Pressure regulation and immobilized atoms

Andrew Jewett (jewett.aij gmail), Shea Lab
University of California Santa Barbara
Santa Barbara, CA 93106

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Draft version

1 Introduction:

Pressure regulation and atom position restraints

We have been having difficulty running MD simulations at constant pressure whenever a large number of atoms are restrained. From speaking to others, I get the impression that this is a common problem which is not widely reported.

The purpose of this document is to: 1) call attention to the issue of immobile atoms 2) point out a simple solution to fix pressure regulation (*include the constraint forces* used to freeze the atom *in the virial*) 3) ask for feedback. (If you don't think this approach will work, or if I screwed up, I am curious to hear about it and can be reached at jewett.aij on gmail.)

Typically, the virial includes contributions from all pairwise forces between atoms, regardless of whether they act on mobile or immobile atoms. Furthermore, all atomic positions are rescaled during pressure equilibration, including mobile atoms, immobile atoms (and, if applicable, restraint anchors). Although this is consistent with the way the virial is calculated, this behavior can be undesirable. (see figure 1).

It is useful to turn off coordinate rescaling for immobilized atoms. (For example, using the "dilate partial" in LAMMPS.) To compensate, we suggest that the forces acting on immobilized atoms should be omitted from the virial, (pairwise) ... *unless* the forces that are used to immobilize the atoms (and negate these pairwise forces) *are included* in the virial. (Although I could be wrong, my impression is that presently they are not.)

2 The virial in the presence of immobile atoms

The virial, W, is used to compute the instantaneous pressure of the system, and it is an ingredient in barostats implemented in most simulation software, including AMBER and LAMMPS. It is defined as: $W = -3V\ \frac{\mathrm{d}U}{\mathrm{d}V}$, where U is the potential energy *per* unit cell, and V is the volume of the unit cell. (See chapter 5.3 of [1] or [2].) To simplify this discussion, lets assume that the system has a cubic unit cell, and that scaling is isotropic ($V = L^3$,

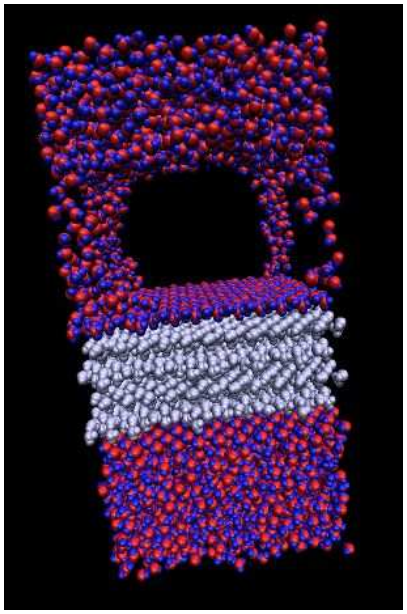

Figure 1: *Snapshot of a simulation containing restrained highly repulsive atoms.* Immobilizing restraints are particularly useful when applied to systems that would otherwise be unstable. As an extreme example, here we show a frame of animation from a simulation of (default TIP3P) water interacting with a slab of immobilized ice (middle) which has been held in place using harmonic restraints under NPT conditions ($T = 300^{\circ}K$, $P = 1$ bar). The innermost layers of ice (white) have had their charges removed, allowing the remaining Lennard-Jones forces to dominate, causing strong intermolecular repulsion. Under NPT conditions, AMBER continues to expand the simulation box in a vain effort to relax the stress between repulsive (white) molecules, which are held in place by restraints. This cavitation problem goes away if either: 1) the charges in the middle layer are restored, or 2) harmonic restraints are removed allowing the neutral (white) molecules to expand to their equilibrium density.

where L is the box size). I will assume that the forces contributing to the virial are dominated by pairwise interactions between atoms (denoted $u_{\mu\nu}(|\vec{r}_\mu - \vec{r}_\nu|)$, where $\vec{r}_\mu$ and $\vec{r}_\nu$ are the positions of atoms μ and ν). (I omitted a discussion of more general N-body interactions [2], because I don't use them in my current work. If someone asks, I'm happy to rewrite this document to include them.)

The potential energy (per unit cell) is the sum of all pairwise energies between atoms, and their images in other cells, and can be written as:

$$U = \frac{1}{2}\sum_{\vec{m}\in\mathbb{Z}^3}\sum_{\mu\neq\nu} u_{\mu\nu}\left(|\vec{r}_\mu - (\vec{r}_\nu + L\vec{m})|\right) \quad (1)$$

$$\text{useful notation: } \vec{r}_{\nu,\vec{m}} \equiv \vec{r}_\nu + L\vec{m} \quad (2)$$

$$= \frac{1}{2}\sum_{\vec{m}\in\mathbb{Z}^3}\sum_{\mu\neq\nu} u_{\mu\nu}\left(\left|\vec{r}_\mu - \vec{r}_{\nu,\vec{m}}\right|\right) \quad (3)$$

where $\sum_{\mu\neq\nu}$ is a sum over all pairs of atoms in the system (mobile or immobile), and $\sum_{\vec{m}\in\mathbb{Z}^3}$ is a sum over an atom's images in all surrounding unit cells (located at position $\vec{r}_\nu + L\vec{m}$, where $\vec{m}$, is a vector with integer x,y,z components). The factor of $\frac{1}{2}$ compensates for redundancy of equivalent pairs ($\mu \leftrightarrow \nu$). This yields:

$$W = -3V\frac{\mathrm{d}U}{\mathrm{d}V} = -L\frac{\mathrm{d}U}{\mathrm{d}L} \quad (\text{where } V = L^3) \quad (4)$$

$$= -\frac{L}{2}\sum_{\vec{m}\in\mathbb{Z}^3}\left(\sum_{\mu\neq\nu}\frac{\mathrm{d}\vec{r}_\mu}{\mathrm{d}L}\cdot\underbrace{\frac{\partial u_{\mu\nu}\left(\left|\vec{r}_\mu - \vec{r}_{\nu,\vec{m}}\right|\right)}{\partial\vec{r}_\mu}}_{=\,-\vec{f}_{\nu,\vec{m}\to\mu}} + \frac{\mathrm{d}\vec{r}_{\nu,\vec{m}}}{\mathrm{d}L}\cdot\underbrace{\frac{\partial u_{\mu\nu}\left(\left|\vec{r}_\mu - \vec{r}_{\nu,\vec{m}}\right|\right)}{\partial\vec{r}_{\nu,\vec{m}}}}_{=\,-\vec{f}_{\mu\to\nu,\vec{m}}}\right) \quad (5)$$

One can recognize $-\frac{\partial}{\partial\vec{r}_\mu}u_{\mu\nu}\left(\left|\vec{r}_\mu - \vec{r}_{\nu,\vec{m}}\right|\right)$ as the force acting on atom μ exerted by atom ν's image in unit cell indicated by $\vec{m}$ (denoted $\vec{f}_{\nu,\vec{m}\to\mu}$). We now split this sum into terms involving mobile and immobile atoms. We use lower-case indices (i, j) to refer to mobile atoms, and upper-case indices (I, J) to refer to immobile atoms, respectively. Expressed this way, $W =$

$$\frac{L}{2}\sum_{\vec{m}\in\mathbb{Z}^3}\left(\sum_{i\neq j}\left(\frac{\mathrm{d}\vec{r}_i}{\mathrm{d}L}\vec{f}_{j,\vec{m}\to i} + \frac{\mathrm{d}\vec{r}_{j,\vec{m}}}{\mathrm{d}L}\ \vec{f}_{i\to j,\vec{m}}\right) + \sum_{I,j}\left(\frac{\mathrm{d}\vec{r}_I}{\mathrm{d}L}\vec{f}_{j,\vec{m}\to I} + \frac{\mathrm{d}\vec{r}_{j,\vec{m}}}{\mathrm{d}L}\ \vec{f}_{I\to j,\vec{m}}\right)\right.$$
$$\left. + \sum_{i,J}\left(\frac{\mathrm{d}\vec{r}_i}{\mathrm{d}L}\vec{f}_{J,\vec{m}\to i} + \frac{\mathrm{d}\vec{r}_{J,\vec{m}}}{\mathrm{d}L}\ \vec{f}_{i\to J,\vec{m}}\right) + \sum_{I\neq J}\left(\frac{\mathrm{d}\vec{r}_I}{\mathrm{d}L}\vec{f}_{J,\vec{m}\to I} + \frac{\mathrm{d}\vec{r}_{J,\vec{m}}}{\mathrm{d}L}\ \vec{f}_{I\to J,\vec{m}}\right)\right) \quad (6)$$

We use the notation: $\vec{s}_i \equiv \vec{r}_i/L$ to denote the normalized coordinates of atom i. The x,y,z components of $\vec{s}_i$ lie in the range from 0 and 1. Because mobile (unconstrained, lower-case) atom positions are rescaled during pressure equilibration, this means that $\vec{r}_i$ and $\vec{r}_j$ are proportional to L ($\vec{r}_j = L\vec{s}_i$), and consequently, $\vec{s}_i$ and $\vec{s}_j$ are independent of L. Consequently:

$$L\frac{\mathrm{d}\vec{r}_i}{\mathrm{d}L} = \vec{r}_i \quad \text{and} \quad L\frac{\mathrm{d}\vec{r}_{j.\vec{m}}}{\mathrm{d}L} = \vec{r}_{j,\vec{m}} = \vec{r}_j + L\vec{m} \quad (7)$$

(See equation 2.) Let us assume, for the moment that immobilized atoms are *not* rescaled during pressure equilibration. This means that:

$$\frac{\mathrm{d}\vec{r}_I}{\mathrm{d}L} \;=\; \frac{\mathrm{d}\vec{r}_J}{\mathrm{d}L} \;=0 \quad \text{and thus} \quad \frac{\mathrm{d}\vec{r}_{I,\vec{m}}}{\mathrm{d}L} \;=\; \frac{\mathrm{d}\vec{r}_{J,\vec{m}}}{\mathrm{d}L} \;=\; \vec{m} \tag{8}$$

After substituting equations 7 and 8 into 6, and some additional simplification (appendix A) we find that the following terms (denoted ΔW_{im}) are *left out* of the virial:

$$\Delta W_{\mathrm{im}} = \sum_I \vec{r}_I \cdot \sum_{\vec{m}\in\mathbb{Z}^3} \left(\sum_j \vec{f}_{j,\vec{m}\to I} + \sum_{J>I} \vec{f}_{J,\vec{m}\to I} \right) \tag{9}$$

These terms would otherwise be present if the immobilized atoms (with indices I, and J) *were* scaled with the box-size during pressure equilibration.

Simulation programs typically include all of these pairwise force terms. To correct the virial, one *could* subtract these terms (ΔW_{im}) from the virial as calculated by the simulation program. We can recognize the sum over $\sum_{\vec{m}\in\mathbb{Z}^3}$ as the *net pairwise force* acting on atom I. Hence we can calculate this correction to the virial knowing only the net force acting on each atom.

Alternately, one can apply the restraint forces which negate these *before* calculating the virial. (This is really the same thing, because these constraint forces would have contributed $-\Delta W_{\mathrm{im}}$ to the virial.) For completeness, an expression for the full virial is given in equation 10 in appendix A.

Appendices:

A Simplifying the virial

I skipped a few steps when deriving equation 9. The are included here. Substituting equations 7 and 8 into equation 6 completely eliminates terms containing $\vec{f}_{j,\vec{m}\to I}$, $\vec{f}_{J,\vec{m}\to I}$, and reduces the number of terms containing $\vec{f}_{i\to J,\vec{m}}$, and $\vec{f}_{I\to J,\vec{m}}$. We are left with:

$$W = \frac{1}{2} \sum_{\vec{m}\in\mathbb{Z}^3} \left(\sum_{i\neq j} \left(\vec{r}_i \cdot \vec{f}_{j,\vec{m}\to i} + (\vec{r}_j + L\vec{m}) \cdot \vec{f}_{i\to j,\vec{m}} \right) + \sum_{I,j} \left((\vec{r}_j + L\vec{m}) \cdot \vec{f}_{I\to j,\vec{m}} \right) \right.$$
$$\left. + \sum_{i,J} \left(\vec{r}_i \cdot \vec{f}_{J,\vec{m}\to i} + L\vec{m} \cdot \vec{f}_{i\to J,\vec{m}} \right) + \sum_{I\neq J} \left(L\vec{m} \cdot \vec{f}_{I\to J,\vec{m}} \right) \right) \tag{10}$$

This expression for the virial can be written in multiple equivalent ways. Note that: $\vec{f}_{i\,\to\,j,\vec{m}}$ (the force from atom i acting on the image of atom j in unit cell $\vec{m}$) is identical to $\vec{f}_{i,-\vec{m}\,\to\,j}$ (the force acting on immobilized atom j, coming from the image of atom i in unit cell $-\vec{m}$).

The terms which (as a result of immobilizing of some of the atoms), are

absent from this summation (denoted $\Delta W_{\rm im}$), are:

$$\Delta W_{\rm im} = \frac{1}{2} \sum_{\vec{m} \in \mathbb{Z}^3} \left(\sum_{I,j} \vec{r}_I \cdot \vec{f}_{j,\vec{m} \to I} + \sum_{i,J} \vec{r}_J \cdot \vec{f}_{i \to J,\vec{m}} + \sum_{I \neq J} \left(\vec{r}_I \cdot \vec{f}_{J,\vec{m} \to I} + \vec{r}_J \cdot \vec{f}_{I \to J,\vec{m}} \right) \right) \tag{11}$$

By using the identities: $\vec{f}_{i \,\to\, J,\vec{m}} = \vec{f}_{i,-\vec{m} \,\to\, J}$ and $\vec{f}_{I \,\to\, J,\vec{m}} = \vec{f}_{I,-\vec{m} \,\to\, J}$, and replacing $\vec{m}$ by $-\vec{m}$, in the sum $\sum_{\vec{m} \in \mathbb{Z}^3}$ (since we are summing over both positive and negative x,y,z components of $\vec{m}$), and combining and eliminating redundant terms (and eliminating the factor of $\frac{1}{2}$), we can justify equation 9.

References

[1] Louis, A., "Computer Simulation Methods in Chemistry and Physics, Part III", Section 5.3, 94-95, (2005) `http://www-thphys.physics.ox.ac.uk/people/ArdLouis/teaching.shtml`

[2] Thompson, A.P., Plimpton, S.J., Mattson, W., "General formulation of pressure and stress tensor for arbitrary many-body interaction potentials under periodic boundary conditions" *J. Chem. Phys.*, **131**, 154107, (2009)