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Note

Energy Conservation in Molecular Dynamics

In molecular dynamics (MD) calculations of the classical mechanical trajectories of N particles, the energy, E, is not strictly conserved, but it fluctuates with time during the computation. The fluctuation is mainly caused by the short-range interactions and can be diminished decades by a new algorithm [1]. Furthermore, many algorithms result in a (small) drift in energy, δE, and this note deals with the problem of ensuring energy conservation in MD calculations.

The simplest way to get rid of an energy drift is of cause to choose a sufficient small time increment, h, but this is often an unnecessary and expensive way to solve the problem. A much simpler way is to adjust the kinetic energy for the drift, which can be done during the calculation by making use of the fact that the heat capacity, $c_V = (\partial E/\partial T)_V$ is given by the time means, $\langle\ \rangle$, of the fluctuations in temperature, T [2],

$$\frac{\langle T^2\rangle - \langle T\rangle^2}{\langle T\rangle^2} = \frac{3}{2N}\left(1 - \frac{3kN}{2c_V}\right). \tag{1}$$

The energy, produced per time step and per particle, δE, is many decades smaller than the change in kinetic energy per step. It dissipates into the system and causes a corresponding small drift in the temperature, δT, which can be obtained from (1) during the calculation as

$$\delta T = c_V^{-1}\,\delta E. \tag{2}$$

By a few scalings of the velocities during the MD computations one can constrain the system to constant energy by means of (1) and (2).

The algorithm in [1] exhibits a negligible drift in energy for a traditional choice of time increment, h. However, for a larger time increment and/or at high temperatures one can spot [1, 3] a small drift in the energy which can be removed by (1) + (2) or it can be diminished a decade by the following procedure: In [1] the time-derivatives of the forces $\mathbf{a}'_{ij}(t+h)$, $\mathbf{a}''_{ij}(t+h)$ between particle Nos. i and j are calculated from $\mathbf{a}_i(t+h)$ and the predicted velocities $\mathbf{r}'_{i,pr}(t+h)$. The velocities $\mathbf{r}'_{i,pr}(t+h)$ are calculated from a second-order formula (A2 in [1]) and this formula is the Achilles' heel in the algorithm which introduces the drift. Heyes and Singer [3] use a third-order Taylor expansion of the velocities from $\mathbf{r}'_i(t)$. It is, however, possible to use a corresponding fourth-order predictor without any increase in computer time or

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storage, and this diminishes δE a decade. The fourth-order term in the velocity, $(1/4!)\, h^4 \mathbf{a}_i'''(t)$, can be obtained from

$$\frac{1}{3!} h^3 \mathbf{a}_i'''(t) = \mathbf{a}_i(t+h) - \mathbf{a}_i(t) - h\mathbf{a}_i'(t) - \frac{1}{2} h^2 \mathbf{a}_i''(t) + \mathcal{O}(h^4). \tag{3}$$

(It can also be calculated directly but this is more complicated.) The velocities at time t are correspondingly given by

$$\mathbf{r}_i'(t) = [\mathbf{r}_i(t+h) - \mathbf{r}_i(t-h)]/2h - \frac{1}{3!} h^2 \mathbf{a}_i'(t) - \frac{1}{5!} h^4 \mathbf{a}_i'''(t) + \mathcal{O}(h^6). \tag{4}$$

This procedure was tested on a Lennard–Jonesium at a high temperature fluid state ($kT/\varepsilon = 2$, $\rho\sigma^3 = 0.75$) and for the time increment $h = 0.01(m\sigma^2/\varepsilon)^{1/2}$. The result is given in Table I. For smaller h or/and lower temperatures there is no drift in E. An energy drift of the magnitude given in Table I will normally not be observed due to the much larger statistical error caused by the finite size of the system and finite time in the MD simulations.

Conservation of energy is a necessary condition for MD algorithm, but it is not a sufficient criterion. A simple third-order Verlet-algorithm [4] has no drift in the energy even for large time increments, although the energy fluctuates from step to step. This algorithm conserves the mean energy because it is symmetrical with respect to time and therefore reversible ($dE = T\,dS - p\,dV$, and $dS = 0$ and $dV = 0$). But it does not lead to the correct trajectories for large h which can be demonstrated by calculating the root mean square deviation (r.m.s.) in the end positions of the particles after an integration time, τ, obtained for different time increments. Already after 10 steps with $h = 0.01$ the end positions differed from the end positions obtained as 40 steps with $h = 0.0025$. The r.m.s. was $1.0 \times 10^{-3}\sigma$ for the Verlet-algorithm and about 30 times less for [1]. A factor ≈ 30 was also obtained by integrating 20 time steps with $h = 0.005$; the r.m.s. was $2.4 \times 10^{-4}\sigma$, and $7.3 \times 10^{-6}\sigma$, respectively.

TABLE I

Algorithm [1], $\mathbf{r}_{i,pr}'(t+h)$	$\delta E/\varepsilon$
A2 in [1]	$+1.0 \times 10^{-5}$
3-order Taylor expansion	-3.9×10^{-5}
4-order Taylor expansion	$+1.0 \times 10^{-6}$

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SØREN TOXVAERD
Department of Chemistry
Panum Institute
University of Copenhagen
DK-2200 Copenhagen N, Denmark