Daresbury Laboratory
INFORMATION QUARTERLY for COMPUTER SIMULATION
of CONDENSED PHASES
Number 36 1993

An other 'clever' idea down the drain ...

Mihaly Mezei
Department of Physiology and Biophysics
Mount Sinai School of Medicine, CUNY,
New York, NY 10029, USA.

As readers of this Newsletter know all too well, the efficient simulation of dense liquids is seriously hampered by the fact that the molecules diffuse rather slowly, instead they spend most of their time just rattling around in the cage of their neighbours. This is less of a problem for homogeneous liquids but more pronounced for mixtures.

The 'clever' idea referred to in the title was an attempt to used the cavity biased insertion, developed for grand-canonical ensemble simulation [1,2] in the canonical ensemble to perform simultaneously the removal and the insertion of a molecule. This idea grew out of the observation in [2] that the insertion - deletion feature of the grand-canonical ensemble simulations are mimicking large jumps. Such a pair of moves would be indistinguishable from a big jump — just the kind of move one would like to have. The idea appeared to be clever, because if one inserts the just removed molecule into a cavity, the removal also leaves behind a cavity and thus microscopic reversibility would be maintained without further corrections in the acceptance expression. To be rigorous, one should exlude from removal those molecules that have neighbours closer than the cavity radius.

This idea was put to test on 91 room-temperature SPC water molecules in a cubic box under periodic boundary conditions at experimental density. This system was shown to have sufficient number of cavities for the cavity-biased insertions [2]. Two million attempted Monte Carlo displacements were performed of the usual kind and after every 10-th conventional step a 'cavity jump' was also attempted. This, of course, required significant extra work since a grid whad to be maintained to track the location of cavities, as described in [2]. However, none of these attempted jumps were accepted, reflecting the fact that the algorithm also has to 'pay' for the removal of the molecule, and dearly, at that.

Naturally, one can still switch to the grand-canonical ensemble, but otherwise, until a truly clever idea comes along, we have to stay with the simulation moves of the kind we are used to.

References:

1. M. Mezei, Molec. Phys. **40**, 901 (1980).

2. M. Mezei, Molec. Phys. **61**, 565 (1987); erratum: **67**, 1207 (1989).