

Simulation of a Diatomic Liquid Using Hard Spheres Model

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In this work we demonstrate the possibility of including constraints in hard systems, using the simple case of a dimer of hard spheres, where the analytical solution exists. We make a detailed description of the model and show that the system's dynamics can be solved in a rigorous way. We also illustrate our theoretical results with some numerical calculations on a simple diatomic liquid.

KEY WORDS: Hard spheres; constraints; molecular dynamics.

1. INTRODUCTION

Molecular dynamics simulation was introduced by Alder and Wainwright⁽¹⁾ for studying the motion of hard systems. Hard models have been extremely useful for simulating a variety of fluids. Let us recall briefly the peculiarities of the (exact) integration algorithm. In hard potential models, the particles move freely and the only interaction occurs at the moment of collision. Therefore, the simulation is essentially based on the calculation of the collision times and on the kinematics of the collision: once the shortest collision time has been computed, we propagate inertially the positions up to that collision time and calculate the velocities of the hard spheres after the collision. Then we reset all the velocities, define the new collision time, and repeat the process. The major advantage of this method is that there is no algorithmic error in the integration of motion. Moreover, when, as in the case of hard spheres, the calculation of the collision times is simple, the integration is very fast and one can follow the model dynamics for very long times.

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There have been several successful attempts to model more complex systems using hard molecules of different forms, e.g., hard lines,^(2,3) spherocylinders,⁽⁴⁾ fused hard spheres,⁽⁵⁾ etc. However, except for the case of hard lines, described with detail in ref. 3, for any other non-spherical body, the calculation of the collision time between two molecules is a complex matter. In two examples given,^(4,5) the authors had to deal with a highly complex equation for the collision time which was not trivial to solve numerically. Therefore, they used a step-by-step approach, losing the major advantage of hard systems. As for large polyatomic molecules, a single polymeric molecule represented by a chain of hard spheres has been simulated.^(6,7) There, the length of the bond between two hard spheres in the chain was restricted to lie between the values σ and $\sigma + \delta\sigma$, and the atoms were moving freely between the collisions with other atoms or "bond collisions." Although brave, this approach has the problem of too many bond collisions.

In the simulation of molecular systems, using molecular dynamics based on continuous interaction potentials, the intramolecular strong interactions are usually substituted by holonomic constraints.⁽⁸⁾ It is an old credo that models involving hard spheres are incompatible with exact constraints, and no work has been pursued in this area. In this paper we show that it is possible to include constraints in hard systems and solve for their dynamics in a rigorous way. An important difference between hard spheres and hard molecules, is that our non-spherical molecules may re-collide before hitting other molecules.^(9,10) In our algorithm re-collisions events are taken into account.

The aim of this work is to highlight what is precisely implied in the introduction of holonomic constraints into a model of hard spheres.

In the following three sections we describe the model for the case of a diatomic liquid, where an analytical solution is at hand. The generalization to polyatomic molecules connected by rigid bonds is analytically much heavier although still feasible. Non-quadratic constraints are also treatable but only using a numerical, non exact, integration algorithm. Therefore, they lose some of the attractiveness of the hard systems. In Section 5 we illustrate our results with a simple model calculation and in Section 6 we draw some conclusions.

2. FREE MOTION OF TWO BOND CONSTRAINED HARD SPHERES

In this section we will discuss the motion in between collisions of a single molecule consisting of two identical hard spheres each of mass m connected by a bond constraint. The molecule translates and rotates

around its center of mass. There are no external forces acting on the molecule.

Let us call the two identical hard spheres forming a diatomic molecule, S1 and S2, and their atomic positions r_1 and r_2 . The center of mass (COM) position $R = \frac{1}{2}(r_1 + r_2)$ at time t is:

$$\vec{R}(t) = \vec{R}(0) + \vec{V}(0) t \quad (1)$$

where $\vec{R}(0)$, and $\vec{V}(0)$ are the initial COM position and velocity. If a is the distance between the centers of the spheres S1 and S2, the constraint condition is:

$$\sigma = (\vec{r}_2 - \vec{r}_1)^2 - a^2 = 0. \quad (2)$$

The expression for the constraint force, G_i , on the atom i ($i = 1, 2$), using the constraint condition, is:

$$G_i = -\lambda \frac{\partial \sigma}{\partial r_i} \quad (3)$$

where λ is the Lagrange multiplier associated to σ . In our case the constraint force is the only force acting on the atoms in between collisions. Denoting $\vec{r}_{12} = \vec{r}_2 - \vec{r}_1$, we write:

$$\begin{aligned} m\ddot{\vec{r}}_1 &= \vec{G}_1 = 2\lambda\vec{r}_{12} \\ m\ddot{\vec{r}}_2 &= \vec{G}_2 = -2\lambda\vec{r}_{12}. \end{aligned} \quad (4)$$

Using these expressions, we can also write the equations of motion of our molecule in between collisions as:

$$\begin{aligned} M\ddot{\vec{R}} &= 0 \\ m\ddot{\vec{r}}_{12} &= -4\lambda\vec{r}_{12}. \end{aligned} \quad (5)$$

The solution of the last differential equation is:

$$\vec{r}_{12}(t) = \vec{A} \cos(\omega t) + \vec{B} \sin(\omega t) \quad (6)$$

with

$$\omega = \sqrt{\frac{4\lambda}{m}}. \quad (7)$$

Imposing the initial conditions and solving for \vec{A} and \vec{B} we get:

$$\begin{aligned}\vec{A} &= \vec{r}_{12}(0) = \vec{r}_2(0) - \vec{r}_1(0) \\ \vec{B} &= \frac{\vec{v}_2(0) - \vec{v}_1(0)}{\omega} = \frac{\vec{v}_{12}(0)}{\omega}.\end{aligned}\quad (8)$$

Inserting the expression (6) in the constraint condition (2), we get:

$$A^2 \cos^2(\omega t) + B^2 \sin^2(\omega t) + 2\vec{A}\vec{B} \sin(\omega t) \cos(\omega t) - a^2 = 0 \quad (9)$$

where, in principle, \vec{B} and ω are functions of λ . At $t = 0$ we get $A^2 = a^2$, and at $\omega t = \frac{\pi}{2}$ we get $B^2 = a^2$, therefore, for any time t from (9) we obtain:

$$2\vec{A}\vec{B} \sin(\omega t) \cos(\omega t) = 0 \quad (10)$$

which means that \vec{A} must be orthogonal to \vec{B} . From Eq. (8) we see that Eq. (10) just gives the kinematic condition to be satisfied by the initial conditions, i.e., $\vec{r}_2(0) - \vec{r}_1(0)$ orthogonal to $\vec{v}_2(0) - \vec{v}_1(0)$. Using Eq. (8) and remembering that $B^2 = a^2$, for ω we get:

$$\omega = \sqrt{\frac{(\vec{v}_2(0) - \vec{v}_1(0))^2}{a^2}} \quad (11)$$

and, for the Lagrange multiplier λ ,

$$\lambda = \frac{m(\vec{v}_2(0) - \vec{v}_1(0))^2}{4a^2}. \quad (12)$$

Returning to cartesian coordinates of each hard sphere in the molecule,

$$\vec{r}_i(t) = \vec{R}(t) \mp \frac{1}{2} \vec{r}_{12}(t) \quad (13)$$

with $i = 1, 2$, we can rewrite the parametric equations for their motion as:

$$\begin{aligned}\vec{r}_1(t) &= \vec{R}(0) + \vec{V}(0) t - \frac{1}{2} (\vec{r}_2(0) - \vec{r}_1(0)) \cos(\omega t) - \frac{\vec{v}_2(0) - \vec{v}_1(0)}{2\omega^2} \sin(\omega t) \\ \vec{r}_2(t) &= \vec{R}(0) + \vec{V}(0) t + \frac{1}{2} (\vec{r}_2(0) - \vec{r}_1(0)) \cos(\omega t) + \frac{\vec{v}_2(0) - \vec{v}_1(0)}{2\omega^2} \sin(\omega t)\end{aligned}\quad (14)$$

with ω defined by Eq. (11). Equation (14) describe the dynamics of the rigid dimer of hard spheres in between collisions.

3. SOLVING FOR THE COLLISION TIMES

Let us consider two molecules, the first (molecule 1) consisting of hard spheres S1 and S2, and the second (molecule 2) consisting of hard spheres S3 and S4. The COM's of both molecules move on a straight line, until the collision occurs:

$$\begin{aligned}\vec{R}_1(t) &= \vec{R}_1(0) + \vec{V}_1(0) t \\ \vec{R}_2(t) &= \vec{R}_2(0) + \vec{V}_2(0) t.\end{aligned}\quad (15)$$

To calculate the collision time between these two molecules, we have to calculate the times of the collisions between all the possible pairs of hard spheres (S1 and S3, S1 and S4, S2 and S3, S2 and S4). The conditions for these collisions are:

$$\begin{aligned}(\vec{r}_3 - \vec{r}_1)^2 &= d^2 \\ (\vec{r}_3 - \vec{r}_2)^2 &= d^2 \\ (\vec{r}_4 - \vec{r}_1)^2 &= d^2 \\ (\vec{r}_4 - \vec{r}_2)^2 &= d^2\end{aligned}\quad (16)$$

where d is the diameter of each hard sphere. Substituting the equations for the position of each hard sphere as a function of time, Eq. (14), in the collision conditions (16) we get a set of equations in t to be solved numerically. The solution gives the four collision times from which we take the smallest one as the collision time of the two molecules.

Let us suppose that the collision occurs between the sphere S1 of the molecule 1 and the sphere S3 of the molecule 2. We write the initial distance between the two molecules $R_2(0) - R_1(0) = R_{12}(0)$ and the difference of molecular velocities $V_2(0) - V_1(0) = V_{12}(0)$. The angular velocities of the molecules are ω_1 and ω_2 . In this case, the first collision condition of Eq. (16) reads:

$$\begin{aligned}(\vec{r}_3 - \vec{r}_1)^2 &= \left\{ \vec{R}_{12}(0) + \vec{V}_{12}(0) t + \frac{1}{2} (\vec{r}_{12}(0) \cos(\omega_1 t) - \vec{r}_{34}(0) \cos(\omega_2 t)) \right. \\ &\quad \left. + \frac{\vec{v}_{12}(0)}{2\omega_1^2} \sin(\omega_1 t) - \frac{\vec{v}_{34}(0)}{2\omega_2^2} \sin(\omega_2 t) \right\}^2 = d^2\end{aligned}\quad (17)$$

Clearly, this collision condition is rather complex. Nevertheless, we can try to simplify the problem. Consider two spherical molecules having the same

diameter $D = d + a$. In this case we could solve the problem of this fictitious collision the same way it has been solved in the standard hard sphere models.⁽¹⁾ The quadratic equation in terms of the molecular centers of mass is:

$$(\vec{R}_2 - \vec{R}_1)^2 = (d + a)^2 \quad (18)$$

where the COM positions are described by the Eqs. (15). To solve this equation we will first decide if the collision is possible. If the distance between the COM's of the two molecules is bigger than $d + a$, and the molecules are receding or moving parallel, so

$$(\vec{R}_2 - \vec{R}_1) \cdot (\vec{V}_2 - \vec{V}_1) \geq 0, \quad (19)$$

the collision will not be possible. In this case we reject the molecular pair and proceed to the next one. Instead, if the left hand side of Eq. (19) is smaller than 0, the two molecules are approaching and we have to proceed to find the fictitious collision time, propagate the molecules till this point, and then solve the Eq. (17). If the initial distance between the molecular COM is less than $d + a$, we also have to proceed to solve Eq. (17), both if the two molecules are approaching or receding.

In Fig. 1 we present the development of an example collision between two molecules as a function of time (f_{cm} corresponds to the value of $(\vec{R}_2 - \vec{R}_1)^2 - (d + a)^2$ for the fictitious molecules of diameter $d + a$ and f_{13} , f_{14} , f_{23} , and f_{24} to the values $(\vec{r}_3 - \vec{r}_1)^2 - d^2$, $(\vec{r}_4 - \vec{r}_1)^2 - d^2$, etc., respectively, for the four possible pairs of atoms inside each molecule.

As can be seen from Fig. 1, the first collision between the two molecules (in this example $f_{24} = 0$) occurs AFTER the fictitious collision between the two molecules of diameter $d + a$ has occurred. In this example the initial distance between the two COM's is less than $d + a$.

Thus, in this case, we can proceed directly to solve for exact collision times, i.e., find where the various particle separation trajectories shown in Fig. 1 cross the time axis. There are a number of methods to find roots of equations, including for example Newton's method, which we can apply in a straightforward fashion at the moment when the distance between the two molecules is equal (or less) to $d + a$. We have just to assure that the first derivatives of the functions of Fig. 1 are negative. This will be a sufficient condition to apply Newton, because it means that the two atoms under consideration are approaching. Otherwise, if the first derivative is positive, the two atoms are receding and a possible collision between them may only happen much later than any collision between the pair of approaching atoms.

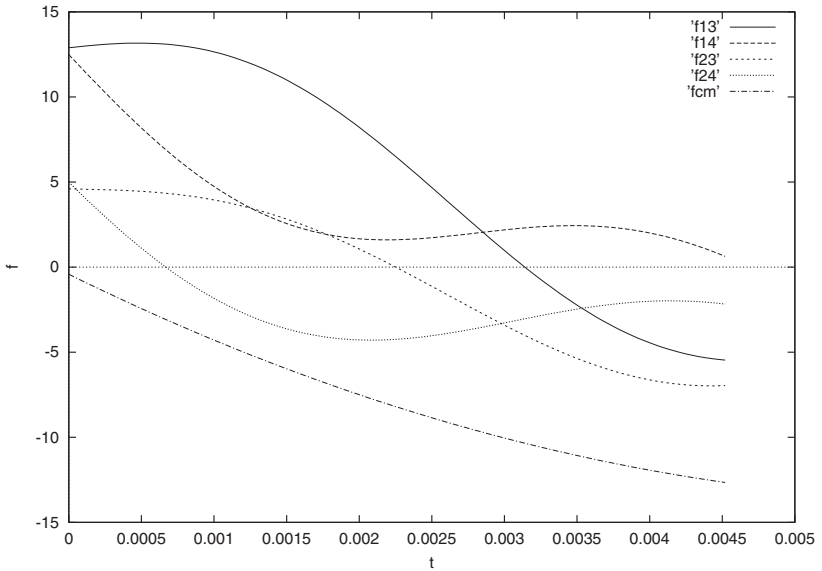


Fig. 1. Development of a collision between two molecules: $f_{cm} = (\vec{R}_2 - \vec{R}_1)^2 - (d+a)^2$, $f_{13} = (\vec{r}_3 - \vec{r}_1)^2 - d^2$, $f_{14} = (\vec{r}_4 - \vec{r}_1)^2 - d^2$, $f_{23} = (\vec{r}_3 - \vec{r}_2)^2 - d^2$, and $f_{24} = (\vec{r}_4 - \vec{r}_2)^2 - d^2$. The intersections with zero correspond to the collisions between the hard spheres. All the functions are in Å, the time unit is 10^{-13} s.

4. SOLVING FOR THE COLLISION BETWEEN TWO MOLECULES

Once we have the shortest collision time t , we have to solve the collision between the two molecules, finding the velocities of each hard sphere after the collision in terms of their initial velocities. Let us suppose that the first collision occurs between the hard sphere S1 of the molecule 1 and the hard sphere S3 of the molecule 2. To find the final velocities we have to use the conservation laws acting during the collision and to impose the constraint. The conservation laws are: 3 conservation conditions for linear momenta, 3 for angular momenta and the conservation of the total kinetic energy (assuming that the collision is completely elastic). They read:

$$\vec{v}_{1i} + \vec{v}_{2i} + \vec{v}_{3i} + \vec{v}_{4i} = \vec{v}_{1f} + \vec{v}_{2f} + \vec{v}_{3f} + \vec{v}_{4f}. \quad (20)$$

$$\begin{aligned} \vec{r}_{1i} \times \vec{v}_{1i} + \vec{r}_{2i} \times \vec{v}_{2i} + \vec{r}_{3i} \times \vec{v}_{3i} + \vec{r}_{4i} \times \vec{v}_{4i} \\ = \vec{r}_{1f} \times \vec{v}_{1f} + \vec{r}_{2f} \times \vec{v}_{2f} + \vec{r}_{3f} \times \vec{v}_{3f} + \vec{r}_{4f} \times \vec{v}_{4f} \end{aligned} \quad (21)$$

$$\frac{v_{1i}^2}{2} + \frac{v_{2i}^2}{2} + \frac{v_{3i}^2}{2} + \frac{v_{4i}^2}{2} = \frac{v_{1f}^2}{2} + \frac{v_{2f}^2}{2} + \frac{v_{3f}^2}{2} + \frac{v_{4f}^2}{2} \quad (22)$$

Now we have to take into consideration the constraint contribution during the collision. Let us assume that the constraint force between the two atoms can be split into two parts, i.e., $G = -\lambda \frac{\partial \sigma}{\partial r_i} \equiv (v + \mu' \delta(t)) \frac{\partial \sigma}{\partial r_i}$. One is the continuous part equal to $v \frac{\partial \sigma}{\partial r_i}$, another is the discontinuous part which acts only during the collision and can be written as $\mu' \delta(t) \frac{\partial \sigma}{\partial r_i}$. The collisions are instantaneous, so for an atom of mass m we can write the relation between the impulse (the only force present is the constraint force) and the change in the linear momentum as:

$$m\vec{v}_f - m\vec{v}_i = \int_{0_-}^{0_+} -\lambda \frac{\partial \sigma}{\partial r} dt = \int_{0_-}^{0_+} v \frac{\partial \sigma}{\partial r} dt + \int_{0_-}^{0_+} \mu' \delta(t) \frac{\partial \sigma}{\partial r} dt. \quad (23)$$

The first integral is equal to zero, while from the second one we get the correction for the velocity due to the constraint force:

$$\vec{v}_f - \vec{v}_i = \frac{1}{m} \frac{\partial \sigma}{\partial r} \int_{0_-}^{0_+} \delta(t) \mu' dt = 2 \frac{\mu' \vec{r}_{12}}{m} \equiv \mu \vec{r}_{12}. \quad (24)$$

Therefore, in the following equations describing the collision between the molecules 1 and 2, we will denote this correction as $\mu_1 \vec{r}_{12}$ for the atoms belonging to the molecule 1, and as $\mu_2 \vec{r}_{34}$ for the atoms belonging to the molecule 2.

In this case the solution, taking into account constraint contribution during the collision, can be written as:

$$\begin{aligned} \vec{v}_{1f} &= \vec{v}_{1i} + \Delta \vec{v} + \mu_1 \vec{r}_{12} \\ \vec{v}_{2f} &= \vec{v}_{2i} - \mu_1 \vec{r}_{12} \\ \vec{v}_{3f} &= \vec{v}_{3i} + \Delta \vec{w} + \mu_2 \vec{r}_{34} \\ \vec{v}_{4f} &= \vec{v}_{4i} - \mu_2 \vec{r}_{34} \end{aligned} \quad (25)$$

defining the vectors $\Delta \vec{v}$ and $\Delta \vec{w}$. Substituting into the momentum conservation law, (20), we conclude that $\Delta \vec{w} = -\Delta \vec{v}$.

Now, let us differentiate the constraint condition $\sigma = 0$ with respect to time, obtaining, (see Eq. (2)):

$$\dot{\sigma} = \dot{\vec{r}} \frac{\partial \sigma}{\partial r} = 2\vec{r}_{12} \dot{\vec{r}}_{12} = 2\vec{r}_{12} \vec{v}_{12} = 0. \quad (26)$$

This gives us that the difference between the atomic velocities inside the same molecule must be orthogonal to the distance between the two atoms before and after the collision:

$$\begin{aligned}
 (\vec{v}_{2i} - \vec{v}_{1i}) \cdot \vec{r}_{12} &= 0 \\
 (\vec{v}_{2f} - \vec{v}_{1f}) \cdot \vec{r}_{12} &= 0 \\
 (\vec{v}_{4i} - \vec{v}_{3i}) \cdot \vec{r}_{34} &= 0 \\
 (\vec{v}_{4f} - \vec{v}_{3f}) \cdot \vec{r}_{34} &= 0.
 \end{aligned} \tag{27}$$

From these expressions we get the following solutions for μ_1 and μ_2

$$\begin{aligned}
 \mu_1 &= -\frac{\Delta\vec{v} \cdot \vec{r}_{12}}{2a^2} \\
 \mu_2 &= \frac{\Delta\vec{v} \cdot \vec{r}_{34}}{2a^2}.
 \end{aligned} \tag{28}$$

Let us proceed with the remaining two conservation laws, (21) and (22). We will use the standard approach to get the value of $\Delta\vec{v}$, with a slight modification to take into account the new terms containing μ_1 and μ_2 .

Substituting (25) into the angular momentum conservation law (21) and remembering that the atomic positions do not change during the collision, Eq. (21) can be reduced to

$$(\vec{r}_1 - \vec{r}_3) \times \Delta\vec{v} = 0 \tag{29}$$

meaning that $\Delta\vec{v}$ is parallel to $(\vec{r}_1 - \vec{r}_3)$. Denoting with Δv the magnitude of the $\Delta\vec{v}$, we write:

$$\Delta\vec{v} = \pm \Delta v \frac{(\vec{r}_1 - \vec{r}_3)}{|\vec{r}_1 - \vec{r}_3|} = \pm \Delta v \frac{(\vec{r}_1 - \vec{r}_3)}{d} \tag{30}$$

where we have used the fact that at the moment of collision $|\vec{r}_1 - \vec{r}_3| = d$. Now, substituting (28) in (25); Eq. (25) in the kinetic energy conservation law (22), and using once more Eq. (27), we get:

$$\begin{aligned}
 \Delta v^2 + \frac{1}{4a^2} \{ (+\Delta\vec{v} \cdot \vec{r}_{12})^2 + (\Delta\vec{v} \cdot \vec{r}_{34})^2 \} - \\
 - \frac{1}{2a^2} \{ (\Delta\vec{v} \cdot \vec{r}_{12})^2 + (\Delta\vec{v} \cdot \vec{r}_{34})^2 \} + \Delta\vec{v} \cdot (\vec{v}_{1i} - \vec{v}_{3i}) = 0
 \end{aligned} \tag{31}$$

from which, substituting $\Delta\vec{v}$ from Eq. (30), we obtain:

$$\Delta v = \pm \frac{(\vec{v}_{1i} - \vec{v}_{3i}) \cdot (\vec{r}_1 - \vec{r}_3)}{d \cdot \text{factor}} \quad (32)$$

with

$$\text{factor} = 1 - \frac{[(\vec{r}_1 - \vec{r}_3) \cdot \vec{r}_{12}]^2 + [(\vec{r}_1 - \vec{r}_3) \cdot \vec{r}_{34}]^2}{4a^2d^2}. \quad (33)$$

Summarizing the above developments, Eqs. (25), (28), (32), and (33) can be used to obtain the final velocities of the four hard spheres participating in the collision in terms of their initial velocities.

5. COMPUTER SIMULATION OF A TEST CASE

We simulated liquid nitrogen at 93 K with the density of 781 kg/m^3 , corresponding to the liquid nitrogen sample simulated by Barojas and Levesque near the boiling point,⁽¹²⁾ and a sample at 80 K with the density of 874 kg/m^3 , corresponding to the nitrogen at the triple point. The initial configuration consisted of 256 molecules, and corresponds to the alpha-phase of nitrogen described in ref. 11. Initial molecular translation and rotation velocities were assigned according to equipartition. We took the distance between the centers of the nitrogen atoms equal to 1.0999 \AA , same as in ref. 12, and the atomic diameter equal to 3.341 \AA , equal to the σ of the Lennard Jones potential of ref. 12.

The initial model crystal was relaxed during 0.15 ns. In order to know if our model describes properly a diatomic liquid, we measured velocity autocorrelation functions, separating the components parallel and perpendicular to the molecule. Using these functions, we obtained corresponding diffusion coefficients.

Denoting as $\vec{R}(0)$ the initial molecular positions and $\vec{R}(t)$ the molecular positions at time t , the self-diffusion coefficient D is given by the expression:⁽¹³⁾

$$D = \frac{1}{6t} \langle |\vec{R}(t) - \vec{R}(0)|^2 \rangle \quad (34)$$

where

$$\langle |\vec{R}(t) - \vec{R}(0)|^2 \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T |\vec{R}(t+\tau) - \vec{R}(t)|^2 d\tau \quad (35)$$

is equal to the ensemble average in thermodynamic limit. Using the velocity autocorrelation functions, we can obtain the diffusion coefficient in terms of relaxation time τ_G , using the expression:⁽¹²⁾

$$D = \frac{k_B T_s \tau_G}{m} \quad (36)$$

where k_B is the Boltzmann constant, T_s is the system's temperature and the relaxation time can be calculated as

$$\tau_G = \int_0^\infty F_v dt \quad (37)$$

where F_v is the normalized velocity autocorrelation function,

$$F_v = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \vec{v}(t+\tau) \cdot \vec{v}(t) d\tau. \quad (38)$$

It is possible to use an intrinsic reference frame attached to each molecule to study anisotropic behavior of the time-correlation functions. In this frame the molecular velocity has been separated into parallel and perpendicular components, and the time correlation functions for these components have been computed. These quantities are never equivalent to the time correlation functions in the laboratory frame although one can obtain the exact correspondence $\langle \vec{V}(t) \cdot \vec{V}(0) \rangle = \langle \vec{V}_\parallel(t) \cdot \vec{V}_\parallel(0) \rangle + 2\langle \vec{V}_\perp(t) \cdot \vec{V}_\perp(0) \rangle$.

The molecular velocity autocorrelation functions for the parallel and perpendicular components for the sample with density 781 kg/m^3 and temperature 93 K are presented in Fig. 2, while the total and angular velocity autocorrelation functions are presented in Fig. 3. Our results compare favorably with those obtained by Allen and Imbierski,⁽⁵⁾ for the total molecular velocity, and with those calculated by Ryckaert *et al.*⁽¹⁴⁾ From Figs. 2 and 4 we see that the diffusion coefficients for perpendicular component of molecular velocity for both samples are considerably smaller than those for the parallel component, in good agreement with,⁽¹⁴⁾ where it was observed that the perpendicular component autocorrelation function goes to zero faster, then the parallel one. The calculated value of the diffusion coefficient in the direction parallel to the molecule gives $2.76 \times 10^{-5} \text{ cm}^2/\text{s}$ for the temperature of 93 K and density 781 kg/m^3 , and in the perpendicular direction $2.04 \times 10^{-5} \text{ cm}^2/\text{s}$ (i.e., $D = \frac{1}{3}(D_\parallel + 2D_\perp) = 2.28 \times 10^{-5} \text{ cm}^2/\text{s}$). The corresponding value of the self-diffusion coefficient obtained from the total velocity autocorrelation function using the Lennard-Jones model of Barojas *et al.*,⁽¹²⁾ is $2.5 \times 10^{-5} \text{ cm}^2/\text{s}$ in satisfactory

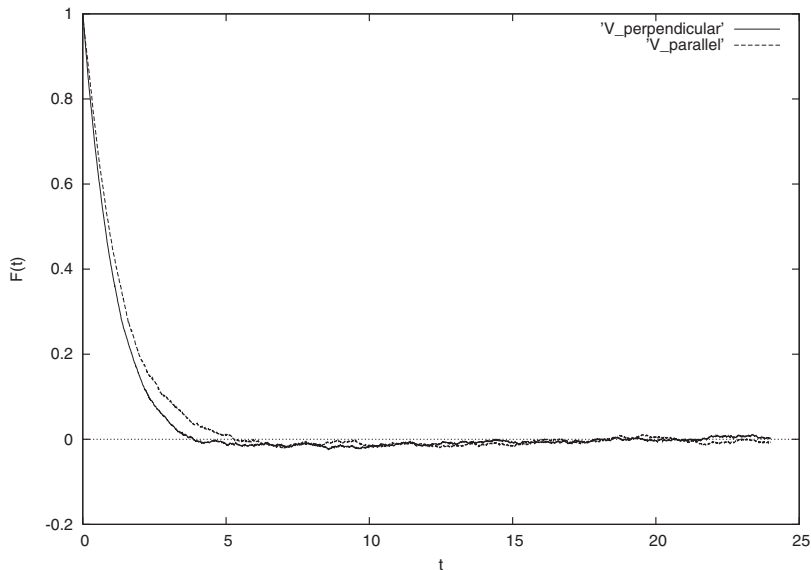


Fig. 2. Molecular velocity autocorrelation function of the parallel component, $\langle \vec{V}_{\parallel}(t) \cdot \vec{V}_{\parallel}(0) \rangle$ and perpendicular component, $\langle \vec{V}_{\perp}(t) \cdot \vec{V}_{\perp}(0) \rangle$. Density 781 kg/m^3 , temperature 93 K and the time unit is 10^{-13} s.

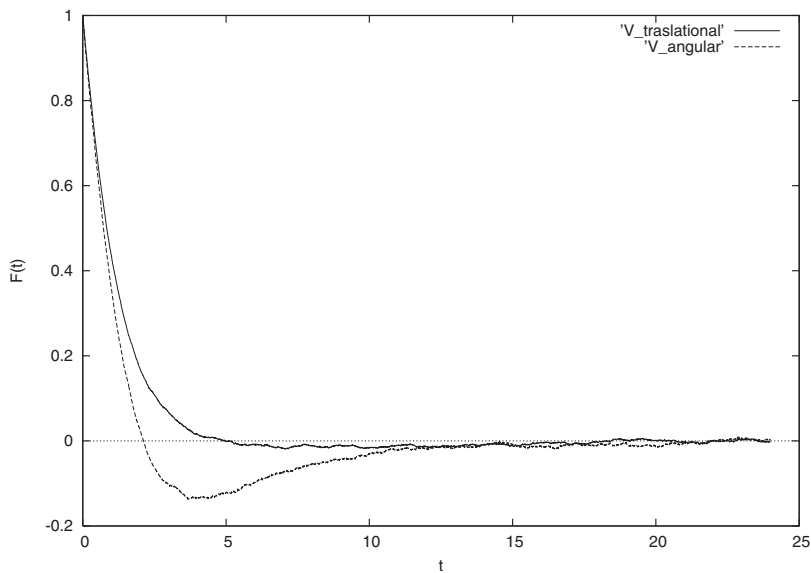


Fig. 3. Translational velocity, $\langle \vec{V}(t) \cdot \vec{V}(0) \rangle$ and angular velocity autocorrelation function, $\langle \vec{\omega}(t) \cdot \vec{\omega}(0) \rangle$. Density 781 kg/m^3 , temperature 93 K and the time unit is 10^{-13} s.

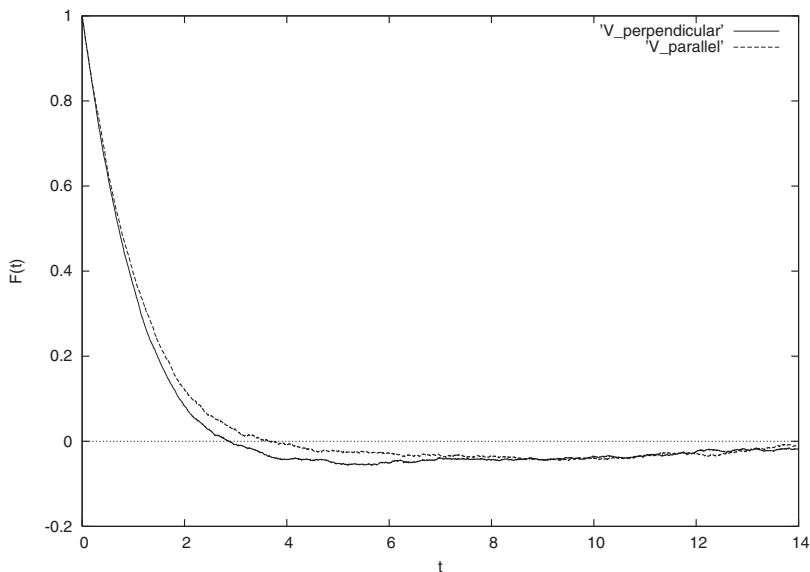


Fig. 4. Molecular velocity autocorrelation function of the parallel component, $\langle \vec{V}_{\parallel}(t) \cdot \vec{V}_{\parallel}(0) \rangle$ and perpendicular component, $\langle \vec{V}_{\perp}(t) \cdot \vec{V}_{\perp}(0) \rangle$. Density 874 kg/m^3 , temperature 80 K and the time unit is 10^{-13} s .

agreement with our result. In Fig. 4 we present the molecular velocity autocorrelation functions for the velocity components parallel and perpendicular to the molecule for the case of the density 874 kg/m^3 and temperature 80 K , which shows the correct trend as a function of density.

6. CONCLUSIONS

We have shown, in the simple case of a dimer of hard spheres, where one can provide an analytic solution, that bond constraints and percussive forces can be combined together in a simple and elegant way. In presence of many bond constraints the solution, conceptually, does not change much: the equations of motion give, instead of a simple harmonic oscillation, a coupled system of oscillators which in principle can be solved through normal modes (so determining the values of Lagrange multipliers in between collisions). The collision is solved in the same way we presented here and the total procedure keeps its feasibility. It can be useful when modeling linear polymers or otherwise, but only using bond constraints.

In principle the situation with general holonomic constraints is not difficult. However, since the solution of the equations of motion for given

λ 's is no longer analytic, one has to solve it in a step by step fashion using an approximate algorithm. As a result the simplicity of the approach is lost and such a model does not seem worth pursuing.

ACKNOWLEDGMENTS

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DEDICATION

The work presented here is, in some sense, a theoretical divertissement which the senior author (GC) is pleased to dedicate to Gianni Jona Lasinio on the occasion of his 70th birthday.

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