Extension of a Generalized Quartic Equation of State to Pure Polar Fluids

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A generalized four-parameter quartic equation of state (EOS) proposed by Shah and coworkers (1992, 1994) was extended to polar fluids. To use the new generalized quartic EOS for polar fluids, only four characteristic properties of the pure compound are required—critical temperature, critical volume, acentric factor, and dipole moment. For nonpolar fluids, the previous equation is recovered and its superior performance for nonpolar fluids is retained. A new set of coefficients for polar fluids for the EOS was determined from multiproperty regressions using literature data for various physical and thermodynamic experimental properties of 30 pure compounds. These regressed coefficients, which are functions of the critical temperature, critical pressure, acentric factor, and the dipole moment of the fluid, were generalized. The accuracy of this equation of state is evaluated with the new set of regressed coefficients to predict thermodynamic properties of pure polar compounds, including vapor pressure, density, residual enthalpy, enthalpy of vaporization, and second virial coefficient. The capability and accuracy of this quartic equation of state are also compared with the well-known Peng-Robinson EOS.

Introduction

The contributions of EOSs have been beneficial to the chemical and petroleum industries, particularly in process design and simulation analysis. Improved EOSs are needed for wide use in the chemical industry for the description of thermodynamic properties and phase equilibria of fluids. Most EOSs are applicable to hydrocarbons and slightly polar compounds. These equations are broadly developed for the calculation of thermodynamic properties of nonpolar substances and their mixtures, but are not highly developed for polar fluids such as alcohols, ethers, esters, ketones, refrigerants, etc.

This work extends a reliable and generalized EOS developed for nonpolar fluids to polar fluids. Shah (1992) and Shah et al. (1994) have developed a generalized four-parameter quartic EOS for nonpolar fluids. The objective of this research was to obtain a new set of regressed coefficients for polar and nonpolar fluids using the generalized quartic EOS. The performance of the generalized quartic EOS in evaluating various physical and thermodynamic properties of polar fluids is demonstrated. A comparison is made between the generalized quartic EOS and the Peng-Robinson EOS for prediction of various thermodynamic properties.

Cubic EOSs have received much attention in the natural gas and chemical industries since the first practical equation of state was introduced by van der Waals (Rowlinson, 1988) in 1873. After the van der Waals equation was used for several decades, Redlich and Kwong (1949) modified the attractive pressure term of the van der Waals equation of state. The Redlich-Kwong EOS was widely popular and was used in the place of the van der Waals equation in industry. Soave (1972) and Peng and Robinson (1976) proposed EOSs that are able to more accurately predict the vapor pressure, liquid density, and equilibrium ratios than the Redlich-Kwong equation. However, these cubic equations are not accurate at high densities, predict a fixed value of the critical compressibility factor for all compounds, and have limited applicability to polar compounds.

Perturbed hard-sphere EOSs are a comparatively recent and highly promising development. Several EOSs based on perturbed hard-sphere EOSs have been proposed (Carnahan

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and Starling, 1969; Nakamura et al., 1976; Lin et al., 1983; Chung et al., 1984; Guo et al., 1985; Bryan and Prausnitz, 1987; Mulia and Yesavage, 1989). Shah (1992) and Shah et al. (1994) developed a four-parameter perturbed hard-sphere EOS which is a generalized quartic EOS, by combining a repulsive term, fitted to the molecular dynamics data of Alder and Wainwright (1960), with an empirical attractive term. One root of this equation has no physical significance, because it is always less than the close packed volume of the fluid (see Appendix B); the behavior of the remaining three roots is equivalent to that of the three roots of a cubic EOS. Thus, the resulting equation retains the advantages of the cubic EOS, existence of analytical solutions and unequivocal identification of roots. With its simplicity and accuracy, the resulting equation only requires three properties of nonpolar fluids: the critical temperature, the critical volume, and the acentric factor. Moreover, it marks a significant improvement over the Peng-Robinson EOS in the supercritical and condensed phase regions.

Generalized Quartic EOS

To aid understanding of the current work, a short summary of the earlier work of Shah et al. (1994) is presented. Most traditional cubic equations of state used the repulsive term in the van der Waals hard-sphere equation as their repulsion pressure term. However, Shah (1992) and Shah et al. (1994) adopted a mathematically simple repulsive term as the repulsive force of the hard spheres in the generalized quartic EOS. This term is a new fitting of computer simulation results for hard spheres (Alder and Wainwright, 1960), as given below:

$$P_{\text{rep}} = \frac{RT}{(V - k_0\beta)} + \frac{\beta k_1 RT}{(V - k_0\beta)^2} \tag{1}$$

where β is the hard-sphere molar volume and values of $k_0 = 1.2864$ and $k_1 = 2.8225$ were obtained by regression analysis.

The attractive pressure term used in earlier equations of state was not used in the quartic EOS. Instead, Shah approximated the attractive pressure term by taking the real fluid data for argon and hard-sphere compressibilities calculated from Eq. 1. This term is an empirical fitting that was obtained by plotting Z_{att} vs. the reduced density at different reduced temperatures. Z_{att} is defined as the difference between the experimental compressibility (Z_{exp}) and the hard-sphere contribution to the compressibility (Z_{hs}). Z_{hs} and Z_{att} are given by Eqs. 2 and 3:

$$Z_{hs} = \frac{V}{(V - k_0\beta)} + \frac{\beta k_1 V}{(V - k_0\beta)^2} = \frac{1}{(1 - k_0\beta^*\rho^*)} + \frac{k_1\beta^*\rho^*}{(1 - k_0\beta^*\rho^*)^2} \tag{2}$$

$$Z_{att} = -\frac{aV^2 + k_0\beta cV}{V(V+e)(V - k_0\beta)RT} \tag{3}$$

where V is the molar volume of argon, $\rho^* = \rho/\rho_c$ is the reduced density of argon, $\beta^* = \beta\rho_c$, the reduced hard-sphere molar volume of argon, ρ_c = the critical density of argon, a and c are parameters that are functions of the temperature, and e is a constant.

From Eqs. 1 and 3 combined, the generalized quartic EOS has the following form:

$$P = \frac{RT}{(V - k_0\beta)} + \frac{\beta k_1 RT}{(V - k_0\beta)^2} - \frac{aV + k_0\beta c}{V(V+e)(V - k_0\beta)} \tag{4}$$

To give the best estimation of various thermodynamic properties of a pure compound, the parameters a, c, and e were determined by nonlinear regression. The four parameters a, β, c, and e are given in reduced forms below; the parameters a, β, and c represent the temperature dependency of the fluid.

$$\beta = \beta_c\left\{\exp\left[-0.03125\ln(T_r) - 0.0054[\ln(T_r)]^2\right]\right\}^3 \tag{5}$$

where $\beta_c = b_r V_c$ and

$$a = a_c\alpha(T_r) \tag{6}$$

where for $T_r \le 1$

$$\alpha(T_r) = \left[1 + X_2\left(1 - \sqrt{T_r}\right) + X_3\left(1 - \sqrt{T_r}\right)^2 + X_4\left(1 - \sqrt{T_r}\right)^3\right]^2 \tag{7}$$

and for $T_r > 1$

$$\alpha(T_r) = \left[1 + X_2\left(1 - \sqrt{T_r}\right) + X_5\left(1 - \sqrt{T_r}\right)^2 + X_6\left(1 - \sqrt{T_r}\right)^3\right]^2 \tag{8}$$

$$c = c_c\xi(T_r) \tag{9}$$

$$\xi(T_r) = \left[1 + X_7\left(1 - \sqrt{T_r}\right)\right]^2 \tag{10}$$

where a_c and c_c are the values of a and c at the critical temperature of the fluid, and X_2, X_3, X_4, X_5, X_6, and X_7 are the constants determined by regressions.

The regressed constants X_2 through X_7, a_c, c_c, and e were made functions of the acentric factor (ω). The regressed constants X_2 through X_7 were assumed to be linear functions of ω, and the regressed constants a_r, c_r, and e_r were assumed to be quadratic functions of ω. These constants are expressed as follows:

$$X_i = X_{i1} + X_{i2}\omega \quad \text{for} \quad i = 2,3,4,5,6,\text{and } 7. \tag{11}$$

$$a_c = \frac{a_r RT_c}{\rho_c} \tag{12}$$

$$c_c = \frac{c_r RT_c}{\rho_c} \tag{13}$$

$$e = \frac{e_r}{\rho_c} \tag{14}$$

$$a_r = a_{r0}(1 + a_{r1}\omega + a_{r2}\omega^2) \tag{15}$$

$$c_r = c_{r0}(1 + c_{r1}\omega + c_{r2}\omega^2) \tag{16}$$

$$e_r = e_{r0}(1 + e_{r1}\omega + e_{r2}\omega^2) \tag{17}$$

Therefore, for nonpolar fluids Eqs. 1 through 17 constitute the generalized quartic equation with coefficients expressed in terms of the critical temperature, the critical volume, and the acentric factor.

Extension of Generalized Quartic EOS to Polar Fluids

Most EOSs do not consider the polarity of the fluid (characterized, for example, by the dipole, quadrupole, and octupole moment) which results in additional attractive forces between molecules. Only the dipole moment is considered here as the measure of polarity of a fluid. Thus, even though a carbon dioxide (fitted well by the generalized quartic EOS) possesses a quadrupole moment, it is still regarded as a nonpolar fluid in this work. Therefore, this study concentrates on the dipole moment when considering pure polar fluids.

To apply the quartic equation of state to polar compounds, the parameters a and c are assumed to be functions of the acentric factor and the dipole moment of the fluid. Also, to express the parameters of the quartic equation in dimensionless form, the reduced dipole moment (μ^*) is used, as shown below:

$$\mu^* = \frac{0.3976\mu}{(RT_cV_c)^{0.5}} \tag{18}$$

where μ is the dipole moment of the polar fluid in debye units.

Thus, when investigating polar fluids, the regressed coefficients X_2 through X_7 were made linear functions of the acentric factor and quadratic functions of the reduced dipole moment. The regressed constants a_r and c_r were made quadratic functions of the acentric factor and the reduced dipole moment. Equations 11, 15, and 16 were rewritten in the following forms:

$$X_i = X_{i1} + X_{i2}\omega + X_{i3}\mu^* + X_{i4}\mu^{*2} \quad \text{for} \quad i = 2,3,4,5,6,\text{and}\,7 \tag{19}$$

$$a_r = a_{r0}(1 + a_{r1}\omega + a_{r2}\omega^2 + a_{r3}\mu^* + a_{r4}\mu^{*2}) \tag{20}$$

$$c_r = c_{r0}(1 + c_{r1}\omega + c_{r2}\omega^2 + c_{r3}\mu^* + c_{r4}\mu^{*2}) \tag{21}$$

Replacing Eqs. 11, 15, and 16 by Eqs. 19, 20 and 21, the constants of the generalized quartic equation for polar fluids are expressed by Eqs. 1 through 17. Hence, only requiring four properties of the fluid (the critical temperature, the critical volume, the acentric factor, and the dipole moment) the generalized quartic EOS is extended to predict the behavior of polar fluids. If the dipole moment of the fluid is zero, then the entire system is reduced to the nonpolar fluid system.

Regression Technique

In this study, the Nelder-Mead simplex algorithm (Nelder, 1965; Nash, 1987) and an adaptive nonlinear least-squares algorithm (Dennis, 1981) were used to determine the regressed constants in the nonlinear regressions. The experimental data for polar fluids were fitted by minimizing the following objective function using nonlinear regression algorithms:

$$F = \sum_{i=1}^{N_1}\left[\left(\frac{\Delta P_{s,i}}{P_{s,i}}\right)^2 + \left(\frac{\Delta \rho_{sv,i}}{\rho_{sv,i}}\right)^2 + \left(\frac{\Delta \rho_{sl,i}}{\rho_{sl,i}}\right)^2\right] + \sum_{j=1}^{N_2}\left(\frac{\Delta \rho_{g,j}}{\rho_{g,j}}\right)^2 + \sum_{k=1}^{N_3}\left(\frac{\Delta H_{r,k}}{H_{r,k}}\right)^2 + \sum_{l=1}^{N_4}\left(\frac{\Delta H_{\text{vap},l}}{H_{\text{vap},l}}\right)^2 + \sum_{m=1}^{N_5}\left(\frac{\Delta B_{v,m}}{B_{v,m}}\right)^2 \tag{22}$$

The criterion for determination of the regressed constants with which we are concerned in this study is the deviation between the calculated and experimental data for pure polar systems. The objective function, Eq. 22, contains the evaluations of various thermodynamic properties of a pure polar compound. Thus, defined multiproperty regressions were used to locate the new regressed coefficients corresponding to the items of the reduced dipole moment. The previously reported regressed constants (Shah, 1992; Shah et al., 1994) for nonpolar fluids were not changed during regressions for 30 pure polar compounds. Experimental data for the vapor pressure and saturation densities near the critical region, approximately 0.97–$1.0T_r$, were not used during regressions. It was a deliberate decision of this work to sacrifice some accuracy in the critical regions [where no analytical equations can model the critical regions accurately anyway (Sengers and Levelt Sengers, 1986)] in exchange for improved accuracy over a wide range of temperature-volume states.

Results and Discussion

The new generalized quartic EOS has been applied to calculate thermodynamic properties of 30 polar compounds, such as refrigerants, esters, ethers, ketones, alcohols, and so on. These thermodynamic properties were taken from experimental literature values for 30 polar compounds, which constitute the database. The parameters in the generalized quartic EOS are expressed by the nondimensional forms. Thus, the reduced dipole moment, expressed in terms of the critical temperature, the critical volume, and the dipole moment, is used to represent the dipole moment of the fluid.

To determine this new set of regressed constants, the parameters a and c of the generalized quartic EOS have been made functions of the acentric factor and the dipole moment of the fluids. The validity of this approach was demonstrated by observing that there was only weak correlation between the reduced dipole moment and the acentric factor of 30 polar fluids. Therefore, four properties of the fluid (the critical temperature, the critical volume, the acentric factor, and the dipole moment) characterize this generalized quartic EOS. The data ranges and sources of 30 pure polar compounds and their physical properties are given in Table 1. Table 2 reports the new set of regressed constants obtained using multiproperty regressions for 30 pure polar compounds. This new set of regressed constants is applicable to both nonpolar

Table 1. Data Ranges and Component Physical Properties Used in the Regressions and Data Sources for 30 Pure Polar Fluids (Daubert and Danner, 1989)

Compound	T (K)	P (MPa)	T_c (K)	V_c (dm^3/mol)	ω	μ (debye)	Data Source*
Acetone	320–1,000	0–100	508.2	0.209	0.3064	2.880	Daubert and Danner (1989) Thermodynamics Res. Ctr. (1993)
Carbon Monoxide	68–1,000	0–100	132.92	0.0931	0.0663	0.112	Goodwin (1985)
Carbonyl Sulfide	150–680	*	378.8	0.1351	0.1041	0.712	Daubert and Danner (1989)
Methyl Acetate	250–505	*	506.8	0.228	0.3253	1.679	Daubert and Danner (1989)
Ethyl Acetate	250–650	*	523.25	0.286	0.3611	1.780	Daubert and Danner (1989)
n-Propyl Acetate	260–620	*	549.4	0.345	0.3935	1.790	Daubert and Danner (1989)
n-Butyl Acetate	300–750	*	579.15	0.389	0.4101	1.840	Daubert and Danner (1989)
Freon-11 (CCl_3F)	220–1,000	0–50	471.2	0.248	0.1837	0.450	Daubert and Danner (1989), Thermodynamics Res. Ctr. (1993), Platzer et al. (1990)
Freon-13 ($CClF_3$)	150–1,000	0–50	301.96	0.18028	0.18	0.510	Thermodynamics Res. Ctr. (1993), Platzer et al. (1990)
Freon-21 ($CHFCl_2$)	250–1,000	0–90	451.58	0.196	0.2069	1.290	Thermodynamics Res. Ctr. (1993), Platzer et al. (1990)
Freon-22 ($CHClF_2$)	180–800	0–100	369.3	0.166	0.2192	1.420	Thermodynamics Res. Ctr. (1993), Platzer et al. (1990), Altunin et al. (1987), Reynolds (1979)
Freon-23 (CHF_3)	145–600	0–100	298.89	0.1333	0.2672	1.649	Thermodynamics Res. Ctr. (1993), Platzer et al. (1990)
Freon-114 ($C_2Cl_2F_4$)	250–600	0–100	418.85	0.29368	0.252	0.560	Daubert and Danner (1989), Thermodynamics Res. Ctr. (1993), Platzer et al. (1990)
Methyl Chloride	206–623	0–35	416.25	0.139	0.1529	1.870	Daubert and Danner (1989), Suh and Storvick (1967), Hsu and McKetta (1964)
Methyl Fluoride	168–950	*	317.7	0.113	0.2037	1.851	Daubert and Danner (1989)
Ethyl Chloride	200–450	*	460.35	0.200	0.1905	2.050	Daubert and Danner (1989)
Chloroform	250–514	*	536.4	0.239	0.2129	1.010	Daubert and Danner (1989)
Chlorobenzene	353–900	0–100	632.35	0.308	0.2505	1.690	Daubert and Danner (1989), Thermodynamics Res. Ctr. (1993)
Dimethyl Ether	180–396	*	400.1	0.170	0.2036	1.300	Daubert and Danner (1989)
Diethyl Ether	255–600	0–100	466.7	0.280	0.2846	1.150	Daubert and Danner (1989) Thermodynamics Res. Ctr. (1993)
Methyl Ethyl Ether	320–435	*	437.8	0.221	0.2189	1.230	Daubert and Danner (1989)
Hydrogen Bromide	200–360	*	363.15	0.10026	0.0693	0.820	Daubert and Danner (1989)
Hydrogen Iodide	230–420	*	423.35	0.12194	0.0381	0.440	Daubert and Danner (1989)
Water	273–1,273	0–100	647.13	0.05595	0.3449	1.850	Daubert and Danner (1989), Reynolds (1979), Keenan et al. (1978)
Hydrogen Sulfide	200–493	0–170	373.53	0.09849	0.0827	0.970	Daubert and Danner (1989), Thermodynamics Res. Ctr. (1993), Lewis and Fredericks (1968)
Methanol	300–800	0–70	512.58	0.11905	0.5656	1.700	Daubert and Danner (1989), Goodwin (1987)
Ammonia	200–800	0–100	405.65	0.07247	0.2520	1.470	Daubert and Danner (1989), Haar and Gallagher (1978)
Nitrous Oxide	190–520	0–32	309.57	0.09737	0.1418	0.167	Daubert and Danner (1989), Couch and Kobe (1961), Hirth and Kobe (0000)
Sulfur Dioxide	205–900	0–100	430.75	0.1220	0.2451	1.630	Daubert and Danner (1989), Thermodynamics Res. Ctr. (1993), Kang et al. (1961)
Acrylonitrile	810–970	*	535	0.212	0.3498	3.870	Daubert and Danner (1989),

*Saturation pressure only.

and polar fluids. The major difference between nonpolar and polar fluids in this study lies in the dipole moment. For nonpolar fluids, the terms in Eqs. 19, 20 and 21 representing the dipole moment are zero. Thus, the new set of regressed constants reduce to the previous set of constants reported by Shah (1992) and Shah et al. (1994) for nonpolar fluids.

Most cubic EOSs have been developed to fit experimental vapor pressure data. When these EOSs are used to predict some thermodynamic properties of pure polar fluids in other regions, such as the region above the critical temperature, large deviations appear. Thus, in general, the applicability and flexibility of most cubic EOSs are limited to certain regions when dealing with pure polar compounds. In order to overcome this disadvantage, the generalized quartic EOS has been extended to polar fluids over a wide range of states and for a wide variety of properties, such as pressure-volume-tempera-

Table 2. Quartic Equation of State Coefficients Obtained by Nonlinear Regressions for 30 Pure Polar Compound Data

Regressed Coefficients		Regressed Coefficients	
a_{r0}	1.84713	X_{21}	0.14988
a_{r1}	−0.05218	X_{22}	0.97848
a_{r2}	1.06446	X_{31}	−0.32379
b_r	0.16500	X_{32}	1.84591
c_{r0}	1.78336	X_{41}	0.14833
c_{r1}	−1.29690	X_{42}	−3.46693
c_{r2}	2.78945	X_{51}	0.11048
e_{r0}	0.63189	X_{52}	0.57743
e_{r1}	−0.81660	X_{61}	0.02581
e_{r2}	3.25246	X_{62}	−0.02700
k_0	1.28650	X_{71}	−0.77357
k_1	2.82250	X_{72}	−1.45342
a^*_{r3}	−0.02730	X^*_{43}	−0.39170
a^*_{r4}	0.02048	X^*_{44}	−0.01597
c^*_{r3}	0.07000	X^*_{53}	0.41218
c^*_{r4}	0.01188	X^*_{54}	−0.10676
X^*_{23}	−0.01390	X^*_{63}	0.38327
X^*_{24}	0.02928	X^*_{64}	−0.09008
X^*_{33}	0.39338	X^*_{73}	−0.04725
X^*_{34}	−0.25483	X^*_{74}	−0.09669

*These coefficients (for terms involving the reduced dipole moment) were varied during regressions. When the reduced dipole moment is equal to zero, these terms drop out.

ture relations, vapor pressure, saturated vapor density, saturated liquid density, enthalpy departure, enthalpy of vaporization, and the second virial coefficient. A comparison of the accuracy and capability of the generalized quartic EOS with those of the widely used Peng-Robinson EOS has been made. Since the Peng-Robinson EOS was not refitted using our 30 pure polar fluid database and data ranges, the comparison was not entirely fair, but the comparison is against the Peng-Robinson EOS as it is currently used. Figure 1 shows the calculation of pressure vs. density for ammonia in the supercritical region by these two EOSs. The average absolute deviation (AAD) calculated for ammonia was 0.76% for the generalized quartic equation and 1.56% for the Peng-Robinson equation. Vapor-liquid equilibrium calculations for water using two EOSs are presented in Figure 2. The result shows that the quartic equation is not very reliable near the critical point of the fluid. The reason is that pure polar compound data close to the critical point were not used in fitting the regressed constants during the regressions. For saturated liquid density calculation, the Peng-Robinson EOS has much larger errors. The AAD calculated for the saturated liquid density for water was 3.5% for the generalized quartic equation and 17.59% for the Peng-Robinson equation. To illustrate low-pressure regions, 0.0–0.1 MPa, the comparison for hydrogen sulfide is presented in Figure 3. The AAD calculated for hydrogen sulfide was 1.82% for the generalized quartic equation; however, for the Peng-Robinson equation the results for this compound was 14.5%. A summary of the AAD calculations for seven physical and thermodynamic properties for 30 pure polar compounds obtained using the generalized quartic and Peng-Robinson EOSs is presented in Table 3. The *overall* performance of the quartic EOS ap-

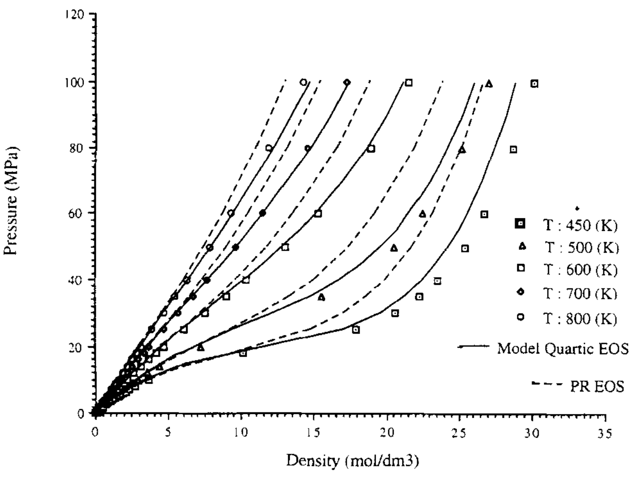

Figure 1. Comparison of pressure-density calculation for ammonia (Haar and Gallagher, 1978).

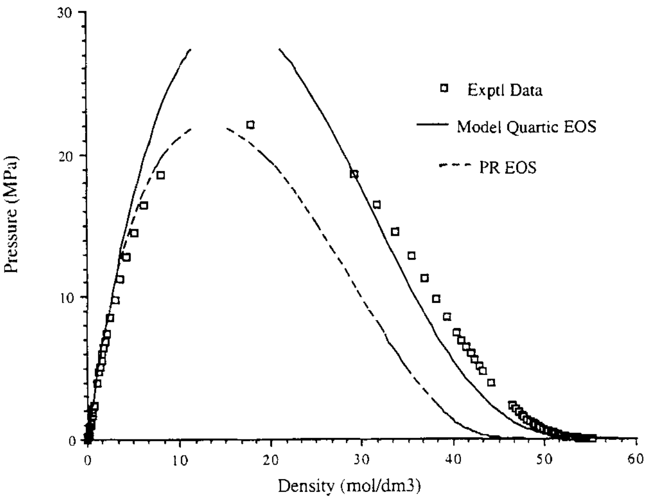

Figure 2. Comparison of saturated VLE calculation for water (Keenan et al., 1978).

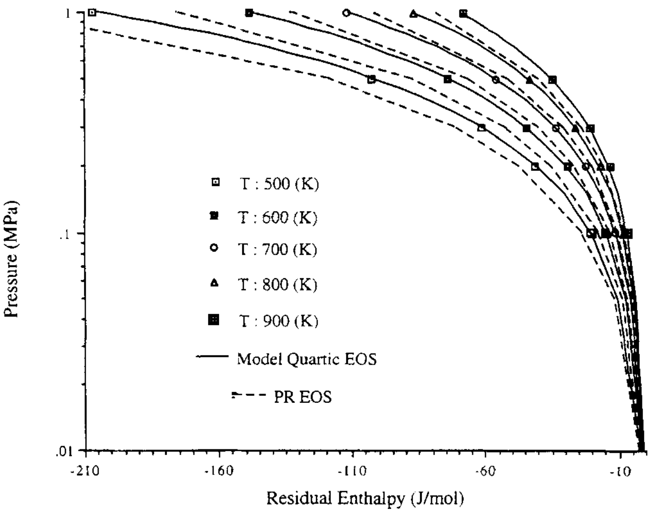

Figure 3. Comparison of residual enthalpy calculation for hydrogen sulfide (Thermodynamics Research Center, 1993).

Table 3. AAD Summary for Regressed Thermodynamic Properties of 30 Polar Compounds Using the Generalized Quartic and Peng-Robinson Equations of State

Thermodynamic and Physical Properties	Generalized Quartic EOS AAD (%)	Peng-Robinson EOS AAD (%)	Number of Data Points
P_s	1.98	1.82	1,456
ρ_{sv}	2.68	2.90	541
ρ_l	2.40	6.74	1,586
ρ_g	0.89	2.08	2,289
H_r	3.29	15.46	913
B_{vir}	1.71	57.05	609
H_v	1.91	1.82	1,118

$\text{AAD}(\%) = \frac{1}{N_d}\sum_{i=1}^{N_d}\left|\left(\frac{y_i^{\text{exp}} - y_i^{\text{calc}}}{y_i^{\text{exp}}}\right)\right| \times 100\%$ where y^{exp} = the experimental data, y^{calc} = the calculated data, and N_d = the number of data points.

pears to be better than that of the Peng-Robinson EOS for pure polar fluid systems. The Peng-Robinson EOS performs slightly better than the generalized quartic EOS with regard to saturated vapor pressure and enthalpy of vaporization calculations.

To demonstrate the ability of the generalized quartic EOS for nonpolar and polar fluids to represent polar systems, we arbitrarily chose seven pure polar substances (Freon-12 (CCl_2F_2), methyl ethyl ketone, m-xylene, toluene, ethylbenzene, 1H-pyrrole, and 1,1-difluoroethane) which were not included in the regressions. These seven polar fluids were examined using the new set of regressed coefficients in the generalized quartic EOS. Table 4 reports the data ranges and sources of seven pure polar compounds and their physical properties. The results of some thermodynamic property calculations for these compounds can be seen in Figures 4–7.

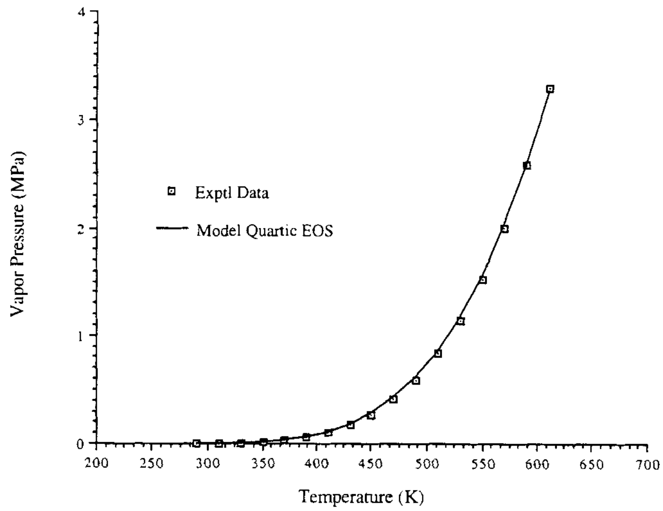

Figure 4. Vapor pressure calculation for ethylbenzene (Daubert and Danner, 1989).

The AAD calculated for saturated liquid density for 1,1-difluoroethane was 1.48% for the generalized quartic equation; however, for the Peng-Robinson equation the results for this compound was 9.63%. The AAD calculated for the second virial coefficient for methyl ethyl ketone was 0.92% for the generalized quartic equation and 35.04% for the Peng-Robinson equation, respectively.

One objective in extending the quartic equation to polar fluids was to develop a fourth parameter which would model the polarity effects independent of the acentric factor. Figure 8 demonstrates that there is only a weak correlation between acentric factor and dipole moment. Preliminary results indi-

Table 4. Description of Seven Polar Fluid Data Ranges Used and Their Data Sources and Physical Properties (Daubert and Danner, 1989)

Compound	Properties	T (K)	P (MPa)	T_c (K)	V_c (dm³/mol)	ω	μ (debye)	Ref.
Dichloro-difluoro-methane (CCl_2F_2)	P_s, ρ_{sv}, ρ_{sl}	230–383	*	384.95	0.217	0.1796	0.510	Platzer et al. (1990)
	ρ_g	390–470	0–80					Platzer et al. (1990)
	H_r	400–520	0–50					Thermodynamics Res. Ctr. (1993)
	B_{vir}	340–470						Daubert and Danner (1989)
	H_v	230–365	*					Platzer et al. (1990)
Methyl ethyl ketone	P_s, ρ_{sl}	200–530	*	535.5	0.267	0.3241	2.760	Daubert and Danner (1989)
	B_{vir}	850–1,150						Daubert and Danner (1989)
	H_v	200–510	*					Daubert and Danner (1989)
m-xylene	P_s, ρ_{sl}	350–610	*	617.05	0.3758	0.3260	0.300	Daubert and Danner (1989)
	H_v	350–590	*					Daubert and Danner (1989)
Ethyl Benzene	P_s, ρ_{sl}	290–610	*	617.17	0.37381	0.3036	0.590	Daubert and Danner (1989)
	B_{vir}	550–800						Daubert and Danner (1989)
	H_v	290–590	*					Daubert and Danner (1989)
Toluene	P_s, ρ_{sl}	250–590	*	591.79	0.31579	0.2641	0.360	Daubert and Danner (1989)
	H_v	250–570	*					Daubert and Danner (1989)
1,1-Difluoro-enthane	P_s, ρ_{sl}	160–385	*	639.75	0.230	0.2876	1.840	Daubert and Danner (1989)
	H_r	400–550	0–75					Thermodynamics Res. Ctr. (1993)
	H_v	160–360	*					Daubert and Danner (1989)
1H-pyrrole	P_s	320–630	*	386.6	0.181	0.2629	2.270	Daubert and Danner (1989)
	H_v	320–600	*					Daubert and Danner (1989)

*Saturation pressure only.

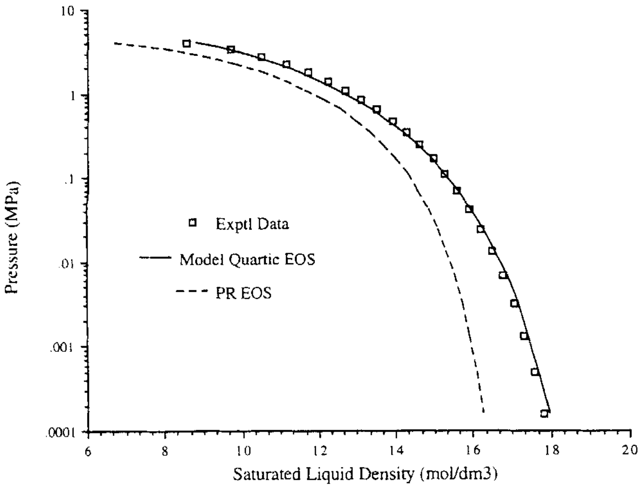

Figure 5. Comparison of saturated liquid density calculation for 1,1-difluoroethane (Daubert and Danner, 1989).

cate that the quartic equation will accurately predict mixture properties if the van deer Waals mixing rules are used for the attractive portion of the equation and Boublik-Mansoori for the hard-sphere part.

Conclusions

A quartic EOS, previously developed and generalized for nonpolar fluids, has been extended and generalized for polar fluids. A summary of the overall performance for the generalized quartic and Peng-Robinson equations for seven polar compounds is reported in Table 5. Various thermodynamic properties predicted from the generalized quartic EOS are in satisfactory agreement with the experimental data over a wide range of states and for a variety of thermodynamic properties. The generalized quartic EOS makes a significant improvement in calculating the enthalpy departure, second virial coefficients, and the pressure-volume-temperature properties. From all results presented in this study, it appears that the new set of generalized constants has been reliably determined using an effective regression technique. This set of regressed constants is applicable to the thermodynamic property calculations for nonpolar and polar fluids. In order to evaluate the thermodynamic properties of a fluid, this EOS is

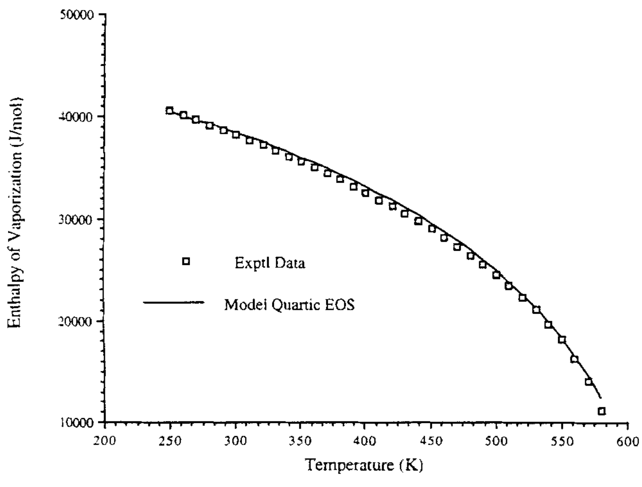

Figure 6. Enthalpy of vaporization calculation for toluene (Daubert and Danner, 1989).

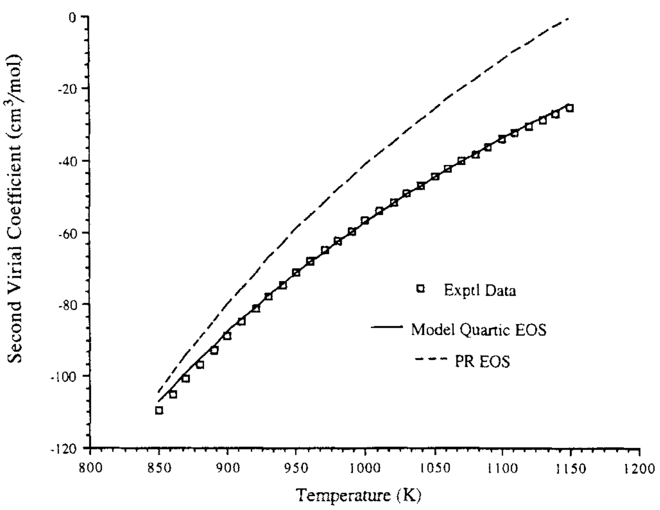

Figure 7. Comparison of second virial coefficient calculation for methyl ethyl ketone (Daubert and Danner, 1989).

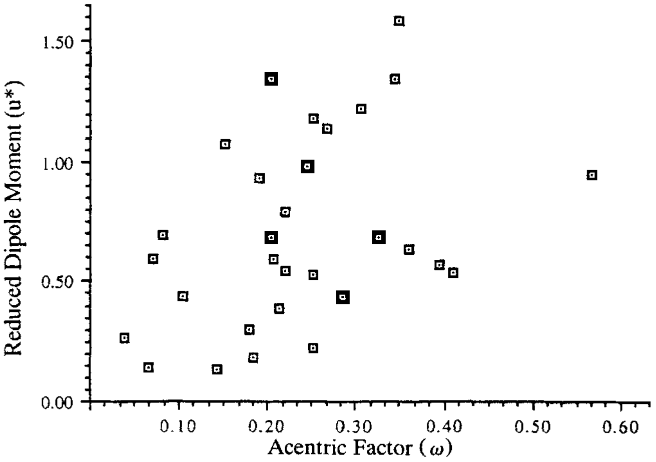

Figure 8. Acentric factor and reduced dipole moment for 30 polar fluids.

Table 5. AAD Summary for Predicted Thermodynamic Properties of Seven Polar Compounds Using the Generalized Quartic and Peng-Robinson Equations of State

Thermodynamic and Physical Properties	Generalized Quartic EOS AAD (%)	Peng-Robinson EOS AAD (%)	Number of Data Points
P_s	2.45	1.61	199
ρ_{sv}	2.78	1.57	30
ρ_{sl}	2.43	6.20	167
ρ_g	1.17	2.45	72
H_r	3.90	17.18	136
B_{vir}	1.25	19.33	84
H_v	2.18	1.76	182

characterized by four properties of the fluid—the critical temperature, the critical volume, the acentric factor, and the dipole moment. The new generalized quartic equation of state is offered as a simple and accurate alternative to the commonly used cubic equations of state for modeling properties of both polar and nonpolar fluids.

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Notation

a = parameter of the quartic equation of state, MPa/dm^6
b = van der Waals volume, mol/dm^3
B_v = second virial coefficient, cm^3/mol
c = parameter of the quartic equation of state, MPa/dm^6
e = parameter of the quartic equation of state, mol/dm^3
f = fugacity, MPa
H_r = residual enthalpy, J/mol
H_v = enthalpy of vaporization, J/mol
k_0, k_1 = quartic equation of state constants
N = number of data points
P = pressure, MPa
R = universal gas constant, 0.008314 MPa·dm^3/mol·K
T = temperature, K
V = molar volume, dm^3/mol
X_i = quartic equation of state regressed coefficients
Z = compressibility factor of a compound

Greek letters

$\alpha(T_r)$ = temperature dependence of parameter a
β = hard core volume, dm^3/mol
$\xi(T_r)$ = temperature dependence of parameter c
ρ = density, mol/dm^3

Superscripts

calc = calculated value
exp = experimental value
$*$ = reduced variable

Subscripts

g = gas, single phase region
hs = hard sphere
l = liquid phase
v = vapor phase
r = reduced property or constant
rep = repulsive
s = saturated, two-phase envelope
sl = saturated liquid phase
sv = saturated vapor phase

Literature Cited

Alder, B. J., and T. E. Wainwright, "Studies in Molecular Dynamics. II: Behavior of a Small Number of Elastic Spheres," *J. Chem. Phys.*, **33**, 1439 (1960).

Altunin, V. V., V. Z. Geller, E. A. Kremenevskaya, I. I. Perelshtein, and E. K. Petrov, *Thermophysical Properties of Freons*: 2, Hemisphere, New York (1987).

Bryan, P. F. and J. M. Prausnitz, "Thermodynamic Properties of Polar Fluids from a Perturbed-Dipolar-Hard-Sphere Equation of State," *Fluid Phase Equil.*, **38**, 201 (1987).

Burnside, W. S., and A. W. Panton, *The Theory of Equations with an Introduction to the Theory of Binary Algebraic Forms*, Vol. 1, Dover Publications, Mineola, NY (1912).

Carnahan, N. F., and K. E. Starling, "Equation of State for Non-attracting Rigid Spheres," *J. Chem. Phys.*, **51**, 635 (1969).

Chung, T. H., M. M. Khan, L. L. Lee, and K. E. Starling, "A New Equation of State for Polar and Nonpolar Fluids," *Fluid Phase Equil.*, **17**, 351 (1984).

Couch, E. J., and K. A. Kobe, "Volumetric Behavior of Nitrous Oxide: Pressure-Volume Isotherms at High Pressures," *J. Chem. Eng. Data*, **6**(2), 229 (1961).

Daubert, T. E., and R. P. Danner, *Physical and Thermodynamic Properties of Pure Chemicals*: *Data Compilations*, Hemisphere, New York, Vols. 1–4 (1989).

Dennis, J. E., D. M. Gay, and R. E. Welsch, "Algorithm 573.NL 2SOL-An Adaptive Nonlinear Least-Squares Algorithm," *ACM Trans. Math. Soft.*, 7, 369 (1981).

Goodwin, R. D., "Carbon Monoxide Thermophysical Properties from 68 to 1000 K at Pressures to 100 MPa," *J. Phys. Chem. Ref. Data*, **14**, 849 (1985).

Goodwin, R. D., "Methanol Thermodynamic Properties from 176 to 673 K at Pressures to 700 Bar," *J. Phys. Chem. Ref. Data.*, **16**(4), 799 (1987).

Guo, T.-M., H. Kim, H.-M. Lin, and K.-C. Chao, "Cubic Chain-of-Rotators Equation of State for Polar Fluids," *Fluid Phase Equil.*, **24**, 43 (1985).

Haar, L., and J. S. Gallagher, "Thermodynamic Properties of Ammonia," *J. Phys. Chem. Ref. Data.*, **7**(3), 635 (1978).

Hirth, L. J., and K. A. Kobe, "Volumetric Behavior of Nitrous Oxide: Gas Compressibility Factors at Low Pressures," *J. Chem. Eng. Data*, **6**(2), 229 (1961).

Householder, A. S., *The Numerical Treatment of a Single Nonlinear Equation*, McGraw-Hill, New York (1970).

Hsu, C. C., and J. J. McKetta, "Pressure-Volume-Temperature Properties of Methyl Chloride," *J. Chem. Eng. Data*, **9**(1), 45 (1964).

Kang, T. L., K. Li, K. A. Kobe, and J. J. McKetta, "Pressure-Volume-Temperature Properties of Sulfur Dioxide," *J. Chem. Eng. Data*, **6**(2), 220 (1961).

Keenan, J. H., F. G. Keyes, P. G. Hill, and J. G. Moore, *Steam Tables*, Wiley, New York (1978).

Lewis, L. C., and W. J. Fredericks, "Volumetric Properties of Supercritical Hydrogen Sulfide," *J. Chem. Eng. Data*, **13**, 482 (1968).

Lin, H. M., H. Kim, T. M. Guo, and K. C. Chao, "Cubic Chain-of-Rotators Equation of State and VLE Calculation," *Fluid Phase. Equil.*, **13**, 143 (1983).

Mulia, K., and V. F. Yesavage, "Development of a Perturbed Hard Sphere Equation of State for Nonpolar and for Polar/Associating Fluids," *Fluid Phase Equil.*, **52**, 67 (1989).

Nakamura, R., G. J. F. Breedveld, and J. M. Prausnitz, "Thermodynamic Properties of Gas Mixtures Containing Common Polar and Nonpolar Compounds," *Ind. Eng. Chem. Process Des. Dev.*, **15**(4), 557 (1976).

Nash, J. C., and M. Walker-Smith, *Nonlinear Parameter Estimation*, Marcel Dekker, New York (1987).

Nelder, J. A., and R. Mead, "A Simplex Method for Function Minimization," *Comput. J.*, **7**, 308 (1965).

Peng, D. Y., and D. B. Robinson, "A New Two Constant Equation of State," *Ind. Eng. Chem. Fundam.*, **15**, 59 (1976).

Platzer, B., A. W. Polt, and G. Maurer, *Thermophysical Properties of Refrigerants*, Springer-Verlag, Berlin Heidelberg (1990).

Redlich, O., and J. N. S. Kwong, "On the Thermodynamics of Solutions V: An Equation of State and Fugacities of Gaseous Solutions," *Chem. Rev.*, **44**, 233 (1949).

Reynolds, W. C., *Thermodynamic Properties in SI*: *Graphs, Tables, and Computational Equations for Forty Substances*, Dept. of Mechanical Engineering, Stanford Univ. (1979).

Rowlinson, J. S., *J. D. van der Waals*: *On the Continuity of Gaseous and Liquid State*, North-Holland, New York (1988).

Shah, V. M., "Development of a Generalized Quartic Equation of State for Pure Fluids," PhD Disser., Univ. of Tennessee, Knoxville (1992).

Shah, V. M., P. R. Bienkowski, and H. D. Cochran, "Generalized Quartic Equation of State for Pure Nonpolar Fluids," *AIChE J.*, **40**(1), 152 (1994).

Sengers, J. V., and M. H. Levent Sengers, Jr., "Thermodynamic Behavior of Fluids Near the Critical Points," *Ann. Rev. Phys. Chem.*, **37**, 189 (1986).

Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Sci.*, **27**, 1197 (1972).

Suh, K. W., and T. S. Storvick, "Gas Compressibility Factors at High Temperature and High Pressure by the Burnett Method: Methyl Chloride," *AIChE J.*, **13**(2), 231 (1967).

Thermodynamics Research Center, *TRC Thermodynamic Tables*: *Non-hydrocarbons*, Texas A&M University, College Station (1993).

Turnbull, H. W., *Theory of Equations*, Oliver and Boyd, Edinburgh (1952).

Young, J. R., *Theory and Solution of Equations of Higher Order*, Souter and Law, London (1843).

Appendix A: Quartic EOS

The equation of state (Eq. 4) can be written as a quartic in volume:

$$V^4 + q_3 V^3 + q_2 V^2 + q_1 V + q_0 = 0 \tag{A1}$$

where

$$q_3 = \left(-2k_0 \beta + e - \frac{RT}{P} \right) \tag{A2}$$

$$q_2 = \left\{ \frac{RT}{P} [\beta(k_0 - k_1) - e] + k_0 \beta (k_0 \beta - 2e) \right\} + \frac{a}{P} \tag{A3}$$

$$q_1 = e \left[k_0^2 \beta^2 + \frac{RT}{P} \beta (k_0 - k_1) \right] + \left[\frac{k_0 \beta (c - a)}{P} \right] \tag{A4}$$

$$q_0 = -\frac{c k_0^2 \beta^2}{P} \tag{A5}$$

Appendix B: Behavior of the Roots of the Quartic EOS

Several authors (Young, 1843; Burnside and Panton, 1912; Turnbull, 1952) have discussed and reviewed the properties of quartic equations. The roots obtained by solving the quartic EOS have the following properties:

(1) One root is always real and negative and has no physical significance. The proof of this is given in the latter part of the discussion.

(2) At the critical point, three roots are real, positive and equal. This also requires that both $(\partial P/\partial V)_T$ and $(\partial^2 P/\partial V^2)_T$ equal to zero at this pressure and temperature. Details on using these conditions to determine parameters of the EOS are given elsewhere (Shah, 1992). The parameters (a, β, c, and e) of the EOS have not been determined in this manner. Hence, the critical point represented by the EOS is not the same as the experimentally determined critical point of the fluid.

(3) Below the critical temperature, all four roots are real. The smallest positive root in volume corresponds to the liquid phase and the largest positive root corresponds to the vapor phase.

(4) Above the critical temperature, two roots are real and the remaining two complex. The only positive root corresponds to the volume of the fluid.

The quartic EOS can be written as:

$$V^4 + q_3 V^3 + q_2 V^2 + q_1 V + q_0 = 0 \tag{B1}$$

Let V_1, V_2, V_3, and V_4 be the four roots to Eq. B1. These roots satisfy the following relationship also:

$$V_1 V_2 V_3 V_4 = q_0 \tag{B2}$$

It can be easily shown that c is always positive for all possible values of the acentric factor and reduced dipole moments. This implies that q_0 is always negative (Eq. A5) and so is the product of all the roots of the quartic EOS. At subcritical temperatures, three roots are always positive implying that the fourth one is always negative. At supercritical temperatures, two roots are complex. Since the quartic EOS is a real polynomial in V, complex roots appear in pairs and one is the complex conjugate of the other (Householder, 1970). Since the product of the two conjugate complex numbers is always positive and the root of physical significance is positive, the fourth root has to be negative.

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