



# Yang–Yang critical anomaly strength parameter from the direct two-phase isochoric heat capacity measurements near the critical point

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## ARTICLE INFO

### Article history:

Received 24 December 2015

Received in revised form

20 January 2016

Accepted 21 January 2016

Available online 23 January 2016

### Keywords:

Coexistence curve

Complete scaling

Critical point

Isochoric heat capacity

Saturated density

Yang–Yang anomaly strength parameter

## ABSTRACT

New technique of the Yang–Yang critical anomaly strength function,  $R_{\mu}(T)$ , determination from direct two-phase liquid ( $C'_{V2}$ ) and vapor ( $C''_{V2}$ ) isochoric heat capacity and liquid ( $V'$ ) and vapor ( $V''$ ) specific volumes measurements at the saturation have been developed. Our measured two-phase (liquid and vapor) isochoric heat capacities ( $C'_{V2}, C''_{V2}$ ) and liquid and vapor specific volumes ( $V', V''$ ) data at saturation near the critical point have been used to accurately determine the Yang–Yang anomaly strength parameter,  $R_{\mu}(T = T_c) = R_{\mu 0}$ , for various molecular liquids. The derived values of the Yang–Yang critical anomaly strength function show trend to negative infinity near the critical point as predicted by the theory (Cerdeiriña et al., 2015) based on compressible cell gas (CCG) model that obey complete scaling with pressure mixing. The physical nature and details of the temperature and the specific volume dependences of the  $C_{V2}$  and correct estimations of the contributions of various terms (chemical potential  $C_{V\mu}$  and vapor-pressure  $C_{VP}$ ) to the measured total two-phase heat capacity were discussed in terms of the Yang–Yang anomaly parameter.

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## 1. Introduction

As well-known,  $C_p$  data are widely used for practical application (engineering calculations), while,  $C_v$  data are used to gain a better understanding of theory and thermodynamic property models (theory and modeling). Isochoric heat capacity is closely related with other important thermodynamic properties and is very important tool to study phase transition and critical phenomena. A sharp discontinuity of the measured  $C_v$  occurs at the liquid–vapor phase transition temperature  $T_S(\rho)$  for each filling density ( $\rho$ ). Thus,  $C_v$  measurements for various isochores can be used to accurately determine the locus (shape) of the phase transition curve  $T_S(\rho)$  near the critical point, i.e., nature of the coexistence curve asymmetry. In this work we propose new technique of accurate calculation of the Yang–Yang anomaly strength parameter using measured two-phase isochoric heat capacity data, saturated temperatures, and saturated liquid and vapor specific volumes, ( $C'_{V2}, C''_{V2}, V', V''$ ).

## 2. Two-phase isochoric heat capacities ( $C'_{V2}, C''_{V2}$ ) and specific volumes ( $V', V''$ ) at saturation

In our previous publications [1–24] we have reported two-phase liquid ( $C'_{V2}$ ) and vapor ( $C''_{V2}$ ) and saturated liquid ( $V'$ ) and vapor ( $V''$ ) specific volumes for several molecular fluids ( $H_2O, D_2O, CO_2, C_3H_8, N_2O_4, DEE, \text{methanol, ethanol, 1-butanol, 2-butanol, etc.}$ ) near the critical point. The experimental details of the isochoric heat-capacity measurements have been described previously (see, for example [1–24]). The measurements of ( $C_vVT$ ) properties were performed with a high-temperature and high-pressure adiabatic calorimeter. The semiconductor ( $Cu_2O$ , highly sensitive thermo-element) layer between the inner and outer spheres was used to maintain adiabatic conditions. Simultaneously, the layer of semiconductor ( $Cu_2O$ ), was used as a medium transmitting pressure from inner to outer sphere. The adiabatic condition was maintained within ( $10^{-6} \div 10^{-5}$  K). The details of the uncertainty assessment is given in Ref. [18]. The combined expanded (coverage factor  $k = 2$ ) uncertainty of the density, temperature, and heat-capacity measurements at the 95% confidence level is estimated to be 0.06%, 15 mK, (2–3) %, respectively. In our previous works [9,16,18,24] we detailed described the method of quasi-static thermo- and barogram techniques for accurately determine location of the phase

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transition temperatures for each measured isochores (shape of the liquid–gas coexistence curve) and the values of one- ( $C'_{V1}, C''_{V1}$ ) and two-phase ( $C'_{V2}, C''_{V2}$ ) isochoric heat capacities at saturation curve. These methods were applied to study the phase transition and critical phenomena in complex multicomponent systems where occurs L-V, L-L, L-S, V-S, L-S-V, and L-L-S phase-transitions (see, for example [23–26]). Some selected results of the two-phase isochoric heat capacity measurements as a function of specific volume for various isotherms are showing in the Figs. 1 and 2, including the saturation curve. The temperature dependence of the two-phase  $C'_{V2}$  and  $C''_{V2}$  for some selected fluids near the critical point are depicted in Figs. 3 and 4. The critical anomaly one- ( $C_{V1}$ ) and two-phase ( $C_{V2}$ ) heat capacities along the critical isochores are showing in Figs. 5–7 (see also Figs. 1S–5S for *n*-alkanes and alcohols in Supplementary Material) together with the values calculated from the reference and crossover equation of states. Measured liquid ( $\rho'_S$ ) and vapor ( $\rho''_S$ ) saturated densities or specific volumes ( $V'_S = 1/\rho'_S$  and  $V''_S = 1/\rho''_S$ ) data in the same calorimetric experiments for some selected molecular fluids are depicted in Figs. 8 and 9 (see also Figs. 6S–8S for argon, *n*-alkanes, and alcohols in Supplementary Material).

### 3. Yang–Yang equation for the two-phase isochoric heat capacity

The phase transition parameters ( $T_S, \rho'_S, \rho''_S$ ) and isochoric heat capacities ( $C'_{V1}, C''_{V1}, C'_{V2}, C''_{V2}$ ) are providing reliable thermodynamically consistent data at saturation which are required for interpretation of the “complete” scaling theory of the Yang–Yang anomaly strength results. The Yang–Yang equation [27] for two-phase isochoric heat capacity  $C_{V2}$  can be presented as

$$C_{V2} = -T \frac{d^2\mu}{dT^2} + T \frac{d^2P_S}{dT^2} V, \quad (1)$$

where  $C_{V2}$  is the two-phase isochoric heat capacity;  $V$  is the specific volume ( $V = 1/\rho$ );  $\mu$  is the chemical potential; and  $P_S$  is the vapor-pressure. As one can see from Eq. (1), two-phase  $C_{V2}$  is the linear function of specific volume  $V$  for each constant temperature (see Figs. 1 and 2). The slope of two-phase ( $C_{V2} - V$ ) isotherm is the second temperature derivative of the vapor pressure,  $T(d^2P_S/dT^2)$ , while the intercept for  $V = 0$  is the second temperature derivative of the chemical potential,  $-T(d^2\mu/dT^2)$ . As one can see from Figs. 1 and 2, the slopes,  $(d^2P_S/dT^2)$ , of two-phase isotherms,  $C_{V2} - V$ , exhibit rapid increasing (singularity) for near-critical temperatures (isotherms) [70].

In the Yang–Yang relation (1) the specific volume  $V$  changes from the saturated liquid specific volume  $V'$  to the saturated vapor specific volume  $V''$ , i.e.,  $V' \leq V \leq V''$ . Therefore, at the end points of the two-phase region for each fixed isotherms,  $V = V'$  and  $V = V''$ , the second temperature derivatives of the vapor-pressure and chemical potential from the Yang–Yang Eq. (1) can be expressed as

$$\frac{d^2P_S}{dT^2} = \frac{C''_{V2} - C'_{V2}}{T(V'' - V')} \quad \text{and} \quad \frac{d^2\mu}{dT^2} = \frac{V''C'_{V2} - V'C''_{V2}}{T(V' - V'')}. \quad (2)$$

As can be note from Eq. (2), both derivatives completely defined from the experimental values of ( $C'_{V2}, C''_{V2}, V'', V'$ ) at saturation curve. Simultaneously measured in our previous publications [1–24] thermodynamically consistence quantities ( $T_S, V', V'', C'_{V2}, C''_{V2}$ ) in Eq. (2), were used to calculate  $(d^2P_S/dT^2)$  and  $(d^2\mu/dT^2)$ . Some results for  $(d^2P_S/dT^2)$  and  $(d^2\mu/dT^2)$ , as an example, for very well

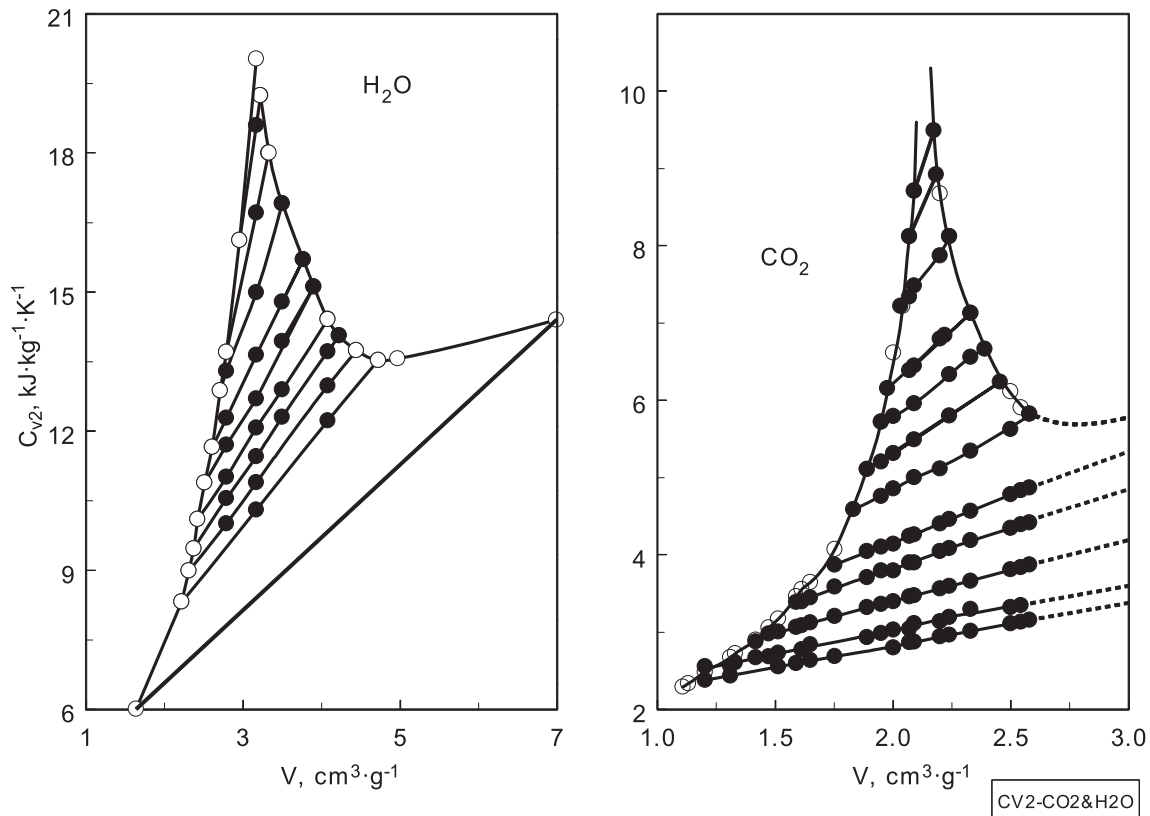


Fig. 1. Measured two-phase isochoric heat capacities of light water [47] (left) and carbon dioxide (right) [49–51] as a function of specific volume along the various near-critical isotherms. ●-two-phase along the various isotherms; ○- two-phase liquid and vapor  $C_{V2}$  at saturation.

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