On the Calculation of the Chemical Potential

Using the Particle Deletion Scheme

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Abstract

A new formulation is presented for the calculation of the chemical potential from molecular simulation based on a test particle removal (inverse Widom) scheme. The new formulation introduces an intermediate stage in the calculation, where the test particle to be removed is substituted by a hard particle. Chemical potential calculations at high densities from NVT and NPT Monte Carlo simulations, using a fast analytical algorithm for the computation of volume accessible to the hard-core particle, are presented for the pure Lennard-Jones fluid and found to be in excellent agreement with predictions from an accurate equation of state and from simulations using the test particle insertion scheme (Widom insertion scheme). Binary mixture simulations are also presented and the new scheme is applied in the Gibbs ensemble [1]. In all cases where the system is highly dense, the new inverse Widom scheme affords a significant reduction of the CPU time compared to the widely used test particle insertion method of Widom (1963). In addition, the new scheme is compared to a recently proposed scheme based on staged insertion.
1. Introduction

The chemical potential is an important thermodynamic quantity for phase equilibrium calculations. Over the years, several methods have been proposed in the literature for the calculation of the chemical potential through molecular simulation (either Molecular Dynamics or Monte Carlo, Allen and Tildesley, 1987 [2]). One of the most elegant, efficient and widely used methods is based on Widom’s approach [3]. According to this method, the chemical potential is calculated from the ratio of the partition function of a system containing $N+1$ molecules divided by the partition function of a system containing $N$ molecules, where both systems are under the same conditions of temperature and total volume or pressure. In practice, this ratio is evaluated through random insertions of ‘ghost’ molecules in the $N$-molecule system and calculation of the interaction energy of the inserted molecule with the remaining molecules of the system (Allen and Tildesley, 1987 [2]). This method becomes very inefficient for dense systems where space vacancies are rare and so molecule insertion is very difficult, and for systems where the $N$-molecule state and the $(N+1)$-molecule state are very different, as in the case of an organic molecule dissolved in water [4].

Alternatively, Widom’s method can be implemented through the deletion of a molecule from the system under consideration, so that the chemical potential can be evaluated by comparing the $N$-molecule state with the $(N-1)$-molecule state. The so-called “inverse Widom scheme” was first introduced by Shing and Gubbins [5]. However, their calculations indicated that it is not possible to estimate correctly the
chemical potential by the removal of a molecule, due to inefficient sampling of the highly positive energies felt by the removed molecule. The inefficient sampling was believed to be caused by the use of importance sampling, whereby the \( N \)-particle system is ‘visiting’ the most probable configurations and is not providing an accurate picture of the highly positive energy configurations, which on the other hand contribute greatly to the chemical potential.

Recently, Parsonage [6-7] proposed a methodology to overcome the problems related to the inverse Widom method by modifying the intermolecular potential with the introduction of a hard core. In this way, he succeeded in estimating the chemical potential of highly dense Lennard-Jones fluids [8]. Although his calculations are accurate enough, there is no clear physical justification for the alteration of the intermolecular potential other than to avoid numerical overflow. More recently, Kofke and Cummings [9-10] presented a very thorough and exhaustive analysis of the methods available for the evaluation of the chemical potential with molecular simulation techniques. Recommendations were presented based on the simulation of hard-sphere and Lennard-Jones systems, emphasizing the effectiveness of insertion-based techniques over deletion-based methodologies.

In this work, a new, detailed formulation of the inverse Widom method is presented based on particle deletion, which allows accurate calculation of the chemical potential. The new formulation is based on the simple concept that if one removes a molecule from a system of \( N \) molecules, the new system is not simply a system of \( N-1 \)
molecules, but rather a system of \(N-1\) molecules and a “hole”, since the remaining \(N-1\) molecules can never occupy the volume accessed by the \(N^{th}\) molecule. So, if one removes a molecule in the way prescribed by Shing and Gubbins [5], one will always sample configurations with a hole, adding a bias to the calculation. To remove this bias, one has to account explicitly for the difference between a system with \(N-1\) molecules and one hole and a system with \(N-1\) molecules. A measure of this difference can be obtained by calculating the accessible volume for inserting a hard sphere into the \((N-1)\)-molecule system. The formulation presented in this work has a rigorous physical basis that explains the use of a hard core potential without the need to alter the intermolecular potential. The new methodology is developed for Monte Carlo simulation, but is equally well applicable for Molecular Dynamics. Calculations are presented for the pure Lennard-Jones fluid and binary mixtures and results are compared with simulations using the Widom insertion scheme and the staged insertion scheme of Kofke and Cummings [9-10].

2. Theory

According to the Widom insertion method, the chemical potential of a species is calculated in a molecular simulation by comparing the free energy of a system of \(N\) molecules with the free energy of a system of \(N+1\) molecules. In the inverse Widom scheme comparison is made between the free energy of a system of \(N\) molecules with the free energy of a system of \(N-1\) molecules. Although in the direct Widom scheme the \((N+1)\)-molecule system can be constructed simply by the insertion of a molecule in the reference \(N\)-molecule system, the \((N-1)\)-molecule system can not be generated in an
equivalent way, that is by simply deleting a molecule from the \( N \)-molecule system. The reference system (the \( N \)-molecule system in both cases) should be able to sample the complete configurational space that the perturbed system samples. However, in the case of the inverse Widom scheme the perturbed system has additional void space over the reference system, generated from the removal of the \( N^{th} \) molecule. To overcome this bias, it is proposed here that the inverse Widom scheme be implemented in two stages, as shown schematically in Figure 1. The initial \( N \)-molecule system (I) is perturbed to an \((N-1)\)-molecule and one hard core molecule system (II). This intermediate system can be also considered as a perturbation of the final \((N-1)\) molecule system (III). In other words, the free energy difference between systems I and III can be calculated based on the free energy differences for the pairs I - II and III - II systems.

The mathematical formulation presented here concerns simulation in the \( NPT \) ensemble. The Gibbs free energy of a system of \( N \) molecules at temperature \( T \) and pressure \( P \) can be calculated from the expression:

\[
G(N, P, T) = -\frac{1}{\beta} \ln (Q(N, P, T))
\]  

(1)

where \( Q(N, P, T) \) is the isothermal-isobaric partition function of the system. Subsequently, the chemical potential is calculated from the expression:
\[ \beta \mu = \beta \frac{\partial G}{\partial N} \bigg|_{P,T} = \frac{\beta (G(N,P,T) - G(N-1,P,T))}{N - (N-1)} = -\ln \frac{Q(N,P,T)}{Q(N-1,P,T)} \]

\[ = -\ln \left( \frac{\left[ q_{\text{int}} \right]^{N} (N-1)! \Lambda_{3(N-1)}^{3N}}{N! \Lambda_{3N}^{3N}} \right) \frac{Z(N,P,T)}{Z(N-1,P,T)} = \beta \mu^i - \ln \left( \frac{1}{V} \frac{Z(N,P,T)}{Z(N-1,P,T)} \right) \]

(2)

where \( \beta \mu^i \) is the ideal gas chemical potential at temperature \( T \) and molecular density \( \langle N/V \rangle \). The ratio of the configurational integrals can be further transformed according to the expression:

\[ \frac{Z(N,P,T)}{Z(N-1,P,T)} = \frac{\int \exp(-\beta PV) dV Z(N,V,T)}{\int \exp(-\beta PV) dV Z(N-1,V,T)} = \frac{\int \exp(-\beta PV) V^N dV Z'(N,V,T)}{\int \exp(-\beta PV) V^{N-1} dV Z'(N-1,V,T)} \]

\[ = \frac{\int \exp(-\beta PV) V^N dV \int \exp(-\beta U_N(s_1, \ldots, s_N)) d^3 s_1 \ldots d^3 s_N}{\int \exp(-\beta PV) V^N dV \int \exp(-\beta U_{N-1}(\tilde{s}_1, \ldots, \tilde{s}_{N-1})) d^3 \tilde{s}_1 \ldots d^3 \tilde{s}_{N-1}} \]

(3)

where \( \tilde{s}_i = \frac{r_i}{L} \) is the reduced position vector of the molecule \( i \) with respect to the simulation box length \( L \). At this point, the intermediate system of \( N-1 \) molecules and a hard sphere is introduced. After straightforward mathematical manipulation, the ratio of configurational integrals is written as:
\[
\frac{Z(N, P, T)}{Z(N-1, P, T)} = \frac{\int \exp(-\beta PV) V^N dV \int \exp(-\beta U_N(\tilde{s}_1, \ldots, \tilde{s}_N)) d^3 s_1 \ldots d^3 s_N}{\int \exp(-\beta PV) V^N dV \int \prod_{i=1}^{N-1} \tilde{H}(s_{i,N}) \frac{\exp(-\beta U_{N_i}(\tilde{s}_1, \ldots, \tilde{s}_{N-1}))}{V} d^3 s_1 \ldots d^3 s_N}
\times \frac{\int \exp(-\beta PV) V^N dV \int \exp(-\beta U_{N_i}(\tilde{s}_1, \ldots, \tilde{s}_{N-1})) d^3 s_1 \ldots d^3 s_N}{\int \exp(-\beta PV) V^N dV \int \prod_{i=1}^{N-1} \tilde{H}(s_{i,N}) \exp(-\beta U_{N_i}(\tilde{s}_1, \ldots, \tilde{s}_{N-1})) d^3 s_1 \ldots d^3 s_N}
\]

= \frac{1}{\int \exp(-\beta PV) V^N dV \int \prod_{i=1}^{N-1} \tilde{H}(s_{i,N}) \exp(-\beta U_{N_i}(\tilde{s}_1, \ldots, \tilde{s}_{N-1})) d^3 s_1 \ldots d^3 s_N}
\times \frac{\int \exp(-\beta PV) V^{N-1} dV \int \prod_{i=1}^{N-1} \tilde{H}(s_{i,N}) \exp(-\beta U_{N_i}(\tilde{s}_1, \ldots, \tilde{s}_{N-1})) d^3 s_1 \ldots d^3 s_N}{\int \exp(-\beta PV) V^{N-1} dV \int \prod_{i=1}^{N-1} \tilde{H}(s_{i,N}) \exp(-\beta U_{N_i}(\tilde{s}_1, \ldots, \tilde{s}_{N-1})) d^3 s_1 \ldots d^3 s_N}
\]

\[
\left\langle \prod_{i=1}^{N-1} H(r_{i,N}) \right\rangle_{N-1, P, T} = \frac{\left\langle \prod_{i=1}^{N-1} H(r_{i,N}) \frac{\exp(\beta U^{(0)}(\tilde{r}_1, \ldots, \tilde{r}_N))}{V} \right\rangle_{N, P, T}}{\left\langle \prod_{i=1}^{N-1} H(r_{i,N}) \frac{\exp(\beta U^{(0)}(\tilde{r}_1, \ldots, \tilde{r}_N))}{V} \right\rangle_{N, P, T}}
\]

In Eq. (4), the following Heaviside step functions were introduced:

\[
\tilde{H}(s_{i,N}) = \begin{cases} 
0 & \text{if } |\tilde{s}_i - \tilde{s}_N| < s_{\text{core}}(\beta, P) \\
1 & \text{if } |\tilde{s}_i - \tilde{s}_N| \geq s_{\text{core}}(\beta, P)
\end{cases} \quad i = 1, \ldots, N - 1
\]

(5a)

\[
H(r_{i,N}) = \begin{cases} 
0 & \text{if } |\tilde{r}_i - \tilde{r}_N| < d_{\text{core}}(\beta, P) \\
1 & \text{if } |\tilde{r}_i - \tilde{r}_N| \geq d_{\text{core}}(\beta, P)
\end{cases} \quad i = 1, \ldots, N - 1
\]

(5b)
The same results can be obtained from the Bennett formula by the correct choice of weighting function \[11\].

The hard core diameter \(d_{\text{core}}\) or \(s_{\text{core}} = d_{\text{core}}/L\) in reduced units is arbitrarily chosen. It has to be larger than the distance of closest approach between two molecules under the prevailing conditions, but at the same time an excessively large value would not allow proper sampling of the free space available in the \((N-1)\)-molecule system. As a result, the optimal choice for \(d_{\text{core}}\) depends on the conditions of the system under investigation (temperature and pressure). This parameter is essentially equivalent to the hard core parameter introduced by Parsonage \[6-7\] in his formulation of the inverse Widom scheme. In the proposed formulation, this parameter is utilized during molecule removal only, unlike Parsonage’s formulation where it was used to modify the intermolecular potential.

On the right-hand side of Eq. (4),

\[
U^{(N)}(\vec{r}_1, \ldots, \vec{r}_N) \equiv U_N(\vec{r}_1, \ldots, \vec{r}_N) - U_{N-1}(\vec{r}_1, \ldots, \vec{r}_{N-1})
\]

stands for the intermolecular energy felt by the \(N^{th}\) molecule due to its interactions with the remaining \(N-1\) molecules of the system.

Substitution of Eq. (4) back in Eq. (2) provides the expression for the excess chemical potential \(\mu^{ex}\) at temperature \(T\) and pressure \(P\):
\[
\beta \mu^e = \beta \mu - \beta \mu^i = - \ln \left\langle \frac{1}{V} \left( \prod_{i=1}^{N-1} H(r_{i,N}) \exp(\beta U^{(N)}(\vec{r}_i, \ldots, \vec{r}_N)) \right) \right\rangle_{N,P,T}
\]

(6)

The analysis presented above for the \textit{NPT} ensemble can be easily applied to other ensembles, such as the \textit{NVT}, grand canonical, or the Gibbs ensemble. A more general expression for the calculation of \(\mu^e\) is:

\[
\beta \mu^e = - \ln \left\langle \frac{1}{V} \frac{1}{\prod_{i=1}^{N-1} H(r_{i,N}) \exp(\beta U^{(N)}(\vec{r}_i, \ldots, \vec{r}_N))} \right\rangle - \ln \left\langle \prod_{i=1}^{N-1} H(r_{i,N}) \right\rangle
\]

\[
= \beta \mu^e_{\text{energy}} + \beta \mu^e_{\text{volume}}
\]

The term \(\left\langle \prod_{i=1}^{N-1} H(r_{i,N}) \right\rangle\) in Eqs. (6) and (7) is the accessible volume fraction for a molecule of diameter \(d_{\text{core}}\) interacting through hard-sphere repulsive interactions with a system of \(N-1\) molecules and was neglected in the analysis of Shing and Gubbins [5].
It is clear from Eq. (6) that the analysis presented here invokes calculations in an ensemble of $N$ molecules and an ensemble of $N$-1 molecules with all other parameters being the same. Although in the thermodynamic limit there is no difference between the two ensembles, special attention should be paid in the case of molecular simulation of finite size systems. A rigorous approach would require two separate simulations. However, when calculations are performed in the $NPT$ ensemble, the difference between the $(N-1)$- and $N$-ensembles corresponds only to a weak size effect, whereas for calculations in the $NVT$ ensemble there is a small density difference.

The situation is complicated even further for the case where the number of molecules in the ensemble varies, as is the case for the $\mu VT$ ensemble or the Gibbs ensemble. A rigorous approach requires that the distribution $g(N)$ (where $\int g(N)dN = 1$) of the number of molecules in the system be known, so that:

$$\left\langle \prod_{i}^{N-1} H(r_{i,N}) \right\rangle = \int \frac{g(N-1)}{g(N)} g(N) \left\langle \prod_{i}^{N-1} H(r_{i,N}) \right\rangle_N dN$$

(8)

It is safe to assume that $g(N) = g(N-1)$ though, and so small variations in the number of molecules do not introduce any further complications in the calculations.
The formulation presented here provides the exact result for the hard sphere system where the hard sphere size is equal to $d_{\text{core}}$. In such a case, the excess chemical potential can be calculated simply from the free volume fraction as predicted by Eq. (6):

$$\beta \mu^e = -\ln \left( \prod_{i=1}^{N-1} H(r_{i,N}) \right)_{N-1}$$  \hspace{1cm} (9)

3. Simulation Details

The newly proposed formulation for the calculation of the $\mu^e$ was tested for systems of spheres interacting through the Lennard-Jones potential. The Lennard-Jones potential is quite realistic for the representation of non-polar fluids such as noble gases and hydrocarbons. Furthermore, an accurate 32-parameter equation of state (EoS) exists for pure Lennard-Jones spheres [12]. Monte Carlo simulations were performed in the $NVT$, $NPT$ and Gibbs ensembles focusing mainly on high density conditions where the Widom method becomes inefficient and computationally intensive. Both pure component systems and mixtures of different size spheres were examined. The efficiency of the Widom scheme and of the inverse Widom scheme was measured based on the CPU time required for a given calculation.

A key quantity in the inverse Widom scheme is the accessible volume. In this work, two different approaches were used for its calculation. The first was based on
Monte Carlo integration via random insertions of hard spheres, and the second on the analytical scheme proposed by Dodd and Theodorou (1991) [13]. The ability to calculate the accessible volume analytically provides considerable advantage, especially in the case of highly dense systems. In the calculations presented in the Results and Discussion Section, the analytical method was used.

In all simulations, unless otherwise stated, systems of 300-350 molecules were subjected to Monte Carlo simulations with an equilibration period of 0.5 million steps, followed by an average of 2.5 - 3.5 million steps for the calculation of the $\mu_{\text{energy}}^{\text{ex}}$ term and 9.5 million steps for the calculation of the accessible volume. NVT simulations employed only particle displacement moves, NPT simulations consisted of 95% particle displacements and 5% volume fluctuations, whereas Gibbs ensemble simulations consisted of 80% particle displacements, 5% volume fluctuations and 15% particle interchanges between the two boxes. Standard Metropolis acceptance criteria were used (Allen and Tildesley, 1987 [2]). Results unless otherwise indicated, are reported in dimensionless LJ units ( $\sigma$ for length, $\sigma^{-3}$ for density, $\varepsilon$ for energy and chemical potential, $\varepsilon/\sigma$ for pressure).

Statistical uncertainty was measured using block averaging analysis, where each run was divided into five blocks, so that the variance was calculated from the expression:

$$\delta \mu_{\text{ex}} = \sqrt{\left(\delta \mu_{\text{energy}}^{\text{ex}}\right)^2 + \left(\delta \mu_{\text{volume}}^{\text{ex}}\right)^2},$$
\[
\delta \mu_{\text{volume}}^{ex} = k_B T \delta \ln \left( \prod_{i=1}^{N-1} H(r_{i,N}) \right) = k_B T \left( \delta \prod_{i=1}^{N-1} H(r_{i,N}) \right)
\]

\[
\delta \mu_{\text{energy}}^{ex} = k_B T \delta \ln \left( \frac{\prod_{i=1}^{N-1} H(r_{i,N}) \exp(\beta U^{(S)}(\vec{r}_1, \ldots, \vec{r}_N))}{\langle N \rangle / V} \right) =
\]

\[
k_B T \left( \frac{\delta < N / V >}{< N / V >} \right)^2 + \delta \left( \frac{\prod_{i=1}^{N-1} H(r_{i,N}) \exp(\beta U^{(S)}(\vec{r}_1, \ldots, \vec{r}_N))}{\langle N \rangle / V} \right)^2
\]

where \( \delta |\ln(<A>)| = \left| \delta <A> \right| / <A> \) and \( \left( \delta <A> \right)^2 = \frac{1}{N} \sum_{b=1}^{5} (\langle A \rangle_b - \langle A \rangle_{run})^2 \) (10)

The hard sphere diameter utilized in the simulations was chosen to be 0.11 reduced units larger than the minimum distance between two molecules encountered in the simulation, so that \( d_{\text{core}} \) was set in the range 0.95-0.98, depending on the temperature and pressure of the system. Calculations in this work were based on either a single run or on two runs, to accumulate averages for the \( N \) and \( N-1 \) molecule systems separately. The value of \( d_{\text{core}} = 0.95 \) was chosen to minimize the length of the second run, for a two-run
simulation (see results section). Smaller values of $d_{\text{core}}$ result in large uncertainties of the $\beta \mu_{\text{energy}}^{\text{ex}}$ term, whereas larger values result in large uncertainties of the $\beta \mu_{\text{volume}}^{\text{ex}}$ term. For the case of a single run, a smaller $d_{\text{core}}$ value is preferable and results in more accurate estimation.

4. Results and Discussion

Simulation results for the $\mu^{\text{ex}}$ of the pure Lennard-Jones fluid are reported in Table 1 for $NVT$ Monte Carlo simulation and Table 2 for $NPT$ Monte Carlo simulation. In addition, predictions from a very accurate EoS [12] are also reported. Calculation of the $\mu^{\text{ex}}$ from simulation was performed using the Widom insertion scheme and the inverse Widom scheme developed in this work. As explained earlier, a rigorous methodology for the inverse Widom scheme requires two separate runs, one with $N-1$ molecules, where the accessible volume for a hard sphere ($\beta \mu_{\text{volume}}^{\text{ex}}$ term) is calculated, and a second one with $N$ molecules, where the $\beta \mu_{\text{energy}}^{\text{ex}}$ term is evaluated. In Tables 1 and 2, simulation results based on two runs are labeled as inverse 2, whereas simulation results obtained from a single run on a system of N-1 molecules are labeled as inverse 1.

Simulation results at all state points examined are in very good agreement with each other, within the statistical uncertainty of the calculations, and with EoS predictions. The inverse Widom scheme with a single run provides consistently lower values for $\mu^{\text{ex}}$ than with two runs for the $NVT$ simulations. On the other hand, in $NPT$ simulations the
difference in the results from one and from two runs does not show a consistent trend, this is an indication that reliable estimates for the chemical potential can be obtained from a single run.

The efficiency of the inverse Widom scheme over the Widom insertion scheme was tested by comparing the CPU time required by each of the two methods in order to calculate the chemical potential at given conditions with the same statistical uncertainty. Results are presented in Table 1 for NVT simulations and Table 2 for NPT simulations for the ratios \( \frac{(\text{CPU time})_{\text{inverse}}}{(\text{CPU time})_{\text{Widom}}} \) and \( \frac{(\text{CPU time})_{\text{inverse}}}{(\text{CPU time})_{\text{Widom}}} \). At all the conditions examined, the inverse Widom scheme with a single run is an order of magnitude faster than the Widom insertion scheme. The inverse Widom scheme with two runs obviously requires more CPU time than the single run scheme but, in all of the cases examined it is still two to three times faster than the Widom insertion scheme. It should be emphasized that the size of the hard core diameter used in all the calculations was optimized with respect to the dual run inverse Widom scheme. One might be able to achieve further reduction in the CPU time for a single run simulation by using a different hard core size.

The size of the hard core that is utilized in the intermediate step of the proposed method is quite important for the consistency of the calculation and for the optimization of the computational time required. This issue has been addressed previously by Parsonage [7] and Kofke and Cummings [10]. The hard core diameter can not be smaller than the minimum distance between two particles interacting with the full potential,
otherwise the perturbed system II of figure 1 samples configurational space that is unreachable by the reference system I. A series of NVT Monte Carlo simulations were performed for a pure Lennard-Jones fluid at \( T = 1 \) and \( \rho = 0.8 \) with different hard core diameters. In all cases, a run with 199 molecules consisting of 500,000 equilibration moves followed by 9,000,000 production moves and a run with 200 molecules consisting of 1,000,000 equilibration moves followed by 2,500,000 production moves were performed. The \( \mu^{ex} \) from the different runs is displayed in Figure 2 as a function of the hard sphere diameter. In addition, the free volume term and the energy term (Eq. 6) that provide \( \mu^{ex} \) are shown separately. A constant \( \mu^{ex} \) value is obtained, as expected. In Figure 3, the statistical uncertainty for \( \mu^{ex} \) is presented together with the statistical uncertainty of the free volume and energy terms. There is a clear optimum value for the hard core diameter, around 0.95, as a result of the combined effect of the two terms. Similar calculations were performed under other conditions and small perturbations of the optimum diameter around the 0.95 value were observed.

At this point, the new methodology is compared to the staged insertion scheme proposed by Kofke and Cummings [9-10] according to which the chemical potential is calculated by inserting a hard sphere into a \((N-1)\)-molecule system and, in a second stage, transforming the hard sphere into a Lennard-Jones sphere. In the second stage of this scheme, system II of Figure 1 is the reference system and system I is the perturbation system, and so the hard sphere diameter employed should be smaller than the minimum distance between two Lennard-Jones molecules. We have implemented the staged insertion method for exactly the same system as the one studied in Figures 2 and 3: The
conditions, number of molecules and number of moves are identical, allowing a direct comparison between inverse Widom and staged insertion schemes. For both methods two runs have been used, one with 9 million steps for calculating the $\beta \mu_{\text{volume}}^{ex}$ and a second with 3 million steps to calculate $\beta \mu_{\text{energy}}^{ex}$. In Figures 4 and 5, the $\mu^{ex}$ and its constituent terms and the statistical uncertainty and its constituent terms are shown, respectively, as functions of the hard sphere diameter. The maximum value for the hard sphere diameter at those conditions is 0.865. In contrast to what happens with the inverse Widom scheme, the energy term accounts for almost the entire $\delta \mu^{ex}$ in the case of staged insertion for all the diameters examined. Furthermore, the minimum value for $\delta \mu^{ex}$ obtained from the staged insertion scheme (at approximately $d_{\text{core}} = 0.85$) is almost three times higher than the value obtained from the inverse Widom scheme (at $d_{\text{core}} = 0.95$).

Another test has been performed for comparison of the two methods. In this test, only one run of 9 million steps was used for both methods. The Inverse Widom for hard core diameter 0.95 gave $\mu^{ex} = -2.27\pm0.055$, while the staged insertion method for hard core diameter 0.83 gave $\mu^{ex} = -2.49\pm0.245$. Again, the statistical uncertainty of the inverse Widom scheme is much smaller under the conditions examined here.

The new inverse Widom scheme was tested for binary Lennard-Jones mixtures. In all cases, Lorentz-Berthelot mixing rules were used to calculate the cross parameters. A large sphere ($\sigma_2 = 1.25$) was considered being dissolved at infinite dilution in a solvent at $T = 1$ and $P = 1.03$ (calculations for the pure Lennard-Jones fluid at these conditions are shown in Table 2) and its $\mu^{ex}$ was calculated using the Widom insertion and the inverse Widom scheme with one and two runs. The values obtained were as follows:
-1.83 ± 0.45 (Widom), -2.10 ± 0.43 (inverse 1), and -1.98 ± 0.40 (inverse 2). All three values agree with each other within the statistical uncertainty. Furthermore, the CPU time required by the inverse 1 method was 7% of the CPU time required by the Widom insertion method and the CPU time required by the inverse 2 method was 9% of the CPU time required by the Widom insertion method.

The new method was tested for the calculation of the chemical potential in the case of a Gibbs ensemble simulation of vapor-liquid equilibrium for a Lennard-Jones fluid at $T=1$. In Table 3, calculations results are shown for the coexisting densities, the $\mu^e$, and the total $\mu$. The $\mu^e$ values obtained with the new (inverse Widom) method are in good agreement with the values using the Widom method.
5. Conclusions

The inverse Widom method (particle deletion) for the calculation of the chemical potential in the course of a molecular simulation was re-formulated by introducing an intermediate stage where the molecule deleted is substituted by a hard sphere whose optimum size is approximately of 0.95 of the size parameter of the molecule. $\mu^{ex}$ values from the new scheme are in good agreement with values obtained using the Widom insertion scheme. Furthermore, the new scheme is much more efficient for highly dense systems than the Widom insertion approach and should be preferred for calculations at these conditions. Finally, the new scheme was shown to be more efficient than the stage insertion scheme proposed recently by Kofke and Cummings [9-10], at least for the system and conditions examined.

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References


Table 1. NVT simulation results and EoS predictions [12] for the excess chemical potential of the pure Lennard-Jones fluid. Simulation results were obtained using the Widom insertion scheme (Widom) and the inverse Widom scheme with one (inverse 1) and two (inverse 2) runs, respectively. The CPU time for the inverse Widom scheme is given as a fraction of the time required to calculate the excess chemical potential under the same conditions using the Widom scheme. All property values are presented in reduced units.

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<th>inverse 2</th>
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<td>0.850</td>
<td>-3.62</td>
<td>-3.49</td>
<td>0.15</td>
<td>-3.59</td>
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</table>

Table 2. NPT simulation results and EoS predictions [12] for the excess chemical potential of the pure Lennard-Jones fluid. Simulation results were obtained using the Widom insertion scheme (Widom) and the inverse Widom scheme with one (inverse 1) and two (inverse 2) runs, respectively. The CPU time for the inverse Widom scheme is given as a fraction of the CPU time required to calculate the excess chemical potential under the same conditions using the Widom scheme. All property values are presented in reduced units.
Table 3. Gibbs simulation results for the excess chemical potential of a Lennard-Jones fluid at $T = 1$. Simulation results were obtained using the Widom insertion scheme (Widom) and the inverse Widom scheme. All property values are presented in reduced units.

<table>
<thead>
<tr>
<th>$T$</th>
<th>$P$</th>
<th>EoS</th>
<th>Widom</th>
<th>inverse 1</th>
<th>inverse 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\mu^{ex}$</td>
<td>$\mu^{ex}$</td>
<td>$\delta \mu^{ex}$</td>
</tr>
<tr>
<td>0.90</td>
<td>1.370</td>
<td>-2.14</td>
<td>-2.44</td>
<td>0.24</td>
<td>-2.26</td>
</tr>
<tr>
<td>1.00</td>
<td>1.030</td>
<td>-2.27</td>
<td>-2.30</td>
<td>0.09</td>
<td>-2.25</td>
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</table>

<table>
<thead>
<tr>
<th>Phase</th>
<th>$\rho$</th>
<th>Widom</th>
<th>inverse</th>
<th>Widom</th>
<th>inverse</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\mu^{ex}$</td>
<td>$\delta \mu^{ex}$</td>
<td>$\mu^{ex}$</td>
<td>$\delta \mu^{ex}$</td>
</tr>
<tr>
<td>Liquid</td>
<td>0.701</td>
<td>-3.494</td>
<td>0.076</td>
<td>-3.444</td>
<td>0.123</td>
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<tr>
<td>Vapor</td>
<td>0.027</td>
<td>-0.303</td>
<td>0.040</td>
<td>-0.286</td>
<td>0.011</td>
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</tbody>
</table>
Figure Captions.

Figure 1. Representation of the new inverse Widom scheme for the calculation of the chemical potential via the deletion methodology.

Figure 2. Excess chemical potential ($\mu^e$) and its two constituent (free volume, $\mu^e_{volume}$ and energy, $\mu^e_{energy}$) terms for a Lennard-Jones fluid at $T = 1$ and $\rho = 0.8$ from NVT Monte Carlo simulation using the two-stage inverse Widom scheme as a function of the hard sphere diameter. The statistical uncertainty in $\mu^e$ is shown in the inset, where the scale of the coordinate has been expanded.

Figure 3. Statistical uncertainty of the excess chemical potential ($\delta \mu^e$) and its two constituent (free volume, $\delta \mu^e_{volume}$ and energy, $\delta \mu^e_{energy}$) terms for a Lennard-Jones fluid at $T = 1$ and $\rho = 0.8$ from NVT Monte Carlo simulation using the two-stage inverse Widom scheme as a function of the hard sphere diameter.

Figure 4. Excess chemical potential ($\mu^e$) and its two constituent (free volume and energy) terms for a Lennard-Jones fluid at $T = 1$ and $\rho = 0.8$ from NVT Monte Carlo simulation using the staged insertion scheme of Kofke and Cummings (1998) [9-10] as a function of the hard sphere diameter. The statistical uncertainty in $\mu^e$ is shown in the inset, where the scale of the coordinate has been expanded.
Figure 5. Statistical uncertainty of the two constituent (free volume and energy) terms of the excess chemical potential for a Lennard-Jones fluid at \( T = 1 \) and \( \rho = 0.8 \) from \( NVT \) Monte Carlo simulation using the staged insertion scheme of Kofke and Cummings [9-10] as a function of the hard sphere diameter. The uncertainty of the total excess chemical potential \( (\delta \mu^e) \) is practically identical to that of the energy term.