

RELATIONSHIPS BETWEEN RECTILINEAR DIAMETER AMPLITUDES AND MOLECULAR POLARIZABILITIES OF FLUIDS NEAR THEIR CRITICAL POINTS

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Abstract: This work reports on the relationships that exist between the amplitudes of liquid-vapor average densities of several fluids and their molecular polarizabilities. The slope of the coexistence-curve diameter has been determined from an equation of state based on the crossover model. We found that the slope for each fluid near the critical point is directly correlated with its molecular polarizability. This correlation is the consequence of the three-body Axilrod-Teller interaction.

Keywords: *Axilrod-Teller interaction, fluids, molecular polarizability, slope*

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. The thermodynamic surface of fluids exhibits a singularity at the critical point. This behavior can be characterized in terms of scaling laws with universal critical exponents and universal scaling functions [1-3]. Unlike 3-dimensional Ising-like systems, fluids exhibit a lack of vapor-liquid symmetry.

It is well established that a mathematically analytic equation of state does not yield the correct thermodynamic behavior of fluids in the critical region. On the other hand, an equation of state that is valid in the critical region cannot be extrapolated outside this region either. Therefore, for the study of the thermodynamic properties of fluids over a wide range of temperatures and densities, one must use a unified equation of state that yields a good agreement with experimental data in the critical region as well as in the classical region, far away from the critical point. Such an equation is available and is based on the crossover model formalism [4, 5].

The present study reports on the application of the crossover model to the coexistence-curve diameter, and in turns shows that the molecular polarizability follows a certain trend with the slope of the rectilinear diameter far away from the critical region.

In order to explain this application, the article is divided into four sections. After the first *Introductory Section*, *Section II* briefly reviews the six-term Landau crossover model. *Section III* presents the common prediction of the behavior of the coexistence-curve diameter equation for one-component fluid, meanwhile *Section IV* explains the relationships that exist between the slope of the rectilinear diameters close to the critical points and their respective molecular polarizabilities due to the three-body dispersion (Axilrod-Teller) forces.

SPECIFICATION OF THE CROSSOVER MODEL

The modern theoretical description of systems close to the critical point is based on the renormalization-group theory (RG) [6]. Different physical systems with the same space dimensionality d , and the same number of components of the order parameter can be grouped within the same universality class. Based on earlier work of Nicoll and coworkers [7 – 9], a crossover model has been developed to represent the thermodynamic properties of fluids in the critical region [3, 4]. The crossover model is based on the renormalization-group theory of critical phenomena. Let ρ 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, 5].

$$\tilde{\rho} = \frac{\rho}{\rho_c}; \quad \tilde{T} = -\frac{T}{T_c}; \quad \tilde{P} = \frac{PT_c}{P_c T}; \quad \tilde{\mu} = \frac{\mu \rho_c T_c}{P_c T}; \quad \tilde{A} = \frac{AT_c}{P_c VT} \quad (1)$$

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:

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

where $\mu_0(T)$ and $A_0(T)$ are analytic background functions of T subject to the conditions that at the critical temperature $\Delta\mu = 0$ and $A_0 = -1$. 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. In the classical mean-field theory, the classical Helmholtz free energy A_{cl} can be represented by analytic Landau expansion that can be written in the form:

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

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 (4) as $u_0 = u \cdot \Lambda$, where Λ is a dimensionless cutoff wave number [7, 8], $a_{05}, a_{06}, a_{14}, a_{22}$ are also system-dependent parameters. As shown by Chen et al. [4, 5] the theoretically predicted asymptotic behavior can be recovered from this expansion by the following transformation:

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

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

$$\begin{aligned} T = Y^{\frac{(2-1/\nu)}{\omega}}; \quad D = Y^{-\frac{\eta}{\omega}}; \quad U = Y^{\frac{1}{\omega}} \\ V = Y^{\frac{2\omega_a - 1}{2\omega}}; \quad K = \frac{\nu}{a\bar{u}\Lambda} \left(Y^{-\frac{\alpha}{\nu\omega}} - 1 \right) \end{aligned} \quad (6)$$

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

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

with:

$$\kappa^2 = tT + \frac{1}{2}u\Lambda M^2DU \quad (8)$$

The symbols $\alpha, \eta, \nu, \omega$ and ω_a [8] in the above relations are the universal critical exponents, while u is defined by $u = u/u^*$, where u^* is also a universal constant, or also called the fixed-point coupling constant [8, 9]. The values of the universal critical-region parameters are listed in Table 1. The variable κ that appears in the crossover model is related to inverse correlation length ζ .

Table 1. Universal critical-region constants

$\alpha = 2 - 3\nu$	η	Δ	$\omega = \Delta/\nu$	ω_a	u^*
0.11	0.0333	0.51	0.80952	2.1	0.472

Crucial for the application of the crossover model to fluids is a suitable transformation of the field variables t and M [3, 4]. This transformation is accomplished as follows:

$$\Delta\tilde{A} = \Delta\tilde{A}_r - c \left[\left(\frac{\partial \Delta\tilde{A}_r}{\partial M} \right)_t \right] \left[\left(\frac{\partial \Delta\tilde{A}_r}{\partial t} \right)_M \right] \quad (9)$$

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

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

Where c_t , c_ρ and d_1 are system-dependent constants and c is the mixing constant that takes account of the fluids asymmetry. Finally, the total Helmholtz free-energy density is obtained from (3). To specify the Helmholtz free-energy density completely, the analytic background functions $\mu_0(T)$ and $A_0(T)$ are represented by truncated Taylor expansion of the form defined elsewhere, and a complete set of equations specifying the crossover model can be found in [4, 5].

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. With ρ_{liq} and ρ_{vap} being the liquid and the vapor densities respectively, ρ_c as the critical density and $\Delta\tilde{T}$ the reduced temperature. Close to the critical point, the renormalization-group theory [10] predicts that:

$$\rho_d = \frac{(\rho_{liq} + \rho_{vap})}{2\rho_c} = 1 + d_1 \Delta\tilde{T} + d_{1-\alpha} |\Delta\tilde{T}|^{(1-\alpha)} + d_{1-\alpha+\Delta} |\Delta\tilde{T}|^{(1-\alpha+\Delta)} + \dots, \quad (12)$$

where α , is the critical exponent that characterizes the divergence of the specific heat at constant volume. 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 sulfur hexafluoride [11], whose data have been further analyzed by Ley-Koo and Green [12], indicate that the singular term is present, with:

$$d_{1-\alpha} = -9.547 (c/c_\rho) \cdot c_t^{(1-\alpha)} \cdot (\bar{u}\Lambda)^{-3(2\nu-1)} \quad (13)$$

THREE-BODY INTERACTIONS

The Hamiltonian operators for the fluid systems contains odd terms in the density-like variable, which normally leads to the exhibition of the asymmetry behavior of the coexistence-curve diagram, in accordance with the previous section. The three-body dispersion forces of the from given by Axilrod and Teller are traditionally the most dominant forces, in spite of the fact these three-body interactions are of importance in

the lighter and less polarizable molecules [13].

The Axilrod-Teller potential for three-particle system located at the position (r_1, r_2, r_3) forming a triangle with vertex angles θ_i is given by [13]:

$$V_{AT} = V_3^0 \frac{[3 \cos(\theta_1) \cos(\theta_2) \cos(\theta_3) + 1]}{r_{12}^3 r_{13}^3 r_{23}^3} \quad (14)$$

where the term $V_3^0 \sim I\alpha_0$ is an amplitude, with I as the energy of the first excited electronic state, which is approximated by the ionization energy, and α_0 the polarizability. Pestak *et al.* [14] have concluded that the appropriate measure of the relative strength of the triplet potentials at the critical point characterized by a critical temperature T_c , critical density ρ_c and a critical pressure P_c is given by the dimensionless critical polarizability product $\alpha_0\rho_c$.

CORRELATION OF THE AMPLITUDE $d_{1-\alpha}$ AND THE CRITICAL POLARIZABILITY $\alpha_0\rho_c$

The analysis of the linear and the $(1 - \alpha)$ terms amplitudes when correlated with the critical amplitude gives a linear trends as suggested by Pestak *et al.* [14] in the analysis of the amplitudes of several fluids, however, as noted by Chen and coworkers [4], we found that in spite of the agreement with the coexistence-curve diameters of different fluids in this work, the values of the linear amplitudes of the coexistence-curve diameters differs considerably from those deduced by Pestak and coworkers [14], this is mainly due to the correlation between the linear term and the $(1 - \alpha)$ term that severely hampers the mere determination of the actual amplitudes from the coexistence-curve diameters. The values of the amplitudes of the rectilinear diameters for different fluids along with their critical polarizabilities as well as their critical temperatures and densities are given in Table 2.

The variation of $(1 - \alpha)$ amplitude of the coexistence-curve diameters and that of the critical compressibility factor with $\alpha_0\rho_c$ of C_2H_4 , C_2H_6 , H_2O , CO_2 and SF_6 are given by least-squares fits represented by the linear curve shown in Figures 1 and 2, represented by the following equations:

$$d_{1-\alpha} = (-168.47 \pm 67.38)\alpha_0\rho_c + (3.61 \pm 1.24) \quad (15)$$

$$Z_c = (12.65 \pm 4.3)\alpha_0\rho_c + (0.0275 \pm 0.080) \quad (16)$$

Table 2. Critical polarizabilities and amplitudes of the rectilinear diameter for several fluids

Fluid	α_0 (Å ³)	T_c (K)	ρ_c (kg/m ³)	$\alpha_0\rho_c$	$d_{1-\alpha}$: eq. (13)
Ethylene C ₂ H ₄	4.25	282.35	214.165	0.0196	0.604 ^a
Ethane C ₂ H ₆	4.50	305.33	206.6	0.0186	0.325 ^b
Steam H ₂ O	1.73	647.067	322.788	0.0187	1.0745 ^b
Carbon dioxide CO ₂	2.911	304.127	467.83	0.0186	0.290 ^b
Sulfur hexafluoride SF ₆	6.54	318.733	743.807	0.0200	0.255 ^c

a – [16]; b – [4]; c – [15,16]

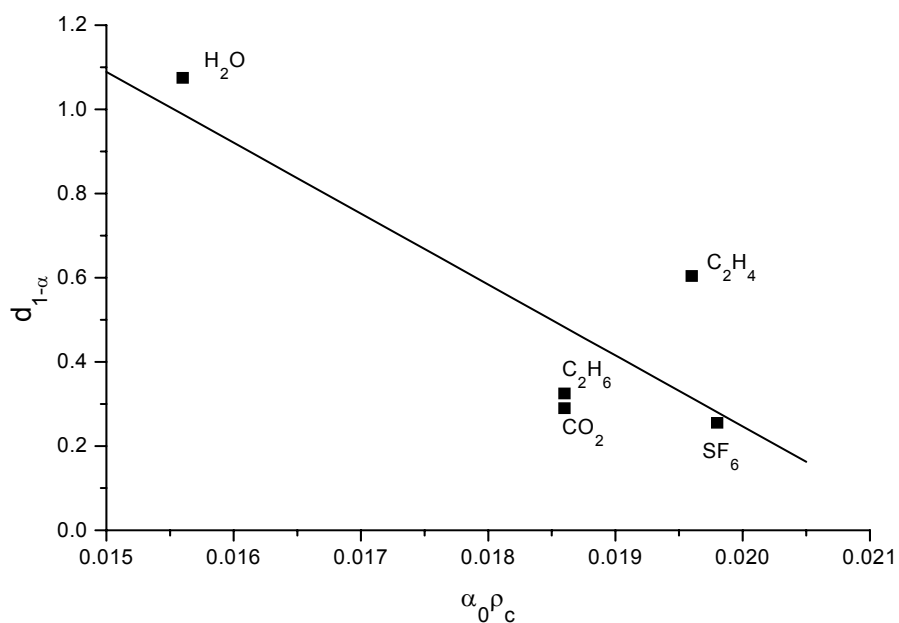


Figure 1. $(1 - \alpha)$ amplitude term in the rectilinear diameter of fluids near the critical point vs. critical polarizability product.
The line represents the fitted linear equation (15)

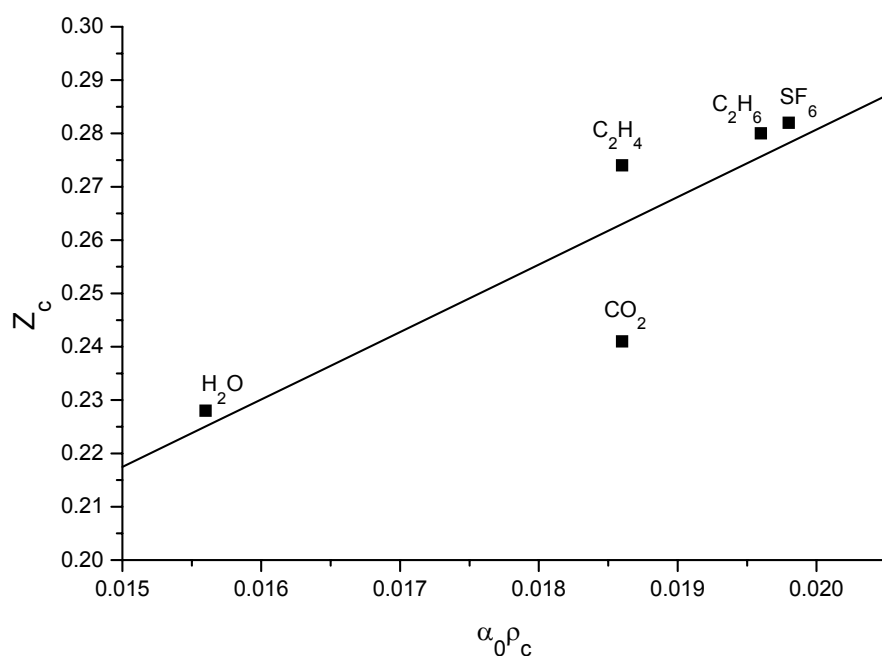


Figure 2. Compressibility factor vs. critical polarizability product.
The line represents the fitted linear equation (16)

DISCUSSION

In this work, we made a direct linkage between the three-body interactions that appears into the Hamiltonian of fluid systems represented by the odd terms (especially the cubic term). The presence of the odd terms is a consequence of the liquid-vapor coexistence curve diameter asymmetry. This characteristic is absent in magnetic systems which Hamiltonian lacks the odd terms in the field M terms and therefore have a perfectly symmetric coexistence-curve diameter.

CONCLUSION

We believe that the correlation made in the work of Pestak and coworkers [14] should have included the $(1 - \alpha)$ amplitude term as well instead of only using the linear amplitudes of the rectilinear diameters.

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NOTES

The critical molecular polarizability is reduced according to the expression:

$$\text{reduced } \alpha_0 \rho_c = \frac{\alpha_0 \rho_c}{M_w} N_A$$

with M_w being the molecular weight, N_A is the Avogadro's number. For instance, the reduced molecular polarizability of ethane is calculated as follows:

$$\text{reduced } \alpha_0 \rho_c = \frac{4.50 \cdot 10^{-24} \text{ cm}^3 \times 0.2066 \text{ g} \cdot \text{cm}^{-3}}{30.07 \text{ g} \cdot \text{mol}^{-1}} \times 6.023 \cdot 10^{23} \text{ mol}^{-1} = 0.0186$$