

ALGORITHMS FOR CONSTANT TEMPERATURE AND/OR CONSTANT PRESSURE ENSEMBLES IN  
MOLECULAR DYNAMICS SIMULATIONS OF ATOMIC LIQUIDS

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Conventionally molecular dynamics (MD) simulations of liquids at equilibrium are carried out using the constant energy ensemble. This is the usual microcanonical  $(N,V,E)$  ensemble of constant number of particles,  $N$ , constant volume,  $V$ , and constant total energy,  $E$ , augmented by the fourth constraint of zero total linear momentum. Over the years several schemes have been proposed for performing MD calculations in alternative ensembles more comparable with the usual laboratory conditions of constant temperature and/or constant pressure. These include the  $(N,V,T)$  [1-4], the  $(N,P,H)$  and  $(N,P,T)$  ensembles [3,5] and also the  $(N,\underline{S},H)$  ensemble [6], where  $\underline{S}$  is the stress tensor. In most cases the relevant articles [1-11] have concentrated on the theoretical justification of the methods and the results obtained using them. In some cases results obtained from different ensembles have been compared [5,7-10] but in general little information is given of the specific algorithms used to integrate the different equations of motion. This can be disheartening for the potential user of these methods who finds that apparently rigorous mathematical expressions do not lend themselves to easy numerical integration and is thus left to ponder how the originator circumvented the problems. Having spent many happy hours in trying to develop ways in which some of the methods can be implemented in a MD program it may be of some use to relate these ideas to those most likely to be interested through the pages of this newsletter. Most of the ideas applied in what follows will be familiar to anyone who has ever written a MD program but the context in which they are used may not be. The 'new' algorithms presented for  $(N,V,T)$ ,  $(N,P,H)$  and  $(N,P,T)$  MD are by no means the last word and there is certainly room for improvement. They do work, however, and hopefully this article will spur others into revealing their better integration schemes.

Given below are the five algorithms which have been recently compared in a series of five MD simulations on the well worn LJ argon system close to the triple point. The results from these simulations will be presented and discussed in detail elsewhere [12]. As has been found previously [7,9,10] all these methods produce essentially identical results for the thermody-

dynamic properties, the velocity auto-correlation function and the time dependence of the mean squared displacement. The first two algorithms contain nothing new but are included for completeness and for comparison with the three 'new' algorithms. The five MD algorithms are then:-

ALG 1 Constant energy

ALG 2 Constant temperature, using 'ad hoc' rescaling [1]

ALG 3 Constant temperature, using the damped force method of Hoover [4] and Evans [11]

ALG 4 Constant pressure, Andersen's method [3]

ALG 5 Constant temperature and pressure, combination of damped force and Andersen's method.

ALG 1, (N,V,E)

The equations of motion are integrated using the 'leapfrog' form of the Verlet algorithm [10]

$$\underline{V}_i(t + \Delta t/2) = \underline{V}_i(t - \Delta t/2) + \underline{F}_i(t) \Delta t/m \quad (1.1)$$

$$\underline{R}_i(t + \Delta t) = \underline{R}_i(t) + \underline{V}_i(t + \Delta t/2) \Delta t \quad (1.2)$$

$$\underline{V}_i(t) = [\underline{V}_i(t - \Delta t/2) + \underline{V}_i(t + \Delta t/2)]/2 \quad (1.3)$$

where

$$\underline{V}_i(t - \Delta t/2) = (\underline{R}_i(t) - \underline{R}_i(t - \Delta t))/\Delta t \quad (1.4)$$

The total internal energy  $U(t)$  is calculated from the total potential energy,  $\Phi(t)$ , and the temperature at time  $t$ ,  $T(t)$ .

ALG 2, (N,V,T) ('ad hoc' rescaling of velocities).

In this case the only modification is that velocities at the previous half time step are scaled, so that

$$\underline{V}_i(t + \Delta t/2) = \underline{V}_i(t - \Delta t/2)\beta + \underline{F}_i(t) \Delta t/m \quad (2.1)$$

where

$$\beta^2 = (3(N - 1)kT_r/m) / \sum_{i=1}^N \underline{V}_i^2(t - \Delta t/2) \quad (2.2)$$

and  $T_r$  is the required temperature. The factor  $N-1$  rather than  $N$  occurs in equation (2.2) as a result of the removal of three degrees of freedom by the constraint of zero total linear momentum.

ALG 3, (N,V,T) (damped force method)

This involves the integration of a modified set of Hamiltonian equations of motion [4]

$$\dot{\underline{p}}_i = \underline{F}_i - \alpha \underline{p}_i/m \text{ or } \dot{\underline{v}}_i = (\underline{F}_i - \alpha \underline{v}_i)/m \quad (3.1)$$

$$\dot{\underline{q}}_i = \underline{p}_i/m \text{ or } \dot{\underline{R}}_i = \underline{v}_i \quad (3.2)$$

where  $\alpha$  is a constant. For constant temperature we require that  $dT/dt = 0$ .

Since  $T = (m/3(N-1)k) \sum_{i=1}^N \underline{v}_i \cdot \underline{v}_i$  differentiation w.r.t. time gives

$$\dot{T} = (2m/3(N-1)k) \sum_{i=1}^N \dot{\underline{v}}_i \cdot \underline{v}_i \quad (3.3)$$

Substituting for  $\dot{\underline{v}}_i$  from eqn.(3.1) gives

$$\dot{T} = (2m/3(N-1)k) \sum_{i=1}^N (\underline{F}_i \cdot \underline{v}_i - \alpha \underline{v}_i \cdot \underline{v}_i)/m \quad (3.4)$$

and for  $\dot{T} = 0$

$$\alpha = \frac{\sum_{i=1}^N \underline{F}_i \cdot \underline{v}_i}{\sum_{i=1}^N \underline{v}_i \cdot \underline{v}_i} \quad (3.5)$$

Equation (1.1) now becomes

$$\underline{v}_i(t + \Delta t/2) = \underline{v}_i(t - \Delta t/2) + \underline{F}_i(t) \Delta t/m - \alpha \underline{v}_i(t) \Delta t/m \quad (3.6)$$

The constant  $\alpha$  can be found by the following procedure. Firstly, we implement the Verlet algorithm, eqn.(1.1), to obtain a projected velocity  $\underline{v}_i'(t)$  which is different from the constrained velocity  $\underline{v}_i(t)$

$$\underline{v}_i'(t) = \underline{v}_i(t - \Delta t/2) + \underline{F}_i(t)\Delta t/2m . \quad (3.7)$$

Then

$$\underline{v}_i(t) = \underline{v}_i'(t) - \alpha \underline{v}_i(t)\Delta t/2m = \underline{v}_i'(t)\beta \quad (3.8)$$

where

$$\beta = (1 + \alpha\Delta t/2m)^{-1} . \quad (3.9)$$

The constant temperature condition requires  $\sum_{i=1}^N \underline{v}_i^2(t) = 3(N - 1)kT_r/m$  and

since the constants  $\alpha$  and  $\beta$  are ensemble properties

$$\beta^2 = (3(N - 1)kT_r/m) / \sum_{i=1}^N \underline{v}_i'^2(t) \quad (3.10)$$

It is unnecessary to calculate  $\alpha$  and  $\underline{v}_i(t)$  explicitly since it is easily shown that eqn.(3.6) becomes

$$\underline{v}_i(t + \Delta t/2) = \underline{v}_i(t - \Delta t/2) (2\beta - 1) + \beta \underline{F}_i(t)\Delta t/m \quad (3.11)$$

Thus for the 'leapfrog' algorithm the damped force method reduces to simple scaling of the velocities and the forces at each integration step (for other algorithms this may not be the case). It does ensure that  $T(t)$  is constant at every time step whereas the method in ALG 2 only produces a mean constant temperature.

#### ALG 4, (N,P,H) (Andersen's method)

In the constant pressure method of Andersen [3] the Hamiltonian for the system in terms of the scaled variables

$$\underline{r}_i = \underline{R}_i/V^{1/3} \quad (4.1)$$

and

$$\underline{\dot{r}}_i = \underline{p}_i/mV^{1/3} \quad (4.2)$$

can be written as [7]

$$H(\{\underline{r}\}, \{\dot{\underline{r}}\}, V, \dot{V}) = \frac{V^{2/3}}{2} \sum_{i=1}^N m \dot{\underline{r}}_i \cdot \dot{\underline{r}}_i + \sum_{i=1}^N \sum_{j>i}^N \phi(r_{ij} V^{1/3}) + (1/2)M\dot{V}^2 + P_E V \quad (4.3)$$

where  $V$  is the volume of the system,  $M$  is a constant and  $P_E$  is the external pressure. The first two terms are exactly equivalent to the internal energy,  $U$ , of the particles of the system whereas terms three and four are the kinetic and potential energy associated with the change in volume. The conserved quantity is the total energy  $H$  associated with the Hamiltonian given in eqn.(4.3). The ensemble average  $\langle H(t) \rangle$  differs from the enthalpy of the  $N$ -particle system by  $1/2kT$  which is the average kinetic energy associated with the volume functions i.e.  $\langle 1/2 M \dot{V}^2(t) \rangle$ .

The coupled Newtonian equations of motion for this system have been given previously [7].

$$\ddot{\underline{r}}_i = \underline{F}_i / m V^{1/3} - (2/3) \dot{\underline{r}}_i \dot{V} / V \quad (4.4)$$

$$\ddot{V} = (P - P_E) / M \quad (4.5)$$

$P$  is the calculated pressure in the system and is given by

$$P = (1/3V) \left( \sum_{i=1}^N m (\underline{p}_i / m) \cdot (\underline{p}_i / m) + \sum_{i=1}^N \sum_{j>i}^N \underline{R}_{ij} \cdot \underline{F}_{ij} \right) \quad (4.6)$$

Where  $\underline{R}_{ij} = \underline{R}_i - \underline{R}_j$  and  $\underline{F}_{ij}$  is the force on molecule  $i$  due to molecule  $j$ .

The direct application of the 'leapfrog' algorithm to integrate eqn. (4.4) is not possible because of the term involving  $\dot{\underline{r}}_i$ . However, this difficulty can be overcome by transforming the equation back into cartesian space [14]. Differentiating eqn.(4.1) w.r.t. time gives

$$\dot{\underline{r}}_i = (1/V^{1/2}) (\dot{\underline{R}}_i - \underline{R}_i \dot{V}/3V) \quad (4.7)$$

which defines the relationship between the momentum and the velocity, since  $\dot{\underline{r}}_i V^{1/3} = \underline{p}_i / m$ , as

$$\underline{p}_i / m = \dot{\underline{R}}_i - \underline{R}_i \dot{V}/3V \quad (4.8)$$

Differentiating eqn.(4.7) w.r.t. time and substituting for  $\dot{\underline{r}}_i$  and  $\ddot{\underline{r}}_i$  in eqn.(4.4) gives

$$\ddot{\underline{R}}_i = \underline{F}_i/m + (\underline{R}_i/3V) [\ddot{V} - (2/3) (\dot{V}/V)^2] \quad (4.9)$$

which can be integrated as we do know  $\underline{R}_i$  and  $\ddot{\underline{R}}_i$  at the time  $t$ .

A similar problem exists in the integration of eqn.(4.5) as strictly speaking the momenta at time  $t$  are needed to evaluate the pressure from eqn.(4.6) but these are generally calculated after eqn.(4.9) has been integrated. The procedure adopted is to evaluate the kinetic contribution to the pressure,  $NkT/V$ , using an approximation to the momenta calculated from the previous two time steps,  $\underline{p}_i(t) = 2\underline{p}_i(t - \Delta t) - \underline{p}_i(t - 2\Delta t)$ , and to combine this with the potential part evaluated at the present time step to obtain a pressure,  $P(t)$ . The approximation used is simply the result of applying Verlet's algorithm to momenta rather than positions and ignoring the terms in  $\Delta t^2$ . A test of the stability of the numerical integration of eqns.(4.5) and (4.9) using the method outlined is the constancy of the total energy,  $H$ , of the system given by the Hamiltonian, eqn.(4.3).

Prior to integrating the equations of motion of the particles the Verlet algorithm is used to obtain  $V(t + \Delta t)$  and  $\dot{V}(t)$  as follows

$$V(t + \Delta t) = 2V_i(t) - V(t - \Delta t) + (P(t) - P_E)\Delta t^2/M \quad (4.10)$$

$$\dot{V}_i(t) = (V(t + \Delta t) - V(t - \Delta t))/2\Delta t \quad (4.11)$$

The leapfrog algorithm for updating the velocities in ALG 4 becomes

$$\begin{aligned} \underline{v}_i(t + \Delta t/2) = & \underline{v}_i(t - \Delta t/2) \\ & + \left[ \underline{F}_i(t)/m + (\underline{R}_i(t)/3V(t)) \left( \ddot{V}(t) - \frac{2}{3} \left( \frac{\dot{V}(t)}{V(t)} \right)^2 \right) \right] \Delta t \end{aligned} \quad (4.12)$$

The remaining steps in the algorithm are as in ALG 1.

#### ALG 5, (N,P,T)

In ALG 5 the methods used in ALG 3 and ALG 4 are combined. Projected velocities at time  $t$  are calculated using

$$\begin{aligned} \underline{v}_i'(t) = & \underline{v}_i(t - \Delta t/2) \\ & + \left[ \underline{F}_i(t)/m + (\underline{R}_i(t)/3V(t)) \left[ \ddot{V}(t) - 2\dot{V}^2(t)/3V^2(t) \right] \right] \Delta t/2 \end{aligned} \quad (5.1)$$

Eqn.(4.8) is then used to calculate the projected momenta at time  $t$

$$\underline{p}_i'(t)/m = \underline{v}_i'(t) - \underline{R}_i(t)\dot{V}(t)/3V(t) \quad (5.2)$$

and thus the scaling factor,  $\beta$ , from

$$\beta^2 = (3(N-1)kT_r/m) / \sum_{i=1}^N (\underline{p}_i'(t)/m)^2 \quad (5.3)$$

It is then straightforward to show that the leapfrog algorithm for updating the velocities becomes

$$\begin{aligned} \underline{v}_i(t + \Delta t/2) = & \underline{v}_i(t - \Delta t/2) (2\beta - 1) + [2\underline{R}_i(t)\dot{V}(t)/3V(t)] (1 - \beta) \\ & + \beta(\underline{F}_i(t)/m + (\underline{R}_i(t)/3V(t))[\ddot{V}(t) - 2\dot{V}^2(t)/3V^2(t)])\Delta t. \end{aligned} \quad (5.4)$$

It is important to note that in the constant pressure methods that the velocity of a particle is dependent upon its position since from eqn.(4.8)

$$\dot{\underline{R}}_i = \underline{p}_i/m + \underline{R}_i\dot{V}/3V.$$

So if at a particular time  $t$  the sidelength of the MD cell is  $L$  then the velocities of its images are, for the  $x$ -direction,

$$\dot{\underline{R}}_x' = p_x/m + (R_x \pm L)\dot{V}/3V$$

so that

$$\dot{\underline{R}}_x' = R_x \pm L\dot{V}/3V.$$

Therefore, both the position and velocity of a particle have to be altered if a boundary is crossed. It is also worth noting that the time dependence of the particle mean squared displacements,  $\langle R^2 \rangle(t)$ , was evaluated as

$$\langle R^2 \rangle(t) = \langle N^{-1} \sum_{i=1}^N \left( \int_0^t \underline{p}_i(t)/m dt \right)^2 \rangle$$

so as not to include any displacements due to volume fluctuations in the constant pressure simulations, and similarly the auto-correlation function for the 'velocity' was calculated from

$$C_V(t) = M^{-2} \langle \underline{p}_i(0) \cdot \underline{p}_i(t) \rangle.$$

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