

Thermodynamic Properties of Supercritical Fluids: Example of n-hexane

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Abstract: Accurate information on the thermodynamic properties of supercritical fluids is highly sought for the chemical technology, especially, supercritical extraction technology. The thermodynamic properties of fluids near the critical region are strongly affected by the presence of fluctuations and therefore, can not be described by conventional equation. We have investigated the behavior of the thermodynamic properties of n-hexane in the vicinity of the critical region. For this reason we have used the so-called the crossover model to describe the thermodynamic properties of hexane in a wide range of temperatures and densities around the critical point.

INTRODUCTION

N-Hexane is a key substance due to its technological importance. 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 n-hexane 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 n-hexane 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].

SPECIFICATION OF THE CROSSOVER MODEL

The so-called crossover model used earlier by Chen, Abbaci, Tang and Sengers CATS [2] is developed to give a new theoretically based equation of state for n-hexane in the critical region that incorporate the crossover from the scaled thermodynamic behavior asymptotically close to the critical point to the analytic classical thermodynamic behavior far away from the

critical point. CATS [2] verified that their crossover model yields an accurate representation of the thermodynamic properties of several fluids in the critical region covering a large range of densities and temperatures around the critical point and extending into the far-critical region where analytic equations of state should be accurate. Hence, we decided to apply this crossover model to n-hexane.

FUNDAMENTAL EQUATION

Asymptotically close to the critical point the thermodynamic properties of fluids satisfy scaling laws with universal critical exponents and universal scaling functions [3, 4]. Equations of state for fluids incorporating these scaling laws have been developed earlier. In previous works, a linear-model parametric equation of state revised to include a lack of vapor-liquid symmetry and extended to incorporate the first corrections beyond asymptotic scaling [5-7] has been used. The range of validity of such a scaled equation of state is still somewhat restricted and the agreement with the experimental data deteriorates very rapidly as soon as the scaled equations are extrapolated outside the near-critical region. On the other hand, outside the critical region the thermodynamic properties can be adequately represented by classical equations that are analytic everywhere. In order to combine the scaling laws near the critical point with classical equations one needs to use a certain mechanism that includes the crossover from scaled behavior near the critical point to analytic behavior far away from the critical point.

Starting from earlier work Nicoll et al. [8-10], we have developed a crossover model to represent the thermodynamic properties of fluids in the critical region [8, 9]. 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 [7]:

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

In addition we define

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

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

Where t and M are temperature-like and density-like variables related to ΔT and Δp 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 (4) as $u_0 = u\Lambda$, where Λ is a dimensionless cutoff wave number [5-7].

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 (4) for ΔA_{cl} :

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

As shown by Abbaci [7] the theoretically predicted asymptotic behavior can be recovered from this expansion by the following transformation:

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

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

$$\begin{aligned} T &= Y^{(2-1/\nu)/\omega}, & D &= Y^{-\eta/\omega}, & U &= Y^{1/\omega} \\ V &= Y^{(2\omega_a - 1)/2\omega}, & K &= \nu/\alpha\bar{u}\Lambda \left[Y^{-\alpha/\nu\omega} - 1 \right] \end{aligned} \quad (7)$$

In terms of a crossover function Y to be determined from

$$1 - (1 - \bar{u})Y = \bar{u} \left(1 + \Lambda^2/\kappa^2 \right)^{1/2} Y^{1/\omega} \quad (8)$$

With

$$\kappa^2 = tT + 1/2 u\Lambda M^2 DU, \quad (9)$$

And

$$\bar{u} = u/u^* \quad (10)$$

In these expressions, the constants, 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 I.

In order to apply the crossover model (6) to fluids we need to introduce a proper translation to fluids variables [8]. This is accomplished by the transformation [8, 9]:

$$\Delta\tilde{A} = \Delta\tilde{A}_r - c \left(\frac{\partial\Delta\tilde{A}_r}{\partial M} \right)_t \left(\frac{\partial\Delta\tilde{A}_r}{\partial t} \right)_M \quad (11)$$

$$\begin{aligned} t &= c_t \Delta\tilde{T} + c \left(\frac{\partial\Delta\tilde{A}_r}{\partial M} \right)_t, \\ M &= c_\rho (\Delta\tilde{\rho} - d_1 \Delta\tilde{T}) + c \left(\frac{\partial\Delta\tilde{A}_r}{\partial t} \right)_M \end{aligned} \quad (13)$$

The coefficients c , c_t , c_ρ and d_1 are system-dependent constants. Finally, the total Helmholtz free-energy density is obtained from (3) as

$$\Delta\tilde{A} = \tilde{A} - \tilde{\rho} \tilde{\mu}_0(\tilde{T}) - \tilde{A}_0(\tilde{T}) \quad (14)$$

With

$$\tilde{\mu}_0(\tilde{T}) = \sum_{j=1}^{j=4} \tilde{\mu}_j (\Delta\tilde{T})^j \text{ and } \tilde{A}_0(\tilde{T}) = -1 + \sum_{j=1}^{j=4} \tilde{A}_j (\Delta\tilde{T})^j \quad (15)$$

The pressure is deduced from (15) as

$$\tilde{P} = \Delta\tilde{\mu} + \Delta\tilde{\rho} \Delta\tilde{\mu} - \Delta\tilde{A} - \tilde{A}_0(\tilde{T}) \quad (16)$$

Table I: Universal critical-region constants

$\nu = 0.630, \eta = 0.033, \alpha = 2 - 3\nu = 0.110, \Delta = 0.51, \omega_a = 2.1, u^* = 0.472$
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APPLICATION TO N-HEXANE

The crossover model as applied to n-hexane 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_p 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 Grigoriev and Abdulagatov [11], and finally the caloric background $\tilde{\mu}_i$ which can be determined from experimental speed of specific heat data reported by Abdulagatov [12]. Actually, the coefficients $\tilde{\mu}_i$ ($i=0, 1$) are related to the zero-point values of energy and entropy and are not considered here. A survey of the available experimental information for the thermodynamic properties of n-hexane can be found in the paper of Grigoriev and Abdulagatov [11]. The primary experimental information for developing a thermodynamic surface in the critical region is provided by the P - ρ - T data reported by Grigoriev and Abdulagatov [11] from which the system-dependent parameters of equation of state were determined.

A decision must be made concerning the values of the critical parameters for C_6H_{14} . For a reason of consistency of our work, the critical parameters for n-hexane are those used by Grigoriev and Abdulagatov [11], which are as follows:

$$T_c = 507.2 \text{ K}, \quad \rho_c = 233.60 \text{ kg.m}^{-3}, \quad P_c = 3.0282 \text{ MPa}$$

The values of the system-dependent parameters adopted for C_6H_{14} in this work are presented in Table II. Figures 1 and 2 present the percentage deviation in pressure and the specific heat for n-hexane respectively. The points are the experimental data and the curve in figure 2 represents the prediction from our equation of state.

CONCLUSION

Although the goodness of the equation of state we have formulated, we intend to pursue our investigation in order to find a more comprehensive equation for n-hexane.

Table II: System-dependent constants for C_6H_{14}

Critical parameters	$T_c = 507.2\text{K}$, $P_c = 3.0282 \text{ MPa}$, $\rho_c = 233.60 \text{ kg/m}^3$
Crossover parameters	$\bar{u} = 0.2303$, $\Lambda = 1.415$
Scaling-field parameters	$c_t = 1.739$, $c_p = 2.498$, $c = -0.0823$
Pressure background parameters	$\tilde{A}_0 = -1$, $\tilde{A}_1 = -6.543$, $\tilde{A}_2 = 9.642$, $\tilde{A}_3 = 6.846$, $\tilde{A}_4 = -16.840$, $d_1 = -0.9565$
Classical parameters	$a_{05} = 0.4002$, $a_{06} = 0.904$, $a_{14} = 2.376$, $a_{22} = 0.775$
Caloric background parameters	$\tilde{\mu}_2 = -72.96$, $\tilde{\mu}_3 = -0.223$, $\tilde{\mu}_4 = -114.86$, $\tilde{\mu}_5 = -68.03$

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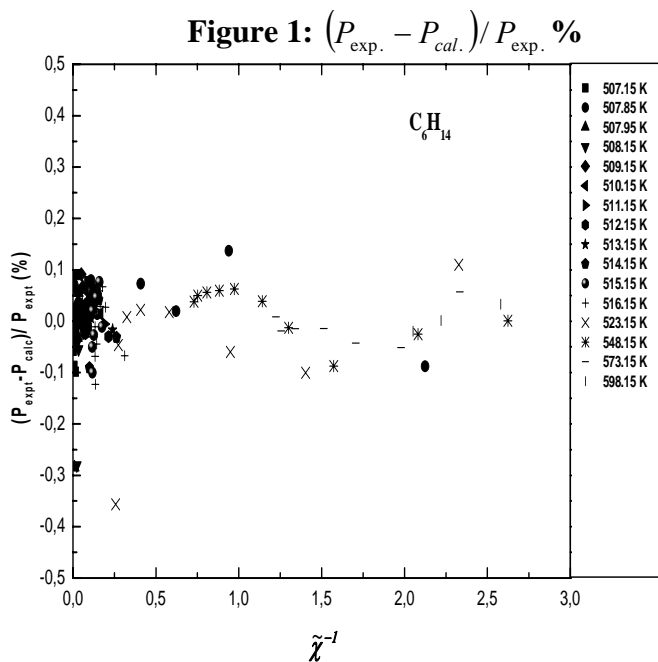


Figure 2: C_v data of Abdulagatov

