International Journal of Thermophysics, Vol. 26, No. 6, November 2005 (© 2005)
DOI: 10.1007/s10765-005-8595-2

An Approach to Calculate Thermodynamic Properties of Mixtures Including Propane, *n*-Butane, and Isobutane[1]

J. Avsec[2,3] and K. Watanabe[4]

This paper discusses a mathematical model for computing the thermodynamic properties of propane, *n*-butane, isobutane, and their mixtures, in the fluid phase using a method based upon statistical chain theory. The constants necessary for computations such as the characteristic temperatures of rotation, electronic state, etc. and the moments of inertia are obtained analytically applying a knowledge of the atomic structure of the molecule. The paper presents a procedure for calculating thermodynamic properties such as pressure, speed of sound, the Joule-Thomson coefficient, compressibility, enthalpy, and thermal expansion coefficient. This paper will discuss, for the first time, the application of statistical chain theory for accurate properties of binary and ternary mixtures including propane, *n*-butane, and isobutane, in their entire fluid phases. To calculate the thermodynamic properties of Lennard-Jones chains, the Liu-Li-Lu model has been used. The thermodynamic properties of the hydrocarbon mixtures are obtained using the one-fluid theory.

KEY WORDS: chain theory; hydrocarbons; isobutane; *n*-butane; mixtures; propane; refrigerant; thermodynamic properties.

1. INTRODUCTION

In engineering practice, energy-conversion systems operating in both liquid and gas regions, are of vital importance. In order to design such systems, it

---

[1] Paper presented at the Fifteenth Symposium on Theremophysical Properties, June 22–27, 2003, Boulder, Colorado, U.S.A.

[2] Faculty of Mechanical Engineering, University of Maribor, Smetanova 17, 2000 Maribor, Slovenia.

[3] To whom correspondence should be addressed. E-mail: jurij.avsec@uni-mb.si

[4] Department of System Design Engineering, Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan.

is necessary to know the thermodynamic properties of states in both one- and two-phase environments for pure hydrocarbons and their mixtures.

In most cases thermodynamic property tables or diagrams or empirical functions obtained from measurement are used (classical thermodynamics). Today, there are numerous equations of state (EOS) reported in the literature for describing the behavior of fluids, e.g., Van der Waals (VDW) EOS, Peng-Robinson (PR) EOS, Redlich-Kwong (RK) EOS, Soave EOS, etc. [1]. However, these equations have exhibited some noticeable defects, such as poor agreement with experimental data at moderate densities. On the other hand, we can use complex equations of state with many constants (Benedict-Webb-Rubin [1] (BWR) EOS, Lee-Kessler [1] EOS, Benedict-Webb-Rubin-Starling-Nishiumi [1] EOS, modified BWR [1, 2] (MBWR) EOS, Jacobsen-Stewart (JS) [2, 3] EOS, Tillner-Roth-Watanabe-Wagner (TRWW) [4–9] EOS, etc.). These equations are more complicated and highly accurate for states where data are available, but they have no insight into the microstructure of matter and often exhibit poor agreement with experimental data outside interpolation limits.

Statistical thermodynamics [10–24], on the other hand, calculates the properties of the state on the basis of molecular motions in a space and intramolecular interactions. The calculation of the thermodynamic functions of state is possible by making use of many statistical theories. One of the most successful approaches is perturbation theory. Several equations of state have been published that are based on perturbation theory [10, 11]. The evolution of perturbation theory is well described by Barker and Henderson [10, 12], Münster [13], Lucas [14], and Gray and Gubbins [15]. In recent years thermodynamic theories based on statistical thermodynamics have been rapidly developing. Fluids with chain bonding and association have received much attention in recent years. Interest in these models is accelerated by the fact that they cover much wider ranges of real fluids than spherical ones [25]. Reference no. [21] explains in detail, the advantage of SAFT models in comparison with classical statistical models over the entire fluid region.

In this paper we have developed a mathematical model for computing equilibrium properties of fluid states on the basis of statistical chain theory. All these models are based on the Lennard-Jones intermolecular potential function. The Lennard-Jones intermolecular potential is an important model for studying simple fluids in one- and two-phase regions. It is widely used as a reference potential in perturbation theories for more complex potentials [15, 16].

We compared the deviations of the results between properties calculating using various models for thermodynamic functions of state, and also for their derivatives (enthalpy, pressure, entropy, isothermal compressibility, coefficient of thermal expansion, heat capacities, and speed of sound).

The results of the analysis are compared with the TRWW model obtained on the basis of classical thermodynamics, and show relatively good agreement, especially for real gases. Somewhat larger deviations can, however, be found in real liquids due to the large influence of the attraction and repulsion forces, because the Lennard-Jones potential is an approximation of the actual real intermolecular potential.

2. STATISTICAL ASSOCIATING FLUID THEORY (SAFT) [25–51]

Over the last 50 years, quite accurate models based upon statistical thermodynamics have been developed for predicting the thermodynamic properties of simple molecules. We are defining simple molecules as molecules for which the most important intermolecular forces are repulsion and dispersion with weak electrostatic forces due to dipoles, quadrupoles, and higher multipole moments. Many hydrocarbons, natural gas constituents, simple organic and simple inorganic molecules fall within this category. But many other components such as electrolytes, polar solvents, hydrogen-bonded fluids, polymers, liquid crystals, plasmas, and particularly mixtures do not belong to this group. The reason for this is that, for such fluids, new intermolecular forces become important: Coloumbic forces, strong polar forces, complexing forces, the effects of association, and chain formation.

An important group of these complex fluids consists of those that associate to form relatively long-lived dimers or higher n-mers. Such fluids include hydrogen bonding, where charge transfer of other types can occur. The intermolecular forces involved are stronger than those due to dispersion or weak electrostatic interactions but still weaker than forces due to chemical bonds.

A good theory for these fluids will be very beneficial to chemical engineering applications by reducing the number of parameters and making them physically meaningful and predictable. To calculate the thermodynamic properties of a real Lennard-Jones (LJ) fluid, the Liu-Li-Lu (LLL) (revised Cotterman) equation of state based on simple perturbation theory and the statistical associating fluid theory (SAFT) equation of state for an LJ chain fluid was applied. The developed radial distribution function (RDF) has been applied to the development of a new SAFT model. The present model has been used to calculate several typical properties of LJ chains and associating LJ chains.

The original derivation of SAFT models can be be found in papers by Wertheim [41–44]. They require a comprehensive knowledge of graph theory to be fully understood. With the help of SAFT theory we can express the residual part of the free energy as

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

For the pure components we can express A^{res} a more detailed equation:

$$A^{\mathrm{res}} = A^{\mathrm{seg}}\,(m\rho, T, \sigma_s, \varepsilon) + A^{\mathrm{chain}}\,(\rho, d, m) + A^{\mathrm{assoc}}\left(\rho, T, d, \varepsilon^{\mathrm{AB}}, \kappa^{\mathrm{AB}}\right) \tag{2}$$

where ρ is the molar density of the molecules, m is the number of segments, $\varepsilon^{\mathrm{AB}}$ is the association energy of interaction between two sites, and κ^{AB} is the volume interaction between two sites.

The residual Helmholtz energy consists of three terms representing contributions from different intermolecular forces. The first term A^{seg} represents segment–segment interactions. In the present paper segment–segment interactions are represented through the Lennard-Jones interaction potential. Each segment is characterized by its diameter σ_{s}, segment interaction parameter ε_{s}, and each molecule is characterized by the number of segments, m. The second term A^{chain} is the result of the presence of covalent chain-forming bonds between the LJ segments.

The third term A^{assoc} is the result of site–site interactions between segments, for example, hydrogen bonding. For the hydrocarbons the association term is not important and will be neglected in our equations.

3. LIU-LI-LU MODEL [26]

The present model was developed on the basis of SAFT and perturbation theory around hard spheres with new coefficients determined by fitting reduced pressure and internal energy data from molecular simulation:

$$A^{\mathrm{seg}} = A^{\mathrm{hs}} + A^{\mathrm{pert}} \tag{3}$$

The hard-sphere term A^{hs} is calculated with the expression given by Mansoori et al. [51]:

$$\frac{A^{\mathrm{hs}}}{R_m T} = \frac{6}{\pi\rho}\left[\frac{3\xi_1\xi_2}{1-\xi_3} + \frac{\xi_2^3}{\xi_3^2\,(1-\xi_3)^2} + \left(\frac{\xi_2^3}{\xi_3^2} - \xi_0\right)\ln\,(1-\xi_3)\right] \tag{4}$$

where the symbol ξ_i is expressed as

$$\xi_i = \left(\frac{\pi}{6}\right)\rho\sum_i \psi_i m_i {d_i}^i \tag{5}$$

In Eq. (5) d_i represents the hard-sphere diameter and is a temperature-dependent function and ψ_i is the mole fraction of component i. In our case we have used the equation developed by Cotterman et al. [52]:

$$d_i = \sigma_i \frac{1 + 0.2977T^*}{1 + 0.33163T^* + c_3 T^{*2}} \tag{6}$$

where T^* is the reduced temperature, and

$$c_3 = \left(0.0010477 + 0.025337\frac{m_i - 1}{m_i}\right) \tag{7}$$

For the case of a pure fluid, Eq. (4) is reduced to the Carnahan–Starling equation [12]:

$$\frac{A^{\text{hs}}}{R_m T} = m\frac{4\eta - 3\eta^2}{(1-\eta)^2}, \tag{8}$$

For the dispersion term we have used an equation by Cotterman et al. [52] and one-dimensional VDW theory for mixtures [26]:

$$A^{\text{pert}} = m_x \frac{A^{(1)}}{T_x^*} + m_x \frac{A^{(2)}}{T_x^{*2}} \tag{9}$$

$$\frac{A^{(1)}}{R_m T} = \sum_{m=1}^{4} A_{1m}\left(\frac{\eta}{\tau}\right)^m, \qquad \frac{A^{(2)}}{R_m T} = \sum_{m=1}^{4} A_{2m}\left(\frac{\eta}{\tau}\right)^m, \tag{10}$$

$$\tau = 0.7405, \quad \eta = \frac{\pi \rho d_s^3}{6} m_x, \tag{11}$$

The effective segment diameter d_s is determined using the Barker perurbation theory. We use a function developed in the work of Chapman et al. [27].

$$d_s = \sigma_x \frac{1 + 0.2977T^*}{1 + 0.33163T^* + c_3 T^{*2}} \tag{12}$$

$$c_3 = 0.0010477 + 0.025337\frac{m_x - 1}{m_x} \tag{13}$$

where

$$T_x^* = \frac{\mathrm{k}T}{\varepsilon_x} \tag{14}$$

For the mixtures we have used one-fluid Van der Waals (VDW1) mixing rules [17, 18]:

$$\begin{aligned} m_x &= \sum_i \psi_i m_i \\ m_x^2 \sigma_x^3 &= \sum_i \sum_j \psi_i \psi_j m_i m_j \sigma_{ij} \\ m_x^2 \varepsilon_x \sigma_x^3 &= \sum_i \sum_j \psi_i \psi_j m_i m_j \varepsilon_{ij} \sigma_{ij} \end{aligned} \tag{15}$$

For the determination of mixing parameters, we have used the Lorentz-Berthelot equations:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}, \quad \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \tag{16}$$

According to Wertheim, in first-order thermodynamic perturbation theory, the contribution to the free energy due to chain formation of the LJ system is expressed as

$$\frac{A^{\text{chain}}}{N\mathrm{k}T} = \sum_i \psi_i \left(1 - m_i\right) \ln g^{\mathrm{LJ}}\left(\sigma\right) \tag{17}$$

Johnson et al. [29] gave a correlation result of the radial distribution function for LJ fluids dependent on reduced temperature and reduced density:

$$g^{\mathrm{LJ}}\left(\sigma_s\right) = 1 + \sum_{i=1}^{5} \sum_{j=1}^{5} a_{ij} \left(\rho^*\right)^i \left(T^*\right)^{1-j} \tag{18}$$

4. RESULTS AND COMPARISON WITH EXPERIMENTAL DATA

For the purpose of comparison of the present statistical model with available analytical models, we have selected the thermodynamic models for hydrocarbons recently published by Miyamoto and Watanabe [6–9] which cover a wide range of temperatures and pressures. For propane the equation covers from the triple point temperature (85.48 K) to 623 K, at pressures up to 103 MPa, and at densities up to 741 kg · m^{-3}; for *n*-butane from 134.87 to 589 K, at pressures up to 69 MPa, and at densities up to 745 kg · m^{-3}; and for isobutane from 113.56 K (the triple point temperature) to 573 K, at pressures up to 35 MPa, and at densities up to $749\,\mathrm{kg\cdot m^{-3}}$. At present the model is one of the most accurate models for calculation of equilibrium thermodynamic properties for propane in the gaseous and liquid states. The absolute deviations of experimental thermodynamic property data from analytical model are mostly within ± 1% in pressure.

The most important data for analytical calculations are presented in Table I. The constants necessary for computations such as the characteristic rotation, electronic, etc. temperatures are obtained from data [53–56]. The vibration constants are obtained from the NIST Chemistry Web Book. The moments of inertia are obtained analytically by applying a knowledge of the atomic structure of the molecule. We carried out calculations for mixtures of *n*-butane, isobutane (C_4H_{10}), and propane (C_3H_8). The comparison of our calculations for hydrocarbon mixtures with the TRWW model is presented in Figs. 1–4. They show the relative deviations of the results for mixtures of butane and propane in the real-gas region between the analytical computation (Liu-Li-Lu model (LLL)) and the TRWW model obtained by classical thermodynamics. For the purpose of calculation of thermodynamic properties of mixtures containing propane, *n*-butane, and isobutane, we have selected the TRWW thermodynamic model with new constants published by Miyamoto and Watanabe (MW) [6–9] for a range of temperatures from the triple point temperature to 600 K, at pressures up to 10 MPa. The absolute deviations of experimental thermodynamic property data from the analytical model are mostly within ± 1%.

The relative deviation is defined by the following expression:

$$\text{Relative deviation} = RD = (data_{\mathrm{LLL}} - data_{\mathrm{TRWW}})/data_{\mathrm{TRWW}} \quad (19)$$

where $data_{\mathrm{LLL}}$ are the analytical results obtained by the LLL model and $data_{\mathrm{TRWW}}$ are analytical results obtained by the TRWW model.

The results for all the models obtained by statistical thermodynamics show relatively good agreement. The computed vapor pressure, isother-

Table I. Important Constants for Analytical Calculations

	n-butane	isobutane	propane
σ_s (m)	3.87×10^{-10}	4.04×10^{-10}	3.77×10^{-10}
ε_s (J)	3.84×10^{-21}	3.219×10^{-21}	3.20×10^{-21}
m (-)	2.134	2.201	1.85

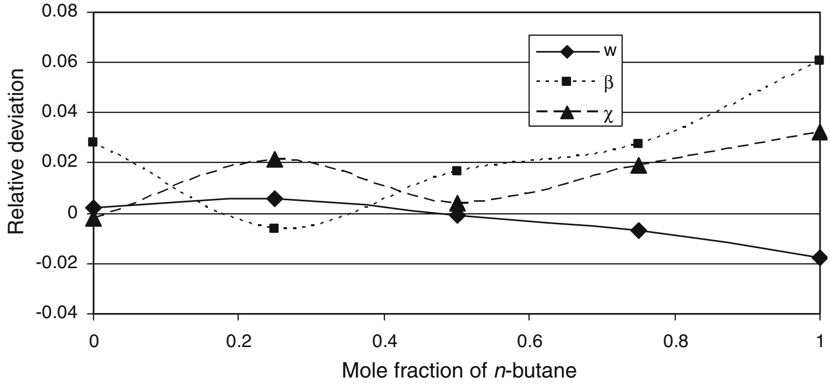

Fig. 1. Deviations of thermodynamic properties of propane + *n*-butane mixtures at 5 MPa and 500 K calculated using the model of this work from values calculated using a classical model (TRWW [6–9]).

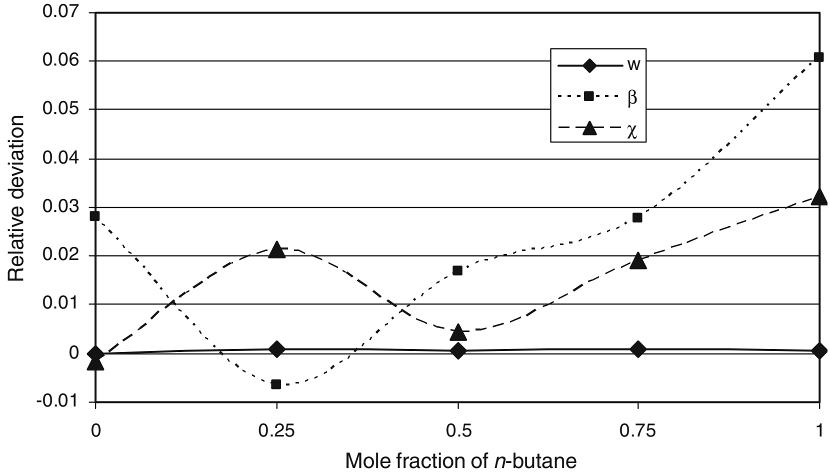

Fig. 2. Deviations of thermodynamic properties of propane + *n*-butane mixtures at 0.1 MPa and 300 K calculated using the model of this work from values calculated using a classical model (TRWW [6–9]).

mal compressibility, molar isobaric heat capacity, and speed of sound were confirmed for all the models obtained by statistical thermodynamics. Somewhat larger deviations can be found in the region near the critical point due to the large influence of fluctuation theory and the singular behavior of some thermodynamic properties in the near-critical region. The perturbation models based upon SAFT theory (LLL) yield

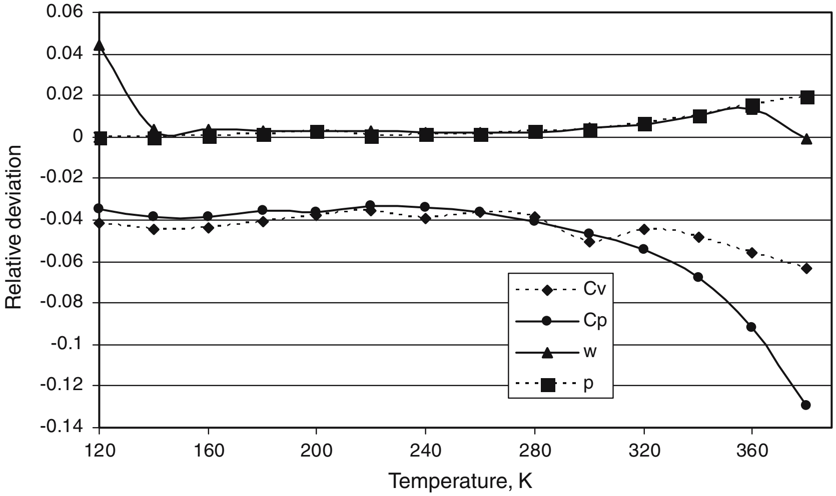

Fig. 3. Relative deviations of thermodynamic properties of the saturated vapor for equimolar mixture of propane + *n*-butane calculated using the model of this work from values calculated using a classical model (TRWW [6–9]).

surprisingly good results. The models based upon SAFT theory give better results in comparison with models based upon classical statistical thermodynamics, especially in high-temperature and high-pressure regions.

Figures 1 and 2 show a comparison between the LLL and TRWW models for speed of sound w, isothermal compressibility β, and volumetric coefficient of expansion χ. These figures are for propane + *n*-butane mixtures for the gas phase at 5 MPa, 500 K and at 0.1 MPa, 300 K. The largest deviations are 1.8% for speed of sound, 6% for volumetric coefficient of expansion, and 3.1% for isothermal compressibility.

Figure 3 shows a comparison between the LLL and TRWW models for speed of sound, pressure, isobaric molar heat capacity and isochoric molar heat capacity for propane + *n*-butane mixtures at 0.5 mole fraction of butane at saturated vapor conditions. The largest deviations are 1.8% for speed of sound w, 4.1% for pressure p, 4.1% for isochoric molar heat capacity C_v, and 13.1% for isobaric molar heat capacity C_p.

Figure 4 shows a comparison between LLL and TRWW models for speed of sound w, pressure, p, isobaric molar heat capacity, C_p and isochoric molar heat capacity, C_v, for *n*-butane + isobutane mixtures at 0.5 mole fraction of *n*-butane at saturated-gas and saturated-liquid conditions.

The analysis shows that multi-pole effects must be taken into account for the regions of very low compressibility factors [31] to be able to

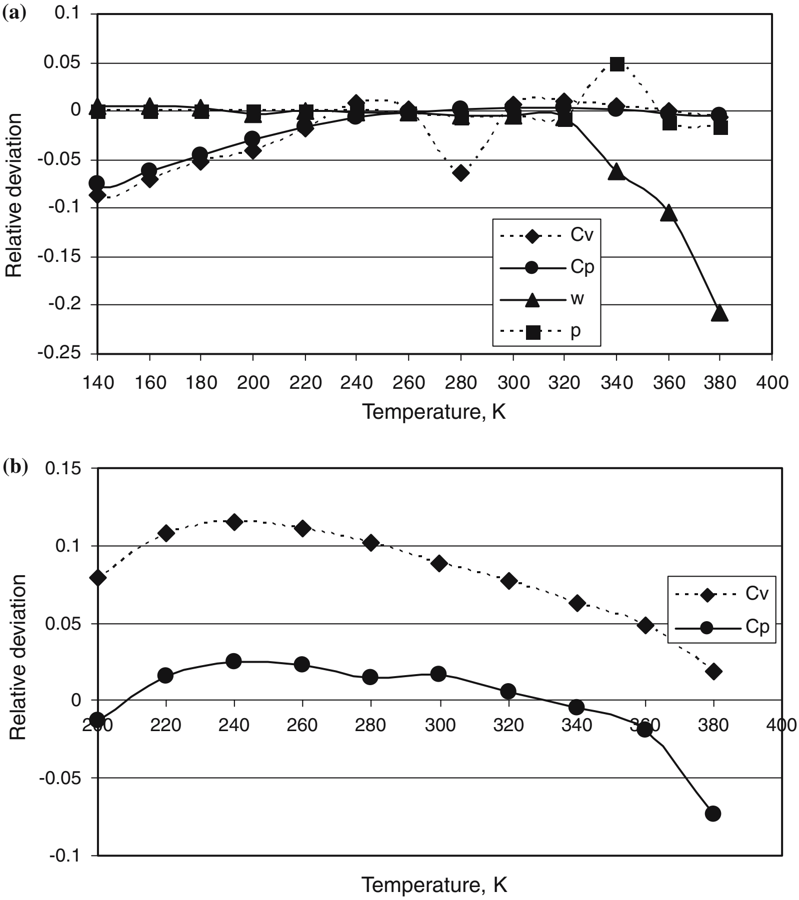

Fig. 4. Relative deviation of thermodynamic properties at the (a) saturated vapor and (b) saturated liquid for equimolar mixture of isobutane + *n*-butane calculated using the model of this work from values calculated using a classical model (TRWW [6–9]).

improve the matching of results, even though the matching is satisfactory. The present analysis provides a good basis for a further upgrade of this model allowing the calculation of very accurate thermodynamic properties in liquid and gas phases as well as in the super- and sub-critical regions.

The results for all models obtained using statistical thermodynamics show relatively good agreement. The computed vapor pressure, isothermal compressibility, isobaric molar heat capacity, and speed of sound have been well confirmed by our analytical model obtained by statistical thermodynamics. Somewhat larger deviations can be found in the region near the critical point due to the significant influence of fluctuation theory and singular behavior of some thermodynamic properties in the near-critical condition. The perturbation models based upon SAFT theory (LLL) yield surprisingly good results.

5. CONCLUSION AND SUMMARY

The paper presents a mathematical model for computation of thermodynamic functions of the state for hydrocarbons in the fluid state on the basis of statistical chain theory. The same procedure can be applied for calculation of thermophysical properties for hydrofluorocarbons, of course with the knowledge of multipolar effects [20, 21]. The analytical results are compared with the analytical calculation obtained by classical thermodynamics and show relatively good agreement.

REFERENCES

1. S. M. Walas, *Phase Equilibria in Chemical Engineering* (Butterworths, Boston, 1984).
2. B. A. Younglove and J. F. Ely, J. Phys. Chem. Ref. Data **16**:577 (1987).
3. R. T Jacobsen, R. B. Stewart, M. Jahangiri, and S. G. Penoncello, *Adv. Cryo. Eng.* **31**:1161 (1986).
4. R. Tillner-Roth, A. Yokezeki, H. Sato, and K. Watanabe, *Thermodynamic Properties of Pure and Blended Hydrofluorocarbon (HFC) Refrigerants* (Japan Society of Refrigerating and Air Conditioning Engineers, Tokyo, 1997).
5. R. Tillner-Roth, *Die Thermodynamischen Eigenschaften von R152a, R134a und ihren Gemischen* (Ph. D. Thesis, Univ. Hannover, Germany, 1993).
6. H. Miyamoto and K. Watanabe, *Int. J. Thermophys.* **21**:1045 (2000).
7. H. Miyamoto and K. Watanabe, *Int. J. Thermophys.* **22**:459 (2001).
8. H. Miyamoto and K. Watanabe, *Int. J. Thermophys.* **23**:477 (2002).
9. H. Miyamoto and K. Watanabe, *Proc. 5th IIR Gustav Lorentzen Conference*, Guangzhou, China (Sept. 16–20, 2002).
10. J. A. Barker and D. Hendersom, *J. Chem. Phys.* **47**:4714 (1967).
11. J. D. Weeks and D. Chandler, *J. Chem. Phys.* **54**:5237 (1971).
12. J. A. Barker and D. Hendersom, *Rev. Mod. Phys.* **48**:587 (1976).
13. A. Münster, *Statistical Thermodynamics* (Springer-Verlag, New York, 1974).
14. K. Lucas, *Applied Statistical Thermodynamics* (Springer-Verlag, New York, 1992).
15. C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids* (Clarendon Press, Oxford, 1984).
16. B. J. McClelland, *Statistical Thermodynamics* (Chapman and Hall, London, 1980).
17. J. Avsec and M. Marčič, *J. Thermophys. Heat Transfer* **14**:496 (2000).
18. J. Avsec and M. Marčič, *J. Thermophys. Heat Transfer* **16**:455 (2002).
19. J. Avsec and M. Marčič, *J. Thermophys. Heat Transfer* **16**:463 (2002).
20. J. Avsec, M. Marcic, A. Leipertz, and A. P. Fröba, *Proc. IIR Thermodyn. Conf.*, Paderborn (2001).
21. J. Avsec, M. Marčič, and K. Watanabe, *J. Thermophys. Heat. Transfer* **18:**243 (2004).
22. Y. Tang and B. C.-Y. Lu, *AIChE J.* **43**:2215 (1997).

23. Y. Tang and B. C.-Y. Lu, *Fluid Phase Equilib.* **146**:73 (1998).
24. L. Chunxi, L. Yigui, and L. Jiufang, *Fluid Phase Equilib*. **127**:71 (1997).
25. Y. Tang and B. C.-Y. Lu, *Fluid Phase Equilib*. **171**:27 (2000).
26. Z.-P. Liu, Y.-G. Li, and J.-F.Lu, *Fluid Phase Equilib*. **173**:189 (2000).
27. W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, *Ind. Eng. Chem.* **29**:1709 (1990).
28. P. D. Condo and M. Radosz, *Fluid Phase Equilib*. **117**:1 (1996).
29. J. K. Johnson and K. E. Gubbins, *Mol. Phys*. **77**:1033 (1992).
30. Y. S. Wie and R. J. Sadus, *AIChE J*. **46**:169 (2000).
31. M. Banaszak, C. K. Chen, and M. Radosz, *Macromolecules* **29**:6481 (1996).
32. S. H. Huang and M. Radosz, *Ind. Eng. Chem. Res*. **29**:2284 (1990).
33. L. A. Davies, A. Gil-Villergas, and G. Jackson, *Int. J. Thermophys*. **19**:234 (1998).
34. W. G. Chapman, G. Jackson, and K. E. Gubbins, *Mol. Phys*. **65**:1057 (1988).
35. S. H. Huang and M. Radosz, *Ind. Eng. Chem. Res*. **30**:1994 (1991).
36. C.-K. Chen, M. Banaszak, and M. Radosz, *J. Phys. Chem. B* **102**:2427 (1998).
37. G. Jackson, W. G. Chapman, and K. E. Gubbins, *Mol. Phys*. **65**:1 (1988).
38. S. B. Kiselev and J. F. Ely, *Ind. Eng. Chem. Res*. **38**:4993 (1999).
39. E. A. Müller and K. E. Gubbins, *Ind. Eng. Chem. Res*. **40**:2193 (2001).
40. H. Adidharma and M. Radosz, *Ind. Eng. Chem. Res.* **37**:4453 (2000).
41. M. S. Wertheim, *J. Stat. Phys*. **35**:19 (1984).
42. M. S. Wertheim, *J. Stat. Phys*. **35**:35 (1984).
43. M. S. Wertheim, *J. Stat. Phys*. **42**:459 (1986).
44. M. S. Wertheim, *J. Stat. Phys*. **42**:477 (1986).
45. J. K. Johnson, E. A. Müller, and K. E. Gubbins, *J. Phys. Chem.* 98:6413 (1994).
46. T. Kraska and K. E. Gubbins, *Ind. Eng. Chem. Res*. **35**:4727 (1996).
47. T. Kraska and K. E. Gubbins, *Ind. Eng. Chem. Res*. **35**:4738 (1996).
48. J. V. Sengers, R. F. Kayser, C. J. Peters, and H. J. White, Jr., *Equations of State for Fluids and Fluid Mixtures* (Elsevier, Amsterdam, 2000).
49. Y. Tang, Z. Wang, and B. C.-Y. Lu, *Mol. Phys*. **99**:65 (2001).
50. J. C. Pamies and L. F. Vega, *Ind. Eng. Chem. Res*. **40**:2532 (2001).
51. G. A. Mansoori, N. F. Carnahan, K. E. Starling, and T. W. Leland, *J. Chem. Phys*. **54**:1523 (1971).
52. R. L. Cotterman and J. M. Prausnitz, *AIChE J*. **32**:1799 (1986).
53. L. J. Bellamy, *The Infrared Spectra of Complex Molecules* (Chapman and Hall, London, 1980).
54. G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (Van Nostrand Reinhold Co., London. Toronto, Melbourne, 1966).
55. G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand Reinhold Company, New York, 1984).
56. U. Delfs, *Berechnung der Idealgaswarmekapazität der Fluor-Chlorderivate von Methan und Ethan unter Verwendung eines Modifizierten Urey-Bradley-Modells, Wärmetechnik*, *Kältetechnik* (VDI Fortschritt-Bericht, Reihe Nr. 81, Reihe 19, 1995).