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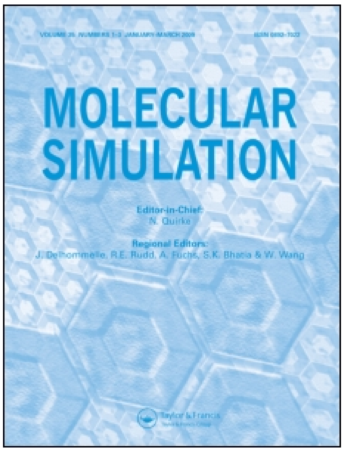

## Molecular Simulation

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

# An Extended Gibbs Ensemble

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**To cite this Article** Strnada, Martin and Nezbeda, Ivo(1999) 'An Extended Gibbs Ensemble', Molecular Simulation, 22: 3, 183 — 198

**To link to this Article: DOI:** 10.1080/08927029908022095

**URL:** http://dx.doi.org/10.1080/08927029908022095

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*Molecular Simulation*, 1999, Vol. 22, pp. 183–198
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Printed in Malaysia.

# AN EXTENDED GIBBS ENSEMBLE

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*(Received May 1995; accepted October 1998)*

A general extended Gibbs ensemble, obtained by augmenting the standard Gibbs ensemble by intermediate states in the spirit of the scaled particle method of Nezbeda and Kolafa [Molec. Simul., 5, 391 (1991)], is introduced. The intermediate states span the states with different number of particles in the simulation boxes and facilitate the transfer of particles even in such complex systems as *e.g.*, mixtures of very different components, systems of flexible polymeric molecules, or systems at very high densities. A general formulation of the ensemble is given and two implementations are considered in detail. The method is very general and is exemplified by studying the fluid–fluid coexistence in a dense binary mixture of the hard-sphere and square-well fluids. It is found that its efficiency is about by factor three greater in comparison with the standard Gibbs ensemble simulations.

*Keywords:* Gibbs ensemble; scaled particle method; fluid–fluid coexistence

## 1. INTRODUCTION

Since its invention in 1987, the Gibbs ensemble (GE) method [1] has become the best available and versatile technique for the direct determination of phase equilibria by computer simulations. A review on the variety of its applications can be found in [2]. Yet its application to some systems (*e.g.*, very dense fluids or mixtures with very different components) is not without problems because it suffers from the same defect which is common to all methods employing insertion (transfer) of particles or their interchange. For instance, for dense fluid phases, configurations with 'holes' in which an additional

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particle could be accommodated are highly improbable making thus the probability of successful particle transfers prohibitively low.

To overcome this problem, several different modifications of the original simple scheme have been proposed. Kofke and Glandt [3] proposed a semi-grand-canonical ensemble in which the identity of different particles is interconverted. Instead of inserting the full particle, a smaller particle is let to grow into the full size of the larger particle of the mixture, which evidently improves the efficiency of the insertion. However, the chemical potential of one of components of the mixture must be known or calculated. A similar idea was used also by Panagiotopoulos [4] in his application of the GE to mixtures of spheres of different sizes. De Pablo and Prausnitz [5] proposed to increase the rate of successful insertions by adding to the studied pure fluid a negligible amount of impurity in the form of a small number of small particles (inflating flea method). These particles facilitate the transfer of particles between the boxes by finding first a 'hole' for the normal particle. Although the impact of these small particles on the numerical values of the thermodynamic functions is negligible, the presence of the impurities makes, strictly speaking, the simulated system different from the original system of interest. Stapleton and Panagiotopoulos [6] used the excluded volume map sampling introduced by Deitrick *et al.* [7]. They claim the gain in efficiency of about sixty per cent but the programming effort is quite demanding. Finally, in order to avoid the transfer of particles at all, Camp and Allen [8] extended the 'pseudo-grand-canonical' ensemble approach of Mehta and Kofke [9] to Gibbs ensemble simulations: By lifting the constraint of coupling the changes of volumes of the boxes, the volumes may change independently so as to mimic the transfer. In addition to these general methods it is possible to implement the Gibbs methodology also by devising a specific (and, as a rule, quite complicated) scheme using biased particle transfers tailored to the system considered. As an example there may serve the scheme used by Bolhuis and Frenkel [10] in their study of mixtures of hard spheres and hard rods. Another possibility is an implementation of the Gibbs methodology for molecular dynamics simulation [11].

Some time ago we proposed a new version of the insertion particle method [12] for the calculation of the chemical potential, the scaled (fluctuating) particle method. The method augments the set of states of the standard canonical or grand-canonical ensembles by introducing unphysical (intermediate) states that span the states of the systems with $N$ and $N + 1$ particles. Specifically, the problem of the insertion/deletion of a particle is bypassed by allowing its *gradual* coupling into/decoupling from the system instead of the straightforward transition between the states with $N$ and

$N + 1$ particles. For both pure fluids and mixtures, the method is conceptually very simple and has been implemented for the efficient direct determination of the chemical potential of the pure dense fluids of hard spheres [12] and Lennard-Jones particles [13], and a ternary mixture of hard spheres and heteronuclear dumbbells [14]. The idea of the gradual insertion was later reconsidered by Attard [15], Kaminsky [16] and Wilding and Müller [17]. In the course of revising this paper we also learnt on an application of this idea to the Gibbs ensemble: Escobedo and de Pablo [18] defined an expanded ensemble tailored to polymer systems by allowing the polymer molecule to be transferred from one box to another segment by segment.

In this paper we introduce a general extended Gibbs ensemble (EGE) whose preliminary results were already published in [19]. In this paper we give the rigorous general formulation of the EGE which comprises, as one of its possible implementations, the expanded ensemble of Escobedo and de Pablo. The method is exemplified by calculating the phase equilibrium in the dense binary mixture of the hard sphere and square-well fluids. Comparison of the EGE simulations with the conventional GE ones demonstrates clearly the superiority of the former method whose efficiency in the considered case may be three times greater.

## 2. EXTENDED GIBBS ENSEMBLE

The GE method enables one to simulate two or more phases, each in a separate box, that are in equilibrium with each other. The boxes represent samples of the respective bulk phases far from the interface. The simulated system may be a pure fluid or a mixture. For the sake of simplicity we will confine our considerations in the following to a one component system, *i.e.*, to the two-phase equilibrium; extension to mixtures is straightforward.

Two simulation boxes $a$ and $b$ are at the same temperature, $T$, to guarantee the thermal equilibrium, each containing $N_a$ and $N_b$ particles, respectively. For a pure fluid, the two boxes together constitute an NVT ensemble, where $N = N_a + N_b$ is the total number of particles, and $V = V_a + V_b$ is the total volume; both $N$ and $V$ are kept fixed. The simulations consists of three kinds of moves. In addition to the standard trial MC moves, *i.e.*, displacement of a particle within its box and mutual change of volumes ensuring the equality of pressures, the exchange of particles between the boxes preserving the equality of chemical potentials must be attempted in order to keep the boxes in the phase equilibrium. The respective acceptance probabilities of these moves can be derived directly from the partition function $Q_{\mathrm{GE}}$ [20],

$$Q_{\mathrm{GE}} = \frac{1}{\Lambda^{3N} V N!} \sum_{N_a=0}^{N} \binom{N}{N_a} \int_0^V dV_a V_a^{N_a} V_b^{N_b} \int d\xi^{(N_a)} \exp[-U_a(N_a)/k_B T] \times \int d\xi^{(N_b)} \exp[-U_b(N_b)/k_B T], \tag{1}$$

where $\Lambda$ is the thermal de Broglie wavelength, $k_B$ is the Boltzmann constant, $U_n(N_n)$ is the total intermolecular potential energy of box $n$ containing $N_n$ particles, and integration is carried out over the scaled coordinates of particles denoted symbolically as $\xi^{(N_n)}$. The standard moves pose no problems and their detailed description can be found *e.g.*, in [21] along with the acceptance probabilities. The transfer of a randomly chosen particle *e.g.*, from box $a$ into box $b$ is governed by the acceptance probability $P_{\mathrm{acc}}$, which can be written, in general, in the form similar to that given in [22] as

$$P_{\mathrm{acc}} = \min\left\{1;\ \frac{p_{b\to a}}{p_{a\to b}} \frac{V_b N_a}{V_a(N_b+1)} \frac{\exp\{-[U_b(N_b+1) - U_b(N_b)]/k_B T\}}{\exp\{-[U_a(N_a) - U_a(N_a-1)]/k_B T\}}\right\}, \tag{2}$$

where $p_{a\to b}$ and $p_{b\to a}$ are fixed probabilities with which the respective transfers are attempted. Although it is usual to set $p_{a\to b} = p_{b\to a} = 1/2$, this is not necessary and the use of other values may improve efficiency of the simulation.

In dependence on the thermodynamic conditions and/or the system considered, probability (2) may become prohibitively small. To find a recipe to overcome the difficulty associated with the particle insertion and increase its effectiveness, Nezbeda and Kolafa [12] modified the original Widom insertion particle method for determining the chemical potential [23] by introducing unphysical intermediate states. Mathematically, if $u(N)$ is an interaction potential of one selected particle with the set of $N$ other particles, $i$-th intermediate state, $i = 1, \ldots, k$, is defined by the potential $u(N; \sigma_i)$, by means of which the selected 'scaled' particle interacts with $N$ normal (full) particles; $\sigma_i$ is referred to as 'size' but in general it denotes a set of potential parameters. For $i = 0$ the scaled particle becomes identical to the remaining particles and we have the state with $N + 1$ particles, whereas for $i = k + 1$ the scaled particle is annihilated and we get the state with $N$ particles. The states (ensembles) with $N$ and $N + 1$ full particles are thus connected by the following scheme of transitions:

$$\underset{1}{[N+1 \equiv N+\sigma]} \rightarrow\leftarrow \underset{w_1}{[N+\sigma_1]} \rightarrow \cdots \leftarrow \underset{w_k}{[N+\sigma_k]} \rightarrow\leftarrow \underset{w_{k+1}}{[N]}, \tag{3}$$

where the brackets denote the ensembles weighted by appropriate weights $w_i$ and the arrows represent the transitions among them attempted with certain *a priori* transition probabilities $p_{i\rightarrow j}\,(p_{i\rightarrow i+1} + p_{i\rightarrow i-1} = 1)$. We remind in passing that for the sake of convenience the order of indexing in (3) is reversed with respect to the original scheme given in [12].

Provided that two such transition schemes are considered in each box of the GE and the annihilation/creation of the scaled particle is substituted by its transfer from/into the other box (*i.e.*, the total number of particles of the entire system is conserved), it is possible to implement the exchange of particles between the boxes of the GE in the following way: A randomly chosen particle from either box, selected according to the associated *a priori* transition probability, starts shrinking (decoupling from the system) until it reaches its 'smallest size'; then it is transferred into the other box in which it may start swelling (coupling into the system) until it becomes indistinguishable from other full particles comprising the system. This process of transferring a particle from one box to another is repeated by choosing the box and particle to attempt the transfer. The algorithm of this intuitive scheme can be formulated rigorously using the partition function of a pseudo-Gibbs ensemble (PGE).

Let us consider a system of $N-1$ full particles and one scaled particle in state $i$. The full particles may be distributed between two boxes, $a$ and $b$, but the scaled particle remains permanently in either box, *i.e.*, it is not subject to any transfer. If the scaled particle resides in box $b$, the partition function of such PGE is

$$\begin{aligned} Q_{b,i} = {} & \frac{1}{\Lambda^{3N} V N!} \sum_{N_b=1}^{N} \binom{N}{N_b} \int_0^V dV_a V_a^{N_a} V_b^{N_b} \int d\xi^{(N_a)} \exp[-U_a(N_a)/k_B T] \\ & \times \int d\xi^{(N_b)} \exp\{-[U_b(N_b-1) + u_b(N_b-1;\sigma_{b,i})]/k_B T\} \quad (i=1,\ldots,k_b) \end{aligned} \tag{4}$$

and similarly if the scaled particle resides in box $a$. If the scaled particle is in the fully coupled state, $i = 0$, the considered PGE corresponds to the standard GE. By combining together all such ensembles we get an extended Gibbs ensemble (EGE) whose partition function is

$$Q_{\mathrm{EGE}} = Q_{\mathrm{GE}} + \sum_{i=1}^{k_a} w_{a,i} Q_{a,i} + \sum_{i=1}^{k_b} w_{b,i} Q_{b,i}, \tag{5}$$

where $w_{n,i}$ stands for the weight of the PGE with the scaled particle in state $i$ in box $n$. With respect to this definition, all configurations of the GE form a subset of configurations of the EGE and only this subset has to be used to define the physically meaningful ensemble averages in the EGE.

The acceptance probabilities of the individual steps are directly available from the partition function (5). The decoupling/coupling of the scaled particle in its own box is realized with the probability

$$P_{\mathrm{acc}} = \min\left\{1; \frac{p_{n,i\pm 1\to n,i}}{p_{n,i\to n,i\pm 1}} \frac{w_{n,i\pm 1}\exp[-u_n(N_n-1;\sigma_{n,i\pm 1})/k_BT]}{w_{n,i}\exp[-u_n(N_n-1;\sigma_{n,i})/k_BT]}\right\} \quad (n=a,b), \tag{6}$$

and the transfer of the scaled particle from state $k_a$ in box $a$ to state $k_b$ in box $b$ is governed by the acceptance probability

$$P_{\mathrm{acc}} = \min\left\{1; \frac{p_{b,k_b\to a,k_a}}{p_{a,k_a\to b,k_b}} \frac{V_b N_a}{V_a(N_b+1)} \frac{w_{b,k_b}\exp[-u_b(N_b;\sigma_{b,k_b})/k_BT]}{w_{a,k_a}\exp[-u_a(N_a-1);\sigma_{a,k_a})/k_BT]}\right\}, \tag{7}$$

(for $k_a = k_b = 0$ the standard GE transfer is recovered).

Although the chemical potential need not be calculated in the phase equilibrium simulations, its knowledge provides very useful information on the development of the simulated system and it is thus desirable to evaluate it in the course of simulations. To obtain the chemical potential from the GE, an expression derived by Smit and Frenkel [20], or a numerically equivalent Widom-like method [2, 20], can be used. The former expression, generalized for the EGE, reads as

$$\begin{aligned}\mu_n = {} & -k_B T\ln\left\langle\frac{V_n}{N_n+1}\exp[-u_n(N_n;\sigma_{n,k_n})/k_B T]\right\rangle - k_B T\ln\left(w_{n,k_n}\frac{\langle\chi[Q_{\mathrm{GE}}]\rangle}{\langle\chi[Q_{n,k_n}]\rangle}\right) \\ & + 3k_B T\ln\Lambda \quad (n=a,b),\end{aligned} \tag{8}$$

where the ensemble averages are considered over all distributions of particles and the quantity $\chi[Q_m]$ is equal to unity when the state belonging to the sub-ensemble $Q_m$ is detected and to zero otherwise. The first term on the right-hand side includes both the density term and the residual chemical potential of the scaled particle in its most decoupled state, and the second term, where $\langle\chi[Q_m]\rangle$ means the frequency of occurrence, is then proportional to the difference of this potential and that of the fully coupled particle, *cf.* [12]. It is easy to see that for $k_n = 0$ expression (8) becomes identical to the well known formula derived in [20].

The above described algorithm, referred to as EGE1, represents only one of possible implementations of the idea of splitting the transfer of a particle into several steps. Another straightforward implementation within the EGE is to combine the partial decoupling of the scaled particle in one box with the simultaneous partial coupling of another scaled particle in the other box. As it will be shown later, such implementation, referred to as EGE2, is equivalent to the expanded GE [18] provided that the acceptance probability of the simultaneous decoupling/coupling in the 'direction' resulting in the transfer of a particle from box $a$ into box $b$ is chosen in the form

$$P_{\mathrm{acc}} = \min\left\{1; \frac{p_{i+1\to i}}{p_{i\to i+1}}\left[\frac{V_b N_a}{V_a(N_b+1)}\right]^{1/(k+1)} \frac{w_{i+1}\exp[-u_a(N_a-1;\sigma_{a,i+1})/k_BT]}{w_i\exp[-u_a(N_a-1;\sigma_{a,i})/k_BT]} \right.$$
$$\left. \times \frac{\exp[-u_b(N_b;\sigma_{b,k-i})/k_BT]}{\exp[-u_b(N_b;\sigma_{b,k-i+1})/k_BT]}\right\}, \tag{9}$$

where $k$ stands for the total number of intermediate states, and where the subscripts both for the weights and *a priori* probabilities associated with the boxes have been omitted. We remark that, because of the simultaneous presence of $N+1$ (although incomplete) particles in $k$ pseudo-ensembles, there is no possibility to measure the chemical potential in the spirit of Eq. (8). Nonetheless, the distribution of states in the subsystem with $N$ full particles really is that of the GE as can be easily verified by multiplying $k+1$ terms in (9); the same holds also true in the case of EGE1 if we multiply $k_a + k_b$ terms from (6) with the last term of (7). Both products give the total acceptance probability for one particle transfer in the form given by Eq. (2).

## 3. COMPUTATIONAL DETAILS

To implement, test and explore the abilities of the EGE approach introduced in the preceding section, we considered the system investigated recently by Green *et al.* [24]: A binary mixture of a square-well (SW) fluid defined by the intermolecular pair potential $u(r)$,

$$u(r) \begin{aligned} &= \infty && \text{for } r < \sigma \\ &= -\varepsilon && \text{for } \sigma \le r < \lambda\sigma \\ &= 0 && \text{for } r \ge \lambda\sigma \end{aligned} \tag{10}$$

and the fluid of hard spheres (HS) of the same diameter $\sigma$; for the cross interaction the additivity of the hard spheres was assumed.

Unlike the implementation reported in [24] where the transfer of particles of both species had been used, we applied the following trial moves to reach equality of the chemical potentials: (i) transfer of a particle of *one*, in advance selected component and (ii) interchange of particles of both species. For evident advantages, HS particles were chosen as those to be transferred (in the EGE being subject to decoupling/coupling). A trial interchange of a randomly selected SW particle from box $a$ with a randomly selected HS from box $b$ is governed by the acceptance probability

$$P_{\mathrm{acc}} = \min\left\{1; \frac{N_a^{\mathrm{SW}} N_b^{\mathrm{HS}}}{(N_a^{\mathrm{HS}}+1)(N_b^{\mathrm{SW}}+1)} \exp\left[-\left(\Delta U_a^{\mathrm{SW/HS}} + \Delta U_b^{\mathrm{HS/SW}}\right)/k_B T\right]\right\}, \tag{11}$$

where $N_n^X$ denotes the number of particles of type $X$ in box $n$, and $U_n^{X/Y}$ denotes the change in energy of box $n$ in which particle of type $X$ has been replaced by particle of type $Y$. The equality of chemical potentials is then verified by the direct measurement of the chemical potential of the HS fluid and by the measurement of the *difference* of chemical potentials of both species according to [25],

$$\mu_n^{\mathrm{SW}} - \mu_n^{\mathrm{HS}} = -k_B T \ln\left\langle \frac{N_n^{\mathrm{HS}}}{N_n^{\mathrm{SW}}+1} \exp\left(-\Delta U_n^{\mathrm{HS/SW}}/k_B T\right)\right\rangle + 3 k_B T \ln \frac{\Lambda^{\mathrm{SW}}}{\Lambda^{\mathrm{HS}}} \quad (n = a, b). \tag{12}$$

We remark in passing that the above algorithm of coupled transfer/interchange trial moves yields the associated measurement of the chemical potentials at higher densities with better statistics than the usual algorithm of independent transfers of particles of both species.

Due to the presence of the scaled particle in the EGE, the use of preferential sampling is obvious. To sample preferentially the vicinity of the scaled particle, we used a rapidly decaying function $f(r) = (\sigma/2 + \sigma_{n,i}/2)^4/r^4$ in the following algorithm [12]: (i) if the scaled particle is in box $n$, choose at random an unscaled particle from this box and calculate its distance $r$ from the scaled particle; (ii) abandon a trial move with the probability $1 - f(r)$; (iii) generate a new position $r'$ of the selected particle; (iv) abandon a trial move with the probability $1 - \min\{1; f(r')/f(r)\}$; (v) test the trial move for acceptance (overlap). Concerning the mutual frequencies of the respective moves, we adopted the recommendation given in [12] and considered one trial decoupling/coupling move *versus* one trial displacement of the scaled particle *versus* one trial displacement of the normal particle (*i.e.*, that actually tested for the overlap).

We considered only one intermediate state of the HS particles in both boxes, $k_a = k_b = 1$, for the EGE1 method. Furthermore, different diameters were used in each box in order to minimize the number of preferential displacements and decoupling/coupling steps necessary for the complete exchange of the full HS particles between the boxes. Setting initially the weights to $w_{a,1} = w_{b,1} = 1$ and all *a priory* transition probabilities to 1/2, test runs showed that the values $\sigma_{a,1} = 0.7\sigma$, and $\sigma_{b,1} = 0.8\sigma$ were reasonable estimates provided that there was a majority of HS particles in box *a* and majority of SW particles in box *b*. Since the acceptance ratios of swelling of the scaled HS particle into its full size in both boxes were found comparable, and hence also comparable frequencies of occurrence of both PGE's, it seemed reasonable to keep both weights identical permanently. As regards the EGE2 implementation, we used only one set of intermediate states, $k = 1$, and the same diameters of the scaled HS particle as above to make a direct comparison with the EGE1 scheme possible.

Simulations were performed with different number of particles in dependence on the thermodynamic conditions. One cycle of trial moves in the GE simulations consisted of one trial volume change of either box (both containing the comparable number of particles), $N$ trial displacements in both boxes, a large number of trial particle transfers to obtain about $N/500$ up to $N/200$ successful particle transfers per cycle (the higher temperature, the larger number of particles) and $N/10$ trial interchanges. In the cycle of the EGE simulations, the regular displacements were substituted by $10 \times N$ attempted preferential moves (finally tested for an overlap) accompanied by coupling/decoupling and displacement trial steps of the scaled particle. All different types of trial moves were undertaken at random. The size of trial displacements and volume changes was adjusted so as to maintain the acceptance ratios at about 0.3. Concerning error estimation, each run was divided into a set of subruns ranging from 4 to 32; the maximum error obtained from the varying number of blocks was taken for the estimate of standard deviations.

## 4. RESULTS AND DISCUSSION

To conduct a thorough test of the method, we performed phase equilibrium simulations on the above defined mixture with $\lambda = 1.5$ at a very high pressure, $P^* = 10.0$, $P^* = P\sigma^3/\varepsilon$, over the temperature range $1.8 \leq T^* \leq 2.3$,

$T^* = k_BT/\varepsilon$. At these thermodynamic conditions the fluid–fluid equilibrium occurs at high densities (up to $\rho^* = N_n\sigma^3/V_n \approx 0.85$), so that all substantial features of the EGE can really be reliably tested and discussed with respect to the standard GE. At higher temperatures the standard transfer step is feasible and the EGE need not be used. Going to low temperatures, the density of both phases increases and the probability to succeed in transferring directly a particle from one box to another becomes negligible. At the intermediate temperature of $T^* = 2.1$ the efficiency of the GE and EGE is similar.

In the simulations we used 512 particles for lower temperatures where no swapping of boxes was observed, and 1728 particles at higher temperatures. After the necessary equilibration period, the averages were accumulated over $2 \times 10^5$ and $1 \times 10^5$ of such cycles in the system of 512 or 1728 particles, respectively. For all thermodynamic conditions, approximately $500 \times N$ of the HS particles were transferred successfully resulting in a reasonable statistics with sufficiently smooth higtograms of densities and number frequencies of particles in boxes. Since the cores of the HS and SW particles were of the same size, very high acceptance ratio of their interchanges (about 0.5) was detected, having as a consequence good sampling of the mole fractions, too.

The overall coexistence densities, $\rho_n^*$, mole fractions, $x_n^{\mathrm{SW}} = N_n^{\mathrm{SW}}/N_n(x_n^{\mathrm{HS}} = 1 - x_n^{\mathrm{SW}})$, and the chemical potentials $\mu_n^{*\mathrm{SW}}$ and $\mu_n^{*\mathrm{HS}}$, $\mu_n^{*X} = (\mu_n^X - 3\ln\Lambda^X)/k_BT$, of the components of the studied binary mixture at the fluid–fluid equilibrium at $P^* = 10.0$ obtained from the EGE1 and GE simulations are given in the table. The temperature-density, $T - \rho$, and temperature-composition, $T - x$, slices through the fluid–fluid coexistence at this pressure are then shown in the figure. It is common, for not too low temperatures, to fit the equilibrium data to the theoretical functional form [24]

$$\xi_\pm = \xi_c + C_2|t| \pm \frac{1}{2}B_0|t|^\beta, \tag{13}$$

where $t = 1 - T/T_c$, $T_c$ is the critical temperature, $\beta = 1/3$, $\xi_c$ stands for the critical density or composition, and $C_2$ and $B_0$ are numerical constants. This fit, providing an estimate of the location of the critical point without corrections for the non-classical behavior, may serve as an additional check of consistency of the simulation data. From the least-square fitting the following values have been obtained: $\rho_c^* = 0.741$, $T_c^* = 2.318$, $C_2 = 0.313$, $B_0 = 0.124$ in the case of the $T - \rho$ coexistence slice, and $x_c^{\mathrm{SW}} = 0.503$, $T_c^* = 2.320$, $C_2 = 0.037$, $B_0 = 1.527$ in the case of the $T - x$ coexistence slice. The coexistence curve given by the fit is also shown in the figure.

TABLE The coexistence densities, $\rho^*$, mole fractions, $x^{SW}$, and components' chemical potentials, $\mu^*$, of the binary mixture of SW and HS fluids at the fluid–fluid equilibrium obtained from the GE and EGE1 simulations at $P^* = 10.0$; Uncertainty of the chemical potentials are of the order of 1%

| *Method* | $N$ | $T^*$ | $\rho^*_{f1}$ | $\rho^*_{f2}$ | $x^{SW}_{f1}$ | $x^{SW}_{f2}$ | $\mu^{*SW}_{f1}$ | $\mu^{*SW}_{f2}$ | $\mu^{*HS}_{f1}$ | $\mu^{*HS}_{f2}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| EGE1 | 512 | 1.80 | 0.777 ± 0.001 | 0.843 ± 0.001 | 0.048 ± 0.014 | 0.939 ± 0.010 | 5.783 | 5.781 | 9.151 | 9.149 |
| EGE1 | 512 | 1.90 | 0.763 ± 0.001 | 0.832 ± 0.001 | 0.076 ± 0.016 | 0.933 ± 0.013 | 5.643 | 5.639 | 8.671 | 8.669 |
| EGE1 | 512 | 2.00 | 0.751 ± 0.002 | 0.820 ± 0.002 | 0.129 ± 0.024 | 0.924 ± 0.019 | 5.526 | 5.524 | 8.270 | 8.269 |
| EGE1 | 512 | 2.10 | 0.740 ± 0.002 | 0.802 ± 0.002 | 0.144 ± 0.017 | 0.884 ± 0.021 | 5.305 | 5.302 | 7.936 | 7.935 |
| GE | 512 | 2.10 | 0.739 ± 0.002 | 0.801 ± 0.002 | 0.184 ± 0.023 | 0.889 ± 0.022 | 5.277 | 5.278 | 7.853 | 7.854 |
| GE | 1728 | 2.20 | 0.731 ± 0.002 | 0.776 ± 0.003 | 0.200 ± 0.025 | 0.773 ± 0.028 | 5.130 | 5.132 | 7.626 | 7.627 |
| GE | 1728 | 2.25 | 0.730 ± 0.003 | 0.767 ± 0.003 | 0.259 ± 0.031 | 0.728 ± 0.035 | 5.083 | 5.083 | 7.493 | 7.494 |
| GE | 1728 | 2.30 | 0.734 ± 0.004 | 0.758 ± 0.004 | 0.345 ± 0.053 | 0.651 ± 0.049 | 5.072 | 5.072 | 7.410 | 7.411 |

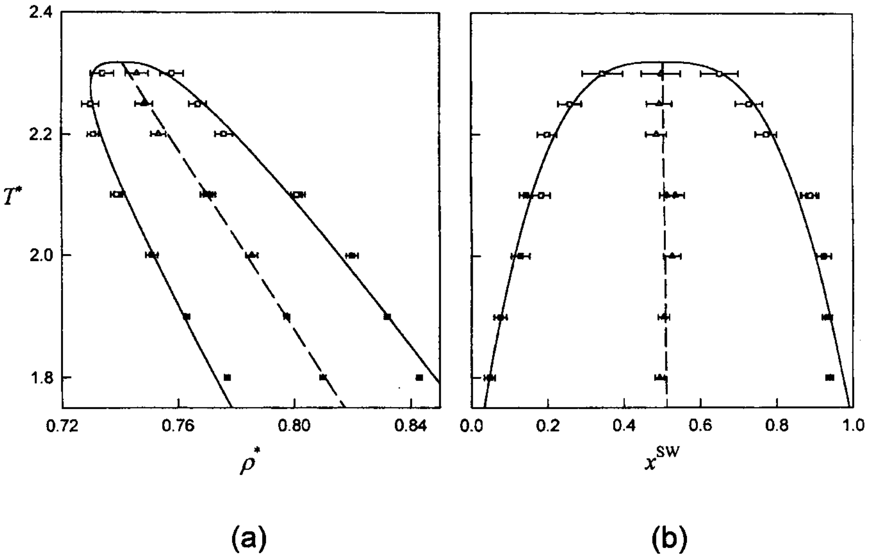

FIGURE (a) The temperature-density, $T-\rho$, and (b) temperature-composition, $T-x$, slices through the phase boundary of the binary mixture of the SW and HS fluids at the fluid–fluid equilibrium at $P^* = 10.0$. The empty and filled symbols denote the results of the GE and EGE1 simulations, respectively, the solid curves result from fitting Eq. (13) to the data, and the dashed lines denote the rule of rectilinear diameters.

Examination of the results at $T^* = 2.1$ shows that the EGE1 method yields, within experimental uncertainties, the same results as the standard GE simulation. Consistency of the simulation results (both EGE1 and GE) can be further deduced from the fit of all the data to (13). The critical temperatures, which represent coefficients of the fit, estimated from two different sets of data, the $T-\rho$ and $T-x$ slices, are practically identical. From the table it is also seen that equality of the chemical potentials of both phases has been maintained with high accuracy even at high densities, which is a straightforward consequence of the nature of the scaled particle method designed originally for this purpose.

The performed simulations have definitely shown that the transfer of particles *via* the EGE schemes is feasible even at very high densities. The question then remains how its efficiency compares with the standard GE simulation. Since the preferential sampling is an integral part of our implementation of the EGE scheme, the efficiency of the particle transfer cannot be measured directly by comparing acceptance ratios. As a plausible unambiguous criterion thus seems the total CPU time required for comparable sampling: It means to achieve (approximately) the same number of successful volume changes, particle transfers, particle interchanges, and number of particle displacements. Using the same algorithms in the codes for both the GE and EGE, it has been found that starting from $T^* = 2.1$ the EGE1 method has become more efficient. In the case of the lowest temperature considered, $T^* = 1.8$, it has been observed that the CPU time required by the EGE1 method has been about three times shorter than that by the GE scheme.

As regards the second EGE implementation, the EGE2 scheme, one might intuitively expect further gain in efficiency of the particle transfer because of its *simultaneous* decoupling/coupling in both boxes resulting thus in fewer intermediate states. However, this was not the case. If we account for the fact that every step aiming at decrease of the scaled HS in the EGE1 is accepted, this is not surprising and the above finding seems only an artifact of the studied system without general validity.

The idea to use nonphysical intermediate states in the GE simulations was implemented also by Escobedo and de Pablo [18] resulting in the 'expanded GE'. As we already mentioned earlier, the expanded GE is one of possible implementations of the EGE method. It is easy to see that when (i) the interaction potential of the scaled particle (residing in both boxes) is constructed as the 'tagged chain' [18], (ii) the Boltzmann factors are replaced by the Rosenbluth weights, and (iii) the relation $w_i P_{i \to i+1} = w_{i+1} P_{i+1 \to i}$ holds true, the EGE2 acceptance probability (9) comes directly over to the acceptance criterion given in [18].

Despite the above equivalence, there is a substantial difference between the EGE2 and expanded ensemble methods. The expanded ensemble was derived in a way different from that proposed here and its formula for the acceptance probability of the particle transfer contains neither weights of the intermediate states nor *a priori* probabilities of transitions between them. Besides the choice of 'tagged' pieces of particles, there is therefore no tool available to affect the resulting efficiency. The EGE offers this possibility but, on the other hand, there is no evident recipe how to set its parameters. It has been common, making usually use of *a priori* knowledge of the chemical potential, to set the parameters of the simulation scheme so as to obtain the uniform sampling of the intermediate states. However, Kofke and Cummings [26] examined in detail the methods of expanded ensembles and concluded that the efficiency can be considerably increased by *non-uniform* sampling. To be more specific, the procedure of error minimization of the chemical potential resulted, in general, in the population of the intermediate states very different from the uniform one. Unlike such NVT computations, the main goal of the EGE is to exchange the particles as 'quickly' as possible. Using trial-and-error, the maximum efficiency has been found in the case when the population of states with the fully coupled particle has been approximately by two orders smaller then that of the intermediate states. It is worth to remark that this important feature of the expanded ensembles was independently revealed and discussed also in [18] and [26].

The last question which seems to remain open is the 'topology' of the scheme connecting all intermediate states. In general, the scaled particle should not be prevented to make any transition beyond its closest neighbors [15, 19, 26]. However, our experience with EGE shows that, at least for a small number of intermediate states, the 'ring' scheme considered here is quite sufficient.

## 5. CONCLUSIONS

In the present paper we have extended the idea of the gradual insertion (scaled particle) method, originally proposed to improve the chemical potential computations, to the Gibbs ensemble. The formulation is very general allowing different implementations in dependence on the way how the scaled particle is transferred from one box to another. Advantage of the present formulation is that it leaves the weights and *a priori* probabilities of intermediate states as free adjustable parameters, whose appropriate setting may considerably affect the overall efficiency of the simulation.

We have considered two implementations, EGE1 and EGE2, and applied them to the determination of the high pressure fluid–fluid equilibria in the binary mixture of the hard sphere and square-well fluids. The former scheme maintains the total number of particles, whereas in the latter, expanded GE-like, the simultaneous decoupling/coupling of the scaled particle in both boxes takes place. The standard GE simulations have also been used for comparison. The results show, at least for the studied mixture, that there is no significant difference in efficiency between the EGE1 and EGE2 schemes. This is however not the case when EGE methods are compared with the standard GE. At high density, the efficiency of the EGE1 method with a non-uniform population of states is by factor three more efficient than the GE simulation.

### *Acknowledgement*

We wish to thank an anonymous referee for his useful comments which have led to a considerable revision of the original manuscript. This research was supported by the Grant Agency of the Czech Republic (Grants No. 203/93/2284 and 203/96/0494).

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