An Equation of State for Pure Fluids Describing the Critical Region

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Density fluctuations of a pure fluid are treated by a cell model, in which the fluid is divided into cells containing different numbers of particles. A probability function for the particle number is derived. This function, after convolution with a classical (mean field) equation of state, leads to an improved equation of state which is valid in the critical region. The equation of state is analytical, hence not exact in the immediate vicinity of the critical point. As an example, the convolution is applied to the Carnahan-Starling/van der Waals equation of state; the resulting equation of state is used to correlate thermodynamic properties of several simple fluids.

KEY WORDS: critical behavior; equation of state; fluctuations.

1. INTRODUCTION

One of the most difficult problems in the thermodynamics of fluids is the description of the critical region. In this region, all analytical mean field equations of state exhibit a systematic deviation from the observed behavior. In principle, the thermodynamic properties of fluids in the vicinity of the critical point can be described by so-called power laws. The exponents in these power laws, the so-called critical exponents, are predicted incorrectly by all classical equations of state, which are expandable into Taylor series at the critical point. Correct values of the critical exponents can be obtained from renormalization theory [1]. Even with these critical exponents, however, the power laws describe the real fluid behavior only in a short range

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around the critical point. Therefore, in the previous two decades several theories were developed, with the aim of describing the classical behavior far from the critical point as well as the nonclassical behavior near the critical point with only one equation of state.

One of the first attempts to accomplish a "crossover" from classical to nonclassical behavior was the introduction of the switch function by Chapela and Rowlinson [2]. With this function, a mathematical combination of an analytical and a nonanalytical equation of state is made: The switch function runs from zero to one while the model turns from nonclassical to classical behavior and determines the weight of the classical contribution to the total equation of state. As shown by Woolley [3], the inflection point of the switch function gives rise to artificial extrema of derived thermodynamic functions, which are at variance with experiment.

Another mathematical method of crossover was proposed by Fox [4]. He transformed the density and the temperature into a coordinate system with a nonequidistant axis scaling. This axis distortion increases with decreasing distance from the critical point. The transformation is weighted with a so-called damping function. Its argument is another function that describes the distance to the critical point.

Another approach, with a more physically rigid foundation, was developed by Sengers and his co-workers [5, 6]. In this model, the diverging wave length of the fluctuation at the critical point is limited by a ultraviolet cutoff parameter. This theory is based on the classical Landau expansion around the critical point, whose coordinates are transformed with functions depending on a crossover function. The more terms of the Landau expansion are used, the more of the mean field region can be described. The transition to the perfect gas or the dense liquid regime is still difficult.

In this work, an equation of state is proposed which is based on the virial expansion, a Taylor expansion around zero density. Because this series converges very rapidly, only a few terms are needed. This theory is able to describe fluctuations, which are significant both in the near-critical region and in a part of the classical region.

2. THE CELL MODEL

In this section it is shown how fluctuation can be considered in the partition function. The influence of the density fluctuations on the partition function is described by a cell model. The use of the mean field approximation with a r^{-6} attraction potential, together with the approximation that the free volume is the difference between the total volume and the

covolume of all molecules, leads to the partition function underlying the van der Waals equation of state:

$$Z_N = \Lambda^{-3N} \frac{(V - Nb)^N}{N!} \exp\left(\frac{aN\rho}{k_B T}\right) \tag{1}$$

$$A = -N k_B T \ln Z_N \tag{2}$$

$$p = -\left(\frac{\partial A}{\partial V}\right)_T = -N k_B T \left(\frac{\partial \ln Z_N}{\partial V_m}\right)_T = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \tag{3}$$

Here ρ denotes the inverse volume, $1/V$, N the particle number, Z_N the canonical partition function, and Λ the thermal de Broglie wavelength.

This partition function represents a mean field of interaction over the whole fluid with N molecules. In the next step, the fluid is divided into M equal-sized cells with the volume V_z. The number of particles K in each of these cells can be different. The mean field approximation is applied to every single cell. The resulting partition function is

$$Z_K = \Lambda^{-3K} \frac{(V_z - Kb)^K}{K!} \exp\left(\frac{aK\rho}{k_B T}\right) \tag{4}$$

with

$$V_z = \frac{V}{M} \quad \text{and} \quad \rho = \frac{K}{V_z} = \frac{KM}{V_z}$$

Because the cells are independent for large systems, with only the restriction $\sum K = N$, the partition function of the whole fluid is the product of the cell partition functions weighted with a density distribution $\omega(K)$. Hence the introduction of the cells represents a step beyond the mean field approximation in the transition from the micropartition function to the system partition function. The physical reason of this model is that the cell size corresponds to the correlation length [7, 8] of the density fluctuations.

MFA $\quad z(i) \quad\rightarrow\quad \rightarrow \quad Z_N = \prod_{i=1}^{N} z(i)$

single-particle p.f. $\qquad\qquad$ system partition function

CMFA $\quad z(i) \quad\rightarrow\quad Z_K = \prod_{i=1}^{K} z(i) \quad\rightarrow\quad Z_N = \prod_{K=0}^{K_{max}} Z_K^{\omega(K)}$

single-particle p.f. $\quad$ cell partition function $\quad$ system partition function

where MFA is the transition with the normal mean field approximation and CMFA the transition with the cell mean field approximation.

This model describes a mean fluctuation which increases with the cell size. With Z_N of the cell model, the equation of state can be derived. If the number of cells is large, it is possible to change the discrete density distribution $\omega(K)$ into a continuous density distribution $\tilde{\omega}(\rho)$ and to replace the summation by an integration.

$$A = -k_B T \ln Z_N \tag{5}$$

$$p = -\left(\frac{\partial A_m}{\partial V_m}\right)_T = RT \int_0^{\rho'} \tilde{\omega}(\rho') \left[\frac{1}{1/\rho' - b} - a\rho'^2\right] d\rho' \tag{6}$$

Comparison of Eqs. (5) and (6) with the van der Waals equation of state leads to a general prescription for deriving an equation of state that includes fluctuations:

$$\langle p \rangle = \frac{\int \tilde{\omega}(\rho)\, p(\rho)\, d\rho}{\int \tilde{\omega}(\rho)\, d\rho} \tag{7}$$

3. MATHEMATICAL FORMALISM

Now we have to find a mathematical formalism that makes it possible to calculate a fluctuation term for every mean field equation of state. First, the basic classical equation has to be expanded into a Taylor series with respect to the reduced density $\xi = b\rho$. The coefficients of this expansion are the f_n:

$$p = p(\xi, T) = \sum_{n=0}^{r} f_n \xi^n \quad \text{with} \quad \xi = \frac{b}{V_m} \tag{8}$$

Then the powers of the reduced density ξ^n have to be convoluted, as written in Eqs. (5) and (6), with the continuous density distribution $\tilde{\omega}(\xi)$.

$$\langle p \rangle = \sum_{n=0}^{r} f_n I_n \quad \text{with} \quad I_n = \int_{,}^{+'} \xi^n \tilde{\omega}(\xi)\, d\xi \tag{9}$$

If a Gaussian distribution function is substituted for the density distribution $\tilde{\omega}(\xi)$, the following integrals I_n are obtained:

$$I_n = \int_{,}^{+'} \xi^n \frac{1}{\sqrt{2\pi}\,\sigma} \exp\left(\frac{-(\xi - \mu)^2}{2\sigma^2}\right) d\xi \tag{10}$$

The analytical solutions of these integrals can be calculated with the following recursive series [9].

$$I_n = -\sum_{i=1}^{n} (-\mu)^i \binom{n}{i} I_{n-i} + \begin{cases} \prod_{i=1}^{n-2} (2i-1)\,\sigma^2, & n = 2, 4, 6,\dots \\ 0, & n = 3, 5, 7,\dots \end{cases} \tag{11}$$

To separate the mean field term and the fluctuation term, some solutions of the I_n have to be calculated. The first nine moments are listed below:

$$I_0 = 1$$
$$I_1 = \mu$$
$$I_2 = \mu^2 + \sigma^2$$
$$I_3 = \mu^3 + 3\mu\sigma^2$$
$$I_4 = \mu^4 + 6\mu^2\sigma^2 + 3\sigma^4 \qquad (12)$$
$$I_5 = \mu^5 + 10\mu^3\sigma^2 + 15\mu\sigma^4$$
$$I_6 = \mu^6 + 15\mu^4\sigma^2 + 45\mu^2\sigma^4 + 15\sigma^6$$
$$I_7 = \mu^7 + 21\mu^5\sigma^2 + 105\mu^3\sigma^4 + 105\mu\sigma^6$$
$$I_8 = \mu^8 + 28\mu^6\sigma^2 + 210\mu^4\sigma^4 + 420\mu^2\sigma^6 + 105\sigma^8$$

The second integral I_1 is equal to the convoluted value of the density $I_1 = \langle \xi \rangle = \mu$. Therefore the parameter μ of the Gaussian distribution is equal to the measured density. To simplify the formulas, $\langle \xi \rangle$, and hence every μ, is replaced by ξ. Insertion of these I_n into Eq. (9) and rearrangement with respect to powers of density yields the following form of the total equation of state:

j	k	1	2	3	4	5
	0	$\{\xi^0(f_0$	$+ f_2\sigma^2$	$+ 3f_4\sigma^4$	$+ 15f_6\sigma^6$	$+ 105f_8\sigma^8 + \cdots)$
	1	$\xi^1(f_1$	$+ 3f_3\sigma^2$	$+ 15f_5\sigma^4$	$+ 105f_7\sigma^6 + \cdots$	$)$
	2	$\xi^2(f_2$	$+ 6f_4\sigma^2$	$+ 45f_6\sigma^4$	$+ 420f_8\sigma^6 + \cdots$	$)$
	3	$\xi^3(f_3$	$+ 10f_5\sigma^2$	$+ 105f_7\sigma^4 + \cdots$		$)$
	4	$\xi^4(f_4$	$+ 15f_6\sigma^2$	$+ 210f_8\sigma^4 + \cdots$		$)$
$\langle p \rangle =$	5	$\xi^5(f_5$	$+ 21f_7\sigma^2 + \cdots$			$)$
	6	$\xi^6(f_6$	$+ 28f_8\sigma^2 + \cdots$			$)$
	7	$\xi^7(f_7$	$+ \cdots$			$)$
	8	$\xi^8(f_8$	$+ \cdots$			$)$
	$\vdots$					$\}$

or, after further rearrangement,

$$\langle p \rangle = \sum_{i=0}^{i} B_i^* \xi^i \qquad (13)$$

where the coefficients B_j^* can be expressed as

$$B_j^* = f_j + \sum_{k=1}^{\infty} \sigma^{2k} f_{j+2k} \binom{2k+j}{2k} \prod_{i=1}^{k} (2i-1) \tag{14}$$

With

$$\prod_{i=1}^{k} (2i-1) = \frac{(2k)!}{k!\, 2^k}$$

$$B_j^* = f_j + \sum_{k=1}^{\infty} \sigma^{2k} f_{j+2k} \frac{(2k+j)!}{k!\, j!\, 2^k} \tag{15}$$

and the separation of B_j^* into a mean field term f_j and a fluctuation term B_j

$$B_j^* = f_j + B_j \tag{16}$$

one finally obtains

$$\langle p \rangle = \sum_{j} f_j \xi^j + \sum_{j=0}^{\infty} \sum_{k=1}^{\infty} \sigma^{2k} f_{j+2k} \frac{(2k+j)!}{k!\, j!\, 2^k} \xi^j$$

$$= \underset{\text{mean field term}}{p(\xi, T)} + \underset{\substack{j=0 \\ \text{fluctuation term}}}{\sum_{j=0}^{\infty} B_j \xi^j} \tag{17}$$

In this equation, the first term refers to the mean field fluid and can be identified with the basic equation of state. The remaining term represents the fluctuations.

4. THE MEASURE OF FLUCTUATION

The last unknown variable is σ, the width of the density distribution, which is a measure of the fluctuation. Its density dependence was determined by fitting σ to density and pressure values along the critical isotherm. Critical isotherm data were obtained in three ways, to study the influence of the critical exponents.

(i)   We used the power law

$$p = p_c(1 + k_\xi \, \Delta\xi \, |\Delta\xi|^{\delta-1}) \tag{18}$$

with

$$\Delta\xi = \frac{\xi - \xi_c}{\xi_c}$$

with a classical exponent $(\delta = 3.0)$.

(ii)   We used the same power law, Eq. (18), with a nonclassical $(\delta = 4.76)$ exponent.

(iii)   We used experimental data for carbon dioxide along the critical isotherm.

The critical isotherm data thus obtained were then used with Eq. (17) to calculate σ as a function of the density. We refer to the σ function obtained from the power law Eq. (18) with $\delta = 3.0$ as *classical*, to that obtained from the same power law with $\delta = 4.76$ as *nonclassical*, and to that obtained from carbon dioxide data as *experimental*. In Fig. 1 the results of these three fits are shown. It is obvious that the nonclassical curve clings to the curve of CO_2 in the vicinity of the critical point. At zero density, the classical curve and the CO_2 curve meet each other at the origin. It is unexpected that the nonclassical σ curve does not run to the origin, though the critical amplitude k_ξ of the power law has been set to one and therefore Eq. (18)
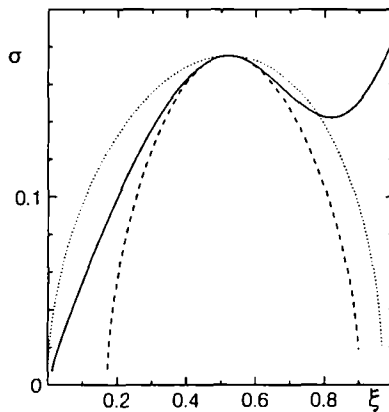

Fig. 1.   Crossover from classical to nonclassical behavior in the fluctuation distribution width σ. (———) Calculated from experimental data for carbon dioxide; (······) calculated with the classical power law; (————) calculated with the nonclassical power law.

yields the pressure zero at zero density. Hence the "experimental" σ curve of CO_2 represents the transition from the classical to the nonclassical behavior. The increase in the CO_2 curve at a high density is an effect of the critical amplitude of CO_2. As shown in Fig. 2, it depends only on k_ξ whether σ decreases or increases at the liquid side.

The nonclassical σ curve cannot be represented analytically: An analytical σ curve inevitably leads to an analytical equation of state, which is not able to describe the real behavior of a real fluid at its critical point. Nevertheless, an analytical polynomial can be used to approximate the σ function of CO_2 with a high degree of accuracy. With this polynomial one can describe the classical fluctuations, which are significant over a wide range of the state variables. It is also possible to describe the correct behavior very close to the critical point as shown below. The polynomial must meet the following conditions.

(i)   At the critical point $\sigma(\xi)$ has a maximum with the value σ_c.

(ii) In the perfect gas limit, σ must be zero.

$$\sigma = \xi \left(f_0 + f_1 y + \sum_{i=1}^{n} A_i y^{i+1} \right) \qquad \text{with} \quad y = \frac{\xi - \xi_c}{B_\xi}$$

$$f_0 = \frac{\sigma_c}{\xi_c} \qquad \text{and} \qquad f_1 = -\frac{\sigma_c B_\xi}{\xi_c^2} \tag{19}$$
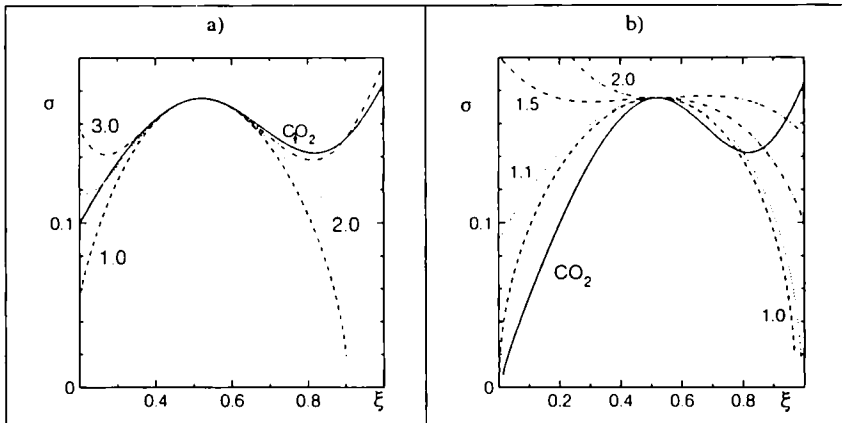
$$B_\xi(CO_2) \equiv 1.0$$

Fig. 2. The effect of variation of the critical amplitude k_ξ on the density dependence of σ. Curves calculated from the power law given by Eq. (18): (a) using the classical value for δ; (b) using the nonclassical value for δ.

This definition of y makes it possible to apply the σ function, which had originally been fitted for CO_2 only, to other substances by merely changing the parameter B_ξ. The parameters A_i (see Table I) are also useful for other substances whose critical compressibility factor Z_c is close to the value of CO_2. For substances with a very low Z_c, such as water, a different set of A_i has to be used. The temperature dependence of the fluctuations can be described with a Gaussian. The complete function $\sigma(\xi, T)$ is the product of the two terms [$\sigma(\xi)$ is given by Eq. (19)]:

$$\sigma(\xi, T) = \sigma(\xi)\, \sigma(T) \tag{20}$$

$$\sigma(T) = \exp\left(-\left(\frac{\Delta T}{B_T}\right)^2\right) \quad \text{with} \quad \Delta T = \frac{T - T_c}{T_c} \tag{21}$$

5. THE EQUATION OF STATE

The CMFA fluctuation terms described above can be coupled to any classical equation of state. To demonstrate the effect of the fluctuation terms on the representation of thermodynamic properties, we have used a rather simple basic equation, namely, a Carnahan-Starling repulsion [10] and a van der Waals attraction term [11], combined with the Kreglewski temperature dependence $\Psi(T)$ [12, 13].

The complete equation of state is listed below. The coefficients Γ_{jk} are defined according to Eq. (22) to simplify the program. Because they are independent of ξ and T, they have to be calculated only once, at the beginning of a program.

Table I. The Parameters of Eq. (19), Determined for CO_2 in the Range $0 \leqslant \xi \leqslant 1.4$

i	A_i
1	−0.450380736929359
2	1.44851592280812
3	6.65311221101693
4	−3.00132583637774
5	−28.7833837850716
6	19.99268347760946
7	46.2213250355894
8	−60.9581774885587
9	16.57810592282334
10	2.91103151685535

$$\langle p \rangle = \frac{RT}{b}\left(\xi + \frac{\xi^2 + \frac{1}{8}\xi^3}{(1 - \frac{1}{4}\xi)^3}\right) + \frac{RT}{b}\sum_{j=0}^{n_x} B_j \xi^j - \frac{a\Psi(T)}{b^2}\xi^2 - \frac{a\Psi(T)}{b^2}\sigma^2$$

$$B_j = \sum_{k=1}^{n_x} \Gamma_{jk}\sigma^{2k}$$

$$\Gamma_{jk} = f_{j+2k}^{CS}\frac{(2k+j)!}{j!\,k!\,2^k}$$

$$f_i^{CS} = \begin{cases} 0, & i = 0, 1 \\ \dfrac{3(i-1) + (i-1)^2}{4^{i-1}}, & i \geqslant 2 \end{cases}$$

$$\sigma(\xi, T) = \exp\left(-\left(\frac{\Delta T}{B_T}\right)^2\right)\xi\left(f_0 + f_1 y + \sum_{i=1}^{n_\sigma} A_i y^{i+1}\right)$$

(22)

$$y = \frac{\xi - \xi_c}{B_\xi}$$

$$f_0 = \frac{\sigma_c}{\xi_c}$$

$$f_1 = -\frac{f_0 B_\xi}{\xi_c}$$

$$\Psi(T) = 1 + \frac{1}{f_T}\left(\frac{T_c}{T} - 1\right)$$

$$n_x = \begin{cases} [8 + 21\xi], & \Delta p\,\dfrac{b}{RT} < 10^{-10} \\ [10 + 28\xi], & \Delta p\,\dfrac{b}{RT} < 10^{-14} \end{cases}$$

The number of terms in the summation, n_x, is not kept constant but made density dependent, using an empirical relationship, $n_x(\xi)$. This speeds up the calculations at the gas side and guarantees convergence at high densities. The brackets in $n_x(\xi)$ denote the largest integer below the real argument value; Δp is the absolute desired pressure inaccuracy. n_σ is the number of parameters A_i, which is 10 for the parameters listed in Table I:

a = attraction parameter, substance dependent

b = covolume, substance dependent

ξ_c = reduced critical density, substance dependent (value depending on Z_c)

σ_c = value of σ at the critical point, substance dependent (value depending on Z_c)

f_T = temperature dependence parameter of the attraction, substance dependent

B_ξ = density dependence parameter of the fluctuation distribution width, substance dependent

B_T = temperature dependence parameter of the fluctuation distribution width, substance dependent

A_i = polynomial coefficients of the density dependence of the fluctuation distribution width, universal for substances within a certain Z_c interval.

6. CALCULATIONS

6.1. Data Reduction

Calculation of the parameters of Eq. (22) requires a two-step data reduction. In the first step, the parameters of the basic equation, a and b, as well as the value of the fluctuation measure, σ_c, have to be fitted to the critical data of pressure, density, and temperature by means of the critical conditions.

$$\left(\frac{\partial p}{\partial \xi}\right)_T = 0, \qquad \left(\frac{\partial^2 p}{\partial \xi^2}\right)_T = 0, \qquad p(\xi_c, \tilde{T}_c) - p_c = 0 \tag{23}$$

It is recommended to use reduced parameters $\tilde{T}_c$ and ξ_c instead of a and b.

$$b = V_{mc}\xi_c, \qquad a = 8bR\frac{T_c}{\tilde{T}_c} \tag{24}$$

Because it is possible to describe the critical point of every substance exactly, the values of $\tilde{T}_c$, ξ_c, and σ_c depend on the critical compressibility factor Z_c, and it is possible to represent these properties by polynomials in Z_c. This makes it possible to calculate the critical parameters directly from Z_c via the polynomials without any fit. The coefficients of these polynomials are listed in Table II. Table III contains the experimental critical data used in this work, and Table IV contains the resulting values of ξ_c and σ_c.

The second step is the calculation of the parameters of Eq. (22), which describe the density and temperature dependence of σ. The parameter B_ξ is fitted to the critical isotherm. In Fig. 3 the effect of the B_ξ variation is shown. B_T and f_T, which represent the temperature dependence of the attraction in the basic equation, have to be fitted simultaneously to the vapor pressure curve. The parameters of the calculated substances are listed in Table V.

Table II. Polynomial Coefficients for Calculation of the Critical Parameters from the Critical Compressibility Factor $[Y(Z_c) = d_1 + d_2 Z_c + d_3 Z_c^2 + d_4 Z_c^3 + \cdots]$ in the Range $0.21 \leqslant Z_c \leqslant 0.30$

	$Y(Z_c)$		
	$\xi_c(Z_c)$	$\tilde{T}_c(Z_c)$	$\sigma_c(Z_c)$
1	0.5161021349438131	2.47644923389038	1.95650074626909
2	0.01878710569107966	1.13135709380211	-47.824968433112
3	-0.01028961440626288	0.172285498944218	592.3143850071386
4	0.02057919382591271	3.62817764202945	-4113.57177545814
5	-0.04188957246634467	-6.36694271368859	17142.47144279727
6		8.66549119997775	-42952.6885993735
7			59950.27507260358
8			-36050.7956382499

Table III. Critical Data of the Pure Substances

Substance	T_c (K)	p_c (bar)	V_{mc} (cm$^3 \cdot$mol^{-1})	Z_c
Argon	150.718	48.6647	74.53	0.28942
Fluorine	144.121	51.724	66.55	0.28725
Methane	190.498	45.949	98.55	0.28589
Propane	369.85	42.4709	201.82	0.27873
Carbon dioxide	304.21	73.825	94.43	0.27561

Table IV. Critical Values of the Reduced Density ξ and the Fluctuation Distribution Measure σ

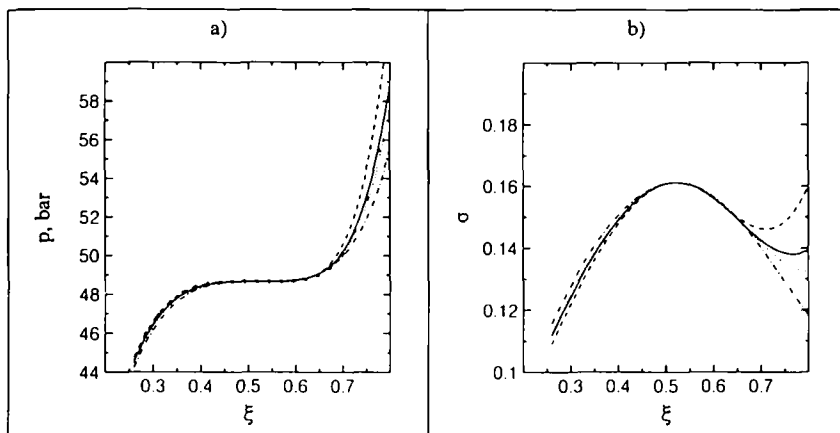| Substance	ξ_c	σ_c
Argon	0.52088277	0.16125848
Fluorine	0.52085228	0.16359201
Methane	0.52083332	0.16501701
Propane	0.52073212	0.17230781
Carbon dioxide	0.52068764	0.17535879

Fig. 3. The effect of variation of the parameter B_ξ (a) on the critical isotherm and (b) on the fluctuation distribution function. ($\cdots$) $B_\xi = 1.0$ (CO_2); ($----$) $B_\xi = 0.8$; ($-\cdot-\cdot-$) $B_\xi = 1.3$; ($---$) $B_\xi = 0.93$ (Ar).

It appears that B_ξ and B_f are close to 1 for all substances studied in this work, with the exception of fluorine. In this case, one might suspect that the quality of the experimental data used for the data reduction was not as good as for the other fluids. The critical density ξ_c is almost a constant for all fluids studied here, whereas B_ξ and σ_c seem to increase slightly with nonsphericity.

6.2. Prediction

With the known parameters of Eq. (22) the $p\rho T$ surface was calculated. The two-phase region was determined by numerical solution of the Maxwell criterion.

In Figs. 4–8 we compare experimental values with calculated results from the full equation of state given by Eq. (22) as well as from the basic

Table V. Parameters of the Complete Equation of State for Pure Fluids

Substance	a ($dm^6 \cdot mol^{-1} \cdot bar$)	b ($dm^3 \cdot mol^{-1}$)	B_ξ	B_f	f_i
Argon	1.3517058815	0.03882163932	0.93	1.0	53.651
Fluorine	1.1556242554	0.03466109548	1.0	0.5	18.016
Methane	2.2639369929	0.05132812380	0.9	0.9	20.000
Propane	9.0399646569	0.10509225471	1.0	1.0	7.440
Carbon dioxide	3.4855201195	0.04916785707	1.0	1.0	5.727

equation of state, which is obtained from Eq. (22) by setting $\sigma = 0$. The basic equation is not capable of representing all three critical coordinates p_c, T_c, and V_{mc}. We chose the critical pressure and volume to calculate a and b, calculated the (classical) critical temperature from these parameters, and then rescaled the temperature with the factor $T_{c,calc}/T_c$ for the graphic presentation. The parameters for the basic equation of state are given in Table VI.

In all cases, the CMFA equation of state leads to superior results in the critical region. The plots of the orthobaric densities vs pressure always show a significant flattening at the top for real substances, which can be reproduced by classical equations of state only if a disproportional number
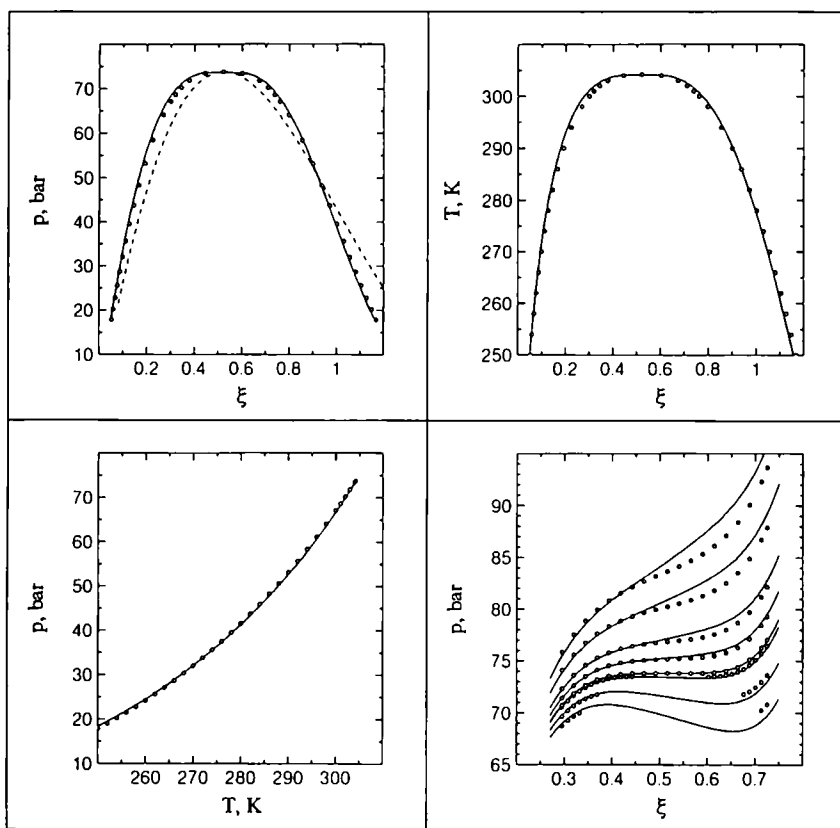
Fig. 4. The coexistence curves, the vapor pressure curve, and some near-critical isotherms of CO_2 (at 302, 303, 304, 304.21, 305, 306, 308, and 310 K). Experimental data [16]: (——) calculated from Eq. (22); (– – – –) calculated with the basic equation ($\sigma = 0$).
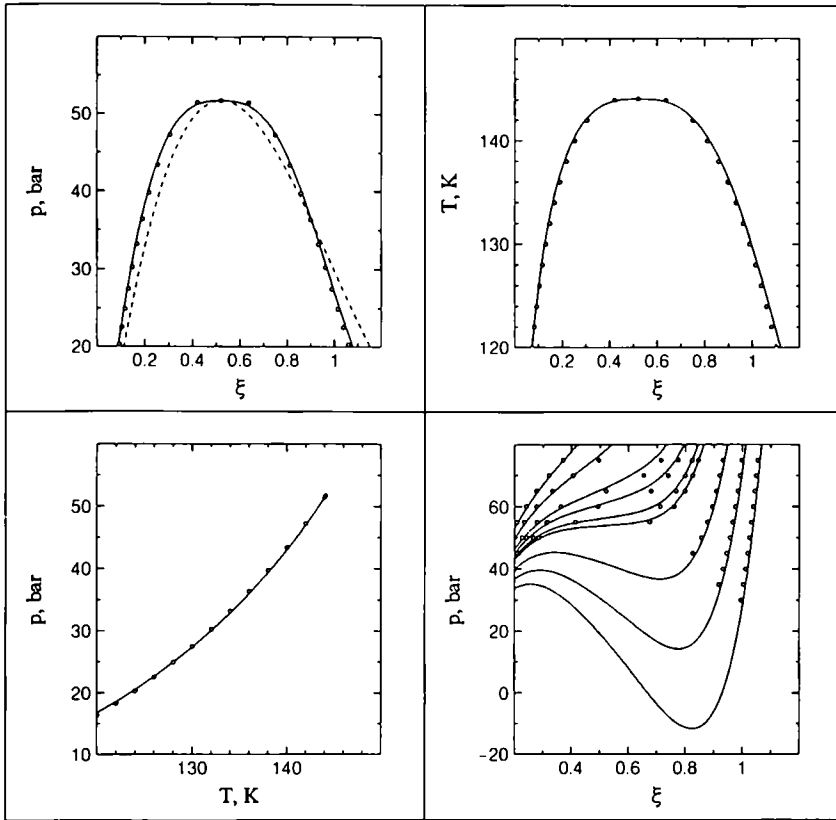
Fig. 5. The coexistence curves, the vapor pressure curve, and some near-critical isotherms of fluorine (at 130, 135, 140, 145, 146, 148, 150, 155, and 160 K). Experimental data [17]: (———) calculated from Eq. (22); (————) calculated with the basic equation ($\sigma = 0$).

Table VI. Parameters of the Basic Equation of State for Pure Fluids

Substance	a (dm$^6 \cdot$ mol$^{-1} \cdot$ bar)	b (dm$^3 \cdot$ mol^{-1})	$T_{c,calc}$ (K)	f_r
Argon	1.04139	0.0388879	121.527	53.651
Fluorine	0.88252	0.0347242	115.337	18.016
Methane	1.71921	0.0514210	151.726	20.000
Propane	6.66436	0.1053050	287.199	7.440
Carbon dioxide	2.53607	0.0492713	233.583	5.727

of adjustable parameters is used. The new equation of state leads to a good agreement with experimental data with few substance-specific parameters only. As mentioned before, the polynomial for σ is a universal function for the molecules considered in this work.

7. DISCUSSION

As shown in the last section, Eq. (22) is able to predict phase behavior in the critical region as well as in the classical region. This is remarkable, because the equation of state is an analytical one. To understand the source
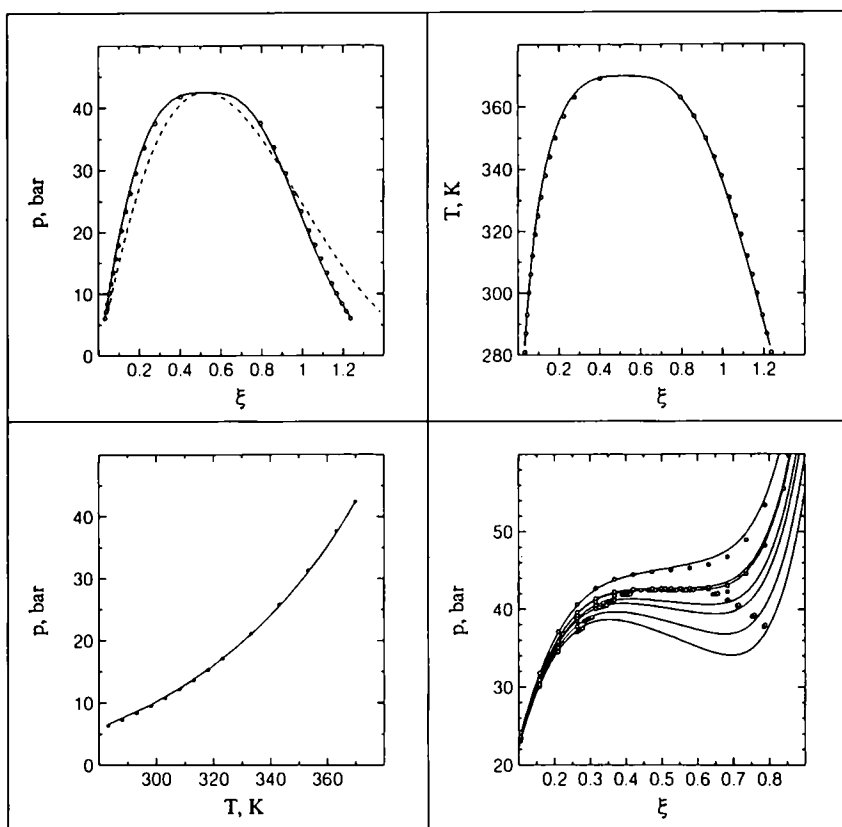
Fig. 6. The coexistence curves, the vapor pressure curve, and some near-critical isotherms of propane (at 363.15, 365.15, 367.15, 368.15, 369.15, 369.85, 370.15, and 373.15 K). Experimental data [18, 19]: (———) calculated from Eq. (22); (- - - -) calculated with the basic equation ($\sigma = 0$).

of this behavior, it is necessary to investigate the exponent of the calculated critical isotherm. The exponent δ and the critical amplitude k_ξ of the power law given by Eq. (18) can be obtained with the following equations:

$$\delta(\xi) = \ln \left| \frac{p(\xi) - p_c}{p_c} \right| \bigg/ \ln |\Delta \xi| \tag{25}$$

$$k_\xi(\xi) = \left| \frac{p(\xi) - p_c}{p_c} \right| \bigg/ |\Delta \xi|^{\delta(\xi)} \tag{26}$$

The results are plotted in Fig. 9 as the dependence of the distance from the critical point. The dotted vertical line marks the critical density. In the
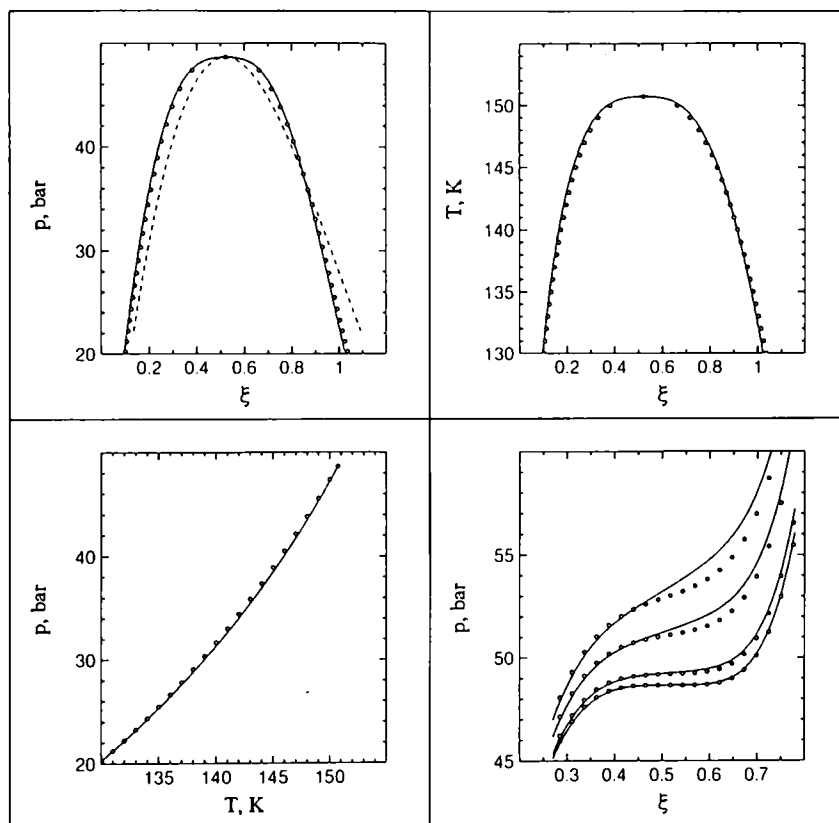
Fig. 7. The coexistence curves, the vapor pressure curve, and some near-critical isotherms of argon (at 150, 150.718, 151, 152, and 153 K). Experimental data [20, 21]: (———) calculated from Eq. (22); (– – – –) calculated with the basic equation ($\sigma = 0$).

classical region, the value of δ increases when the distance to the critical point decreases. In the near-critical region the slope changes its sign, and δ is forced to the classical value three. Because the critical isotherm is very flat in the vicinity of the critical point, the high value of the slope of $\delta = \delta(\xi)$ has little effect on the pressure values. The reason is a corresponding maximum of the critical amplitude at ξ_c. The interaction of δ and k_ξ is responsible for the good reproduction of the experimental data in the near critical region. The more coefficients are used in the fit of Eq. (19), the nearer the domain of nonclassical values of δ can be moved toward the critical point, though the classical value at the critical point cannot be avoided.

An analogous investigation of the binodal line leads to the same results. In Fig. 10 the values of $1/\beta$ and the corresponding critical amplitude are
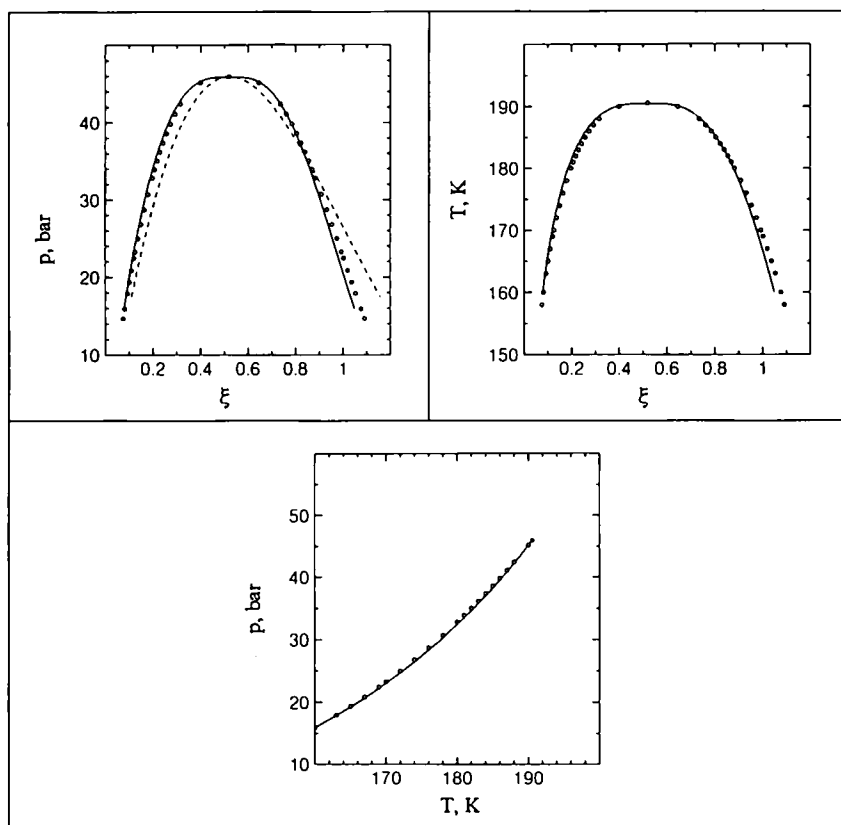
Fig. 8. The coexistence curves and the vapor pressure curve of methane. Experimental data [21, 22]: (———) calculated from Eq. (22); (- - - -) calculated with the basic equation ($\sigma = 0$).
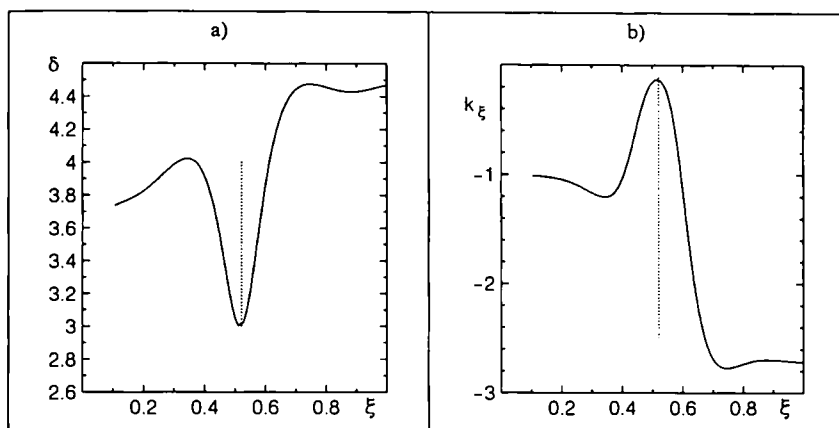
Fig. 9. Behavior of the critical exponent δ along the critical isotherm, calculated from Eq. (22). (a) Critical exponent δ; (b) associated critical amplitude of the power law (18).

plotted. $1/\beta$ runs through a sharp minimum with the classical value. If one extrapolated the functions $\delta(\xi)$ and $1/\beta(\xi)$ over ξ_c without considering the minimum, these functions would pass through the nonclassical value at ξ_c.

Also, the weakly divergent behavior of the isochoric heat capacity C_V at the critical point is not reproduced correctly by our approach. This is due partly to the fact that the nonclassical behavior of C_V is apparent at very small distances from the critical point only, where the CMFA approximation is already returning to its classical limiting value. Further-
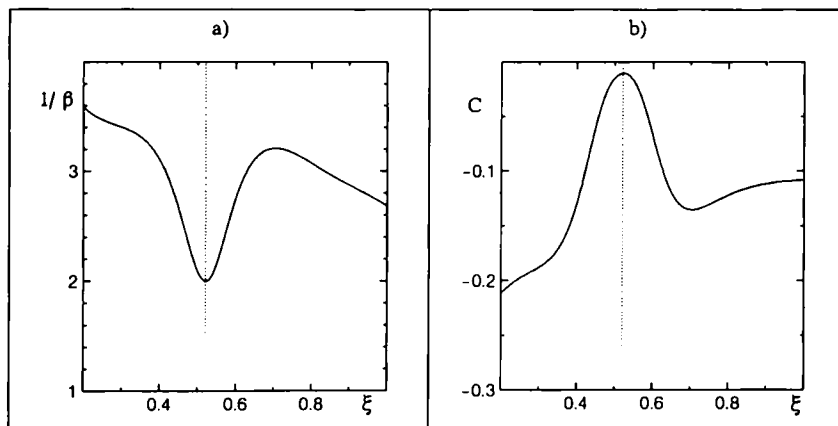

Fig. 10. Behavior of the critical exponent β along the phase boundary, calculated from Eq. (22). (a) Reciprocal value of β; (b) associated critical amplitude of the binodal power law.

more, the basic equation of state used in this work is too simple; to describe the behavior of C_V correctly, an improved classical equation must be used which exhibits a maximum of C_V at the critical point.

The reason the CMFA equation does not converge exactly to the nonclassical value of the critical exponents at the critical point is the use of equal-sized cells. The size of the cells is connected to the measure of the fluctuation σ. Because the cells have equal sizes, we have an averaging of fluctuation. The nonclassical behavior, however, is caused by diverging fluctuations, which cannot be described accurately with a model using finite and uniform cells. In this work, we replaced the mean field approximation by a mean fluctuation approximation. The mean fluctuation approximation (CMFA in Section 2) represents the classical fluctuations in the fluid.

The other restriction of our model is that fluctuations of all length scales are not coupled. This property makes our model equivalent to the Gaussian model [14], which has been shown to yield classical critical exponents in the immediate vicinity of the critical point [15].

To describe the nonanalytical behavior, the mean fluctuation approximation has to change to a multiple fluctuation approximation. This can be done by introducing a distribution of cell sizes. If it is possible to consider infinite cell sizes, the nonclassical values will be reached at the critical point. Hence the CMFA is the first step in the development of the new kind of crossover. Nevertheless, it is useful for describing experimental data of real substances as shown in Section 6. We intend to generalize this model to a model using a range of cell sizes which will yield the complete crossover.

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