

## Accurate CO<sub>2</sub> Joule–Thomson inversion curve by molecular simulations

Coray M. Colina<sup>a,\*</sup>, Martin Lísal<sup>b</sup>, Flor R. Siperstein<sup>a</sup>, Keith E. Gubbins<sup>a</sup>

<sup>a</sup> *Chemical Engineering Department, North Carolina State University, Raleigh, NC 27695, USA*

<sup>b</sup> *E. Hála Laboratory of Thermodynamics, Institute of Chemical Process Fundamentals,  
Academy of Sciences of the Czech Republic, Prague, Czech Republic*

Received 14 February 2002; accepted 30 April 2002

### Abstract

We present simulation of the Joule–Thomson inversion curve (JTIC) for carbon dioxide using two different approaches based on Monte Carlo (MC) simulations in the isothermal–isobaric ensemble. We model carbon dioxide using a two-center Lennard–Jones (LJ) plus point quadrupole moment (2CLJQ) potential. We show that a precision of four significant figures in ensemble averages of thermodynamic quantities of interest is needed to obtain accurately the JTIC. The agreement between the experimental data, Wagner equation of state (EOS) and our simulations results indicates that the 2CLJQ potential represents an excellent balance between simplicity and accuracy in modeling of carbon dioxide. Additionally, we calculate the JTIC using the BACKONE EOS (that uses the same intermolecular potential as in our simulations) and show that the BACKONE EOS performs very well in predicting the JTIC for carbon dioxide.

© 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Carbon dioxide; Joule–Thomson inversion curve; Molecular simulation; Monte Carlo method

### 1. Introduction

The Joule–Thomson inversion curve (JTIC) is the locus of states where fluid temperature is invariant upon isenthalpic expansion [1,2]. Knowledge of the inversion curve is essential for the design and operation of throttling processes (such as, refrigeration, production of petroleum fluids), as well as for the evaluation of equations of state (EOSs) and their prediction capabilities. Unfortunately, direct measurement of inversion points is difficult and unreliable.

Experimental JTICs are rarely obtained by direct measurement of inversion points because this would demand extremely accurate temperature determinations. Instead, experimental pressure–volume–

\* Corresponding author. Tel.: +1-919-513-2051; fax: +1-919-513-2470.  
*E-mail address:* ccolina@eos.ncsu.edu (C.M. Colina).

temperature ( $PvT$ ) data are processed, e.g. by fitting them with a high-precision multiparameter EOS and the JTIC is then computed from thermodynamic relations [3]. Even so, the complete JTICs of many fluids cannot be established because they extend into inaccessible regions of high temperatures and pressures. Hence, experimental data on the JTICs are too scarce to permit a rigorous test of the various predictions.

An alternative way to obtain the JTICs is from molecular simulations. JTICs are obtained from molecular simulations via calculation of either compressibility or thermal expansivity along isotherms [4–6]. It should be mentioned that calculations of JTICs in high-temperature regions require very long simulation in comparison with low-temperature regions to obtain results with sufficient accuracy, because temperature changes of isenthalps in the high-temperature regions are less sensitive to changes in pressure in comparison with low-temperature regions.

The JTIC of a Lennard–Jones (LJ) fluid has been obtained by different techniques. Heyes and Llaguno [7] were the first to attempt to calculate the LJ JTIC by molecular dynamics (MD), generating isenthalps in the isothermal–isobaric (NPT) ensemble. Their results show reliable values only at low temperatures and high scatter of results is presented near the peak of the curve (high-pressure zone) as well as in the high-temperature branch. Recently, Kioupis and Maginn [8] developed a new algorithm, which enables the direct simulation of isenthalpic pressure changes using MD. The determination of JTICs is a natural choice to test this technique. Kioupis et al. [9] computed the LJ JTIC using their proposed pressure–enthalpy driven (PHD) MD method and obtained very good agreement with previously published data.

Colina and Müller [4,5] used NPT Monte Carlo (MC) simulation to obtain a series of isobars to predict the LJ JTIC. They simulated the inversion points in the same way as they are obtained experimentally, i.e. by looking for the location of an extremum in the compressibility factor along the isobars.

Escobedo and Chen [10] have recently reported results for the LJ JTIC using a novel integration scheme in conjunction with NPT MC simulations. Their results follow those of Colina and Müller [4,5], but show an ever closer match when comparing them with prediction using the Johnson et al.'s EOS for LJ fluid [11].

Lagache et al. [6] proposed to use simultaneous determination of derivative properties from statistical fluctuations. They obtained the thermal expansivity, the residual heat capacity and the isothermal compressibility from an explicit isothermal–isobaric partition function. They found excellent agreement of these properties with experimental measurements for pure light hydrocarbons (methane, ethane and butane) in the vapor and liquid states. Furthermore, they showed that this method can be used to accurately determine the Joule–Thomson coefficient.

The determination of JTICs of real fluids by molecular simulations may help in understanding practical problems, such as the possibility of heating that occurs during expansion of high-temperature, -pressure gas condensate due to the Joule–Thomson effect. The JTICs of real fluids, such as carbon dioxide [12] and a series of alkanes up to heptane [6,10] have been calculated using molecular simulation. The importance of carbon dioxide, especially in the supercritical state, is broadly known in a variety of fields, e.g. the oil industry (as a carrier gas for enhanced oil recovery) and “green chemistry”, where research efforts are underway to identify sustainable processes and products using CO<sub>2</sub>-related technology.

Chacín et al. [12] observed an anomalous behavior of the CO<sub>2</sub> JTIC in the high-temperature range. The simulated JTIC deviated from the expected quasi-parabolic shape, exhibiting a change of slope and curvature (a “hump”). Their results appeared to be consistent with the original experimental data of Price [13] and the predictions of the Pitzer–Sterner EOS [14]. However, Colina and Olivera-Fuentes [15] have recently shown that the CO<sub>2</sub> JTIC obtained from the Pitzer–Sterner EOS is incorrect at high temperatures, due to physically erroneous prediction of the third virial coefficients.

In this work, we show that the anomalous behavior of the CO<sub>2</sub> JTIC obtained by Chacín et al. is not due to the potential model used (two-center LJ plus point quadrupole moment (2CLJQ) potential), but arises from high uncertainty in the high-temperature branch of the JTIC. The JTIC for carbon dioxide is calculated using the compressibility and thermal expansivity routes. Both routes appear to be equally accurate and efficient for calculating the JTIC when simulation averages are taken over  $1.5 \times 10^8$  configurations. The 2CLJQ potential gives an accurate description of the JTIC even outside the range where the potential model was originally developed.

## 2. Joule–Thomson inversion curves (JTICs)

JTICs are usually represented in the pressure ( $P$ ) and temperature ( $T$ ) plane. The JTIC starts from a saturated liquid state at low temperature and pressure, passes through a pressure maximum at intermediate temperature and goes to zero pressure at maximum temperature as the fluid approaches ideal gas behavior. The inversion criterion can be expressed as

$$\left(\frac{\partial T}{\partial P}\right)_h = 0 \quad (1)$$

where  $h$  is the enthalpy. The inversion criterion given by Eq. (1) may be written in several alternative forms, e.g. for use with a pressure-explicit EOS  $P = P(T, \rho)$ , as

$$T \left(\frac{\partial P}{\partial T}\right)_\rho - \rho \left(\frac{\partial P}{\partial \rho}\right)_T = 0 \quad (2)$$

where  $\rho$  is the density, or for use with corresponding states models  $Z = Z(T, P)$ , as

$$\left(\frac{\partial Z}{\partial T}\right)_P = 0 \quad (3)$$

where  $Z = P/(\rho RT)$  is the compressibility factor and  $R$  the universal gas constant. Alternatively, the inversion criterion can be expressed as a function of the thermal expansivity ( $\alpha$ ) as

$$T\alpha - 1 = 0 \quad (4)$$

where

$$\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P \quad (5)$$

The compressibility and thermal expansivity routes use Eqs. (3) and (4), respectively, to determine JTICs.

## 3. Potential model

We model carbon dioxide as a 2CLJQ fluid [16]. The 2CLJQ molecule is composed of two identical LJ sites a distance ( $l$ ) apart and a point quadrupole ( $Q$ ) placed in the geometric center of the molecule. The 2CLJQ potential ( $u_{2CLJQ}$ ) can be written as

$$u_{2CLJQ}(r_{ij}, \omega_i, \omega_j, l, Q^2) = u_{2CLJ}(r_{ij}, \omega_i, \omega_j, l) + u_Q(r_{ij}, \omega_i, \omega_j, Q^2) \quad (6)$$

where

$$u_{2\text{CLJ}}(r_{ij}, \omega_i, \omega_j, l) = 4\varepsilon \sum_{a=1}^2 \sum_{b=1}^2 \left[ \left( \frac{\sigma}{r_{ab}} \right)^{12} - \left( \frac{\sigma}{r_{ab}} \right)^6 \right] \quad (7)$$

and

$$u_{\text{Q}}(r_{ij}, \omega_i, \omega_j, Q^2) = \frac{3}{4} \frac{Q^2}{4\pi\varepsilon_0|r_{ij}|^5} [1 - 5(c_i^2 + c_j^2) - 15c_i^2c_j^2 + 2(c - 5c_ic_j)^2] \quad (8)$$

In Eqs. (7) and (8),  $r_{ij}$  is the distance between the centers of molecules  $i$  and  $j$ ,  $\omega_i$  and  $\omega_j$  the orientations of molecules  $i$  and  $j$ ,  $r_{ab}$  the distance between the center of two LJ sites  $a$  and  $b$  of different molecules,  $\varepsilon$  the LJ energy parameter,  $\sigma$  the LJ size parameter,  $c_i = \cos \theta_i$ ,  $c_j = \cos \theta_j$  and  $c = \cos \theta_i \cos \theta_j + \sin \theta_i \sin \theta_j \cos \phi_{ij}$ , where  $\theta_i$  and  $\theta_j$  are the polar angles of the molecular axis with respect to a line joining the molecular centers,  $\phi_{ij}$  the difference in the azimuthal angles and  $\varepsilon_0$  the permittivity of free space. We used potential parameters suggested by Möller and Fischer [16]:  $\varepsilon/k = 125.317$  K,  $\sigma = 3.0354$  Å,  $l/\sigma = 0.699$  and  $Q^2/4\pi\varepsilon_0\varepsilon\sigma^5 = 3.0255$ .

#### 4. Simulation details

A total of  $N = 500$  molecules was initially placed in a random configuration in a cubic simulation box. Periodic boundary conditions and minimum image conventions were applied. Simulations were organized in cycles. Each cycle consists of  $N$  attempts to displace or rotate a randomly chosen molecule and an attempt of volume change. Acceptance probabilities of displacement and volume changes were adjusted to be about 30%. Averages have been taken over  $5 \times 10^5$  cycles, after a stabilization period of at least  $3 \times 10^5$  cycles.

#### 5. Results and Discussion

Two different approaches, the compressibility [4] and thermal expansivity [6] routes, were used to simulate the JTIC of CO<sub>2</sub>. We restrict ourselves to methodologies that rely exclusively on MC simulations to determine the JTIC and do not include Escobedo and Chen's technique that uses a combination of EOS and MC simulations for accurate determination of  $PvT$  properties. Simulations were performed in the entire range of temperatures and pressures where the JTIC is expected for carbon dioxide.

Colina and Müller [4,5] suggested that to find an inversion curve point, a series of NPT simulations (generally from 5 to 10) need to be carried out in the vicinity of an expected inversion point. The compressibility factor  $Z = P/\rho RT$  is calculated from densities obtained from NPT MC simulations. The derivative in Eq. (3) is calculated numerically from a collection of simulations at constant pressure.

Fig. 1a shows the compressibility factor as a function of reduced temperature  $T^* = Tk/\varepsilon$  for a typical isobar ( $P^* = P\sigma^3/\varepsilon = 1.15$  and  $P = 73.24$  MPa). The low-temperature inversion point can be easily found from a well-pronounced minimum ( $T^* = 3.13$  and  $T = 398.5$  K). On the other hand, the high-temperature inversion point corresponds to a maximum that is less obvious in this figure. Fig. 1b shows only the high-temperature points with a more refined scale, where now the maximum is clearly observed ( $T^* = 6.89$  and  $T = 877.3$  K). Even though the error bars are relatively bigger for

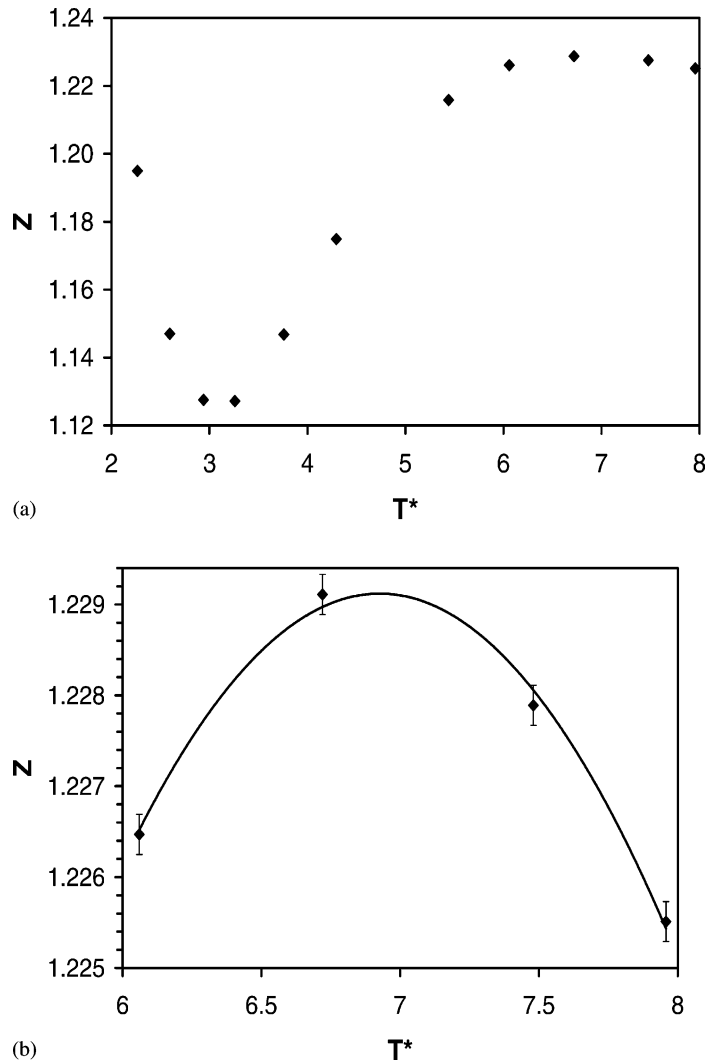


Fig. 1. (a) Compressibility factor as a function of reduced temperature ( $T^*$ ) for a typical isobar ( $P^* = 1.15$ ); (b) high-temperature points at the same conditions as in (a).

the high-temperature branch, the maximum is still clearly observed. It is important to note that precision of four significant figures in the compressibility factor is needed to have good statistics. Although this level of accuracy is not normally pursued in molecular simulations, nowadays it is possible to obtain it in a reasonable simulation time and this opens the door to the possibility of using computer simulations as a convenient method to extrapolate experimental data to other conditions of difficult experimental access.

Fig. 2 shows a typical  $Z$  versus number of cycles plot for the determination of a point after equilibration have been reached. Due to the high precision that is needed for the determination of the JTIC, at least  $3 \times 10^5$  cycles ( $1.5 \times 10^8$  configurations) have to be performed to have good statistics.

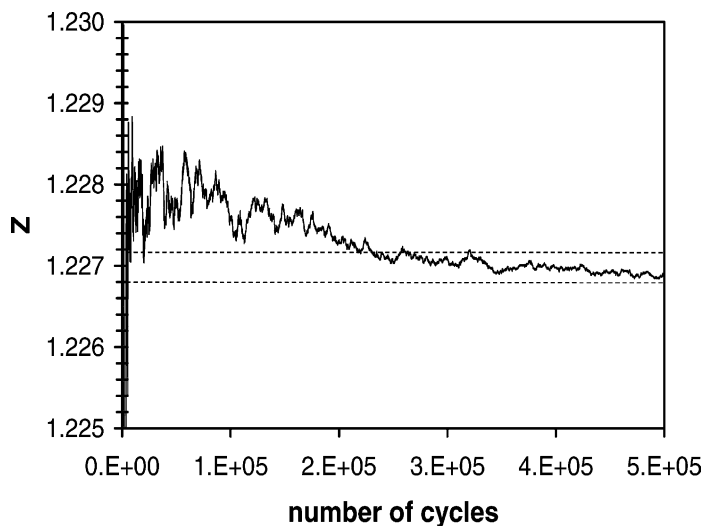


Fig. 2. Compressibility factor vs. number of cycles for a typical isobar.

The JTIC of carbon dioxide was also calculated using the thermal expansivity method proposed by Lagache et al. [6], where the inversion condition given by Eq. (4) is obtained from fluctuations in the enthalpy ( $h$ ) and volume ( $v$ )

$$T\alpha - 1 = \frac{\langle vh \rangle - \langle v \rangle \langle h \rangle}{\langle v \rangle kT} - 1 = 0 \quad (9)$$

Fig. 3 shows, as an example, the  $T^*\alpha - 1$  function for  $P^* = 1.15$  for a complete range of temperatures ( $\blacklozenge$ ). For the determination of the JTIC, it is not necessary to generate all these points. In fact, for the determination of the inversion point, only the points near the inversion condition (usually four) were taken and correlated with a linear approximation ( $T\alpha - 1 = mT + b$ ) to obtain the inversion temperatures at the pressure under study. From a linear approximation the low-temperature inversion point was  $T^* = 3.17$  ( $T = 404.1$  K) and the high-temperature inversion point  $T^* = 6.90$  ( $T = 879.0$  K). These temperatures correspond to the values obtained as  $T_{\text{inv}} = -b/m$  from the different linear correlations. The error propagation in the inversion temperature is given by

$$\sigma_{T_{\text{inv}}}^2 = \frac{b^2}{m^4} \sigma_m^2 + \frac{1}{m^2} \sigma_b^2 + \dots \quad (10)$$

where  $\sigma_i$  is the standard deviation of  $i$ .

Therefore, low values of  $m$  result in larger errors in the determination of the inversion point for equivalent scatter in the slope and intercept ( $\sigma_b$ ,  $\sigma_m$ ). To obtain an accurate JTIC in the whole temperature range, it is important to be extremely careful at high temperatures where changes in  $(T\alpha - 1)$  are less sensitive than in the low-temperature range. This effect is more evident at low pressures, as is also shown in Fig. 3 ( $\circ$ ).

The simulated JTIC of carbon dioxide, expressed in reduced units:  $T_r = T^*/T_c^*$ ,  $P_r = P^*/P_c^*$ , is shown in Fig. 4. The simulation results of this work using both approaches are compared with previously published simulations from Chacín et al. [12] and with our calculations using the BACKONE EOS

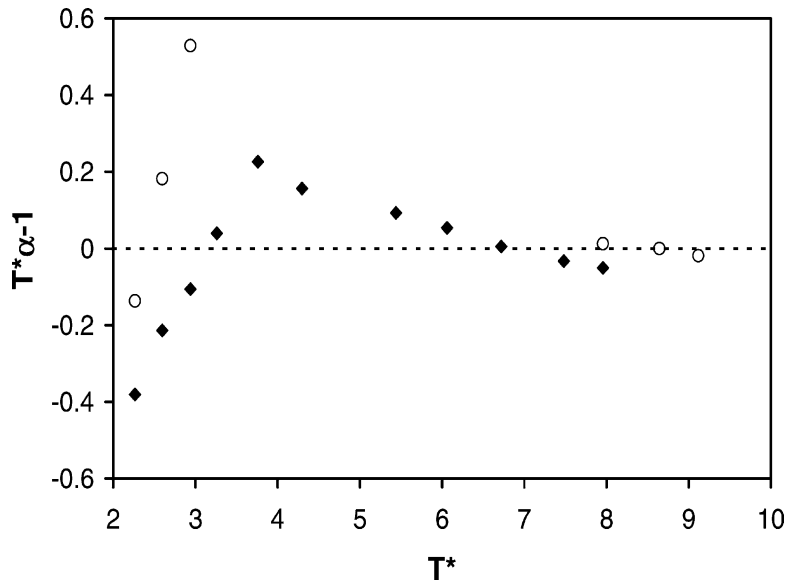


Fig. 3.  $T^*\alpha - 1$  function vs.  $T^*$  at high and low pressure: ( $\blacklozenge$ )  $P^* = 1.15$  ( $P = 73.24$  MPa); ( $\circ$ )  $P^* = 0.65$  ( $P = 41.40$  MPa).

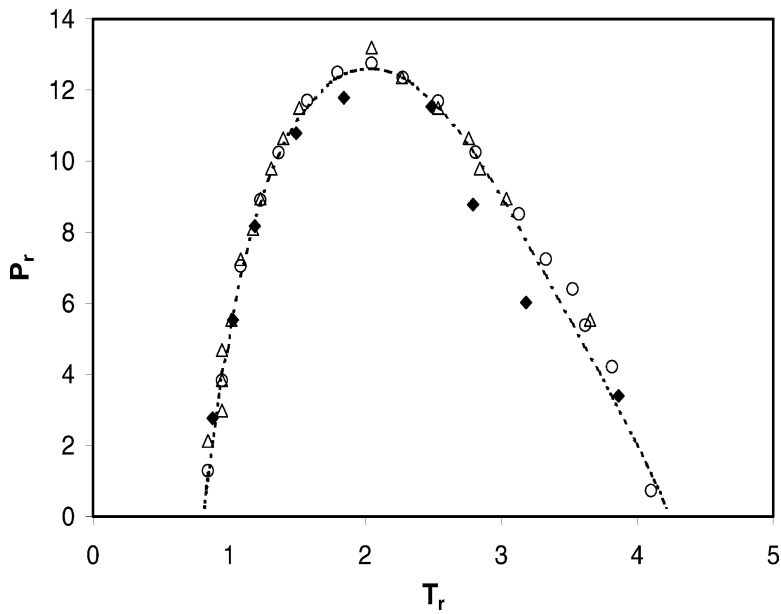


Fig. 4. JTIC for carbon dioxide modeled as 2CLJQ fluid: ( $\Delta$ ) from compressibility factor; ( $\circ$ ) from  $T^*\alpha - 1$  function; ( $\blacklozenge$ ) previous simulation of Chacín et al. [12]; (---) BACKONE EOS.

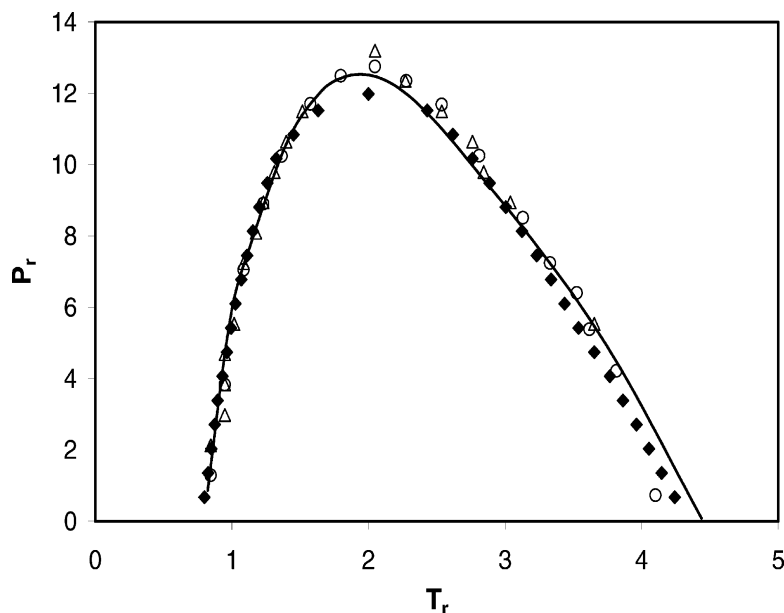


Fig. 5. JTIC of carbon dioxide predicted by: (—) the Span–Wagner EOS; ( $\Delta$ ) from compressibility factor; ( $\circ$ ) from  $T^*\alpha - 1$  function; ( $\blacklozenge$ ) experimental data as reported in Perry’s Chemical Engineers’ Handbook [21].

[17–19]. This EOS was selected because it uses the same intermolecular potential as is used in this simulation. The agreement between our simulations and the BACKONE EOS is remarkable and we believe that the anomalous behavior of the JTIC obtained by Chacín et al. [12] is not due to the 2CLJQ potential model but is due to the high uncertainty of Chacín et al.’s results in the high-temperature branch of the JTIC. The calculation of the JTIC is a “stringent” test for EOSs and the almost quantitative agreement between our simulations and the BACKONE EOS indicates its excellent performance for this 2CLJQ fluid at such extreme conditions.

Fig. 5 shows the JTIC of carbon dioxide computed from the Span–Wagner EOS [20], experimental values interpolated from Vukalovich and Altunin’s interpolation of data of Price, given in Perry’s Chemical Engineers’ Handbook [21]. Fig. 5 shows very good agreement between the experimental data, Span–Wagner EOS and our simulations results. Such agreement indicates that the 2CLJQ potential represents an excellent balance between simplicity and accuracy in modeling thermodynamic properties of carbon dioxide in the supercritical region, outside the range of thermodynamic conditions where the 2CLJQ potential parameter were fitted.

## 6. Conclusions

In this work, two different approaches, the compressibility [4,5] and thermal expansivity [6] routes, were used to simulate the JTIC of carbon dioxide. We showed that precision of four significant figures in the thermodynamic quantities of interest was needed in both methods, to obtain good statistics especially for the high-temperature branch of the JTIC.

Our results illustrate the predictive capabilities of molecular simulations. We have found quantitative agreement for JTIC with both experimental measurements [21] and EOS predictions [20]. We have found excellent agreement, however, despite not including all properties in the optimization of the intermolecular potential.

#### List of symbols

$h$	enthalpy
$l$	distance between two LJ sites
$P$	pressure
$P_c$	critical pressure
$P_r$	reduced pressure
$Q$	point quadrupole
$r_{ab}$	distance between two LJ sites $a$ and $b$ of different molecules
$r_{ij}$	distance between the centers of molecules $i$ and $j$
$R$	universal gas constant
$T$	temperature
$T_c$	critical temperature
$T_r$	reduced temperature
$v$	volume
$Z$	compressibility factor

#### Greek letters

$\alpha$	thermal expansivity
$\varepsilon$	LJ energy parameter
$\varepsilon_0$	permittivity of free space
$\theta_i, \theta_j$	polar angles of the molecular axis
$\rho$	density
$\sigma$	LJ size parameter
$\phi_{ij}$	difference in the azimuthal angles
$\omega_i, \omega_j$	orientations of molecules $i$ and $j$

#### Acknowledgements

We thank Edward Maginn for providing us a copy of [8,9] prior to publication. This material is based upon work supported in part by the STC Program of the National Science Foundation under Agreement no. CHE 9876674 and by the Grant Agency of the Czech Republic under Grant no. 203/02/0805.

#### References

- [1] P.W. Atkins, Physical Chemistry, 6th Edition, Oxford University Press, Oxford, 1998.
- [2] M.J. Moran, H.N. Shapiro, Fundamentals of Engineering Thermodynamics, 2nd Edition, Wiley, New York, 1992.
- [3] C.M. Colina, C. Olivera-Fuentes, Cryogenics 38 (1998) 721–728.
- [4] C.M. Colina, E.A. Müller, Int. J. Thermophys. 20 (1999) 229–235.

- [5] C.M. Colina, E.A. Müller, *Mol. Simulat.* 19 (1997) 237–246.
- [6] M. Lagache, P. Ungerer, A. Boutin, A.H. Fuchs, *Phys. Chem. Chem. Phys.* 3 (2001) 4333–4339.
- [7] D.M. Heyes, C.T. Llaguno, *Chem. Phys.* 168 (1992) 61–68.
- [8] L.I. Kioupis, E.J. Maginn, *Fluid Phase Equilib.*, in press.
- [9] L.I. Kioupis, G. Arya, E.J. Maginn, *Fluid Phase Equilib.*, in press.
- [10] F.A. Escobedo, Z. Chen, *Mol. Simulat.* 26 (2001) 395–416.
- [11] J.K. Johnson, J.A. Zollweg, K.E. Gubbins, *Mol. Phys.* 78 (1993) 591–618.
- [12] A. Chacín, J.M. Vázquez, E.A. Müller, *Fluid Phase Equilib.* 165 (1999) 147–155.
- [13] D. Price, *Ind. Eng. Chem.* 1 (1956) 83–86.
- [14] K.S. Pitzer, S.M. Sterner, *J. Chem. Phys.* 101 (4) (1994) 3111–3116.
- [15] C.M. Colina, C. Olivera-Fuentes, *Ind. Eng. Chem. Res.* 41 (5) (2002) 1064–1068.
- [16] D. Möller, J. Fischer, *Fluid Phase Equilib.* 100 (1994) 35–61.
- [17] A. Müller, J. Winkelmann, J. Fischer, *AIChE J.* 42 (4) (1996) 1116–1126.
- [18] M.A. Mecke, J. Müller, J. Winkelmann, J. Fischer, *Int. J. Thermophys.* 18 (1997) 683–698;  
M.A. Mecke, J. Müller, J. Winkelmann, J. Fischer, *Erratum, Int. J. Thermophys.* 19 (1998) 1495.
- [19] B. Saager, J. Fischer, *Fluid Phase Equilib.* 72 (1992) 67–88.
- [20] R. Span, W. Wagner, *J. Phys. Chem. Ref. Data* 25 (6) (1996) 1509–1596.
- [21] R.H. Perry, D.W. Green, *Perry's Chemical Engineers' Handbook*, 7th Edition, McGraw-Hill, New York, 1997, pp. 2–134.