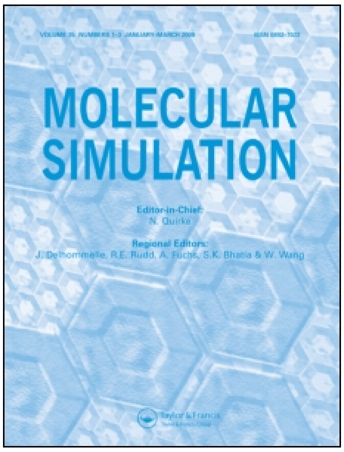

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A MOLECULAR DYNAMICS SIMULATION STUDY OF RIGID AND NON-RIGID HARD DUMB-BELLS

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We present a comparative study, using molecular dynamics, of systems of diatomic, hard dumb-bell, molecules in which the interatomic distance is either constrained to a fixed value or is allowed to vary freely between preset limits. A significant improvement in simulation effciency can be attained by allowing the bond length to vary. We find that thermodynamic properties, and some time correlation functions, are only slightly affected by the removal of the rigid bond-length constraint. The atomic velocity correlation function responds dramatically at short times to changes in the degree of non-rigidity, but at long times these differences are much less important.

KEY WORDS: Dynamics, dumb-bells, hard bodies

1. INTRODUCTION

Since the earliest molecular dynamics simulations of Alder and Wainwright [1, 2], the hard sphere model has been used as a reference system for simple atomic fluids. It is now accepted that the harsh repulsive elements of the atomic pair potential play a leading role in determining liquid structure [3]. Hard non-spherical bodies should be of comparable value in the molecular case, and the hard dumb-bell or fused hard-sphere diatomic molecule is the prototype of a range of interaction-site models. Monte Carlo simulations of this model were conducted many years ago [4], and for recent reviews see [5, 6].

Recently, there has been some effort to conduct molecular dynamics (MD) simulations of these same systems (see reference [7] and references therein). MD is essential if one is interested in dynamical properties, and also, for hard systems, MD is good for calculating structural and thermodynamic properties that characterize molecules in contact. The pressure, for example, is calculated quite straightforwardly via the collisional virial, whereas the calculation of the pressure in conventional constant-volume Monte Carlo simulations is less direct. We return to this point shortly.

In this paper, we describe molecular dynamics simulations of two versions of the hard dumb-bell system: in one, the distance between the atoms is fixed, while in the other it is allowed to vary between two preset limits. We present the first direct comparison of dynamical properties determined by both methods, highlighting those functions for which good agreement between the two is obtained, and also showing where differences appear. Our work is preliminary, in the sense that we only discuss one state point in the liquid region. Nonetheless, some of our conclusions may be expected to hold more generally, and indicate that further work, to investigate systematically the influence of non-rigidity on larger molecules, may be desirable.

This paper is arranged as follows. In section 2 we discuss the implementation of molecular dynamics for rigid and non-rigid hard dumb-bells, and touch on some theoretical points concerning these models. These points are pursued a little further in the appendix. Simulation details are outlined in section 3, results are presented in section 4, and our conclusions follow in section 5.

2. MOLECULAR DYNAMICS: RIGID AND NON-RIGID DUMB-BELLS

The principal difficulty with MD simulation of hard, rigid, dumb-bells is that the free-flight dynamics, although exactly known, generate a highly nonlinear equation for the time of collision between a pair of molecules. The solution of such a nonlinear equation, by a combination of the Newton-Raphson formula and interval bisection, is a standard numerical exercise [8]. Nonetheless, it is far more time-consuming than in the case of hard spheres, for which the equation is simply quadratic in the time. Possible roots of the equation must first be bracketted by advancing through a small time step, and searching for pair overlaps, a method first used by Rebertus and Sando [9] for hard spherocylinders. Recently, hard lines [10], dumb-bells [11, 12], hard ellipsoids [13] and hard spherocylinders [14] have been treated by this or similar methods (see reference [7] for a review). However, the expense of solving the collision equation many times, in an iterative way, in the course of such a simulation is a significant deterrent.

One way around this was suggested by Rapaport [15, 16]: molecules are built up out of atomic hard spheres but the bonds between atoms in a molecule are not rigid. Instead they take the form of narrow square wells, with infinite potential barriers. Thus the bond lengths are not constrained absolutely, but 'rattle' within pre-defined limits. The dynamics is that of atomic free flight between collisions, and so the basic collisional problem is very simple, and cheap to solve. The trade-off however is that as the bond lengths are more closely prescribed, so more computer time is spent on frequent intramolecular collisions, rather than on the more interesting intermolecular ones.

Nonetheless, in a brief report, Bellemans and co-workers [11] compared the two approaches for a two-dimensional system and suggested that the 'rattling bond' method might be cost-effective. They reproduced the equation of state of the rigid dumb-bells quite accurately, and efficently, with suitably-chosen limits on the allowed bond-length variation. More recently, Chapela and co-workers [17] have shown that the liquid-state structural distribution functions of non-rigid hard molecules, simulated in this way, satisfactorily reproduce those of their rigid counterparts, as determined by Monte Carlo.

The intention of the current work is to extend these comparisons to include dynamical properties. The technical details of our rigid dumb-bell simulations can be found elsewhere [7]. The non-rigid simulation programs are fairly standard, and we use the basic methods described by Chapela [17] and Rapaport [15, 16].

Our rigid hard dumb-bell model consists of two hard spheres, of diameter σ (taken as a unit of length), and unit mass m, a fixed distance l apart. The non-rigid model is the same, except that the distance between the atomic centres is allowed to vary freely in the range $[l - \frac{1}{2}\delta l, l + \frac{1}{2}\delta l]$, where δl is a small parameter. It is clear that not all the properties of the non-rigid model converge to those of the rigid model in the limit $\delta l \rightarrow 0$. However, the averages of some configurational quantities may be expected to be well-behaved in this limit, and we present an argument relating to this in the appendix. It is not our intention, however, in this paper, to examine this point with any degree of rigour.

A technical point concerns the evaluation of the pressure in Monte Carlo and molecular dynamics. In conventional MC simulations of hard bodies, molecules never come into contact. To calculate the pressure, one may extrapolate a pair distribution function to contact [4], use a volume-scaling 'fake' Monte Carlo move [20] or, of course, switch to constant-pressure Monte Carlo [21, 22]. Another alternative is to measure the contact density at a hard wall in the system [23, 24]. For systems in which a wall is naturally present, this is a convenient route, and indeed Henderson and van Swol used it as a check for proper equilibration in their simulations of wetting phenomena; however, in general, the inhomogeneity associated with the introduction of however, in general, the inhomogeneity associated with the introduction of a wall is undesirable.

By contrast, in molecular dynamics, pressure evaluation is easy once the basic collisional problem has been solved. Each collision contributes a term proportional to the scalar product of the collisional impulse and the vector joining the centres of the colliding particles. For the non-rigid model, this is a simple atom–atom calculation, exactly analogous to the case of hard spheres or square-well systems: all collisions, including the intramolecular ones, are treated in the same way. For the rigid model, the calculation is best expressed in molecular terms: we calculate the scalar product of the impulse (directed along the atom–atom vector between the colliding molecules) and the vector joining the *molecular* centres . These points are considered further in the appendix.

3. SIMULATION DETAILS

For the case of the rigid dumb-bells, we assume rectilinear motion of the centre of mass of each molecule, and rotation about the centre of mass with constant angular momentum, between collisions. The molecules behave as axially symmetric, linear rotors: end-over-end rotation occurs, with the angular velocity perpendicular to the symmetry axis at all times. When collisions occur, the colliding surfaces are treated as perfectly smooth: the impulse is perpendicular to the contact plane. The collisions are perfectly elastic, and the laws of conservation of energy, linear momentum and angular momentum, determine the post-collisional momenta. The appropriate formulae are given in the appendix. Full details of the method used to locate collision times, and implement the collision dynamics, appear elsewhere [7].

The non-rigid-molecule program used conventional collision-by-collision hard-sphere dynamics [1, 2, 18, 19]. The bond length was allowed to vary in the range $[l - \frac{1}{2}\delta l,\ l + \frac{1}{2}\delta l]$, i.e. at the lower limit an intramolecular hard-sphere repulsive collision (a 'wall' collision) would occur while at the upper limit an intramolecular square-well attractive collision (a 'well' collision) would occur. External, intermolecular collisions at distance σ were handled as usual.

In all cases the system size was $N = 108$ molecules, and cubic periodic boundaries were employed. We used a Verlet-type neighbour list [25] based on the distances between atoms to speed up the programs. We chose unit values of atomic mass m, atomic diameter σ and $k_B T$.

We report results for hard dumb-bells having a distance $l/\sigma = 0.6$ between the

Table 1 Rigid and non-rigid dumb-bell collisions

δl	*collisions*				*cpu time /s*	*speed*
	total	*wall*	*well*	*external*		
0.1	60935	15951	8949	36035	12065	2.99
0.05	85937	28344	21299	36294	15759	2.30
0.02	158796	64596	57708	36492	26829	1.36
0.01	278967	124896	117870	36201	45495	0.80
0	33915	–	–	33915	28923	1.17

spheres, at a molecular density of $N\sigma^3/V = 0.5$. We investigated the non-rigid model for maximum bond-length variations $\delta l = 0.1, 0.05, 0.02, 0.01$.

4. RESULTS

In Table 1 we compare the performance of the programs for the rigid and non-rigid models. For runs of the same length in simulation time, we give the cpu time used (on a VAX 11/750 with floating point accelerator), the total number of collisions, and the breakdown of this quantity into 'external' contributions and the two types of intramolecular collision, 'well' and 'wall'. We compare program speeds in terms of intermolecular collisions per unit cpu time. In Table 2 we also give the various contributions to the pressure arising from these sources. As expected, the intramolecular collisions become dominant as the 'rattling' bond is tightened up, but their contributions to quantities such as the pressure tend to cancel. The computer time spent on these internal collisions makes the simulation program less efficient for $\delta l = 0.01$ than for the rigid molecule case; however, the efficiency is greater for the larger values of δl, and even $\delta l = 0.05$ seems quite a satisfactory value for predicting the pressure. This confirms the conclusions of Chapela *et al.* [17]. Our results indicate that the pressure in the rigid dumb-bell case is slightly higher than would be predicted by extrapolating the non-rigid values to this limit. However, differences are small ($\approx \frac{1}{2}\%$ for $\delta l = 0.01$) and we have not attempted to establish the true form of the asymptotic dependence on δl as $\delta l \to 0$.

Our interest is primarily in the dynamical properties of this system. Molecular rotation is characterized by the single-molecule orientational time correlation functions

$$\begin{aligned} C_1(t) &= \langle P_1(\mathbf{u}_i(0)\cdot\mathbf{u}_i(t))\rangle \\ C_2(t) &= \langle P_2(\mathbf{u}_i(0)\cdot\mathbf{u}_i(t))\rangle \end{aligned} \qquad (1)$$

Table 2 Rigid and non-rigid dumb-bell pressures

δl	*PV/Nk* PV/Nk_BT *contributions*				
	total	*wall*	*well*	*external*	*ideal*
0.1	12.67	2.40	−1.59	9.87	2.0
0.05	12.77	4.50	−3.67	9.94	2.0
0.02	12.79	10.43	−9.63	9.99	2.0
0.01	12.79	20.18	−19.35	9.96	2.0
0	12.86	–	–	11.86	1.0

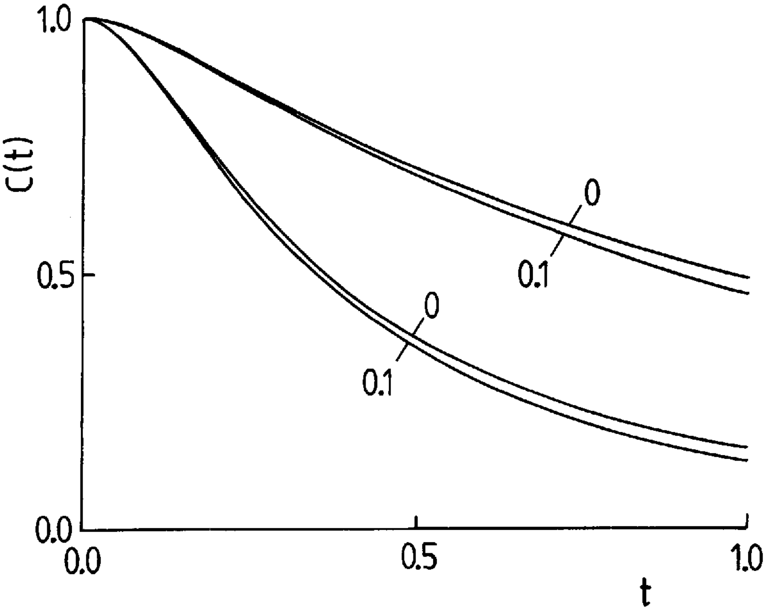

Figure 1 Orientational time correlation functions $C_1(t)$ (upper curves) and $C_2(t)$ (lower curves) for the rigid (δl = 0) and non-rigid (δl = 0.1) hard dumb-bells.

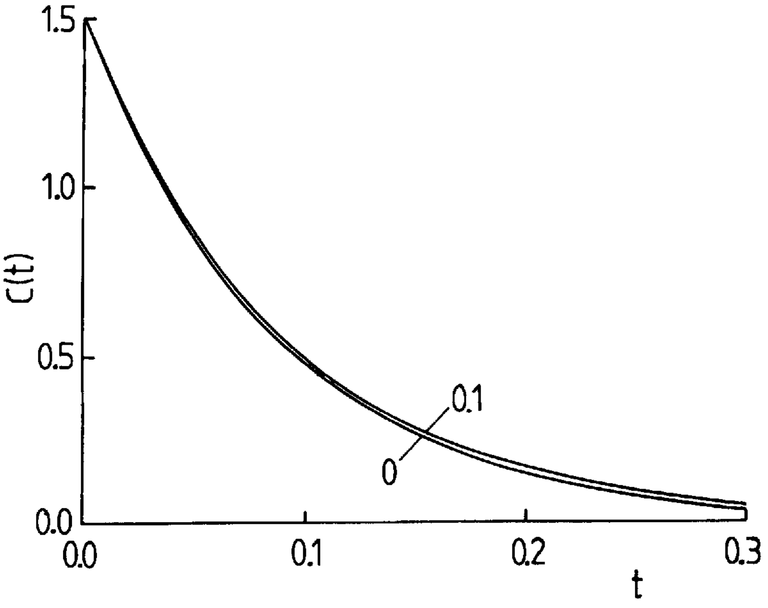

Figure 2 Centre-of mass velocity autocorrelation functions for rigid (δl = 0) and non-rigid (δl = 0.1) hard dumb-bells.

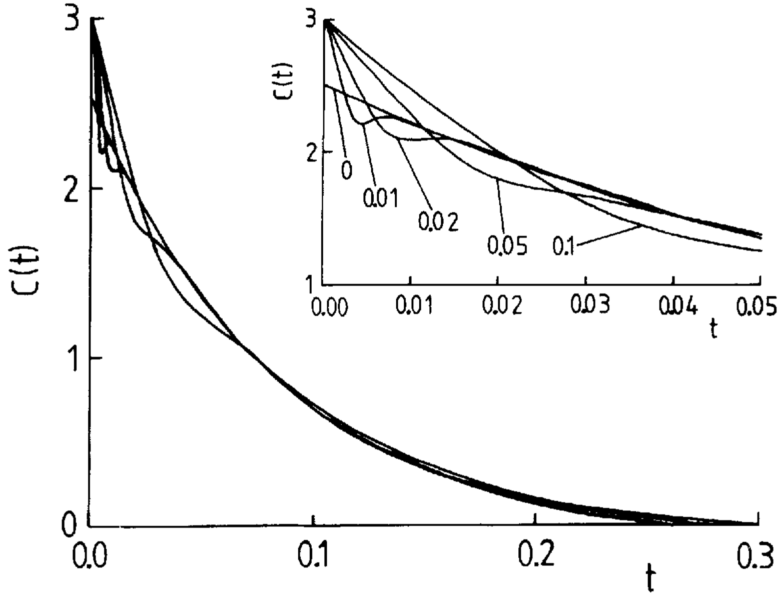

Figure 3 Atomic velocity autocorrelation functions for rigid ($\delta l = 0$) and non-rigid ($\delta l = 0.01, 0.02, 0.05, 0.1$) hard dumb-bells. The inset shows the short-time behaviour.

where P_1 and P_2 are first and second rank Legendre polynomials, and $\mathbf{u}_i$ is the orientation unit vector of molecule i. In Figure 1 we show $C_1(t)$ and $C_2(t)$ for the rigid model and for the least rigid approximation ($\delta l = 0.1$). In Figure 2 we show the centre-of-mass velocity autocorrelation function for these same cases. These figures show that overall molecular rotation and translation are quite insensitive to the degree of flexibility. However, it is possible to pick out functions that show directly the effect of relaxing the rigid bond constraint. In Figure 3 we show the atomic velocity autocorrelation functions for the rigid model and the various non-rigid approximations. We have left these functions un-normalized: with our chosen scale (unit temperature and atomic mass) the initial value $\langle v^2 \rangle$ for atoms in the non-rigid model is equal to 3 while that in the rigid model is 2.5, corresponding to one fewer degree of freedom per molecule. Nonetheless, the curves for the non-rigid case rapidly approach that for the rigid dumb-bell, in a decaying oscillatory fashion, with the period of oscillation decreasing as the parameter δl decreases. Thus, the internal degree of freedom equilibrates more-or-less rapidly, leaving the atomic correlations at long times unaffected. It should be possible to choose other dynamical quantities which are sensitive to the state of the internal bond: the rate of energy transfer to and from the surrounding liquid, for example, will presumably reflect this.

5. CONCLUSIONS

Our results confirm that the non-rigid version of the hard dumb-bell model can be used in molecular dynamics simulations, with advantages of program efficiency over the rigid model, while giving reasonable agreement with thermodynamic and some dynamical properties. It is possible to pick certain time correlation functions, for example the atomic velocity autocorrelation function, for which there are obvious differences at short times. Nonetheless, in this study, the long-time behaviour even of this function, for rigid molecules, seems to be well-represented by the non-rigid counterparts.

It would be dangerous to draw far-reaching conclusions from this study, at a single state point. Clearly, it is desirable to extend this preliminary work and investigate the dependence of the diffusion coeffcient on the degree of non-rigidity. Also, it is still of interest to examine closely the $\delta l \rightarrow 0$ limit. Even if further investigations show that serious discrepancies exist between the properties of rigid and non-rigid models, we should emphasize that the non-rigid model is worthy of study in its own right. The systematic investigation of the quantitative effects of molecular flexibility on dense fluid properties, particularly for elongated molecules, is of great interest. Simulation using models of this kind [15, 16, 24] seems to be a suitable approach to this problem.

Acknowledgements

The simulations described here were carried out on the Bristol University Physics Department VAX 11/750: we are grateful to those who support this machine.

APPENDIX

In this appendix we address some technical and theoretical points relating to rigid and non-rigid dumb-bell simulations.

A question arises as to whether or not the static statistical-mechanical properties of the non-rigid model may be expected to converge to those of the rigid one, in the limit $\delta l \rightarrow 0$. In general, as is well-known [26, 27], the introduction of constraints will have a non-trivial effect on the distribution functions of the unconstrained variables. In the particular case of dumb-bells, however, we believe that there should be no effect. Consider the analogous situation in which harmonic spring potentials between the atoms are replaced by rigid bond constraints. Then, ensemble averages for the two models may be related by incorporating into the configurational integral a term involving the determinant $|\mathbf{H}|$ of a matrix $\mathbf{H}$ as discussed by Fixman and Helfand [26, 27]

$$H_{kk'} = \sum_i \sum_\alpha m_i \frac{\partial q_k^c}{\partial r_{i\alpha}} \frac{\partial q_{k'}^c}{\partial r_{i\alpha}}. \tag{2}$$

Here i labels a particular atom whose Cartesian coordinates are $\mathbf{r}_i$; α ranges over components x, y, z. The idea is to transform to a set of generalized coordinates $\{q_k\}$, a subset of which, $\{q_k^c\}$ are constrained in the rigid model, but vary under the influence of harmonic spring potentials in the non-rigid case. Here, for a system of N diatomic molecules, there are $6N$ coordinates, of which N correspond to the intramolecular bonds. They are all of the form

$$q_k^c = |\mathbf{r}_{2k} - \mathbf{r}_{2k-1}|^2 \tag{3}$$

and are fixed at the value l^2 in the rigid model. Since each atom is only associated with one constraint, $H_{kk'} = 0$ unless $k = k'$, and the determinant is trivially evaluated to give a constant. Consequently, the statistical properties are unaffected. In our case, of

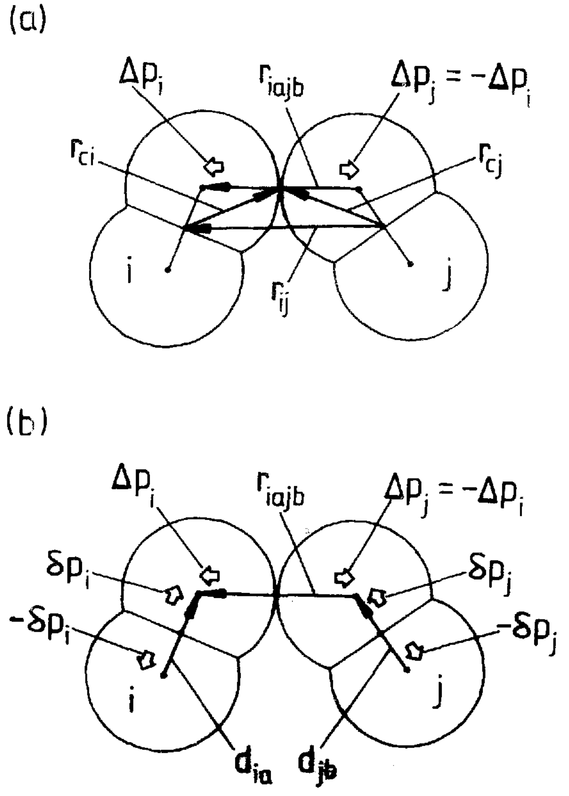

Figure 4 Collision geometry for rigid hard dumb-bells (a) For discussion of 'molecular' calculation of pressure. (b) For discussion of 'atomic' calculation of pressure.

course, we have narrow square-well potentials in the non-rigid model, rather than harmonic springs, and this difference may be important for some properties. This feature is highlighted, for example, by the divergent, but cancelling, contributions of the intramolecular 'wall' and 'well' collisions to the pressure. We make no attempt to pursue this point here: it seems reasonable to assume that, for properties reflecting intermolecular rather than intramolecular correlations, an argument similar to the one above will hold, and the two models should be identical in the limit $\delta l \to 0$.

A second question concerns the way in which we solve the collision equations, and evaluate the pressure, for the rigid dumb-bell system. Let us assume that the simulation program has determined that molecules i and j, with centre-of-mass velocities v_i, v_j and angular velocities ω_i, ω_j, collide at time t_{ij}. The system is advanced up to the moment of contact; the collision geometry is shown schematically in Figure 4. Let the centres of the molecules be at positions $\mathbf{r}_i$ and $\mathbf{r}_j$ respectively. Suppose that the colliding atoms are labelled a, on molecule i, at position $\mathbf{v}_{ia}$ and b, on molecule j, at position $\mathbf{r}_{jb}$. Let the vectors $\mathbf{d}_{ia}$ and $\mathbf{d}_{jb}$ point to these atoms from the other atom on the same molecule (see Figure 4). The linear momenta $\mathbf{p}_i$, $\mathbf{p}_j$ ($\mathbf{p} = M\mathbf{v}$ where M is the molecular mass) and angular momenta $\mathbf{J}_i$, $\mathbf{J}_j$ ($\mathbf{J} = I\omega$ where I is the moment of inertia) now change discontinuously. Denoting post-collisional values with primes, we can write these changes in terms of the collision impulse $\Delta\mathbf{p}_i$:

$$\begin{aligned}\mathbf{p}'_i &= \mathbf{p}_i + \Delta\mathbf{p}_i\\ \mathbf{p}'_j &= \mathbf{p}_j - \Delta\mathbf{p}_i\\ \mathbf{J}'_i &= \mathbf{J}_i + \mathbf{r}_{ci} \times \Delta\mathbf{p}_i\\ \mathbf{J}'_j &= \mathbf{J}_j - \mathbf{r}_{cj} \times \Delta\mathbf{p}_i.\end{aligned}$$

$\mathbf{r}_{ci} = \mathbf{r}_c - \mathbf{r}_i$ (e.g.) is the position of the point of impact measured relative to the centre of molecule i (i.e. midway between the atoms in this case). This equation guarantees conservation of linear and angular momentum. Applying conservation of energy leads to

$$\frac{\Delta p_i^2}{M} + \mathbf{g}_{ij}\cdot\Delta\mathbf{p}_i + \frac{1}{2I}\left(|\mathbf{r}_{ci} \times \Delta\mathbf{p}_i|^2 + |\mathbf{r}_{cj} \times \Delta\mathbf{p}_i|^2\right) = 0 \tag{5}$$

where

$$\mathbf{g}_{ij} = \mathbf{v}_{ij} + \boldsymbol{\omega}_i \times \mathbf{r}_{ci} - \boldsymbol{\omega}_j \times \mathbf{r}_{ci} \tag{6}$$

is the relative velocity of the two impacting points. Finally, since the impulse is normal to the surface (the smoothness condition), $\Delta\mathbf{p}_i = \mathbf{n}\Delta\mathbf{p}_i$, so

$$\Delta\mathbf{p}_i = \frac{-\mathbf{g}_{ij}\cdot\mathbf{n}}{(1/M) + (|\mathbf{r}_{ci} \times \mathbf{n}|^2 + |\mathbf{r}_{cj} \times \mathbf{n}|^2)/2I}. \tag{7}$$

For hard dumb-bells, the surface normal is just

$$\mathbf{n} = \mathbf{r}_{iajb}/\sigma \tag{8}$$

where $\mathbf{r}_{iajb} = \mathbf{r}_{ia} - \mathbf{r}_{jb}$ is the vector between the atoms in contact. Note that, as usual in molecular systems, the impulse is not necessarily directed along the line joining the *molecular* centres, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$.

The usual virial expression for the pressure gives

$$PV = (PV)^{\mathrm{kin}} + (PV)^{\mathrm{col}} = Nk_BT + \frac{1}{t}\sum_{\langle ij\rangle}\frac{1}{3}\mathbf{r}_{ij}\cdot\Delta\mathbf{p}_i \tag{9}$$

where the sum is over all pair collisions occurring in the time t. This is the expression used in our rigid dumb-bell simulations. It is instructive to reformulate these equations purely in 'atomic' terms. The ideal gas or kinetic contribution to PV is

$$(PV)^{\mathrm{kin}} = \left\langle\frac{1}{3}\sum_i\sum_a mv_{ia}^2\right\rangle = \frac{5}{3}Nk_BT \tag{10}$$

where we sum over the two atoms for each of the N molecules. $m = M/2$ is the atomic mass. The right-hand side follows by equipartition, since there are 5 degrees of freedom (one bond constraint) per molecule. Equivalently,

$$\langle mv_{ia}^2\rangle = 2.5k_BT \tag{11}$$

This kinetic contribution is partly cancelled by a term $-\frac{2}{3}Nk_BT$ arising from the virial contribution of *intra*molecular forces during free flight. To see this, note that the force between the two atoms a and b of a given molecule i is

$$\mathbf{f}_{iaib} = -\frac{1}{2} m\omega_i^2 \mathbf{d}_{ia}. \tag{12}$$

Thus the contribution to the virial is

$$\begin{aligned}(PV)^{\mathrm{intra}} &= \left\langle \sum_i \frac{1}{3} \mathbf{d}_{ia} \cdot \mathbf{f}_{iaib} \right\rangle = -\frac{1}{6} \left\langle \sum_i m\omega_i^2 l^2 \right\rangle \\ &= -\frac{1}{3} \left\langle \sum_i I\omega_i^2 \right\rangle = -\frac{2}{3} Nk_BT. \end{aligned} \tag{13}$$

Again, the right-hand side follows by equipartition, there being two degrees of rotational freedom per molecule. This term is conveniently combined with the kinetic term, to give Nk_BT as before. The collisional impulse contributions are also equivalent to those in the case of the molecular formulation. Consider the collision geometry of Figure 4b. This time, on collision, there are three impulses all acting along the lines joining the atomic centres. The intermolecular impulse $\Delta\mathbf{p}_i = -\Delta\mathbf{p}_j$ has been discussed above. Equations for the intramolecular impulses $\delta\mathbf{p}_i$, $\delta\mathbf{p}_j$ may be obtained by requiring that the bond length remain constant:

$$\begin{aligned} \mathbf{d}_{ia} \cdot (2\delta\mathbf{p}_i + \Delta\mathbf{p}_i) &= 0 \\ \mathbf{d}_{jb} \cdot (2\delta\mathbf{p}_j + \Delta\mathbf{p}_j) &= 0 \end{aligned} \tag{14}$$

From this, the collisional contribution to the virial follows:

$$(PV)^{\mathrm{coll}} = \frac{1}{3} (\mathbf{r}_{iajb} \cdot \Delta\mathbf{p}_i + \mathbf{d}_{ia} \cdot \delta\mathbf{p}_i + \mathbf{d}_{jb} \cdot \delta\mathbf{p}_j) = \frac{1}{3} \mathbf{r}_{ij} \cdot \Delta\mathbf{p}_i \tag{15}$$

as before, with $\mathbf{r}_{ij} = \mathbf{r}_{iajb} - \frac{1}{2}\mathbf{d}_{ia} + \frac{1}{2}\mathbf{d}_{jb}$ measured between the molecular centres.

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