COMMENTS

Comment on ''Molecular dynamics simulations in the grand canonical ensemble: Formulation of a bias potential for umbrella sampling'' [J. Chem. Phys. 110, 8295 (1999)]

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In a recent paper describing a significant improvement in the grand canonical ensemble (GCE) molecular dynamics (MD) method of Çağın and Pettitt,[1] Shroll and Smith[2] remarked that '' . . . it is possible that this dynamical approach may circumvent some of the computational difficulties associated with discrete insertion and deletion methods.'' While the focus of Ref. 2 was a different aspect of the GCE-MD methodology, Fig. 2 of that paper showing the fluctuation of the number of molecules as a function of time provides an opportunity for the examination of this possibility. Accordingly, this comment compares the fluctuation of particle numbers during the simulation as obtained by this MD run and by the cavity-biased Monte Carlo method.[3,4]

To allow comparison with the data of Ref. 2, the SPC/E model for liquid water[5] was simulated in a periodic cube of edge 14.74 Å and the targeted number of waters was 107, to reproduce the experimental water density at 300 K, the temperature set. All interactions were treated under the minimum image convention. This differs from the treatment of Ref. 2, where Ewald summation was used to evaluate the electrostatic energy, but this difference is unlikely to affect significantly the fluctuation characteristics under study here.

The program MMC[6] was used to perform the Monte Carlo calculations with the cavity-biased insertions. The cavity radius was set to 2.5 Å. Each metropolis displacement attempt was followed by an insertion or deletion attempt.

The computational effort involved in 1 ns MD with a timestep of 2 fs is approximately equivalent to $10^6 * N/2$ MC steps. Here it is assumed that the extra time involved in the insertion/deletion attempts (ca. 20%) is about the same as the extra time required to calculate the forces (in addition to the energy). Thus a run of 10 million MC steps targeting 107 water molecules represents about 400 ps of molecular dynamics.

Figure 1 shows the number of molecules during our 10 million step long MC run and the first half ns of the MD simulation. It is clear that fluctuations of the order of 8–10 molecules occur with a period of about half million MC steps (i.e., in a run equivalent to ~20 ps), while the MD runs require about half ns to produce the same fluctuation. Furthermore, the range of the number of molecules in the 2.5 ns MD run was 11.5 while the 10 million step long MC run sampled in the range of 20 molecules. These results show that this MC simulation outperformed the corresponding MD run by an order of magnitude. This difference is large enough that optimization of the mass of the number extension variable (not done in Ref. 2) would be unlikely to reverse the comparison.

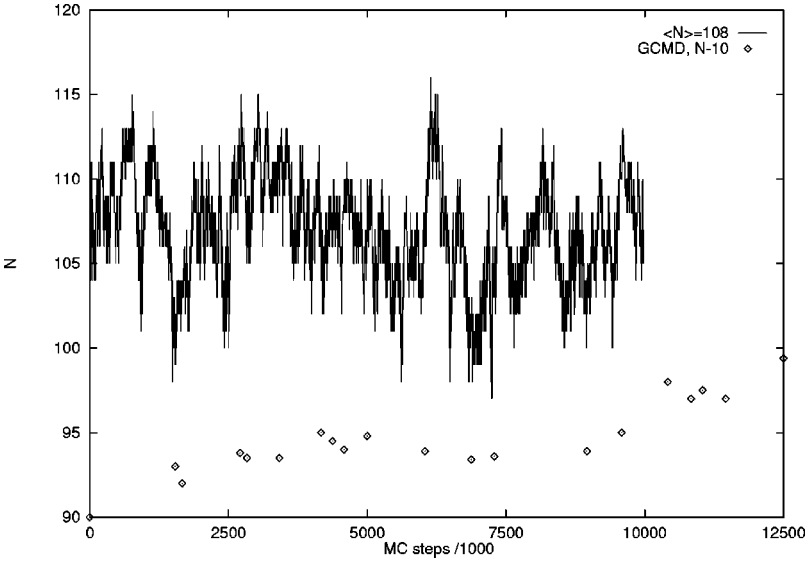

FIG. 1. Change in the number of molecules during the MC run (line) and the MD run of corresponding length (◇), as read from Fig. 2 of Ref. 2.

It should also be pointed out, however, that this comparison is limited for systems where the molecule undergoing insertions is of comparable size to the rest of the system. Once the size of the molecule to be inserted exceeds the maximum conceiveable size of cavities, discrete insertion will not be feasible any more, while the continuous insertion techniques described in Refs. 1–3 will retain their viability.

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