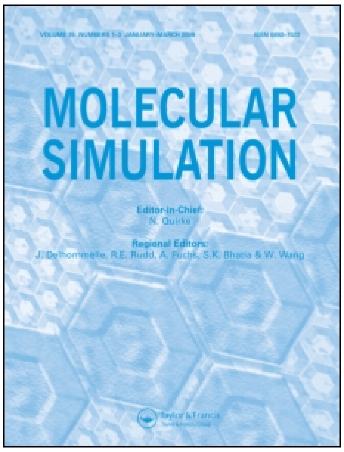

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Further Validation of a Set of Quadrupolar Potential Models for Ethylene and Propylene from the Prediction of some Binary Mixture Vapor-Liquid Equilibria by Gibbs-ensemble Molecular Simulation

Javier Carrero-Mantilla[a]; Mario Llano-Restrepo[a]
[a] School of Chemical Engineering, Universidad del Valle, Cali, Colombia

To cite this Article Carrero-Mantilla, Javier and Llano-Restrepo, Mario(2003) 'Further Validation of a Set of Quadrupolar Potential Models for Ethylene and Propylene from the Prediction of some Binary Mixture Vapor-Liquid Equilibria by Gibbs-ensemble Molecular Simulation', Molecular Simulation, 29: 9, 549 — 554

To link to this Article: DOI: 10.1080/0892702031000103275

URL: http://dx.doi.org/10.1080/0892702031000103275

Molecular Simulation, Vol. 29 (9), September 2003, pp. 549–554

Taylor & Francis
Taylor & Francis Group

Further Validation of a Set of Quadrupolar Potential Models for Ethylene and Propylene from the Prediction of some Binary Mixture Vapor–Liquid Equilibria by Gibbs-ensemble Molecular Simulation

JAVIER CARRERO-MANTILLA and MARIO LLANO-RESTREPO*

School of Chemical Engineering, Universidad del Valle, Apartado 25360, Cali, Colombia

(Received February 2003; In final form February 2003)

A set of two-center Lennard–Jones plus point quadrupole (2CLJQ) effective pair potential models for ethylene and propylene, that have already been shown to be capable of fitting the saturated densities, the vapor pressures, and the enthalpies of vaporization of the pure liquids, is tested for vapor–liquid equilibrium (VLE) of mixtures in this work. Monte Carlo simulations in the Gibbs ensemble were carried out in order to obtain VLE data for the binary systems methane + ethylene, ethylene + ethane, and ethane + propylene. No binary adjustable parameters were needed to compute the unlike-pair Lennard–Jones interactions in the binary systems. Simulation results were found to be in good agreement with the experimental data available for pressure and phase composition of the binary systems methane + ethylene at 150 and 190 K, ethylene + ethane at 233.15 and 255.37 K and ethane + propylene at 277.59 and 310.93 K.

Keywords: Quadrupolar fluids; Gibbs ensemble; Vapor liquid equilibria; Ethylene; Propylene

INTRODUCTION

Ethylene and propylene are olefinic hydrocarbons used for the production of various petrochemicals. An accurate knowledge of the vapor–liquid equilibrium (VLE) of mixtures of these components with methane and ethane is quite important for the design of the cryogenic separation trains that follow the turbo expansion and pyrolysis processing of natural gases containing significant amounts of ethane and propane [1].

Molecular simulation methods have already gained considerable importance for the prediction of fluid phase equilibria [2]. In particular, the Gibbs-ensemble Monte Carlo (GEMC) method, devised by Panagiotopoulos [3], and further developed by Panagiotopoulos *et al.* [4–7] and Smit *et al.* [8,9], has been implemented by various authors in order to predict VLE data for pure components and binary and multicomponent mixtures.

A set of two-center Lennard–Jones plus point quadrupole (2CLJQ) effective pair potential models for ethylene and propylene was recently developed by Vrabec *et al.* [10]. These potential models were shown by their proponents to be capable of fitting thermodynamic properties of the liquids such as the saturated densities, vapor pressures and enthalpies of vaporization. Because the development and testing of potential models that remain valid over wide ranges of state conditions and for a variety of systems of practical significance has been identified as one of the most important tasks for the continuing application of molecular simulation methods to the prediction of phase equilibria [11], it would be of interest to find out whether the potential models for ethylene and propylene proposed by Vrabec *et al.* [10] are capable of predicting the VLE behavior of mixtures of these substances with methane and ethane, which as pointed out above, is an important issue for the petrochemical industry.

In consequence, the aim of this work is to test, for VLE calculations, the potential models for ethylene and propylene proposed by Vrabec *et al.* [10].

---

*Corresponding author. Tel.: +57-2-3312935. Fax: +57-2-3392335. E-mail: mllano@mafalda.univalle.edu.co

ISSN 0892-7022 print/ISSN 1029-0435 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/0892702031000103275

For that purpose, Monte Carlo simulations in the Gibbs ensemble are carried out to obtain VLE data for the binary systems methane + ethylene, ethylene + ethane, and ethane + propylene. In the second section, details are given for the potential models used to describe the molecular interactions of the pure substances and binary systems considered in this study. In third section, simulation results are reported and compared with available experimental data. In the Appendix A, important computational details are provided for the purpose of making the results of this work as reproducible as possible.

INTERMOLECULAR POTENTIAL MODELS

In the present work, methane is described as a one-center Lennard–Jones (1CLJ) fluid, and ethane, ethylene and propylene as 2CLJQ fluids. A 1CLJ potential model validated by Vrabec *et al.* [10] is chosen for methane. The 2CLJQ potential models developed by Vrabec *et al.* [10], are chosen for ethane, ethylene and propylene. These potential models were shown by their proponents to be capable of fitting thermodynamic properties of the liquids, such as the saturated densities, vapor pressures and enthalpies of vaporization. The quadrupolar potentials for ethane, ethylene and propylene have not yet been tested for VLE of mixtures.

These molecular models are used to compute the total configurational energy U of these fluids by use of the pairwise additivity approximation with effective pair potentials given by the sum of Lennard–Jones (LJ) 12–6 interactions ϕ_{kl}^{LJ} between all pairs of intermolecular sites k (in molecule i) and l(in molecule j), and the point quadrupole-point quadrupole (QQ) intermolecular interactions (in the case of ethane, ethylene and propylene) between molecules i and j:

$$U = \sum_{k\in i}\sum_{l\in j}\phi_{kl}^{\mathrm{LJ}} + \sum_{i}\sum_{j}\phi_{ij}^{\mathrm{QQ}} \tag{1}$$

The LJ interaction between intermolecular sites k and l is given by the expression:

$$\phi_{kl}^{\mathrm{LJ}} = 4\varepsilon_{kl}\left[\left(\frac{\sigma_{kl}}{r_{kl}}\right)^{12} - \left(\frac{\sigma_{kl}}{r_{kl}}\right)^{6}\right] \tag{2}$$

where r_{kl} is the intersite separation distance and σ_{kl}, ε_{kl} are the size and energy parameters for the site k-site l interaction, respectively, which are defined in terms of the size parameters σ_k and σ_l of the molecules that lodge the sites by the commonly used combining rules:

$$\sigma_{kl} = \frac{\eta}{2}(\sigma_k + \sigma_l) \tag{3}$$

$$\varepsilon_{kl} = \xi(\varepsilon_k\varepsilon_l)^{1/2} \tag{4}$$

where η and ξ are adjustable coefficients (known as binary interaction parameters).

If $\eta = \xi = 1$, Eqs. (3) and (4) simplify to the well-known Lorentz–Berthelot (LB) combining rules [12]:

$$\sigma_{kl} = \frac{1}{2}(\sigma_k + \sigma_l) \tag{5}$$

$$\varepsilon_{kl} = (\varepsilon_k\varepsilon_l)^{1/2} \tag{6}$$

Table I lists values for the size and energy parameters σ and ε, and for the intramolecular center-to-center separation distance (elongation) L (if required) in the molecular models used for methane, ethane, ethylene and propylene. The bonding angle of propylene is not explicitly dealt with in the potential model proposed by Vrabec *et al.* [10], so that the charge distribution of that molecule is simplified to an axially symmetrical one.

Due precisely to the fact that the aim of this work is to ascertain the ability of the potential models proposed by Vrabec *et al.* [10] for pure ethylene and propylene to reproduce the experimental VLE data for some of the binary mixtures of these substances with methane and ethane, then no binary interaction parameters should be involved in the calculations, and in consequence, the LB combining rules, Eqs. (5) and (6), are employed to compute the unlike-pair LJ interactions.

Because the ethane, ethylene and propylene molecules are regarded as having axially symmetric charge distributions in the potential models by Vrabec *et al.* [10], the point quadrupole-point quadrupole (QQ) interaction between molecules i and j is given by the expression [13]:

$$\phi_{ij}^{\mathrm{QQ}} = \frac{3Q_iQ_j\Omega_{ij}}{4(r_{ij})^5} \tag{7}$$

The values of the quadrupole moments for ethane, ethylene and propylene are given in Table I. In reduced units, the quadrupole moment of molecule k is written as $(Q_k)^* = Q_k/(\varepsilon_k\sigma_k^5)^{1/2}$. For ethane, $(Q^*)^2 = 0.0700$, for ethylene, $(Q^*)^2 = 2.3483$ and for propylene, $(Q^*)^2 = 2.0922$.

The relative orientation of two linear molecules i and j is shown in Fig. C.2 (in Appendix C) of the classic textbook by Allen and Tildesley [12]. If vector $\mathbf{r}_{ij}$ is the intermolecular center-to-center separation vector, and θ_i and θ_j are the angles between $\mathbf{r}_{ij}$ and the unit vectors directed along the molecular axes $\mathbf{e}_i$ and

TABLE I Parameters for the potential models used in this work

Substance	*σ (Å)*	*ε/k (K)*	*L (Å)*	*Q (D Å)*	*Reference*
Methane	3.7281	148.55			[10]
Ethane	3.4896	136.99	2.3762	0.8277	[10]
Ethylene	3.7607	76.95	1.2695	4.3310	[10]
Propylene	3.8169	150.78	2.5014	5.9387	[10]

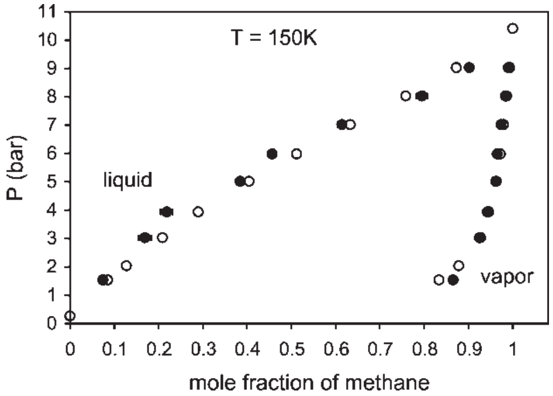

FIGURE 1 Pressure-composition diagram for methane + ethylene at 150 K. Filled circles: simulation results; Empty circles: experimental data [14]. Error bars, relative to the ensemble averages of the liquid and vapor mole fractions of methane, are on the average, 3 and 0.3%, respectively.

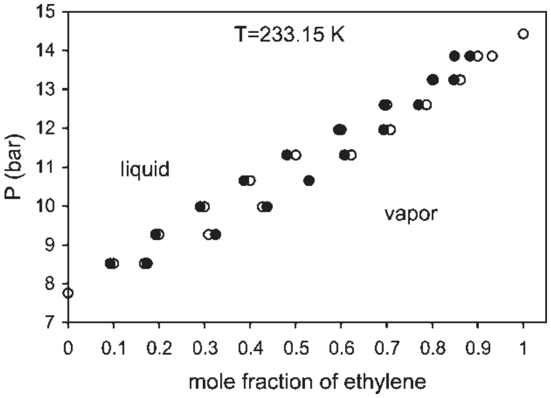

FIGURE 3 Pressure-composition diagram for ethylene + ethane at 233.15 K. Filled circles: simulation results; Empty circles: experimental data [15]. Error bars, relative to the ensemble averages of the liquid and vapor mole fractions of ethylene, are on the average, 1.3 and 0.5%, respectively.

$\mathbf{e}_j$, then the factor Ω_{ij} in Eq. (7) is given in terms of these angles by the following expression [12,13]:

$$\Omega_{ij} = 1 - 5\cos^2\theta_i - 5\cos^2\theta_j - 15\cos^2\theta_i\cos^2\theta_j + 2\left(\mathbf{e}_i\cdot\mathbf{e}_j - 5\cos\theta_i\cos\theta_j\right)^2 \tag{8}$$

where

$$\cos\theta_i = \frac{\left(\mathbf{e}_i\cdot\mathbf{r}_{ij}\right)}{\left|\mathbf{r}_{ij}\right|} \tag{9}$$

and

$$\cos\theta_j = \frac{\left(\mathbf{e}_j\cdot\mathbf{r}_{ij}\right)}{\left|\mathbf{r}_{ij}\right|} \tag{10}$$

SIMULATION RESULTS

Methane + ethylene

Simulation results for the pressure-composition (*P-xy*) diagrams of the system methane + ethylene at 150 and 190 K are presented in Figs. 1 and 2 together with the experimental data reported by Miller *et al.* [14]. As mentioned in "Intermolecular Potential Models" Section, no binary interaction parameters were used to compute the unlike-pair LJ interactions. As indicated by the position of the filled circles relative to the empty circles, the GEMC simulation results for methane + ethylene, are found to be in good agreement with experiment at the two temperatures considered in this study. The best agreement for liquid compositions is obtained at 190 K, and for vapor compositions at 150 K. In the lower and middle pressure ranges at 150 K, the mole fraction of methane in the liquid phase tends to be slightly underpredicted by simulation.

Ethylene + ethane

Simulation results for the pressure-composition (*P-xy*) diagrams of the system ethylene + ethane at 233.15 and 255.37 K are presented in Figs. 3 and 4

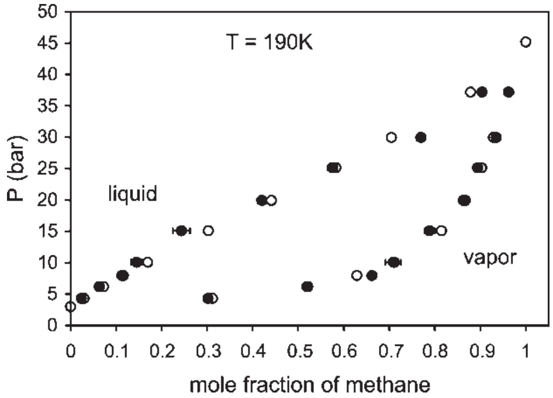

FIGURE 2 Pressure-composition diagram for methane + ethylene at 190 K. Filled circles: simulation results; Empty circles: experimental data [14]. Error bars, relative to the ensemble averages of the liquid and vapor mole fractions of methane, are on the average, 3.8 and 0.7%, respectively.

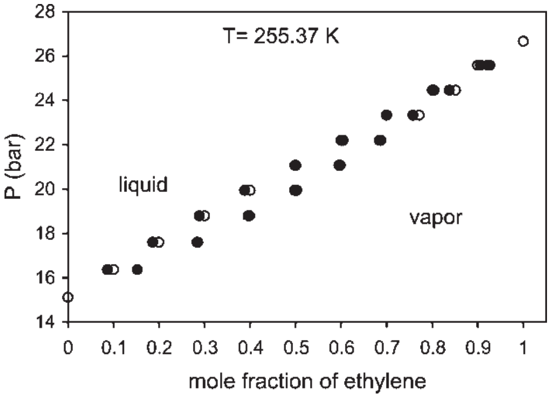

FIGURE 4 Pressure-composition diagram for ethylene + ethane at 255.37 K. Filled circles: simulation results; Empty circles: experimental data [15]. Error bars, relative to the ensemble averages of the liquid and vapor mole fractions of ethylene, are on the average, 1.2 and 0.7%, respectively.

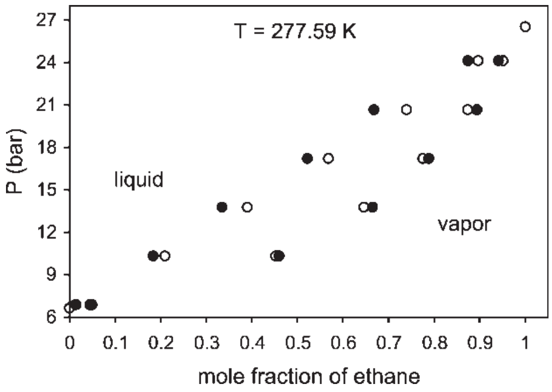

FIGURE 5 Pressure-composition diagram for ethane + propylene at 277.59 K. Filled circles: simulation results; Empty circles: experimental data [16]. Error bars, relative to the ensemble averages of the liquid and vapor mole fractions of ethane, are on the average, 1.3 and 0.9%, respectively.

together with the experimental data reported by Hanson *et al.* [15]. As mentioned in "Intermolecular Potential Models" Section, no binary interaction parameters were used to compute the unlike-pair LJ interactions. As indicated by the position of the filled circles relative to the empty circles, the GEMC simulation results for ethylene + ethane at the two temperatures considered in this study, are found to be in very good agreement with experiment. The best agreement for the liquid and vapor compositions is obtained at 255.37 K for all pressures.

Ethane + propylene

Simulation results for the pressure-composition (*P-xy*) diagrams of the system ethane + propylene at 277.59 and 310.93 K are presented in Figs. 5 and 6 together with the experimental data reported by McKay *et al.* [16]. As mentioned in "Intermolecular Potential Models" Section, no binary interaction parameters were used to compute the unlike-pair LJ interactions. As indicated by the position of the filled circles relative to the empty circles, the GEMC simulation results for ethane + propylene at the two temperatures considered in this study, are found to be in relatively good agreement with experiment. At both temperatures, the liquid compositions tend to be underpredicted by simulation in the middle pressure range.

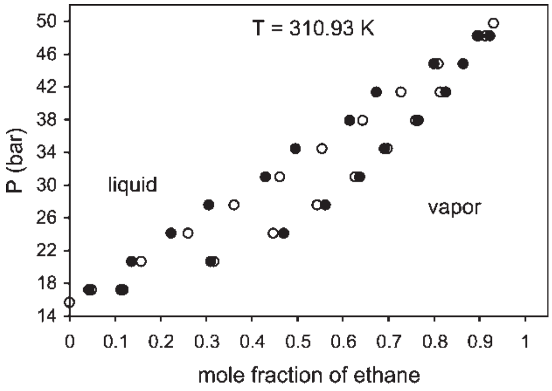

FIGURE 6 Pressure-composition diagram for ethane + propylene at 310.93 K. Filled circles: simulation results; Empty circles: experimental data [16]. Error bars, relative to the ensemble averages of the liquid and vapor mole fractions of ethane, are on the average, 1 and 0.8%, respectively.

CONCLUSIONS

The good agreement between the GEMC simulation results obtained in this work and the corresponding experimental data for the VLE of the binary systems methane + ethylene, ethylene + ethane and ethane + propylene, may be regarded as a further validation of the predictive capabilities of the potential models for ethylene and propylene proposed by Vrabec *et al.* [10]. With a set of potential parameters that are independent of temperature and density, it is possible to predict not only the VLE behavior of pure ethylene and propylene [10] but also the VLE of some of its binary mixtures with methane and ethane, as shown in the present work, without needing any binary interaction parameters to compute the unlike-pair LJ interactions. This validation seems to indicate the importance of taking the effect of the quadrupole interactions on VLE into account for the development of more refined potential models for ethylene and propylene.

Acknowledgements

Financial support from the School of Chemical Engineering, Universidad del Valle, Colombia, is gratefully acknowledged by the authors.

APPENDIX A

The methodology of the GEMC method has been described in detail elsewhere [3–9,17]. Two regions (cubic boxes) are used to simulate the two phases (liquid and vapor). Four kinds of trial moves are performed in the boxes: molecule translational (and rotational, if applicable) displacements, box volume changes, molecule transfers and molecule identity exchanges. The transfer moves are applied to the smaller molecules and the identity exchange moves are applied to the larger molecules. These four kinds of moves, when performed for a sufficiently large number of simulation steps, make possible for the two boxes to attain phase equilibrium. A Boolean scheme, devised by the present authors [18], was chosen for programming the transfer and identity exchange trial moves.

Since both temperature and pressure are specified at the beginning of a simulation run for a mixture, the condition of equilibrium is verified through the fulfillment of two sets of equalities: one for the chemical potential of the component of smaller molecules in each box, and the other for the difference between the chemical potentials of the components of larger molecules and the component of smaller molecules in each box. The expression to calculate the chemical potential of the component of smaller molecules was given by Smit and Frenkel [9], and the expression to calculate the difference between the chemical potentials of the components of larger molecules and the component of smaller molecules was recently derived by the present authors [19] and had previously been used by Liu and Beck [17].

Periodic boundary conditions (PBC) and the minimum image convention (MIC), as explained in detail by Allen and Tildesley [12], were applied for the computation of the total configurational energy U or any energy changes ΔU. The LJ interactions were spherically truncated at intersite distances $r_{kl} > 3.5\,\sigma_M$, where σ_M is the LJ size parameter of methane. In consequence, a long-range correction was added to the total configurational energy U, applying the analytical expression given by Allen and Tildesley [12] and extended to mixtures by de Pablo and Prausnitz [20].

Following Street and Tildesley [21] and Weingerl and Fischer [22], no long-range corrections were applied to the QQ interactions since a cutoff correction to the QQ potential vanishes due to the absence of angular ordering beyond the cutoff distance for fluids with quadrupole moments like those of ethane, ethylene and propylene.

Following a computational strategy used by Möller and Fischer [23], Vrabec and Fischer [24] and Stoll *et al.* [25] to calculate the chemical potential of quadrupolar fluids by the test particle method, a hard core of diameter 0.4σ (where σ is the LJ size parameter of ethylene or propylene) centered at the quadrupole site of the corresponding molecule, was used in this work to avoid large negative values of the quadrupolar interactions at the short intermolecular distances that may occur during the identity exchange moves for ethylene and propylene in the binary systems ethylene + ethane and ethane + propylene, respectively.

Simulation runs were initiated with 256 molecules in each box, with starting configurations generated from previous NPT-ensemble runs. GEMC simulation runs required an equilibration phase and a production phase, each consisting of a certain number of cycles, which in turn comprised all four kinds of trial moves. Typically, GEMC simulation runs consisted of a total of 5000 cycles with the first 2000 cycles for equilibration and the last 3000 cycles for production. In this way, a sufficiently large number of trial moves were performed during the equilibration phase as to attain stable values of the properties to be sampled in the production phase. A given cycle consisted of as many translational (and orientational, if required) sequential displacements as molecules were contained in each box, followed by one volume change trial move, 250 transfer attempts for randomly chosen molecules of the smaller size, and 50 identity exchange moves for randomly chosen molecules of the larger size. The value of 5 for the ratio of transfer to identity exchange moves was found to minimize in most cases the difference between the number of successful moves of each kind. The formulas for the probabilities of acceptance for the various kinds of moves [3–9,17] were applied to accept or reject a new configuration of the system according to the Metropolis importance sampling technique [12].

For the rotational moves required for ethane, ethylene, and propylene, random orientational displacements were applied following the scheme based on Euler angles, as described by Allen and Tildesley [12]. This method was chosen only for simplicity in developing the simulation code, even though it seems not to be the most efficient one when applied to linear molecules [12].

In this work, the blocking transformation method developed by Flyvbjerg and Petersen [26], and explained in practical detail by Frenkel and Smit [27], was implemented to compute the estimates of the statistical uncertainties (error bars) of the ensemble averages obtained from simulation. Typically, for each fluctuating property, a total of 2.5×10^5 values were saved to a one-dimensional array during the simulation run. At the end of the run, the entries of this array were collected to define the initial data block on which to apply Flyvbjerg and Petersen's blocking transformation.

References

[1] Matar, S. and Hatch, L.F. (2001) *Chemistry of Petrochemical Processes* (Gulf Professional Publishing, Boston) pp 7–8, pp 32–33.

[2] Panagiotopoulos, A.Z. (2000) "Monte Carlo methods for phase equilibria of fluids", *Journal of Physics and Condensed Matter* **12**, R25–R52.

[3] Panagiotopoulos, A.Z. (1987) "Direct determination of phase coexistence properties of fluids by Monte Carlo simulation in a new ensemble", *Molecular Physics* **61**, 813–826.

[4] Panagiotopoulos, A.Z., Quirke, N., Stapleton, M. and Tildesley, D.J. (1988) "Phase equilibria by simulation in the Gibbs ensemble, Alternative derivation, generalization and application to mixture and membrane equilibria", *Molecular Physics* **63**, 527–545.

[5] Panagiotopoulos, A.Z. and Stapleton, M.R. (1989) "The Gibbs method for molecular-based computer simulations of phase equilibria", *Fluid Phase Equilibria* **53**, 133–141.

[6] Panagiotopoulos, A.Z. (1989) "Exact calculations of fluid phase equilibria by Monte Carlo simulation in a new

statistical ensemble", *International Journal of Thermophysics* **10**, 447–457.

[7] Panagiotopoulos, A.Z. (1992) "Direct determination of fluid phase equilibria by simulation in the Gibbs ensemble: a review", *Molecular Simulation* **9**, 1–23.

[8] Smit, B., de Smedt, Ph. and Frenkel, D. (1989) "Computer simulations in the Gibbs ensemble", *Molecular Physics* **68**, 931–950.

[9] Smit, B. and Frenkel, D. (1989) "Calculation of the chemical potential in the Gibbs ensemble", *Molecular Physics* **68**, 951–958.

[10] Vrabec, J., Stoll, J. and Hasse, H. (2001) "A set of molecular models for symmetric quadrupolar fluids", *Journal of Physical Chemistry B* **105**, 12126–12133.

[11] Cummings, P.T., Peterson, B.K., Hall, C.K., Neurock, M., Panagiotopoulos, A.Z. and Westmoreland, P.R. (1997) *Final Report of the Workshop Future Directions in Molecular Modeling and Simulation: Fundamentals and Applications* (National Science Foundation, Arlington).

[12] Allen, M.P. and Tildesley, D.J. (1990) *Computer Simulation of Liquids* (Clarendon Press, Oxford) pp 21, pp 332–333.

[13] Buckingham, A.D. (1959) "Molecular quadrupole moments", *Quarterly Reviews of the Chemical Society* **13**, 183–214.

[14] Miller, R.C., Kidnay, A.J. and Hiza, M.J. (1977) "Liquid + vapor equilibria in methane + ethene and in methane + ethane from 150.0 to 190.0 K", *Journal of Chemical Thermodynamics* **9**, 167–178.

[15] Hanson, G.H., Hogan, R.J., Ruehlen, F.N. and Cines, M.R. (1953) "Ethane–ethylene system vapor–liquid equilibria at 0°, −40°, and −100° F", *Chemical Engineering Progress Symposium Series* **49**(6), 37–44.

[16] McKay, R.A., Reamer, H.H., Sage, B.H. and Lacey, W.N. (1951) "Volumetric and phase behavior in the ethane-propene system", *Industrial and Engineering Chemistry* **43**, 2112–2116.

[17] Liu, A. and Beck, T.L. (1998) "Vapor–liquid equilibria of binary and ternary mixtures containing methane, ethane and carbon dioxide from Gibbs ensemble simulation", *Journal of Physical Chemistry B* **102**, 7627–7631.

[18] Carrero-Mantilla, J. and Llano-Restrepo, M. (2003) "Boolean scheme for programming trial moves that involve molecule insertion and removal in Monte Carlo simulation", *Molecular Simulation* **29**(1), 23–28.

[19] Carrero-Mantilla, J. and Llano-Restrepo, M. (2003) "Derivation of the formula to calculate the chemical potential difference for the components involved in identity exchange moves in Gibbs ensemble simulation of mixtures", *Molecular Simulation* **29**(4), 255–257.

[20] De Pablo, J.J. and Prausnitz, J.M. (1989) "Phase equilibria for fluid mixtures from Monte Carlo simulation", *Fluid Phase Equilibria* **53**, 177–189.

[21] Street, W.B. and Tildesley, D.J. (1977) "Computer simulations of polyatomic molecules. Part II. Molecular dynamics studies of diatomic liquids with atom-atom and quadrupole-quadrupole potentials", *Proceedings of the Royal Society of London A* **355**, 239–266.

[22] Weingerl, U. and Fischer, J. (2002) "Consideration of dipole-quadrupole interactions in molecular based equations of state", *Fluid Phase Equilibria* **202**, 49–66.

[23] Möller, D. and Fischer, J. (1994) "Determination of an effective intermolecular potential for carbon dioxide using vapour–liquid phase equilibria from NpT + test particle simulations", *Fluid Phase Equilibria* **100**, 35–61.

[24] Vrabec, J. and Fischer, J. (1997) "Vapor–liquid equilibria of the ternary mixture $CH_4 + C_2H_6 + CO_2$ from molecular simulation", *American Institute of Chemical Engineers Journal* **43**, 212–217.

[25] Stoll, J., Vrabec, J., Hasse, H. and Fischer, J. (2001) "Comprehensive study of the vapour-liquid equilibria of the pure two-centre Lennard-Jones plus point quadrupole fluid", *Fluid Phase Equilibria* **179**, 339–362.

[26] Flyvbjerg, H. and Petersen, H.G. (1989) "Error estimates on averages of correlated data", *Journal of Chemical Physics* **91**, 461–466.

[27] Frenkel, D. and Smit, B. (1996) *Understanding Molecular Simulation* From Algorithms to Applications, (Academic Press, San Diego), pp 381–384.