LIQUID-VAPOR DENSITY OF ETHANE IN THE CRITICAL POINT

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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 ethane. We also present a comparison of the crossover model equation with the experimental data.

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KEY WORDS: Crossover model, Fluids, Rectilinear diameter, ethane.

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. With $\tilde{\rho} = \dfrac{\rho}{\rho_c}$, $\tilde{T} = -\dfrac{T_c}{T}$, $\tilde{P} = \dfrac{PT_c}{P_c T}$, $\qquad$ (1)

we can write asymptotically:

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

and

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

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:

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

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 [2-4]. 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 [3]:

$$\Delta \tilde{A}_{cl} = \frac{1}{2}tM^2 + \frac{u_0}{4!}M^4 + ...,$$ (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, 3]. 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 (5) for ΔA_{cl} as shown by Abbaci [4]. The theoretically predicted asymptotic behavior can be recovered from this expansion by the following transformation so that:

$$\Delta \tilde{A}_r = \frac{1}{2}tM^2 TD + \frac{u_0}{4!}M^4 D^2 U + \frac{a_{05}}{5!}M^5 D^{5/2} VU +$$ (6)

$$\frac{a_{06}}{6!}M^6 D^3 U^{3/2} + \frac{a_{14}}{4!}tM^4 TD^2 U^{1/2} +$$

$$\frac{a_{22}}{2!2!}t^2 M^2 T^2 DU^{-1/2} - \frac{1}{2}t^2 K$$

The coefficients $a_{05},$ $a_{06},$ $a_{14},$ a_{22} are also system-dependent parameters, and where the functions T, D, U, V and K are defined by:

$$T = Y^{(2-1/\nu)/\omega}, \quad D = Y^{-\eta/\omega}, \quad U = Y^{1/\omega}$$ (7)

$$V = Y^{(2\omega_a - 1)/2\omega}, \quad K = \frac{\nu}{\alpha \bar{u} \Lambda}\left[Y^{-\alpha/\nu\omega} - 1 \right]$$ (8)

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

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

With

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

and

$$\bar{u} = u / u^*$$ (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. (6) the scaled critical behavior, while for large values of κ the crossover function Y approaches unity and Eq. (6) reduces to the classical Landau expansion of Eq. (5).

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:

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

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

$$M = c_\rho (\Delta\widetilde{\rho} - d_1 \Delta\widetilde{T}) + c \left(\frac{\partial \Delta\widetilde{A}_r}{\partial t} \right)_M$$ (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 $\Delta\widetilde{T}$ the reduced temperature. Then close to the critical point, the renormalization-group theory predicts that [6]:

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

Table 1: Universal critical-region constants

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

Since $(1-\alpha)$ is close to unity, the singularity in the coexistence-curve diameter is very difficult to detect. However, early experiments performed by Weiner, Langley and Ford on ethane[7], whose data have been further analyzed by Ley-Koo and Green [6], indicate that the singular term is present. Subsequent experiments performed by Pestak and coworkers for nitrogen, neon, and for ethane and ethylene [8] 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:

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

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

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

$$\frac{\rho_{liq}-\rho_{vap}}{2\rho_c} = A_\beta \left|\Delta\tilde{T}\right|^{\beta} + A_{\beta+\Delta}\left|\Delta\tilde{T}\right|^{\beta+\Delta} + A_{\beta+2\Delta}\left|\Delta\tilde{T}\right|^{\beta+2\Delta}, \tag{18}$$

with β a new critical exponent with a value listed on Table1. 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 ETHANE

Ethane is an important substance sure to its presence in most natural gases and petroleum. The crossover parameters $\bar{u}$ and Λ as well as the background parameter $\tilde{A}_j$ and the classical parameters a_{ij} by fitting the crossover model to the P-ρ-T to the data of Fuke et al. [9] associated to those of Claus et al. [10]. The system dependent parameters are presented into Table 2. The comparison of Funke et al. and those of Claus et al. along with the liquid-vapor data of Douslin and Harrison [11] are presented in Fig. 1 and 2.

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

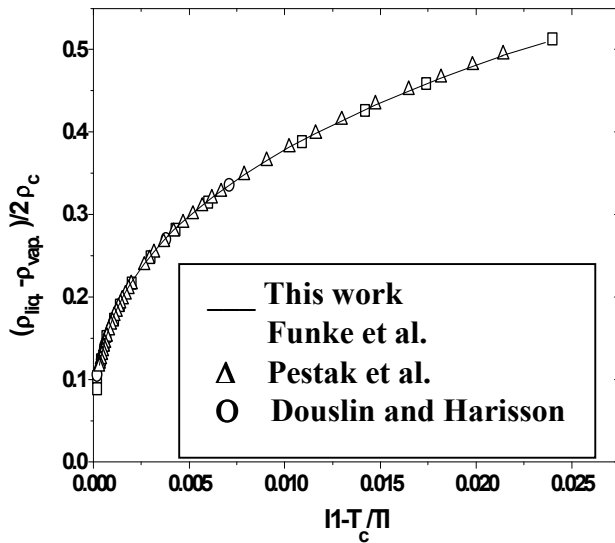| |
|---|
| Crossover parameters: $\Lambda=3.288$, $\bar{u}=0.2269$, $c_t=1.9836$, $c_\rho=2.4318$, $c=-0.0224$ |
| Background parameters:
 $\tilde{A}_0=-1$, $\tilde{A}_1=-5.453$, $\tilde{A}_2=3.988$, $\tilde{A}_3=-2.306$, $\tilde{A}_4=7.541$, $d_1=-0.2782$ |
| Classical parameters: $a_{05}=-0.499$, $a_{06}=1.453$, $a_{14}=0.299$, $a_{22}=0.207$ |
| Range of validity: $-0.0246\leq \Delta\tilde{T} \leq 0.1965$ and $0.496\leq \Delta\tilde{\rho} \leq 1.68$ |
| Critical parameters: $T_c=305.322$ K, $\rho_c=6.86$ mol/L, $P_c=4.8722$ MPa |

FIGURE 1:
Rectilinear diameter of ethane
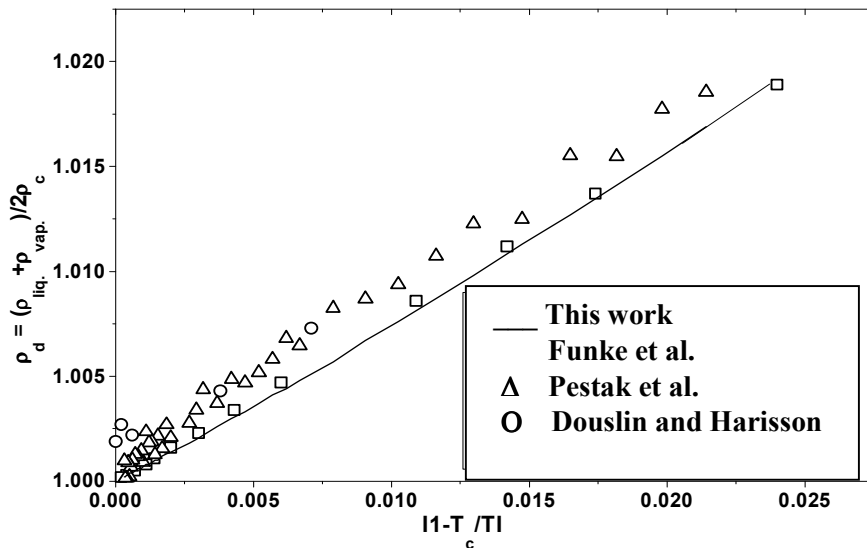$$\frac{\left(\rho_{liq.} - \rho_{liq.}\right)}{2\rho_c}$$

FIGURE 2: Liquid-vapor coexistence curve of ethane
$$\frac{\left(\rho_{liq.} + \rho_{liq.}\right)}{2\rho_c}$$

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

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