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Short Note

Correcting mesh-based force calculations to conserve both energy and momentum in molecular dynamics simulations

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The high cost of evaluating forces in molecular dynamics makes it necessary to use approximations. The most effective approximations for nonbonded 2-body interactions, such as particle–particle particle–mesh, particle–mesh Ewald, and multilevel summation, split the potential into a short-range part which is evaluated directly and a long-range part which is interpolated from a mesh. This results in a force that, though still conservative, is not translation-invariant, resulting in drift in the linear momentum. A common remedy is to apply a uniform correction to all forces to conserve linear momentum, but this results in a force that is not conservative. Described here is a mass-weighted correction, based on the simple idea of constraining the center of mass, which does yield a conservative force.

Consider a system of N particles with masses m_i and positions $\vec{r}_i = \vec{r}_i(t)$, $i = 1, 2, \ldots, N$, which evolve in time t as dictated by Newton's second law of motion

$$m_i \ddot{\vec{r}}_i = \vec{F}_i(\mathbf{R}, \dot{\mathbf{R}}, t), \tag{1}$$

where $\mathbf{R}$ denotes $\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N$. Often linear momentum $\sum_i m_i \dot{\vec{r}}_i$ is conserved, which is equivalent to $\sum_i \vec{F}_i = \vec{0}$. In particular, a translation-invariant potential energy function

$$U(\vec{r}_1 + \vec{d}, \ldots, \vec{r}_N + \vec{d}) = U(\vec{r}_1, \ldots, \vec{r}_N)$$

yields forces $\vec{F}_i = -\nabla_i U(\mathbf{R})$ that sum up to zero.

For a computer simulation the cost of evaluating forces can be very high. In particular, 2-body nonbonded interactions require $\mathcal{O}(N^2)$ operations unless approximations are used. The most efficient approximations are obtained with methods such as particle–particle particle–mesh [1], particle–mesh Ewald (PME) [2], and multilevel summation [3–5], which split the potential into a short-range part calculated directly and a long-range

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part interpolated from a mesh. The use of a mesh yields an approximation $U^{\mathrm{a}}(\mathbf{R})$ to the long-range part of the potential energy which is not translation-invariant. This leads not only to a violation of Newton's third law but causes particles to exert forces on themselves [6]! (Methods based on a hierarchical clustering of interactions, such as the fast multipole method [7], do not have this problem; however, they compute forces that are not conservative [8] and appear to be otherwise less efficient for molecular dynamics [9,4], though these studies are based on older versions of the methods.)

Failure to conserve linear momentum is at best a nuisance, since it means that even if the center of mass is initially at rest, it will start moving as the simulation progresses. A common remedy [2,10,11] is to subtract out the average net force $(1/N)\sum_k \vec{F}_k^{\mathrm{a}}$ from each force $\vec{F}_i^{\mathrm{a}}$. However, the resulting force is not conservative even if the original approximate force is conservative. For a conservative force, the Jacobian matrix of $\vec{F}_i$ with respect to $\vec{r}_j$ must equal the transpose of the Jacobian matrix of $\vec{F}_j$ with respect to $\vec{r}_i$. However, such is not the case for the adjusted force $\vec{F}_i^{\mathrm{a}}(\mathbf{R}) - (1/N)\sum_k \vec{F}_k^{\mathrm{a}}(\mathbf{R})$, whose Jacobian matrix with respect to position $\vec{r}_j$ is given by

$$\frac{\partial}{\partial \vec{r}_j}\left(\vec{F}_i^{\mathrm{a}} - \frac{1}{N}\sum_k \vec{F}_k^{\mathrm{a}}\right) = -\overleftrightarrow{\mathscr{H}}_{ij}^{\mathrm{a}} + \frac{1}{N}\sum_k \overleftrightarrow{\mathscr{H}}_{kj}^{\mathrm{a}},$$

where $\overleftrightarrow{\mathscr{H}}_{ij}^{\mathrm{a}}$ is the (i,j)th 3×3 block of the Hessian of the potential energy function U^{a}.

The negative effect of this simple force correction on conservation of energy is observed in [12, p. 30]. A system of 216 rigid SPC waters is simulated for 10 ns in a cube of side length 18.7 Å. PME is used with a $18\times 18\times 18$ grid, a direct sum cutoff of 8 Å, and the Verlet integrator with a 2 fs time step. The use of the force correction produces a drift of -0.14 kcal/mol amidst fluctuations of ± 0.05 kcal/mol. Without the force correction the drift is not discernible.

A mass-weighted correction to the force is conservative, however. Assume that the initial linear momentum is zero:

$$\sum_i m_i \dot{\vec{r}}_i(0) = 0$$

(which is attained by subtracting a constant velocity from each velocity). Denote the displacement of the center of mass by

$$\vec{g}(\mathbf{R}) = \frac{1}{m_{\mathrm{tot}}}\sum_k m_k(\vec{r}_k - \vec{r}_k(0)),$$

where $m_{\mathrm{tot}} = \sum_k m_k$, and conservation of linear momentum is equivalent to the holonomic constraint

$$\vec{g}(\mathbf{R}) = 0.$$

This can be combined with the equations of motion (1) by adding constraint forces

$$m_i \ddot{\vec{r}}_i = \vec{F}_i(\ldots) + \frac{m_i}{m_{\mathrm{tot}}}\vec{\lambda},$$

where $\vec{\lambda}$ is a set of Lagrange multipliers and its coefficient is obtained from the Jacobian matrix of $\vec{g}(\mathbf{R})$ with respect to $\vec{r}_i$. Eliminating $\vec{\lambda}$ (by twice differentiating the constraints and substituting in the equations of motion) leads to

$$m_i \ddot{\vec{r}}_i = \vec{F}_i(\ldots) - \frac{m_i}{m_{\mathrm{tot}}}\sum_k \vec{F}_k(\ldots).$$

A direct proof that the corrected force is conservative is obtained by defining a corrected potential energy function

$$U^{\mathrm{c}}(\mathbf{R}) = U^{\mathrm{a}}(\vec{r}_1 - \vec{g}(\mathbf{R}), \ldots, \vec{r}_N - \vec{g}(\mathbf{R})).$$

This is translation-invariant, and the use of a potential leads to conservative forces

$$\begin{aligned}\vec{F}_i^{\mathrm{c}}(\vec{r}_1,\ldots,\vec{r}_N) &= -\nabla_i U^{\mathrm{c}}(\vec{r}_1,\ldots,\vec{r}_N)\\ &= \vec{F}_i^{\mathrm{a}}(\vec{r}_1 - \vec{g}(\mathbf{R}),\ldots,\vec{r}_N - \vec{g}(\mathbf{R})) - \frac{m_i}{m_{\mathrm{tot}}}\sum_k \vec{F}_k^{\mathrm{a}}(\vec{r}_1 - \vec{g}(\mathbf{R}),\ldots,\vec{r}_N - \vec{g}(\mathbf{R})).\end{aligned} \tag{2}$$