PREDICTION OF THE DENSITIES AND PRESSURES OF ETHANE ON THE COEXISTENCE

A. Abbaci[*], Faculté des Sciences, Département de Chimie, Université Badji-Mokhtar, B. P.12, El-Hadjar, Annaba (23200), Algeria, e-mail : azzedineabbaci@hotmail.com, Tél : +213-71-35-87-15, Fax: +213-38-86-85-10

Abstract:

The coexisting liquid and vapor densities and the pressure of ethane are predicted from a global equation of state in the vicinity of the critical point. Specifically, a crossover thermodynamic potential is used to represent the thermodynamic data of ethane accurately. The hook of the rectilinear diameter very close to the critical point is reproduced using this model and the scaling laws.

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Keywords: Coexisting densities, critical point, crossover model, ethane, equation of state, pressure.

INTRODUCTION:

The critical thermodynamic behavior of fluid systems has been the subject of several investigators [1], conducted in analogy with the 3-dimensional Ising-like systems. The thermodynamic surface of fluids exhibits a singularity at the critical point. This behavior can be characterized in terms of scaling laws with universal critical exponents and universal scaling functions [1-3]. Unlike 3-dimensional Ising-like systems, fluids exhibit a lack of vapor-liquid symmetry in its coexistence-curve. In the present work, we give the application of the crossover model to the coexistence-curve diameter to ethane, and show that we can reproduce the liquid-vapor coexistence curve diameter only by using a newly formulated equation of state for ethane [4].

FUNDAMENTAL EQUATION:

Starting from earlier work Nicoll et al. [5-7], we have developed a crossover model to represent the thermodynamic properties of fluids in the critical region [5]. This crossover model is based on the renormalization group theory of critical phenomena to include the cooperative effects associated with the long-range critical fluctuations up to a maximum microscopic wavenumber.

Let ρ be the density, T the temperature, P the pressure, μ the chemical potential and A/V the of Helmholtz free energy per unit volume. We make these properties dimensionless with the aid of the critical parameters [4, 8]:

$$\widetilde{\rho}=\rho/\rho_c, \quad \widetilde{T}=-T_c/T, \quad \widetilde{P}=PT_c/P_cT, \quad \widetilde{\mu}=\mu\rho_cT_c/P_cT, \quad \widetilde{A}=AT_c/P_cVT \tag{1}$$

In addition we define

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

(2)

and

$$\Delta\widetilde{A}=\widetilde{A}-\tilde{\rho}\tilde{\mu}_0(\widetilde{T})-\widetilde{A}_0(\widetilde{T}).$$

(3)

Here $\tilde{\mu}_0(\widetilde{T})$ and $\widetilde{A}_0(\widetilde{T})$ are analytic background functions of T subject to the conditions that at the critical temperature $\Delta\tilde{\mu}(T=T_c)=0$ and $\widetilde{A}_0(T=T_c)=-1$.

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:

$$\Delta\widetilde{A}_{cl} = \frac{1}{2}tM^2 + \frac{u_0}{4!}M^4 + \frac{a_{05}}{5!}M^5 + \frac{a_{06}}{6!}M^6 + \frac{a_{14}}{4!}tM^4 + \frac{a_{22}}{2!2!}t^2M^2 .$$

(4)

Where t and M are temperature-like and density-like variables related to ΔT and $\Delta\rho$ in a manner to be specified below. The coefficient u_0 of the M^4 term in (4) is $u_0=u\Lambda$, where Λ a dimensionless cutoff wave number [9] is. In order to obtain a fundamental equation that can be applied in a large range of densities and temperatures around the critical point we renormalize t, M and u_0 to obtain:

$$\Delta\widetilde{A}_r = \frac{1}{2}tM^2 \mathbf{TD} + \frac{u_0}{4!}M^4 \mathbf{D}^2\mathbf{U} + \frac{a_{05}}{5!}M^5 \mathbf{D}^{5/2}\mathbf{VU} + \frac{a_{06}}{6!}M^6 \mathbf{D}^3\mathbf{U}^{3/2}$$

$$+ \frac{a_{14}}{4!}tM^4 \mathbf{TD}^2\mathbf{U}^{1/2} + \frac{a_{22}}{2!2!}t^2M^2\mathbf{T}^2\mathbf{DU}^{-1/2} - \frac{1}{2}t^2\mathbf{K}$$

(5)

where the functions $\mathbf{T}$, $\mathbf{D}$, $\mathbf{U}$, $\mathbf{V}$ and $\mathbf{K}$ are defined by

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

(6)

The crossover function Y in Eq. (6) is to be determined from:

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

(7)

with

$$\kappa^2 = t\mathbf{T}+1/2 \, u\Lambda M^2 \, \mathbf{DU},$$

(8)

The constants ν, η, ω and ω_a are universal critical exponents, u^* is another universal constant presented in Table 1. The variable κ is related to the inverse correlation length and is a measure of distance from the critical point.

The effect of the lack of symmetry in fluids can be incorporated by the mixing of the field variables t and M through the following definition

$$\Delta\widetilde{A} = \Delta\widetilde{A}_r - c\left(\partial\Delta\widetilde{A}_r/\partial M\right)_t\left(\partial\Delta\widetilde{A}_r/\partial t\right)_M \tag{9}$$

where c is the mixing parameter. The variables t and M are related to ΔT and $\Delta\rho$ as:

$$t = c_t\Delta\widetilde{T} + c\left(\partial\Delta\widetilde{A}_r/\partial M\right)_t, \tag{10}$$

$$M = c\rho(\Delta\widetilde{\rho} - d_1\Delta\widetilde{T}) + c\left(\partial\Delta\widetilde{A}r/\partial t\right)_M \tag{11}$$

where d_1 is a constant representing global symmetry. The expression of (9) for $\Delta\widetilde{A}$ is to be substituted into (3). To specify the Helmholtz free–energy density completely the analytic background functions $\widetilde{\mu}_0(\widetilde{T})$ and $\widetilde{A}_0(\widetilde{T})$ are represented by truncated Taylor expansions through the relations:

$$\widetilde{\mu}_0(\widetilde{T}) = \sum_{j=1}^{j=4}\widetilde{\mu}_j(\Delta\widetilde{T})^j \; and \; \widetilde{A}_0(\widetilde{T}) = -1 + \sum_{j=1}^{j=4}\widetilde{A}_j(\Delta\widetilde{T})^j \tag{12}$$

APPLICATION TO ETHANE:

Ethane is an important substance due to Its presence In most natural gases and petroleum. The crossover parameters $\bar{u}$ and Λ, the scaling-field parameters c, c_t, c_ρ and d_1, the classical parameters a_{05}, a_{06}, a_{14} a_{22} and the background parameters $\widetilde{A}_j$ which can be determined by fitting the crossover model to the P-ρ-T data of Funke et al. [10] associated with those of Claus et al. [11]. The system dependent parameters are presented into Table 1.

We denote the liquid density by $\rho_{liq.}$ and the vapor density by $\rho_{vap.}$, ρ_c as the critical density, and $\Delta\widetilde{T}$ the reduced temperature. Then close to the critical point, the renormalization-group theory predicts [12] the following equation:

$$\rho_d = \frac{(\rho_{liq} + \rho_{vap})}{2\rho_c} = 1 + d_1\Delta\widetilde{T} + d_{s1}\left|\Delta\widetilde{T}\right|^{(1-\alpha)} + d_{s2}\left|\Delta\widetilde{T}\right|^{(1-\alpha+\Delta)} + \ldots, \tag{13}$$

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 given in Table 2. A comparison of the obtained equation of state [4] with experimental data of Pestak et al. [13] and Douslin

and Harrison [14] and those of Funke et al. [10] rectilinear diameter is presented in Figure 1. In this comparison the offset of Pestak's

Finally, we present in Figs. 1-3, the comparison of the crossover model with the experimental data of the rectilinear diameter, liquid and vapor densities and their differences, as reported by Funke et al. [10], Pestak et al. [13], Douslin and Harrison [14], and those reported by Khazanova and Sominskaya [15].

The data sets reported by Funke et al. [10] show satisfactory consistency, if one keeps in mind that none of the saturated density-data for ethane were used to determine any of the system-dependent parameters in the crossover equation of state. The offset of Pestak's data 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, and even at moderate densities the deviations of the Lorentz-Lorentz formula from the true values could amount to as much as a few percent.

Table 1: Critical exponents

$v = 0.630,\ \eta = 0.033,\ \alpha = 2-3v = 0.110,\ \Delta = 0.51,\ \omega_a = 2.1,\ u^* = 0.47$

Table 2: System-dependent constants for C_2H_6

Critical parameters: $T_c = 305.322$, $P_c = 4.8722$ MPa, $\rho_c = 6.86$ mol L^{-1}

Crossover parameters: $\bar{u} = 0.2269$, $\Lambda = 3.288$

Scaling-field parameters: $c_t = 1.9836$, $c_\rho = 2.4318$, $c = -0.0224$
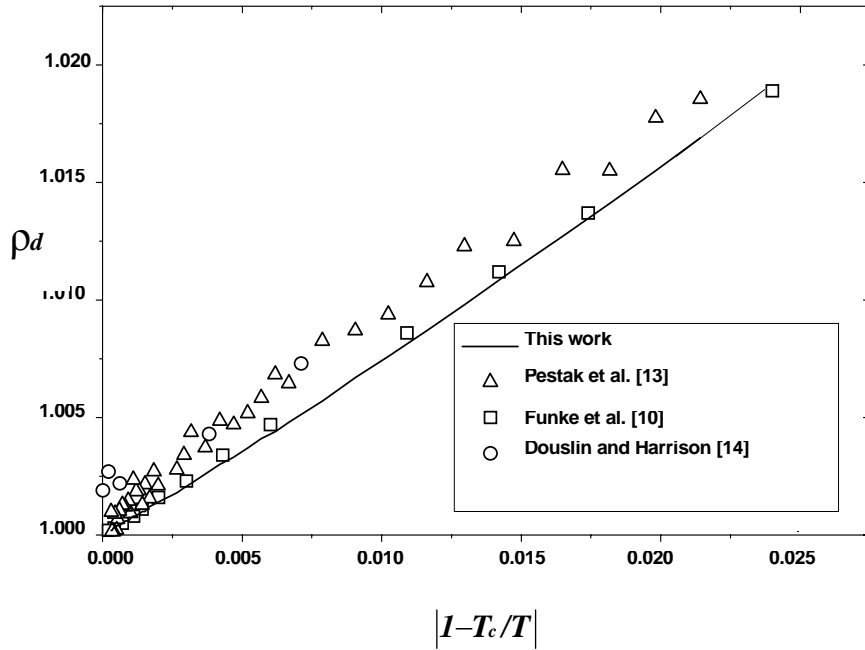
P-ρ-T background parameters: $\tilde{A}_0 = -1$, $\tilde{A}_1 = -5.453$, $\tilde{A}_2 = 3.988$, $\tilde{A}_3 = -2.306$, $\tilde{A}_4 = 7.541$, $d_1 = -0.2782$

Classical Parameters: $a_{05} = -0.499$, $a_{06} = 1.453$, $a_{14} = 0.299$, $a_{22} = 0.207$

Range of validity of the equation of state:

$-0.0246 \leq \Delta\tilde{T} \leq 0.1965$ and $0.496 \leq \rho/\rho_c \leq 1.68$

Figure 1: Coexistence diameter $\rho_d = \dfrac{(\rho_{liq.} + \rho_{vap.})}{2\rho_c}$ for ethane as a function of reduced temperature. The squares indicate the experimental data obtained by Pestak et al., Funke et al. and Douslin and Harrison. The Solid curve represents the values from the crossover model.
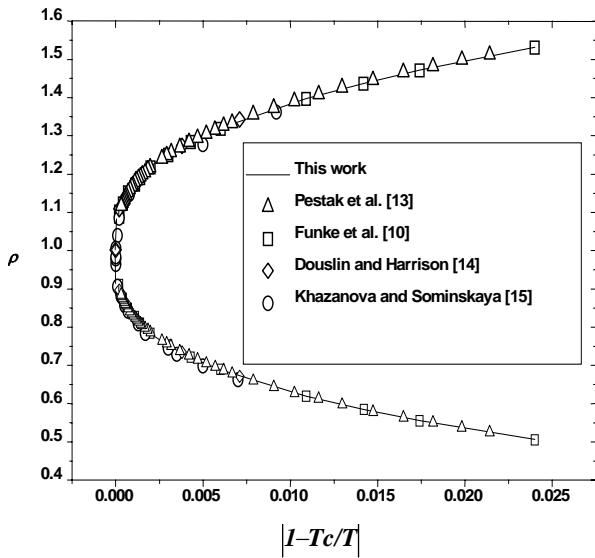
Figure 2: Liquid and vapor densities of ethane as a function of reduced temperature. The squares indicate the experimental data obtained by Pestak et al., Funke et al. and Douslin and Harrison. The Solid curve represents the values from the crossover model.
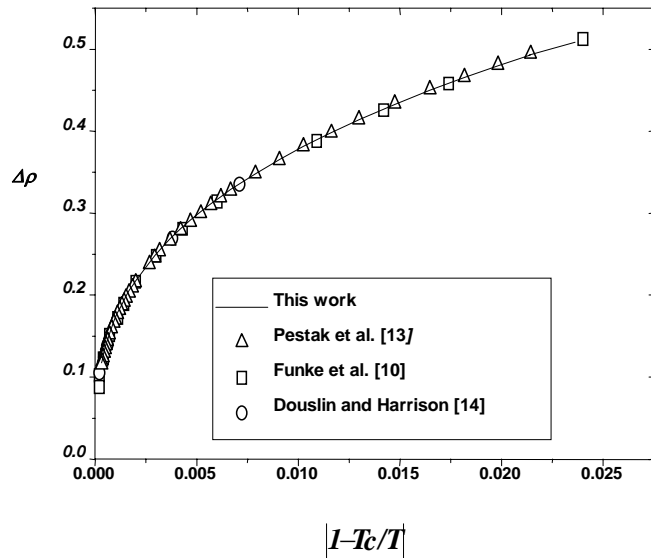
Figure 3: Density differences $\rho_d = \dfrac{(\rho_{liq.} - \rho_{vap.})}{2\rho_c}$ of ethane as a function of reduced temperature. The squares indicate the experimental data obtained by Pestak et al., Funke et al. and Douslin and Harrison. The Solid curve represents the values from the crossover model.

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