ACKNOWLEDGMENT

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NOTATION

a = wave amplitude, m
c = wave velocity, m/s
c^* = $c\rho_s/\overline{N}$
f = friction factor = $\tau_W/\frac{1}{2}U^2_b$, dimensionless
h = surface height, cm
ΔH = heat of fusion
N = mass flux from the surface or heat flux to surface in the units of mass or heat per unit area per unit time
Q = surface heat flux
Re^* = Reynolds number based on the friction velocity = $\lambda u^*/\nu$
t = time, s
U_b = bulk averaged velocity, m/s
u^* = friction velocity equal to $(\overline{\tau}_W/\rho)^{1/2}$, m/s
x = coordinate in the direction of mean flow
y = coordinate perpendicular to mean solid surface, m

Greek Letters

α = wave number, m^{-1}
α^+ = wave number made dimensionless using u^* and ν
β = time constant for growth, s^{-1}
β^+ = $\rho\nu\rho_s/Nu^*$
θ = phase angle to be defined by (8)
λ = wave length, m
ν = kinematic viscosity, m^2/s
ρ = density of the fluid, kg/m^3
ρ_s = density of solid, kg/m^3
τ_W = shear stress acting on the wave surface, N/m^2
$\overline{\tau}_W$ = average value of τ_W over one wavelength, N/m^2

Other symbols

$\overline{N}(y)$ = average value of N over one wavelength
$a|\hat{n}|$ = amplitude of wave induced variation of N, $n = N - \overline{N}$
Z = Schmidt number of Prandtl number

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An Equation of State for Polyatomic Fluids

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An equation of state has been developed for convex nonspherical particles with nonpolar and multipolar forces. The effects of nonsphericity and multipolarity on phase behavior are characterized by a geometric shape parameter and an energy fluctuation parameter, respectively. The equation performs for real fluids better than the Van der Waals equation and as well as the Redlich-Kwong and Peng-Robinson equations.

SCOPE

An equation of state is developed for attracting, nonspherical particles with rigid, convex cores. The method makes use of mean field approximations and the scaled particle theory. The effect of nonsphericity and polarity on phase behavior is investigated. Spherocylindrical, tetragonal, and hexagonal cores are considered. The equation of state is tested for nitrogen, carbon dioxide, methane, and benzene and is compared to the Van der Waals, Redlich-Kwong, and Peng-Robinson equations as well as new variations of these equations.

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CONCLUSIONS AND SIGNIFICANCE

As the particles become more nonspherical, the critical compressibility factor decreases and the acentric factor increases. Increasing polarity does not affect the critical compressibility factor, but it increases the acentric factor sharply. These are in qualitative agreement with experimental trends. Also nonsphericity increases critical volume and decreases critical pressure. The equation of state developed here agrees with experiment considerably better than the Van der Waals equation, a little better than the Redlich-Kwong equation, and about the same as the Peng-Robinson equation. Introduction of nonsphericity into the Redlich-Kwong equation makes no improvement.

The statistical theory of fluids is not yet sufficiently developed to accurately predict thermodynamic properties of real systems. But considerable progress has been achieved for fluids of idealized particles. The structure and thermodynamics of a fluid of nonattracting hard spheres has been well described by the Percus-Yevick (PY) theory (Percus and Yevick, 1960; Wertheim, 1963; Lebowitz, 1965). The Percus-Yevick hard sphere equation of state was earlier derived in a different way from scaled particle theory by Reiss et al. (1959). The equation of state agrees with the results of numerical simulations made by Alder and co-workers (1960; 1964) over a wide range of density.

The behavior of nonspherical particles has also been studied. The effect of particle shape on the second virial coefficient was investigated by Isihara and Hayashida (1951) and Kihara (1953; 1953). Gibbons (1969; 1970) extended the scaled particle theory to mixtures of rigid, nonattracting convex particles of arbitrary shape. MacRury and Steele (1977) have modeled the intermolecular interaction of nonspherical particles by representing each particle as an assembly of overlapping hard spheres. A realistic theory of the fluid state must take into account attractive nonpolar (dispersion) forces and long range multipolar forces as well as short range nonspherical repulsive forces. Gubbins et al. (1973; 1978), Sandler (1974), and Twu et al. (1975; 1976) have studied the effect of multipole interactions introduced as perturbations on the nonspherical hard core potential. The objective of this paper is to construct an equation of state that includes through mean field approximations dispersion and multipolar interactions and through scaled particle theory rigid body nonsphericity.

Our chief interest lies in establishing a simple equation of state which predicts how the various interactions affect fluid properties. However, we do demonstrate that our equation performs as well as or better than some well-known similar equations of state.

GENERAL FORMALISM

The interaction between a pair of classical nonspherical molecules will be described by the potential model introduced by Kihara (1953). He assumed that molecules have an inner hard core of some geometrical shape and that pairs of molecules interact via a potential depending only on the distance ρ, defined as the shortest distance between two cores. The Lennard-Jones type of pair potential u is given by

$$u(\mathbf{r}_{12}, \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2) = \infty, \quad r_{12} < \sigma\,(\hat{\mathbf{r}}_{12}, \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2)$$

$$= u_0 \left[\frac{\mu}{\nu - \mu} \left\{ \frac{\rho_0}{\rho(\mathbf{r}_{12}, \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2)} \right\}^{\nu} \right.$$

$$\left. - \frac{\nu}{\nu - \mu} \left\{ \frac{\rho_0}{\rho(\mathbf{r}_{12}, \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2)} \right\}^{\mu} \right],$$

$$r_{12} > \sigma\,(\hat{\mathbf{r}}_{12}, \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2), \quad \nu > \mu > 3 \quad (1)$$

where $\sigma(\hat{\mathbf{r}}_{12}, \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2)$ denotes the distance of separation of the centers of rigid convex bodies 1 and 2 in contact with $\hat{\mathbf{r}}_{12}$, a unit vector along $\mathbf{r}_{12}$, the line joining their centers of mass. $\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2$ are vectors indicating the orientations of molecules 1 and 2.

When the rigid convex bodies are nonattracting, the potential reduces to

$$\begin{aligned} u^{CB} &= \infty, \qquad r_{12} < \sigma(\hat{\mathbf{r}}_{12}, \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2) \\ &= 0, \qquad r_{12} > \sigma(\hat{\mathbf{r}}_{12}, \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2) \end{aligned} \quad (2)$$

Gibbons' (1969) extension of scaled particle theory to nonattracting convex bodies of arbitrary shape assumes the above kind of pair potential. For such a fluid, he obtained for pressure P^{CB} the equation

$$\frac{P^{CB}}{nkT} = \frac{1}{1 - nv} + \frac{s\overline{R}n}{(1 - nv)^2} + \frac{(s\overline{R}n)^2}{3(1 - nv)^3} \quad (3)$$

The pair potential between attracting convex molecules, Equation (1), can be approximated by

$$u(\mathbf{r}_{12}, \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2) = u^{CB}(\mathbf{r}_{12}, \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2) - w(\mathbf{r}_{12}, \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2) \quad (4)$$

where $- w(\mathbf{r}_{12}, \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2)$ is a negative potential accounting for the attractive interactions between molecules of the fluid, and u^{CB} is chosen to mimic the shape of the repulsive core of the molecules. If the potential is pairwise additive, the configuration partition function of the fluid can be written as

$$Z_N = \int \ldots \int e^{-u_N{}^{CB}/kT}\, e^{\sum_{i>j=1}^{N} w(\mathbf{r}_{ij}, \hat{\mathbf{e}}_i, \hat{\mathbf{e}}_j)/kT} \, (d^3r)^N (d^{2+\chi}e)^N \quad (5)$$

$\chi = 0$ if the molecules are linear, and $\chi = 1$ otherwise. We introduce here the mean field approximation made in the Van der Waals theory. It is assumed that w is long ranged and sufficiently slowly varying that the value of $\sum_{i>j=1}^{N} w(\mathbf{r}_{ij}, \hat{\mathbf{e}}_i, \hat{\mathbf{e}}_j)$ for all accessible molecular configurations does not differ greatly from the mean value

$$\frac{N(N-1)}{2} \langle w(\mathbf{r}_{ij}, \hat{\mathbf{e}}_i, \hat{\mathbf{e}}_j) \rangle,$$

where

$$<w(\mathbf{r}_{ij}, \hat{\mathbf{e}}_i, \hat{\mathbf{e}}_j)> \equiv V^{-2} \int \ldots \int w(\mathbf{r}_{12}, \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2) \, g(\mathbf{r}_{12}, \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2) \, d^3r_1 d^3r_2 d^{2+\chi}e_1 d^{2+\chi}e_2 \quad (6)$$

g is the pair correlation function, $d^{2+\chi}e_i \equiv \sin \theta_i d\theta_i \cdot d\phi_i(d\psi_i)^\chi$, and θ_i, ϕ_i, ψ_i Eulerian angles.
Define

$$a \equiv \frac{1}{2V} \int w(\mathbf{r}_{12}, \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2) \, g(\mathbf{r}_{12}, \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2) \, d^3r_1 d^3r_2 d^{2+\chi}e_1 d^{2+\chi}e_2 \quad (7)$$

Then

$$Z_N \simeq e^{N^2a/VkT} \cdot Z_N^{CB} \quad (8)$$

where

$$Z_N^{CB} = \int \ldots \int e^{-u_N^{CB}/kT} \, (d^3r)^N (d^{2+\chi}e)^N \quad (9)$$

u_N^{CB} being the total potential of N rigid convex bodies. If a is assumed to be independent of V, then

$$P = kT\left(\frac{\partial \ln Z_N}{\partial V}\right)_{N,T} = -\frac{aN^2}{V^2} + kT\left(\frac{\partial \ln Z_N^{CB}}{\partial V}\right)_{N,T} \quad (10)$$

Since the second quantity on the right-hand side of Equation (10) is P^{CB}, we obtain

$$\frac{P}{nkT} = \frac{1}{1-nv} + \frac{s\bar{R}n}{(1-nv)^2} + \frac{(s\bar{R}n)^2}{3(1-nv)^3} - \frac{na}{kT} \quad (11)$$

by approximating P^{CB} as the scaled particle pressure, Equation (3). We shall refer to this equation as the convex body Van der Waals (CBVDW) equation.

In the original Van der Waals theory, the parameter a was assumed to be independent of temperature. Such assumption neglects multipolar forces (and the temperature dependence of g). The dipole-dipole pair potential of spherical molecules is

$$u_{dd} = \frac{\mathbf{D}_1 \cdot \mathbf{D}_2 - 3(\mathbf{D}_1 \cdot \mathbf{r}_{12})(\mathbf{D}_2 \cdot \mathbf{r}_{12})}{r_{12}^3} \quad (12)$$

where $\mathbf{D}_i$ represents the dipole moment vector of molecule i. The contribution of u_{dd} to the parameter a may be developed as a series in T^{-1}, the lead term going as T^{-1} (Hirschfelder et al., 1954). In fact, to lowest order, any multipolar contribution to a goes as T^{-1} for spherical molecules. But Sandler (1974) has shown that for nonspherical molecules there will be an additional contribution which is proportional to the square of the multipole and is independent of T. Thus, the equation of state introduced here is

$$\frac{P}{nkT} = \frac{1}{1-nv} + \frac{s\bar{R}n}{1-nv} + \frac{(s\bar{R}n)^2}{3(1-nv)^2} - \frac{na}{kT}\left(1 + \frac{\lambda}{vkT}\right) \quad (13)$$

where the parameter λ is to account for multipolar force contributions and for the temperature dependence of the traditional Van der Waals a arising from the temperature dependence of the pair correlation function (that is, of the fluid structure).

In what follows, the qualitative features and quantitative ability of Equation (13), to be referred to as the present model (PM), will be examined.

The traditional Van der Waals (VDW) equation of state is obtained from Equation (10) if $kT(\partial \ln Z_N^{CB}/\partial V)_{N,T}$ is approximated by the Clausius relation $nkT/1 - nv$

$$\frac{P}{nkT} = \frac{1}{1-nv} - \frac{na}{kT} \quad (14)$$

A popular variation of the VDW equation of state is the Redlich-Kwong (1949) equation

$$\frac{P}{nkT} = \frac{1}{1-nv} - \frac{na}{(1+nv)kT^{3/2}} \quad (15)$$

The Redlich-Kwong (RK) equation accounts for multipolar forces and the temperature and density dependence of g through the group $a/T^{1/2}(1 + nv)$ which replaces the constant a of the VDW equation. The RK equation is generally more accurate than the VDW equation in describing real fluid behavior. The convex body version of the RK equation (to be referred to as the CBRK equation) is

$$\frac{P}{nkT} = \frac{1}{1-nv} + \frac{s\bar{R}n}{(1-nv)^2} + \frac{(s\bar{R}n)^2}{3(1-nv)^2} - \frac{na}{(1+nv)kT^{3/2}} \quad (16)$$

The various models represented by Equations (11), (13), (14), (15), and (16) will be compared later. We shall also compare these equations with the Peng-Robinson (1976) equation

$$\frac{P}{nkT} = \frac{1}{1-nv} - \frac{a \cdot \alpha(T_r, \omega_a)}{kT[1 + nv(2-nv)]} \quad (17)$$

where

$$\alpha = [1 + \kappa(1 + T_r^{1/2})]^2 \quad (18)$$

$$\kappa = 0.37464 + 1.5422\,\omega_a - 0.26992\,\omega_a^2 \quad (19)$$

The Peng-Robinson (PR) equation is similar in performance and in spirit to modifications of the RK equations (Soave, 1972). These three-parameter equations are somewhat better than the RK equation and are probably the best of the two- and three-parameter descendents of the VDW equation.

EFFECT OF NONSPHERICITY AND POLARITY ON PHASE BEHAVIOR

Equation (13) can be made dimensionless with the following definitions:

$$\theta = \frac{s\bar{R}}{v}, \quad n^* = nv, \quad P^* = \frac{Pv^2}{a}, \quad T^* = \frac{kTv}{a}$$

So

$$P^* = \frac{n^*T^*}{1-n^*} + \frac{n^{*2}\,\theta T^*}{(1-n^*)^2} + \frac{n^{*3}\theta^2 T^*}{3(1-n^*)^3} - n^{*2}\left(1 + \frac{\lambda}{T^*}\right) \quad (20)$$

Note that the effect of the shape of the particles on phase behavior only enters through the parameter θ. Figure 1 shows convex bodies obtained from spherocylindrical, tetrahedral, and hexagonal cores. The following equations give the variation of parameter θ with shape which is also shown in Figure 2.

Spherocylinder

$$\theta = \frac{\{4\pi(R/L)^2 + 2\pi(R/L)\}\{(R/L) + 1/4\}}{\frac{4}{3}\pi(R/L)^3 + \pi(R/L)^2} \quad (21a)$$

Regular tetrahedron

$$\theta = \frac{\{4\pi(R/L)^2 + 12(\tan^{-1}\sqrt{2})R/L + \sqrt{3}\}\,\{(R/L) + (6/4\pi)\tan^{-1}\sqrt{2}\}}{\frac{4}{3}\pi(R/L)^3 + 6(\tan^{-1}\sqrt{2})(R/L)^2 + \sqrt{3}(R/L) + \frac{1}{6\sqrt{2}}} \tag{21b}$$

Regular hexagon

$$\theta = \frac{\{4\pi(R/L)^2 + 6\pi(R/L) + \sqrt{3}\,3\}\,\{(R/L) + (3/4)\}}{\frac{4}{3}\pi(R/L)^3 + 3\pi(R/L)^2 + 3\sqrt{3}\,(R/L)} \tag{21c}$$

The two length parameters, R and L, are defined in Figure 1. Observe that as $R/L \to \infty$, $\theta \to 3$, the value for a sphere.

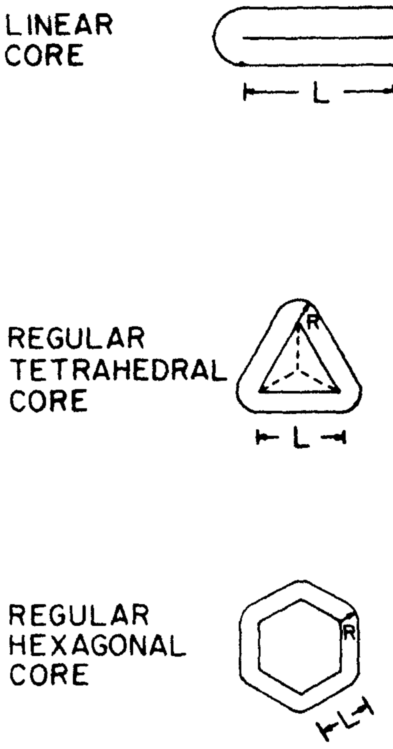

Fig. 1. Convex parallel bodies obtained from spherocylindrical, tetrahedral, and hexagonal cores.

The phase behavior of a fluid following Equation (20) has been computed. Table 1 shows the effect of shape (denoted by θ) on various thermodynamic properties. Here, $\lambda = 0$. Note that the critical compressibility Z_c is smaller than that of a Van der Waals fluid (0.375), and it increases with decreasing θ. P_c^* and T_c^* decrease, and V_c^* increases with increasing θ. The acentric factor ω_a increases as θ increases. ω_a is defined, as usual, by

$$\omega_a = -\log\left(\frac{P_s}{P_c}\right)_{T_r=0.7} - 1 \tag{22}$$

where $T_r \equiv T/T_c$, and P_s is the pressure of saturated vapor at $T_r = 0.7$.

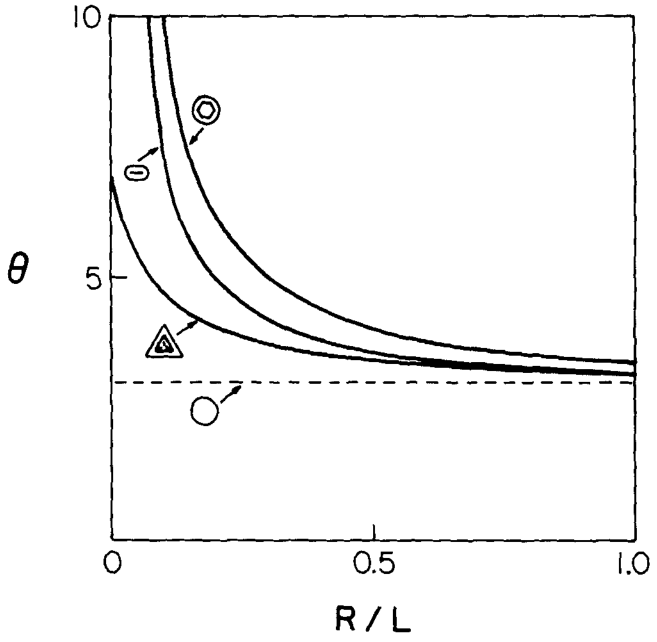

Fig. 2. Variation of parameter r with particle shape.

TABLE 1. EFFECT OF NONSPHERICITY OF PARTICLES ON THERMODYNAMIC PROPERTIES

θ	3.0	4.0	5.0	6.0	10.0
Z_c	0.3598	0.357	0.355	0.354	0.349
P_c^*	4.34×10^{-3}	3.1×10^{-3}	2.34×10^{-3}	1.83×10^{-3}	8.79×10^{-4}
V_c^*	7.77	9.00	10.18	11.32	15.72
T_c^*	0.094	0.078	0.067	0.059	0.039
ω_a	−0.106	−0.062	−0.025	0.007	0.106

TABLE 2. EFFECT OF POLAR INTERACTIONS OF PARTICLES ON THERMODYNAMIC PROPERTIES

λ	0	0.1	0.2	0.5	1.0
Z_c	0.3598	0.3598	0.3598	0.3598	0.3598
P_c^*	4.34×10^{-3}	7.15×10^{-3}	8.88×10^{-3}	1.24×10^{-2}	1.65×10^{-2}
V_c^*	7.77	7.77	7.77	7.77	7.77
T_c^*	0.094	0.154	0.192	0.268	0.357
ω_a	−0.106	0.341	0.481	0.6498	0.756

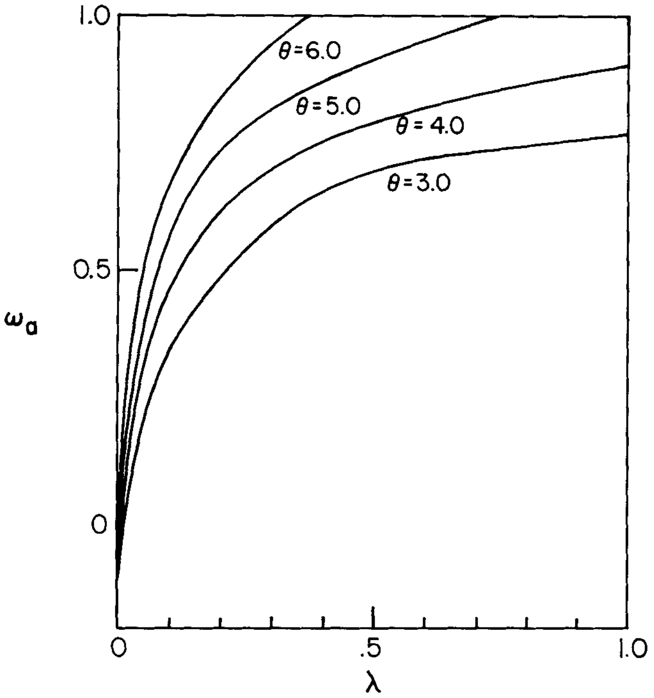

Fig. 3. Acentric factor as a function of polar interaction parameter λ and shape parameter θ.

TABLE 3. PARAMETERS USED IN EVALUATION OF EQUATIONS

	N_2	CO_2	C_6H_6	CH_4
R, Å	1.8	1.71	1.5	1.87
L, Å	0.86	1.73	1.16	0.28
θ	3.063	3.008	3.277	3.218
λ	0.016	0.013	0.044	0.048

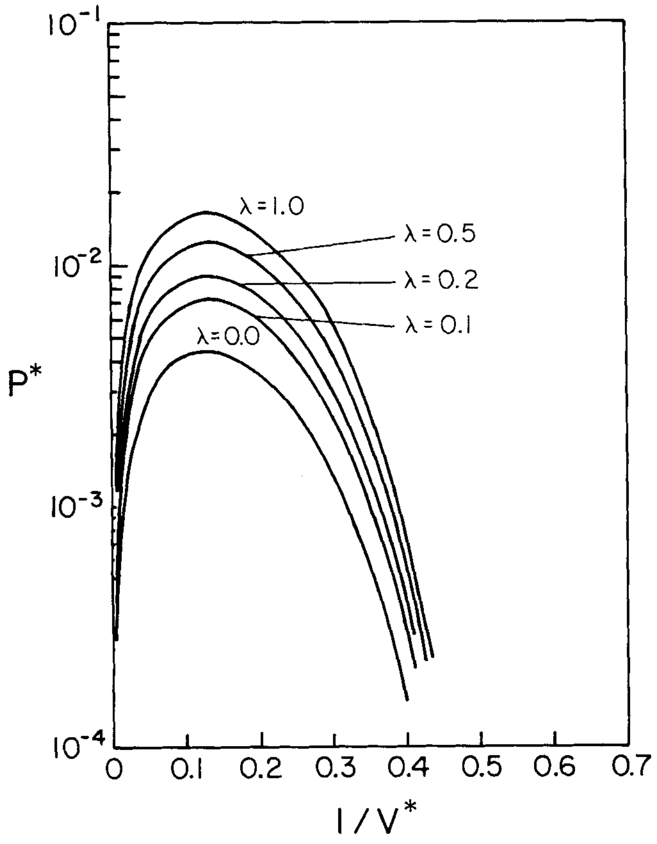

Fig. 5. Dimensionless phase envelope for varying polar interaction. *r* = 3.0.

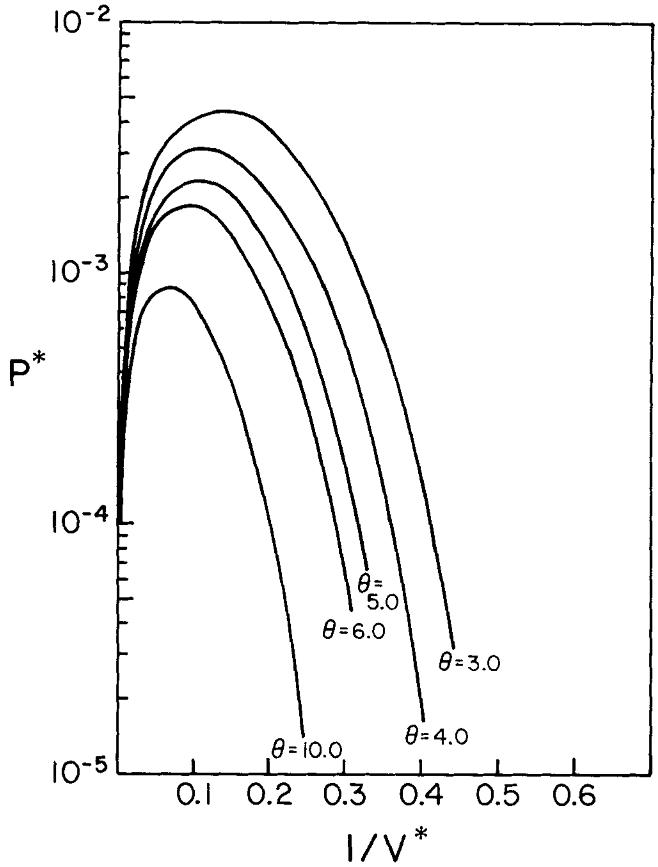

Fig. 4. Dimensionless phase envelope for varying nonsphericity. λ = 0.

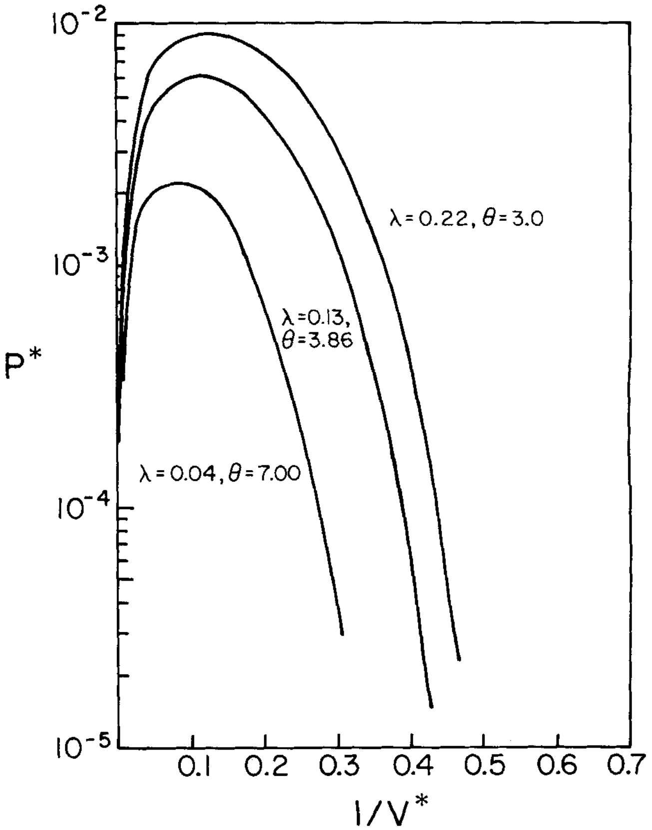

Fig. 6. Dimensionless phase envelope for constant acentric factor but varying nonsphericity and polar interaction.

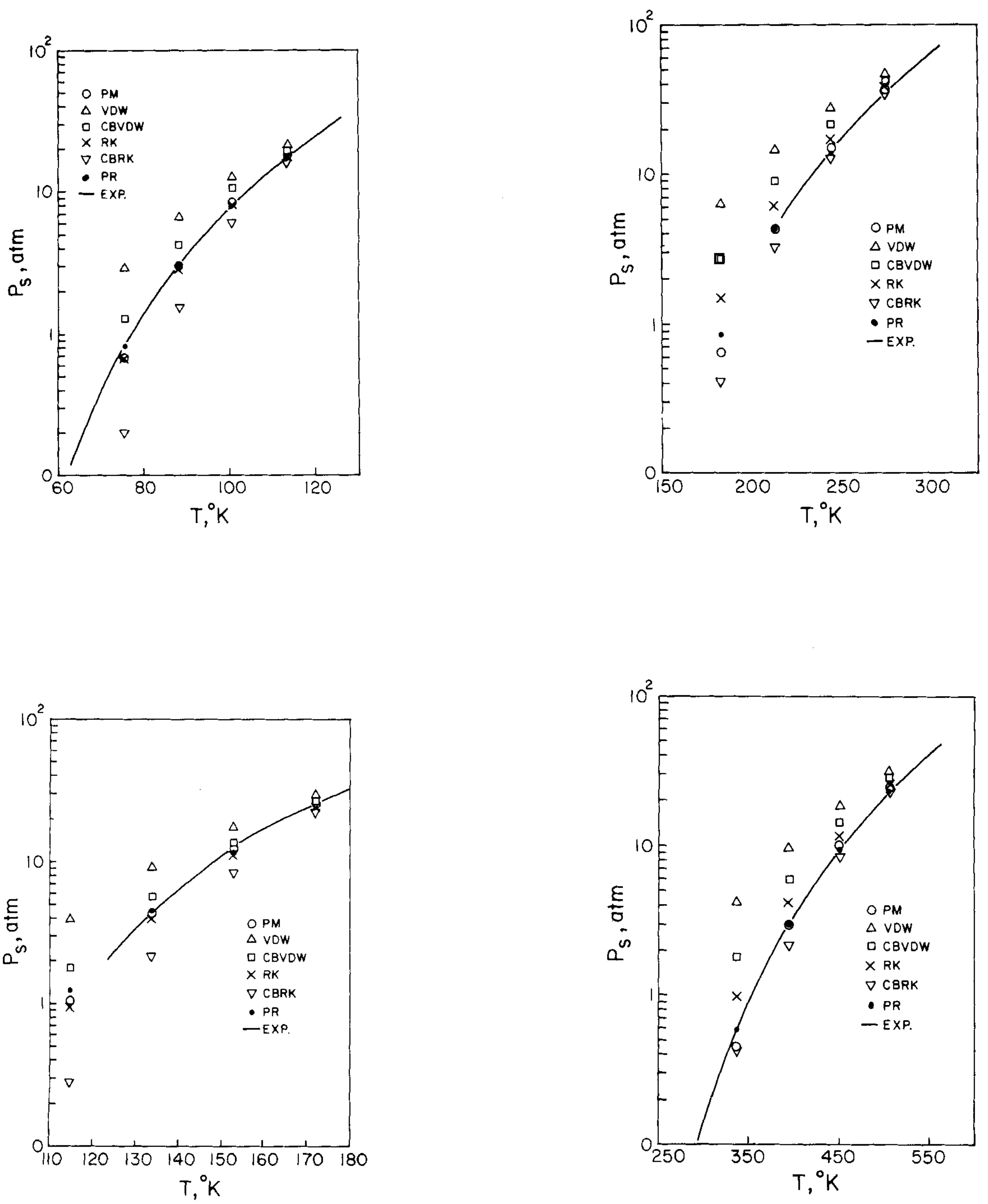

Fig. 7. Comparison of experimental vapor pressure data with predictions by the PM [Equation (13)], VDW [Equation (14)], CBVDW [Equation (11)], RK [Equation (15)], CBRK [Equation (16)], and PR [Equation (17)] equations. *a.* nitrogen, *b.* Carbon dioxide, *c.* benzene, *d.* methane.

The effect of polar interactions (λ) on various properties is shown in Table 2, where $\theta = 3.0$ (that of a sphere). The critical compressibility is not a function of λ, nor is V_c^*. But P_c^*, T_c^*, and ω_a all increase with increasing λ.

Figure 3 shows the acentric factor ω_a as a function of λ for various θ's. Note that for small λ, ω_a is a very steeply increasing function. For most molecules of interest, ω_a is less than 0.5. That limits the range of λ to be within 0 and 0.2. But a small change in λ, that is, in the dipolar or other multipolar interaction, can give large changes in acentric factor. Increasing ω_a with increasing polarity is in qualitative agreement with experimental trends.

The dependence of vapor-liquid phase envelope on shape of molecules and polar interactions is shown in Figures 4 and 5, respectively. The pressure and specific volume have been reduced by molecular size and interaction parameters. As the molecule becomes more and more nonspherical, the pressure needed for criticality goes down but volume occupied increases. This, too, is in qualitative agreement with experimental trends. For a fixed acentric factor, increasing λ is accompanied by de-

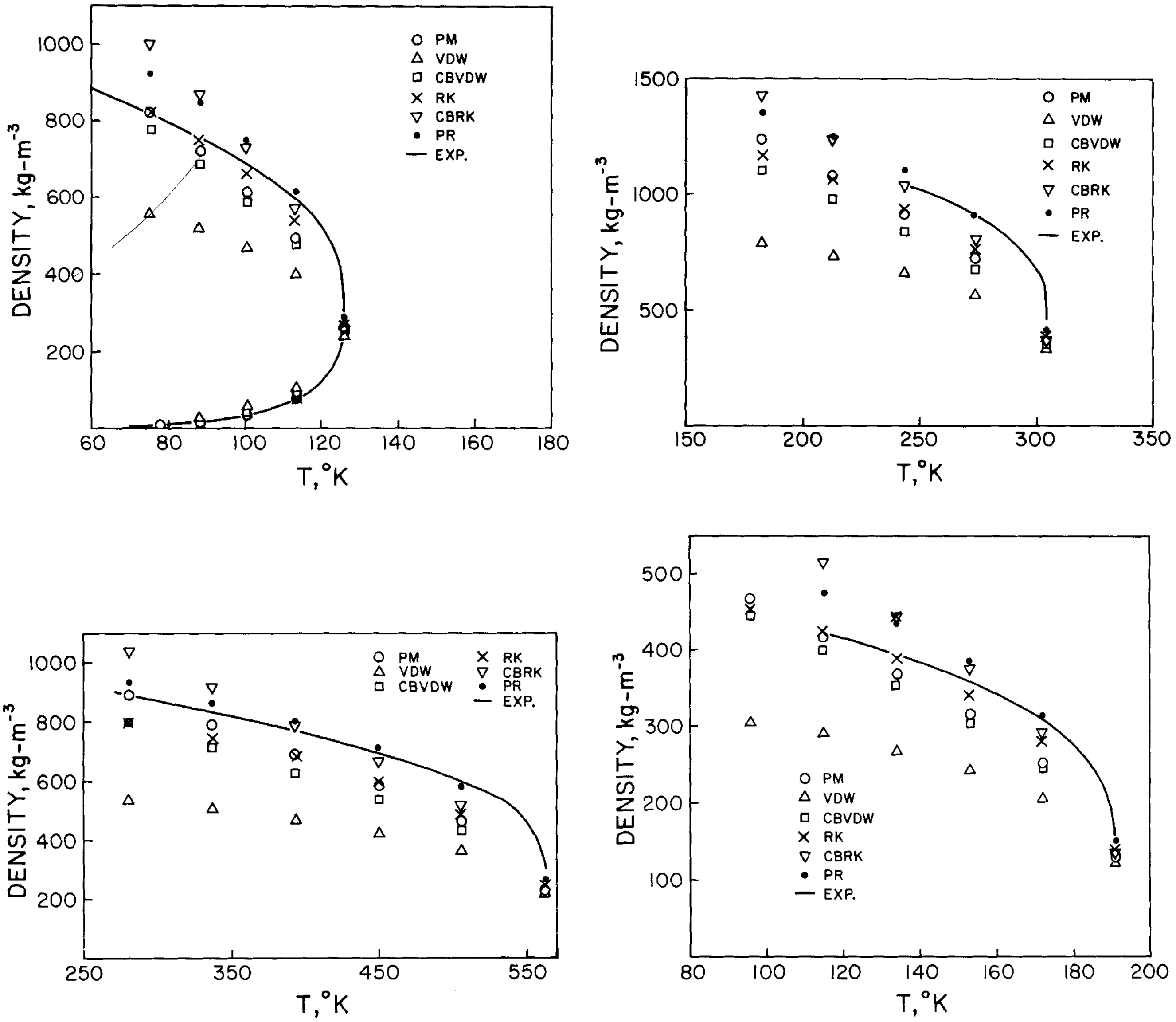

Fig. 8. Comparison of experimental saturated liquid density data with predictions by the model equations of state. Points correspond to assignments made in Figure 7. *a*. nitrogen, *b*. carbon dioxide, *c*. benzene, *d*. methane.

creasing θ, increasing P_c^*, and decreasing V_c^*. This behavior is illustrated in Figure 6.

COMPARISON OF EXPERIMENTAL DATA AND THE MODEL EQUATIONS OF STATE

Both v and a are parameters that occur in the present model (PM) and in the VDW, RK, and PR equations of state. They can be estimated from critical point data. Here T_c and P_c will be used to determine v and a. Choice of θ depends on the shape and size of the molecules.

The molecules chosen for illustration are nitrogen, carbon dioxide, benzene, and methane. The first two are spherocylinders, whereas the third and fourth are hexagonal and tetrahedral, respectively. Danon and Pitzer (1962) provide the geometric parameters R and L, which were obtained from second virial coefficient data. The shapes of the molecules proposed by Bienkowski and Chao (1975) were not used because they were determined empirically for an equation of state different from the present one. λ was chosen in order to give the experimental ω_a. Table 3 lists the relevant parameters used in evaluating the equation of state.

We compare predictions of the model equations with experiment in the liquid-vapor coexistence region. Figure 7 shows vapor pressure vs. temperature. Introduction of the convex body modification definitely improves the VDW equation (compare VDW and CBVDW points) but not the RK equation (compare RK and CBRK). The present model, obtained by introduction of the convex body modification and polar interactions, agrees with experiment considerably better than the VDW equation, slightly better than the RK equation, and as well as the PR equation.

The model equations results for coexisting liquid and vapor densities are compared with experiment in Figure 8. The vapor density is plotted only in Figure 8*a* since the trend is the same in all others and the differences of the equations tend to wash out as they all go to the ideal gas limit at low density. At temperatures close to critical, none of the equations gives good results, since the critical compressibility factor of each is quite different from experiment. Such an observation has previously been made for the RK equation (Horvath, 1972) and is well known for the VDW equation. As was noted from the vapor pressure data, the CBVDW equation performs considerably better than the VDW equation, and the PM, RK, and PR equations perform quite similarly and are superior to all the others.

DISCUSSION

In this paper we have presented an equation of state of the VDW type but in which molecular nonsphericity and multipolarity are accounted for explicitly by the shape parameter $s\bar{R}$ and the energy parameter λ. The equation has four parameters, v, a, $s\bar{R}$, and λ. Our recommendation is to determine them from second virial coefficient data, critical point data, and the acentric factor. However, a least-squares fit to data might improve agreement between experiment and predictions.

As an empiricism, the equation offers no advantage over the RK and PR equations, since the latter involve only two and three parameters whereas the present model contains four. However, the present equation has the advantages that its form and parameters have a theoretical basis and that the qualitative effects of molecular shape and polarity on the thermodynamic properties of polyatomic fluids can be investigated with the equation. It would be interesting to extend the model to multicomponent systems. Molecular shape may play a more important role in mixtures than in one-component systems, since the packing geometry of a dense fluid is more complex in the former.

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NOTATION

a = energy parameter in equation of state
$\mathbf{D}_i$, $\mathbf{D}_j$ = dipole vectors of molecules
$\hat{e}_1$, $\hat{e}_2$ = orientations of molecules 1 and 2
g = pair correlation function
k = Boltzmann's constant
L = defined in Figure 1
R = defined in Figure 1
n = density, molecules/volume
N = number of particles
P = pressure
$\mathbf{r}_{12}$ = vector joining centers of mass of molecules 1 and 2
$\hat{\mathbf{r}}_{12}$ = unit vector in direction of $\mathbf{r}_{12}$
s = surface area of a convex particle
$\bar{R}$ = average radius of curvature of a convex particle
T = temperature
u_o = Lennard-Jones energy parameter
u = pair potential between molecules
u_{dd} = pair potential from dipole interaction alone
v = volume of a convex particle and volume parameter in equation of state
V = volume of the fluid of N particles
w = nonpolar attractive potential
Z_N = configurational partition function

Greek Letters

θ = molecular shape parameter, $s\bar{R}/v$
λ = energy term in equation of state accounting for fourth-order multipolar contributions
ρ = shortest distance between two convex particles
ρ_o = Lennard-Jones length parameter
σ_{12} = distance of separation of centers of molecules 1 and 2
ω_a = acentric factor

Subscripts and Superscripts

c = critical value
CB = for convex body
r = reduced by critical value
s = saturation value
$*$ = dimensionless quantity

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