# Toward a Molecular Equation of State for Real Materials

An equation of state based on molecular interaction concepts has been developed. This equation contains three parameters corresponding to a square-well potential characterized by a molecular radius, a well depth, and a well width. It is obtained by perturbation theory with a hard sphere reference system and, with appropriate choice of parameters, yields good agreement with experimental PVT properties of 12 nonaqueous substances. The agreement is in all cases far superior to that obtained with the usual implementation of the Peng-Robinson equation, and is better for most cases than that obtained by optimizing the parameters in the Peng-Robinson equation.

For water, neither the reported equation nor the Peng-Robinson equation is in agreement with experiments. To obtain acceptable agreement, it is necessary to employ an equation that treats the particular geometry of attractive interactions characteristic of water. The Fleming-Gibbs lattice equation of state for water does give reasonable agreement with PVT properties.

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## Introduction

Attempts to determine equations of state of fluids in terms of molecular interactions date back to the classic work of van der Waals (1890, 1899). The van der Waals equation is the simplest equation that gives a qualitatively correct account of liquid and vapor states. It is easy to manipulate, and never predicts physically absurd results. Its simple form, and the physically appealing interpretation of its terms, have made it the basis for the many empirical equations that have attracted much interest in the engineering literature (Redlich and Kwong, 1949; Martin, 1967, 1979; Usdin and McAuliff, 1976; Lee and Edmister, 1971; Soave, 1972; Fuller, 1971; Peng and Robinson, 1976; Schmidt and Wenzel, 1980; Patel and Teja, 1982; Coats and Smart, 1982).

The important recognition in obtaining an equation of state that properly reflects the molecular interactions is that the molecular interaction potential consists of two distinct parts. These parts, first recognized by van der Waals, are a harsh, short-range repulsion along with a relatively weak, long-range attraction. Using this separation, van der Waals derived his equation as one describing hard spheres interacting with weak long-range attraction. His ideas were largely intuitive, and it was not until the 1960's that Kac et al. (1963 a, b; 1964) showed that the van der Waals equation is exact for a one-dimensional system of hard rods interacting with an infinistesimally weak but infinitely long-range attraction. Kac's ideas were extended to three dimensions by van Kampen (1964), and by Lebowitz and Penrose (1966), when it was shown that an equation much like that of van der Waals was obtained for the same sort of long-range interactions. However, the van der Waals form for the repulsive term was shown to be incorrect, except in one dimension.

In van der Waals' time, of course, the correct hard sphere equation of state was not known. It has been only in the last quarter-century, with the advent of computer simulations (Metropolis et al., 1953; Alder and Wainwright, 1957, 1959; Wood and Jacobson, 1957; Hoover and Ree, 1967, 1968) of the hard sphere fluid and of the analytic solution of the Percus-Yevick (1958) integral equation for this system by Wertheim (1963, 1964) and Thiele (1963), that this equation of state has been well determined. Both the virial and compressibility equations of state obtained from the Percus-Yevick solution for hard spheres are in excellent agreement with the machine simulations. Carnahan and Starling (1969) derived an equation that interpolates between the Percus-Yevick virial and compressibility equations of state and agrees well with all seven of the known virial coeffi-

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cients. Their equation has a simple functional form and is virtually indistinguishable from the simulation results.

With the properties of the hard sphere fluid well known, the possibility of obtaining the equation of state of a system by a perturbation expansion, with the hard sphere fluid as a reference system, became possible. Using the Carnahan-Starling equation and the Percus-Yevick pair correlation function, Barker and Henderson (1967 a, b) were able to derive accurate equations of state for molecular interaction potentials possessing both attractive and repulsive parts. In particular, they considered the square-well and Lennard-Jones 6-12 fluids. Variations on these perturbation calculations were presented by Andersen, Chandler, and Weeks with good success (Andersen and Chandler, 1970, 1972a, b; Andersen et al. 1971a, b, 1972; Weeks and Chandler, 1970).

Recently, progress has been made on molecular theories for fluids containing nonspherical molecules (see the review by Gubbins, 1983). These theories have been of two types, one based on perturbation theory about a reference system of spherical molecules (Gubbins, 1983; Williams et al., 1984a, b; Nezbeda, 1985; Johnson and Shaw, 1985), and the other based on perturbation theory about a system of nonspherical reference molecules (Gubbins, 1983; Fischer and Lago, 1983; Wertheim, 1984a, b). These efforts have achieved varying degrees of success, often running into convergence problems.

While the molecular theory was flourishing, research on empirical equations of state continued. Most of these equations utilize the van der Waals repulsive term with different modifications of the attractive contribution. However, Carnahan and Starling (1972) utilized their hard-sphere repulsive term along with either the van der Waals or Redlich-Kwong attractive terms, with significant improvement over the van der Waals-based equations. For all of these empirical equations, the parameters were determined by fixing the critical pressure and temperature. Some of these (Soave, 1972; Peng and Robinson, 1976; and Patel and Teja, 1982) also fix the acentric factor (Pitzer, 1955; Pitzer et al. 1955) and therefore yield very good vapor pressure curves although, as we shall see later, this does not necessarily guarantee good agreement over the full phase diagram.

Fixing the critical properties is actually a weakness of the empirical equations because they, like all van der Waals-type equations (including thde perturbation theoretic equations as well), yield classical behavior in the critical region. As is well known, the critical region in real fluids is described by singularities characterized by a set of nonclassical critical exponents (Widom, 1965; Kadanoff, 1966; Stanley, 1971). The origin of this behavior is now understood as a result of the work by Wilson and others formulating the critical phase transition in terms of the so-called renormalization group theory (Wilson, 1971a, b, 1983; Wilson and Fisher, 1972; Ma, 1976). In order to properly describe the behavior of fluids in the critical region, scaling equations of state (Schofield, 1969; Schofield et al., 1969; Levelt-Sengers, 1983) have been developed. These equations are very accurate in the critical region, and are recommended for calculations of thermodynamic properties in this part of the phase diagram. It makes little sense, therefore, to determine the parameters in a classical equation of state by fixing the critical properties when the equation is known to yield the wrong shape of the thermodynamic surface in the critical region.

In this work we employ a classical equation of state based on the square-well potential and perturbation theory. We employ the square-well potential because it is simple in form, while possessing the essential properties of real potentials, and its properties are well known as the result of molecular dynamics (Alder et al., 1972) and Monte Carlo simulation (Henderson et al., 1976, 1980). The use of the square-well system as a model for real fluids is reinforced by the work of deLonngi and del Rio (1983), who employed the square-well potential as the reference system for a perturbation theory.

We will see that the equation of state based on the square-well potential, with molecular diameter, well depth, and well width chosen by least-squares fit to the data, gives a good description of the PVT properties of all simple fluids (nearly spherical molecules) and some not so simple fluids. For all materials considered, the molecular equation of state gives significantly better agreement with the PVT properties over a large region of the phase diagram than does the most recently proposed three-parameter empirical equation of state, the Peng-Robinson equation. However, if the parameters $T_c$, $P_c$, and $\omega$ (acentric factor) are determined by least-squares fit instead of being set to their experimental values, as is suggested by the discussion above concerning the critical region, then the Peng-Robinson equation will, as seen below, give improved agreement with PVT properties, but still not as good as the molecular equation in most cases.

For the case of water, neither the molecular equation nor the optimized Peng-Robinson equation give acceptable agreement with the experimental properties. This is not too surprising since the anomalous properties of water are well known. It is generally accepted (Eisenberg and Kauzmann, 1969; Gibbs et al., 1973) that these anomalous properties result from the propensity of water to form hydrogen bonds with fourfold coordination. To show that, unlike simple fluids where the repulsive forces dominate, for water the geometry of attractive forces is the most important factor, we have compared the PVT properties of water with the Fleming-Gibbs (1974a, b) lattice model. We find that this model, with its naive treatment of intermolecular repulsions, gives a better description of the properties of water than does either the square-well based or the Peng-Robinson equation of state.

## Formulation

In this section we describe our model equation of state. We assume that the molecules of the fluid interact with a pairwise-additive potential that can be approximated as a square well. This potential is defined by

$$u(r) = \begin{matrix} \infty & r < \sigma \\ -\epsilon & \sigma < r < \lambda\sigma, \\ 0 & r > \lambda\sigma \end{matrix} \tag{1}$$

where $\sigma$ is the hard-core diameter, $\epsilon$ is the net strength of attraction and, $\lambda\sigma$ is the range of attraction. The use of a square well as an approximation to a realistic potential was discussed by deLonngi and del Rio (1983). The parameters $\sigma$, $\epsilon$, and $\lambda$ will be assumed to be adjustable, to be determined by least-squares fit.

To calculate the thermodynamic properties of a square-well fluid we utilize perturbation theory (Barker and Henderson, 1967a, b; Andersen and Chandler, 1970, 1972a, b; Andersen et al., 1971a, b, 1972; Weeks and Chandler, 1970), which has been very successful in reproducing the thermodynamic properties of fluids with known potentials. Following Barker and Henderson (1967, 1976), we write the Helmholtz free energy of the system as

$$\beta F = \sum_{n=0}^{\infty} (\beta\epsilon)^n \beta F_n, \tag{2}$$

where $\beta = 1/kT$. In this expansion, $F_0$ is the free energy of the hard sphere fluid with diameter $\sigma$. $F_1$, the first-order term, is given by

$$\frac{\beta F_1}{N} = -2\pi n \int_{\sigma}^{\lambda\sigma} dr r^2 g_0(r), \tag{3}$$

where $g_0(r)$ is the pair correlation function of the hard sphere fluid, and $n = N/V$ is the number density of the fluid. The second-order term, $F_2$, has been written by Barker and Henderson (1972, 1976) as

$$\frac{\beta F_2}{N} = -\pi n \int_{\sigma}^{\lambda\sigma} dr r^2 g_0(r) + \int_{\sigma}^{\lambda\sigma} dr_1 \int_{\sigma}^{\lambda\sigma} dr_2 F(r_1, r_2), \tag{4}$$

where $F(r_1, r_2)$ is a function of three- and four-particle correlation functions of the hard sphere fluid. Barker and Henderson calculated $F(r_1, r_2)$ by Monte Carlo calculations and fitted it to an expansion in a set of basis functions. We could use this expansion, but for simplicity we will employ the local compressibility approximation employed in the original papers by Barker and Henderson (1967a, b). In this approximation we take

$$\frac{\beta F_2}{N} = -\pi n \int_{\sigma}^{\lambda\sigma} dr r^2 \left(\frac{\partial n g_0(r)}{\partial \beta p_0}\right), \tag{5}$$

where the derivative is evaluated for the hard sphere reference system. We use the chain rule to evaluate the derivative in Eq. 5 to obtain

$$\begin{aligned}\frac{\beta F_2}{N} &= -\pi n \left(\frac{\partial n}{\partial \beta p_0}\right) \frac{\partial}{\partial n}\left[n \int_{\sigma}^{\lambda\sigma} dr r^2 g_0(r)\right], \\ &= \frac{1}{2} \frac{\partial n}{\partial \beta p_0} n \frac{\partial}{\partial n} \frac{\beta F_1}{N}\end{aligned} \tag{6}$$

We take the hard sphere free energy to be (de Lonngi and del Rio, 1983)

$$\beta f_0 \equiv \beta \frac{F_0}{N} = \ln \frac{6\lambda_T^3}{\pi\sigma^3} + \ln \eta - 1 + \eta \frac{4 - 3\eta}{(1 - \eta)^2}, \tag{7}$$

where $\eta = \frac{1}{6} \pi n \sigma^3$ is a dimensionless density (i.e., volume fraction) and $\lambda_T = h/(2\pi m k T)^{1/2}$ is the thermal wavelength. The first-order term can be written as

$$\beta f_1 \equiv \beta \frac{F_1}{N} = -\eta \Delta(\eta), \tag{8}$$

where

$$\Delta(\eta) = 12 \int_{1}^{\lambda} dx x^2 g_0(\sigma x).$$

Following Barker and Henderson, we utilize the Percus-Yevick (1958) compressibility equation of state

$$\frac{\beta p}{n} = \frac{1 + \eta + \eta^2}{(1 - \eta)^3}, \tag{9}$$

to evaluate the inverse compressibility in Eq. 6. Thus, we finally obtain the approximate free energy,

$$\begin{aligned}\beta f \equiv \frac{\beta F}{N} &= \ln \frac{6\lambda_T^3}{\pi\sigma^3} + \ln \eta - 1 + \eta \frac{4 - 3\eta}{(1 - \eta)^3} \\ &\quad - \left[\beta\epsilon + \frac{1}{2} (\beta\epsilon)^2 \frac{(1 - \eta)^4}{1 + 4\eta + 4\eta^2} \eta \frac{\partial}{\partial \eta}\right] \eta \Delta(\eta).\end{aligned} \tag{10}$$

In principle, we could use the Carnahan-Starling (1969) equation to evaluate the derivative, but Eq. 10 gives better agreement with Monte Carlo data.

Thus, the determination of our equation of state is reduced to determination of the quantity $\Delta$. We will approximate $g_0$ by the Percus-Yevick analytic solution. Using the analytic forms obtained by Smith and Henderson (1970) and assuming $\lambda < 2$, we obtain for $\Delta(\eta)$:

$$\begin{aligned}\Delta(\eta) &= 12 \int_{1}^{\lambda} \sum_{\alpha=0}^{2} a_0^{\alpha} e^{t_{\alpha}(x-1)} x dx \\ &= 12 \sum_{\alpha=0}^{2} a_0^{\alpha} \left[\left(\frac{\lambda}{t_{\alpha}} - \frac{1}{t_{\alpha}^2}\right) e^{t_{\alpha}(\lambda-1)} + \frac{1}{t_{\alpha}^2} - \frac{1}{t_{\alpha}}\right],\end{aligned} \tag{11}$$

where

$$t_{\alpha} = [-2\eta + (2\eta \mathscr{f})^{1/3}(y + e^{2\pi\alpha i/3} + y - e^{-2\pi\alpha i/3})]/(1 - \eta),$$

with

$$\mathscr{f} = 3 + 3\eta - \eta^2$$

and

$$y_{\pm} = [1 \pm (1 + 2(\eta^2/\mathscr{f})^2)^{1/2}]^{1/3},$$

is a solution of the cubic polynomial equation

$$\begin{aligned}S(t_{\alpha}) = (1 - \eta)^2 t_{\alpha}^3 + 6\eta(1 - \eta) t_{\alpha}^2 + 18\eta^2 t_{\alpha} \\ - 12\eta(1 + 2\eta) = 0.\end{aligned} \tag{12}$$

The coefficients $a_0^{\alpha}$ are given by

$$a_0^{\alpha} = \frac{t_{\alpha} L(t_{\alpha})}{S_1(t_{\alpha})}, \tag{13}$$

where

$$L(t) = (1 + \tfrac{1}{2}\eta)t + 1 + 2\eta$$

and

$$S_1(t) = S'(t).$$

Equation 11 is the desired analytic expression for $\Delta(\eta)$. It is cumbersome and requires complex arithmetic (all adding up to a real result, of course). To avoid the complex arithmetic, we will fit the result of Eq. 11 to a real function of the form suggested by Barker and Henderson (1976),

$$\Delta(\eta) = \frac{6\lambda C_1}{\pi\sqrt{2}} - \frac{C_1}{\eta}\left[1 - \exp\left(\frac{-6\lambda\eta}{\pi\sqrt{2} - 6\eta}\right)\right] - \frac{6}{\pi}P_1 - \left(\frac{6}{\pi}\right)^2 Q_1\eta. \tag{14}$$

$C_1$, $P_1$, and $Q_1$ were fitted to polynomials as a function of $\lambda$, yielding

$$C_1 = 189.20237\lambda - 252.91144\lambda^2 + 81.826210\lambda^3, \tag{15a}$$

$$P_1 = -0.37394704\lambda + 4.312674094\lambda^2 - 4.162936468\lambda^3, \tag{15b}$$

$$Q_1 = -14.397069\lambda + 14.096318\lambda^2 - 3.7110026\lambda^3. \tag{15c}$$

The pressure and chemical potential are readily obtained by differentiating Eq. 10. Thus, we have

$$\frac{\beta p}{n} = \eta\frac{\partial \beta f}{\partial \eta} = \frac{\beta p_0}{n} + \beta\epsilon\frac{\beta p_1}{n} + (\beta\epsilon)^2\frac{\beta p_2}{n}, \tag{16}$$

where

$$\frac{\beta p_0}{n} = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3},$$

$$\frac{\beta p_1}{n} = \eta[\Delta(\eta) + \eta\Delta'(\eta)]$$

and

$$\frac{\beta p_2}{n} = -\frac{1}{2}\eta\left[\frac{(1-\eta)^3(1 - 5\eta - 20\eta^2 - 12\eta^3)}{(1 + 4\eta + 4\eta^2)^2}\Delta(\eta) + \frac{(1-\eta)^3(3 + \eta - 20\eta^2 - 20\eta^3)\eta}{(1 + 4\eta + 4\eta^2)^2}\Delta'(\eta) + \frac{(1-\eta)^4\eta^2}{1 + 4\eta + 4\eta^2}\Delta''(\eta)\right]$$

Likewise, for the chemical potential

$$\beta\mu = \frac{\partial\beta\eta f}{\partial\eta} = \beta\mu_0 + \beta\epsilon\beta\mu_1 + (\beta\epsilon)^2\beta\mu_2, \tag{17}$$

where

$$\beta\mu_0 = \ln\frac{6\lambda_t^3}{\pi\sigma^3} + \ln\eta + \eta\frac{8 - 9\eta + 3\eta^2}{(1-\eta)^3},$$

$$\beta\mu_1 = -\eta[2\Delta(\eta) + \eta\Delta'(\eta)],$$

$$\beta\mu_2 = -\eta\left[\frac{(1-\eta)^3(1 - \eta - 10\eta^2 - 8\eta^3)}{(1 + 4\eta + 4\eta^2)^2}\Delta(\eta) + \frac{(1-\eta)^3(2 + 2\eta - 10\eta^2 - 12\eta^3)\eta}{(1 + 4\eta + 4\eta^2)^2}\Delta'(\eta) + \frac{1}{2}\frac{(1-\eta)^4\eta^2}{(1 + 4\eta + 4\eta^2)}\Delta''(\eta)\right].$$

This completes the formulation of our equation of state, which we designate the PT equation.

## Other Equations of State

In this section we discuss two equations of state from the literature, one empirical and one theoretical, whose accuracy will be compared with experiments and the PT equation.

### *Peng-Robinson equation*

The Peng-Robinson (PR) equation of state was originally proposed as an improvement over the Redlich-Kwong (RK) and Soave-Redlich-Kwong (SRK) equations of state. The PR equation gave much better values of coexisting liquid and vapor densities than either the RK or SRK equations. We write the PR equation in a form that facilitates comparison with the PT equation.

$$\frac{\beta p}{n} = \frac{1}{1 - 4\eta} - \frac{4\eta\beta a(T)}{(1 + 4\eta) + 4\eta(1 - 4\eta)}, \tag{18}$$

where

$$\eta = \tfrac{1}{4}nb,$$

$$a(T) = a_c\alpha(T/T_c),$$

and

$$\alpha(t) = (1 + \kappa(1 - \sqrt{t}))^2.$$

This equation contains three parameters, $b$, $a_c$, and $\kappa$. Thus, it is well suited for comparison with our three-parameter square-well equation of state. These parameters are usually expressed in terms of the corresponding critical pressure and temperature and acentric factor, $P_c$, $T_c$, and $\omega$, respectively. The relationships are given numerically by

$$\beta_c p_c b = 0.077196 \tag{19a}$$

$$\beta_c a_c = 5.87736 \tag{19b}$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2. \tag{19c}$$

Equations 19a and 19b are determined by the form of Eq. 18, while Eq. 19c was obtained by fitting $\kappa$ to a quadratic function of $\omega$.

The PR equation can be expanded in a form similar to Eq. 16,

$$\frac{\beta p}{n} = \frac{\beta p_0}{n} + \frac{\beta p_{1/2}}{n}(\beta a_c)^{1/2} + \frac{\beta p_1}{n}(\beta a_c), \tag{20}$$

where

$$\frac{\beta p_0}{n} = \frac{1}{1 - 4\eta} - \frac{4\eta\kappa^2\beta_c a_c}{1 + 4\eta + 4\eta(1 - 4\eta)},$$

$$\frac{\beta p_{1/2}}{n} = \frac{8\eta(\beta_c a_c)^{1/2}\kappa(1 + \kappa)}{1 + 4\eta + 4\eta(1 - 4\eta)},$$

and

$$\frac{\beta p_1}{n} = -\frac{4\eta(1+\kappa)^2}{1+4\eta+4\eta(1-4\eta)}.$$

We see that $p_1$ plays the role of an attractive contribution to the pressure, while the other two terms

$$\frac{\beta p_0}{n} + \frac{\beta p_{1/2}}{n}(\beta a_c)^{1/2} = \frac{1}{1-4\eta} + \frac{4\eta\kappa\beta_c a_c[2(1+\kappa)\sqrt{T_c/T} - \kappa]}{1+4\eta+4\eta(1-4\eta)} \quad (21)$$

combine to form a temperature-dependent repulsive contribution to the pressure. This gives insight into why the PR equation has had some success in comparison with the properties of real materials. A similar observation applies to the SRK equation.

Expressions for the free energy and chemical potential corresponding to the PR equation can readily be obtained from Eq. 18 by integration. These are

$$\beta\mu = \ln\frac{4\lambda_T^3}{b} - 1 + \ln\frac{\eta}{1-4\eta} + \frac{1}{1+4\eta} + \beta a(T)\left[\sqrt{2}\ln\left(\frac{4\eta-1+\sqrt{2}}{4\eta-1-\sqrt{2}}\right) - \left(\frac{4\eta\beta a}{1+8\eta-16\eta^2}\right)\right]. \quad (23)$$

### *Fleming-Gibbs equation*

The Fleming-Gibbs (1974a, b) or FG equation of state was originally introduced as part of a theory for the structure and thermodynamics of liquid water. This theory is basically a lattice gas model with orientational dependent interactions. This model was seen to give reasonable agreement with the properties of water in the normal liquid range (0–100°C, 1 atm [101.3 kPa]), in addition to yielding a density maximum as a function of temperature. The free energy per molecule for the Fleming-Gibbs model is given by

$$\beta f = \ln\frac{n_L}{Z} + \left(\frac{1}{n_L} - 1\right)\ln(1-n_L) - n_L B_2 - \frac{1}{2}n_L^2 B_3 - \frac{1}{3}N_L^3 B_4 \quad (24)$$

where

$$\bar{Z} = \frac{v_c}{\lambda_T^3},$$

$$B_2 = 4(\tfrac{5}{8}\beta\epsilon_1 + \tfrac{1}{4}\beta\epsilon_2 + \tfrac{1}{8}\beta E) + 2[\tfrac{5}{8}(\beta\epsilon_1)^2 + \tfrac{1}{4}(\beta\epsilon_2)^2 + \tfrac{1}{8}(\beta E)^2],$$

$$B_3 = -8[\tfrac{1}{8}(\beta\epsilon_1 + \beta\epsilon_2)^2 + \tfrac{1}{8}(\tfrac{3}{2}\beta\epsilon_1 + \beta E)^2]$$

and

$$B_4 = 6(\tfrac{5}{8}\beta\epsilon_1 + \tfrac{1}{4}\beta\epsilon_2 + \tfrac{1}{8}\beta E)^2.$$

In this equation $n_L$ is the number of molecules per lattice site and $v_c$ is the volume of a unit cell of the body-centered cubic lattice. $E$ is the hydrogen bond energy, $\epsilon_1$ is a (presumably) weak attractive energy, and $\epsilon_2$ is an "anti-hydrogen bond" repulsion. The number density $n$ is related to the lattice density $n_L$ by

$$n = n_L v_c \quad (25)$$

For the body-centered cubic lattice the unit cell volume is related to the nearest neighbor distance, $R_{NN}$, according to

$$v_c = \frac{4}{3\sqrt{3}} R_{NN}^3. \quad (26)$$

The equation of state obtained by differentiation of Eq. 24 is

$$\frac{p\beta}{n} = -\frac{1}{n_L}\ln(1-n_L) - n_L B_2 - n_L^2 B_3 - n_L^3 B_4. \quad (27)$$

Likewise, the chemical potential is given by

$$\beta\mu = \ln\frac{n_L}{\bar{Z}(1-n_L)} - 2n_L B_2 - \frac{3}{2}n_L^2 B_3 - \frac{4}{3}n_L^3 B_4. \quad (28)$$

In the following section these two equations will be used in comparison with Eq. 16 and experimental results.

## Comparison with Experiments

In this section we compare the different equations of state with the PVT properties of real materials. Before doing so, we will check the accuracy of Eq. 16 as a square-well equation of state. Figure 1 shows a comparison of Eq. 16 with the pressure obtained from the Monte Carlo (MC) simulations of Henderson

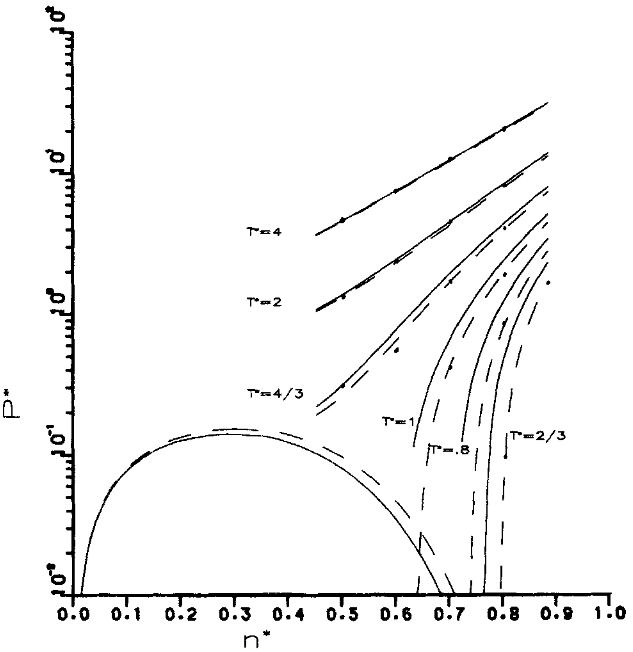

**Figure 1. Equation 16 as EOS for square-well fluid.**

Comparison with Monte Carlo data of Henderson et al. (1976, 1980)

——— Eq. 16, approx.; — — — Eq. 16, optimized.

$P^* = P\sigma^3/\epsilon$; $n^* = n\sigma^3$; $T^* = kT/\epsilon$.

Table 1. Errors Obtained with Equations of State when Compared with Different Materials

| Substance | No. of Points | Mean Error, % |  |  | RMS Error, % |  |  | Substance Data Source |
|---|---|---|---|---|---|---|---|---|
|  |  | UPR | OPR | PT | UPR | OPR | PT |  |
| Ethane | 82 | 4.52 | 3.59 | 1.78 | 7.86 | 4.89 | 2.93 | Sage et al. (1937a) |
| $H_2S$ | 68 | 45.9 | 4.15 | 1.95 | 263 | 6.52 | 3.15 | Reamer et al. (1950 |
| Nonane | 25 | 343 | 12.0 | 3.19 | 577 | 14.2 | 4.53 | Carmichael et al. (1953) |
| Nitrogen | 92 | 110 | 5.42 | 5.28 | 427 | 7.58 | 6.95 | Marshall (1976) |
| Propane | 79 | 18.1 | 5.24 | 4.51 | 28.1 | 7.50 | 7.38 | Marshall (1976) |
| Argon | 92 | 219 | 6.95 | 6.62 | 811 | 10.8 | 8.83 | Marshall (1976) |
| Hexane | 19 | 29.7 | 11.6 | 7.23 | 55.0 | 13.0 | 9.51 | Stewart et al. (1954) |
| $CO_2$ | 92 | 40.8 | 4.78 | 6.13 | 160 | 6.74 | 9.62 | Stewart et al. (1954) |
| Pentane | 20 | 422 | 28.7 | 7.97 | 1240 | 35.2 | 10.8 | Sage & Lacey (1942) |
| Butane | 92 | 43.8 | 7.43 | 7.71 | 102 | 11.0 | 10.8 | Sage et al. (1973b), Kay (1940) |
| Octane | 12 | 377 | 14.4 | 9.53 | 590 | 15.5 | 11.0 | Felsing & Watson (1942) |
| Methane | 92 | 424 | 9.23 | 8.52 | 2311 | 12.6 | 18.0 | Keenan et al. (1969) |

UPR, Usual implementation of Peng-Robinson EOS; OPR, Optimized-parameter Peng-Robinson EOS; PT, This work EOS.

et al. (1976, 1980) for 108 square wells having $\lambda = 1.5$. The agreement with the simulations is excellent for all but the lowest temperatures where $\beta\epsilon \geq 1$. The average error for the three high-temperature isotherms is about 6% (closer to 3%, of the order of the accuracy of the Monte Carlo calculations, if the point at $n\sigma^3 = 0.6$ and $\beta\epsilon = 0.75$ is ignored). The corresponding rms errors are 12 and 5%, respectively.

To show that the errors in Eq. 16 can be compensated for by varying the parameters, we have determined the best fit values of the square-well parameters for the MC data. Also shown in Figure 1 is this fit obtained from Eq. 16 with $\lambda = 1.46$ and replacing $\epsilon$ by $\epsilon' = 1.07\ \epsilon$. This fit gives an average error of about 4% (again, about 3% if the one point is ignored). The corresponding RMS errors are about 6 and 5%, respectively. Thus, Eq. 16 is accurate for high temperatures, as it should be, and can be made more accurate at low temperatures by slightly adjusting the parameters. Therefore it should be well suited for comparison with the PVT properties of real materials.

The critical constants obtained are as follows:

|  | Straight Fit | Mol. Dynam. Simulation | Optimized Fit |
|---|---|---|---|
| $T_c^* = (\beta_c\epsilon)^{-1} =$ | 1.32 | 1.26 | 1.34 |
| $n_c^* = n_c\sigma^3 =$ | 0.286 | 0.33 | 0.30 |
| $P_c^* = P_c\sigma^3 =$ | 0.139 | 0.12 | 0.151 |
| $Z_c = P_c\beta_c/n_c =$ | 0.369 | 0.287 | 0.377 |

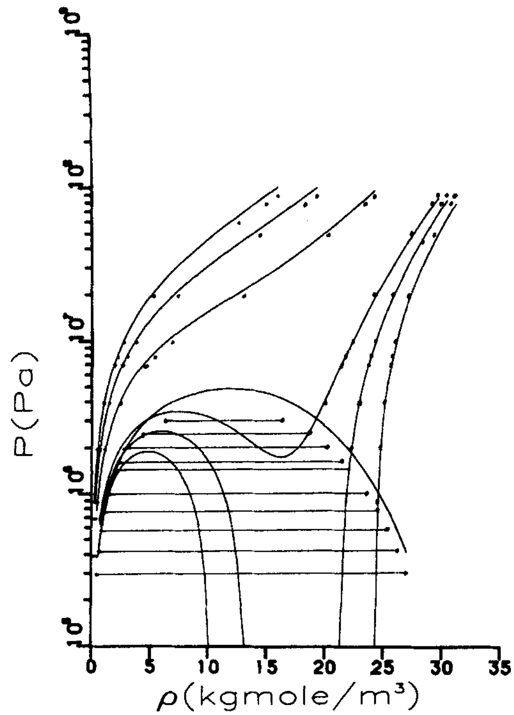

Figure 2. Pressure-density phase diagram for nitrogen calculated from PT EOS.

Comparison with experimental coexistence data and isotherms at 100, 110, 120, 200, 300, 400 K reported by Marshall (1976).

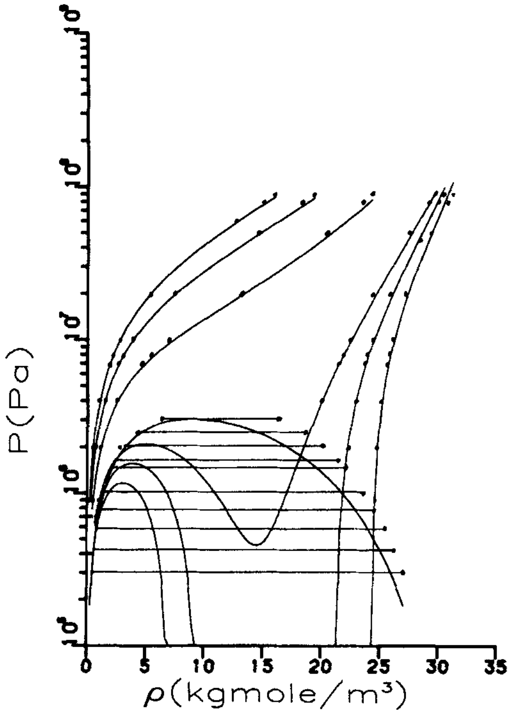

Figure 3. Pressure-density phase diagram for nitrogen calculated from OPR EOS.

Comparison as in Fig. 2.

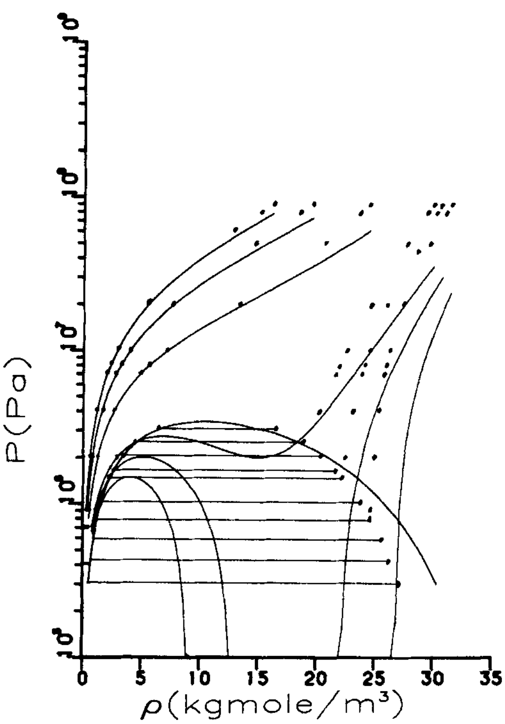

**Figure 4. Pressure-density phase diagram for nitrogen calculated from UPR EOS.**
Comparison as in Fig. 2.

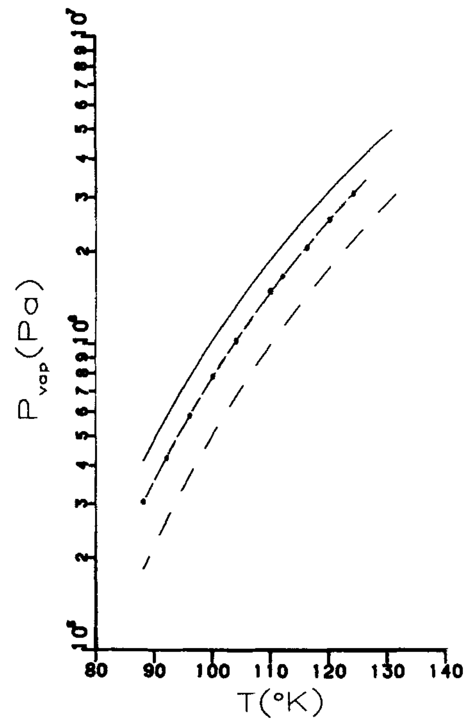

**Figure 5. Vapor pressure curve for nitrogen.**
Curve calculated by:
——— PT EOS; — — — OPR EOS; —·— UPR EOS
Comparison with experimental values reported by Marshall (1976).

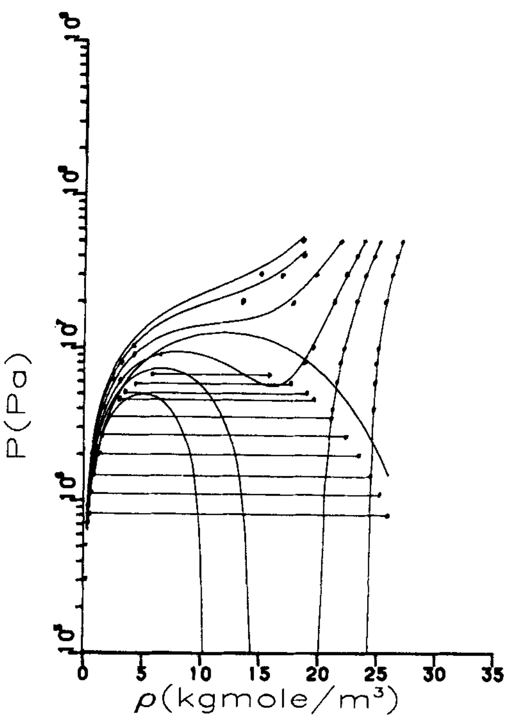

**Figure 6. Pressure-density phase diagram for $CO_2$ calculated from PT EOS.**
Comparison with experimental coexistence data and isotherms at 243, 273, 293, 323, 353, 373 K reported by Marshall (1976).

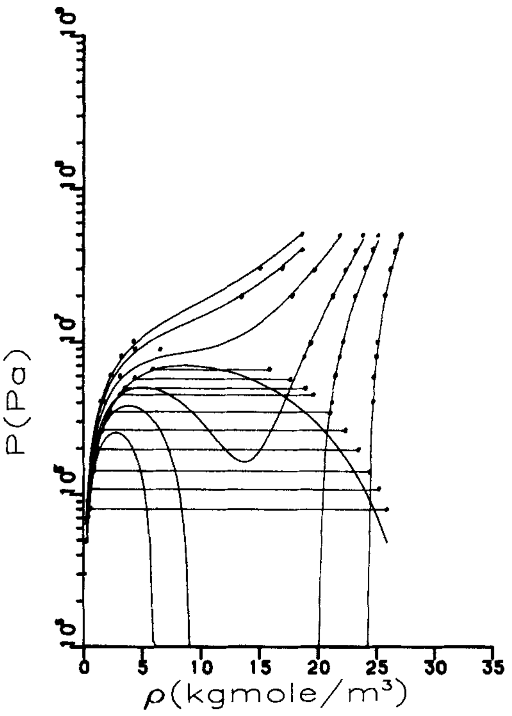

**Figure 7. Pressure-density phase diagram for $CO_2$ calculated from OPR EOS.**
Comparison as in Fig. 6.

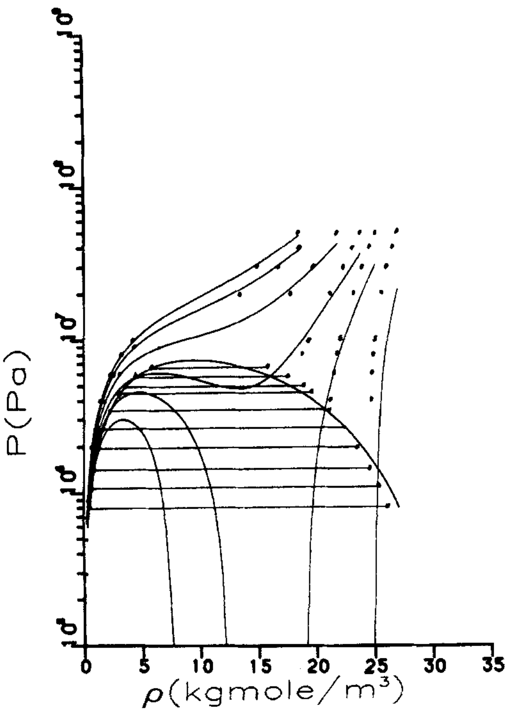

**Figure 8. Pressure-density phase diagram for $CO_2$ calculated from UPR EOS.**
Comparison as in Fig. 6.

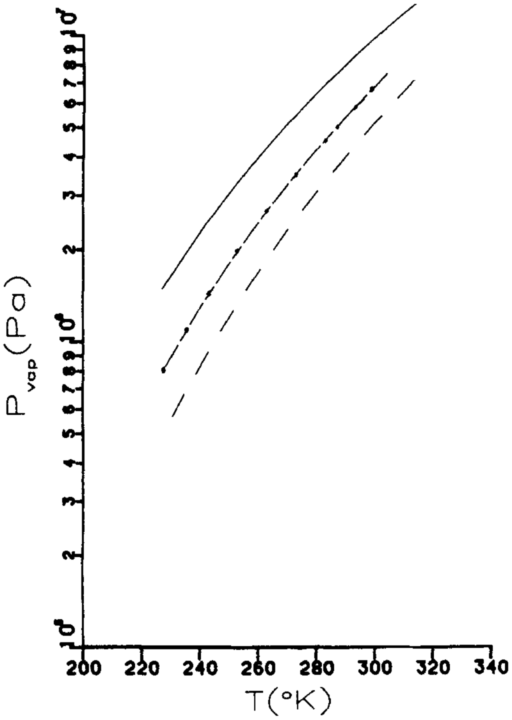

**Figure 9. Vapor pressure curve for $CO_2$.**
Curve calculated by:
——— PT EOS; — — — OPR EOS; —·— UPR EOS
Comparison with experimental values presented by Marshall (1976).

Values of the three parameters λ, ϵ, and σ in Eq. 16 were determined by a nonlinear least-squares regression analysis of PVT data for 12 different pure components. The results are summarized in Table 1 along with the corresponding results obtained from the usual implementation of the Peng-Robinson equation (UPR) and those obtained by an optimization of the Peng-Robinson parameters (OPR). In the UPR the parameters $T_c$, $P_c$, and $\omega$ are taken as their experimental values. In the OPR these parameters are adjusted to achieve the best least-squares fit over all the data. As seen in Table 1, both the absolute average errors and the RMS errors obtained from the PT equation are much less than those obtained with the UPR. The same is true for the OPR, but the PT equation yields smaller absolute errors than the OPR for all except $CO_2$ and butane, and smaller RMS errors for all but $CO_2$ and methane.

To get some insight into the differences in the various fits, we consider two cases in more detail. Figure 2 shows the fits to data for nitrogen obtained from the PT equation. The corresponding fits for the UPR and OPR are shown in Figures 3 and 4, respectively. As seen in the figures, the PT equation yields a phase envelope that is above the experimental one, while the UPR and OPR yield phase envelopes below the experimental ones. Both the PT and OPR give good fits to all of the isotherms considered, while the UPR yields poor low-temperature isotherms and fair high-temperature isotherms. With such poor PVT properties, why is the UPR a popular equation for engineering calculations? One answer is seen by looking at the vapor pressure curves predicted by the different equations, shown in Figure 5. The PT vapor pressure curve is systematically higher than the experimental one, while the OPR vapor pressure curve is lower. The UPR vapor pressure curve, however, is in excellent agreement with the experimental points. This is not surprising, and is typical, since the UPR equation was designed to yield a good vapor pressure curve. The price that is paid for such a tight fit to the vapor pressure curve is a very poor fit to the remaining PVT data. This points out the danger in deducing the parameters characterizing a two-dimensional function by optimizing along a single line, a one-dimensional optimization.

The various fits to data for $CO_2$ are given in Figures 6–8. As with nitrogen, the phase envelope for the PT equation is higher and the two Peng-Robinson implementations are lower than the experimental ones. Both the PT and OPR yield more correct isotherms than the UPR, with the OPR being better for the higher temperature isotherms. The PT does, however, yield better agreement with the experiments for the higher, liquidlike densities than does the OPR. The mean errors in the calculated pressures for densities higher than the critical density is 5.9% for the PT, as against 6.6% for the OPR with the corresponding RMS

**Table 2. Errors with Various Equations of State for Water Data**

| No. of Points | Mean Error, % | | | | RMS Error, % | | | |
|---|---|---|---|---|---|---|---|---|
| | UPR | OPR | PT | FG | UPR | OPR | PT | FG |
| 92 | 268,000 | 24.6 | 108 | 11.9 | 2,010,000 | 46.6 | 293 | 19.9 |

Water data from Keenan et al. (1969).
UPR, Usual implementation of Peng-Robinson EOS.
OPR, Optimized-parameter Peng-Robinson EOS.
PT, This work EOS.
FG, Fleming-Gibbs EOS.

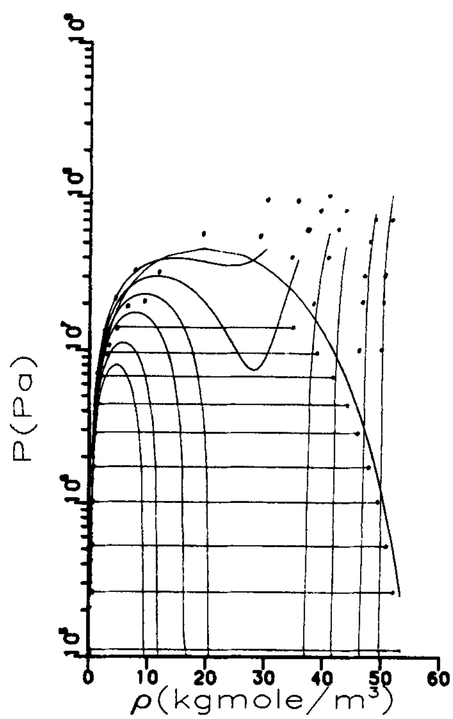

**Figure 10. Pressure-density phase diagram for water calculated from PT EOS.**
Comparison with experimental coexistence data and isotherms at 450, 506, 589, 644, 700, 756 K reported by Keenan et al. (1969).

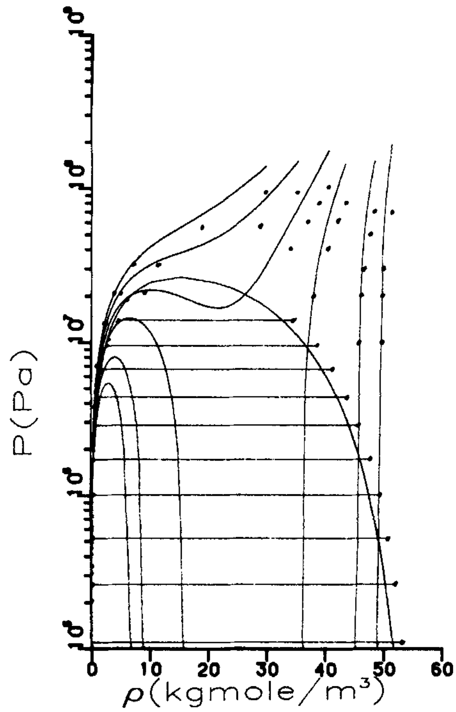

**Figure 11. Pressure-density phase diagram for water calculated from OPR EOS.**
Comparison as in Fig. 10.

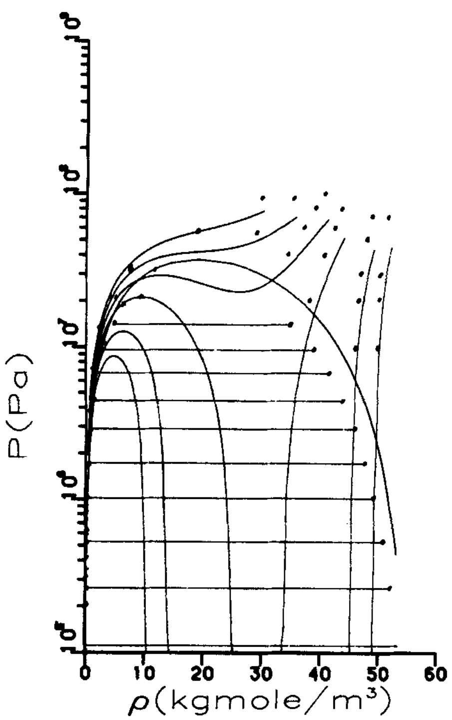

**Figure 12. Pressure-density phase diagram for water calculated from FG EOS.**
Comparison as in Fig. 10.

errors being 7.7 and 8.2%, respectively. The calculated vapor pressure curves shown in Figure 9 are similar to those for nitrogen, with the UPR again yielding excellent agreement with the data.

In all of the cases discussed so far, the OPR and PT have both given good agreement with the experiments, with the PT being better in most cases. Such is not the case for water. Table 2 shows a summary of the results obtained by comparison with water data (Keenan et al., 1969). As seen there, the UPR yields enormous errors, even though the vapor pressure curve is again very good. Both the PT and OPR give large errors, although the OPR is somewhat better than the PT. Plots of the PVT data compared with the PT and OPR are given in Figures 10 and 11.

Not surprisingly, we see that equations of state, which are reasonable for most materials, are not very good for water. It is interesting to compare the results obtained here with those obtained from equations of state designed specifically for water. The FG lattice equation is one such equation; it has been shown to predict much of the peculiar behavior that is characteristic of water, and to be in good agreement with experiments for water in the normal liquid range (0–100°C, 1 atm). To obtain a fair comparison with the three-parameter equations discussed here, we must reduce the FG equation to three parameters. We take these to be $R_{NN}$, $E$, and $\epsilon_1$ and set $\epsilon_2 = -E$. This corresponds to the anti-hydrogen bond energy being equal and opposite to the hydrogen bond energy. The fit to the water data, obtained with $R_{NN} = 2.88$ A, $E/k = 1{,}462$ K, and $\epsilon_1/k = 548$ K, is shown in Figure 12 and the corresponding vapor pressure fit is shown in Figure 13 along with the corresponding fits from the OPR and PT. As seen in Table 2, the FG equation is significantly better than either the PT or OPR equations. Thus, we conclude that

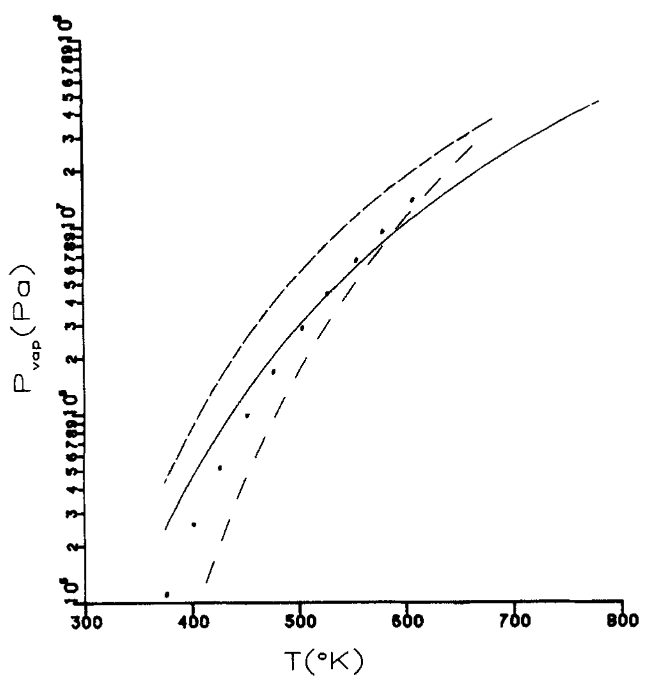

**Figure 13. Vapor pressure curve for water.**

Curve calculated by:

—— PT EOS; ——— OPR EOS; —·— FG EOS

Comparison with experimental values presented by Keenan et al. (1969).

even with the very unrealistic geometry imposed by the lattice, the FG equation yields better thermodynamic properties because it treats the geometry of the attractive interactions realistically. This again points out a fact that has been known for a long time: the peculiar thermodynamic properties of water are a consequence of the geometry of hydrogen bonding and any equation of state that does not take this into account will be in great error.

A summary of all the values of the parameters obtained for the PT, UPR, and OPR equations is given in Table 3.

## Discussion

We have formulated an equation of state,..the PT equation, based on molecular interactions, that is superior to the usual Peng-Robinson equation for all materials considered. This equation, based on a square-well potential and perturbation theory about a hard sphere reference, is also better than the Peng-Robinson equation for most normal substances when the PR parameters are optimized to give the best fit to the data. For water, neither the PT equation nor the optimized-parameter PR equation give good agreement with PVT properties. Instead, we find that a lattice gas equation, which possesses the correct geometry of attractive interactions, is in better agreement with experiment than either the PT or OPR equations.

The advantage of a molecular-based equation of state is that the parameters appearing in the equation all have a well-defined physical interpretation. Irrespective of its utility, the physical basis for the acentric factor is far from understood.

Another advantage of the molecular-based equation is in the generalization to mixtures. The analytic solution of the Percus-Yevick equation for binary mixtures of hard spheres with additive diameters, by Lebowitz (1964), makes the generalization to binary mixtures of square wells straightforward. The work by Baxter (1967, 1970) on the solution to the Percus-Yevick equation for $N$-component mixtures of hard spheres allows us to formulate a theory of mixtures of real materials without the invocation of *ad hoc* mixing rules, which are required in empirical equations of state. This helps to keep the mixture equation on a sound physical basis. The resulting mixture equation could be used to model thermodynamics and phase behavior associated with chemical and physical processes and with recovery of oil by thermal, chemical, or miscible methods.

In conclusion, we have seen that good agreement with experimental results for real materials can be obtained with a molecular-based equation of state. Such equations can serve as a sound physical basis for interpretation of experimental results in both pure components and nonaqueous mixtures. Any theory of aqueous systems, however, must treat the particular geometry of the attractive interactions of water molecules to be useful. Thus, the aqueous system case must also be based on molecular consider-

**Table 3. Values of the Parameters Obtained for Equations of State and Various Materials**

| | UPR | | | OPR | | | PT | | |
|---|---|---|---|---|---|---|---|---|---|
| Substance | $T_c$ | $P_c$ (atm) | $\omega$ | $T_c$ | $P_c$ (atm) | $\omega$ | $\lambda$ | $\epsilon$ | $\sigma$(A) |
| Ethane | 305.4 | 48.2 | 0.098 | 311.0 | 46.55 | 0.1132 | 1.788 | 151.2 | 4.050 |
| $H_2S$ | 373.2 | 88.2 | 0.100 | 388.1 | 83.01 | 0.0250 | 1.598 | 258.9 | 3.487 |
| Nonane | 594.6 | 22.8 | 0.444 | 524.0 | 20.90 | 0.965 | 1.840 | 312.0 | 6.819 |
| Nitrogen | 126.2 | 33.5 | 0.040 | 131.3 | 30.09 | 0.069 | 1.421 | 110.9 | 3.535 |
| Propane | 359.8 | 41.9 | 0.152 | 382.9 | 39.15 | 0.283 | 1.365 | 360.4 | 4.696 |
| Argon | 150.8 | 48.1 | 0.004 | 158.4 | 43.24 | 0.013 | 1.445 | 129.2 | 3.323 |
| Hexane | 507.4 | 29.3 | 0.296 | 498.5 | 28.65 | 0.450 | 1.806 | 307.3 | 5.920 |
| $CO_2$ | 304.2 | 72.8 | 0.225 | 313.6 | 69.34 | 0.308 | 1.331 | 314.4 | 3.680 |
| Pentane | 469.6 | 33.3 | 0.251 | 473.5 | 32.30 | 0.272 | 1.842 | 228.0 | 5.648 |
| Butane | 425.0 | 37.5 | 0.201 | 442.1 | 36.10 | 0.229 | 1.357 | 418.9 | 5.076 |
| Octane | 568.8 | 24.5 | 0.394 | 565.3 | 24.80 | 0.487 | 1.815 | 315.5 | 6.429 |
| Methane | 191.0 | 45.8 | 0.013 | 202.0 | 42.37 | −0.049 | 1.485 | 157.7 | 3.612 |
| Water | 647.3 | 217.6 | 0.344 | 664.3 | 258.9 | 0.599 | 1.544 | 559.0 | 2.869 |

UPR, Usual implementation of Peng-Robinson EOS.
OPR, Optimized-parameter Peng-Robinson EOS.
PT, This work EOS.

ations, although the simple spherically symmetric equation derived here is not adequate for those systems.

## Notation

$a(T)$ = defined in Eq. 18
$a_c$ = $a(T_c)$
$a_0^\alpha$ = defined by Eq. 13
$B_n$ = coefficients, Eq. 24
$b$ = van der Waals parameter
$C_1$ = defined in Eq. 14
$F$ = Helmholtz free energy
$F_n$ = $n$th-order term in high-temperature expansion of Helmholtz free energy
$f$ = Helmholtz free energy per particle
$f_n$ = $n$th expansion coefficient of $f$
$\ell$ = defined in Eq. 11
$g_0(r)$ = pair correlation function for hard sphere fluid
$k$ = Boltzmann's constant
$L(t)$ = defined in Eq. 13
$N$ = number of molecules in system
$n$ = number density of molecules
$n_L$ = lattice density
$p$ = pressure of system
$p_c$ = critical pressure
$p_n$ = $n$th-order term in high-temperature expansion of pressure
$P_1$ = defined in Eq. 14
$Q_1$ = defined in Eq. 14
$R_{NN}$ = nearest neighbor distance in lattice model
$r$ = separation distance
$S(t)$ = defined in Eq. 12
$S_1(t)$ = $S'(t)$
$T$ = temperature
$T_c$ = critical temperature
$t_\alpha$ = defined in Eq. 11
$u(r)$ = potential energy function
$v_c$ = unit cell volume for Fleming-Gibbs model
$y_\pm$ = defined in Eq. 11
$Z$ = defined in Eq. 24

### *Greek letters*

$\alpha(t)$ = defined in Eq. 18
$\beta$ = $1/kT$
$\beta_c$ = critical value of $\beta$
$\epsilon$ = strength of attractive energy
$\eta$ = volume fraction, defined after Eq. 7
$\kappa$ = defined in Eq. 19c
$\lambda$ = range of attraction in units of $\sigma$
$\lambda_T$ = thermal wavelength
$\mu$ = chemical potential
$\omega$ = acentric factor

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*Manuscript received Apr. 16, 1985, and revision received July 2, 1986.*