

Apparent Energy Conservation

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One of the constant concerns of a molecular dynamic is his energy conservation. New programs rarely conserve energy and in nine out of ten cases this will be a programming error which calls for prolonged staring. There is an unhappy moment when all the apparent bugs have been removed and the internal energy still fluctuates. One possibility is that the differential equations are too stiff and the choice of algorithm is inappropriate. If this is the case energy conservation normally improves as the timestep is reduced. A more likely cause is that all the relevant contributions to the total energy have not been included. We recently came across an interesting example of the latter problem.

We were developing a program to simulate Lennard-Jonesium in the gas-liquid interface. To begin the project we wrote a simple program to simulate 256 LJ atoms in the bulk liquid. As is our wont we used a fifth-order predictor-corrector method and an interaction cut-off of 2.5σ . We were particularly concerned about energy conservation since we planned long runs in the interface. The program seemed to run well but the energy fluctuation, 1 part in 1200, was too large for comfort. For this system Verlet claims an energy conservation of 1 part in 10^7 (Verlet, 1967) and although we had never seen the energy this steady we were anxious to try and reproduce the result. We obtained little improvement by reducing the timestep and increasing the cut-off to 3σ and we wondered if the leapfrog algorithm was intrinsically more accurate than the Gear method. The problem was eventually traced to the

definition of the potential. The force on a particle i from its neighbour j is defined by

$$f(r) = 48\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - 0.5 \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad r_{ij} < r_c$$

$$f(r) = 0 \quad r_{ij} > r_c \quad (1)$$

There is a small discontinuity at the cut-off, if $r_c = 2.5\sigma$ this is $0.039 \epsilon \sigma^{-1}$, which is less than 2% of the well-depth in the force.

The potential at r_{ij} is minus the force integrated from infinity to r_{ij} ,

$$U(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] - 4\epsilon \left[\left(\frac{\sigma}{r_c} \right)^{12} - \left(\frac{\sigma}{r_c} \right)^6 \right] \quad r_{ij} < r_c \quad (2)$$

This is the simulation potential; the normal U_{LJ} plus a small constant correction. This means that any time-step the internal energy is given by

$$E = \frac{3}{2} N_c kT + \sum_{\substack{i < j \\ r_{ij} < r_c}} U_{LJ}(r_{ij}) - \frac{N_c(N_c - 1)}{2} U_{LJ}(r_c) \quad (3)$$

where N_c is the number of atoms in the cut-off sphere. It is this quantity which is conserved and since N_c fluctuates, failure to include the third term in (3) distorts the real energy conservation. The improvement obtained by including the third term as a correction is shown in table 1. These remarks apply equally to simulations of molecular liquids with discontinuous cut-offs in the force. Even when r_c is taken as half the box-length N_c can still fluctuate. The problem will not occur if we use the minimum image method and include all interactions in the basic cube since the last term in (3) is then a constant, but this will nearly double the number of interactions which have to be considered

explicitly and this is prohibitively expensive.

Cut-off	Corrected	Conservation	T^*	U^*	P^*
2.5 σ	No	1 part in 1200	1.05	-4.52	-0.05
2.5 σ	Yes	1 part in 300000			
3.0 σ	No	1 part in 1700	1.02	-4.53	-0.11
3.0 σ	Yes	1 part in 500000			

TABLE 1: A simulation of Lennard-Jonesium, ($\rho^* = 0.650$), timestep, (0.863×10^{-14} s). The figures for energy conservation represent the total spread in energies based on timesteps 2500 - 2600 after equilibration. The thermodynamic properties after 3000 timesteps include the long range corrections. All simulations are started from the same point in phase space and equilibrated for 1300 timesteps. (note that micro-fiche copies of the results are available on request).

These problems can be avoided by using a shifted force potential (Streett *et al.* 1978) defined by

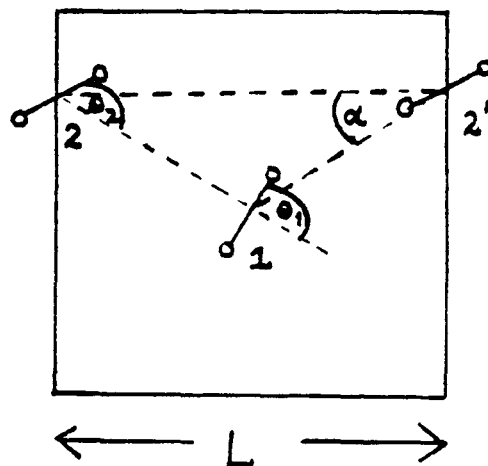
$$\begin{aligned}
 U(r_{ij}) &= U_{LJ}(r_{ij}) - U'_{LJ}(r_c)r_{ij} + U'_{LJ}(r_c)r_c - U_{LJ}(r_c) \quad r_{ij} < r_c \\
 U(r_{ij}) &= 0 \quad r_{ij} > r_c. \quad (4)
 \end{aligned}$$

This kind of potential has a force that goes to zero at r_c , (although it does have a regulation cusp at this point). For those who have simulated with the first term in (2) the energy conservation is probably better than it looks.

Those who believe that snipping at 2.5 σ can have very little effect on properties of interest will remember that the critical temperature

of Lennard-Jonesium has been estimated at $T_C^* = 1.32 - 1.36$, (Barker and Henderson, 1976). At the last CCP5 meeting on interfaces a number of estimates were given for the critical temperature of truncated Lennard-Jonesium; none of these were over $T_C^* = 1.2$ and for a potential which had been cut and shifted at 2.5σ there was an estimate of $T_C^* = 0.99$, (Saville, 1982). It has also been known for some time that the densities of the coexisting liquid and gas depend on the truncation of the potential (Lee *et al.* 1974)

If we include all the contributions to the internal energy then, in the case of an atomic fluid, we might expect time-step to time-step conservation of energy of better than 1 part in 10^5 , (for the Gear method). In the case of a molecular fluid there is an additional problem. Imagine simulating a quadrupolar fluid with a minimum image convention. During a time-step molecule 2 crosses the boundary and 2' enters through the opposite face.



If the relative orientations of molecules 1 and 2 are θ_1, θ_2 then the relative orientations of 1 and 2' are $\theta_1 - 2\alpha$ and $\theta_2 - 2\alpha$. Now $U_{QQ}(\theta_1, \theta_2)$ does not equal $U_{QQ}(\theta_1 - 2\alpha, \theta_2 - 2\alpha)$ unless $\alpha = 0$, or $\theta_1 + \theta_2 = n\pi + 2\alpha$;

($n = 0$, or 1), and there will be a small jump in energy of order $Q^2(0.5L)^{-5}$ during the crossing. For a model of liquid nitrogen, (256 molecules, $33.85 \text{ cm}^3 \text{ mole}^{-1}$) we estimate that this energy jump will be of order 1 part in 10^6 of the total energy, (allowing ten particles to cross a boundary at each time-step). Energy would then be conserved at the level of 1 part in 10^5 which is the general experience with this kind of system. In the case of fluids of dipolar molecules the energy jump is of order $\mu^2(0.5L)^{-3}$. For small systems the fluctuations caused by the boundary crossing may well be visible at the level of 1 part in 10^5 , (Adams *et al.* 1979; Impey, 1982). In the case of a dipolar molecule, with no symmetry plane perpendicular to the molecular axis, the jump in energy may be more pronounced since the interaction falls off as r^{-3} ; energy is still conserved at $\alpha = 0$, but many of the other relative orientations which conserve for quadrupoles do not for dipoles. These small fluctuations in the total energy will mean that properties such as the specific heat, which is measured by monitoring fluctuations in the kinetic energy, are difficult to calculate accurately. For a simulation of water it may be necessary to abandon the minimum image convention for the Ewald sum not just for collective correlation functions but to maintain a sufficiently high standard of energy conservation throughout the simulation (Impey, 1982).

In the case where the multipoles are modelled by partial charges, rather than idealized point moments, we have to consider what happens when a molecule lies across a boundary. In this case one of the charges will be outside the box. If we consider the minimum image of this charge, the central molecule will think itself surrounded by charged ions at approximately half the box length. This problem can be avoided by always using a centre of mass cut-off for models with partial charges.

Finally, although we used the same time-step as Verlet, (1967), in our simulation of atoms we never found the energy constant to 1 part in 10^7 so it is possible that leap-frog algorithms are slightly more stable than predictor-corrector techniques for the simulations of liquids.

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