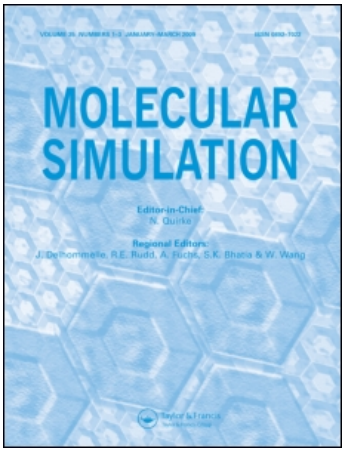

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THE FORCE OF CONSTRAINT IN PREDICTOR-CORRECTOR ALGORITHMS FOR SHAKE CONSTRAINT DYNAMICS

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A lack of clarity in the definition of the force of constraint in a previously reported implementation of SHAKE within a Gear predictor-corrector algorithm (W. F. van Gunsteren and H. J. C. Berendsen, 1977, *Mol. Phys.*, **34**, 1311) is pointed out and a more thorough description given. The new formulation is verified by comparison with an analytical calculations and by reference to an implementation of SHAKE within the leapfrog form of the Verlet algorithm. The modification has no direct effect on the propagation of the trajectories but enables a correct determination of the force of constraint which is often required in free energy and pressure calculations.

Keywords: SHAKE; constraint force; predictor-corrector algorithms

1. INTRODUCTION

Some time ago now van Gunsteren and Berendsen [1] introduced an algorithm, henceforward referred to as vGB, which incorporated the routine SHAKE [2] for maintaining rigid holonomic constraints in a molecular dynamics (MD) simulation within the framework of a Gear predictor-corrector algorithm [3]. The aims of this short note are to point out a lack of clarity in the calculation of the force of constraint in this algorithm and to provide a more precise formulation. It should be emphasised immediately that none of this has any direct effect on the particle trajectories. The point that is made clear here is that *both* applications of SHAKE at each time

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step in the vGB algorithm contribute to the forces of constraint. Explicit calculations of the forces of constraint are not always required for the propagation of the trajectory but are required, for instance, for free energy calculations [4, 5] and in the determination of the pressure tensor within the atomic framework [6]. The latter is particularly important if the pressure enters the equation of motion, e.g. in the NPT and NPH ensembles.

In the following section some clarifying remarks are first made concerning the vGB algorithm as originally presented. In section 3a freely rotating rigid dumbell model is used to demonstrate the problem with the vGB algorithm and in section 4a modified calculation of the force of constraint is outlined. Finally the problem is illustrated by reference to a rigid dumbell model rotating in the presence of a potential field.

2. NOTES ON THE ORIGINAL vGB ALGORITHM

Extensive details of the vGB algorithm were given in the original paper [1] and will not be reproduced here. The vGB algorithm is based on the force or *F-representation* of the Gear predictor-corrector algorithm in which present positions and velocities and present and past forces are used to propagate the trajectory. In the original notation of a k-value predictor-corrector algorithm in the *F-representation*, the vector $\boldsymbol{y}_n(F) \equiv \{y_n, hy'_n, h^2y''_n/2, h^2y''_{n-1}/2, \ldots, h^2y''_{n-k+3}/2\}^T$, where the prime denotes a derivative with respect to time and h is the time step, is used to specify the system after n discrete integration steps. The vGB algorithm is referred to as being that described [1] by the six steps *plus* the two modification. (a) and (b), included to maintain stability. Given in the Appendix is a brief description of the vGB algorithm, as it has been interpreted here, taking into account the following clarifying remarks:-

(i) Eqs. 3.4, 3.5 and 3.7 are dimensionally incorrect; the forces appearing must be divided by the mass of the particle.

(ii) In Eq.3.11b $h'y_{n+1}$ must be hy'_{n+1}.

(iii) At step (6) the literal interpretation of "The final step consists of using f_{tot} in the corrector, Eq. (3.4)." implies applying the corrector to the positions themselves which would reset the $y_{n+1,\,(\text{tot})}$ determined at Step 4 (Eq. 3.6). We assume that the corrector is not applied to positions as this would destroy the constraints. Instead the positions resulting from the application of SHAKE at Step 4 are those which are used at the next step.

3. PROBLEM WITH THE ORIGINAL vGB ALGORITHM

To best illustrate the problem with the original vGB algorithm consider the case of a simple dumbell in two dimensions. We have two point masses, each of mass m, maintained at a fixed distance apart, d, by a rigid bond. Consider now that there are no external forces so only the forces of constraint are acting, i.e. f_{free} is identically zero in Eq. A3. If the dumbell is at rest lying along the y-axis up until a time $t = nh$ at which point one mass is given a velocity in the positive x direction and the other mass given an equal but opposite impulse the system is specified as $\boldsymbol{y}_0 = \{y_0, hy'_0, 0, 0, \ldots, 0\}^T$.

Following the scheme set out in the appendix we first obtain from the predictor step

$$y_{n+1,(p)} = B_{00}\, y_n + B_{01}\, y'_n h = y_n + y'_n h \tag{1}$$

and

$$y'_{n+1,(p)} = B_{11}\, y'_n = y'_n \tag{2}$$

with all higher terms being identically zero on account of the initial conditions. We also obtain

$$Y = (B_{10} - B_{11}\, B_{00})\, y_n = -y_n \tag{3}$$

Note that equations 1–3 follow since for all k the coefficients B_{00}, B_{01} and B_{11} are all equal to 1 (see Appendix 2 of [1]). From Eq. A5 the corrected positions in the absence of any forces become, in this specific case,

$$y_2 = y_{n+1,(p)} \tag{4}$$

Step III then is equivalent to SHAKE $(y_n, y_{n+1,(p)}, y_3)$ and as we have no "free" forces

$$y_{n+1,(\text{free})} = y_3 \tag{5}$$

So as the positions y_3 satisfy the constraints the second application of SHAKE at step V has no effect and simply returns

$$y_{n+1,(\text{tot})} = y_3 \tag{6}$$

Thus from Eq. A9 (Eq. 3.7 of [1]) the "force of constraint" comes out to be zero which clearly cannot be correct. It is at this point where it is not clear in the original paper whether Eq. 3.7 is the only calculation of the force of constraint that is required when the original vGB modification (a) is applied. This is not so surprising since, as stated above, the force of constraint is not directly required for the propagation of trajectories.

4. CORRECT CONSTRAINT FORCE CALCULATION IN THE vGB ALGORITHM

It can easily be shown that in the absence of forces from continuous potentials the algorithm actually reduces to the leapfrog form of the Verlet algorithm. Continuing the procedure set out in the appendix for the case given in the last section, the positions are updated according to A10

$$y_{n+1} = y_{n+1,(\text{tot})} = y_{n+1,(\text{free})} = y_3 \tag{7}$$

the velocities as Eq. A11 become

$$y'_{n+1} = \{B_{11}\, y_{n+1} + Y\}/h = \{y_{n+1} - y_n\}/h \tag{8}$$

and all higher terms remain identically zero as both $y''_{n+1,(p)}$ and $f_{\text{tot}}(y_{n+1,(p)})$ are zero. Clearly in the $f_{\text{free}} = 0$ case the trajectory followed is the same as that of the leapfrog algorithm and as such the true force of constraint should be obtained after step III from the equation

$$f_{c_1} = (y_3 - y_2)\, m/h^2; \tag{9}$$

the corresponding form of Eq. A9 for the lower order leapfrog algorithm.

In general, when $f_{\text{free}} \neq 0$ the application of SHAKE at step V does produce a non-zero f_{constr} but it is *not the total force of constraint.* One must add the f_{constr} at Eq. A9 (Eq. 3.7 of [1]) to that given above, f_{c_1} Eq. 9, in order to get the total force of constraint.

$$f_{c_{\text{tot}}} = f_{c_1} + f_{\text{constr}}. \tag{10}$$

It must be emphasised though that, as stated already, one must continue to use the algorithm as given in the appendix to propagate the trajectories.

Eqs. 9 and 10 are ancillary and simply return the true constraint force to be used in, say, the pressure calculation.

A rigorous justification of the new procedure is not offered here as this would require first a justification of the modifications (a) and (b) given in the original paper [1] and this was not done. It is clear though, that the first application of SHAKE at step III ultimately has some effect on the eventual position at time $t = (n+1)h$ and so must contribute something to the overall force. In the next section it is demonstrated that the new procedure agrees with results from the leapfrog algorithm and with analytical results in the case where $f_{\text{free}} \neq 0$.

5. CASE STUDY: RIGID DUMBELL IN AN EXTERNAL FIELD

The model chosen for the case study is once again the dumbell in two dimensions with the exception that an external field, given by

$$\Phi(\theta) = \frac{k_\theta}{2}\theta^2 \tag{11}$$

where the angle θ is that which the dumbell makes with the y-axis (See Fig. 1), is applied. In terms of the angular coordinate it is straightforward to show that the Lagrangian for the system is just

$$L = \frac{m d^2 \dot{\theta}^2}{4} - \frac{k_\theta}{2}\theta^2 \tag{12}$$

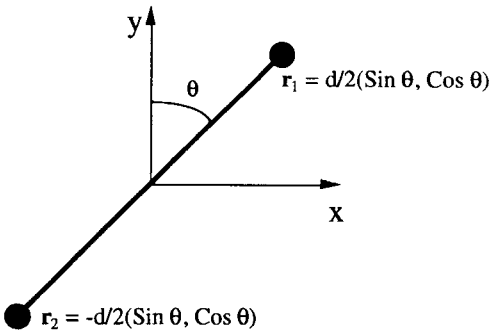

FIGURE 1 A schematic diagram of the model dumbell system in two dimensions.

and thus the equation of motion is

$$\frac{m\,d^2\ddot{\theta}}{2} = -k_\theta \theta \tag{13}$$

Given the initial condition, $\theta(0) = 0$ and $\dot{\theta}(0) = \dot{\theta}_0$, the analytic solution of this problem is

$$\theta(t) = \dot{\theta}_0 \frac{1}{\omega} \mathrm{Sin}(\omega t) \tag{14}$$

with

$$\omega^2 = \frac{2k_\theta}{md^2}.$$

Alternatively the equations of motion can be written in Cartesian coordinates

$$m\ddot{\mathbf{r}}_1 = \mathbf{f}_1 + \mathbf{g}_1 = \mathbf{f}_1 + \lambda \mathbf{r}_{12} = -m\ddot{\mathbf{r}}_2 \tag{15}$$

where $\mathbf{f}_1$ is the force on the first particle due to the continuous potential and $\mathbf{g}_1$ is the as yet undetermined force of constraint directed along the bond vector. The force from the continuous potential is given by

$$\mathbf{f}_1 = \frac{-\partial\Phi(\theta)}{\partial \mathbf{r}_1} = \frac{-\partial\Phi(\theta)}{\partial\theta} \frac{\partial\theta}{\partial \mathrm{Cos}(\theta)} \frac{\partial \mathrm{Cos}(\theta)}{\partial \mathbf{r}_1}$$

$$= \frac{k_\theta \theta}{\mathrm{Sin}(\theta)} \frac{1}{|\mathbf{r}_{12}|} (\hat{\mathbf{y}} - \mathrm{Cos}(\theta)\hat{\mathbf{r}}_{12}) \tag{16}$$

which we note is always perpendicular to the bond vector as $\mathrm{Cos}(\theta) = \hat{\mathbf{y}} \cdot \hat{\mathbf{r}}_{12}$.

The above Cartesian equations of motion have been integrated using both the vGB algorithm and the leapfrog algorithm, both incorporating SHAKE, with a reduced time step $h\omega \approx 0.03$ for the case where $\dot{\theta}_0 \approx 0.09\omega$. The variation in the angle θ with time is shown in Figure 2 from both algorithms and the analytic solution (Eq. 14). No differences are detectable on the scale shown. In Figure 3 the values of the undetermined multiplier λ are shown as a function of time. In this case the value determined from the interpretation of the original vGB algorithm and the modified version are

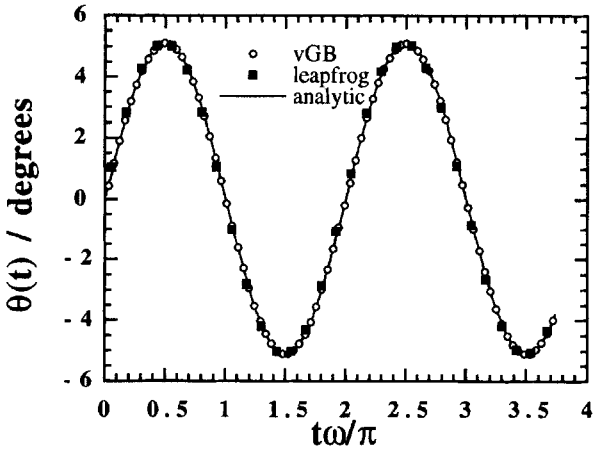

FIGURE 2 The variation of the angle θ between the axis of the dumbell and the y-axis as a function of time for both integration algorithms compared to the analytic result (Eq. 14).

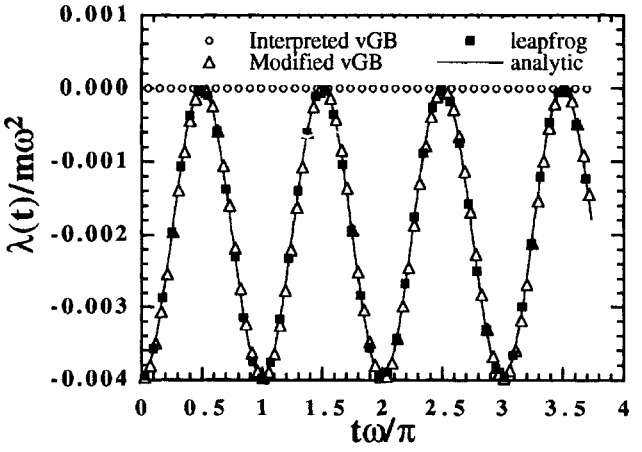

FIGURE 3 The variation of the multiplier λ, determining the magnitude of the force of constraint, as a function of time for both algorithms compared to the analytic result. The interpretation of the original vGB definition (Eq. A9) is clearly incorrect whereas the modified definition (Eq. 10) is in agreement with both the leapfrog and analytic result.

compared to that obtained from the leapfrog algorithm and the analytic result. The latter can be found by determining the contribution to the acceleration of particle 1 which is directed along the bond vector, i.e. $\ddot{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_{12}$. Substituting the analytic solution for $\theta(t)$ (Eq. 14) into the expression for $\mathbf{r}_1 = d/2\{\mathrm{Sin}(\theta), \mathrm{Cos}(\theta)\}$, differentiating twice and taking the dot product

with the unit bond vector gives a first expression for this quantity as

$$\ddot{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_{12} = -\frac{d\dot{\theta}^2}{2} \tag{17}$$

However, from Eq. 15 a second can be derived as

$$m\ddot{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_{12} = \mathbf{f}_1 \cdot \hat{\mathbf{r}}_{12} + \lambda \mathbf{r}_{12} \cdot \hat{\mathbf{r}}_{12} = \lambda d \tag{18}$$

Given the form of $\mathbf{f}_1$ in this case (Eq. 16) it follows immediately that

$$\lambda = -\frac{m\dot{\theta}^2}{2} \tag{19}$$

From Figure 3 it can be seen that the values of λ determined from the modified vGB and leapfrog algorithm are in agreement with the analytical result Eq. 19. In contrast the interpretation of the original vGB algorithm gives a completely incorrect value as expected.

6. CONCLUSION

The original vGB algorithm does not make clear the calculation of the force of constraint and this problem is rectified here. It has been demonstrated that the modified procedure gives answers consistent with a different algorithm and an analytic solution for a rigid dumbell rotating in a potential field. No judgement is passed on the relative merits of the vGB algorithm as compared to the leapfrog, or any other, algorithm for integrating the dynamics of systems containing rigid constraints. However, it should be noted that at each step vGB makes two calls to SHAKE whereas leapfrog only makes one which obviously affects efficiency. On the other hand the incorporation into a predictor-corrector format may have some advantages in that the method lends itself more easily to the integration of more complicated equations of motion.

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APPENDIX: THE ORIGINAL vGB ALGORITHM

The vGB algorithm, as it has been implemented here, proceeds as follows:-

I. (vGB step 1) Predict values at next time step

$$\mathbf{y}_{n+1,(p)} = \mathbf{B}\mathbf{y}_n \tag{A1}$$

where the predictor matrix **B** is as given in [1] and depends on the value of k chosen. At the same time it is useful to store some values required for the velocity modification (vGB step (b), see Eq. 3.10 of [1])

$$Y = \sum_{\substack{i=0 \\ i \neq 1}}^{k-1} (B_{1i} - B_{11} B_{0i}) y_{n,i} \tag{A2}$$

NB. Normally at this point the forces would be calculated from the predicted positions, $y_{n+1,(p)}$. However, as explained before at step 2 of [1]), for constraint dynamics only that part of the force from the continuous potentials can be determined at this point, $f_{\text{free}}(y_{n+1,(p)})$. The total force, f_{tot}, is actually the sum of this term and the as yet unknown force of constraint

$$f_{\text{tot}} = f_{\text{free}} + f_{\text{constr}} \tag{A3}$$

If we knew the total force the algorithm would then procede to the corrector step

$$\mathbf{y}_{n+1} = \mathbf{y}_{n+1,(p)} + \mathbf{b}\frac{1}{2}h^2 (f_{\text{tot}}(y_{n+1,(p)})/m - y''_{n+1,(p)}) \tag{A4}$$

where $\mathbf{b} = (b_0, b_1, b_2, \ldots\ldots, b_{k-1})$ is the vector of corrector coefficients (see Appendix 2 of [1]). As this is not possible the vGB algorithm continues with the following step.

II. (vGB modification (a)) Obtain the corrected positions in the absence of any forces (Eq. 3.8 of [1])

$$y_2 = y_{n+1,(p)} - b_0 \frac{1}{2} h^2 y''_{n+1,(p)} \tag{A5}$$

III. (vGB modification (a)) SHAKE the position y_2 determined at step II using the positions y_n as reference (Eq. 3.9 of [1])

$$\text{SHAKE}(y_n, y_2, y_3) \tag{A6}$$

IV. Obtain the positions corrected for the "free" forces

$$y_{n+1,(\text{free})} = y_3 + b_0 \frac{1}{2} h^2 f_{\text{free}}(y_{n+1,(p)})/m \tag{A7}$$

V. SHAKE the positions $y_{n+1,(\text{free})}$ determined at step IV using the positions $y_{n+1,(p)}$ as reference (Eq. 3.6 of [1])

$$\text{SHAKE}\ (y_{n+1,(p)}, y_{n+1,(\text{free})}, y_{n+1,(\text{tot})}) \tag{A8}$$

VI. Obtain the force of constraint (Eq. 3.7 of [1])

$$f_{\text{constr}} = (y_{n+1,(\text{tot})} - y_{n+1,(\text{free})})\, m \Big/ \left(b_0 \frac{1}{2} h^2 \right) \tag{A9}$$

VII. After obtaining the total force from Eq. A3 the corrector is applied (Eq. A4) *but* not for the positions, which are kept as those resulting from the application of SHAKE at step V.

$$y_{n+1} = y_{n+1,(\text{tot})} \tag{A10}$$

(see note (iii) in Section 2) and the velocities which are updated according to modification (b) of [1]

$$y'_{n+1} = \{B_{11} y_{n+1} + Y + (b_1 - B_{11} b_0) \frac{1}{2} h^2 (f_{\text{tot}}(y_{n+1,(p)})/m - y''_{n+1,(p)})\}/h \tag{A11}$$

where Y is the term stored as step I.

References

[1] van Gunsteren, W. F. and Berendsen, H. J. C. (1977). "Algorithms for macromolecular dynamics and constraint dynamics", *Mol. Phys.*, **34**, 1311–1327.

[2] Ryckaert, J.-P., Ciccotti, G. and Berendsen, H. J. C. (1977). "Numerical integration of the cartesian equations of motion of a system with constraints: molecular dynamics of liquid alkanes", *J. Comput. Phys.*, **23**, 327–41.

[3] Gear, C. W. (1971). *Numerical initial value problems in ordinary differential equations*, Prentice-Hall, Englewood Cliffs, NJ.

[4] Straatsma, T. P., Zacharias, M. and McCammon, J. A. (1992). "Holonomic constraint contributions to free energy differences from thermodynamic integration molecular dynamics simulations", *Chem. Phys. Letts.*, **196**, 297–302.

[5] Mülders, T., Krüger, P., Swegat, W. and Schlitter, J. (1996). "Free energy as the potential of mean constraint force", *J. Chem. Phys.*, **104**, 4869–4870.

[6] Brown, D. and Neyertz, S. (1995). "A general pressure tensor calculation for molecular dynamics simulations", *Mol. Phys.*, **84**, 577–595.