

# Thermodynamic properties of ethane in the critical region<sup>☆</sup>

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## Abstract

The thermodynamic properties of fluids are predicted using global equations of state. Among these thermodynamic properties, we consider the densities of the liquid and vapor phases, pressure, the caloric properties such as specific heat at constant volume and specific heat at constant pressure and the speed of sound. In the present work, we apply the crossover theory to these thermodynamic properties and give a comparison of the crossover model equation of state with the experimental thermodynamic property data of ethane.

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## 1. Introduction

The asymptotic singular behavior of the thermodynamic properties of fluids in the vicinity of the critical point can be described in terms of scaling laws with universal scaling exponents and universal scaling functions [1,2]. A revised and extended parametric equation, which incorporates the theoretically predicted asymptotic scaling behavior, was formulated by Balfour et al. [3]. This parametric equation yields an accurate representation of the thermodynamic properties of fluids such as ethane near the critical point as documented by Levelt Sengers et al. [4,5].

The validity of the scaled parametric equations, however, is limited to a small range of temperatures and densities around the critical point. In order to represent the thermodynamic properties in a wider range of temperatures and densities, a theory for the nonasymptotic thermodynamic behavior has to be implemented. The singular thermodynamic behavior is obtained from the renormalization group theory of critical phenomena by linearizing the renormalization equation around the fixed point [6]. The nonasymptotic thermodynamic behavior can be obtained by considering the full nonlinear renormalization equations [6–

8]. The theory needs to account for the effect of critical fluctuations up to a maximum wave number comparable to an inverse microscopic length. Since near the critical point the correlation length becomes large, the dependence of the solution of the renormalization equations on the cutoff wave number is unimportant. However, to obtain a complete crossover from critical behavior to regular behavior, the effect of the cutoff wave number must be retained, since one must recover the regular behavior when the correlation length becomes microscopic [8–10].

Based on these principles, Albright et al. [11] and Chen et al. [12] have formulated a theory for this crossover behavior. In their earlier approach, the classical theory was presented by a two-term Landau expansion. While a two-term crossover theory was sufficient to describe some of the basic features of the crossover theory, it is restricted to a limited range of validity around the critical point. The point is that far away from the critical point, where the classical theory should become valid, a two-term classical equation itself will not be adequate. The reasons for the formulation of this new equation of state of ethane encompass significant new and accurate pressure data reported by Funke et al. [15] and Claus et al. [16] and improvements in the extension of the crossover theory to be used in connection with a six-term Landau expansion [8]. Therefore, Abbaci [13] and Abbaci et al. [14] have subsequently extended the crossover theory to be used in conjunction with a six-term Landau expansion.

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In this work, we shall proceed as follows. In Section 2, we present the crossover theory, in Sections 3 and 4, we discuss the application of the model to ethane and use it to analyze the available experimental data for C<sub>2</sub>H<sub>6</sub> in the critical region.

## 2. Crossover theory

Let  $\rho$  be the density,  $T$  the temperature,  $P$  the pressure,  $\mu$  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 [13,14]:

$$\begin{aligned}\tilde{\rho} &= \rho/\rho_c, \tilde{T} = -T_c/T, \tilde{P} = PT_c/P_c T, \\ \tilde{\mu} &= \mu\rho_c T_c/P_c T, \tilde{A} = AT_c/P_c V T\end{aligned}\quad (1)$$

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  $\Delta\tilde{\mu}(T = T_c) = 0$  and  $\tilde{A}_0(T = T_c) = -1$ .

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:

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

where  $t$  and  $M$  are temperature-like and density-like variables related to  $\Delta T$  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 Eq. (4) as  $u_0 = uA$ , where  $A$  is a dimensionless cutoff wave number [7–9], the coefficients  $a_{05}$ ,  $a_{06}$ ,  $a_{14}$ ,  $a_{22}$  are the classical system-dependent parameters.

The theoretically predicted asymptotic behavior can be recovered from this expansion by the following transformation:

$$\begin{aligned}\Delta\tilde{A}_r &= (1/2)tM^2TD + (u_0/2!)M^4D^2U \\ &+ (a_{05}/5!)M^5D^{5/2}VU + (a_{06}/6!)M^6D^3U^{3/2} \\ &+ (a_{14}/4!)tM^4TD^2U^{1/2} \\ &+ (a_{22}/2!2!)t^2M^2T^2DU^{-1/2} - (1/2)t^2K\end{aligned}\quad (5)$$

Table 1  
Universal critical-region constants

$v=0.630$
$\eta=0.033$
$\alpha=2-3v=0.110$
$\Delta=0.51$
$\omega_a=2.1$
$u^*=0.472$

where the functions  $T$ ,  $D$ ,  $U$ ,  $V$  and  $K$  are defined by

$$\begin{aligned}T &= Y^{(2-1/v)/\omega}, D = Y^{-\eta/\omega}, U = Y^{1/\omega} \\ V &= Y^{(2\omega_a-1)/2\omega}, K = v/\alpha\bar{u}A \left[ Y^{-\alpha/v\omega} - 1 \right]\end{aligned}\quad (6)$$

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

$$1 - (1 - \bar{u})Y = \bar{u}(1 + \Delta^2/\kappa^2)^{1/2}Y^{1/\omega} \quad (7)$$

with

$$\kappa^2 = tT + 1/2 uAM^2 \quad DU, \quad (8)$$

and

$$\bar{u} = u/u^* \quad (9)$$

In these expressions  $v$ ,  $\eta$ ,  $\omega$  and  $\omega_a$  are universal critical exponents,  $u^*$  is another universal constant. The values of the universal critical-region parameters are specified in Table 1.

The crossover model depends parametrically on the variable  $\kappa^2$  defined by Eq. (8). For the small values of  $\kappa$  one recovers from Eq. (5), the scaled critical behavior, while for large values of  $\kappa$  the crossover function  $Y$  approaches unity and Eq. (5) reduces to the classical Landau expansion Eq. (4). In order to apply the crossover model to fluids, we need to introduce a proper translation to fluid variables [13]. This is accomplished by the transformation:

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

$$M = c_\rho(\Delta\tilde{\rho} - d_1\Delta\tilde{T}) + c\left(\partial\Delta\tilde{A}_r/\partial t\right)_M \quad (11)$$

with the corresponding transformation:

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

where  $c$ ,  $c_t$ ,  $c_\rho$  and  $d_1$  are system-dependent constants. Finally, the total Helmholtz free-energy density is obtained from Eq. (3) as:

$$\Delta\tilde{A} = \tilde{A} - \tilde{\rho}\tilde{\mu}_0(\tilde{T}) - \tilde{A}_0(\tilde{T}) \quad (13)$$

with

$$\begin{aligned}\tilde{\mu}_0(\tilde{T}) &= \sum_{j=1}^{j=4} \tilde{\mu}_j(\Delta\tilde{T})^j \text{ and } \tilde{A}_0(\tilde{T}) \\ &= -1 + \sum_{j=1}^{j=4} \tilde{A}_j(\Delta\tilde{T})^j\end{aligned}\quad (14)$$

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