Coexisting densities and critical asymmetry between gas and liquid

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ABSTRACT

We assess currently available experimental data of the diameter of the coexistence curve for the gas–liquid phase transition of pure fluids. Various approaches, including the direct evaluation of dielectric-constant data and the analysis of calorimetric experiments, are found to support a leading $|T - T_c|^{2\beta}$ singular term in the diameter, with $\beta \cong 0.326$ and T_c the critical temperature. This is consistent with the predictions from "complete scaling" formulation of asymmetric fluid criticality.

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1. Introduction

The central role the gas–liquid phase transition of pure substances has played in the development of the theory of critical phenomena originates in the work of van der Waals. While such "classical" theory describes a wide range of features, it was seriously challenged in 1945 by Guggenheim's observation [1] that the curve describing the temperature dependence of the density ρ of the coexisting gas and liquid phases (see Fig. 1 for illustration) is flatter than predicted. Specifically, asymptotically close to the critical temperature T_c

$$\rho^{liq} - \rho^{gas} \sim B|t|^{\beta}, \qquad (1)$$

where $t \equiv (T - T_c)/T_c$ and β is the critical exponent that describes the shape of the coexistence curve near the critical point. The van der Waals value is $\beta = 1/2$ whereas, on the basis of experimental data for many fluids, Guggenheim reported $\beta \approx 1/3$. A great amount of experimental information now strongly supports that β approaches 0.326 (see, e.g., Ref. [3]).

Another prominent aspect of the gas–liquid coexistence curve is the behavior of the coexistence-curve diameter, $\rho_d \equiv (\rho^{liq} + \rho^{gas})/2$, that is, the mid-points of the phase boundary (see Fig. 1). For this property one has [4–8]

$$\Delta \rho_d(T) \equiv \frac{\rho_d(T)}{\rho_c} - 1 = A_{2\beta}|t|^{2\beta} + A_{1-\alpha}|t|^{1-\alpha} + A_1|t| \ldots, \qquad (2)$$

where $\alpha \cong 0.109$ and ρ_c is the critical density. This means that, despite not apparent from Fig. 1, ρ_d bends as T_c is approached. Such a curved ρ_d goes beyond the "classical" Law of the Rectilinear Diameter predicted by van der Waals theory and reflects an asymmetry between coexisting gas and liquid phases near the critical point.

Despite Eq. (2) is actually accepted, the experimental characterization of the diameter—a volumetric property—is a nontrivial task. For instance, the original data for sulfur hexafluoride [9], regarded the first manifestation of the breakdown of the Law of the Rectilinear Diameter, have been the subject of a number of reanalyses [2,6–8,10–12]. Some of these works also included reanalysis of data for alkali metals [2,6,11] and other fluids [2,7,8]. With this background and having at hand added, updated information appeared over the last years, we analyze here literature data for the 13 fluids listed in Table 1. It is our aim to assess what is the current experimental evidence supporting the $|t|^{2\beta}$ term in $\rho_d(T)$.

The manuscript is organized as follows. Section 2 introduces the thermodynamics of asymmetry-related effects in the critical region. Then, we show in Section 3 the general features of $\rho_d(T)$ as well as the problems that an unambiguous experimental resolution of the various leading contributions in Eq. (2) raise. Section 4 describes some of the difficulties associated with the determination of the density in the gas–liquid critical region. In Sections 5 and 6 we discuss "nonstandard" approaches based on the behavior of the dielectric constant and on calorimetric experiments. Concluding remarks are made in Section 7.

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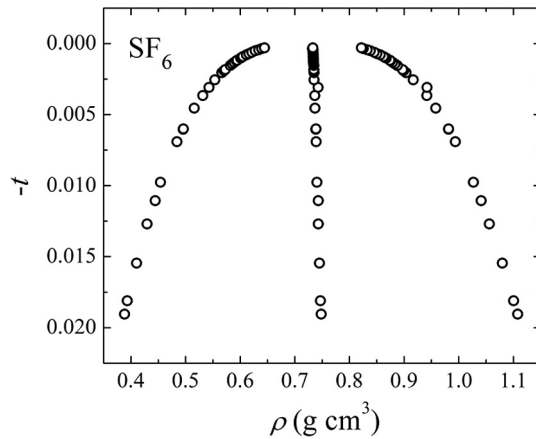 E-mail address: calvarez@uvigo.es (C.A. Cerdeiriña).

Fig. 1. Coexistence curve of sulfur hexafluoride (SF$_6$) in the density-temperature plane. Data were taken from Ref. [2], the mid-points represent the diameter ρ_d, and $t = (T - T_c)/T_c$, with T_c the critical temperature.

Table 1
Fluids studied in this work, effective critical exponents in Eq. (7), experimental techniques used for the determination of the coexistence-curve diameter in the density-temperature plane, and sources of data.

Fluid	ψ_{eff}	Technique
Sulfur hexafluoride	0.78	Dielectric constant measurements [2,9]
Heptane	0.66	Magnetic float densitometry [13]
Ethene	0.92	Refractive index measurements [2,14,15]
Ethane	0.86	Refractive-index measurements [2,14,15]
Freon-113	0.63	Magnetic float densitometry [16]
Neon[a]	1.01	Dielectric constant measurements [2,17]
Nitrogen[a]	0.99	Dielectric constant measurements [2,17]
Hydrogen deuteride[a]	0.87	Dielectric constant measurements [2,17]
Rubidium	0.62	Direct ρpT measurements [18]
Argon[b]	0.83	Calorimetry [19]
Nitrogen tetroxide[b]	0.83	Calorimetry [19]
Hexane[b]	0.59	Calorimetry [19]
1-Butanol[b]	0.77	Calorimetry [19]

[a] As explained in Section 5, dielectric-constant data have also been analyzed for these fluids and for diethyl ether [20]; those data have been provided by M.H.W. Chan and S.J. Rzoska.
[b] Data provided by I.M. Abdulagatov.

2. What does "asymmetric fluid criticality" mean?

The singular, nonanalytical behavior of the diameter required the original Widom's scaling formulation of the thermodynamics of a fluid in the critical region [21] to be revised. While the $|t|^{1-\alpha}$ term in $\rho_d(T)$ was implemented in scaling theory in the early 70 s [22], it was only in 2000 that Fisher and coworkers firmly established a "complete scaling" formulation that predicts the existence of the $|t|^{2\beta}$ term [4,5].

Complete scaling arose, however, from a careful analysis of experimental data of the two-phase heat capacity C_V in the critical region that demonstrated the existence of the so-called Yang-Yang (YY) anomaly [4,23]. This issue started with 1964 original work by Yang and Yang [24], who derived the following exact thermodynamic relation

$$\frac{\rho}{\rho_c} C_V(T) = \tilde{C}_p(T) + \frac{\rho}{\rho_c}\tilde{C}_\mu, \tag{3}$$

where $\tilde{C}_p \equiv \rho_c^{-1} T d^2 p_{sat}/dT^2$ and $\tilde{C}_\mu \equiv -T d^2 \mu_{sat}/dT^2$, with p_{sat} and μ_{sat} the pressure and chemical potential at coexistence. According to (3) ρC_V is linear in ρ at a given temperature T, with $\tilde{C}_\mu(T)$ and $\tilde{C}_p(T)$ being the slope and the intercept, respectively (see Fig. 2 for
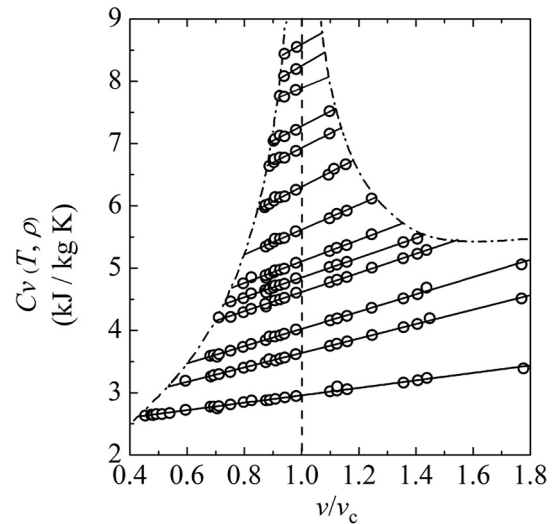

Fig. 2. Literature experimental data [25] of the isochoric heat capacity C_V of propane as a function of temperature T and volume v (or, equivalently, the density $\rho = 1/v$). Solid lines fit experimental data along isotherms and dash-dot lines are the phase boundaries delimitating liquid and gas phases; as expected, C_V diverges for the critical isochore $v = v_c$.

illustration via a fully equivalent C_V vs v plot, where $v = 1/\rho$). Then, one easily finds [19]

$$\tilde{\mathfrak{R}}_\mu(T) \equiv \frac{\tilde{C}_\mu}{\tilde{C}_p + \tilde{C}_\mu} = \frac{\rho_c(\rho^{liq}C_V^{liq} - \rho^{gas}C_V^{gas})}{\rho^{liq}C_V^{liq}(\rho_c - \rho^{gas}) + \rho^{gas}C_V^{gas}(\rho^{liq} - \rho_c)}, \tag{4}$$

where $C_V^{liq}(T)$ and $C_V^{gas}(T)$ denote the heat capacity of the coexisting phases. Clearly, $\tilde{\mathfrak{R}}_\mu \neq 0$ whenever the ρC_V of gas and liquid are different. This is the case for $T < T_c$.

But from the point of view of critical behavior, that is, asymptotically close to the critical point, the issue of interest concerns the so-called Yang-Yang ratio

$$\mathfrak{R}_\mu = \tilde{\mathfrak{R}}_\mu(T_c). \tag{5}$$

A Yang-Yang anomaly is said to exist whenever $\mathfrak{R}_\mu \neq 0$. From Eqs. (4) and (5) as well as the critical behavior of the heat capacity per unit volume of gas and liquid coexisting phases, i.e., $\rho^{liq}C_V^{liq} \sim A_{liq}|t|^{-\alpha}$ and $\rho^{gas}C_V^{gas} \sim A_{gas}|t|^{-\alpha}$, it comes out that $\mathfrak{R}_\mu \neq 0$ as soon as $A_{liq} \neq A_{gas}$. The YY anomaly thus reflects, like the behavior of the diameter, the asymmetry between gas and liquid. As a matter of fact, complete scaling establishes [5] that

$$A_{2\beta} = B^2 \mathfrak{R}_\mu, \tag{6}$$

implying that the YY anomaly and the $|t|^{2\beta}$ singularity in the diameter have the same physical origin.

Associated with nonvanishing $\mathfrak{R}_\mu$ and $A_{2\beta}$, complete scaling contemplates a comprehensive set of singularities in the whole thermodynamic behavior of fluids near the gas–liquid critical point [5]. In other words, the YY anomaly and the $|t|^{2\beta}$ singularity are two of the many faces—but certainly the most widely studied—of what is termed "asymmetric fluid criticality".

3. General features and effective critical exponents

Fig. 3 shows the temperature dependence of the diameter for neon and sulfur hexafluoride. As is the general case, $\rho_d(T)$ develops towards lower densities as the critical temperature is approached. Close to T_c, neon displays little deviation from linearity while a small but detectable curvature is observed for sulfur hexafluoride.