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A NON-CUBIC HARD-SPHERE PERTURBED EQUATION OF STATE FOR REPRESENTING *PVT* AND PHASE EQUILIBRIA BEHAVIOR OF FLUIDS*

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A new equation of state is proposed by combining a hard-sphere reference model with a general inverse quadratic attractive term, used previously by the author, in a general cubic equation of state (GEOS). Similarly to the cubic GEOS, a parameterization based on four critical conditions is applied to the hard-sphere perturbed equation of state (PHSGEOS). Moreover, the procedure can be generalized for many reference hard-sphere or chain-hard-sphere forms proposed in literature. To exemplify, the Carnahan-Starling equation of state for hard spheres is used together with a van der Waals hard-sphere term as a reference form. The main result is the good representation of *PVT* and phase behavior of fluids. For pure fluids both vapor pressure and liquid density are accurately represented for an extensive range of temperature and a diversity of substances, by using a temperature dependence of the attractive term. The temperature function has three parameters (C_1, C_2, C_3) estimated by matching points on the saturation curve (vapor pressure and the corresponding liquid volumes). The equation can be extended to mixtures using the Boublik-Mansoori scaled-particle theory and the one-fluid theory.

Key words: Equation of state; Perturbed hard sphere; Phase equilibria; *PVT* properties.

INTRODUCTION

Equations of state models are commonly used in thermodynamic and phase equilibrium calculations. For standard chemical engineering applications, the most used equations of state are the simple cubic van der Waals forms. On the other hand much attention has been given toward development of semi-theoretical equations of state. For correlation and prediction of pressure-volume-temperature (*PVT*) and phase equilibria behavior, a useful reference system is a hard-sphere model. Many attempts are presented in the literature to add corrections, called perturbations, to the reference system. The simplest result is the perturbation of a hard-sphere term with a van der Waals attraction term, as suggested by Carnahan and Starling.[1] They used also the perturbation term of Redlich and Kwong. It was shown by Wong and Prausnitz[2] that both equations lead to poor liquid densities. Different perturbation terms, more or less complex, were proposed in the literature after 1972, some of them being reviewed by Dohrn and Prausnitz.[3] They studied several simple perturbation terms on Carnahan-Starling hard-sphere equation and proposed a new simple perturbation term. Seven two-parameter equations of state were applied for 11 non-polar pure fluids, and compared with the equation proposed by the authors. Their equation of state represents liquid densities significantly better, but it is not superior to other equations for vapor pressures.

Later, Aly and Ashour[4] reinvestigated the equation of state with a van der Waals perturbation term, corrected with a temperature function. The equation gives good vapor pressures but poor densities, especially at low temperatures and high pressures in the liquid region.

For polar compounds, the Carnahan-Starling hard-sphere equation was modified by Bryan and Prausnitz.[5]

Recently, Yelash et al.[6,7] proposed two new simple hard-sphere reference equations which, in combination with a van der Waals attraction term, lead to a biquadratic, respectively a cubic equation of state. The new equations, having poles close to the physical packing fraction of hard spheres, were studied for their global phase behavior and predicted closed-loop liquid-liquid immiscibility.

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[*] Paper presented by Mircea Banciu

More complicated equations of state have been proposed and applied to real systems using the statistical association fluid theory (SAFT) by Huang and Radosz,[8,9] Fu and Sandler,[10] or the perturbed hard-sphere-chain (PHSC) theory by Song et al.,[11] and Hino and Prausnitz.[12]

The Carnahan-Starling equation of state for hard spheres was extended to mixtures using either a one-fluid mixing rules, or the generalization of scaled-particle (called also Percus-Yevick) theory proposed by Bublik[13] and Mansoori et al.[14] Equations of state using the two reference systems, combined with a perturbation term of the van der Waals form, were used by Dimitrelis and Prausnitz[15] to correlate the phase behavior of binary mixtures of nonpolar molecules differing significantly in size.

In this work, a new equation of state is proposed by combining a hard-sphere reference model with a general inverse quadratic attractive term, used previously by the author[16-18] in a general cubic equation of state (GEOS). Similarly to the GEOS, a parameterization based on four critical conditions is applied to the hard-sphere perturbed equation of state. Moreover, the procedure can be generalized for many reference hard-sphere or chain-hard-sphere forms proposed in literature. To exemplify, the Carnahan-Starling equation of state for hard spheres is used together with a van der Waals hard-sphere term as a reference form. The main result is a good representation of pressure-volume-temperature (*PVT*) properties and phase behavior of fluids. For pure fluids both vapor pressure and liquid density are accurately represented for an extensive range of temperature and a diversity of substances, by using a temperature dependence of the attractive term. The temperature function has three parameters (C_1, C_2, C_3) estimated by matching points on the saturation curve (vapor pressure and the corresponding liquid volumes). The equation can be extended to mixtures using the Boublik-Mansoori scaled-particle theory[13,14] and the one-fluid theory.

THE PERTURBED HARD-SPHERE EQUATION OF STATE

Following van der Waals, it is usual to represent the compressibility factor Z by the contributions of a reference term and a perturbation term:

$$Z = Z_{\text{ref}} + Z_{\text{pert}} \tag{1}$$

In previous works, the van der Waals reference term was combined with a general inverse quadratic perturbation term leading to a general cubic equation of state, called GEOS.[16] Using the reduced density, η, the last version GEOS3C[19] takes the form:

$$Z = \frac{1}{1-4\eta} - \frac{4a(T_r)}{RTb}\eta\frac{1}{(1-4\frac{d}{b}\eta)^2 + 16\frac{c}{b^2}\eta^2} \tag{2}$$

with the reduced density

$$\eta = \frac{1}{4}\frac{b}{V} = \frac{1}{4}b\rho \tag{3}$$

The equation has four parameters (a, b, c, d), and the function of temperature is:

$$a(T_r) = a\beta^2(T_r) \tag{4}$$

and

$$\beta(T_r) = 1 + C_1 y + C_2 y^2 + C_3 y^3 \quad \text{for } T_r \le 1 \tag{5}$$

$$\beta(T_r) = 1 + C_1 y \quad \text{for } T_r > 1 \tag{6}$$

$$y = 1 - \sqrt{T_r} \tag{7}$$

with T_r - the reduced temperature by its critical value (T/T_c) and C_1, C_2, C_3 - constants.

This equation of state was applied to pure substances[19] as well as to mixtures.[20,21]

For many purposes, the van der Waals reference term is satisfactory, and because of its algebraic simplicity it is used extensively. From a theoretical point of view, more appropriate is a reference term based on the equation for hard spheres.

Then the cubic form (2) can be generalized to the hard-sphere equation combined with the same general inverse quadratic perturbation term (PHSGEOS):

$$Z = Y - \frac{4a(T_r)}{RTb}\eta\frac{1}{(1-4\frac{d}{b}\eta)^2 + 16\frac{c}{b^2}\eta^2} \tag{8}$$

where Y is a short notation for any kind of hard-sphere reference function $Y(\eta)$. For the van der Waals repulsive term:

$$Y \equiv Z^{vdW} = \frac{1}{1-4\eta} = 1 + \frac{4\eta}{1-4\eta} \tag{9}$$

Much attention has received the Carnahan-Starling (CS) expression:[1]

$$Y \equiv Z^{CS} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} = 1 + \frac{4\eta-2\eta^2}{(1-\eta)^3} \tag{10}$$

which, for preserving the cubic form of the equation of state, was simplified to

$$Y \equiv Z^{CS}_{simpl} = \frac{1+4m\eta}{1-4n\eta} = 1 + \frac{4(m+n)\eta}{1-4n\eta} \tag{11}$$

with m=n=0.5 by Scott, m=0.77, n=0.42 by Kim et al., and m=0.62, n=0.47 by Mohsen-Nia et al.[22]

Other expressions appeared in the literature and may be also used, as for example that proposed by Bryan and Prausnitz[5] for polar fluids.

A hard-sphere-chain expression, as that used by Huang and Radosz[8] in the SAFT equation of state, may be considered too.

Coming back to the PHSGEOS equation (8), the following notations can be introduced:

$$a = \Omega_a \frac{R^2 T_c^2}{P_c} \qquad b = \Omega_b \frac{RT_c}{P_c} \tag{12}$$

$$c = \Omega_c \frac{R^2 T_c^2}{P_c^2} \qquad d = \Omega_d \frac{RT_c}{P_c} \tag{13}$$

by using the critical temperature and pressure (T_c, P_c). R is the universal gas constant, and Ω_a, Ω_b, Ω_c, Ω_d are nondimensional parameters.

Then the PHSGEOS equation (8) becomes:

$$Z = Y - \frac{4\Omega_a \beta(T_r)}{\Omega_b T_r} \eta \frac{1}{(1-4\frac{\Omega_d}{\Omega_b}\eta)^2 + 16\frac{\Omega_c}{\Omega_b^2}\eta^2} \tag{14}$$

In reduced variables the equation of state (14) takes the form:

$$P_r = \frac{T_r}{Z_c V_r} Y - \frac{\Omega_a \beta(T_r)}{(Z_c V_r - \Omega_d)^2 + \Omega_c} \tag{15}$$

with $T_r = T/T_c$, $P_r = P/P_c$, $V_r = V/V_c$, and the critical compressibility factor $Z_c = P_c V_c / RT_c$. V_c is the critical molar volume.

Imposing four critical conditions to the equation (15) (see appendix), it results:

$$Y_c = \frac{Z_c}{B}; \quad B = \frac{1+C_1}{\alpha_c + C_1}; \quad \beta^{'}(T_r = 1) = -C_1 \tag{16}$$

and the following expressions for the parameters:

$$\Omega_a = \frac{4(Y_c - Z_c)^3}{Z_c u^2 (1+h)} \qquad \Omega_b = 4\eta_c Z_c \tag{17}$$

$$\Omega_c = \frac{4(Y_c - Z_c)^2 h}{u^2 (1+h)^2} \qquad \Omega_d = Z_c - \frac{2(Y_c - Z_c)}{u(1+h)} \tag{18}$$

The notations in the above expressions are:

$$u = \frac{1}{Z_c}(Y_c + \eta_c Y_c^{'}) \tag{19}$$

$$w = \frac{1}{Z_c}(2Y_c + 4\eta_c Y_c^{'} + \eta_c^2 Y_c^{"}) \tag{20}$$

$$h = 3 - \frac{2w(Y_c - Z_c)}{Z_c u^2} \tag{21}$$

where the notations Y_c, $Y_c^{'}$, $Y_c^{"}$ are used for the function Y, and their first and second derivatives at the critical point. The η_c is the value of the reduced density at the critical point, obtained as the solution of the equation $Y_c = Z_c /B$.

The calculation of the parameters is made as follows:

- Given (adjusting) α_c and C_1;
- Calculation of B and Z_c /B;
- Solving for η_c from the equation Y_c=Z_c /B;
- Calculation of $Y_c^{'}$, $Y_c^{"}$ and u, w, h from (19-21);
- Calculation of Ω_a, Ω_b, Ω_c, Ω_d from (17, 18).

The procedure is general, this means that every suitable expression for the hard sphere reference term, Y, may be used for applications. Moreover, in the general inverse quadratic attractive term, special cases can be easily obtained, by setting restrictions on the parameters (as in the cubic GEOS[18,19]). For example, the van der Waals attractive term results by setting:

$$\Omega_c = \Omega_d = 0 \tag{22}$$

The Redlich-Kwong attractive term is obtained by setting:

$$\Omega_c = -(\Omega_b/2)^2 \qquad \Omega_d = -(\Omega_b/2) \tag{23}$$

The Peng-Robinson attractive term is obtained by setting:

$$\Omega_c = -2\,\Omega_b^2 \qquad \Omega_d = -\,\Omega_b \tag{24}$$

This explains the meaning of the "general inverse quadratic" term. The implications of such settings, in relation with many other attractive terms proposed in literature, were discussed on the basis of a generalized diagram[21] using the coordinates Ω_c/Ω_b^2 and Ω_d/Ω_b.

As it was mentioned before, many expressions suggested in the literature for the reference hard sphere term can be used to obtain a special equation of state. In this work we present an example of the application of a simple type of perturbed hard sphere equation of state, following the general described procedure. At first, the most simple equation of state may be obtained by combining the Carnahan-Starling expression with the general inverse quadratic perturbation term, used previously in the GEOS forms:

$$Z = Z^{CS} - \frac{4a(T_r)}{RTb}\eta\frac{1}{(1-4\frac{d}{b}\eta)^2 + 16\frac{c}{b^2}\eta^2} \tag{25}$$

with Z^{CS} given by equation (10).

Equations of state, in the general form (8), may be derived from the canonical van der Waals partition function.[23]

For the free volume term, a van der Waals hard sphere expression

$$\frac{v_f}{v} = 1 - 4\eta \tag{26}$$

leads to equation (2). The expression of hard spheres:

$$\frac{v_f}{v} = \exp\left[\frac{\eta(3\eta-4)}{(1-\eta)^2}\right] \tag{27}$$

is considered for equation (25)

In both cases the potential field is given by:

$$\Phi = \frac{a(T_r)}{N_A\sqrt{-c}}\ln\frac{V-d+\sqrt{-c}}{V-d-\sqrt{-c}} \tag{28}$$

where the molar volume $V = N_A v/N$, N_A is the Avogadro's number, and *a, c, d* are energy and size parameters, and $c < 0$.

The equations of state are obtained using the statistical thermodynamic relationship between the compressibility factor and the canonical partition function.

NEW PERTURBED HARD-SPHERE EQUATION OF STATE

Taking into consideration the relative good representation of *PVT* and phase equilibrium behavior achived by the cubic equation of state, it is interesting to study the transition between the limiting cases discussed in the above paragraph. The following equation of state is proposed:[23]

$$Z = 1 + c_0\frac{4\eta - 2\eta^2}{(1-\eta)^3} + f\frac{4\eta}{1-4\eta} - \\ - \frac{4a(T_r)}{RTb}\eta\frac{1}{(1-4\frac{d}{b}\eta)^2 + 16\frac{c}{b^2}\eta^2} \tag{29}$$

The reference term is a combination of a hard sphere Carnahan-Starling expression (10) with a van der Waals form:

$$Y = 1 + c_0\frac{4\eta - 2\eta^2}{(1-\eta)^3} + f\frac{4\eta}{1-4\eta} \tag{30}$$

The parameters c_0 and f enable the transition between the limiting cases: $c_0 = 0$ and $f = 1$ (the cubic GEOS equation) and $c_0 = 1$ and $f = 0$ (the CS + inverse quadratic equation). Formally, the van der Waals term in equation (29) can be included in the attractiv part of the equation of state. But for the algebra of the equation and applications the coupling of the two terms in equation (30) leads to simpler expressions. The first and second derivative of the *Y* function (30) are given in appendix.

Different combinations of hard-sphere and van der Waals terms were tested, by using particular values for c_0 and f in equation (30). The results show that an appropiate combination is with the values $c_0 = 1$ and $f = 0.6$. The new equation is:

$$Z = 1 + \frac{4\eta - 2\eta^2}{(1-\eta)^3} + \frac{2.4\eta}{1-4\eta} - \\ - \frac{4a(T_r)}{RTb}\eta \frac{1}{(1-4\frac{d}{b}\eta)^2 + 16\frac{c}{b^2}\eta^2} \qquad (31)$$

This empirical choice is reasonable, conserving the correct theoretical hard-sphere reference term. The corrective term of van der Waals type is needed by two reasons suggested in the literature: to change the pole of the equations of state (as discussed by Yelash and Kraska[6]), and/or to complicate the attractiv term (as discussed by Dohrn and Prausnitz[3]). The recent papers of Polishuk et al.[27] investigating the global phase diagrams of hard-sphere and cubic equations of state confirm also the need of such kind of transition. Surely, other approaches may be imaginated.

RESULTS AND DISCUSSION

In the following part we present the results obtained by applying the new equation of state (31) to represent *PVT* and phase behavior of pure fluids.

Using experimental values of the critical constants (T_c, P_c, Z_c) and the acentric factor for the calculation of Riedel parameter (α_c) from the equation:

$$\alpha_c = 5.808 + 4.93\omega \qquad (32)$$

the C_1, C_2, C_3 were obtained by matching points on the saturation curve (vapor pressures together with the corresponding saturated-liquid molar volumes). Thus, the EOS is forced to properly reproduce the saturation region from the triple point to the critical point. In many cases three fixed temperatures, the triple point, the boiling point and the reduced temperature $T_r = 0.7$, can be used as a minimum available data for obtaining the parameters values.

The values of the C_1, C_2, C_3 parameters for the equation (31), for several substances are presented in Table 1. Table 2 gives the average absolute deviations (AAD) for vapor pressure, saturated-liquid volume and vapor volume, between calculated values by equation (31) and experimental data (when available, IUPAC recommended data). The data used in the calculations are collected in a database, called LVV1DAT.[21] The corresponding tables of the parameters values and average absolute deviations for the cubic GEOS are reported elsewhere[21].

Table 1. The C_1, C_2, C_3 parameters of equation of state (31).

Component	C_1	C_2	C_3	α_c
NH_3	–0.0165	0.9498	–0.3987	7.0695
Ar	–0.0915	0.2661	0.7197	5.7869
CO_2	0.0479	0.2923	3.5754	6.9173
He	–0.4952	0.0920	–0.1689	3.9008
H_2O	0.0311	1.0544	–0.7619	7.5027
H_2	–0.2923	0.2007	–0.2179	4.7272
CH_4	–0.0774	0.3312	0.2997	5.8573
C_2H_6	0.0272	0.3813	0.1431	6.2909
C_3H_8	0.0432	0.5159	0.0734	6.5549
i-C_4H_{10}	0.0792	0.3727	1.0314	6.7195
n-C_4H_{10}	0.0222	0.6493	0.8173	6.7906
i-C_5H_{12}	0.0161	0.8828	0.2820	6.9145
n-C_5H_{12}	0.0391	0.8373	0.5373	7.0484
n-C_6H_{14}	0.0938	0.8575	–0.0043	7.2822
n-C_7H_{16}	0.0745	1.2357	–0.3078	7.5384
n-C_8H_{18}	0.1090	1.4298	–1.4201	7.7504
CH_3Cl	–0.0519	0.7843	0.8471	6.5771
F_2	–0.0167	0.3513	0.1759	6.0526
N_2O	–0.0524	0.5031	4.1690	6.5968
SO_2	0.0248	0.8544	1.0558	7.0454
H_2S	–0.0554	0.4466	2.0550	6.3010
C_2H_4	–0.0046	0.4009	0.2576	6.2363
C_3H_6	–0.0460	0.7722	0.9647	6.5376
C_6H_6	0.0397	0.6429	0.3826	6.8270
cyclo-C_3H_6	0.0576	–1.8387	13.491	7.1095
Ne	–0.0549	–0.2088	1.5980	5.8080
N_2	–0.0471	0.3263	0.4863	5.9805
O_2	–0.0502	0.3585	0.1189	5.9174
CO	0.0074	0.1162	1.0489	6.0355
CH_3OH	0.0525	2.4073	–3.6874	8.5528
C_2H_5Cl	0.0017	0.6357	0.6370	6.7523
CCl_4	0.0095	0.6876	0.6189	6.7640
Cl_2	–0.0816	0.5041	0.7495	6.1679
HCl	–0.0574	0.6462	0.0309	6.4361
SO_3	0.1396	0.3981	5.4876	7.9367

Using the same parameter values, the densities (volumes) of the pure fluids were predicted in the single-phase region, on several isotherms. The absolute average deviations in volumes on the isotherms, in the single-phase region are reported also in the table 2 (AAD 1PV).

Examples of such calculations are presented in Figs. 1 – 3. Fig. 1 shows the isotherms of argon. Points figure

IUPAC data,[25] while the curves represent predictions performed by the equation of sate (31).

Table 2. *PVT* Average Absolute Deviations of equation of state (31).

Component	%AAD Ps	%AAD Vl	%AAD Vv	%AAD 1PV
NH_3	0.76	6.68	2.86	5.04
Ar	0.26	2.91	1.45	1.52
CO_2	0.34	2.55	2.01	1.43
He	0.18	0.31	1.56	8.54
H_2O	0.76	6.07	2.07	3.10
H_2	0.12	1.66	1.07	2.90
CH_4	0.46	3.54	1.22	3.09
C_2H_6	1.13	5.15	1.69	3.36
C_3H_8	1.09	5.57	1.75	3.90
$i\text{-}C_4H_{10}$	0.36	2.56	1.62	3.07
$n\text{-}C_4H_{10}$	0.35	3.05	1.49	3.74
$i\text{-}C_5H_{12}$	0.19	2.83	2.64	2.92
$n\text{-}C_5H_{12}$	0.26	3.28	1.54	4.48
$n\text{-}C_6H_{14}$	0.41	4.73	1.56	3.86
$n\text{-}C_7H_{16}$	0.29	3.39	1.94	7.45
$n\text{-}C_8H_{18}$	0.29	3.86	1.97	5.21
CH_3Cl	0.35	2.42	2.50	3.48
F_2	0.93	4.55	1.59	2.71
N_2O	0.22	1.69	2.72	3.82
SO_2	0.33	2.93	0.90	4.01
H_2S	0.32	2.06	1.88	2.90
C_2H_4	1.06	5.23	2.12	3.86
C_3H_6	0.37	1.66	2.65	3.68
C_6H_6	0.77	4.70	5.23	4.47
$cyclo\text{-}C_3H_6$	1.04	2.41	2.55	2.97
Ne	0.69	2.17	1.58	1.32
N_2	0.47	3.59	1.74	3.75
O_2	0.97	4.14	2.07	2.84
CO	0.69	3.20	2.76	1.66
CH_3OH	0.64	6.68	4.01	-
C_2H_5Cl	0.55	3.47	3.74	-
CCl_4	0.23	3.37	2.30	-
Cl_2	0.41	3.22	5.13	-
HCl	0.20	4.79	4.59	-
SO_3	0.97	3.61	6.07	-

The agreement with IUPAC data is very good at high temperatures (200 – 1100 K) and reasonable good at the critical temperature (150.86 K). At subcritical temperatures (85, 120 K), larger errors of calculations were observed, but still acceptable (average absolute deviations on isotherms 1.52%, table 2).

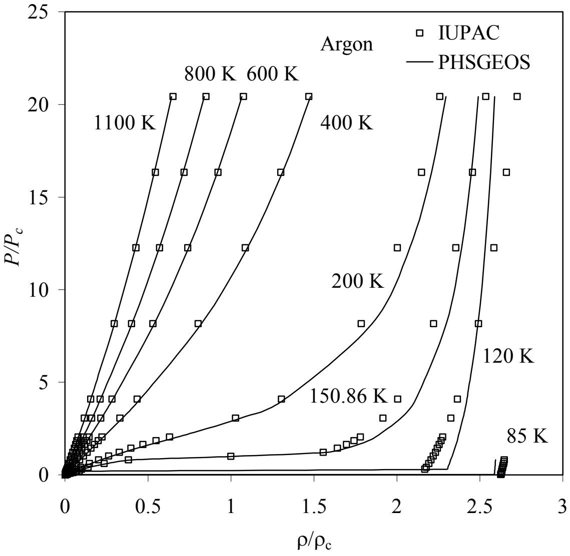

Fig. 1. Argon isotherms. Comparison between calculations with the equation of state (31) and IUPAC recommended data.[25]

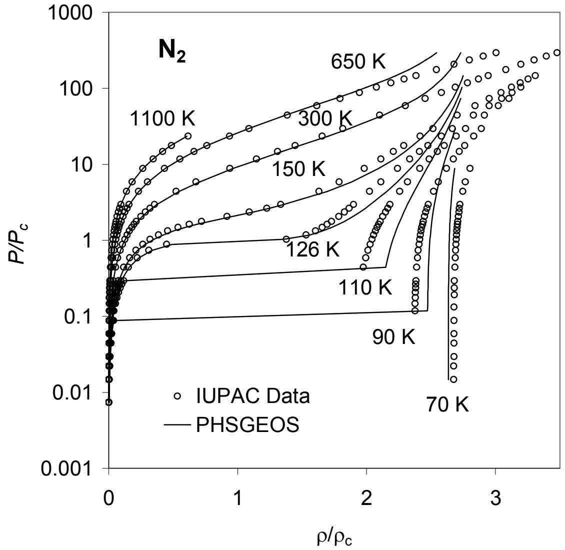

Fig. 2. Nitrogen isotherms. Comparison between calculations with the equation of state (31) and IUPAC recommended data.[24]

A similar plot is presented in Fig. 2 for N_2. The agreement with IUPAC data[24] is acceptable at reduced pressures (under 100) but larger errors of calculations should be, however, counted in the high-pressure range ($P/P_c > 100$).

A similar behavior is observed for CH_4, as shown in Fig. 3. The agreement with IUPAC data[26] is reasonable at pressures under 1000 bar.

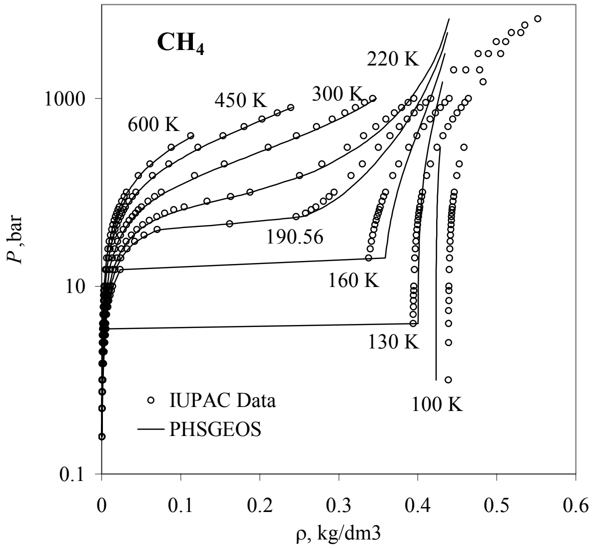

Fig. 3. Methane isotherms. Comparison between calculations with the equation of state (31) and IUPAC recommended data.[26]

CONCLUSIONS

A generalized equation of state is proposed by combining a hard-sphere reference model with a general inverse quadratic attractive term (PHSGEOS) used previously by the author, in a cubic general equation of state (GEOS). Similarly to the cubic GEOS, a parameterization based on four critical conditions is applied to the hard-sphere perturbed equation of state. The procedure can be generalized for many reference hard-sphere or chain-hard-sphere forms proposed in literature. To exemplify, the Carnahan-Starling equation of state for hard spheres is used together with a van der Waals hard-sphere term as a reference form. The main result is a good representation of *PVT* properties and phase behavior of fluids. For pure fluids both vapor pressure and liquid density are accurately represented for an extensive range of temperature and a diversity of substances, by using a temperature dependence of the attractive term. The temperature function has three parameters (C_1, C_2, C_3) estimated by matching points on the saturation curve (vapor pressure and the corresponding liquid volumes). The equation can be extended to mixtures using the Boublik-Mansoori scaled-particle theory for the hard sphere reference term and the one-fluid theory for the other parameters in the attractive term of the equation of state.

APENDIX

Setting four critical conditions at $T_r = 1$ and $V_r = 1$ in the equation (15):

$$P_r = 1; \quad \frac{\partial P_r}{\partial V_r} = 0; \quad \frac{\partial^2 P_r}{\partial V_r^2} = 0; \quad \frac{\partial P_r}{\partial T_r} = \alpha_c \tag{A1}$$

the following system of equations is obtained:

$$1 = \frac{1}{Z_c} Y_c - \frac{\Omega_a}{(Z_c - \Omega_d)^2 + \Omega_c} \tag{A2}$$

$$u = \frac{2\Omega_a Z_c (Z_c - \Omega_d)}{[(Z_c - \Omega_d)^2 + \Omega_c]^2} \tag{A3}$$

$$w = \frac{2\Omega_a Z_c^2 [3(Z_c - \Omega_d)^2 - \Omega_c]}{[(Z_c - \Omega_d)^2 + \Omega_c]^3} \tag{A4}$$

$$\alpha_c = \frac{1}{Z_c} Y_c + \frac{\Omega_a C_1}{(Z_c - \Omega_d)^2 + \Omega_c} \tag{A5}$$

with

$$u = \frac{1}{Z_c}(Y_c + \eta_c Y_c^{'}) \tag{A6}$$

$$w = \frac{1}{Z_c}(2Y_c + 4\eta_c Y_c^{'} + \eta_c^2 Y_c^{"}) \tag{A7}$$

By combining of (A2) with (A5) it results:

$$Y_c = \frac{Z_c}{B} \qquad B = \frac{1 + C_1}{\alpha_c + C_1} \tag{A8}$$

The notation B for the above expression is the same used in the cubic general form (GEOS), in the previous papers.[16-21]

The corresponding expressions of the derivatives for the new equation of state (29) are:

$$Y_c^{'} = (Z_c^{CS})^{'} + \frac{4f}{(1 - 4\eta_c)^2} \tag{A9}$$

$$Y_c^{"} = (Z_c^{CS})^{"} + \frac{32f}{(1 - 4\eta_c)^3} \tag{A10}$$

$$(Z_c^{CS})' = \frac{2(2+2\eta_c-\eta_c^2)}{(1-\eta_c)^4} \tag{A11}$$

$$(Z_c^{CS})'' = \frac{4(5+2\eta_c-\eta_c^2)}{(1-\eta_c)^5} \tag{A12}$$

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