ESTIMATION OF THE DIFFERENCE BETWEEN MOLECULAR DYNAMICS AND MONTE CARLO AVERAGES DUE TO THE TRUNCATION OF THE POTENTIAL

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A particular discrepancy between Monte Carlo and molecular dynamics calculations using a truncated potential is analysed and an approximate method for its estimate based on Monte Carlo calculation is presented. Results are given for the configurational internal energy of the ST2 water at 10°C

1. Introduction

Ensemble averages obtained by the Monte Carlo and molecular dynamics calculations of the same (finite) system should show a slight difference ($O(1/N)$, N being the number of particles considered) [1], due to the difference in the ensembles employed. If the interaction between the particles is described with a truncated non-spherical potential, a further discrepancy arises [2–4]. The purpose of this letter is to present an approximate procedure to calculate the difference in expectation values due to this latter discrepancy and to present the estimated difference in the internal energy of the ST2 water [2] based on the recent very long Monte Carlo calculation in this laboratory [5].

2. Theory

There is a difference between the ways the Monte Carlo and molecular dynamics methods implement the truncation of the potential, giving rise to a difference in the ensemble averages computed. For the evaluation of the internal energy, both methods set to zero the interaction energy, V_{ij}, between molecules i and j, if the distance between the two molecules, r_{ij}, is greater than a predetermined cut-off, R_c:

$$E_T = \sum_{\{i,j \mid r_{ij} < R_c\}} V_{ij}. \tag{1}$$

In the Monte Carlo method E_T is then used to generate the Markov chain in the configuration space, while in the molecular dynamics method the analogously truncated forces are used to obtain the trajectory of the system. This implies that the trajectory generated will have a Boltzmann distribution with internal energy $E_T + E_c$, where

$$E_c = \sum_{\{i,j \mid r_{ij} \geq R_c\}} V_{ij}(R_c). \tag{2}$$

Here $V_{ij}(R_c)$ denotes the most recent value of the pair potential such that $r_{ij} = R_c$. Since the potential is not spherically symmetric, $V_{ij}(R_c)$ will depend on the particular relative orientation of the molecules i and j at that time. As a consequence, E_c depends on the history of the system and is therefore non-conservative. Note, however, that the value of E_c does not appear explicitly in the calculations.

In general, given a Markov chain, generated by a potential energy function E^0, for any property P it is possible to obtain its expectation value that is generated by the potential energy function $E^0 + \delta E$ using the following expression [6]:

$$\langle P \rangle_{E^0+\delta E} = \langle P \rangle_{E^0} + \sum_{k=1}^{n} P^{(k)} \exp(-\beta \delta E^{(k)}) / \sum_{k=1}^{n} \exp(-\beta \delta E^{(k)}), \tag{3}$$

where n is the number of Monte Carlo steps and the superscript k refers to a particular configuration. Eq. (3)

is exact in the limit $n \to \infty$, but for runs of practicable length it is valid only for small δE. If we apply eq. (3) to the property $P \equiv E_T$ and use $E^0 \equiv E_T$ and $\delta E \equiv E_c$ the result is the estimate of the difference between the expectation value of E_T computed by the Monte Carlo method, $\langle E_T \rangle_{MC}$, and the expectation value of E_T computed by the molecular dynamics method, $\langle E_T \rangle_{MD}$. This arises because the Markov chain and the molecular dynamics trajectory are generated using E_T and $E_T + E_c$, respectively

$$\langle \Delta E_T \rangle = \langle E_T \rangle_{MC} - \langle E_T \rangle_{MD} = (1/n) \sum_{k=1}^{n} E^{(k)} - \sum_{k=1}^{n} E^{(k)} \exp(-\beta E_c^{(k)}) / \sum_{k=1}^{n} \exp(-\beta E^{(k)}). \quad (4)$$

It should be stressed that it should be more appropriate to use eq. (4) in conjunction with the molecular dynamics trajectory, but we expect our estimate to be good too since the comparison of the results by the two methods shows the differences to be quite small [2–4].

The computation of E_c presents two problems. While the definition of $V_{ij}(R_c)$ involves pair energies at exactly the cut-off distance, the Markov chain consists of a discrete set of configurations. Also, at the beginning of the calculation the $V_{ij}(R_c)$ values are undefined

The first problem was solved by linear interpolation. An exact solution to the second problem would follow the trajectory of the system until all values are assigned and discard this "initial" portion of the run. This, unfortunately, requires much longer calculations than the one analysed here. Our approximate solution follows the Markov chain until a significant portion of the $V_{ij}(R_c)$ values were obtained and subsequently assigned the remaining pairs the average computed over a previous stretch of the Markov chain.

3. Results and discussion

A very long Monte Carlo simulation was recently performed in this laboratory [1] on the ST2 water [2] at 10°C temperature, 1.000 g/ml density using 216 molecules under simple cubic periodic boundary condition, with a spherical cut-off $R_c = 8.46$ Å (a value that is smaller than the half-edge of the periodic cell), in order to study the convergence characteristics of the conventional Metropolis Monte Carlo method since this particular system was reported to show convergence problems [3]. We present here an estimate of the effect of the truncation on the configurational internal energy of this system using eq. (4).

The actual estimation was performed on the last 2090 K configurations, using the preceding 70K to initialize $V_{ij}(R_c)$ values. The $V_{ij}(R_c)$ values not initialized were given an average value obtained from a previous 300K segment. The computed values of the estimate $\langle \Delta E_T \rangle$ and the value of E_c at successive stages of the analysis are given in table 1. The number of $V_{ij}(R_c)$ terms that were actually computed and the number that were estimated are also given in table 1.

We can estimate from table 1 that the initialization of all $V_{ij}(R_c)$ values would require at least an additional ≈ 10000K long run. However, the oscillatory behaviour of E_c indicates that our approximate procedure for the computation of E_c did not introduce serious bias into the calculation.

The final estimate of $\langle \Delta E_T \rangle$ can be read from table 1 as 0.1 kcal/mol The result on the molecular dynamics calculation on the same system is $\langle E_T \rangle_{MD} = -10.4$ kcal/mol [2]. This results in a corrected $\langle E_T \rangle$ value of −10.3 kcal/mol that can be compared with $\langle E_T \rangle_{MC}$. The Monte Carlo calculation in this laboratory produced two regions with internal energy averages of −10.49 ± 0.03 kcal/mol and −10.70 ± 0.02 kcal/mol, respectively [5]. This implies an overall average of −10.60 ± 0.13 kcal/mol. Calculations by Rao et al. [4] using the force-biased Monte Carlo method gave −10.6

Table 1
Results of the estimation of $\langle \Delta E_T \rangle$

Number of steps (in thousands)	Number of $V_{ij}(R_c)$		E_c (kcal/mol)	$\langle \Delta E_T \rangle$ (kcal/mol)
	computed	estimated		
0	1037	13095		
300	3253	10886	0.633	−0.0096
600	3968	10171	0.630	−0.103
1100	4714	9427	0.613	−0.0458
1250	4937	9205	0.642	0.111
1550	5247	8892	0.651	0.0991
1850	5577	8562	0.616	0.0982
2090	5819	8320	0.630	0.113

kcal/mol on the same system. This leaves a difference of 0.3 kcal/mol that can be attributed to the $\mathcal{O}(1/N)$ difference between the finite realizations of the two methods.

In summary, we can conclude that the discrepancy introduced by the truncation into the configurational internal energy is quite small, being comparable to the uncertainty of the Monte Carlo calculations. This, of course, does not exclude the possibility that it could be more significant for other properties. In any case, the procedure described here is applicable to the estimation of this discrepancy in the expectation value of any property.

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