Extension of the Shape-Factor Method to Highly Polar Systems

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While successful for nearly spherical molecules, the simple two-parameter corresponding states principle is inappropriate for molecules which are strongly nonspherical. To deal with the latter, Leach et al. (1968) have introduced the shape-factor method, an extension of the two-parameter corresponding states principle, in which an arbitrary fluid is made conformal to a reference fluid by relating the reduced properties of both fluids via dimensionless factors which depend on the shape of the molecules. This method has been widely applied to determine densities, vapor-liquid equilibria, enthalpies, critical states, surface tensions, thermal conductivities, viscosities, Joule-Thomson coefficients and azeotropic states. An extensive review of this method can be found in Mentzer et al. (1980).

From experimental data for paraffin hydrocarbons ranging methane to *n*-pentadecane, Leach et al. (1968) evaluated shape factors by the simultaneous solution of two equations which relate the compressibility factor and the residual Helmholtz free energy of a fluid to the corresponding quantities of the *methane* reference fluid.

The shape factors, θ_{ij} and ϕ_{ij}, were correlated in the form

$$\theta_{ij} = 1 + (\omega_i - \omega_j)\left[0.0892 - 0.8493 \ln T_{ri} + \left(0.3063 - \frac{0.4506}{T_{ri}}\right)(V_{ri} - 0.5)\right] \quad (1a)$$

and

$$\phi_{ij} = \frac{Z_{ci}}{Z_{cj}}\{1 + (\omega_i - \omega_j)[0.3903(V_{ri} - 1.0177) - 0.9462(V_{ri} - 0.7663)\ln T_{ri}]\}, \quad (1b)$$

respectively, where ω_j is the acentric factor of methane, and T_{ri} and V_{ri} are the reduced temperature and reduced volume, respectively, of component i. In Eqs. 1, V_{ri} is set equal to 2.0 when it is larger than 2.0, and to 0.5 when it is smaller than 0.5, and T_{ri} is set equal to 2.0 when it is larger than 2.0.

In this paper, two new findings pertaining to the shape-factor method will be presented. First, a method is proposed to change the reference fluid with much less computational effort than in the original iterative "ratio rules" method (Leach et al., 1968) and without any loss of accuracy. Next, a modified shape-factor method is proposed to account for the properties of highly polar fluids, in contrast to the restriction of Eqs. 1 to nonpolar fluids.

Change of Reference Fluid

Instead of using the original "ratio rules" method, we have found that the reference fluid may be changed simply by replacing in Eqs. 1 the acentric factor ω_j of the methane reference fluid by the acentric factor of the new reference fluid. The density calculations are performed at given temperature and pressure, and the properties of the reference fluid are evaluated from a 32-constant modified BWR equation of state (Ely, 1984). Results obtained with this method for different reference fluids are essentially identical, as shown in Table 1.

Modified Shape-Factor Method for Highly Polar Fluids

Little work has been done on the application of the shape-factor method to polar fluids. Mentzer et al. (1981) have shown that the shape-factor method is fairly accurate for slightly and moderately polar fluids, but the agreement with experimental data for highly polar and associating fluids is very poor.

In order to extend the shape-factor method to highly polar systems, we introduce a modified shape-factor method by incorporating the idea of a recently developed four-parameter corresponding states method (Wu and Stiel, 1985; Wilding and Rowley, 1986) into the original shape-factor method. This four-parameter corresponding states method was developed successfully to predict the properties of polar fluids by using the perturbation theory to separate any dimensionless residual property

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*Deceased

Table 1. Average Absolute Percentage Deviations (AAD) of Compressibility Factor Calculations for Different Reference Fluids

Substance	Temp. Range (K)	Pres. Range (MPa)	No. of Pts.	AAD (%) for reference fluid				Data Sources
				CH_4	C_2H_6	C_3H_8	C_4H_{10}	
Heptane	548–623	2.5–32	14	1.19	1.42	1.21	0.74	a
Nonane	303–573	5.1–200	12	1.20	1.03	1.00	0.91	a
Undecane	303–573	5.1–200	12	1.93	1.14	1.11	1.13	a
Carbon dioxide	191–298	0.05–100	34	0.30	—	—	0.76	b

a. Doolittle (1964); b. Din (1956).

into three parts: the contribution from the nonpolar reference fluid, the contribution from geometrical deviations, and the polar contribution.

In the shape-factor method, it is assumed that the potential function is of the form of $u = \epsilon F(r/\sigma)$ for all components, and the function F is taken to be universal. However, the shape-factor method fails to predict the properties of highly polar and associating fluids. It is indeed believed that the function F of a nonpolar fluid is not directly conformal to that of a highly polar fluid. We thus assume that the function F of a highly polar fluid can be separated into two parts: a nonpolar part and a polar one. The nonpolar part is assumed to be conformal to the potential function of any nonpolar fluid and the polar parts of different polar fluids are assumed to be proportional to one another. More precisely, we propose that:

$$u_3 = \epsilon_1 f_{31} F_1\left(\frac{r}{\sigma_1 g_{31}}\right) + \kappa\left[\epsilon_2 f_{32} F_2\left(\frac{r}{\sigma_2 g_{32}}\right) - \epsilon_1 f_{31} F_1\left(\frac{r}{\sigma_1 g_{31}}\right)\right], \quad (2)$$

where the subscripts 1, 2, and 3 represent the nonpolar reference fluid, the polar reference fluid, and the fluid of interest, respectively, the conformal parameters f_{ij} and g_{ij} are defined by $f_{ij} = \epsilon_i/\epsilon_j$ and $g_{ij} = \sigma_i/\sigma_j$, and κ is a scaling factor, which varies with the reference fluids and the fluid of interest. The conformal parameters are applied to account for the geometrical deviations and the polar scaling factor κ accounts for the polar contribution to the potential energy of the fluid of interest.

In the following we use statistical thermodynamics to derive a new version of conformal solution theory for our proposed potential function (Eq. 2). Consider N molecules of fluid 3 confined to a volume V_3 at a temperature T_3, and an equal number of molecules of fluid 1 confined to another volume $V_3/h_{31}(=V_1)$ at a temperature $T_3/f_{31}(=T_1)$. The ratio of the configurational integrals of fluid 3, Q_3, to that of fluid 1, Q_1, is then to be given by:

$$\frac{Q_3(T_3, V_3)}{Q_1\left(\frac{T_3}{f_{31}}, \frac{V_3}{h_{31}}\right)} = \frac{\frac{1}{N!}\int \cdots \int e^{-\beta U_3}\, dr_1 \cdots dr_N}{\frac{1}{N!}\int \cdots \int e^{-\beta f_{13} U_1}\, dr_1 \cdots dr_N} = h_{13}^N \langle e^{-\beta\kappa\Delta U}\rangle, \quad (3)$$

where $\langle\,\rangle$ indicates a canonical average over reference 1, $\beta = 1/kT_3$, and $h_{ij} = g_{ij}^3$. ΔU is defined as the difference between the total potential energy of references 2 and 1, and is assumed to be small enough that we can write

$$\langle \exp(-\beta\kappa\Delta U)\rangle \approx 1 - \beta\kappa\langle\Delta U\rangle \approx \exp(-\beta\kappa\langle\Delta U\rangle).$$

Substituting this last relationship into Eq. 3 yields

$$\frac{Q_3(T_3, V_3)}{Q_1\left(\frac{T_3}{f_{31}}, \frac{V_3}{h_{31}}\right)} = h_{13}^N e^{-\beta\kappa\langle\Delta U\rangle}. \quad (4)$$

The ratio of the configurational integrals of fluid 2 to that of fluid 1 can be derived following the same procedure, with the result:

$$\frac{Q_2\left(\frac{T_3}{f_{32}}, \frac{V_3}{h_{32}}\right)}{Q_1\left(\frac{T_3}{f_{31}}, \frac{V_3}{h_{31}}\right)} = h_{12}^N e^{-\beta\langle\Delta U\rangle}. \quad (5)$$

The configurational Helmholtz free energy is given by $A = -kT \ln Q(T, V)$, and combining Eqs. (4) and (5), we have

$$\frac{A_3}{kT_3} = \frac{A_1}{kT_3/f_{31}} - N \ln h_{13} + \kappa\left(\frac{A_2}{kT_3/f_{32}} - \frac{A_1}{kT_3/f_{31}} + N \ln h_{12}\right). \quad (6)$$

The shape factors, θ_{ij} and ϕ_{ij}, are introduced to relate conformal parameters to critical properties by: $f_{ij} = \theta_{ij}(T_{ci}/T_{cj})$ and $h_{ij} = \phi_{ij}(V_{ci}/V_{cj})$. In addition, using $Q^{id} = V^N/N!$, the dimensionless residual free energy becomes

$$\left(\frac{A_3 - A_3^{id}}{kT_3}\right)_{T_3,V_3} = \left(\frac{A_1 - A_1^{id}}{kT_1}\right)_{T_1=T_3T_{C1}/T_{C3}\theta_{31},\,V_1=V_3V_{C1}/V_{C3}\phi_{31}} + \kappa\left[\left(\frac{A_2 - A_2^{id}}{kT_2}\right)_{T_2=T_3T_{C2}/T_{C3}\theta_{32},\,V_2=V_3V_{C2}/V_{C3}\phi_{32}} - \left(\frac{A_1 - A_1^{id}}{kT_1}\right)_{T_1=T_3T_{C1}/T_{C3}\theta_{31},\,V_1=V_3V_{C1}/V_{C3}\phi_{31}}\right]. \quad (7a)$$

Differentiation of Eq. 7a with respect to volume gives the compressibility factor in the form

$$z_3(T_3, V_3) = z_1\left(\frac{T_3T_{C1}}{T_{C3}\theta_{31}}, \frac{V_3V_{C1}}{V_{C3}\phi_{31}}\right) + \kappa\left[z_2\left(\frac{T_3T_{C2}}{T_{C3}\theta_{32}}, \frac{V_3V_{C2}}{V_{C3}\phi_{32}}\right) - z_1\left(\frac{T_3T_{C1}}{T_{C3}\theta_{31}}, \frac{V_3V_{C1}}{V_{C3}\phi_{31}}\right)\right]. \quad (7b)$$

Equations 7 are the expressions of the modified shape-factor method. Note that Eqs. 7 reduce to those of the original shape-factor method if the polar factor of fluid 3 is set equal to zero.

Table 2. Average Absolute Percentage Deviations (AAD) of Compressibility Factor Calculations for Polar Fluids by Three Different Methods

				SFM*	MSFM**		WRM†	
Substance	Reduced Temp. Range	Reduced Pres. Range	No. of Pts.	AAD (%)	Polar Factor	AAD (%)	AAD (%)	Data Sources
Ammonia	0.49–1.43	0.001–9.88	65	10.76	0.90	1.11	1.25	a
Acetone	0.92–1.21	2.05–6.47	34	16.73	0.82	0.55	0.21	b
Methanol	0.58–1.1	0.012–12.4	41	11.15	0.85	2.41	2.42	c, d
Ethanol	0.92–1.2	1.30–10.8	61	4.16	0.33	1.77	2.95	e
Hydrogen Chloride	0.49–2.07	0.002–24.5	49	6.68	0.82	3.30	2.60	f, g, h
Sulfur Dioxide	0.75–0.98	1.5–2.6	30	2.77	0.32	1.10	1.27	i
Methyl Acetate	0.50–0.62	4.2–33.4	12	4.74	0.45	1.49	0.52	j
Ethyl Acetate	0.48–0.60	5.1–40.9	32	3.51	0.325	1.22	0.44	k
Ethylene Oxide	0.63–1.02	0.0003–2.8	46	4.03	0.84	1.14	1.07	l
Methyl Fluoride	0.42–0.91	0.0001–0.51	37	10.11	0.95	2.26	2.24	m
Methyl Chloride	0.74–1.2	0.015–4.7	72	2.57	0.39	1.15	1.24	n
Methyl Iodide	0.48–0.59	4.4–24.2	12	6.44	0.56	1.17	0.40	j
Difluoromethane	0.71–1.4	0.15–3.5	38	10.32	0.87	1.53	—	o
Dichloromethane	0.58–0.68	0.01–17.0	15	8.12	0.64	1.87	0.25	p
Trifluoromethane	0.47–0.97	0.0003–0.97	31	3.82	0.71	1.80	2.18	m
Difluorochloromethane	0.69–0.85	1.9–32.1	12	2.88	0.25	0.51	0.39	j

*Shape-factor method

**Modified shape-factor method

†Four-parameter corresponding states method of Wilding and Rowley

a. Din (1958), b. Keller and Stiel (1977), C. Machado and Streett (1983), d. Zubarev and Bagdonas (1967), e. Lo and Stiel (1969), f. Nunes da Ponte and Staveley (1981), g. Thomas (1962), h. Frank et al. (1962), i. Kang et al. (1961), j. Kumagain and Iwasaki (1978), k. Kumagai and Iwasaki (1979), l. Walters and Smith (1952), m. Smith and Srivastava (1986), n. Hsu and McKetta (1964), o. Malbrunot et al. (1968), p. Singh and Kunchadker (1979).

Results

In Table 2, we compare the values of the compressibility factor of highly polar fluids calculated from three different methods at given temperature and pressure:

Shape-Factor Method. Methane is used as the reference fluid in Eqs. 1, and the properties of methane are obtained from the 32-constant modified BWR equation of state (Ely, 1984).

Modified Shape-Factor Method. Water and methane are chosen as the two reference fluids in Eqs. 7. The properties of water are obtained from the accurate equation of state developed by Keenan et al. (1978). The polar factor κ is fitted to experimental PVT data. For the liquid phase, the predicted value is seen to be quite sensitive to the polar factor, while it is not for the vapor phase.

Four-Parameter Corresponding States Method of Wilding and Rowley (1986). The geometrical factor is obtained from a general equation, which is a function of radius of gyration (Wilding and Rowley, 1986). The polar factor is also determined by fitting experimental PVT data.

The composite average absolute deviations of the compressibility factor are 6.90, 1.56, and 1.58% for the shape-factor, Wilding-Rowley, and modified shape-factor methods, respectively. The modified shape-factor method is a significant improvement over the original shape-factor method. Both modified shape-factor method and Wilding and Rowley's method perform well, and it is difficult to tell which one is better. It should be noted that the modified shape-factor method makes very good predictions for associating fluids such as ammonia, in contrast to the original shape-factor method.

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Notation

A = Helmholtz free energy at a given temperature and density
A^{id} = Helmholtz free energy of an ideal gas state of a fluid at the same temperature and density as the actual fluid
f_{ij} = energy conformal parameter of component i which relates its energy parameter ϵ to a reference j
g_{ij} = length conformal parameter of component i which relates its length parameter σ to a reference j
h_{ij} = cube of g_{ij}
k = Boltzmann's constant
N = number of molecule in a system
Q = configurational integral
Q^{id} = configurational integral of an ideal gas state of a fluid
r_i = a vector represents the position of molecule i
T = temperature
T_{ci} = critical temperature of component i
T_{ri} = reduced temperature of component $i (= T/T_{ci})$
U = total potential energy
u = pair potential
V = volume
V_{ci} = critical volume of component i
V_{ri} = reduced volume of component $i (= V/V_{ci})$
z_i = compressibility factor of component i
z_{ci} = critical compressibility factor of component i

Greek Letters

$\beta = 1/kT_3$
ϵ = energy parameter for a two-parameter pair potential
ϕ_{ij} = volume shape factor of component i which relates its critical volume relative to a reference j
η = geometrical scaling factor
κ = polar scaling factor
θ_{ij} = energy shape factor of component i which relates its critical temperature relative to a reference j
σ = length parameter for a two-parameter pair potential
ω = acentric factor

Literature Cited

Din, F., *Thermodynamic Functions of Gases,* Vol. 1, Butterworths, London (1956).

Din, F., *Thermodynamic Functions of Gases*, Vol. 3, Butterworths, London (1958).

Doolittle, A. K., "Specific Volumes of *n*-Alkanes," *J. Chem. Eng. Data*, **9**, 276 (1964).

Ely, J. F., "Application of the Extended Corresponding States Model to Hydrocarbon Mixtures (Computer program EXCST)," *Proc. Convention of Gas Processors Assoc.*, New Orleans, LA (1984).

Frank, E. U., M. Brose, and K. Mangold, *Progress in International Research on Thermodynamic and Transport Properties*, Academic Press, New York, 159 (1962).

Hsu, C. C., and J. J. McKetta, "Pressure-Volume-Temperature Properties of Methyl Chloride," *J. Chem. Eng. Data*, **9**, 45 (1964).

Kang, T. L., L. J. Hirth, K. A. Kobe, and J. J. McKetta, "Pressure-Volume-Temperature Properties of Sulfur Dioxide," *J. Chem. Eng. Data*, **6**, 220 (1961).

Keenan, J. H., F. G. Keyes, P. G. Hill, and J. G. Moore, *Steam Table*, Wiley, New York (1978).

Keller, R. M., and L. I. Stiel, "The P-V-T Behavior of Acetone in the Dense Gaseous Region," *J. Chem. Eng. Data*, **22**, 241 (1977).

Kumagai, A., and H. Iwasaki, "Pressure-Volume-Temperature Relations of Several Polar Liquids," *J. Chem. Eng. Data*, **23**, 193 (1978).

Kumagai, A., and H. Iwasaki, "Pressure-Volume-Temperature Relations of $CH_3COOC_2H_5$ and Generalized Tait Equation for Liquids at High Pressures," *J. Chem. Eng. Data*, **24**, 261 (1979).

Leach, J. W., P. S. Chappelear, and T. W. Leland, "Use of Molecular Shape Factors in Vapor-Liquid Equilibrium Calculations with the Corresponding States Principle," *AIChE J.*, **14**, 568 (1968).

Lo, H. Y., and L. I. Stiel, "The PVT Behavior of Ethyl Alcohol at Elevated Pressures and Temperatures," *I & EC Fund.*, **8**, 713 (1969).

Machado, J. R. S., and W. B. Streett, "Equation of State and Temperature Properties of Liquid Methanol from 298 to 489 K and Pressures to 1040 bar," *J. Chem. Eng. Data*, **28**, 218 (1983).

Malbrunot, P. F., P. A. Meunier, G. M. Scatena, W. H. Mears, K. P. Murphy, and J. V. Sinka, "Pressure-Volume-Temperature Behavior of Difluoromethane," *J. Chem. Eng. Data*, **13**, 16 (1968).

Mentzer, R. A., R. A. Greenkorn, and K. C. Chao, "The Principle of Corresponding States and Prediction of Gas-Liquid Separation Factors and Thermodynamic Properties: A Review," *Sep. Sci. Tech.*, **15**, 1613 (1980).

Mentzer, R. A., R. A. Greenkorn, and K. C. Chao, "Principle of Corresponding States and Vapor-Liquid Equilibria of Molecular Fluids, and Their Mixtures with Light Gases," *Ind. Eng. Chem. Proc. Des. Dev.*, **20**, 240 (1981).

Nunes da Ponte, M., and L. A. K. Staveley, "The Equation of State and Thermodynamic Properties of Liquid Hydrogen Chloride," *J. Chem. Thermody.*, **13**, 179 (1981).

Singh, R. P., and A. P. Kudchadker, "Pressure-Volume-Temperature Relations of Dichloromethane Gas from 250 to 510 K," *J. Chem. Thermody.*, **11**, 205 (1979).

Smith, B. D., and R. Srivastava, *Thermodynamic Data for Pure Compounds*, Elsevier (1986).

Thomas, W., *Progress in International Research on Thermodynamic and Transport Properties*, Academic Press, New York, 166 (1962).

Walters, C. J., and J. M. Smith, "Volumetric Behavior and Thermodynamic Properties of Ethylene Oxide," *Chem. Eng. Prog.*, **48**, 337 (1952).

Wilding, W. V., and R. L. Rowley, "A Four-Parameter Corresponding States Method for the Prediction of Thermodynamic Properties of Polar and Nonpolar Fluids," *Int. J. Thermophys.*, **7**, 525 (1986).

Wu, G. Z. A., and L. I. Stiel, "A Generalized Equation of State for the Thermodynamic Properties of Polar Fluids," *AIChE J.*, **31**, 1632 (1985).

Zubarev, V. N., and A. V. Bagdonas, "Experimental Determination of the Specific Volumes of Methanol at Temperature of 140–300 C and Pressures up to 200 bar," *Teploenergtika*, **14**, 79 (1967).

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