Pair approximation for polarization interaction: efficient method for Monte Carlo simulations of polarizable fluids

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A new method is presented for the Monte Carlo simulations of polarizable models with induced dipole moments. This method updates induced dipole moments on all molecules when a single molecule is moved, without evaluating all pair interactions. Thus, depending on the number of molecules, it is 10–20 times faster than Monte Carlo simulations with full iteration. The efficiency makes it a powerful tool for the study of phase equilibria of polarizable models in grand canonical and Gibbs ensembles.

1. Introduction

Polarizable models of fluids are expected to be superior to their non-polarizable counterparts, e.g. in the prediction of properties over wide ranges of thermodynamic states, including vapour–liquid equilibria. At least for water, at the present time, this does not seem to be the case [1]. Evidently, the reason for this is the poor parametrization of polarizable models used, since most (if not all) of these models were fitted at ambient conditions only. The goal of developing a polarizable model for water which yields an accurate phase envelope remains elusive and will continue to be so until we can routinely and efficiently predict the phase envelope of polarizable fluids.

Only a few papers have reported the determination of the phase coexistence of polarizable models for water. For example, Kiyohara \textit{et al.} [2] used grand canonical Monte Carlo simulations together with the histogram reweighting technique. Another method for the determination of phase equilibria, the Gibbs ensemble Monte Carlo (GEMC) simulation [3], has been applied by Medeiros and Costas [4] to a fluctuating charge polarizable water model.

There is an inherent problem with the Monte Carlo (MC) technique for the simulation of polarizable models. In molecular dynamics, all $O(N^2)$ interactions between $N$ molecules are evaluated every integration timestep, and the polarization interaction does not increase the calculation time significantly (usually by a factor of 2–3 depending on the method of solving the self-consistency of induced dipoles). However, in MC the electronic configuration of all molecules must be updated after each move of a single molecule, a feature that makes this method by $O(N)$ slower in comparison with the MC of non-polarizable models.

The first method for fast MC simulation of polarizable models was introduced by Meideiros and Costas [4] for fluctuating charge (FQ) models, in which only the partial charges of the molecule being moved are updated. Martin \textit{et al.} [5] suggested a sequential algorithm (SFQ-MC), where a molecule displacement is accepted or rejected without any change of its charges. As an independent move, the charges of randomly selected molecules are frequently updated. Chen \textit{et al.} [6] later recognized that SFQ-MC samples inappropriately the configurational space and presented its improvement, the adiabatic and electronic sampling (ANES-MC) algorithm, to correct such a deficiency. In the latter method, a molecule displacement is followed by a series of electronic moves (updates of charges) of randomly selected molecules, and the resulting configuration is treated as a trial configuration. The electronic moves are accepted using a very low electronic temperature to restrict the charges close to the electronic ground state. The ANES-MC method has been applied successfully also to GEMC simulation [7].

We are not aware of any efficient MC method for the simulation of fluids involving induced dipole moments. For that purpose, in this paper we investigate two
approximate methods for the MC simulations of polarizable fluids. Both methods are based on the evaluation of interactions between the molecule being displaced and other molecules; thus, they scale as a conventional MC method.

As a first step, we test the ‘single molecule update’ method, which is a straightforward generalization of Medeiros’ and Costas’ method. Next, we introduce in this paper the ‘pair approximation for polarization interaction’ (PAPI). Unlike the single-update method, PAPI updates induced dipoles on all molecules when a single molecule is displaced. This feature gives PAPI the ability to produce results accurately within (or close to) a standard deviation at times by an order of magnitude or more better in comparison with those for full iteration MC.

2. Model

We tested both methods for a simple polarizable model of water, namely the SCPDP model devised by Chialvo and Cummings [8]. This model originates from the SPC and TIP4P non-polarizable models with fixed geometry and charges. However, in SCPDP the fixed partial charges are rescaled to give the correct dipole moment 1.85 D of an isolated molecule, and the Lennard Jones (LJ) parameters are refitted to give the best agreement with experimental data of pressure and configurational energy under ambient conditions. We used the set of parameters for oxygen–negative charge distance |OM| = 0.2 Å, which has also been studied by Jedlovszky and Richardi [1] using NVT-MC simulation with full iteration. We used N = 256 molecules and a cutoff radius of 9 Å. Long range interactions were accounted for by LJ correction and reaction field technique with εRF = 78.

The polarizability is accounted for by a point-dipole interaction. There is a single induced moment \( p_i \) located at the centre of mass of each molecule \( i \), proportional to the total electric field \( E_i \) at that point, which is a sum of electric field from the charges on other molecules, \( E_i^q \), and that from the induced moments on other molecules, \( E_i^p \).

\[
\begin{align*}
p_i &= \alpha(E_i^q + E_i^p) \\
E_i^p &= \sum_{i \neq j} T_{ij} \cdot p_j. \quad (1)
\end{align*}
\]

Here we assume the polarizability \( \alpha \) to be scalar, \( T_{ij} \) is the dipole tensor

\[
T_{ij} = \frac{1}{r_{ij}^3} \left( \frac{3 r_{ij} f_{ij}}{r_{ij}^5} - \mathbf{1} \right), \quad (2)
\]

and \( \mathbf{1} \) is the unit tensor. Since equation (1) represents a set of coupled equations for induced moments, the fastest and simplest method for solving these equations in simulations is by an iterative procedure [9]. The total potential is given by the sum of the non-polarizable potential \( U_{nonpol} = U_{LJ} + U_{qp} \) and the polarizable potential \( U_{pol} = U_{qp} + U_{pp} + U_{self} = -\frac{1}{2} \sum_{i=1}^{N} p_i \cdot E_i^q \) (for details, see [8]).

3. Single-molecule update method

In the single-molecule update method, the electric field at the new position of a displaced molecule \( i \) is used, according to expression (1), to assign a new induced dipole \( p_i \). The inaccuracy of this method arises from the lack of update of the induced dipoles on other molecules, even though they experience a change in the local electric field due to the displacement of the molecule \( i \).

To gain some insight into this method, we performed a set of simulations for the thermodynamic state \( \rho = 1 \text{ g cm}^{-3} \) and \( T = 298 \text{ K} \). In each simulation, after \( M \) accepted displacements the full iteration was performed to update accurately all induced moments and the configurational energy. The difference \( \delta E = E - E_{\text{full}} \) of configurational energies before \( (E) \) and after the full iteration \( (E_{\text{full}}) \) at fixed molecular positions and orientations was monitored.

The average values of the correction \( \delta E \) and the average configurational energy \( E \) for different values of \( M \) are given in table 1. These values must be compared with the average energy obtained from the exact full iteration simulation, \( E_0 = -40.71 \pm 0.06 \text{ kJ mol}^{-1} \). This average is in good agreement with the value

<table>
<thead>
<tr>
<th>Single update</th>
<th>PAPI, ( R_{\text{iter}} = 0 )</th>
<th>PAPI, ( R_{\text{iter}} = 5.73 \text{ Å} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M )</td>
<td>( \delta E / \text{J mol}^{-1} )</td>
<td>( E / \text{kJ mol}^{-1} )</td>
</tr>
<tr>
<td>1</td>
<td>0.8</td>
<td>-35.52 ± 0.05</td>
</tr>
<tr>
<td>10</td>
<td>8.4</td>
<td>-35.52 ± 0.03</td>
</tr>
<tr>
<td>100</td>
<td>76</td>
<td>-35.44 ± 0.03</td>
</tr>
<tr>
<td>( \infty )</td>
<td>416</td>
<td>-35.04 ± 0.03</td>
</tr>
</tbody>
</table>

Table 1. Average configurational energy \( E \) and average energy correction \( \delta E \) due to full update after \( M \) accepted MC steps. For \( M = \infty \), \( \delta E \) was evaluated without modifying the configuration. The exact configurational energy at the state point considered, \( T = 298 \text{ K} \) and \( \rho = 1 \text{ g cm}^{-3} \), is \(-40.71 \pm 0.06 \text{ kJ mol}^{-1} \). MC runs are \( \approx 10^5 \) cycles.
-40.35 ± 0.35 kJ mol⁻¹ given by Jedlovszky and Richardi [1]. The oxygen–oxygen pair correlation function \( g_{OO}(r) \) from the single-update method is compared in figure 1 with that corresponding to a full iteration procedure. Evidently, the single-update method gives unacceptable departure from the correct results. The disagreement in both the average energy \( E \) and the pair correlation function \( g_{OO}(r) \) is independent of the frequency \( M \) of corrective full updates. With increasing \( M \), \( \delta E \) becomes larger, yet this deviation is relatively small and cannot explain the 5 kJ mol⁻¹ error in average energy. At this point we can make the following observations. The single-update method introduces two kinds of error. (i) The configurations which are accepted violate equation (1), because of the incomplete update of dipole moments. This error, estimated by \( \delta E \), is not crucial and can be controlled by an appropriate choice of the update parameter \( M \). (ii) Because it does not account for the significant part of the multibody interactions, the single-update method gives an inaccurate estimate of the energy difference between old and new positions of a molecule. This inaccuracy biases the MC sampling. The bias proves to be fatal, inherent to the method, independent of \( M \), and thus difficult to overcome.

The bias is most pronounced for small molecular separations. The positive average Lennard-Jones energy of the system indicates a repulsive LJ interaction, which is compensated for by the negative charge–charge and polarization contributions. The latter becomes more important for small separations because it scales as \( r^{-3} \).

With full iteration, when molecule 1 moves closer to molecule 2, both induced moments are enhanced and reoriented to produce a polarization contribution negative enough to compensate the LJ repulsion. However, if only the induced dipole 1 is updated without the response on molecule 2, the polarization contribution is much smaller, and such a trial move is likely to be rejected. The inverse is true as well in that if we start from a configuration obtained by the correct full iteration method, with the single-update method it becomes easier to separate two molecules at a close distance, since molecule 2 will still keep its enhanced dipole, making the change of polarization energy less positive in comparison with that from the full update. Therefore, within a few hundred cycles the total energy will drift from the correct value to the corresponding average given in table 1.

With the single-update method, the molecules will not approach each other as closely as they should, therefore the resulting structure is shifted, and subsequently the thermodynamics are erroneous as well. This behaviour is a consequence of the unphysical nature of the single update.

4. Pair approximation for polarizable interactions

As a more sophisticated approximation method for the MC simulations of polarizable models involving induced dipole moments, we present here the pair approximation for polarization interaction (PAPI). This method updates the induced dipoles on all molecules when a single molecule \( i \) is displaced. The information from the interaction between particle \( i \) and another molecule \( j \) is used not only to calculate the new value of \( \mathbf{p}_i \), but also to update \( \mathbf{p}_j \). The induced dipole on displaced molecule \( i \) is calculated from the new values of \( E_{ij}^q \) and \( E_{ij}^p \), which are evaluated directly as a sum of contributions \( E_{ij}^q \) and \( E_{ij}^p \) from neighbouring molecules, i.e.

\[
E_{ij}^q \text{ new} = \sum_{j \neq i} E_{ij}^q \text{ new} \quad \text{and} \quad E_{ij}^q \text{ new} = \sum_{q=1}^3 q_j^i \frac{r_{ij}^{\text{new}}}{|r_{ij}^i - r_{ij}^j|} , \tag{3}
\]

where contributions from the charges \( q_j^i \) of molecule \( j \) are summed, and

\[
E_{ij}^p \text{ new} = \sum_{j \neq i} E_{ij}^p \text{ new} \quad \text{and} \quad E_{ij}^p \text{ new} = \mathbf{r}_{ij}^\text{new} \cdot \mathbf{p}_j , \tag{4}
\]

The electric fields \( E_{ij}^q \) and \( E_{ij}^p \) on molecule \( j \) are modified by the displacement of molecule \( i \) and their new values are used to assign a new value of induced dipole \( \mathbf{p}_i \). The electric field from charges \( E_{ij}^q \) is updated using the old value \( E_{ij}^q \text{ old} \), saved in an array, and the difference in the contribution \( E_{ij}^q \) from molecule \( i \) to the total electric field from charges \( E_{ij}^q \) = \( \sum_{j \neq i} E_{ij}^q \) on molecule \( j \).

\[
E_{ij}^q \text{ new} = E_{ij}^q \text{ old} + \Delta E_{ij}^q \quad \text{and} \quad \Delta E_{ij}^q = E_{ij}^q \text{ new} - E_{ij}^q \text{ old} . \tag{5}
\]

Only the interactions between molecules \( i \) and \( j \) need to be considered to update \( E_{ij}^q \) accurately.
The change of electric field $\mathbf{E}_j'$ from induced dipole moments is given not only by the change of $\mathbf{p}_i$, but also by the change of all other induced moments $\mathbf{p}_k$, because all induced moments respond to the displacement of molecule $i$, i.e.

$$E_{j}'_{\text{new}} = E_{j}'_{\text{old}} + \Delta E_{j}' ; \quad \Delta E_{j}' = \sum_{k \neq j} E_{j,k}^{p \text{new}} - E_{j,k}^{p \text{old}}.$$  \hfill (6)

Exact evaluation of this equation implies the calculation of all pair interactions ($\propto N^2$), which is the most time consuming part of the full iterative procedure. It turns out, however, that most of the terms in the last sum are very small and can be neglected.

The simplest approximation to equation (6) is to consider only direct interactions between molecule $i$ and its neighbours to update their induced dipole moments as follows,

$$\Delta E_{j}' \approx E_{j}'_{\text{new}} - E_{j}'_{\text{old}}.$$  \hfill (7)

This equation is simple and fast for calculation purposes, yet it captures part of the dipolar interactions which is completely ignored by single-update method: the change in other induced dipoles when molecule $i$ is displaced. In fact, equation (7) is exact for the first iteration after a displacement of molecule $i$, because during the first iteration all induced dipole moments except that of molecule $i$ still have their old values.

This is no longer true for the second and higher iterations, when the induced dipoles are already modified according to the updated electric fields in the previous iterations. Therefore, we use a more general approximation than equation (7) for the second and higher iterations. Since the strength of the polarization interaction decreases as $r^{-3}$, the change in induced dipole moment $\Delta \mathbf{p}_i$ is small for molecules distant from both the old and new location of molecule $i$. The term $\Delta \mathbf{E}_{jk}',$ proportional to $\Delta \mathbf{p}_k$ must also be small, especially when molecules $k$ and $j$ are far away, because $\Delta \mathbf{E}_{jk}' = T_{jk} \cdot \Delta \mathbf{p}_k$ and $T_{jk}$ are proportional to $r_{jk}^{-3}$. Therefore, we consider for the update of induced dipoles interactions between the displaced molecule $i$ and all molecules within the cutoff radius of the new location of molecule $i$ (as in the first iteration, see figure 2) plus all interactions between molecules $j,j'$ which are distant from the old or new location of molecule $i$ by less than a parameter $R_{\text{iter}}$, which will be further discussed, i.e.

$$\Delta \mathbf{E}_{j}' \approx E_{j,j}^{p \text{new}} - E_{j,j}^{p \text{old}} + \sum_{j', \text{iter}} E_{j,j'}^{p \text{new}} - E_{j,j'}^{p \text{old}}.$$  \hfill (8)

The calculation of all interactions between molecules within $R_{\text{iter}}$ guarantees proper handling of multibody interactions for short separations, which is essential for the correct update of induced dipole moments and sampling of configurations. Because for a given $R_{\text{iter}}$ the number of these interactions is limited and not a function of the number of molecules, PAPI scales linearly with the number of molecules $N$, as for non-polarizable molecules. The $N^2$ dependence of the number of interactions evaluated by the exact procedure for polarizable interactions after each MC step is avoided.

From $E_{j}'_{\text{new}}$ and $E_{j}'_{\text{old}}$ the new induced moment $p_{j}'_{\text{new}}$ is calculated according to equation (1). Since $p_{j}'_{\text{old}} = \alpha (E_{j}^{q \text{old}} + E_{j}^{p \text{old}})$, there is no need to calculate or save the values of $E_{j}'$, and only the difference related to the move of molecule $i$ is relevant, i.e.

$$p_{j}'_{\text{new}} = p_{j}'_{\text{old}} + \alpha \Delta E_{j}'$$ \hfill (9)

The update of both $\mathbf{p}_i$ and all $\mathbf{p}_j$’s is iterated until an appropriate convergence is achieved. The convergence criterion is the same as for the full iteration: the iteration stops when it changes all of the induced dipoles by less than 0.2%. On average, 3 iterations are required. The electric field from the charges, $E_{j}'$, is updated throughout the simulation according to equation (5), because its value is needed to calculate the energy difference

$$\Delta U_{\text{pol}} = -\frac{1}{2} \sum_{k=1}^{N} (p_{k}'_{\text{new}} \cdot E_{k}^{q \text{new}} - p_{k}'_{\text{old}} \cdot E_{k}^{q \text{old}}),$$  \hfill (10)

used in the MC step.

There are several points which make the pair approximation for polarization interactions quite accurate and physically justifiable. (a) As long as all the induced dipoles do not differ significantly from the exact values given by the self-consistent full iteration (equation (1)), the first iteration is identical to that of full iteration, because during the first iteration equation (7) is exact. (b) The approximation used in higher iterations has a simple interpretation. We neglect the change in electric
field $\mathbf{E}'_{ik}$ on molecule $j$ arising from the change of induced dipole $\mathbf{p}_k$ on a molecule $k$ distant from $i$ by more than $R_{\text{iter}}$, i.e. when the change in induced dipole moment $\mathbf{p}_k$ is small and its effect on other molecules even smaller. (c) PAPI is exact for a single pair of molecules, a system for which the single-update method already fails. (d) Typically, the largest contribution to $E_i$ (60–70%) originates from $\mathbf{E}'_{ij}$, which is evaluated accurately, as well as $\mathbf{p}_i$ and $\mathbf{E}'_{ji}$. The approximation affects only a small part of the total electric field calculation.

5. Results and discussion

The performance of PAPI with full updates after 100 accepted steps, i.e. $M = 100$, is documented at ambient conditions in table 2 and figure 1 for different values of the iteration radius $R_{\text{iter}}$. Even for $R_{\text{iter}} = 0$, when equation (7) is used for all iterations, PAPI is much better than the single-update method, the average configurational energy is only 2% higher than that obtained by the full iteration, and the pair correlation functions are close to or indistinguishable from the correct ones. Inclusion of all interactions between nearest neighbours of the displaced molecule, $R_{\text{iter}} = 3.3\,\text{Å}$, which corresponds to the location of first minimum of $g_{OO}$, does not improve the accuracy significantly. However, when the location of the second minimum of $g_{OO}$ is used for $R_{\text{iter}}$, $R_{\text{iter}} = 5.73\,\text{Å}$, the results differ from the exact ones by less than 0.3%. The simulation using PAPI is more than 10 times faster than that using the full iteration. When interactions between all molecules within the cutoff distance of the displaced molecule are used to update the dipole moments, $R_{\text{iter}} = 9.0\,\text{Å}$, PAPI recovers the exact results. However, because there is on average 101 molecules within the cutoff distance under the conditions studied here, this simulation is considerably slower than the previous cases, and is only 5 times faster than that for the full iteration. The CPU times are given in minutes per 1000 MC cycles on a desktop computer; it is not the absolute values that are important but the ratios.

The pair correlation functions for different values of $R_{\text{iter}}$ are shown in figure 1. For $R_{\text{iter}} = 0$ and $R_{\text{iter}} = 3.3\,\text{Å}$, there is a slight shift in the correlation functions towards larger distances, especially for the oxygen–oxygen pair correlation function. This complies with the neglecting of a part of the multibody interactions and its consequences, as we discussed for the single-update method. The curves for $R_{\text{iter}} = 5.73\,\text{Å}$ and $R_{\text{iter}} = 9.0\,\text{Å}$ (not shown) are indistinguishable from the correct ones obtained by the full iteration.

The second parameter affecting the performance of PAPI is the frequency of the full updates using the exact full iterative procedure, performed after $M$ accepted displacements. Thus the trial configurations are always accepted/rejected using PAPI, but the full iteration at infrequent intervals brings the induced dipole moments to agreement with the self-consistent equation (1). For $M = 1$, each accepted move is followed by a full iteration. Such a simulation is a perfect test of the pair approximation, because in this case the only source of error can be the sampling of the configurational space. As seen in table 1, the sampling is not exact for $R_{\text{iter}} = 0$ when the configurational energy differs from the exact one by 2%. For $R_{\text{iter}} = 5.73\,\text{Å}$ we get exact result for $M = 1$. With increasing $M$, the induced dipole moments depart from the self-consistent values and the accuracy of simulations deteriorates. For simulations without any full updates, $M = \infty$, we get 0.6% error in the average energy for $R_{\text{iter}} = 5.73\,\text{Å}$. With the PAPI approximation, the induced dipole moments do not obey the self-consistent equation strictly; however, they keep close to those values and do not diverge from them even in the absence of any full updates. Carrying out the full updates after 10 accepted MC steps (i.e. on average after 33 trial steps) slows down the simulation only by 23%, but gives accurate results for both the average energy and the correlation functions.

Table 2. Average configurational energy $E$, CPU time, and average number of molecules within $R_{\text{iter}}$ of displaced molecule for $M = 100$ and different values of $R_{\text{iter}}$.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>$E$/kJ mol$^{-1}$</th>
<th>CPU time</th>
<th>$N_{\text{iter}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full iteration</td>
<td>$-40.71 \pm 0.06$</td>
<td>195</td>
<td></td>
</tr>
<tr>
<td>PAPI, $R_{\text{iter}} = 0$</td>
<td>$-39.93 \pm 0.04$</td>
<td>14.9</td>
<td>0</td>
</tr>
<tr>
<td>PAPI, $R_{\text{iter}} = 3.3,\text{Å}$</td>
<td>$-40.02 \pm 0.04$</td>
<td>15.4</td>
<td>4</td>
</tr>
<tr>
<td>PAPI, $R_{\text{iter}} = 5.73,\text{Å}$</td>
<td>$-40.61 \pm 0.04$</td>
<td>17.6</td>
<td>25</td>
</tr>
<tr>
<td>PAPI, $R_{\text{iter}} = 9.0,\text{Å}$</td>
<td>$-40.72 \pm 0.02$</td>
<td>39.6</td>
<td>101</td>
</tr>
</tbody>
</table>

Figure 3. Probability distribution of energy correction $\delta E$ due to a full update of all induced dipole moments after $M$ accepted displacements of a molecule.
different values of \( M \). The iteration involved in PAPI modifies all the induced dipoles to minimize the energy between the moved molecule and the others, which can make the energy even lower than that obtained by the full iteration procedure for a given configuration (\( \delta E < 0 \)). This effect is possible only by violating the self-consistent expression (1). The distribution for PAPI with \( M = 100 \) is shifted by 0.007\% towards lower energies for \( R_{\text{iter}} = 0 \text{ Å} \), but it is perfectly centred and more peaked for \( R_{\text{iter}} = 5.73 \text{ Å} \). Increasing \( M \) makes the distribution even sharper. The flat and by 0.02 \% shifted distribution obtained by the single-update method for \( M = 10 \) clearly confirms the inferiority of that method.

With a constant acceptance ratio of MC steps close to 30\%, the speed enhancement of PAPI with respect to the full iterative procedure is independent of the thermodynamic state. For \( R_{\text{iter}} = 5.73 \text{ Å} \) and \( N = 256 \) molecules, PAPI is 9 times (\( M = 10 \)) and 11 times (both \( M = 100 \) and \( M = \infty \)) faster than the full iteration counterpart; for \( N = 512 \) molecules, these ratios become 13 and 20. Thus, even though PAPI works quite well without any full updates of induced moments (\( M = \infty \)), the inclusion of these updates at infrequent intervals can increase the accuracy without a significant loss of computational speed. The best choice of PAPI parameters depends on the model, the state point studied, and the required accuracy. As a rule of thumb, the value of \( R_{\text{iter}} \) corresponding to the second minimum of \( g_{\infty} \) and full updates after from 10 to 100 accepted MC steps can be recommended. We found that the use of these recommended parameters in the simulation of the SCPDP model needed only twice the CPU time as that for the simulation of the corresponding non-polarizable model. Because of the combination of speed per MC step and phase space sampling efficiency, thanks to the large trial displacements, 0.27 Å and 0.37 rad, used here, it appears that PAPI may be much faster than ANES-MC [6].

The state point studied here presents one of the most stringent tests. At higher temperatures and lower densities, PAPI gives even more accurate results, as indicated in table 3. Jedlovszky and Richardi [1] found the average energy at this state point to be \(-23.48 \pm 0.58 \text{ kJ mol}^{-1}\), which agrees perfectly with our results. The pair correlation functions under these conditions are indistinguishable from the exact ones obtained by full iteration, for this state point even those for \( R_{\text{iter}} = 0 \) and \( M = \infty \).

<table>
<thead>
<tr>
<th>Simulation</th>
<th>( E ) (kJ mol(^{-1}))</th>
<th>CPU time</th>
<th>( N_{\text{iter}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full iteration</td>
<td>(-23.53 \pm 0.02)</td>
<td>154</td>
<td></td>
</tr>
<tr>
<td>PAPI, ( R_{\text{iter}} = 0 \text{ Å} )</td>
<td>(-23.28 \pm 0.02)</td>
<td>11.7</td>
<td>0</td>
</tr>
<tr>
<td>PAPI, ( R_{\text{iter}} = 5.73 \text{ Å} )</td>
<td>(-23.45 \pm 0.02)</td>
<td>13.4</td>
<td>18</td>
</tr>
</tbody>
</table>

This feature makes PAPI a convenient tool for the study of phase equilibria of polarizable models at high temperatures and supercritical states. The extension of PAPI to Gibbs ensemble MC is planned for a subsequent paper [10].

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