

Liquid-Vapor Density of Sulfur Hexafluoride in the Critical Point

Abbaci, Azzedine^{*+}

*Faculté des Sciences, Département de Chimie, Université Badji-Mokhtar, B.P. 12, El-Hadjar,
Annaba (23200), ALGERIA*

ABSTRACT: *The thermodynamic properties of fluids can be predicted using the global equations of state. Among these thermodynamic properties of fluids, we choose the densities of the liquid and vapor phases. This paper considers the application of the crossover model to the vapor-liquid rectilinear diameter of sulfurhexafluoride. We also present a comparison of the crossover model equation with the experimental data.*

KEY WORDS: *Crossover model, Fluids, Rectilinear diameter, Sulfurhexafluoride.*

INTRODUCTION

The critical thermodynamic behavior of fluid systems has been the subject of several investigations [1], conducted in analogy with the 3-dimensional Ising-like systems. Asymptotically close to the critical point the thermodynamic properties of fluids show anomalous behaviors. Such behavior can be characterized in terms of scaling laws with universal critical exponents and universal scaling functions [1-3]. Unlike the 3-dimensional Ising-like systems, fluids exhibit a lack of vapor-liquid symmetry in the shape of their coexistence curve.

It is well known that an empirical analytic equation of state does not reproduce the correct thermodynamic behavior of fluids in the critical region. On the other hand, an equation of state that is valid in the critical region cannot be extrapolated in the classical region. Therefore, a unified equation of state is needed in order to take account of the thermodynamic properties of fluids over a wide range of temperatures and densities; while

having a good agreement with experimental data in the critical region as well as in the classical region, far away from the critical point. Such an equation is available and is based on the crossover model formalism [4, 5].

In the present work, we give the application of the crossover model to the coexistence-curve diameter, and show that we can reproduce the liquid-vapor coexistence curve diameter, only by using the already formulated equation of state for sulfurhexafluoride [4,5].

This article is organized as follows; after the introduction, we briefly review the six-term Landau crossover model in section 2. Then, we present the common prediction of the behavior of the coexistence-curve diameter equation for one-component fluid in section 3. We finally discuss the application of the crossover model to the coexistence-curve diameter of sulfurhexafluoride in section 4, and give a comparison of the experimental data with those of the model.

* To whom correspondence should be addressed.

+ E-mail: azzedineabbaci@hotmail.com

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THEORY

The modern theoretical description of systems close to the critical point is based on the renormalization-group theory (RG) [6]. Different physical systems with the same space dimensionality d , and the same number n of components of the order parameter can be grouped within the same universality class. Based on earlier work of Nicoll et al. [7, 8] and Bagnuls and Bervillier [9], a crossover model has been developed to represent the thermodynamic properties of fluids in the critical region [4,5]. The crossover model is based on the renormalization-group theory of critical phenomena. Let ρ be the density, T the temperature, P the pressure, μ the chemical potential and A/V the Helmholtz free energy per unit volume. We make these properties dimensionless with the aid of the critical parameters [2,4,5].

$$\tilde{\rho} = \frac{\rho}{\rho_c}, \quad \tilde{T} = \frac{T_c}{T}, \quad \tilde{P} = \frac{PT_c}{P_c T}, \quad (1)$$

$$\tilde{\mu} = \frac{\mu \rho_c T_c}{P_c T}, \quad \tilde{A} = \frac{AT_c}{P_c VT}$$

In addition we define

$$\Delta\tilde{\rho} = \tilde{\rho} - 1, \Delta\tilde{T} = \tilde{T} - 1, \Delta\tilde{\mu} = \tilde{\mu} - \tilde{\mu}_0(\tilde{T}) \quad (2)$$

and

$$\Delta\tilde{A} = \tilde{A} - \tilde{\rho}\tilde{\mu}_0(\tilde{T}) - \tilde{A}_0(\tilde{T}) \quad (3)$$

Here $\tilde{\mu}_0(\tilde{T})$ and $\tilde{A}_0(\tilde{T})$ are analytic background functions of T subject to the conditions that at the critical temperature $\Delta\tilde{\mu} = 0$ and $\tilde{A}_0 = -1$ which in principle should be obtained from a classical equation. Since the precise functional form of these background functions are not important ingredients of our crossover model, we represent $\tilde{A}_0(\tilde{T})$ by a truncated Taylor expansion to specify the Helmholtz free-energy density completely:

$$\tilde{A}_0(\tilde{T}) = -1 + \sum_{j=1} \tilde{A}_j (\Delta\tilde{T})^j \quad (4)$$

The quantity $\Delta\tilde{A}$ in Eq. (3) represents the singular part of the Helmholtz free-energy density. The coefficients \tilde{A}_j are background parameters which can be determined by fitting the crossover model to P - ρ - T data (P is pressure, ρ density and T temperature). The relevant thermodynamic relations in terms of these reduced

thermodynamic properties can be found elsewhere [4,5]. Classical equations of state for the Helmholtz free energy density A imply that the classical part A_{cl} has an asymptotic expansion of the form [10]:

$$\Delta\tilde{A}_{cl} = \frac{1}{2} t M^2 + \frac{u_0}{4!} M^4 + \dots, \quad (5)$$

Where t and M are temperature-like and density-like variables related to ΔT and $\Delta\rho$ in a manner to be specified below. In the sequel we find it convenient to write the coefficient u_0 of the M^4 term in (5) as $u_0 = \Lambda u$, where Λ is a dimensionless cutoff wave number [1,4]. In order to obtain a fundamental equation that can be applied in a large range of densities and temperatures around the critical point we retain six terms in the classical Landau expansion (4) for ΔA_{cl} so that:

$$\Delta\tilde{A}_{cl} = \frac{1}{2} t M^2 + \frac{u_0}{4!} M^4 + \frac{a_{05}}{5!} M^5 + \frac{a_{06}}{6!} M^6 + \frac{a_{14}}{4!} t M^4 + \frac{a_{22}}{2!2!} t^2 M^2 \quad (6)$$

the coefficients $a_{05}, a_{06}, a_{14}, a_{22}$ are also system-dependent parameters. As shown by Chen et al. [4] the theoretically predicted asymptotic behavior can be recovered from this expansion by the following transformation:

$$\Delta\tilde{A}_r = \frac{1}{2} t M^2 T D + \frac{u_0}{4!} M^4 D^2 U + \frac{a_{05}}{5!} M^5 D^{5/2} V U + \frac{a_{06}}{6!} M^6 D^3 U^{3/2} + \frac{a_{14}}{4!} t M^4 T D^2 U^{1/2} + \frac{a_{22}}{2!2!} t^2 M^2 T^2 D U^{-1/2} - \frac{1}{2} t^2 K \quad (7)$$

Where the functions T, D, U, V and K are defined by:

$$T = Y^{(2-1/\nu)/\omega}, \quad D = Y^{-\eta/\omega}, \quad U = Y^{1/\omega} \quad (8)$$

$$V = Y^{(2\omega_a - 1)/2\omega}, \quad K = \frac{\nu}{a\bar{u}\Lambda} \left[Y^{-\alpha/\nu\omega} - 1 \right]$$

In terms of a crossover function Y to be determined from:

$$1 - (1 - \bar{u})Y = \bar{u} \left(1 + \frac{\Lambda^2}{\kappa^2} \right)^{1/2} Y^{1/\omega} \quad (9)$$

With

$$\kappa^2 = tT + \frac{1}{2} u\Lambda M^2 D U \quad (10)$$

and

$$\bar{u} = u / u^* \quad (11)$$

In these expressions, β , ν , η , ω and ω_a are universal critical exponents, u^* is also a universal constant. The values of the universal critical-region parameters are specified in table 1. The crossover model depends parametrically on the variable κ^2 defined by Eq. (10). For small values of κ one recovers from Eq. (7) the scaled critical behavior, while for large values of κ the crossover function Y approaches unity and Eq. (7) reduces to the classical Landau expansion of Eq. (6).

Crucial for the application of the crossover model to fluids is a suitable transition of the field variables t and M [4, 5]. This idea can be accomplished by the following transformation:

$$\Delta\tilde{A} = \Delta\tilde{A}_r - c_t \left(\frac{\partial\Delta\tilde{A}_r}{\partial M} \right)_t \left(\frac{\partial\Delta\tilde{A}_r}{\partial t} \right)_M \quad (12)$$

$$t = c_t \Delta\tilde{T} + c \left(\frac{\partial\Delta\tilde{A}_r}{\partial M} \right)_t, \quad (13)$$

$$M = c_\rho (\Delta\tilde{p} - d_1 \Delta\tilde{T}) + c \left(\frac{\partial\Delta\tilde{A}_r}{\partial t} \right)_M \quad (14)$$

where, c_t , c_ρ and d_1 are system-dependent constants. The coefficient c is another system-dependent parameter that mixes the field variables t and M .

COEXISTENCE-CURVE DIAMETER

One of the most important consequences of the mixing of the field variables t and M is the existence of a weak singularity in the coexistence-curve diameter. We denote the liquid density by ρ_{liq} and the vapor density by ρ_{vap} , ρ_c as the critical density, and $\Delta\tilde{T}$ the reduced temperature. Then close to the critical point, the renormalization-group theory predicts that [11]:

$$\frac{(\rho_{\text{liq}} + \rho_{\text{vap}})}{2\rho_c} = 1 + d_1 \Delta\tilde{T} + d_{s1} |\Delta\tilde{T}|^{(1-\alpha)} + d_{s2} |\Delta\tilde{T}|^{(1-\alpha+\Delta)} + \dots, \quad (15)$$

where α is the critical exponent that characterizes the divergence of the specific heat at constant volume, β , Δ , and $\Delta_a = \omega_a \nu$ are other critical exponents given in Table 1.

Since $(1-\alpha)$ is close to unity, the singularity in the

Table 1: Universal critical-region constants

| | | |
|--|-------------------|-----------------|
| $\alpha = 0.11$, | $\eta = 0.0333$, | $\beta = 0.325$ |
| $\Delta = 0.51$ ($\omega = \Delta\nu = 0.80952$), $\omega_a = 2.1$, $u^* = 0.472$ | | |

coexistence-curve diameter is very difficult to detect. However, early experiments performed by Weiner, Langley and Ford on sulfurhexafluoride [12], whose data have been further analyzed by Ley-Koo and Green [13], indicate that the singular term is present. Subsequent experiments performed by Pestak and coworkers for nitrogen, neon, and for ethane and ethylene [14] have also confirmed the presence of the hook characterized by this weak singular term with the predicted exponent $(1-\alpha)$. With $\Delta = \omega\nu$, the crossover model reproduces this expansion with the coefficients d_{s1} and d_{s2} given by the following expressions:

$$d_{s1} = -9.547 c_\rho^{-1} c_t^{(1-\alpha)} (\bar{u} \Lambda)^{-3(2\nu-1)} \quad (16)$$

$$d_{s2} = 8.820 c_\rho^{-1} c_t^{(1-\alpha+\Delta)} (\bar{u}-1)(\bar{u} \Lambda)^{-3(2\nu-1)-2\Delta} \quad (17)$$

The coexisting liquid and vapor densities may be presented by the following relation:

$$\frac{\rho_{\text{liq}} - \rho_{\text{vap}}}{2\rho_c} = A_\beta |\Delta\tilde{T}|^\beta + A_{\beta+\Delta} |\Delta\tilde{T}|^{\beta+\Delta} + \quad (18)$$

$$A_{\beta+2\Delta} |\Delta\tilde{T}|^{\beta+2\Delta}$$

with β a new critical exponent with a value listed on Table 1. The coefficients A_β , $A_{\beta+\Delta}$, and $A_{\beta+2\Delta}$ can be determined from the model or by fitting the experimental data to Eq. (18).

APPLICATION TO SULFURHEXAFUORIDE

Sulfurhexafluoride can be used in particular, by the electrical power industry, where the fluid is used in equipment such as high-voltage circuit breakers and gas-insulated transmitters, due to this industrial importance; it has been the focus of our study.

For a comparison of our crossover model with experimental data of sulfurhexafluoride, we consider the coexistence-curve diameter of sulfurhexafluoride for which an equation of state in the critical region has been proposed earlier by Abbaci and Sengers [15, 16].

The system-dependent constants in the crossover model [3,4] were determined from a fit to the P - ρ - T data of Biswas et al. [17] with temperature and density ranges

Table 2: System-dependent constants in the crossover model of sulfurhexafluoride

| | | |
|--|-------------------------------|-------------------------------|
| $\Lambda=1.1382$, $\bar{u} = 0.44868$, $c_l = 1.9535$, $c_p = 2.3957$, $c = -0.02092$ | | |
| $a_{05} = -0.25834$, $a_{06} = 1.4306$, $a_{14} = 0.63984$, $a_{22} = 0.60844$ | | |
| $\tilde{A}_0 = -1$, | $\tilde{A}_1 = -6.0726$, | $\tilde{A}_2 = 4.7809$ |
| $\tilde{A}_3 = 1.4783$, | $\tilde{A}_4 = -0.55502$, | $d_1 = -0.45778$, |
| $d_{s1} = 0.255^a$, | $d_{s2} = 0.383^a$ | |
| $A_\beta = 1.66^b$, | $A_{\beta+\Delta} = 1.26^b$, | $A_{\beta+2\Delta} = -3.66^b$ |
| $d_l = 6.47^c$, | $d_{s1} = 3.99^c$, | $d_{s2} = 6.94^c$ |

^a: Equations (16) and (17), ^b: direct fitting to Eq. (18),

^c: direct fitting to Eq. (15)

of $312 \text{ K} \leq T \leq 365 \text{ K}$ and $350 \text{ kg/m}^3 \leq \rho \leq 1075 \text{ kg/m}^3$ respectively. The critical parameters used here are the same one used by Abbaci and Sengers [15, 16]:

$$T_c = 318.733 \text{ K}, \quad P_c = 3.7543 \text{ MPa}, \quad (19)$$

$$\rho_c = 743.807 \text{ kg/m}^3$$

With a fixed system-dependent parameters shown in Table 2. A comparison of the crossover model equation with the density experimental data reported by Pestak and coworkers [14] is shown in Fig. 1. We also show the densities of the coexisting vapor and liquid phases of sulfurhexafluoride as a function of the temperature in Fig. 2. As expected, the data reported by Pestak and coworkers tend toward quite satisfactory agreement when fitted to Eq. (15). Two liquid-vapor points measured by Gilgen and coworkers [18] are also shown in Fig. 1 and Fig. 2. We notice in Fig. 1 that these two points are slightly off the curve. The offset of Pestak's data with respect to the curve predicted from the crossover model equation is probably due to the fact that these density-data were obtained from measurements of the refractive index, then the data of this latter were converted to densities using values from Lorentz-Lorentz formula. However, it is well known that the Lorentz-Lorentz formula is only valid at low densities. The coefficient of the $(1-\alpha)$ term and the coefficient of the linear term deduced from the crossover model differ appreciably from the values of the same terms deduced from a direct Eq. (15). These differences are due to the correlation

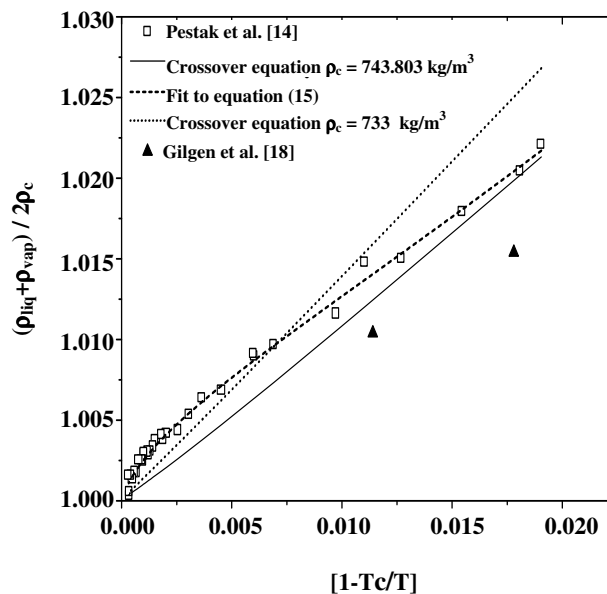


Fig. 1: Rectilinear diameter as a function of reduced temperature. The squares represent the experimental data of Pestak et al. [14] and the triangles are those of Gilgen et al. [18], the line represents the prediction of the crossover model.

between the $(1-\alpha)$ and the linear amplitudes from coexistence-curve data only. This fact explains the discrepancies between the slopes in Fig. 1.

Fig. 1 is too coarse a scale to permit any conclusions about the quality of the comparison. The agreement of the Pestak et al. [14] sets of data with the coexistence curves are typically measured on the level of a few 0.1 % uncertainty. It is therefore, more appropriate and even more informative to show deviation plots. Fig. 3 shows the deviation plots of Pestak et al. experimental data [14] with respect to the values calculated from the crossover model as well as the curve fit to Eq. (15). The experimental data are reproduced with the crossover model with standard deviations of 0.07 % and 0.17 % using $\rho_{c=743.807} \text{ kg/m}^3$ and $\rho_c = 733 \text{ kg/m}^3$ respectively, and an average deviation of 0.04 % with Eq. (15).

DISCUSSION

Although the discussion in this paper has focused on the application of the crossover model to the liquid-vapor coexistence-curve diameter, it can also be extended to other thermodynamic properties. The comparison made here for sulfurhexafluoride is not based on any fitting to the experimental data in question. Furthermore, it can be seen that the hook that is characterized by the

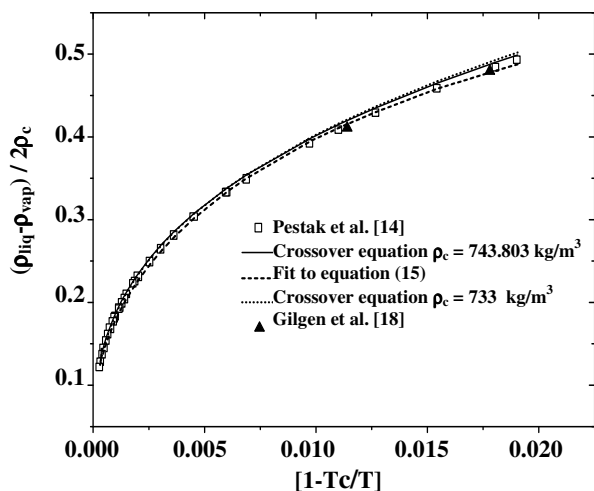


Fig. 2: Density-temperature diagram. The squares represent the experimental data of Pestak et al. [14], and the triangles are those of Gilgen et al. [18]. The line represents the prediction from the crossover model.

term $|\Delta\tilde{T}|^{(1-\alpha)}$ in the rectilinear diameter for sulfurhexafluoride is so small that it can not be noticed.

Furthermore, our crossover equation implies a value of the specific-heat-amplitude ratio A^+/A^- which is about 5 % below the theoretical value, that is the best ratio as obtained from renormalization-group calculations for the Ising model [4,5], and the amplitude of the hook of the coexistence-curve diameter is intimately connected with the specific-heat amplitude A^- . Therefore, it is sometimes very difficult to make any statement about the magnitude of this hook as long as the amplitude ratio is not known correctly. Kostrowicka and Sengers [19] proposed a new equation of state for the thermodynamic properties of sulfurhexafluoride. This equation does not differ from the one we proposed earlier, for it could fix the caloric properties problem, but in our view it leaves the other properties unchanged in general, this is because, we tested our equation of state with the P - ρ - T data of Gilgen et al. [18], and found that it gives quite satisfactory results, this suggests that the density calculations from our equation of state are as good as the one if they were calculated with the equation proposed by Kostrowicka and Sengers [19].

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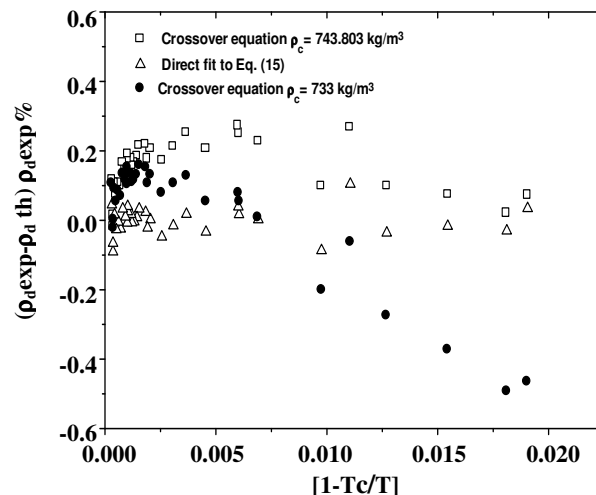


Fig. 3: Percent deviation Plot of the experimental coexistence-curve diameter from its calculated values from the crossover model with $\rho_c = 743.807 \text{ kg/m}^3$ and $\rho_c = 733 \text{ kg/m}^3$, and from Eq. (15).

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