Molecular Thermodynamics for Fluids at Low and High Densities

Part I: Pure Fluids Containing Small or Large Molecules

A correlation is presented for the thermodynamic properties of pure fluids containing small or large molecules. The residual Helmholtz energy is given in terms of perturbed-hard-chain (PHC) theory, extended to polar fluids with a multipolar expansion. The novel feature of this correlation is a separation of the Helmholtz energy into low-density and high-density contributions. The low-density contribution follows from a virial expansion and the high-density contribution from a perturbation expansion. For intermediate densities, a continuous function is used to interpolate between the two density limits. This modification of PHC theory improves agreement with experimental second virial coefficients, vapor pressures, and saturated liquid densities. Since all molecular parameters used here have a well-defined physical significance, they can be reliably estimated for high-molecular-weight-fluids where experimental data are scarce. More important, separation into low-density and high-density contributions allows separate mixing rules for each density region; this flexibility in mixing rules significantly improves representation of mixture properties, as discussed in Part II.

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Introduction

Equations of state are commonly used to correlate thermodynamic properties for computer-aided design of chemical processes. For engineering purposes, the most commonly used equations of state are either semitheoretical or empirical; the equations contain adjustable parameters that are fitted to experimental data. Empirical multiparameter equations, such as the Bennedict-Webb-Rubin equation (1940) and its extensions (Starling and Han, 1972; Watanasiri et al., 1982), have been widely used for engineering calculations. Such equations are useful if sufficient data are available to determine the large number of parameters; however, extension to mixtures is often difficult because essentially arbitrary mixing rules must be applied to a relatively large number of equation-of-state constants.

Semitheoretical equations are based on simplified molecular models; the parameters of such equations usually have some physical significance. The most common class of semitheoretical equations are based on van der Waals theory (Vera and Prausnitz, 1972; Sandler, 1985). The two main parameters are related to molecular size and to intermolecular potential energy; a third empirical parameter, e.g., the acentric factor, may be used to reflect the molecules' (small) deviation from spherical symmetry. Examples of this class are discussed in numerous references (Redlich and Kwong, 1949; Soave, 1972; Peng and Robinson, 1976); for a comprehensive review, see Martin (1979).

Extension of van der Waals theory to large molecules is based on the dense-fluid theories of Prigogine (1957) and Flory (1970) for chain molecules, or on the theory of Boublik (1975) for elongated hard convex bodies. Examples of this class are the perturbed-hard-chain (PHC) equation (Beret and Prausnitz, 1975a), the chain-of-rotators equation (Chien et al., 1983) and the hard-convex-body equations of Chen and Kreglewski (1977)

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and Chung et al. (1984). These equations use a third molecular parameter in addition to the two of the simple van der Waals theory. The third parameter is used to take into account the ellipticity or flexibility of high-molecular-weight molecules. Equations of this class are slightly more complex than the simple van der Waals equations, but they may be used to represent simultaneously liquid densities and vapor pressures for fluids containing large molecules. Extension to mixtures has been reported by several authors, notably Donohue and Prausnitz (1978), Chien et al. (1983) and Kreglewski and Chen (1978).

The semitheoretical equations tend to give good results at high densities and advanced temperatures. Although these equations approach the correct ideal-gas limit, they are generally poor at moderate densities. This effect is seen in the poor agreement between experimental and calculated second virial coefficients. For example, Kaul and Donohue (1980) found it necessary to add to the PHC equation an empirical correction to give a good second virial coefficient. Similar modifications for simpler equations of state were proposed by El-Twaty and Prausnitz (1980) and Brandani and Prausnitz (1981).

In this work, both high-density and low-density regions are represented with a single equation of state; however, instead of adding a correction term for the low-density region, we separate the high-density and low-density regions as suggested by Dimitrelis and Prausnitz (1982). This separation improves results for pure fluids but, more important, it allows flexibility to select mixing rules for mixtures, as discussed in Part II.

An Expression for Residual Helmholtz Energy

We seek an expression for the molar residual Helmholtz energy a^r; derivatives of that quantity give the equation of state, enthalpy, and chemical potential. The residual Helmholtz energy represents the effect of intermolecular forces; it is the difference between the Helmholtz energy for a real fluid and that for an ideal gas at the same temperature and volume

$$a^r(T,V) = a(T,V) - a^{IG}(T,V) \tag{1}$$

where superscript IG refers to ideal gas.

Following van der Waals, we separate a^r into reference and perturbation terms:

$$a^r = a^{ref} + a^{pert} \tag{2}$$

The reference term includes repulsive intermolecular forces; the perturbation term includes attractive intermolecular forces.

The principal novelty of our work is the separation of a^{pert} into high-density and low-density contributions

$$a^{pert} = a^{sv}(1 - F) + a^{df} F \tag{3}$$

where a^{sv} and a^{df} are the attractive contributions to the Helmholtz energy at the second-virial and the dense-fluid limits, respectively. To provide a smooth interpolation between the two density limits, we use a generalized interpolation function F that depends on density and temperature.

Perturbed-Soft-Chain Theory

As suggested by PHC theory, there are three characteristic molecular parameters for each pure fluid: $r\sigma^3$, $\epsilon q/k$, and c; these parameters characterize soft-core volume, potential energy, and the number of external degrees of freedom of the molecule, respectively.

Each molecule is considered to be made up of equisized segments; a molecule has r segments and an external surface area q. The soft-core volume, per mole of molecules, is

$$v^* = r\sigma^3 N_{av}/\sqrt{2} \tag{4}$$

where N_{av} is Avogadro's number and σ is the segment diameter.

The potential energy per molecule is given by $\epsilon q/k$ where ϵ is potential energy per unit surface area and k is Boltzmann's constant. A characteristic temperature is defined by

$$T^* \equiv \epsilon q/ck \tag{5}$$

Parameter $(c - 1)$ accounts for the density dependence of external molecular vibrations and rotations (Prigogine, 1957); for a chain molecule, it is a measure of flexibility and asymmetry. For simple molecules such as methane, $(c - 1)$ is zero.

Reduction of pure-fluid data yields parameter c and the products $\epsilon q/k$ and $r\sigma^3$. For correlation of mixture data, it is necessary to factor these products, as discussed in Part II.

The residual Helmholtz energy a^r in Eq. 2 is defined per mole of molecules. Expressions for reference and perturbation contributions to a^r are derived for spherical molecules; those expressions are generalized to nonspherical molecules using parameter c and number of segments r. For simple molecules ($c = 1$), the residual Helmholtz energy per mole of molecules may be written

$$a^r = r\, a^r_{seg} \tag{6a}$$

where a^r_{seg} is the residual Helmholtz energy per mole of *segments*. By introducing parameter c per segment (c/r), Eq. 6a becomes:

$$a^r = r\,(c/r)\, a^r_{seg} = c\, a^r_{seg} \tag{6b}$$

Equation 6b indicates that expressions for the residual Helmholtz energy derived for simple molecules (or molecular segments) can be generalized to chain molecules by multiplying by parameter c. Further, parameter c may be defined either per molecule or per molecular segment; the resulting expressions are numerically equivalent.

Reference Term

For the reference term a^{ref}, we use a generalized form of the hard-sphere Carnahan-Starling (1972) equation

$$\frac{a^{ref}}{RT} = c\,\frac{(3\tau/\tilde{v} - 4)(\tau/\tilde{v})}{(1 - \tau/\tilde{v})^2} \tag{7}$$

with

$$\tau = \pi\sqrt{2}/6 = 0.7405$$

The reduced volume $\tilde{v}$ may be defined per molecule or per segment; the two choices are equivalent. To illustrate, the reduced volume per segment is given by

$$\tilde{v}_{seg} = \frac{V}{n_{seg}\sigma^3/\sqrt{2}} \tag{8a}$$

where V is total volume and n_{seg} is the number of segments. Since n_{seg} is equal to the product of number of segments per molecule r and number of molecules n, Eq. 8a becomes

$$\tilde{v}_{seg} = \frac{V}{nr\sigma^3/\sqrt{2}} = \tilde{v} \tag{8b}$$

where $\tilde{v}$ is the reduced volume defined per molecule (or mole of molecules).

To define the reduced volume, we allow for softness of the core volume; following Barker and Henderson (1967), we use a temperature-dependent core diameter d. This temperature dependence follows from the Lennard-Jones intermolecular potential. We define the hard-core (temperature-dependent) diameter d by relating it to the Lennard-Jones soft-core (temperature-independent) diameter σ:

$$\frac{d}{\sigma} = \int_0^1 \{1 - \exp[-u(z)/kT]\}\,dz \tag{9}$$

where $u(z)$ is the Lennard-Jones potential and z is the center-to-center distance between interacting (nonbonded) segments divided by σ. For spherical Lennard-Jones molecules ($c = 1$), the integral in Eq. 9 depends on reduced temperature $kT/\epsilon q$; for nonspherical molecules ($c > 1$), the reduced temperature is generalized to $\tilde{T} = ckT/\epsilon q$.

Figure 1 shows the ratio d/σ as a function of reduced temperature ($\tilde{T} = T/T^*$). The points in Figure 1 are calculated from Eq. 9 for several reduced temperatures; these points are fitted as a function of reduced temperature $\tilde{T}$:

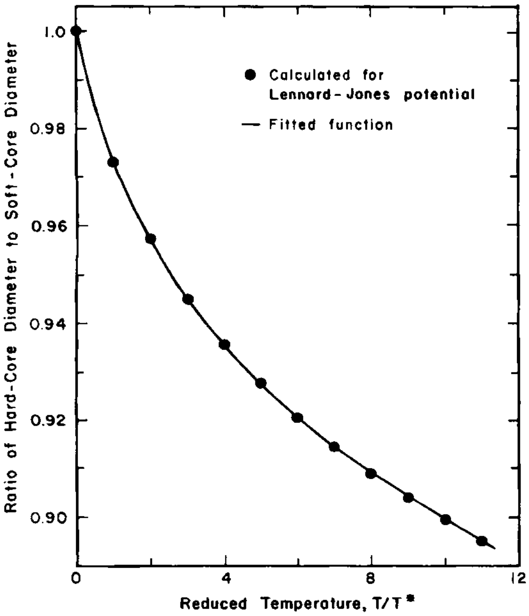

Figure 1. Temperature dependence of hard-core diameter for a Lennard-Jones fluid.

$$\frac{d}{\sigma} = \frac{1 + 0.29770\,\tilde{T}}{1 + 0.33163\,\tilde{T} + 0.0010477\,\tilde{T}^2} \tag{10}$$

for $0 < \tilde{T} < 15$. Equation 10 accurately represents d/σ values calculated from Eq. 9 and matches the theoretical limits $d/\sigma \rightarrow 1$ at $\tilde{T} = 0$ and $d/\sigma \rightarrow 0$ at $\tilde{T} = \infty$.

A temperature-dependent hard-core volume $v^\dagger$ is defined by

$$v^\dagger = v^*(d/\sigma)^3 \tag{11}$$

The reduced volume in Eq. 8 is given by $\tilde{v} = v/v^\dagger$.

For large temperature changes, the temperature dependence of the hard-core volume can be significant. For example, for a change in reduced temperature from $\tilde{T} = 0.5$ to $\tilde{T} = 5.0$, the hard-core volume $v^\dagger$ decreases almost 17%.

Dense-Fluid Perturbation Term

The dense-fluid perturbation term is given by the sum of dispersion and polar contributions:

$$a^{df} = a^{df}(\text{dispersion}) + a^{df}(\text{polar}) \tag{12}$$

Following Barker and Henderson (1967), we express the dispersion contribution as a perturbation expansion in reciprocal temperature for a Lennard-Jones intermolecular potential; we then generalize that result for nonspherical molecules using parameter c. We truncate the perturbation series following the second-order term:

$$a^{df}(\text{dispersion}) = \frac{a^{(1)}}{\tilde{T}} + \frac{a^{(2)}}{\tilde{T}^2} \tag{13}$$

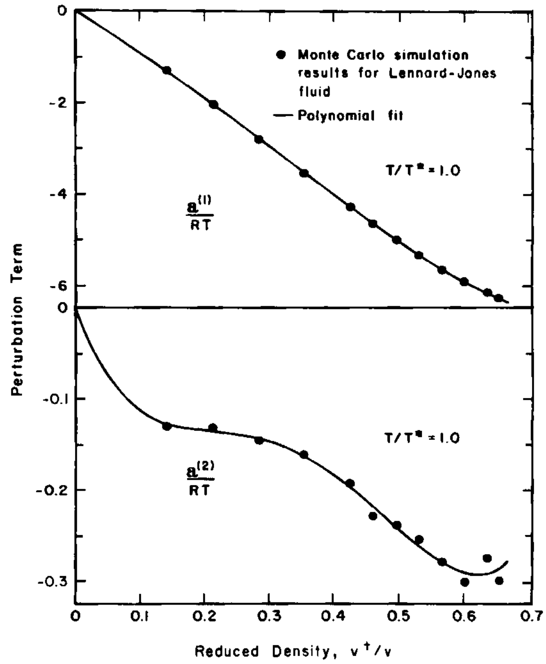

Figure 2. First-order and second-order perturbation terms in Helmholtz energy as a function of reduced density for a Lennard-Jones fluid.

Functions $a^{(1)}$ and $a^{(2)}$ are determined from Monte Carlo computer simulations for Lennard-Jones molecules (Henderson and Barker, 1971). For spherical molecules ($c = 1$), these functions depend only on reduced volume; for nonspherical molecules ($c > 1$), $a^{(1)}$ and $a^{(2)}$ depend also on parameter c, as shown in Appendix A.

Figure 2 shows Monte Carlo results for a Lennard-Jones fluid as a function of reduced hard-core density. The first-order perturbation from $a^{(1)}$ is nearly linear in density; this linearity is consistent with the density dependence of the perturbation term in the original van der Waals model. The magnitude of the second-order term is much smaller than that of the first-order term; the perturbation series converges rapidly. The simulation results in Figure 2 are fitted with polynomials in reduced hard-core density. Appendix A gives coefficients for the polynomials.

Similar to the work of Vimalchand and Donohue (1985) and Vimalchand et al. (1986), we have extended the PHC theory to fluids containing dipole and/or quadrupole moments using the multipolar expansions of Gubbins and Twu (1978). Polar contributions arise from dipolar, quadrupolar, and dipolar-quadrupolar interactions. Reduced dipole and quadrupole moments are defined by

$$\tilde{\mu} = \frac{\mu}{(\epsilon q)^{1/2}(r\sigma^3)^{1/2}} \tag{14}$$

$$\tilde{Q} = \frac{Q}{(\epsilon q)^{1/2}(r\sigma^3)^{5/6}} \tag{15}$$

where μ and Q are dipole and quadrupole moments, respectively. The expressions given by Gubbins and Twu are derived for linear molecules. For nonlinear molecules, effective values of dipole and quadrupole moments are used in Eqs. 14 and 15.

Following Gubbins and Twu, we express the polar contribution a^{df} (polar) as a multipole expansion

$$a^{df}(\text{polar}) = a^{\mu\mu} + a^{QQ} + a^{\mu Q} \tag{16}$$

where $a^{\mu\mu}$, a^{QQ}, and $a^{\mu Q}$ are contributions due to dipolar, quadrupolar, and dipolar-quadrupolar forces. Equation 16 neglects induction effects. Appendix B gives details of the expressions for each term in Eq. 16.

Second Virial Perturbation Term

At low densities we use a virial expansion to derive an expression for a^{sv} in Eq. 3. We truncate the virial expansion after the second virial coefficient. The resulting expression for the low-density limit becomes

$$a^{sv} = \frac{RT}{v}(B^{disp} + B^{\mu\mu} + B^{QQ}) \tag{17}$$

where B^{disp} is the contribution to the second virial coefficient from dispersion forces, B^{QQ} is the contribution from quadrupolar forces, and $B^{\mu\mu}$ is the contribution from dipolar forces. Only leading polar contributions are included in Eq. 17; induction forces and dipolar-quadrupolar forces are neglected.

The expression for the dispersion term is correlated as a function of $v^\dagger$, c, and $\tilde{T}$ using experimental second virial coefficients for the normal alkane series. The polar contributions are fitted to experimental second virial coefficients for quadrupolar and dipolar fluids. Appendices A and B give details for these contributions.

The top part of Figure 3 shows calculated and observed second virial coefficients for normal alkanes. Parameter c for each fluid is indicated in parentheses. Since the virial coefficients are reported in reduced units, the top diagram illustrates the influence of increasing values of c.

The bottom part of Figure 3 shows results for several polar fluids. These fluids have similar c values; differences in reduced second virial coefficients are due to different strengths of multipolar moments.

Interpolation Function

Function F in Eq. 3 interpolates between the two density limits. The interpolation function is not unique but must meet several boundary conditions: it must be zero at zero density, it must approach unity at high densities, and it must approach zero at very high temperatures. Further, it must not contribute to the second virial coefficient. We choose an exponential function; the argument of the exponential is selected to meet the necessary boundary conditions:

$$F = 1 - \exp\left[-\left(\frac{6}{\tilde{T}}\right)\frac{(\epsilon q/k)^{\text{total}}}{T\tilde{v}}\right] \tag{18}$$

where $(\epsilon q/k)^{\text{total}}$ is the sum of the dispersion and polar contributions to the potential energy:

$$(\epsilon q/k)^{\text{total}} = cT^*(1 + \tilde{\mu}^2 + \tilde{Q}^2 + 2\tilde{\mu}\tilde{Q}) \tag{19}$$

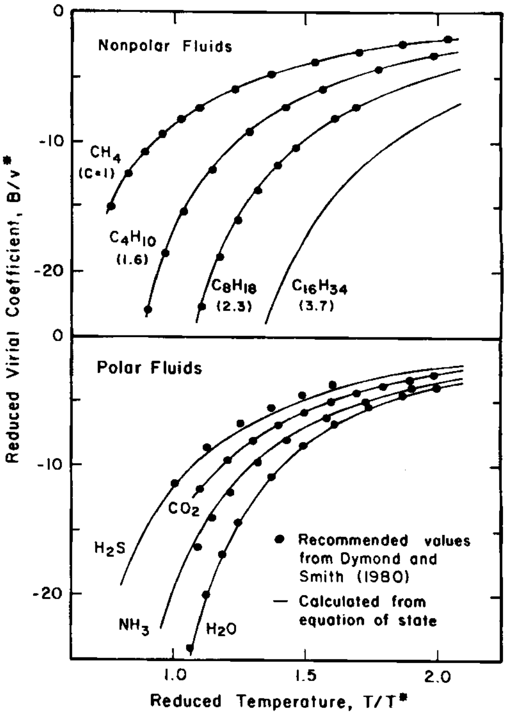

Figure 3. Calculated and experimental second virial coefficients for several polar and nonpolar fluids.

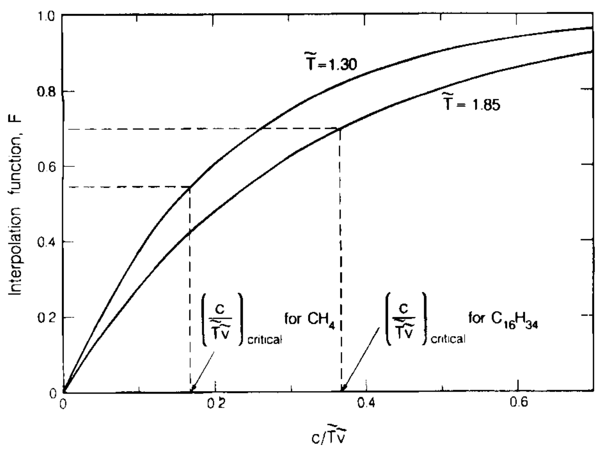

Figure 4. Universal function for interpolation between low-density and high-density limits.

The coefficient $(6/\tilde{T})$ is determined empirically from experimental data for a large number of fluids.

Figure 4 shows the interpolation function at two reduced temperatures corresponding to the reduced critical temperatures of methane and hexadecane. At the critical density of methane, there are nearly equal contributions to the residual Helmholtz energy from the low-density and the high-density expressions. At the critical density of hexadecane, the relative contribution from the high-density limit is larger than from the low-density limit. Increased molecular size increases high-density contributions at the critical density.

Data Reduction

The method of data reduction is extremely important for evaluating the ability of a molecular model to represent experimental data. Regression methods should give not only reliable estimates of molecular parameters but also uncertainties in those parameters. If molecular parameters are fitted to only one thermodynamic property (such as vapor pressure or density), they tend to be correlated to each other. The uniqueness of parameters is much improved if more than one property is used for the regression, as suggested, for example, by Cox et al. (1971).

We fit parameters simultaneously to vapor pressure and density data. For most fluids, we use liquid densities at saturation or atmospheric pressure; however, for low-molecular-weight compounds (H_2) and polymers, we use fluid densities in the single-phase region at high pressures.

A data reduction method should take into account experimental uncertainties. We use a maximum-likelihood procedure described by Anderson et al. (1978) to account for errors in both dependent and independent variables. Anderson and Prausnitz (1980) discuss maximum-likelihood techniques for obtaining equation-of-state parameters.

We assume standard error estimates for each type of data. Typical expected errors are: temperatures ±0.05 K and pressures ±1.0% for vapor pressure data; temperatures ±0.05 K, densities ±2.0%, and pressures ±2.0% for density data. These estimates suffice to account for typical experimental uncertainties. Since uncertainties for vapor pressure data are lower than those for density data, vapor pressure data are in effect given preferential weight in data reduction.

We use experimental second virial coefficients from Dymond and Smith (1980) to determine universal constants for each contribution to the virial coefficient in Eq. 17; expressions for these contributions are given in Eq. A3 and Eqs. B10 and B12 in the appendices.

Gray and Gubbins (1984) give experimental dipole and quadrupole moments for a variety of fluids. While dipole moments can be measured accurately, experimental quadrupole moments have large uncertainties; therefore, for molecules with both dipole and quadrupole moments we adjust the quadrupole moment slightly to give good agreement with vapor pressure and density data.

Comparison of Calculated and Experimental Thermodynamic Properties

To illustrate applicability, Figure 5 shows the calculated and experimental pressure vs. density phase diagram for pentane. Agreement between calculated and experimental PVT and saturation properties is good, except in the critical region.

The dotted line in Figure 5 indicates behavior of the equation of state in the two-phase region. The equation gives a simple van der Waals loop inside the two-phase region, similar to that of cubic equations such as the Redlich-Kwong equation or the Peng-Robinson equation.

Figure 6 shows a pressure vs. density phase diagram for carbon dioxide. Due to the large quadrupole moment of carbon dioxide, the quadrupolar perturbation terms contribute significantly to the equation of state. the equation of state behaves smoothly throughout the phase diagram, producing a van der Waals loop (not shown) in the two-phase region. As with pentane, our equation of state overpredicts the critical pressure. This overprediction is a common feature of virtually all semitheoretical equations of state.

Phase diagrams may also be calculated for strongly polar fluids such as water or ammonia. The qualitative behavior of the

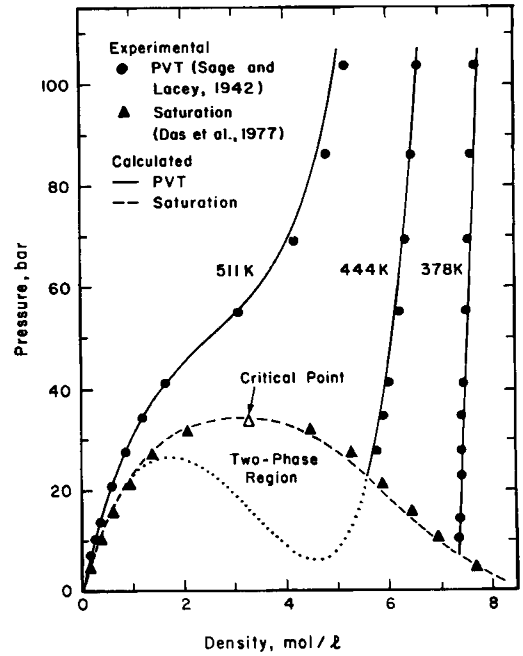

Figure 5. Calculated and experimental phase diagram for pentane showing equation-of-state behavior in two-phase region.

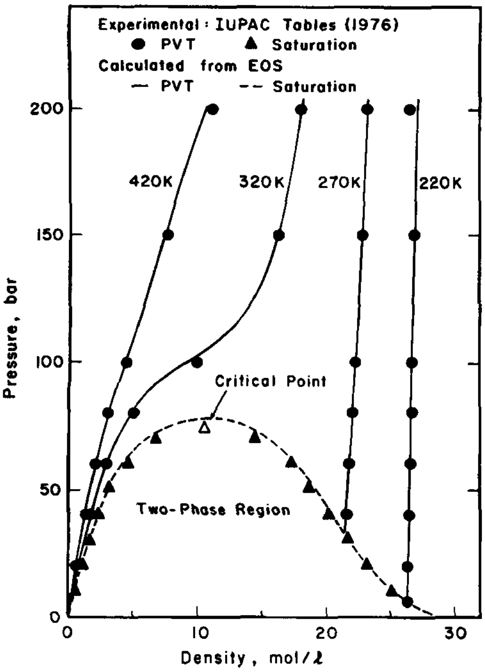

Figure 6. Calculated and experimental phase diagram for carbon dioxide.

equation of state is similar to that for nonpolar fluids; however, agreement between calculated and experimental properties, while good, is somewhat less favorable. Tables 1 and 2 show average deviations between calculated and observed fluid densities and saturation properties for several fluids, including water.

Figure 7 shows calculated and experimental densities for hydrogen at three temperatures. To avoid quantum effects, only density data above 100 K are used to determine hydrogen parameters. Above 100 K, hydrogen is supercritical; the parameters given here should not be used to calculate saturation properties for hydrogen.

Table 2 shows typical agreement between calculated and experimental saturation properties for several polar and nonpolar fluids. For each fluid, the range of reduced temperature is indicated; deviations between calculated and observed results are reported as percent average absolute deviations.

Additional comparisons between calculated and experimental saturation properties are deposited as supplementary material.

Table 1. Percent Deviation of Experimental and Calculated Fluids Densities for Several Nonpolar and Polar Fluids

Fluid	Temp. Range K	Pres. Range Bar	Density % AAD*
Methane	200–600	1–500	0.19
Propane	390–700	1–700	0.70
Pentane	344–510	1–100	1.19
Hydrogen	100–700	1–500	0.04
Carbon Dioxide	220–720	1–200	0.14
Water	273–773	1–250	1.54

*Average absolute deviation.

Table 2. Percent Deviation of Calculated and Experimental Saturation Properties for Several Nonpolar and Polar Fluids

Fluid	Temp. Range T/T_c	% Avg. Absolute Deviation Vapor Press.	 Liquid Density
Methane	0.48–0.95	0.62	0.81
Pentane	0.31–0.95	0.61	1.57
Decane	0.45–0.85	0.89	1.42
Eicosane	0.40–0.85	1.18	0.18
Isobutane	0.46–0.95	0.22	0.96
Cyclohexane	0.50–0.95	0.28	0.10
Benzene	0.50–0.95	0.20	0.24
Anthracene	0.56–0.76	0.23	0.21
Tetralin	0.40–0.94	1.25	1.85
Nitrogen	0.50–0.95	0.49	0.54
Carbon Dioxide	0.72–0.95	0.02	0.55
Water	0.42–0.95	1.32	1.74
Ammonia	0.49–0.95	0.14	3.00

Molecular Parameters for Pure Fluids

Molecular parameters have been fitted for several polar and nonpolar fluids. Table 3 gives some typical parameters. With the exception of hydrogen, these parameters were fitted simultaneously to vapor pressure and density data. A more extensive list of parameters with data references is deposited as supplementary material.

Table 4 lists dipole and quadrupole moments for several polar fluids. The quadrupole moments for quadrupolar fluids are experimental values with the exception of carbon dioxide. The experimental quadrupole moment for carbon dioxide is 4.3 B (1 Buckingham = 10^{-26} *esu cm*^{2}); a slightly smaller value of 3.9 B improves agreement with experimental vapor pressure and density data. Quadrupole moments for dipolar fluids are selected to agree with vapor pressure and density data. However, all dipole moments are independently reported experimental values.

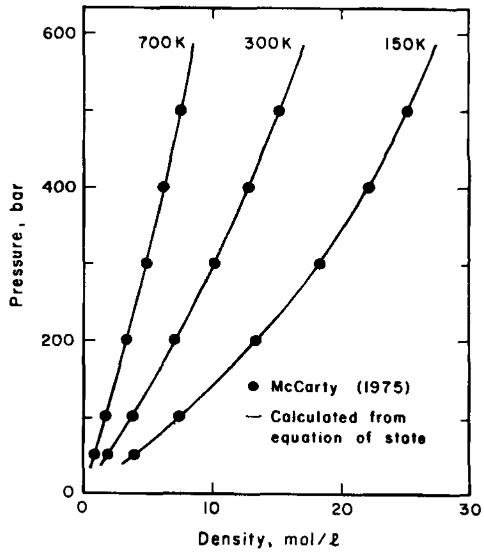

Figure 7. Calculated and experimental supercritical densities for hydrogen at three temperatures.

Table 3. Molecular Parameters for Nonpolar and Polar Fluids

Fluid	T^* K	v^* cm^3/mol	c
Normal Alkanes			
Methane	147.1	21.94	1.000
Propane	253.5	40.46	1.447
Decane	357.3	110.9	2.689
Tetratetracontane	434.9	463.2	7.773
Alkylnaphthalenes			
Cyclohexane	358.5	61.71	1.705
Decylcyclohexane	418.8	165.9	3.223
Alkylbenzenes			
Benzene	368.1	50.61	1.678
Decylbenzene	423.9	154.9	3.181
Fused-ring Aromatics			
Tetralin	443.9	81.19	2.090
Triphenylene	626.2	128.2	2.325
Quadrupolar Fluids			
Carbon dioxide	200.8	21.09	1.220
Nitrogen	95.84	20.06	1.000
Dipolar Fluids			
Water	401.1	12.27	1.052
Ammonia	274.8	15.99	1.051
Sulfur dioxide	287.9	27.20	1.223
Hydrogen sulfide	277.0	21.75	1.097
Light Gases			
Hydrogen	30.43	11.02	1.000

Representation of Volumetric Data for Molten Polymers

Our modified PHC theory is useful for representing volumetric data for high molecular weight fluids such as molten polymers. Figure 8 shows calculated and experimental densities for two polymers, polyethylene ($MW_n = 25{,}000$) and polyisobutylene ($MW_n = 36{,}000$). As discussed, for example, by Liu and Prausnitz (1979), it is inconvenient to use molar quantities for polymeric fluids; therefore, we replace everywhere the molar quantities v^* and c with specific soft-core volume v^*_{sp} and characteristic parameter P^*, defined by $P^* = cRT^*/v^*$. While both v^* and c are molar quantities, the ratio P^* is independent of molecular weight.

Table 4. Dipole and Quadrupole Moments for Several Fluids

Fluid	Q B*	$\tilde{Q}$	μ D**	$\tilde{\mu}$
Quadrupolar Fluids				
Carbon dioxide	3.90†	0.821	—	—
Nitrogen	1.47	0.516	—	—
Chlorine	3.23	0.470	—	—
Carbon disulfide	4.30	0.413	—	—
Ethylene	2.00	0.333	—	—
Cyclopropane	1.60	0.185	—	—
Dipolar Fluids				
Water	1.25†	0.315	1.850	1.428
Ammonia	1.15†	0.281	1.470	1.201
Acetone	—	—	2.880	1.157
Sulfur dioxide	3.00†	0.426	1.630	0.925
Hydrogen sulfide	1.00†	0.184	0.974	0.665
Carbon monoxide	1.00†	0.331	0.112	0.133

*B, Buckingham; **D, Debye.

†Value of quadrupole moment adjusted to experimental vapor pressure and density data.

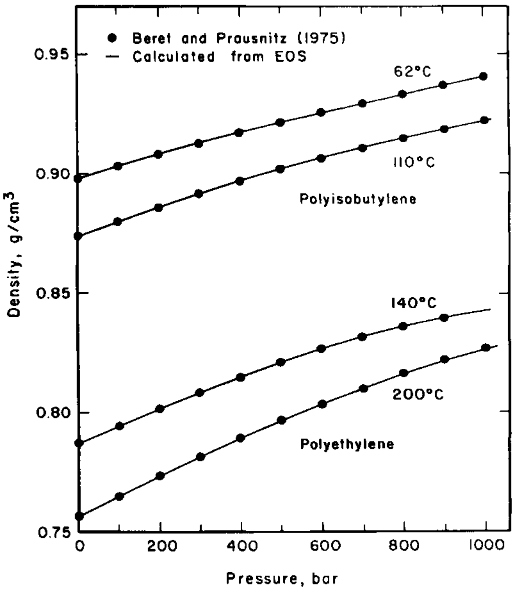

Figure 8. Calculated and experimental densities for two molten polymers.

Table 5 gives pure-component molecular parameters for the two molten polymers shown in Figure 8. These parameters were fitted to the polymer compressibility data of Beret and Prausnitz (1975b).

Correlation of Molecular Parameters

As discussed by Wilhelm and Prausnitz (1985), pure-fluid PHC parameters can be correlated as simple functions of molecular weight for various hydrocarbon classes. Such correlations are useful to estimate parameters for those fluids where experimental data are not available. These correlations are also useful for continuous-thermodynamics calculations (Cotterman and Prausnitz, 1985) where parameters are expressed as continuous functions of some characterizing property such as molecular weight.

We have correlated equation-of-state parameters for four hydrocarbon classes: normal paraffins, *n*-alkylbenzenes, *n*-alkylcyclohexanes, and fused-ring aromatics. Appendix C gives correlation functions and constants. Figures 9 and 10 show correlation results as a function of molecular weight for normal alkanes and fused-ring aromatics, respectively. As these figures show, and as suggested by their physical significance, the potential-energy parameter $\epsilon q/k(=cT^*)$ and soft-core volume v^* are linear functions of molecular weight. Since (for a given chemical series) parameters c and q are expected to be linear functions of molecular weight for intermediate and high molecular weights,

Table 5. Molecular Parameters for Two Molten Polymers

Polymer	T^* K	v^*_{sp} cm^3/g	P^* bar
Polyethylene	511.0	0.7519	946.4
Polyisobutylene	517.6	0.6903	1250.

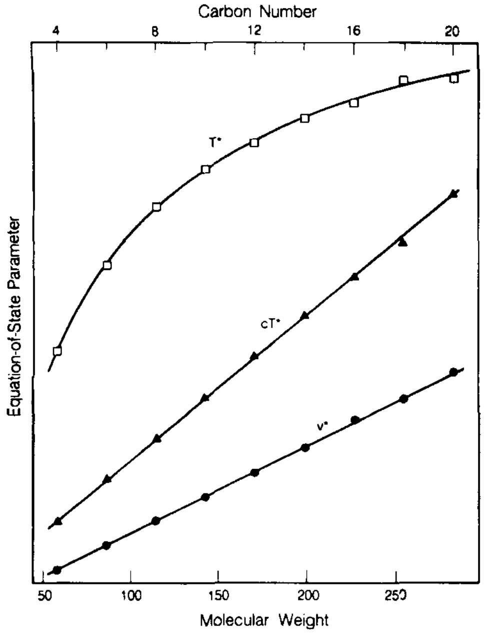

Figure 9. Correlation of equation-of-state parameters for normal alkanes as a function of molecular weight.

Figure drawn to scale.

we expect characteristic temperature T^* to approach a constant as molecular weight becomes large. Therefore, these parameter correlations may be extrapolated with confidence to higher molecular weights where experimental data are scarce.

To illustrate such extrapolation, we use the correlation shown in Figure 9 to determine molecular parameters for polyethylene. Extrapolating our parameter correlations to molecular weight 25,000, we find an average deviation of 1.6% between the calculated densities and experimental densities shown in Figure 8. This deviation is necessarily, but not much, higher than that of using the fitted parameters in Table 5. This example suggests that the generalized correlations can give reasonable estimates of molecular parameters for large molecules.

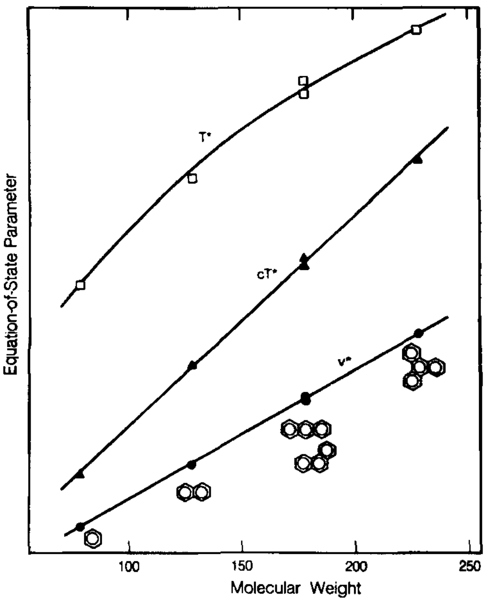

Figure 10. Correlation of equation-of-state parameters for fused-ring aromatics as a function of molecular weight.

Figure drawn to scale.

Throughout this work, we have stressed the physical significance of molecular parameters. Well-defined physical significance is important for parameter correlations and for establishing meaningful mixing rules for calculating mixture properties. Physical significance is particularly important for polar fluids. When polar effects are neglected, "molecular" parameters may be determined that fit pure-fluid data well, but these nonmeaningful parameters give poor results for mixture calculations. Appendix D discusses briefly the importance of including polar effects when fitting data for polar fluids and lists parameters for several polar fluids, neglecting polar effects.

Conclusion

A molecular-thermodynamic correlation is presented for representing thermodynamic properties of pure fluids containing small or large molecules. The novel feature of this correlation is a separation of high-density and low-density contributions to an expression for the residual Helmholtz energy. While this separation leads to accurate representation of pure-fluid properties, the primary advantage follows from extension to mixtures, as discussed in Part II.

The applicability of the correlation is illustrated for fluids of interest in the petroleum and related industries. Thermodynamic properties are correlated for polar and nonpolar fluids ranging in molecular size from hydrogen to polyisobutylene. For each pure component, three characteristic molecular parameters are fitted to experimental vapor pressure and/or density data. Calculated and experimental results are in good agreement over wide ranges of temperature and pressure except in the critical region.

Molecular parameters are reported for a variety of pure fluids. For a homologous series, these parameters are simple functions of molecular weight. Parameters are correlated for four hydrocarbon series: normal paraffins, *n*-alkylbenzenes, *n*-alkylcyclohexanes, and fused-ring aromatics. These correlations can be used to estimate molecular parameters for high-molecular-weight fluids where experimental data are scarce; they are also useful for continuous-thermodynamics calculations where parameters are expressed as continuous functions of molecular weight.

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Notation

a = molar Helmholtz energy
$a^{(1)}, a^{(2)}$ = coefficients for correlation in Eq. C1
$b^{(1)}, b^{(2)}$ = coefficients for correlation in Eq. C2
B = second virial coefficient (attractive contribution)
$c^{(1)}, c^{(2)}, c^{(3)}$ = coefficients for correlation in Eq. C3
c = shape and flexibility parameter

d = hard-core (temperature-dependent) diameter
F = interpolation function
J = integral of two-body radial distribution function
K = integral of three-body radial distribution function
k = Boltzmann's constant
n = number of moles (or molecules)
n_{seg} = number of molecular segments
P = absolute pressure
P^* = characteristic pressure, $P^* = cRT^*/v^*$
q = external molecular surface area
Q = molecular quadrupole moment
$\tilde{Q}$ = reduced quadrupole moment
r = number of segments per molecule
R = gas constant
T = absolute temperature
$\tilde{T}$ = reduced temperature, $\tilde{T} = T/T^*$
T^* = characteristic temperature, $T^* = \epsilon q/ck$
u = intermolecular potential
v = molar volume
$\tilde{v}$ = reduced volume, $\tilde{v} = v/v\dagger$
$\tilde{v}_{seg}$ = reduced volume per segment
$\bar{v}$ = reduced volume, $\bar{v} = v/v^*$
v^* = soft-core molar-volume parameter
v_{sp}^* = soft-core specific-volume parameter, $v_{sp}^* = v^*/MW$
$v\dagger$ = hard-core molar-volume parameter
V = total volume

Greek letters

μ = molecular dipole moment
$\tilde{\mu}$ = reduced dipole moment
ϵ = potential energy per unit surface area
σ = soft-core diameter (independent of temperature)
τ = hard-sphere packing factor (0.7405)
Ω = correction to second virial coefficients due to parameter c

Superscripts

df = dense-fluid contribution
$disp$ = dispersion contribution
IG = ideal-gas property
$pert$ = perturbation term
QQ = quadrupolar contribution
ref = reference term
sv = second virial contribution
$\mu\mu$ = dipolar contribution
μQ = dipolar-quadrupolar contribution

Appendix A. Nonpolar Contributions to Perturbation Term of Residual Helmholtz Energy

This appendix gives expressions for the dispersion (nonpolar) contributions to the high-density and low-density perturbation terms. Dispersion contributions to the high-density term are determined from computer-simulation results; low-density contributions are determined empirically to represent experimental second virial coefficients.

Equation 13 gives an expression for the dispersion contributions to the dense-fluid term a^{df} as a truncated perturbation series. The first-order and second-order terms of this series, $a^{(1)}$ and $a^{(2)}$, are fitted to computer-simulation results for Lennard-Jones molecules

$$\frac{a^{(1)}}{RT} = \frac{c}{\tilde{v}} \cdot (-8.5959 - 4.5424/\tilde{v} - 2.1268/\tilde{v}^2 + 10.285/\tilde{v}^3) \quad \text{(A1)}$$

$$\frac{a^{(2)}}{RT} = \frac{c}{\tilde{v}} \cdot (-1.9075 + 9.9724/\tilde{v} - 22.216/\tilde{v}^2 + 15.904/\tilde{v}^3) \quad \text{(A2)}$$

where $\tilde{v}$ is reduced hard-core volume. Parameter c in Eqs. A1 and A2 follows from the derivation of the PHC theory (Beret and Prausnitz, 1975a). The polynomials in Eqs. A1 and A2 are plotted in Figure 2 as a function of reduced density for spherical molecules ($c = 1$) at $\tilde{T} = 1.0$.

The dispersion contribution to the second virial coefficient B^{disp} is fitted to second virial coefficient data for normal alkanes

$$B^{disp} = -cv\dagger(12.541 + \Omega(c)/\tilde{T}^6) \cdot [\exp(0.67372/\tilde{T}) - 0.98071] \quad \text{(A3)}$$

Universal constants for simple molecules ($c = 1$) are fitted to second viral coefficients for methane. Function $\Omega(c)$ extends Eq. A3 to fluids with larger c values; it is fitted to second virial coefficient data for alkanes from ethane to *n*-octane

$$\Omega = \frac{6.9261(c-1)^2}{1.0 + 0.87720(c-1)} \quad \text{(A4)}$$

Function Ω is zero for simple fluids and is linear in c for high-molecular-weight fluids.

Equations A3 and A4 contain molecular parameters T^*, v^*, and c. These parameters are fitted to vapor pressure and density data. Since the second virial term B^{disp} contributes to calculated vapor pressures and densities, universal constants in Eqs. A3 and A4 and molecular parameters must be determined by sequential and repeated fitting of second virial coefficients and dense-fluid properties, until convergence is achieved. Therefore, the constants in Eqs. A3 and A4 are consistent with the molecular parameters reported in Table 3.

Appendix B. Perturbation Term for Polar Contributions to Residual Helmholtz Energy

This appendix gives expressions for multipolar contributions to the high-density and low-density perturbation terms. The high-density contributions follow from a multipole expansion for a Lennard-Jones (dispersion) reference system; low-density contributions are correlated to experimental second virial coefficients for several polar and quadrupolar fluids.

Polar and quadrupolar interactions are characterized using reduced dipole and quadrupole moments, defined by Eqs. 14 and 15. These equations may be written more conveniently in terms of molecular parameters T^*, v^*, and c:

$$\tilde{\mu} = \frac{\mu}{(cT^*v^*)^{1/2}}\left[\frac{N_{av}}{k\sqrt{2}}\right]^{1/2} \quad \text{(B1a)}$$

$$\tilde{Q} = \frac{Q}{(cT^*)^{1/2}(v^*)^{5/6}}\, k^{1/2}\left[\frac{N_{av}}{\sqrt{2}}\right]^{5/6} \quad \text{(B1b)}$$

For T^* in K, v^* in cm^3/mol, μ in D (1 Debye = 10^{-18} *esu cm*), and Q in B (1 Buckingham = 10^{-26} *esu cm*^{2}). Eqs. B1a and B1b become:

$$\tilde{\mu} = 55.537\frac{\mu}{(cT^*v^*)^{1/2}} \quad \text{(B2a)}$$

$$\tilde{Q} = 41.783\frac{Q}{(cT^*)^{1/2}(v^*)^{5/6}} \quad \text{(B2b)}$$

High-density contributions

As suggested by several authors (Gubbins and Twu, 1978; Stell et al., 1974), multipolar effects may be introduced into molecular-thermodynamic models as multipolar perturbation expansions to the Helmholtz energy. Since these series expansions converge slowly for strong multipole moments, they are replaced by a Padé approximant due to Stell et al.

The multipolar contribution due to dipole-dipole forces is

$$a^{\mu\mu} = a_{\mu\mu}^{(2)}\left[1 - \frac{a_{\mu\mu}^{(3)}}{a_{\mu\mu}^{(2)}}\right]^{-1} \qquad \text{(B3)}$$

Since the multipolar expansion is a perturbation to a Lennard-Jones (nonpolar) reference system, first-order perturbation terms do not appear. The second-order and third-order perturbation terms are given by

$$\frac{a_{\mu\mu}^{(2)}}{RT} = -2.9619\,\frac{c\tilde{\mu}^4}{\tilde{T}^2\bar{v}}\,J^{\mu\mu}(\tilde{T},\bar{v}) \qquad \text{(B4)}$$

$$\frac{a_{\mu\mu}^{(3)}}{RT} = 43.596\,\frac{c\tilde{\mu}^6}{\tilde{T}^3\bar{v}^2}\,K^{\mu\mu\mu}(\tilde{T},\bar{v}) \qquad \text{(B5)}$$

where $J(\tilde{T},\bar{v})$ and $K(\tilde{T},\bar{v})$ are integrals based on two-body and three-body radial-distribution functions. Analytical expressions for these integrals, given by Gubbins and Twu (1978), are shown in the supplementary material. Reduced volumes $\bar{v}$ for polar perturbation terms are defined using the soft-core volume ($\bar{v} = v/v^*$).

The multipolar contribution due to quadrupole-quadrupole forces is

$$a^{QQ} = a_{QQ}^{(2)}\left[1 - \frac{a_{QQ}^{(3)}}{a_{QQ}^{(2)}}\right]^{-1} \qquad \text{(B6)}$$

The second-order and third-order perturbation terms are given by

$$\frac{a_{QQ}^{(2)}}{RT} = -12.440\,\frac{c\tilde{Q}^4}{\tilde{T}^2\bar{v}}\,J^{QQ}(\tilde{T},\bar{v}) \qquad \text{(B7)}$$

$$\frac{a_{QQ}^{(3)}}{RT} = 2.6113\,\frac{c\tilde{Q}^6}{\tilde{T}^3\bar{v}}\,J^{QQQ}(\tilde{T},\bar{v}) + 77.716\,\frac{c\tilde{Q}^6}{\tilde{T}^3\bar{v}^2}\,K^{QQQ}(\tilde{T},\bar{v}) \qquad \text{(B8)}$$

For dipole-quadrupole forces, the perturbation series is truncated after the second-order term since contributions from higher-order terms are expected to be small. The resulting expression for the dipole-quadrupole contribution is

$$\frac{a^{\mu Q}}{RT} = -8.8858\,\frac{c\tilde{\mu}^2\tilde{Q}^2}{\tilde{T}^2\bar{v}}\,J^{\mu Q}(\tilde{T},\bar{v}) \qquad \text{(B9)}$$

As used here, constants reported by Gubbins and Twu for each of the above integrals must be multiplied by $\sqrt{2}$ wherever reduced density appears because the reduced volume in this work is based on a close-packed molecular volume. Analytical expressions for the integrals are included in the supplementary material.

Low-density contributions

As discussed in Appendix A, low-density contributions to a^{pert} are fitted to experimental second virial coefficient data. Contributions are included for quadrupole-quadrupole forces and for dipole-dipole forces; dipole-quadrupole contributions are neglected because their magnitude is much smaller than that of dipole-dipole contributions.

Expressions for the multipolar contributions are fitted initially to second virial coefficients for Lennard-Jones molecules with point dipoles (Stockmayer, 1941) or with point quadrupoles (Buckingham and Pople, 1955). Universal constants in these expressions are then adjusted using experimental second virial coefficients.

For dipole-dipole contributions,

$$B^{\mu\mu} = cv^*\left(7.6445 - 7.4678c - \frac{\Omega^{\mu\mu}}{\tilde{T}}\right) \cdot \left[\exp\left(1.6578\,\frac{\tilde{\mu}^{3/2}}{\tilde{T}}\right) - 1\right] \qquad \text{(B10)}$$

where

$$\Omega^{\mu\mu} = 8.9110 - 9.8386c \qquad \text{(B11)}$$

For quadrupole-quadrupole contributions,

$$B^{QQ} = cv^*\left(-0.090323 + \frac{\Omega^{QQ}}{\tilde{T}}\right) \cdot \left[\exp\left(2.8285\,\frac{\tilde{Q}^{3/2}}{\tilde{T}}\right) - 1\right] \qquad \text{(B12)}$$

where

$$\Omega^{QQ} = 0.85613 - 0.28108c \qquad \text{(B13)}$$

As discussed in Appendix A, the final expressions for Eqs. B10 to B13 are determined by sequential and repeated fitting of universal constants and molecular parameters in those expressions to second virial coefficient data and to dense fluid data.

Appendix C. Correlation of Equation-of-State Parameters for Various Hydrocarbon Classes

Figures 9 and 10 show that for a given hydrocarbon class, molecular parameters can be correlated as simple functions of molecular weight. Parameters v^*, $\epsilon q/k$ ($=cT^*$), and c are nearly linear in molecular weight; however, over a wide range of molecular weight, parameter c shows nonnegligible deviations from linearity. Therefore, we correlate characteristic temperature T^* instead of c, since T^* approaches a constant value at high molecular weights.

For a given hydrocarbon class, the functions chosen to corre-

Table C1. Calculated and Experimental Vapor Pressures and Liquid Densities for Several Hydrocarbon Classes

Hydrocarbon Class	Mol. Wt. Range	% Avg. Absolute Deviation	
		Vapor Press.	Liquid Density
Paraffins			
(*n*-alkanes)	58–619	2.03	1.55
Naphthenes			
(*n*-alkylcyclohexanes)	84–365	2.98	0.38
Alkyl aromatics			
(*n*-alkylbenzenes)	78–359	2.26	0.79
Fused-ring aromatics	78–228	2.77	1.27

late parameters v^*, cT^*, and T^* are

$$v^* = a^{(1)} + a^{(2)}MW \tag{C1}$$

$$cT^* = b^{(1)} + b^{(2)}MW \tag{C2}$$

$$T^* = c^{(1)} - c^{(2)} \exp\left(-c^{(3)}MW^{1/2}\right) \tag{C3}$$

Constants $a^{(1)}$, $a^{(2)}$, $b^{(1)}$, and $b^{(2)}$ are fitted directly to molecular parameters. Likewise, constants $c^{(1)}$, $c^{(2)}$, and $c^{(3)}$ are fitted initially to molecular parameters; however, these constants are later adjusted by fitting, all at once, vapor pressure and density data for the components in a hydrocarbon class.

Table C1 lists ranges of molecular weight and comparisons between calculated and observed vapor pressures and densities for four hydrocarbon classes. Agreement between calculation and experiment is reported for each class as overall percent average absolute deviations.

Table C2 gives constants for Eqs. C1 to C3 for four hydrocarbon classes. With the exception of the *n*-alkylcyclohexanes, these constants are used to calculate the deviations listed in Table C1. For the *n*-alkylcyclohexanes, the value of cT^* for cyclohexane does not lie on the same straight line with the other compounds in that hydrocarbon class. Therefore, we add the term $[243.90/(MW - 78)]$ to Eq. C2 to include cyclohexane, it being understood that the correlation is valid only for $MW \geq 84$. This correction does not contribute significantly to the other compounds; for molecular weights above 90, this correction may be omitted.

Table C2. Correlation of Molecular Parameters for Several Hydrocarbon Classes; Constants for Eqs. C1, C2, C3

Hydrocarbon Class	v^*, cm^3/mol		
	$a^{(1)}$	$a^{(2)}$	
Paraffins	8.6855	0.71820	
Naphthenes	0.2703	0.73628	
Alkyl aromatics	−7.2913	0.74042	
Fused-ring aromatics	10.1030	0.51714	
	cT^*, K		
	$b^{(1)}$	$b^{(2)}$	
Paraffins	120.72	5.8408	
Naphthenes	98.527	5.6016	
Alkyl aromatics	199.16	5.3269	
Fused-ring aromatics	180.04	5.6413	
	T^*, K		
	$c^{(1)}$	$c^{(2)}$	$c^{(3)}$
Paraffins	419.86	643.89	0.19945
Naphthenes	445.04	554.67	0.20018
Alkyl aromatics	474.58	269.62	0.10780
Fused-ring aromatics	1,351.4	1,522.3	0.04939

Appendix D. Physical Significance of Molecular Parameters for Polar Fluids

Pure-fluid molecular parameters v^*, $\epsilon q/k(=cT^*)$, c have a well-defined physical significance; they characterize the size, potential energy, and flexibility (or asymmetry) of a molecule. This physical significance of parameters is important for two reasons. First, we correlate fitted parameters to estimate parameters for fluids where experimental data are scarce. These correlations require unique estimates of molecular parameters. Second, and more important, for extension to mixtures, physically significant parameters are necessary to determine mixture parameters using appropriate mixing rules.

As suggested by Figures 9 and 10, parameters for a class of nonpolar fluids are simple functions of molecular weight. For polar fluids, by including dipolar and quadrupolar effects, values of fitted molecular parameters are consistent with those for nonpolar fluids. However, if polar effects are neglected, molecular parameters for polar fluids are not physically reasonable. For example, Table D1 lists molecular parameters for several polar fluids, neglecting polar effects. These parameters may be compared to the corresponding values for fluids in Table 3.

The parameters in Table D1 are fitted to vapor pressure and density data. The quality of fit is nearly the same with or without polar effects. However, the c parameters in Table D1 are much larger than those for the same fluids in Table 3. When polar effects are neglected, these polar fluid c parameters are not consistent with parameters for nonpolar fluids with similar size and shape.

When polar effects are included, larger c parameters follow since the product cT^* now accounts for both dispersion and polar energetic contributions. While physically unreasonable parameters may not be important for pure-fluid calculations, mixture calculations may be highly sensitive to unrealistic parameters. The use of physically unreasonable parameters tends to produce temperature-dependent adjustable binary parameters.

Table D1. Molecular Parameters for Several Polar Fluids, Neglecting Polar Effects

	T^* K	v^* cm^3/mol	c
Carbon dioxide	198.08	18.214	1.7064
Water	433.14	10.516	1.8041
Ammonia	273.94	14.018	1.6526
Hydrogen sulfide	264.01	20.345	1.2931

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