

Yang–Yang Critical Anomaly[†]

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15.1 Background

Isochoric heat capacity, c_V , is a thermodynamic property of fluids and fluid mixtures with a variety of scientific applications. c_V is distinctly different from the commonly measured isobaric heat capacity, c_P , which is often used by engineers in process design calculations. On the one hand, c_V and c_P show similar behaviors as a function of temperature and pressure in the single-phase (liquid or vapor) region. On the other hand, only c_V is measurable inside the vapor + liquid coexistence region, while c_P is not a measurable property. In terms of a process explanation, with a pure substance in a calorimeter when P is held constant in the vapor + liquid coexistence region, then energy added by heating (ΔH) serves solely to evaporate liquid to the vapor phase without increasing the temperature of the sample ($\Delta T = 0$); thus, the apparent heat capacity $\approx (\Delta H / \Delta T)_P$ would have an indeterminate value. In this study, we will take advantage of c_V measurements that are made inside, outside and on the boundary of the vapor + liquid coexistence region. Careful measurements of

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c_V heat capacities close to this boundary have demonstrated a step change in magnitude, which can be exploited for this study as a sensitive indicator of the occurrence of a phase transition, and hence can be used to determine the phase transition temperature, T_S , at a fixed density, ρ . This approach is equally applicable at conditions near the gas–liquid critical point where many other methods fail to discern the phase change. Thus, even at the critical point, the discontinuity behavior of c_V at the phase transition point is pronounced (see Figures 15.1 to 15.3). Isochoric heat capacity is a property that is very sensitive to its treatment in terms of theory and modeling, since it is a measure of the average energy stored by molecules. Of special interest is the critical region where the structure changes are of enormous interest for the understanding and theoretical modeling of the molecular structure in materials. According to the thermodynamic definition, the isochoric heat capacity c_V is the first temperature derivative of the internal energy at constant volume,

$$c_V(T, V) = \left(\frac{\partial U}{\partial T} \right)_V, \quad (15.1)$$

where $U(V, T)$ is the internal energy. The residual internal energy, defined as the difference between that of the real fluid and the ideal gas, $U^r(V, T) = U(V, T) - U^0(V \rightarrow \infty, T)$, can be expressed in terms of the intermolecular potential $\phi(r)$ and the pair correlation function $g(r)$ as:

$$U^r(V, T) = \int g(r) \phi(r) dr. \quad (15.2)$$

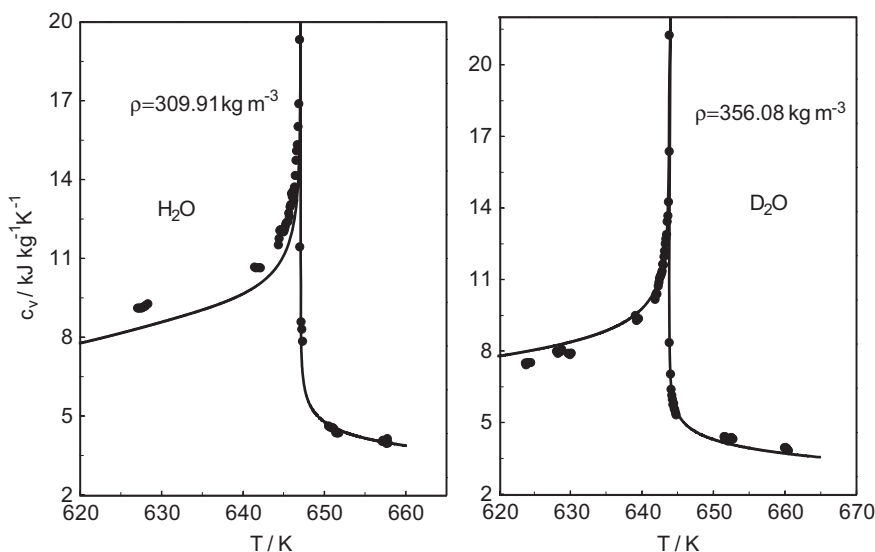


Figure 15.1 Measured and calculated isochoric heat capacities of *light* and *heavy* water along the near critical isochores. H_2O ^{81,84} and D_2O ^{28,33,82}; (—) crossover models.^{82,83}

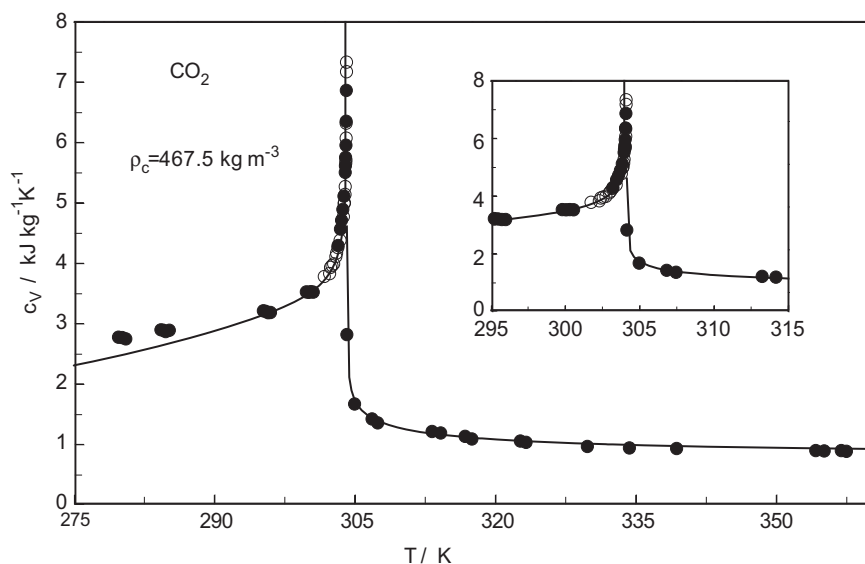


Figure 15.2 Measured and calculated isochoric heat capacities of carbon dioxide along the critical isochore. (—), crossover model;⁷⁴ ● Abdulagatov *et al.*^{34,76} and Amirkhanov *et al.*;^{77–79} ○ Adamov *et al.*⁸⁰

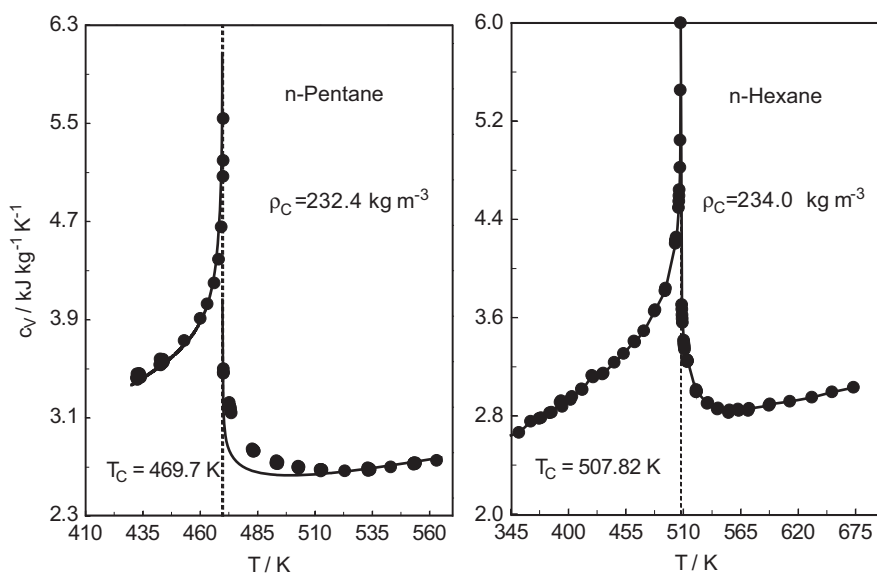


Figure 15.3 Measured and calculated isochoric heat capacities of *n*-pentane and *n*-hexane along each critical isochore (Amirkhanov *et al.*⁷¹); (—), crossover model.⁷²

For short-range intermolecular potentials, $\varphi(r)$ decays to zero in the region of r where the critical “tail” of the distribution function develops; therefore, $U^r(V, T)$ is determined by the short-range part of the radial distribution function $g(r)$. The theory of critical phenomena is primarily concerned with the long-range behavior of the total correlation function $h(r) = g(r) - 1$. In classical theory, the internal energy reflects the short-range behavior of $h(r)$ and has no critical anomalies, *i.e.*, along the critical isochore, c_V exhibits a finite jump upon crossing the critical temperature, $c_V = z_C(3a_0^2/u_0)R$, where $z_C = P_C/RT_C\rho_C$, $u_0 = 9$, and $a_0 = 6$. In non-classical theory,^{1–4} something subtle happens with the short-range behavior of $h(r)$, resulting in a weak anomaly ($c_V \propto t^{-\alpha}$), where α is the universal critical exponent of c_V and $t = (T - T_C)/T_C$ is a measure of deviation from the critical temperature T_C . Therefore, the short-range structure of $g(r)$ and $h(r)$ must be such that this weak anomaly in the derivative property is generated, *i.e.*, along the critical isochore, c_V exhibits an infinite jump upon crossing the critical temperature (see Figure 15.4). The internal energy along the critical isochore as a function of temperature exhibits a scaling type behavior,⁵ $U(\rho_C, T) \propto t^{1-\alpha}$, *i.e.*, the internal energy remains finite at the critical point, but its first temperature derivative diverges weakly like the isochoric heat capacity, $(\partial U/\partial T)_V \propto t^{-\alpha}$ (see Figure 15.5). Since the isothermal compressibility K_T diverges at the

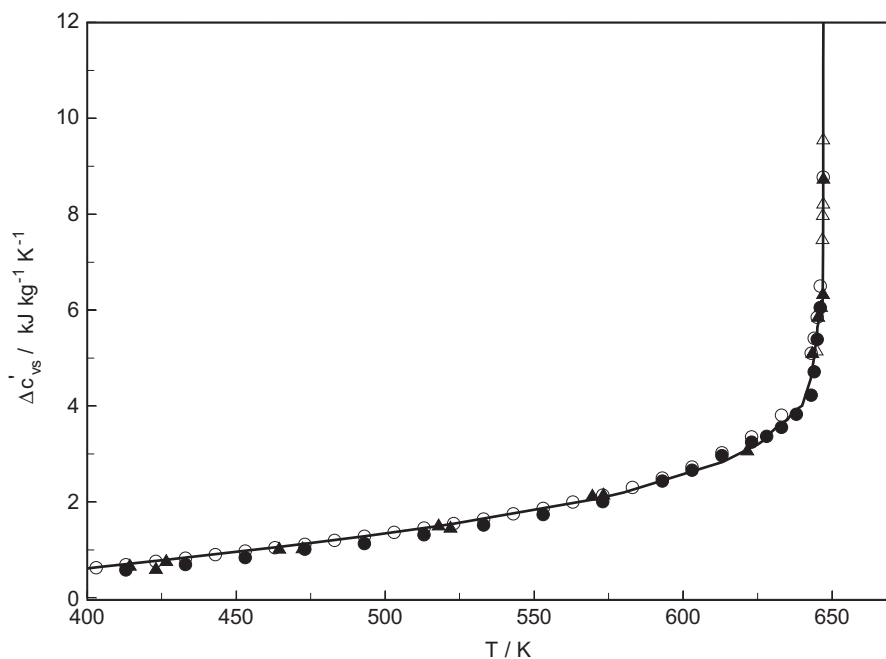


Figure 15.4 Experimental isochoric heat capacity jumps ($\Delta c'_{vs}$) for light water as a function of temperature near the critical point. $\blacktriangle$ Abdulgatov *et al.*;⁷⁴ $\bullet$ Kerimov;⁸⁶ $\circ$ Amirkhanov *et al.*;⁸⁴ Δ Abdulgatov *et al.*;⁸¹ $\times$ Polikhronidi *et al.*;⁷⁶ (—) IAPWS.⁵⁸

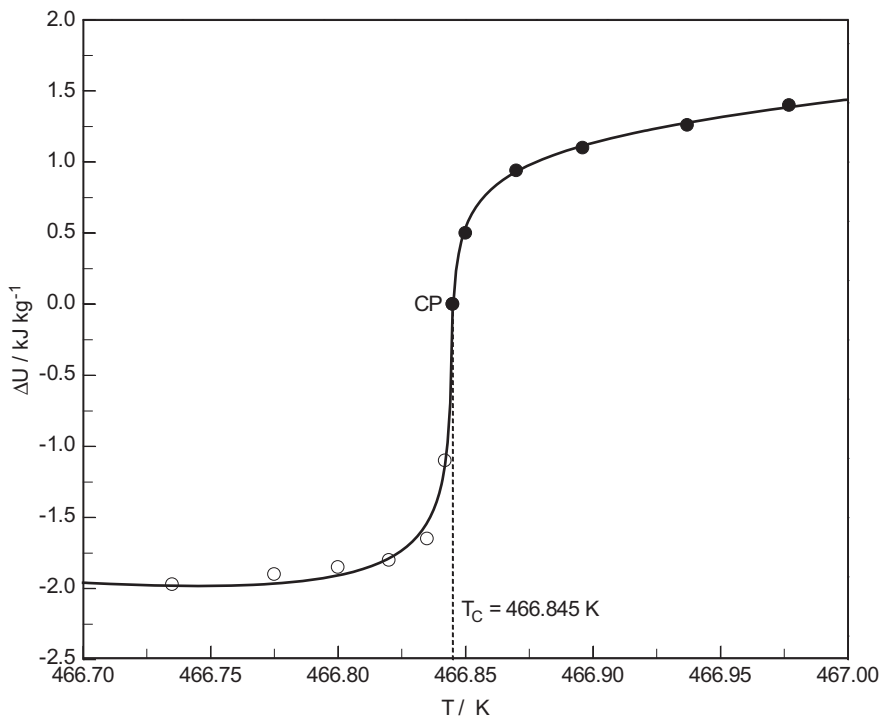


Figure 15.5 Internal energy of diethyl ether along the critical isochore,⁵ $\Delta U(\rho_C, T)$, near the critical point. Solid curve is the scaling equation.

critical point and is related to the correlation function as $RT\rho K_T = 1 + \rho \int h(r) dr$, the integral of $h(r)$ must diverge at this point, so that $h(r)$ becomes long-ranged both in the classical and non-classical cases. In classical Ornstein-Zernike theory, $h(r)$ decays as r^{-1} at the critical point. Away from this point, $h(r)$ decays as $h(r) \approx \exp(-r/\xi)/r$, where r is large and the decay parameter ξ is finite. The decay parameter ξ , which is a function of temperature and density, is the correlation length. At the critical point the correlation length diverges to infinity according to the simple scaling power law $\xi = \xi_0 t^{-\nu}$ (at $\rho = \rho_C$), where $\nu = \gamma/2$ is the universal critical exponent, and ξ_0 is on the order of molecular dimensions, typically ≈ 0.1 nm to 0.3 nm for small molecules. When the critical point is approached, the large values of ξ shows the existence of large clusters in the near-critical region. Thus, this physical effect in the critical region causes the critical anomaly of c_V .

15.2 Isochoric Heat Capacity and Liquid-Gas Asymmetry

Accurate isochoric heat capacity experiments near the critical point for pure fluids are needed to confirm the conclusions and physical bases of a

Complete Scaling Theory of critical phenomena.^{6,7} As established by careful measurements, the coexistence curve diameter, $\rho_d = (\rho'_s + \rho''_s)/2\rho_c$, where a single-prime mark denotes the saturated liquid and a double-prime mark denotes the saturated vapor, exhibits strong curvature in the immediate vicinity of the critical point. This means that measured rectilinear diameter data exhibit some deviations from a straight line (rectilinear behavior) in the temperature range for which $t < 10^{-2}$. According to renormalization group theory⁸ of liquid–gas critical phenomena, the first temperature derivative of the coexistence-curve diameter, $(d\rho_d/dT)$, diverges as the isochoric heat capacity^{9–12} $t^{-\alpha}$. The current theory of complete scaling^{6,7,13,14} predicts a “ 2β ” anomaly of the singular diameter of the coexistence curve, $(d\rho_d/dT) \propto t^{2\beta-1}$, *i.e.*, according to the complete scaling theory,^{6,7,13,14} densities of the liquid–gas coexistence curve can be represented by:

$$\Delta\rho = \pm B_0 t^\beta \pm B_1 t^{\beta+\Delta} + B_2 t^{1-\alpha} - B_3 t + B_4 t^{2\beta}, \quad (15.3)$$

where $B_i (i=0,4)$ are the adjustable system-dependent critical amplitudes. In eqn (15.3), $\pm B_0 t^\beta$ is the asymptotic (symmetric) term, $\pm B_1 t^{\beta+\Delta}$ is the non-asymptotic (symmetric Wegner’s correction) term, $B_2 t^{1-\alpha}$ is the *singular diameter* (the first non-analytical contribution to the liquid–gas asymmetry predicted by *incomplete* scaling), $B_4 t^{2\beta}$ is the new (second) non-analytical contribution of the liquid–gas asymmetry (new complete scaling term), and $B_3 t$ is the *rectilinear diameter*. According to definition,^{6,7} the Yang–Yang anomaly strength parameter defines the contribution of the chemical potential, $(d^2\mu/dT^2)$, to the measured two-phase isochoric heat capacity, c_{V2} , singularity at the critical point (details are in Section 15.4). The effect of the Yang–Yang anomaly strength parameter, $R_{\mu 0} = A_\mu/(A_\mu + A_P)$, on the coexistence curve diameter is given by:^{6,7,13,14}

$$\rho_d = 1 + (B_2 t^{1-\alpha} - B_3 t + B_4 t^{2\beta}), \quad (15.4)$$

Where the complete scaling asymmetry parameter $B_4 \propto A_\mu/A_P$, and where A_μ and A_P are the asymptotic critical amplitudes of $(d^2\mu/dT^2) \propto A_\mu t^{-\alpha}$ and $(d^2P_s/dT^2) \propto A_P t^{-\alpha}$ which diverge at the critical point. A Yang–Yang anomaly implies a leading correction, $\rho_d \propto B_4 t^{2\beta}$, (complete theory correction) would dominate the previously expected $\rho_d \propto B_2 t^{1-\alpha}$ correction (incomplete theory correction). Therefore, the first temperature derivative of the coexistence-curve diameter diverges as the isochoric heat capacity $(d\rho_d/dT) \propto t^{-\alpha}$ and as $(d\rho_d/dT) \propto t^{2\beta-1}$ ($2\beta - 1 \approx -0.352$), *i.e.*, the divergence of the liquid–gas coexistence curve diameter is shared between the two terms, incomplete $B_2 t^{1-\alpha}$ and complete $B_4 t^{2\beta}$ scaling terms. As was discussed in earlier work,^{15,16} the coefficients $\bar{A}_0^-$, $\bar{B}_{cr}$, B_2 , and B_3 in eqn (15.3)–(15.5) are not independent. We then present the relation:

$$\frac{c_{V2}}{k_B} = \bar{A}_0^- t^{-\alpha} (1 + \bar{A}_1^- t^\Delta) - \frac{\bar{B}_{cr}}{k_B}, \quad (15.5)$$

where k_B is Boltzmann's constant. As shown previously,^{6,7} the first non-asymptotic asymmetric coexistence curve complete scaling parameter B_2 and rectilinear parameter B_3 are directly related to the two-phase isochoric heat capacity asymptotic critical amplitude $\bar{A}_0^-$ and fluctuation induced "critical background" parameter $\bar{B}_{cr}$, respectively, in eqn (15.5). In our previous publications¹⁷⁻²⁰ (see also Anisimov and Wang^{15,16}), the measured two-phase c_{V2} results along the critical isochore were used to estimate the values of the asymptotic critical amplitude $\bar{A}_0^-$ and "critical background" parameter $\bar{B}_{cr}$ in eqn (15.5). The values of the coexistence curve parameters (B_2 , B_3 , and B_4 , in eqn (15.3) are related to the isochoric heat capacity critical amplitudes [$\bar{A}_0^-$ and $\bar{B}_{cr}$ in eqn (15.5)] as in the following:¹⁶

$$B_3 = -b_2 \frac{\bar{B}_{cr}}{k_B}, \quad B_4 = \frac{a_3}{1+a_3} B_0^2, \quad (15.6)$$

Therefore, according to the complete scaling theory the coexistence curve diameter [eqn (15.4)] $B_2 = -b_2 \frac{\bar{A}_0^-}{(1-\alpha)}$ can be represented as:¹⁶

$$\rho_d - 1 = \frac{a_3}{1+a_3} B_0^2 t^{2\beta} - b_2 \left[\frac{\bar{A}_0^-}{(1-\alpha)} t^{1-\alpha} - \frac{\bar{B}_{cr}}{k_B} t \right], \quad (15.7)$$

where a_3 is the pressure mixing coefficient (complete scaling term), *i.e.*, the scaling field h_1 is a linear combination of physical field variables^{6,7} ΔT , ΔP , and $\Delta\mu$:

$$h_1 = a_1 \Delta\mu + a_2 \Delta T + a_3 \Delta P, \quad (15.8)$$

while b_2 is the temperature mixing coefficient (incomplete scaling term), *i.e.*, the scaling field h_2 is a linear combination of physical field variables^{6,7} ΔT , ΔP , and $\Delta\mu$:

$$h_2 = b_1 \Delta\mu + b_2 \Delta T + b_3 \Delta P. \quad (15.9)$$

The pressure (a_3 , complete scaling) and temperature (b_2 , incomplete scaling) mixing coefficients are system dependent asymmetry coefficients, which are determined by the details of intermolecular interactions.¹⁶ Therefore, $R_{\mu 0} \neq 0$ for real fluids, if $a_3 \neq 0$. For previous incomplete scaling models, $a_3 = 0$, $R_{\mu 0} = 0$. In general, the singular liquid-gas coexistence curve diameter [eqn (15.7)] contains only two adjustable parameters a_3 and b_2 . Both saturated densities (ρ'_S and ρ''_S) and two-phase isochoric heat capacity (c_{V2}) measurements together provide very useful information about the qualitative behavior of the liquid-gas coexistence curve shape near the critical point. This information is very important to interpret the coexistence curve diameter singularity, the nature of the asymmetry of the coexistence curve,

and to precisely evaluate the Yang–Yang anomaly strength parameter, $R_{\mu 0}$. Thus, simultaneous measurements of two-phase c_{v2} and saturated liquid (ρ'_S) and vapor (ρ''_S) densities are sufficient to completely determine the values of the Yang–Yang anomaly parameter $R_{\mu 0}$ through the asymmetric coefficient of the coexistence curve [eqn (15.3)] or singular diameter [eqn (15.7)]. The critical amplitudes of the coexistence curve diameter (complete scaling term, B_4) and asymptotic coexistence curve amplitude (B_0) are related to the Yang–Yang anomaly strength as $R_{\mu 0} = a_3/(a_1 + a_3)$ or $R_{\mu 0} = B_4/B_0^2$,^{6,7} where $a_1 \approx 1$. As one can see from eqn (15.3) and (15.7), the pressure mixing coefficient a_3 (asymmetric coefficient of the complete scaling theory) can be directly determined experimentally in a calorimetric experiment by measuring both sides of the coexistence curve (saturated-liquid ρ'_S and saturated-vapor ρ''_S densities) near the critical point and two-phase c_{v2} along the critical isochore ($\bar{A}_0^-$ and $\bar{B}_{cr}$). Eqn (15.3) together with restrictions [eqn (15.6)] (*i.e.*, at fixed values of $\bar{A}_0^-$ and $\bar{B}_{cr}$) was applied to the saturated-liquid and saturated-vapor density (T_S, ρ'_S, ρ''_S) data derived from calorimetric experiments^{17–20} for several molecular liquids, as was demonstrated by Wang and Anisimov.^{15,16} Both asymmetry coefficients (a_3 and b_2) for various fluids show different signs. The sign of the asymmetric coefficients plays a very important role in determination of the qualitative behavior of the shape of the top of the coexistence curve and singular diameter behavior [eqn (15.7)]. For example, if $a_3 > 0$ (positive) and $b_2 < 0$ (negative), the contribution of both asymmetric coefficients to the singular diameter is positive and ρ_d shifts to the high density side (liquid side), while if $a_3 < 0$ (negative) and $b_2 > 0$ (positive), ρ_d shifts to the low density side (vapor side), and finally if both coefficients have the same sign, then the contribution of the asymmetric terms (complete and incomplete terms) compensate each other and the diameter behaves as “rectilinear” $\left(\text{classical behavior, } \rho_d = 1 + b_2 \frac{B_{cr}}{k_B} t \right)$.

The same positive values of both asymmetric parameters $a_3 > 0$ and $b_2 > 0$ of the coexistence curve diameter were found for (*n*-pentane, *n*-heptane, SF₆, and R-113),¹⁶ methanol,²¹ 1-propanol,²² *n*-butanol,¹⁹ and diethyl ether.²³ This means that for these fluids, the two non-analytical contributions ($t^{1-\alpha}$ and $t^{2\beta}$) in eqn (15.7) compensate each other, thereby producing an imitation of a rectilinear diameter,¹⁶ where complete scaling term is positive, $\frac{a_3}{1+a_3} B_0^2 t^{2\beta} > 0$, while the incomplete scaling term is negative, $-b_2 \frac{A_0^-}{(1-\alpha)} t^{1-\alpha} < 0$. This compensation can explain why the coexistence curve diameter observed for some fluids (especially liquid metals) can be quite close to rectilinear,^{24,25} depending on the magnitude of the amplitudes of these terms. The opposite results, *i.e.*, the negative ($a_3 < 0$) contribution of the complete scaling term, $t^{2\beta}$, and positive ($b_2 < 0$) contribution of the incomplete scaling term, $t^{1-\alpha}$, was found for (neon, methane, nitrogen, ethane),¹⁶ *tert*-butanol,¹⁷ *sec*-butanol,²⁰ and hard-core square-well fluids.^{13,14} In this case also, the asymmetric terms in ρ_d compensate each other and

their contributions depend on the magnitudes of their amplitudes. For some fluids (ethane, water),¹⁶ ethanol,²⁶ isobutanol,¹⁸ RPM, and HCSW theory fluids,^{13,14} the value of the asymmetric coefficient of the complete scaling a_3 is positive, but very small (<0.1), while the incomplete scaling asymmetric coefficient is negative, $b_2 < 0$. This means that the singularity of the ρ_d is determined by the incomplete scaling term $t^{1-\alpha}$. The negative value of the Yang–Yang anomaly strength $R_{\mu 0}$ was found previously for CO_2 (-0.4),^{6,7} Ne (-0.018), CH_4 (-0.024), N_2 (-0.018), C_2H_4 (-0.0035),¹² *tert*-butanol (-0.036),¹³ and *sec*-butanol (-0.52).²⁰ Numerical MC simulation^{13,14} of the hard-core square-well fluid also indicates that $R_{\mu 0}$ has a small absolute value and a negative sign. Thus, in previous publications the value of $R_{\mu 0}$ for various fluids was evaluated by using saturated liquid and vapor density data (or singular diameter data) to determine the asymmetric coefficient a_3 as^{15,16} $R_{\mu 0} = a_3/(1 + a_3)$ or, by using the asymptotic amplitudes (A_μ and A_p) of $(d^2 P_S/dT^2)$ and $(d^2 \mu/dT^2)$, derived from two-phase isochoric heat capacity measurements. Classical equations of state (lattice gas, cubic EOS, van der Waals, Redlich–Kwong, Peng–Robinson) predict positive values for asymmetric parameters from 0 to 0.493 for a_3 and from 0 to 0.089 for b_2 . Thus, depending on the physico-chemical nature of fluids and the nature of their intermolecular interactions, the sign of the asymmetry coefficients of fluids is different and their effect on coexistence curve and singular diameter behavior near the critical point is also different.

Recently Cerdeiriña *et al.*²⁷ studied the Yang–Yang anomaly by using the compressible cell gas (CCG) model that obeys complete scaling with pressure mixing. They found that when the discrete local CCG cell volumes fluctuate freely the Yang–Yang anomaly parameter $R_{\mu 0}$ may take any value between $-\infty$ and 0.5. As we discuss in Section 15.5, our calorimetric (two-phase c_{V2}) measurements near the critical point clearly confirm the prediction of the theory proposed by Cerdeiriña *et al.*²⁷ As was mentioned by Cerdeiriña *et al.*²⁷ theory does provide some guidance, but the absolute value, the physical meaning, magnitude or even the sign of the $R_{\mu 0}$ are not firmly established. For the time being, we must rely on the best values from accurate experimental measurements.

Both properties c_{V2} , and (ρ'_S, ρ''_S) which are used to evaluate the Yang–Yang anomaly property ($R_{\mu 0}$) and the nature of the liquid–gas coexistence curve asymmetry ρ_d can be simultaneously measured by applying the quasi-static thermogram technique while conducting experiments with an adiabatic calorimeter.^{28–57} Some selected results of the two-phase liquid and vapor isochoric heat capacities (c'_{V2}, c''_{V2}) measurements at saturation are shown in Figures 15.6 and 15.10.

It is well known^{59,60} that the isochoric heat capacity jump Δc_V diverges at the critical point as $\Delta c_V \propto (T - T_c)^{-\alpha}$ (see also our experimental results^{17–45} and Figure 15.4), where $\alpha = 0.11$ is the universal critical exponent. The quasi-static thermogram technique based on isochoric heat capacity jumps is suitable to precisely determine the phase boundary properties (shape of

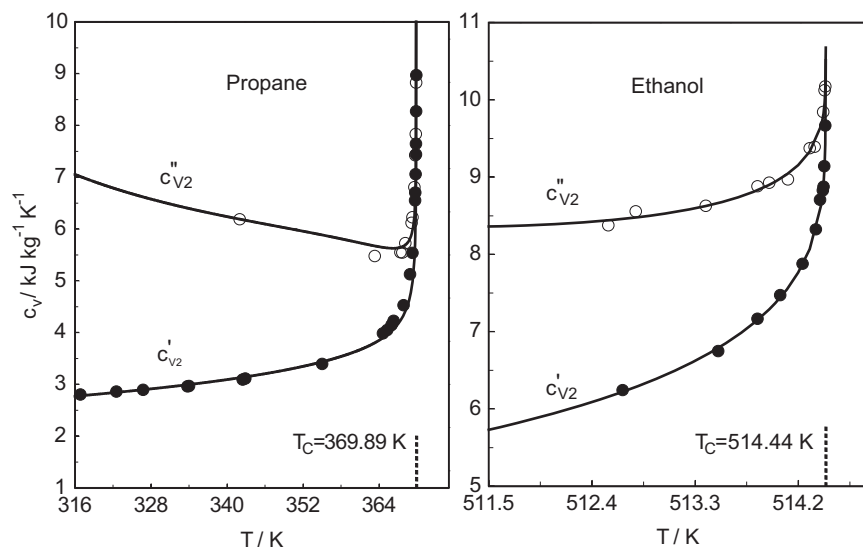


Figure 15.6 Measured and calculated two-phase liquid (c'_{V2}) and vapor (c''_{V2}) isochoric heat capacities of propane (left) and ethanol (right) at saturation as a function of temperature near the critical point. Left: $\circ$ (vapor) and $\bullet$ (liquid) Abdulagatov *et al.*,^{36–38} (—), crossover model Kiselev and Rainwater.⁷⁴ Right: $\circ$ (vapor) and $\bullet$ (liquid) Polikhronidi *et al.*,²⁶ (—), crossover model Kiselev *et al.*⁷⁰

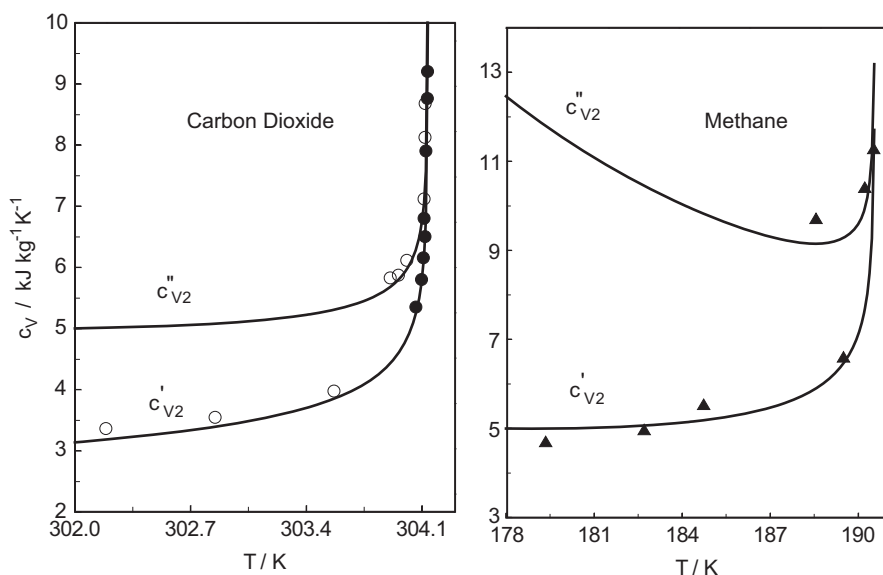


Figure 15.7 Measured and calculated two-phase liquid (c'_{V2}) and vapor (c''_{V2}) isochoric heat capacities of carbon dioxide (left) and methane (right) at saturation as a function of temperature near the critical point. Left: $\bullet$ Abdulagatov *et al.*,^{34,76} $\circ$ Amirkhanov *et al.*,^{77–79} Right: $\blacktriangle$ Anisimov *et al.*,⁸⁷ (—), crossover model Kiselev and Rainwater.⁷⁴

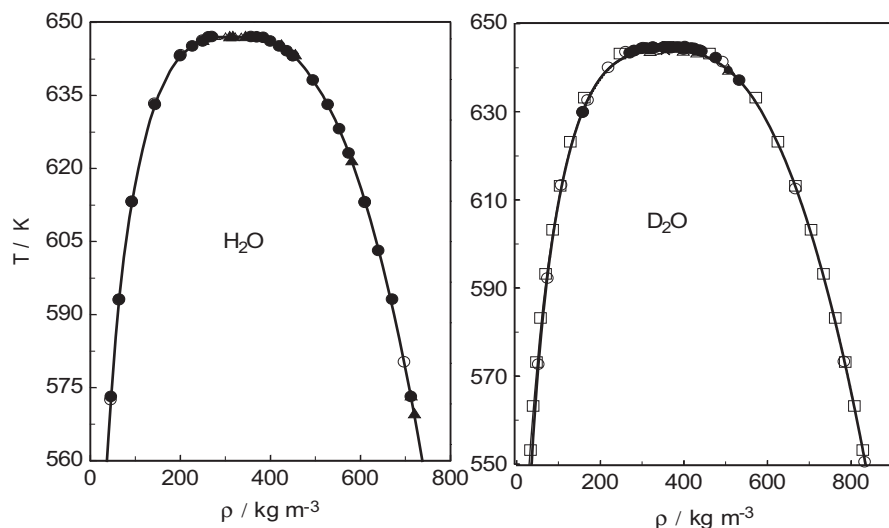


Figure 15.8 Saturated liquid–gas densities of light (left) and heavy water (right) derived from isochoric heat capacity measurements (quasi-static thermograms method) together with the data reported by other author's and calculated from equations of state.^{75,88} The solid lines are calculated from the crossover models.^{82,83} Right: ○ Mursalov *et al.*;³³ ● and △ Polikhronidi *et al.*;^{28,40} □ Hebert *et al.*⁸⁹ Left: ▲ Abdulagatov *et al.*;⁸¹ △ Abdulagatov *et al.*;⁸⁴ ● Amirkhanov *et al.*;⁹⁰ ■ Kerimov.⁸⁶

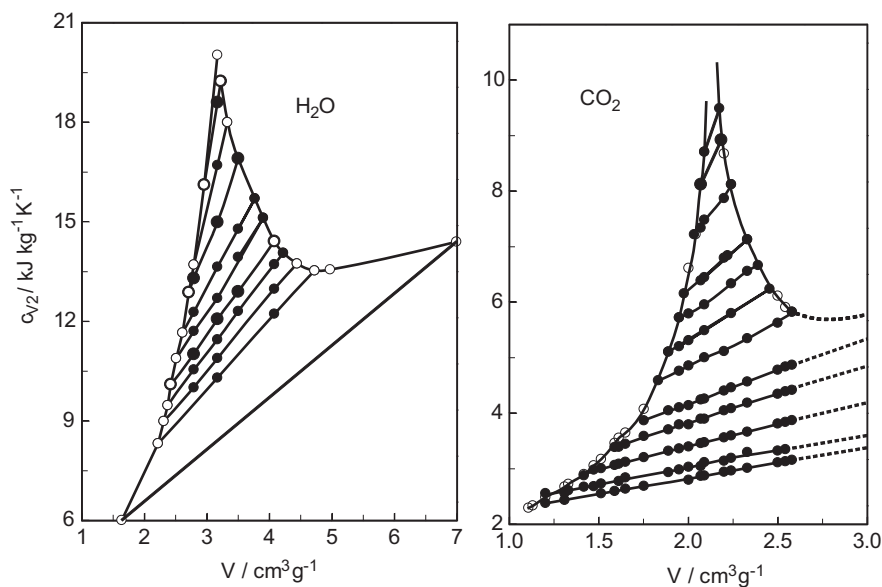


Figure 15.9 Measured two-phase isochoric heat capacities of light water⁹⁰ (left) and carbon dioxide^{77–79} (right) as a function of specific volume along the various near-critical isotherms. ● two-phase along the various isotherms; ○ two-phase liquid and vapor c_{V2} at saturation.

the top of the coexistence curve and the critical parameters) in the critical region. In contrast to the more commonly used method of observing a meniscus disappearance, our electronic sensors are in close contact with the fluid, and are not limited by the phenomenon of critical opalescence which makes visual observation of a meniscus increasingly difficult as the critical point is approached. Further, the quasi-static thermogram technique allows us to observe other types of phase transitions (L–L, L–S, L–V, S–V) occurring in the system, even weak phase transition phenomena. This technique was successfully used by Voronel *et al.*^{61–64} However, a key difference from the method used by Voronel *et al.*^{61–64} is that we supplement quasi-static thermograms with recorded readings of the adiabatic control sensor. Our combination of the quasi-static thermogram method and adiabatic control ensures sufficient information on the changes in the sample's thermodynamic state (for example, presence of any temperature gradient in the volume of the sample) in different places (in the middle and near the inner surface) of the calorimetric vessel. Thus, using this method the phase diagram of the fluids and fluid mixtures near the critical point can be constructed by measuring the phase transition temperatures and pressures and their variation with density. Examples from our previous measurements are shown in Figures 15.8 to 15.11.

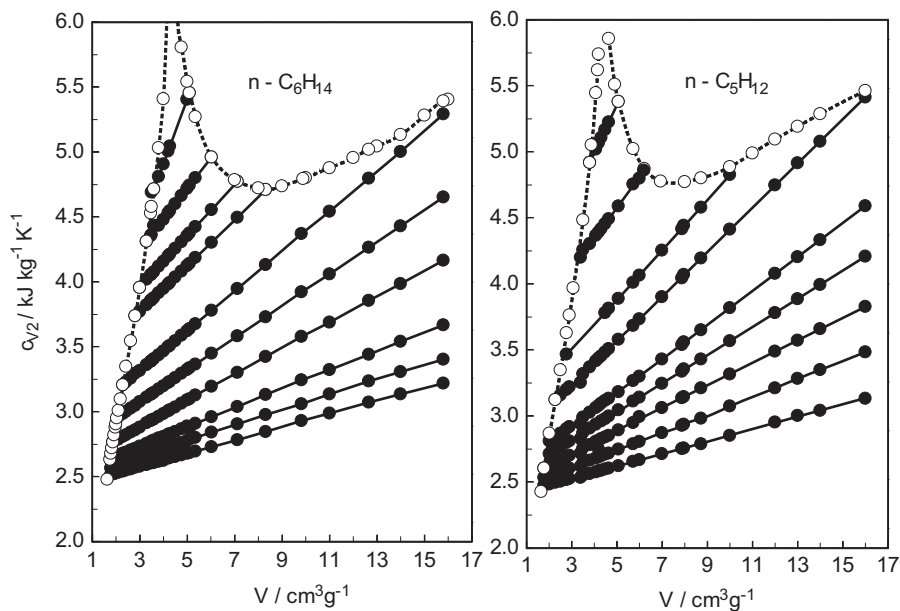


Figure 15.10 Measured two-phase isochoric heat capacities of n -pentane (right) and n -hexane (left) as a function of specific volume along the various near-critical isotherms.⁷¹ $\bullet$ values of c_{v2} along the various isotherms; $\circ$ values of liquid and vapor c_{v2} at the saturation curve.

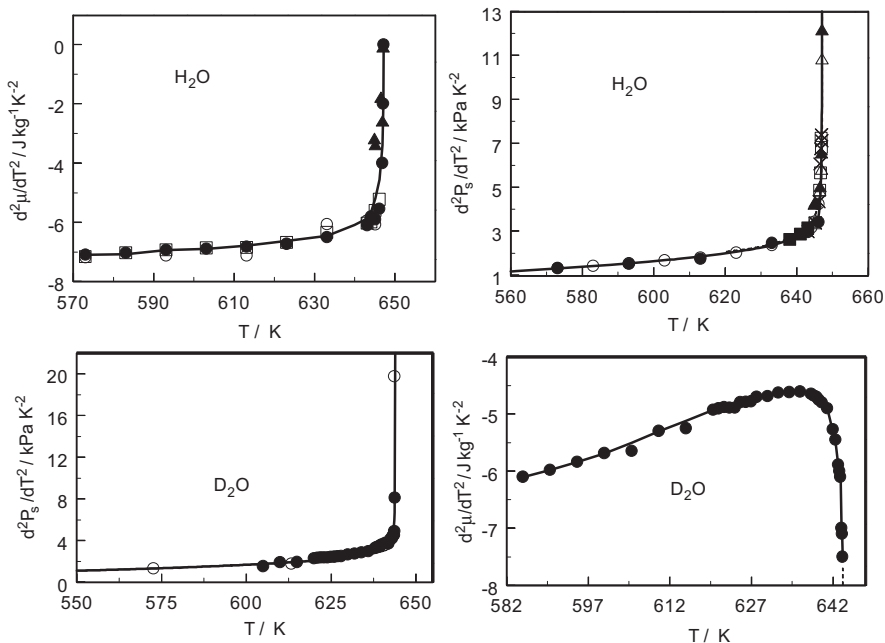


Figure 15.11 Second temperature derivatives of chemical potential and vapor pressure of light and heavy water derived from two-phase isochoric heat capacities and specific volume measurements at saturation using relation (15.12). H_2O : ● Amirkhanov *et al.*,⁹⁰ ○ Kerimov;⁸⁶ ▲ Abdulagatov *et al.*,⁸¹ △ Abdulagatov *et al.*,⁸⁴ × Levelt Semgers;⁷ D_2O : ● Polikhronidi *et al.*,^{28,40} ○ Mursalov *et al.*,³³ solid line is calculated from crossover model.^{82,83}

15.3 Yang–Yang Critical Anomaly Strength and Distinct Two-phase Isochoric Heat Capacity Contributions near the Liquid–Gas Critical Point

As was shown above, the technique of the simultaneous measurements of the phase transition parameters and isochoric heat capacity at saturation near the critical point are providing reliable and thermodynamically consistent data (T_s , ρ'_s , ρ''_s , c'_{V1} , c''_{V1} , c'_{V2} , c''_{V2}) at saturation, which can be used for interpretation of the complete scaling theory results for the Yang–Yang anomaly strength. According to the Yang–Yang relation⁶⁵ for liquid-vapor phase coexistence, the temperature dependence of the total measured two-phase isochoric heat capacity c_{V2} of pure fluids near the critical point can be presented as a sum of two distinct contributions:

$$c_{V2} = -T \frac{d^2\mu}{dT^2} + T \frac{d^2P_s}{dT^2} V, \quad (15.10)$$

or

$$c_{v2} = c_{v\mu} + c_{vp}, \quad (15.11)$$

where $c_{vp} = V_C T \frac{d^2 P_S}{dT^2}$ is the vapor pressure and $c_{v\mu} = -T \frac{d^2 \mu}{dT^2}$ is the chemical potential contributions to the total measured two-phase isochoric heat capacity c_{v2} along the critical isochore; V is the specific volume. An accurate determination of the contributions of the distinct heat capacities, c_{vp} and $c_{v\mu}$, is very important for correct interpretations of the experimental observed singularity of c_{v2} and the physical nature of the coexistence curve asymmetry near the critical point, and therefore, also for the Yang–Yang parameter. According to eqn (15.10), two-phase c_{v2} is a linear function of specific volume V along each fixed temperature (isotherm). Therefore, the slopes of two-phase ($c_{v2} - V$) isotherms are directly related to the values of the second temperature derivative of the vapor pressure, $T(d^2 P_S/dT^2)$, while the intercepts for $V=0$ are related to the second temperature derivative of the chemical potential $-T(d^2 \mu/dT^2)$. Rapid increases of the slopes of $c_{v2} - V$ isotherms,^{17–21,28–31,33–44} (see also Figures 15.9 and 15.10) as the critical temperature (isotherm) is approached is the result of increasing of the second temperature derivative, $(d^2 P_S/dT^2)$.

Since the Yang–Yang relation [eqn (15.10)] is valid at any specific volumes V from saturated liquid specific volume V' to saturated vapor specific volume V'' ($V' \leq V \leq V''$), the following relations can be derived for the second temperature derivatives of the vapor pressure and chemical potential:

$$\frac{d^2 P_S}{dT^2} = \frac{c'_{v2} - c'_{v2}}{T(V'' - V')} \quad \text{and} \quad \frac{d^2 \mu}{dT^2} = \frac{V'' c'_{v2} - V' c'_{v2}}{T(V' - V'')}, \quad (15.12)$$

where c'_{v2} , c''_{v2} are the two-phase liquid and vapor isochoric heat capacities at saturation, respectively, V'' and V' are the specific vapor and liquid volumes at saturation, μ is the chemical potential, and P_S is the vapor pressure. Simultaneously measured in our previous publications,^{28–45} thermodynamic quantities (T_S , V' , V'' , c'_{v2} , c''_{v2}) at saturation on the right-hand sides of eqn (15.12), can be used to directly calculate the temperature derivatives $(d^2 P_S/dT^2)$ and $(d^2 \mu/dT^2)$ from the calorimetric experimental data. As an example, some results for $(d^2 P_S/dT^2)$ and $(d^2 \mu/dT^2)$ for very well studied pure fluids such as carbon dioxide, water, *n*-alkanes, and some alcohols, from our direct measured values of (T_S , V' , V'' , c'_{v2} , c''_{v2}), as a function of temperature are shown in Figures 15.11 to 15.15 together with the values calculated by twice differentiating the vapor-pressure correlations, $P_S(T)$. Thus, we can quantitatively estimate the contributions of both $(d^2 P_S/dT^2)$ and $(d^2 \mu/dT^2)$ terms to the singularity of the two-phase isochoric heat capacity c_{v2} near the critical point [eqn (15.10)] As Figures 15.11 to 15.15 demonstrate, the values of $(d^2 P_S/dT^2)$ derived from the measured two-phase c_{v2} are rapidly increasing (or diverging) upon approaching the critical point. It is established that the

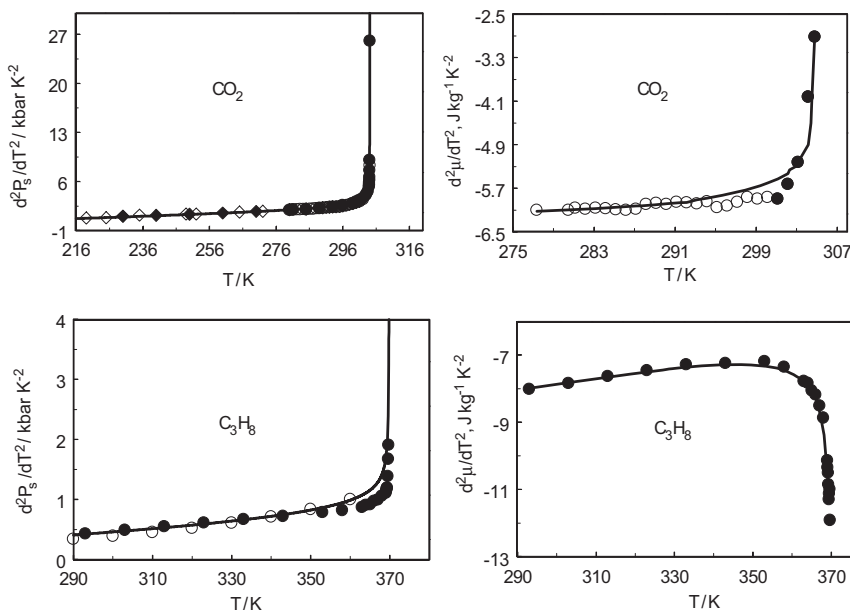


Figure 15.12 Second temperature derivatives of vapor pressure of carbon dioxide and propane derived from two-phase isochoric heat capacities and specific volume measurements at saturation using relation (15.12). CO_2 : ● Abdulgatov *et al.*^{34,76} and Amirkhanov *et al.*;^{77–79} ○ Gaddy and White;⁹¹ ◆ Magee and Ely;⁹² ◇ Adamov *et al.*;⁸⁰ (—) crossover model.⁷⁴ C_3H_8 : ● Abdulgatov *et al.*;^{36–38} ○ Anisimov *et al.*;⁷³ (—) calculated from the correlation by Lemmon and Goodwin.⁸⁵

asymptotic critical behavior of real fluids can be characterized in terms of the same physical variables as that of the lattice gas. This assumption implies that, below T_C , the second derivative of the pressure with respect to temperature should asymptotically diverge like the isochoric heat capacity c_V , as a simple scaling power law $(d^2P_s/dT^2) \propto t^{-\alpha}$, while the second derivative of the chemical potential $(d^2\mu/dT^2)$ should remain finite (referred to as *incomplete* scaling theory^{9,66,67}) at the critical point.⁹⁴ The validity of this assumption^{6,7} has been questioned, on the basis of an analysis of experimental two-phase c_V data, given in terms of the Yang–Yang relation, [eqn (15.10)].

Kostrowicka Wyczalkowska *et al.*⁹⁴ have studied the effect of the presence of a small amount of an impurity and the effect of other nonasymptotic deviations from lattice-gas symmetry which would lead to a considerable change in the slope of two-phase $c_{V2} - V$ isotherms and at the same time, changes in (d^2P_s/dT^2) and $(d^2\mu/dT^2)$ behaviors. When corrections for a small amount of an impurity are applied and an allowance is made for the leading asymmetric Wegner correction, the experimental c_V data are not inconsistent with previous treatments in which the second derivative of the chemical

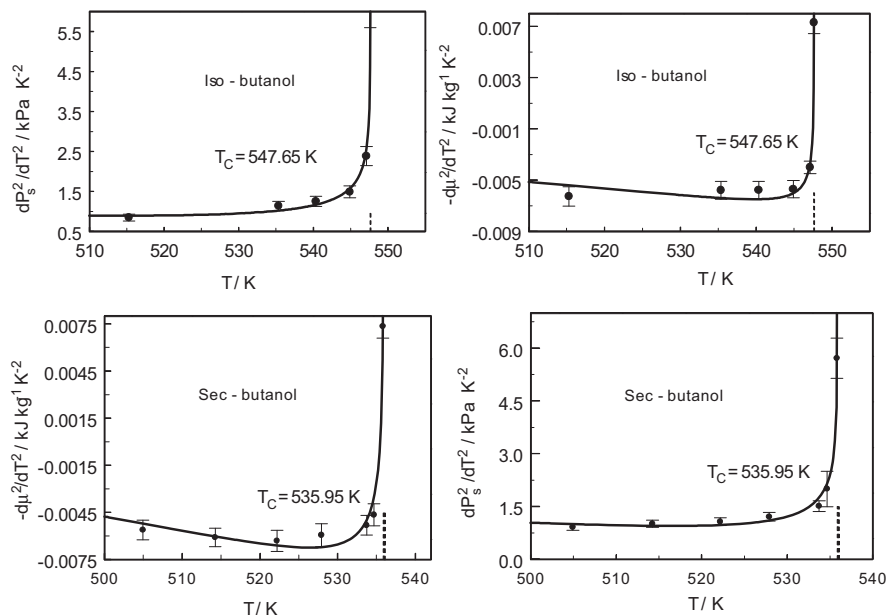


Figure 15.13 Second temperature derivatives of vapor pressure and chemical potential of *iso*-butanol and *sec*-butanol derived from two-phase isochoric heat capacities and specific volume measurements^{18,20} at saturation using relation (15.12).

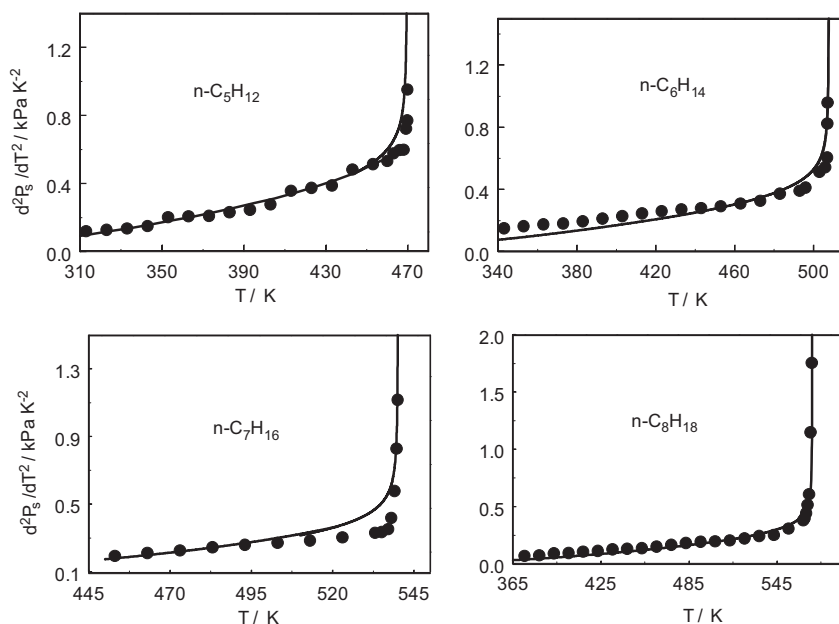


Figure 15.14 Second temperature derivatives of vapor pressure of some selected *n*-alkanes derived from two-phase isochoric heat capacities and specific volume measurements⁷¹ at saturation using relation (15.12). (—) calculated from the correlation by Lemmon and Goodwin.⁸⁵

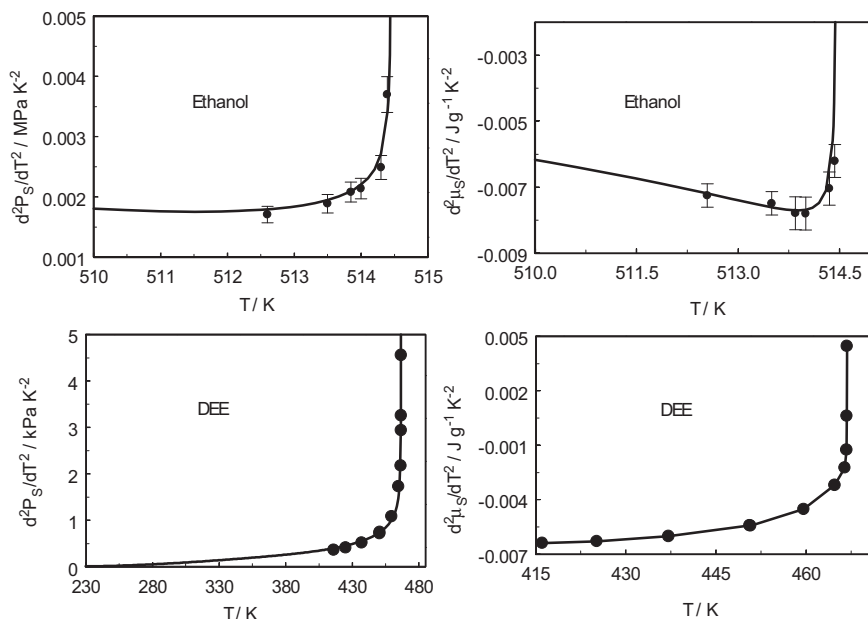


Figure 15.15 Second temperature derivatives of vapor pressure and chemical potential of ethanol²⁶ and diethyl ether²³ derived from two-phase isochoric heat capacities and specific volume measurements at saturation using relation (15.12). Ethanol: solid lines are calculated from crossover model of Kiselev *et al.*⁷⁰

potential would exhibit a cusp-like singularity with a finite limiting value at the critical temperature.⁹⁴

We have observed from experiments that the actual behavior of the ($d^2\mu/dT^2$) near the critical point is complicated. As one can see from Figures 15.11 to 15.15, the values of ($d^2\mu/dT^2$) that were derived from measured two-phase c_{V2} and saturation specific volumes also diverge (in most cases, to negative values). Thus, the experimentally observed singularity of the c_{V2} is shared between the simultaneous singularities of (d^2P_S/dT^2) and ($d^2\mu/dT^2$). *Incomplete* scaling theory^{9,66,67} predicts finite values of ($d^2\mu/dT^2$) at the critical point, that $\mu(T)$ is an analytic function of temperature, *i.e.*, the singularity of c_{V2} at the critical point would be completely caused by the divergence of c_{VP} , *i.e.*, (d^2P_S/dT^2). This is the result of the gas-liquid symmetry of the coexistence curve. The derived values of (d^2P_S/dT^2) and ($d^2\mu/dT^2$) can be used to quantitatively estimate the contributions of the both terms (chemical potential and vapor pressure parts) in the Yang-Yang relation [eqn (15.10)] to the singularity of the experimentally observed total two-phase c_{V2} near the critical point. The distinct heat capacity c_{V2} contributions, (c_{VP} and $c_{V\mu}$) terms can be separated and extracted from the measured total two-phase isochoric heat capacity near the critical point using the Yang-Yang equation [eqn (15.10)]. Accurate measurements

of the specific volume dependence of the total c_{v2} for various near critical isotherms allow us to correctly estimate the contribution of the vapor-pressure c_{vP} and chemical potential $c_{v\mu}$ parts using the Yang–Yang relation [eqn (15.10)] and understand the microscopic physical nature of the heat capacity singularity near the critical point. Extending these concepts to mixtures, Wang *et al.*⁹⁵ have generalized the *complete* scaling theory for binary mixtures, *i.e.*, the principle of isomorphism has been reformulated in terms of complete scaling.

15.4 New Method for Evaluation of the Yang–Yang Anomaly Parameter from Direct Measurements of Two-phase Isochoric Heat Capacity and Saturated Liquid and Vapor Density

Experimentally^{17–21,28–31,33–41} and theoretically^{1–3} it is well known^{4,59} that c_{v2} , the left side of the Yang–Yang equation [eqn (15.10)], diverges at the critical point as a simple scaling power law, $c_{v2} \propto t^{-\alpha}$, therefore, the right-hand side of eqn (15.1) should also diverge as $\propto t^{-\alpha}$. The question naturally arises of what are the contributions of $(d^2\mu/dT^2)$ and (d^2P_S/dT^2) to the c_{v2} singularity near the critical point. As the experiment data shows (see Figures 15.11 to 15.15), both $(d^2\mu/dT^2)$ and (d^2P_S/dT^2) are sharing the singularity of experimentally observing behavior of c_{v2} , *i.e.*, the singularity of c_{v2} can be caused by the divergence of (d^2P_S/dT^2) or $(d^2\mu/dT^2)$, or both of them. As one can see from Figures 15.11 to 15.15, the singularity of c_{v2} for most studied fluids is caused by the positive divergence of (d^2P_S/dT^2) and positive or negative divergences of $(d^2\mu/dT^2)$. For quantitative estimation of the contribution of (d^2P_S/dT^2) and $(d^2\mu/dT^2)$ to the singularity of c_{v2} the Yang–Yang anomaly strength parameter $R_{\mu0}$ (Yang–Yang anomaly in fluid criticality) concept^{6,7} can be used. The Yang–Yang anomaly strength parameter was first introduced by Fisher and co-authors.^{6,7,13,14} Previous incomplete scaling theory was extended by Fisher and Orkoulas⁶ and Orkoulas *et al.*,⁷ by introducing the pressure into the ordering scaling field h_1 [see eqn (15.8)].

According to the definition,^{6,7} the Yang–Yang anomaly strength parameter $R_{\mu0}$ defined as:

$$R_{\mu0} = A_{\mu}/(A_{\mu} + A_P), \quad (15.13)$$

where A_{μ} and A_P are the asymptotic critical amplitudes of the power law for $-T(d^2\mu/dT^2) \approx A_{\mu}t^{-\alpha}$ and $TV_C(d^2P_S/dT^2) \approx A_Pt^{-\alpha}$. This method was used in our previous publications^{17,18,20,21,23} to estimate the value of the Yang–Yang anomaly strength parameter, $R_{\mu0}$. Correct determination of the asymptotical critical amplitudes, A_{μ} and A_P , caused by the fluctuation (fluctuation contribution) using the experimental c_{v2} data, are very difficult (see, for example, Perkins *et al.*⁶⁸) due to contribution of the regular part caused by fluctuation. As was mentioned above, the value of the Yang–Yang anomaly strength

parameter, $R_{\mu 0}$, can also be estimated through the coexistence curve diameter asymmetry coefficient⁷ a_3 as $R_{\mu 0} = a_3/(1 + a_3)$ or $R_{\mu 0} = B_4/B_0^2$. According to the definition, it is apparent that if $R_{\mu 0} = 0$ ($a_3 = 0$), then $A_\mu = 0$, and the divergence of the c_{V2} is caused by the divergence of $T(d^2P_S/dT^2)$ only, while $-T(d^2\mu/dT^2)$ remains finite, as incomplete scaling predicts.^{9,66,67} If $R_\mu \neq 0$, therefore, $A_\mu \neq 0$ ($a_3 \neq 0$), and the singularity of the c_{V2} in eqn (15.10) is caused by divergence of both or just by $-T(d^2\mu/dT^2)$, *i.e.*, the divergence of c_{V2} is shared between both terms, $TV_C(d^2P_S/dT^2)$ and $-T(d^2\mu/dT^2)$. Derived in a calorimetric experiment, values of saturated liquid (ρ'_S) and vapor (ρ''_S) densities together with c_{V2} measurements along the critical isochore can be used to accurately determine a thermodynamically consistent asymmetric parameter a_3 , and therefore the value of $R_{\mu 0}$ (see, for example, Anisimov and Wang^{15,16} and our previous works^{17,18,20}).

Recently⁵⁷ we have proposed a new technique to accurately evaluate the Yang–Yang strength parameter from direct measurements of (V' , V'' , c'_{V2} , c''_{V2}) at the saturation curve near the critical point. In order to estimate the contribution of the chemical potential to the experimentally observed two-phase c_{V2} at any temperatures, the Yang–Yang anomaly function:

$$R_\mu(T) = \frac{c_{V\mu}(T)}{c_{VP}(T) + c_{V\mu}(T)}, \quad (15.14)$$

can be introduced. It is apparent that the value of the Yang–Yang anomaly function at the critical point is the Yang–Yang anomaly parameter, $R_\mu(T=T_C) = R_{\mu 0}$ or $R_{\mu 0} \equiv \lim_{T \rightarrow T_C} R_\mu(T)$, initially introduced by Fisher and co-authors.^{6,7} Therefore, the Yang–Yang anomaly function defines the contribution of the chemical potential to a measured c_{V2} value at any temperatures, while the Yang–Yang anomaly parameter is defined as the contribution of chemical potential to the c_{V2} singularity at the critical temperature. We used our previous^{17–21,28–31,33–44} measurements of (c'_{V2} , c''_{V2}) and specific volumes (V' , V'') at saturation to calculate the Yang–Yang anomaly strength function (or Yang–Yang anomaly parameter $R_{\mu 0}$). Using eqn (15.14) for $R_{\mu 0}(T)$ and eqn (15.12) for temperature derivatives (d^2P_S/dT^2) and ($d^2\mu/dT^2$), we can calculate R_μ from the directly measured values of (c'_{V2} , c''_{V2} , V' , V'') as:

$$R_\mu = \frac{V''c'_{V2} - V'c''_{V2}}{c'_{V2}(V'' - V_C) - c''_{V2}(V' - V_C)}. \quad (15.15)$$

The relation (15.5) can be used to interpret the physical meaning of the Yang–Yang anomaly function or parameter. As one can see from eqn (15.5), the value of R_μ is completely determined from the measured values of liquid (c'_{V2}) and vapor (c''_{V2}) two-phase isochoric heat capacities and specific volumes (V' , V'') at saturation, *i.e.*, some combination of the calorimetric (c'_{V2} , c''_{V2}) and volumetric (V' , V'') properties along the liquid–gas coexistence curve. It is obvious that in Anisimov's^{15,16} approach $R_{\mu 0}$ also was determined

using the asymptotic critical amplitude ($\bar{A}_0, \bar{B}_{cr}$) of two-phase c_{v2} and coexistence curve asymmetric parameter (a_3) (see above eqn (15.5) to (15.7)). Actually, in our case in eqn (15.10) and (15.12) we can use (or replace) one of the specific volumes (V'' or V') with the critical isochore V_C as a reference (isochore) curve. Then, the relation (15.5) is simplified as:

$$R_\mu = \frac{V_C c'_{v2} - V' c_{v2}^{cr}}{-c_{v2}^{cr}(V' - V_C)}, \quad (15.16)$$

where c_{v2}^{cr} is the isochoric heat capacity along the critical isochore defined from eqn (15.5). Now it is clear that eqn (15.16) completely defined R_μ through the two-phase isochoric heat capacities along the critical isochore (c_{v2}^{cr}) and along the liquid side of the coexistence curve (c'_{v2}) and liquid side of the coexistence curve ($V' - V_C$) behavior. Thus, we note from eqn (15.5) and (15.16), the values of R_μ directly related with the asymmetry factor, *i.e.* with the ratio of the differences ($V' - V_C$) and ($V'' - V_C$) at the coexistence curve near the liquid–gas critical point, $k = (V'' - V_C)/(V_C - V')$ ($k \geq 1$, asymmetry factor). In the simple case when $k = 1$ (no asymmetry of the coexistence curve), the Yang–Yang anomaly function or parameter is defined as:

$$R_\mu^{sym} = 2 \frac{V_C}{(V_C - V')} \frac{c'_{v2}}{(c'_{v2} + c''_{v2})} - \frac{V'}{V_C - V'}. \quad (15.17)$$

In this case the value of R_μ^{sym} calculated from eqn (15.17) diverges to large positive values. Therefore, the asymmetry of the liquid–gas coexistence curve (singular diameter behavior near the critical point) depends on a combination of the (c'_{v2}, c''_{v2}) and (V', V'') temperature behaviors near the critical point. The same conclusion was made by Anisimov and Wang,^{15,16} *i.e.*, the coexistence curve asymmetry parameters (a_3 and b_2) are related to the critical amplitude ($\bar{A}_0$) of the two-phase c_{v2} along the critical isochore. Since $c'_{v2}, c''_{v2}, V', V''$ in eqn (15.5) are functions of temperature, R_μ depends on temperature, which means that the contribution of the chemical potential part of the total two-phase c_{v2} [eqn (15.10)] changes with temperature.

As can be noted, the denominator of the relation (15.5) always is positive, because $(V'' - V_C) > 0$, $(V' - V_C) < 0$, $c''_{v2} > c'_{v2}$, and $V'' > V'$. Therefore, relation (15.5), for the Yang–Yang anomaly strength function, $R_\mu(T)$, can lead to various different sequences, depending on the sign and magnitude of the numerator, $(V'' c'_{v2} - V' c''_{v2})$:

- (1) If $V'' c'_{v2} > V' c''_{v2}$ at the critical point, the Yang–Yang anomaly strength parameter is positive, $R_{\mu 0} > 0$, or if $V' c'_{v2} < V' c''_{v2}$, negative, $R_{\mu 0} < 0$. Since at the critical point $V'' = V' = V_C$, the positive value of $R_{\mu 0}$ can be derived if $c''_{v2} < c'_{v2}$. However, as was mentioned above, always $c''_{v2} > c'_{v2}$ at any temperature. Therefore, $R_{\mu 0}$ is always negative. As will be

shown below, our calorimetric experiment confirms the negative trend ($R_\mu \rightarrow -\infty$) of R_μ near the critical point. In other words, the amplitude of $V''c'_{V2} - V'c''_{V2}$ near the critical point diverges greater than $V''c'_{V2}$;

- (2) If $V''c'_{V2} - V'c''_{V2} = 0$ or $V''c'_{V2} = V'c''_{V2}$, the value of $R_{\mu0}$ is zero and the contribution of the chemical potential to the singularity of c_{V2} is zero and the singularity of c_{V2} is completely caused by (d^2P_S/dT^2) (*incomplete* scaling);
- (3) If $V_C(c''_{V2} - c'_{V2}) \equiv 0$ or $c''_{V2} \cong c'_{V2}$, the magnitude $R_{\mu0}$ is close to 1 and the contribution of the vapor pressure to the singularity of c_{V2} is very small and completely caused by the singularity of $(d^2\mu/dT^2)$. This means that two-phase c_{V2} is independent of specific volume, and the vapor pressure of the fluid is zero. This case is realized for ionic liquids near ambient temperature with vanishingly small vapor pressure, and;⁶⁹
- (4) If $(V''c'_{V2} - V'c''_{V2}) = 0.5 [(V''c'_{V2} - V'c''_{V2}) + V_C(c''_{V2} - c'_{V2})]$, or $V_C(c''_{V2} - c'_{V2}) = (V''c'_{V2} - V'c''_{V2})$, both chemical potential and vapor pressure contributions are equal, *i.e.*, the singularity of c_{V2} is equally shared between both derivatives.

Thus, the sign of the combination, $(V''c'_{V2} - V'c''_{V2})$, of the measured coexistence curve properties (V'', V') and (c''_{V2}, c'_{V2}) , is defining the sign of the Yang–Yang anomaly strength function R_μ . The sign and magnitude of R_μ strongly depend (very sensitively) on the relation between the specific volumes (V'', V') or densities (ρ'', ρ') at the saturation and two-phase saturated heat capacities (c''_{V2}, c'_{V2}) and their relative changes with temperature in the immediate vicinity of the critical point. Now the physical meaning of the Yang–Yang anomaly strength parameter is very clear, namely, $R_{\mu0}$ is the parameter characterizing the deformation (variation) of the coexistence curve shape (asymmetry) when approaching the critical point, which is a very sensitive parameter to the asymmetry of the coexistence curve. Also, it is obvious that $R_{\mu0}$ strongly depends on how fast (V'', V') and (c''_{V2}, c'_{V2}) change when the critical temperature is approached, $T \rightarrow T_C$. If the liquid side (V') of the coexistence curve approaches the critical point faster than the vapor side (V''), then the value of $R_{\mu0}$ is negative (or $a_3 < 0$), otherwise it is positive. In other words, if the rate of change of the saturated liquid volume V' is higher than the rate of change of the saturated vapor volume V'' , which means that $V''c'_{V2} < V'c''_{V2}$, *i.e.*, singular diameter shift to the left side, *i.e.*, $R_{\mu0}$ is negative. According to the above discussion, in our calorimetric experiments we observed values of $R_{\mu0}$ that are negative for most substances. Previous studies^{6,7,15–20} on different substances have reported either positive or negative finite values of $R_{\mu0}$. Thus, the relation (15.5) defines a new technique of determining the Yang–Yang anomaly strength parameter from direct simultaneous measurements of the saturation properties $(c'_{V2}, c''_{V2}, V', V'')$ near the critical point. Below we provide the result of application of the method to our previously

reported isochoric heat capacity (c'_{V2}, c'_{V2}) and specific volumes (v', v'') measurements at saturation near the critical point.

In our previous publications^{17–21,28–45} which report experimental data, we have reported two-phase isochoric heat capacities (c'_{V2}, c'_{V2}) and liquid and vapor specific volumes (v'', v'), or density (ρ'', ρ'), data at saturation for various pure fluids (*n*-alkanes, alcohols, light and heavy water, nitrogen tetroxide, carbon dioxide, diethyl ether, *etc.*) in the vicinity of the critical point. Selected results are depicted in Figures 6 to 8. These data ($c'_{V2}, c'_{V2}, v', v''$) were used to directly estimate the value of the Yang–Yang anomaly strength function (R_μ) for some selected molecular fluids by using eqn (15.5). The results are depicted in Figures 15.16 to 15.19. As one can see from Figures 15.16 to 15.19, experimental values of the Yang–Yang anomaly function R_μ show a trend to negative values when the temperature approaches the critical point. Indeed, if we examine the asymptotic behaviors of all the measured thermodynamic quantities ($c'_{V2}, c'_{V2}, v', v''$) in eqn (15.15) for the Yang–Yang function R_μ they will follow well-known and simple asymptotic power laws,^{4,59} namely $c'_{V2} \propto A'_0 t^{-\alpha}$, $c'_{V2} \propto A''_0 t^{-\alpha}$, $v' \propto V_C(1 - B_0 t^\beta)^{-1}$, and $v'' \propto V_C(1 - B_0 t^\beta)^{-1}$. In these expressions, A'_0 and A''_0

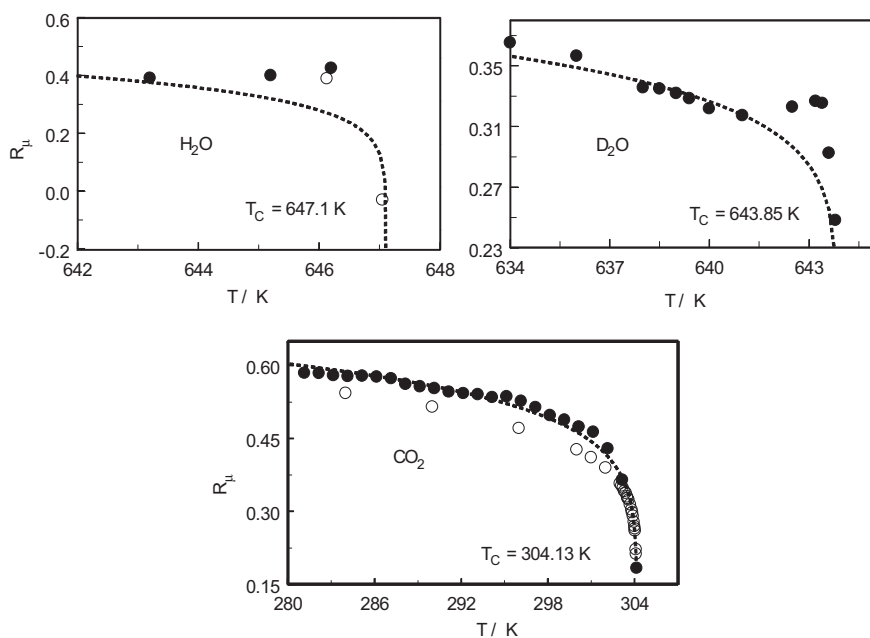


Figure 15.16 Temperature dependence of the Yang–Yang anomaly strength function, $R_\mu(T)$, derived from our direct calorimetric measurements [eqn (15.15)] for light and heavy water and carbon dioxide. ● Amirkhanov *et al.*;⁹⁰ ○ Abdulagatov *et al.*;^{81,84} D₂O: ● Polikhronidi *et al.*;^{28,40} and Mursalov *et al.*;³³ CO₂: ○ Adamov *et al.*;⁸⁰ ● Abdulagatov *et al.*^{34,76} and Amirkhanov *et al.*^{77–79} The dashed lines are calculated from eqn (15.19).

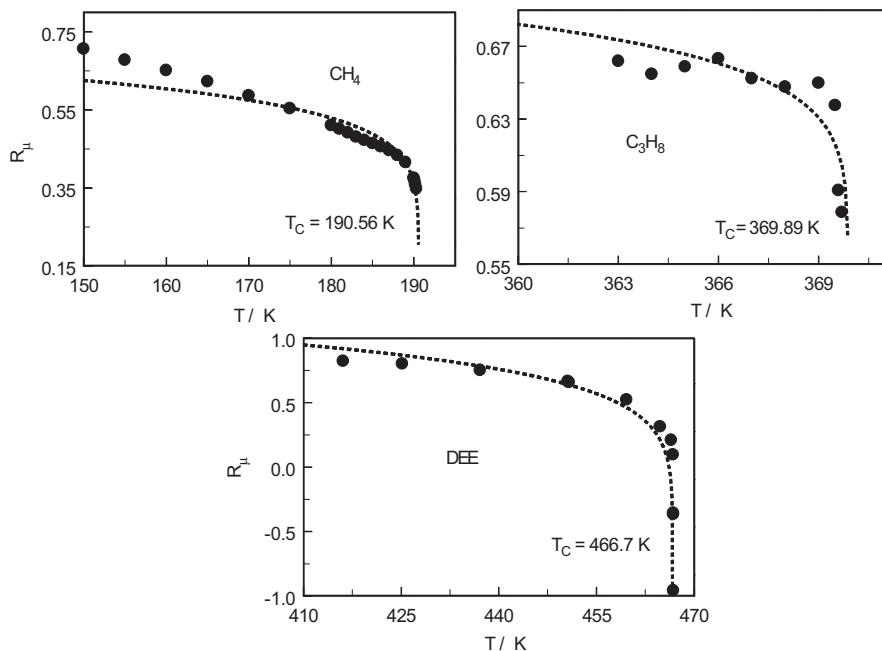


Figure 15.17 Temperature dependence of the Yang-Yang anomaly strength function, $R_\mu(T)$, derived from our direct calorimetric measurements [eqn (15.15)] for methane, propane, and diethyl ether (DEE). CH_4 : ● Anisimov *et al.*;⁸⁷ C_3H_8 : ● Abdulagatov *et al.*;^{36–38} DEE: ● Polikhronidi *et al.*²³ The dashed lines are calculated from eqn (15.19).

are the asymptotical critical amplitudes of two-phase c_{V2} along the liquid and vapor saturation curves, respectively; B_0 is the amplitude of the asymptotic (symmetric) term of the coexistence curve; and $\alpha = 0.109$, $\beta = 0.324$ are the universal asymptotic critical exponents of heat capacity and saturated liquid and gas density, respectively. Thus, the amplitude of the asymptotic scaling behavior of the Yang-Yang anomaly function from eqn (15.5) is proportional to:

$$R_\mu \propto \frac{1}{B_0} \left(\frac{A'_0 - A''_0}{A'_0 + A''_0} \right) \quad \text{or} \quad R_\mu \propto \frac{1}{B_0} \left(\frac{A'_0 - \bar{A}_0^-}{A'_0 + \bar{A}_0^-} \right) \quad (15.18)$$

It follows from eqn (15.18) that the sign of the singularity depends on the difference between the critical amplitudes of the two-phase liquid and vapor heat capacities, *i.e.*, $(A'_0 - A''_0)$ or $(A'_0 - \bar{A}_0^-)$, where $\bar{A}_0^-$ is the critical amplitude of two-phase c_{V2} along the critical isochore [eqn (15.5)]. It is well-known from direct experimental c'_{V2} and c''_{V2} measurements (see, for example Figures 15.6 to 15.7), that $A''_0 > A'_0$ or $\bar{A}_0^- > A'_0$ (meaning that c''_{V2} is always

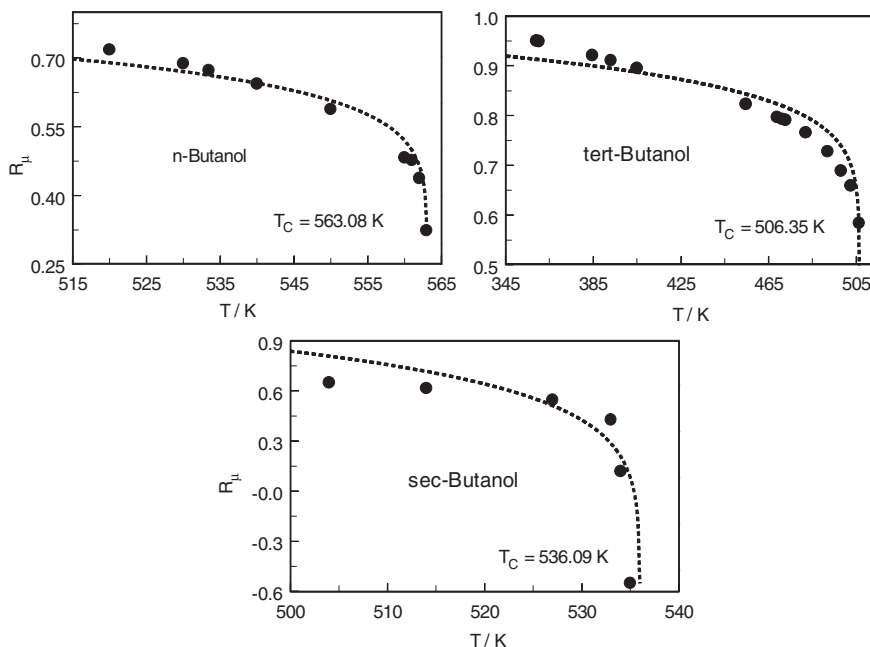


Figure 15.18 Yang–Yang anomaly strength function, $R_\mu(T)$, of alcohols derived from direct two-phase isochoric heat capacity and specific volume measurements^{17–19} at saturation. The dashed lines are calculated from eqn (15.19).

greater than c'_{v2}); therefore, $R_\mu < 0$ (would have a negative sign) at the critical temperature. A recent theoretical study by Cerdeiriña *et al.*²⁷ has contributed a fresh understanding. They studied the Yang–Yang anomaly by using a compressible cell gas (CCG) model that obeys *complete* scaling with pressure mixing. They found that when the discrete local CCG cell volumes fluctuate freely, the Yang–Yang anomaly parameter may take any value between $-\infty$ and $+0.5$. Thus, our calorimetric measurements confirm the prediction of the theory proposed by Cerdeiriña *et al.*²⁷ In the standard lattice gas (SLgas) model, chemical potential would be an analytic function of temperature $\mu(T)$. This is the result of the gas–liquid symmetry of the coexistence curve. Thus, for the SLgas model $R_\mu \equiv 0$. As Cerdeiriña *et al.*²⁷ have pointed out, the exact values of R_μ , their physical meaning, their magnitude and even their sign are still not fully understood. However, experimental results depicted in Figures 15.16 to 15.19 clearly demonstrate that the Yang–Yang anomaly strength R_μ is a strong function of temperature in the immediate vicinity of the critical point, *i.e.*, R_μ changes sharply as the critical temperature is approached. It is also clear that the amplitude, $R_{\mu 0} = \frac{1}{B_0} \left(\frac{A'_0 - A''_0}{A'_0 + A''_0} \right)$, of R_μ is

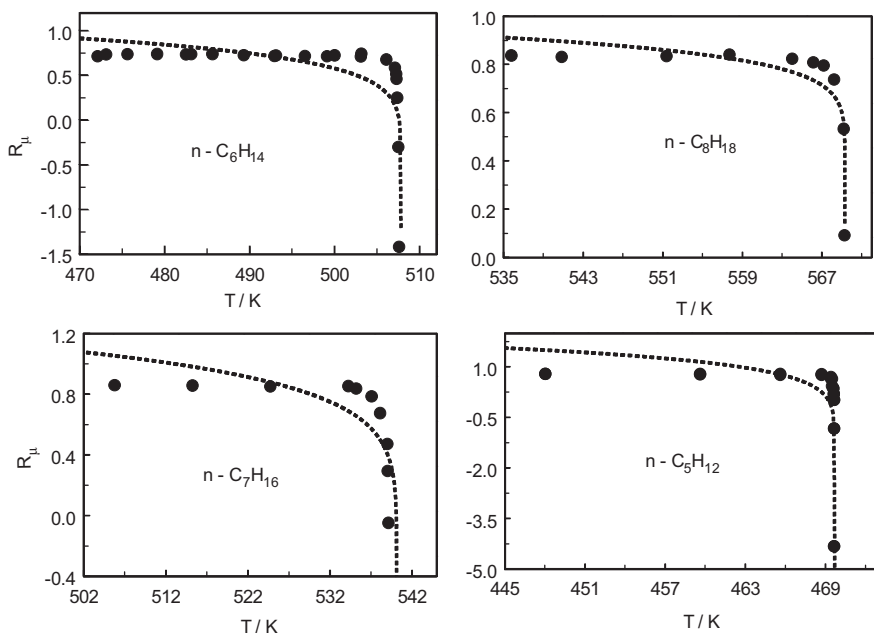


Figure 15.19 Temperature dependence of the Yang-Yang anomaly strength function, $R_\mu(T)$, derived from direct calorimetric measurements [eqn (15.15)] for various n -alkanes.⁷¹ The dashed lines are calculated from eqn (15.19).

an individual parameter for each molecular fluid like other critical amplitudes ($\bar{A}_0^-$, B_0 , for example) and always has a negative sign. Our calorimetric measurements (see Figures 15.16 to 15.19) clearly illustrate that R_μ tends to a negative value as $T \rightarrow T_C$. While it isn't possible to conclude, based solely on experimental measurements in Figures 15.16 to 15.19, that R_μ becomes infinite at the critical point, we observe that the trend of the R_μ behavior confirms large negative values at T_C . The experimentally observed (Figures 15.16 to 15.19) behavior of R_μ as a function of temperature can be represented by the *complete* scaling prediction, which is:⁹³

$$R_\mu(T) = R_\mu(T_C) + C_\mu t^\alpha, \quad (15.19)$$

where C_μ is a system-dependent amplitude. At the critical point $R_\mu(T) = R_\mu(T_C)$. In the present work, we analyzed experimental R_μ data for several molecular fluids using eqn (15.19). The results are given in Table 15.1. As shown in Table 15.1, the values of the Yang-Yang parameter $R_\mu(T_C)$ for various molecular fluids vary in the range of -8 to 0.46 , which is consistent with the theory.²⁷

Table 15.1 Values of the fitting parameters of the eqn (15.19) for selected fluids calculated from the derived Yang–Yang function.

Fluid	Yang–Yang parameter/ $R_\mu(T_C)$	C_μ
Argon	−0.0536	0.6085
Carbon dioxide	−0.1967	1.0548
Light water	−0.3727	1.3071
Heavy water	0.0503	0.4826
Methane	−0.3287	1.2347
Propane	0.4598	0.3299
<i>n</i> -Pentane	−2.8535	6.0848
<i>n</i> -Hexane	−1.2109	2.8205
<i>n</i> -Heptane	−1.0297	2.8134
<i>n</i> -Octane	0.1371	1.0521
Toluene	−8.0909	14.912
Nitrogen tetroxide	−1.9090	3.7753
<i>n</i> -Butanol	0.0134	0.8952
<i>iso</i> -Butanol	−1.0802	2.5761
<i>tert</i> -Butanol	0.2675	0.7388
<i>sec</i> -Butanol	−1.4766	3.1079
DEE	−1.4437	3.0097

15.5 Conclusions

A new technique was proposed to evaluate two distinct contributions to measured c_{V2} values (vapor pressure, c_{VP} , and chemical potential, $c_{V\mu}$) to the measured total two-phase isochoric heat capacity, by using the well-known Yang–Yang relation. The extracted c_{VP} and $c_{V\mu}$ can be used to estimate the value of the Yang–Yang anomaly strength parameter, $R_\mu(T_C) = R_{\mu 0}$. Our previously reported two-phase isochoric heat capacity (c''_{V2} , c'_{V2}) and specific volume (V'' , V') data at saturation were used to directly calculate the Yang–Yang anomaly strength function $R_\mu(T)$. The proposed new technique was applied for various molecular fluids (water, carbon dioxide, alcohols, *n*-alkanes, diethyl ether, *etc.*) to accurately determine the value of the Yang–Yang anomaly strength function, $R_\mu(T_C) = R_{\mu 0}$. It was shown that the sign and magnitude of R_μ strongly depend on the combination of the liquid–gas co-existence specific volumes (V'' , V') and two-phase isochoric heat capacities (c''_{V2} , c'_{V2}), namely, $(V''c'_{V2} - V'c''_{V2})$. We also demonstrated that the Yang–Yang anomaly strength R_μ is a strong function of temperature in the immediate vicinity of the critical point, *i.e.*, it sharply changes when the critical temperature is approached. Based on our experimental calorimetric data (c''_{V2} , c'_{V2} , V'' , V') we showed that the Yang–Yang function $R_\mu(T_C) = R_{\mu 0}$ at the critical point (Yang–Yang anomaly parameter) for most studied molecular fluids tends to take large negative values, which means that the contribution of the chemical potential dominates the total experimentally observed two-phase isochoric heat capacity singularity at the critical point.

Far from the critical point, the contribution of the vapor pressure is greater than that of the chemical potential. The negative value of the Yang–Yang parameter from our calorimetric measurements near the critical point is in good agreement with the recent theoretical prediction by Cerdeiriña *et al.*²⁷ based on a compressible cell gas (CCG) model that obeys *complete* scaling with pressure mixing. Moreover, the proposed new technique correctly predicts the sign of the R_μ and provides a correct explanation and interpretation of the physical meaning of the Yang–Yang anomaly strength parameter and its relation to liquid–vapor coexistence asymmetry. Experimentally obtained values of the Yang–Yang function $R_\mu(T)$ were fitted with the *complete* scaling relation by Cerdeiriña *et al.*²⁷ for various molecular fluids. The values of $R_\mu(T_C)$ (Yang–Yang strength parameter) for these substances vary from -8 to 0.46 , which is consistent with theory.²⁷

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