Backone Family of Equations of State: 1. Nonpolar and Polar Pure Fluids

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The Helmholtz energy F is written as the sum $F = F_H + F_A + F_{Pol}$, *where* F_H *is the hard-body contribution,* F_A *the attractive dispersion force contribution, and* F_{Pol} *either the quadrupolar or dipolar contribution. Here, a new expression for* F_A *is constructed by a simultaneous correlation of experimental data of methane, oxygen, and ethane. The resulting equations for F with only three or four substance-specific parameters are tested for several nonpolar, quadrupolar, and dipolar fluids. In the correlation of large data sets good results are obtained. The significance of the approach, however, is in the good to excellent prediction of all thermodynamic properties in the whole fluid region based on a parameter fit to only four experimental data—two vapor pressures and two saturated liquid densities.*

Introduction

The importance of equations of state (EOS) for the design of various engineering processes is well known. For the construction of accurate equations, two routes may be considered. The one route is to correlate large data sets by equations with many substance-specific parameters (Bender, 1971; Jacobsen et al., 1990; Setzmann and Wagner, 1991). This approach yields very accurate equations, but the problem is already in the measurement of the required large data sets for pure fluids and even more for mixtures. Alternatively, one can construct physically based equations of state with only a few substance specific parameters of physical significance; examples are the BACK (Boublik–Alder–Chen–Kreglewski) equation (Chen and Kreglewski, 1977; Kreglewski, 1984) and subsequent equations (Lee and Chao, 1988; Saager and Fischer, 1994). This route allows, in principle, the prediction of thermodynamic data. The problem with this approach, however, is that existing equations still show some shortcomings. It is the purpose of this article to improve these physically based equations of state and hence to allow more accurate predictions.

The equations to be considered here start out from the fact that the intermolecular interactions consist of several characteristic parts like the short-range repulsion, the dispersion force attraction, or polar interactions. Generalizing the idea of van der Waals, it is assumed that each of these characteristic parts yields a separate contribution to the Helmholtz energy F. Hence, for nonpolar fluids F is written as

$$F = F_H + F_A, \tag{1}$$

with F_H being the contribution of the hard molecular cores representing the short-range repulsion, and F_A being the contribution of the attractive dispersion forces. For fluids with polar forces, the contribution of these interactions is accounted for by an additional term F_{Pol}. In case of quadrupolar forces, this term is F_Q and the equation is

$$F = F_H + F_A + F_Q; \tag{2}$$

for dipolar forces, it is F_D and the equation is

$$F = F_H + F_A + F_D. \tag{3}$$

A prominent example of these physically based equations for nonpolar fluids is the BACK equation (Chen and Kreglewski, 1977; Kreglewski, 1984), which contains the hard-body contribution F_H of Boublik (1975) and an attractive

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force term F_A with a functional form suggested by Alder et al. (1972). Modifications of that equation are the MOBACK equation (Saager et al., 1992) and the NIK equation (Nguyen et al., 1993). An extension of BACK to polar fluids was made by Lee and Chao (1988), who added the polar pressure of water. Alternatively, the quadrupolar contribution F_Q and the dipolar contribution F_D were constructed on the basis of molecular simulations (Saager and Fischer, 1992). The resulting extensions of the MOBACK equation by addition of one of these terms were called the QUABACK and the DIBACK equations (Saager and Fischer, 1992, 1994).

Accounting for the nonspherical behavior of the attractive dispersion forces in F_A, however, still remains a problem. In the BACK and MOBACK equations, F_A is a function of the hard-body packing fraction ξ and a rescaled temperature

$$\tau=(T/T_0)/(1+\eta/kT), \tag{4}$$

with T the temperature, T_0 some reference temperature, and η represents the nonspherical shape of the molecules. This temperature rescaling dates back to earlier work of Rowlinson (1954). On the basis of a rather accurate perturbation theory (Fischer, 1980), however, we have come to the conclusions that this temperature rescaling transformation yields only qualitatively correct results. Consequently, it turns out that, with the functional form of F_A fitted to ethane (Saager et al., 1992), it is not possible to arrive at an accurate description of methane by using the transformation equation, Eq. 4. An additional shortcoming of this concept is that one needs one anisotropy parameter η for the attractive forces and another anisotropy parameter α for the hard bodies. An attempt to construct an F_A term for nonspherical molecules on the basis of molecular simulations was made by Sowers and Sandler (1992), but they considered only supercritical temperatures.

In this article we will derive an expression for F_A that is able to account for spherical as well as for nonspherical molecules in the whole fluid region. The construction of F_A is based on experimental data for methane, oxygen, and ethane, and on previously derived potential models for these substances (Fischer et al., 1984; Bohn et al., 1986a,b). The functional form of F_A is found by a simultaneous correlation of data of all three substances using the method for optimizing the structure of thermodynamic equations due to Setzmann and Wagner (1989). The resulting expression for F_A will have the same parameters as the hard-body contribution F_H, namely, a characteristic density ρ_0, a characteristic temperature T_0, and an anisotropy parameter α. The class of equations that combines the new F_A with Boublik's (1975) hard-body term F_H and, in the case of polar fluids, adds either F_Q or F_D (Saager and Fischer, 1992) is called BACKONE family. For nonpolar fluids, these equations need three substance-specific parameters, and for polar fluids, they need only one additional parameter—a reduced multipole moment.

In the next section we will construct F_A as indicated earlier. In the subsequent sections, the resulting BACKONE equations are tested in the correlative and predictive mode according to nine nonpolar and polar substances: methane, oxygen, ethane, argon, nitrogen, ethylene, carbon dioxide, R22, and R152a. According to our previously introduced notation (Saager and Fischer, 1994), the correlative mode means that the parameters of the equation of state are fitted to a large set of experimental data with the aim of reproducing these and all other data as accurately as possible. The use of physically based equations of state in the correlative mode is not a goal by itself; the quality of reproduction, however, indicates whether the equations are sound. The real power of the BACKONE equations is expected to be in the predictive mode. Here, the three or four substance-specific parameters are fitted to only two experimental vapor pressures and two saturated liquid densities. The thereupon based predictions for the full saturation curve, for pvT-data, isochoric heat capacities, and second virial coefficients, are compared with experimental data.

While the present article deals only with pure fluids, an extension and application of the BACKONE equations to mixtures will be given in a subsequent article.

Construction of the New Attractive Dispersion Force Contribution F_A

For nonpolar molecules the Helmholtz energy F will be composed of a hard-body contribution F_H and the attractive dispersion force contribution F_A,

$$F=F_H+F_A. \tag{1}$$

Following Boublik (1975) and Boublik and Nezbeda (1986), we write the hard-body contribution F_H as

$$F_H/RT=(\alpha^2-1)\ln(1-\xi)+[(\alpha^2+3\alpha)\xi-3\alpha\xi^2]/(1-\xi)^2. \tag{5}$$

The anisotropy parameter α is specific for a given substance and considered to be independent of the state conditions. The volume of the hard bodies is assumed to be temperature-dependent according to a modification (Smith, 1973) of Barker and Henderson (1967) theory called BH1 or hBH. On this basis, a closed expression for the packing fraction ξ was derived (Saager et al., 1992), which is also used here

$$\xi=0.1617(\rho/\rho_0)[a+(1-\alpha)(T/T_0)^{\gamma}]^{-1}, \tag{6}$$

with $a=0.689$ and $\gamma=0.3674$. Here, ρ_0 denotes a characteristic density and T_0 a characteristic temperature that are intended to be the critical quantities for nonpolar substances. Hence, the hard-body contribution to the Helmholtz energy F_H is a function of the density ρ and the temperature T and of the three substance-specific parameters ρ_0, T_0, and α in the form

$$F_H=F_H(\rho/\rho_0,T/T_0,\alpha). \tag{7}$$

We want to construct the attractive contribution F_A as a function of the same three parameters. Hence, we make the ansatz

$$F_A=F_A(\rho/\rho_0,T/T_0,\alpha). \tag{8}$$

Table 1. Parameters ρ_0, T_0, and α Required for the Hard-Body Helmholtz Energy F_H of Methane, Oxygen, and Ethane According to Eqs. 5 and 6

	ρ_0 mol/dm^3	T_0 K	α
Methane	10.139	190.564	1.0000
Oxygen	13.630	154.581	1.0244
Ethane	6.800	305.330	1.2126

The functional form of F_A will be found by a simultaneous fit to the experimental data of methane, oxygen, and ethane. In the first step, this requires subtraction of the hard-body thermodynamic properties from the experimental data, and as a consequence the specification of the parameters ρ_0, T_0, and α for these three substances. The quantities ρ_0 and T_0 are simply taken to be the critical density and temperature. We take the value of the parameter α at the critical point using perturbation theory results. For ethane, the calculation of α is described in detail in a previous paper (Saager et al., 1992), yielding $\alpha = 1.2126$. In the case of methane, it was shown that the spherical Lennard-Jones potential is a good to excellent model potential (Saager and Fischer, 1990, 1991b), and hence $\alpha = 1.0000$ for that substance. Oxygen can be modeled by a two-center Lennard-Jones potential with elongation $L = 0.22$ (Saager and Fischer, 1991a), and using previous perturbation theory results (Bohn et al., 1986a,b; Fischer et al., 1984), one obtains $\alpha = 1.0244$. Table 1 summarizes the three parameters ρ_0, T_0, and α for the substances methane, oxygen, and ethane.

As experimental input data of methane, oxygen, and ethane, we used available data compilations. For methane we used the data of Setzmann and Wagner (1991), for oxygen the data of Schmidt and Wagner (1985), and for ethane we took Goodwin et al.'s (1976) compilation used previously (Saager et al., 1992). In the subsequent optimization procedure we referred to the uncertainties given in the original sources.

For the construction of F_A from the available data we used only the pvT data, the phase equilibrium or Maxwell data, the enthalpies of vaporization, the isochoric heat capacities, and the second virial coefficients. This selection was made for the sake of simplicity in the application of the optimization procedure.

Having specified the experimental data as well as the hard-body contribution F_H for methane, oxygen, and ethane, we look for a function F_A in the form

$$F_A/RT = \sum_{i=1}^{28} c_i (T/T_0)^{n_i/2} (\rho/\rho_0)^{m_i} \alpha^{j_i} \exp\left[-(\rho/\rho_0)^{l_i}\right], \quad (9)$$

with coefficients c_i, half-integer exponents $n_i/2$, and integer exponents m_i, j_i, and l_i. The search for relevant terms was performed by the optimizing procedure of Setzmann and Wagner (1989) after having prescribed a suitable "bank of terms." The resulting coefficients and exponents for the optimized expression of F_A/RT are given in Table 2.

Table 2. Coefficients and Exponents for the Attractive Dispersion Force Contribution F_A/RT $(T/T_0,\ \rho/\rho_0,\ \alpha)$, Eq. 9

i	c_i	n_i	m_i	j_i	l_i
1	0.75134293525E−02	−5	1	1	0
2	0.16605902280E+00	−4	2	−4	0
3	−0.17669033205E+00	−4	2	−3	0
4	0.14199996651E−02	−3	4	4	0
5	0.44333059390E−06	−3	10	−1	0
6	−0.15731874520E+01	−2	1	0	0
7	−0.62556385182E−01	−2	2	4	0
8	−0.73141715005E−01	−2	3	−3	0
9	0.16582913621E−01	−2	4	−4	0
10	0.13920791757E+00	−1	1	−2	0
11	0.19260424146E+01	−1	2	−1	0
12	−0.16491266440E+02	−1	2	1	0
13	0.30473509420E+02	−1	2	2	0
14	−0.21129652724E+02	−1	2	3	0
15	0.51677847972E+01	−1	2	4	0
16	−0.17884035610E−04	−1	8	4	0
17	−0.35690255303E−01	0	2	−4	0
18	0.43167070851E−01	0	3	−2	0
19	−0.40116173206E−02	1	4	−4	0
20	−0.29208867194E+00	−4	1	0	1
21	−0.41274021904E+00	−14	2	−3	2
22	0.40093366775E+00	−14	2	−2	2
23	−0.96431590546E−01	−12	2	4	2
24	0.21941739780E−01	−10	5	−1	2
25	−0.43064150362E−01	−8	1	4	2
26	0.71945839092E−01	−6	2	4	2
27	0.24387090115E−02	−4	8	4	2
28	−0.46464433632E−01	−2	1	1	2

Since up to now our knowledge about F_A was still limited, a closer inspection of the present results seems to be rewarding. We remind the reader that in the original van der Waals equation F_A was assumed to be linear in the density. Without further justification, the same assumption'was also made in the NIK equation (Nguyen et al., 1993). In order to check this assumption, it is useful to define the quantity $\tilde{F}_A = (\rho/\rho_0)(F_A/RT_0)$, which in the case of linear density dependence should be a constant as a function of the density. The values for $\tilde{F}_A$ can be calculated from Eq. 9, and are shown in Figures 1 and 2 for several reduced temperatures T/T_0 as a function of the reduced density ρ/ρ_0 for two different values of the anisotropy parameter α, namely $\alpha = 1.0$ and $\alpha = 1.2$. We learn from Figures 1 and 2 that in general $\tilde{F}_A$ is not constant with the density. At high densities $\tilde{F}_A$ yields roughly a straight line with a negative slope that increases with increasing molecular anisotropy.

Correlative Applications

After the construction of the new attractive dispersion force contribution, Eq. 9, the equations of the BACKONE family are fully defined. Recall that the hard-body term is given by Eqs. 5 and 6. For nonpolar substances, the resulting equation is Eq. 1 ($F = F_H + F_A$), which we call the SIMBACKONE equation. This equation has only three substance-specific parameters, namely, T_0, ρ_0, and α. For quadrupolar fluids, the quadrupolar contribution to the Helmholtz energy F_Q has to be added, resulting in Eq. 2 ($F = F_H + F_A + F_Q$), which we call the QUABACKONE equation. The term F_Q was derived previously (Saager and Fischer, 1992) as

$$\frac{F_Q}{RT} = \sum_{i=1}^{17} c_i \left(\frac{T}{T_p}\right)^{n_i/2} \left(\frac{\rho}{\rho_0}\right)^{m_i/2} (Q^{*2})^{k_i/4} \exp\left[-o_i\left(\frac{\rho}{\rho_0}\right)^2\right]. \quad (10)$$

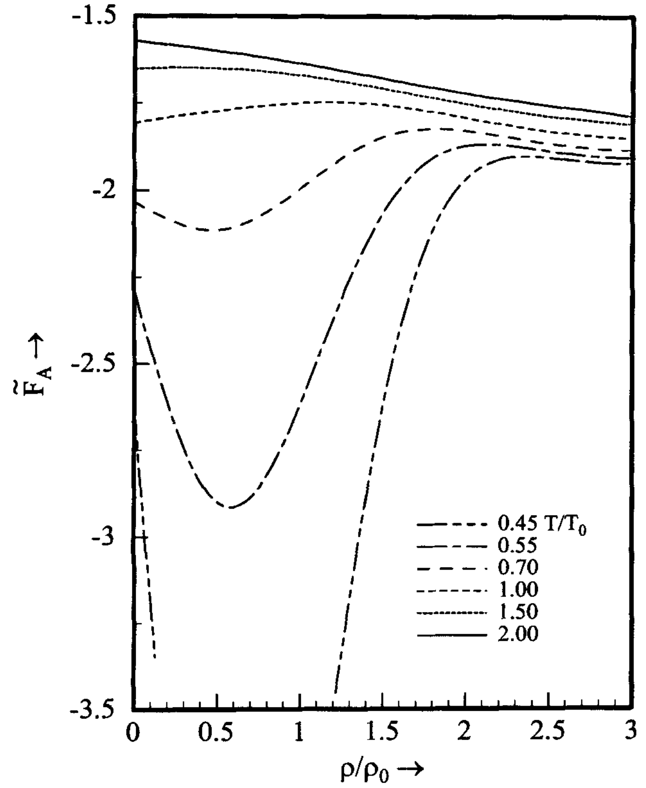

Figure 1. Reduced attractive dispersion force contribution $\tilde{F}_A = (\rho_0/\rho)/(F_A/RT_0)$ from Eq. 9 for the anisotropy parameter $\alpha = 1.0$.

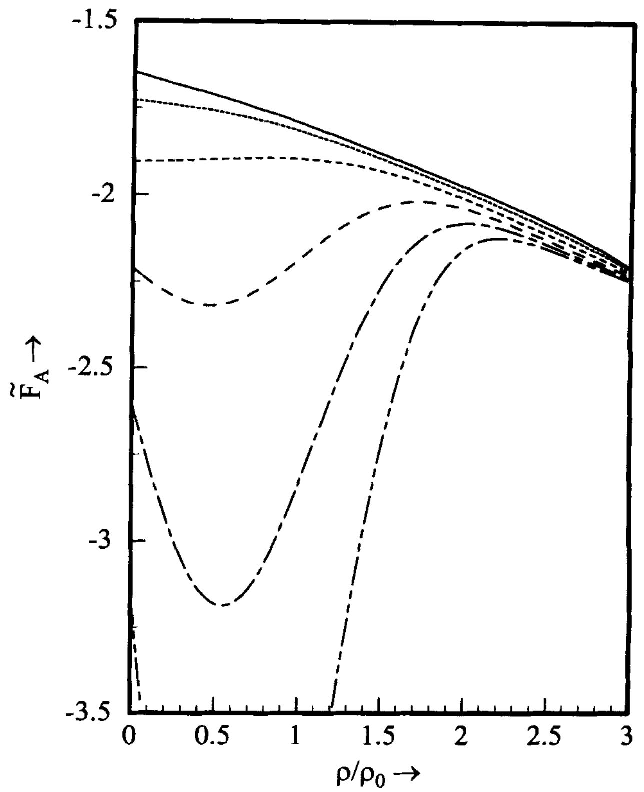

Figure 2. Reduced attractive dispersion force contribution $\tilde{F}_A = (\rho_0/\rho)/(F_A/RT_0)$ from Eq. 9 for the anisotropy parameter $\alpha = 1.2$.

The coefficients c_i and the exponents n_i, m_i, k_i, and o_i are given in Table 3. The quantity T_p is the pseudocritical temperature (Fischer et al., 1992) which according to recent results (Lotfi et al., 1992) is related to T_0 by $T_p = 1.13\ T_0$. The quantity Q^{*2} is a reduced quadrupole moment and the fourth substance-specific parameter in the QUABACKONE equation. For dipolar fluids, the procedure is similar to that for quadrupolar fluids. The dipolar contribution to the Helmholtz energy F_D has to be added, and the resulting equation is Eq. 3 ($F = F_H + F_A + F_D$), which is called DIBACKONE equation. As before, the term F_D was derived previously (Saager and Fischer, 1992b) as

$$\frac{F_D}{RT} = \sum_{i=1}^{28} c_i \left(\frac{T}{T_p}\right)^{n_i/2} \left(\frac{\rho}{\rho_0}\right)^{m_i/2} (\mu^{*2})^{k_i/4} \exp\left[-o_i\left(\frac{\rho}{\rho_0}\right)^2\right], \tag{11}$$

with the coefficients c_i and the exponents n_i, m_i, k_i, and o_i given in Table 4. Again, $T_p = 1.13\ T_0$, and the quantity μ^{*2} is a reduced dipole moment and the fourth substance-specific fit parameter in the DIBACKONE equation. It should be mentioned that for a given substance, either F_Q or F_D will be added according to the dominant multipole moment; the equations cannot yet account for cross combinations.

In the application of the BACKONE equation, the parameters ρ_0, T_0, α, and if necessary either Q^{*2} or μ^{*2} have to be fitted to the experimental data. In the correlative mode we use large data sets for the determination of the parameters. Out of several thermophysical properties we have decided to use only pvT and phase equilibrium data. In the fitting procedure, the vapor pressures, and the bubble and dew densities were calculated for each trial set of parameters at the temperature of the experimental data; hence, for each

Table 3. Coefficients and Exponents for the Quapolar Contribution to the Helmholtz Energy F_Q/RT $(T/T_p,\ \rho/\rho_0,\ Q^{*2})$, Eq. 10

i	c_i	n_i	m_i	k_i	o_i
1	−0.412154280896E−02	−8	2	11	1
2	0.355780441736E−02	−6	2	12	1
3	−0.888093798389E−03	−4	2	13	1
4	0.973791559609E−04	−10	2	16	1
5	−0.604233719326E−07	−20	2	19	1
6	−0.304478633146E−04	−8	2	20	1
7	−0.378930196337E−03	−3	8	7	0
8	−0.275388267352E−01	−3	2	8	0
9	0.118301888420E−01	−2	2	8	0
10	−0.283451230562E−02	0	2	8	0
11	−0.567703874828E−04	−5	8	8	0
12	0.314708573212E−02	−1	2	9	0
13	0.963786052569E−03	−3	5	10	0
14	−0.127591002424E−02	−1	5	10	0
15	0.363746463238E−03	0	5	10	0
16	0.301067943096E−04	0	8	10	0
17	0.291778231128E−06	−10	7	18	0

Table 4. Coefficients and Exponents for the Dipolar Contribution to the Helmholtz Energy F_D/RT $(T/T_p,\ \rho/\rho_0,\ \mu^{*2})$, Eq. 11

i	c_i	n_i	m_i	k_i	o_i
1	−0.423652173318E−01	−5	2	5	1
2	0.204459397242E−01	−8	2	6	1
3	0.664266837321E−01	−4	2	7	1
4	−0.324168341478E−01	−3	2	7	1
5	−0.741263275720E−02	−10	2	9	1
6	−0.160855507113E−01	−7	2	9	1
7	0.435623305093E−02	−10	2	11	1
8	−0.105933370736E−03	−11	2	15	1
9	−0.132000046519E−05	−15	2	18	1
10	0.838157718194E−05	−10	3	18	1
11	0.109144074057E−01	−2	2	5	0
12	0.257960188278E−01	−2	3	5	0
13	−0.544140085185E−03	−1	6	5	0
14	0.349568484468E−02	−5	2	6	0
15	−0.421407562467E−01	−3	3	6	0
16	−0.745992658113E−02	−1	3	6	0
17	0.146102252152E−03	1	6	6	0
18	0.566611094911E−03	−9	2	7	0
19	−0.378643890614E−02	−7	2	7	0
20	−0.365824539450E−01	−2	2	7	0
21	0.169287932475E−01	−1	2	7	0
22	0.663866480778E−02	−5	3	7	0
23	0.294409406715E−01	−2	3	7	0
24	−0.112110434947E−01	−1	3	7	0
25	−0.182144939032E−05	−8	10	7	0
26	0.758594753989E−07	−5	16	7	0
27	−0.216942306418E−04	1	4	8	0
28	−0.274025042954E−05	−4	9	10	0

Table 5. Assigned Uncertainties of the Pseudoexperimental pvT and Vapor-Liquid Phase Equilibrium Data

pvT data	$\Delta p/p$	0.1%
	$\Delta \rho/\rho$	0.2%
	$\Delta T/T$	0.005%
Phase equilibrium data	$\Delta p_s/p_s$	0.05%
	$\Delta \rho'/\rho'$	0.05%
	$\Delta \rho''/\rho''$	0.15%

For argon, nitrogen, ethylene, and carbon dioxide, pseudoexperimental data were created from the thermophysical calculation package of Jacobsen et al. (1992).

experimental phase equilibrium point the deviation of the corresponding calculated point should be assessed individually. The final parameters were selected as those that minimize the standard deviations with respect to all pvT data and to all phase equilibrium data simultaneously.

The quality of the equations in the correlative and in the predictive mode is tested using nine substances as examples: the nonpolar fluids methane, oxygen, ethane, and argon; the quadrupolar fluids nitrogen, ethylene, and carbon dioxide; and the dipolar refrigerants R22 and R152a. For methane we used the experimental data set of Setzmann and Wagner (1991); for oxygen the file of Schmidt and Wagner (1985); for ethane the compilation of Goodwin et al. (1976); for R22 the experimental data of Kohlen (1987) and Marx (1989); and for R152a, the set of Saager and Fischer (1994). For the calculation of the relative standard deviations in the fitting proce-

Table 6. Equation Parameters and Results for $\mathrm{STA}_{\mathrm{pvT}}$ According to Eq. 12 for the Correlative Mode*

Substance	Equation	α	T_0	ρ_0/v_{00}	η	μ^{*2}	Q^{*2}	$\mathrm{STA}_{\mathrm{pvT}}$
Methane	BACK†	1.0	190.29	21.576	1.0	—	—	60.3
	MOBACK	1.193	194.81	9.946	−8.110	—	—	44.0
	SIMBACK1	1.0	190.57	10.139	—	—	—	3.48
Oxygen	BACK	1.014	154.75	15.919	1.543	—	—	29.6
	MOBACK	1.205	162.12	13.607	−8.858	—	—	10.1
	SIMBACK1	1.0244	154.58	13.629	—	—	—	2.56
Ethane	BACK†	1.037	298.03	31.118	19.0	—	—	79.5
	MOBACK	1.2126	305.33	6.800	0.0	—	—	0.71
	SIMBACK1	1.2127	305.32	6.800	—	—	—	1.24
Argon	BACK†	1.0	150.86	16.290	0.0	—	—	3.31
	MOBACK	1.1951	155.16	13.229	−7.783	—	—	16.4
	SIMBACK1	0.9876	150.16	13.487	—	—	—	2.53
Nitrogen	BACK	1.0124	124.93	19.337	2.668	—	—	5.23
	MOBACK	1.1945	126.62	10.993	−3.307	—	—	14.8
	QUABACK1	1.0471	125.74	11.133	—	—	0.489	2.75
Ethylene	BACK†	1.0330	279.55	28.031	12.0	—	—	6.06
	MOBACK	1.2066	280.10	7.569	0.045	—	—	6.76
	QUABACK1	1.1716	281.78	7.577	—	—	0.522	3.32
Carbon dioxide	BACK†	1.0571	284.28	19.703	40.0	—	—	11.85
	QUABACK	1.3024	291.57	10.666	−8.635	—	3.539	4.12
	QUABACK1	1.3919	291.28	10.549	—	—	2.181	5.78
R22	BACK‡	1.055	339.40	35.199	55.960	—	—	8.70
	DIBACK‡	1.244	337.22	6.110	15.695	4.054	—	1.96
	DIBACK1	1.3813	331.83	6.120	—	5.316	—	3.70
R152a	BACK‡	1.102	378.81	36.531	51.360	—	—	24.6
	DIBACK‡	1.2633	337.94	5.808	18.184	6.150	—	6.47
	DIBACK1	1.409	342.80	5.787	—	6.494	—	4.56

*T_0 is in K and ρ_0 is in mol/dm^3, and for the BACK EOS v_{00} is in cm^3/mol.

†Parameters from Chen and Kreglewski, (1977); or Kreglewski, (1984).

‡Parameters from Saager and Fischer (1994).

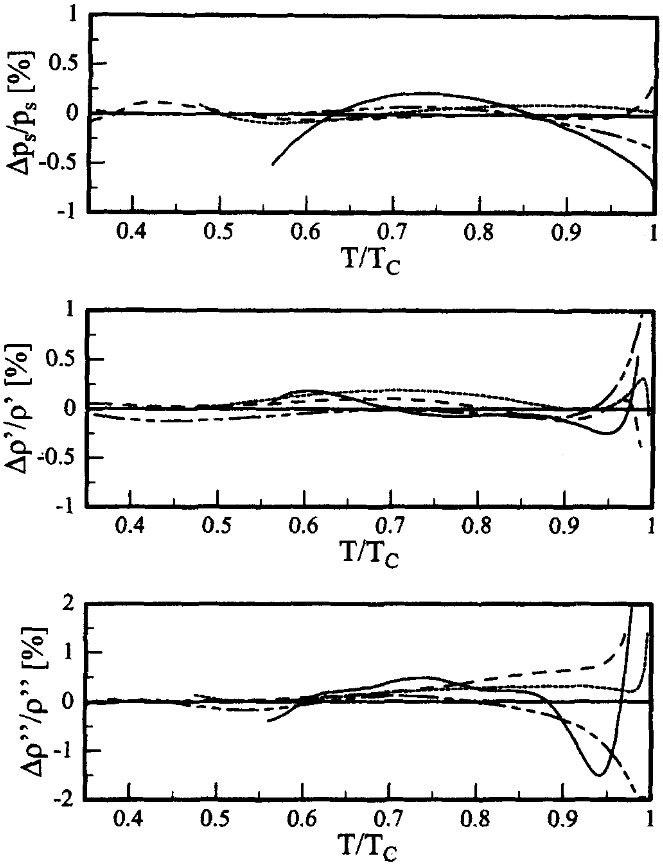

Figure 3. Deviation of vapor pressures, bubble, and dew densities for nonpolar substances argon (——), methane (· · · ·), oxygen (–· · ·–· · ·–), and ethane (– – –) obtained from the SIMBACKONE equation in the correlative mode vs. correlations of experimental data (Jacobsen et al., 1992).

$\Delta p_s/p_s = (p_{s,\mathrm{exp}} - p_{s,\mathrm{EOS}})/p_{s,\mathrm{exp}}$, $\Delta\rho'/\rho' = (\rho'_{\mathrm{exp}} - \rho'_{\mathrm{EOS}})/\rho'_{\mathrm{exp}}$ and $\Delta\rho''/\rho'' = (\rho''_{\mathrm{exp}} - \rho''_{\mathrm{EOS}})/\rho''_{\mathrm{exp}}$.

dure, the experimental uncertainties were taken for these fluids. For the other four substances, the experimental data together with their experimental uncertainties were not easily accessible to us. Hence, we created pseudoexperimental pvT and vapor-liquid equilibrium data for these fluids from the highly accurate equations of state contained in the thermophysical calculation package of Jacobsen et al. (1992). In order to calculate the standard deviations of these pseudoexperimental data in the fits, we assigned some uncertainties to them. These are given in Table 5.

Table 6 contains the parameters for the BACKONE equations obtained in the correlative mode, together with parameters for the BACK equation and for equations of the MOBACK family, for all substances under consideration. This table also contains the resulting relative standard deviations STA$_{\mathrm{pvT}}$ based on the equation

$$\mathrm{STA}_{\mathrm{pvT}} = \left(\frac{1}{N} \sum_{i}^{N} \frac{(p_{i,\mathrm{exp}} - p_{i,\mathrm{EOS}})^2}{\Delta p_{i,\mathrm{exp}}^2} \right)^{1/2}, \qquad (12)$$

where $p_{i,\mathrm{exp}}$ denotes the experimental value of the pressure, $\Delta p_{i,\mathrm{exp}}$ its experimental error, and $p_{i,\mathrm{EOS}}$ represents the value obtained from the equations of state. Further, we show the percentage of deviations of the BACKONE vapor pressures, bubble, and dew densities from direct correlations of the experimental data in Figures 3 to 5.

Let us first discuss the results from SIMBACKONE for the four nonpolar fluids. We learn from Figure 3 that the deviations calculated from the experimental phase equilibrium are mostly below 0.25%, with the exception of the near critical region, which we consider an excellent performance. The STA$_{\mathrm{pvT}}$ results in Table 6 obtained from the correlative application show that we succeeded in constructing F_A. A considerable improvement in the description of fluids from spherical to dumbbell shape was achieved. Hence, the SIMBACKONE equation of state no longer has the disadvantage of the BACK and MOBACK equations, which were not able to give reasonable results for fluids with molecular shapes other than the one used for the construction of F_A. This is a

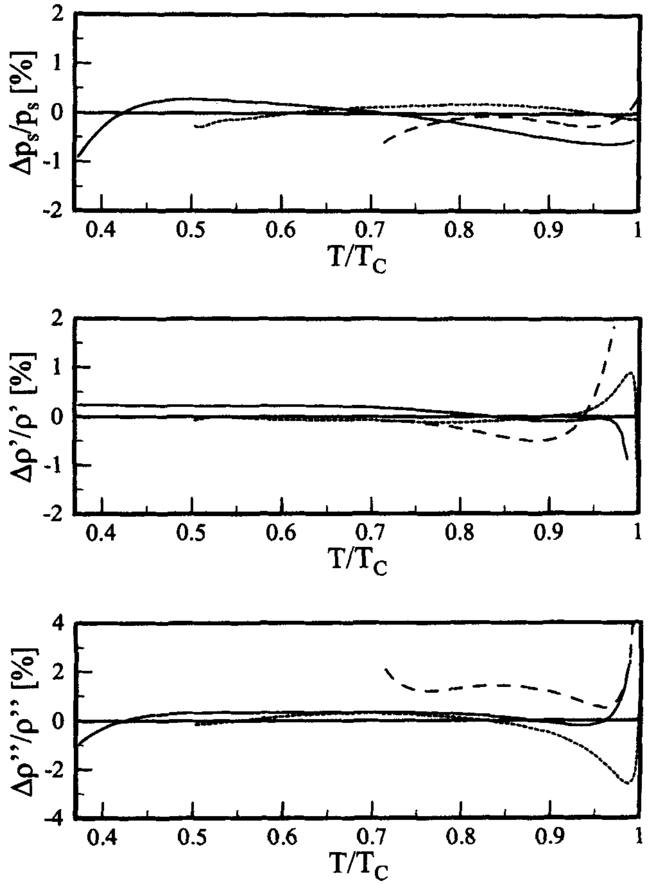

Figure 4. Deviation of vapor pressures, bubble, and dew densities for quadrupolar substances ethylene (——), nitrogen (· · · ·), and carbon dioxide (– – –) obtained from the QUABACKONE equation in the correlative mode vs. correlations of experimental data (Jacobsen et al., 1992).

$\Delta p_s/p_s = (p_{s,\mathrm{exp}} - p_{s,\mathrm{EOS}})/p_{s,\mathrm{exp}}$, $\Delta\rho'/\rho' = (\Delta\rho'_{\mathrm{exp}} - \rho'_{\mathrm{EOS}})/\rho'_{\mathrm{exp}}$ and $\Delta\rho''/\rho'' = (\rho''_{\mathrm{exp}} - \rho''_{\mathrm{EOS}})/\rho''_{\mathrm{exp}}$.

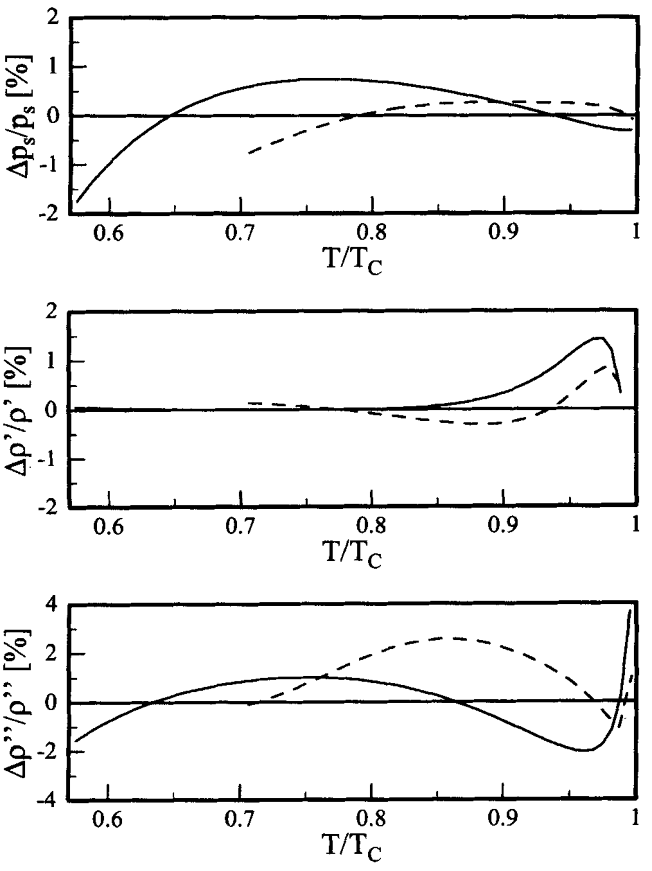

Figure 5. Deviation of vapor pressures, bubble, and the dew densities for dipolar substances R22 (——) and R152a (- - -) obtained from the DIBACKONE equation in the correlative mode vs. correlations of experimental data (Kohlen, 1987; Marx, 1989).

$\Delta p_s/p_s = (p_{s,\text{exp}} - p_{s,\text{EOS}})/p_{s,\text{exp}}$, $\Delta\rho'/\rho' = (\rho'_{\text{exp}} - \rho'_{\text{EOS}})/\rho'_{\text{exp}}$ and $\Delta\rho''/\rho'' = (\rho''_{\text{exp}} - \rho''_{\text{EOS}})/\rho''_{\text{exp}}$.

prerequisite for a proper description of mixtures and the development and testing of mixing rules.

The quadrupolar fluids nitrogen, ethylene, and carbon dioxide are described with the QUABACKONE equation. The phase equilibrium data shown in Figure 4 behave in general quite well. In contrast to nitrogen, for ethylene at lower temperatures we observe a larger deviation for the calculated vapor pressures and the dew densities. This performance can be attributed to the validity range of the quadrupolar contribution to the Helmholtz energy F_Q, which is limited to temperatures higher than 0.5 T_0. The triple point of ethylene, however, is $T_{Tr} = 0.37\ T_0$, and thus outside the range of validity of F_Q. The results for carbon dioxide show that the dew density calculated with the QUABACKONE equation of state is always roughly 1.3% too low in comparison with the experimental values. This effect was also observed in the application of the QUABACK equation and molecular dynamic simulations (Möller, 1991), and may be due to some vibrational effects. The STA_{pvT} results in Table 6 show that a considerable improvement was achieved in the description of quadrupolar fluids with the QUABACKONE equation when compared with the BACK and the MOBACK equations.

The last group of fluids are the dipolar refrigerants R22 and R152a. From Figure 5 we learn that a proper description of the bubble densities with deviations below 0.25%, except near the critical region, was achieved for both substances. The vapor pressures show deviations on the order of 1%, while the dew densities deviate by 2% from correlations of experimental values. With respect to the relative standard deviations STA_{pvT}, given in Table 6, the DIBACKONE equation yields a very large improvement over the BACK equation. In comparison with the previous DIBACK equation, the results are worse for R22 and better for R152a. We should, however, keep in mind that the DIBACKONE equation needs only four substance-specific parameters, as opposed to the DIBACK equation, which has five substance-specific parameters.

Predictive Applications

The real power of physically based equations of state is expected in the predictive mode. In that case the few substance-specific parameters are fitted to only a few of the experimental data, with the aim of predicting all thermodynamic quantities. As the equations of the BACKONE family have either three or, in the case of polar substances, four parameters, we fitted these parameters only to the vapor pressures and the bubble densities at two temperatures. The resulting parameters for all substances considered in this article are given in Table 7.

Table 7. Parameters and Results for STA_{pvT} for the Predictive Application of the BACKONE Family of Equations of State*

Equation	Substance	α	T_0	ρ_0	μ^{*2}	Q^{*2}	STA_{pvT}
SIMBACK1	Methane	1.0	190.57	10.139	—	—	3.48
	Oxygen	1.0244	154.58	13.629	—	—	2.56
	Ethane	1.2127	305.32	6.800	—	—	1.24
	Argon	0.9879	150.16	13.491	—	—	2.56
QUABACK1	Nitrogen	1.0403	125.19	11.112	—	0.707	2.96
	Ethylene	1.1259	290.98	7.560	—	0.913	2.36
	Carbon dioxide	1.3915	291.29	10.533	—	2.182	5.76
DIBACK1	R22	1.3722	326.12	6.126	5.778	—	4.65
	R152a	1.4035	336.02	5.791	7.028	—	5.09

*T_0 is in K and ρ_0 is in mol/dm^3.

Table 8. pvT Data of Argon from SIMBACKONE in the Predictive Mode in Comparison with Experimental Results*

T K	ρ mol/dm^3	p_{exp} MPa	p_{EOS} MPa	$\Delta p/p_{\text{exp}}$ %
90.0	34.57845	0.97800	0.97954	0.00
100.0	32.95184	0.97281	0.83211	0.05
150.7	0.862967	1.00335	1.00343	−0.01
200.0	0.619363	1.00004	1.00005	0.00
340.0	0.354859	1.00036	1.00060	−0.02
90.0	35.35822	11.98851	11.58023	0.08
100.0	33.94413	12.02845	11.55126	0.11
150.7	24.79706	12.02723	11.76402	0.40
200.0	10.73268	12.03119	12.08785	0.59
340.0	4.328452	12.03170	12.04310	−0.09

*From Gilgen (1994).

Table 9. Isochoric Heat Capacities of Argon from SIMBACKONE in the Predictive Mode in Comparison with Experimental Results*

T K	ρ mol/dm^3	$(C_v/R)^{\text{exp}}$	$(C_v/R)^{\text{EOS}}$	$\Delta C_v/C_v^{\text{exp}}$ %
88.468	34.88	2.57	2.50	−2.56
92.419	34.86	2.57	2.47	−3.92
100.667	32.89	2.41	2.37	−1.77
103.376	32.89	2.44	2.35	−3.65
116.759	29.95	2.24	2.25	0.68
120.681	29.94	2.24	2.22	−0.91
124.929	28.17	2.19	2.22	1.33
134.588	28.15	2.18	2.15	−1.27
134.303	25.87	2.18	2.22	2.07
144.583	25.85	2.14	2.12	−1.02
141.171	23.41	2.27	2.30	0.95
150.464	23.40	2.14	2.16	0.59
149.251	18.47	2.79	2.61	−6.56

*From Gladun (1971).

Using the parameters of Table 7, we predicted pvT data and compared them with experimental results. The relative standard deviations of the predicted pvT data are also presented in Table 7. We observe that for all substances the standard deviations in the predictive mode are of about the same magnitude as in the correlative mode (cf. Table 6).

Table 10. Second Virial Coefficients of Argon from SIMBACKONE in the Predictive Mode in Comparison with Experimental Results*

T K	B_{exp} cm^3/mol	B_{EOS} cm^3/mol	$\Delta B/B_{\text{exp}}$ %
80.0	−288.0	−271.37	−5.77
88.0	−238.7	−227.40	−4.73
96.0	−202.0	−194.13	−3.90
112.0	−151.3	−147.19	−2.72
132.0	−111.4	−109.40	−1.80
164.0	−73.5	−72.59	−1.24
200.0	−48.7	−47.92	−1.59
300.0	−15.7	−14.52	−7.49
500.0	6.9	8.31	20.41
1,000.0	21.1	21.77	3.17

*From Levelt-Sengers et al. (1972).

Table 11. pvT Data of Ethylene from QUABACKONE in the Predictive Mode in Comparison with Experimental Results*

T K	ρ mol/dm^3	p_{exp} MPa	p_{EOS} MPa	$\Delta p/p_{\text{exp}}$ %
160.0	21.670	36.288	37.716	−0.15
160.0	21.330	21.988	23.282	−0.15
160.0	21.025	10.403	11.748	−0.18
160.0	20.894	5.665	7.182	−0.22
252.0	17.690	31.178	32.368	−0.36
252.0	16.962	19.785	20.498	−0.30
252.0	15.874	8.383	8.556	−0.13
252.0	15.319	4.661	4.625	0.04
320.0	14.373	29.784	30.307	−0.41
320.0	14.017	26.879	27.313	−0.40
320.0	13.721	24.781	25.119	−0.36
320.0	12.919	20.133	20.327	−0.30

*From Straty (1980).

For a more detailed study of the predictive mode we selected one representative substance from each substance class: argon as the nonpolar substance described by SIMBACKONE, ethylene as the quadrupolar substance described by QUABACKONE, and R152a as the dipolar substance described by DIBACKONE. Comparisons of predicted with experimental data for each of these substances are shown for pvT data, for heat capacities, and for second virial coefficients in Tables 8–17 , and in Figures 6–8 for the phase equilibrium data. The figures also contain results from previous equations in the correlative mode. The results for argon are contained in Tables 8–10 and Figure 6; the results for ethylene in Tables 11–14 and Figure 7; and, finally, the results for R152a are contained in Tables 15–17 and Figure 8.

We noted earlier that the relative standard deviations of the pvT data in the predictive mode are of the same order of magnitude as in the correlative mode when the BACKONE

Table 12. Isochoric Heat Capacities of Ethylene from QUABACKONE in the Predictive Mode in Comparison with Experimental Results*

T K	ρ mol/dm^3	$(C_v/R)^{\text{exp}}$	$(C_v/R)^{\text{EOS}}$	$\Delta C_v/C_v^{\text{exp}}$ %
246.358	15.67	4.57	4.43	−2.87
271.568	15.61	4.72	4.60	−2.55
283.777	15.58	4.81	4.71	−2.28
291.005	15.57	4.89	4.77	−2.40
144.122	21.60	4.94	4.91	−0.59
148.698	21.57	4.92	4.89	−0.54
153.288	21.54	4.90	4.87	−0.56
157.837	21.52	4.88	4.86	−0.46

*From Weber (1982).

Table 13. Heat Capacities on the Bubble Line of Ethylene from QUABACKONE in the Predictive Mode in Comparison with Experimental Results*

T K	$(C_\sigma/R)^{\text{exp}}$	$(C_\sigma/R)^{\text{EOS}}$	$\Delta C_\sigma/C_\sigma^{\text{exp}}$ %
139.876	8.09	8.24	1.86
159.356	8.09	8.16	0.84
195.662	8.37	8.38	0.04
228.558	9.22	9.19	−0.33
255.457	10.89	11.01	1.12
271.352	14.31	14.33	0.14
275.437	17.21	16.39	−4.81

*From Weber (1982).

Table 14. Second Virial Coefficients of Ethylene from QUABACKONE in the Predictive Mode in Comparison with Correlations of Experimental Results*

T K	B_{exp} cm^3/mol	B_{EOS} cm^3/mol	$\Delta B/B_{\mathrm{exp}}$ %
250.0	−200.5	−196.4	−2.04
300.0	−138.1	−136.5	−1.18
350.0	−98.4	−97.9	−0.49
400.0	−71.3	−71.1	−0.30
500.0	−51.8	−51.4	−0.82

*From Levelt-Sengers and Hastings (1982).

Table 15. pvT Data of R152a from DIBACKONE in the Predictive Mode in Comparison with Experimental Data

T K	ρ mol/dm^3	p_{exp} MPa	p_{EOS} MPa	$\Delta p/p_{\mathrm{exp}}$ %
197.97	17.00050	9.073†	10.0461	−0.11
205.06	16.98687	20.4710†	19.4762	0.10
212.95	16.97325	32.6940†	29.9143	0.28
217.89	16.96416	40.6630†	36.3421	0.43
223.75	16.95508	49.5580†	43.9928	0.54
261.140	15.02324	3.2381‡	3.5380	−0.07
267.531	15.01688	9.4451‡	9.4073	0.01
274.386	15.01022	16.0468‡	15.6847	0.07
281.409	15.00341	22.7517‡	22.0867	0.13
289.575	14.99553	30.4679‡	29.4886	0.18

†Geller et al. (1979).
‡Blanke and Weiss (1992).

Table 16. Isobaric Heat Capacities of R152a from DIBACKONE in the Predictive Mode in Comparison with Experimental Results*

T K	p MPa	$(C_p/R)^{\mathrm{exp}}$	$(C_p/R)^{\mathrm{EOS}}$	$\Delta C_p/C_p^{\mathrm{exp}}$ %
263.15	0.181	13.473†	13.755	2.10
	1.630	13.330†	13.628	2.23
	5.170	13.251†	13.586	2.53
273.15	0.264	13.672†	14.090	3.06
	1.190	13.680†	14.048	2.69
	5.748	13.402†	13.864	3.45
283.15	0.372	13.815†	14.442	4.54
	1.347	13.863†	14.385	3.76
	3.990	13.632†	14.254	4.50
	5.520	13.640†	14.174	3.92
293.15	0.513	14.085†	14.829	5.28
	2.220	13.998†	14.701	5.02
	4.100	13.934†	14.578	4.62
	6.210	13.950†	14.457	3.63
303.15	0.689	14.570†	15.269	4.80
	1.840	14.299†	15.151	5.96
	3.360	14.292†	15.013	5.04
	6.200	14.220†	14.797	4.05
330.85	5.0	15.435‡	16.202	4.97
381.15	5.0	25.017‡	26.166	4.59
390.35	5.0	72.911‡	82.960	13.78
403.91	5.0	24.961‡	26.606	6.59

*The ideal contribution to the isobaric heat capacities was taken from Beckermann and Kohler (1995).
†Gross et al. (1992).
‡Porichanskii et al. (1982).

Table 17. Second Virial Coefficients of R152a from SIMBACKONE in the Predictive Mode in Comparison with Experimental Results*

T K	B_{exp} cm^3/mol	B_{EOS} cm^3/mol	$\Delta B/B_{\mathrm{exp}}$ %
296.15	−534.0	−509.4	−4.61
273.15	−671.0	−626.5	−6.64
253.15	−844.0	−764.8	−9.39
233.15	−1109.0	−956.7	−13.74

*From Schramm et al. (1992).

equations are used. By comparing the phase equilibrium deviations calculated from the correlative and predictive mode that are presented for argon in Figures 6 and 3, for ethylene in Figures 7 and 4, and for R152a in Figures 8 and 5, we arrive at the same conclusions.

We come now to a closer inspection of the predictions of the BACKONE family of equations in comparison with the experimental data. Tables 6–15 and Figures 6–8 show that for argon, ethylene, and R152, as representatives of different classes of substances, the predictions of all types of thermodynamic data are good to excellent.

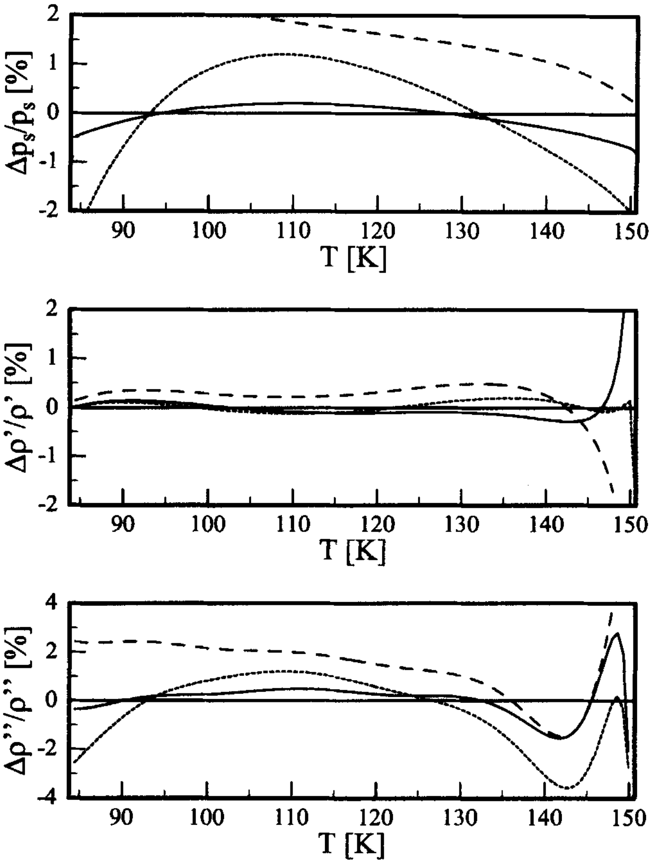

Figure 6. Deviation of vapor pressures, bubble, and dew densities for argon obtained from the SIMBACKONE equation in the predictive mode.

With parameters from Table 7 (——); same quantities are shown for the correlative application of the BACK (- - -) and MOBACK (····) equation with the parameters of Table 6.
$\Delta p_s/p_s = (p_{s,\mathrm{exp}} - p_{s,\mathrm{EOS}})/p_{s,\mathrm{exp}}$, $\Delta\rho'/\rho' = (\rho'_{\mathrm{exp}} - \rho'_{\mathrm{EOS}})/\rho'_{\mathrm{exp}}$ and $\Delta\rho''/\rho'' = (\rho''_{\mathrm{exp}} - \rho''_{\mathrm{EOS}})/\rho''_{\mathrm{exp}}$.

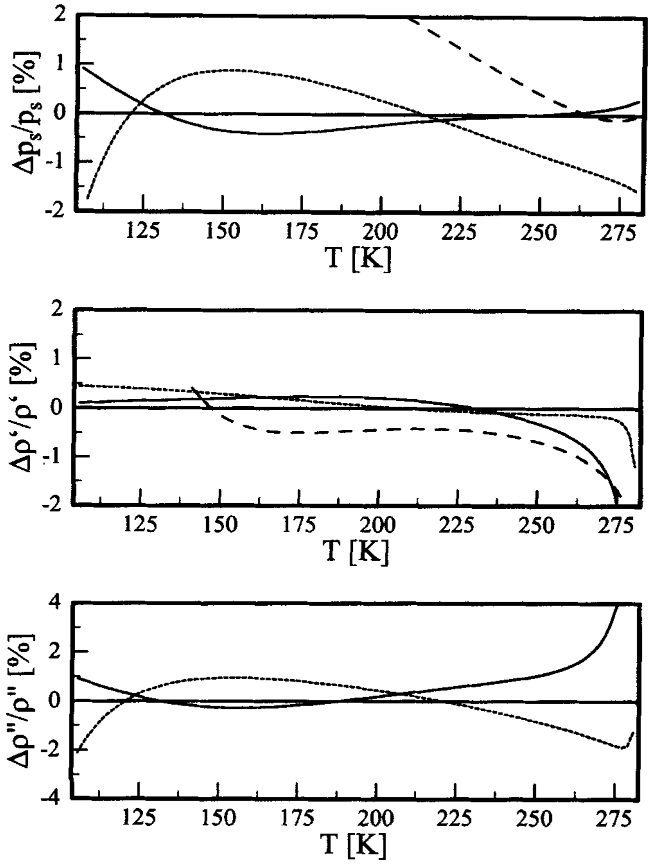

Figure 7. Deviation of vapor pressures, bubble, and dew densities for ethylene obtained from the QUABACKONE equation in the predictive mode.

With parameters from Table 7 (——); same quantities are shown for the correlative application of the BACK (– – –) and MOBACK (····) equation with the parameters of Table 6.

$\Delta p_s/p_s = (p_{s,\mathrm{exp}} - p_{s,\mathrm{EOS}})/p_{s,\mathrm{exp}}$, $\Delta \rho'/\rho' = (\rho'_{\mathrm{exp}} - \rho'_{\mathrm{EOS}})/\rho'_{\mathrm{exp}}$ and $\Delta \rho''/\rho'' = (\rho''_{\mathrm{exp}} - \rho''_{\mathrm{EOS}})/\rho''_{\mathrm{exp}}$.

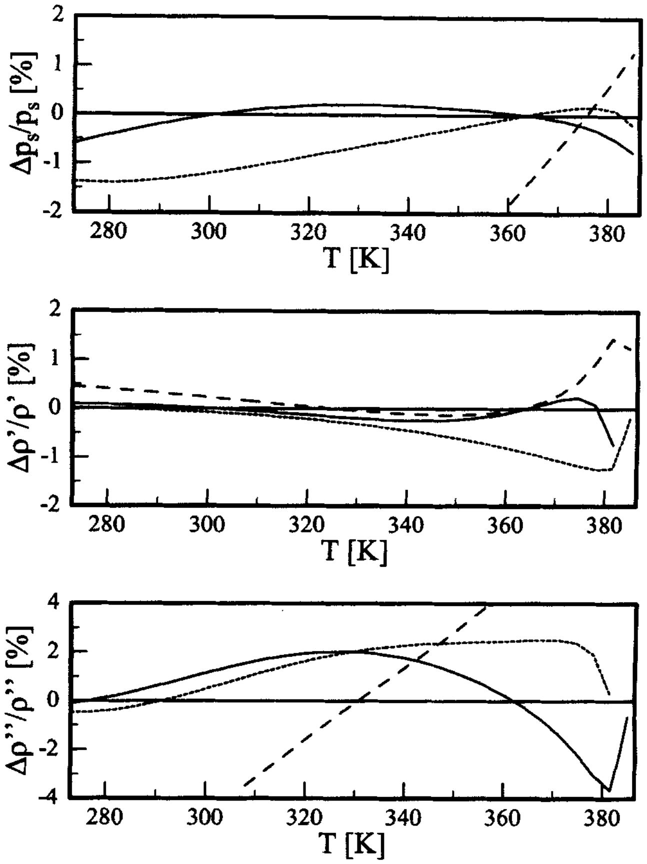

Figure 8. Deviation of vapor pressures, bubble, and dew densities for R152a obtained from the DIBACKONE equation in the predictive mode.

With parameters from Table 7 (——); same quantities are shown for the correlative application of the BACK (– – –) and DIBACK (····) equation with the parameters of Table 6.

$\Delta p_s/p_s = (p_{s,\mathrm{exp}} - p_{s,\mathrm{EOS}})/p_{s,\mathrm{exp}}$, $\Delta \rho'/\rho' = (\rho'_{\mathrm{exp}} - \rho'_{\mathrm{EOS}})/\rho'_{\mathrm{exp}}$ and $\Delta \rho''/\rho'' = (\rho''_{\mathrm{exp}} - \rho''_{\mathrm{EOS}})/\rho''_{\mathrm{exp}}$.

Finally, we compare the predictive power of the BACKONE equations with the correlative ability of previous equations, namely the original BACK equation as well as the MOBACK, QUABACK, and DIBACK equations. This is done by comparing Tables 4 and 5 and inspecting Figures 6–8. In comparison with the original BACK equation, the BACKONE equations are substantially improved. In comparison with the MOBACK, QUABACK, and DIBACK equations, the BACKONE equation results are remarkably improved for the nearly spherical molecules.

Summary

We have constructed a new attractive dispersion force contribution F_A to the Helmholtz energy that allows the description of spherical as well as of elongated molecules, with the same three parameters occurring in the hard-body term F_H. The resulting equations of state, the SIMBACKONE equation $F = F_H + F_A$, with three parameters for nonpolar substances, the QUABACKONE equation $F = F_H + F_A + F_Q$, with four parameters for quadrupolar substances, as well as the DIBACKONE equation $F = F_H + F_A + F_D$, with four parameters for dipolar substances, were applied to several substances in the correlative as well as in the predictive mode. Of special interest is the predictive mode, where fits of the three or four substance-specific parameters to only the vapor pressures and bubble densities of two temperatures resulted in good to excellent predictions of all thermodynamic properties in all different classes of substances. The equations of the BACKONE family together with appropriate mixing rules will be applied to mixtures in a forthcoming article.

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