The Yang-Yang Anomaly in Fluid Criticality: Experiment and Scaling Theory

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Yang and Yang proved that the divergence of $C_V(T)$ at a gas-liquid critical point implies that *either* $d^2p/dT^2 \equiv p''_\sigma$ *or* $d^2\mu/dT^2 \equiv \mu''_\sigma$ *or both* diverge when $T \to T_c-$ on the phase boundary σ. They queried the lattice-gas prediction that μ''_σ remains finite. Analysis of two-phase heat-capacity data provides, for the first time, evidence for such a Yang-Yang anomaly ($\mu''_\sigma \to \pm\infty$) in propane and suggests an anomaly of opposite sign in CO_2. A revision of standard scaling theory for fluid criticality is demanded: specifically, $p - p_c$ must appear in the ordering field. The coexistence diameter hence gains a $|T - T_c|^{2\beta}$ term.

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In 1962 Voronel' and co-workers [1] demonstrated for fluid argon that the constant-volume specific heat on the critical isochore $C_V^c(T) \equiv C_V(T; \rho = \rho_c)$ becomes infinite when T approaches T_c (contrary to the prediction of all classical theories). Oxygen was soon found to behave similarly [1]. Two years later Yang and Yang [2] derived the general relation

$$C_V^{\rm tot} = VT(\partial^2 p/\partial T^2)_V - NT(\partial^2\mu/\partial T^2)_V\,, \qquad (1)$$

where $N/V = \rho = 1/v$, and applied it to the two-phase region $\rho_{\rm gas} < \rho < \rho_{\rm liq}$ beneath T_c where, *on* the phase boundary or vapor pressure curve σ, one has $p = p_\sigma(T)$ and $\mu = \mu_\sigma(T)$. Noting that the divergence of $C_V^c(T)$ then implies that one, the other, or both of the second derivatives p''_σ and μ''_σ must diverge when $T \to T_c-$, they stressed the importance of deciding what actually occurs.

This problem gains significance on recalling that simple lattice gases—on which much of our understanding of criticality in fluids is based—and all previous extensions of such models [3] predict that $\mu_\sigma(T)$ is analytic through T_c so that $\mu''_\sigma(T_c-)$ must remain finite. But Yang and Yang felt that for real gases it was more reasonable to expect that *both* p''_σ *and* μ''_σ should diverge [4]. If so, it is clearly of interest to find *how* the singularity in C_V^c is shared, in other words, to determine the strength of the Yang-Yang "anomaly," that is, the divergence of $\mu''_\sigma(T)$.

Here we answer these questions by carefully analyzing extensive data recently published for the two-phase heat capacity of propane (C_3H_8) [5]. We find, in fact, that the singularity is split almost equally between μ''_σ and p''_σ [when suitably normalized (see below)]. Earlier data for carbon dioxide (CO_2) [6] support a similar conclusion but with μ''_σ diverging in the opposite sense [7]. Historically, the first experiments to be examined (1967–1971) were for water (or steam, H_2O) [8]; these were interpreted as consonant with μ''_σ finite through T_c. However, our reexamination indicates that these early data lack consistency and are too imprecise to draw reliable conclusions.

It has been recognized for many years [3] that an asymptotic scaling description of fluid criticality requires two *scaling fields,* say $\tilde{t}$ and $\tilde{\mu}$—a thermal field and an ordering field—that, in contrast to symmetric systems like ferromagnets, are *both* "mixtures," i.e., in leading order linear combinations, of the "bare" fields, $t = (T/T_c) - 1$ and $(\mu - \mu_c)$. But that assumption is *inadequate* to explain the presence of a Yang-Yang anomaly. Rather, as demonstrated below, the pressure deviation $(p - p_c)$ should, in general, *also* mix into the scaling fields. That, in turn, induces a $|t|^{2\beta}$ correction term in the coexistence curve diameter, $\bar{\rho}(T) = \frac{1}{2}(\rho_{\rm liq} + \rho_{\rm gas})$. [Here, as usual, $\beta = 0.326\,(\pm 0.0015)$ [9] describes the coexistence curve via $\rho_{\rm liq} - \rho_{\rm gas} \sim |t|^\beta$ as $t \to 0$.] This $|t|^{2\beta}$ term is new and actually *dominates* the previously anticipated $|t|^{1-\alpha}$ term [3] [where $\alpha = 0.109\,(\pm 0.004)$ [9] is the specific heat exponent]. By the same token, the necessity of allowing for pressure mixing casts doubt on the validity of recently devised finite-size scaling algorithms for extrapolating the effective coexistence curves obtained in precise modern simulations of continuum fluid models [10].

To justify the claims summarized above observationally, we focus exclusively on the *two-phase region:* $T < T_c, \rho_{\rm gas} < \rho < \rho_{\rm liq}$. It is then helpful to rewrite the Yang-Yang (Y-Y) relation (1) as

$$C_V(T, \rho) = (v/v_c)\widetilde{C}_p(T) + \widetilde{C}_\mu(T)\,, \qquad (2)$$

[11] where we may expect the critical behavior [12]

$$\widetilde{C}_\mu(T) \equiv -T\mu''_\sigma = \widetilde{A}_\mu/t'^\alpha + \widetilde{B}_\mu + \tilde{a}_\mu t'^{\theta-\alpha} + \cdots\,, \qquad (3)$$

and similarly for $\widetilde{C}_p(T) \equiv Tv_c p''_\sigma$, with amplitudes $\widetilde{A}_p$, $\widetilde{B}_p$, etc. For later convenience we have introduced $t' = (T_c/T) - 1 = -t/(1+t)$, while $\theta \simeq 0.52\,(\pm 0.02)$ [9] is the leading correction-to-scaling exponent. Our aim is to estimate the strength of the Y-Y anomaly as measured by the ratio

$$R_\mu = \frac{\widetilde{A}_\mu}{\widetilde{A}_p + \widetilde{A}_\mu} = \lim_{t\to 0-}\left[\widetilde{R}_\mu(T) \equiv \frac{\widetilde{C}_\mu}{\widetilde{C}_p + \widetilde{C}_\mu}\right], \qquad (4)$$

from experimental data for $C_V(T, \rho)$.

For propane, Abdulagatov *et al.* [5] present two-phase data for 36 isochores, $\rho = \rho_i$, $i = 1, 2, \ldots$, for each of which C_V is tabulated for a series of 17 to 75 temperatures

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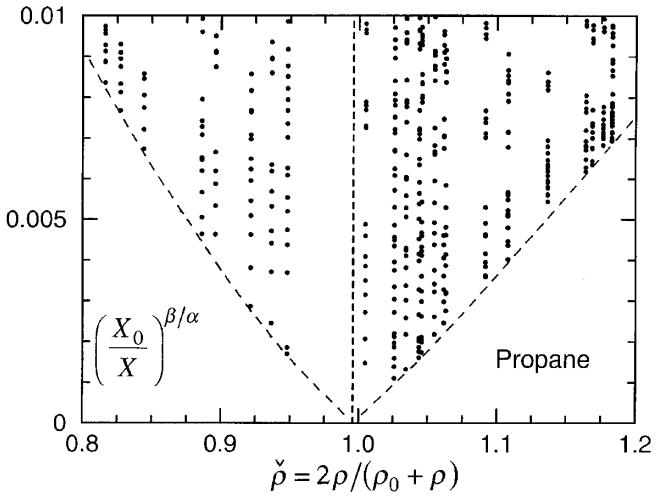

FIG. 1. Plot of transformed propane data for $X = \sqrt{\rho}\, C_V$ [5] normalized by $X_0 = 1(\rho_0)^{1/2}$ kJ/kg K vs the transformed density $\check{\rho}(\rho)$; see text. The linear intercept of the envelope (dashed curve) with the $\check{\rho}$ axis locates ρ_c.

T_{ij} in the range $t' = (0.29\text{–}7) \times 10^{-5}$. Apart from a few misprints, slips, and defects [13], the data exhibit remarkable precision and internal consistency. Some are displayed in Fig. 1 which depicts $(\sqrt{\rho}\, C_V)^{-\beta/\alpha}$ vs $\check{\rho} = 2\rho/(\rho_0 + \rho)$, where for ρ_0 the estimate ρ_c^{Ab} of [5] has been used [13]. The advantage of this plot is that the lower envelope (corresponding to $\rho = \rho_{\mathrm{gas}}+$ or $\rho = \rho_{\mathrm{liq}}-$) should extrapolate linearly and symmetrically to zero at $\check{\rho} = \check{\rho}_c$. Thereby we estimate $\rho_c = 1/v_c = 218.495$ kg/m^3, 0.8% lower than ρ_c^{Ab}. This value plays a role, although not a sensitive one, in estimating R_μ.

Now, given isothermal data, it follows from (2) that a plot of C_V vs v or, equally, of ρC_V vs ρ for *fixed* T should be *linear* with slopes and intercepts determined by $\widetilde{C}_p(T)$ and $\widetilde{C}_\mu(T)$. However, to the precision required, the isochoric observation temperatures T_{ij} do not *match* from one isochore to another. To overcome this, *explicit nonlinear fits* [using forms like (3) and various extensions [13]] were used to represent the data for each ρ_i. The high quality of these fits $C_{\rho_i}(T)$ can be gauged from Fig. 2 which displays the "core data set," running from $\rho_{21} = 245.82$ kg/m^3 to $\rho_{28} = 194.06$ kg/m^3. All the data are represented to within the experimentally assessed precision [5,13].

The eight isochores of the core set "survive" (i.e., do not enter the one-phase region) down to $t' \simeq 5 \times 10^{-4}$. By evaluating the corresponding fits $C_{\rho_i}(T)$ at appropriately selected fiducial temperatures T_k, the resulting isothermal values for C_V can be used to estimate $\widetilde{C}_p(T_k)$ and $\widetilde{C}_\mu(T_k)$ from linear fits vs v (and ρ); see (2) and Fig. 3. In fact, the C_{ρ_i} values always agree with the least-squares linear fits to within the expected uncertainties [5,13]. Furthermore, the values of $\widetilde{C}_p$ and $\widetilde{C}_\mu$ found from plots vs ρ and vs v agree, with very few exceptions, to within 1%. For $t' < 4 \times 10^{-4}$ only one isochore above ρ_c (namely, $i = 27$) survives, and the fitted slopes can no longer be trusted [13]. However, the mean values $\frac{1}{2}(\widetilde{C}_p + \widetilde{C}_\mu)$ remain well behaved and, via (2), provide reasonably precise and reliable estimates for $\frac{1}{2} C_V^c(T)$; see the final estimates presented in Fig. 4. Granted that C_V^c diverges when

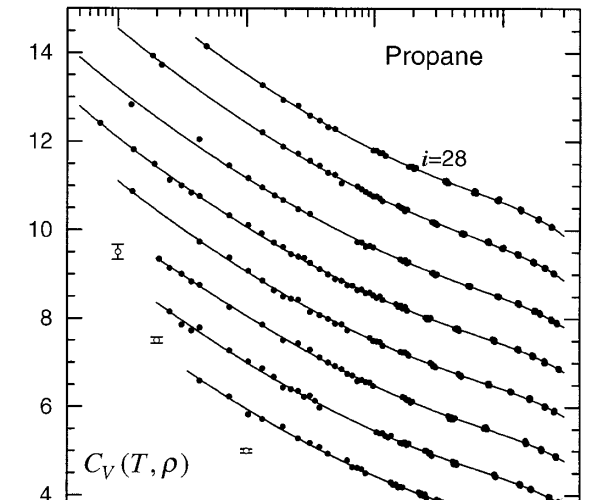

FIG. 2. The nonlinear fits $C_{\rho_i}(T)$ to the isochoric data for $C_V(T_{ij}, \rho_i)$ [5] for the core set $i = 21\text{–}28$, in units of kJ/kg K. For clarity, successive isochores have been shifted by $\Delta C_V = 1$ kJ/kg K; the uncertainty bars indicate the quoted precision [5]; the critical density lies between ρ_{26} and ρ_{27}.

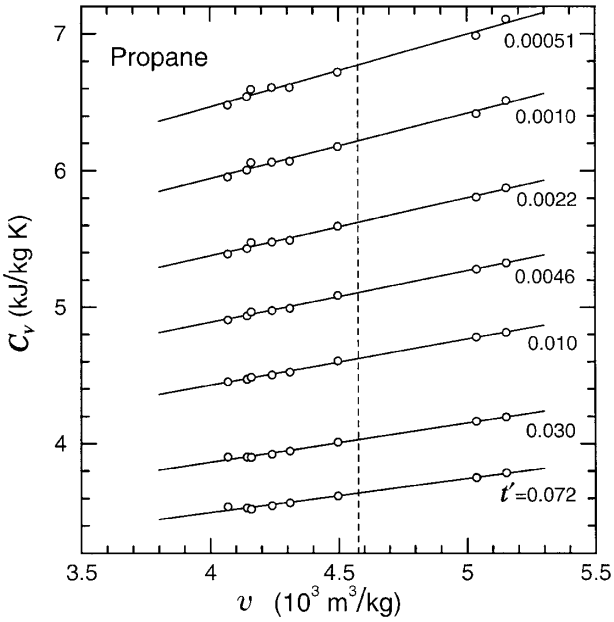

FIG. 3. Linear isothermal fits of C_V vs specific volume $v = 1/\rho$ for the core set ($i = 21\text{–}28$) at selected fiducial temperatures T_k, yielding estimates of $\widetilde{C}_p$ and $\widetilde{C}_\mu$ over 2.6 decades of t'. The dashed vertical line locates the critical volume.

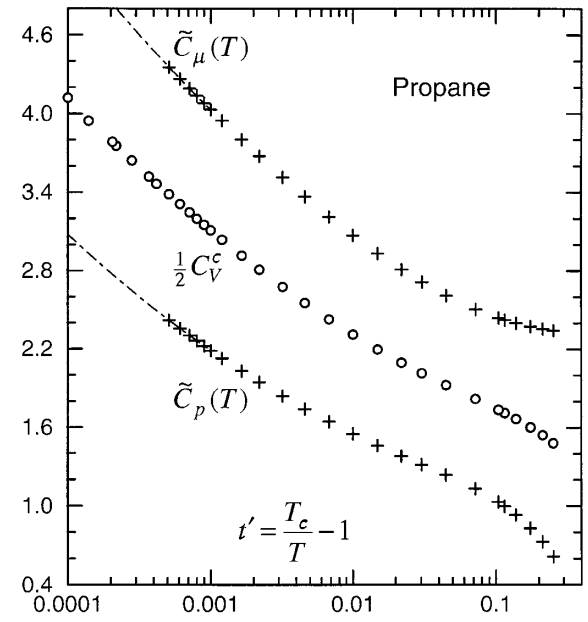

FIG. 4. Final estimates of the chemical potential and pressure contributions $\tilde{C}_\mu(T)$ and $\tilde{C}_p(T)$, respectively, to the specific heat $C_V^c(T)$, on the critical isochore of propane (kJ/kg K). The dot-dashed curves represent fits modeled on Eq. (3).

$T \to T_c$ there seem to be few grounds for doubting that $\tilde{C}_\mu(T)$ diverges in a very similar manner; in other words, propane exhibits a clear Yang-Yang anomaly.

To assess the strength of the anomaly as defined in (4), one may recall (3) and examine $\tilde{R}_\mu$ vs t'^α as in Fig. 5.

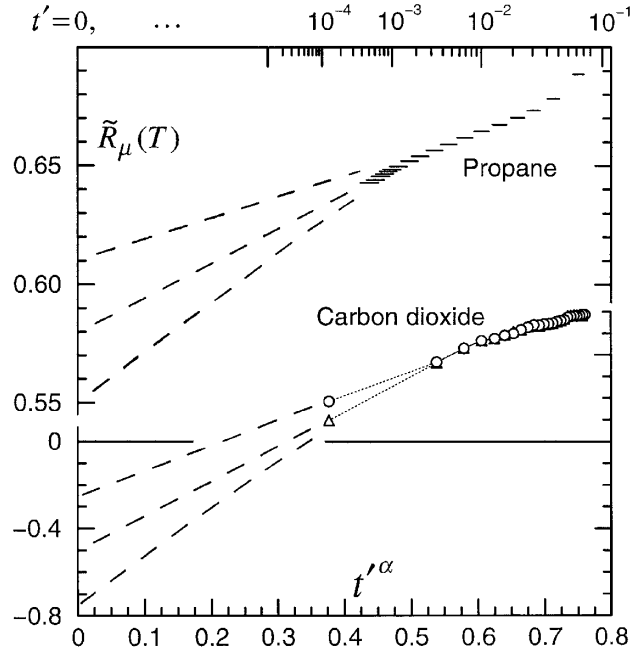

FIG. 5. The strength R_μ of the Yang-Yang anomaly estimated by linear extrapolation of $\tilde{R}_\mu(T)$ [see Eq. (4)] vs t'^α. For CO_2 the triangles and circles represent the 1978 and 1982 analyses, respectively [6]. Note the breaks in the vertical scale. The dashed lines represent a range of plausible extrapolations.

On this plot R_μ should be approached *linearly* when $x \equiv t'^\alpha \to 0$ with leading corrections of order x^Θ, where $\Theta = \theta/\alpha \simeq 4.8$. The main uncertainties arise from those of α, as indicated by the horizontal bars in the figure [14]. By extrapolation we conclude

$$R_\mu \simeq 0.56 \quad \text{for propane,} \tag{5}$$

with confidence limits of ± 0.04 [13]. This clearly represents a major deviation from lattice-gas predictions.

We have examined similarly [13] the careful estimates of p_σ'' and μ_σ'' made by Gaddy and White for CO_2 [6,7]. These clearly suggest that $\mu_\sigma'' \to +\infty$ which is the *opposite* sign of divergence found for propane. The plots of $\tilde{R}_\mu$ vs t'^α for CO_2 shown in Fig. 5 are sparse for $t' \lesssim 4 \times 10^{-3}$, but the evidence suggests $R_\mu \simeq -0.4\,(\pm 0.3)$ [13]. As mentioned, more recent data for CO_2 [7] support $R_\mu < 0$ but, owing to lack of sufficient internal consistency, cannot be used to sharpen our estimate [13].

The data for propane [5], while precise and internally consistent (see especially the linearity in Fig. 3) may be subject to systematic errors owing to the relatively high impurity level of 0.5% [13] and, close to T_c, owing to gravity effects (the cell being ~10 cm high). However, the samples were vigorously stirred which reduces the effects of gravity. Furthermore, neglecting the data for $t' < 10^{-3}$ *increases* the estimate for R_μ. Stirring also homogenizes the system which tends to reequilibrate the impurities; so our pseudo-single-component treatment may not be safe. Theoretical studies to check this issue, at least, semiquantitatively are planned.

How should the customary scaling description be modified to accommodate a Y-Y anomaly? A full thermodynamic description of a one-component fluid is provided by a relation $\Upsilon(p, \mu, T) = 0$. Near a critical point (p_c, μ_c, T_c), convenient dimensionless variables are t and

$$\check{p} = (p - p_c)/\rho_c k_B T_c, \quad \check{\mu} = (\mu - \mu_c)/k_B T_c\,. \tag{6}$$

Scaling then asserts that a reduced description

$$\Phi(\tilde{p}/|\tilde{t}|^{2-\alpha}; \tilde{\mu}/|\tilde{t}|^{2-\alpha-\beta}) \approx 0 \tag{7}$$

becomes valid (where the vanishing corrections to scaling require further arguments $|\tilde{t}|^\theta, |\tilde{t}|^{\theta_5}, \ldots$). Here $\tilde{p}$, $\tilde{\mu}$, and $\tilde{t}$ are *nonlinear scaling fields* which, neglecting terms beyond linear order, may be written

$$\tilde{p} = \check{p} - k_0 t - l_0 \check{\mu} + \cdots, \tag{8}$$

$$\begin{aligned} \tilde{\mu} &= \check{\mu} - k_1 t - j_2 \check{p} + \cdots, \\ \tilde{t} &= t - l_1 \check{\mu} - j_1 \check{p} + \cdots. \end{aligned} \tag{9}$$

The terms after $\check{p}$ in (8) generate the usual "smooth background" $p_0(\mu, T)$. The original scaling formulations included the coefficient $k_1 \propto (d\mu_\sigma/dT)_c$ in (9) but neglected j_1, j_2, and l_1. Studies of models required the introduction of $l_1 \neq 0$ [3] but $j_1 = j_2 \equiv 0$ was, implicitly, still accepted. However, for fluids this assumption

also is unjustifiable as seen explicitly in an exactly soluble "compressible cell gas" derived from the Ising model [15,16,4].

Now the full phase boundary is determined by $\tilde{\mu} = 0$. From (7)–(9) one hence finds [16]

$$p_\sigma(T) = p_c + p_1 t + A_p|t|^{2-\alpha} + p_2 t^2 + \cdots, \quad (10)$$

$$\mu_\sigma(T) = \mu_c + \mu_1 t + A_\mu|t|^{2-\alpha} + \mu_2 t^2 + \cdots, \quad (11)$$

with $\rho_c A_\mu = j_2 A_p$. Thus a Y-Y anomaly of strength $R_\mu = -j_2/(1 - j_2)$ arises provided that $j_2 \neq 0$. In addition, the coexistence curve diameter is given by [16]

$$\bar{\rho} = \rho_c[1 + \bar{b} j_2|t|^{2\beta} + \bar{a} l_1|t|^{1-\alpha} + c_1 t + \cdots] \quad (12)$$

so that a Y-Y anomaly *also* implies a leading correction $\sim|t|^{0.65}$, *dominating* the previously expected $\sim|t|^{0.89}$ correction [3]. Unfortunately, experimental resolution of the three corrections in (12) is unlikely to be feasible.

In conclusion, we have answered the question raised by Yang and Yang in 1964 by presenting strong evidence that the second derivative of $\mu_\sigma(T)$, the chemical potential on the vapor pressure curve, diverges like the specific heat $C_V(T)$ when T approaches the gas-liquid critical point from below. The appropriately scaled strength of the anomaly in propane is large: $R_\mu \simeq 0.56$. For CO_2 evidence suggests an anomaly of comparable magnitude but of opposite sign. Previous scaling descriptions must be extended by introducing the pressure p into the ordering field. More generally it is tempting to speculate that the magnitude of the anomaly is related to molecular shape and flexibility: The anomalies in, e.g., argon and helium, might well be significantly smaller. This idea is supported by simulations of the hard-core square-well fluid and by the exactly soluble compressible cell gas [15].

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[4] Furthermore, the exactly soluble one-dimensional continuum "cluster-interaction models," [M. E. Fisher and B. U. Felderhof, Ann. Phys. (N.Y.) **58**, 217 (1970), Secs. 8 and 9] although rather artificial, do display a divergence of $\mu''_\sigma(T)$ at criticality. But note [Y.-C. Kim (private communication)] that classical theory, because of its underlying analytic character, cannot provide hints regarding the existence or magnitude of the Yang-Yang anomaly.

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[10] See A. D. Bruce and N. B. Wilding, Phys. Rev. Lett. **68**, 193 (1992); used, e.g., by G. Orkoulas and A. Z. Panagiotopoulos, J. Chem. Phys. **110**, 1581 (1999).

[11] Note that $\tilde{C}_p(T)$ and $\tilde{C}_\mu(T)$ are *not* the usual isobaric and isopotential specific heats C_p and C_μ.

[12] A stronger divergence, say, $1/t'^{\psi}$ with $\psi > \alpha$, is not obviously excluded but seems improbable. If present it would dictate $R_\mu = -1$ in (4) [redefining $\tilde{A}_\mu$ appropriately in (3), etc.].

[13] See a detailed analysis by G. Orkoulas, M. E. Fisher, and C. Üstün (to be published). Dr. Abdulagatov kindly approved of the discards and corrections made to his data in [5]; [7].

[14] Uncertainties in the values of ρ_c and T_c, for which we accepted T_c^{Ab} [5], have relatively small effects.

[15] G. Orkoulas, M. E. Fisher, and A. Z. Panagiotopoulos (to be published).

[16] Details will be presented elsewhere.