Extending the GERG-2008 Equation of State: Improved departure function and interaction parameters for methane + butane.

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ABSTRACT

The Groupe European de Recherche Gaziere 2008 (GERG) multi-parameter equation of state (EOS) is considered the reference model for the prediction of natural gas mixture properties. However, the limited quality of thermodynamic property data available for many key binary mixtures at the time of its development constrained both its range of validity and achievable uncertainty. The data situation for the binary system $CH_4 + C_4H_{10}$ in particular was identified previously as limiting the ability of the GERG-EOS to describe rich natural gases at low temperatures. Recently, new vapour-liquid equilibrium (VLE) and liquid mixture heat capacity data measured at low temperatures and high pressures have been published which significantly improve the data situation for this crucial binary, allowing erroneous literature data to be identified and the predictive behaviour of the GERG-EOS when extrapolated to be tested. The ten basis functions in the generalised departure function used by the GERG-EOS for several binaries including $CH_4 + C_4H_{10}$ were examined to eliminate the term causing a divergence between measured and predicted liquid mixture isobaric heat capacities at $T <$ 150 K. Using a simplified nine-term departure function, the maximum relative deviation between the measured and predicted heat capacities was reduced from nearly 110 % to 7 %. The interaction parameters in the GERG equation for this binary were also re-determined by including, for the first time, reliable low temperature VLE data together with most of the other high temperature data used in the original development of the model. The new interaction parameters for $CH_4 + C_4H_{10}$ reduced the relative deviation of bubble point pressures measured and predicted at 244 K from 9 % to 1.4 %, without affecting the accuracy of property predictions at higher temperatures.

INTRODUCTION

Accurate equations of state (EOS) for natural gas mixtures are essential in process engineering to help reduce over-design and allow more effective optimization of gas pipeline networks and processing equipment. The GERG-2008 wide-range EOS is based on accurate experimental thermodynamic property data for 21 components of natural gas (alkane hydrocarbons methane through decane, isobutane, isopentane, hydrogen, helium, nitrogen, oxygen, argon, water, carbon monoxide, carbon dioxide and hydrogen sulfide) and their binary mixtures, and is valid for describing mixtures of these components over the range (60 to 700) K and up to 70 MPa [1]. However, while it has been adopted as the ISO Standard for calculating the equilibrium properties of natural gases [1], there is considerable scope for improving the GERG-2008 EOS. Many of these opportunities for development require new experimental data: for example, only seven of the 210 combinations of binary fluids in the natural gas model have experimental data of sufficient quantity and quality to justify the most accurate level of representation possible in the GERG-2008 EOS [1]. In particular, Kunz and Wagner [1] stated that the paucity of quality vapour liquid equilibrium data available limited the accuracy achievable in the development of the GERG-EOS, and specifically identified a need for low temperature VLE data in mixtures of $CH_4 + C_4H_{10}$ to improve the description of rich natural gases at conditions of significant industrial importance.

The methane + butane binary is an important mixture where large deviations between the GERG-2008 EOS predictions and accurate experimental measurements are known to occur. (In this work, the term "butane" refers to the isomer often called normal butane). In the development of the GERG-2008 EOS the VLE data for methane + butane at low temperatures from several sources [2-5] were found to be mutually inconsistent so only VLE data at $T > 278$ K from Sage et al. [6] and Wiese et al. [7] were used in the optimizwere found
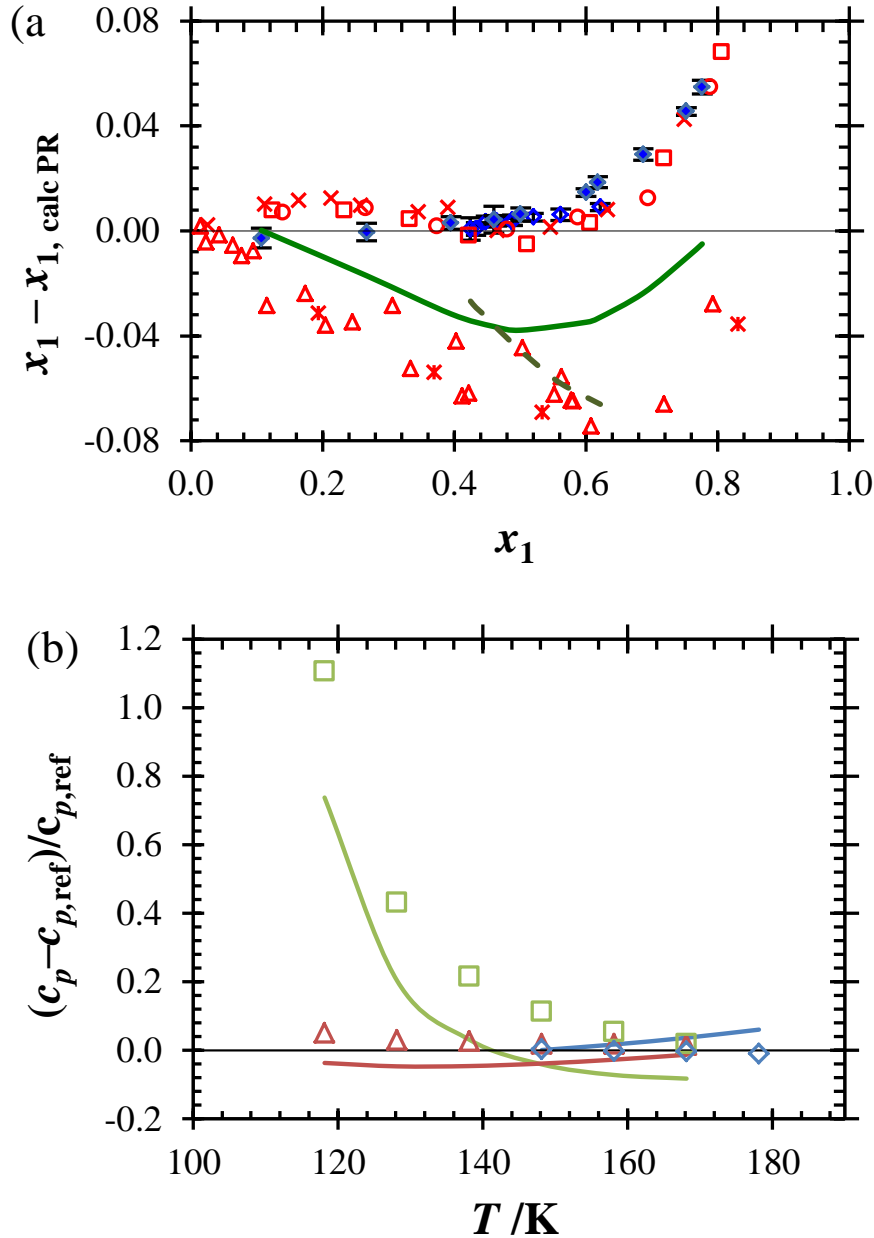
Figure 1. (a) Deviations of methane + butane literature VLE data and the GERG-2008 EOS predictions from the Peng-Robinson EOS. Symbols: △, 244 K, Roberts et al. [5]; , 244 K, Wang et al. [12]; ○, 233 K, Elliot et al. [3]; □, 244 K, Elliot et al. [3]; , 255 K, Elliot et al. [3]; ◇, (203 to 273) K isochore, May et al. [10]; ◆ 244 K, May et al. [10]. Curves: – – –, GERG-2008 EOS prediction of May et al. [10] isochore data; —, GERG-2008 EOS prediction of May et al. [10] isotherm data. (b) Relative deviations $(c_p-c_{p,ref})/c_{p,ref}$ of isobaric heat capacity c_p for methane + butane of Syed et al. [11] and HYSYS Peng-Robinson predictions (—) from $c_{p,ref}$ calculated from the GERG-2008 EOS [1]. Symbols: ◇, x_1=0.95, p=5.05 MPa; △, x_1=0.88, p=5.15 MPa; □, x_1=0.60, p=5.15 MPa.

THEORETICAL BACKGROUND

The GERG-2008 EOS is based on a multi-fluid approximation [1]. The dimensionless Helmholtz free energy, $\alpha = a/(RT)$, is related to mixture variables density ρ, reduced density $\delta = \rho/\rho_r$, temperature T, inverse reduced temperature $\tau = T_r/T$, and the molar composition vector $\boldsymbol{x}$ by

$$\alpha(\delta,\tau,\boldsymbol{x}) = \alpha^o(\rho,T,\boldsymbol{x}) + \alpha^r(\delta,\tau,\boldsymbol{x}) \tag{1}$$

The reduced density and inverse reduced temperature depend on ρ_r and T_r, the so-called 'composition-dependent reducing functions' for the density and temperature of the mixture, which depend in turn on the molar composition of the mixture i.e. $\rho_r = \rho_r(\boldsymbol{x})$; $T_r = T_r(\boldsymbol{x})$.

The ideal-gas contribution α^o to the mixture Helmholtz free energy is given by

$$\alpha^o(\rho,T,\boldsymbol{x}) = \sum_{i=1}^{N} x_i \left[\alpha_{oi}^o(\rho,T) + \ln x_i \right] \tag{2}$$

where N is the number of mixture components, x_i is the mole fraction of component i, and α_{oi}^o is the dimensionless Helmholtz free energy of component i in the ideal-gas state. The term $x_i \ln x_i$ is the entropy-of-mixing contribution [1].

The residual part of the dimensionless Helmholtz free energy α^r contains free energy contributions from each pure fluid in the mixture (at reduced conditions) and a non-ideal contribution from the so-called 'departure function' $\Delta\alpha^r$:

$$\alpha^r(\delta,\tau,\boldsymbol{x}) = \sum_{i=1}^{N} x_i \alpha_{oi}^r(\delta,\tau) + \Delta\alpha^r(\delta,\tau,\boldsymbol{x}) \tag{3}$$

The function α_{oi}^r depends implicitly on the mixture composition $\boldsymbol{x}$ through δ and τ. The GERG-2008 EOS mixture model is compatible with all types of pure fluid equations of state [1]. Most of the mixture behaviour is captured through the summation over $x_i \alpha_{oi}^r$, and the use of the composition-dependent reducing functions for density and temperature, which determine δ and τ. The purpose of the departure function is to improve the accuracy of the multi-fluid approximation when these composition-dependent reducing functions are unable to reproduce highly-accurate data within experimental uncertainty. For many mixtures, where there are little or no experimental data with sufficient accuracy, the departure function is set to zero.

The composition-dependent reducing functions for density and temperature, ρ_r and T_r, are based on the quadratic mixing rules proposed by Klimeck [1, pg. 3045].

$$\frac{1}{\rho_r(\boldsymbol{x})} = \sum_{i=1}^{N} x_i^2 \frac{1}{\rho_{c,i}} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{2x_i x_j}{\rho_{c,ij}}, \tag{4}$$

$$T_r(\mathbf{x}) = \sum_{i=1}^{N} x_i^2 T_{c,i} + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} 2 x_i x_j T_{c,ij} \tag{5}$$

where

$$\frac{1}{\rho_{c,ij}} = \beta_{v,ij}\gamma_{v,ij}\frac{x_i + x_j}{\beta_{v,ij}^2 x_i + x_j}\cdot\frac{1}{8}\left(\frac{1}{\rho_{c,i}^{1/3}} + \frac{1}{\rho_{c,j}^{1/3}}\right)^3 \quad \text{and} \tag{6}$$

$$T_{c,ij} = \beta_{T,ij}\gamma_{T,ij}\cdot\frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j}\sqrt{T_{c,i}T_{c,j}} \tag{7}$$

The parameters $\rho_{c,i}$ and $T_{c,i}$ are, respectively, the critical density and critical temperature of pure fluid i [1, Table A5].

Given sufficient data for the binary mixture of components i and j, the four binary interaction parameters (BIPs) – $\beta_{v,ij}$, $\gamma_{v,ij}$, $\beta_{T,ij}$, $\gamma_{T,ij}$ – can be adjusted. However, in the case of fluid component pairs for which little or no experimental information is available, the BIPs can be set to unity, resulting in the quadratic mixing rules of Lorentz and Berthelot [1], i.e.

$$1/\rho_{c,ij} = \left(\rho_{c,i}^{1/3} + \rho_{c,j}^{1/3}\right)^3\Big/8 \tag{8}$$

$$T_{c,ij} = \sqrt{T_{c,i}T_{c,j}} \tag{9}$$

Other parameter-free combining rules are possible and utilised within the framework of the GERG-2008 EOS. For certain binary mixtures involving a heavy hydrocarbon (C_{4+}) with either another hydrocarbon, carbon monoxide or hydrogen, 'linear' combining rules are used [1], which are implemented by substituting the following expressions

$$\beta_{v,ij} = 4\left(\frac{1}{\rho_{c,i}} + \frac{1}{\rho_{c,j}}\right)\Bigg/\left(\frac{1}{\rho_{c,i}^{1/3}} + \frac{1}{\rho_{c,j}^{1/3}}\right)^3 \tag{10}$$

$$\beta_{T,ij} = \tfrac{1}{2}\left(T_{c,i} + T_{c,j}\right)\Big/\sqrt{T_{c,i}T_{c,j}} \tag{11}$$

into eqs (6) and (7), with the corresponding γ parameters set to unity. Thus, varying degrees of complexity are used for modelling binary mixtures in the GERG-2008 EOS as determined by the number and quality of the available data. In those cases where the mixture data are sufficient, departure functions are used to improve upon the description provided through the composition-dependent reducing functions. Adjusting the binary interaction parameters in the latter also modifies values calculated with the departure function through its dependence on δ and τ.

The overall departure function for a mixture is the sum of the binary departure functions from the constituents taken pairwise, i.e.:

$$\alpha^{\mathrm{r}}\left(\delta, \tau, \boldsymbol{x}\right) = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_i x_j F_{ij}\, \alpha^{\mathrm{r}}_{ij} ,\tag{12}$$

The GERG-2008 EOS contains two kinds of non-trivial binary departure function $\alpha_{ij}^{r}(\delta,\tau)$: 'binary-specific' departure functions for well-measured binary fluids and 'generalised' departure functions for certain classes of similarly-behaved binary fluids. For those binary mixtures having a binary-specific departure function, the parameter F_{ij} is set to unity while for binary mixtures covered by the generalised departure function F_{ij} is treated as an adjustable parameter. However, in the case of the methane + butane system, which is the archetype for the generalised departure function, the value of F_{ij} is set to unity. For all other binary mixtures, where the availability of reliable property data is insufficient to justify the inclusion of a departure function to improve upon the predictions achieved with the reducing functions in eqs (6) and (7), F_{ij} is set to zero. Of the 210 binary fluid combinations covered in the GERG-2008 EOS, 31 are modelled (mostly hydrocarbon mixtures) with the 'linear' combining rules, 54 are modelled with the Lorentz-Berthelot combining rules, 110 are modelled with adjusted BIPs in the composition-dependent reducing functions and eight binary alkane mixtures, including methane + butane, are modelled using the (single) generalised departure function (see Figure 1 of [1]). Binary-specific departure functions were only able to be developed for the seven binary mixtures methane + nitrogen, methane + carbon dioxide, methane + ethane, methane + propane, nitrogen + carbon dioxide, nitrogen + ethane, and methane + hydrogen [1] because these binaries had a sufficient number of high-quality property data available at the time. Kunz and Wagner [1, pg. 3080] postulated that it would be worthwhile to develop distinct generalised departure functions for binary mixtures of air components (e.g. nitrogen + oxygen, nitrogen + argon), of carbon dioxide with hydrocarbons, of heavier hydrocarbons (pentane to nonane), and of helium, hydrogen or water with other components. Recently, Gernert and Span [13] published a multi-parameter EOS based on the GERG-2008 formalism with improved interaction parameters and departure functions to give more accurate descriptions of mixtures containing CO_2, H_2O, N_2, O_2, Ar, and CO.

The binary departure functions in the GERG-2008 EOS have the form

$$\alpha^{\mathrm{r}}_{ij}(\delta,\tau) = \sum_{k=1}^{K_{\mathrm{Pol},ij}} n_{ij,k}\, \delta^{d_{ij,k}}\tau^{t_{ij,k}} + \sum_{k=K_{\mathrm{Pol},ij}+1}^{K_{\mathrm{Pol},ij}+K_{\mathrm{Exp},ij}} n_{ij,k}\, \delta^{d_{ij,k}}\tau^{t_{ij,k}}\cdot\exp\left[-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^2 - \beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)\right]\tag{13}$$

where $K_{\mathrm{Pol},ij}$ is the number of 'polynomial' terms and $K_{\mathrm{Exp},ij}$ is the number of 'exponential' terms [1]. The values of the coefficients $n_{ij,k}$ and the exponents $d_{ij,k}$, $t_{ij,k}$, $\eta_{ij,k}$, $\varepsilon_{ij,k}$, $\beta_{ij,k}$ and $\gamma_{ij,k}$ appearing in the binary-specific and generalised departure functions were obtained via the structure optimization process [8].

The properties of the methane + butane binary fluid were represented in the GERG-2008 EOS using optimized BIPs (Table 1) and the generalised departure function with the properties of pure methane and pure butane calculated using so-called 'technical equations of state' [1].

Table 1. Methane + butane binary interaction parameters compatible with the GERG-2008 EOS.

Parameter	Original GERG-2008 EOS parameters [8]	Benchmark results (this work)	New BIPs (this work)
$\beta_{v,ij}$	0.979105972	0.978678	0.991509
$\gamma_{v,ij}$	1.045375122	1.046648	1.055790
$\beta_{T,ij}$	0.994174910	0.986612	0.981759
$\gamma_{T,ij}$	1.171607691	1.172916	1.177286

To fit the BIPs, experimental data for the methane + butane binary fluid were collected by Kunz et al. [1,8] from 21 literature sources with the most recent published in 2007. The selection of reliable data for use in optimization was made on the basis of comparisons of the data against predictions made with different equations of state (e.g. AGA8-DC92 equation of Starling and Savidge [14] and the cubic equation of state of Peng and Robinson [15]) as well as on the basis of comparisons between different datasets (see [8], pg. 80). Based on these comparative analyses, of the 21 total datasets, eight sources were wholly or partially used for optimization of the methane + butane BIPs [8, Table A 2.1]. For p- -T properties, the main data sources used for optimization were Fenghour et al. [9], Reamer et al. [16] and Ruhrgas [17]. All of these data lie in the supercritical fluid region (270 to 511) K. Approximately 40 p- -T and saturated liquid density data from Haynes [18], Hiza et al. [19] and Pan et al. [20] in the temperature range (108 to 140) K were also used. The only other datasets included in the optimization were the high-temperature VLE (bubble point pressure) data of Sage et al. [6] and Wiese et al. [7]. The average absolute deviations (AAD) between the model and the p- -T datasets were less than 0.7 %, while the AAD between the model and the optimized VLE data were 2.2 % or better [8, Table A 2.1]. The prediction of p- -T values that were not included in the optimization was generally as accurate as for those data that were optimized. However, the prediction of VLE data that were not included in the optimization was typically much worse: the average absolute deviations for the relatively large datasets of Roberts et al. [5], Chen et al. [2], Elliot et al. [3] and Kahre [4] varied from (6 to 12) %.

RESULTS AND DISCUSSION

Benchmarking the optimization algorithm

To improve upon and extend the GERG-2008 EOS description of the methane + butane system's thermodynamic properties in light of the new high-quality data measured after 2007, we developed a Levenberg-Marquardt nonlinear least squares optimization procedure [21] to enable determination of improved values for the BIPs $_{v,ij}$, $_{v,ij}$, $_{T,ij}$, $_{T,ij}$. To validate this optimization procedure, we used 833 data points from the same eight sources from which Kunz et al. [8] used 1027 data points. It was not possible to match exactly the data set used in

the original optimization of the GERG-2008 EOS because the number of points from the Ruhrgas database used in the optimization as reported in Table A2.1 of Kunz et al. [8] is greater than the number of data points listed in the corresponding literature source [22] and some of the data points in the literature sources used were excluded from the optimization [8]; however Kunz et al. [8] did not state exactly which points were excluded, or provide criteria for doing so. Since the values of the weighting factors controlling the influence of the different properties and different data on the original optimization [8, pg. 20] were not stated explicitly, the process of benchmarking our optimization algorithm comprised several trial calculations varying the weights on the datasets until reasonable agreement was found between the GERG-2008 EOS parameters and the benchmark parameters. The final weighting assigned to each dataset is given in Table 2 as a percentage of the measured property value.

Table 2: Sources and number of experimental data used in the GERG-2008 EOS optimization of methane + butane binary interaction parameters, and number of data from each source that were used for benchmarking the current optimization algorithm. The assigned uncertainty of each datum in the current benchmark optimization is given as the percentage $100u$ of the measured property value.

p-ρ-T	N_{total}	N_{used} [a]	N_{used} [b]	$100u$	AAD % [c]	AAD % [d]
Fenghour et al. (1999) [9]	71	71	66	1.0	0.94	1.02
Hiza et al. (1977) [19]	4	4	4	0.3	0.39	0.35
Pan et al. (1975) [20]	2	2	2	0.3	0.38	0.36
Reamer et al. (1947) [16]	512	262	492	0.5	0.53	0.49
Ruhrgas (1990), Bu [17]	42	29	14	0.02	0.01	0.01
Ruhrgas (1990), Op [17]	511	511	106	0.02	0.01	0.01
Saturated liquid density						
Haynes (1983) [18]	19	19	19	0.3	0.42	0.40
Hiza et al. (1977) [19]	12	12	8	0.3	0.71	0.68
VLE data						
Sage et al. (1940) [6]	117	108	107	0.5	2.4	1.3
Wiese et al. (1970) [7]	25	9	15	2.0	1.8	0.9
Total		*1027*	*833*			

[a] Number of data used to optimize the BIPs for the GERG-2008 EOS as reported in ref. [8]
[b] Number of data used for the benchmark optimization in this work.
[c] Average absolute deviations between the data used in the benchmark optimization and the GERG-2008 EOS with the original BIPs.
[d] Average absolute deviations between the data used in the benchmark optimization and the GERG-2008 EOS with the optimized BIPs.

The BIPs optimized during the benchmarking of the optimization algorithm are compared with the original GERG-2008 EOS BIPs in Table 1, the largest difference being less than 0.8 % for $_{v,ij}$. As shown in Table 2, the AAD between the benchmark data and the EOS with optimized BIPs closely match the AAD between the benchmark data and the GERG-2008 EOS with its original BIPs. The distribution of the residuals from both models of the p- -T data of Fenghour et al. [9] and the VLE data of Sage et al. [6] also match closely (Figure 2).
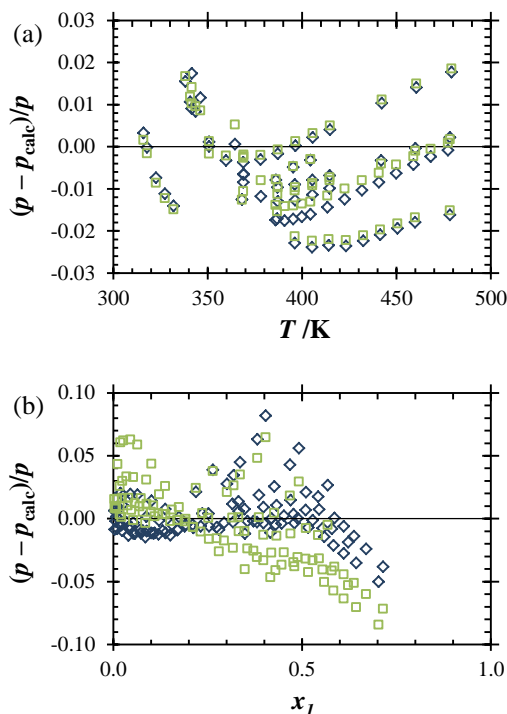
Figure 2. Relative deviations $(p–p_{calc})/p$ of pressure p for methane + butane from p_{calc} calculated from the GERG-2008 EOS ($\square$) and our benchmark optimization model ($\diamond$). (a) p--T data of Fenghour et al. [9]; (b) VLE data of Sage et al. [6].

These benchmarking results help establish (1) that the optimization procedure is sufficiently reliable to be used in optimizations involving additional datasets and modified departure functions, and (2) that the weightings assigned in this work to the existing datasets used by Kunz et al. [8] are likely to be sufficiently representative of those used in the original EOS development.

An improved departure function for methane + butane

Finding the cause of the divergence of the (extrapolated) low-temperature heat capacity predictions made using the GERG-2008 EOS from the data of Syed et al. [11] was a key motivation of the present work. To do so, we investigated the mixture model's performance when the linear or quadratic mixing rules (eqs (8) to (11)) were used for the methane + butane system. Although large systematic deviations compared to the methane + butane experimental data are incurred for most properties when these mixing rules are used (Table SI3, SI4), all of the isobaric heat capacity of Syed et al. [11] are reproduced within 3.4 %. Therefore, the reference equations of state for the pure fluids can be ruled out as the cause of the divergent behaviour in the low temperature region. Accordingly, with elimination of the equations for the pure fluids as the cause, the generalised departure function remains as the likely source of the divergence.

The generalised departure function is comprised of ten polynomial terms [1], i.e.

$$\alpha_{ij}^{r}(\delta, \tau) = \sum_{k=1}^{10} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} \tag{14}$$

Its structure was determined almost completely from results obtained using data from the methane + ethane, methane + propane, and methane + butane binary systems [8, pg. 172]. The values of the coefficients and exponents appearing in eq (14) are shown in Table 3.

Table 3. Coefficients and exponents of the generalised departure function α_{ij}^{r} (eq (14)) for modelling secondary alkanes in the GERG-2008 EOS [1].

k	$d_{ij,k}$	$t_{ij,k}$	$n_{ij,k}$
1	1	1.000	0.25574776844118E+01
2	1	1.550	-0.79846357136353E+01
3	1	1.700	0.47859131465806E+01
4	2	0.250	-0.73265392369587
5	2	1.350	0.13805471345312E+01
6	3	0.000	0.28349603476365
7	3	1.250	-0.49087385940425
8	4	0.000	-0.10291888921447
9	4	0.700	0.11836314681968
10	4	5.400	0.55527385721943E-04

The relation between the reduced Helmholtz free energy and the isobaric heat capacity is [1, Table B1]

$$c_p/R = -\tau^2 \left(\alpha_{\tau\tau}^{o} + \alpha_{\tau\tau}^{r} \right) + \frac{\left(1 + \delta\alpha_{\delta}^{r} - \delta\tau\alpha_{\delta\tau}^{r} \right)^2}{1 + 2\delta\alpha_{\delta}^{r} + \delta^2\alpha_{\delta\delta}^{r}} \tag{15}$$

where $\alpha_{\tau}^{o} = (\partial\alpha^{o}/\partial\tau)$, $\alpha_{\tau\tau}^{o} = (\partial^2\alpha^{o}/\partial\tau^2)$, etc. The contributions of the generalised departure function's derivatives to the calculated isobaric heat capacities were systematically examined in the region of the Syed et al. [11] data where the largest deviations were observed ($p = 5.0$ MPa, $T = (110 \text{ to } 180)$ K, $x_1 = 0.6$) and a probl1 0 ET 0 1 212.45 304.49 Tm G1 0 0 192 reW* nBT/F2 12
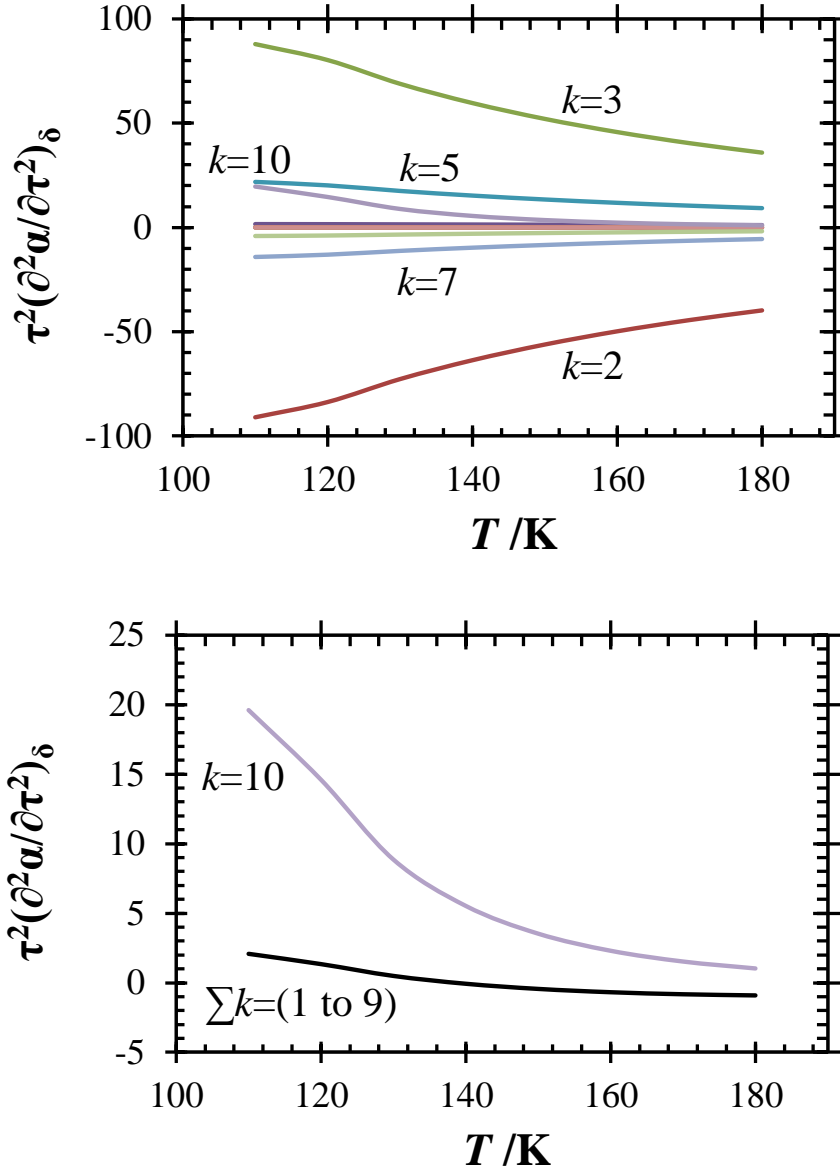
Figure 3. Contributions to the isobaric heat capacity at $p = 5.0$ MPa and $x_1 = 0.6$. (a) Derivatives $\tau^2(\partial^2 \alpha / \partial \tau^2)$ of terms $k = 1$ to $k = 10$ in the generalised departure function. (b) Derivative of the $k = 10$ term in the generalised departure function compared to the sum of the derivatives for terms $k = (1 \text{ to } 9)$.

However, the term for $k = 10$ is not cancelled out. Therefore, the tenth term dominates the other terms in the departure function and appears to be the major cause of the divergent behaviour of the heat capacity predictions in the cryogenic ($T < 150$ K) region. To verify this the isobaric heat capacities were calculated using the BIPs of Kunz et al. [8] with and without the tenth term in the generalised departure function, and the results are shown in Figure 4.
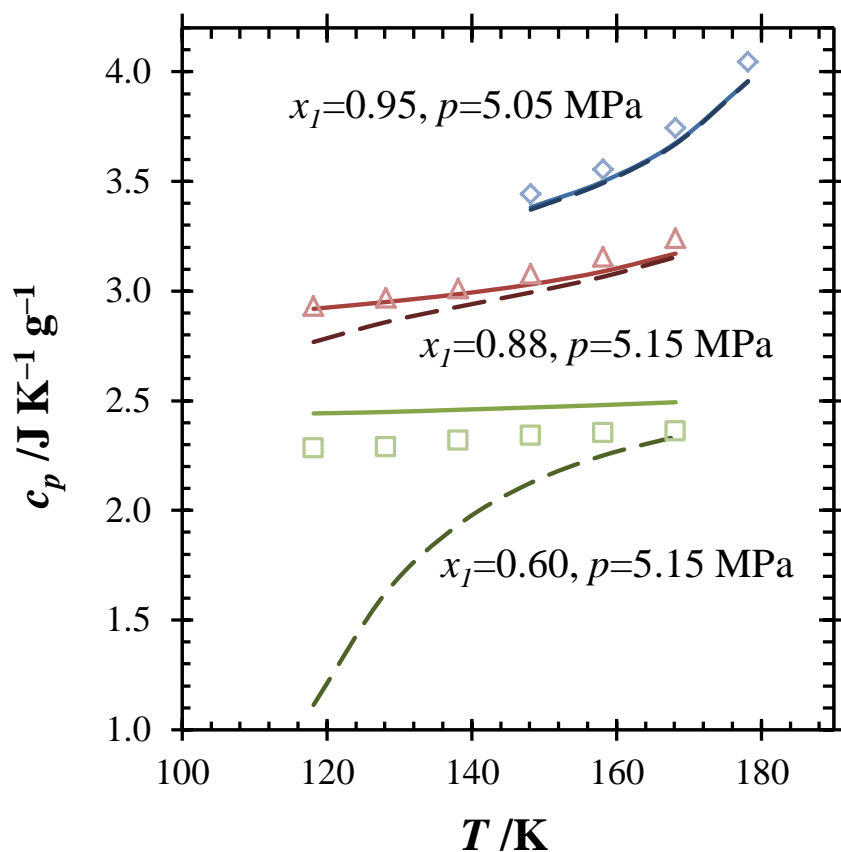
Figure 4. The isobaric heat capacity c_p predicted with the GERG-2008 EOS (– – –) diverges toward negative values at $T < 150$ K when $x_1 = 0.60$. Omitting the tenth term from the generalised departure function (—), while keeping all interaction parameters at their original values, improves agreement with the measured data of Syed et al. [11]. Symbols: ◇, x_1=0.95, p=5.05 MPa; △, x_1=0.88, p=5.15 MPa; □, x_1=0.60, p=5.15 MPa.

The agreement between the c_p predicted when the tenth term in the departure function was omitted and the experimental data of Syed et al. [11] was significantly improved and yielded a more reasonable extrapolation of the heat capacity for temperatures below 150 K. Omitting the tenth term has only minor effects on the prediction of other thermodynamic properties for the methane + butane system: differences in p- -T predictions are less than 0.02% and the AAD between the VLE data of Sage et al. [6] increases marginally from 2.4 % to 2.6 % (Table SI5). Overall, it seems that the generalised departure function with only nine terms improves both the correlation and the prediction of the properties of methane + butane. Investigating the use of this improved departure function with other binary mixtures is an area of future work.

Improving the binary interaction parameters for methane + butane.

Improving the prediction of thermodynamic properties of methane + butane requires new BIPs based on reliable property data measured over a wide range of conditions. Bubble point

pressures are one of the properties to which the BIPs are most sensitive [8], and therefore it is important that consistent, high-quality VLE data are used in optimizations. In the development of the GERG-2008 EOS only high-temperature VLE data from Sage et al. [6] and Wiese et al. [7] were included in the optimization [8]. The most reliable low-temperature VLE data prior to 2007 appear to be those of Elliot et al. [3] which are systematically over-predicted by the GERG-2008 EOS [8, Table A 2.1]. The recent high-quality low-temperature VLE data from May et al. [10] seem to be consistent with the data set of Elliot et al. [3] and are similarly over-predicted by the GERG-2008 EOS. New BIPs were optimized using the reference equations for pure methane [23] and butane [24], the improved departure function (with F_{ij} equal to unity and the tenth term omitted from the generalised departure function) and the data and weights in Table 4.

Table 4: Sources and number of experimental data used in the optimization of new binary interaction parameters for methane + butane. The assigned uncertainty of each datum is given as the percentage $100u$ of the measured property value.

p-ρ-T	N_{total}	N_{used}	$100u$	AAD %
Fenghour et al. (1999) [9]	71	66	1.0	1.20
Hiza et al. (1977) [19]	4	4	0.3	0.96
Pan et al. (1975) [20]	2	2	0.3	0.23
Reamer et al. (1947) [16]	512	492	0.5	0.37
Ruhrgas (1990), Bu [17]	42	14	0.02	<0.01
Ruhrgas (1990), Op [17]	511	106	0.02	0.02
Saturated liquid density				
Haynes (1983) [18]	19	19	0.3	0.18
Hiza et al. (1977) [19]	12	8	0.3	0.50
VLE data				
Sage et al. (1940) [6]	117	106	2.0	2.5
Wiese et al. (1970) [7]	25	15	2.0	2.4
Data not included in Kunz et al. [8]				
VLE data				
Elliot et al. (1974) [3]	109	81	2.0	2.5
May et al. (2015) [10]	20	20	1.0	1.4
Isobaric heat capacity				
Syed et al. (2014) [11]	16	16	3.0	3.3

The predictions of p-ρ-T data sets from both the GERG-2008 EOS [1] and the optimized model with the new BIPs are largely in accord (e.g. Figure 5a): however, the Ruhrgas [17] data at 290 K measured by optical interferometry deviate systematically from predictions made using the new BIPs compared to the other Ruhrgas data in the range (270 to 330) K (Figure 5b).
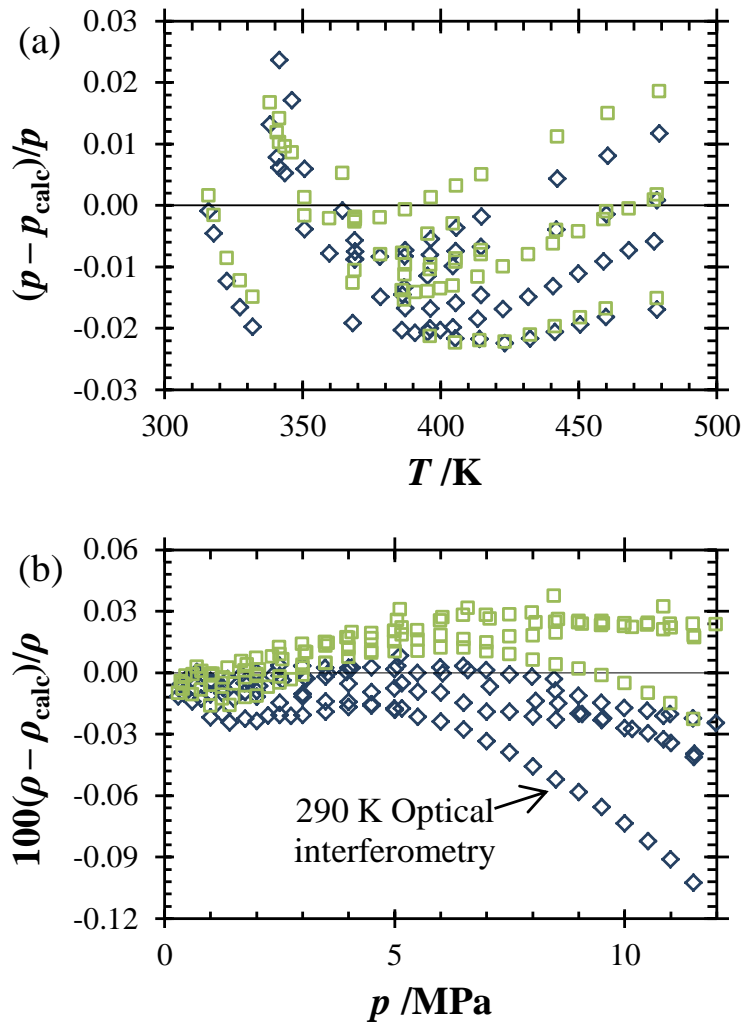
Figure 5. (a) Relative deviations $(p–p_{calc})/p$ of pressure p for methane + butane of Fenghour et al. [9] from p_{calc} calculated from the GERG-2008 EOS (□) and the new BIPs of this work (◇). (b) Relative deviations $(\rho - \rho_{calc})/\rho$ of absolute density ρ for methane + butane of Ruhrgas [17] from ρ_{calc} calculated from the GERG-2008 EOS (□) and the new BIPs of this work (◇). Ruhrgas [17] data at 290 K ($x_1 = 0.985$) measured by optical interferometry deviate systematically from the improved EOS at high pressure.

The data of Sage et al. [6] are represented approximately equally well by both the GERG-2008 EOS [1] and the optimized model with the new BIPs (2.4 % vs. 2.5 %) (Figure 6). The data of Elliot et al. [3] at 278 K deviated systematically from the new model compared to the data of Sage et al. [6] at 294 K and were excluded from the current optimization. Several other Elliot et al. [3] data at low temperature were also excluded because the associated low absolute pressures of those measurements lead to large relative deviations in the least-squares fit. Overall, the improvements in the predictions of the VLE data are substantial. The new BIPs improve the representation of both the data of Elliot et al. [3] for which the AAD is reduced from 6.3 % to 2.5 % (Figure 6) and the data of May et al. [10] for which the AAD is reduced from 9 % to 1.4 % (Figure 7).
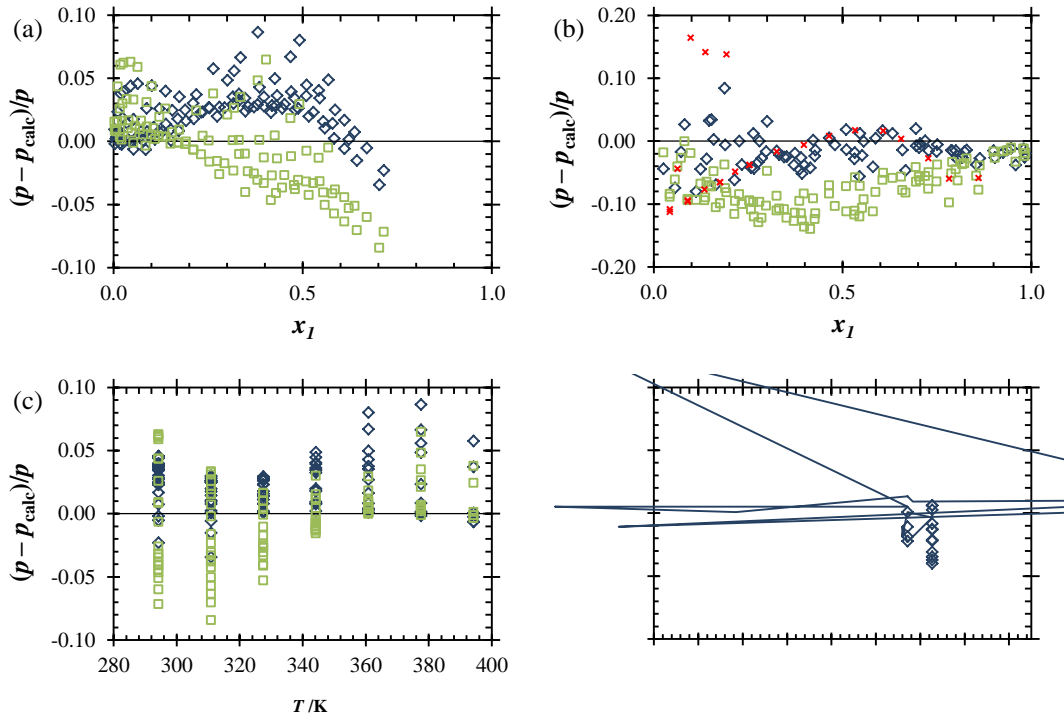
Figure 6. Relative deviations $(p - p_{calc})/p$ of pressure p for methane + butane from p_{calc} calculated from the GERG-2008 EOS (□) and the new BIPs of this work (◇,). (a) and (c) Sage et al. [6] VLE data. (b) and (d) Elliot et al. [3] data (denotes data excluded from optimization).

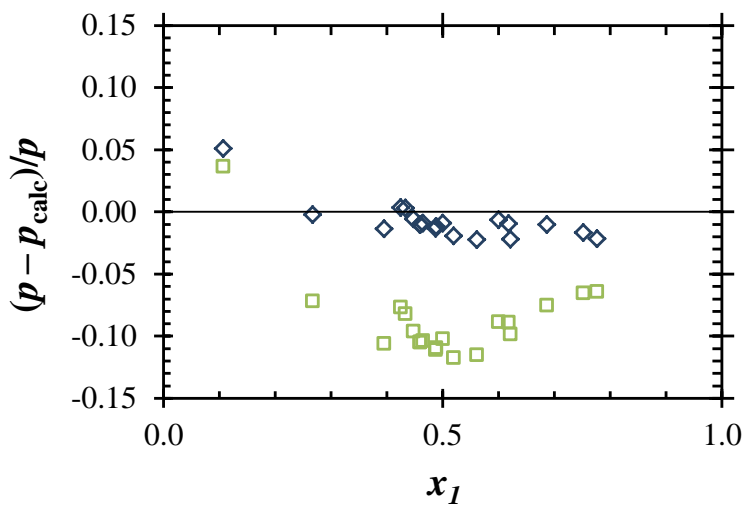**Figure 7.** Relative deviations $(p - p_{calc})/p$ of pressure p for methane + butane VLE data in the range $T = (203 \text{ to } 273)$ K [10] from p_{calc} calculated from the GERG-2008 EOS (□) and the new BIPs of this work (◇).

Similarly, the maximum deviation relative to the isobaric heat capacity data of Syed et al. [11] improved from 106 % using the GERG-2008 EOS to 7 % using the new BIPs. The

extrapolations into the cryogenic region are much more robust using the new model, largely due to the improved departure function.

CONCLUSION

Large systematic differences occur between predictions made for the methane + butane binary using the default GERG-2008 EOS and the mixture heat capacity data measured by Syed et al. [11] as well as the low temperature VLE data of May et al [10] and Elliot et al. [3]. In the case of the isobaric heat capacity, the tenth term in the generalised binary departure function was found to cause the default model to diverge from experiment in the cryogenic region. It has also been shown above that neglecting the tenth term from the generalised departure function corrects this problem at low temperature while having almost no effect on the predictions of high temperature data which were available during the development of the GERG-2008 EOS [8]. An avenue for future work would be to determine whether predictions of the thermodynamic properties of other binary alkane mixtures for which the generalised departure function is recommended, such as methane + isobutane, ethane + butane, and ethane + isobutane, would improve by truncating the generalised departure function at nine terms.

To extend and improve upon the GERG-2008 EOS for the methane + butane system, the following refinements were made in this work. First, the generalised departure function was truncated from ten terms to nine terms. Second, the reference equations were used for the pure fluids instead of the compact revised equations. Third, new binary interaction parameters for this binary were obtained by regression to datasets which included VLE data from the wider temperature range (144 to 394) K. None of these changes had a detrimental effect on the calculated properties for other datasets compared to the default GERG-2008 EOS. Regarding the second point, the differences between different pure fluid EOS are typically much less than the uncertainty of the mixture data and the effect of using different EOS for the pure fluids is therefore usually insignificant, particularly for this binary. A revised methane + butane binary fluid file containing the truncated departure function, compatible with the TREND 2.0 software distribution [25], is included as Supporting Information and can be used as a standalone replacement for the existing file in the 'BINARY_MIX_FILES' directory folder.

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