<u>Constant Pressure Molecular Dynamics for Polyatomics</u>

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The equations relating absolute to scaled coordinates from reference [1] are:-

$$V = s^3 \tag{1}$$

$$\underline{\rho}_i = \underline{R}_i / V^{1/3} \tag{2}$$

$$\begin{aligned} \dot{\underline{R}}_i &= \underline{p}_i/m_i + (\underline{R}_i/3)\frac{d}{dt}(\ln V) \\ &= \underline{p}_i/m_i + \underline{R}_i\,\dot{V}/(3V) \end{aligned} \tag{3}$$

$$\underline{p}_i/m_i = \dot{\underline{\rho}}_i\, V^{1/3} \tag{4}$$

where: $V$ = value of MD cell

$s$ = side length of MD cell

$\underline{R}_i$ = position of $i^{th}$ molecule centre-of-mass

$\underline{\rho}_i$ = scaled position if $i^{th}$ molecule centre-of-mass

$\underline{p}_i$ = momentum of $i^{th}$ molecule

$m_i$ = mass of $i^{th}$ molecule

and the equations of motion are:-

$$\ddot{\underline{\rho}}_i = V^{-1/3}\,\underline{F}_i/m_i - 2\,\dot{\underline{\rho}}_i\,\dot{V}_i/(3V) \tag{5}$$

$$\ddot{V} = M^{-1}(P_{cal} - P_{req}) \tag{6}$$

where: $M$ is the 'mass' of the piston

$P_{cal}$ is the calculated pressure

$P_{req}$ is the required pressure

After calculating the pressure at the present time step in the usual way it is possible to integrate (6) using Verlet's algorithm, which gives:-

$$V\,(t+\Delta t) = 2V(t) - V(t-\Delta t) + (P_{cal} - P_{req})\,\Delta t^2/M \tag{7}$$

$$\dot{V}(t) = (V(t+\Delta t)-V(t-\Delta t))/(2\Delta t) \qquad (8)$$

where $\Delta t$ is the time step.

Using equation (1) gives:-

$$s(t+\Delta t) = (V(t+\Delta t))^{1/3}$$

Integrating (5) using Verlet's algorithm gives:-

$$\underline{\rho}_i(t+\Delta t) = 2\,\underline{\rho}_i(t)-\underline{\rho}_i(t-\Delta t) + \left[\bar{V}^{1/3}\,\underline{F}_i/m_i - 2\,\dot{\underline{\rho}}_i\,\dot{V}/(3V)\right]\Delta t^2 \qquad (9)$$

If we define $\dot{\underline{\rho}}_i = (\underline{\rho}_i(t)-\underline{\rho}_i(t-\Delta t))/\Delta t$ and substitute this into (9) we get:

$$\underline{\rho}_i(t+\Delta t) = \underline{\rho}_i(t) + \dot{\underline{\rho}}_i(t)\,\Delta t + \left[V^{-1/3}\,\underline{F}_i/m_i - 2\,\dot{\underline{\rho}}_i\,\dot{V}/(3V)\right]\Delta t^2 \qquad (10)$$

Now substituting equations (1), (2) and (4) in (10) gives:-

$$\underline{R}_i(t+\Delta t)/s(t+\Delta t) = \underline{R}_i(t)/s(t) + \underline{p}_i(t)\Delta t/(m_i\,s(t)) + \left[\underline{F}_i(t)/(m_i\,s(t)) - 2\,\underline{p}_i(t)\,\dot{V}(t)/(3m_i\,s(t)\,V(t))\right]\Delta t^2$$

which gives us an algorithm for updating the centre of mass as:-

$$\underline{R}_i(t+\Delta t) = \frac{s(t+\Delta t)}{s(t)}\left[\underline{R}_i(t)+\underline{p}_i(t)\Delta t/m_i + \left[\underline{F}_i(t)/m_i-2\underline{p}_i(t)\dot{V}(t)/(3m_iV(t))\right]\Delta t^2\right] \qquad (11)$$

and the momenta are updated in the usual way:-

$$\underline{p}_i(t+\Delta t)/m_i = \underline{p}_i(t)/m_i + \underline{F}_i(t)\Delta t/m_i \qquad (12)$$

Using equation (11) for the centre-of-mass motion allows the use of an absolute coordinate system with only minor changes to the nearest image transformation in the calculation of forces and the update routine.

If we are using a system such that s(0) = 2 box units and $-1 \leq \underline{R}_i^{\alpha} \leq 1$. Then if HS = 0.5 * s(t) and RHS = 1.0/HS, the nearest image transformation is performed by:

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XD = X(I)-X(J)
XD = XD - 2 *INT(XD*RHS)*HS
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and the update for atoms or centre-of-mass leaving the box is:-

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U = HS * INT(RHS*X(I))
X(I) = X(I) - U - U
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If the corrections are calculated for the potential energy and the virial, then these will also have to be scaled at each time step by:-

VIRLRC $(t+\Delta t)$ = VIRLRC(t)*V(t)/V$(t+\Delta t)$

and the same for the potential energy.

The advantages of retaining an absolute coordinate system, are that no changes are required in the rotational algorithm and the calculation of properties such as temperature, pressure, radial distribution function and correlation function remain the same as in a constant volume program.

References

[1] J.M. Haile, H.W. Graben, J. Chem. Phys. (1980) 73. 2412.