OPEN ACCESS

The Journal of Engineering and Exact Sciences – jCEC, Vol. 10 N. 09 (2024)
journal homepage: https://periodicos.ufv.br/jcec
eISSN: 2527-1075
ISSN: 2446-9416

Liquid-vapor phase diagram of carbon dioxide near the critical point

Article Info:
Article history: Received 2024-11-03 / Accepted 2024-12-12 / Available online 2024-12-16
doi: 10.18540/jcecvl10iss9pp20832

Azzedine Abbaci
ORCID: https://orcid.org/0000-0002-4112-9287
Laboratoire de Synthèse et de Biocatalyse Organique, Faculté des Sciences, Départementde Chimie, Université Badji-Mokhtar, B.P. 12, Sidi-Amar, Annaba (23200), Algeria
E-mail:Azzedine.abbaci@univ-annaba.dz

Abstract

Reliable information on the properties of supercritical fluids is sought due to their importance in chemical technology. For this purpose, we consider the crossover model to explain the behavior of the thermodynamic properties of fluids in the vicinity of the critical point. In particular, we present an up-to-date examination of the coexistence densities of carbon dioxide near the critical point and compare it the experimental data of Duschek et al. as well as with the data generated from NIST REFPROP package.

Keywords: Carbon dioxide, crossover model, equation of state, supercritical fluids

1. Introduction

The studies of the critical thermodynamic behavior of pure fluid systems are of increasing interest for many fields Hutchenson and Foster (1995). Pure compound fluids can be found under different phases depending on the temperature and pressure. In particular, a subcritical fluid is characterized by its temperature above its boiling point and below critical point under pressure. However, a supercritical fluid temperature is above the critical point. Fluids at the sub-and supercritical conditions have different physical and chemical properties, such as the density, the dielectric constant, etc..., when compared to their properties at ambient conditions. Carbon dioxide is one of the frequently used sub-and supercritical fluid. By changing the temperature and pressure, the enhanced thermodynamic properties of sub-and supercritical fluids used to improve biowastes, plastic wastes, biocrude, supercritical fluid separation in petroleum-chemistry separation and purification, food industry (Akgerman and Madras, 1994; Beckman, 1996; Cansell et al., 1997; McHugh and Krukonis, 1998) and supercritical fluid chromatography in analytical and preparative separation, determination of physicochemical properties (Page et al., 1994; Schneider, 1983) amongst other utilizations (Kiran, 1994; Cansell et al. 1999; Chen et al. 1995; Savage et al. 1995).
Conventionally, equations of state are used to describe the thermodynamic properties of fluids and fluid mixtures in the critical region in the vicinity of the critical point as well as in the classical region far away from the critical point. Nonetheless, empirical analytic equations of state do not reproduce the correct thermodynamic behavior of fluids in the critical region. Furthermore, equations of state that are valid in the critical region cannot be extrapolated to 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 around the critical point, with good agreement with experimental data in the critical region and in the classical region far away from the critical point. An equation of state that is based on the crossover model formalism should take into account the description of the thermodynamic properties of pure fluids both in the critical

region as well as far away in the classical region (Chen et al. 1990; Rizi and Abbaci 2024; Abbaci, 2005; Abbaci and Berrezeg, 2004; Rizi and Abbaci, 2012).

The present work delineates the application of the crossover model to the coexistence-curve diameter to carbon dioxide, and substantiates the reproducibility of the liquid-vapor coexistence curve diameter only by a using the already formulated equation of state for carbon dioxide based on the crossover model (Chen et al. 1990; Rizi and Abbaci 2024). This work is divided into 5 sections and we shall proceed as follows: Section 2 provides the general theoretical framework for the six-term crossover model. Section 3, presents the formulation that predict the behavior of the coexistence-curve diameter equation for one-component fluid. Section 4, discusses the application of the crossover model to the coexistence-curve diameter of carbon dioxide and address the comparison of the experimental data of carbon dioxide with the crossover model as well as the data generated from REFPROP package (NIST, 2023). We conclude with a discussion in section 5.

2. Theory

1.1 Specification of the crossover model

Close to the critical point, the description of fluid systems is based on modern theoretical of the renormalization-group theory (RG) (Nicoll and Albright, 1985). In particular, diverse physical systems with the same space dimensionality *d*, and the same number *n* of components of the order parameter belong to the same universality class. Based on earlier works of Nicoll et al. (Nicoll, 1983; Nicoll and Bhattacharjee, 1981), a crossover model based on the renormalization-group theory of critical phenomena has been developed to predict the thermodynamic properties of fluids in the critical region (Chen et al. 1990; Rizi et al. 2024; Abbaci, 2005; Abbaci and Berrezeg, 2004; Rizi and Abbaci, 2012).

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 (Chen et al. 1990; Rizi and Abbaci 2024):

$$\tilde{\rho} = \frac{\rho}{\rho_c}, \tilde{T} = \frac{T}{T_c}, \tilde{P} = \frac{PT_c}{P_cT}, \tilde{\mu} = \frac{\mu T_c \rho_c}{TP_c}, \tilde{A} = AT_c/VTP_c \qquad (1)$$

In addition, we define;

$$\Delta\tilde{\rho} = \tilde{\rho} - 1, \Delta\tilde{T} = \tilde{T} + 1,$$
$$\Delta\tilde{\mu} = \widetilde{\mu_c} - \tilde{\mu}_0 \qquad (2-3)$$

and

$$\Delta\tilde{\boldsymbol{A}} = \tilde{\boldsymbol{A}}\,\tilde{\mu}_0(\tilde{T}) - \tilde{A}_0\,(\tilde{T}) \qquad (4)$$

Here, the terms $\tilde{\mu}_0\,(\widetilde{T})$ and $\tilde{A}_0\,(\widetilde{T})$ are analytic backgrounds of functions of *T* subjects to the conditions that at the critical temperature, $\Delta\tilde{\mu}(T = T_c) = 0$, $\Delta\tilde{A}(T = T_c) = -1$. The equation of state used here is expressed in the form of a reduced Helmholtz energy which can be written as (Abbaci et al., 2004; Rizi et al., 2023):

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

Where *t* and *M* are temperature-like and density-like variables respectively related to $\Delta\tilde{T}$ and $\Delta\tilde{\rho}$ defined by:

$$t = c_t \Delta\tilde{T} + c\left(\frac{\partial\Delta\tilde{A}}{\partial t}\right)_M \tag{6}$$

$$M = c_\rho(\Delta\tilde{\rho} - d_1\Delta\tilde{\rho}) + c\left(\frac{\partial\Delta\tilde{A}}{\partial M}\right)_t \tag{7}$$

with the corresponding transformation:

$$\Delta\tilde{A} = \Delta\,\tilde{A}_r - c\left(\frac{\partial\Delta\tilde{A}}{\partial t}\right)_M \left(\frac{\partial\Delta\tilde{A}}{\partial M}\right)_t \tag{8}$$

Where, c_t, c_ρ and d_1 are system-dependent constants. The coefficient c arises because of the vapor-liquid asymmetry of fluids. Thus, the coefficient c is also system-dependent parameter that mixes the field variables t and M. The coefficients $a_{05,}$ $a_{06,}$ $a_{14,}$ a_{22} are system-dependent parameters and $u_0 = u\cdot\Lambda$, where Λ is a dimensionless cutoff wave number and u is defined below, whilst the crossover functions $\mathcal{T}, \mathcal{D}, \mathcal{U}, \mathcal{V}$and $\mathcal{K}$ are defined by:

$$\mathcal{T} = \mathcal{Y}^{(2-1/v)/\omega},\ \ \mathcal{D} = \mathcal{Y}^{-\eta/\omega},\ \ \mathcal{U} = \mathcal{Y}^{1/\omega}, \tag{9}$$
$$\mathcal{V} = \mathcal{Y}^{(2\omega_a-1)/\omega}\ \ , \mathcal{K} = \frac{v}{\alpha \bar{u}\Lambda}\left[\mathcal{Y}^{-\alpha/v\omega} - 1\right]$$

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

$$1 - (1-\bar{u})\mathcal{Y}\ = u\left(1 + \frac{\Lambda^2}{\kappa^2}\right)^{1/2} \mathcal{Y}^{1/\omega} \tag{10}$$

with

$$\kappa^2 = t\mathcal{T} + \frac{1}{2}\,u\Lambda M^2\mathcal{D}\mathcal{U} \tag{11}$$

With $\bar{u} = u/u^*$.In these expressions ν, η, ω and ω_a are universal critical exponents, u^* is another universal constant, called the fixed-point coupling constant found elsewhere (Rizi and Abbaci 2024). The values of the critical exponents that will be used in this work are presented in Table 1.

Table 1: Universal critical-region constant

Critical exponent/Values
α=0.11
η=0.033
ν=0.63
Δ=0.51
$\omega=\Delta/\nu$=0.80952
ω_a=2.1
u^*=0.472

In order to apply the crossover model to fluid systems, an appropriate transformation of the field variables t related to the temperature T and M related to the density ρ is presented by the following conversion (Chen et al. 1990; Rizi and Abbaci 2024):

The coefficients, 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.

3. The Coexistence-curve diameter

The presence of the weak singularity in the coexistence-curve diameter is the consequence of the mixing of the field variables t and M as shown in Eq. (7). By denoting $\rho_{liq.}$ as the liquid density and $\rho_{vap.}$ as the vapor density, ρ_c as the critical density, and $\Delta\tilde{T}$ as the reduced temperature; then, near the critical point, the renormalization-group theory predicts that (Weiner et al., 1974; Ley-Koo and Green, 1972):

$$\rho d = \frac{(\rho_{liq}+\rho_{vap})}{2\rho_c} = 1 + d_1\Delta\tilde{T} + d_{s1}\Delta\tilde{T}^{(1-\alpha)} d_{s2}\Delta\tilde{T}^{(1-\alpha+\Delta)} + \cdots, \tag{12}$$

By inverting Eq. (2), the densities of the liquid and the vapor phases can be computed as:

$$\rho_{liq.,vap.} = \rho_c \left[1 + {}^{1}\!/_{c_\rho} \left\{M - c \left({}^{\partial \Delta \tilde{A}_r}\!/_{\partial t}\right)_M\right\} + d_1 \Delta \tilde{T}\right]_{liq.,vap.} , \tag{13}$$

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

Since (1-α) is close to unity, the hook in the coexistence-curve diameter is very too difficult to distinguish from its linear term. Nonetheless, experiments performed by Weiner, Langley and Ford on sulfurhexafluoride (Weiner et al., 1974), that have been latter on analyzed by Ley-Koo and Green (Ley-Koo Green, 1972), indicate that the singular term is present. Subsequently, Pestak and coworkers (Pestak et al. 1987) have performed experiments on nitrogen and neon, and Burton and Balzarini, (1974) and coworkers on ethane and ethylene who have established the existence of the hook characterized by this weak singular term with the predicted exponent (1-α)/ With Δ = ων.

The crossover model reproduces expansion in Eq. (12) with the coefficients d_{s1} and d_{s2} given by the following expressions:

$$d_{s1} = -9.547\, {c_t}^{(1-\alpha)}\, (\Lambda \bar{u})^{-3(2\upsilon-1)} c/c_\rho, \tag{14}$$

$$d_{s1} = 8.820 {c_t}^{(1-\alpha+\Delta)}\, (1-\bar{u})(\Lambda \bar{u})^{-3(2\upsilon-1)-2\Delta} c/c_\rho, \tag{15}$$

The coexisting liquid and vapor densities are represented by the relation:

$$\frac{(\rho_{liq} - \rho_{vap})}{2\rho_c} = A_\beta \left[\Delta \tilde{T}\right]^\beta + \cdots, \tag{16}$$

With the critical exponents Δ=ωυ and β and values listed on Table1. The coefficient A_β, can be deduced from the crossover model. The expression of this dominant coefficient in Eq. (8) is calculated from the crossover model as follow:

$$A_\beta = \left[\frac{2(1+x)}{x^{2\beta}} \left({}^{(\Lambda \bar{u})^{-2(2-1/\upsilon)\beta-\eta}}\!/_{u^*}\right)^{1/2}\right] {c_t}^\beta / c_\rho, \tag{17}$$

With

$$x = {}^{\left[2(3\upsilon - 1) - \sqrt{4 - 54\upsilon + 9(9-u^*)\, \upsilon^2}\right]}\!/_{[10 - 3\upsilon(5-u^*)]}, \tag{18}$$

4. Application to the phase diagram of carbon dioxide

In particular, a comparison of the crossover model EOS with the experimental data of the coexistence-curve diameter of carbon dioxide is made based on system-dependent constants in the crossover model that were determined previously (Chen et al., 1990) from a fit to the P-ρ-T data of Michels and coworkers (1935 a, b) and Michels et al., (1937) with temperatures and densities ranges of $291 \leq T/\mathrm{K} \leq 373K$ and $193 \leq \rho/\mathrm{kg.m}^{-3} \leq 712$. For the critical parameters, we adopted the following values, T_c = 304.127 K, P_c = 7.3757 MPa ρ_c = 467.83 kg m^{-3}.

With fixed system-dependent parameters shown in Table 2, we generated liquid and vapor densities and the rectilinear diameter values of carbon dioxide as shown in Table 3. A comparison of the crossover model equation with the experimental coexistence diameter data for carbon dioxide reported by Duschek and coworks (Duschek et al., 1990), the values generated from REFPROP packages (NIST, 2023) is shown in figure 1. In addition, we also show in figure 2 the densities of the coexisting vapor and liquid phases of the fluid as a function of temperature.

Table 2- System-dependent constants for carbon dioxide

Crossover parameters $\bar{u} = 0.39803$, $\Lambda = 1.4214$
Scaling parameters $c_t = 1.5951,\ c_\rho = 2.4145$, $c = -0.02590$
Classical Parameters $a_{05} = -0.27063,\ a_{06} = 1.14228$, $a_{14} = 0.39839,\ a_{22} = 0.30116$
Pressure background parameters $\tilde{A}_0 = -1,\ \tilde{A}_1 = -6.0079,\ \tilde{A}_2 = 4.5139$, $\tilde{A}_3 = -1.9509,\ \tilde{A}_4 = 5.1371$, d_1 =-0.33231, d_{S1}= 0.2905, d_{S2}= 0.424

Figure 1 is too roughly scaled to make any conclusions about the goodness of the comparison and agreement of the Duschek et al. (Duschek et al., 1990) sets of data and the coexistence curve are typically measured on the level of a few tenth of a percent uncertainty, especially very close to the critical point. It is therefore, more adequate and even more informative to show deviation plots. In figure 3, we present the deviation plots of REFPROP (NIST, 2023) against the experimental data measured by Duschek et al. (Duschek et al., 1990) from the values calculated from the crossover Model as well as values calculated from Eq. (12).

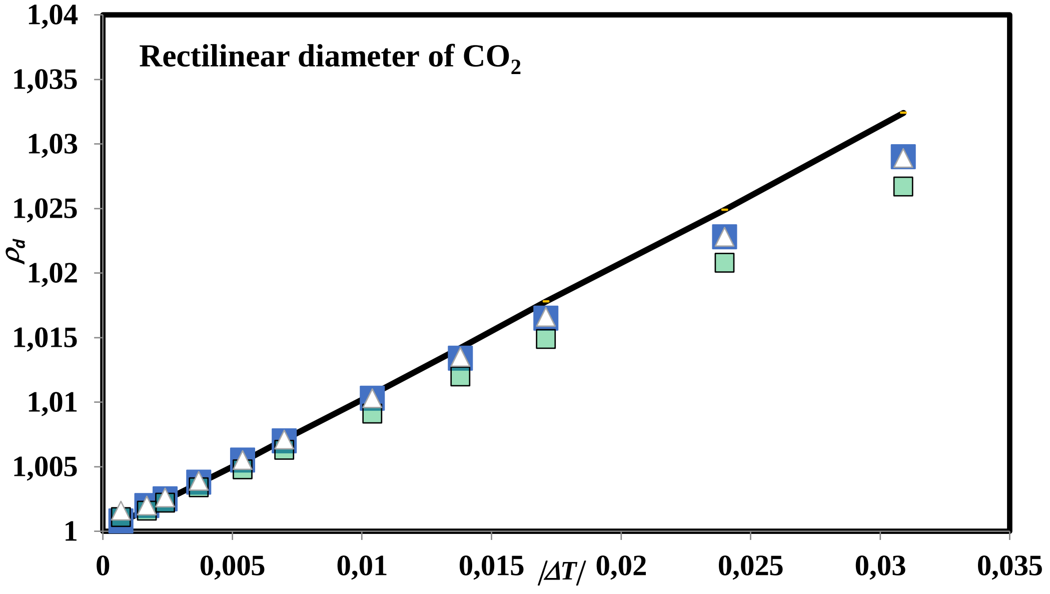

Figure 1 - Coexistence-curve diameter for carbon dioxide as a function of reduced temperature. The green squares indicate the experimental data obtained by Duschek et al., (1990). The Solid curve represents the values from the crossover model and the blue squares are the values calculated from Eq. (12).

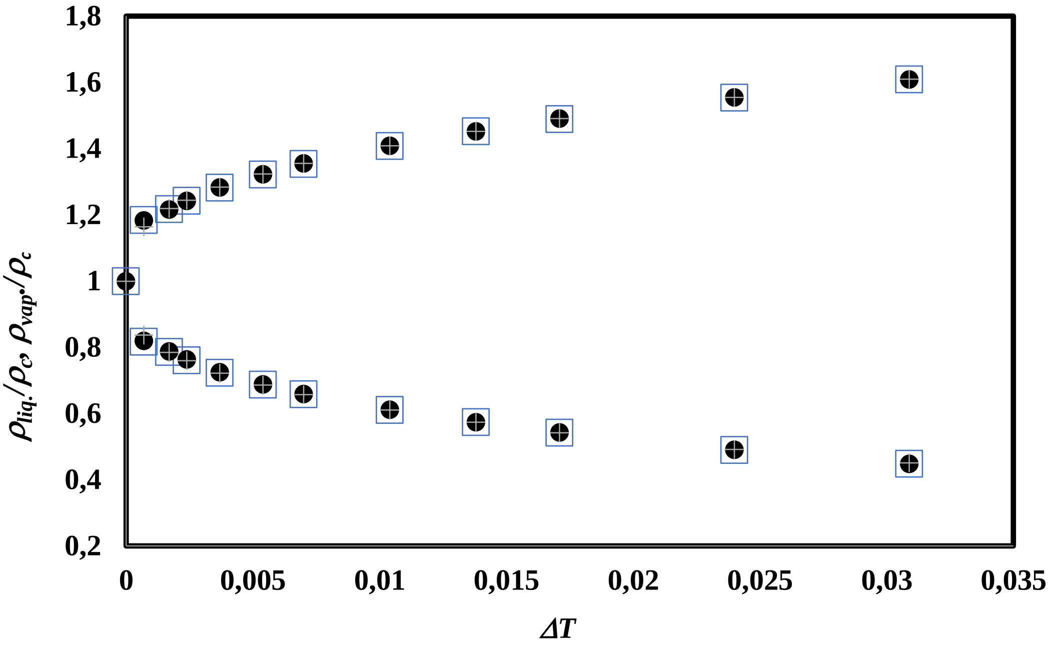

Figure 2 - Density-temperature diagram.

The open squares represent the experimental data of Duschek et al., the crosses represent the prediction from the crossover model and the closed circles represent the data generated form REFPROP. The point on the top of the curve is the critical point characterized by (T_c, ρ_c).

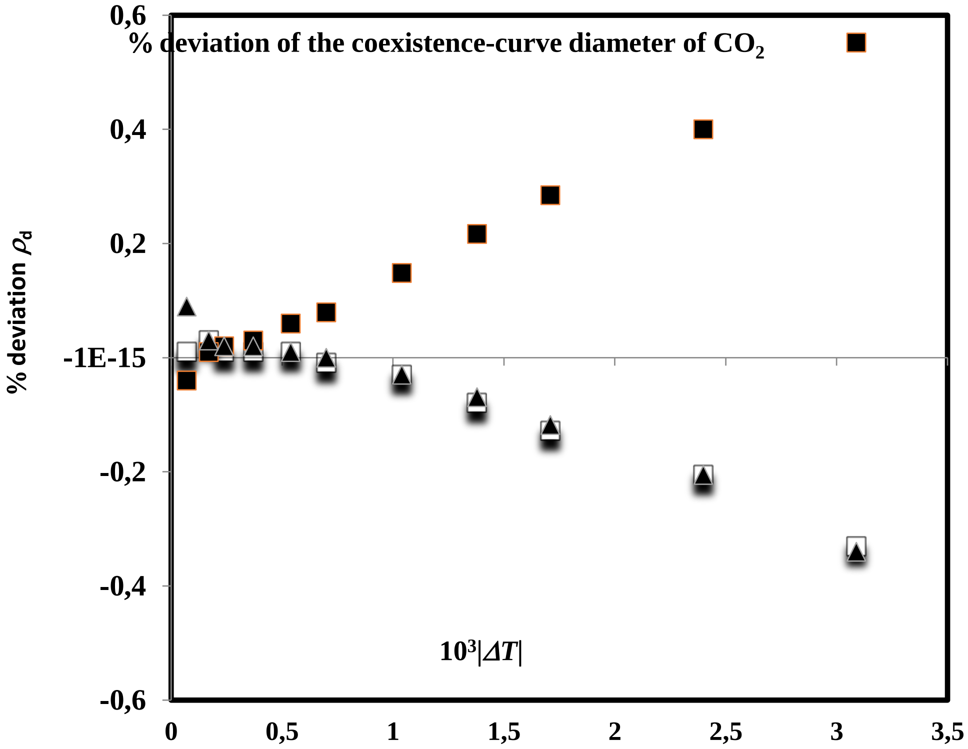

Figure 3 - Percent deviation plot of the experimental coexistence-curve diameter

Data obtained by Duschek et al., (1990) from its calculated values from the crossover model (open circles), those calculated from Eq. (12) (closed triangles) and those with respect to the data generated form REFPROP (open squares).

Table 3: Equilibrium liquid and vapor densities of carbon dioxide

T (K)	$\Delta\tilde{T}$	$\tilde{\rho}_{vap.}{}^{a}$	$\tilde{\rho}_{liq.}{}^{a}$	$\rho_{d}{}^{a}$	$\tilde{\rho}_{vap.}{}^{b}$	$\tilde{\rho}_{liq.}{}^{b}$	$\rho_{d}{}^{b}$	$\rho_{d}{}^{c}$	$\rho_{d}{}^{d}$
295.0	0.0309	0.4507	1.6102	1.0324	0.4480	1.6090	1.0290	1.0267	1.0289
297.0	0.0240	0.4917	1.5552	1.0249	0.4900	1.5540	1.0228	1.0208	1.0228
299.0	0.0171	0.5425	1.4905	1.0178	0.5420	1.4890	1.0165	1.0149	1.0166
300.0	0.0138	0.5736	1.4527	1.0142	0.5740	1.4520	1.0134	1.0120	1.0135
301.0	0.0104	0.6106	1.4090	1.0106	0.6110	1.4080	1.0103	1.0091	1.0103
302.0	0.0070	0.6570	1.3560	1.0071	0.6580	1.3540	1.0070	1.0063	1.0071
302.5	0.0054	0.6862	1.3236	1.0054	0.6870	1.3220	1.0055	1.0048	1.0055
303.0	0.0037	0.7223	1.2844	1.0037	0.7230	1.2820	1.0038	1.0034	1.0039
303.4	0.0024	0.7600	1.2443	1.0024	0.7610	1.2420	1.0025	1.0022	1.0026
303.6	0.0017	0.7844	1.2187	1.0017	0.7860	1.2170	1.0020	1.0016	1.0020
303.8	0.0007	0.8370	1.1643	1.0007	0.8172	1.1842	1.0008	1.0011	1.0016

a: This work; b: Ref. (Duschek et al., 1990); c: Eq. (12); d: REFPROP (NIST, 2024)

5. Discussion and conclusion

In this work, a comparison of the liquid and vapor densities experimental data is made for carbon dioxide based on a previously formulated crossover model EOS for carbon dioxide and without performing any fitting to the liquid-vapor phase experimental data, i.e., the equilibrium liquid and vapor densities. The hook characterized by the term $\left|\Delta\tilde{T}\right|^{(1-\alpha)}$ in the rectilinear diameter for carbon dioxide in Figure 1 is hardly noticeable. In addition, the crossover model equation yields a value of the specific-heat-amplitude ratio A^{+}/A^{-} that is about 5 % below the most accurate values calculated from Renormalization-Group-Theory for Ising-like model. Also, the amplitude of the hook of the coexistence-curve diameter is closely linked to the specific-heat amplitude A^{-} which makes so often very difficult to make any conclusion in regards to the magnitude of this hook as long as the amplitude ratio is not accurately determined (Chen et al. 1990; Rizi and Abbaci 2024).

Acknowledgments

We acknowledge the financial support from the Direction Générale de la Recherche Scientifique et technologique (DGRST) for the computer time and the grant awarded to the "Laboratoire de Synthèse et de Biocatalyse Organique/ FNRE/MESRS Algeria".

References

Abbaci, A., (2005). Thermodynamic properties of ethane in the critical region. *J. Mol. Liq.*, 118, 31-36. https://doi.org/10.1016/j.molliq.2004.07.006

Abbaci A. and Berrezeg. A. (2004). A Thermodynamic Equation of State for the Critical Region of Ethylene. *Int. J. of Thermophys.*, 25, 739–752. https://doi.org/10.1023/B:IJOT.0000034235.06616.97

Abbaci, A., Berrezeg, A. and Samar, M. E. H. (2003/2007). Prediction of the coexisting liquid and vapour densities of ethylene near the critical point, *High temperatures-High Pressures*, 35/36, , 691-697.

Abbaci, A. (2004). The coexistence curve diameter of Sulfur Hexafluoride in the critical point, *Iran. J. Chem. & Chem. Eng.*, 23 (1), 103-108, 10.30492/ijcce.2004.8167.

Akgerman, A. and Madras, G. (1994). Supercritical fluids-Fundamentals for application. *Nato ASI Ser. E 273*, Kluwer, Dordrecht, 669-695.

Beckman, E. J. (1996). Carbon dioxide extraction of biomolecules. *SCIENCE*, 271(5249), 613-614. *American Association for the Advancement of Science* (AAAS). https://doi: 10.1126/science.271.5249.613.

Burton M., and Balzarini, D. A. (1974). Lorentz–Lorenz Coefficient of Ethane. Can. J. Phys., 52, 2011-2013. https://doi.org/10.1139/p74-266

Cansell, F., Botella, Ph., Garrabos, Y., Six, J.L., Gnanou Y., and Tufeu, R. (1997). Thermodynamic aspects of supercritical fluids processing: applications to polymers and wastes treatment. *Polymers J.*, 29, 910-916. https://ogst.ifpenergiesnouvelles.fr/articles/ogst/pdf/1998/01/cansell_v53n1.pdf

Cansell, F., Chevalier, B., Demourgues, A., Etourneau, J., Even, C., Pessey, V., Petit, S., Tressaud, A. and Weill, F. (1999). Supercritical fluid processing: a new route for materials synthesis. *J. Mater. Chem.*, 9, 67-75. https://DOI: 10.1039/A804964E.

Chen, D. T., Craig, A. P., Reichert E. and Hoven, J. (1995). Depolymerization of tire and natural rubber using supercritical fluids. *J. Hazar. Mat.*, 44, 53-60. https://DOI:10.1016/0304-3894(95)00047-X

Chen, Z. Y., Abbaci, A., Tang, S. and Sengers, J. V. (1990). Global thermodynamic behavior of fluids in the critical region. *Phys. Rev. A*, 42, 4470-4484. https://doi.org/10.1103/PhysRevA.42.4470

Duschek, W., Kleinrahm, R., Wagner, W. (1990). Measurement and correlation of the (pressure, density, temperature) relation of carbon dioxide II. Saturated-liquid and saturated-vapour densities and the vapour pressure along the entire coexistence curve. *J. Chem. Thermodyn.*, 22, 841-864. doi:10.1016/0021-9614(90)90173-N

Hutchenson, K.W. and Foster N.R. (1995). Innovations in supercritical fluids science and technology. *ACS Symposium,* Serie 608, Washington. https://DOI: 10.1021/bk-1995-0608.ch001

Kiran E. (1994). Supercritical fluids-Fundamentals for application. *Nato ASI Ser. E 273*, Kluwer, Dordrecht, 541-588.

Ley-Koo M. and Green M.S. (1977). Revised and extended scaling for coexisting densities of SF_6. *Phys. Rev. A*, 16, 2483- 2487. DOI:https://doi.org/10.1103/PhysRevA.16.2483

Michels, A. and Michels, C. (1935). Isotherms of CO_2 between 0° and 150° and pressures from 16 to 250 atm (Amagat densities 18-206), *Proc. R. Soc A*, London Ser., 53, 201-214.

Michels, A. and Michels, C., and Wooters, H. (1935). Isotherms of CO_2 between 70 and 3000 atmospheres (Amagat densities between 200 and 600), *Proc. R. Soc. A*, London Ser., 153, 214-224.

Michels, A. and Blaisse, B. (1937). The isotherms of CO_2 in the neighbourhood of the critical point and round the coexistence line, *Proc. R. Soc. A*, London Ser., 160, 358-375. https://doi.org/10.1098/rspa.1937.0114

Nicoll, J. F., and Albright, P.C. (1985). Crossover functions by renormalization-group matching: Three-loop results. Phys. Rev. B, 31, 4576-4589. Doi:10.1103/PhysRevB.31.4576.

Nicoll, J. F. (1983). Nonlinear Solutions of Renormalization-Group Equations. *Phys. Rev. A*, 24, 2203-2220. https://Doi:10.1103/PhysRevLett.33.1524.3

Nicoll, J. F., and Bhattacharjee, J. K. (1983). Crossover functions by renormalization-group matching: $O(\varepsilon 2)$ results. *Phys. Rev. B.*, (1981), 23, 389-401. DOI:https://doi.org/10.1103/PhysRevB.23.389

NIST Chemistry WebBook, (2023). *NIST Standard Reference* Database SRD Number *69*. Last update to data, DOI: https://doi.org/10.18434/T4D303.

Page, S.H. , Morrison J.F. and Lee, M.L. (1994). Supercritical fluids-Fundamentals for application. *Nato ASI Ser. E 273*, Kluwer, Dordrecht, 641-652.

Pestak, M. W., Goldstein, R. E., M. H. W. Chan, J. R.,De Bruyn, Balzarini D. A. & Ashcroft N. W. (1987). Three-body interactions, scaling variables, and singular diameters in the coexistence curves of fluids. *Physical Review B, 36*(1), 599-614. https://doi.org/10.1103/PhysRevB.36.599

Rizi, A., and Abbaci, A. (2024). An Equation of State for the Thermodynamic Properties of Fluid n-Butane in the Critical Region. *Int. J. Thermophys.*, 45 (5), https://DoI:10.1007/s10765-024-03354-y

Rizi, A. and Abbaci, (2012), A. A thermodynamic equation of state for the critical region of argon.

J. Mol. Liq., 171, 64-70. https://doi.org/10.1016/j.molliq.2012.04.010

Schneider, G.M. (1983). Physicochemical aspects of fluid extraction, Fluid Phase Equilib. 10, 141-157.

Weiner J., Langley K. H., and Ford N. C., Jr. (1974). Experimental evidence for a departure from the law of the rectilinear diameter. *Phys. Rev. Lett.*, 32, 879- 881. https://doi.org/10.1103/PhysRevLett.32.879