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# DETERMINATION OF THERMODYNAMIC PROPERTIES OF REFRIGERANTS BY USING MOLECULAR SIMULATION AND EXPERIMENT: APPLICATION TO DEVELOPMENT OF PREDICTIVE THERMODYNAMIC MODELS

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## ABSTRACT

Since 1987, several protocols have banned the use and the production of CFC's and HCFC's, and limited the utilisation of HFC's owing to ozone depletion and global warming. In Europe, the F-gas regulation gives the objective in terms of GWP of fluids authorized in the market. These working fluids can be pure component or blends of refrigerants with low GWP (like CO<sub>2</sub>). In all cases, the production and uses of these fluids require knowledge of thermodynamic properties in order to estimate their performance in machines and to design compressors, heat exchangers or turbines. The best strategy consists in developing predictive equations of state. These models are very useful to screen and select the best candidates for the considered application (refrigeration, heat pump, etc.). The parameters of the predictive models, mainly based on group contribution approach, have to be determined. It exists two methods to obtain thermodynamic properties: the first one consists in using molecular simulation, and the second one consists in measuring thermodynamic data experimentally. Herein, we consider the capabilities of Monte Carlo simulations in the Gibbs ensemble to provide vapor-liquid equilibrium data of refrigerant mixtures. Experimental work can be done considering techniques based on either analytic or synthetic methods.

## 1. INTRODUCTION

Since 1985, several regulations have appeared concerning the utilisation of refrigerants. After the Montreal protocol, regulations concerning ozone-depleting substances have prohibited the use and the production of chlorofluorocarbons (CFC's) and of hydrochlorofluorocarbons (HCFC's) worldwide. Consequently, hydrofluorocarbons (HFC's) were proposed as alternative refrigerants. Unfortunately, HFC's have non negligible global warming potentials (GWP's). After the Kyoto protocol in 1997, regulations concerning GWP have progressively prohibited the utilisation of these latter chemicals. The F-gas regulations were created in order to plan the utilisation and replacement of these refrigerants. The 2009 F-gas regulation fixes the limits of GWP for each year. Today, the objective is to use fluids (pure compounds or mixtures) with  $GWP < 2200$ . In 2018, the objective is to use fluids with  $GWP < 1300$  close to the GWP of R134A ( $GWP = 1300$ ; Bolaji, 2010). In 2020, the objective is to use fluids with  $GWP < 1000$ . In order to reach the objectives in terms of GWP, two solutions exist: the first one consists in developing new fluids with low GWP values, such as hydrofluoroolefines (HFO's), and the second one consists in developing new blends of refrigerants (less than 3 components). The GWP of mixtures is calculated by means of the GWP of each component and of the composition. The development of refrigerators, heat pumps or organic Rankine cycle machines requires the knowledge of the thermodynamic properties and the phase diagram of fluids. For example, to design heat exchangers with and without phase changing, it is important to know the state of the fluid and to evaluate the level of the temperature or pressure glide. In this case, it is important to know if the fluid behaves like a pure component (azeotropic behaviour) or not. So, knowledge of phase diagram is essential. Coquelet and Richon (2009) and Privat and Jaubert (2013) have revisited the Scott and van Konynenburg (1980) classification and applied it to refrigerant-containing systems. Figure 1 presents the main types of phase diagrams.

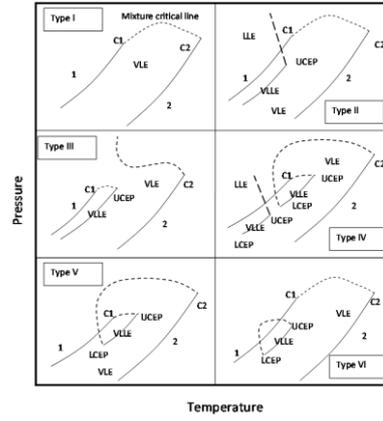


Figure 1: Scott and van Konynenburg classification.

Regarding the design of the heat exchangers, chemical engineers use correlations with adimensional numbers, such as equation 1.

$$Nu = A Re^\alpha Pr^\beta \quad (1)$$

where Nu is the Nusselt number  $Nu = \frac{hD}{\lambda}$ , Re is the Reynolds number  $Re = \frac{\rho v D}{\mu}$  and Pr is the Prandtl number

$Pr = \frac{\mu C_p}{\lambda}$ , with  $h$  the heat transfer coefficient [ $J.m^{-2}$ ],  $D$  a characteristic length [m],  $\lambda$  the thermal conductivity

[ $J.m^{-1}$ ],  $\rho$  the density [ $kg.m^3$ ],  $\mu$  the viscosity [Pa.s],  $C_p$  the heat capacity [ $J.mol^{-1}.K^{-1}$ ] and  $v$  the speed of the fluid [ $m.s^{-1}$ ]. The thermodynamic properties are obtained by using equations of state (EoS's). In the process simulators, the most famous EoS's are of cubic type, such as equation 2, and all the thermodynamic properties like residual enthalpy can be calculated from such an EoS (cf. equation 3).

$$P = \frac{RT}{v-b} - \frac{a(T)}{v+ubv-wb^2} \quad (2)$$

where  $u$  and  $w$  are EoS parameters (for the Peng-Robinson EoS,  $u = 2$  and  $w = -1$ ),  $a$  is the attractive term [ $Pa.m^3.mol^{-1}$ ] and  $b$  is the molar co-volume [ $m^3.mol^{-1}$ ].

$$(h - h^0)_{T,P} = \int_0^P \left( v - \frac{\partial v}{\partial T} \right)_P dP \quad (3)$$

Concerning the transport properties, different approaches exist. One consists in using the corresponding state method. The most famous approach is the TRAPP method developed by the NIST. Huber et al. (2003) and Klein et al. (1997) have developed a series of equations adapted to the prediction of viscosities and thermal conductivities of pure components and mixtures. The approach consists in modifying the transport properties in the ideal dilute gas state taking into account the molecular interactions (and so the density of the fluid with temperature and pressure). For the calculation of phase equilibrium, the thermodynamic approach is based on the isofugacity criterion (equation 4).

$$f_i^V(T, P, y) = f_i^L(T, P, x) \quad (4)$$

There are two main ways to solve equation 4. The dissymmetric or “ $\gamma$ - $\Phi$ ” approach consists in using two different models for describing the vapor phase and the liquid phase: for instance, a cubic EoS like equation 2 for the vapor phase and an activity coefficient model for the liquid phase. Unfortunately, this method is limited to the low or moderate pressures and can not calculate the critical point of a mixture. The second one consists in using a symmetric (or “ $\Phi$ - $\Phi$ ”) approach. The model is identical for the liquid and vapour phases. This approach needs a cubic EoS with an alpha function. This alpha function permits to calculate more precisely the pure component vapour pressures. Recently, Privat et al. (2014) have published an interesting

paper discussing alpha functions to be used with cubic EoS. Mixing rules are necessary to calculate the parameters  $a$  and  $b$  of the EoS for the mixtures. Two types of mixing rules are frequently used:

- The van der Waals mixing rules (known as quadratic mixing rules).
- $g^E$  type mixing rules combining an EoS with an activity coefficient model. The first mixing rule belonging to this approach was developed by Huron and Vidal (1979) with an infinite pressure reference. Wong and Sandler (1992) developed more accurate mixing rules at high pressure. Other authors used zero pressure reference for low pressure VLE.

As mentioned above, the new regulations impose to chemist the development of new fluids, pure components or mixtures. The selection of the fluids is mainly based on their energetic performances evaluated on energetic machines. The performance (COP) is generally evaluated from a process simulator (see one example on figure 2) and confirmed after several tests on existing machines.

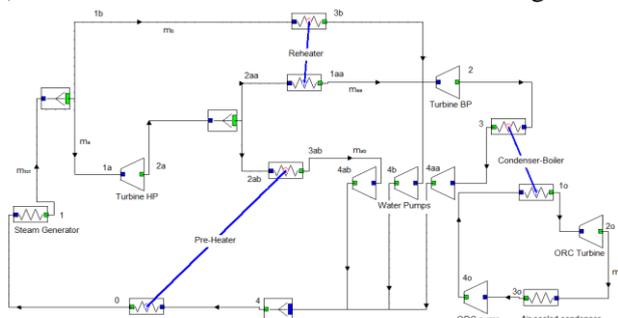


Figure 2. Structure of the Two Stage Rankine Cycle represented in THERMOPTIM™ (2010).  
Extracted from Bo LIU thesis (2014)

In order to obtain the parameters of a cubic EoS, experimental data are needed, mainly VLE data. We can easily imagine the huge number of experimental studies required to qualify a fluid in terms of performance. So, predictive tools based on the group contribution concept are of precious help to chemical engineers. Among these latter tools, the most famous ones are the UNIFAC (1975) or PSRK UNIFAC (1991) models. Since the beginning of 2000's, Jaubert and coworkers develop the PPR78 GC model (Jaubert and Mutelet, 2004) which combines the Peng-Robinson EoS (1978) and a mathematical relation which allows one to estimate the binary interaction parameters from the partitioning of the molecules in elementary groups. The determination of the group-interaction parameters requires many phase equilibrium data which can be obtained either by molecular simulation or by experiment.

## 2. MOLECULAR SIMULATION APPROACH

By complementing experimental work, molecular simulation techniques provide a useful tool for the investigation of phase coexistence of pure fluids and fluid mixtures. For instance, to study VLE, two-phase simulations can be considered. This type of simulation is based on a single simulation box containing three regions: the liquid phase, the interfacial region, and the vapor phase. This situation corresponds to the numerical twin of the experimental observation, but this two-phase simulation method presents several disadvantages. In particular, simulations can be slow because of the difficulties encountered generally to equilibrate the interfacial region. In the case where interfacial phenomena are not of concern, simulations in the Gibbs ensemble (Panagiotopoulos 1987) are usually considered. For studying the VLE, the Gibbs ensemble method is based on two boxes containing homogeneous phases (liquid phase and vapor phase boxes) that are in thermodynamic equilibrium but not physically in contact. In this method, the simulation of the interface is thus avoided. Equilibrium between the boxes is reached by attempting molecular displacements in each box, volume changes and molecule interchanges between the boxes. Although several implementations have been proposed for molecular dynamics, the Gibbs ensemble method was originally developed for Monte Carlo simulations, and widely used in this latter framework nowadays. This Gibbs ensemble method has been used in conjunction with several intermolecular interaction potentials describing the Van der Waals interaction, and particularly the 12-6 Lennard-Jones potential. For the Lennard-Jones potential parameters for unlike atoms, by far the most commonly employed combining rule is that of Lorentz and Berthelot. The Gibbs ensemble calculations yield thermodynamic properties for pure fluids and mixtures, such as VLE curves, densities, vapor pressures, heats of vaporization, heat capacities, etc. To reach transport properties, such as shear viscosity and thermal conductivity, by molecular simulation, molecular

dynamics techniques have to be considered. The transport properties can be determined from the time evolution of autocorrelation functions in a system in equilibrium, based on the Green-Kubo formalism. For example, the Green-Kubo relation for shear viscosity,  $\eta$ , is given by equation 5.

$$\eta = \frac{V}{k_B T} \int_0^{\infty} dt \langle P_{xy}(0) \cdot P_{xy}(t) \rangle \quad (5)$$

where  $k_B$  is the Boltzmann constant, and the bracket term is the autocorrelation function of the  $xy$  component of the pressure tensor. Beside the Green-Kubo formulation, transport properties can be calculated by non equilibrium molecular dynamics (NEMD) methods. These methods consist in applying a perturbation to a system that drive it out of the equilibrium and in recording the response of the system to the imposed perturbation. For instance, in the case of the computation of the shear viscosity, the perturbation is the shear rate and the response of the system is the momentum flux. The shear rate dependent viscosity is then defined as the proportionality constant between the momentum flux and the shear rate.

### 3. EXPERIMENTAL APPROACH

The accuracy of the experimental data depends strongly on the method used. Experimental methods for the investigation of phase equilibrium belong either to closed or open circuit methods (Fonseca et al., 2011; Richon and de Loos, 2005). The closed circuit methods can be divided into two main classes depending on how the composition is determined: static-analytic methods and static-synthetic methods. For the analytic methods, the composition of each phase is obtained by analysis after sampling (direct sampling method). For the synthetic methods, the global composition of the mixture is known a priori, so that no sampling is necessary. The composition of each phase is determined by solving mass balance equations (indirect methods) or the system is brought to its bubble or dew point. The variable volume cell technique (or PVT technique) can be cited as a static-synthetic method. The components of the mixture are introduced separately and the composition is known by weighing procedure. The volume of the cell is modified with a piston to study bubble or dew points. With the static methods, the chemical system reaches equilibrium state with a good agitation either through the use of a magnetic stirrer or through circulating one or several phases with pumps. At equilibrium (constant temperature and pressure), samples of phases are withdrawn and analysed, leading to PTxy data determination. Two categories can be distinguished:

- Dynamic-analytic methods with one or more circulating phases using pumps. With these methods, special care must be taken to ensure the circulating phase is in equilibrium. Samples are directly taken in the circulation line with valves and analysed, generally by chromatographic analysers.

- Static-analytic method with a sampler system. The mixture is enclosed in an equilibrium cell. An internal stirring system permits to reach fast equilibrium. When this latter is reached, small quantities of the phases are sampled and analysed through chromatographic analysers. Details are given by Raal and Mühlbauer (1997). Since the beginning of eighties, CTP research aims for developing and improving reliable tools (capillary sampler; Guilbot et al., 2000) in order to obtain the most representative sampling in different domains of pressure. Zhang et al. (2014) have presented a new static-analytic equipment dedicated to the measurement at low pressure.

Open circuit methods include several different techniques. Only the densimeter technique developed by Galicia Luna et al. (1994), and Bouchot and Richon (1998), and critical point measurement (Soo et al., 2010; Juntarachat et al., 2012), which are synthetic methods are considered here. Concerning density measurement, a mixture with known composition circulates through a vibrating U-tube. Density is deduced from the Forced Path Mechanical Calibration Model developed in the CTP research group (Bouchot and Richon, 2001). This model linked the density to the acquired data (vibration period of U-tube, temperature and pressure). This apparatus can be used to obtain (P $\rho$ T) data of compressed phases and to estimate saturating properties. Concerning critical point measurements, the technique consists in observing the critical opalescence by controlling the temperature and the flow of the mixture circulating through the equilibrium cell. Figure 3 describes the critical point apparatus.

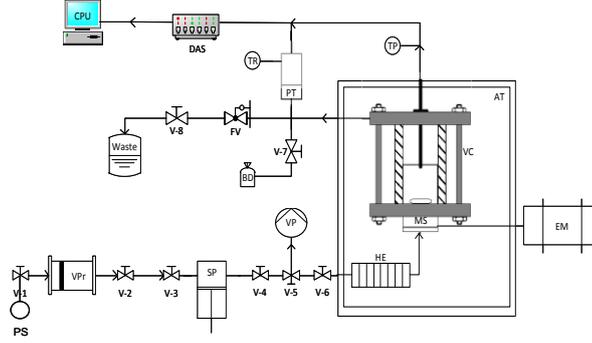


Figure 3: Schematic diagram of the critical point measurement apparatus. PS: pressurized source; VPr: volumetric press; SP: syringe pump; VP: vacuum pump; HE: heat exchanger; EM: electric motor; MS: magnetic stirrer; VC: view cell; AT: air thermostat bath (oven); TP: platinum resistance temperature probe; PT: pressure transducer; TR: temperature regulator; BD: bursting disc; FV: flow regulation valve; DAS: data acquisition system; CPU: central processor unit; V: valve.

#### 4. GROUP CONTRIBUTION APPROACH

Our data were correlated with the well-established 1978 version of the Peng-Robinson EoS, referred as PR78 in this communication. For a pure component, the PR78 EoS is described by equations 6 and 7.

$$P = \frac{RT}{v - b_i} - \frac{a_i(T)}{v(v + b_i) + b_i(v - b_i)} \quad (6)$$

and

$$\begin{cases} R = 8.314472 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ \eta_c = \left[ 1 + \sqrt[3]{4 - 2\sqrt{2}} + \sqrt[3]{4 + 2\sqrt{2}} \right]^{-1} \approx 0.253076587 \\ b_i = \Omega_b \frac{RT_{c,i}}{P_{c,i}} \text{ with: } \Omega_b = \frac{\eta_c}{\eta_c + 3} \approx 0.0777960739 \\ a_i = \Omega_a \frac{R^2 T_{c,i}^2}{P_{c,i}} \alpha(T) \text{ with: } \Omega_a = \frac{8(5\eta_c + 1)}{49 - 37\eta_c} \approx 0.457235529 \text{ and } \alpha(T) = \left[ 1 + m_i \left( 1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right]^2 \\ \text{if } \omega_i \leq 0.491 \quad m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \\ \text{if } \omega_i > 0.491 \quad m_i = 0.379642 + 1.48503\omega_i - 0.164423\omega_i^2 + 0.016666\omega_i^3 \end{cases} \quad (7)$$

where  $P$  is the pressure,  $R$  is the gas constant,  $T$  is the temperature,  $a_i$  and  $b_i$  are the EoS parameters of pure component  $i$ ,  $v$  is the molar volume,  $T_{c,i}$  is the critical temperature,  $P_{c,i}$  is the critical pressure and  $\omega_i$  is the acentric factor of pure  $i$ . To apply this EoS to a mixture, mixing rules are necessary to calculate the values of  $a$  and  $b$  of the mixture. Classical van der Waals one-fluid mixing rules were used in this study:

$$\begin{cases} a(T, \mathbf{z}) = \sum_{i=1}^N \sum_{j=1}^N z_i z_j \sqrt{a_i(T) \cdot a_j(T)} [1 - k_{ij}(T)] \\ b(\mathbf{z}) = \sum_{i=1}^N z_i b_i \end{cases} \quad (8)$$

where  $z_i$  represents the mole fraction of component  $i$  and  $N$  is the number of components in the mixture. The  $k_{ij}(T)$  parameter, whose choice is difficult even for the simplest systems, is the so-called binary interaction parameter (BIP) characterizing the molecular interactions between molecules  $i$  and  $j$ . The dependence in temperature of the  $k_{ij}$  was determined following the equations developed for the PPR78 (Jaubert and Mutelet, 2004) model. We thus used:

$$k_{12}(T) = \frac{A_{12} \cdot \left( \frac{298.15}{T} \right)^{\left( \frac{B_{12}-1}{A_{12}} \right)} - \left( \frac{\sqrt{a_1(T)}}{b_1} - \frac{\sqrt{a_2(T)}}{b_2} \right)^2}{2 \frac{\sqrt{a_1(T) \cdot a_2(T)}}{b_1 \cdot b_2}} \quad (9)$$

Such an equation comes from the combination of the Peng-Robinson EoS and a Van Laar type activity coefficient ( $g^E$ ) model under infinite pressure and thus follows the well-established Huron-Vidal mixing rules. Eq. 9 highlights that one needs to estimate two constant parameters ( $A_{12}$  and  $B_{12}$ ) for each binary system. VLE data published in the open literature as well as new data measured can be used to determine the optimal values of these parameters. For each system,  $A_{12}$  and  $B_{12}$  parameters are those which minimize the following objective function (equation 10).

$$\begin{cases}
F_{obj} = \frac{F_{obj,bubble} + F_{obj,dew} + F_{obj,crit,comp} + F_{obj,crit,pres}}{n_{bubble} + n_{dew} + 2n_{crit}} \\
F_{obj,bubble} = 100 \sum_{i=1}^{n_{bubble}} 0.5 \left( \frac{|\Delta x|}{x_{1,exp}} + \frac{|\Delta x|}{x_{2,exp}} \right)_i \\
\text{with } |\Delta x| = |x_{1,exp} - x_{1,cal}| = |x_{2,exp} - x_{2,cal}| \\
F_{obj,dew} = 100 \sum_{i=1}^{n_{dew}} 0.5 \left( \frac{|\Delta y|}{y_{1,exp}} + \frac{|\Delta y|}{y_{2,exp}} \right)_i \\
\text{with } |\Delta y| = |y_{1,exp} - y_{1,cal}| = |y_{2,exp} - y_{2,cal}| \\
F_{obj,crit,comp} = 100 \sum_{i=1}^{n_{crit}} 0.5 \left( \frac{|\Delta x_c|}{x_{c1,exp}} + \frac{|\Delta x_c|}{x_{c2,exp}} \right)_i \\
\text{with } |\Delta x_c| = |x_{c1,exp} - x_{c1,cal}| = |x_{c2,exp} - x_{c2,cal}| \\
F_{obj,crit,pres} = 100 \sum_{i=1}^{n_{crit}} \left( \frac{|P_{cm,exp} - P_{cm,cal}|}{P_{cm,exp}} \right)_i
\end{cases} \quad (10)$$

where  $n_{bubble}$ ,  $n_{dew}$  and  $n_{crit}$  are the number of experimental bubble points, dew points and mixture critical points, respectively. Subscripts *exp* and *cal* mean *experimental value* and *calculation with the PR78 EoS*, respectively;  $x_i$  and  $y_i$  are the mole fractions of component  $i$  in the liquid and gas phases, respectively, at a fixed temperature and pressure;  $x_{ci}$  and  $P_{cm}$  are the critical mole fraction of component  $i$  and critical mixture pressure at a given temperature. The optimization problem was solved using the quasi-Newton BFGS algorithm.

## 5. EXAMPLE OF RESULTS

The PPR78 EoS can be used to predict phase diagram for several applications. As mentioned above, its development required either experimental or molecular simulation data. These data will be used in order to determine the parameters of the groups (like  $CH_3$ ,  $CH_2$ ,  $CH$ ,  $CF_3$  or  $CO_2$  if the size of the group is very small). As an example for the determination of group parameters, experimental works were done concerning the  $CO_2 + R1234yf$  system. No molecular simulation calculations were done. We have combined the data obtained using two equipments, one for critical point data (figure 3) and another one for VLE data measurements.

This system was also investigated by Juntarachat et al. (2014). We can notice that the system can be a good candidate for car's air conditioning. The R1234yf is used to replace R134a. Phase equilibrium measurements were obtained from by means of an equipment whose technique is based on a static-analytic method. The parameterization of the model was done from critical point data measured with the equipment described on figure 3 (cf. results on figure 4). The combination of two techniques of measurement leads to a perfect representation of the phase diagram and so to a better estimation of the thermodynamic properties. This system was also investigated using molecular simulation technique (Monte Carlo). The figure 5, shows the accuracy of the method in comparison with experimental investigation.

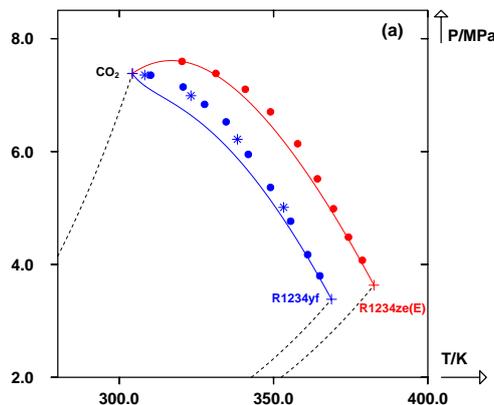


Figure 4: Comparison between experimental and calculated critical values and correlation with the PR78 model: (a): P-T projection, (b): P-x projection and (c): T-x projection. (●): Experimental critical points of the  $CO_2$  (1) + R1234yf (2) system. (\*): Calculated critical points of the  $CO_2$  (1) + R1234yf (2) system. (●): Experimental critical points of the  $CO_2$  (1) + R1234ze(E) (2) system. (+): Experimental critical points of the pure compounds. (Solid line): critical line calculated with the PR78 model. (Dashed line): vaporization curves predicted by the PR78 model.

Figure 5: rajouter VLE + molecular simulation (ajouter ref  $CO_2 + R1234yf$ ) voir Niramol

From PPR78, it is also possible to predict phase diagram of refrigerant mixtures. PPR78 parameters were obtained from experimental data adjustment on data

Jean Noel peux tu montrer un exemple de calcul d'utilisation de PPR78 pour predire le diag de pahse d'un refrigerant.

## 6. CONCLUSIONS

Considering the large number of candidate fluids and the different combinations possible for these fluids, it does not seem appropriate to rely only on experimental work to develop accurate EoS's, as experimental work can be rapidly substantial. In consequence, the development of predictive EoS's like group contribution EoS is very important. Parameterisation of these equations requires experimental work, but molecular simulation techniques can also be helpful. Molecular simulation calculations can also provide densities or transport properties. Measurements can be done on VLE properties including critical point data. Densities are determined in order to check the predictive capacity of the models and can help for parameterisation of interaction potentials used in molecular simulation (Monte Carlo simulation, for instance).

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