

## Constrained impulsive molecular dynamics†

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An exact procedure for treating the molecular dynamics of holonomically constrained systems in the presence of impulsive forces is presented. Because of its simplicity it can be applied not only to purely impulsive situations, but (if it is used in conjunction with existing continuous forces constrained dynamics algorithms) to combined impulsive/continuous force systems as well. The possibility of application to fused hard sphere and polymer dynamics is discussed in some detail.

### 1. INTRODUCTION

Ever since the pioneering work of Alder and Wainwright [1], molecular dynamics has been an invaluable aid in studying the classical dynamics of what are effectively atomic systems. Unfortunately, the relatively simple conceptual leap to studying the much richer behaviour of genuinely *molecular* systems has proven numerically difficult. In particular, if one actually tries to include the internal motion of molecules on the same basis as their translational motion, the much faster time scale of the vibrations ( $10^{-5}$  ps versus  $10^{-2}$  ps) makes the equations of motion stiff and their solution extremely inefficient. Yet, since in many cases the vibrations are practically irrelevant to the properties being investigated (and since the highly quantal nature of the vibrations makes classical trajectory descriptions of them dubious anyway), this inefficiency would seem to be purposeless.

One way to avoid this problem would be to get rid of the high frequency, small amplitude, vibrational motion by imposing constraints on bondlengths and (sometimes) on bond angles. This would lead to a model which is both computationally tractable and physically reasonable. Moreover, the small error introduced by imposing the constraints could often be approximately removed by inserting the proper metric once the calculation was finished [2-4]. However, the use of constraints introduces a new problem. The relevant equations of motion for an asymmetric *rigid* body are Euler's equations and the usual coordinate description, Euler angles [5]. For anything other

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than linear molecules though, a straightforward solution in these terms requires a complicated and awkward calculation.

Fortunately, it is possible to circumvent this difficulty by employing an algorithm which allows one to run the classical trajectory in cartesian (non-eulerian) coordinates while ignoring the constraints. What the algorithm does is correct for the constraints at the end of each time step. In fact, the so-called SHAKE algorithm [6] does this by iteratively solving whatever version of the equations of motion is being used for the magnitude of the constraint forces (to within the intrinsic error of the version). These forces are then substituted back in the equation of motion to find out how much the coordinates at the end of a time step of the unconstrained trajectory have to be corrected to include the constraints.

Of course, implicit in the SHAKE method is the assumption that the forces involved are continuous and well behaved. Should one desire any type of impulsive forces, a procedure based on solving finite difference equations of motion, such as SHAKE, would not be able to deal with the fact that the forces act instantaneously. As a result, even with SHAKE, there are a large number of systems which are still beyond our computational capabilities. For example, the general study of the dynamics of polyatomic fluids is severely hindered because it is not practical to run trajectories with a fused hard sphere representation of the molecules<sup>†</sup>. Thus, unlike the equilibrium case, we have no convenient reference system from which to investigate the behaviour of real molecular liquids, nor do we have an unambiguous way to isolate the effects of geometry and packing. Along somewhat different lines, the lack of a technique for treating constraints in the presence of impulses also prevents us from examining the dynamical behaviour of molecular liquids near a hard surface (which is an idealized model for non-uniform fluids).

With these difficulties in mind, the remainder of this article will be devoted to describing a computationally convenient new approach for dealing with this problem of the dynamics of constrained systems under the influence of impulses. Section 2 will outline the basic procedure and derive the necessary equations for several general cases. Section 3 will then discuss their implementation and provide a numerical example. The final section will comment on the application of this work to problems in statistical mechanics.

## 2. A PROCEDURE FOR CONSTRAINED IMPULSIVE DYNAMICS

Without any loss of generality, the dynamics of constrained molecular systems may be divided into segments involving motion in the presence of continuous forces alone (if any are present) and motion involving impulses. However, because impulses are instantaneous they do not allow coordinates to change, so we may rigorously ignore the presence of continuous forces in calculating the effect of an impulse on the dynamics. Accordingly, in running a trajectory we will always be able to employ the following approach: (1) use SHAKE to take continuous force time steps up until an impulse, (2) apply some sort of algorithm which does not depend on the forces or the trajectory

<sup>†</sup> A two dimensional fused hard sphere calculation with *relaxed* constraints has been recently reported however. See BELLEMANS, A., ORBAN, J., and VAN BELLE, D., 1980, *Molec. Phys.*, **39**, 781.

history to compute the velocity changes of the constrained system due to the impulse, and finally (3) propagate forward to the next impulse, again using SHAKE and continuous force time steps.

The problem that remains, then, is that of defining the algorithm in step (2)—that is, finding a way to use the coordinates and velocities before the impulse (which fixes what the impulse would have been without constraints) to figure out the post-impulse velocity. Inasmuch as this is formally analogous to the continuous force problem, let us proceed in a similar manner [7]. The equation of motion for a single constrained molecule feeling an impulse may be written

$$\Delta \mathbf{p}_j = \mathbf{I}_j + \mathbf{i}_j \quad j = 1, \dots, N, \tag{2.1}$$

where  $j$  labels the  $N$  sites (e.g. atoms) of the molecule,  $\Delta \mathbf{p}_j$  is the change in momentum of the  $j$ th site due to the impulse,  $\mathbf{I}_j$  is the impulse the  $j$ th site would feel if there were no constraints, and  $\mathbf{i}_j$  is the impulse on the  $j$ th site due to the constraints.

If the constraints are assumed to be holonomic [5], as they are in SHAKE, then they may always be represented in terms of fixed distances between certain sites. By way of example, bondlengths and angles in a straight chain polymer may be constrained by fixing the distances between every other site and the distances between every adjacent site. Thus, for our purposes the constraint impulse,  $\mathbf{i}_j$ , must have the form

$$\mathbf{i}_j = \sum_{k=1}^N \mathbf{i}_{jk} = \sum_{k=1}^N \lambda_{jk} \hat{b}_{jk} \tag{2.2}$$

with  $\mathbf{i}_{jk}$  the impulse on site  $j$  due to any constraint between site  $j$  and site  $k$ ,  $\lambda_{jk}$  the magnitude of  $\mathbf{i}_{jk}$ , and  $\hat{b}_{jk}$  a unit vector pointing from  $j$  to  $k$ . Moreover, since we know that these constraint impulses are nothing but the response of the molecule to the original impulse,  $I$

$$I = |\mathbf{I}| = \left| \sum \mathbf{I}_j \right| \tag{2.3}$$

the  $\mathbf{i}_j$ s must actually *scale* with the value of  $I$ . It is therefore convenient to define quantities in terms of a unit impulse†

$$\begin{aligned} \mathbf{I}_j^0 &= (\mathbf{I}_j)/I \\ \mathbf{i}_{jk}^0 &= (\mathbf{i}_{jk})/I = \lambda_{jk}^0 \hat{b}_{jk} \end{aligned}$$

and to rewrite (2.1)

$$\Delta \mathbf{p}_j = I \left( \mathbf{I}_j^0 + \sum_{k=1}^N \lambda_{jk}^0 \hat{b}_{jk} \right) \tag{2.4}$$

The task now is to calculate the  $\lambda_{jk}^0$ s from the original scaled impulse vectors  $\mathbf{I}_j^0$ . This can be accomplished by using the fact that the presence of a constraint between two sites means that the sites must have zero relative velocity along the line joining them. For each constraint between sites  $j$  and  $k$  this in turn implies that the impulse does not induce a velocity change parallel to  $\hat{b}_{jk}$

$$\left( \frac{\Delta \mathbf{p}_j}{m_j} - \frac{\Delta \mathbf{p}_k}{m_k} \right) \cdot \hat{b}_{jk} = 0, \tag{2.5}$$

where  $m_j$  is the mass of the  $j$ th site.

† If *two* molecules are colliding then Newton's third law makes them feel equal but opposite impulses. Thus there is still only one  $I$ —namely that given by (2.3) applied to either molecule. This is illustrated in the Appendix.

Substituting (2.4) into (2.5) and factoring out  $I$  then gives an equation for each  $jk$  constraint

$$\sum_{l=1}^N \left[ \frac{1}{m_j} \lambda_{jl}^0 (\hat{b}_{jl} \cdot \hat{b}_{jk}) - \frac{1}{m_k} \lambda_{kl}^0 (\hat{b}_{kl} \cdot \hat{b}_{jk}) \right] = \left( \frac{\mathbf{I}_k^0}{m_k} - \frac{\mathbf{I}_j^0}{m_j} \right) \hat{b}_{jk}. \quad (2.6)$$

However, all of the  $\lambda_{jk}^0$ s are not independent because Newton's third law (action/reaction) requires that

$$\mathbf{i}_{jk} = -\mathbf{i}_{kj}$$

so that

$$\lambda_{jk}^0 = \lambda_{kj}^0. \quad (2.7)$$

Therefore each of the (say)  $M$  constraints is associated with exactly one unknown  $\lambda_{jk}^0$  ( $j < k$ ). As a result, the  $M$  linear equations of (2.6) constitute a complete solution of the problem of finding the  $\lambda_{jk}^0$ s from the  $\mathbf{I}_j^0$ s.

The only remaining step is to determine the magnitude  $I$ . By conservation of energy we know that an impulse cannot change the total kinetic energy of the system, so that if only *one* molecule is involved in the impulse

$$\sum_{j=1}^N \frac{1}{2m_j} (\mathbf{p}_j^{(i)} + \Delta \mathbf{p}_j)^2 = \sum_{j=1}^N \frac{1}{2m_j} (\mathbf{p}_j^{(i)} \cdot \mathbf{p}_j^{(i)}), \quad (2.8)$$

where  $\mathbf{p}_j^{(i)}$  is the initial (pre-impulse) momentum. If we now define

$$\Delta \mathbf{p}_j^0 = (\Delta \mathbf{p}_j / I)$$

rearranging (2.8) and using (2.4) leads to the desired expression for  $I$

$$I = - \frac{\sum_{j=1}^N \frac{1}{m_j} \mathbf{p}_j^{(i)} \cdot \Delta \mathbf{p}_j^0}{\sum_{j=1}^N \frac{1}{2m_j} (\Delta \mathbf{p}_j^0)^2}, \quad (2.9)$$

$$I = - \frac{\sum_{j=1}^N \frac{1}{m_j} \mathbf{p}_j^{(i)} \cdot \left[ \mathbf{I}_j^0 + \sum_{k=1}^N \lambda_{jk}^0 \hat{b}_{jk} \right]}{\sum_{j=1}^N \frac{1}{2m_j} \left[ \mathbf{I}_j^0 + \sum_{k=1}^N \lambda_{jk}^0 \hat{b}_{jk} \right]^2}.$$

Similarly if *two* molecules,  $A$  and  $B$ , are involved in the impulse (as in the case of a collision)

$$I = - \frac{\sum_{j_A=1}^{N_A} \frac{1}{m_{j_A}} \mathbf{p}_{j_A}^{(i)} \cdot \Delta \mathbf{p}_{j_A}^0 + \sum_{j_B=1}^{N_B} \frac{1}{m_{j_B}} \mathbf{p}_{j_B}^{(i)} \cdot \Delta \mathbf{p}_{j_B}^0}{\sum_{j_A=1}^{N_A} \frac{1}{2m_{j_A}} [\Delta \mathbf{p}_{j_A}^0]^2 + \sum_{j_B=1}^{N_B} \frac{1}{2m_{j_B}} [\Delta \mathbf{p}_{j_B}^0]^2}, \quad (2.10 a)$$

$$\Delta \mathbf{p}_{j_A}^0 = \mathbf{I}_{j_A}^0 + \sum_{k_A=1}^{N_A} \lambda_{j_A k_A}^0 \hat{b}_{j_A k_A}, \quad (2.10 b)$$

$$\Delta \mathbf{p}_{j_B}^0 = \mathbf{I}_{j_B}^0 + \sum_{k_B=1}^{N_B} \lambda_{j_B k_B}^0 \hat{b}_{j_B k_B}. \quad (2.10 c)$$

Note that the quantities  $\Delta \mathbf{p}_{j_A}^0$  and  $\Delta \mathbf{p}_{j_B}^0$  are computed independently by applying (2.6) to each molecule separately.

Equations (2.4), (2.6), (2.9) and (2.10) then are the necessary equations for solving the constrained impulsive dynamics problem. Unlike the situation with constrained continuous dynamics, application of the impulsive procedure does not introduce its own error† or require an iterative solution. All that is needed is to (1) compute the  $\mathbf{I}_j^0$ s and  $\hat{b}_{jk}$ s from the initial momenta and coordinates, (2) find the  $\lambda_{jk}^0$ s by solving  $M$  linear equations in  $M$  unknowns, (2.6), (3) calculate  $I$  from (2.9) or (2.10), and (4) read off the desired momentum changes from (2.4).

As an illustrative example, consider the dynamics of an  $n$ -alkane (an unbranched chain) with fixed bondlengths. If we regard the methyl and methylene groups as the sites, constraints must be imposed between every site and its nearest neighbours, so we will have to find the following  $(n-1)$  parameters

$$\lambda_{12}^0, \lambda_{23}^0, \lambda_{34}^0, \dots, \lambda_{n-1,n}^0$$

(all the other  $\lambda$ s being either equal to these by (2.7) or zero). This means that for every set of bond angles

$$\cos \theta_j = \hat{b}_{j,j-1} \cdot \hat{b}_{j,j+1} \quad (j=2, 3, \dots, n-1), \quad (2.11)$$

we will have to solve the matrix equation

$$\begin{pmatrix} \frac{1}{\mu_{12}} & \frac{\cos \theta_2}{m_2} & 0 & \dots & 0 & 0 \\ \frac{\cos \theta_2}{m_2} & \frac{1}{\mu_{23}} & \frac{\cos \theta_2}{m_3} & \dots & 0 & 0 \\ 0 & \frac{\cos \theta_3}{m_3} & \frac{1}{\mu_{34}} & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & \frac{1}{\mu_{n-2,n-1}} & \frac{\cos \theta_{n-1}}{m_{n-1}} \\ 0 & 0 & 0 & \dots & \frac{\cos \theta_{n-1}}{m_{n-1}} & \frac{1}{\mu_{n-1,n}} \end{pmatrix} \begin{pmatrix} \lambda_{12}^0 \\ \lambda_{23}^0 \\ \lambda_{34}^0 \\ \vdots \\ \lambda_{n-2,n-1}^0 \\ \lambda_{n-1,n}^0 \end{pmatrix} = \begin{pmatrix} \Delta v_{12}^0 \\ \Delta v_{23}^0 \\ \Delta v_{34}^0 \\ \vdots \\ \Delta v_{n-2,n-1}^0 \\ \Delta v_{n-1,n}^0 \end{pmatrix}, \quad (2.12)$$

where we have defined

$$\left. \begin{aligned} \mu_{j,j+1} &= 1/(m_j^{-1} + m_{j+1}^{-1}), \\ \Delta v_{j,j+1}^0 &= \left( \frac{\mathbf{I}_{j+1}^0}{m_{j+1}} - \frac{\mathbf{I}_j^0}{m_j} \right) \cdot \hat{b}_{j,j+1}. \end{aligned} \right\} \quad (2.13)$$

Equation (2.12) is of course precisely (2.6) specialized to this example. We may also rewrite (2.9) by using

$$\left. \begin{aligned} \Delta \mathbf{p}_1^0 &= \mathbf{I}_1^0 + \lambda_{12}^0 \hat{b}_{12}, \\ \Delta \mathbf{p}_j^0 &= \mathbf{I}_j^0 + \lambda_{j-1,j}^0 \hat{b}_{j,j-1} + \lambda_{j,j+1}^0 \hat{b}_{j,j+1} \quad (j=2, \dots, n-1), \\ \Delta \mathbf{p}_n^0 &= \mathbf{I}_n^0 + \lambda_{n-1,n}^0 \hat{b}_{n,n-1}. \end{aligned} \right\} \quad (2.14)$$

† However an error is introduced when this algorithm is interfaced with an approximate trajectory routine. See the comments in § 3.

The final result would then be

$$\Delta \mathbf{p}_j = I \Delta \mathbf{p}_j^0$$

as always.

A more detailed example, which demonstrates the calculation of the unconstrained impulses,  $\mathbf{I}$ , is given in the Appendix.

### 3. IMPLEMENTATION

If the procedure we have been describing is to be used in treating systems with both continuous and impulsive forces, it is clearly necessary to consider the *interface* between the algorithms which deal with them. Although there is no real need to limit our considerations to a particular trajectory routine, it is convenient to focus on the standard Verlet [7] approach to continuous forces. Briefly, this approach calculates a new coordinate,  $\mathbf{r}(t + \Delta t)$ , from the current coordinates and forces,  $\mathbf{r}(t)$  and  $\mathbf{F}[\mathbf{r}(t)]$ , and the previous coordinate,  $\mathbf{r}(t - \Delta t)$

$$\mathbf{r}(t + \Delta t) \approx 2\mathbf{r}(t) - \mathbf{r}(t - \Delta t) + (\Delta t)^2 \mathbf{F}[\mathbf{r}(t)]/m \quad (3.1)$$

accurate to  $\theta(\Delta t)^4$ . The routine does not normally deal with the velocities in any direct sense, but when velocities are explicitly included (as in the *first* step of a trajectory)

$$\mathbf{r}(t + \Delta t) \approx \mathbf{r}(t) + (\Delta t)v(t) + \frac{1}{2}(\Delta t)^2 \mathbf{F}[\mathbf{r}(t)]/m \quad (3.2)$$

the accuracy drops to  $\theta(\Delta t)^3$ .

For this Verlet technique the basic problem of matching the trajectory routine with impulsive situations is shown in figure 1. In general, a trajectory time step starting at  $(x_2, t)$  will strike a hard wall sometime in the middle of the step,  $(x_3, t + \alpha\Delta t)$ . However, since the routine does not know of the impulsive forces, it will predict an incorrect final position,  $x_4$ , at the end of the time step.

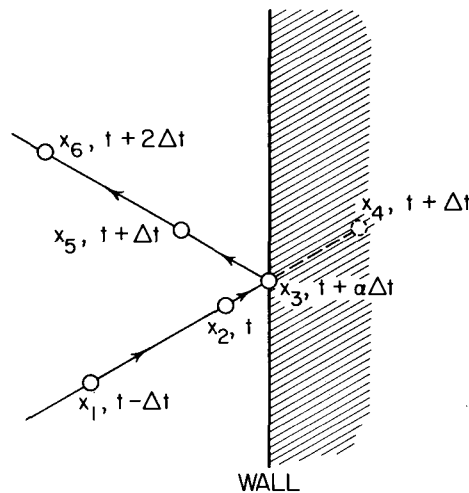


Figure 1. Verlet time steps near a hard wall. The correct sequence of coordinates is  $x_1, x_2, x_3, x_5, x_6$  but without a knowledge of the hard wall the sequence is  $x_1, x_2, x_4$ . The number  $\alpha$  is the fraction of a time step required to go from  $x_2$  to  $x_3$ .

Therefore the constrained impulsive dynamics algorithm will not have the necessary positions and velocities  $(x_3, v_3)$  to work with.

We can resolve this difficulty as follows : Because the coordinates of the wall are known, we know  $x_3$  (for at least one of the degrees of freedom). In combination with  $x_1, x_2$ , and  $x_4$ , this is sufficient to compute the fraction  $\alpha$  through quadratic inverse interpolation [8].

$$\alpha^2(x_1 + x_4 - 2x_2) + \alpha(x_4 - x_1) + 2(x_2 - x_3) \approx 0, \quad 0 \leq \alpha \leq 1. \quad (3.3)$$

Once we know the collision time  $(t + \alpha\Delta t)$ , we can apply an unequal time step Verlet algorithm, such as

$$\left. \begin{aligned} \mathbf{r}(t + \alpha\Delta t) &= -\alpha\mathbf{r}(t - \Delta t) + (1 + \alpha)\mathbf{r}(t) + \frac{1}{2}\alpha(1 + \alpha)(\Delta t)^2 \mathbf{F}(t)/m, \\ \mathbf{v}(t + \alpha\Delta t) &= [(1 + \alpha)^2 \mathbf{r}(t + \Delta t) - (1 - \alpha)^2 \mathbf{r}(t - \Delta t) \\ &\quad - 4\alpha\mathbf{r}(t + \alpha\Delta t)]/[2(1 - \alpha^2)\Delta t] \end{aligned} \right\} \quad (3.4)$$

to provide the coordinates and velocities at impact. Then, after these values are substituted into the impulsive dynamics algorithm, the resulting new velocities can be used to restart the Verlet trajectory (3.2), which will continue until the next impulse.

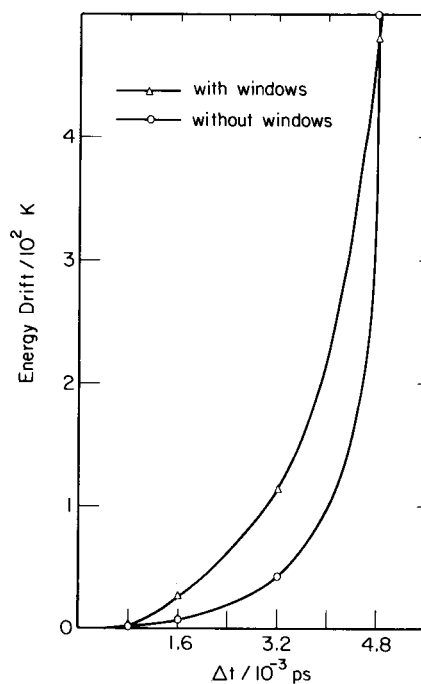


Figure 2. Energy drift in units of  $10^2$  K versus the size of the Verlet time step for two different kinds of 3000 step trajectories of butane. The lower curve uses Verlet and SHAKE alone. The upper curve uses infinitely steep windows to constrain the dihedral angle and must therefore also include the constrained impulsive force algorithm. The total energy of the butane molecule in these runs was about  $8 \times 10^3$  K.

Actually, in practice, it is often useful to let the first time step after the impulse be the remaining fraction,  $(1 - \alpha)\Delta t$ , of the time step interrupted by the impulse. This not only makes the overall trajectory bookkeeping easier, but, more importantly, prevents the distribution of coordinates from being biased away from a hard wall. Of course, in order to implement the fractional time step start-up, the next Verlet step must use an unequal time step formula, but otherwise the procedure is identical to that described above.

It should be noted that the interpolation, the unequal time step Verlet propagation, and the Verlet start-up all have errors of  $\theta(\Delta t)^3$ . Thus even though the impulsive dynamics algorithm itself is rigorous, the machinery required to interface it smoothly with the trajectory routine automatically introduces a larger error than that of the trajectory routine alone. For example, the interpolation is limited to a quadratic one by the fact that the Verlet routine saves only the current coordinate and the previous coordinate at each step.

Nevertheless, it seems unlikely that this will cause any noticeable difficulty. After all, in most applications of combined impulsive/continuous trajectories, the continuous force time steps will far outnumber those with impulses. Yet, it still might be possible that some combination of round-off errors and the  $(\Delta t)^3$  errors might introduce some sort of instability. To rule this out, we decided to test the numerical properties of a simple system which combined constraints, continuous forces, and impulsive forces. The system chosen was a single butane molecule (considered as four extended atoms arranged consecutively) modelled by fixing the three bondlengths but allowing the two tetrahedral bond angles to move under harmonic forces. [For simplicity, the torsional potential was neglected.] As a control, the Verlet algorithm was used in conjunction with SHAKE to evolve the butane trajectories in cartesian coordinates. Infinite walls were then inserted in the torsional potential—restricting the dihedral angle to bouncing back and forth inside a ‘window’ of 30 degrees†—and the numerical behaviour was investigated with and without the windows.

Some of the results of this comparison are illustrated in figure 2. In this graph the energy drift of two equal length trajectories (one requiring Verlet, SHAKE, and the impulsive dynamics routine, and one with just Verlet and SHAKE) is plotted versus the size of the time step. Examining the graph, we see that for a normal time step ( $0.8 \times 10^{-3}$  ps) there is no apparent difference between the two, but as the time step is increased the trajectory with windows shows slightly more drift. The significant point, though, is that the addition of the impulses produces a negligible effect whenever the energy conservation of the trajectory *without* impulses is satisfactory.

Similarly, looking at the small amounts of energy artificially introduced into the constrained degrees of freedom by SHAKE (something the impulsive routine does not do) again reveals that the addition of impulses has no real effect on the magnitude or stability of these errors. Moreover the distribution of the dihedral angle inside the windows displays the behaviour expected without a torsional potential, independent of whether or not windows are present. Thus it certainly seems that we can be fairly confident in attaching our impulsive force algorithm to a constrained continuous force trajectory.

† This is a convenient way of doing dynamical umbrella sampling which will be discussed in a future paper: HOLMGREN, S., and CHANDLER, D. (in preparation).

## 4. COMMENTS

Because it is so simple to include a constrained impulsive dynamics algorithm in any calculation that uses SHAKE and a trajectory routine, it would certainly seem that we now have an efficient way to do molecular dynamics on any system with holonomic constraints. This opens up the possibility of investigating a wide variety of chemical problems. One of these problems, the conformational behaviour of polymers, provides an especially tempting situation since the use of hard core interactions would produce a ready test of our understanding of excluded volume effects. In a similar fashion, a study of a polyatomic fluid near a corrugated hard wall would lead to an enhanced knowledge of surface kinetics and catalytic phenomena.

However, besides these relatively specific applications there is also the possibility of a more general usage. It may be possible to devise a *molecular* version of the extremely economical techniques which are currently employed in treating the dynamics of systems of hard spheres [9]. In place of hard spheres, one would work with fused hard spheres, but like the existing algorithms, the dynamics between collisions would still be trivial. SHAKE could be modified so as to enable this constrained, force free motion to be accomplished in a single step. The actual collision dynamics could then be taken care of by the procedure described in this article.

There is, nevertheless, one impediment to this type of approach which should be noted. In the existing hard sphere programmes much of the efficiency is a result of being able to predict the time of the next collision analytically. Thus one does not actually need to propagate from collision to collision; it is possible to 'jump' to the desired times. Unfortunately, in molecular systems it is no longer an easy matter to invert the force free part of the trajectory,  $\mathbf{x}(t)$ , to find the necessary times. This is due to the fact that the definition of a collision can no longer be expressed in terms of the relative centre of mass positions alone but must also include the internal degrees of freedom.

Yet even with this difficulty, it is still clear that fused hard sphere molecular dynamics is eminently practical—one may just have to take several simple time steps between collisions. Indeed, it may be possible to completely avoid taking these time steps if a rapid numerical method for inverting the trajectory can be devised. Alternatively, for low density systems one could also envision defining a 'sphere of influence' about the centre of mass of each molecule. Since a collision cannot occur unless two spheres of influences collide, one would therefore recover a simple way for predicting collision times. In either case, the use of the constrained impulsive dynamics for molecular fluids is worthy of serious investigation.

## APPENDIX

The purpose of this Appendix is to illustrate the constrained impulsive dynamics procedure in somewhat more detail than was done with the example in the text. Suppose we wish to study the molecular dynamics of a system of homonuclear diatomic molecules with an interaction which includes a fused hard sphere repulsive core (with or without an attractive component). If we let the molecular sites be the two nuclear centres (1 and 2), the most general geometry for a collision between two molecules (*A* and *B*) will be as pictured in

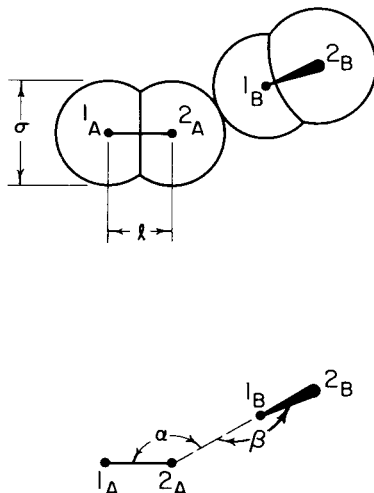


Figure 3. General collision geometry for two diatomics.

figure 3. Given this collision geometry (i.e., the coordinates  $\mathbf{r}_{1A}$ ,  $\mathbf{r}_{2A}$ ,  $\mathbf{r}_{1B}$ ,  $\mathbf{r}_{2B}$  at the time of impact) and the pre-collision velocities ( $\mathbf{v}_{1A}^{(i)}$ ,  $\mathbf{v}_{2A}^{(i)}$ ,  $\mathbf{v}_{1B}^{(i)}$ ,  $\mathbf{v}_{2B}^{(i)}$ ) what we will need to calculate are the velocities immediately after the collision ( $\mathbf{v}_{1A}^{(f)}$ ,  $\mathbf{v}_{1B}^{(f)}$ ,  $\mathbf{v}_{2A}^{(f)}$ ,  $\mathbf{v}_{2B}^{(f)}$ ).

To do this it is helpful to define the unit vectors

$$\hat{b}_{1A2A} = (\mathbf{r}_{2A} - \mathbf{r}_{1A})/l, \quad \hat{b}_{1B2A} = (\mathbf{r}_{2A} - \mathbf{r}_{1B})/\sigma,$$

$$\hat{b}_{1B2B} = (\mathbf{r}_{2B} - \mathbf{r}_{1B})/l$$

and the angles

$$\cos \alpha = \hat{b}_{1A2A} \cdot \hat{b}_{1B2A}, \quad \cos \beta = \hat{b}_{1B2A} \cdot \hat{b}_{1B2B}.$$

It is now straightforward to compute the  $\mathbf{I}^0$  vectors because if there were no constraints, only sites  $2A$  and  $1B$  would feel the impulse. By Newton's third law

$$\mathbf{I}_{2A} = -\mathbf{I}_{1B}, \quad \mathbf{I}_{1A} = \mathbf{I}_{2B} = 0$$

so that if we scale the impulse each molecule would feel without constraints

$$\mathbf{I}_{2A}^0 = \mathbf{I}_{2A}/I, \quad \mathbf{I}_{1B}^0 = \mathbf{I}_{1B}/I,$$

$$I = |\mathbf{I}_{1A} + \mathbf{I}_{2A}| = |\mathbf{I}_{1B} + \mathbf{I}_{2B}|$$

we can write

$$\left. \begin{aligned} \mathbf{I}_{1A}^0 &= 0, & \mathbf{I}_{1B}^0 &= -\hat{b}_{1B2A}, \\ \mathbf{I}_{2A}^0 &= \hat{b}_{1B2A}, & \mathbf{I}_{2B}^0 &= 0. \end{aligned} \right\} \quad (\text{A } 1)$$

Calculating the constraint forces is also particularly simple since each molecule has but one constraint. Equation (2.6) therefore becomes a single equation for each molecule

$$\lambda_{1A2A}^0 = \frac{1}{2}(\mathbf{I}_{2A}^0 - \mathbf{I}_{1A}^0) \cdot \hat{\mathbf{b}}_{1A2A},$$

$$\lambda_{1B2B}^0 = \frac{1}{2}(\mathbf{I}_{2B}^0 - \mathbf{I}_{1B}^0) \cdot \hat{\mathbf{b}}_{1B2B}$$

From (A 1) then

$$\lambda_{1A2A}^0 = \frac{1}{2} \cos \alpha, \quad \lambda_{1B2B}^0 = \frac{1}{2} \cos \beta. \quad (\text{A } 2)$$

However, once the  $\lambda$  parameters are known we may use (2.10 b) and (2.10 c) to find the scaled momentum changes

$$\left. \begin{aligned} \Delta \mathbf{p}_{1A}^0 &= \frac{1}{2} \cos \alpha \hat{b}_{1A2A}, & \Delta \mathbf{p}_{1B}^0 &= -\hat{b}_{1B2A} + \frac{1}{2} \cos \beta \hat{b}_{1B2B}, \\ \Delta \mathbf{p}_{2A}^0 &= \hat{b}_{1B2A} - \frac{1}{2} \cos \alpha \hat{b}_{1A2A}, & \Delta \mathbf{p}_{2B}^0 &= -\frac{1}{2} \cos \beta \hat{b}_{1B2B}, \end{aligned} \right\} \quad (\text{A } 3)$$

which, in turn, can be used to find  $I$  via (2.10 a)

$$I = -2m \frac{\mathbf{v}_{1A}^{(i)} \cdot \Delta \mathbf{p}_{1A}^0 + \mathbf{v}_{2A}^{(i)} \cdot \Delta \mathbf{p}_{2A}^0 + \mathbf{v}_{1B}^{(i)} \cdot \Delta \mathbf{p}_{1B}^0 + \mathbf{v}_{2B}^{(i)} \cdot \Delta \mathbf{p}_{2B}^0}{(\Delta \mathbf{p}_{1A}^0)^2 + (\Delta \mathbf{p}_{2A}^0)^2 + (\Delta \mathbf{p}_{1B}^0)^2 + (\Delta \mathbf{p}_{2B}^0)^2} \quad (\text{A } 4)$$

(with  $m$  the mass of each site in the molecule). The final velocities may then be written

$$\left. \begin{aligned} \mathbf{v}_{1A}^{(f)} &= \mathbf{v}_{1A}^{(i)} + (I/m) \Delta \mathbf{p}_{1A}^0, & \mathbf{v}_{1B}^{(f)} &= \mathbf{v}_{1B}^{(i)} + (I/m) \Delta \mathbf{p}_{1B}^0, \\ \mathbf{v}_{2A}^{(f)} &= \mathbf{v}_{2A}^{(i)} + (I/m) \Delta \mathbf{p}_{2A}^0, & \mathbf{v}_{2B}^{(f)} &= \mathbf{v}_{2B}^{(i)} + (I/m) \Delta \mathbf{p}_{2B}^0. \end{aligned} \right\} \quad (\text{A } 5)$$

For example, if the collision is collinear ( $\alpha = \beta = \pi$ ,  $\mathbf{v}_{1A}^{(i)} = \mathbf{v}_{2A}^{(i)} = \mathbf{v}_A^{(i)}$ ,  $\mathbf{v}_{1B}^{(i)} = \mathbf{v}_{2B}^{(i)} = \mathbf{v}_B^{(i)}$ ) then

$$\begin{aligned} I &= 2m |v_A^{(i)} - v_B^{(i)}|, \\ v_{1A}^{(f)} &= v_{2A}^{(f)} = v_B^{(i)}, \quad v_{1B}^{(f)} = v_{2B}^{(f)} = v_A^{(i)}. \end{aligned}$$

This is just a particularly roundabout way of deriving the well known fact that when two billiard balls collide they exchange velocities.

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