We compute second order derivatives of the Gibbs energy by Monte Carlo simulation in the isobaric–isothermal ensemble for fluids made of rigid and flexible molecules and test the accuracy of the simple interactions potential. The thermal expansivity and the isothermal compressibility can be calculated directly during a simulation run. The total heat capacity is obtained as the sum of the residual heat capacity computed using the fluctuation method and the ideal heat capacity, which cannot be determined by Monte Carlo simulation and must be taken from experimental data. The Joule–Thomson coefficient is obtained by the combined use of thermal expansivity and total heat capacity. The fluctuation method proves to converge very well, with limitation at low pressure for the Joule–Thomson coefficient. The fluctuation method has been extensively tested on pure light hydrocarbons (methane, ethane and butane) in the vapour and liquid states. In the case of methane, we used a united atom Lennard-Jones potential (D. J. Oprzynski, A. and J. Møller, Møller, Robinson, Soave–Redlich–Kwong) do not provide satisfactory predictions for heat capacity in high pressure conditions. These equations of state have been used for the prediction of the Joule–Thomson coefficient of natural gases at high pressure but without prior validation against experimental measurements. Their reliability is uncertain, as illustrated by the poor prediction of the inversion curve of nitrogen and methane modelled by Dilay et al. It is known that cubic equations of state suffer large difficulties in representing correctly the liquid densities, which difficulties must be solved by empirical correction terms. As a consequence, it can be expected that any derivative property based on the volume derivatives will be poorly predicted by cubic equations of state. Corresponding states methods, such as the Lee–Kesler equation, show better performance for heat capacity but this appears insufficient to determine the Joule–Thomson inversion curve accurately. These methods are also known to exhibit a severe decrease in performance for alkanes heavier than C12.

An alternative route to equations of state and corresponding state methods is now provided by Monte Carlo simulation that enables calculations to be made over a large range of temperature and pressure. In this field, the availability of thermal effects, to provide perfect heat insulation, and to impose a high flow rate. This is why no reliable technique is presently available to provide direct measurements of Joule–Thomson coefficients in representative conditions.

As shown by Barreau et al., cubic equations of state such as those frequently used in the oil and gas industry (Peng–Robinson, Soave–Redlich–Kwong) do not provide satisfactory predictions for heat capacity in high pressure conditions. These equations of state have been used for the prediction of the Joule–Thomson coefficient of natural gases at high pressure but without prior validation against experimental measurements. Their reliability is uncertain, as illustrated by the poor prediction of the inversion curve of nitrogen and methane modelled by Dilay et al. It is known that cubic equations of state suffer large difficulties in representing correctly the liquid densities, which difficulties must be solved by empirical correction terms. As a consequence, it can be expected that any derivative property based on the volume derivatives will be poorly predicted by cubic equations of state. Corresponding states methods, such as the Lee–Kesler equation, show better performance for heat capacity but this appears insufficient to determine the Joule–Thomson inversion curve accurately. These methods are also known to exhibit a severe decrease in performance for alkanes heavier than C12.

An alternative route to equations of state and corresponding state methods is now provided by Monte Carlo simulation that enables calculations to be made over a large range of temperature and pressure. In this field, the availability of
accurate intermolecular potentials makes it now possible to predict standard thermodynamic properties (saturations pressures, vaporisation enthalpies, molar volumes) with a good accuracy.\textsuperscript{6–9} Therefore, an interesting question is whether Monte Carlo simulation can provide quantitative prediction of derivative properties. Chacin et al.\textsuperscript{10} investigated the prediction of Joule–Thomson coefficients using very simple potential models. To evaluate the required differentials numerous Monte Carlo simulations at various temperatures must be performed.

In the present work, we propose a simultaneous determination of several derivative properties from statistical fluctuations on the basis of a single simulation run. Indeed, it is well known that the derivative of a property X with respect to a fixed intensive state variable Y can be obtained from the analysis of the fluctuations \( \langle XZ \rangle - \langle X \rangle \langle Z \rangle \) in the related statistical ensemble, where Z is the conjugate extensive variable of Y.\textsuperscript{11} This relationship may be used for instance to obtain volume derivatives (thermal expansivity, isothermal compressibility) by Monte Carlo simulation. However, the prediction of heat capacity is more delicate. Indeed, the kinetic part of the energy is not considered in Monte Carlo simulation, and also the concept of united atoms used in many intermolecular potentials results in erroneous predictions of ideal heat capacity. As already pointed out by Jörgensen,\textsuperscript{12} total heat capacity can be obtained as the sum of residual heat capacity from Monte Carlo simulation and ideal heat capacity from experimental correlations. Finally, the Joule–Thomson coefficient may be determined from a combined use of thermal expansivity and heat capacity.\textsuperscript{13} These basic relationships will be derived in the first section. A second section will be dedicated to simulation methods (Monte Carlo algorithm, intermolecular potential models, ideal heat capacity and numerical aspects of fluctuation determination).

The third section will be devoted to the results concerning the derivative properties (thermal expansivity, isothermal compressibility, residual heat capacity and Joule–Thomson coefficient) on pure hydrocarbons (methane, ethane, butane) and their mixtures at temperature up to 380 K and pressures up to 100 MPa compared to experimental data.\textsuperscript{14–17}

2 Theoretical background

In this section, we will first define the isobaric–isothermal partition function. We will subsequently derive to obtain the thermal expansivity and the residual heat capacity and finally the isothermal compressibility. We will use a capital letter \( \mathcal{X} \) for an extensive property of a system of \( N \) molecules and a lower case letter x for the associated molar property.

The isobaric–isothermal partition function of a system composed of \( N_1 \) molecules of type 1, \( N_2 \) molecules of type 2 ... is given by:\textsuperscript{18}

\[
\mathcal{A} = \int \frac{V^{N_1 + N_2 + \ldots}}{N_1! N_2! \ldots A_1^{N_1} A_2^{N_2} \ldots} \exp(-\beta \tilde{H}) dV d\xi^n \tag{1}
\]

where, \( V \) is the volume of the system, \( A_i \) is the equivalent de Broglie wavelength of the molecule i, \( \tilde{H} \) is the configurational enthalpy, \( \tilde{H} = H^\text{ext} + H^\text{int} + PV \) where \( H^\text{ext} \) is the intermolecular potential energy and \( H^\text{int} \) the intramolecular potential energy, \( \xi \) are the dimensionless degrees of freedom and \( n \) the number of degrees of freedom. As discussed in ref. 19, eqn. (1) results from the factorisation of the partition function in the case of a rigid molecule and is only an approximation for a flexible molecule presenting several conformations. Nevertheless, we will use eqn. (1), in the same way as is always done in Monte Carlo simulation of such systems.\textsuperscript{6–9} An average property \( X \) can be written as:

\[
\langle X \rangle = \frac{1}{\mathcal{A}} \int \frac{X V^{N_1 + N_2 + \ldots}}{N_1! N_2! \ldots A_1^{N_1} A_2^{N_2} \ldots} \exp(-\beta \tilde{H}) dV d\xi^n \tag{2}
\]

The equivalent de Broglie wavelength \( \lambda_i \) for a molecule i is proportional to \( \beta^{m_i/2} \), where \( m_i \) is its number of degrees of freedom.\textsuperscript{19} As the temperature derivative of the de Broglie wavelength \( \lambda_i \) cancels out, it can be demonstrated that:

\[
\frac{\partial \langle X \rangle}{\partial \beta} = \langle X \rangle \langle \tilde{H} \rangle - \langle X \rangle \langle \tilde{H} \rangle \tag{3}
\]

From this equation, the thermal expansivity \( x_T \) can be calculated:

\[
x_T = \frac{1}{V} \frac{\partial V}{\partial T} = \frac{1}{V} \frac{1}{kT^2} \langle \langle V \rangle \langle \tilde{H} \rangle - \langle V \rangle \langle \tilde{H} \rangle \rangle \tag{4}
\]

A similar derivation leads to the following expression of the isothermal compressibility \( \beta_T \):

\[
\beta_T = -\frac{1}{V} \frac{\partial V}{\partial P} = \frac{1}{V} \frac{1}{kT} \langle \langle V^2 \rangle - \langle V \rangle^2 \rangle \tag{5}
\]

The derivation of heat capacity at constant pressure is more delicate. Indeed, the kinetic part of the energy is not considered in Monte Carlo simulation. As already pointed out by Jörgensen\textsuperscript{12} but without giving any fluctuation formula, residual and ideal parts have to be clearly separated in the expression of the heat capacity.

\[
C_p(T, P) = \left( \frac{\partial \langle H \rangle}{\partial T} \right)_P
\]

where the enthalpy, \( H = U^\text{ext} + U^\text{int} + K + PV \), differs from \( \tilde{H} \) because it includes the kinetic energy \( K \).

The enthalpy is expressed by introducing the residual and ideal contributions according to:

\[
\langle H \rangle = \langle H^\text{id} \rangle + \langle H^\text{res} \rangle
\]

\( H^\text{id} = U^\text{int} + K + NkT \) is the ideal gas enthalpy which is a function of temperature only. \( H^\text{res} = U^\text{ext} + PV - NkT \) is the residual enthalpy.

Thereby, introducing,

\[
C_p^\text{id}(T, P) = \left( \frac{\partial \langle H^\text{id} \rangle}{\partial T} \right)_P
\]

\[
C_p^\text{res}(T, P) = \left( \frac{\partial \langle H^\text{res} \rangle}{\partial T} \right)_P
\]

we obtain,

\[
C_p(T, P) = C_p^\text{id}(T, P) + C_p^\text{res}(T, P) \tag{7}
\]

The residual heat capacity which will be determined by Monte Carlo simulation is expressed as follows,

\[
C_p^\text{res}(T, P) = \left( \frac{\partial \langle U^\text{res} \rangle}{\partial T} \right)_P + P \left( \frac{\partial \langle V \rangle}{\partial T} \right)_P - Nk
\]

The derivative of \( \langle U^\text{res} \rangle \) is obtained by applying eqn. (3):

\[
C_p^\text{res} = \frac{1}{kT^2} \langle \langle U^\text{ext} \rangle \langle \tilde{H} \rangle \rangle - \langle \langle U^\text{ext} \rangle \langle \tilde{H} \rangle \rangle + \frac{1}{kT^2} \langle \langle V \rangle \langle \tilde{H} \rangle - \langle V \rangle \langle \tilde{H} \rangle \rangle - Nk \tag{8}
\]

The molar heat capacity is obtained from:

\[
\frac{c_p}{C_p} = \frac{c_p^\text{res}}{C_p^\text{res}} = \frac{c_p^\text{id}}{C_p^\text{id}} = \frac{N'}{N}
\]

where \( N' \) is the Avogadro number. For a mixture, \( c_p^\text{res}(T) \) can be easily calculated from the pure component ideal heat capacities:

\[
c_p^\text{res}(T) = \sum x_i c_p^\text{res}(T) \]

where \( x_i \) is the mole fraction of each compound. Pure component ideal heat capacities can be obtained\textsuperscript{1} from experimental correlations\textsuperscript{20} and from group contribution methods.\textsuperscript{21,22} Finally, the Joule–Thomson coeffi-
To calculate the desired variables and where $v$ is the molar volume.

As a consequence of eqn. (9), (8) and (10), a single Monte Carlo simulation in the isobaric-isothermal ensemble enables us to calculate the desired variables $x_c$, $y_c$, and $z_c$.

### 3 Simulation methods

#### 3.1 Monte Carlo algorithms

The isothermal-isobaric ensemble has been simulated using standard Monte Carlo procedures including periodic boundary conditions of the cubic simulation box and Metropolis sampling.\(^\text{23}\) The implemented Monte Carlo moves consisted in molecular translations, rotations, and box volume changes. In the case of $n$-butane, we also used partial regrowth with the configurational bias algorithm\(^\text{6}\) in order to sample all possible internal conformations. This move was used with five positions tested for each force centre. The maximum amplitude of displacement, rotation and volume change were continuously monitored in order to obtain a 50% acceptance probability of a given move.

In the case of methane and ethane the fraction of attempted volume changes was 0.02, the complement being translations (and rotations if needed). For $n$-butane, the probability of attempting the various moves was 0.248 for translations and rotations, 0.5 for regrowth and 0.004 for volume changes. A cut-off radius was systematically implemented with a long range correction. In a first implementation, we introduced a variable cut-off radius $r_c$ equal to half the box length. In a second implementation, a constant cut-off radius of 10 Å was used. Although, the implementations did not exhibit significant differences, we used preferably the first option because it was presumed to give a better account of possible statistical fluctuations. The initial configuration was prepared by placing molecules randomly on a cubic lattice. Averages were taken after a stabilisation period of at least 10\(^6\) iterations. In order to estimate uncertainties on average properties obtained by Monte Carlo simulation, we used the block average method of Allen and Tildesley.\(^\text{18}\)

### 3.2 Intermolecular potential functions

For alkane systems, intermolecular interactions are restricted to the dispersion and repulsion forces. These are modelled by Lennard-Jones potential functions whose parameters are described in Table 1. Methane is represented by the united atom (UA) potential of Müller et al.\(^\text{24}\) Ethane and $n$-butane are represented by the anisotropic united atoms (AUA) potential proposed by Ungehrer et al.\(^\text{9}\) Compared with more classical UA potentials for alkanes, AUA potentials use the same groups ($\text{CH}_2$, $\text{CH}_3$, . . .) but the Lennard-Jones force centre is shifted to an intermediate position between the carbon and hydrogen atoms of the related group instead of being placed on the carbon nuclei. The distance separating the force centre from the carbon nucleus is represented by $\delta$. The potential parameters $\sigma$, $\epsilon$ and $\delta$ of the $\text{CH}_2$ and $\text{CH}_3$ groups have been optimised to predict several equilibrium properties (vapour pressure, liquid density, vapourisation enthalpy) of alkanes in a large range of temperature. The carbon-carbon distance is fixed at 1.535 Å. The evolution of the $\epsilon$ parameter with the sequence $\text{CH}_4$, $\text{CH}_3$, $\text{CH}_2$ and $\text{CH}$ is logical and regular. In the case of $\sigma$, the decreasing sequence for the AUA potential indicates a better physical meaning than the UA potentials, for which $\sigma_{\text{CH}_3}$ is greater than $\sigma_{\text{CH}_2}$.\(^\text{25}\) Torsion and bending potentials are also included in this AUA potential. We have used the bending potential $U_{\text{bend}}/k = \delta_{\text{bend}} \cos \theta - \cos^2 \theta_0$. The general expression for the torsion potential $U_{\text{tors}}/k = \sum_{i=0}^{26} \alpha_i \cos^i \phi$ has been taken identical to Toxvaerd.\(^\text{26}\) Torsion and bending parameters are described in Table 2.

### 3.3 Ideal heat capacity

The ideal heat capacities of pure components at the temperatures investigated have been obtained from the Dortmund Data Bank.\(^\text{20}\) We have checked that these estimates were consistent with other recommended values\(^\text{14,27,28}\) within 0.5%.

### 3.4 Numerical aspects of fluctuation determination

In order to estimate the fluctuations, the cross products $\langle V^2 \rangle$, $\langle V U \rangle$ . . . were stored at regular intervals of typically 100 iterations with an accuracy of 15 digits. A good statistical convergence of second order derivatives of the Gibbs energy is obtained but it requires longer simulation than for the convergence of primary derivative properties like volume or energy. The uncertainties on the second order derivative properties were estimated by a simplified block average method. For a typical run of $10^7$ iterations, 10 blocks of $10^6$ iterations, assumed independent, were defined to estimate the standard deviation. Confidence intervals were plotted by assuming statistical uncertainties twice the standard deviation.

We can expect the fluctuation method to be less accurate at very low pressure. For instance, thermal expansivity involves a difference between cross products which both tend to infinity in the limit of zero pressure (eqn. (4)). We have tested the accuracy of the fluctuation formulae at pressures down to 1 Pa. In the limit of low pressure, we can compare simulation results with perfect gas behaviour at the temperature considered. ($T = 294.25$ K) $c_v = 20\rho M P R T^2 = 6.55 \times 10^{-6}$ $\text{J} \text{mol}^{-1} \text{K}^{-1}$, $\sigma_p = 1/S = 3.40 \times 10^{-6}$ in SI units. Simulation results show that the expected density is obtained within an accuracy of 0.2%. $\sigma_p^\text{ex}$ is indeed lower than 0.1 $\text{J} \text{mol}^{-1} \text{K}^{-1}$, $\sigma_p$ and $\beta_p$ are estimated within 0.5% of the theoretical low pressure limit. These results are highly satisfactory. However, the computed Joule–Thomson coefficient diverges at pressures lower than 0.1 MPa. This can be explained by eqn. (10) in which molar volume tends to infinity while $T \sigma_p$ - 1 tends to zero in the low pressure limit. Therefore it is not surprising that the Joule–Thomson coefficient diverges while $\sigma_p$ is still converging.

### Table 1 Lennard-Jones parameters of the $\text{CH}_4$, $\text{CH}_3$ and $\text{CH}_2$ group. $\delta$ stands for the carbon to force centre distance

<table>
<thead>
<tr>
<th>Group</th>
<th>$\sigma$/Å</th>
<th>$\epsilon$/K</th>
<th>$\delta$/Å</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_4$</td>
<td>3.7327</td>
<td>149.92</td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>$\text{CH}_3$</td>
<td>3.6072</td>
<td>120.15</td>
<td>0.21584</td>
<td>9</td>
</tr>
<tr>
<td>$\text{CH}_2$</td>
<td>3.4612</td>
<td>86.291</td>
<td>0.38405</td>
<td>9</td>
</tr>
</tbody>
</table>

### Table 2 Torsion and bending parameters

<table>
<thead>
<tr>
<th>Bending</th>
<th>$\theta_0$/degrees</th>
<th>$k_{\text{total}}$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-CH$_2$-C</td>
<td>114</td>
<td>74 900</td>
</tr>
<tr>
<td>Torsion</td>
<td>C-CH$_2$-CH$_3$-C</td>
<td>$a_1$/degrees</td>
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<td></td>
<td></td>
<td>$a_2$/degrees</td>
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<td></td>
<td>$a_8$/degrees</td>
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<td></td>
<td></td>
<td>$a_9$/degrees</td>
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</table>

\(^{13}\) \(\mu_{RT} = \frac{\partial T}{\partial P} = \frac{1}{c_P} \left[ \frac{\partial T}{\partial P} \right]_p - \frac{
u}{c_P} [T x_P - 1] (10)\)

\(^{14}\) | $\theta_0$/degrees | $k_{\text{total}}$/K |
<table>
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</thead>
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<tr>
<td>C-CH$_2$-C</td>
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<td>C-CH$_2$-CH$_3$-C</td>
<td>$a_1$/degrees</td>
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<td>$a_3$/degrees</td>
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<td></td>
<td></td>
<td>$a_9$/degrees</td>
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</tbody>
</table>

\(^{24}\) \(\mu_{RT} = \frac{\partial T}{\partial P} = \frac{1}{c_P} \left[ \frac{\partial T}{\partial P} \right]_p - \frac{
u}{c_P} [T x_P - 1] (10)\)
4 Results and discussion

ESI on numerical simulation results is available for methane (Tables S1 and S2), ethane (Table S3), methane-ethane mixture (Table S4) and n-butane (Table S5).

4.1 Methane

We performed calculations for pressures between 1 and 100 MPa and at 294.25 K and higher (corresponding to supercritical conditions). As discussed in the previous section, Joule–Thomson simulation results are valid only for pressures higher than 0.1 MPa. Temperature and pressure conditions have been selected to correspond to experimental measurements of the Joule–Thomson coefficient indicated by Landolt and Börnstein. Fig. 1 shows the compressibility factor $Z = PV/RT$ as a function of pressure at two temperatures: 294.25 and 377.55 K. Comparison is made with the IUPAC recommended values. As the pressure is approaching zero, the compressibility factor approaches unity, as expected for an ideal gas. Smaller departures to ideal behaviour at higher temperature are also well described. These results confirm that the potential of Möller et al. accurately represents the volumetric properties of methane, as already pointed out by Neubauer et al.

Fig. 2 represents the residual heat capacity (eqn. 8) as a function of pressure at 294.25 and 377.55 K. Here again the vanishing residual heat capacity in the limit of zero pressure is well described. Similarly the maximum in heat capacity at pressures of 20 MPa at 294.25 K and 40 MPa at 377.55 K is satisfactorily predicted. In most cases, the difference between simulation results and IUPAC data is smaller than the estimated statistical uncertainty. This tends to prove that we have correctly separated the residual and the ideal contribution in the expression of the total heat capacity (eqn. 7). Although the potential of Möller et al. contains only two parameters, it appears remarkably efficient in describing the sharpening of the heat capacity maximum with decreasing temperatures. Indeed, this effect tends to be more and more pronounced for temperatures closer to the critical temperature.

The change in total heat capacity with temperature at constant pressure (10.3 MPa) is illustrated in Fig. 3. Simulation results accurately reproduce the decrease in residual heat capacity with increasing temperature, which overweights the increase in ideal heat capacity.

Fig. 4(a) and (b) show the Joule–Thomson coefficient as a function of pressure at 294.25 and 377.55 K. The dispersion of simulation results at pressures lower than 10 MPa originates...
from the statistical uncertainty as already discussed above. Nevertheless, an excellent agreement with IUPAC data\textsuperscript{14} is observed. The inversion pressure of the Joule–Thomson effect, \(B_{45} = 45\) MPa at 294.25 K and \(B_{50} = 50\) MPa at 377.55 K, is well described.

Fig. 5 represents the variation of the Joule–Thomson coefficient with temperature at constant pressure (10.3 MPa). The decrease in the Joule–Thomson coefficient with temperature is in better agreement with the IUPAC recommendation\textsuperscript{14} than the direct measurements indicated by Landolt and Börmstein.\textsuperscript{16} As pointed out by Setzmann and Wagner,\textsuperscript{29} some direct measurements of Joule–Thomson coefficient appear less reliable than careful estimates from heat capacity and volumetric behaviour. The difference between our results and experimental data is in any case comparable to the difference between the two sources of data.

The accurate prediction of the Joule–Thomson coefficient confirms the excellent representation of methane by the potential of Möller et al.\textsuperscript{24} at the pressure and temperature conditions of our study.

4.2 Ethane
Simulations have been performed at a temperature of 377.55 K \(i.e.,\) higher than the critical temperature of ethane (305.3 K), at pressures between 1.7 and 10.3 MPa. The total heat capacity as a function of pressure is illustrated by Fig. 6 compared with the direct experimental measurements of Bier et al.\textsuperscript{15} whose uncertainty is estimated to be 0.2%. The simulation results are consistent with experimental behaviour within statistical uncertainty. The increase in the total heat capacity is entirely due to the residual contribution because the ideal heat capacity is constant at fixed temperature. Fig. 7 represents the Joule–Thomson coefficient as a function of pressure. The experimental data are also taken from Bier et al.\textsuperscript{15} whose uncertainty is estimated to be 1%. The simulation results are in good agreement with these direct measurements. The results show that the AUA4 potential represents correctly the derivative properties tested here although it was calibrated only on the first order derivatives of the Gibbs energy.

4.3 Methane–ethane mixture
The mixture investigated is composed of 75 mol% methane and 25 mol% ethane. Among the various methane–ethane mixtures documented by Landolt and Börmstein\textsuperscript{16} this composition was selected because it was more representative of an average natural gas where methane is by far the most abundant hydrocarbon. Simulation results at 377.55 K and pressures between 1.7 and 10.3 MPa are reported on Fig. 7. Here again, simulation results are in good agreement with the experimental Joule–Thomson coefficient. As expected the behaviour of the mixture is intermediate between that of the pure components.

4.4 Butane
The case of n-butane allows us to extend our tests to flexible molecules and liquid phase properties. For this purpose, n-butane was investigated at 380 K (the critical temperature is
Results are indicated in Fig. 8 to 12. Comparison was made with the correlation of experimental data from Sychev et al.\textsuperscript{17} for the thermal expansion coefficient, the isothermal compressibility coefficient and the Joule–Thomson coefficient and from Younglove et al.\textsuperscript{28} for the residual heat capacity. As can be seen from the pressure–volume diagram of Fig. 8, the AUA4 potential of Ungerer et al.\textsuperscript{9} provides a good representation of n-butane volumetric behaviour and saturation pressure at 380 K. This is not surprising because the potential has been calibrated on similar properties on ethane, n-pentane and n-dodecane.

Fig. 9 represents the predicted thermal expansivity as a function of pressure, which presents a discontinuity at the saturation pressure. In the vapour state, uncertainties are small but the thermal expansion coefficient appears slightly underestimated. In the liquid state, statistical uncertainties are larger but the agreement is nevertheless satisfactory without systematic discrepancy.

The isothermal compressibility as a function of pressure is illustrated by Fig. 10(a) for the gas state and Fig. 10(b) for the liquid state. Departures from experimental behaviour are generally lower than estimated statistical uncertainties.

Fig. 11 represents the residual heat capacity as a function of pressure. Simulation represents correctly the large difference between the gas and the liquid states.

The Joule–Thomson coefficient as a function of pressure is illustrated by Fig. 12. The experimental trend is well reproduced in the vapour phase although a significant underestimation is observed at low pressure. The observed deviations which are approximately 10% are not greater than some discrepancies observed between various literature sources\textsuperscript{17,30} for the Joule–Thomson coefficient (see Fig. 5). A more detailed evaluation of data sources would be needed to know whether or not our deviations are really meaningful. From this investigation of the n-butane system, two major conclusions can be drawn.

The first is that the proposed fluctuation method applies to flexible molecules in the vapour state and in the liquid state. Convergence is slower in the liquid state as can be noticed from the larger statistical uncertainties. The second conclusion is that the AUA4 potential represents in a satisfactory way the thermodynamic derivative properties of n-butane although it was calibrated on standard properties. Particularly, the difference in behaviour between the gas state and the liquid state is well predicted for all four coefficients investigated.
References