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Global thermodynamic behaviour of supercritical fluids: example of methane and ethane

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Abstract. Do to the fluctuations associated with the critical region of fluids. The behavior of thermodynamic properties these can not be predicted by mean field theories. To do so, a global equation of state based on the crossover model has been used. This equation of state is formulated on the basis of comparison of selected measurements of pressure-density-temperature data, isochoric and isobaric heat capacity of fluids.The model can be applied in a wide range of temperatures and densities around the critical point for ethane and methane. It is found that the developed model represents most of the reliable experimental data accurately.

1 Introduction

Methane and ethane are important fluids which are present in natural gas and Petroleum. Many efforts are diploid to formulate an equation of state for describing the thermodynamic properties of these two systems.

In fact, the work described in this paper is part of a research effort to develop a comprehensive but preliminary fundamental equation for the thermodynamic properties of ethane and methane in the critical region that extends to the classical region. The formulated equation of state covers the entire range of temperatures and densities around the critical region and also can describe the behavior of the thermodynamic properties of ethane and methane in the classical region far away from the critical region. Several analytic equations of state as well as non-analytical equations of state were proposed earlier [1].

Accurate information on the thermodynamic properties of fluids is highly sought for the chemical technology. The thermodynamic properties of fluids near the critical region are strongly affected by the presence of fluctuations and therefore, cannot be described by conventional equation. We have investigated an interim formulation for the behavior of the thermodynamic properties of methane and ethane in the vicinity of the critical region. For this reason we have used the so-called "Crossover Model" to describe the thermodynamic properties of methane and ethane in a wide range of temperatures and densities [2, 3].

2 Crossover model

The description of the thermodynamic properties in the neighborhood of the critical region, as well as in the classical region by using two different formalisms, will introduce discontinuities of the caloric properties; such as Cv, Cp and Cs. Therefore, we introduce another alternative: a unified function that describes these properties with a smooth transition from the critical region to the classic region (without a jump).

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 [4]:

$$\tilde{T} = -\frac{Tc}{T},$$

$$\tilde{u} = \frac{\mu\rho_c T_c}{TP_c},$$

$$\tilde{P} = \frac{PT_c}{TP_c}$$

$$\tilde{\rho} = \frac{\rho}{\rho_c},$$

$$\tilde{A} = \frac{AT_c}{VTP_c},$$

$$\tilde{U} = \frac{U}{VP_c}$$

$$\tilde{S} = \frac{ST_c}{VP_c},$$

$$\tilde{H} = \frac{HT_c}{VTP_c},$$

$$\tilde{\chi} = \left[\frac{\partial\tilde{\rho}}{\partial\tilde{\mu}}\right]_T$$

$$\tilde{C}_V = \frac{C_V T_c}{VP_c},$$

$$\tilde{C}_P = \frac{C_P T_c}{V P_c},$$
$$\tilde{W} = W\left[\frac{\rho_c T_c}{P_c T}\right]^{1/2} \quad (1)$$

in addition we define

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

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 $\tilde{A}_0(T = T_c) = -1$.

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 $\Delta A cl$:

$$\Delta\tilde{A}_{cl} = (1/2)tM^2 + (u_0/2!)M^4 + (a_{05}/5!)M^5 + (a_{06}/6!)M^6 + (a_{14}/4!)tM^4 + (a_{22}/2!2!)t^2M^2 + \ldots \quad (3)$$

As shown by Abbaci (1991) [4] the theoretically predicted asymptotic behavior can be recovered from this expansion by the following transformation

$$\Delta\tilde{A}_r = \frac{1}{2}tM^2TD + \frac{1}{4!}u_0M^4D^2U + \frac{1}{5!}a_{05}M^5D^{5/2}VU + \frac{1}{6!}a_{06}M^6D^3U^{3/2} + \frac{1}{4!}a_{14}tM^4TD^2U^{1/2} + \frac{1}{2!2!}a_{22}t^2M^2T^2DU^{-1/2} - \frac{1}{2}t^2K \quad (4)$$

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

$$T = Y^{\left(2-\frac{1}{\nu}\right)/\omega},$$
$$D = Y^{(-\eta/\omega)}, \qquad V = Y^{(2\omega_a - 1)/2\omega},$$
$$U = Y^{1/\omega},$$
$$K = \frac{\nu}{\alpha\bar{u}\Lambda}\left[Y^{-\alpha/\Delta}(1) - 1\right] \quad (5)$$

In terms of a crossover function Y to be determined from

$$1 - (1-\bar{u})Y = \bar{u}\left(1 + \Lambda^2/\kappa^2\right)^{1/2}Y^{1/\omega}$$
$$K^2 = t\,T + 1/2\ \mathrm{u}\Lambda M^2\ \ DU \quad (6)$$

and

$$\bar{u} = \mathrm{u}/\mathrm{u}^*$$

Fluid system do not exhibit the symmetry in coexistence curve as magnetic systems, also colled mixing of the field variable is needed [6,7] such as

$$t = c_t\Delta\tilde{T} + c\left(\partial\Delta\tilde{A}_r/\partial M\right)_t,$$
$$M = c_\rho(\Delta\tilde{\rho} - d_1\Delta\tilde{T}) + c\left(\partial\Delta\tilde{A}_r/\partial\right)_M$$
$$\Delta\tilde{A} = \Delta\tilde{A}_r - c\left(\frac{\partial\Delta\tilde{A}_r}{\partial M}\right)_t\left(\frac{\partial\Delta\tilde{A}_r}{\partial}\right)_M \quad (7)$$

The coefficients c, c_t, c_ρ and d_1 are system-dependent constants. Finally, the total Helmholtz free-energy density is obtained

$$\Delta\tilde{A} = \tilde{A} - \tilde{\rho}\tilde{\mu}_0(\tilde{T}) - \tilde{A}_0(\tilde{T}) \quad (8)$$

$$\tilde{\mu}_0(\tilde{T}) = \sum_{j=1}^{j=4}\tilde{\mu}_j(\Delta\tilde{T})^j$$

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

with

$$\tilde{P} = \Delta\tilde{\mu} + \Delta\tilde{\rho}\Delta\tilde{\mu} - \Delta\tilde{A} - \tilde{A}_0(\tilde{T})$$

Table 1. Universal critical-region constants.

ν= 0.630, η= 0.033, α=2-3ν=0.110, Δ=0.51, ω_a=2.1 u^*=0.472

3 Application to methane and ethane

The crossover model as applied to these two fluids contains the following system-dependent parameters: The critical parameters T_c, ρ_c, and P_c to be deduced either from an asymptotic analysis of the thermodynamic–property data near the critical point or reported by several experiments. 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 $\tilde{A}_j$ which can be determined by fitting the crossover model to the P-ρ-T data of Douslin [8] for ethane, with σ_p= 0.007%, σ_T= 0.001K, and σ_ρ= 0.02% as

an estimated errors in pressure, temperature and density. For methane, we used P-ρ-T data of Wagner and CO [9], with σ_p= 0.0001MP, σ_T= 0.005K, and σ_ρ= 0.01%. Finally the caloric background $\tilde{\mu}_i$ which can be determined from experimental isochoric specific heat capacity data reported by Shmakov [10] for ethane and Abdulagatov data [11] for methane.

The values of the critical parameters for C_2H_6 are those used by Douslin [8], which are as follows

Tc= 305.322 K, ρc= 206.18 Kg.m-3,
Pc= 4.8722MPa (9)

The values of the critical parameters for CH_4 used by Wagner [9] are

T_c= 190.564 K, ρ_c= 162.66 Kg.m^{-3},
P_c= 4.5992MPa (10)

The values of the system-dependent parameters adopted for C_2H_6 in this work are presented in Table 2. The equation of state of ethane is valid in the range of temperature, density and susceptibility correspond to

$$298K \le T \le 380K \text{ at} \rho=\rho_c,$$
$$84Kg.m^{-3} \le \rho \le 340Kg.m^{-3} \text{ at} T=T_c, \quad (11)$$
$$\tilde{\chi}_T^{-1} \le 2.15$$

The depended system parameters of CH_4 are represented in Table 3. The equation of state of methane is valid in the range of temperature, density and susceptibility correspond to $280K \le T \le 220K$ at $\rho=\rho_c$,

$$70Kg.m^{-3} \le \rho \le 300Kg.m^{-3} \text{ at } T=T_c, \quad (12)$$
$$\tilde{\chi}_T^{-1} \le 2.2$$

Table 2. System-dependent constants for C_2H_6.

Critical parameters	T_c= 305.322 K,ρ_c= 206.18 Kg.m^{-3}, P_c=4.8722MPa
Crossover parameters	$\bar{u}$ = 0.269, Λ = 3.288
Scaling-field parameters	c_t = 1.9836, c_ρ = 2.4318, c = -0.0224
Pressure 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
Caloric background parameters	$\tilde{\mu}_2 = -15.802$, $\tilde{\mu}_3 = -8.341$

Table 3. System-dependent constants for CH_4.

Critical parameters	T_c= 190.564 K, ρ_c= 162.66 Kg.m^{-3} P_c= 4.5992MPa
Crossover parameters	$\bar{u}$ 0.5432, Λ = 1.373
Scaling-field parameters	c_t = 1.27980, c_ρ = 2.61650, c = -0.04326
Pressure background parameters	$\tilde{A}_0$ = -1, $\tilde{A}_1$ = -4.9838, $\tilde{A}_2$ = 2.4568, $\tilde{A}_3$ = -0.1756, $\tilde{A}_4$ =1.0242, d_1= 0.21568
Classical parameters	a_{05} =- 0.2071, a_{06} = 0.8695, a_{14} =0.2206, a_{22} =0.1596
Caloric background parameters	$\tilde{\mu}_2 = -8.5637$, $\tilde{\mu}_3 = -5.4329$, $\tilde{\mu}_4 = 5.2509$, $\tilde{\mu}_5 = -18.286$

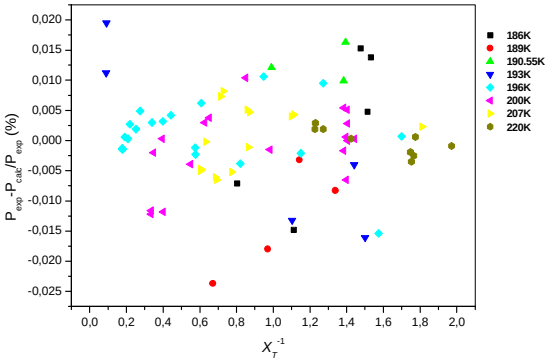

Figure1. Percentage deviation of the experimental pressure data of methane obtained by Wagner and CO.[9] from calculated value**.**

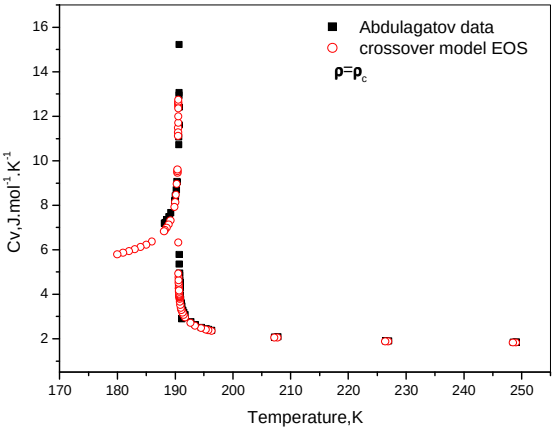

Figure2. Isochoric specific heat Cv of methane. The data points indicate the experimental data obtained by Abdulagatov [11] and the values calculated by the crossover model.

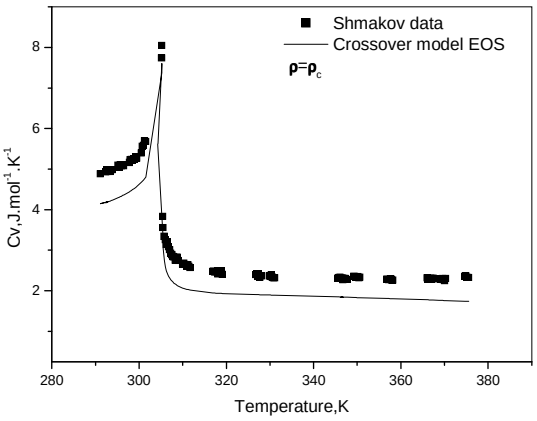

Figure3. Isochoric specific heat *Cv* of ethane. The data points indicate the experimental data obtained by Shmakov [10] and the solid curve represent the values calculated by the crossover model.

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