Generalized Quartic Equation of State for Pure Nonpolar Fluids

Vinod M. Shah and Paul R. Bienkowski
Dept. of Chemical Engineering, University of Tennessee, Knoxville, TN 37996

Hank D. Cochran
Oak Ridge National Laboratory, Oak Ridge, TN 37831

A generalized quartic equation of state has been developed for pure nonpolar fluids. The equation of state contains four parameters which depend on three properties of the fluid—critical temperature, critical volume, and acentric factor. A mathematical approximation based on previously reported hard-sphere molecular dynamics simulations has been used to model repulsive contributions to the pressure. Attractive forces were modeled using an empirical term. While the quartic equation yields four roots, one root is always negative and hence physically meaningless, and three roots behave like three roots of a cubic equation. Thus, the new equation of state has the advantages of a cubic, simplicity and unequivocal identification of the roots, while correctly modeling the attractive and repulsive contributions to the pressure. The new equation of state is more accurate than either the Peng-Robinson or a previously proposed quartic equation of state. Accuracy in the supercritical and compressed liquid regions is improved substantially.

Introduction

Equations of state (EOS) are used to describe phase equilibrium, calculate physical properties such as pressure and molar volume of substances at different temperatures, and predict thermodynamic properties such as specific heat, isothermal compressibility, and enthalpy. EOSs based only on pure fluids and binary mixtures are very valuable tools in predicting the complex behavior of multicomponent mixtures. These equations are widely used in the chemical and petroleum industries to model and predict phase equilibrium and in process design and economic evaluation calculations. Different equations of state predict these properties with different degrees of accuracy and require vastly different amounts of resources for proper application.

Cubic equations of state, which are the industry standard, model the repulsive forces incorrectly resulting in inaccuracies in representing thermodynamic properties, especially in the supercritical fluid and condensed-phase regions. Cubic equations are widely accepted in the petroleum and chemical industries because of their simplicity and reasonable accuracy. Van der Waals (vdW) proposed the first cubic equation of state in 1873. In most cubic equations of state, the contribution to the pressure due to repulsive forces between molecules is given by the van der Waals repulsive term:

$$P_{rep} = \frac{RT}{(V-b)} \tag{1}$$

It was based on the assumption that only collisions between a pair of molecules occur in dilute gases. As a result, four times the volume of one molecule was not available to any other molecule. While this assumption is true for dilute gases, it is no longer valid at higher densities. The Redlich-Kwong equation of state (Redlich and Kwong, 1949) was considerably superior to other equations of state available at that time.

The RK equation retained the van der Waals P_{rep} term, a practice followed in all the popular cubic equations of state. Soave (1972) introduced a temperature dependence in the a parameter of the RK equation (SRK) and let it be a function of the acentric factor of the fluid. Peng and Robinson (PR) proposed an equation of state in 1976 which offer better liquid density predictions than the Soave equation of state.

Presently, SRK and PR equations are the most frequently

Correspondence concerning this article should be addressed to V. M. Shah.

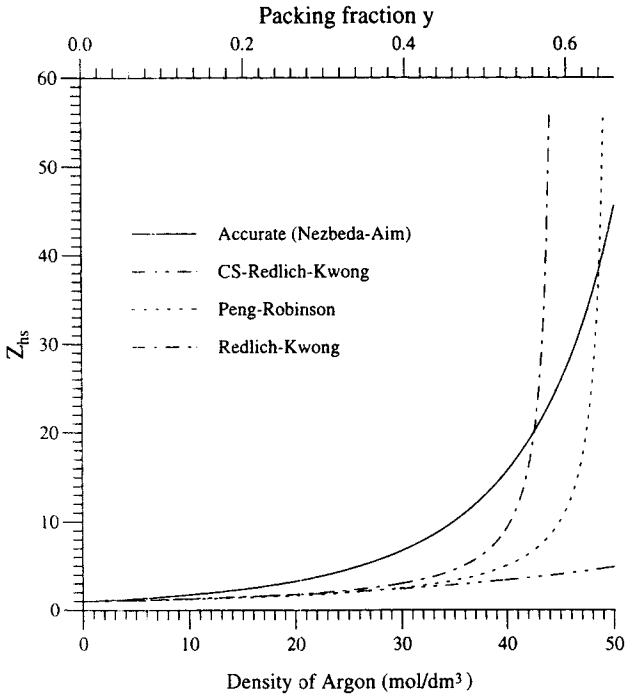

Figure 1. Hard-sphere compressibility from various equations of state.

used cubic equations of state. Rowlinson and Swinton (1982) pointed out that the vdW equations of state are more correct in the attractive a/V^2 term than in the repulsive term $RT/(V-b)$. Carnahan and Starling (CS) (1969) proposed an equation of state for hard spheres which agrees with molecular dynamics and Monte Carlo simulations. Alder et al. (1968) performed molecular dynamics simulations of hard spheres at high densities. At high density, their results no longer agreed with those predicted by the CS equation. The CS equation is more accurate and theoretically correct as compared to the vdW repulsive term.

A common misconception about the vdW repulsive term, when used in cubic equations, is that the parameter b is four times the true hard sphere volume of the molecule. If the true hard sphere volume of a fluid was used with the van der Waals term, it would fail at packing fractions of greater than 0.25. In reality, the imposition of the critical constraints on the vdW-type cubic equations of state leads to a value of b which is much smaller, allowing the cubics to perform much better than expected at high density.

Table 1. Hard-Sphere Volume of Argon at 83.8 K Calculated by Various Equations of State

Equation of State	V_{hs} dm³/mol
Peng-Robinson	0.00501
Redlich-Kwong	0.00558
CS-Peng-Robinson	0.00629
Kubic's Quartic EOS	0.00884
Soave's Quartic EOS	0.00611
Nezbeda-Aim (Perturbation Theory)	0.0132
New Quartic EOS	0.0130

Other equations of state use the correct hard-sphere equation to model the repulsive forces. Some of these, however, use the wrong hard-sphere volumes and hence model the repulsive forces incorrectly. Figure 1 compares the hard sphere compressibility (Z_{hs}) for argon vs. density for several equations. The accurate determination of the hard-sphere volume of Nezbeda and Aim (1984) was used with the Carnahan-Starling equation for comparison. Clearly, Z_{hs} determined by the vdW-type equations and some of the CS-type equations of state are incorrect at the high-density limit. The CS-type equations in Figure 1 use the correct Z_{hs} equation, but use the wrong hard-sphere volume. The wrong hard-sphere volumes are obtained as a result of forcing the EOS to satisfy the critical point constraints. Table 1 shows the hard-sphere volumes used by various EOSs for Argon at 83.8 K. The hard-sphere volume for the cubic EOSs is given by $b/4$. Table 1 shows that only a few EOSs use the correct hard-sphere volume. In practice, the cubic equations are able to give reasonable predictions for PVT data despite a fundamentally flawed repulsive term. This is accomplished by creating a distortion in the attractive term to compensate for the deficiencies of the repulsive term.

Our goal here is to develop a new equation of state that retains desirable features of the popular cubic equations of state with improved accuracy. We propose to improve accuracy by using a form of the repulsive term with better accuracy than the van der Waals form, which leads to an equation of state that can be solved efficiently and has roots that can be unequivocally identified. We chose to test forms for the repulsive contribution that lead to an equation of state which is quartic in volume. Kubic (1986b) proposed the first quartic equation of state and extended it to mixtures (1986a). Soave (1990) has also proposed a quartic equation of state for pure fluids.

New Quartic Equation of State

A mathematically simple, yet correct, hard-sphere equation was used to model the repulsive interactions between molecules. To keep the equation of state a quartic in volume, the equation had to be simpler than the Carnahan-Starling equation. It was found that a mathematically simple repulsive term could be made to fit the MD results of Alder et al. closely in the packing fraction range of 0.0 to 0.6:

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

where β is the molar hard-sphere volume. Regression of the MD results led to values of k_0 and k_1 of 1.2864 and 2.8225, respectively. Figure 2 shows that the simple expression for Z_{hs} represents remarkably the molecular dynamics data of Alder et al. Equation 2 was used to represent the repulsive pressure in the new equation of state. Because of its algebraic simplicity, Eq. 2 could be used to develop a quartic equation of state.

The attractive forces were modeled using an empirical equation. The following approach was used to develop the attractive term: using real fluid data for argon and hard-sphere compressibilities calculated from Eq. 2, plots of Z_{att} vs. reduced density were prepared for various reduced temperatures:

$$Z_{att}=Z_{exp}-Z_{hs} \tag{3}$$

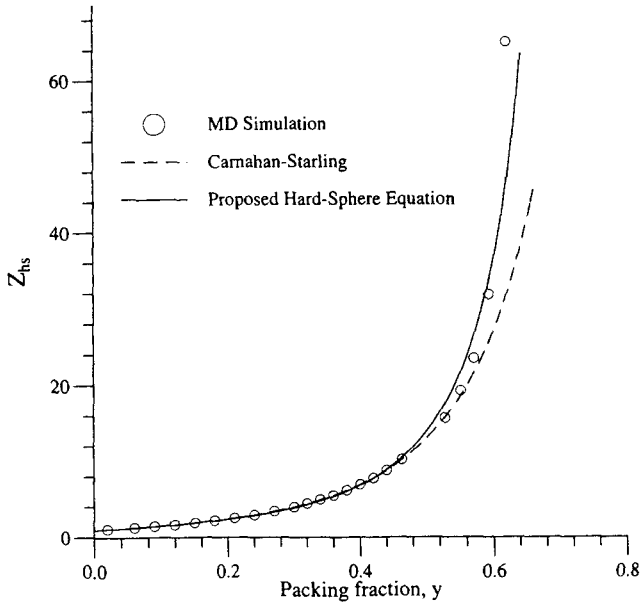

Figure 2. Hard-sphere compressibility predicted by the new equation.

Molecular dynamics results of Adler et al. (1968).

where Z_{att} is the attractive contribution to the compressibility, Z_{exp} is the experimental compressibility value, and Z_{hs} is the hard-sphere contribution given by Eq. 2. Plots of Z_{att} vs. reduced density were constructed for different reduced temperatures and fit with an empirical equation for Z_{att}. Z_{att} given by,

$$Z_{att} = -\frac{aV^2 + k_0\beta cV}{V(V+e)(V-k_0\beta)RT}, \tag{4}$$

where e is a constant, and a and c are temperature-dependent, gave the best results. Combining Eqs. 2 and 4, the resulting equation of state can be written as:

$$P = \frac{RT}{(V-k_0\beta)} + \frac{\beta k_1 RT}{(V-k_0\beta)^2} - \frac{aV + k_0\beta c}{V(V+e)(V-k_0\beta)} \tag{5}$$

The equation of state can be rewritten as a quartic:

$$V^4 + q_3V^3 + q_2V^2 + q_1V + q_0 = 0 \tag{6}$$

where

$$q_3 = \left(-2k_0\beta + e - \frac{RT}{P}\right) \tag{7}$$

$$q_2 = \left[\frac{RT}{P}(\beta(k_0-k_1)-e) + k_0\beta(k_0\beta-2e)\right] + \frac{a}{P} \tag{8}$$

$$q_1 = e\left[k_0^2\beta^2 + \frac{RT}{P}\beta(k_0-k_1)\right] + \left[\frac{k_0\beta(c-a)}{P}\right] \tag{9}$$

$$q_0 = -\frac{ck_0^2\beta^2}{P} \tag{10}$$

Most equations of state determine the hard-sphere volume of a fluid by using the critical pressure. Such an approach requires that the critical compressibility of the fluid be known or specified by an empirical equation. If the critical volume is used, however, the critical compressibility does not have to be specified. The hard-sphere volumes of the fluids at the critical temperature were fixed to 0.165 times the critical volume of the fluid. It can be seen from Table 1 that this leads to a hard-sphere volume for argon comparable to those used in more accurate equations of state. A temperature dependence was incorporated into β according to Nezbeda and Aim (1984):

$$\beta = \beta_c\{\exp[-0.03125\ \ln(T_r) - 0.0054[\ln(T_r)]^2]\}^3 \tag{11}$$

where $\beta_c = 0.165V_c$. A temperature dependence was incorporated into a and c in the following manner:

$$a = a_c\alpha(T_r) \tag{12}$$

where for $T_r <= 1$

$$\alpha(T_r) = [1 + X_2(1-\sqrt{T_r}) + X_3(1-\sqrt{T_r})^2 + X_4(1-\sqrt{T_r})^3]^2 \tag{13}$$

and for $T_r > 1$

$$\alpha(T_r) = [1 + X_2(1-\sqrt{T_r}) + X_5(1-\sqrt{T_r})^2 + X_6(1-\sqrt{T_r})^3]^2 \tag{14}$$

Finally,

$$c = c_c\xi(T_r) \tag{15}$$

and

$$\xi(T_r) = [1 + X_7(1-\sqrt{T_r})]^2 \tag{16}$$

where X_2, X_3, X_4, X_5, X_6 and X_7 are constants. The equation of state was extended to nonspherical fluids with the introduction of the acentric factor, ω, as the third property to characterize the fluid. The parameters a, c and e, and the constants X_1 through X_7 were made functions of the acentric factor. The parameters a_c, c_c and e were defined and related to the acentric factor as shown in Eqs. 17-22.

$$a_c = \frac{a_r RT_c}{\rho_c} \tag{17}$$

$$c_c = \frac{c_r RT_c}{\rho_c} \tag{18}$$

$$e = \frac{e_r}{\rho_c} \tag{19}$$

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

$$e_r = e_{r0}(1 + e_{r1}\omega + e_{r2}\omega^2) \tag{21}$$

$$c_r = c_{r0}(1 + c_{r1}\omega + c_{r2}\omega^2) \tag{22}$$

where a_c and c_c are the values of a and c at the critical tem-

Table 2. Pure-Component Data Used in Regressions and Their Sources

Fluid	Temp. K	Pres. MPa	Source
Argon	84–140	0–100	(Stewart & Jacobsen, 1989)
Krypton	116–204	0–100	(Vargaftik, 1975)
Xenon	164–280	0–100	(Vargaftik, 1975)
Oxygen	56–152	0–100	(Vargaftik, 1975)
Nitrogen	64–1,000	0–100	(Jacobsen et al., 1986)
Methane	100–600	0–100	(Younglove & Ely, 1987)
Ethane	140–600	0–100	(Younglove & Ely, 1987)
Propane	170–600	0–100	(Younglove & Ely, 1987)
n-Butane	130–600	0–70	(Younglove & Ely, 1987)
Carbon Dioxide	220–1,000	0–100	(Angus et al., 1976)
n-Pentane	299–455	0–1.44	(Starling, 1973)
n-Hexane	266–494	0–2.45	(Starling, 1973)
n-Octane	277–533	0–1.49	(Starling, 1973)
n-Nonane	253–573	0–20	(Vargaftik, 1975)
n-Decane	263–393	0–10	(Vargaftik, 1975)
n-Undecane	303–573	0–100	(Vargaftik, 1975)

perature. Equations 20–22 were required to keep the critical compressibility, calculated by the equation of state, dependent on the nature of the fluid. The constants X_2 to X_7 were made functions of ω as:

$$X_i = X_{i1} + X_{i2}\omega \text{ for } i = 2,3,4,5,6,7 \tag{23}$$

A multiproperty nonlinear regression analysis was employed using data from 16 nonpolar fluids to determine all of the constants necessary to specify the equation of state. Second virial coefficient data, high-temperature residual enthalpy data, and density data were used for parameter evaluation. The database used is shown in Table 2. Accurate equations of state were used to generate the database whenever possible. Pure-component physical properties, T_c, P_c, and ω, used in the regressions were obtained from Reid et al. (1987). Table 3 provides the regressed constants for the equation of state.

Figure 3 represents the PVT data of carbon dioxide by the equation of state; Figure 4 the VLE data of *n*-octane and Figure 5 the vapor pressure of *n*-nonane. The new EOS reproduces the second virial coefficient of fluids quite accurately at supercritical temperatures. At subcritical temperatures there is some deterioration in the fit of the second virial coefficient. Figure 6 shows the second virial coefficient predictions of

Table 3. Equation of State Constants Obtained by Regressions (Quartic EOS)

Parameter	Parameter		
a_{r0}	1.84713	X_{21}	0.14988
a_{r1}	−0.05218	X_{22}	0.97848
a_{r2}	1.06446	X_{31}	−0.32379
c_{r0}	1.78336	X_{32}	1.84591
c_{r1}	−1.29690	X_{41}	0.14833
c_{r2}	2.78945	X_{42}	−3.46693
e_{r0}	0.63189	X_{51}	0.11048
e_{r1}	−0.81660	X_{52}	0.57743
e_{r2}	3.25246	X_{61}	0.02581
		X_{62}	−0.02700
k_0^*	1.2865	X_{71}	−0.77357
k_1^*	2.8225	X_{72}	−1.45342

*These quantities were kept fixed during regressions.

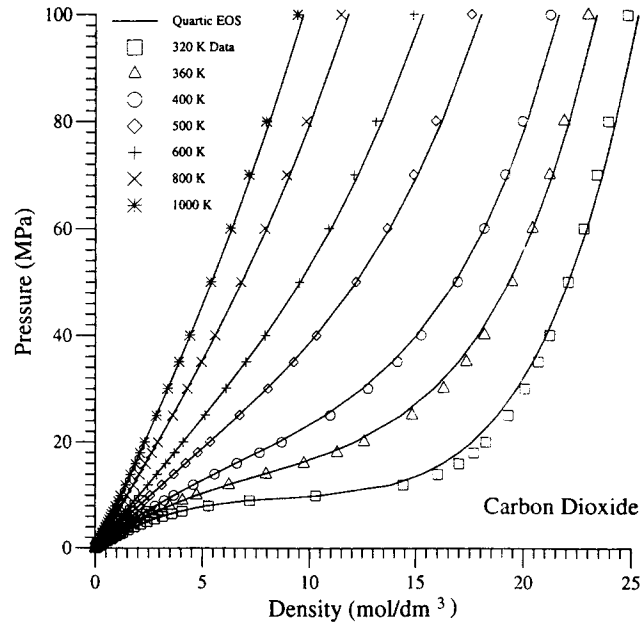

Figure 3. Pressure-density calculations for carbon dioxide.

Smoothed data of Angus et al. (1976).

carbon monoxide and ethylene using only the critical temperature, critical volume, and acentric factor for these fluids. Figure 7 is a prediction of the PVT of benzene. Figure 8 shows the residual enthalpy predictions for ethylene. Benzene, carbon monoxide, and ethylene were not used in the development of the new equation, thus the excellent agreement with the experimental data is predictive in nature.

The equation of state shows classical behavior at the critical point: three roots of the EOS become equal. Table 4 gives the critical constants calculated using the equation of state and the relative error between the calculated and the true critical properties for six fluids. The calculated critical point of a fluid

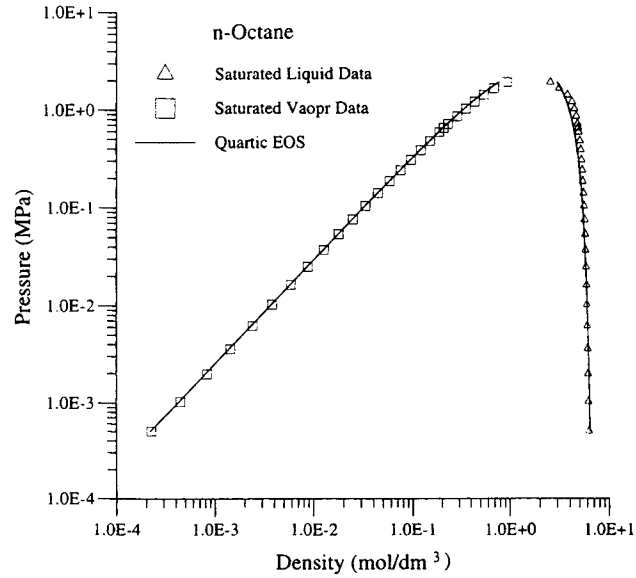

Figure 4. Saturated VLE calculations for *n*-octane.

Data of Starling (1973).

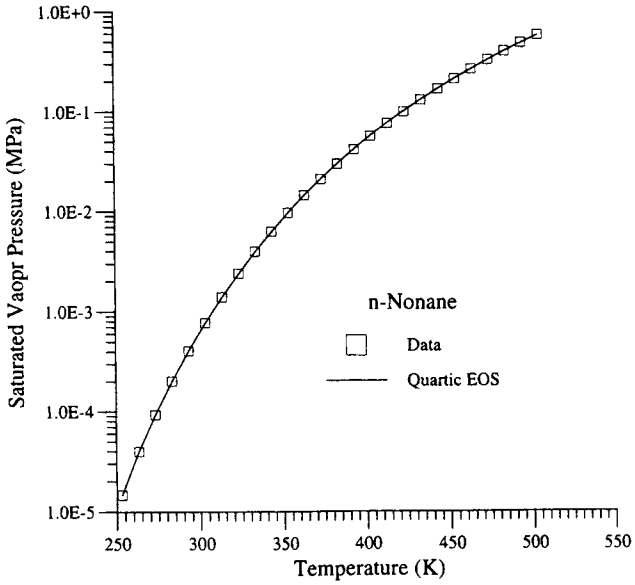

Figure 5. Vapor pressure calculations for *n*-nonane.

Data of Vargaftik (1975).

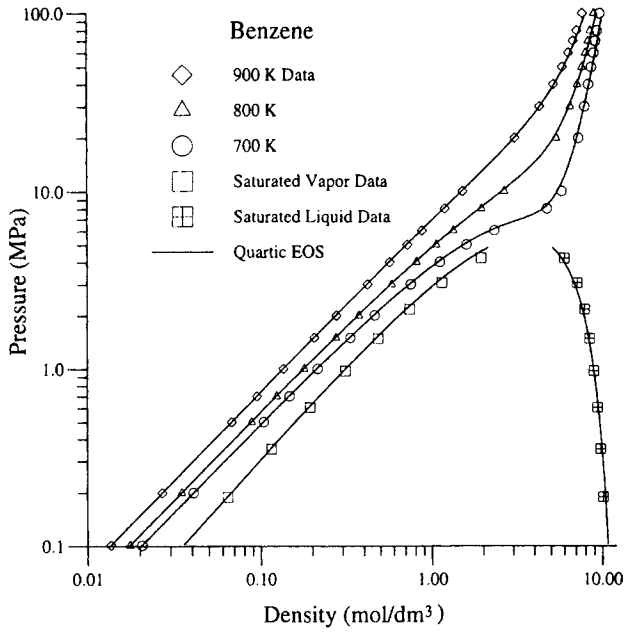

Figure 7. PVT calculations for benzene.

Smoothed data of Goodwin (1988).

was obtained by numerically determining the pressure, temperature and density where critical point conditions are satisfied by the new EOS.

Comparison with Kubic and Peng-Robinson Equations of State

The performance of the new EOS is substantially superior to those of the Peng-Robinson (PR) and Kubic's quartic equation. Both the PR and Kubic EOSs overpredict densities at high pressures and supercritical temperatures. Density calculations for argon at supercritical temperatures by all the equations of state are presented in Figure 9.

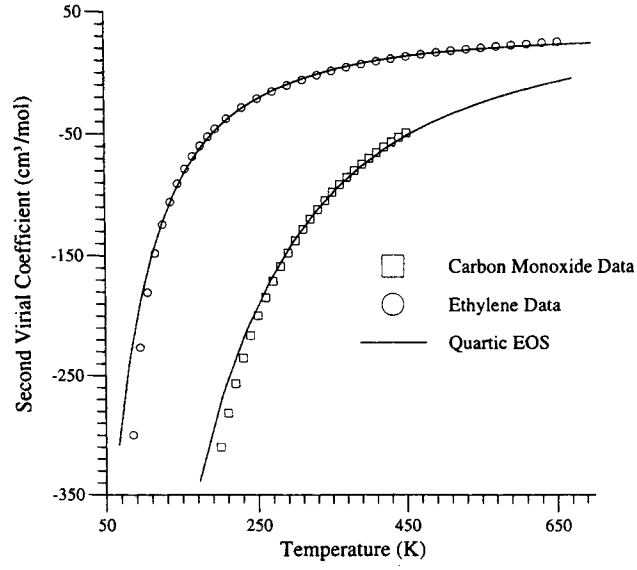

Figure 6. Second virial coefficient calculations.

Ethylene data of Jahangiri et al. (1986); carbon monoxide data of Goodwin (1985).

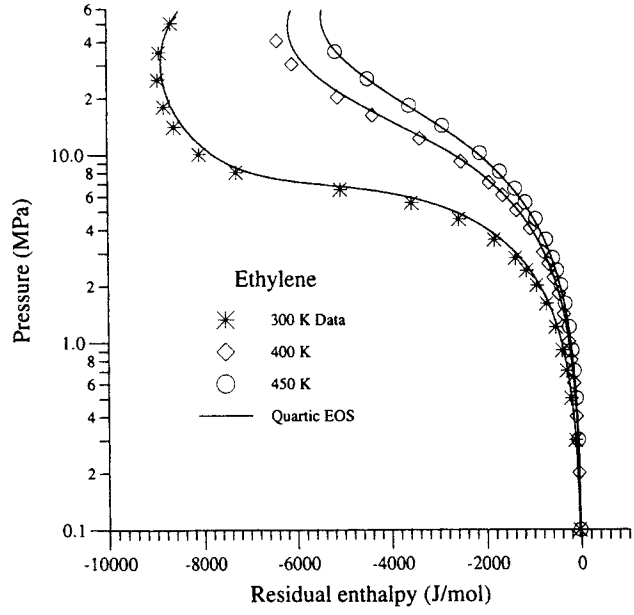

Figure 8. Residual enthalpy calculations for ethylene.

Smoothed data of Jahangiri et al. (1986).

Table 4. Calculated Critical Properties Using Quartic EOS

Fluid	Critical Pres. MPa	% Error*	Critical Temp. K	% Error*	Critical Density mol/dm³	% Error*
Argon	5.278	8.38	152.90	1.39	12.42	−6.97
Methane	5.038	9.52	193.16	1.45	9.40	−6.75
Nitrogen	3.696	9.03	128.17	1.56	10.38	−6.74
n-Butane	4.254	11.95	433.71	2.00	3.56	−9.26
CO_2	8.170	10.70	310.20	2.01	9.59	−9.95
n-Heptane	2.933	7.04	550.58	1.90	1.99	−14.12

*% Error = $((C^{calc} - C^{exp})/C^{exp})100$

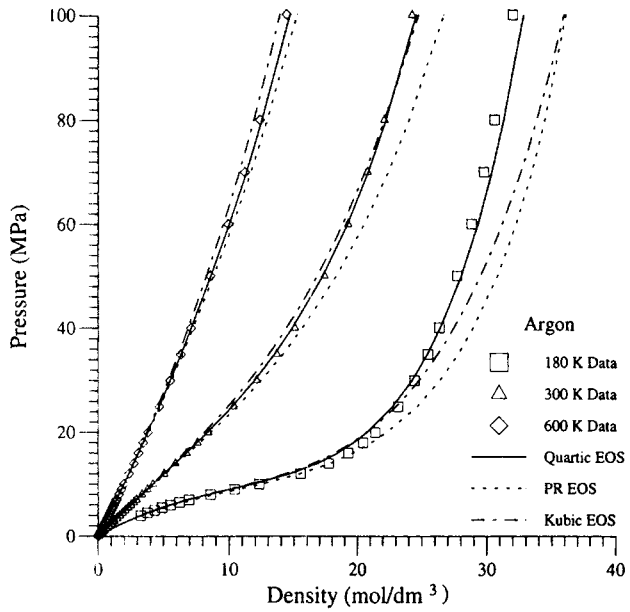

Figure 9. Pressure-density calculations for argon.

Smoothed data of Stewart and Jahangiri (1989).

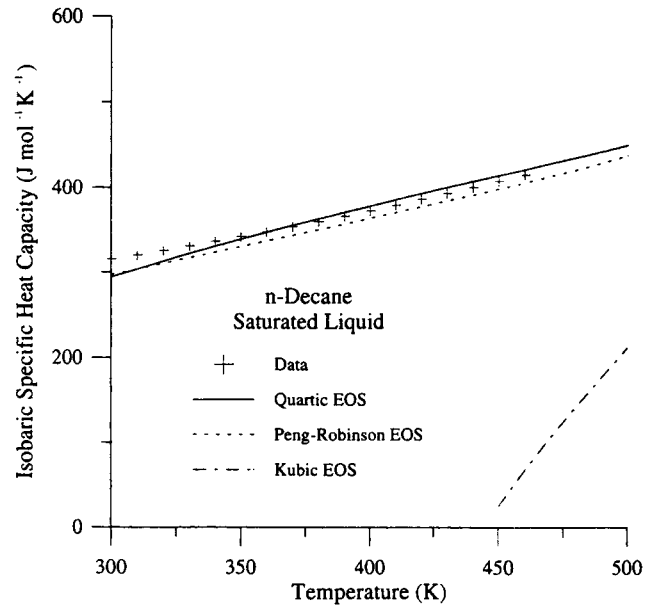

Figure 11. Comparison of specific heat calculations for *n*-decane.

Smoothed data of Rizicka et al. (1991).

At subcritical temperatures the new EOS performs better, particularly for liquid density calculations. For argon the PR equation gives too high a liquid density at lower reduced temperatures. For nonpolar hydrocarbons, as the chain length of the molecule increases from methane to *n*-octane, the performance of the PR EOS becomes comparable to that of the new EOS for orthobaric liquid densities and saturated vapor pressures. Kubic's EOS shows incorrect orthobaric liquid density calculations at low reduced temperatures, as shown in Figure 10.

The new EOS is more accurate in predicting derived thermodynamic properties such as specific heat, the Joule-Thomson coefficient and the adiabatic coefficient of bulk compressibility. The last property can be obtained from the speed of sound data for fluids. Figure 11 shows the isobaric specific heat calculations for the three EOSs for *n*-decane. At subcritical temperatures the Kubic EOS tends to predict negative values for heat capacities. Figure 12 compares the calculations of the Joule-Thomson coefficient for nitrogen; Figure 13 the speed of sound calculations in methane. The quartic

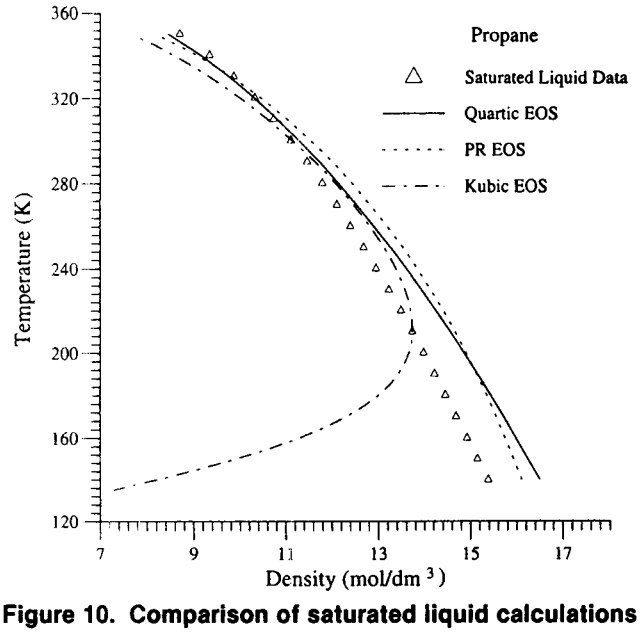

Figure 10. Comparison of saturated liquid calculations for propane.

Smoothed data of Younglove and Ely (1987).

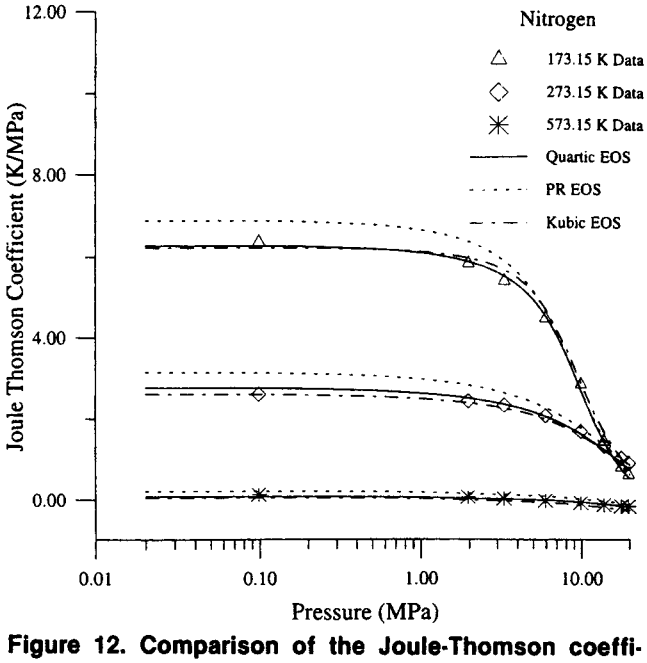

Figure 12. Comparison of the Joule-Thomson coefficient calculation of nitrogen.

Data of Roebuck and Osterberg (1935).

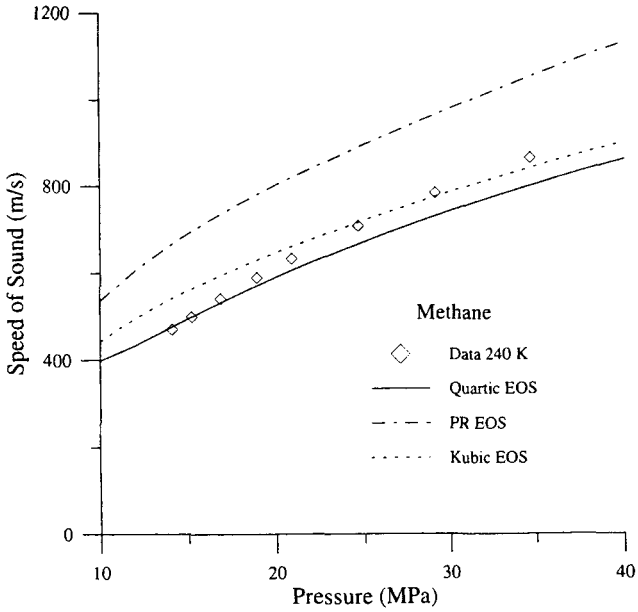

Figure 13. Comparison of speed of sound calculations for methane.

Data of Voronov et al. (1969).

EOS is better than the other two EOSs at supercritical temperatures, as seen in Figure 13. Figure 14 shows the speed of sound calculations for saturated liquid methane. Both the Peng-Robinson and the quartic EOS are unable to accurately predict the speed of sound in the saturated liquid methane. The Kubic EOS calculations show large errors in the speed of sound calculations, as seen in Figure 14. In general, the quartic EOS is better than or comparable to the Peng-Robinson EOS, and more accurate than the Kubic EOS in estimating derived thermodynamic properties.

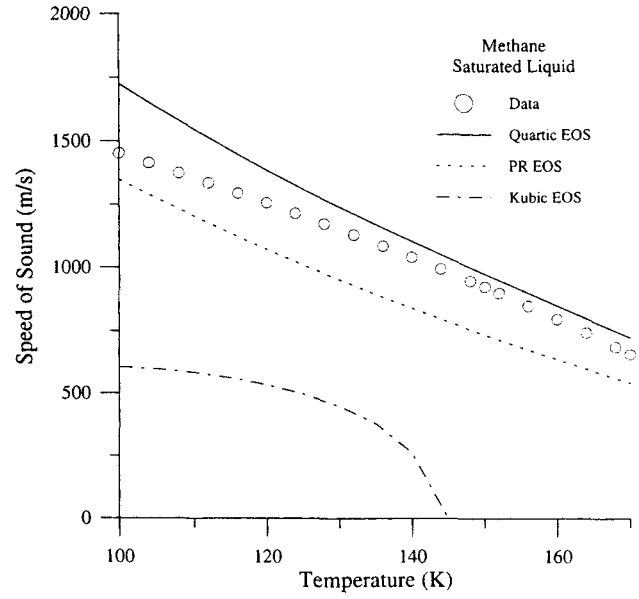

Figure 14. Comparison of the speed of sound in saturated liquid methane.

Data of Straty (1974).

Table 5. Comparison of Physical and Thermodynamic Properties: AAD Summary

Property	New Eq. AAD %	Peng-Robinson AAD %	Kubic's Quartic AAD %	Data Points
P_{sat}	1.52	1.31	118.3	409
ρ_{sv}	2.00	2.20	130.0	409
ρ_l	3.46	6.31	5.78	581
ρ_g	0.60	1.67	1.58	2,763
B_{vir}	6.09	46.46	48.04	537
H_r	4.03	22.27	13.18	1,204

Table 5 presents the absolute average deviation (AAD) for various physical properties calculated from the new EOS, the PR EOS, and the Kubic EOS. The AAD summary was generated using data from all 16 fluids used in the regressions. Table 5 shows that the new EOS is remarkably superior to the other two equations. The PR EOS is slightly better than the new EOS with regard to saturated vapor pressure representation. The new EOS, however, gives a much better overall representation of fluid behavior than either the PR or Kubic equations.

Conclusions

We have presented a quartic equation of state which models the forces between molecules correctly, unlike the cubic equations of state. The equation of state has been generalized for simple and nonpolar fluids. Only three properties of a fluid need to be specified to reproduce PVT and thermodynamic properties accurately. The identification of the roots obtained on solving the equation of state is very easy as one of them is always negative. Hence, the rules used to identify the roots of a cubic equation of state can be used with the quartic EOS. The proposed EOS is more accurate than the Peng-Robinson or the Kubic equation of state. Further work is in progress regarding 1) extending the equation of state to polar fluids and 2) testing the capabilities for representation of mixture properties by developing the proper expressions for the derived properties of mixtures based on vdW mixing rules and testing with experimental data.

Notation

a = parameter of the quartic equation of state, MPa/dm^6
b = van der Waals volume, mol/dm^3
B_{vir} = second virial coefficient
c = parameter of the quartic equation of state, MPa/dm^6
C^{exp} = experimental critical property
C^{calc} = calculated critical property
e = parameter of the quartic equation of state, mol/dm^3
H_r = residual enthalpy, J/mol
k_0, k_1 = quartic equation of state constants
P = pressure, MPa
P_{sat} = saturated vapor pressure
R = universal gas constant, (MPa·dm^3)/(mol·K)
T = temperature, K
V = molar volume, dm^3/mol
X_i = quartic equation of state constants
y = packing fraction
Z = compressibility of a fluid

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
ρ_g = single-phase gas density
ρ_l = liquid density
ρ_{sv} = saturated vapor density
ω = acentric factor

Subscripts and superscripts

c = value at the critical temperature or the critical point
calc = calculated value
exp = experimental value
g = gas, single-phase region
hs = hard sphere
l = liquid phase
r = reduced property or constant
s = saturated, two-phase envelope
sl = saturated liquid phase
sv = saturated vapor phase
v = vapor phase
* = reduced variable

Literature Cited

Alder, B. J., W. G. Hoover, and D. A. Young, "Studies in Molecular Dynamics, v. High-Density Equation of State and Entropy for Hard Disks and Spheres," *J. Chem. Phys.*, **49**, 3688 (1968).

Angus, S., B. Armstrong, and K. M. de Rueck, *International Tables of the Fluid State Carbon Dioxide*, Permagon (1976).

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

Goodwin, R. D., "Carbon Monoxide Thermophysical Properties from 68 to 1,000 K at Pressures to 100 MPa," *J. Chem. Phys. Ref. Data*, **14**, 849 (1985).

Goodwin, R. D., "Benzene Thermophysical Properties from 279 to 900 K at Pressures to 1,000 bar," *J. Chem. Phys. Ref. Data*, **17**, 1541 (1988).

Jacobsen, R. T., R. B. Stewart, and M. Jahangiri, "Thermodynamic Properties of Nitrogen from Freezing Line to 2,000 K with Pressures to 1,000 MPa," *J. Phys. Chem. Ref. Data*, **15**, 735 (1986).

Jahangiri, M., R. T. Jacobsen, and R. B. Stewart, "Thermodynamic Properties of Ethylene from the Freezing Line to 450 K at Pressures to 260 MPa," *J. Phys. Chem. Ref. Data*, **15**, 593 (1986).

Kubic, W. L., Jr., "Application of the Quartic Hard Chain Equation of State to Polymer Mixtures," *Fluid Phase Equilib.*, **31**, 56 (1986a).

Kubic, W. L., Jr., "A Quartic Hard Chain Equation of State for Normal Fluids," *Fluid Phase Equilib.*, **31**, 35 (1986b).

Nezbeda, I., and K. Aim, "Perturbed Hard-Sphere Equations of State of Real Fluids: II. Effective Hard-Sphere Diameters and Residual Properties," *Fluid Phase Equilib.*, **17** (1984).

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

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

Reid, R. C., J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw Hill, New York (1987).

Roebuck, J. R., and H. Osterberg, "The Joule-Thomson Effect in Nitrogen," *Phys. Rev.*, **48**, 450 (1935).

Rowlinson, J. S., and F. L. Swinton, *Liquids and Liquid Mixtures*, Butterworths Press (1982).

Ruzicka, V., M. Zabransky, and V. Majer, "Heat Capacities of Organic Compounds in the Liquid State II. c_1 to c_{18} n-Alkanes," *J. Chem. Phys. Ref. Data*, **20**, 405 (1991).

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

Soave, G., "A Non-Cubic Equation of State for PVT and Phase Equilibrium Calculations (Pure Compounds)," *Fluid Phase Equilibria*, **56**, 39 (1990).

Starling, K. E., *Fluid Thermodynamic Properties for Light Petroleum Systems*, Gulf Publishing (1973).

Stewart, R. B., and R. T. Jacobsen, "Thermodynamic Properties of Argon from Triple Point to 1,200 K with Pressures to 1,000 MPa," *J. Phys. Chem. Ref. Data*, **18**, 640 (1989).

Straty, G. C., "Velocity of Sound in Dense Fluid Methane," *Cryogenics*, 367 (1974).

van der Waals, J. D., "Over de Continuiteit van den Gas- en Vloeistoftestand," PhD Thesis, University of Leiden (1873).

Vargaftik, N. B., *Tables on the Thermophysical Properties of Liquids and Gases*, Hemisphere (1975).

Voronov, F. F., L. L. Pitaevskaya, and A. V. Bilevich, "Rate of Propogation of Ultrasound in Nitrogen at Pressures Up to 4 kbar and Temperatures in the Range 25–175°C," *Russ. J. Phys. Chem.*, **43**, 321 (1969).

Younglove, B. A., and J. F. Ely, "Thermophysical Properties of Fluids: II. Methane, Ethane, Propane, Isobutane and Normal Butane," *J. Phys. Chem. Ref. Data*, **16**, 577 (1987).

Manuscript received Aug. 24, 1992, and revision received May 21, 1993.