

A molecular-dynamics algorithm for mixed hard-core/continuous potentials

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Abstract

We present a new molecular-dynamics algorithm for integrating the equations of motion for a system of particles interacting with mixed continuous/impulsive forces. This method, which we call Impulsive Verlet, is constructed using operator splitting techniques similar to those that have been used successfully to generate a variety molecular-dynamics integrators. In numerical experiments, the Impulsive Verlet method is shown to be superior to previous methods with respect to stability and energy conservation in long simulations.

I. INTRODUCTION

Purely collisional systems were among the first to be studied by molecular-dynamics simulation¹. These systems include hard spheres or hard ellipsoids, which undergo purely elastic collisions, and square-well fluids, in which an attractive impulse force at a particular interparticle position is present in addition to the hard-core interactions. The algorithms for such systems are exact, to within roundoff error, and consist of free particle motion punctuated by exact resolution of the impulsive collisions—the resulting phase space trajectory is discontinuous. On the other hand, the vast majority of current molecular-dynamics simulations are performed on systems with continuous potentials. For such systems, the trajectory must be approximated using a numerical timestepping scheme such as the popular Verlet algorithm².

There exist, however, systems that are neither purely collisional, nor continuous, but are hybrids of the two. Important examples of such systems are the restricted primitive model (RPM) for electrolyte solutions and dipolar hard spheres³. In addition, the use of hard-core potentials with attractive continuous tails is common in perturbative treatments of liquids⁴. Since the the algorithms for simulating impulsive and continuous systems are fundamentally different from one another, the construction of hybrid methods for mixed systems is non-trivial and little studied. Consequently, the vast majority of studies on such systems have utilized Monte Carlo simulation techniques, eliminating the possibility of obtaining dynamical information.

In this paper, we present a new method for mixed hard-core/continuous potentials, which we call the Impulsive Verlet algorithm. This algorithm is suitable for any continuous potential, is less likely than alternatives to miss collisions, and exhibits good stability and energy conservation in long time simulation. In the construction of this new method we have been guided by recent work in the use of Hamiltonian splitting methods for the development of efficient and stable molecular-dynamics algorithms^{5,6}.

A few *ad hoc* hybrid methods have been constructed for mixed (hard/soft) systems^{7–10}. All of these methods are rather similar, in that the particles are advanced according to the continuous forces by a time step using a standard algorithm for continuous potentials, usually some variant of the Verlet algorithm, and the trajectories are checked for the existence of particle overlaps at the end or during the step. If no overlaps occur, the procedure is repeated for the next step. If overlaps (collisions) do occur, the system is returned to its state before the step and then is advanced without momentum modification by the forces to the time of collision, and the momenta are then modified according to the rules of elastic collision. This process is repeated until all collisions have been resolved and the end of the time step is reached. (One major difference between the algorithms is whether overlaps are checked only at the end of each step, or throughout the step. In the former case⁸, it is possible that glancing collisions are missed during the dynamics.) Heyes⁹ and Suh, *et al.*¹⁰ apply such algorithms to the restricted primitive model for electrolytes (hard-sphere with embedded charges in a dielectric continuum) with some apparent success. Unfortunately, as with the other papers on algorithms for mixed systems, no quantitative discussion on the stability or accuracy of the algorithm is given, making it difficult to evaluate the quality of the methods.

The Impulsive Verlet method is developed in the next two sections, followed by a discussion of certain numerical experiments on two model systems, comparing our scheme with the algorithm used in Suh, *et al.*¹⁰.

II. SPLITTING METHODS FOR MIXED DYNAMICS

Consider a system of N particles with instantaneous positions $\mathbf{q} = (q_1, q_2, \dots, q_N)$ in d dimensions interacting according to a continuous potential $V_c(\{\mathbf{q}_i\})$, assumed for simplicity to be spherically symmetric and pairwise additive, that is,

$$V_c(\mathbf{q}) = \sum_{i=1}^N \sum_{j>i} \phi_c(q_{ij}) , \quad (1)$$

where $q_{ij} \equiv |\mathbf{q}_j - \mathbf{q}_i|$, and ϕ is any smooth function of one variable. In addition, suppose the particles to have a hard core of diameter σ ; that is, when the distance between two particles is σ an elastic collision occurs that reflects the momentum of each particle along the collision vector. Such a hard-sphere core can be represented formally by a discontinuous pair potential of the form

$$\phi_{\text{hs}}(q_{ij}) = \begin{cases} \infty & q_{ij} \leq \sigma, \\ 0, & q_{ij} > \sigma. \end{cases} \quad (2)$$

We will define the energy function of the mixed system by analogy with continuous dynamics as the sum of the kinetic and formal potential energies:

$$H(\mathbf{q}, \mathbf{p}) = T(\mathbf{p}) + V_{\text{hs}}(\mathbf{q}) + V_c(\mathbf{q}), \quad (3)$$

where,

$$V_{\text{hs}} = \sum_{i=1}^N \sum_{j>i} \phi_{\text{hs}}(q_{ij})$$

and

$$T(\mathbf{p}) = \frac{1}{2} \mathbf{p}^T \mathbf{M}^{-1} \mathbf{p}, \quad (4)$$

is the kinetic energy (\mathbf{M} is the mass matrix) and $\mathbf{p} = (p_1, p_2, \dots, p_N)$, where each p_i is a d -dimensional vector. Despite appearances, this energy function is not, properly speaking, a Hamiltonian. Nonetheless, we can view the dynamics of the hard-sphere fluid as the limiting dynamics in repulsive inverse-power potentials of the form $V_{\text{sw}}(r) = 1/r^\beta$, with β a large positive integer. In this sense and for the purpose of constructing numerical methods, we can interpret the formal energy H as representing a very hard repulsive inverse-power Hamiltonian. We will often refer to H as the *pseudo-Hamiltonian*.

We define the flow map as the generator of the phase space trajectory,

$$\begin{pmatrix} \mathbf{q}(\tau + t) \\ \mathbf{p}(\tau + t) \end{pmatrix} = \psi_{t,H} \begin{pmatrix} \mathbf{q}(\tau) \\ \mathbf{p}(\tau) \end{pmatrix}. \quad (5)$$

The family of flow maps is closed under composition,

$$\psi_{t_1,H} \circ \psi_{t_2,H} = \psi_{t_2,H} \circ \psi_{t_1,H} = \psi_{t_1+t_2,H}, \quad (6)$$

for any times t_1 and t_2 .

A continuous Hamiltonian system can often be split into integrable subproblems with Hamiltonians H_1 and H_2 ⁶:

$$H(\mathbf{q}, \mathbf{p}) = H_1(\mathbf{p}) + H_2(\mathbf{q}). \quad (7)$$

The flow map of the full Hamiltonian can then be approximated as the concatenation of flow maps for the subproblems. There are a variety of ways of doing this, but the most common is based on a Trotter factorization

$$\psi_{h,H} = \psi_{\frac{h}{2},H_2} \circ \psi_{h,H_1} \circ \psi_{\frac{h}{2},H_2} + \mathcal{O}(h^3), \quad (8)$$

where h is the time step. For a separable Hamiltonian such as Eq. 3 with $V_{\text{hs}} = 0$, this factorization reduces to the usual velocity-Verlet algorithm¹¹ when $H_1 = T(\mathbf{p})$ and $H_2 = V_c(\mathbf{q})$.

The splitting framework for continuous Hamiltonians suggests a means of constructing integrators for mixed impulsive/continuous systems. A natural splitting for the pseudo-Hamiltonian is to let $H_1 = T(\mathbf{p}) + V_{\text{hs}}(\mathbf{q})$ and $H_2 = V_c(\mathbf{q})$. (Note that in this case H_1 is a function of both \mathbf{p} and \mathbf{q} , but since this represents a system with free particle motion punctuated by elastic collisions, it is exactly integrable.) This gives

$$\begin{pmatrix} \mathbf{q}^{n+1} \\ \mathbf{p}^{n+1} \end{pmatrix} = \psi_{\frac{h}{2},V_c} \circ \psi_{h,T+V_{\text{hs}}} \circ \psi_{\frac{h}{2},V_c} \begin{pmatrix} \mathbf{q}^n \\ \mathbf{p}^n \end{pmatrix}, \quad (9)$$

where \mathbf{q}^n and \mathbf{p}^n are the approximations to the phase space variables after the n -th time step. In other words, the momenta are adjusted at the beginning of each time step by one-half step according to the continuous forces (“kick”). The positions are next advanced for one time step, resolving all elastic collisions, but without further momentum

modification by the continuous forces (“push”). At the end of the step, the momenta are advanced again by a half step using the forces calculated from the new positions (another “kick”). This is nearly identical to the algorithm of Suh, *et al.*¹⁰ except that there momenta are only defined at half steps and a leap-frog formulation is used:

$$\begin{pmatrix} \mathbf{q}^{n+1} \\ \mathbf{p}^{n+1/2} \end{pmatrix}_{\text{Suh}} = \psi_{h,T+V_{hs}} \circ \psi_{h,V_c} \begin{pmatrix} \mathbf{q}^n \\ \mathbf{p}^{n-1/2} \end{pmatrix}. \quad (10)$$

Viewing the hard-sphere potential as being approximated by a very hard inverse-power repulsive potential, we see that either of the above two splitting methods is symmetric (i.e. time-reversible). From Eq. 8 we naively expect that such a method (applied to the inverse-power potential approximation) is second order accurate, meaning that in one step a *local error* of size $O(h^3)$ is introduced; on a finite fixed time interval, these errors accumulate, but the total growth or *global error* is at most $O(h^2)$. However, the demonstration of third-order local error requires a C^3 solution, and this assumption will break down in the limit of hard-sphere dynamics, in particular during a collision step. In fact, the local error introduced during a collision is really $O(h)$.

We illustrate this point with the simple example of a nonlinear “impact oscillator” with one degree-of-freedom pseudo-Hamiltonian

$$H = \frac{p^2}{2} + \phi_{hs}(q) + \phi_c(q), \quad (11)$$

describing a point mass acted on by some potential ϕ_c in collisional dynamics with a hard wall at $q = \delta$. The particle moves in the continuous potential ϕ_c according to Newton’s equations, until an impact, when $q = \delta$, then the momentum changes sign and the motion continues from the impact point.

Consider a numerical step from the point (q_0, p_0) at time $t = 0$ for a timestep of size h during which the particle motion includes a single collision event. (We mostly use subscripts to index particle number and superscripts for timestep, but for the discussion that follows we need to indicate powers of the momenta; so for this one-particle model, we will use subscripts for the timestep index.) We need to compute the local energy error contribution during a collisional step for this single degree-of-freedom model problem. The sequence of computations is

$$\hat{p} = p_0 - \frac{h}{2}\phi'_c(q_0), \quad (12)$$

$$h_{\#} = -\frac{q_0 - \delta}{\hat{p}}, \quad (13)$$

$$h_{\flat} = h - h_{\#}, \quad (14)$$

$$\tilde{p} = -\hat{p}, \quad (15)$$

$$q_1 = \delta - h_{\flat}\tilde{p}, \quad (16)$$

$$p_1 = \tilde{p} - \frac{h}{2}\phi'_c(q_1), \quad (17)$$

where $h_{\#}$, and h_{\flat} are the time to the next collision and the time from that collision to the end of the time step, respectively.

Substituting the endpoint values into the energy relation, we quickly find

$$\begin{aligned} \Delta H &= H(q_1, p_1) - H(q_0, p_0) = \frac{1}{2}(\tilde{p} - \frac{h}{2}\phi'_c(q_1))^2 + \phi_c(q_1) - \frac{1}{2}p_0^2 - \phi_c(q_0), \\ &= \frac{1}{2}(-p_0 + \frac{h}{2}\phi'_c(q_0) - \frac{h}{2}\phi'_c(q_1))^2 \\ &\quad + \phi_c(q_1) - \frac{1}{2}p_0^2 - \phi_c(q_0). \end{aligned}$$

Expand ϕ_c in a Taylor series about $q = \delta$, substitute, and cancel like terms to obtain

$$\begin{aligned} \Delta H &= -\frac{h}{2}p_0(\phi'_c(q_0) - \phi'_c(q_1)) + \frac{h^2}{8}(\phi'_c(q_0) - \phi'_c(q_1))^2 \\ &\quad + \phi'_c(\delta)(q_1 - q_0) + \frac{1}{2}\phi''_c(\delta)((q_1 - \delta)^2 - (q_0 - \delta)^2) + E_h. \end{aligned}$$

The remainder E_h contains terms of order the third power of h or higher, i.e. $|E_h/h^3|$ is bounded for all $h < 1$ such that the step contains a collision. Indeed, $\frac{h^2}{8}(\phi'_c(q_0) - \phi'_c(q_1))^2$ is also of this order, since $q_1 - q_0$ is proportional to h . From the equations

$$q_1 = \delta - h_b \hat{p}, \quad q_0 = \delta - h_{\#} \hat{p},$$

and the use of a Taylor series expansion of ϕ'_c , we arrive after discarding terms of order three or higher at,

$$\Delta H = \frac{h(h_{\#} - h_b)}{2} \phi''_c(\delta) \hat{p}^2 - \phi'_c(\delta)(h_b - h_{\#}) \hat{p} + \frac{1}{2} \phi''_c(\delta)(h_b^2 - h_{\#}^2) \hat{p}^2 + \tilde{E}_h.$$

with \tilde{E}_h again of third order. This finally leads to

$$\begin{aligned} \Delta H &= \frac{(h_{\#} - h_b)}{2} (h - (h_{\#} + h_b)) \phi''_c(\delta) \hat{p}^2 - \phi'_c(\delta)(h_b - h_{\#}) \hat{p} + \tilde{E}_h \\ &= -\phi'_c(\delta)(h_b - h_{\#}) \hat{p} + \tilde{E}_h. \end{aligned}$$

Therefore, the expected energy error introduced in this one collisional step is

$$H(q_1, p_1) - H(q_0, p_0) = -\phi'_c(\delta)(h_b - h_{\#}) \hat{p} + \tilde{E}_h, \quad (18)$$

where the quantity $|\tilde{E}_h/h^3|$ is bounded independent of h . (A similar result would hold for the solution error.)

Technically speaking, it is incorrect to say that the energy jump in one step is $O(h)$ since if we decrease the timestep h sufficiently, there will be no collision event within the particular step, and so the error will revert to $O(h^3)$. Nonetheless, in any timestepping simulation in which there are collision events, these steps will introduce errors proportional to h . If we define the *local approximation error* e_{loc} as the maximum of magnitudes of the local errors introduced, then e_{loc} is of first order in h , not third order as we would expect in the continuous case. Since there are, in general, a finite number of such collisions in any finite interval, the accumulation is bounded and the global error is also $O(h)$. The apparent contradiction of an odd-order symmetric method is just one of several anomalies that result from the complex transition from the smooth problem to the discontinuous limit. In another terminology, we could say that the splitting method undergoes an *order reduction* for stiff potential wells.

From this discussion and Eq. 18, we expect the naive splitting method to give rather poor energy conservation, except in three special cases:

Case 1 Collisions do not occur *within* timesteps but precisely *at* the timesteps, so third order is recovered.

Case 2 The collisions occur at precisely the middle of a timestep, so that the first order term in the error formula vanishes and third order local energy drift is again recovered.

Case 3 Third order will be recovered if the *derivative of the continuous pair potential vanishes for two spheres in contact*.

To illustrate this last point, we apply the method to one degree-of-freedom anharmonic “impact oscillator” with a continuous potential, $\phi_c(q) = \frac{1}{2}q^2 + \frac{1}{4}q^4$. We show in Fig. 1 the maximum total energy error as a function of the time step when the wall is placed at $q = 0.00$ and $q = -4.00$. One can see that the naive splitting is a second order method when the derivative at the wall vanishes .

Because it is only applicable for a relatively limited class of potentials the naive splitting method is not a candidate for a viable general technique, however, it does provide a good starting point for the development of a general method, which we call the Impulsive Verlet (IV) algorithm.

III. IMPULSIVE VERLET

To develop our method, we deliberately exploit two of the special cases in the naive algorithm for which third order can be expected, namely Cases 1 and 3 mentioned at the end of the previous section. (Case 2, the situation that

collisions occur at the midpoint of the time interval, does not appear to be of practical use.) We begin by introducing an artificial splitting of the continuous potential, $\phi_c(q_{ij})$, into a short-ranged part, $\phi_1(q_{ij})$, and a long-range part, $\phi_2(q_{ij})$, according to

$$\phi_c(q_{ij}) = \phi_1(q_{ij}) + \phi_2(q_{ij}) . \quad (19)$$

(This decomposition is similar to that invoked in multiple timestepping^{5,12-14} molecular-dynamics algorithms.) For the reasons discussed above, the long-range (and therefore most expensive to calculate) part of the potential is defined so that the derivative vanishes at the hard-core separation. We define $\phi_2(q_{ij})$ as follows:

$$\phi_2(q) = \begin{cases} P(q_1), & q < q_1, \\ P(q), & q_1 \leq q < q_2, \\ \phi_c(q), & q \geq q_2, \end{cases} \quad (20)$$

where, q_1 and q_2 are parameters, and $P(r) = A_0 + A_1 r + A_2 r^2 + A_3 r^3$ is a Hermite interpolant introduced so that the two potentials are smooth to the order C^1 for any continuous potential. From Eqns. 19) and 20), $\phi_1(q)$ is given by

$$\phi_1(r_{ij}) = \begin{cases} \phi_c(q) - P(q_1) & q < q_1 \\ \phi_c(q) - P(q) & q_1 \leq q < q_2, \\ 0 & q \geq q_2. \end{cases} \quad (21)$$

The continuity condition, $P(q_2) = \phi_c(q_2)$, and the smoothness conditions, $P'(q_2) = \phi'_c(q_2)$, $P'(q_1) = 0$, and $P''(q_1) = 0$, allow us to calculate the coefficients of the Hermite interpolant, giving

$$A_3 = \frac{\phi'_c(q_2)}{6r_1(q_1 - q_2) + 3(q_2^2 - q_1^2)} \text{ for } q_1 \neq q_2, \quad (22)$$

$$A_2 = -3q_1 A_3, \quad (23)$$

$$A_1 = 3q_1^2 A_3, \quad (24)$$

$$A_0 = -(A_1 q_2 + A_2 q_2^2 + A_3 q_2^3) + V_c(q_2) . \quad (25)$$

(An example of this potential splitting for an inverse-sixth-power attractive potential, $\phi_c(q) = -c(\sigma/q)^6$, is shown in Fig. 2.)

Next, we define N -body potentials V_1 and V_2 as a sum of pair contributions from ϕ_1 and ϕ_2 , respectively. We then split the total Hamiltonian in the following way:

$$H_1(\mathbf{q}, \mathbf{p}) = T(\mathbf{p}) + V_{\text{hs}}(\mathbf{q}) + V_1(\mathbf{q}) \quad (26)$$

and

$$H_2(\mathbf{q}) = V_2(\mathbf{q}) . \quad (27)$$

The Trotter factorization (Eq. 8) is now applied to this splitting. The problem now is that H_2 is not integrable and its flow map must be approximated. This is done in the following way:

$$\psi_{H_2, h} \approx \prod_{i=1}^{n_c+1} \psi_{V_{\text{hs}}} \circ \psi_{V_1, \tau_i^{(c)}/2} \circ \psi_{T, \tau_i^{(c)}} \circ \psi_{V_1, \tau_i^{(c)}/2} , \quad (28)$$

where n_c is the number of hard-sphere collisions between during the time step h , $\tau_i^{(c)}$ is the time between each collision (with $\tau_1^{(c)}$ being measured from the beginning of the time step until the first collision and $\tau_{n+1}^{(c)}$ measured from the

last collision to the end of the time step), and $\psi_{V_{hs}}$ is an operator representing the resolution of each elastic collisions. This is essentially the execution of a Verlet step of length $\tau^{(c)}$ between each elastic collision. The collision times can be calculated since the Verlet step generates a quadratic trajectory, which together with the collision condition for two particles i and j can be written as

$$\|\mathbf{q}_i(\tau^{(c)}) - \mathbf{q}_j(\tau^{(c)})\|^2 - \sigma^2 = 0, \quad (29)$$

generates a quartic equation for $\tau^{(c)}$.

We describe below the algorithm for the Impulsive Verlet molecular-dynamics simulation in more detail.

Impulsive Verlet Timestepping Algorithm

$$\mathbf{p}_i^{n+1/2,0} = \mathbf{p}^{n,0} + \frac{1}{2}\mathbf{F}_{2,i}(\mathbf{q}^{n,0})h$$

do $i_c = 1, n_c$

$$\mathbf{p}_i^{n+1/2,i-1/2} = \mathbf{p}^{n+1/2,i-1} + \frac{1}{2}\mathbf{F}_{1,i}(\mathbf{q}^{n,i-1})\tau_c^i$$

$$\mathbf{q}^{n,i} = \mathbf{q}^{n,i-1} + \mathbf{M}^{-1}\mathbf{p}^{n+1/2,i-1/2}\tau_c^i$$

$$\tilde{\mathbf{p}}_i^{n+1/2,i} = \mathbf{p}^{n+1/2,i-1/2} + \frac{1}{2}\mathbf{F}_{1,i}(\mathbf{q}^{n,i})\tau_c^i$$

$$\mathbf{p}^{n+1/2,i} = \psi_{V_{hs}} \left(\begin{array}{c} \mathbf{q}^{n,i} \\ \tilde{\mathbf{p}}^{n+1/2,i} \end{array} \right)$$

end do

$$\mathbf{p}_i^{n+1/2,n_c+1/2} = \mathbf{p}^{n+1/2,n_c} + \frac{1}{2}\mathbf{F}_{1,i}(\mathbf{q}^{n,n_c})(h - \sum_{i=1}^{n_c} \tau_c^i)$$

$$\mathbf{q}^{n+1,0} = \mathbf{q}^{n,n_c} + \mathbf{M}^{-1}\mathbf{p}^{n+1/2,n_c+1/2}(h - \sum_{i=1}^{n_c} \tau_c^i)$$

$$\mathbf{p}_i^{n+1/2,n_c+1} = \mathbf{p}^{n+1/2,n_c+1/2} + \frac{1}{2}\mathbf{F}_{1,i}(\mathbf{q}^{n+1,0})(h - \sum_{i=1}^{n_c} \tau_c^i)$$

$$\mathbf{p}_i^{n+1,0} = \mathbf{p}^{n+1/2,n_c} + \frac{1}{2}\mathbf{F}_{2,i}(\mathbf{q}^{n+1,0})h$$

To make sure that no collisions are missed it is necessary to ensure that the quartic equation (Eq. 29) is accurately solved to give the nearest root to zero. This is not a trivial problem as the solution becomes increasingly unstable as smaller time steps are used (i.e. when the time to collision is small). To ensure the inaccuracies are not large enough to affect the overall accuracy and order of the method, we employ Laguerre's method¹⁵ to find all roots of the quartic and take the smallest, positive real root, which is then refined using Newton-Raphson. This proved to be sufficient at all but the very smallest time steps studied.

There is a small probability that the Impulsive Verlet method can miss a grazing collision, since the trajectories that are followed in determining collisions are quadratic approximations. However, this probability is greatly reduced in comparison to the method of Suh, *et al.* or any other algorithm that uses linear motion to determine the collisions.

IV. NUMERICAL EXPERIMENTS

We test the Impulsive Verlet algorithm using as our continuous potentials, $\phi_c(q)$, the Lennard-Jones potential

$$\phi_{c,LJ} = 4\epsilon \left[\left(\frac{\sigma}{q} \right)^{12} - \left(\frac{\sigma}{q} \right)^6 \right]. \quad (30)$$

and an attractive inverse-sixth-power potential

$$\phi_{c,6} = -\epsilon \left(\frac{\sigma}{q} \right)^6. \quad (31)$$

In both potentials σ is the same as the hard-core diameter. We truncate both potentials at the distance $q_c^* = q_c/\sigma = 2.5$ and, to ensure their continuity, they are shifted so that the value of the potential at the cutoff is zero. In implementing the Impulsive Verlet algorithm, we split each potential as prescribed in Eq. 19- 25, with q_1 and q_2 as input parameters. For the Lennard-Jones potential there is, of course, a natural splitting, namely that of Weeks, Chander and Anderson (WCA)⁴, where the potential is split at the minimum with $q_1^* = q_2^* = 2^{1/6}$, which gives the following splitting:

$$\phi_{1,LJ}(q; \text{WCA}) = \begin{cases} 4\epsilon[(\frac{\sigma}{q})^{-12} - (\frac{\sigma}{q})^{-6}] + \epsilon & q < 2^{\frac{1}{6}}\sigma, \\ 0, & q \geq 2^{\frac{1}{6}}\sigma. \end{cases} \quad (32)$$

$$\phi_{2,LJ}(q, \text{WCA}) = \begin{cases} -\epsilon, & q < 2^{\frac{1}{6}}\sigma, \\ 4\epsilon[(\frac{\sigma}{q})^{-12} - (\frac{\sigma}{q})^{-6}], & q \geq 2^{\frac{1}{6}}\sigma, \end{cases} \quad (33)$$

The MD simulations were carried out on systems of 108 particles. The system of reduced units was chosen so that all quantities are dimensionless. So, as units of distance and energy we used the potential parameters σ and ϵ , respectively, and the mass of one atom as the unit mass. The unit of time is $(m\sigma^2/\epsilon)^{1/2}$. An asterisk superscript indicates reduced units. Except where otherwise indicated all simulations are performed using a reduced density $\rho^* = \rho\sigma^3 = 0.9$ and reduced temperature $T^* = kT/\epsilon = 2.5$. In addition, a cubic box with periodic boundary conditions is used. For greater efficiency, the MD program incorporates three neighbor lists¹⁶ for the evaluation of the short-range force, the long-range force, and the collision times.

The results of the Impulsive Verlet on the instantaneous total energy for the Lennard-Jones and the attractive inverse sixth continuous potentials are illustrated in Fig. 3 and 4. A comparison to the naive splitting algorithm of Suh, *et al.*¹⁰ is also made for both potentials. The superiority in energy conservation and stability of the Impulsive Verlet algorithm over the naive splitting method is striking.

We study in Fig. 5 the order of the method while varying q_1 and q_2 . The order is obtained by plotting (on a log-log) the maximum energy error for a fixed-length simulation versus the time step. A comparison with a straight line of slope two tells us that the method is of second order for various values of q_1^* and q_2^* . (Note the slight deviation of the slope at very small time steps from the theoretical value of 2.0 is due to the difficulty in solving the quartic equation for the collision times when the time to collision is very small. This is not a real problem in practice since the goal of molecular-dynamics simulation is to use the largest time steps possible.)

Finally, to demonstrate the ability of the Impulsive-Verlet method to yield relevant dynamical quantities, we show in Fig. 6 the result for the normalized velocity autocorrelation function, $C(t) = \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle / \langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle$, for the Lennard-Jones system (108 particles) with $\rho^* = 0.9$ and $T^* = 0.9$. In this calculation we use a splitting with $q_1^* = 1.122$ and $q_2^* = 1.5$.

V. CONCLUSION

We have introduced a molecular-dynamics method for mixed hard-core/continuous potentials, which we refer to as the Impulsive Verlet algorithm. This algorithm is produced by extending general potential splitting methods to the specific case of mixed potentials. In addition to providing a mechanism for generating the Impulsive Verlet method, the potential splitting formalism helps to understand the failings of previous methods. The Impulsive Verlet algorithm uses a quadratic trajectory between collisions and does not miss any collisions of the approximate trajectory. As a result the algorithm is suitable for any type of continuous potential, is second order, has good energy preservation, and is far more stable over long time simulation than previously integrators for such systems. (A detailed theoretical analysis of the algorithm is the subject of current research.)

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FIGURES

FIG. 1. The maximum total energy error as a function of the time step for one degree-of-freedom anharmonic “impact oscillator” is using the naive splitting approach. The wall is placed at $q = -4.00$ (square) and at $q = 0.00$ (circle). Comparison is made with lines of slope two (solid line) and one (dashed line).

FIG. 2. A potential splitting of a inverse-sixth-power attractive interaction, $-(\frac{\sigma}{q})^6$, with $q_1/\sigma = 1.1$ and $q_2/\sigma = 1.200$. The short range and the long potentials are (a) and (b) respectively.

FIG. 3. Instantaneous total energy for a 108 particle simulation using a Lennard-Jones continuous potential with a hard-sphere core, using both Impulsive Verlet (solid line) and the naive splitting algorithm of Suh, *et al.* (dashed line). The time step is $h^* = 4 \times 10^{-3}$.

FIG. 4. Instantaneous total energy for a 108 particle system interacting via an inverse sixth-power attractive potential with a hard-sphere core, using both Impulsive Verlet (solid line) and the naive splitting algorithm of Suh, *et al.* (dashed line). The time step is $h^* = 4 \times 10^{-3}$.

FIG. 5. The maximum total energy error as a function of the time step for a system of 108 particles using the Impulsive Verlet algorithm and the Lennard-Jones potential. Comparison is made with a line of slope two.

FIG. 6. Normalized velocity autocorrelation as a function of time for 108 Lennard-Jones particles at $\rho^* = 0.9$ and $T^* = 0.9$, using the Impulsive Verlet algorithm with a time step $h^* = 1 \times 10^{-2}$.











