

## AN INTERIM THERMODYNAMIC PROPERTY FORMULATION FOR SUPERCRITICAL *n*-HEXANE

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Received: March 2, 2010

Accepted: April 9, 2010

**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 an interim formulation for 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 “crossover model” to describe the thermodynamic properties of *n*-hexane in a wide range of temperatures and densities around the critical point.

**Keywords:** *crossover, fluctuations, n-hexane, supercritical, thermodynamic properties.*

## INTRODUCTION

*n*-hexane is a key substance due to its technological importance for which reference data tables are considered necessary. 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 incorporates 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 wave number.

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 [7]:

$$\tilde{\rho} = \frac{\rho}{\rho_c}, \quad \tilde{T} = -\frac{T_c}{T}, \quad \tilde{P} = \frac{P \cdot T_c}{P_c \cdot T}, \quad \tilde{\mu} = \mu \cdot \frac{\rho_c \cdot T_c}{P_c \cdot T}, \quad \tilde{A} = A \cdot \frac{T_c}{P_c \cdot V \cdot T} \quad (1)$$

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:

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

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:

$$\Delta\tilde{A}_{cl} = \frac{1}{2}t M^2 + \frac{1}{2}u_0 M^4 + \dots \quad (4)$$

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 (4) as  $u_0 = u\Lambda$ , where  $\Lambda$  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  $\Delta A_{cl}$ :

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

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

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

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

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

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

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

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

with:

$$\mathcal{K} = t\mathcal{T} + 1/2u\Lambda M^2\mathcal{D}\mathcal{U} \quad (9)$$

and:

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

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

**Table 1.** Universal critical-region constants

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

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]:

$$t = c_t \Delta \tilde{T} + c \left( \partial \Delta \tilde{A}_r / \partial M \right)_t \quad (11)$$

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

$$M = c_\rho (\Delta \tilde{\rho} - d_1 \Delta \tilde{T}) + c \left( \partial \Delta \tilde{A}_r / \partial t \right)_M \quad (13)$$

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

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

with

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

The pressure is deduced from (14) as

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

## APPLICATION TO *n*-HEXANE

The crossover model as applied to *n*-hexane contains the following system-dependent parameters: The critical parameters  $T_c, \rho_c$ , 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  $\Delta$ , the scaling-field parameters  $c, c_t, c_\rho$  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  $P$ - $\rho$ - $T$  data of Grigoryev *et al.* [11], and finally the caloric background  $\tilde{\mu}_i$  which can be determined from experimental specific heat data reported by Abdulagatov *et al.* [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 Grigoryev *et al.* [11]. The primary experimental information for developing a thermodynamic surface in the critical region is provided by the  $P$ - $\rho$ - $T$  data reported by Grigoryev *et al.* [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<sub>6</sub>H<sub>14</sub>. For a reason of consistency of our work, we adopted the critical parameters for *n*-hexane used by Kurumov [13], which are as follows:

$$T_c = 507.2 \text{ K}, \quad \rho_c = 233.60 \text{ kg.m}^{-3}, \quad P_c = 3.0282 \text{ MPa} \quad (17)$$

The values of the system-dependent parameters adopted for C<sub>6</sub>H<sub>14</sub> in this work are presented in Table 2. The equation of state for *n*-hexane is valid in the range of temperatures defined by:

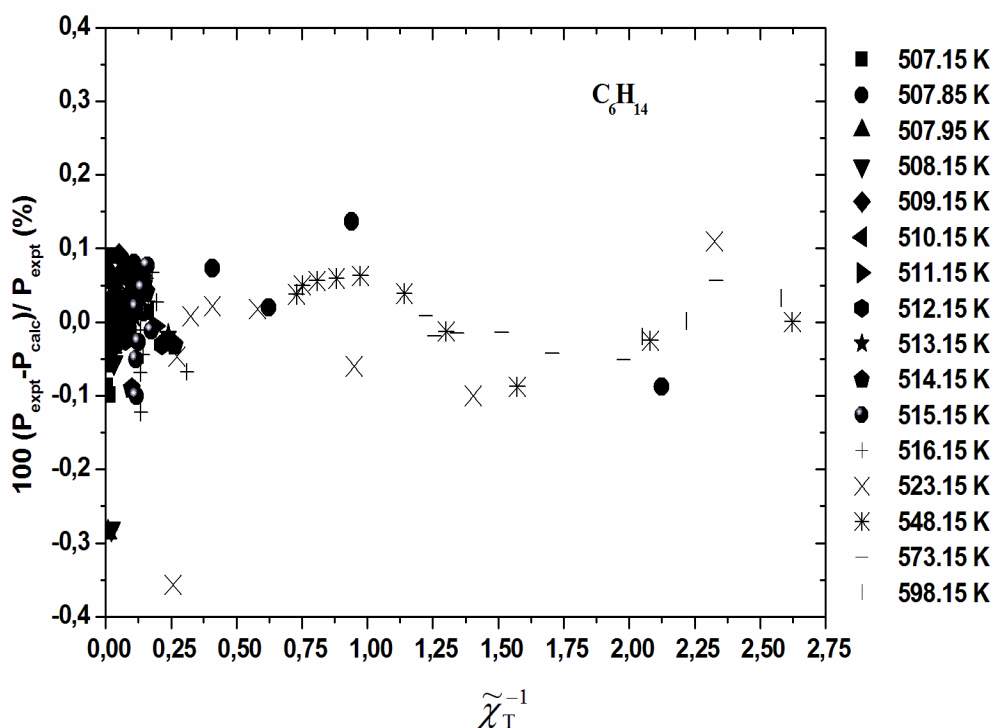
$$97 \text{ K} \leq T \leq 293 \text{ K}$$

and densities defined by:

$$85 \text{ kg.m}^{-3} \leq \rho \leq 300 \text{ kg.m}^{-3}$$

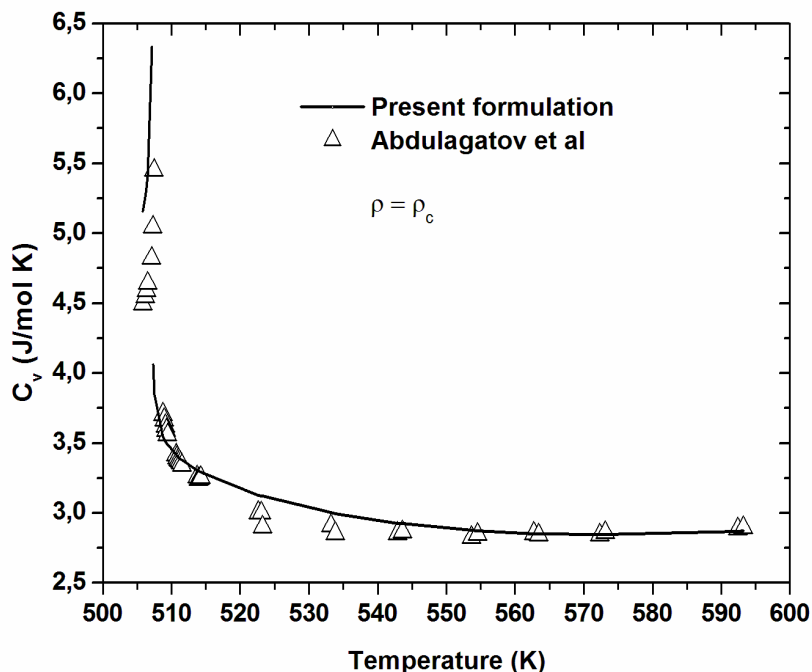
**Table 2.** System-dependent constants for C<sub>6</sub>H<sub>14</sub>

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	$c_t = 1.739, c_p = 2.498, c = -0.04367$
Pressure background parameters	$\tilde{A}_0 = -1, \tilde{A}_1 = -6.543, \tilde{A}_2 = 9.642, \tilde{A}_3 = 6.846,$ $\tilde{A}_4 = -16.840, d_I = -0.9565$
Classical parameters	$a_{05} = 0.904, a_{06} = 2.376, a_{14} = 0.775, a_{22} = 1.485$
Caloric background parameters	$\tilde{\mu}_2 = -72.96, \tilde{\mu}_3 = -0.223, \tilde{\mu}_4 = -114.86,$ $\tilde{\mu}_5 = -68.03$



**Figure 1.** Percent deviation in pressure as a function of the inverse compressibility

The formulated equation of state reproduced the pressure data measured by Grigoryev *et al.* [11] with an average percent deviation of 0.0405. 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.



**Figure 2.** Specific heat  $C_v$  as a function of temperature. The data points are those of Abdulagatov *et al.* [12] and the curve is the prediction of our crossover formulation.

## CONCLUSION

In a previous publication we have developed an equation of state for carbon dioxide [14]. We extend this work to *n*-alkanes. The present equation of state is only a tentative formulation of the thermodynamic properties of *n*-hexane that is a part of series in *n*-alkanes equations that we are developing based on the crossover model, which parameters will in turn be correlated in terms of the accentric factors of the corresponding *n*-alkanes.

## ACKNOWLEDGMENTS

We acknowledge the financial support from the *Agence Nationale pour le Développement de la Recherche Universitaire* (ANDRU) for the computer time and the grant awarded to the "LSBO FNRE/MESRS Algeria".

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