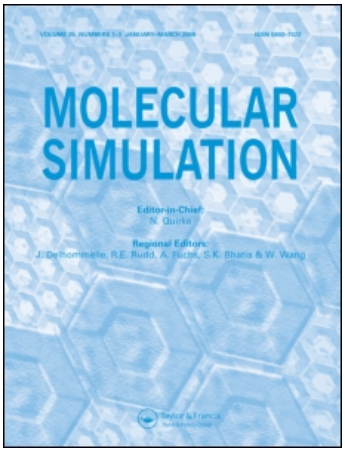

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Gibbs Ensemble Calculations with an Equation of State: An Application to Vapor-Liquid Equilibria

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To cite this Article Tsangaris, D. M. and McMahon, P. D.(1992) 'Gibbs Ensemble Calculations with an Equation of State: An Application to Vapor-Liquid Equilibria', Molecular Simulation, 9: 3, 223 — 238
To link to this Article: DOI: 10.1080/08927029208047429
URL: http://dx.doi.org/10.1080/08927029208047429

Molecular Simulation, 1992, Vol. 9, pp. 223–238
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GIBBS ENSEMBLE CALCULATIONS WITH AN EQUATION OF STATE AN APPLICATION TO VAPOR-LIQUID EQUILIBRIA

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(*Received December 1991, accepted December 1991*)

A new modification of the Gibbs ensemble Monte Carlo computer simulation method for fluid phase equilibria is described. The modification is based on a thermodynamic model for the vapor phase, and uses an equation of state to account for the weak interactions between the vapor phase molecules. Reductions in the computational time by 30–40% as compared to the original Gibbs ensemble method are obtained. The algorithm is applied to Lennard-Jones – (12, 6) fluids and their mixtures and the results are in good agreement with results obtained from simulations using the full Gibbs ensemble method.

KEY WORDS: Monte Carlo, Gibbs ensemble, vapor–liquid equilibrium, Lennard-Jones

1 INTRODUCTION

Following our previous work [1] we describe another algorithm for the calculation of vapor–liquid equilibria based on the Gibbs ensemble method introduced by Panagiotopoulos [2, 3]. The power of this technique and its modifications comes from the fact that a point on the vapor–liquid saturation curve can be located by performing a single simulation at the temperature of interest.

In the original approach of Pangiotopoulos [2, 3] the thermal equilibrium is established by using the Metropolis algorithm to control particle movements separately in each phase [4]. Mechanical equilibrium is achieved by performing volume exchanges between the two phases and chemical equilibrium is achieved by transferring particles from one phase into the other. The above steps are essential since they satisfy the necessary and sufficient Gibbs conditions for phase equilibria.

As it was shown in the modified Gibbs ensemble method [1], it is possible to reduce the computational effort required for vapor–liquid equilibrium (VLE) simulations by avoiding the exact calculation of the interactions between the particles in the vapor phase. Such a modification results in significant reductions since each phase typically accounts for about half the total computational effort. However, the lack of interactions between the vapor phase particles is equivalent to an ideal gas vapor phase model which can not predict very accurately vapor-liquid equilibrium properties at relatively high saturation pressures.

In this paper we describe a new approach to the modified Gibbs ensemble method. The proposed algorithm has the same computational complexity with our previous method but predicts more accurately the equilibrium properties. The method is based on statistical mechanics and uses an equation of state to predict the properties of the

vapor phase. In contrast to the modified Gibbs ensemble of [1] where the vapor phase was assumed to behave as an ideal gas, this version treats the vapor phase as a real gas and uses an equation of state to describe its non-ideal behavior.

The rest of the paper is organized as follows: In section 2 the theory for the proposed method with application to pure fluids is given and next the theory for the application of both versions of the modified Gibbs ensemble to mixtures is developed. In section 3 the theory needed for the application of the newly proposed algorithm to vapor–liquid equilibrium is presented and in section 4 simulation results for both pure fluids and mixtures are reported. In the appendix the reader can find technical details of the simulations.

2 THEORY

In this section we give the theoretical background of the proposed modified Gibbs ensemble method. The derivation following is for vapor–liquid equilibrium of pure Lennard-Jones fluids and mixtures. However, the method can be applied to any phase equilibrium problem when an analytic equation for the thermodynamic properties of one phase is available.

2.1 Pure Fluids

Starting from the partition function for the Gibbs ensemble we have that

$$Q_{NVT} = \frac{1}{\Lambda^{3N} N!} \sum_{N_v=0}^{N} \frac{N!}{N_v! N_l!} \int_0^V \mathrm{d}V_v V_v^{N_v} V_l^{N_l} \times \int \mathrm{d}r_v^{N_v} \exp(-\beta U_v) \int \mathrm{d}r_l^{N_l} \exp(-\beta U_l), \tag{1}$$

where Λ is the thermal de Broglie wavelength, $\beta = 1/k_B T$, r_v and r_l are the scaled coordinates of the particles, and $U_i(r_i;\ i = 1, \ldots, N)$ is the intermolecular potential of the N interacting particles. This is the exact expression for a system of simple monoatomic molecules but it can be extended very easily to polyatomic molecules; the derivation that follows however, deals with monoatomic molecules.

The contribution of the vapor phase to the partition function can be factored out by introducing the canonical partition function of this phase.

$$Q^v_{N_v V_v T} = \frac{V^{N_v}}{N_v! \Lambda^{3N_v}} \int \mathrm{d}r_v^{N_v} \exp(-\beta U_v). \tag{2}$$

For the canonical partition function of an ideal gas we have

$$Q^{ig}_{N_v V_v T} = \frac{V^{N_v}}{N_v! \Lambda^{3N_v}}, \tag{3}$$

which gives for the configurational partition function of a real gas in the canonical ensemble

$$Z_{N_v V_v T} = \int \mathrm{d}r_v^{N_v} \exp(-\beta U_v) = \frac{Q_{N_v V_v T}}{Q^{ig}_{N_v V_v T}}. \tag{4}$$

Substitution of Equation (4) into Equation (1) gives

$$Q_{NVT} = \frac{1}{\Lambda^{3N} N!} \sum_{N_v=0}^{N} \frac{N!}{N_v! N_l!} \int_0^V \mathrm{d}V_v V_v^{N_v} V_l^{N_l} \frac{Q_{N_v V_v T}}{Q^{ig}_{N_v V_v T}} \int \mathrm{d}r_l^{N_l} \exp(-\beta U_l). \tag{5}$$

The above partition function suggest a pseudo-Boltzmann weight factor

$$\exp\left[\ln \frac{N!}{N_v! N_l!} + N_v \ln V_v + N_l \ln V_l + \ln Q_{N_v V_v T} - \ln Q^{ig}_{N_v V_v T} - \beta U_l\right]. \tag{6}$$

For the canonical partition function of the vapor phase we can use the bridge equation and write

$$\ln Q_{N_v V_v T} - \ln Q^{ig}_{N_v V_v T} = -\beta(A_{N_v V_v T} - A^{ig}_{N_v V_v T}), \tag{7}$$

where $A_{N_v V_v T}$ is the Helmholtz energy of N_v particles at the temperature T and volume V_v. If we substitute Equation (7) back into Equation (6), the psuedo-Boltzmann weight factor will be

$$\exp\left[\ln \frac{N!}{N_v! N_l!} + N_v \ln V_v + N_l \ln V_l - \beta A^R_{N_v V_v T} - \beta U_l\right], \tag{8}$$

where A^R now is the residual Helmholtz energy of the vapor phase. Finally, from Equation (8) we can define a generalized energy Γ for this modified Gibbs ensemble (this quantity is analogous to the configurational energy of the canonical ensemble) as

$$\Gamma = -\frac{1}{\beta} \ln\left(\frac{N!}{N_v! N_l!}\right) - \frac{1}{\beta} N_v \ln V_v - \frac{1}{\beta} N_l \ln V_l + A_v^R + U_l. \tag{9}$$

Using Equation (9) we can implement a new Metropolis algorithm [4] which will sample the state space by displacing only the liquid phase particles, by changing the volume of both phases under constant total volume, and, finally, by transferring particles between the two phases.

The new configurations will be accepted with a probability P given by:

$$P = \min[1, \exp(-\beta \Delta\Gamma)] \tag{10}$$

where for $\Delta\Gamma$ we have:

(1) Particles displacement in liquid phase.

$$\Delta\Gamma = U_l^{\text{new}} - U_l^{\text{old}}. \tag{11}$$

(2) Exchange of volume between the liquid and the vapor phases, ΔV

$$\Delta\Gamma = (U_l^{\text{new}} - U_l^{\text{old}}) + (A_v^{R,\text{new}} - A_v^{R,\text{old}}) - \frac{N_v}{\beta} \ln\left(\frac{V_v^{\text{new}}}{V_v^{\text{old}}}\right) - \frac{N_l}{\beta} \ln\left(\frac{V_l^{\text{new}}}{V_l^{\text{old}}}\right). \tag{12}$$

(3) Transfer of a particle from the liquid to the vapor phase

$$\Delta\Gamma = (U_l^{\text{new}} - U_l^{\text{old}}) + (A_v^{R,\text{new}} - A_v^{R,\text{old}}) + \frac{1}{\beta} \ln\left(\frac{V_l(N_v + 1)}{V_v N_l}\right). \tag{13}$$

(4) Transfer of a particle from the vapor to the liquid phase

$$\Delta\Gamma = (U_l^{\text{new}} - U_l^{\text{old}}) + (A_v^{R,\text{new}} - A_v^{R,\text{old}}) + \frac{1}{\beta} \ln\left(\frac{V_v(N_l + 1)}{V_l N_v}\right). \tag{14}$$

We emphasize that the above equations are exact and do not involve any approximation. Furthermore, this modified Gibbs ensemble has fewer degrees of freedom because the particle positions of the vapor phase have been integrated out, and any Monte Carlo algorithm implemented along these guidelines will sample from a lower dimension state space. However, an expression for the Helmholtz energy of the vapor phase (or, in general, for the phase that is not simulated) is needed. For some classes of problems such expressions are available and one of those classes will be examined next.

2.2 Mixtures

For the *NPT* version one has to modify the previously given partition function for the *NVT* system of pure fluids in order to take into account the fluctuating total volume and the different mixture components. Thus, the partition function is given by

$$\begin{aligned} Q_{NPT} &= \frac{1}{\Lambda^{3N} N!} \sum_{N_v=0}^{N} \frac{N!}{N_v^{\alpha}! N_v^{\beta}! N_l^{\alpha}! N_l^{\beta}!} \\ &\quad \times \int_0^V \mathrm{d}V_v V_v^{N_v} V_l^{N_l} \exp(-\beta P V_v) \exp(-\beta P V_l) \\ &\quad \times \int \mathrm{d}r_v^{N_v} \exp(-\beta U_v) \int \mathrm{d}r_l^{N_l} \exp(-\beta U_l), \end{aligned} \tag{15}$$

Therefore, the ensemble average of any function $f(r^N)$ is simply

$$\begin{aligned} \langle f(r^N) \rangle &= \frac{1}{Q_{NPT} \Lambda^{3N} N!} \sum_{N_v=0}^{N} \frac{N!}{N_v^{\alpha}! N_v^{\beta}! N_l^{\alpha}! N_l^{\beta}!} \\ &\quad \times \int_0^V \mathrm{d}V_v V_v^{N_v} V_l^{N_l} \exp(-\beta P V_v) \exp(-\beta P V_l) \\ &\quad \times \int \mathrm{d}r_v^{N_v} \exp(-\beta U_v) \int \mathrm{d}r_l^{N_l} \exp(-\beta U_l) f(r^N). \end{aligned} \tag{16}$$

This partition function differs from the *NVT* form (Equation (1)) in two ways: the $N_{\text{phase}}^{\text{species}}$ terms, and the $\exp(-\beta P V_{\text{phase}})$ terms. The first one accounts for the way that N^{species} molecules can be distributed between the two phases, and the second one for the contribution of the fluctuating volumes.

Equation (15) gives rise to the following pseudo-Boltzmann factor:

$$\exp\left[\ln\left(\frac{N!}{N_v^{\alpha}! N_v^{\beta}! N_l^{\alpha}! N_l^{\beta}!}\right) + N_v \ln V_v + N_l \ln V_l - \beta P(V_v + V_l) - \beta U_v - \beta U_l\right]. \tag{17}$$

If we assume that the vapor phase behaves as an ideal gas mixture (version-1 of the modified Gibbs ensemble method, MGE) then the U_v term drops out and it is not necessary to keep track of the particle positions in this phase. So the probability distribution will be

$$\exp\left[\ln\left(\frac{N!}{N_v^{\alpha}! N_v^{\beta}! N_l^{\alpha}! N_l^{\beta}!}\right) + N_v \ln V_v + N_l \ln V_l - \beta P(V_v + V_l) - \beta U_l\right]. \tag{18}$$

Using the generalized energy Γ we have that

$$\Gamma_{MGE} = -\frac{1}{\beta}\ln\left(\frac{N!}{N_v^\alpha!N_v^\beta!N_l^\alpha!N_l^\beta}\right) - \frac{1}{\beta}N_v \ln V_v - \frac{1}{\beta}N_l \ln V_l + PV_v + PV_l + U_l. \tag{19}$$

If however, we use the version-2 of the modified Gibbs ensemble method (MGEV) described above for pure fluids then the generalized energy Γ will have the Helmholtz residual energy in place of the configurational energy of the vapor phase.

$$\Gamma_{MGEV} = -\frac{1}{\beta}\ln\left(\frac{N!}{N_v^\alpha!N_v^\beta!N_l^\alpha!N_l^\beta}\right) - \frac{1}{\beta}N_v \ln V_v + -\frac{1}{\beta}N_l \ln V_l + PV_v + PV_l + A_v^R + U_l. \tag{20}$$

Using Equation (19) and Equation (20) we can implement the steps of the modified algorithms described previously for studying mixtures vapor–liquid equilibria. However, the algorithm will slightly differ in the interchange step. As suggested by Panagiotopoulos *et al.* [3] this step should take place as follows:

(1) First, the phase that receives a particle should be determined with equal probability,

(2) Then the species that will undergo the transfer should be determined. The two species do not have to be chosen with equal probability, but their relative ratio must remain constant during the course of the simulation.

Finally, we should emphasize again that it is neither necessary to move particles in the vapor phase, nor to keep track of their exact positions. All we need is to monitor the number of particles of each species and the volume of the simulation sub-box.

3 APPLICATION TO VLE

3.1 Virial Equation of State

The Helmholtz free energy of a real gas can be evaluated using an equation of state. In this application we had the choice of the virial equation in the density form given by

$$z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \cdots \tag{21}$$

and in the pressure form given by

$$z = \frac{Pv}{RT} = 1 + \frac{BP}{RT} + \cdots \tag{22}$$

Here B is the second virial coefficient and z is the compressibility factor.

The choice of the EOS was motivated by the simplicity of the calcultions and the existence of statistical mechanical background. The virial coefficients can be calculated exactly from the molecular potential and, therefore, no extra parameters are introduced into the problem. In addition to that, the virial equation is particularly appropriate for studying vapor–liquid equilibria of mixtures due to the exactness on

the composition dependence. For example, the B_{mix} for a binary mixture can be calculated rigorously from

$$B_{mix} = y_\alpha^2 B_{\alpha\alpha} + 2y_\alpha y_\beta B_{\alpha\beta} + y_\beta^2 B_{\beta\beta}, \tag{23}$$

where for the $B_{\alpha\beta}$ is the virial coefficient for the interaction between molecules of species α and β.

In this work we assumed that the vapor phase is modeled accurately by the truncated form of the virial equation. Among the available pressure and density expressions we choose the pressure equation because on one hand it is more accurate, and on the other hand, experimental virial coefficients are often calculated by fitting experimental data to the truncated pressure equation.

3.2 Residual Helmholtz Energy

Using Equation (22) the pressure at given specific volume and temperature will be

$$P = RT/(v - B). \tag{24}$$

The Helmholtz energy (per mole) at given temperature and specific volume is given by [8]

$$\alpha = \int_v^\infty [P - RT/v]\, dv + \alpha^{ig} \tag{25}$$

where α^{ig} is the free energy of the ideal gas at the same conditions. Therefore, the residual part will be

$$\begin{aligned} \alpha^R &= \int_v^\infty [P - RT/v]\, dv \\ &\approx \int_v^\infty [RT/(v - B) - RT/v]\, dv \end{aligned} \tag{26}$$

After the integration the final expression for the residual Helmholtz energy is

$$\alpha^R = -RT \ln (1 - B/v) \tag{27}$$

The above equation is valid for both pure components and mixtures if in the latter case the virial coefficient of mixtures is used.

The equation of state has also been used to calculate other thermodynamic quantities needed in this work. The reader should refer to the appendix for the derivation of those quantities and for more details on the implementation of the algorithm.

4 RESULTS AND DISCUSSION

4.1 Pure Fluids

Table 1 contains the values for the second virial coefficient used in the simulations. The values have been evaluated through numerical integration of the following exact expression by Hierschfelder, Curtiss and Bird [5]

$$B^{HCB}(T) = -\frac{1}{2V} \int\int [\exp(-\beta u(r_{12})) - 1]\, d\mathbf{r}_1 d\mathbf{r}_2$$

Table 1 Second virial coefficient values for Lennard-Jones – (12, 6) potential. B^{HCB} is the reduced second virial coefficient reported in [5] with $B = b_0 B^{HCB}$ and $b_0 = 2\pi N\sigma^3/3$, the hard sphere virial coefficient. B^* is the reduced virial coefficient used in this work, $B^* = 2\pi B^{HCB}/3$. Also $B_1^{HCB} = T^*(dB^{HCB}/dT^*)$.

T^*	B^{HCB}	B^*	B_1^{HCB}	T^*dB^*/dT^*
0.75	−4.17592830	−8.74604378	7.25401350	15.19277035
0.90	−3.04711430	−6.38186127	5.26491840	11.02681931
1.00	−2.53808140	−5.31574525	4.42826160	9.27452941
1.15	−1.98264920	−4.15245077	3.55929250	7.45456478
1.20	−1.83594920	−3.84520301	3.33748930	6.99002124
1.25	−1.70377840	−3.56838514	3.14040740	6.57725388
1.30	−1.58410470	−3.31774113	2.96420400	6.20821434

where $u(r_{12})$ is the pair intermolecular potential of a simple Lennard-Jones – (12, 6) fluid.

For the Helmholtz free energy Equation (A.1) was used. No major modifications in the programming code was necessary since the above equation replaces the function that calculates the configurational energy (of the vapor phase) in the full Gibbs ensemble. To avoid other modifications, Equation (A.6) was used, within the same function call, in place of the explicit evaluation of the virial. The chemical potential of the vapor phase was calculated at the end of the simulation using Equation (A.12) and the ensemble average vapor density.

Table 2 and Figure 1 show that the new modified Gibbs ensemble is able to predict the properties of simple Lennard-Jones fluids adequately. At temperatures up to $T^* = 1.15$ the results are within the experimental error. The above temperature correponds to a reduced temperature (with respect to the critical temperature) of $T' = T/T_c = 0.87$. Up to these temperatures the truncated virial equation of state sufficiently describes the behavior of real gas and no discrepancies are expected. For temperatures of $T^* = 1.20$ and above, or $T_r \geqslant 0.90$, the model predicts a density for the vapor phase which is lower than the one obtained using the full Gibbs ensemble, but there is significant improvement over the previous model that treated the vapor phase as an ideal gas. At much higher temperatures, the algorithm still converges in contrast to the "ideal vapor" model which fails to reach the equilibrium values. The results for the liquid phase are very much in agreement with the full Gibbs ensemble results up to $T^* = 1.20$. This is something that we also observed in the "ideal vapor" model and confirms that the liquid phase is not very sensitive to the small changes in the behavior of the vapor phase at those conditions.

Table 3 contains the values of the configurational chemical potential. The vapor phase chemical potential was obtained at the end of simulation using the ensemble average vapor density and Equation (A.12). For the liquid phase, we used Equation (C.1) (Widom's expression) and Equation (C.2) (Smit and Frenkel's expression). Both equations give almost the same estimates for the chemical potential of the liquid phase especially at low temperatures where the fluctutions in the number density are very small. Comparison between the chemical potentials of the two phases shows that there is a very good mutual agreement between the "configurational" chemical potential of the vapor and the liquid phase. It should be mentioned here that no error estimates for the chemical potential were obtained because the values were calculated from the total length of the simulation.

The overhead associating with the equation of state is insignificant and as a result

Table 2 Comparison of the calculated vapor–liquid coexistence properties of the Lennard-Jones – (12, 6) fluid as obtained from the Gibbs ensemble method (GE) the modified Gibbs ensembles, version-1(MGE) and the version-2 with an EOS discussed in the text (MGEV). References: [1] Tsangaris (1991); [2] Panagiotopoulos (1988); [3] Frenkel (1989). $T^* = k_B T/\varepsilon$, $\rho = N\sigma^3/V$, $P^* = P\sigma^3/\varepsilon$ and $\mu^* = \mu/\varepsilon$. The number in the brackets is the accuracy of the last digit(s).

N	*Method*	T^*	ρ_v^*	ρ_l^*	P_v^*	P_l^*	U_v^*	U_l^*	μ_v^*	μ_l^*
216	VMGE	0.75	0.0025(1)	0.815(4)	0.0018(1)	0.0096(313)	−0.028(2)	−5.84(3)	−4.54	−4.64
216	MGE[1]		0.0023(2)	0.814(6)	0.0017(2)	0.005(36)	−0.000	−5.84(5)	−4.56	−4.46
216	GE[1]		0.0023(2)	0.819(3)	0.0016(1)	0.0012(313)	−0.045(2)	−5.87(3)	−4.59	−4.62
500	GE[2]		0.0031(3)	0.819(3)	0.0023(3)	0.019(36)	−0.035(3)	−5.88(3))	−4.38	−4.35
216	VMGE	0.90	0.0117(13)	0.749(6)	0.0098(10)	0.002(14)	−0.108(11)	−5.29(5)	−4.13	−4.00
216	MGE[1]		0.0105(10)	0.750(6)	0.0095(9)	0.016(33)	−0.000	−5.29(5)	−4.10	−4.03
216	GE[1]		0.0120(8)	0.747(4)	0.0117(8)	0.014(21)	−0.083(6)	−5.26(3)	−4.12	−4.10
300	GE[2]		0.0151(3)	0.758(9)	0.0123(6)	0.014(37)	−0.145(15)	−5.36(6)	−3.95	−3.86
216	VMGE	1.00	0.0258(23)	0.700(5)	0.0227(17)	0.036(29)	−0.211(16)	−4.88(34)	−3.91	−3.90
216	MGE[1]		0.0202(13)	0.698(8)	0.0202(13)	0.027(19)	−0.000	−4.87(6)	−3.89	−3.83
216	GE[1]		0.0252(9)	0.695(6)	0.0203(6)	0.010(23)	−0.218(7)	−4.85(5)	−3.94	−3.95
300	GE[2]		0.0291(6)	0.702(6)	0.0246(12)	0.024(27)	−0.275(18)	−4.90(3)	−3.90	−3.85
216	VMGE	1.15	0.062(8)	0.598(14)	0.057(6)	0.059(23)	−0.424(42)	−4.11(9)	−3.69	−3.65
216	MGE[1]		0.038(3)	0.594(15)	0.044(3)	0.045(16)	−0.000	−4.09(10)	−3.76	−3.73
216	GE[1]		0.069(7)	0.602(10)	0.051(13)	0.059(20)	−0.616(22)	−4.14(7)	−3.70	−3.65
300	GE[2]		0.083(6)	0.612(9)	0.064(5)	0.075(24)	−0.712(18)	−4.20(6)	−3.63	−3.63
216	GE[3]		0.075(3)	0.607(8)	0.062(3)	0.07(2)	−0.67(5)	−4.18(7)	−3.71	−3.69
216	VMGE	1.20	0.084(12)	0.584(15)	0.076(8)	0.119(27)	−0.53(56)	−3.99(10)	−3.60	−3.65
216	MGE[1]		0.047(5)	0.548(27)	0.056(6)	0.057(20)	−0.00	−3.76(17)	−3.67	−3.68
216	GE[1]		0.090(13)	0.551(33)	0.071(9)	0.073(21)	−0.75(11)	−3.87(20)	−3.66	−3.69
216	GE[3]		0.112(31)	0.564(24)	0.079(7)	0.08(3)	−0.95(26)	−3.87(16)	−3.66	−3.66
216	VMGE	1.25	0.120(10)	0.574(19)	0.105(6)	0.196(30)	−0.69(4)	−3.89(13)	−3.47	−3.49
300	GE[2]		0.148(3)	0.526(15)	0.101(6)	0.108(20)	−1.18(3)	−3.59(9)	−3.59	−3.56

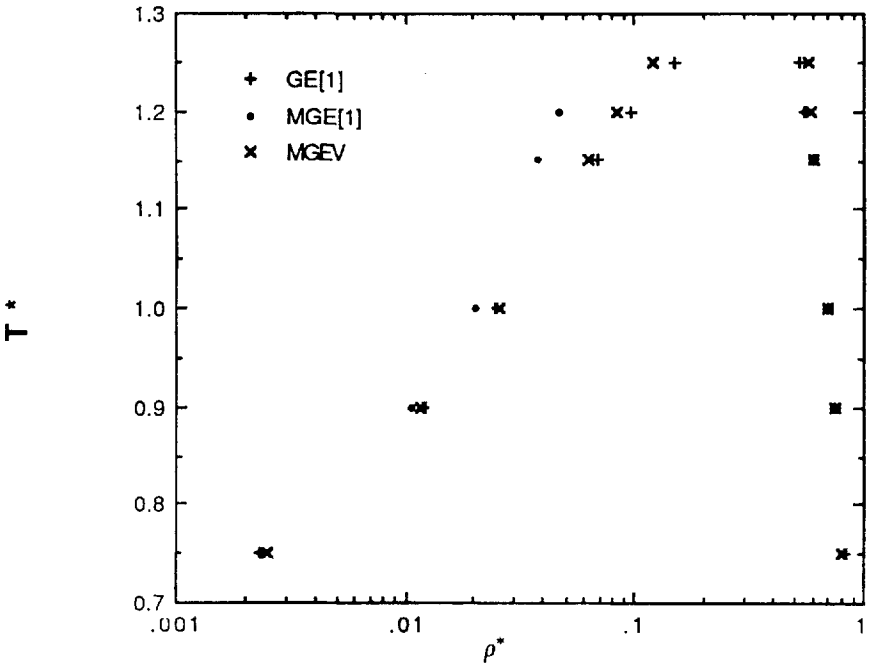

Figure 1 Vapor–liquid coexistence curve for a Lennard-Jones – (12, 6) fluid as obtained from the standard Gibbs ensemble (GE) and the modified methods described in [1] (MGE) and in the text (MGEV).

the proposed algorithm falls into the same class with the first version of the modified Gibbs ensemble. Complete time analysis of the modified Gibbs ensemble method can be found in our previous paper [1].

4.2 Mixtures

For the simulation of mixtures one has a choice between an NPT and an NVT system. That is, the composite vapor–liquid system can have constant number density or constant pressure. Both systems however, must have constant temperature and constant total number of particles. This choice rises from the fact that a binary mixture has an extra degree of freedom compared to a pure fluid. For vapor–liquid

Table 3 Comparison between the chemical potential of the vapor phase as obtained from the virial EOS using Equation (A.12) and the chemical potential of the liquid phase as obtained from the simulation using (C.1) and (C.2).

T^*	μ_v^{EOS}	μ_l^W	μ_l^F
0.75	−4.535	−4.639	−4.639
0.90	−4.130	−4.003	−4.003
1.00	−3.905	−3.901	−3.897
1.15	−3.694	−3.654	−3.648
1.20	−3.547	−3.546	−3.545
1.25	−3.459	−3.495	−3.457

Table 4 Lennard-Jones mixture parameters and virial coefficients for the various interaction types. Symbols are as in Table 1.

T^*	*Interaction type*	ε	σ	B^*	dB^*/dT
1.00	1 – 1	1	1	−5.315745	9.274529
	2 – 2	1	1	−5.315745	9.274529
	1 – 2	0.750	1	−3.165761	4.493785

calculations the NPT version is more useful than the NVT because it allows the pressure to be specified externally, whereas in the NVT system the pressure is calculated from the virial equation as an ensemble average and therefore is subject to random error. Accurate knowledge of the pressure is important because one is usually interested in constructing a P, T, x rather than a ρ, T, x diagram. For those reasons in the application of the modified Gibbs ensembles to mixtures we chose the NPT system. The implementation of the NVT would be a simple modification that would require minor changes in the computer code.

The mixture simulated was a mixture of simple spherical Lennard-Jones particles. Table 4 gives the values of the LJ parameters of the mixture and the values of the virial coefficients for the three types of interactions.

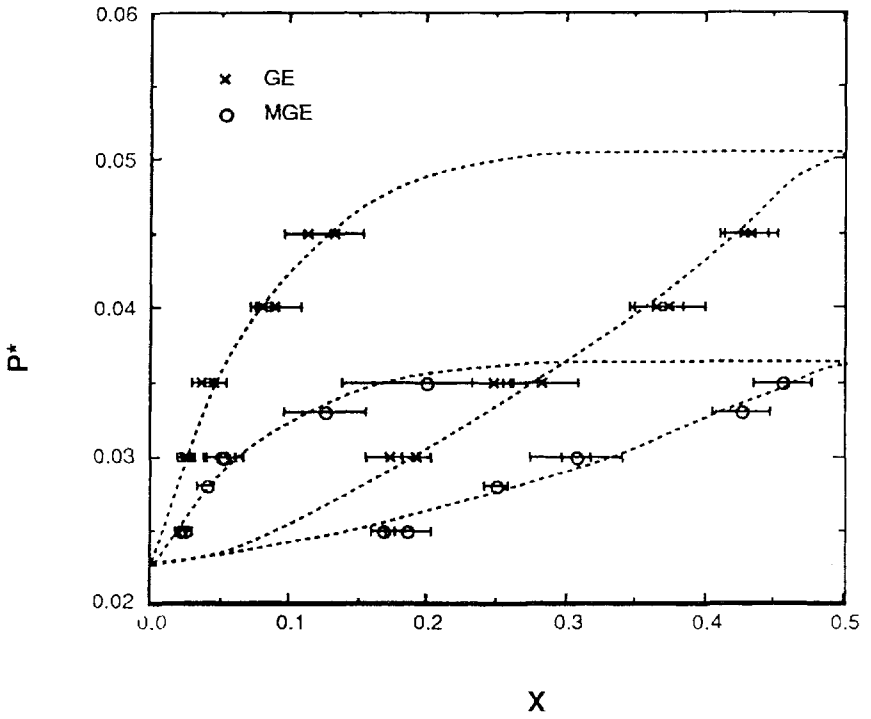

Figure 2 Vapor–liquid coexistence curve for a Lennard-Jones – (12, 6) mixture as obtained from the standard Gibbs ensemble (GE) and the modified method which assumes ideal gas mixture vapor phase (MGE). The dashed lines are drawn as a guide to the eye.

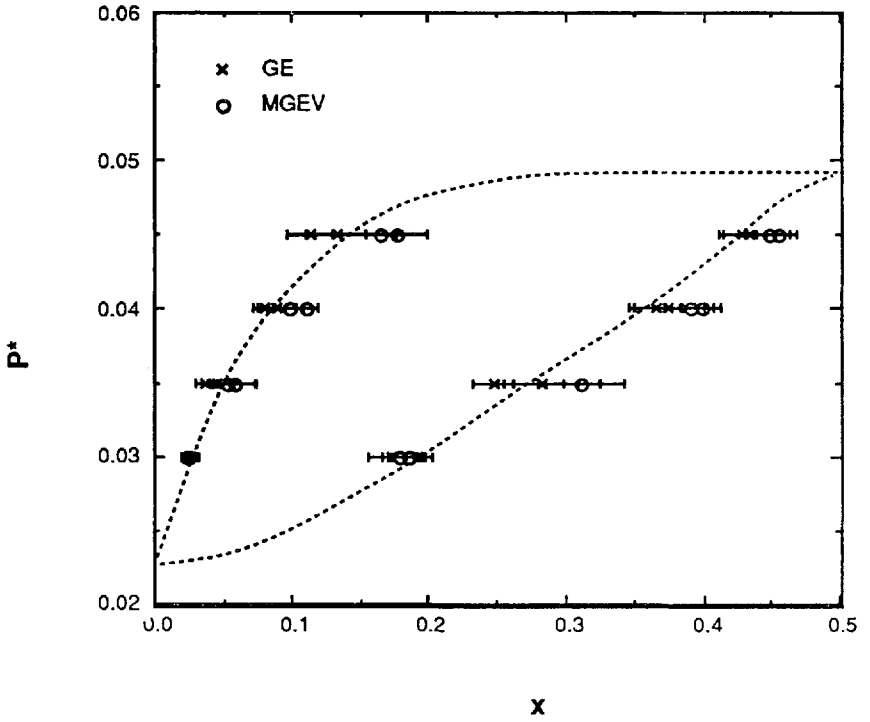

Figure 3 Vapor–liquid coexistence curve for a Lennard-Jones – (12, 6) mixture as obtained from the standard Gibbs ensemble (GE) and the modified method which uses the virial equation of state for the vapor phase (MGEV). The dashed lines are drawn as a guide to the eye.

For this mixture the size parameters of the two species are the same. The energies of interaction between like molecules (ε_{11}, ε_{22}) are also the same but the unlike interaction parameter, ε_{12}, differs giving rise to positive excess Gibbs energies. This kind of mixture is symmetric and shows an azeotrope for a mole fraction of 0.5. Table 5 compares the calculated properties from the full and the modified Gibbs ensembles. In Figures 2 and 3 the P, T, x diagram for the reduced temperature of $T^* = 1.00$ is given. From Figure 2 we can conclude that the modified model which assumes ideal gas vapor phase (MGE) is able to predict the azeotrope and to give a qualitative description of the system. For mixtures "rich" in α (or β since it is symmetric) the modified and the original model gives almost indistinguishable results. As the mixture composition approached $x = 0.5$ the deviations increases and the model underestimates the azeotrope. The newly proposed algorithm however (*MGEV*), which uses the virial equation of state to describe the behavior of the vapor phase, gives excellent results and slightly underestimates the azeotrope (Figure 4).

The above results are in full agreement with the results obtained for the pure fluids. First of all, at any fixed composition the mixture can be thought of as a pure fluid that has an "effective" ε which depends on the compositions. As the mixture composition moves away from the azeotrope the ε_{mix} approaches the value of 1 (pure α) and the mixture behaves as a pure component at $T^* = 1.00$ ($T^* = T/k_B\varepsilon_\alpha$). As it was shown

Table 5 Comparison of the calculated vapor–liquid coexistence properties of the Lennard-Jones – (12, 6) mixture as obtained from the Gibbs ensemble method (GE) and the modified Gibbs ensembles, (MGE) and (MGEV). The vapor phase properties were calculated at the end of the simulation using Equations (A.9) for the energy, (A.5) for the pressure and (B.16) for the chemical potential. The other symbols are as in Table 2.

	Phase coexistence properties of Lennard-Jones mixture. $T^* = 1.00$											
Method	P^*	U_v^*	U_l^*	P_v^*	P_l^*	ρ_v^*	ρ_l^*	$x_{v\alpha}^*$	$x_{l\alpha}^*$	$\mu_{v\alpha}^*$	$\mu_{l\alpha}^*$	$\mu_{v\beta}^*$	$\mu_{l\beta}^*$
GE	0.030	−0.299(4)	−4.767(56)	0.030(0)	0.028(25)	0.036(0)	0.693(7)	0.192(11)	0.027(4)	−5.222	−5.302	−3.885	−3.878
GE	0.030	−0.304(6)	−4.795(57)	0.030(0)	0.042(11)	0.036(0)	0.696(6)	0.173(17)	0.024(5)	−5.333	−5.278	−3.863	−3.868
GE	0.035	−0.351(5)	−4.787(53)	0.035(0)	0.048(21)	0.043(0)	0.699(5)	0.248(15)	0.037(8)	−4.846	−4.915	−3.830	−3.856
GE	0.035	−0.346(3)	−4.704(75)	0.035(1)	0.037(17)	0.043(0)	0.690(8)	0.283(27)	0.046(8)	−4.727	−4.751	−3.872	−3.883
GE	0.040	−0.397(6)	−4.553(41)	0.040(0)	0.040(11)	0.051(0)	0.679(4)	0.365(19)	0.081(6)	−4.381	−4.411	−3.882	−3.893
GE	0.040	−0.394(8)	−4.502(81)	0.040(0)	0.025(13)	0.051(1)	0.674(7)	0.375(26)	0.090(19)	−4.360	−4.374	−3.894	−3.908
GE	0.045	−0.466(13)	−4.466(68)	0.045(1)	0.039(16)	0.060(1)	0.675(6)	0.428(18)	0.113(16)	−4.135	−4.253	−3.879	−3.884
GE	0.045	−0.459(8)	−4.387(82)	0.045(0)	0.052(9)	0.060(1)	0.668(7)	0.434(19)	0.132(21)	−4.128	−4.057	−3.895	−3.882
MGE	0.025	0.000(0)	−4.798(29)	0.025(0)	0.026(23)	0.025(0)	0.695(3)	0.168(9)	0.021(4)	−5.472	−5.481	−3.869	−3.802
MGE	0.025	0.000(0)	−4.748(67)	0.025(0)	0.020(22)	0.025(0)	0.689(7)	0.186(16)	0.024(5)	−5.368	−5.308	−3.892	−3.894
MGE	0.028	0.000(0)	−4.734(42)	0.028(0)	0.037(15)	0.028(0)	0.692(5)	0.250(9)	0.040(6)	−4.961	−4.995	−3.861	−3.878
MGE	0.030	0.000(0)	−4.672(78)	0.030(0)	0.024(14)	0.030(0)	0.687(7)	0.308(33)	0.052(14)	−4.681	−4.620	−3.872	−3.876
MGE	0.030	0.000(0)	−4.690(62)	0.030(0)	0.033(22)	0.030(0)	0.689(6)	0.308(10)	0.051(11)	−4.685	−4.737	−3.874	−3.860
MGE	0.033	0.000(0)	−4.374(129)	0.033(0)	0.038(30)	0.033(0)	0.665(13)	0.426(21)	0.126(29)	−4.262	−4.133	−3.964	−3.954
MGE	0.035	0.000(0)	−4.150(200)	0.035(0)	0.035(13)	0.035(0)	0.642(13)	0.456(21)	0.199(61)	−4.138	−4.003	−3.960	−3.902
MGEV	0.030	−0.237(0)	−4.801(13)	0.030(0)	0.039(18)	0.035(0)	0.696(2)	0.179(13)	0.023(4)	−5.298	−5.388	−3.857	−3.888
MGEV	0.030	−0.236(0)	−4.792(79)	0.030(0)	0.024(32)	0.035(0)	0.695(9)	0.185(12)	0.025(4)	−5.265	−5.191	−3.863	−3.811
MGEV	0.035	−0.254(0)	−4.658(39)	0.035(0)	0.027(07)	0.042(0)	0.686(5)	0.312(13)	0.053(4)	−4.627	−4.744	−3.892	−3.927
MGEV	0.035	−0.254(0)	−4.659(83)	0.035(0)	0.036(17)	0.042(0)	0.687(8)	0.312(31)	0.057(17)	−4.626	−4.539	−3.893	−3.901
MGEV	0.040	−0.281(0)	−4.464(43)	0.040(0)	0.031(13)	0.049(0)	0.674(5)	0.398(15)	0.111(8)	−4.284	−4.244	−3.907	−3.899
MGEV	0.040	−0.282(0)	−4.509(45)	0.040(0)	0.041(10)	0.049(0)	0.677(4)	0.390(17)	0.098(11)	−4.306	−4.275	−3.895	−3.908
MGEV	0.045	−0.313(0)	−4.314(59)	0.045(0)	0.051(16)	0.056(0)	0.665(7)	0.448(16)	0.165(12)	−4.079	−4.071	−3.890	−3.889
MGEV	0.045	−3.313(0)	−4.251(65)	0.045(0)	0.043(17)	0.056(0)	0.658(7)	0.454(15)	0.176(23)	−4.068	−4.053	−3.901	−3.896

earlier, the modified methods gives good predictions at this temperature range and the mixture is simulated satisfactorily. As the mixture moves close to the azeotrope, the ε_{mix} approaches a value close to $\varepsilon_{12} = 0.75$ and the mixtures behaves as a pure component at T^* much higher than 1.00. (A value of $\varepsilon_{12} = 0.75$ corresponds to a $T^* = 1.33$). In those conditions the modified models underestimate the vapor phase properties of pure components resulting in the underestimation of the mixture azeotrope. The success of the new method however are due mostly to the higher accuracy of the algorithm at higher saturation pressures.

In conclusion, the newly proposed modified Gibbs ensemble is able to accurately predict the properties of pure components in chemical equilibria. In addition to that, the thermodynamic models proposed have been shown to accurately predict the thermodynamic properties of mixtures when the vapor phase is modeled as an ideal or as a real gas. At extreme conditions the models still give quantitatively reasonable description of the system. Computationally, they reduce the CPU requirements by 30–40%, a reduction independent of the complexity of the intermolecular potential and the number of species.

ACKNOWLEDGEMENT

This work was supported in part by the Greek Government/NATO Fellowship. Special thanks to Pr. S.T. Kim for the allocation of computer resources.

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APPENDIX

A *Statistical Mechanics Notation*

The equation of state can be used to calculate thermodynamic quantities needed for a complete description of the system. However, for a reasonable comparison a reduction in the statistical mechanics notation must take place by initially reducing the above quantities in units "per molecule" and finally by applying another reduction with respect to the Lennard-Jones parameters ε and α. In the later notation $T^* = k_B T/\varepsilon$, $\rho^* = \rho\sigma^3$, and $P^* = P\sigma^3/\varepsilon$. Here ρ is the number density equal to N/v where

v is the molar specific volume. Also for the second virial coefficient B given in volume/mole we define $B^* = B/\sigma^3 N$.

A.1 Residual Helmholtz energy

For the Helmholtz residual energy we have using Equation (27) that

$$\begin{aligned} A^R &= \alpha^R/N = -k_B T \ln (1 - B/v) \\ A^{*R} &= A^R/\varepsilon = -T^* \ln (1 - B^*\rho^*) \end{aligned} \tag{A.1}$$

A.2 Pressure and excess pressure

Using Equation (24) the pressure of the vapor phase is given by:

$$P = RT/(v - B) \tag{A.2}$$

It is also possible to define the excess pressure from

$$P = P^{ig} + P^{ex} \tag{A.3}$$

where $P^{ig} = rT/v$ and therefore $P^{ex} = RTB/v(v - B)$. The P^{ex} is related to the "virial" w (per mole) with $P^{ex} = w/v$. As a result

$$w = RTB/(v - B) \tag{A.4}$$

Returning to the statistical mechanics notation and using Equation (24) the reduced pressure is:

$$\begin{aligned} P &= k_B TN/(v - B) \\ P^* &= P\sigma^3/\varepsilon = T^*\rho^*/(1 - B^*\rho^*) \end{aligned} \tag{A.5}$$

while from Equation (A.4) the reduced virial is:

$$\begin{aligned} W &= w/N = k_B TB/(v - B) \\ W^* &= W/\varepsilon = T^*B^*\rho^*/(1 - B^*\rho^*) \end{aligned} \tag{A.6}$$

The virial pressure ($P^{ex} = W/v$) is due to intermolecular forces. Version-2 of the modified Gibbs ensemble implicitly evaluates the contribution of those forces to the vapor phase mechanical properties (through the second virial coefficient). This in contrast to the full Gibbs ensemble where an explicit calculation takes place.

A.3 Internal energy

For the internal energy (per mole) at given specific volume and temperature we have that

$$u^R = \int_v^\infty \left[P - T\left(\frac{\partial P}{\partial T}\right)_v \right] \mathrm{d}v \tag{A.7}$$

Using the equation of state and carrying out the integration we get that

$$u^R = -RT^2 \frac{\mathrm{d}B}{\mathrm{d}T} \Big/ (v - B) \tag{A.8}$$

In the statistical mechanics notation Equation (A.8) gives:

$$\begin{aligned} U^R &= u^R/N = -k_B T^2 \frac{\mathrm{d}B}{\mathrm{d}T} \Big/ (v - B) \\ U^* &= T^R/\varepsilon = -T^{*2} \frac{\mathrm{d}B^*}{\mathrm{d}T^*} \rho^*/(1 - B^*\rho^*) \end{aligned} \tag{A.9}$$

A.4 Residual chemical potential

For the residual chemical potential (per mole) of a pure component at given specific volume and temperature we have

$$\begin{aligned} \mu^R &= \int_v^\infty [P - RT/v]\,dv + v(P - P^{ig}) \\ &= A^R + v(P - P^{ig}) \\ &= -RT \ln (1 - B/v) + RTB/(v - B) \end{aligned} \tag{A.10}$$

Using Equation (A.10) the statistical mechanics expression gives:

$$\begin{aligned} \mu^R/N &= -k_B T \ln (1 - B/v) + k_B TB/(v - B) \\ \mu^* &= \mu^R/N\varepsilon = -T^* \ln (1 - B^*\rho^*) + T^*B^*\rho^*/(1 - B^*\rho^*) \end{aligned} \tag{A.11}$$

However for the simulations the "configurational" potential is usally reported,

$$\begin{aligned} \mu_c^* &= \mu^* + T^* \ln \rho^* \\ &= -T^* \ln (1 - B^*\rho^*) + T^*B^*\rho^*/(1 - B^*\rho^*) + T^* \ln \rho^* \end{aligned} \tag{A.12}$$

For mixtures, the same equations were used after the virial coefficient of the pure component was replaced by the corresponding one for mixtures (Equation (23)). For the calculation of the chemical potential of the mixture species however, we postpone our discussion to the next section.

B *Vapor Phase Chemical Potential*

For the version-1 of the modified Gibbs ensemble method which treated the vapor phase as an ideal gas mixture the configurational chemical potential of species α was calculated from

$$\mu_\alpha^* = T^* \ln \rho^* x_\alpha \tag{B.13}$$

In version-2, where the vapor phase was treated as a real gas mixture modeled with the virial equation of state, the chemical potential of species α was calculated from:

$$\begin{aligned} \mu_\alpha^R &= \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{V,T,n_j} - RT/V \right] dV \\ &= -RT \ln (1 - B_{\text{mix}}/v) + RTC_\alpha/(v - B_{\text{mix}}) \\ \mu_\alpha^* &= \mu_\alpha^R/N\varepsilon = -T^* \ln (1 - B_{\text{mix}}^*\rho^*) + T^*C_\alpha^*\rho^*/(1 - B_{\text{mix}}^*\rho^*) \end{aligned} \tag{B.14}$$

where

$$\begin{aligned} C_\alpha^* &= 2y_\alpha B_{\alpha\alpha}^* + 2y_\beta B_{\alpha\beta}^* - B_{\text{mix}}^* \\ B_{\text{mix}}^* &= y_\alpha^2 B_\alpha^* + 2y_\alpha y_\beta B_\alpha^* + y_\beta^2 B_{\beta\beta}^* \end{aligned} \tag{B.15}$$

In the statistical mechanics notation the "configurational" chemical potential of species α is finally given by

$$\begin{aligned} \mu_{c\alpha}^* &= \mu_\alpha^* + T^* \ln \rho^* x_\alpha \\ &= -T^* \ln (1 - B_{\text{mix}}^*\rho^*) + T^*C_\alpha^*\rho^*/(1 - B_{\text{mix}}^*\rho^*) + T^* \ln \rho^* x_\alpha \end{aligned} \tag{B.16}$$

C *Liquid Phase Chemical Potential*

For the chemical potential of the liquid phase Widom's expression [6] was used.

$$\mu_l^* = -T^* \ln \langle \exp(-\beta U_t^*)_{N_l} + T^* \ln \rho_l^* \quad \text{(C.1)}$$

where U_t is the intermolecular potential energy of interactions of an imaginary test molecule with all the N molecules in the system.

Equation (C.1) was derived for the canonical ensemble and a modified expression valid for the Gibbs ensemble derived by Smit and Frenkel [7] gives

$$\mu_l^* = -T^* \ln \left\langle \frac{V_l}{N_l + 1} \exp(-\beta U_t) \right\rangle \quad \text{(C.2)}$$

where V is the volume of the simulation box of the liquid phase.

For mixtures, the configurational chemical potential of species α was calculated from Widom's expression using the formula below:

$$\mu_{l\alpha}^* = -T^* \ln \langle \exp(-\beta U_t^*) \rangle_{N_l} + T^* \ln \rho_l^* x_\alpha \quad \text{(C.3)}$$

where U_t is the intermolecular potential energy of interactions of an imaginary test molecule of species α with all the N molecules in the system.

D *Simulation Details*

All the simulations were started from a face-centered-cubic intial configuration. An equilibration period of 10 000 Monte Carlo cycles preceeded the production period of another 10 000 MC cycles to ensure equilibrium independent of the initial conditions. The initial guesses for the liquid and vapor densities were taken from Panagiotopoulos [2] as well as the number of attempts per MC cycle for particle swaps between the two phases. The maximum position change and the maximum volume exchange were automatically adjusted during the course of the simulations to maintain a fifty percent acceptance ratio. Periodic boundary conditions were used and a spherical cutoff distance equal to the half box length was employed. Long range corrections were applied to account for the energy of interactions extending over the cutoff distance [9]. The estimated accuracy of the values reported in tables were calculated from the standard deviation of the block averages, using blocks of 1 000 Monte Carlo cycles. Further details of the Gibbs ensemble simulation method are given in [1] and [2, 3].