MOLECULAR-BASED EQUATIONS OF STATE

at the Graduate Level

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In recent decades, equations of state (EOS) have become a major tool for the correlation and prediction of thermodynamic properties of fluids. They can be applied to pure substances as well as to mixtures, and in view of the variety of chemical species and applications, it is not surprising that hundreds of equations of state have been published to date; if variants are counted, too, the total exceeds 2,000.[1] Therefore, a very large number of publications deal with the development or improvement of equations of state.

Once they enter their careers, chemical engineers will often be in the position of having to select an EOS that is most appropriate for a specific situation. In addition to commonly used empirical equations, graduate students should be exposed to molecular-based equations of state. In this paper, we present a project for graduate thermodynamics courses at North Carolina State University (NCSU) and Simón Bolívar University (USB) in which students are asked to determine the vapor-liquid equilibria, including the critical point, of a pure substance using three different EOS: (a) cubic, (b) multiparametric, and (c) molecular-based. Students are prompted to use the Internet, and to develop a code for the molecular-based EOS.

SELECTING AN EOS

Depending on one's taste and desired application, one can use a cubic EOS, a local-composition model, corresponding-states theory, group-contribution methods, or a more fundamental approach such as perturbation theory. For simple fluids (*i.e.*, molecules for which the most important intermolecular forces are repulsion and dispersion), all of these methods are likely to give good results. For more complex fluids, however, such as electrolytes, polar solvents, hydrogen-bonded fluids, polymers, and so on, conventional predictive tools fail.

Wei and Sadus[2] presented a wide-ranging overview of recent progress in the development of equations of state, encompassing both simple empirical models and theoretically based equations. The main branches of the EOS tree proposed by them correspond to the van der Waals, Carnahan-Starling,

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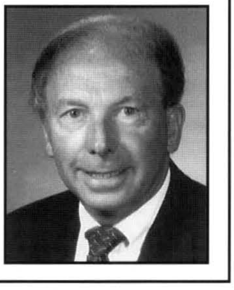

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Hard Convex Body (BACK EOS), Perturbed Hard Chain Theory (PHCT EOS), and Thermodynamic Perturbation Theory (SAFT EOS) models. Among these, the BACK, PHCT, and SAFT equations of state are shown as the precursors of many theoretical attraction terms. (The Redlich-Kwong EOS is similarly presented as the precursor for the development of empirical attraction terms, notably in cubic EOS.) In this project we chose to work with the statistical associating fluid theory[3] (SAFT) EOS.

SAFT is a molecular-based method that is designed to account for effects of molecular association, chain flexibility, and repulsive and dispersion interactions. It has been successfully used to model thermodynamic properties and phase behavior of a large variety of simple and complex fluids and fluid mixtures. The SAFT equation has proven to be a significant improvement over more empirical equations of state, because it has a firm basis in statistical mechanics. Recently Müller and Gubbins,[4,5] Wei and Sadus,[2] and Economou[6] presented reviews of the SAFT EOS and related approaches.

Despite many theoretical improvements, one of the most successful modifications remains the Huang-Radosz[7] version of the SAFT equation. Huang and Radosz have applied SAFT to more than 100 real fluids, fitting the potential parameters to experimental vapor pressure and saturated liquid-density data. A generalized method to estimate these parameters from the critical data and acentric factor of any fluid has also been presented.[8]

SAFT MODEL

In SAFT, molecules are modeled as chains of covalently bonded spheres (see Figure 1). Homologous series, such as n-alkanes and polymers, can be modeled as chains of identical spheres, where the number of spheres in the chain increases with the molecular weight. The residual Helmholtz energy, a^{res}, is of the form

$$a^{res} = a^{seg} + a^{chain} + a^{assoc} \tag{1}$$

where a^{seg} is the part of the Helmholtz energy due to segment-segment interactions (*i.e.*, interactions between monomer units in different molecules, usually modeled as hard sphere, Lennard-Jones, or square-well interactions). Further, a^{chain} is the additional Helmholtz energy due to chain formation, and a^{assoc} is that due to association (*e.g.*, hydrogen bonding) between different molecules.

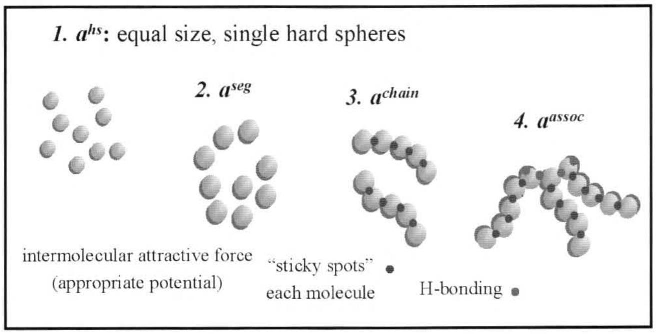


***Figure 1.** SAFT model.*

Granted, the principal value of this theory lies in the strong physical foundation of the characteristic parameters, which permits a reasonable prediction of thermodynamic properties of large molecules (*e.g.*, polymers, hydrocarbons of high molecular weight), and in the explicit inclusion of the association effect. Yet it is also possible to apply this EOS to nonassociating fluids. The widely used Huang and Radosz version of the SAFT EOS for pure nonassociating fluids can be written in terms of the compressibility factor as

$$Z = 1 + Z^{seg} + Z^{chain} \tag{2}$$

where

$$Z^{seg} = m\left[\frac{4\eta - 2\eta^2}{(1-\eta)^3} + \sum_{i=1}^{4}\sum_{j=1}^{9} jD_{ij}\left(\frac{u}{kT}\right)^i\left(\frac{\eta}{\tau}\right)^j\right] \tag{3}$$

$$Z^{chain} = (1-m)\frac{\frac{5}{2}\eta - \eta^2}{(1-\eta)\left(1-\frac{1}{2}\eta\right)} \tag{4}$$

with the auxiliary definitions

$$\eta = \tau m\frac{v^0}{v},\; v^0 = v^{00}\left[1 - C\exp\left(-\frac{3u^0}{kT}\right)\right]^3,\; \frac{u}{k} = \frac{u^0}{k}\left[1 + \frac{e}{kT}\right] \tag{5}$$

In these equations, η represents the reduced fluid density (segment packing fraction), v^0 is the segment molar volume in a close-packed arrangement, v^{00} is the segment volume (temperature-independent segment molar volume at $T = 0$), $\tau = 0.74048$, $C = 0.12$, and $e/k = 10$ except for a few small molecules ($e/k = 0$ for argon; 1 for methane, ammonia, and water; 3 for nitrogen; 4.2 for carbon monoxide; 18 for chlorine; 38 for CS_2; 40 for carbon dioxide, and 88 for SO_2). D_{ij} are universal constants that have been fitted to accurate PvT, internal energy, and second virial coefficient data for argon, by Chen and Kreglewski.[9] For pure nonassociating compounds, there are three essential adjustable parameters: m, the number of hard spheres that forms a molecule; v^{00}, the volume of a mole of these spheres when closely packed (this sets their size); and u^0, the segment energy, which determines segment-segment interactions. As mentioned earlier, pure component parameters for a large variety of nonassociating and associating real fluids have been tabulated.[7]

PROJECT STATEMENT

In this assignment, students are asked to generate predictions for the vapor-liquid equilibria region (including the critical point), using the Huang and Radosz[7] version of the SAFT EOS for the nonassociating fluid assigned to them. They are also asked to compare these with the predictions of a fluid-specific multiparametric EOS and of a cubic EOS — specifically, SRK (Soave-Redlich-Kwong) or PR (Peng-Robinson). To accomplish this task, they need to perform the calculations with the SAFT equation, using any software they feel comfortable with, such as Matlab, Maple, Mathematica, Mathcad, Excel, VisualBasic, and Fortran.

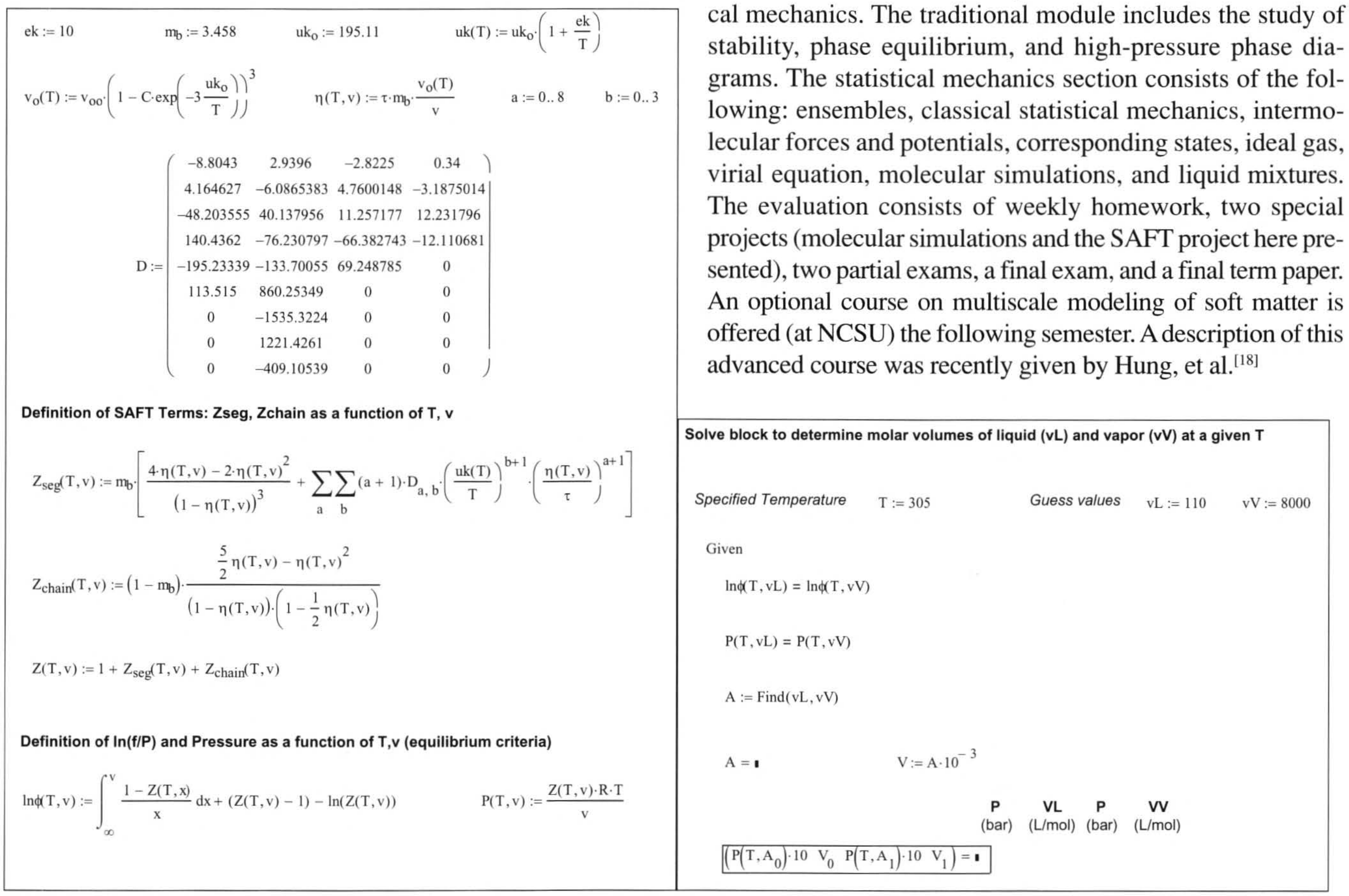
Many useful EOS resources can be found on the Internet. For example, leading institutions such as NIST[10] or DIPPR[11] have user-friendly Web pages, on which up-to-date databases are available for selected fluids. Several sites can also be found where online cubic EOS software is available (see, for example, Reference 12). Students wishing to "program" a cubic EOS are certainly permitted to do so. For example, undergraduate textbooks present computer-aided strategies for solving cubic equation of state, *e.g.*, (a) use of packages such as Maple, Mathematica, Mathcad, and Matlab (see, for example, References 13-15); or (b) use of spreadsheets such as Excel (see, for example, Reference 14). Some textbooks even supply appropriate computer code that can be used for a specific cubic or multiparametric EOS (see, for example, Reference 16).

The results can be presented in graphical and/or tabular form. The use of Pv or Pρ diagrams and of group statistics (see Reference 17) is recommended. A copy of the computer program developed for the SAFT EOS must be provided as an appendix.

Additionally, students are asked to report the acentric factor, $\omega \equiv -1-\log_{10} P_{r,sat}\{T_r = 0.7\}$, predicted from the SAFT EOS for the fluid under study. Finally, comments on applicability range and comparisons among the models are expected.

SOLUTION

The project presented here is part of a graduate thermodynamics course. The course is suitable for students who are already familiar with classical thermodynamics and differential and integral calculus. The course is divided to cover one-third traditional thermodynamics and two-thirds statistical mechanics. The traditional module includes the study of stability, phase equilibrium, and high-pressure phase diagrams. The statistical mechanics section consists of the following: ensembles, classical statistical mechanics, intermolecular forces and potentials, corresponding states, ideal gas, virial equation, molecular simulations, and liquid mixtures. The evaluation consists of weekly homework, two special projects (molecular simulations and the SAFT project here presented), two partial exams, a final exam, and a final term paper. An optional course on multiscale modeling of soft matter is offered (at NCSU) the following semester. A description of this advanced course was recently given by Hung, et al.[18]



$ek := 10$ $\quad m_b := 3.458$ $\quad uk_o := 195.11$ $\quad uk(T) := uk_o \cdot \left(1 + \frac{ek}{T}\right)$

$v_o(T) := v_{oo} \cdot \left(1 - C \cdot \exp\left(-3\frac{uk_o}{T}\right)\right)^3$ $\quad \eta(T,v) := \tau \cdot m_b \cdot \frac{v_o(T)}{v}$ $\quad a := 0..8$ $\quad b := 0..3$

$$D := \begin{pmatrix} -8.8043 & 2.9396 & -2.8225 & 0.34 \\ 4.164627 & -6.0865383 & 4.7600148 & -3.1875014 \\ -48.203555 & 40.137956 & 11.257177 & 12.231796 \\ 140.4362 & -76.230797 & -66.382743 & -12.110681 \\ -195.23339 & -133.70055 & 69.248785 & 0 \\ 113.515 & 860.25349 & 0 & 0 \\ 0 & -1535.3224 & 0 & 0 \\ 0 & 1221.4261 & 0 & 0 \\ 0 & -409.10539 & 0 & 0 \end{pmatrix}$$

Definition of SAFT Terms: Zseg, Zchain as a function of T, v

$$Z_{seg}(T,v) := m_b \cdot \left[\frac{4\cdot\eta(T,v) - 2\cdot\eta(T,v)^2}{(1-\eta(T,v))^3} + \sum_a \sum_b (a+1)\cdot D_{a,b} \cdot \left(\frac{uk(T)}{T}\right)^{b+1} \cdot \left(\frac{\eta(T,v)}{\tau}\right)^{a+1}\right]$$

$$Z_{chain}(T,v) := (1-m_b)\cdot\frac{\frac{5}{2}\eta(T,v) - \eta(T,v)^2}{(1-\eta(T,v))\cdot\left(1-\frac{1}{2}\eta(T,v)\right)}$$

$$Z(T,v) := 1 + Z_{seg}(T,v) + Z_{chain}(T,v)$$

Definition of ln(f/P) and Pressure as a function of T,v (equilibrium criteria)

$$\ln\phi(T,v) := \int_{\infty}^{v} \frac{1-Z(T,x)}{x}\,dx + (Z(T,v)-1) - \ln(Z(T,v)) \qquad P(T,v) := \frac{Z(T,v)\cdot R\cdot T}{v}$$

Solve block to determine molar volumes of liquid (vL) and vapor (vV) at a given T

Specified Temperature $T := 305$ *Guess values* $vL := 110$ $vV := 8000$

Given

$\ln\phi(T, vL) = \ln\phi(T, vV)$

$P(T, vL) = P(T, vV)$

$A := \mathrm{Find}(vL, vV)$

$A = ▮$ $\qquad V := A \cdot 10^{-3}$

P (bar) **VL** (L/mol) **P** (bar) **VV** (L/mol)

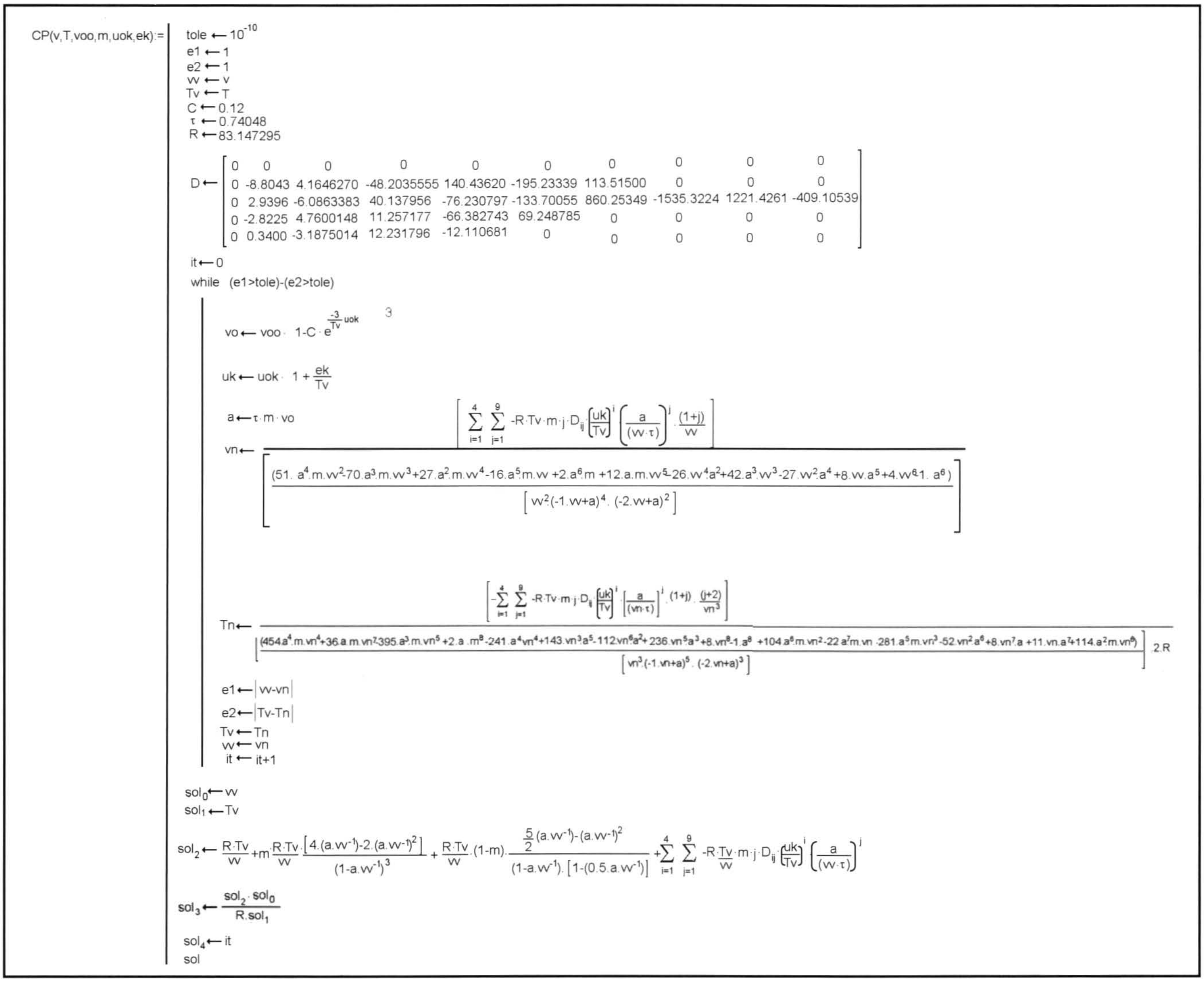
$\boxed{\left(P(T,A_0)\cdot 10 \;\; V_0 \;\; P(T,A_1)\cdot 10 \;\; V_1\right) = ▮}$

Figure 2a. *A typical Mathcad code for the prediction of the vapor-liquid equilibria.*

In a previous paper,[19] we presented a "thermo project" for a first thermodynamics course, in which the undergraduate student was encouraged to use the Internet, handle some software, and read tables to evaluate the PvT prediction capabilities of different models for a pure fluid. In this work, we additionally prompt the graduate student to program a molecular-based EOS, such as the SAFT EOS, using any software they feel comfortable with. Generally students select Mathcad or Excel, and use the same application (Excel) to show the results. The Internet is used to obtain the predictions of multiparametric EOS for different fluids through the NIST Web book[10] or the DIPPR database,[11] and to obtain the predictions of the Peng-Robinson[20] equation (from Reference 14 or 15). The reader is referred to our previous paper for additional details on the use of Internet, software, and computer-aided strategies for this type of project. In this paper we concentrate on the programming of a molecular-based equation of state, *e.g.*, SAFT. Several examples are given below.

EXAMPLES

Figure 2 (a and b) shows a typical Mathcad code for the prediction of the vapor-liquid equilibria of a pure compound using the SAFT EOS for a nonassociating fluid. As can be seen in the figures, the necessary code is relatively straightforward. Students with no previous experience in using this software (or equivalents such as Mathlab, Maple, and Mathematica) are able to program the EOS with the assistance of the "help" section of the software. It is important to keep in mind that the code shown is an example of an actual student submission and should be judged accordingly. In particular, the code uses the simplified



```
CP(v,T,voo,m,uok,ek):=
    tole ← $10^{-10}$
    e1 ← 1
    e2 ← 1
    vv ← v
    Tv ← T
    C ← 0.12
    τ ← 0.74048
    R ← 83.147295
    $D \leftarrow \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -8.8043 & 4.1646270 & -48.2035555 & 140.43620 & -195.23339 & 113.51500 & 0 & 0 & 0 \\ 0 & 2.9396 & -6.0863383 & 40.137956 & -76.230797 & -133.70055 & 860.25349 & -1535.3224 & 1221.4261 & -409.10539 \\ 0 & -2.8225 & 4.7600148 & 11.257177 & -66.382743 & 69.248785 & 0 & 0 & 0 & 0 \\ 0 & 0.3400 & -3.1875014 & 12.231796 & -12.110681 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$
    it ← 0
    while  (e1>tole)-(e2>tole)
        $vo \leftarrow voo \cdot\ 1-C\cdot e^{\frac{-3}{Tv}uok}\quad 3$
        $uk \leftarrow uok \cdot\ 1+\frac{ek}{Tv}$
        $a \leftarrow \tau\cdot m\cdot vo$
        $vn \leftarrow \dfrac{\left[\sum_{i=1}^{4}\sum_{j=1}^{9} -R\cdot Tv\cdot m\cdot j\cdot D_{ij}\cdot\left(\frac{uk}{Tv}\right)^{i}\left(\frac{a}{(vv\cdot\tau)}\right)^{j}\cdot\frac{(1+j)}{vv}\right]}{\left[\dfrac{(51.\ a^{4}.m.vv^{2}\text{-}70.a^{3}.m.vv^{3}+27.a^{2}.m.vv^{4}\text{-}16.a^{5}m.vv+2.a^{6}m+12.a.m.vv^{5}\text{-}26.vv^{4}a^{2}+42.a^{3}.vv^{3}\text{-}27.vv^{2}a^{4}+8.vv.a^{5}+4.vv^{6}1.\ a^{6})}{\left[vv^{2}(-1.vv+a)^{4}.\ (-2.vv+a)^{2}\right]}\right]}$
        $Tn \leftarrow \dfrac{\left[-\sum_{i=1}^{4}\sum_{j=1}^{9} -R\cdot Tv\cdot m\cdot j\cdot D_{ij}\cdot\left(\frac{uk}{Tv}\right)^{i}\cdot\left[\frac{a}{(vn\cdot\tau)}\right]^{j}.(1+j).\frac{(j+2)}{vn^{3}}\right]}{\left[\dfrac{(454a^{4}.m.vn^{4}+36.a.m.vn^{7}\text{-}395.a^{3}.m.vn^{5}+2.a\ .m^{8}\text{-}241.a^{4}vn^{4}+143.vn^{3}a^{5}\text{-}112.vn^{6}a^{2}+236.vn^{5}a^{3}+8.vn^{8}\text{-}1.a^{8}+104.a^{6}m.vn^{2}\text{-}22\ a^{7}m.vn\ \text{-}281.a^{5}m.vn^{3}\text{-}52.vn^{2}.a^{6}+8.vn^{7}.a+11.vn.a^{7}+114.a^{2}m.vn^{6})}{\left[vn^{3}.(-1.vn+a)^{5}.\ (-2.vn+a)^{3}\right]}\right].2.R}$
        e1 ← |vv-vn|
        e2 ← |Tv-Tn|
        Tv ← Tn
        vv ← vn
        it ← it+1
    $sol_0 \leftarrow vv$
    $sol_1 \leftarrow Tv$
    $sol_2 \leftarrow \frac{R\cdot Tv}{vv}+m\cdot\frac{R\cdot Tv}{vv}\cdot\frac{\left[4.(a.vv^{-1})-2.(a.vv^{-1})^{2}\right]}{(1-a.vv^{-1})^{3}}+\frac{R\cdot Tv}{vv}.(1-m).\frac{\frac{5}{2}(a.vv^{-1})-(a.vv^{-1})^{2}}{(1-a.vv^{-1}).\left[1-(0.5.a.vv^{-1})\right]}+\sum_{i=1}^{4}\sum_{j=1}^{9} -R\cdot\frac{Tv}{vv}\cdot m\cdot j\cdot D_{ij}\cdot\left(\frac{uk}{Tv}\right)^{i}\left(\frac{a}{(vv\cdot\tau)}\right)^{j}$
    $sol_3 \leftarrow \frac{sol_2\cdot sol_0}{R.sol_1}$
    $sol_4 \leftarrow it$
    sol
```

Figure 2b. *A typical Mathcad code for the prediction of the critical point of a pure compound using the SAFT EOS for a nonassociating fluid.*

form of the SAFT EOS for pure nonassociating substances. Additionally, good initial density guesses must be supplied in order to achieve convergence.

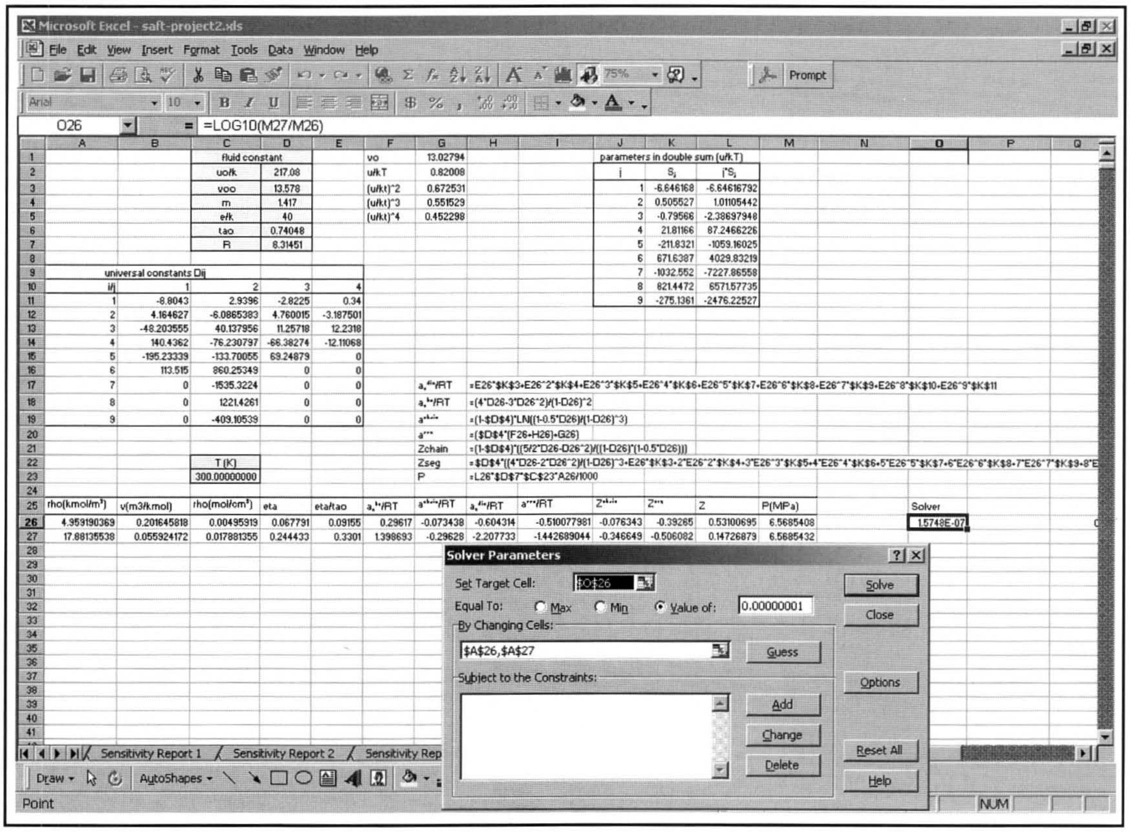
A typical Excel spreadsheet is shown in Figure 3. No macro (such as Visual Basic) is being used in this example. All calculations are made within the spreadsheet. Cells are programmed with the SAFT equation as can be seen in the figure. Many of the intermediate calculations are also shown. This scheme involves more direct input from the student, and it could be computationally less efficient than, for example, the use of Visual Basic objects (macros) embedded in the same application. It is relatively simple, however, and no advanced knowledge of numerical methods is needed from the student. In this example students use the "solver" function (an Excel add-in) to find mechanical equilibrium (equality of pressure) and then calculate the fugacity coefficients at this condition to check that they are equal.

The use of Visual Basic, Fortran, Pascal, etc. requires some knowledge of the application, since a numerical routine (*e.g.*, bisection, Newton-Raphson) is required to obtain the density (or packing fraction) roots of the equation. Examples are not shown here, because only a small percentage of the students chose to use these techniques, even though they were expected to have the necessary numerical tools from their undergraduate courses to pursue this computational project. We have to bear in mind that this is one of the first courses at the graduate level, where differences in background are starting to appear. We place accordingly more emphasis on the correctness of the results and the soundness of their analysis, and less on the sophistication of the calculation procedure employed.

REPRESENTATIVE RESULTS

The phase envelopes (vapor-liquid equilibria or saturation conditions) for carbon dioxide and n-decane are shown in Figures 4 and 5 as examples. Results are shown for the multiparametric EOS (Span and Wagner[10, 21] for CO_2 and saturated liquid densities for n-decane[11]), Peng-Robinson,[14, 20] and SAFT.[7]

These figures illustrate the predictive capabilities of multiparametric equations of state. The Span-Wagner[21] EOS is the equation most frequently used for carbon dioxide, and can be taken as a reference (for a more detailed discussion, see References 17 and 21). It is worth mentioning that even though the Internet[10, 11] was used in this stage of the project, the data for n-decane is relatively old, corresponding to a compilation made from sources dating from 1944 to 1989 (specific references are given in DIPPR[11]). The data's longevity can, however, be used to show that "old" methods (tables and handbooks) are not necessarily less accurate than "new" methods (Internet), or vice versa.



O26 = =LOG10(M27/M26)

fluid constant	
uo/k	217.08
voo	13.578
m	1.417
e/k	40
tao	0.74048
R	8.31451

vo	13.02794
u/kT	0.82008
(u/kt)^2	0.672531
(u/kt)^3	0.551529
(u/kt)^4	0.452298

universal constants Dij

i/j	1	2	3	4
1	-8.8043	2.9396	-2.8225	0.34
2	4.164627	-6.0865383	4.760015	-3.187501
3	-48.203555	40.137956	11.25718	12.2318
4	140.4362	-76.230797	-66.38274	-12.11068
5	-195.23339	-133.70055	69.24879	0
6	113.515	860.25349	0	0
7	0	-1535.3224	0	0
8	0	1221.4261	0	0
9	0	-409.10539	0	0

parameters in double sum (u/kT)

j	S_j	$j*S_j$
1	-6.646168	-6.64616792
2	0.505527	1.01105442
3	-0.79566	-2.38697948
4	21.81166	87.2466226
5	-211.8321	-1059.16025
6	671.6387	4029.83219
7	-1032.552	-7227.86558
8	821.4472	6571.57735
9	-275.1361	-2476.22527

T (K)
300.00000000

a_0^{disp}/RT	=E26*K3+E26^2*K4+E26^3*K5+E26^4*K6+E26^5*K7+E26^6*K8+E26^7*K9+E26^8*K10+E26^9*K11
a_0^{hs}/RT	=(4*D26-3*D26^2)/(1-D26)^2
a^{chain}	=(1-D4)*LN((1-0.5*D26)/(1-D26)^3)
a^{seg}	=(D4*(F26+H26)+G26)
Zchain	=(1-D4)*((5/2*D26-D26^2)/((1-D26)*(1-0.5*D26)))
Zseg	=D4*((4*D26-2*D26^2)/(1-D26)^3+E26*K3+2*E26^2*K4+3*E26^3*K5+4*E26^4*K6+5*E26^5*K7+6*E26^6*K8+7*E26^7*K9+8*E
P	=L26*D7*C23*A26/1000

rho(kmol/m³)	v(m3/kmol)	rho(mol/cm³)	eta	eta/tao	a_0^{hs}/RT	a^{chain}/RT	a_0^{disp}/RT	a^{seg}/RT	Z^{chain}	Z^{seg}	Z	P(MPa)		Solver
4.959190369	0.201645818	0.00495919	0.067791	0.09155	0.29617	-0.073438	-0.604314	-0.510077981	-0.076343	-0.39265	0.53100695	6.5685408		1.5748E-07
17.88135538	0.055924172	0.017881355	0.244433	0.3301	1.398693	-0.29628	-2.207733	-1.442689044	-0.346649	-0.506082	0.14726879	6.5685432		

Solver Parameters

Set Target Cell: O26

Equal To: ○ Max ○ Min ● Value of: 0.00000001

By Changing Cells: A26,A27

Subject to the Constraints:

Figure 3. A typical Excel spreadsheet code for the prediction of the vapor-liquid equilibria of a pure compound using the SAFT EOS for a nonassociating fluid.

Deficiencies of cubic equations of state in the prediction of liquid densities are shown by the PR results. Also worth mentioning is that it was shown in the previous work[19] that for carbon dioxide and in the region under study, the PR equation is more accurate than SRK. It is clear in Figure 4 that in general, the PR EOS performs better than the SAFT EOS for CO_2, especially near the critical point. The prediction of liquid densities in the low temperature region, however, is better from the SAFT EOS. This should lead students to discuss how the fluid-specific parameters of molecular-based EOS such as SAFT are fitted to experimental vapor pressure and liquid-density data; the result is an overestimation of the critical temperature and pressure. On the other hand, the usual practice for a cubic EOS such as Peng-Robinson is to enforce the experimental values of the latter two properties; this results instead in overestimation of the critical volume. Similar conclusions (not shown) are obtained for the lower members of the n-alkane family. In Figure 5, however, it is seen that there is little to choose between the PR and SAFT equations for n-decane. The vapor-liquid phase envelope for n-eicosane ($C_{20}H_{42}$) is shown as a T ρ diagram in Figure 6. For this substance, predictions of the PR EOS are now inferior to those of the SAFT EOS (*e.g.*, AAD — saturation pressure: 8.3% SAFT, 23.4% PR; molar liquid density: 6.2% SAFT, 15.3% PR).

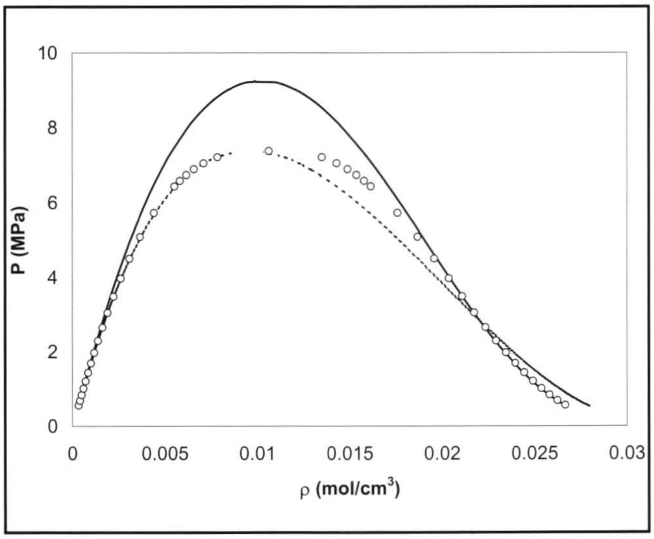


Figure 4. *Vapor-liquid phase envelope for CO_2 shown as a P ρ diagram. Continuous line predicted by the SAFT EOS,*[3, 7] *dashed line predicted by the Peng-Robinson EOS,*[20] *(○) predicted by the Span-Wagner EOS.*[21]

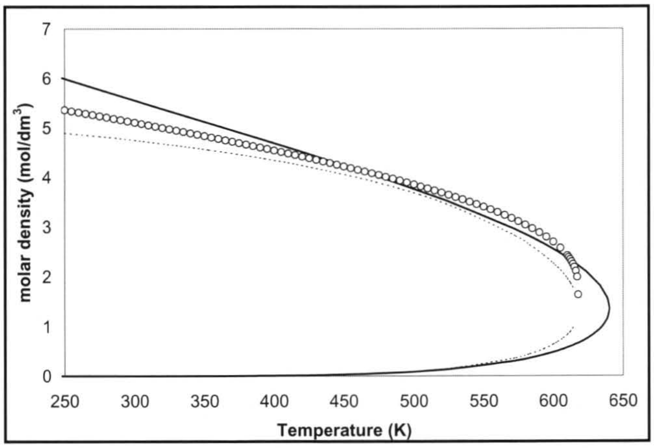


Figure 5. *Vapor-liquid phase envelope for n-decane ($C_{10}H_{22}$) shown as a T ρ diagram. Continuous line predicted by the SAFT EOS,*[3, 7] *dashed line predicted by the Peng-Robinson EOS,*[20] *(○) predicted by the DIPPR database.*[11]

Finally it is worth mentioning than both PR and SAFT — like all analytic (*i.e.*, based on mean field) EOS — predict a *parabolic* instead of the experimentally found *cubic* curve in the critical region. The latter arises from the nonanalytic nature of the coexistence in the critical region, which yields a much flatter curve in this region.

CRITICAL PROPERTIES AND ACENTRIC FACTOR

From the traditional stability conditions at the critical point, it follows that the critical isotherm must exhibit an inflexion point in Pv coordinates

$$\left(\frac{\partial P}{\partial v}\right)_T = 0 \text{ and } \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0 \text{ or } \left(\frac{\partial^2 a}{\partial v^2}\right)_T = 0 \text{ and } \left(\frac{\partial^3 a}{\partial v^3}\right)_T = 0 \quad (6)$$

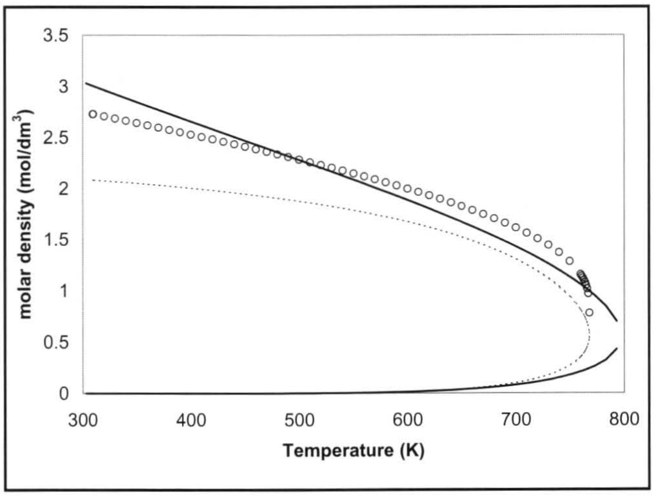


Figure 6. *Vapor-liquid phase envelope for n-eicosane ($C_{20}H_{42}$) shown as a T ρ diagram. Continuous line predicted by the SAFT EOS,*[3, 7] *dashed line predicted by the Peng-Robinson EOS,*[20] *(○) predicted by the DIPPR database.*[11]

A possible algorithm to find the critical properties using Mathcad is shown in Figure 2b. It can be observed that finding the critical point is straightforward with this package (or, in fact, any equivalent package). Results for the critical properties of the fluids mentioned above are given in Table 1.

The acentric factor, ω, specifies a vapor pressure at a reduced temperature of $T_r = 0.7$ and is defined by

$$\omega \equiv -1-\log_{10} P_{r,sat}\{T_r=0.7\} \quad P_r=\frac{P}{P_c} \quad T_r=\frac{T}{T_c} \tag{7}$$

Results for the acentric factor from the equations of state studied above are also shown in Table 1. The primary objective of these calculations is to make students realize that the acentric factor is a thermodynamic property dependent on the saturation pressure at a specific temperature ($T = 0.7\ T_c$). Depending on the accuracy of the experimental data or model, different values are obtained. To stress this point, acentric factors reported in Reid, *et al.*,[22] and Poling, *et al.*,[23] are also included. Differences between these sources and up-to-date databases show the variation on experimental data available. Moreover, these calculations can also be used to dis-

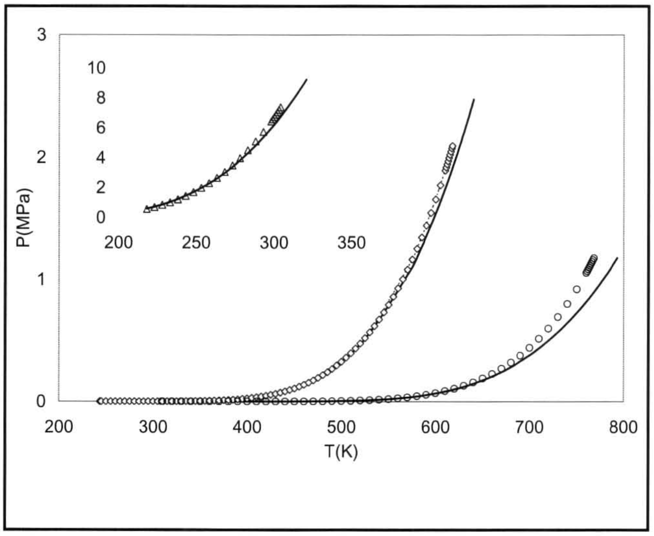


Figure 7. *Pressure-temperature diagram for CO_2, $C_{10}H_{22}$, $C_{20}H_{42}$. Continuous line predicted by the SAFT EOS,[3, 7] dashed line predicted by the Peng-Robinson EOS,[20] symbols predicted by the DIPPR database[11] or NIST[10] for (△) CO_2, (◇) n-decane, and (○) n-eicosane.*

TABLE 1

Acentric Factor and Critical Properties

	ω			Tc (K)		Pc (MPa)		Vc (m^3/kmol)		
FLUID/EOS	MP[c]	PR	SAFT	MP[c] and PR	SAFT	MP[c] and PR	SAFT	MP[c]	PR	SAFT
CO_2	0.228	0.242	0.255[a]	304.13	320.71	7.38	9.25	0.094	0.101	0.098
	0.225[d]		0.085[b]							
	0.239[e]									
n-decane	0.490	0.429	0.428[a]	617.8	639.84	2.11	2.46	0.624	0.687	0.738
	0.490[d]		0.309[b]							
	0.489[e]									
n-eicosane	0.907	0.883	0.914[a]	768.0	796.73	1.16	1.22	1.34	1.71	1.802
	0.865[d]		0.694[b]							
	0.907[e]									

[a] calculated with experimental T_c and P_c

[b] calculated with T_c and P_c predicted by the EOS

[c] NIST webbook

[d] Poling et al.

[e] Reid et al.

cuss the accuracy of different equations. It could appear that there are surprising differences between the acentric factor predicted by the SAFT EOS and the general predictions observed in Figures 4-6. A PT projection of the saturation line predicted for the different equations — n-decane and n-eicosane (shown in Figure 7 for CO_2) — could help clarify the apparent inconsistency as well as the two sets of acentric factors reported in Table 1 for the SAFT EOS. The overprediction of critical temperatures and pressures by the SAFT EOS is responsible for the incorrect acentric factor predicted by the EOS (case b in Table 1). If experimental critical properties are used to obtain the acentric factor, however, then due to the good fit of the EOS to saturation pressures at intermediate temperatures, good predictions on ω are found (case a in Table 1). Regarding carbon dioxide, it is worth noting that $T_r = 0.7$ is below the triple point of this substance. Therefore, an experimental value of the acentric factor does not exist, except as an extrapolation subject to greater uncertainty than for other fluids.

FINAL COMMENTS

It should be made clear to the students that even though similar results were found using an empirical equation such as Peng-Robinson, and an equation with statistical mechanical basis such as SAFT, the selection of the equation should be based on the range of conditions. As mentioned early on, for simple fluids — molecules for which the most important intermolecular forces are repulsion and dispersion — cubic equations are likely to give good results. If, however, mixtures in liquid-liquid equilibrium are the desired objective, these predictive tools will fail. They will also fail for more complex fluids, such as electrolytes, polar solvents, hydrogen-bonded fluids, and polymers. Several examples at these conditions can be found in the graduate thermodynamics book of Prausnitz, *et al.* [24]

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REFERENCES

1. Deiters, U.K., "Remarks on Publications Dealing with Equations of State," *Fluid Phase Equil.*, **161**, 205 (1999); Deiters, U.K., and K.M. de Reuck, "Guidelines for Publication of Equations of State. I. Pure Fluids," *Pure Appl. Chem.*, **69**, 1237 (1997)
2. Wei, Y.S., and R.J. Sadus, "Equations of State for the Calculation of Fluid-Phase Equilibria," *AIChE J.*, **46**, 169 (2000)
3. Chapman, W.G., Gubbins, K.E., Jackson G., and M. Radosz, "New Reference Equation of State for Associating Liquids," *Ind. Eng. Chem. Res.*, **29**, 1709 (1990)
4. Müller, E.A., and K.E. Gubbins, "Associating Fluids and Fluids Mixtures," in J.V. Sengers, R.F. Kayser, C.J. Peters, and H.J. White, Jr. (Eds), *Equations of State for Fluids and Fluid Mixtures. Experimental Thermodynamics, Volume 5*, Elsevier, Amsterdam, p. 435 (2000)
5. Müller, E.A., and K.E. Gubbins, "Molecular-Based Equations of State for Associating Fluids: A Review of SAFT and Related Approaches," *Ind. Eng. Chem. Res.*, **40**(10), 2193 (2001)
6. Economou, I.G., "Statistical Associating Fluid Theory: A Successful Model for the Calculation of Thermodynamic and Phase Equilibrium Properties of Complex Fluid Mixtures," *Ind. Eng. Chem. Res.*, **41**, 953 (2002)
7. Huang, S.H., and M. Radosz, "Equation of State for Small, Large, Polydisperse, and Associating Molecules," *Ind. Eng. Chem. Res.*, **29**, 2284 (1990)
8. Bouza, A., Colina, C.M., and C.G. Olivera-Fuentes, "Parameterization of Molecular-based Equations of State," *Fluid Phase Equilib.*, **228-229C**, 561 (2005)
9. Chen, S.S., and A. Kreglewski, "Applications of the Augmented van der Waals Theory of Fluids. I. Pure Fluids," Ber. Bunsen-Ges. Phys. Chem., **81**, 1048 (1977)
10. Lemmon, E.W., M.O. McLinden, and D.G. Friend, "Thermophysical Properties of Fluid Systems," in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, July 2001, National Institute of Standards and Technology, Gaithersburg, MD, 20899 <http://webbook.nist.gov/chemistry/>
11. Rowley, R.L., W.V. Wilding, J.L. Oscarson, Y. Yang, R.J. Rowley, T.E. Daubert, and R.P. Danner, *DIPPR Data Compilation of Pure Compound Properties*, Design Institute for Physical Property Data, AIChE, New York, NY (2001)
12. <http://www.questconsult.com/~jrm/thermot.html>
13. Smith, J.M., H.C. van Ness, and M.M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 6th Ed., McGraw-Hill, New York (2001)
14. Elliott, J.R., and C.T. Lira, *Introductory Chemical Engineering Thermodynamics*, Prentice Hall (1999)
15. Sandler, S.I., *Chemical and Engineering Thermodynamics*, 3rd Ed., John Wiley & Sons (2001)
16. Van Wylen, J.G., R.E. Sonntag, and C. Borgnakke, *Fundamentals of Classical Thermodynamics*, 4th Ed., John Wiley & Sons (1994)
17. Jacobsen, R.T., S.T. Penoncello, E.W. Lemmon, and R.Span, "Multiparametric Equations of State," in J.V. Sengers, R.F. Kayser, C.J. Peters, and H.J. White, Jr. (Eds), *Equations of State for Fluids and Fluid Mixtures. Experimental Thermodynamics*, Volume 5, Elsevier, Amsterdam, p. 849 (2000)
18. Hung, F.R., S. Franzen, and K.E. Gubbins, "A Graduate Course on Multi-Scale Modeling of Soft Matter," *Chem. Eng. Ed.*, **38**(4), 242 (2004)
19. Colina, C.M., and K.E. Gubbins, "Choosing and Evaluating Equations of State for Thermophysical Properties," *Chem. Eng. Ed.*, **37**(3), 236 (2003)
20. Peng, D.-Y., and D.B. Robinson, "A New Two-Constant Equation of State," *Ind. Eng. Chem. Fundam.*, **15**(1), 59 (1976)
21. Span, R., and W. Wagner, "A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa," *J. Phys. Chem. Ref. Data.*, **25**, 1509 (1996)
22. Reid, R.C., J.M. Prausnitz, and B.E. Poling, *The Properties of Gases and Liquids*, 4th Ed., McGraw-Hill, New York, NY (1987)
23. Poling, B.E., J.M. Prausnitz, and J.P. O'Connell, *The Properties of Gases and Liquids*, 5th Ed., McGraw-Hill, New York, NY (2001)
24. Prausnitz, J. M., Lichtenthaler, R.N., and E. Gomes de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd Ed., Prentice Hall International Series (1999) ❒