Shape Factors for the Light Hydrocarbons[1]

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Abstract

Corresponding-states shape factors for ethane, propane, *iso*-butane, *n*-butane and nitrogen, with methane as the reference fluid, have been determined from the available experimental data. We present simple six-parameter correlations of the results for each substance in a way that enforces thermodynamic consistency. Using the one-fluid model with our shape factors, compression factors of mixtures of ethane and methane have been calculated and found to be in good agreement with experimental values.

Keywords: Corresponding-States, Density, Hydrocarbons, Mixtures, Nitrogen, Shape-Factors

Introduction

The corresponding states principle (CSP), whereby the configurational thermodynamic properties of a fluid of interest are related to those of a chosen reference fluid, is a well-known tool for the prediction of the properties of both pure fluids and mixtures. In its simplest form the CSP requires, in addition to the equation of state of the reference substance, just two substance-dependent parameters (usually critical temperature T^c and pressure p^c); it is then entirely predictive but unfortunately its usefulness is restricted to small sets of very similar substances. The extended three-parameter theory of Pitzer [1], which includes an additional substance-dependent parameter ω known as the acentric factor, is of much wider applicability. The implementation of this theory due to Lee and Kesler [2] is particularly useful and offers an accuracy that is satisfactory for the purposes of many engineering calculations. Nevertheless, there are a number of applications for which a model approaching the accuracy of good experimental data is desirable. One such example is natural gas systems where *pVT* properties are required with high accuracy for custody-transfer purposes.

It is possible to map the thermodynamic properties of the fluid of interest onto those of the reference fluid by associating each state point with a pair of numbers, known as shape factors, that correct the simple CSP relations. To the extent that the simple CSP is a useful first approximation, the shape factors are expected to be of order unity and to vary slowly as functions of temperature and density in a fluid of fixed composition. Unfortunately, there is no efficient and reliable method by which these quantities may be calculated from molecular theory and our present knowledge of shape factors is based entirely on the empirical evidence for various substances.

Leland *et al.* [3] developed a correlation of shape factors for the light hydrocarbons, based on methane as the reference fluid, and this made use of four substance-dependent parameters: T^c, p^c, ω and the critical compression factor Z^c. In the thirty years since that work, there have been many improvements in the quantity and quality of the available experimental

data and it would seem useful to develop new correlations which exploit these facts. The initial objective of the present work is to develop simple correlations of the shape factors for the light hydrocarbons, plus nitrogen, carbon dioxide and a few other substances, and to test their usefulness in connection with a one-fluid theory for the prediction of mixture properties. This approach may provide a useful and accurate thermodynamic model for natural gas systems.

Theory

Definition of the shape factors

The basic relations between the properties of the fluid of interest and those of the reference fluid may be stated as follows [4]:

$$F^{res}(\tau,\delta) = F_0^{res}(\tau_0,\delta_0) \tag{1}$$

$$Z(\tau,\delta) = Z_0(\tau_0,\delta_0)\,. \tag{2}$$

Here, $\tau = T^c/T$ is the inverse reduced temperature, $\delta = \rho/\rho^c$ is the reduced amount-of-substance density, Z is the compression factor, $F^{res} = A^{res}/nRT$ is the dimensionless residual Helmholtz free energy and subscript '0' denotes properties of the reference fluid. The simple CSP asserts that $\tau_0 = \tau$ and $\delta_0 = \delta$, so that Z and F^{res} are universal functions of reduced temperature and density. In the extended CSP, it is recognised that this universality does not hold but that eqns. (1) and (2) may be made exact through the introduction of temperature- and density-dependent shape factors θ and ϕ such that

$$\left.\begin{aligned} \tau_0 &= \theta\tau \\ \delta_0 &= \phi\delta\,. \end{aligned}\right\} \tag{3}$$

The properties of the reference fluid may be obtained conveniently from an equation of state explicit in the dimensionless Helmholtz free energy. In particular, Z_0 is given by

$$Z_0(\tau_0,\delta_0) = 1 + \delta_0(\partial F_0^{res}/\partial\delta_0)_{\tau_0}\,. \tag{4}$$

Shape factors from experimental data

Given a pair of experimental values of Z and F^{res} for the fluid of interest, and an equation of state for the reference fluid, eqns. (1) and (2) may be solved for the values of τ_0 and δ_0 pertaining to the state point in question; the corresponding shape factors are then obtained from eqn. (3). Repeating this calculation at many points leads to a table of the shape factors that map the thermodynamic properties of the fluid of interest onto those of the reference fluid. Obviously this procedure is not in itself predictive.

Thermodynamic consistency

For practical purposes it is usually preferable to have correlations of the shape factors as functions of τ and δ but this must be done with care if thermodynamic consistency is to be maintained. This issue arises because, while eqn. (2) remains true, Z is also given by

$$Z(\tau,\delta) = 1 + \delta(\partial F^{res}/\partial\delta)_\tau \tag{5}$$

and, in view of eqn. (1), this is equivalent to

$$Z(\tau,\delta) = 1 + \delta\left[(\partial F_0^{res}/\partial\delta_0)_{\tau_0}\{\varphi + \delta(\partial\varphi/\partial\delta)_\tau\} + \tau(\partial F_0^{res}/\partial\tau_0)_{\delta_0}(\partial\theta/\partial\delta)_\tau\right]. \tag{6}$$

Eqns. (2) and (6) will agree exactly if and only if the shape factors obey the constraint

$$(\partial\theta/\partial\delta)_\tau = -\left\{\frac{\delta(\partial F_0^{res}/\partial\delta_0)_{\tau_0}}{\tau(\partial F_0^{res}/\partial\tau_0)}\right\}(\partial\varphi/\partial\delta)_\tau . \tag{7}$$

Exact consistency may be enforced by the following procedure: (a) correlate one of the shape factors as a function of both τ and δ; (b) correlate only the zero-density values of the other shape factor as a function of τ; and (c) determine the remaining density dependence by integration of eqn. (7).

Zero-density shape factors

The complexity of most real substances is such that a theoretical evaluation of θ and ϕ is generally impossible. It is nevertheless possible to deduce the zero density shape factors θ_0 and ϕ_0 from the second and third virial coefficients of the fluids and thus, indirectly, from the two- and three-body intermolecular potential functions. To do this, one writes both eqns. (1) and (2) in terms of the virial equations of state for the fluid of interest and for the reference fluid correct to order δ^2. The shape factors are also expanded as polynomials in δ. Then, solving the corresponding states relations correct to order δ^2, one obtains the following equations:

$$\left.\begin{aligned} \rho^c B(\tau) &= (\phi_0 \rho_0^c) B_0(\theta_0 \tau) \\ (\rho^c)^2 C(\tau) &= (\phi_0 \rho_0^c)^2 C_0(\theta_0 \tau) \end{aligned}\right\} \tag{8}$$

These relations may be solved for θ_0 and ϕ_0 given correlations for the second and third virial coefficients (or intermolecular potentials from which these quantities may be calculated). Alternatively, if one of the zero-density shape factors is already determined then the other may be obtained using just the second virial coefficients.

Application to mixtures

In this work, we follow rigorously the van der Waals one-fluid model of mixtures [4] without considering separately mixture pseduo-critical constants and mixture shape factors. Briefly, the one-fluid model expresses the mixture compression factors $Z_x(T,\rho)$ in terms of that of a single reference fluid by means of the relation

$$Z_x(T,\rho) = Z_0(T/f_x, h_x\rho)\,, \tag{9}$$

where f_x and h_x are scaling parameters which are given by the van der Waals mixing rules:

$$h_x = \sum_i \sum_j x_i x_j h_{ij} \tag{10}$$

$$f_x h_x = \sum_i \sum_j x_i x_j f_{ij} h_{ij}\,. \tag{11}$$

The pure component scaling factors are given by

$$\left.\begin{aligned} f_{ii} &= (T_{ii}^{c}/T_{0}^{c})\theta_{ii} \\ h_{ii} &= (\rho_{0}^{c}/\rho_{ii}^{c})\phi_{ii}, \end{aligned}\right\} \tag{12}$$

where θ_{ii} and ϕ_{ii} are the shape factors of pure i evaluated at temperature $(T/f_x)(\theta_{ii}T_{ii}^{c}/T_{0}^{c})$ and density $(h_x\rho)(\rho_{ii}^{c}/\phi_{ii}\rho_{0}^{c})$. The unlike terms in f_x and h_x are given by the Lorentz-Berthelot combining rules,

$$\left.\begin{aligned} f_{ij} &= (1-k_{ij})\left(f_{ii}f_{jj}\right)^{1/2} \\ h_{ij} &= (1-l_{ij})\left(\tfrac{1}{2}h_{ii}^{1/3}+\tfrac{1}{2}h_{jj}^{1/3}\right)^{3}, \end{aligned}\right\} \tag{13}$$

where for completeness we include binary interaction parameters k_{ij} and l_{ij}. These expressions for the mixture compression factor reduce exactly to eqns. (2) and (3) in the case of a pure substance.

Pure-fluid shape factors

The first stage of the present work was to examine the shape factors of nitrogen and of several light hydrocarbons, with methane as the reference fluid, without presuming any particular functional form. To do this we made use of experimental compression factors, vapour pressures p^{σ}, saturated vapour densities ρ'' and saturated liquid densities ρ' for these substances. For all super-critical isotherms we determined values of Φ^{res} by quadrature according to the relation

$$\Phi^{res} = \int_{0}^{\rho}(Z-1)\,d\ln\rho\ . \tag{14}$$

In the sub-critical region, the procedure was to use eqn. (14) to obtain Φ^{res} at densities up to the saturated vapour density, then to add the increment $\Delta\Phi^{res}$ associated with crossing the co-existence region and finally to integrate from the saturated-liquid density up to the greatest desired density. The increment $\Delta\Phi^{res}$ is given by

$$\Delta F^{res} = \frac{p^s(\rho' - \rho'')}{\rho'\rho'' RT} + \ln(\rho''/\rho') . \tag{15}$$

Having obtained F^{res} at the state points where experimental values of Z were available, we solved eqns. (1) - (3) for the shape factors on a point-by-point basis. The properties of the reference fluid were obtained from the accurate equation of state due to Setzmann and Wagner [5].

Figs. 1 - 3 illustrate results for ethane based on the experimental data of Douslin and Harrison [6] along one sub-critical, one near-critical and one super-critical isotherm. Error bars indicate the approximate effect of uncertainties in the experimental data. It is apparent

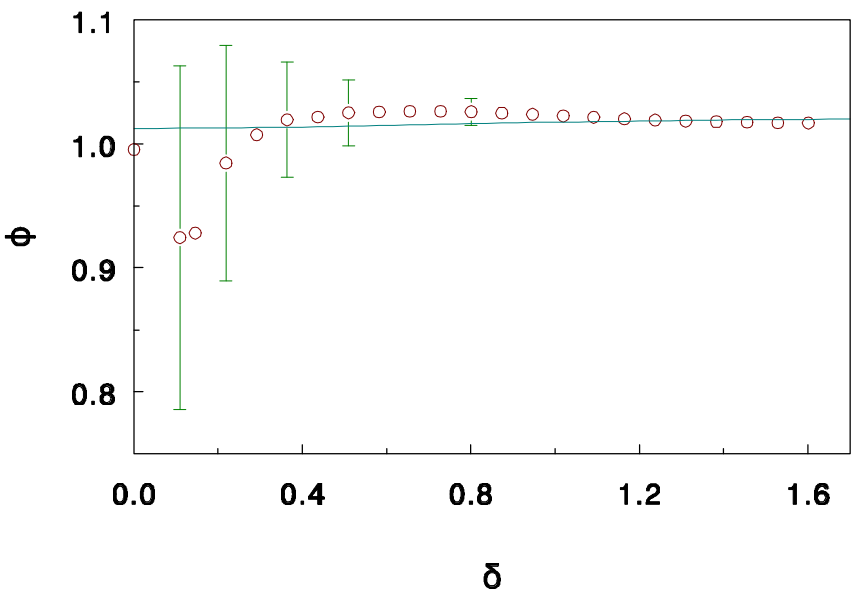

Fig. 1 Shape factor φ for ethane at τ = 1.1178 (T = 273.15 K): ○, derived from experimental [6] data; ———, calculated from eqns. (16) and (17).

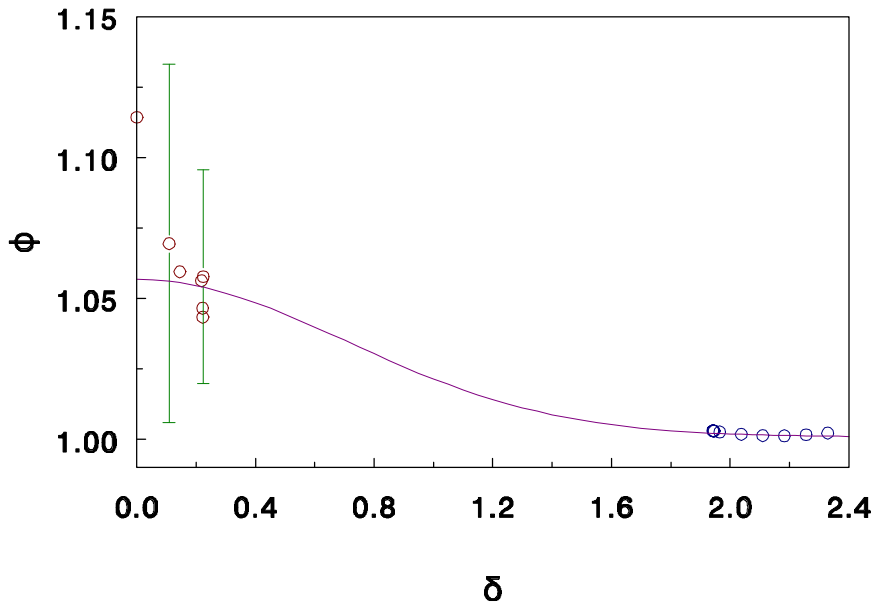

Fig. 2 Shape factor j for ethane at t = 0.99987 (*T* = 305.37 K): ○, derived from experimental [6] data; ———, calculated from eqns. (16) and (17).

that, although quite smooth, the results at low densities are in fact subject to a large uncertainty and this reflects the fact that the solution is illconditioned as $\rho \rightarrow 0$. We also show zero-density shape factors obtained by solving eqns. (7) using correlations of the second and third virial coefficients of ethane based on intermolecular-potential models. For densities such that δ is greater than about 0.5, the effects of the experimental uncertainties become quite small and we see the shape factors approaching constant values as reported by other workers [3]. Very similar behaviour was found on all isotherms, except those near to the critical temperature, for ethane, propane and nitrogen. The isotherms close to T^c show slightly more complicated behaviour which we have not yet attempted to correlate.

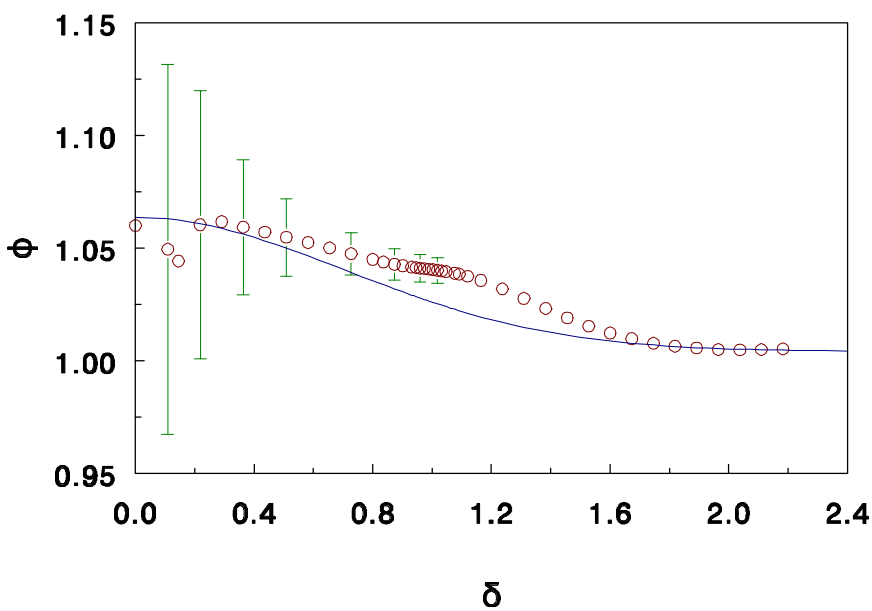

Fig. 3 Shape factor Θ for ethane at τ = 0.7216 (T = 423.15 K): ○, derived from experimental [6] data; ———, calculated from eqns. (16) and (17).

The form of the curves obtained for the shape factor Θ, combined with the associated uncertainties, led us to correlate Θ by means of the simple two-parameter function:

$$\phi = A_1(\tau) + A_2(\tau)\exp(-\delta^2). \tag{16}$$

This has the property of varying smoothly from $A_1(\tau) + A_2(\tau)$ at zero density towards a limiting high density value of $A_1(\tau)$. Having adopted this functional form for ϕ with trial values of the parameters, we solved the first of eqns. (8) for η_0 and then integrated eqn. (7) to obtain η along the whole isotherm. The optimum values of the parameters $A_1(\tau)$ and $A_2(\tau)$ were determined for each of 28 isotherms reported by Douslin and Harrison [6] and, typically, the compression factors on each isotherm were fitted to within about 0.1 per cent. The parameters so determined were found to be correlated well by the relations:

$$\left.\begin{aligned} A_1(\tau) &= b_{11} + b_{12}\exp(-1/\tau) - b_{13}\ln(\tau) \\ A_2(\tau) &= b_{21} + \frac{b_{22}}{\exp(1/\tau^2) + \exp(-1/\tau^2)} + b_{23}\exp(-1/\tau^2) \end{aligned}\right\}. \tag{17}$$

This leads to a total of six parameters in addition to three intermolecular potential parameters used to correlate the second virial coefficients. Finally, these six parameters were optimised in a single global fit to all of the isotherms except those in the range 273.15 < T/K < 323.15 around the critical temperature (T^c = 305.33 K). The parameters determined in this way are given in table 1 and, in table 2, we give the absolute average deviation (AAD) of the fit. Also given in table 2 is the AAD for all isotherms, including those in the critical region, and AAD's for the sub-critical and super-critical regions taken separately. These figures show that the global fit is generally good but clearly less accurate that the fit for a single isotherm.

The same procedure has been applied to nitrogen and propane with similar results which we present in tables 1 and 2. We also report results for *n*-butane and *iso*-butane but we found that these substances conformed less-well to the functional form of ϕ devised for the other substances; the AAD's are consequently somewhat larger.

Application to a methane-ethane mixture

As a test of the model, compression factors of the mixture {0.749CH_4 + 0.251C_2H_6} were calculated and compared with the experimental data of Blanke and Weiss [11] in the temperature range 273.7 K to 333.4 K at pressures up to 7 MPa. The binary interaction parameter k_{ij} was optimised against the datum at the lowest temperature and the highest pressure with the result k_{ij} = -0.0133. Fig. 4 shows the relative deviations of the experimental data from the prediction; the AAD was 0.04 per cent. Broadly similar results were found for other mixture compositions studied by Blanke and Weiss.

Table 1. Parameters of eqn. (17).

	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	N_2
$b_{1,1}$	-0.174570	0.678112	1.323605	0.675455	0.983174
$b_{1,2}$	3.204108	0.874822	-0.843045	0.842524	0.041860
$b_{1,3}$	1.205835	0.365789	-0.245955	0.284092	0.031031
$b_{2,1}$	-0.093284	-0.033634	0.722702	0.282470	-0.013432
$b_{2,2}$	1.705488	0.879460	-2.487791	0.639186	-0.111969
$b_{2,3}$	-1.087056	-0.537378	0.730726	-0.925929	-0.048965

Table 2. Absolute average percentage deviations of experimental data from the model in different regions of the thermodynamic surface.

	Overall	Super-Critical	Near-Critical	Sub-Critical	Non-Critical	Data Sources
C_2H_6	0.31	0.16	0.63	0.12	0.15	[6]
C_3H_8	1.02	0.10	2.02	0.36	0.24	[7]
n-C_4H_{10}	1.11	1.26	1.67	0.29	0.78	[8]
i-C_4H_{10}	0.65	0.57	1.00	0.50	0.52	[9]
N_2	0.16	0.10	0.18	0.36	0.16	[10]

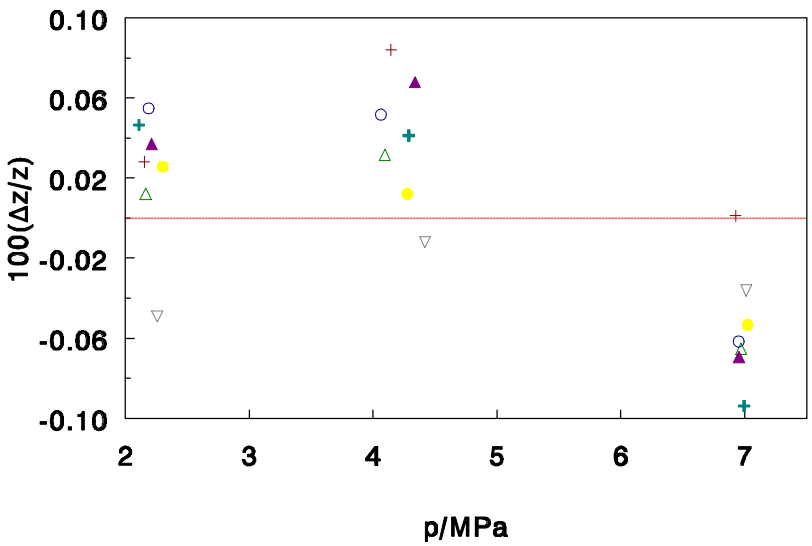

Fig. 4 Fractional deviations $\Delta Z/Z$ of experimental compression factors of {0.749 CH_4 + 0.251 C_2H_6} [20] from the corresponding-states theory and the one-fluid model.).+ , 274 K; △, 283 K; ○, 294 K; +, 304 K; ▲, 313 K; ●, 323 K ▽ , 333 K.

Conclusion

From our mapping of pure-fluid shape factors, we conclude that a relatively simple dependence upon density exists for given substance although there is evidence that the functional form may be somewhat substance dependent. The behaviour of the shape factors in the critical region clearly requires further investigation. Finally, we are optimistic that a one-fluid model will permit reliable predictions of mixture properties.

List of Symbols

A	Helmholtz free energy
B	Second virial coefficient
C	Third virial coefficient
f_x	Mixture temperature-scaling parameter
h_x	Mixture density-scaling parameter
n	Amount of substance
p	Pressure
R	Universal gas constant (R = 8.31451 J·K^{-1}·mol^{-1})
T	Temperature
V	Volume
x	Mole fraction
Z	Compression factor

Greek letters

δ	Reduced density, ρ/ρ^c
θ	Shape factor (inverse temperature)
ρ	Amount-of-substance density, n/V
τ	Inverse reduced temperature, T^c/T
ψ	Shape factor (density)
Φ	Dimensionless residual Helmholtz free energy, A^{res}/nRT

ω Acentric factor

Superscripts

c Critical property

res Residual property

s Saturation value

′ Saturated liquid

″ Saturated vapour

Subscripts

0 Reference-fluid property or zero-density value

i, *j* Component indices

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