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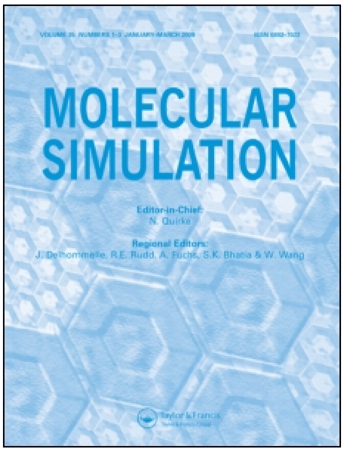

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CHEMICAL POTENTIAL, PARTIAL ENTHALPY AND PARTIAL VOLUME OF MIXTURES BY *NPT* MOLECULAR DYNAMICS

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Equilibrium *NPT* molecular dynamics computer simulations have been used to determine the chemical potential, partial enthalpy and partial volume of model Ar-Kr mixtures using newly devised non-intrusive particle insertion and particle swap techniques [P. Sindzingre *et al. Chemical Physics*, **129** (1989) 213]. In this report we examine, *for the first time*, in some detail the relative convergence statistics of the particle swap and particle insertion methods for these properties for binary Lennard–Jones (LJ) mixtures. Both species are represented by single-site Lennard–Jones pair potentials with Lorentz–Berthelot rules for the cross-species interactions. We show that, over the whole phase diagram and especially in the vicinity of the fluid–solid coexistence line, the particle swap method gives significantly better statistics than the particle insertion method for the difference in chemical potential of the two species, partial enthalpy and partial volume of each species. Also, we find that, using the particle swap method, the difference in the chemical potential converges more rapidly than the differences in the partial enthalpy and volume.

KEY WORDS: Binary mixtures, Argon–Krypton, molecular dynamics chemical potential, partial thermodynamics quantities

1 INTRODUCTION

Molecular simulation is increasingly being applied to study phase equilibria and excess properties of multi-component fluid mixtures. For this it is useful to have an efficient method for determining the chemical potential and partial molar quantities of the components. The chemical potential of each species and other partial molar quantities are more difficult to obtain than the usual ensemble averages, such as pressure, total energy. The equation of state can in principle be numerically integrated to derive the chemical potential [1, 2]. However, this is inconvenient as a general tool to obtain what is, after all a state function. In response, much effort has been spent in determining the chemical potential of single component fluids by a direct method in the 1970s and early 1980s using the non-destructive particle implant method derived by Widom [3, 4].

Recently Sindzingre *et al.* [5, 6] have shown that modifications of the test insertion particle method of Widom can be used in constant pressure Molecular Dynamics (or Monte Carlo) simulations to calculate directly the configurational parts of the chemical potential, partial enthalpy and partial volume in binary mixtures. There is little new in the particule insertion method for the chemical potential, apart from the fact that it is carried out in the *NPT* ensemble. However this approach when applied to the partial enthalpies, h_i, and partial volumes, v_i is new and a major advance in technique. The method differs from the previous approach in that it only requires a single simulation at the composition and state point of interest. Previously, the partial molar quantities were obtained from a numerical differention of the results of a series of simulations at various compositions near the state point of interest. This latter technique has much poorer statistics. The major drawback of this Widom-like route to h_i and v_i is that at high density, close to the fluid–solid phase boundary, trial insertions of test particles are rare events and the statistics deteriorates.

Sindzingre *et al.* [5, 6] proposed yet another particle sampling method, that leads directly to the **difference** in the μ_i, h_i and v_i between the two species in a binary mixture. The individual h_i and v_i can then be determined from the time average enthalpy and volume per particle, h and v, respectively, which are routinely determined as time averages from the simulation. (As the h and v have exceptional statistics in comparison with the sampling chemical potentials and partial quantities, the latter values essentially determine the statistical efficiency of the technique.) This method involves calculating the potential energy change associated with a swapping of a particle of species i with that of a species j. In this process the molecular coordinates are "frozen" and the procedure does not affect the evolution of the mixture through phase space, as the swapped pair are "returned" to their original positions before resumption of the simulation. The advantage of the method is that it determines the **differences** in chemical potential, partial enthalpy and partial volume **as a single average**, rather than as a difference of two separately determined quantities (as is the case with the insertion method) each with some statistical uncertainty. This becomes important when the chemical nature of the species becomes more similar.

In this report we investigate further the convergence characteristics of this new technique. While Sindzingre *et al.* [5, 6] looked at the particle swap method they did not compare the relative convergence characteristics of the particle insertion and swap routes to the partial molar quantities. This is explored here at a number of representative state points for equimolar Ar/Kr mixtures over a wide range of temperature and density.

2 THEORY AND SIMULATION METHOD

Fluid Parameters

Both the argon and krypton molecules are represented by single centre or site particles. We consider a system of N_1 particles ("molecules") of mass m_1 and N_2 molecules of mass m_2 contained in a volume V, mediated through a Lennard-Jones, LJ, (12-6) potential,

$$\phi_{\mu\nu}(r) = 4\varepsilon_{\mu\nu}((\sigma_{\mu\nu}/r)^{12} - (\sigma_{\mu\nu}/r)^6), \tag{1}$$

where μ and ν are the indices of the two species (i.e., ranging from 1 to 2). The cross-interactions are governed by the Lorentz–Berthelot mixing rules,

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2, \tag{2}$$

and

$$\varepsilon_{12} = \varepsilon_{11}^{1/2}\varepsilon_{22}^{1/2}, \tag{3}$$

The MD simulations were performed using cubic unit cells of volume V containing mainly $N = 256$ Lennard-Jones (LJ) particles, although a simulation was conducted

Table 1 Molecular fluid parameters for the Lennard-Jones molecules used in the simulations, taken from reference [7].

Molecule	m_1/u	$(\varepsilon_{11}/k_B)/K$	σ_{11}/nm	m_1^*	ε_{11}^*	σ_{11}^*
Ar	39.95	119.8	0.3405	1	1	1
Kr	83.80	167.0	0.3633	2.0976	1.3940	1.06696

with $N = 108$ to assess the N-dependence of the properties. The interactions were truncated at half the box sidelength ($S/2$). We use both real and LJ reduced units (based on the parameters for species 1, which is Ar) in this report. For example, for temperature, $k_B T/\varepsilon_{11} \rightarrow T^*$, and number density, $\rho^* = N\sigma_{11}^3/V$. Reduced time is in units of $\sigma_{11}(m_1/\varepsilon_{11})^{1/2}$, viscosity in $(m_1\varepsilon_{11})^{1/2}/\sigma_{11}^2$, thermal conductivity in $k_B(m_1/\varepsilon_{11})^{-1/2}\sigma_{11}^{-2}$, self-diffusion coefficient in $\sigma_{11}(\varepsilon_{11}/m_1)^{1/2}$ and pressure tensor components in $\varepsilon_{11}\sigma_{11}^{-3}$. The time step, h, was typically ≈ 0.01 in reduced units. These molecular parameters for the two species are taken from [7] and given in Table 1. Simulations performed on the CRAY-XMP at ULCC using CFT77 were for typically $\sim 2 \times 10^5$ time steps in production for each state point.

Thermodynamic Properties

The mean configurational energy, U, of the N particles is accumulated as the time average,

$$U = 1/2 \sum_i^N \sum_j^N \phi_{ij} + N u_{lrc}, \tag{4}$$

where $N = N_1 + N_2$. For mole fractions, $x_1 = N_1/N$ and $x_2 = N_2/N$, and partial number densities, $\rho_\nu = N_\nu/V = x_\nu \rho$. The interactions need to be truncated at a separation, $r_c \leqslant S/2$. The long range corrections for $r_{ij} > r_c$ are,

$$u_{lrc} = u_{lrc}^r + u_{lrc}^a, \tag{5}$$

where

$$u_{lrc}^r = \frac{8\pi}{9r_c^9}[x_1\varepsilon_{11}\rho_1\sigma_{11}^{12} + 2x_1\varepsilon_{12}\rho_2\sigma_{12}^{12} + x_2\varepsilon_{22}\rho_2\sigma_{22}^{12}], \tag{6}$$

and

$$u_{lrc}^a = \frac{-8\pi}{3r_c^3}[x_1\varepsilon_{11}\rho_1\sigma_{11}^6 + 2x_1\varepsilon_{12}\rho_2\sigma_{12}^6 + x_2\varepsilon_{22}\rho_2\sigma_{22}^6]. \tag{7}$$

The lower case symbols denote intensive (i.e., per particle) quantities, whereas upper case symbols represent the extensive quantities for the entire system, e.g., $u = U/N + u_{lrc}$. Also, $E = K_E + U$ and $e = E/N$. Similarly, the mean enthalpy per particle is $h = H/N$, where

$$H = K_E + U + PV. \tag{8}$$

The kinetic energy per particle, $k_e = K_E/N$ is obtained from,

$$K_E = 1/2 \sum_\nu \sum_i^{N_\nu} \mathbf{p}_{\nu i}^2/m_\nu, \tag{9}$$

where $\mathbf{p}_{vi}$ is the momentum of particle i of species v. The instantaneous temperature is,

$$T = 2K_E/(3N - 4)k_B. \tag{10}$$

The temperature and momenta are fixed, resulting in the removal of four degrees of freedom in Equation (10). The pressure is given by,

$$P = \frac{1}{3V}\left[\sum_{v}\sum_{i=1}^{N_v} \mathbf{p}_{vi}^2/m_v - \sum_{i=1}^{N-1}\sum_{j>i}^{N} r\frac{\mathrm{d}\phi(r_{ij})}{\mathrm{d}r}\right] + P_{lrc}, \tag{11}$$

where the long-range correction to the pressure has a contribution from the repulsive (r) and attractive (a) components of the pair potential,

$$P_{lrc} = P_{lrc}^{r} + P_{lrc}^{a}, \tag{12}$$

where

$$P_{lrc}^{r} = \frac{32\pi}{9r_c^9}[\varepsilon_{11}\rho_1^2\sigma_{11}^{12} + 2\varepsilon_{12}\rho_1\rho_2\sigma_{12}^{12} + \varepsilon_{22}\rho_2^2\sigma_{22}^{12}], \tag{13}$$

and

$$P_{lrc}^{a} = \frac{-16\pi}{3r_c^3}[\varepsilon_{11}\rho_1^2\sigma_{11}^{6} + 2\varepsilon_{12}\rho_1\rho_2\sigma_{12}^{6} + \varepsilon_{22}\rho_2^2\sigma_{22}^{6}]. \tag{14}$$

We also consider a quantity we call the partitioned enthalpy for each species, i, h_i^p **defined** for species 1 as,

$$h_1^p = 3k_BT/2 + P/\rho + \tfrac{1}{2}\left\langle\sum_{i=1}^{N_1}\phi_i\right\rangle\bigg/ N_1, \tag{15}$$

where,

$$\phi_i = \sum_{j\neq i}^{N}\phi_{ij}, \tag{16}$$

This quantity has in the past been confused with the partial enthalpy, h_i, see later. We give the partitioned enthalpies for reference and comparison in the discussion.

Partial Molar Quantities

For intensive property, $y = Y/N$, and mole fractions, x_i we have for an m-component mixture the partial thermodynamic quantity,

$$y_i = (\partial y/\partial x_i)_{x_j,T,P}. \tag{17}$$

From Euler's theorem we can relate the ensemble average thermodynamic quantity, y to these partial derivatives,

$$y = \sum_{i}^{m} x_i y_i. \tag{18}$$

For a binary system this reduces to,

$$y = x_1(\partial y/\partial x_1)_{x_2,T,P} + x_2(\partial y/\partial x_2)_{x_1,T,P}. \tag{19}$$

The total sum of the mole fractions, x is of course,

$$x = \sum_i^m x_i = 1, \tag{20}$$

The partial molar quantities can be determined by *two* new techniques: test particle insertion along the lines of Widom and particle "swap", a novel simultaneous implementation of particle removal and insertion.

Particle Insertion

Consider two species in the mixture, 1 and 2. Following on from Sindzingre *et al.* [5] the chemical potential of component 1 or μ_1 can be separated into a configurational part, μ_1^c and a kinetic or "ideal" part, μ_1^{id} as follows,

$$\mu_1 = \mu_1^{id} + \mu_1^c, \tag{21}$$

where

$$\mu_1^{id} = k_B T \ln(\rho_1) - \tfrac{3}{2} k_B T \ln(T/\Theta) + k_B T, \tag{22}$$

where $\Theta = h^2/2\pi m \varepsilon \sigma^2$ and,

$$\mu_1^c = \left[\int_0^\rho \mathrm{d}\rho (P - \rho k_B T)/\rho^2\right] + P/\rho - k_B T, \tag{23}$$

We use Widom's particle insertion method to obtain μ_1^c and μ_2^c directly. Let ΔU^{1+} be the energy of a test particle of species 1 randomly inserted in the fluid. In the NPT ensemble we have,

$$\mu_1^c = k_B T(\ln(V) - \ln(\langle V \exp(-\beta \Delta U^{1+})\rangle)), \tag{24}$$

where V is the volume of the N particles, $\beta = 1/k_B T$ and ΔU^{1+} is the energy of the inserted particle of species 1. $\langle \cdots \rangle$ denotes a time and particle average. The transposed expression (i.e., 1 → 2 and 2 → 1 in Equation (24) leads to an expression for μ_2). Equation (24) is different from the usual Widom expression encountered for constant volume NVT systems:

$$\mu_i^c = -k_B T \ln(\langle \exp(-\beta \Delta U^{1+})\rangle), \tag{25}$$

The presence of the volume terms above will introduce a small N-dependence. Although, the two expressions will converge in the thermodynamic limit, i.e., as $N \to \infty$. A formally equivalent (but in practice, statistically inferior) method involves sampling the potential energy of a **real** particle in the simulated system [2],

$$\mu_1^c = k_B T(\ln(\langle V \rangle) + \ln(\langle V^{-1} \exp(\beta \Delta U^{1-})\rangle)), \tag{26}$$

where ΔU^1 is the potential energy of a particle in the system. The particle removal method gives more importance to the attractive region of interaction-space, whereas the test insertion particle method samples more readily the repulsive part of interaction-space. Although formally equivalent routes to the chemical potential, the particle insertion method gives much better statistics than the removal method. It appears that a sample real particle within the simulation will not explore all of the necessary phase space in practice to determine μ_i, h_i and v_i.

Similarly for the partial molar enthalpy, h_1 we have,

$$\begin{aligned} h_1 &= \left(\frac{\partial \beta\mu_1}{\partial \beta}\right)_{P,N_1,N_2} \\ &= \frac{\langle(\Delta U^{1+} + U(N_1 - 1, N_2) + PV)V \exp(-\beta\Delta U^{1+})\rangle_{N_1-1,N_2}}{\langle V \exp(-\beta\Delta U^{1+})\rangle_{N_1-1,N_2}} \\ &\quad - \langle U(N_1 - 1, N_2) + PV\rangle_{N_1-1,N_2} \end{aligned} \tag{27}$$

where again 2 is the other species. Similarly for the partial volume, v_1

$$\begin{aligned} v_1 &= \left(\frac{\partial \mu_1}{\partial P}\right)_{T,N_1,N_2} \\ &= \frac{\langle V^2 \exp(-\beta\Delta U^{1+})\rangle_{N_1-1,N_2}}{\langle V \exp(-\beta\Delta U^{1+})\rangle_{N_1-1,N_2}} \langle V\rangle_{N_1-1,N_2}, \end{aligned} \tag{28}$$

The principal drawback of this and all particle insertion methods is its comparative failure at high density, where the majority of locations for particle insertion leads to substantial particle overlap. Therefore the contributions of these Boltzmann factors are negligible [8, 9]. At every time step, irrespective of the values of N_1 and N_2, we randomly positioned $N/2$ molecules of species 1 and $N/2$ molecules of species 2 in the fluid. This is to improve the statistics of the μ_i, h_i and v_i of a dilute component i.e., $x_i \rightarrow 0$.

Particle Swap

If we define,

$$\begin{aligned} \Delta y &= (\partial y/\partial x_1)_{x,T,P} \\ &= (\partial y/\partial x_1)_{x_2,T,P} - (\partial y/\partial x_2)_{x_1,T,P} \\ &= y_1 - y_2, \end{aligned} \tag{29}$$

Therefore,

$$y_1 = y + (1 - x_1)\Delta y, \tag{30}$$

and,

$$y_2 = y - x_1\Delta y. \tag{31}$$

These partial molar quantities have been evaluated for the specific enthalpy, h, and specific volume, $v = V/N$. Each time step in an NPT ensemble molecular simulation, the energy change, ΔU, was evaluated, caused by replacing a particle by one of the other species without altering the configuration. This is a virtual transformation as it is reversed before the dynamics are resumed for the next change of the configuration. For example, for the two species 1 and 2, the energy change on "removing" a 1 atom and "replacing" it by a 2 atom, ΔU^{2+1-},

$$\Delta U^{2+1-} = \sum_{v=1,2}^{2} \sum_{j_v \neq i_1} [\phi_{2v}(r_{i_1 j_v}) - \phi_{1v}(r_{i_1 j_v})]. \tag{32}$$

Also,

$$\begin{aligned}\Delta\mu &= \mu_1 - \mu_2 \\ &= \beta^{-1} \ln \langle \exp(-\beta \Delta U^{2^+1^-}) \rangle_{N_1,N_2} \end{aligned} \tag{33}$$

where $\beta = (k_B T)^{-1}$. In the simulation each particle in turn was chosen every time step as a candidate for this exchange. Clearly, unlike for the particle insertion method, above, the number of swaps of each pair 1–2 is determined by the values of N_1 and N_2. Also,

$$\begin{aligned}\Delta h &= h_1 - h_2 \\ &= -\frac{\langle \Delta U^{2^+1^-} \exp(-\beta\Delta U^{2^+1^-})\rangle_{N_1,N_2}}{\langle \exp(-\beta\Delta U^{2^+1^-})\rangle_{N_1,N_2}} \\ &\quad\times \frac{[\langle H \exp(-\beta\Delta U^{2^+1^-})\rangle_{N_1,N_2} - \langle H\rangle_{N_1,N_2}\langle \exp(-\beta\Delta U^{2^+1^-})\rangle_{N_1,N_2}]}{\langle \exp(-\beta\Delta U^{2^+1^-})\rangle_{N_1,N_2}} \end{aligned} \tag{34}$$

The Δh and h can therefore be obtained directly as time averages from the simulation. Hence from Equations (30) and (31) we have,

$$h_1 = h + (1 - x_1)\Delta h, \tag{35}$$

and

$$h_2 = h - x_1 \Delta h, \tag{36}$$

where $h = \langle H/N \rangle$ and using Equation (8).

Now, for the partial molar volume,

$$\begin{aligned}\Delta v &= v_1 - v_2 \\ &= \frac{\langle V \exp(-\beta\Delta U^{2^+1^-})\rangle_{N_1,N_2}}{\langle \exp(-\beta\Delta U^{2^+1^-})\rangle_{N_1,N_2}} - \langle V \rangle_{N_1,N_2}. \end{aligned} \tag{37}$$

Hence from Equations (30) and (31) we have,

$$v_1 = v + (1 - x_1)\Delta v, \tag{38}$$

and

$$v_2 = v - x_1 \Delta v, \tag{39}$$

and where $v = \langle V/N \rangle$.

We now consider the implementation of the constant temperature and pressure constraints.

NPT equations of motion

The [*NPT*] equations were introduced in the MD code by box sidelength and velocity rescaling. Constant temperature was achieved approximately using a velocity rescaling procedure in a Verlet leapfrog algorithm [10]. For the desired temperature, T_0 and instantaneous temperature, T, (based on the half-time step momenta) we determine a momentum rescaling factor,

$$f = (T_0/T)^{1/2}, \tag{40}$$

$$\mathbf{p}(t + h/2) = \mathbf{p}(t - h/2) + \mathbf{F}(t)h. \tag{41}$$

where **F** is the systematic force. For each molecule, the new half-timestep velocity is rescaled, $\mathbf{p}(t + h/2) \rightarrow f\mathbf{p}(t + h/2)$. The Anderson constant pressure equations of motion were used to fix a pressure P_0 in the system [11]. This can be rewritten as a series of rescaling operations applied to the molecular co-ordinates and velocities as follows. For a position, **r**, and momentum, **p**,

$$\dot{\mathbf{r}} = \mathbf{p} + \dot{\varepsilon}\mathbf{r}, \tag{42}$$

$$\dot{\mathbf{p}} = \mathbf{F} - \varepsilon\dot{\mathbf{p}}, \tag{43}$$

$$\ddot{V} = (P - P_0)/M_A, \tag{44}$$

where the Anderson mass, $M_A = 0.005m_1$, typically.

$$\ddot{\varepsilon} = \frac{\ddot{V}}{3V}. \tag{45}$$

We use the velocity-Verlet algorithm to update the cell volume and implement Equations (42)–(45) in timesteps, h.

$$\dot{V}(t + h/2) = \dot{V}(t - h/2) + \ddot{V}(t)h, \tag{46}$$

$$V(t + h) = V(t) + \dot{V}(t + h/2)h, \tag{47}$$

$$\gamma = [V(t + h)/V(t)]^{1/3} - 1, \tag{48}$$

$$\mathbf{p}(t + h/2) \rightarrow [1 - \gamma]\mathbf{p}(t + h/2), \tag{49}$$

$$\mathbf{r}(t + h) = [1 + \gamma](\mathbf{r}(t) + \mathbf{p}(t + h/2)h). \tag{50}$$

The box sidelength $S = V^{1/3}$ is recalculated each time step to apply the periodic boundary conditions appropriate to the new MD cell dimensions. The long range corrections are also rescaled each time step,

$$u^r_{lrc} = u'^r_{lrc}(S'/S)^{12}, \tag{51}$$

$$u^a_{lrc} = u'^a_{lrc}(S'/S)^6, \tag{52}$$

$$P^r_{lrc} = P'^r_{lrc}(S'/S)^{15}, \tag{53}$$

$$P^a_{lrc} = P'^a_{lrc}(S'/S)^9, \tag{54}$$

where S' is the sidelength used to evaluate reference long range corrections, u'^r_{lrc}, u'^a_{lrc}, P'^r_{lrc}, P'^a_{lrc}.

Each time step, the interaction truncation distance is scaled in proportion to S', in order to maintain the same molecules in each N-coordination shells after rescaling.

3 RESULTS AND DISCUSSION

The purpose of this report is to quantify the convergence properties of the Sindzingre *et al.* methods for obtaining μ_i, h_i and v_i. The state points considered are given in Table 2. Simulations I and II test the number dependence of the quantities. Simulations

Table 2 State points considered in this study and their thermodynamic averages. h_i^p is the partitioned enthalpy of species i. S is the simulation index for future reference. All simulations were equimolar in Ar and Kr, i.e., $x_1 = x_2 = 0.5$.

S	N	T	ρ	u	e	h	P	h_1^p	h_2^p
I	108	1.2546	0.60621	−5.5765	−3.7179	−3.7139	0.00244	−2.9126	−4.4687
II	256	1.2546	0.60414	−5.5648	−3.6927	−3.6887	0.00243	−2.8949	−4.4629
III	256	0.9756	0.71752	−6.7860	−5.3302	−5.3302	0.0000	−4.3881	−6.2571
IV	256	2.0910	0.69256	−5.7290	−2.6088	2.8035	3.7472	3.6570	1.9794
V	256	2.0910	0.53739	−4.5728	−1.4527	0.9904	1.3116	1.6645	0.3443

III–V cover a wider density and temperature range. For a clear comparison between the swap, insertion and removal techniques, we concentrate on the **differences** between the partial properties,

$$\Delta\mu = \mu_1 - \mu_2, \tag{55}$$

$$\Delta h = h_1 - h_2, \tag{56}$$

$$\Delta v = v_1 - v_2, \tag{57}$$

In Table 3 we consider the equimoar state point: $\rho = 0.605 \pm 0.001$, $T = 1.2546$ and $P = 0.00243$ using two system sizes, $N = 108$ and $N = 256$. The time steps are ~ 0.01. The convergence of the difference of the chemical potential is better for the swap method (Equation (33)) than using Equation (55) with Equation (25) (insertion) and certainly better than the removal method, using Equation (26) for μ_i. The $N = 108$ and $N = 256$ chemical potential differences by the swap method are statistically indistinguishable. The power of the swap method becomes apparent, however, when the partial enthalpies and volumes are considered. We note that for short simulations of $t < 500$ reduced time units, the enthalpy difference by the swap method is within $\sim 5\%$ of the exact result, whereas the particle insertion difference values can be $\sim 25\%$ away from convered limit. The convergence of the average quantities h is much faster. For example for $N = 256$ we have, $h = -3.7009$, -3.6942 and -3.6887 for times $t = 161, 321$ and 5223. Therefore the limiting factor

Table 3 Differences in partial quantities for state points I and II from Table 2. t is time in LJ reduced units for argon. $\Delta\mu = \mu_1 - \mu_2$. S, W and R refer to swap, Widom and removal particle sampling method respectively.

N	t	$\Delta\mu_s$	$\Delta\mu_W$	$\Delta\mu_R$	Δh_s	Δh_W	Δv_s	Δv_W
108	281	2.1137	2.0132	2.8517	3.6234	−3.7229	0.09439	−2.0941
108	562	2.0899	2.2476	2.7691	3.6139	0.55431	0.12450	−0.54423
108	2812	2.0810	2.0921	3.8234	3.8778	3.9563	0.23522	0.26368
108	8437	2.0766	2.0798	2.8298	3.9447	3.9091	0.25561	0.24298
108	16874	2.0745	2.0815	1.8394	3.9822	4.0369	0.26610	0.28667
108	22217	2.0745	2.0810	2.0029	3.9747	4.0877	0.26364	0.29296
256	80	2.0681	2.0964	2.1284	4.3930	5.2563	0.41667	0.36076
256	161	2.0734	2.0813	2.0138	4.2850	3.7215	0.37097	−0.01113
256	402	2.0725	2.0902	2.0274	4.1610	3.1334	0.33135	0.002651
256	804	2.0717	2.0774	2.4032	4.0354	3.9077	0.29166	0.20493
256	1607	2.0732	2.0658	2.5323	3.9417	3.4819	0.25783	0.10268
256	3214	2.0717	2.0636	2.7358	3.9580	4.1644	0.26207	0.31985
256	5223	2.0708	2.0650	2.7944	4.0028	4.0075	0.28141	0.24584

Table 4 Differences in partial quantities for state points III, IV and V from Table 2. t is time in LJ reduced units for argon. $\Delta\mu = \mu_1 - \mu_2$. S, W and R denote swap, Widom and removal methods respectively. $N = 256$. The data marked (a) comes from [6] Tables 4, 5 and 6, for which $N = 108$.

State	t	$\Delta\mu_s$	$\Delta\mu_W$	$\Delta\mu_R$	Δh_s	Δh_W	Δv_s	Δv_W
III	91	2.4224	2.3560	3.7212	3.2867	9.6018	−0.042519	0.38217
III	273	2.4213	2.3452	3.6768	3.4139	7.5608	−0.049952	0.26058
III	911	2.4197	2.5060	3.6150	3.4790	1.3728	−0.042236	−0.32566
III	1822	2.4189	2.4388	3.4507	3.4650	2.8161	−0.049419	−0.081623
III	3645	2.4190	2.4416	3.1314	3.5033	2.3371	−0.045094	−0.15128
(a)	800	2.4222	-	-	3.50	-	−0.067	-
IV	62	1.2318	1.1981	2.8112	1.9813	1.1246	−0.17523	−0.10823
IV	187	1.2344	1.1542	3.6447	2.0938	2.8498	−0.15084	−0.13379
IV	373	1.2361	1.1135	3.3081	2.0369	1.3964	−0.15840	−0.23104
IV	622	1.2361	1.1379	3.0067	2.1826	1.3213	−0.14260	−0.30573
IV	1245	1.2363	1.1605	3.0915	2.2190	1.7792	−0.13853	−0.21537
IV	1867	1.2372	1.1801	2.6910	2.417	2.2412	−0.13332	−0.19768
IV	3112	1.2361	1.1886	3.1821	2.2605	2.1502	−0.13003	−0.16976
IV	4357	1.2364	1.2113	3.3840	2.2507	2.0117	−0.13358	−0.16956
IV	4979	1.2361	1.2112	2.7055	2.2591	1.7963	−0.13223	−0.18387
V	62	1.4827	1.6952	3.2539	1.8221	6.9218	−0.19131	1.4703
V	187	1.4346	1.3946	2.1826	2.8429	2.8272	0.062036	0.069492
V	622	1.4325	1.3958	2.0696	2.8957	2.5230	0.074641	−0.017071
V	1245	1.4339	1.4131	2.2517	2.8732	2.6449	0.069564	0.026756
V	1867	1.4336	1.4228	2.2481	2.8443	2.6748	0.062318	0.014029
V	3112	1.4342	1.4232	2.1497	2.8655	2.6878	0.067356	0.033678
V	4979	1.4335	1.4242	2.2779	2.8457	2.6446	0.062142	0.022584
V	5539	1.4331	1.4226	2.4667	2.8477	2.6075	0.063022	0.011825

on the accuracy of h_i by the swap method is in Δh. Similarly for the volume we have 1.6564, 1.6567 and 1.6569, respectively at these times. There is no statistically significant N-dependence between for Δh and Δv using swap or insertion methods. (The results for the removal method were far worse for Δh and Δv and are therefore not reported.)

In Table 4 we consider the three other state points using $N = 256$ particles. State point III is the same one as treated by Sindzingre *et al.* [5, 6] (although they only used $N = 108$ in their simulation for this equimolar mixture state point). The clear superiority of the swap method is apparent. Convergence in $\Delta\mu$ to within three significant figures is reached within $t = 100$ reduced time units. Whereas the insertion method is still only accurate to two significant figures within 3645 reduced time units. The removal method seems to converge onto values which are statistically significant but not the correct values, obviously due to the inadequate exploration of phase space by this method. The same trends are evident for the v_i also. The small value for Δv at $T = 0.9756$ and $\rho = 0.71752$ is obtained to within $\sim 1\%$ after $t = 91$ by the swap method whereas the insertion method for Δv (Equation (57) and Equation (28)) is still an order of magnitude away from the converged limit after 3645 reduced time units.

The previous state points have been at near zero pressure and low (near-triple point) temperature. Now we consider two temperature state points at high pressure. State point IV is supercritical for both components and at a reasonably high density: $T = 2.09$ and $\rho = 0.693$. Table 4 combined with Table 2 reveals that the high pressure causes all partial quantities now to be positive. Here again the convergence rate of the swap sampling techniques is better than the insertion method, although the relative rates of convergence are not as different as in the previous two states (II and III). The convergence of h is $h = 2.8082$, 2.8042 and 2.8035 at reduced time of 311, 622 and 4979. Therefore, again the convergence of the h_i is governed by that of Δh. Similarly for the average volume per particle we have, 1.4449, 1.445 and 1.4444 at the same times, respectively.

Also in Table 4 we give the $\Delta\mu_i$, Δh_i and Δv_i of state point V. This is at the same temperature as state IV but being at a lower pressure, settles down to a lower average density: $\rho = 0.53739$. Table 4 reveals that the $\Delta\mu$ of the insertion method converges again considerably more slowly than the value from the particle swap method. The conclusions are same for the Δh and Δv. After times $t = 62$, 187, 622, 1867 and 5539 we find that the accumulated averages for v are 1.8251, 1.8640, 1.8644, 1.8627 and 1.8626, respectively. The corresponding average enthalpies per particle, h, are: 0.83383, 0.9949, 0.9959, 0.9900 and 0.9904, respectively. These time averages again converge more rapidly than those of the particle sampling methods.

4 CONCLUSIONS

This study has presented strong evidence for the superior convergence of the particle swap method, when compared with all other methods, for obtaining **differences** in chemical potential, and absolute partial enthalpy and volume in molecular simulation. The sampling technique can be implemented in Monte Carlo, Molecular Dynamics and even Brownian Dynamics without any loss of rigour. The technique is a useful tool in the investigation of mixtures by simulation.

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