c$	0.110±0.0045
β	1/2	1/4	0.325±0.0015
γ	1	1	1.241±0.0020
δ	3	5	——
ν	1/2	1/2	0.630±0.0015
η	0	0	0.031±0.004
Δ_1			0.498±0.020

exponent equalities: $2-\alpha=\beta(\delta+1)$ $d\nu=2-\alpha$ (hyperscaling)

$\gamma=\beta(\delta-1)$ $\gamma=(2-\eta)\nu$

TABLE 2. Critical amplitude ratios (n=1, d=3)

Γ^+/Γ^-	4.80	
A^+/A^-	0.55	
$\Gamma^+ D B^{\gamma-1}$	1.66	
$A^+\Gamma^+/B^2$	0.066	
$(A^+k_B)^{1/\delta}\xi_0$		0.270
Ref.	(2)	(3)

The critical-exponent equalities and universal amplitude ratios are all imbedded in the Widom-Kadanoff scaling laws, Refs.(5,6) which follow from the hypothesis of generalized homogeneity near the critical point, Ref. (7). If two independent field variables u_h, u_t are chosen such that u_t is along the coexistence curve in u_h, u_t space, u_h at an angle to it, and u_h, $u_t=0$ at the critical point, then the thermodynamic potential $P(u_h,u_t)$ may be written in terms of a regular and a scaled part as

$$P = P_{reg}(u_h,u_t) + P_{sc}(u_h,u_t)$$

$$P_{sc} = ak|u_t|^{\beta(\delta+1)} \; f\left(\frac{u_h/a}{|u_t|^{\beta\delta}}\right) \quad . \tag{1}$$

Here f, in the class specified by (n,d), is a universal function of the scaled variable $x=(u_h/a)/|u_t|^{\beta\delta}$; k and a are nonuniversal scale factors determining the units of two of the variables u_h, u_t and P_{sc}. The scaled potential, $P_{sc}/|u_t|^{\beta(\delta+1)}=P_{sc}/|u_t|^{2-\alpha}$ is a function of only one (scaled) variable x. A similar hypothesis is made for the correlation length $\xi(u_h,u_t)$. The form of the scaling function f is known approximately from renormalization-group calculations. In practice, variants of the linear-model parametric representation of Schofield, Ho and Litster (8,9) are used. The linear model is of the form

$$u_t = r(1-b^2\theta^2)$$

$$u_h/a = r^{\beta\delta}\,\theta(1-\theta^2)$$

$$P_{sc}/ak = r^{\beta(\delta+1)}\,p(\theta)$$

$$\text{order par.: } \partial(P_{sc}/ak)/\partial(u_h/a) = \theta r^{\beta} \text{ (linear model)} \tag{2}$$

Here p (Θ) is a universal polynomial quadratic in Θ^2 with coefficients which are functions of the critical exponents and the universal constant b^2. Forms algebraically-closed in terms of parametric variables are available for all thermodynamic functions of pure fluids and binary liquid mixtures (Table 3). For a complete listing, see Ref. (10). In ferromagnets, the variable u_t equals $T-T_c$, while u_h equals H, the magnetic field. In fluids, the relation of u_t, u_h to the physical variables is of some subtlety and will be discussed in the next section.

TABLE 3. Linear model equation for one-component fluids and for incompressible binary liquids

One-component fluid	Binary liquid	Parametric expression
	Potential	
$P(\mu,T)$	$-\mu_2(\Delta,T)$	
$dP=(S\rho)dT+\rho d\mu$	$-d\mu_2=SdT+xd\Delta$	
	Reduced variables	
$\Delta\rho^*=(\rho-\rho_c)/\rho_c \equiv \rho^*-1$	$x-x_c\ (x=x_1)$	$kr^{\beta}\Theta$
$\Delta T^*=(T-T_c)/T_c$		$r(1-b^2\Theta^2)$
$P^*=P/P_c$	$-\mu_2^*=-\mu_2/RT_c$	
$\mu^*=\mu\rho_c/P_c$	$\Delta^*=(\mu_1-\mu_2)/RT_c$	
$(A\rho)^*=(A\rho)/P_c$	$G^*=G/RT_c$	
$(S\rho)^*=(S\rho)T_c/P_c$	$S^*=S/R$	
$(U\rho)^*=(U\rho)/P_c$	$H^*=H/RT_c$	
	Regular and scaled parts	
$\Delta\mu^*=\mu^*-\mu^*(\rho_c,T^*)\equiv\mu^*-\mu_0(T^*)$	$\Delta\Delta^*=\Delta^*-\Delta(x_c,T^*)\equiv\Delta^*-\Delta_0(T^*)$	$ar^{\beta\delta}\Theta(1-\Theta^2)$
$P^*=P_0(T^*)+\Delta\mu^*+P^*_{anom}$	$-\mu_2^*=-\mu^*_{20}(T^*)+\Delta\Delta^*-\mu^*_{2anom}$	
P^*_{anom}	$-\mu^*_{2anom}$	$akr^{2-\alpha}p(\Theta)$
$(A\rho)^*=\rho^*\mu_0(T^*)-P_0(T^*)+(A\rho)^*_{anom}$	$G^*=x\Delta_0(T^*)+\mu_{20}(T^*)+G^{E*}$	
$(A\rho)^*_{anom}$	G^{E*}	$akr^{2-\alpha}[\Theta^2(1-\Theta^2)-p(\Theta)]$
$(S\rho)^*=P_0'(T^*)-\rho\mu_0'(T^*)+(S\rho)^*_{anom}$	$S^*=-\mu_{20}'(T^*)-x\Delta_0'(T^*)+S^{E*}$	
$(S\rho)^*_{anom}$	S^{E*}	$akr^{1-\alpha}s(\Theta)$
$(U\rho)^*=-\{P_0(T^*)-T^*P_0'(T^*)\}+$ $+\rho^*\{\mu_0(T^*)-T^*\mu_0'(T^*)\}+(U\rho)^*_{anom}$	$H^*=\{\mu_{20}(T^*)-T\mu_{20}'(T^*)\}+$ $+x\{\Delta_0(T^*)-T^*\Delta_0'(T^*)\}+H^{E*}$	
$(U\rho)^*_{anom}$	H^{E*}	$akr^{1-\alpha}s(\Theta)+$ $+akr^{2-\alpha}[(1-b^2\Theta^2)s(\Theta)+\Theta^2(1-\Theta^2)-p(\Theta)]$

$p(\Theta)=p_0+p_2\Theta^2+p_4\Theta^4$ $\quad p_0=\dfrac{\beta\delta-3\beta-b^2\alpha\gamma}{2b^4(2-\alpha)(1-\alpha)\alpha}$ $\quad s(\Theta)=s_0+s_2\Theta^2$ $\quad s_0=(2-\alpha)p_0$

$p_2=-\dfrac{\beta\delta-2\beta-b^2\alpha(2\beta\delta-1)}{2b^2(1-\alpha)\alpha}$ $\quad s_2=(\beta\delta-3\beta)/2b^2\alpha$

$p_4=(2\beta\delta-3)/2\alpha$

restriction: $b^2=(\delta-3)/[(\delta-1)(1-2\beta)]$

$\mu_0(T^*)$, $P_0(T^*)$, $\mu_{20}(T^*)$ and $\Delta_0(T^*)$ are analytic functions of T^*, to be approximated by polynomials

primes denote differentiation w.r.t. T^*

THE WEGNER EXPANSION

The range of validity of the asymptotic scaling laws (1) has been found to be small in fluids (Refs. (11-15)). Wegner derived the form of the corrections to scaling for the magnetic case from renormalization-group considerations. The Wegner expansion is of the form

$$P_{sc} = au_t^{\beta(\delta+1)}\ [k_0f_0(x) + k_1|u_t|^{\Delta_1}f_1(x)+,\ldots] \tag{3}$$

Here f_0, f_1 ... are all universal functions of the scaling variable $x = (u_h/a)/|u_t|^{\beta\delta}$. Each new term is characterized by a new universal "gap" exponent Δ_i, and only one non-universal amplitude k_i. It follows that the amplitude of the i^{th} Wegner correction for different thermodynamic properties of a given fluid are all related to each other, only one of them being independent.

Renormalization-group calculations give Δ_1=0.498 (Table 1). Although the values of the higher exponents are still quite uncertain, they appear to be spaced by roughly 0.5, so that the Wegner expansion is a slowly-converging series. The importance of the confluent singularities was first recognized by Ahlers (12) in his analysis of the pressure-dependence of the specific heat of He^4 near the λ-line in the early 1970's. In fluids, this recognition arose after the experiments of Balzarini (13), Hocken and Moldover (14) and Greer (15) showed that only very close to the critical point do critical exponents in fluids approach the values for Ising-like systems.

The Wegner expansion is usually applied along selected paths in the space of independent variables. Well-known examples from the literature are the analysis of the coexistence curve of sulphur hexafluoride by Ley-Koo and Green (16), that of the compressibility of xenon from light scattering by Güttinger and Cannell (17) and that of the coexistence curve of partially-miscible binary liquids by Greer (15).

The posters of Ewing et al., Kumaran et al. and Van Dael, Thoen et al., in my poster session, apply the Wegner expansion to coexistence-curve properties such as concentration, speed of sound and dielectric constant of binary liquids. I will discuss these results shortly.

For the case of one-component fluids, we have succeeded in applying the Wegner expansion, Eq. (3), in the entire space of independent variables u_h, u_t rather than along specified paths. This requires a functional form for $f_1(x)$ in addition to that of $f_0(x)$, Eq. (3). Balfour et al. (18) proposed a parametric form for $f_1(x)$ which gives a derivative which is linear in Θ just as that for $f_0(x)$ in the linear model, Eq. (2).

In the application to fluids, a decision needs to be made about the relation between the variables u_h, u_t and the physical variables. The variable u_h, the analogue of the magnetic field H, drives the system away from the coexistence curve in u_h, u_t space. In fluids u_h is chosen as $\Delta\mu \equiv \mu - \mu(\rho_c, T)$, where μ is the chemical potential and $\mu(\rho_c, T)$ the chemical potential at coexistence below T_c, and on the critical isochore at least asymptotically above T_c. It is assumed that $\mu(\rho_c, T)$ is an analytic function of T, to be represented by a polynomial in $\Delta T \equiv T - T_c$. The variable u_t is the analog of $T-T_c$ in the ferromagnet and drives the system away from criticality along the coexistence curve in u_t, u_h space; in Ref. 18 it was chosen as a linear combination of ΔT and $\Delta\mu$. The potential is the pressure $P(\mu, T)$ and thus the density $\rho = (\partial P/\partial \mu)_T$ and the entropy density $s = (\partial P/\partial T)_\mu$. These choices and assumptions are all based on the formal analogy of the ferromagnet and the lattice gas (19), and on the known behavior of the so-called decorated-lattice-gas models (20) which lack particle-hole symmetry just as real fluids do. Each of these assumptions requires further modification if Wegner corrections beyond the leading symmetric one are considered (21,22).

I want to show here some applications of the Wegner expansion that we have recently made in order to formulate the thermodynamic properties of H_2O (23), D_2O (24) and C_2H_4 (25) in a range around the critical point. Especially for H_2O, a large number of accurate experimental data of various kinds were available. For the critical exponents, the theoretical values listed in Table 1 were assumed. Most other model parameters were obtained from a fit to the PVT data for these substances. The model predictions were then compared with experimental data for other properties. In Figs. 1-3 we show the agreement of the model with data for C_p, C_V and the speed of sound of H_2O. In Fig. 4 a comparison is shown with the speed of sound in ethylene. Note that C_p is a sharply-diverging property, C_V a weakly-diverging one, and that the speed of sound goes to zero weakly at the critical point. After some slight adjustments of the temperature scales of the various experiments for H_2O, the agreement of the model and high-quality data for both substances is within the uncertainty of the data. The range of application of the model, if one Wegner correction is used, is of the order of -1% to +8% in reduced temperature, -35 to +35% in reduced density from the critical point. The range in which the asymptotic Ising-like exponents are recovered is very small indeed. If the amplitude of the first correction term in Eq. (3) is of the order of that of the leading one, for the correction term to be no more than 1% of the leading one the reduced temperature range is to be smaller than 10^{-4}.

Our work has shown that various accurate thermodynamic data in one-component fluids in a region up to +8% in temperature, ±35% in density from the critical, appear consistent with a theoretical model that incorporates Ising-like critical exponents, mixing of variables and one Wegner correction term. I will suggest that the same model be used for describing binary liquid data such as excess enthalpies and volumes.

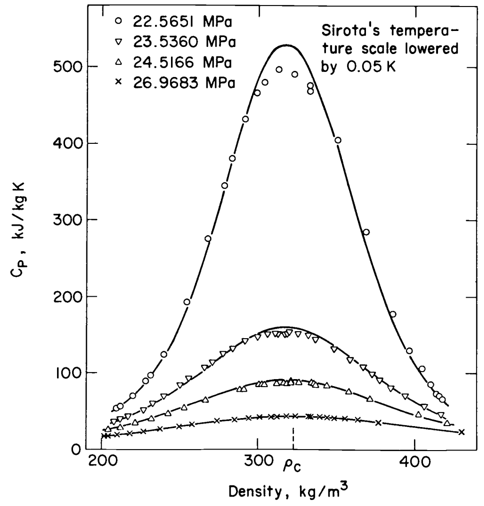

Fig. 1. Isobaric specific heat C_P of steam predicted by a scaled equation fitted to PVT data. The critical isobar is at 22.064 MPa. Apart from a small shift in peak location, which can be corrected by a temperature shift of 0.05 K (T_c=647 K!) the specific heat is quantitatively predicted by the scaling equation with one Wegner correction.

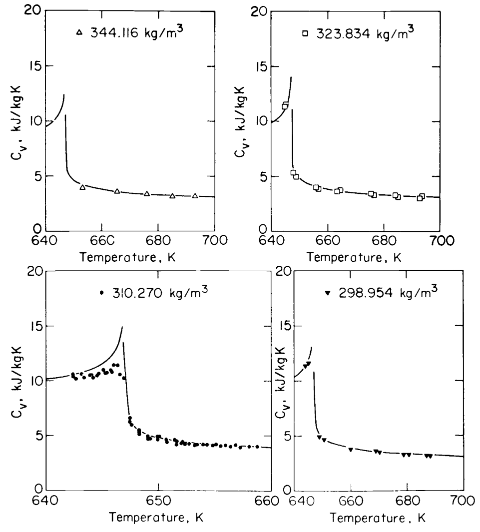

Fig. 2a. Isochoric specific heat C_V of steam, as measured by Baehr et al. along four isochores (ρ_c=322 kg/m^3), compared with the prediction from a scaled equation fitted to PVT data, Ref. (23).

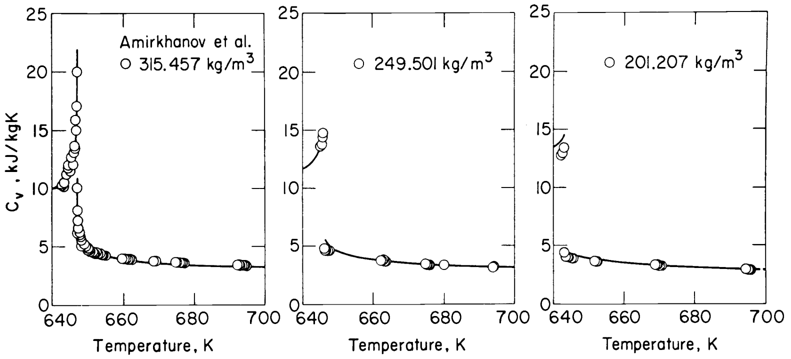

Fig. 2b. A similar comparison for isochoric specific heats measured by Amirkhanov et al. much closer to the coexistence curve. Apart from a shift in temperature scale of 0.3 K between PVT and C_V data, the steep rise of C_V close to the phase transition is accurately predicted.

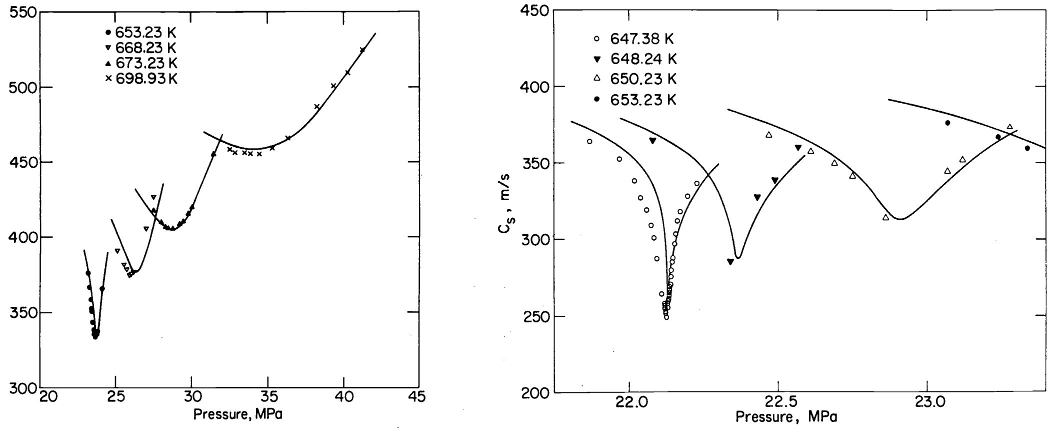

Fig. 3. The deep minimum in the isothermal speed of sound of steam is well predicted by a scaled equation fitted to PVT data.

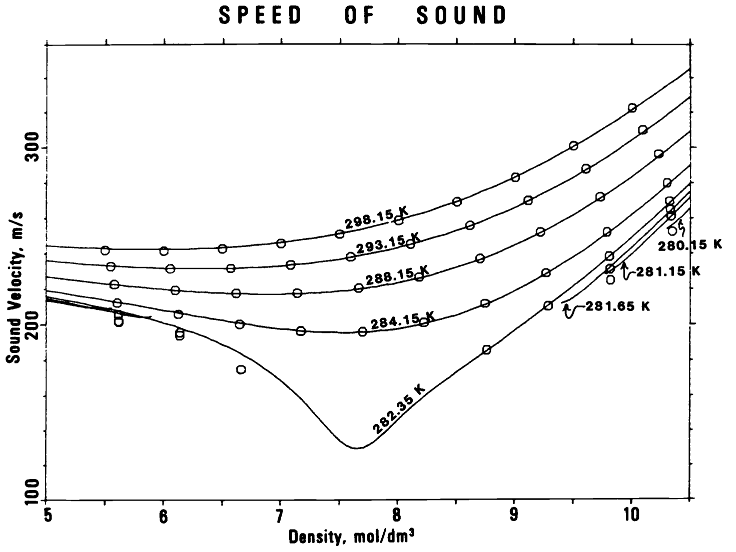

Fig. 4. A scaled equation fitted to PVT data of ethylene predicts the speed-of-sound data within experimental error in a substantial range around the critical point (T_c=282.34 K).

SPECIAL DIRECTIONS AND EXPONENT RENORMALIZATION

As pointed out by Griffiths and Wheeler (26), in the case of two independent variables u_h and u_t there is one direction in the u_h, u_t plane that is singled out by the phase transition itself. The second derivative of the potential taken along this direction diverges at most weakly, while it diverges sharply if taken in any other direction; second derivatives taken in any direction diverge more strongly if the path of approach to criticality is along the special direction than if it is not. Take, as an example, for the one-component fluid the potential $\mu(P,T)$ whose second derivatives are the measurable quantities:

$$-\frac{\partial^2\mu}{\partial T^2} = \frac{C_P}{T} \qquad \frac{\partial^2\mu}{\partial P\partial T} = V\alpha_P \qquad \frac{\partial^2\mu}{\partial P^2} = VK_T \tag{4}$$

The specific heat C_P, the expansion coefficient α_P and the compressibility K_T all diverge strongly, with exponent γ, because both P and T axes intersect the special direction. This is true for classical and nonclassical behavior. If, however, the derivative of the potential is taken along the special direction, that is, along the direction of the vapor pressure curve in the P-T plane, then the second derivative of the potential diverges only weakly, as C_V, with exponent α; or not at all in the classical case. This special direction, moreover, is confluent with the critical isochore both for classical and nonclassical critical behavior: $(\partial P/\partial T)_{V=V_c} \rightarrow (dP/dT)_{vap}$ as $|T-T_c|^{1-\alpha}$ for a scaled equation. Saying it differently, a second derivative taken at constant "density" (volume, entropy, etc.) is in fact taken along the special direction and results in a weak anomaly. Thus, along the special direction:

$$(\partial P/\partial T)_{S=S_c},\ (\partial P/\partial T)_{V=V_c} \rightarrow (dP/dT)_{vap} \text{ as } |T-T_c|^{1-\alpha}$$

$$C_{V=V_c},\ K_{S=S_c},\ \alpha_{S=S_c} \propto |T-T_c|^{-\alpha} \tag{5}$$

The critical exponents γ, α by definition describe the strong divergence of the compressibility K_T and the weak divergence of the specific heat C_V along the special path of approach to the critical point. As pointed out by Griffiths and Wheeler (26), along any other path, such as that of constant temperature or pressure, these exponents become renormalized, because along the special path the high near-critical values are reached faster than along other paths. For example, along the special path the compressibility diverges as $|T-T_c|^{-\gamma}$ or as $|P-P_c|^{-\gamma}$; because of the relation for the critical isotherm: $|P-P_c| \propto |\rho-\rho_c|^{\delta}$ we have, at $T=T_c$, $K_T \propto |P-P_c|^{-\gamma/\beta\delta}$, which means that the exponent is reduced by a factor $\beta\delta$ as compared to the special direction ($\beta\delta \sim 1.5$). This path renormalization by a factor of $\beta\delta$ occurs for both strongly and weakly-diverging properties, but it does not change the intrinsic character of the anomaly, (strong, weak, nondivergent).

In the case of three or more independent variables, there is, in addition to the directions along and intersecting with the coexistence surface, a new way of approaching a critical point, namely along the critical line in the case of three, parallel to the critical space in the case of more independent variables, Ref.(26). Examples of interest to us are: the superfluid phase transition in helium-4 as a function of pressure or in the presence of an admixture of helium-3; partially miscible binary liquid mixtures under pressure; ternary liquid mixtures; a fluid in an electric field; the polymerization of sulphur solutions. For classical critical behavior, the thermodynamics were developed by Ehrenfest: at a coexistence surface, "density" variables change discontinuously, whereas at a critical line, these variables are continuous but their first derivative has a discontinuity. Thus, Ehrenfest predicted finite jumps in quantities such as C_p, α_p of the superfluid or of the binary liquid mixture at the critical line. The Clapeyron equation relates the ratio of jumps in entropy and volume to the slope of the vapor pressure curve. Likewise, Ehrenfest related the jumps in specific heat and expansion coefficient to the slope of the critical line. Once it was realized in the mid-1950's that the specific heat of superfluid helium has a logarithmic divergence at the λ line, a new approach to the thermodynamics was required. The thermodynamics of the λ line was worked out by Pippard (27) in 1957 and by Buckingham and Fairbank (28) in 1961. For C_p to diverge, the entropy surface of helium must have a vertical tangent all along the λ-line. The Maxwell relations then imply that the volume has a similar vertical tangent. Pippard relations such as that between the specific heat and the expansion coefficient near the λ line

$$(C_p/T) \rightarrow (V\alpha_p)\ (dP/dT)_\lambda \tag{6}$$

replace the Ehrenfest relations for the jumps in these quantities in the classical (finite-C_p) case. Griffiths and Wheeler (26) generalized these ideas to the case of critical behavior in systems with more than two independent variables. Thus, the binary liquid mixture, at critical concentration, has weakly-diverging specific heat and expansion coefficients related by the Pippard relation (6).

We noted before three characteristics of the special direction of the first-order transition: it is approached by keeping one density-like variable constant; second derivatives taken along this direction diverge weakly rather than strongly; and divergences on paths along this direction are about 50% sharper than along other directions (exponent renormalization). The direction along the critical line presents similar characteristics. They can be summarized as follows: this direction is approached by keeping <u>two</u> density-like variables constant; second derivatives taken along this direction are <u>nondivergent</u>; and divergences in second derivatives not taken along this direction are about 10% stronger on paths along this direction than along other paths in the coexistence surface (exponent renormalization, Fisher (29)). These facts are readily grasped if one imagines the entropy surface of a binary mixture, constrained to the coexistence surface, that is, maintained at $x=x_c(P)$ asymptotically, as a function of pressure and temperature, with its vertical slope along the λ line. On any path of constant pressure, the S(T) curve has a similar shape. The only effect that pressure has is to shift the value of S_c (and of V_c, x_c) smoothly, and to modify the amplitude of the anomaly in S. On all paths intersecting the λ line (such as constant pressure or constant temperature paths) the steep rise in entropy will be encountered: $(\partial S/\partial T)_{Px} = C_{Px}/T$ and $(\partial S/\partial P)_{Tx} = V\alpha_{Px}$ will diverge as $|T-T_c|^{-\alpha}$. If, however, a path of constant volume is taken, then this path will have to "hug" the critical line, because along paths intersecting the critical line the volume, just like the entropy, varies anomalously. Along the critical line, however, entropy, volume and concentration vary smoothly and uneventfully and since derivatives such as $(\partial S/\partial T)_{Vx}$ are effectively taken along the critical line they do not diverge:

$$C_{Vx},\ K_{Sx},\ \alpha_{Sx} \rightarrow \text{constant as } |T-T_c|^\alpha \tag{7}$$

The approach of $(\partial P/\partial T)_{Vx}$ to $(dP/dT)_\lambda$ is only weak, not strong as in the case of approach to a first-order curve:

$$(\partial P/\partial T)_{Vx},\ (\partial P/\partial T)_{Sx} \rightarrow (dP/dT)_\lambda \text{ as } |T-T_c|^\alpha \tag{8}$$

Since this "hugging" effect is induced by the weak anomalies, it does <u>not</u> occur in the classical case, and we will not be surprised to find that it is hard to detect in fluid mixtures.

Finally, critical exponents of strongly and weakly anomalous derivatives will be renormalized on paths in the coexistence surface that are asymptotically parallel to the critical line. The reason is the same as in the case of the first-order transition discussed before: the high near-critical values are reached faster on paths parallel to the critical line. The enhancement factor of the critical exponent, however, is smaller than the factor of 1.5 we encountered before. Here, it is $1/(1-\alpha)$ or about 1.1 and, again, it does not modify the character of the anomaly (strong, weak, nondivergent).

In Table 4, a list is made of the primary independent variables, the additional field, its conjugate density, the primary weak anomaly, and some of the weak anomalies it induces, for all the cases of interest to us here. In Table 5, Pippard relations for these cases of interest are summarized.

TABLE 4. Weak anomalies in systems with additional fields

	primary ind. vars.	additional field	conjugate density	primary weak anom.	induced weak anom.
Superfluid helium	T	P	V	C_P	α_P, K_T
One-component fluid in electric field	T,P	E^2	ε	C_{V,E^2}	$\left(\frac{\partial\varepsilon}{\partial T}\right)_{V,E^2}$, $\left(\frac{\partial\varepsilon}{\partial E^2}\right)_{V,T}$
Binary liquid under pressure	$T,(\mu_1-\mu_2)$	P	V	C_{Px}	α_{Px}, K_{Tx}
Binary liquid in electric field	$T,(\mu_1-\mu_2)$	E^2	ε/ρ	C_{Px}	$\left(\frac{\partial(\varepsilon/\rho)}{\partial T}\right)_{x,E^2}$, $\left(\frac{\partial(\varepsilon/\rho)}{\partial E^2}\right)_{x,T}$
Partially miscible ternary	$T,(\mu_1-\mu_2)$	μ_3	x_3	$C_{p,x_1/x_2}$	$\left(\frac{\partial x_3}{\partial T}\right)_{x_1/x_2,\mu_3}$, $\left(\frac{\partial x_3}{\partial \mu_3}\right)_{x_1/x_2,T}$

TABLE 5. Pippard relations

Superfluid helium	$\frac{C_P}{T} \rightarrow (V\alpha_P) \left(\frac{dP}{dT}\right)_\lambda$	$\alpha_P \rightarrow K_T \left(\frac{dP}{dT}\right)_\lambda$
One-component fluid in electric field	$\frac{C_V}{VT} \rightarrow \left(\frac{\partial\varepsilon}{\partial T}\right)_{V,E^2} \left(\frac{dE^2}{dT}\right)_\lambda$	$\left(\frac{\partial\varepsilon}{\partial T}\right)_{V,E^2} \rightarrow \left(\frac{\partial\varepsilon}{\partial E^2}\right)_V, \left(\frac{dE^2}{dT}\right)_\lambda$
Binary liquid under pressure	$\frac{C_{Px}}{T} \rightarrow (V\alpha_{Px}) \left(\frac{dP}{dT}\right)_\lambda$	$\alpha_{Px} \rightarrow K_{Tx} \left(\frac{dP}{dT}\right)_\lambda$
Binary liquid in electric field	$\frac{C_{Px}}{T} \rightarrow \left(\frac{\partial(\varepsilon/\rho)}{\partial T}\right)_{x,E^2} \left(\frac{dE^2}{dT}\right)_\lambda$	$\left(\frac{\partial(\varepsilon/\rho)}{\partial T}\right)_{x,E^2} \rightarrow \left(\frac{\partial(\varepsilon/\rho)}{\partial E^2}\right)_{x,T} \left(\frac{dE^2}{dT}\right)_\lambda$
Partially miscible ternary	$\frac{C_{P,x_1/x_2}}{T} \rightarrow \left(\frac{\partial x_3}{\partial T}\right)_{x_1/x_2,\mu_3} \left(\frac{d\mu_3}{dT}\right)_\lambda$	$\left(\frac{\partial x_3}{\partial T}\right)_{x_1/x_2,\mu_3} \rightarrow \left(\frac{\partial x_3}{\partial \mu_3}\right)_{x_1/x_2,T} \left(\frac{d\mu_3}{dT}\right)_\lambda$

BINARY LIQUID MIXTURES

Before discussing some of the results of the six posters in my session that present properties of binary liquid mixtures (LL), I will make some remarks about the analysis of the critical anomalies in binary mixtures. It is generally recognized that the theoretical asymptotic behavior of binaries is limited to the close vicinity of the critical point. Although this close-in region is probed in all experiments in my poster session, in most of the experimental range corrections to scaling are to be expected. The participants in the poster session have been quite aware of this need and you will find reference to the use of the Wegner expansion in almost all posters. There are, however, a few complications that have to be faced. The first one is the choice of order parameter. As was argued forcefully by Scott (30), any choice of order parameter that is not the one theoretically required will induce correction terms in the analysis of the coexistence curve, the lowest-order one being proportional to $|T-T_c|^{2\beta}$. This exponent is lower than any expected from either Wegner corrections or mixing of variables. Since we do not know a priori what the order parameter is in a binary liquid mixture, this ignorance presents an essential limitation to the application of the Wegner expansion in binaries. In the case that enough thermodynamic information is available to try several choices of order parameter (mole fractions, volume fractions, number densities, etc.) it is possible to judge how reliably an amplitude of a Wegner term can be obtained. Such information, however, is seldom available. A second problem is the extreme sensitivity of the amplitude of the Wegner correction to the choice of leading exponent. A third problem is the effect of gravity that affects the entire range where Wegner corrections are small. This is an uncontrolled effect because gravitational sedimentation is almost certainly never fully developed in binary mixtures. In analyzing binary liquid data, it is therefore important to first make a clear choice of the questions to ask. It is certainly unrealistic to expect to derive reliable values for the critical exponents, plus the amplitudes of leading and Wegner correction terms, from an analysis of coexistence-curve properties of a mixture for which even the choice of order parameter is ambiguous. In such cases, it is perhaps wiser to strive for a more limited goal: the demonstration of consistency with a theoretical picture, under the assumption that the theoretical values of the critical exponents are now more precise than most experiments can give.

My second remark pertains to the analysis of excess properties. It has been customary to analyze the excess volume or excess enthalpy of mixing by a power-law analysis of the properties $(\partial^2H^E/\partial x^2)_{PT}$, $(\partial^2V^E/\partial x^2)_{PT}$ on the critical isopleth. Both properties are expected to go to zero as $|\Delta T|^{\gamma-1}$ along this path. Any experimentalist who has tried to derive a value for a second derivative from his data is aware of how difficult this is. If mixtures of varying concentrations are made up separately, the systematic errors will preclude the determination of the second derivative; if the mixture is continuously diluted, there is of course a fighting chance to retain some accuracy in $\partial^2V^E/\partial x^2$. I would like to suggest here a different approach. This is to fit the measured values of H^E, V^E or G^E directly to the appropriate scaled expression at all experimental temperatures and concentrations at which the information is available. As an example, I will use the simple linear model discussed before (cf. Table 3) for the case of incompressible binaries. The generalization to compressible binaries goes in steps. First, the reference values T_c, X_c and Δ_c are to be functions of pressure. Secondly, the scale factors a and k are to be functions of pressure. We will assume them to be linear in P. Thirdly, the excess volume V^E is obtained from the relation for the volume V:

$$V = \left(\frac{\partial\mu_2}{\partial P}\right)_{u_t,u_h} + S\left(\frac{dT}{dP}\right)_\lambda + x\left(\frac{d\Delta}{dP}\right)_\lambda \tag{9}$$

which was obtained by Sengers et al. (33) by transforming the derivative $V = (\partial\mu_2/\partial P)_{T,\Delta}$ to a derivative in which the scaling variables u_h,u_t are kept constant. The relation (9) is valid near the critical line. The derivatives $(dT/dP)_\lambda$, $(d\Delta/dP)_\lambda$ represent the slope of the critical line with pressure. For S and x we take the parametric expressions from Table 3. The pressure-dependence of μ_2 at constant u_t,u_h is solely through the pressure dependence of a and k. The anomalous part of V, which is V^E, therefore consists of three terms; one in r^β, representing the trivial linear dependence on $x-x_c$; one in $r^{1-\alpha}$, which gives rise to the weak anomaly in the expansion coefficient on the critical isopleth and to the fact that $(\partial^2V^E/\partial x^2)_{P,T}$ goes to zero as $|\Delta T|^{\gamma-1}$; and one term which behaves as μ_2, as $r^{2-\alpha}$, which is a confluent singularity of considerably higher order. The parametric expressions for the excess properties are given in Table 6. The regular "background" terms in G, S, and H are those given in Table 3. The background of V is more complex, but it is of the same structure, $V_0(T^*)+xV_1(T^*)$, as that of the other functions. These equations will not be applicable in the entire concentration range, given the experience that the equivalent relations in one-component fluids do not extend over more than ±35% in density even in "apparent" or range-averaged critical exponent values are used. The relations in Table 6 are readily extended to include a Wegner correction, since the generalization of Table 1 that includes the first Wegner correction is available in the literature, Refs. (11, 23-25).

TABLE 6. Linear model equations for compressible binary liquid mixtures

Potential	$-\mu_2(\Delta,T,P)$ $-d\mu_2=SdT+xd\Delta-VdP$
$\Delta T^*=[T-T_c(P)]/T_c(P)$	$r(1-b^2\theta^2)$
$x-x_c(P)$	$kr^\beta\theta$
$\Delta^*-\Delta_0(T^*)$	$ar^{\beta\delta}\theta(1-\theta^2)$
$-\mu_2{}^*{}_{\text{anom}}$	$akr^{2-\alpha}p(\theta)$
S^{E*}	$akr^{1-\alpha}s(\theta)$
G^{E*}	$akr^{2-\alpha}[\theta^2(1-\theta^2)-p(\theta)]$
H^{E*}	$akr^{1-\alpha}s(\theta)+akr^{2-\alpha}[(1-b^2\theta^2)s(\theta)+\theta^2(1-\theta^2)-p(\theta)]$
V^{E*}	$-(a_pk_0+a_0k_p)r^{2-\alpha}p(\theta)+$ $+akr^{1-\alpha}s(\theta)\left(\frac{\partial T}{\partial p}\right)_\lambda + kr^\beta\theta\left(\frac{\partial\Delta}{\partial p}\right)_\lambda$
$a=a_0+a_pP$ $k=k_0+k_pP$	$p(\theta),s(\theta)$ in Table 3

Let me now draw your attention to the material in my poster session. There are two posters that present excess properties. That of Marsh and Rogers gives the results of measurements of concentration, excess volume, excess enthalpy, and vapor pressure of nitroethane-cyclohexane; that of Ewing, Johnson, and McGlashan gives concentration and excess volume of cyclohexane and methanol, by the use of a continuous-dilution dilatometer. The second poster contains a Wegner analysis of the concentration on the coexistence curve. In both posters, the question of extracting the exponent γ from the second derivative of V^E or H^E is encountered. To these two posters my preceding remarks apply.

Then, there are two posters, that of Van Dael, Mijlemans and Vansteenkiste, and that of Kumaran, Halpin and Benson, in which the speed of sound is used as a probe in a variety of binary mixtures. The speed of sound W is related to the adiabating compressibility K_{Sx} by

$$W^2 = \frac{1}{\rho K_{Sx}} \tag{10}$$

Since two "densities" are kept fixed when the derivative is taken, the speed of sound is not expected to diverge. Only its temperature derivative will have an anomaly, Eq. (7). Thus, at the coexistence curve the speed of sound will reach a finite value that is a function of the state of the system. That is, it is not an order parameter but a function of the order parameter. Therefore, the difference of speed of sound in coexisting phases will vary asymptotically as $|T-T_c|^{\beta}$, after which the term in $|T-T_c|^{2\beta}$ appears. In the poster of Van Dael et al. careful analyses of highly-accurate speed of sound data on the coexistence curve in a number of binaries are presented. The asymptotic β values obtained are in agreement, within their uncertainty, with the theoretical ones. The correction terms are not negligible for $(T-T_c)/T_c > 2\times10^{-4}$. The theoretical predictions are well confirmed by these data.

In ternary mixtures, the adiabatic compressibility likewise remains finite, but the path of approach to the critical point, in the coexistence surface at constant overall x_2, x_3, is asymptotically parallel to the critical line so that the exponent β becomes renormalized to $\beta/(1-\alpha)$, Refs. (31,32). Van Dael et al. indeed seem to confirm this predicton: they find $\beta=0.360\pm0.01$ in the ternary water-ethanol-chloroform. It should, however, be kept in mind that the theoretical predictions pertain to the zero-frequency limit of the speed of sound. At nonzero frequency, a critical frequency with accompanying high dispersion, is encountered on an approach to the critical point. Van Dael and coworkers found this to happen within their experimental range in several of the systems they studied. This phenomenon, although of considerable interest, leads to distortion of critical exponent values.

The issue of the Pippard relation is touched upon indirectly in the poster of Siebert, Warowny and Knobler on nucleation, and directly in that of Thoen, Kindt and Van Dael on the dielectric constant of binary mixtures. As to the first poster, the trick used in inducing nucleation is to adiabatically decompress a pressurized binary mixture, thus forcing it to cross the phase boundary. There are two effects involved: the shift of the critical temperature induced by the change of pressure, and the adiabatic cooling. The effect on the critical temperature can be either a raising or a lowering of T_c. The former would seem to be of help, the second counterproductive, but it has been found that mixtures with $(dT_c/dP)_\lambda > 0$, such as 3 methyl-pentane-nitroethane, Ref. (34), and mixtures with $(dT_c/dP)_\lambda < 0$, such as isobutyric acid-water, both nucleate under adiabatic decompression. This must then be due to the $(\partial T/\partial P)_{Sx}$ effect being large enough to override the effect of a negative $(dT_c/dP)_\lambda$. But let us now consider the Pippard relation (8). It predicts that, asymptotically, $(\partial T/\partial P)_{Sx}$ should approach $(dT/dP)_\lambda$, so that an adiabatic expansion should have no effect whatsoever! Given the fact that adiabatic expansion has been found to induce nucleation as close as 0.01°C from the critical point, Ref. (34), we are forced to conclude that the approach of $(\partial T/\partial P)_{Sx}$ to $(dT/dP)_\lambda$ is so slow that it is of no practical importance. A similar conclusion was reached by Doiron et al. (36) in their study of the P-T isochores of helium-3-helium-4 mixtures near the gas-liquid critical line. The critical isochore appears to cross the dew-bubble curve in the P-T plane at an angle while the critical line is tangent to this curve at the critical point. Again, although theory predicts that $(\partial T/\partial P)_{\rho x}$ should approach $(dT/dP)_\lambda$, in practice the region where this happens is experimentally irrelevant. No more than a minor "dip" in $(\partial T/\partial P)_{\rho x}$ is visible in these very careful experiments.

The issue of the weak anomalies and the Pippard relation is also the topic of the poster of Thoen et al. on the dielectric constant of nitroethane-cyclohexane. These authors are to be credited for their discovery of an interesting frequency dependence of the low-frequency dielectric constant in conducting mixtures, Ref. (35). Until this effect was recognized, the studies of dielectric behavior of binary liquid mixtures were a bizarre array of mutually conflicting results. I urge you to visit this poster and have the elegant resolution of these controversies explained. Here I want to discuss the dielectric constant anomaly from the point of view of thermodynamics. In the recent paper by Sengers et al. (33) referred to before, the argument was presented that for a binary liquid mixture in an electric field, the quantity ε/ρ behaves formally analogous to the volume V for a mixture under pressure. That is

$$\frac{\varepsilon}{\rho} = -\left(\frac{\partial\mu_2}{\partial E^2}\right)_{\tau,h,\phi} - S\left(\frac{dT}{dE^2}\right)_\lambda - x\left(\frac{d\Delta}{dE^2}\right)_\lambda \qquad (11)$$

where $\phi = P + \varepsilon E^2/2$. The theory thus predicts an α-type anomaly for $(\partial(\varepsilon/\rho)/\partial T)_x$ on the critical isopleth above T_c, with an amplitude linked to that of the specific heat C_{Px} by $(\partial T/\partial E^2)_\lambda$: according to the Pippard relations

$$\frac{C_{Px}}{T} \rightarrow (V\alpha_{Px}) \left(\frac{dP}{dT}\right)_\lambda$$

$$\frac{C_{Px}}{T} \rightarrow \left(\frac{\partial(\varepsilon/\rho)}{\partial T}\right)_{x,E^2} \left(\frac{dE^2}{dT}\right)_\lambda$$

the anomalies in C_{Px}, α_{Px} and $\partial(\varepsilon/\rho)/\partial T$ are all connected by factors related to the slope of the critical line. A test of these relations was performed by Thoen et al., who measured C_{Px}, the density and the dielectric constant for nitroethane-cyclohexane.

Before summarizing the results of my poster session, I want to make a few remarks about the weak anomalies and exponent renormalization. The primary weak anomaly in C_V in one-component fluids, C_{Px} in binary mixtures has been unequivocally demonstrated in many experiments. For reviews, see Refs. (30, 37, 38). The Pippard relations, Table 5, show that the anomaly in the expansion coefficient has an amplitude which differs from that in C_{Px} by a factor $(dT/dP)_\lambda$. Since the pressure effect on the critical line of binary liquid mixtures is small, the amplitude of α_{Px} must be small. Indeed, there are no more than one or two experiments in which this anomaly has even been detected, Ref. (39). The compressibility K_{Tx} relates to α_{Px} as α_{Px} to C_{Px}; the hope to ever see the weak anomaly in K_{Tx} is thus very slim indeed.

In summary, the posters in my session demonstrate the general agreement with the results of the renormalization-group predictions for critical exponents and correction to scaling; and of the thermodynamics of mixtures as developed by Griffiths and Wheeler on the foundation laid by Pippard, Buckingham and Fairbank, and Fisher. They also illustrate the following intrinsic difficulties: (1) the theory assumes the existence of an order parameter which, in practice, is ambiguous; (2) the critical exponents, because of this ambiguity and because some of them are derived by twice differentiating experimental quantities, cannot be obtained with an accuracy even approaching that of the theoretical predictions, and (3) several of the predicted weak divergences and weak asymptotic confluences are not noticeable in ranges of experimental interest.

It is the view of this author that because of these ambiguities, most experiments in binary liquid mixtures cannot prove or disprove the theoretical results of the renormalization group. At best, a demonstration of consistency can be given. The theory, so far, has passed the test of consistency with validated data in pure fluids and in binaries.

TRICRITICAL POINTS

A tricritical point in a fluid mixture is defined as a point at which three fluid phases become identical. If a binary mixture has phase separation in the liquid phase, it will possess two critical lines, a gas-liquid and a liquid-liquid line. For tricriticality it is required that these lines meet. This is, according to the phase rule, extremely unlikely to happen. Thus, tricritical points, if they occur, have to be looked for in mixtures with a minimum of three components. In four-component mixtures, they can be studied at ambient pressure. This thermodynamic curiosity has come into the limelight recently for two unrelated reasons. The first one is the prediction that at a tricritical point classical theory should be valid in three dimensions. The fluctuation cannot become large enough to wash out the difference in properties of coexisting phases, because the top of the coexistence curve is of the fourth degree for a classical tricritical point (Table 1). The second one is that a relationship was discovered between this fluid tricritical point and a well-known transition point in superfluid helium-3/helium-4 mixtures. At this point the second-order λ line of the superfluid transition goes over into a first-order line along which two phases, a superfluid phase rich in helium-4 and a normal phase rich in helium-3 coexist. Blume, Emery and Griffiths (40) modeled this phase transition by a classical model. If the fictitious field conjugate to the order parameter is included in the model, it turns out that three critical lines meet at this point; this is the origin of the name tricritical point. The tricritical point in helium mixtures is analogous to those found in several solid-state phase transitions, for instance in certain antiferromagnets in which an external magnetic field of sufficient strength disrupts the critical (Néel) line and turns it into a first-order line. This second-order to first-order transition has been known for a long time and was first modeled by Landau in 1937.

That fluid tricritical points and these "symmetric" tricritical points (called this way because the behavior is unchanged if the sign of the fictitious ordering field is reversed) are analogous is not all that easy to see. Griffiths (41) showed that if unsymmetric terms are added to the classical model that was used for the superfluid tricritical point, the characteristic topology of a fluid tricritical point results. It is more complicated than I have suggested, and can only evolve from a situation in a binary when two critical lines, emerging from the respective pure-fluid critical points, are interrupted at a lower and an upper critical endpoint on a line of three-phase coexistence. The role of the third component is to shrink this three-phase line to zero, so that the two critical lines blend into one. In the language of van Konynenburg and Scott (42), who generated almost all known phase diagrams of binary mixtures with the Van der Waals model, the tricritical point happens at the transition of type IV to type II behavior. Contrary to the symmetric tricritical points, the unsymmetric one in a three- or four component fluids has no fictitious fields: in principle, all physical fields are experimentally accessible. In practice, however, this advantage is lost because it is not the fields but rather the conjugate densities that are studied by the experimenter; in terms of densities, the tricritical point is extremely complex. In the frontier study of a four-component mixture by Lang and Widom (43) the three independent composition variables were sampled over the entire extent of the three-phase region at a number of temperatures. This work permitted a test of the classical theory, with the result that the classical exponents 1.5, 1 and 0.5, predicted to characterize the shrinking of the three-phase region, were confirmed within a fairly large experimental uncertainty. The experimental situation brightened considerably when Griffiths and coworkers (44) formulated so-called sum rules, which involve the osmotic susceptibilities of coexisting phases. One such sum rule says that the square root of the susceptibility of the middle phase is equal to the sum of the square roots of the susceptibilities of top and bottom phases or, alternatively, that the correlation length of the middle phase equals the sum of those of top and bottom phases. In principle, such a sum rule can be tested by angle-dependent light scattering at one temperature, near the tricritical one at which three phases are present. No sampling seems necessary. In attempting to do this, Ref. (45), however, we encountered severe difficulties due to the fact that the intensity of scattered light is only proportional to the osmotic susceptibility, but that the proportionality factor, $(\partial\varepsilon/\partial\psi)^2$ with ψ the order parameter, varies strongly from phase to phase in a way that can only be predicted if all compositions are known. This problem is not encountered if the sum rule is tested for the correlation length. It is, however, very difficult to determine the correlation length with good precision from angle-dependent light scattering. The tests of the sum rules for the square root of the susceptibility (corrected for the variable value of $\partial\varepsilon/\partial\psi$) and the correlation length for the Lang-Widom mixture were that the rule was violated in such a way that the value for the middle phase fell about 20% below the sum of those in the other phases. Van Dael and coworkers ascribe these, and other departures from classical behavior that they noted by their measurements of the speed of sound, to the nearness of the critical end points where nonclassical behavior should prevail, Ref. (46) and poster.

A new phase in the research was opened when Scott, Knobler and coworkers (47) realized that a tricritical point can almost be reached in a binary, and that it can be reached in an almost-binary. The trick was to find, in mixtures of component A with a component B_1, B_2,...from a homologous series, a component B_i which forms a type IV, while component B_{i+1} forms a type II mixture with A. The A-B_i mixture will then have a very small three-phase region which is quite close to tricriticality. A typical example is ethane/eicosane. By mixing some B_{i+1} into B_i, the tricritical point can actually be reached. Since the B components may be two high-molecular-weight alkanes, while A is methane or ethane, the heavy alkanes will occur in almost identical proportions in each of the phases and act as if they were "almost" a single component, so that the system is called a quasi-binary. Four-dimensional vision is no longer required if the thinking about tricritical points is done in quasi-binaries. Although it may seem a disadvantage that these systems have to be studied under pressure, the contrary is true. In a variable-volume cell these systems can be readily manipulated, with two field variables, P and T, accessible.

Studies of almost-tricritical binaries and of tricritical quasibinaries are reported by Specovius, Goh, Knobler and Scott in my poster session. I encourage you to hear their results; in addition, they may have a report on their first results of a test of the Griffiths sum rules by a light scattering experiment that they are carrying out in collaboration with Kumar and Cannell.

I am delighted to report that my poster session also contains an example of a symmetric tricritical point. I am referring to the poster by Wheeler on the polymerization of sulphur solutions. Let me first remind you that liquid sulphur polymerizes at a temperature of 159°C, at which the closed rings of eight sulphur atoms open up to an open-chain radical that is capable of joining an existing chain. The Scott-Magat extension of the Flory-Huggins polymer solution theory to mixtures of different chain lengths was the basis for the Tobolsky-Eisenberg treatment of the polymerization of pure liquid sulphur. The transition, although not infiitely sharp, is close to being a second-order phase transition. Scott (48) extended the Tobolsky-Eisenberg treatment to sulphur in solution. By diluting the sulphur by a solvent, the temperature of polymerization is increased, so that a critical line is generated. After the system is sufficiently diluted, it will split into two phases, one rich in sulphur and polymerized, the other poor in sulphur and not polymerized. The situation is quite similar to that in helium-3/helium-4 mixtures, with the temperature direction reversed, but this was realized only recently. Unaware that he was treating what is presently called a tricritical point, Scott developed the classical theory and predicted the various phase diagrams for different solvents, in good qualitative agreement with the data.

Then arrived the renormalization-group approach and the notion of universality classes. DeGennes showed the formal analogy of the polymerization process and the magnetic model for the n-component spin in the limit $n \rightarrow 0$. Wheeler, Kennedy and Pfeuty (49) applied this model to liquid sulphur, and shortly afterwards, Wheeler and Pfeuty (50) extended these results to sulphur solutions by introducing an additional interaction parameter. They solved the model in the classical or mean-field approximation, predicted the phase diagram, and discovered that it contains a tricritical point. They demonstrated the complete equivalence of their results with those Scott obtained in 1965.

INTERFACES

In this section I will sketch some recent developments in the theory and experiments on fluid interfaces.

In the classical theory of the interface by van der Waals (51) the free-energy cost of creation of an interface was set proportional to the square of the density gradient. The free-energy gain in creating the interface is obtained because of the bulk free energy of the two-phase system is lower than that of the corresponding system constrained to remain homogeneous. The resulting density profile is such that half the free energy gain is used to pay the cost of the interfacial energy. Since the gain in free energy due to phase separation diminishes near the critical point, but the cost of the gradient remaining relatively steady, the interface has to become less sharp, and its thickness must diverge. Van der Waals already demonstrated that on approach to the critical point, in the case of a classical free energy, the interfacial tension disappears as $|T-T_c|^{\mu}$, with $\mu=1.5$. He was also aware that the experiments indicated a considerably lower value, $\mu=1.23-1.27$, cf. Ref. (52). Fisk and Widom (53) developed the non-classical counterpart to the theory of surface tension of van der Waals. The Fisk-Widom theory is still a square-gradient theory, but the free energy is assumed to have the non-classical form given by the scaling laws. The coefficient of the gradient-squared term was assumed to be constant. This is equivalent to the assumption that the critical exponent η equals 0. The critical exponent μ was shown to be equal to

$$\mu = \gamma + 2\beta - \nu$$

while the interface thickness was shown to diverge at the critical point as the correlation length ξ, that is as $|T-T_c|^{-\nu}$. With the best values of the critical exponents (Table 1), we find $\mu=1.261$, which is in the center of the experimental range established by van der Waals in 1893, cf. Ref. (52), and has been corroborated by all high-quality modern experiments. The divergence of the interface thickness was confirmed by experiments on light scattering from the interface.

The second modern development was the prediction, by Cahn (57), of a surface-tension phase transition from non-wetting to wetting. This transition should occur at a noncritical interface at some distance in temperature from the point where two fluid phases become identical. A typical example is a binary liquid near its critical point -- call the coexisting phases β and γ, and the corresponding surface tension $\sigma_{\beta\gamma}$. The noncritical phase α might be the wall of the vessel or the vapor phase. The argument, equally valid for classical and nonclassical critical behavior, is that $\sigma_{\beta\gamma}$ disappears as $|T-T_c|^{\mu}$ while the difference between $\sigma_{\alpha\gamma}$ and $\sigma_{\alpha\beta}$ goes to zero no faster than $|T-T_c|^{\beta}$. Assume that $\sigma_{\alpha\gamma}$ is the larger of the two. As soon as $\sigma_{\alpha\gamma}-\sigma_{\alpha\beta} > \sigma_{\beta\gamma}$, the β phase will have to wet the noncritical interface, because the balance of forces $\sigma_{\alpha\gamma}$, $\sigma_{\alpha\beta}$, $\sigma_{\beta\gamma}$ can no longer be maintained along a line of contact between the three phases with nonzero contact angles. In practice, the wetting-nonwetting phase transition has not yet been demonstrated to occur by changing the temperature. In binary liquids where wetting of the vapor by the bottom phase has been observed, the wetting persisted until a liquid phase froze. The transition to incomplete wetting has, however, been induced by addition of a third component, Ref. (54). The theory of the behavior of the three surface tensions $\sigma_{\alpha\beta}$, $\sigma_{\beta\gamma}$ and $\sigma_{\alpha\gamma}$ was first worked out by Widom and coworkers (55) for the particular case of three-phase equilibrium near a tricritical point. Later, the theory was generalized by Khosla and Widom (56) to any noncritical phase α in the presence of near-critical β, γ phases. The theoretical predictions are the following: (1) on the critical isotherm, the surface tension of the (one-phase) ($\beta\gamma$) phase with respect to the noncritical α phase varies as $|x-x_c|^{\mu/\beta}$; (2) on the critical isopleth, the three surface tensions: $\sigma_{\alpha\gamma}-\sigma_c$, $\sigma_{\alpha\beta}-\sigma_c$, below T_c, and $\sigma_{\alpha,\beta\gamma}-\sigma_c$ above T_c, have a common tangent if plotted as a function of temperature, and an anomalous contribution of the form $|T_c-T|^{\mu}$ with different amplitudes for the three phases; (3) finally, near T_c, $\sigma_{\beta\gamma}=\sigma_{\alpha\gamma}-\sigma_{\alpha\beta}$, which is ultimately, a consequence of the fact that there is only one order parameter, Refs. (55,57). The first test of these laws, by Khosla and Widom (56), revealed a departure from the common-tangent rule that the authors suspected to be an artifact. Recent very precise sets of surface tension data in two binaries, one with an upper, another with a lower consolute point, obtained by McLure and Pegg, are displayed in the poster session. These measurements confirm the prediction of the common tangent that was left in doubt by the Khosla-Widom experiments.

The last topic regarding interfaces is a conceptual difficulty that arises when the theory of the diverging interface thickness below T_c, Ref. (53), is confronted with the theory of gravity effects in the supercritical phase, Ref. (58). For convenience, let us consider a one-component fluid. Because of the large compressibility, a density gradient develops according to the relation $\partial\rho/\partial z = g\rho^2 K_T$. This gradient will become sharper and sharper as the critical point is approached from above, while the density profile of the subcritical interface will get thicker and thicker as it is approached from below. Obviously, there is a piece of the puzzle missing. Very recently, Sengers and van Leeuwen (59) have resolved this difficulty by observing that in the field of gravity neither the correlation length nor the interface thickness can grow to infinity, nor can the density profile in the supercritical phase become infinitely sharp. The correlation length ξ can not grow beyond the point that local fluid properties would vary considerably over the height ξ. The very fact that fluid properties are correlated over length ξ implies that sharp variations over distances smaller than ξ cannot occur. Sengers and van Leeuwen introduced these nonlocal effects into the supercritical fluid by the same device of a square-gradient term in the free energy that van der Waals had employed below T_c and under the restriction of $\eta=0$, just as in the Fisk-Widom theory, Ref. (53). They showed that in the field of gravity the correlation length, compressibility and the density profile "saturate" at a finite temperature above the critical point (a few tenths of a millidegree) and remain steady during the passage through T_c until a temperature slightly below T_c is reached. Thus, two apparently conflicting predictions have been reconciled by the use of the tool of the square-gradient theory passed to us by van der Waals.

NUCLEATION

The classical theory of nucleation of Becker and Döring makes it plausible that at a given degree of supersaturation of a vapor, only spontaneous fluctuation of a size at least as large as a critical radius will be able to grow. This critical radius is strongly dependent on the degree of supersaturation, and, as a consequence, an observable rate of nucleation occurs almost abruptly as the degree of supersaturation is increased. If the classical theory is applied near the critical point, it is found that the degree of supersaturation, if measured as δT, the amount of undercooling below the saturation temperature T_σ, is a virtually constant fraction of $T_c - T_\sigma$. A refinement of the theory to incorporate non-classical critical behavior was performed by Langer and Turski (60), with the result that although an increase in the degree of supercooling $\delta T/(T-T_c)$ was predicted on approach to the critical point, the increase was too weak to be of much practical consequence. A large number of experiments in near-critical one- and two-component fluids, however, showed considerable increases in the degree of supercooling, as much as a factor 2 beyond the Becker-Döring limit. Binder and Stauffer (61) suggested that this apparent increase in nucleation rate might in fact be due to a decrease in nucleation growth which is expected to occur because of the slowing-down of the coefficients of thermal diffusivity and of diffusion. A recent paper by Langer and Schwartz (62) works out the different stages of the process of nucleation and droplet growth in meticulous detail. The experimentalist does not observe the onset of nucleation; rather, he sees a late stage of the process of nucleation and growth. In none of the experiments claiming disagreement with the Becker-Döring theory had these two stages been separated.

Such a separation of nucleation and growth was recently achieved by Knobler and coworkers (63) in binary liquid mixtures. A poster in my session reports their results. The means by which this separation is achieved is a so-called double-quench. In previous publications (64) Knobler and coworkers had introduced and refined the pressure-quench technique, by which a binary liquid mixture is forced to enter the metastable region by a sudden release of pressure. To introduce nucleation, the pressure drop is adjusted so that the mixture enters the narrow "window" where droplets of critical size are formed. The system is then quenched again, to enter a part of the metastable region where there is no further nucleation but where the droplets can grow. Knobler and coworkers report in their poster that their recent observations of these two different regimes agree in detail with the predictions of the Langer-Schwartz theory.

SUMMARY

Having reviewed some significant achievements and new insights that have been obtained in the past few years in the theoretical and experimental study of critical phenomena in fluids, I hope I have been able to convey to my audience that any area of this century-old field of physics has recently yielded new phenomena and new ideas, once it was restudied with care. My choice of topics has in no way been exhaustive; I simply used the material presented in the poster session and the additional information my contributors provided me as a guide, and was delighted to see to what lovely places it took me.

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