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A Correlation for the Thermodynamic Properties of Supercritical Fluids at Very High Pressures

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Recently Breedveld and Prausnitz (1973) applied corresponding states theory to the *PVT* data of several simple fluids at very high pressures and developed generalized tables and charts for density, fugacity, enthalpy, and internal energy for the reduced temperature range 1 to 50 and for reduced pressures from 1 to 2000. This work extended the earlier work of Dodge (1944), Hougen et al. (1964), and Pitzer et al. (see Lewis et al., 1961) with respect to both T_R and P_R.

It is interesting to note that the several species, whose data were analyzed by Breedveld and Prausnitz in compiling their extensive tables and charts, are simple molecules of spherical or almost spherical geometry (Ar, N_2, He, H_2, Ne, Xe, CO, CH_4). In this note we propose a correlation with a statistical mechanical basis which allows calculation of pressures from densities and temperatures with results which agree very well with those in the supercritical region of the tables and charts of Breedveld and Prausnitz. It is quite general, with only three temperature-dependent parameters, and provides excellent predictions particularly in the region $T_R \geqq 4$, a situation no doubt due to the absence of the inflection of the isotherms that occurs at temperatures closer to $T_R = 1$. This note presents the correlation and comments on its accuracy and usage in predicting thermodynamic properties. The utility of such a correlation is that a large region of high temperature state data at all pressures and densities becomes available in the form of an equation of state which can be used to predict thermodynamic properties with the aid of a computer. With proper combinatorial rules (see Breedveld and Prausnitz, 1973; Leland and Chappelear, 1968), the correlation could be useful too for predicting the properties of mixtures.

THEORETICAL EQUATION OF STATE

The square-well intermolecular potential can be written

$$
\begin{aligned}
u(x) &= +\infty, \quad x \leq 1 \\
&= -\epsilon, \quad 1 < x \leq R \\
&= 0, \quad x > R
\end{aligned}
$$

where x is a reduced length r/σ, σ being the hard-sphere diameter, ϵ an energetic parameter denoting strength of attractive potential energy of an interacting pair of molecules, and R a parameter denoting extent of the interaction, or more specifically, the width of the attractive well is (R-1) in reduced coordinates. Schrodt et al. (1972a, 1972b) derived an equation of state for $P = P(v, T)$ from statistical mechanics for fluids interacting with a square-well potential for $R = 1.85$ and showed that it could predict features of the liquid-gas coexistence region and the critical region qualitatively well. (See Kozak et al., 1972.)

It should be noted that the choice of the square-well potential model is based on expediency. It is the simplest potential representation that still incorporates the features required for real, condensable fluids. Certainly the square-well potential is not meant to be a precise representation of the intermolecular nature of fluids but the mathematical simplicity attendant to its usage compensates for this shortcoming. Added incentive for undertaking the construction of a correlation for the high temperature regime was provided by the intuitive feeling that the impulsive nature of the intermolecular forces for the square-well model (due to its step-function form) would more closely represent reality in this thermodynamic regime. Experience has shown that a value of $R = 1.85$ represents the nature of spherical molecules (Hirschfelder et al., 1954; Palyvos et al., 1967) for the square-well potential model.

The prediction of pressure via statistical mechanics is one of the more sensitive predictions, in that the pair correlation function $g(x)$ is weighted by the derivative of

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the potential energy $u(x)$:

$$P^*v^*\theta = 1 - 4y\theta \int_0^\infty x^3 u'(x) g(x)\,dx \qquad (1)$$

for spherically symmetric molecules. For the square-well potential, Equation (1) is simply

$$P^*v^*\theta = 1 - 4y[R^3(1 - e^{-\theta})g(R_-) - g(1_+)] \quad (2)$$

Equation (2) is a reduced equation of state for spherical molecules (that is, $R \equiv 1.85$), with (P, v, T) reduced with respect to the size parameter σ and the energy parameter ϵ. Thus $P^*v^*\theta = z$.

Schrodt and Luks (1972) solved the Yvon-Born-Green integral equation for the pair correlation function $g(x)$ using the Kirkwood superposition approximation and presented least-squares fitted representations for $g(1_+)$ and $g(R_-)$, valid for temperatures from about 2/3 T_c up to $T \rightarrow \infty$ and for density from 0 to at least 2.6 ρ_c. These representations are of the form

$$g(x) = \exp\left\{\frac{\psi_0(v^*; x) + \theta\psi_1(v^*; x) + \theta^2\psi_2(v^*; x)}{x}\right\} \qquad (3)$$

where

$$\psi_i(1_+) = \sum_{j=0}^{6} A_{ij}\, y^j \qquad (4)$$

$$\psi_i(R_-) = \sum_{j=0}^{6} B_{ij}\, y^j \qquad (5)$$

The coefficients $\{A_{ij}\}$ and $\{B_{ij}\}$, first appearing in Schrodt and Luks (1972a), are tabulated in Table 2.

EXTENSION TO CORRESPONDING STATES

Equation (2) can be used for any appropriate (approximately spherical) fluid whose parameters (ϵ, σ) for the square-well potential are known. However, since the critical point of Equation (2) can be found accurately (Kozak et al., 1972), Equation (2) can be reduced relative to P_c^*, v_c^*, θ_c, in an internally consistent manner, providing a general corresponding states equation restricted only by the specification of the parameter $R = 1.85$. Physically speaking, it should be appropriate for the several species examined by Breedveld and Prausnitz (1973).

The reduced pressure $P_R{}^\dagger$ for the square well theory described above is easily generated by computer using Equations (2) through (5). When compared with experiment (that is, the tabulations of Breedveld and Prausnitz, 1973), it showed qualitative agreement over the entire state regime of $T_R \geqq 1$. Standard deviations were defined:

$$\sigma' \equiv \sqrt{\sum \left(\frac{P_{R_{\rm exp}} - P_R{}^\dagger}{P_{R_{\rm exp}}}\right)^2 \Big/ (n-1)} \qquad (6)$$

These deviations varied from 10 to 30%, with the worst results for the isotherms representing the extreme temperatures $T_R = 1$ and 50.

The function $P_R{}^\dagger$ was used as a basis for a correlation designed to fit $P_{R_{\rm exp}} = P_{R_{\rm exp}}(\rho_R, T_R)$ at each isotherm. The form assumed was

$$P_{R_{\rm calc}} = P_R{}^\dagger\,[\alpha + \beta\,(\rho_R - 1) + \gamma\,(\rho_R - 1)^2] \quad (7)$$

α, β, and γ were evaluated by the least-squares method, minimizing the function $\sum [(P_{R\rm calc} - P_{R\rm exp})/P_{R\rm exp}]^2$, where $P_{R_{\rm exp}}$ are the tabulations of Breedveld and Prausnitz. The values of α, β and γ and the deviation in % [100 × σ' in Equation (6)] are listed in Table 1 as a function of T_R. The tabulations of Breedveld and Prausnitz were terminated at $\rho_R = 2.6$ in order to be consistent with the limitations of the model for $P_R{}^\dagger$. The agreement between $P_{R_{\rm calc}}$ and $P_{R_{\rm exp}}$ is excellent for $T_R \geqq 4$. All density tabulations below $\rho_R = 2.6$ were used consistent with the limitation of $P_R \geqq 1$ of the tables of Breedveld and Prausnitz.

REMARKS

There are several comments that can be made concerning the usage of Equation (7) as a correlation for $P_{R_{\rm calc}} = P_{R_{\rm calc}}(\rho_R, T_R)$. Interpolation is quite straightforward and can be achieved to an accuracy of ± 1% for isotherms intermediate to those listed in Table 1, exceeding $T_R = 3$; intermediate values of (α, β, γ) are generated merely by interpolating linearly with respect to T_R between the tabulated values of (α, β, γ). Extrapolation to higher densities, although outside of the range of validity of Equation (2), does produce agreement between $P_{R_{\rm calc}}$ and $P_{R_{\rm exp}}$ to within ± 10% up to densities of $\rho_R = 3.6$. Interpolation and extrapolation are somewhat less reliable for $T_R < 3$ as is consistent with the increased values of σ' in this T_R range. See Table 1.

Since Equation (7), with interpolation of (α, β, γ) can provide a continuous picture of $P_R = P_R(\rho_R, T_R)$ for the state regime of interest, it is straightforward to compute other thermodynamic properties such as $\ln(f/P)$ and the enthalpy difference $\dfrac{H(O,T) - H(P,T)}{R'T_c}$. Adopting a value of $z_c = 0.292$ for spherical molecules (see Hirschfelder et al., 1954), one can calculate $\ln(f/P)$ to within about 1% for $T_R = 4$, when compared with the tabulations of Breedveld and Prausnitz (1973). In the case of the enthalpy difference, the corresponding deviation is about ± 10% with the best agreement occurring at high values of T_R (± 2%).

TABLE 1. CORRELATION PARAMETERS AND STANDARD DEVIATION BETWEEN PREDICTED AND EXPERIMENTAL PRESSURES AS A FUNCTION OF REDUCED TEMPERATURE (TO MAXIMUM REDUCED DENSITY OF 2.6). THE MAXIMUM P_R COMPATIBLE WITH $\rho_R = 2.6$ IS ALSO TABULATED

T_R	$P_{R\rm MAX}$	α	β	γ	Standard deviation %
1	25	1.0	−0.729649	1.002404	1.09*
1.05	27	0.887311	−0.241579	0.624773	4.40
1.2	35	0.975667	−0.109278	0.375379	3.71
1.6	52	1.039450	−0.064837	0.198841	2.23
2.0	70	1.053606	−0.064451	0.147322	1.77
3.0	107	1.056710	−0.082086	0.090723	1.34
4.0	137	1.043090	−0.105795	0.065585	0.70
8.0	245	0.998733	−0.158320	0.046102	0.77
14.0	379	0.951722	−0.206920	0.041993	0.38
24.0	572	0.913697	−0.246244	0.041174	0.32
32.0	707	0.883388	−0.267911	0.049311	0.32
44.0	907	0.857279	−0.287675	0.054543	0.29
50.0	992	0.848433	−0.295446	0.054804	0.25

* Since comparison with experiment is limited to isotherms with $P_R \geqq 1$, the isotherm $T_R = 1$ does not include any points at densities less than $\rho_R = 1$. Consequently, the data for $T_R = 1$ are easier to correlate than, say, for $T_R = 1.05$ or 1.2 which include the inflection near the critical point.

It is useful to engineers to have an expression of the form $\rho_R = \rho_R(P_R, T_R)$. However, since ρ and T are fundamental quantities in statistical mechanics and P is a

TABLE 2. VALUES OF THE COEFFICIENTS FOR THE DENSITY EXPANSIONS FOR $\{\psi_i(1_+)\}$ AND $\{\psi_i(R_-)\}$ AS GIVEN IN EQUATION (4) AND (5)

j	A_{0j}	A_{1j}	A_{2j}
0	0.8982×10^{-4}	0.1001×10	-0.1001×10^{-1}
1	0.2494×10	-0.1054×10^{2}	0.1314×10^{2}
2	0.5917	0.2749×10^{2}	-0.1179×10^{3}
3	-0.1675×10	-0.8999×10	0.3453×10^{3}
4	0.4746	-0.7021×10^{2}	-0.2474×10^{3}
5	-0.5340×10	0.1300×10^{3}	-0.4943×10^{3}
6		-0.8969×10^{2}	0.6812×10^{3}

	B_{0j}	B_{1j}	B_{2j}
0	-0.3338×10^{-3}	0.1854×10	-0.6759×10^{-2}
1	0.1474	-0.1186×10^{2}	0.1236×10^{2}
2	-0.4542×10	0.7751×10^{2}	-0.1869×10^{3}
3	0.1193×10^{2}	-0.2902×10^{3}	0.1142×10^{4}
4	-0.4252×10^{2}	0.7089×10^{3}	-0.3577×10^{4}
5	0.9332×10^{2}	-0.1071×10^{4}	0.5732×10^{4}
6	-0.9561×10^{2}	0.7424×10^{3}	-0.3749×10^{4}

derived quantity, inversion of Equation (7) to the form $\rho_R = \rho_R(P_R, T_R)$ is unfeasible. Given P_R and T_R, one would have to perform a trial-and-error computation on Equation (7) to obtain ρ_R.

We feel that the correlation of Equation (7) can be useful not only in the regime discussed but also at values of $T_R > 50$, if the need arises.

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NOTATION

A_{ij}, B_{ij} = coefficients for density expansions in Equations (4) and (5)
f = fugacity
$g(x)$ = pair correlation function
$H(P, T)$ = enthalpy at P and T
$H(O, T)$ = enthalpy at $P = 0$ and T
k = Boltzmann constant
N = Avogadro's number
n = number of data points
P = pressure
$P_R = \dfrac{P}{P_c}$ = reduced pressure
$P_R{}^{\dagger} = \dfrac{P^{*}\epsilon/\sigma^3}{P_c}$ = square well predicted reduced pressure from Equation (2)
$P_{R\text{calc}}$ = reduced pressure calculated from $P_R{}^{\dagger}$ with Equation (7)
$P_{R\text{exp}}$ = experimental reduced pressure
$P_{R\text{MAX}}$ = the maximum P_R compatible with $\rho_R = 2.6$ in Table 1
P_c = critical pressure
$P^{*} = \dfrac{P}{\epsilon/\sigma^3}$ = reduced pressure
$P_c{}^{*} = \dfrac{P_c}{\epsilon/\sigma^3}$ = reduced critical pressure
R = parameter denoting width of square well
R' = gas constant
r = intermolecular separation
T = temperature
$T_R = \dfrac{T}{T_c}$ = reduced temperature, equal to experimental reduced temperature
T_c = critical temperature
$u(x)$ = intermolecular potential function
$u'(x)$ = first derivative of $u(x)$
v = molar volume
$v_R = \dfrac{V}{V_c}$ = reduced molar volume
v_c = critical molar volume
$v^{*} = \dfrac{V}{N\sigma^3}$ = reduced molar volume
$v_c{}^{*} = \dfrac{V_c}{N\sigma^3}$ = reduced critical molar volume
$x = r/\sigma$ = reduced intermolecular distance
$y = \dfrac{\pi}{6v^{*}}$ = density function
z = compressibility factor
z_c = critical compressibility factor
α, β, γ = correlation parameters in Equation (7)
ϵ = energetic parameter of square well
$\theta = \dfrac{\epsilon}{kT}$ = reciprocal reduced temperature
$\theta_c = \epsilon/kT_c$ = reciprocal reduced critical temperature
ρ = density
$\rho_R = \dfrac{\rho}{\rho_c}$ = reduced density
ρ_c = critical density
σ = hard sphere diameter
σ' = standard deviation, Equation (6)
ψ_0, ψ_1, ψ_2 = density dependent components of correlation function, Equations (3) to (5)
$+$ = subscript attached to reduced intermolecular distances defined by $x_+ = \lim\limits_{\Delta x \to 0} (x + \Delta x)$, $\Delta x > 0$
$-$ $x_- = \lim\limits_{\Delta x \to 0} (x + \Delta x)$, $\Delta x < 0$, as explained above

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